Electron Transfer in Rigid and Semi-Rigid Iridium d^8-d^8 Donor-Spacer-Acceptor Complexes

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Humanity's deepest desire for knowledge is justification enough for our continuing quest. And our goal is nothing less than a complete description of the universe we live in.

—Stephen Hawking,
A Brief History of Time

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to my sources of love,
Mom, Dad,
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Abstract

A series of rigid and semi-rigid donor-spacer-acceptor complexes, [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-(CH$_2$)$_n$-py$^+$-R)]$_2$ (pz* = 3,5-dimethylpyrazolyl; C$_6$H$_4$ = phenylene; py$^+$ = pyridinium; R = H, 4-*tert*-butyl, and 4-amide; and n = 0, 1, 2, and 3), has been synthesized for the purpose of studying photoinduced electron-transfer (ET) reactions. The spacers separating the iridium center (electron donor, Ir$_2$) and pyridinium cation (electron acceptor, py$^+$) are based on terminal phosphinite ligands, consisting of a phenylene group and a number of methylene groups ranging from 0 to 3. Three distinct ET reactions can be studied in each complex: singlet excited-state electron transfer (^{1}ET), triplet excited-state electron transfer (^{3}ET), and thermal back electron transfer (ET^b).

Atomic positions, obtained from the X-ray crystal structure of [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-CH$_3$]$_2$, were used as a basis for molecular mechanics calculations, furnishing solution structures for the series of Ir$_2$-py$^+$ donor-acceptor complexes. These results revealed that the spacers in complexes where n = 0 and n = 1 are rigid, and that in complexes where n = 2 and n = 3, the spacers are semi-rigid, taking on either *folded* or *stretched* conformations in fluid solution.

Steady-state and time-resolved emission and absorption experiments were employed to determine ^{1}ET, ^{3}ET, and ET^b rates in these complexes. The ^{1}ET and ^{3}ET rates for the n = 2 and n = 3 complexes exhibit Gaussian free-energy dependence, in excellent agreement with classical ET theory (n = 2: λ = 1.10 eV, H$_{DA}$ = 26 cm^{-1}; n = 3: λ = 1.05 eV and H$_{DA}$ = 7 cm^{-1}). However, the ^{1}ET and ^{3}ET rates in n = 0 and n = 1 complexes exhibit dramatically different behavior: the ^{3}ET rates in these rigid complexes are on the order of 10,000 times slower than the corresponding ^{1}ET rates. H$_{DA}$s for the ET^b reactions (n = 1, 2) are similar to those of the corresponding ^{1}ET reactions. These results are discussed in terms of the solution structure parameters obtained for the series of donor-acceptor complexes. Evidence that through-bond and through-space couplings play different roles in singlet and triplet electron transfer is presented for the first time.

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List of Abbreviations

NMR

br	broad
d	doublet
m	multiplet
s	singlet
t	triplet

Electrochemistry

$E_{1/2}$	half-wave potential
E_{pc}	cathodic peak potential
E_{pa}	anodic peak potential
E_j	junction potential
F	the Faraday; charge on one mole of electrons
SSCE	saturated sodium chloride electrode
TBAH	tetra-n-butylammonium hexafluorophosphate

Spectroscopy

ε	molar absorptivity
Φ_p^o	intrinsic phosphorescence quantum yield
Φ_f^o	intrinsic fluorescence quantum yield
Φ_p	phosphorescence quantum yield
Φ_f	florescence quantum yield
k_r	radiative decay rate constant
k_{nr}	non-radiative decay rate constant
τ_p	triplet excited state lifetime
τ_f	singlet excited-state lifetime
τ_p^o	intrinsic triplet excited-state lifetime
τ_f^o	intrinsic singlet excited-state lifetime
S_0	singlet ground state
S_1	lowest singlet excited-state
T_1	lowest triplet excited-state

Electron Transfer

k_{ET}	electron-transfer rate constant
^1ET	singlet excited-state electron transfer
^3ET	triplet excited-state electron transfer
ET^b	thermal back electron transfer
$^1H_{DA}$	electronic coupling matrix element for ^1ET
$^3H_{DA}$	electronic coupling matrix element for ^3ET
$^bH_{DA}$	electronic coupling matrix element for ET^b

General

Ph	phenyl
C_6H_4	phenylene
py	pyridine
$py^\bullet$	pyridinium radical
py^+	pyridinium cation
py^+-Am	4-amidopyridinium
py^+-tB	4-*tert*-butylpyridinium
pzH	pyrazole
pz	pyrazolyl
pz^*	3,5-dimethylpyrazolyl
$Quin^+$	Quinuclidinium
Q	quinone
UQ	ubiquinone

Chapter 1

Introduction and Background

Electron-transfer (ET) reactions play a central role in many chemical and biological processes.[1-3] For example, energy production in both plants and animals is a direct consequence of ET occurring in cells.[4] The most extensively studied *biological* electron-transport process is photosynthesis occurring in purple bacteria[5-8] (two species of which have been structurally characterized[9-11]). These organisms capture the energy of sunlight and through a series of efficient electron-transfer steps, convert it to chemical energy in the form of long-lived oxidative and reductive species. These remarkable reactions occur between several distinct redox components contained within the so-called reaction center (RC). Following light absorption, a bacteriochlorophyll dimer in its singlet excited state transfers an electron, on a picosecond time-scale, to a monomeric bacteriochlorophyll which in turn reduces a quinone, again on a subnanosecond time-scale. The competing back ET reaction to the ground state is ~4,000 times slower than the forward charge-separating reaction. Clearly, an understanding of the precise role the medium plays in determining ET rates, the nature of the high quantum yields, and the origin of the diminished back ET rates is important in the effort to mimic these reactions that lead to efficient conversion of light into chemical energy. However, there are fundamental limitations at present in the ability to manipulate such a complicated natural system. Model compounds that actually mimic important features of the RC thus have a valuable role to play in unraveling the mysteries of RC function.[12-20]

Many model systems have been prepared in an effort to understand the effects of (1) electronic parameters such as donor-acceptor distance and relative orientation[12,16,17,21,22] and the chemical nature of the medium,[23-26] and (2) nuclear parameters[13,27-29] such as solvent and internal reorganization energies, and thermodynamic driving forces.

This thesis deals with the mechanistic aspects of photoinduced intramolecular electron transfer in iridium d^8-d^8 complexes. Many of the questions posed above will be addressed in the following chapters with the ultimate goal of coupling photoinduced charge transfer to bond-forming chemical reactions (as occurs in photosynthesis) in mind. Our studies have

focused on d^8-d^8 complexes because they are powerful excited state reductants and their corresponding d^8-d^7 complexes are reactive toward C-X and C-H bond activation. This chapter reviews theoretical models associated with electron-transfer reactions, introducing relevant concepts and terminology, and presents a summary of the systems that inspired this research.

Electron Transfer Theory: An in-depth description of all existing electron-transfer theories (for some examples see refs. 2,30-37) is beyond the scope of this thesis (and the author), however, a brief review of classical ET theory[31-33] (where nuclear tunneling effects are neglected) will be provided.

All theoretical expressions for the rate of electron transfer between two redox sites consist of two important components; an electronic factor and a nuclear factor. The nuclear factor can be discussed by considering the potential-energy curves in Figure 1.1. In this figure, the reactant and product potential curves (representations of multi-dimensional potential surfaces) are drawn along a reaction coordinate q which represents the positions of all the nuclei in the system (including solvent). For electron transfer to occur, the system must attain a geometry that is intermediate between that of the reactants and products (a statement of the Franck-Condon principle), corresponding to the intersection of the potential surfaces. The horizontal displacement of the two wells gives an indication of the extent of nuclear motion involved in the electron-transfer event. The energy involved in moving all the nuclei to their appropriate positions is referred to by Marcus as the reorganization energy, λ, from inner sphere effects (λ_{in}) and from outer sphere effects (λ_{out}).[38] λ_{in} includes changes in bond angles and bond lengths in the molecule itself while λ_{out} includes changes in solvent configuration, and is largely due to the repolarization energy of the solvent associated with the charge transfer reaction.

Figure 1.1. Product and reactant potential energy surfaces plotted as a function of nuclear coordinates (q), showing free energy change for the reaction ($\Delta G°$), and solvent and internal reorganization energy (λ).
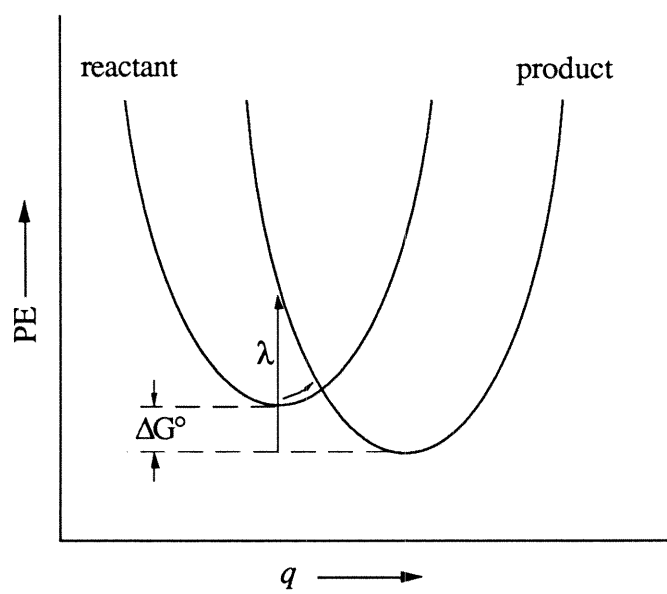
Once a suitable nuclear configuration has been reached, the fate of the transferring electron lies in the electronic factors. If there is no electronic interaction between the wave functions representing the donor and acceptor sites, the surfaces will intersect, and the reaction cannot occur. If, however, there is an electronic interaction, the intersection of the two curves results in an *avoided crossing*, a consequence of overlap between the reactant and product electronic wavefunctions. This situation is represented in Figure 1.2. The overlap causes a splitting of the two surfaces by an amount $2H_{DA}$ (electronic coupling matrix element). The magnitude of this *interaction energy*, which is the main concern of this thesis, depends on structural parameters such as donor-acceptor distance and orientation. If H_{DA} is large enough ($H_{DA} > \sim 100$ cm^{-1}), the system remains on the lower surface when passing through the intersection region, with unit probability. This situation is termed the *adiabatic* limit and is represented by an electronic transmission coefficient, κ_E, equal to one. However, when H_{DA} is small ($H_{DA} < \sim 10$ cm^{-1}), the splitting between surfaces is also small, and the system can sometimes *jump* to the upper surface, retaining an electronic configuration indicative of the reactants. It may therefore pass through the transition state many times without proceeding on to products. Such a system is said to be *nonadiabatic*, and is characterized by a value of κ_E less than unity.

Electron-transfer rates can be expressed in terms of these electronic and nuclear factors by eq 1.1, where ν_N is the effective frequency for nuclear motion ($\kappa_E\nu_N$ represents the activationless reaction rate constant), and FC is the Frank-Condon factor for electron transfer. Electron-transfer rates in the *nonadiabatic* limit have been treated classically by Marcus,[31-33] and can be expressed by eqs 1.2 and 1.3, where $\Delta G°$ is the free energy change for the reaction.

One of the most remarkable predictions of Marcus theory is that for very exergonic reactions the rate constant should *decrease with increasing* driving force. The range in which such behavior is predicted to occur ($-\Delta G° > \lambda$) is termed the *inverted region.* Naturally, the region ($-\Delta G° < \lambda$) where reaction rates behave normally (increasing with

Figure 1.2. Representation of the avoided crossing at the transition state region, showing the interaction energy, H_{DA}. If electron transfer is adiabatic ($\kappa = 1$), the reactants pass with unit probability to the lower product surface. If, however, the reaction is nonadiabatic ($\kappa < 1$), the system can be excited to the higher energy surface and may have to pass through the transition state many times before being converted into products.

product   reactant

$2H_{DA}$

reactant   product
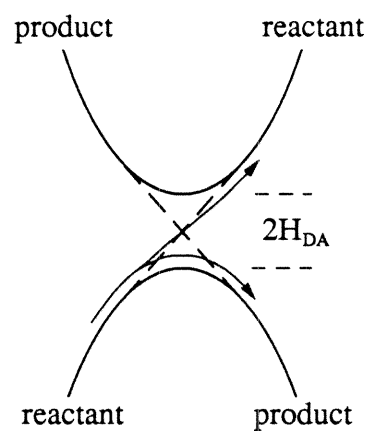
$$k_{ET} = \kappa_E v_N (FC) \tag{1.1}$$

$$k_{ET} = \left(\pi / \hbar^2 \lambda k_B T \right)^{1/2} (H_{ab})^2 \exp\left(\frac{-(\Delta G^{\circ} + \lambda)^2}{4 \lambda k_B T} \right) \tag{1.2}$$

$$\lambda = \lambda_{in} + \lambda_{out} \tag{1.3}$$

increasing driving force) is termed the *normal region*.

The inverted region has attracted a great deal of attention. Its experimental confirmation has only recently become available,[13,22,27,39-42] lending strong support to the validity of Marcus theory for electron transfer. With an adequate knowledge of electron transfer theory in hand, we proceed with an outline of the studies that motivated the research presented in this thesis.

Our research regarding photoinduced electron transfer in d^8-d^8 compounds began several years ago with a driving force study of excited-state electron transfer between a pyrazolyl-bridged iridium dimer and a series of substituted pyridiniums dissolved in fluid solution.[43,44] The results from these bimolecular reactions, summarized in Figure 1.3, demonstrated the reactivity of the metal localized triplet excited state (^{3}Ir$_2^*$) with respect to electron transfer. The expected increase in ET rates at low driving forces was observed; however, the inverted region predicted by Marcus theory was elusive due to diffusion limited reactions at high driving force. The reactivity of the higher lying singlet excited state (^{1}Ir$_2^*$) also remained a mystery, presumably due to the subnanosecond intrinsic lifetime of the iridium dimer, (COD)Ir(μ-pz)$_2$Ir(COD). The limitations inherent in this study led to the synthesis of a redox system that eliminated bimolecular diffusion as a rate limiting process. This was accomplished in a series of complexes, [Ir(μ-pz*)(CO)(Ph$_2$PO-CH$_2$CH$_2$-py$^+$-R)]$_2$ (R = -H, -2,4,6-(CH$_3$)$_3$, -4-CH$_3$, -4-Ph), where the pyridinium cation (acceptor) was covalently linked to the iridium dimer chromophore (donor) via a phosphinite ligand.[27,45,46] With the elimination of bimolecular

Figure 1.3. The driving force dependence data of Marshall et al., displaying diffusion limited electron-transfer rates at high driving forces.

$$^3Ir_2^* + A^+ \xrightarrow{k_q'} Ir_2^+ + A^\bullet$$
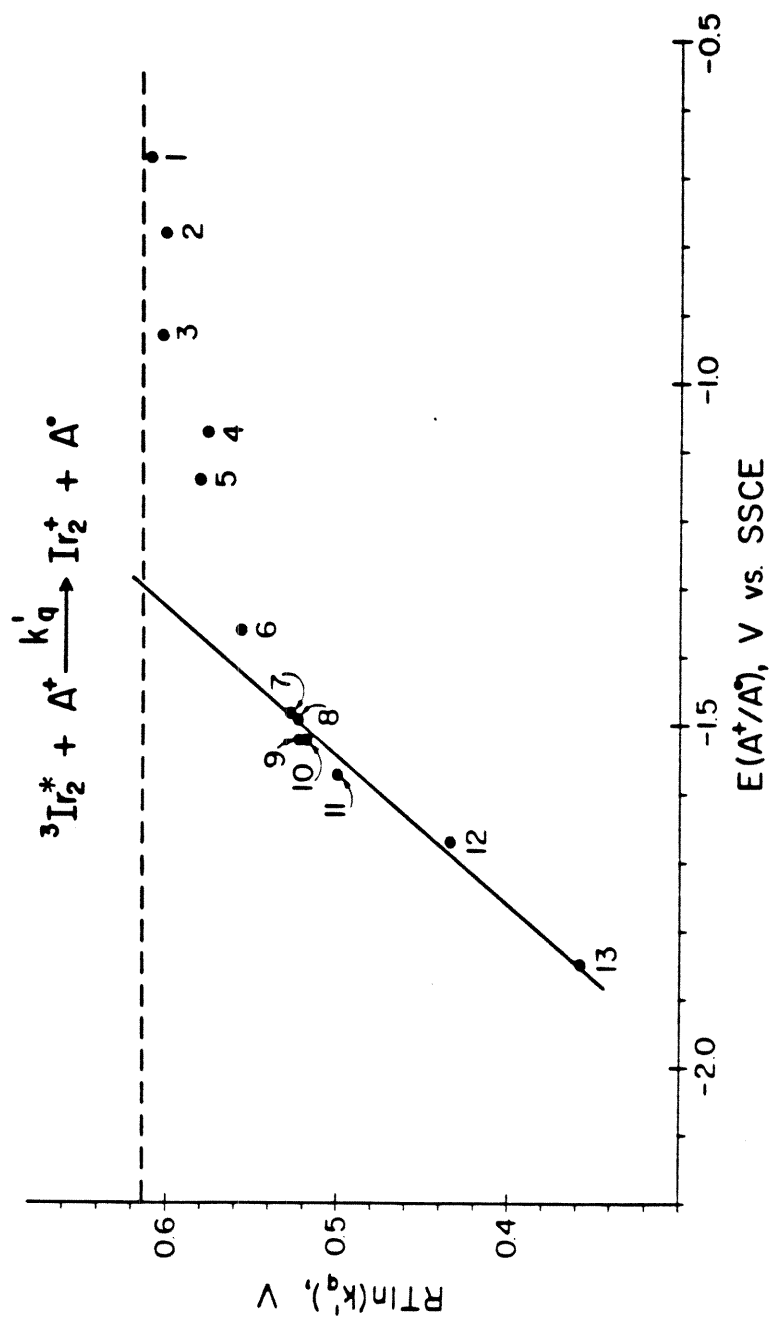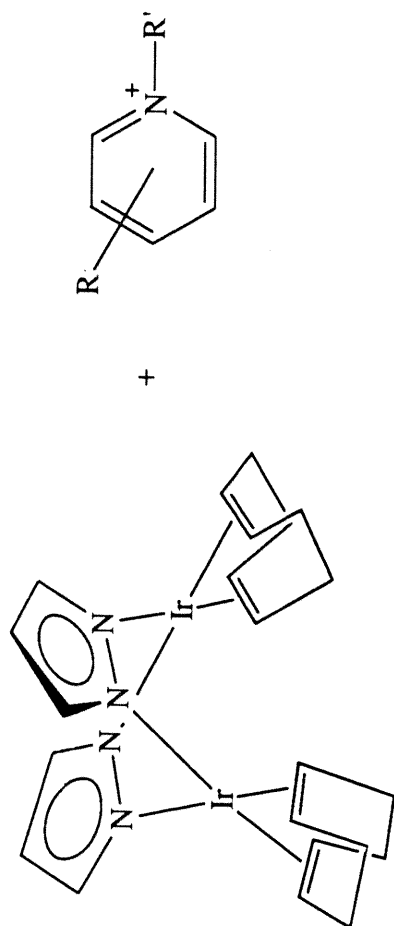
diffusion, this system revealed the reactivity of $^1Ir_2^*$ toward electron transfer and the elusive inverted region. Figure 1.4 summarizes the data obtained from the linked donor-acceptor complexes. The singlet, triplet, and recombination ET rates were fit to classical Marcus theory with the same set of nuclear and electronic parameters ($H_{DA} = 24$ cm^{-1}, $\lambda = 1.05$ eV). The origin of this surprising result was difficult to ascertain due to the flexible nature of the bridge (-P-O-CH$_2$-CH$_2$-) separating the donor and acceptor groups. The effect of the intervening medium on H_{DA} was therefore not possible to determine. Thus, we set out to design a donor-spacer-acceptor system that would facilitate the study of medium effects on intramolecular electron transfer. This was accomplished by incorporating a structurally rigid group into the bridge separating the iridium donor and pyridinium acceptor sites. The goals of this research were (1) to explore the effects of the intervening medium on electron transfer with respect to donor-acceptor distance and orientation, and (2) to determine if differences between singlet and triplet electronic couplings would arise in a system that effectively eliminated direct donor-acceptor interaction.

In this chapter, concepts concerning electron-transfer reactions and the importance of understanding the factors that control them have been presented. Chapter 2 outlines the preparation and characterization of a series of iridium d^8-d^8 donor-acceptor complexes. In Chapter 3, a discussion of their solution structures, obtained from the X-ray crystal structure of [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-CH$_3$)]$_2$, and molecular mechanics calculations, is presented. Chapter 4 is concerned with spectroscopic (steady-state absorption, emission, and excitation) and electrochemical properties of the complexes. These data were used to construct a state diagram of the metal localized and charge-transfer excited states, from which electron-transfer driving forces were extracted. Finally, in Chapter 5, photoinduced (*forward*) and thermal (*back*) electron-transfer rates were measured from time-resolved absorption and emission experiments. These results are discussed in terms of through-bond and through-space mechanisms.

Figure 1.4. The driving force dependence data of Fox et al. ^{1}ET ($\blacksquare$); ^{3}ET ($\blacktriangle$); and ET^b ($\bullet$). The dashed line is the best fit of these data to classical Marcus theory (H_{DA} = 24 cm^{-1}, λ = 1.06 eV).

R-py$^+$-CH$_2$CH$_2$-O-PPh$_2$
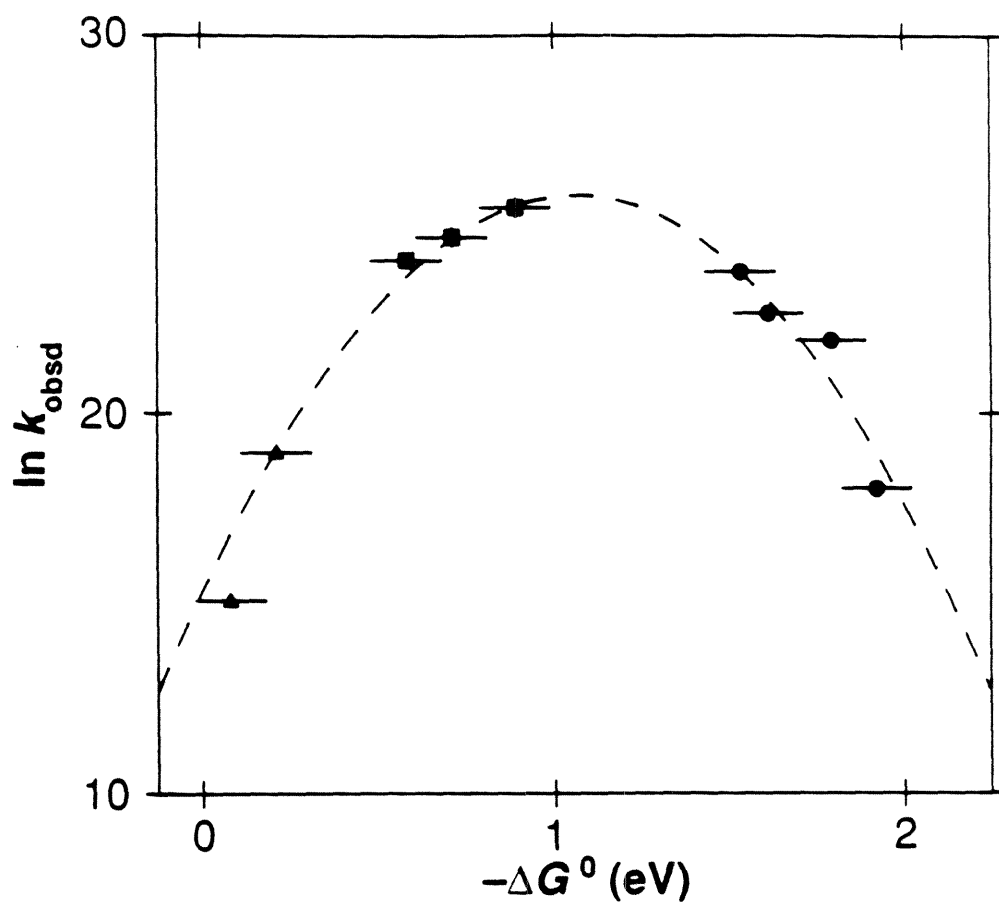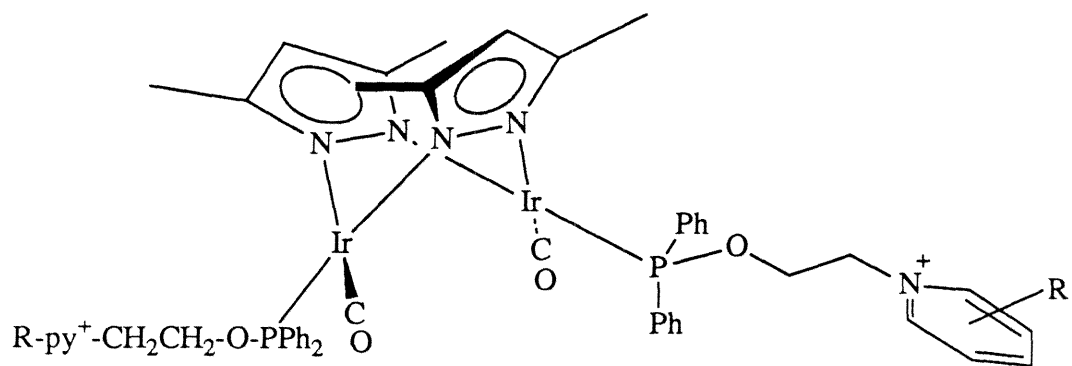
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Chapter 2

Synthesis of
Donor-Spacer-Acceptor Complexes

INTRODUCTION

Electron-transfer (ET) reactions between donor and acceptor groups are governed by parameters that express the nature of the intervening medium, the free energy change for the reaction, and relative donor-acceptor distance and orientation. A majority of studies until the last decade had been conducted on systems where the donor and acceptor were dissolved in fluid solution.[1-4] In these systems, electron transfer occurs only when diffusion brings the donor and acceptor groups within a contact distance necessary for reaction. However, more recently, numerous *linked* donor-acceptor complexes have been synthesized and studied.[5-25] Two major classes of bridges have been used to link donors and acceptors: (1) flexible bridges such as hydrocarbon chains[5, 6, 25-27] and (2) rigid or semi-rigid bridges such as ring systems[7-9, 14-19, 21, 23, 28] or peptide bonds.[24, 29, 30]

If the bridge is flexible and not too long, it serves to bring the donor and acceptor together, much the way donor and acceptor groups interact in bimolecular reactions, but at a much higher frequency. This type of bridge nearly eliminates the troublesome complication of diffusion limited electron-transfer rates.[25]

Alternatively, if the bridge is semi-rigid or completely rigid it can serve to orient the donor and acceptor in a specific geometry. Depending on the nature of the bridge it can also provide multiple electron-transfer pathways. For example, in the hypothetical donor-
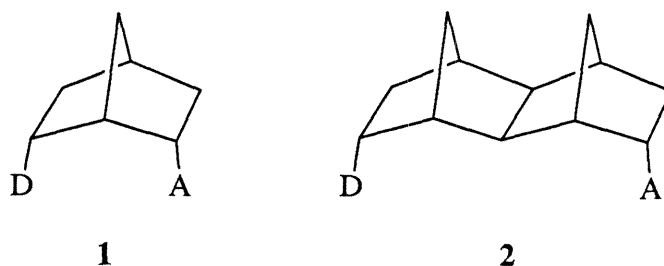
Figure 2.1. Structures of model rigid donor-spacer-acceptor complexes, demonstrating the concept of through-bond versus through-space electron-transfer mechanisms.

acceptor complex **1** (Figure 2.1), bridged by a rigid spacer, electron transfer from the donor to the acceptor can occur via the hydrocarbon chain (through-bond mechanism) and/or via a direct interaction between the donor and acceptor (through-space mechanism). On the other hand, the through-space mechanism in **2** is unlikely to be a contributing factor in the transfer of electrons from the donor to the acceptor due to the large through-space separation. Therefore, only through-bond mechanisms will be important in determining the electron-transfer rate in **2**. From a study of the ET rates in these complexes, a distinction between through-space and through-bond mechanisms can be established. If the ET rates turn out to scale with the number of carbon atoms between the donor and acceptor, we would deduce that the through-bond mechanism in **1** is the only mechanism operable (the dependence of electron-transfer rates on the number of intervening carbon atoms can be determined by extending the series further to include complexes with more than two intervening norbornane groups). However, if the ET rates did not scale with the number of carbon atoms in the bridge, and the electron-transfer rate in **1** was unexpectedly fast, then we would deduce that through-space interactions in **1** are the primary contribution to the overall coupling of the donor and the acceptor. This example demonstrates some of the advantages of linking donors and acceptors with rigid spacers in studies aimed at elucidating orientation, distance, and through-space vs. through-bond effects on electron-transfer rates.

The donor-acceptor complexes used in the present study utilize rigid and semi-rigid bridges to link donor and acceptor groups. These complexes, shown in Figure 2.2, are represented as $[Ir(\mu\text{-pz*})(CO)(Ph_2PO\text{-}C_6H_4\text{-}(CH_2)_n\text{-py}^+\text{-R})]_2(PF_6^-)_2$, where pz* = 3,5-dimethylpyrazolyl, Ph = phenyl, $-C_6H_4-$ = phenylene, py$^+$ = pyridinium, and n = 0, 1, 2, 3. They are similar to d^8-d^8 compounds of previous bimolecular and unimolecular ET studies conducted in our laboratory in which pyrazolyl-bridged iridium dimer chromophores were used as electron donors and pyridinium groups (in solution or covalently attached to the donor) were employed as one-electron acceptors. In the present

Figure 2.2. Structure of donor-spacer-acceptor complexes, $[Ir(\mu\text{-}pz^*)(CO)(Ph_2PO\text{-}C_6H_4\text{-}(CH_2)_n\text{-}py^+\text{-}R)]_2$, where the iridium center (Ir_2) and pyridinium group (py^+) act as electron donor and electron acceptor. Ph = phenyl, n = 0, 1, 2, or 3, and R = H, 4-t-butyl, or 4-amide.
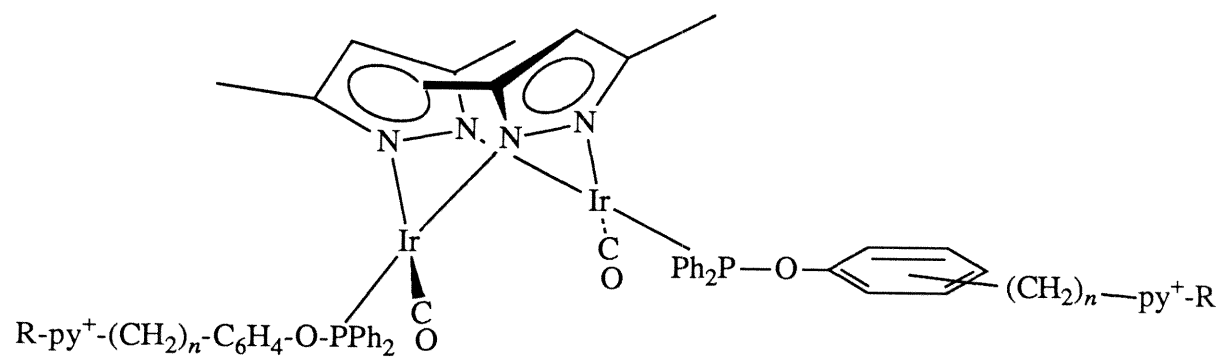
study the pyridinium acceptor was covalently attached via a phosphinite ligand to the metal center. A phenylene bridge was incorporated into the bridge separating Ir_2 (donor) and py^+ (acceptor). In all but one molecule the phenylene bridge was 1,4-disubstituted (in one molecule the phenylene group was 1,3-disubstituted). The number of methylene groups, n, bridging the pyridinium acceptor to the phenylene group, was varied from $n = 0$ to 3. In addition, the pyridinium R group was varied in $n = 1$ complexes.

As will be demonstrated in Chapter 4, intramolecular electron-transfer studies also require that *model* complexes, in which only the donor is incorporated into the complex, be prepared. Therefore, complexes of the type, $[Ir(\mu\text{-pz*})(CO)(Ph_2PO\text{-}C_6H_4\text{-}Y)]_2$, where Y is a poor electron acceptor (CH_3 or $CH_2\text{-}Quin^+PF_6^-$) have been synthesized.

In this chapter the syntheses of the series of donor-acceptor complexes and two model complexes are presented. The characterization of all the molecules by ^1H, ^{31}P NMR and IR spectroscopies is described. The complexes will, from here on, be denoted as $[Ir_2]$-R. $[Ir_2]$ represents the iridium dimer core including the pyrazolyl bridge and carbonyl ligands, the diphenyl phosphine group, and the oxygen atom and phenylene group of the bridge, i.e., $[Ir_2] = (\text{-}C_6H_4\text{-}O\text{-}Ph_2P)(CO)Ir(\mu\text{-pz*})_2Ir(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-})$. R denotes the remainder of the bridge and in all but the two model complexes, the pyridinium acceptor.

EXPERIMENTAL

Materials:

Tetrahydrofuran was distilled from sodium/benzophenone. The color of the solvent/drying agent prior to distillation was dark blue or purple. A yellow color indicated the presence of H_2O or O_2 at unacceptable levels. Methylene chloride was distilled from calcium hydride under argon. Acetone and ethanol were spectral grade in quality and used as received. Acetonitrile was either dried over activated 3Å Linde sieves for 24 hrs and

distilled onto freshly activated 3Å sieves for storage in the dry box (VAC Atmospheres) or

the acetonitrile (Burdick & Jackson) was used directly from freshly opened bottles and

stored over Linde 3Å molecular sieves for at least three days. Synthesis of

N,N-dimethyl-P,P-diphenylphosphine is described elsewhere.[31] Tetracarbonyl-

bis(μ-3,5-dimethylpyrazolyl)diiridium(I), [Ir(μ-pz*)(CO)$_2$]$_2$, was prepared according to

previously established procedures.[32] All other chemicals were of reagent grade or better

and were used as received.

Physical Measurements:

^{1}H spectra were recorded on either a JEOL FX-90Q or JEOL GX-400 FT

spectrometer. ^{1}H chemical shifts are reported in ppm (δ) using the solvent

(CHDCl$_2$ δ5.32, CHD$_2$CN δ1.93, CD$_3$COCHD$_2$ δ2.04, or HOD δ4.63) as an internal

standard. Proton decoupled ^{31}P NMR spectra were recorded on a JEOL FX-90Q

spectrometer and referenced to external 85% aqueous phosphoric acid. IR spectra were

recorded as Nujol or fluorolube mulls, KBr pressure pellets, or in dichloromethane

solutions on a Beckman Instruments IR-4240 spectrometer or on a Perkin-Elmer 1600

FTIR. Elemental analyses were obtained at the Caltech analytical facility.

Synthesis of Phenols:

N-(4-hydroxyphenyl)pyridinium, HO-C$_6$H$_4$-py$^+$ (n = 0):   disodium 4-nitrophenyl

phosphate hexahydrate (0.31 g, 1.4 mmoles), pyridine (4 mL) and H$_2$O (25 mL) were

added to a Schlenk flask. The flask was immersed in an H$_2$O filled, jacketed dewer fitted

with a Pyrex window (Figure 2.3). A refrigerated cold unit was attached to the dewer and

water was circulated at 4°C. While compressed air was directed at the window, to prevent

condensation, the sample was broad-band irradiated with excitation from a 1000 W lamp

for 24 hrs, upon which the solution turned from pale yellow to bright yellow. The reaction

mixture was then evaporated to dryness, leaving a dark yellow residue. The solid was

dissolved in 3 mL H$_2$O followed by the addition of 20 mL of ethanol which forced the
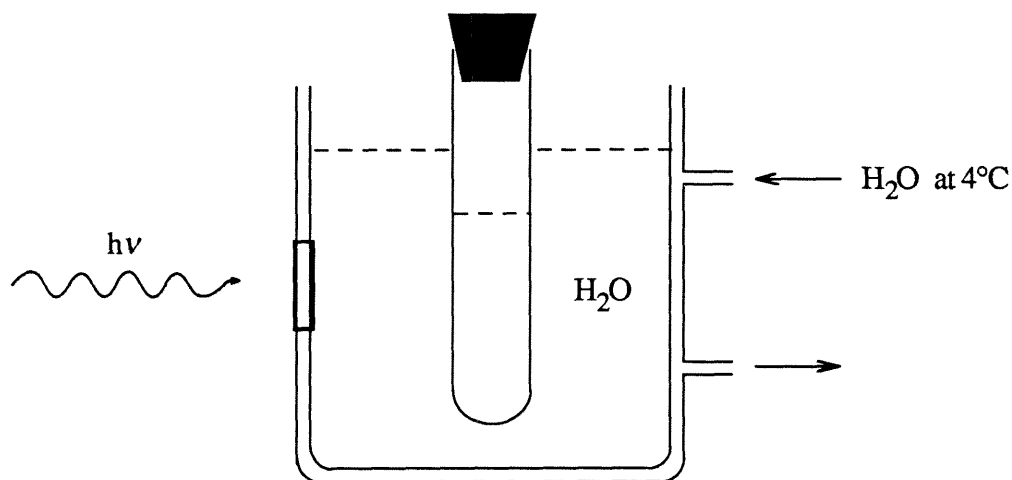
Figure 2.3. Apparatus employed in the synthesis of $HO\text{-}C_6H_4\text{-}py^+$.

precipitation of the pyridinium salt. The solid was collected by filtration and dissolved in

concentrated hydrochloric acid (25 mL) in a round bottom flask fitted with a Kontes Teflon

needle valve. The solution was stirred for 24 hrs at 100°C in the *closed* system which

resulted in the hydrolyzes of the phosphate group. The solvent was again removed in

vacuo. Ethanol was added to the solid (dissolving the desired product), and the solution

was filtered and evaporated in vacuo yielding the crude product as a red oily residue. 1 mL

of H_2O was added followed by 5 mL of a saturated H_2O solution of ammonium

hexafluorophosphate which caused the precipitation of the hexafluorophosphate salt of the

desired product, $HO\text{-}C_6H_4\text{-}py^+$.

N-(4-hydroxyphenylmethyl)pyridinium, **$HO\text{-}C_6H_4\text{-}CH_2\text{-}py^+$** ($n = 1$): p-cresol

(21.13 g, 0.195 moles) was dissolved in dry THF (30 mL) and triethylamine (27.2 mL,

0.195 moles) was added to the solution. Acetylchloride (13.9 mL, 0.195 moles) was

added slowly to the reaction mixture which caused the immediate precipitation of a white

solid. The solution was stirred for ~30 min to ensure complete consumption of the starting material. The product, which is soluble in THF, was separated from the insoluble byproducts by filtration, the solvent was evaporated in vacuo, and the crude product was fractionally distilled yielding $AcO\text{-}C_6H_4\text{-}CH_3$ as a colorless liquid (24.4 g).

$AcO\text{-}C_6H_4\text{-}CH_3$ (24.4 g, 0.163 moles) was dissolved in carbon tetrachloride (50 mL) and freshly recrystallized N-bromosuccinimide (28.9 g, 0.162 moles) was added as well as *tert*-butyl hydroperoxide (0.1 mL) which acts to catalyze the reaction. The reaction vessel was fitted with a condenser and under constant supervision the mixture was stirred vigorously and heated to reflux. Several minutes after reflux temperature was reached a dark orange gas formed above the solution (presumably Br_2 gas) and the solution itself turned red. After ~15 min the solution cleared and the Br_2 gas was consumed. The solvent was removed in vacuo leaving $AcO\text{-}C_6H_4\text{-}CH_2Br$ as yellow oily residue.

$AcO\text{-}C_6H_4\text{-}CH_2Br$ (2 g) without further purification was then dissolved in neat pyridine (20 mL) and stirred for 24 hrs. The reaction mixture was filtered and the solid was dried at 40°C yielding $AcO\text{-}C_6H_4\text{-}CH_2\text{-}py^+Br^-$. A pyridine molecule of solvation still remained (as evidenced by ^1H NMR) after rigorous drying. No further attempts were made to remove the pyridine and the next reaction was conducted with the unpurified compound.

$AcO\text{-}C_6H_4\text{-}CH_2\text{-}py^+Br^-$·pyridine was dissolved in 30 mL H_2O and 0.5 mL of 48% HBr was added. The solution was stirred vigorously for 24 hrs. followed by the addition of a large excess of a saturated water solution of ammonium hexafluorophosphate. The hexafluorophosphate salt of $HO\text{-}C_6H_4\text{-}CH_2\text{-}py^+$ was separated from the solution by filtration and washed extensively with H_2O until the washings were of neutral pH.

N-(4-hydroxyphenylmethyl)quinuclidinium, **$HO\text{-}C_6H_4\text{-}CH_2\text{-}Quin^+$** ($n = 1$): The synthesis of this complex was conducted by the same procedure as described for $HO\text{-}C_6H_4\text{-}CH_2\text{-}py^+$ except quinuclidine was used instead of pyridine. The reaction of 1 eq of quinuclidine with $AcO\text{-}C_6H_4\text{-}CH_2Br$ was conducted in THF.

4-*tert*-butyl-*N*-(4-hydroxyphenylmethyl)pyridinium, **HO-C$_6$H$_4$-CH$_2$-py$^+$-tB**

(*n* = 1): The synthesis of this complex was conducted by the same procedure as described

for HO-C$_6$H$_4$-CH$_2$-py$^+$ except 4-*t*-butylpyridine was used instead of pyridine. The

reaction of 1 eq of 4-*t*-butylpyridine with AcO-C$_6$H$_4$-CH$_2$Br was conducted in THF.

4-amido-*N*-(4-hydroxyphenylmethyl)pyridinium, **HO-C$_6$H$_4$-CH$_2$-py$^+$-Am**

(*n* = 1): The synthesis of this complex was conducted by the same procedure as described

for HO-C$_6$H$_4$-CH$_2$-py$^+$ except isonicotinamide was used instead of pyridine. The reaction

of 1 eq of isonicotinamide with AcO-C$_6$H$_4$-CH$_2$Br was conducted in THF. Analysis

Calculated for C$_{13}$H$_{13}$F$_6$N$_2$O$_2$P: C, 41.73%; H, 3.50%; N, 7.49%. Found: C, 41.71%;

H, 3.50%; N, 7.06%.

N-(4-hydroxyphenethyl)pyridinium, **HO-C$_6$H$_4$-(CH$_2$)$_2$-py$^+$** (*n* = 2):

4-hydroxyphenethyl alcohol (2.56 g, 18.53 mmoles) was dissolved in 48% HBr (35 mL)

and stirred for 3 hrs. at 90°C upon which dark red-brown droplets separated from the

solution. The reaction mixture was then poured onto ice, initiating the precipitation of a

white solid. The crude product was extracted with three portions of 30 mL diethylether.

The ether solution was then washed with water until the washings were at neutral pH (6

times), dried with anhydrous magnesium sulfate, filtered, and evaporated leaving a white

solid. The crude product was collected and recrystallized from hot cyclohexane yielding

1.47 g of white needles. *β*-(p-hydroxyphenyl)ethyl bromide (0.40 g) from the previous

step was dissolved in neat pyridine (3 mL) and stirred for 5 hrs. at 40-50°C at which time a

white precipitate formed. The mixture was filtered, washed with hexane, metathesized to

the hexafluorophosphate salt and washed three times with H$_2$O, yielding 100 mg of the

desired pyridinium salt, HO-C$_6$H$_4$-(CH$_2$)$_2$-py$^+$.

N-(3-hydroxyphenethyl)pyridinium, **HO-C$_6$H$_4$-3-(CH$_2$)$_2$-py$^+$** (*n* = 2): The

synthesis of this complex was conducted by the same procedure as described for

HO-C$_6$H$_4$-(CH$_2$)$_2$-py$^+$ except that 3-hydroxyphenethyl alcohol was used instead of

4-hydroxyphenethyl alcohol.

N-(4-hydroxyphenylpropyl)pyridinium, **HO-C₆H₄-(CH₂)₃-py⁺** (*n* = 3): The
synthesis of this complex was conducted by the same procedure as described for
HO-C₆H₄-(CH₂)₂-py⁺ except that 4-hydroxyphenylpropyl alcohol was used instead of
4-hydroxyphenethyl alcohol.

Synthesis of Phosphinite Ligands:

Ph₂P-O-C₆H₄-CH₃: *p*-cresol (1.83 g, 7.0 mmoles) was dissolved in dry THF
(100 mL) in a 50 mL Schlenk flask with a side arm. The solution was pump-flushed three
times while being stirred. Triethylamine (2.59 mL, 18.6 mmoles) was added via syringe.
After ~1 min of stirring, chlorodiphenylphosphine (3.43 mL) was added slowly via
syringe. The total volume was added over 5 min. Upon contact with the solution, the
insoluble triethylamine hydrochloride precipitated from solution. The reaction mixture was
stirred for 15 min to ensure complete consumption of the starting materials. The solution
was separated from the white powder by cannula filtration. The solution at this point could
be exposed to ambient atmosphere. The flask containing crude product, solvent, and small
amounts of triethylamine hydrochloride was fitted with a short-path distillation apparatus.
The solvent was removed at room temperature in vacuo leaving an oily, cloudy residue.
The crude product was then fractionally distilled, collecting the product between 145° and
180°C at ~10⁻² torr in a cow receiver. The purified phosphinite product at room
temperature solidified in the cow receiver after ~1 hr.

Ph₂P-O-C₆H₄-py⁺, Ph₂P-O-C₆H₄-CH₂-py⁺, Ph₂P-O-C₆H₄-CH₂-Quin⁺,
Ph₂P-O-C₆H₄-CH₂-py⁺-tB, Ph₂P-O-C₆H₄-CH₂-py⁺-Am,
Ph₂P-O-C₆H₄-(CH₂)₂-py⁺, Ph₂P-O-C₆H₄-3-(CH₂)₂-py⁺, and
Ph₂P-O-C₆H₄-(CH₂)₃-py⁺: In all cases, the syntheses of these phosphinite ligands
were accomplished by the following procedure: 0.5 g of the appropriate phenol (syntheses
described above) was dissolved in CH₃CN (~2 mL) in the dry box, followed by the
addition of an CH₃CN solution of *N*,*N*-dimethyl-*P*,*P*-diphenylphosphine, Ph₂PNMe₂

(1 eq). The reaction was stirred for 1 hr, then transferred to a Schlenk flask. The solvent was removed in vacuo outside the box, leaving an oily residue which was not further purified owing to the extreme air-sensitivity of the phosphinite ligands.

Synthesis of Iridium(I) Complexes:

$[Ir_2]$-CH$_3$, $[Ir_2]$-py$^+$, $[Ir_2]$-CH$_2$-py$^+$, $[Ir_2]$-CH$_2$-Quin$^+$, $[Ir_2]$-CH$_2$-py$^+$-tB, $[Ir_2]$-CH$_2$-py$^+$-Am, $[Ir_2]$-(CH$_2$)$_2$-py$^+$, $[Ir_2]$-3-(CH$_2$)$_2$-py$^+$, and $[Ir_2]$-(CH$_2$)$_3$-py$^+$: The iridium complexes were all synthesized by a similar procedure. A concentrated acetonitrile solution of the phosphinite (2.1 eq) was added to an acetonitrile solution of $[Ir(\mu$-pz*$)(CO)_2]_2$ (1 eq) in the dry box (the scale of this reaction was typically 100-200 mg of $[Ir(\mu$-pz*$)(CO)_2]_2$). An immediate liberation of carbon monoxide gas was observed with a corresponding change in solution color from orange to orange/red. The reaction mixture was stirred for ~2 hrs to ensure complete consumption of the starting materials. CH$_3$CN was removed in vacuo, leaving in all cases an orange/red residue, which was taken up in a minimum of dichloromethane. Addition of excess ethanol to the saturated, deep red solutions precipitated the iridium(I) products as light orange powders. $[Ir_2]$-CH$_3$ Analysis: Calculated for Ir$_2$C$_{50}$H$_{48}$N$_4$O$_4$P$_2$: C, 49.42%; H, 3.98%; N, 4.61%. Found C, 49.19%; H, 3.96%; N, 4.69%. $[Ir_2]$-py$^+$ Analysis: Calculated for Ir$_2$C$_{58}$H$_{52}$F$_{12}$N$_6$O$_4$P$_4$: C, 42.65%; H, 3.21%; N, 5.15%. Found: C, 42.34%; H, 3.18%; N, 4.96%. $[Ir_2]$-CH$_2$-py$^+$ Analysis: Calculated for Ir$_2$C$_{60}$H$_{56}$F$_{12}$N$_6$O$_4$P$_4$: C, 43.38%; H, 3.40%; N, 5.06%. Found: C, 44.26%; H, 3.38% N, 4.60%.

RESULTS and DISCUSSION

The series of donor-acceptor complexes,

$[Ir(\mu\text{-pz}^*)(CO)(Ph_2PO\text{-}C_6H_4\text{-}(CH_2)_n\text{-py}^+\text{-R})]_2(PF_6^-)_2$ (n = 0, 1, 2, 3), and two model

complexes, $[Ir(\mu\text{-pz}^*)(CO)(Ph_2PO\text{-}C_6H_4\text{-Y})]_2$ (Y= CH_3 or $CH_2\text{-Quin}^+PF_6^-$) have been

synthesized, and are shown in Figure 2.4. The syntheses of these iridium complexes were

accomplished in three general steps, outlined in Figure 2.5.

Step 1:

The phenol, **1**, was first synthesized by simple, relatively high yield reactions. Four

classes of phenols, categorized by the number of methylene groups in the molecule, have

been synthesized (n = 0: $HO\text{-}C_6H_4\text{-py}^+$; n = 1: $HO\text{-}C_6H_4\text{-}CH_2\text{-py}^+$,

$HO\text{-}C_6H_4\text{-}CH_2\text{-Quin}^+$, $HO\text{-}C_6H_4\text{-}CH_2\text{-py}^+\text{-tB}$, and $HO\text{-}C_6H_4\text{-}CH_2\text{-py}^+\text{-Am}$;

n = 2: $HO\text{-}C_6H_4\text{-}(CH_2)_2\text{-py}^+$, and $HO\text{-}C_6H_4\text{-}3\text{-}(CH_2)_2\text{-py}^+$; n = 3:

$HO\text{-}C_6H_4\text{-}(CH_2)_3\text{-py}^+$). The synthetic schemes used to prepare the four classes of

compounds are outlined in Figures 2.6 (n = 0), 2.7 (n = 1), and 2.8 (n = 2, 3). The final

step in the synthesis of the pyridinium salts was to metathesize them to their corresponding

hexafluorophosphate salts, in order to enhance the solubility of their corresponding

phosphinite ligands and iridium complexes in organic solvents.

The isolated yield of the n = 0 reaction (Figure 2.6) was approximately 40%.

Attempts to increase the yield of **2** by increasing reaction times were unsuccessful and

served only to produce more byproducts, decreasing the overall yield. This reaction was

also found to be specific to pyridine. Attempts to react substituted pyridines with **1** were

unsuccessful due to the poor solubility of the pyridine in H_2O at 4°C.

The syntheses of n = 1 complexes (Figure 2.7) were complicated by the susceptibility

of the intermediate benzyl bromide to attack by base, specifically, the phenol itself; initial

attempts at preparing this class of compounds were frustrated by the unavoidable

production of polymers. This complication necessitated capping the hydroxy group with a

Figure 2.4. Structures of the phosphinite ligands in the two model complexes and the series of Ir$_2$-py$^+$ donor-acceptor complexes.
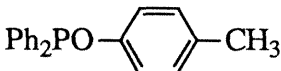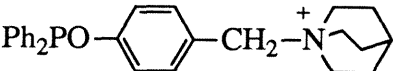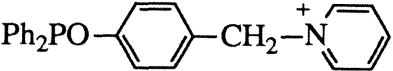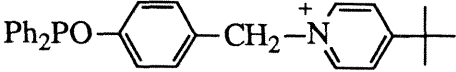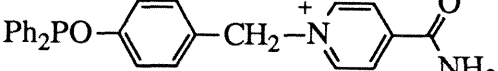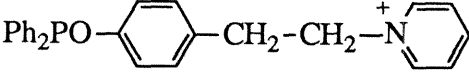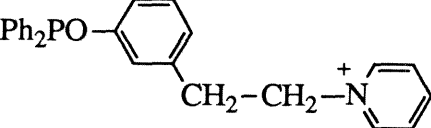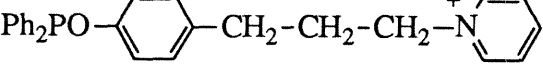
$$[Ir(\mu\text{-pz}^*)(CO)(L)]_2$$

L	Symbol
Ph_2PO—⟨ ⟩—CH_3	$[Ir_2]\text{-}CH_3$
Ph_2PO—⟨ ⟩—CH_2—$\overset{+}{N}$(quinuclidine)	$[Ir_2]\text{-Quin}^+$
Ph_2PO—⟨ ⟩—$\overset{+}{N}$(pyridinium)	$[Ir_2]\text{-py}^+$
Ph_2PO—⟨ ⟩—CH_2—$\overset{+}{N}$(pyridinium)	$[Ir_2]\text{-}CH_2\text{-py}^+$
Ph_2PO—⟨ ⟩—CH_2—$\overset{+}{N}$(pyridinium)—$C(CH_3)_3$	$[Ir_2]\text{-}CH_2\text{-py}^+\text{-tB}$
Ph_2PO—⟨ ⟩—CH_2—$\overset{+}{N}$(pyridinium)—$C(=O)NH_2$	$[Ir_2]\text{-}CH_2\text{-py}^+\text{-Am}$
Ph_2PO—⟨ ⟩—CH_2—CH_2—$\overset{+}{N}$(pyridinium)	$[Ir_2]\text{-}(CH_2)_2\text{-py}^+$
Ph_2PO—⟨ ⟩—CH_2—CH_2—$\overset{+}{N}$(pyridinium) (meta)	$[Ir_2]\text{-}3\text{-}(CH_2)_2\text{-py}^+$
Ph_2PO—⟨ ⟩—CH_2—CH_2—CH_2—$\overset{+}{N}$(pyridinium)	$[Ir_2]\text{-}(CH_2)_3\text{-py}^+$

Figure 2.5. Three step synthesis of Ir$_2$-py$^+$ donor-acceptor complexes. (1) Synthesis of pyridinium phenols. (2) Synthesis of phosphinite ligands. (3) Synthesis of iridium complexes.

$$\text{HO}-\text{C}_6\text{H}_3(\text{Br}) \longrightarrow \longrightarrow \dots \quad \text{HO}-\text{C}_6\text{H}_3(\text{R}) \qquad (1)$$

1

$$\text{HO}-\text{C}_6\text{H}_3(\text{R}) \quad + \quad \text{Ph}_2\text{PNMe}_2 \longrightarrow \text{Ph}_2\text{PO}-\text{C}_6\text{H}_3(\text{R}) \qquad (2)$$

1   **2**

$$(\text{CO})_2\text{Ir}(\mu\text{-pz*})_2\text{Ir}(\text{CO})_2 \quad + \quad \text{Ph}_2\text{PO}-\text{C}_6\text{H}_3(\text{R}) \longrightarrow \qquad (3)$$

$$(\text{R-C}_6\text{H}_4\text{-O-Ph}_2\text{P})(\text{CO})\text{Ir}(\mu\text{-pz*})_2\text{Ir}(\text{CO})(\text{PPh}_2\text{-O-C}_6\text{H}_4\text{-R})$$

3
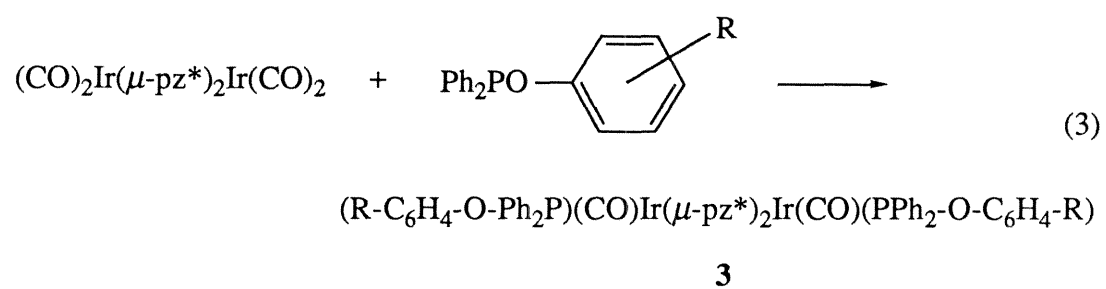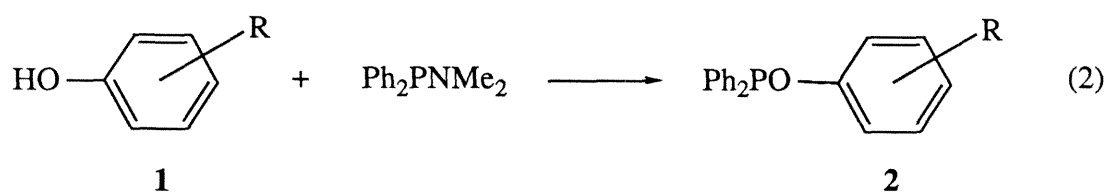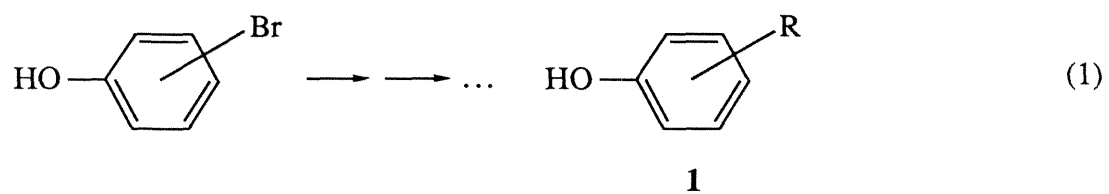
Figure 2.6. Synthesis of complex with $n = 0$.

1   2   3
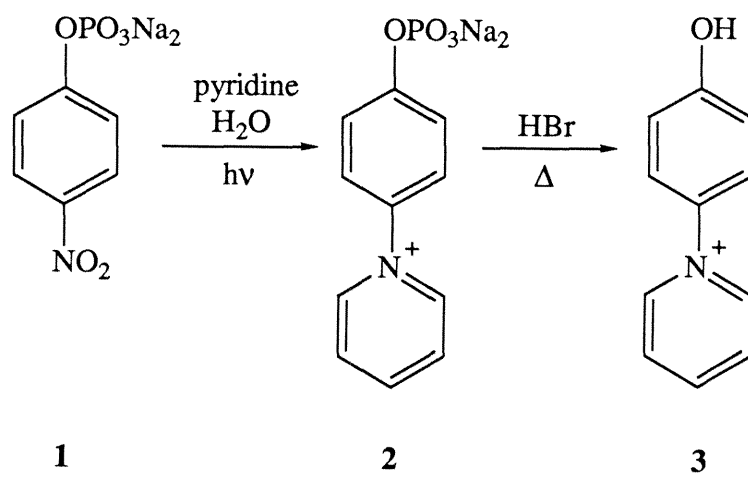
Figure 2.7. Syntheses of complexes with $n = 1$. AcCl = acetyl chloride, Et_3N = triethylamime, NBS = N-bromosuccinimide, t-BuOOH = *tert*-butyl hydroperoxide.
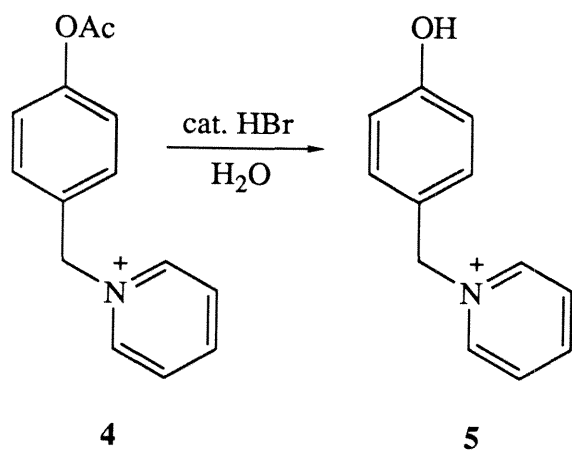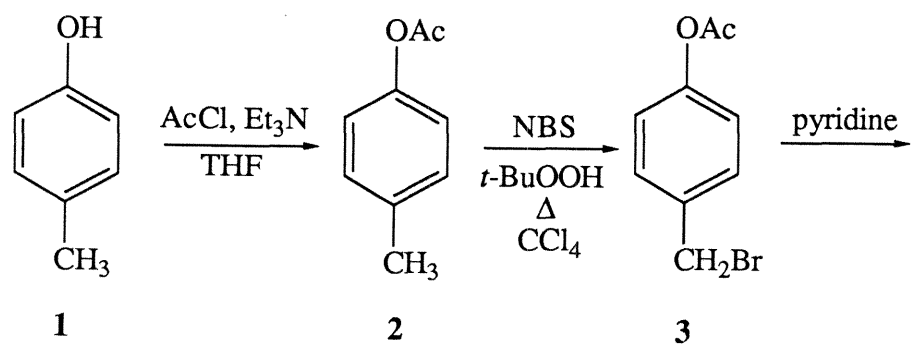
Figure 2.8. Syntheses of complexes with $n = 2$ and $n = 3$.

$$OH{-}\!\!\bigcirc\!\!{-}(CH_2)_n{-}OH \xrightarrow[\Delta]{HBr} OH{-}\!\!\bigcirc\!\!{-}(CH_2)_n{-}Br \xrightarrow{pyridine}$$

1   **2**

$$OH{-}\!\!\bigcirc\!\!{-}(CH_2)_n{-}\overset{+}{N}\!\!\bigcirc$$

3
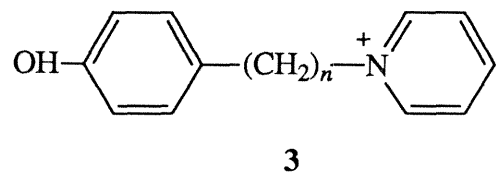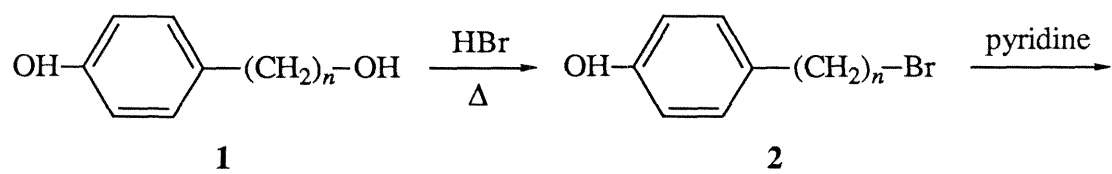
protecting group until the benzyl bromide was converted into the corresponding pyridinium salt, at which point the protecting group was hydrolyzed off.

The reactions used to synthesize complexes with $n = 2$ and 3 (Figure 2.8) are straightforward and will not be discussed further.

Characterization of Phenols:

Each of the phenols was characterized by ^{1}H and ^{31}P NMR spectroscopy. These data are summarized in Table 2.1, and the corresponding numbering scheme is shown in Figure 2.9. The 1,4-phenylene groups of all the molecules exhibit the characteristic AA'BB' doublet of doublets between 6.6 and 7.5 ppm, the precise chemical shift of which depends on the nature of the 4-substituent (columns *j* and *k* in Table 2.1). The methylene groups in $n = 1$ compounds show up as singlets shifted downfield (~5.5 ppm) by the effect of the positive charge on the adjacent pyridinium cation (column *m*). For $n = 2$ and 3 compounds, the methylene resonance closest to the pyridinium is a triplet at ~4.5 ppm, while the remaining resonances are in normal positions (2.2 to 3.2 ppm). The pyridinium resonances are resolved for each unique position (2-position: 8.45-8.81 ppm; 3-position: 7.78-8.23 ppm; 4-position: 8.30-8.59 ppm).

Step 2:

The next step was the alcoholysis of *N*, *N*-dimethyl-*P*, *P*-diphenylphosphine by the phenol synthesized in Step 1.[31] This transformation was carried out in a dry box. The phosphinite product was isolated but not purified for the next step. Characterization by ^{31}P NMR was conducted, showing single peaks between 109.8 and 112.6 ppm for each compound (first column of Table 2.2), identifying the ligands as esters of diphenylphosphinous acid.[33]

Figure 2.9. Numbering scheme used in assigning ^{1}H NMR spectra of phenols. *j* and *k* are phenylene protons; *m*, *n*, and *o* are methylene protons; *p*, *q*, and *r* are pyridinium protons; *s*, *t*, and *u* are quinuclidine protons; and *v* are the methyl protons of the *tert*-butyl group.
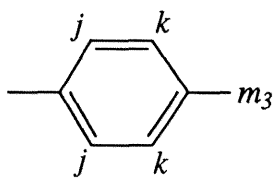
$HO\text{-}C_6H_4\text{-}CH_3$
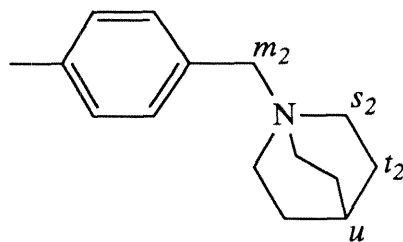
$HO\text{-}C_6H_4\text{-}CH_2\text{-}Quin^+$
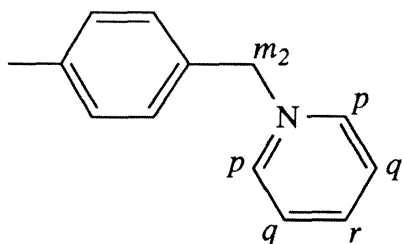
$HO\text{-}C_6H_4\text{-}CH_2\text{-}py^+$
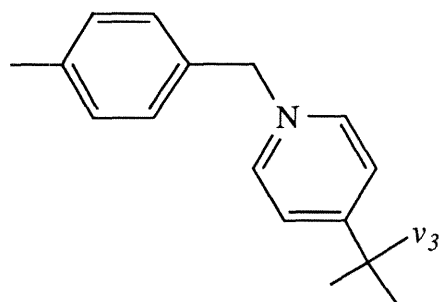
$HO\text{-}C_6H_4\text{-}CH_2\text{-}py^+\text{-}tB$
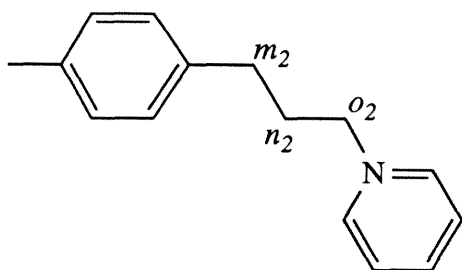
$HO\text{-}C_6H_4\text{-}(CH_2)_3\text{-}py^+$
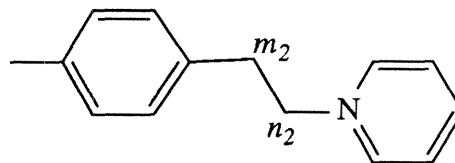
$HO\text{-}C_6H_4\text{-}(CH_2)_2\text{-}py^+$

Table 2.1. ^{1}H NMR Resonances for Phenols ^{e}

Compounds	j	k	m	n	o	p(s)	q(t)	r(u)	v
HO-C$_6$H$_4$-CH$_3$	7.04	7.10	—	—	—	—	—	—	—
HO-C$_6$H$_4$-CH$_2$-Quin$^+$	6.82	7.10	4.08	—	—	3.31 (t)	—^{b}	1.88 (m)	—
HO-C$_6$H$_4$-py$^+$	7.07	7.51	—	—	—	8.81 (d)	8.11 (t)	8.59 (t)	—
HO-C$_6$H$_4$-CH$_2$-py$^+$	6.88	7.32	5.60	—	—	8.68 (d)	7.98 (t)	8.48 (t)	—
HO-C$_6$H$_4$-CH$_2$-py$^+$-Am	6.89	7.34	5.64	—	—	8.80	8.23 (d)	—	—
HO-C$_6$H$_4$-CH$_2$-py$^+$-tB ^{a}	—^{c}	—^{c}	5.31	—	—	8.31	7.81 (d)	—	1.38
HO-C$_6$H$_4$-(CH$_2$)$_2$-py$^+$	6.70	6.93	4.69 (t)	3.16 (t)	—	8.43 (d)	7.92 (t)	8.48 (t)	—
HO-C$_6$H$_4$-3-(CH$_2$)$_2$-py$^+$	—^{d}	—^{d}	4.73 (t)	3.18 (t)	—	8.45 (d)	7.93 (t)	8.38 (t)	—
HO-C$_6$H$_4$-(CH$_2$)$_3$-py$^{+\,a}$	6.58	6.89	4.39 (t)	2.17 (q)	2.48 (t)	8.53 (d)	7.78 (t)	8.30 (t)	—

^{a} Bromide salt in D$_2$O.

^{b} Obscured by phenyl resonances.

^{c} Obscured by resonances from Ph$_4$B$^-$ which are at 6.95 and 7.30 ppm.

^{d} The phenylene resonances are 7.20 (s), 7.11 (s), 7.02 (s), 6.73 (br,s), and 6.55 (m).

^{e} The splitting patterns are given in parentheses; a singlet is inferred unless otherwise indicated.

Table 2.2. ^{31}P NMR Resonances for Phosphinite Ligands and Iridium Complexes

R	Ph$_2$PO-C$_6$H$_4$-R	[Ir$_2$]-R
-CH$_3$ ^{a}	109.8	100.4
-Quin$^+$	110.4	—^{b}
-py$^+$	112.6	103.6
-CH$_2$-py$^+$	111.2	102.5
-CH$_2$-py$^+$-Am	110.9	102.3
-CH$_2$-py$^+$-tB	110.4	102.5
-(CH$_2$)$_2$-py$^+$	110.3	101.0
-(CH$_2$)$_3$-py$^+$	—^{b}	100.6

^{a} In d$_6$-acetone.

^{b} These values were not obtained.

Step 3:

The series of iridium(I) donor-acceptor complexes and corresponding model compounds were prepared using procedures similar to those described previously for an analogous series of pyrazolyl-bridged phosphinite iridium dimers.[31] Two equivalents of the phosphinite ligand were added to a solution of $[Ir(\mu\text{-pz}^*)(CO)_2]_2$ in acetonitrile at room temperature and the immediate liberation of carbon monoxide gas followed by a darkening of the solution from orange to orange/red indicated the formation of the pyrazolyl-bridged dicarbonylbisphosphinite iridium(I) dimer. As observed previously in phosphine reactions with analogous metal complexes,[34] the phosphinite added in a transoid fashion. The *trans* configuration of the terminal ligands has a pronounced effect on the ^1H NMR resonances. There are two separate resonances for the methyl substituents on the pyrazolyl bridge (~1.97 and ~2.10 ppm). As expected, the NMR spectra also reveal two magnetically inequivalent phenyl groups. These NMR data are summarized in Table 2.3, and the numbering scheme is shown in Figure 2.10. An ^1H NMR spectrum of the model complex, $[Ir_2]$-CH_3, is provided in Figure 2.11, showing the inequivalent phenyl and pyrazolyl methyl resonances as well as the AA'BB' doublet of doublets for the phenylene proton resonances (see Table 2.3 for chemical shifts).

^{31}P NMR revealed a singlet for each complex with chemical shifts between 100.4 and 103.6 ppm (second column of Table 2.2), consistent with coordination of the phosphinite ligands to an Ir(I) metal center.[35]

The solution IR spectrum of $[Ir_2]$-CH_3, given in Figure 2.12, reveals a single strong band at 1966 cm^{-1}, corresponding to the carbonyl C-O stretching mode. This is comparable to the value of 1955 cm^{-1} for the analogous compound, $[Ir(\mu\text{-pz}^*)(CO)(Ph_2PO\text{-}C_2H_4\text{-py}^+)]_2(Ph_4B^-)_2$.

Figure 2.10. Numbering scheme used in assigning ^{1}H NMR spectra of iridium complexes. a and b are the methyl protons on the pyrazolyl bridge; c is the proton in the 4-position on the pyrazolyl bridge; d, e, f, g, h, and i are the phenyl protons; j and k are the phenylene protons; and remaining protons m-v are as shown in Figure 2.9.
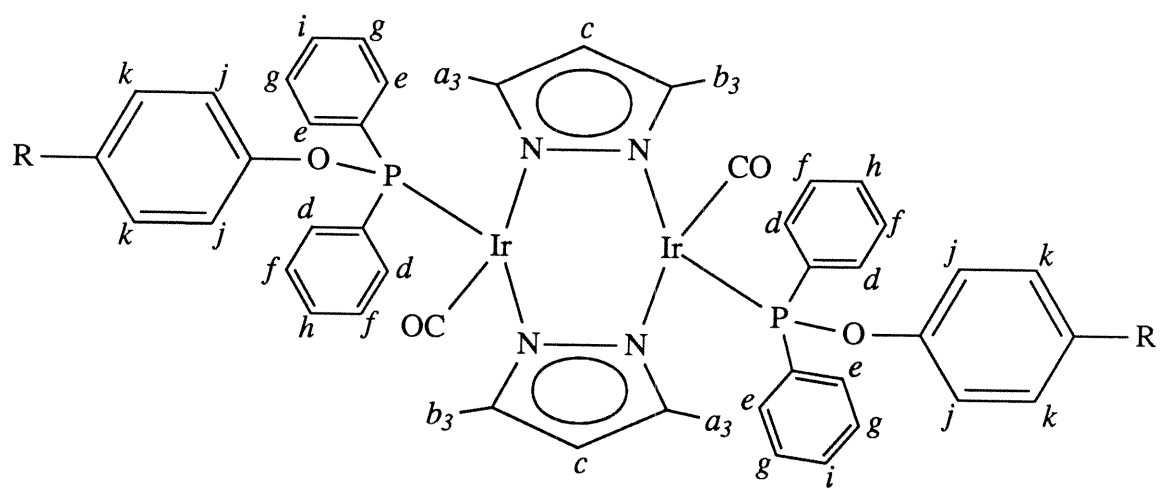
Table 2.3. ^{1}H NMR Resonances for Iridium Complexes

R	a	b	c	d	e	f, g, h, i	j	k
[Ir$_2$]-CH$_3$ ^{a}	1.97	2.14	5.37	7.96	8.28	7.24, 7.48	7.13	7.24
[Ir$_2$]-py$^+$	1.97	2.14	5.46	7.95	8.20	7.50	7.64	7.84
[Ir$_2$]-CH$_2$-py$^+$	1.95	2.00	5.38	7.89	8.17	7.43	6.95	—^{b}
[Ir$_2$]-CH$_2$-py$^+$-Am	1.95	2.18	5.59	—^{b}	—^{b}	—^{b}	6.91	—^{b}
[Ir$_2$]-CH$_2$-py$^+$-tB	1.97	2.00	5.38	7.89	8.18	7.43	6.82	—^{b}
[Ir$_2$]-(CH$_2$)$_2$-py$^+$	1.96	2.12	5.43	7.90	8.19	7.24,7.45	7.08	7.53
[Ir$_2$]-(CH$_2$)$_3$-py$^+$	1.95	2.10	5.39	7.90	8.21	7.42	7.16	7.52

R	m	n	o	p	q	r	s	t	u	v
[Ir$_2$]-CH$_3$ ^{a}	2.27	—	—	—	—	—	—	—	—	—
[Ir$_2$]-py$^+$	—	—	—	8.82	8.16	8.66	—	—	—	—
[Ir$_2$]-CH$_2$-py$^+$	5.65	—	—	8.67	7.98	8.51	—	—	—	—
[Ir$_2$]-CH$_2$-py$^+$-Am	5.62	—	—	8.75	8.24	—	—	—	—	—
[Ir$_2$]-CH$_2$-py$^+$-tB	5.59	—	—	8.55	7.95	—	—	—	—	1.35
[Ir$_2$]-(CH$_2$)$_2$-py$^+$	4.72	3.23	—	8.46	7.91	8.45	—	—	—	—
	(t)	(t)		(d)	(q)	(t)				
[Ir$_2$]-(CH$_2$)$_3$-py$^+$	4.50	2.30	2.67	8.62	7.99	8.48	—	—	—	—
	(t)	(q)	(t)	(d)	(t)	(t)				

^{a} In d$_6$-acetone.

^{b} Obscured by phenyl resonances.

Figure 2.11. ^{1}H NMR (400 MHz) spectrum of [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-CH$_3$)]$_2$ in CD$_3$CN, showing inequivalent pyrazolyl methyl resonances at 1.97 and 2.14 ppm, and *o*-phenyl resonances at 7.96 and 8.28 ppm, indicating transoid configuration of terminal phosphinite ligands.

PPM
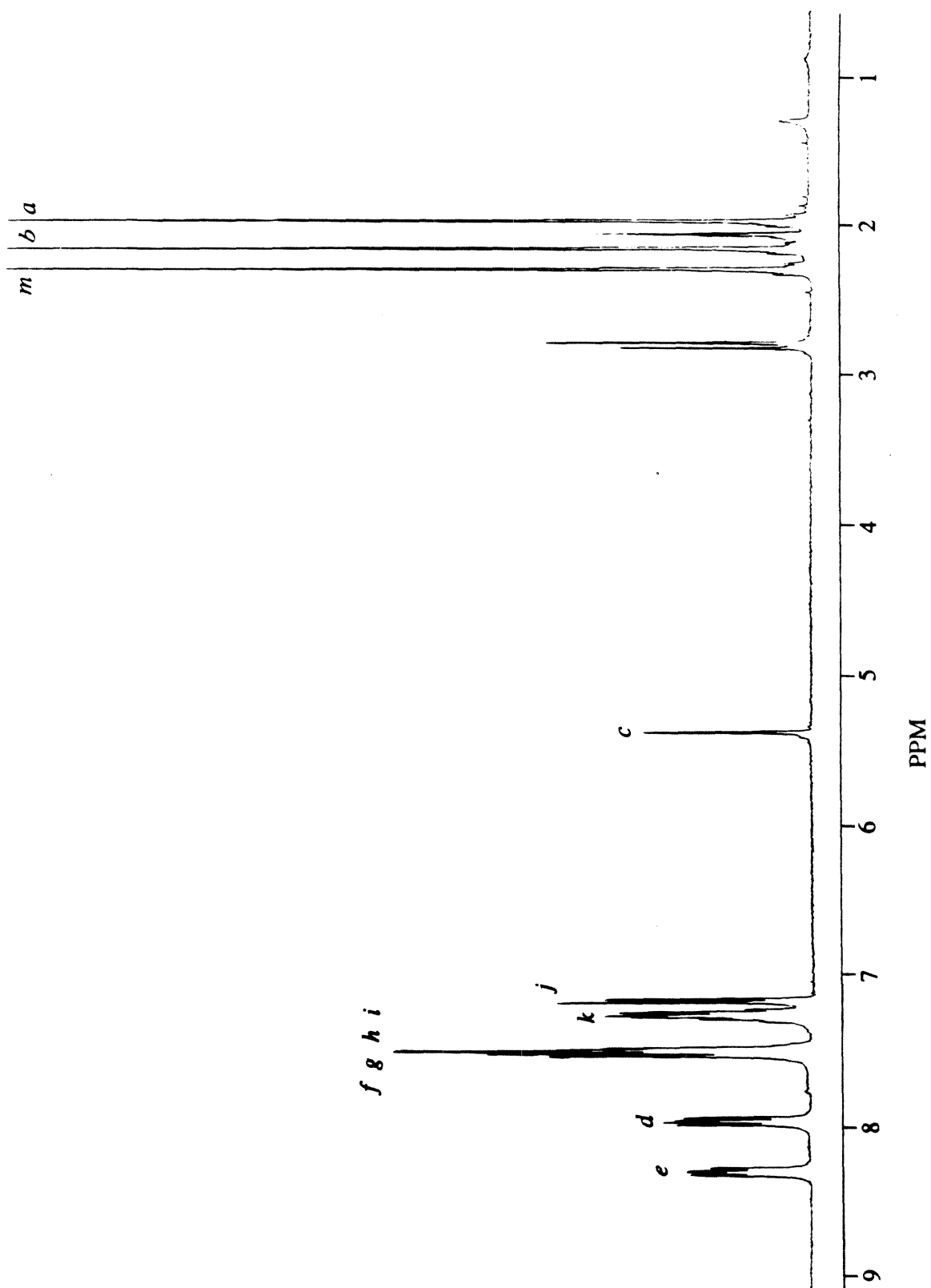
Figure 2.12. Solvent subtracted IR spectrum of Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-CH$_3$)]$_2$ in CH$_2$Cl$_2$, showing single CO band at 1966 cm^{-1}. Other unassigned bands appear at 2350 (d), 1506, 1437, 1206 (d), 1166, and 1102 cm^{-1}. The large feature at ~1270 cm^{-1} corresponds to an intense solvent (CH$_2$Cl$_2$) band assigned.
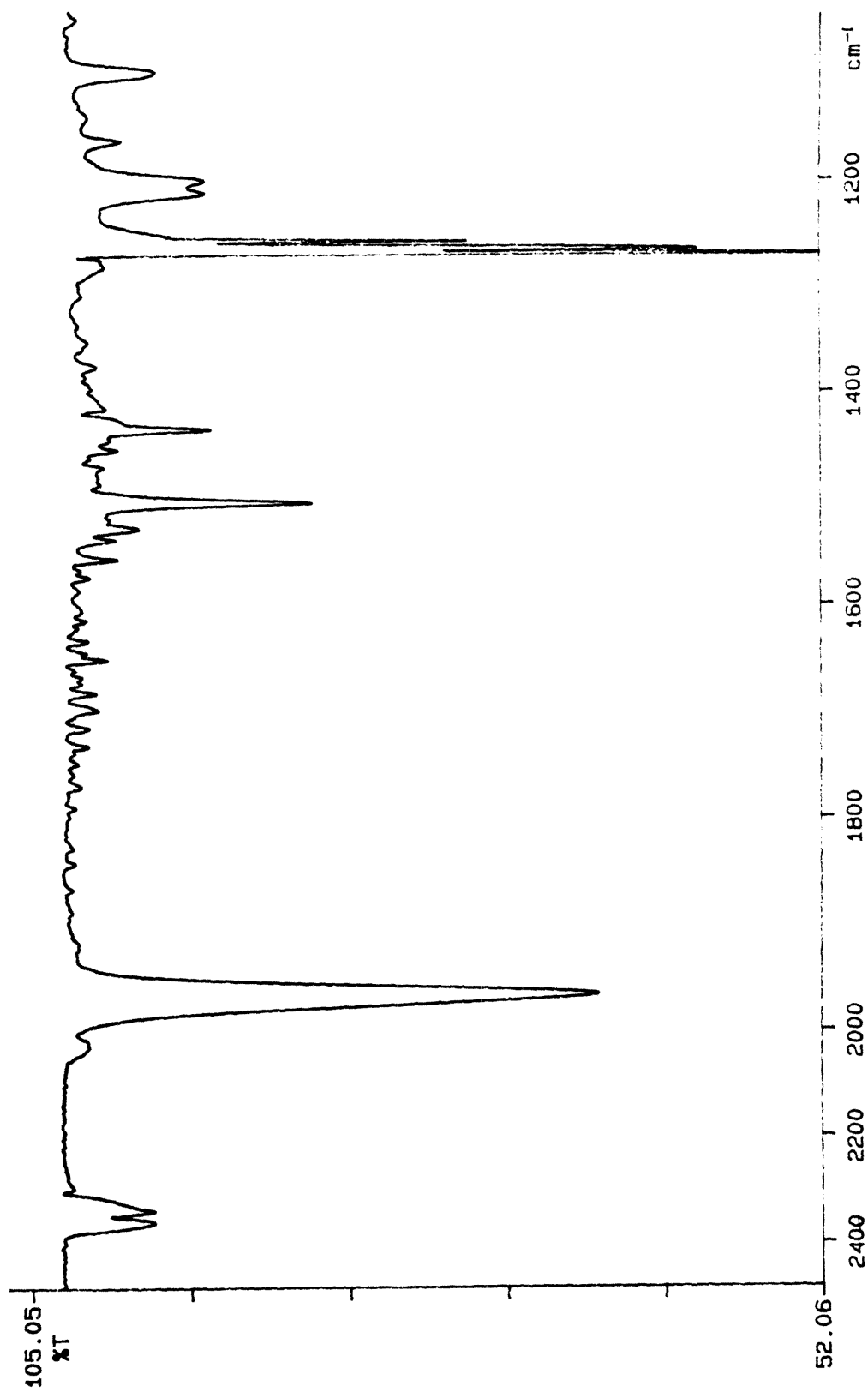
CONCLUDING REMARKS

The synthetic methodology used to prepare the series of donor-acceptor complexes, $[Ir(\mu\text{-}pz^*)(CO)(Ph_2PO\text{-}C_6H_4\text{-}(CH_2)_n\text{-}py^+\text{-}R)]_2(PF_6^-)_2$, can be applied to the preparation of a wider class of donor-acceptor complexes. Three features of these complexes make this an attractive prospect: (1) the phosphinite ligand containing the electron acceptor can be attached to a large variety of chromophores with metal centers that bind phosphines; (2) the nature of the bridge can also be easily varied by either completely replacing the phenylene group or by simple substitution directly on the phenylene group; (3) and the pyridinium acceptor can be replaced with other one-electron acceptors by utilizing similar synthetic methods as described in the previous sections. Research involving the preparation and study of new ligands and complexes is currently being pursued in our laboratory.

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Chapter 3

X-ray Crystal Structure and
Molecular Mechanics Calculations

INTRODUCTION

A main goal of our research is to understand how structural parameters such as distance and orientation affect excited-state and thermal electron-transfer rates in linked donor-acceptor complexes. The series of Ir_2-py^+ donor-acceptor complexes, described in the previous chapter, were prepared with this goal in mind. A study aimed at correlating donor-acceptor distance and orientation to electron-transfer rates must clearly involve a detailed investigation of their solution structures.[1,2] We have therefore obtained conceivable solution structures for the series of donor-spacer-acceptor complexes, $[Ir(\mu\text{-}pz^*)(CO)(Ph_2PO\text{-}C_6H_4\text{-}(CH_2)_n\text{-}py^+)]_2$ (n = 0, 1, 2, and 3). This was accomplished by using data from an X-ray crystal structure of *one* model complex as a basis for constructing the remaining Ir_2-py^+ complexes by computer modeling (in most cases two distinct low energy structures were proposed to exist in solution).

In this chapter, the X-ray crystal structure determination of $[Ir(\mu\text{-}pz^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}CH_3)]_2$ is presented, followed by a description of the molecular mechanics calculations conducted on the four general classes of Ir_2-py^+ donor-acceptor complexes (n = 0, 1, 2, and 3). The results of these calculations will be discussed in relation to donor-acceptor electronic couplings in Chapter 5.

EXPERIMENTAL

X-Ray Structure Determination:

Slow evaporation of a methylene chloride/acetonitrile solution produced acicular crystals of $[Ir(\mu\text{-}pz^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}CH_3)]_2$. A section, cut from a needle, was coated with epoxy to prevent reaction with air and solvent loss. Unit cell parameters and an orientation matrix were obtained on a CAD-4 diffractometer by a least squares calculation from the setting angles of 24 reflections with $30° < 2\theta < 33°$. Two equivalent data sets out

to a 2θ of 45° were collected. The data were corrected for a slight decay in intensity. Since calculated absorption correction increased goodness of fit (GOF) for merging, an absorption coefficient 30% of the calculated value was used (this value was found to minimize GOF for merging). Lorentz and polarization factors were applied and the two data sets were then merged to yield the final data set. Preliminary Weissenberg photographs and systematic absences in the diffractometer data revealed the space group to be $P2_1/c$.

Hydrogen atom positions were determined from difference maps for the methyl groups and by calculation for the remainder. All hydrogen atoms were placed at 0.95 Å from the attached carbon atom and given isotropic B values 20% greater than that of the attached atom. No hydrogen parameters were refined.

Analysis of a Patterson map provided the iridium atom coordinates. The electron density maps indicated the presence of a dichloromethane solvent molecule. The remaining non-hydrogen atoms were located via successive structure factor-Fourier calculations. The complete least squares full matrix, consisting of spatial and anisotropic thermal parameters for the non-hydrogen atoms, a population factor for the solvent molecule, and a scale factor, contained 588 parameters. A final difference Fourier map showed deviations ranging from -0.64 e$Å^{-3}$ to +0.78 e$Å^{-3}$. The refinement converged with an R-factor of 0.0316 (0.0235 for $F_o^2 > 3\sigma(F_o^2)$) and a goodness of fit of 1.46 for all 6662 reflections.

Calculations were done with programs of the CRYM Crystallographic Computing System and ORTEP. Scattering factors and corrections for anomalous scattering were taken from a standard reference.[3] $R = \Sigma|F_o - |F_c||/\Sigma F_o$, for only $F_o^2 > 0$, and goodness of fit = $[\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of data and p the number of parameters refined. The function minimized in least squares was $\Sigma w(F_o^2 - F_c^2)^2$, where w = $1/\sigma^2(F_o^2)$. Variances of the individual reflections were assigned based on counting statistics plus an additional term, $(0.014I)^2$. Variances of the merged reflections were determined by standard propagation of error plus another additional term, $(0.014\langle I\rangle)^2$. The

absorption correction was done by Gaussian integration over an $8 \times 8 \times 8$ grid. Transmission factors varied from 0.39 to 0.54.

Molecular Mechanics Calculations:

Molecular mechanics calculations were carried out on the full series of donor-acceptor complexes using Biograf (the molecular design and analysis program from Biodesign Inc.).[4] version 2.10 with the Dreiding force field. Atomic positions from the X-ray structure of $[Ir(\mu\text{-}pz^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}CH_3)]_2$, $[Ir_2]\text{-}CH_3$, were used as a base upon which the remaining portion of the bridge and pyridinium group were constructed. Energy minimizations of the computer constructed complexes were carried by holding the iridium core atomic coordinates fixed (both Ir atoms, the entire 3,5-dimethylpyrazolyl bridges, and the phosphorous atoms and attached phenyl groups and oxygens), and allowing the atoms of the phenylene groups, the hydrocarbon chains, and the pyridinium groups to be adjustable.

RESULTS and DISCUSSIONS

X-ray Structure:

The structure of dicarbonylbis(μ-3,5-dimethylpyrazolyl)bis(O-4-tolyl-P,P-diphenyl-phosphinite)diiridium(I) ($[Ir_2]\text{-}CH_3$), $Ir_2C_{50}H_{48}N_4O_4P_2\cdot CH_2Cl_2$, has been determined by X-ray diffraction techniques. The molecule crystallized in the monoclinic system, in the space group $P2_1/c$ (#14), with $a = 18.677(2)$ Å, $b = 13.817(1)$ Å, $c = 20.225(3)$ Å, $\beta = 101.37(1)°$, volume $= 5116.8(10)$ Å^3; $Z = 4$ and density $= 1.688$ g cm^{-3}. Crystallographic data are summarized in Table 3.1.

ORTEP diagrams showing the iridium coordination sphere and ligand geometry are presented in Figures 3.1a and b. The atomic numbering scheme is given in Figure 3.2. Selected bond lengths and angles are provided in Table 3.2. All other data pertaining to

Table 3.1. Crystallographic Data for $[Ir(\mu\text{-pz}^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}CH_3)]_2$

Formula: $Ir_2C_{50}H_{48}N_4O_4P_2 \cdot CH_2Cl_2$

$a = 18.677(2)$ Å

$b = 13.817(1)$ Å

$c = 20.225(3)$ Å

$\beta = 101.27(1)°$

$V = 5116.8(10)$ Å^3

Space Group: $P2_1/c$ (#14)

$T = 293°K$

$\lambda = 0.7107$ Å

$\rho_{calc} = 1.688$ g cm^{-3}

$\mu = 57.28$ cm^{-1}

Transmission coeff. $= 0.39 - 0.54$

$R(F_o) = 0.316$

GOF $= 1.46$

Figure 3.1. (a) ORTEP diagram of [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-CH$_3$)]$_2$, showing the nearly eclipsed 3,5-dimethylpyrazolyl groups. (b) A second view of the same complex, showing the square planar coordination of Ir and the *trans* CO and phosphinite ligands. For the sake of clarity, the four phenyl groups have not been shaded.
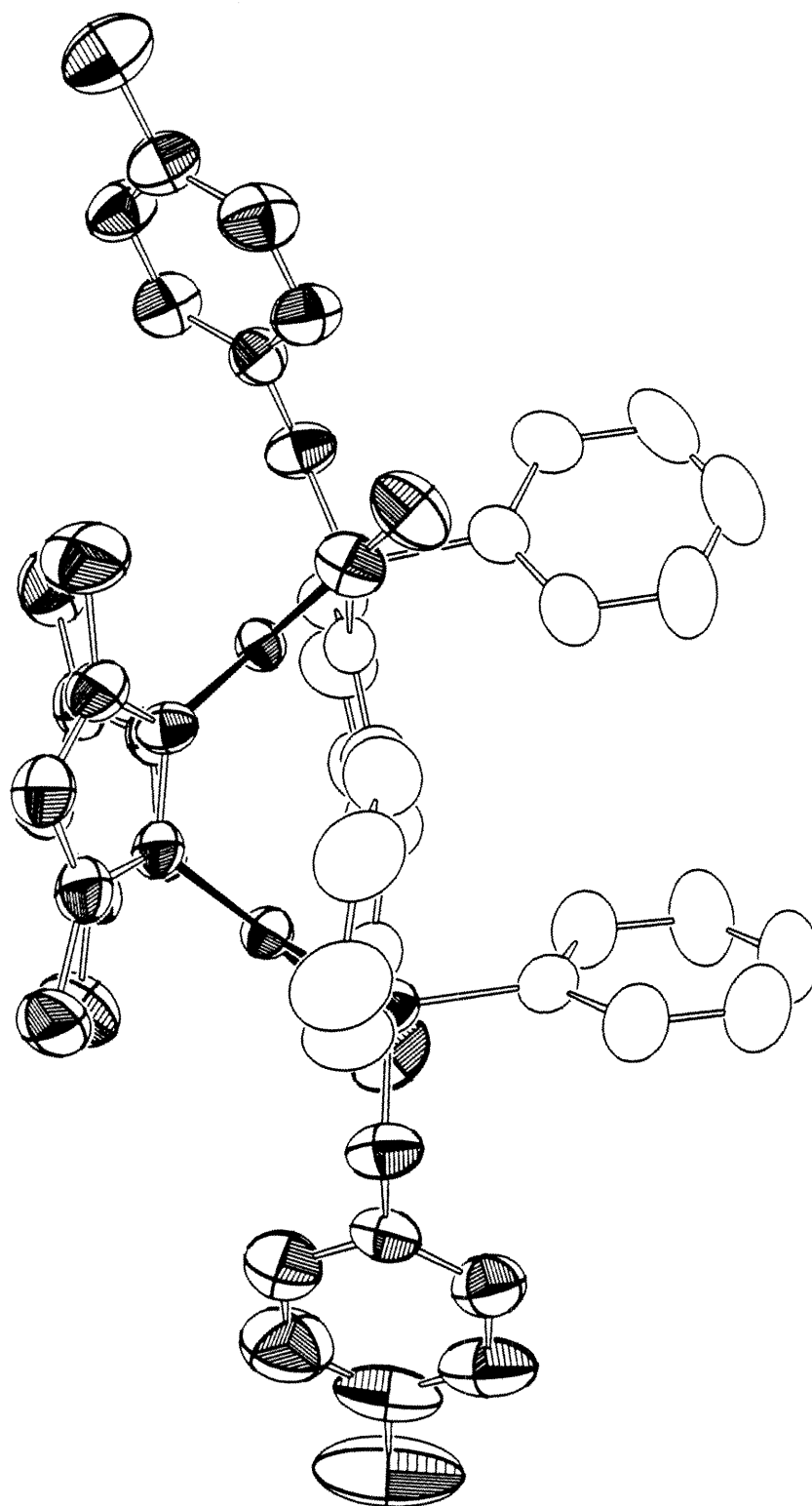
a
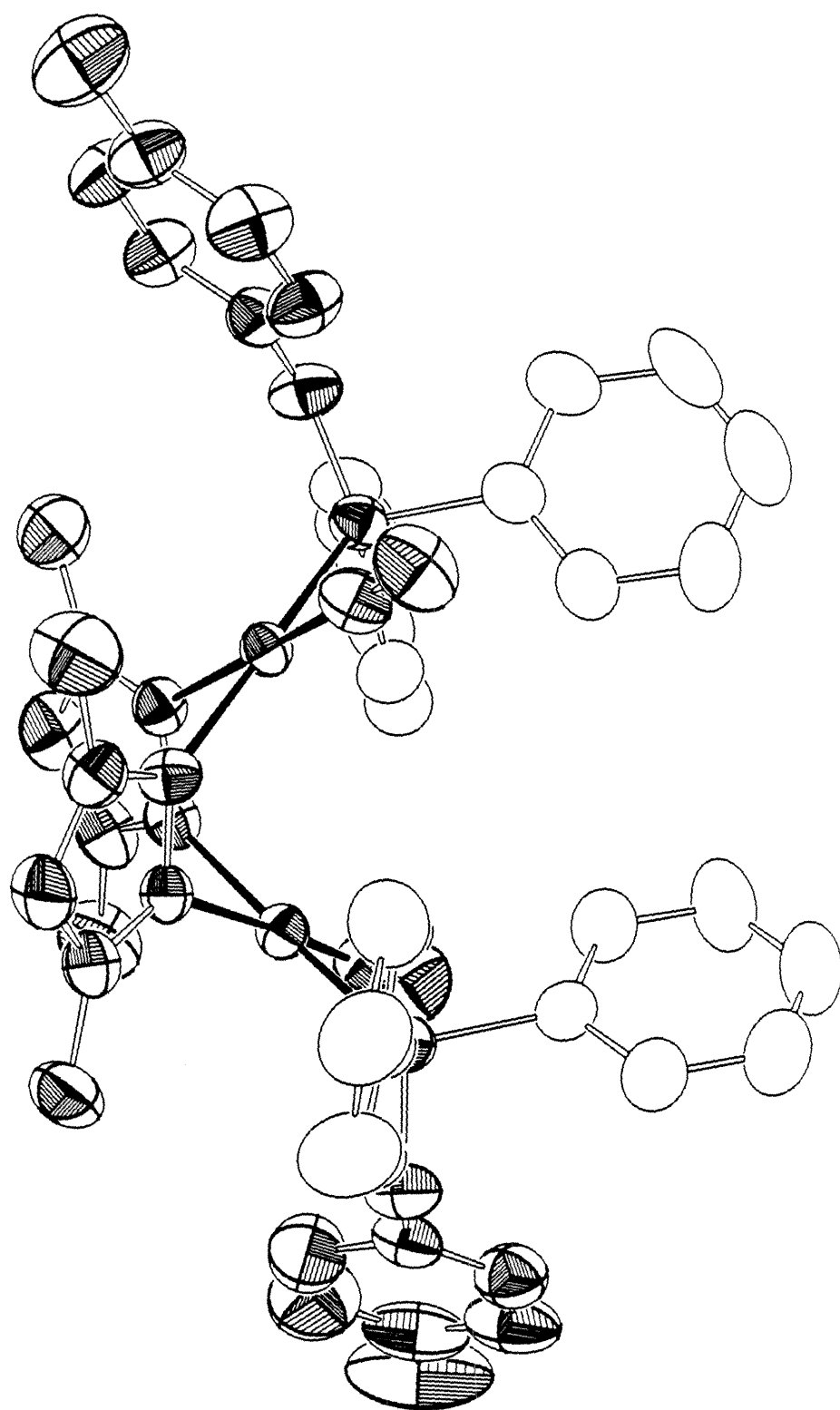
b

Figure 3.2. Atomic number scheme for [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-CH$_3$)]$_2$.
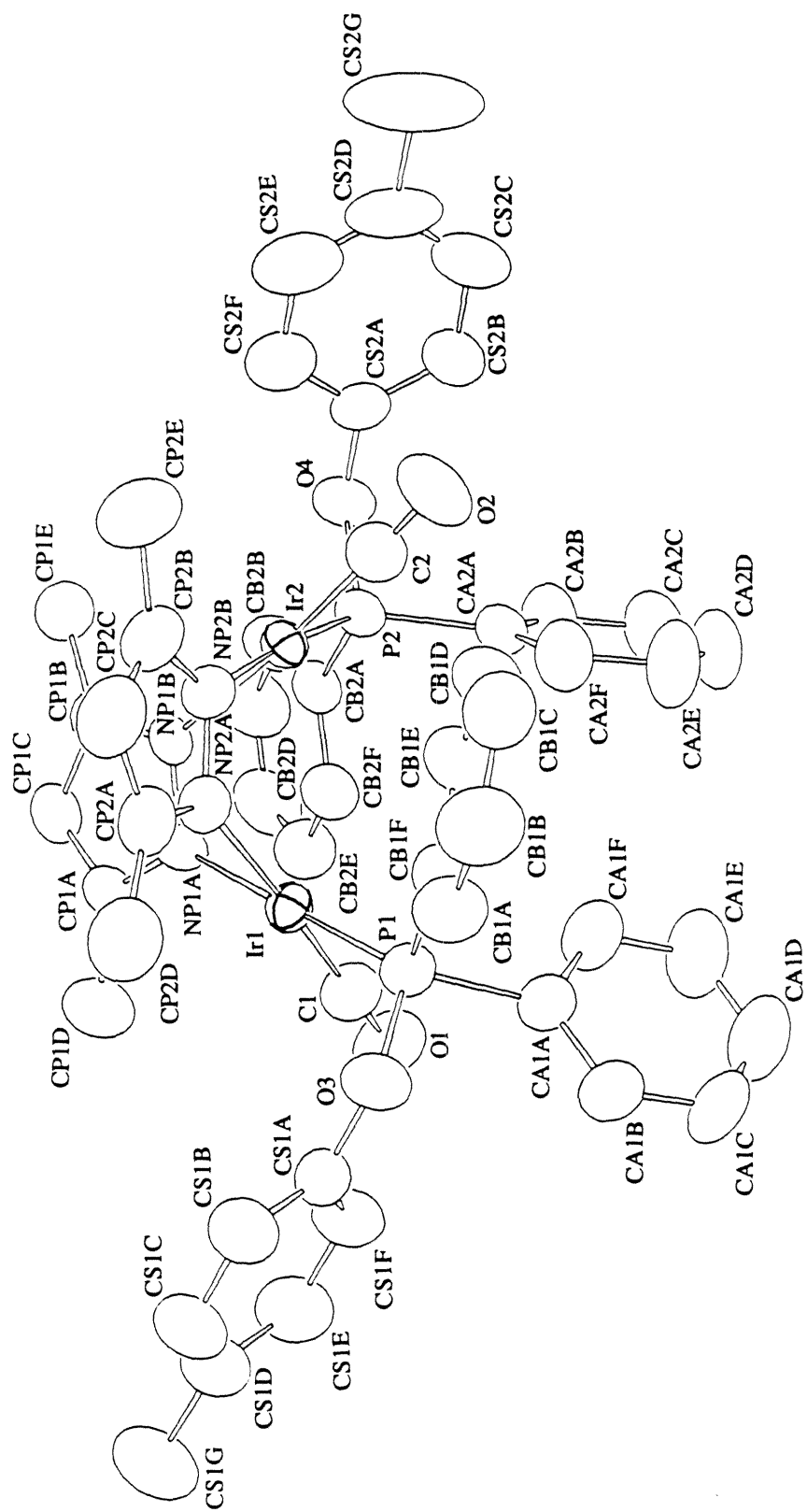
Table 3.2. Selected Bond Lengths and Angles for

$[Ir(\mu\text{-}pz^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}CH_3)]_2$
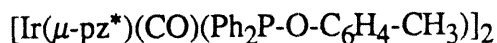
Iridium Coordination Sphere

Distance(Å)			Angle(°)		
Ir1 – Ir2	3.307(1)	NP1A – Ir1 –	NP2A	85.1(2)
Ir1 – C1	1.797(6)	NP1A – Ir1 –	C1	91.6(2)
Ir2 – C2	1.810(6)	P1 – Ir1 –	C1	91.0(2)
Ir1 – P1	2.224(1)	P1 – Ir1 –	NP2A	92.3(1)
Ir2 – P2	2.224(1)	NP2A – Ir1 –	C1	176.3(2)
Ir1 – NP1A	2.075(4)	P1 – Ir1 –	NP1A	177.4(1)
Ir2 – NP1B	2.068(4)	NP1B – Ir2 –	NP2B	83.1(2)
Ir1 – NP2A	2.091(4)	NP2B – Ir2 –	C2	92.9(2)
Ir2 – NP2B	2.073(4)	P2 – Ir2 –	C2	91.8(2)
		P2 – Ir2 –	NP1B	92.5(1)
		NP1B – Ir2 –	C2	174.1(2)
		P2 – Ir2 –	NP2B	174.2(1)
		Ir1 – NP1A –	NP1B	117.9(3)
		Ir1 – NP2A –	NP2B	117.2(3)
		Ir2 – NP1B –	NP1A	117.1(3)
		Ir2 – NP2B –	NP2A	118.0(3)
		NP1A – Ir1 –	Ir2	61.7(1)
		NP2A – Ir1 –	Ir2	62.2(1)
		P1 – Ir1 –	Ir2	117.0(1)
		C1 – Ir1 –	Ir2	117.4(2)
		NP1B – Ir2 –	Ir1	62.3(1)
		NP2B – Ir2 –	Ir1	62.5(1)
		P2 – Ir2 –	Ir1	112.1(1)
		C2 – Ir2 –	Ir1	119.6(2)

CO Ligands

Distance(Å)			Angle(°)		
C1 – O1	1.174(7)	O1 – C1 – Ir1	179.3(5)
C2 – O2	1.165(7)	O2 – C2 – Ir2	178.0(5)

Pyrazole Ligands

Distance(Å)		Angle(°)	
NP1A – NP1B	1.370(6)	Ir1 – NP1A –CP1A	135.1(3)
NP1A – CP1A	1.349(7)	CP1A – NP1A –NP1B	106.8(4)
NP1B – CP1B	1.334(7)	CP1B – NP1B –NP1A	109.3(4)
CP1A – CP1C	1.371(8)	Ir2 – NP1B –CP1B	133.0(3)
CP1A – CP1D	1.493(9)	CP1C – CP1A –NP1A	109.2(5)
CP1B – CP1C	1.377(8)	CP1D – CP1A –NP1A	120.8(5)
CP1B – CP1E	1.494(8)	CP1D – CP1A –CP1C	130.0(5)
NP2A – NP2B	1.376(6)	CP1C – CP1B –NP1B	108.2(5)
NP2A – CP2A	1.337(7)	CP1E – CP1B –NP1B	120.8(5)
NP2B – CP2B	1.332(7)	CP1E – CP1B –CP1C	130.9(5)
CP2A – CP2C	1.365(9)	CP1B – CP1C –CP1A	106.5(5)
CP2A – CP2D	1.488(9)	Ir1 – NP2A –CP2A	134.3(4)
CP2B – CP2C	1.377(9)	CP2A – NP2A –NP2B	108.4(4)
CP2B – CP2E	1.493(9)	CP2B – NP2B –NP2A	107.4(4)
		Ir2 – NP2B –CP2B	134.5(4)
		CP2C – CP2A –NP2A	108.6(5)
		CP2D – CP2A –NP2A	121.6(5)
		CP2D – CP2A –CP2C	129.7(6)
		CP2C – CP2B –NP2B	109.1(5)
		CP2E – CP2B –NP2B	121.5(5)
		CP2E – CP2B –CP2C	129.5(6)
		CP2B – CP2C –CP2A	106.5(5)

Phosphinite Ligands

	Distance(Å)				Angle(°)
P1 – O3	1.629(4)	Ir1	– P1 –	O3	119.3(1)
P2 – O4	1.633(4)	Ir1	– P1 –	CA1A	116.5(2)
P1 – CA1A	1.817(5)	Ir1	– P1 –	CB1A	116.4(2)
P1 – CB1A	1.820(5)	CB1A	– P1 –	CA1A	101.7(2)
P2 – CA2A	1.826(5)	Ir2	– P2 –	O4	119.7(1)
P2 – CB2A	1.815(5)	Ir2	– P2 –	CA2A	116.2(2)
O3 – CS1A	1.410(6)	Ir2	– P2 –	CB2A	117.8(2)
O4 – CS2A	1.404(7)	CB2A	– P2 –	CA2A	102.1(2)
CS1D – CS1G	1.512(9)	CA1B	– CA1A –	P1	122.2(4)
CS2D – CS2G	1.524(14)	CA1F	– CA1A –	P1	119.4(4)
		CB1B	– CB1A –	P1	117.6(4)
		CB1F	– CB1A –	P1	124.0(4)
		CA2B	– CA2A –	P2	119.9(4)
		CA2F	– CA2A –	P2	122.0(4)
		CB2B	– CB2A –	P2	117.5(4)
		CB2F	– CB2A –	P2	123.0(4)
		CA1A	– P1 –	O3	102.4(2)
		CB1A	– P1 –	O3	97.5(2)
		CS1A	– O3 –	P1	125.9(3)
		CA2A	– P2 –	O4	101.8(2)
		CB2A	– P2 –	O4	95.8(2)
		CS2A	– O4 –	P2	121.0(3)
		CS1B	– CS1A –	O3	116.5(5)
		CS1F	– CS1A –	O3	122.7(5)
		CS2B	– CS2A –	O4	119.5(5)
		CS2F	– CS2A –	O4	119.6(5)
		CS1G	– CS1D –	CS1C	121.6(6)
		CS1G	– CS1D –	CS1E	120.9(6)
		CS2G	– CS2D –	CS2C	121.2(8)
		CS2G	– CS2D –	CS2E	120.1(8)

Dihedral Angles

				Angle (°)
CP2D	– CP2A –	NP2A –	Ir1	-1.51
CP1D	– CP1A –	NP1A –	Ir1	-6.19
CP2E	– CP2B –	NP2B –	Ir2	-4.76
CP1E	– CP1B –	NP1B –	Ir2	-11.43
Ir1	– NP2A –	NP2B –	Ir2	4.93
Ir1	– NP1A –	NP1B –	Ir2	12.15
CP1D	– CP1A –	CP1C –	CP1B	178.97
CP2D	– CP2A –	CP2C –	CP2B	-178.37
CP1E	– CP1B –	CP1C –	CP1A	-177.44
CP2E	– CP2B –	CP2C –	CP2A	179.97

Angles Involving Ir···Ir Connectivity

			Angle (°)
Ir1	– Ir2 –	NP1B	62.46
Ir1	– Ir2 –	NP2B	62.23
Ir2	– Ir1 –	NP1A	62.25
Ir2	– Ir1 –	NP2A	61.70
Ir1	– Ir2 –	C2	119.61
Ir2	– Ir1 –	C1	117.36
Ir1	– Ir2 –	P2	112.10
Ir2	– Ir1 –	P1	117.01

this structure have been collected in Appendix I (Table A.1. Crystal and Intensity

Collection Data, Table A.2. Final Non-Hydrogen Coordinates and Displacement

Parameters, Table A.3. Anisotropic Displacement Parameters, Table A.4. Assigned

Hydrogen Parameters, Table A.5. Complete Distances and Angles, and Table A.6.

Observed and Calculated Structure Factors). A brief description of the structure is now

presented.

The molecule has approximate C_{2v} symmetry. Figures 3.3a and b show ORTEP

diagrams for $[Ir_2]$-CH_3 with views down the approximate C_2-symmetry axis. The largest

deviations from perfect C_{2v} symmetry occur between the axial phenyl groups (CA1 and

CA2) and between the tolyl groups (CS1 and CS2). An illustration of the former deviation

is the difference in relative geometry of the CA1/CB1 axial phenyl groups compared to the

equitorial phenyls, CA2/CB2. The CA1 and CB1 phenyl groups are nearly eclipsed

(dihedral angle, CA1B-CA1A-CB1A-CB1B = 3.1°), while phenyls CA2 and CB2 are far

from eclipsed (analogous dihedral angle, CA2B-CA2A-CB2A-CB2B = 44°). Examination

of more than one unit cell reveals the origin of these particular deviations. It appears that

the benzene rings of the molecule (four phenyl groups and two tolyl groups) accommodate

positions that maximize their overlap. Perfect C_{2v} symmetry is, however, not a necessary

condition for this overlap to occur.

The iridium atoms exhibit slightly distorted square planar coordination geometry. The

standard deviation from 90° of the angles N-Ir-N, N-Ir-C, N-Ir-P, and P-Ir-C is 3.8°. The

average of the two N-Ir-N angles is less than 90° (84°), while the average of the N-Ir-C,

P-Ir-C, and P-Ir-N angles is greater than 90° (92°).

The bridging-pyrazolyl groups retain their isolated structure, deviating by no more

than 0.8° from perfect planarity. The angle between the planes of the pyrazolyl groups is

78.8(6)° which is 5.3° less than the average N-Ir-N angle, implying that the pyrazolyl

groups are not perfectly eclipsed (this is indeed apparent in Figure 3.1a).

Figure 3.3. (a) ORTEP diagram of [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-CH$_3$)]$_2$, showing the approximate C$_2$-axis. Two of the phenyl groups and the pyrazolyl groups are superimposed by rotation about the C$_2$-axis. (b) However, the tolyl groups, as seen in this view of the molecule, deviate from perfect C$_2$-symmetry (phenyl groups have been omitted for clarity).

a
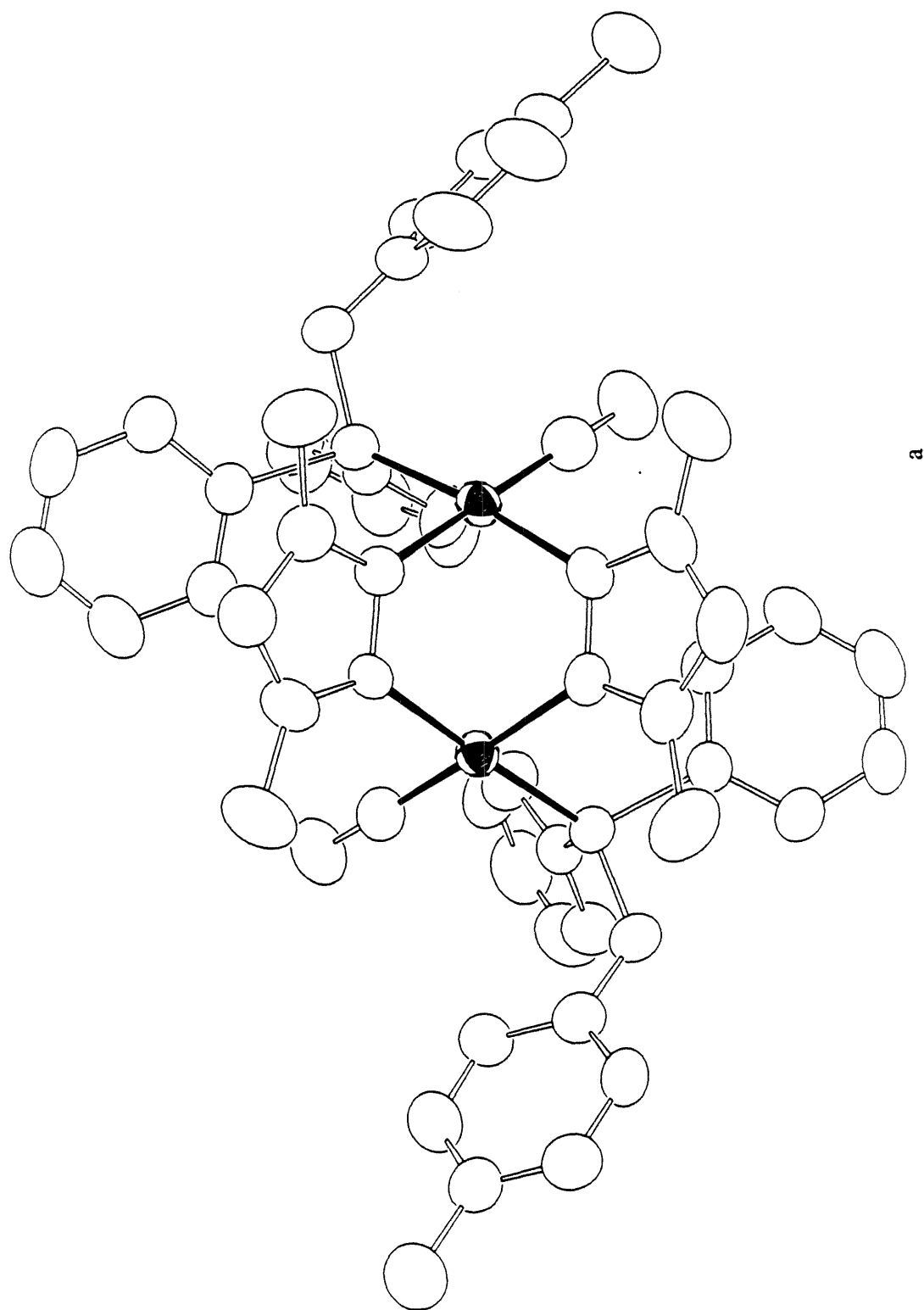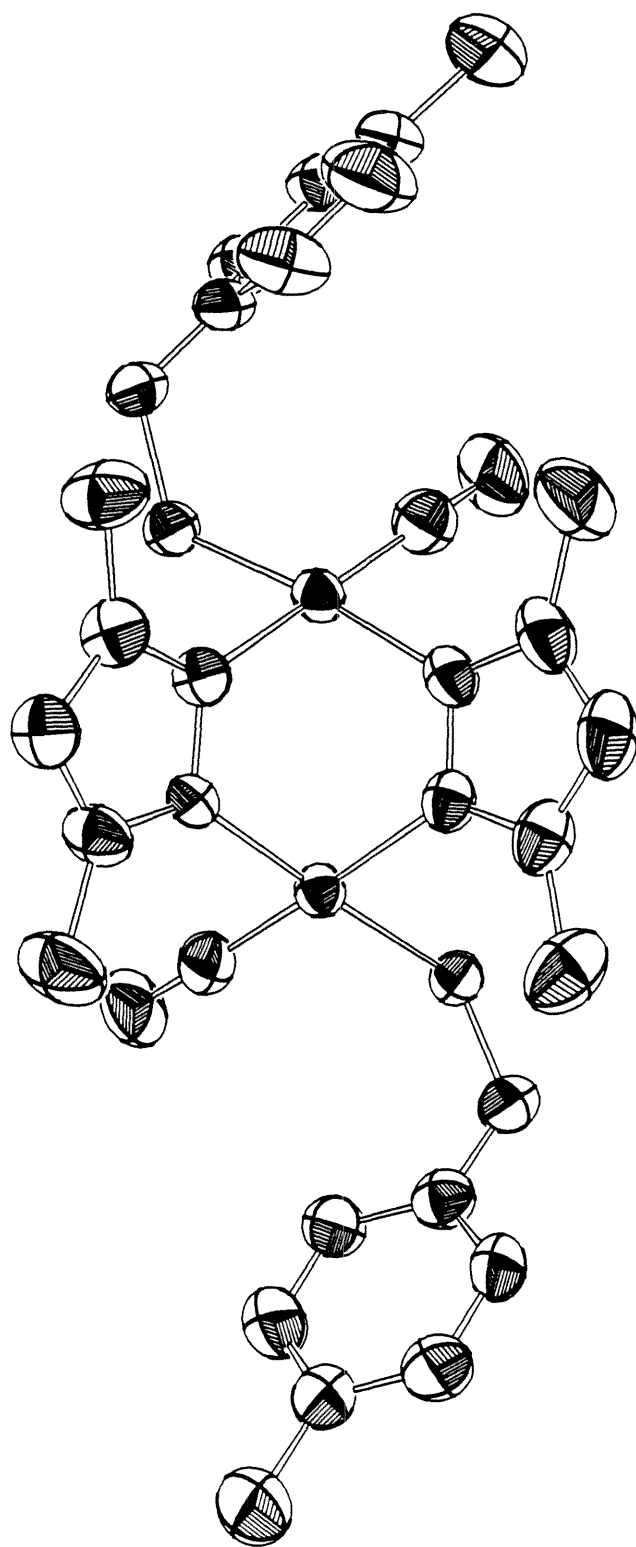
b

The Ir···Ir solid-state non-bonding separation in the present structure is the same as the M···M separations in analogous pyrazolyl-bridged Ir and Rh dimers within the standard deviation of distances (Table 3.3). It appears that the nature of X, Y, R, or M has no consistent effect on the M···M separation. For example, the average M···M separations in Ir and Rh dimers are 3.28 ± 0.12 Å and 3.31 ± 0.18 Å (the same within the standard error), for dimers with R = CH_3 and R = H the average M···M separations are 3.24 ± 0.06 Å and 3.34 ± 0.18 Å , and for dimers with X = Y = CO and X,Y = COD the average M···M separations are 3.34 ± 0.15 Å and 3.21 ± 0.06 Å.
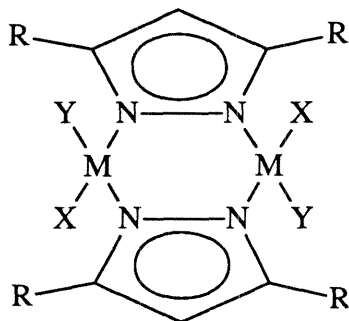
Table 3.3. M···M Separations in Pyrazolyl -Bridged Iridium(I) and Rhodium(I) Dimers

M	R	X	Y	M···M (Å)	Ref.
Ir	CH_3	CO	CO	3.245	5
Ir	CH_3	CO	$Ph_2POC_2H_4$-py^+	3.219	6
Ir	CH_3	CO	$Ph_2POC_6H_4$-CH_3	3.307	here
Ir	H	CO	CO	3.506	5
Ir	H		COD	3.216	7, 8
Ir	H	CO	Ph_3P	3.162	9
Rh	CH_3	CO	CO	3.262	10
Rh	CH_3		COD	3.154	10
Rh	H		COD	3.267	7
Rh	H	CO	$(PhO)_3P$	3.568	11

COD = 1,4-cyclooctadiene; Ph = phenyl; py^+ = pyridinium; C_6H_4 = phenylene; C_2H_4 = ethylene

Having demonstrated that the Ir···Ir separation in $[Ir(\mu\text{-pz}^*)(CO)(Ph_2P\text{-O-}C_6H_4\text{-}CH_3)]_2$ is typical of analogous $d^8\text{-}d^8$ dimers, a comparison of other bond lengths and angles to analogous complexes will be made. This was accomplished by considering the structure of $[Ir(\mu\text{-pz}^*)(CO)(Ph_2PO\text{-}C_2H_4\text{-py}^+)]_2(Ph_4B^-)_2$ (a donor-acceptor complex previously studied in our laboratory), which also contains a 3,5-dimethylpyrazolyl bridge, and CO and phosphinite ligands.[6] Table 3.4 summarizes selected bond lengths and angles for this complex (2) and for the structure of concern (1). The short Ir-C and long C-O bond lengths in 2 have been attributed to systematic errors in correcting the diffraction intensities for iridium absorption effects. Other than this discrepancy, however, deviations were found to be minimal. The iridium coordination spheres show similar structural parameters for both complexes: Ir-P = 2.22 Å, and Ir-N = 2.08(2) Å. The pyrazolyl bridge also exhibits similar structural parameters: N-N = 1.36(2) Å, and Ir-N-N = 117(2)°.

In Chapter 4 it will become apparent that the similarities between these two structures will serve to simplify the analyses of absorption and emission spectra for $[Ir_2]\text{-}CH_3$, as well as the series of donor-acceptor complexes described in Chapter 2.

Table 3.4. Comparison of Bond Lengths and Angles Between $[Ir_2]\text{-}CH_3$, 1, and $[Ir(pz^*)(CO)(Ph_2POC_2H_4\text{-py}^+)]_2$, 2

Bonds and Angles	1	2
Ir1-Ir2	3.31 Å	3.22 Å
Ir1-C1	1.80	1.65±0.01
Ir2-C2	1.81	1.76±0.01
Ir-P (avg)	2.22	2.22
Ir-N (avg)	2.08±0.01	2.07±0.02
C-O (avg)	1.17±0.01	1.23±0.02
P-O (avg)	1.63	1.64±0.01
N-N (avg)	1.37	1.35
Ir-N-N (avg)	117.6±0.5°	116.8±3.0°
N-Ir-P(C) (avg)	175.5	172.9

Molecular Mechanics Calculations:

Possible solution structures for the series of donor-acceptor complexes, $[Ir(\mu\text{-}pz^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}(CH_2)_n\text{-}py^+)]_2$ ($n = 0, 1, 2,$ and 3), have been determined by the method described in the Experimental Section of this chapter. The complexes are categorized based on the number of methylene groups, n, in the bridge between Ir_2 (donor) and py^+ (acceptor). The computer generated structures of the $n = 0$ and $n = 1$ complexes are shown in Figures 3.5 and 3.6a. The angles and distances, defined in Figure 3.4 and summarized in Table 3.5, will be used to structurally describe these two complexes. θ is the angle between the planes of the phenylene and pyridinium rings, and γ is the cant angle between the rings. A more detailed view of the Ir-spacer-py^+ ($Ir\text{-}P\text{-}O\text{-}C_6H_4\text{-}(CH_2)_n\text{-}py^+$, $n = 1$) portion of the complex is provided in Figure 3.6b, showing the interaction between the pyridinium and phenylene rings. This depiction of the electron-transfer pathway also serves to demonstrate that the pyridinium acceptor cannot come within van der Waals contact of the iridium donor.

The pyridinium group of the $n = 2$ complex can exist in one of two possible low energy conformations in relation to the phenylene ring (there are many other possible conformations; however, knowledge of the two extreme conformers will be sufficient to understand the dynamics of the spacer and acceptor). The first conformer, shown in Figure 3.7a, and in more detail in 3.7b, is the lowest energy structure (minimum gauche interactions) in which the methylene chain is completely *stretched*. The relevant distances and angles that characterize the relative orientation of the pyridinium and phenylene rings in the stretched conformer are given in Table 3.5. The second conformer, shown in Figure 3.8a and b, is a slightly higher energy structure in which the pyridinium ring is brought as close to the phenylene group as allowed by van der Waals interactions. In this extreme conformation the pyridinium ring is 3.1 Å from the phenylene ring at its closest contact point , and will therefore be termed the *folded* conformation.
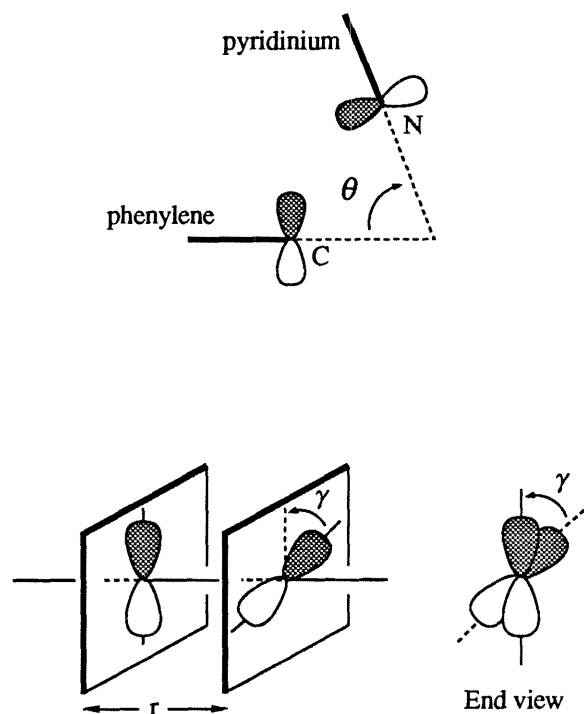
Figure 3.4. Definition of r, θ, and γ between the phenylene and pyridinium rings. These angles and distance are used to characterize the series of Ir_2-py^+ donor-acceptor complexes.

Table 3.5. Structural Parameters Obtained from Molecular Mechanics Calculations for Stretched and Folded Conformations

compounds	stretched			folded			
	Ir-N^s	Ir-N^b	θ (°)	Ir-N^s	θ (°)	γ (°)	r (Å)
[Ir$_2$]-py$^+$	6.5	9.5	180	6.5	180	42	1.4
[Ir$_2$]-CH$_2$-py$^+$	7.0	11.0	110	7.0	110	0	2.4
[Ir$_2$]-(CH$_2$)$_2$-py$^+$	9.4	12.5	180	6.4	50	0	3.1
[Ir$_2$]-(CH$_2$)$_3$-py$^+$	10.4	14.0	110	6.3	40	0	3.7

^{s} Edge-to-edge iridium-pyridinium through-*space* distance in Å.
^{b} Edge-to-edge iridium-pyridinium through-*bond* distance in Å.

Figure 3.5. Computer generated solution structure of $[Ir_2]\text{-py}^+$ ($n = 0$).
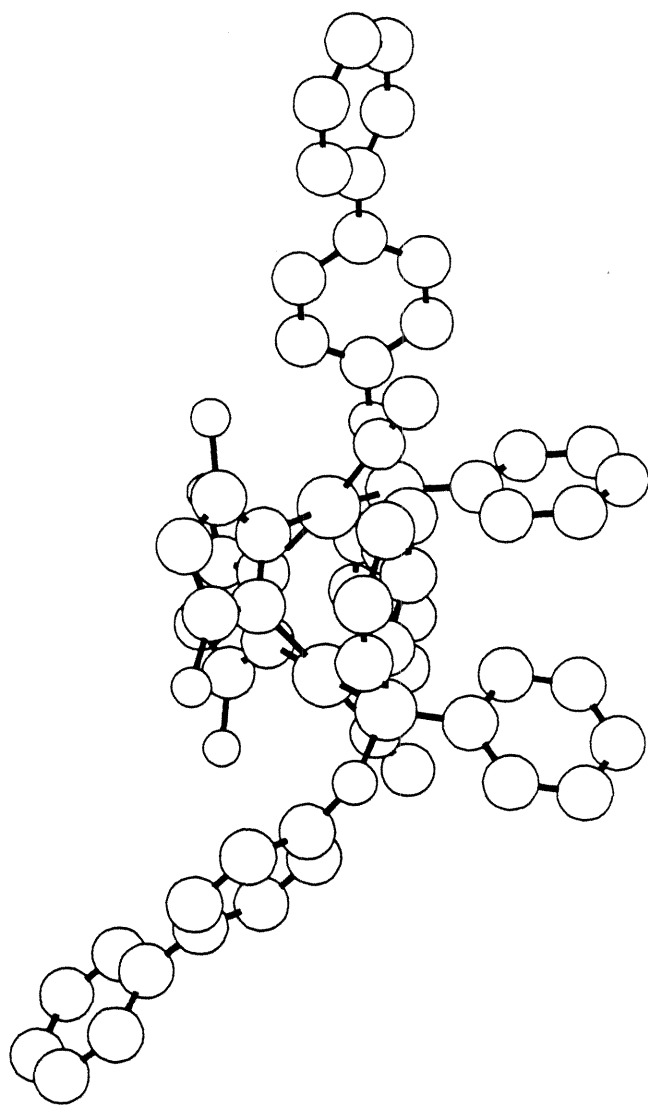
Figure 3.6. (a) Solution structure of $[Ir_2]$-CH_2-py^+ ($n = 1$). (b) Detailed view of electron-transfer pathway.
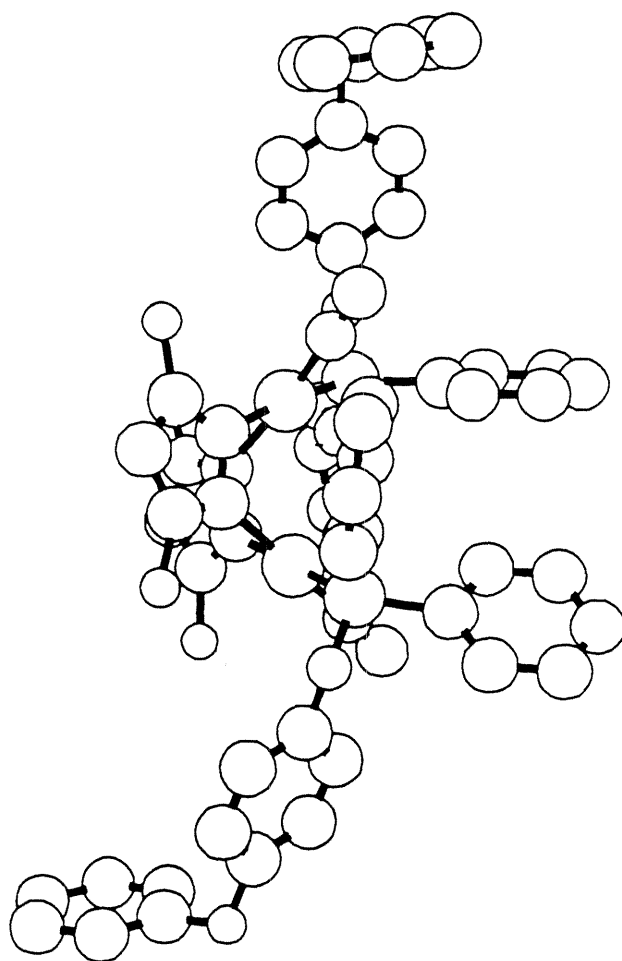
a
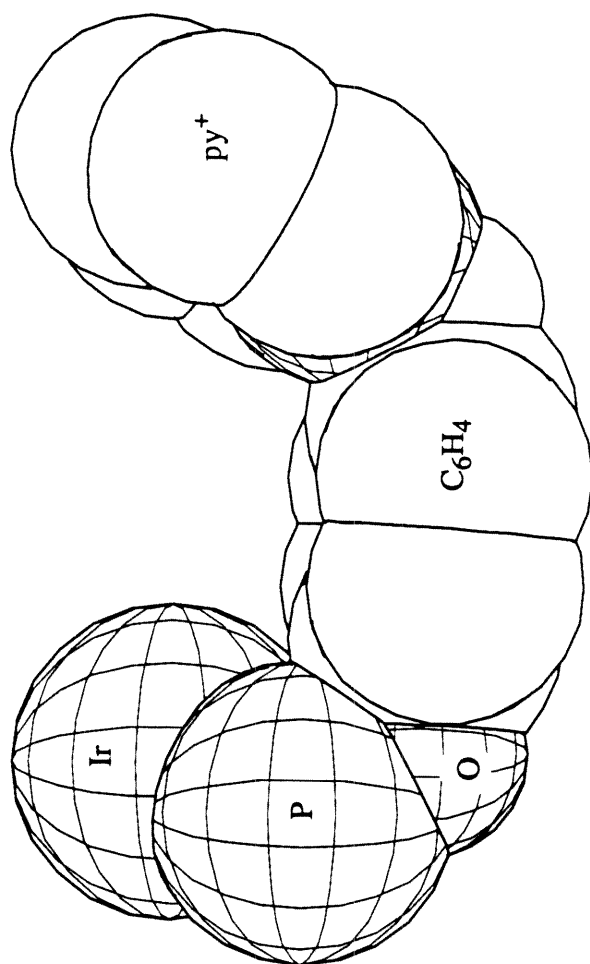
b

Figure 3.7. (a) Solution structure of the stretched conformation of $[Ir_2]$-$(CH_2)_2$-py$^+$ (n = 2). (b) Detailed view.
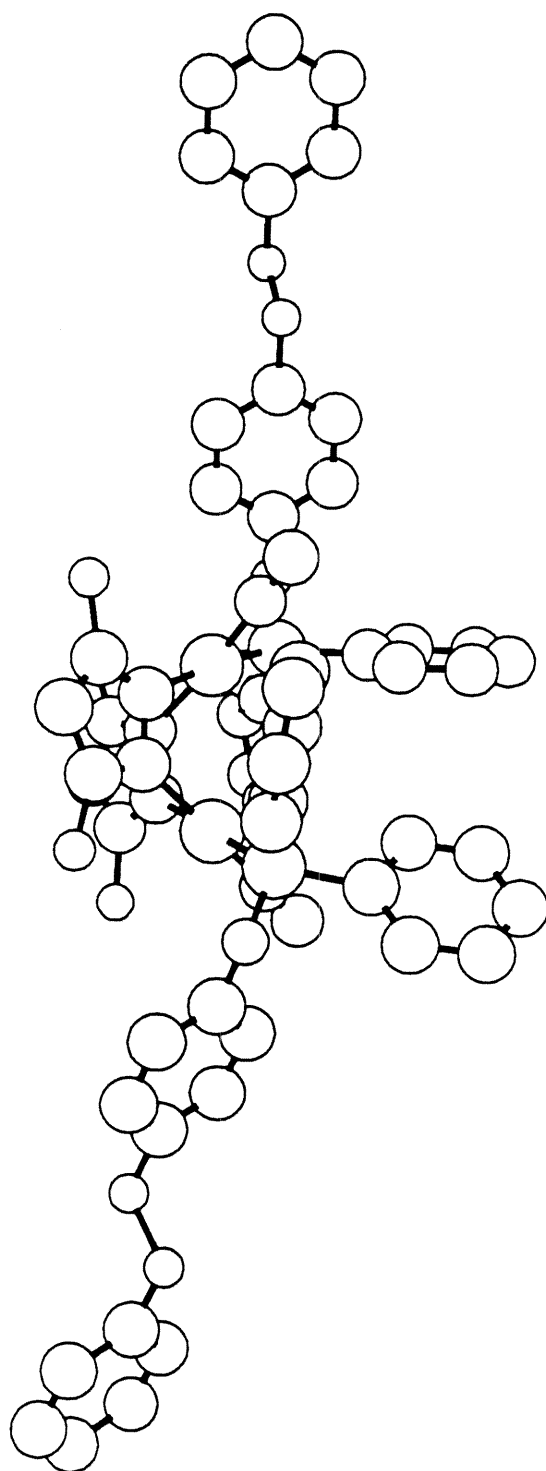
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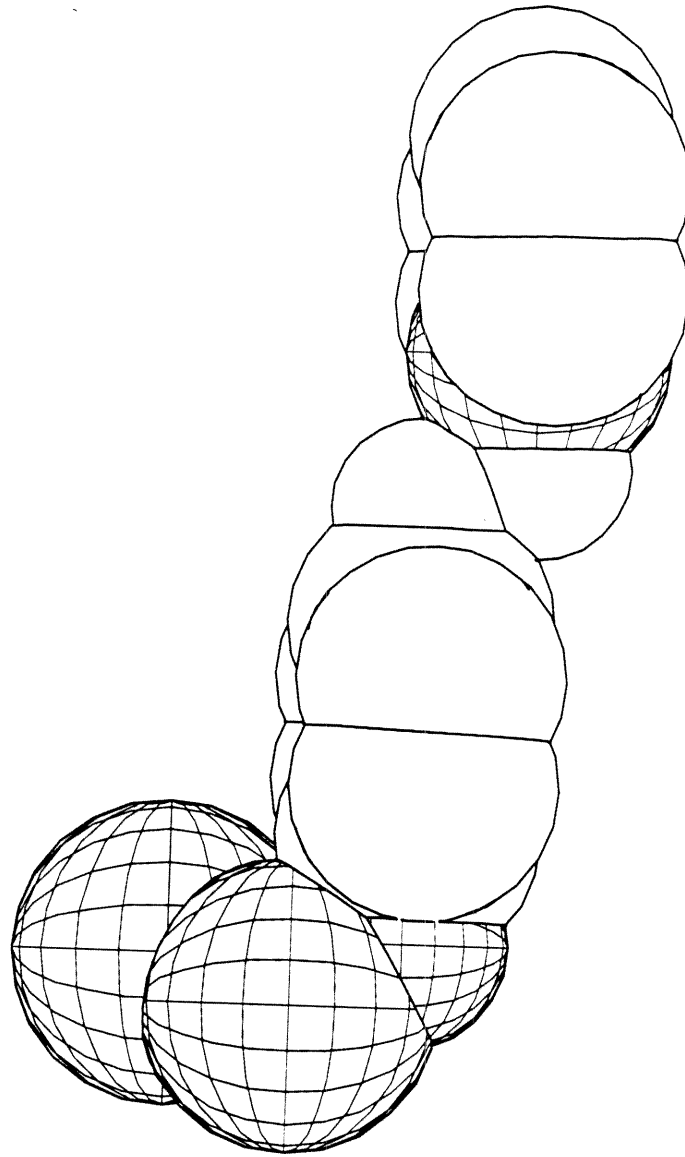
b

Figure 3.8. (a) Solution structure of the folded conformation of $[Ir_2]$-$(CH_2)_2$-py^+ ($n = 2$). (b) Detailed view.
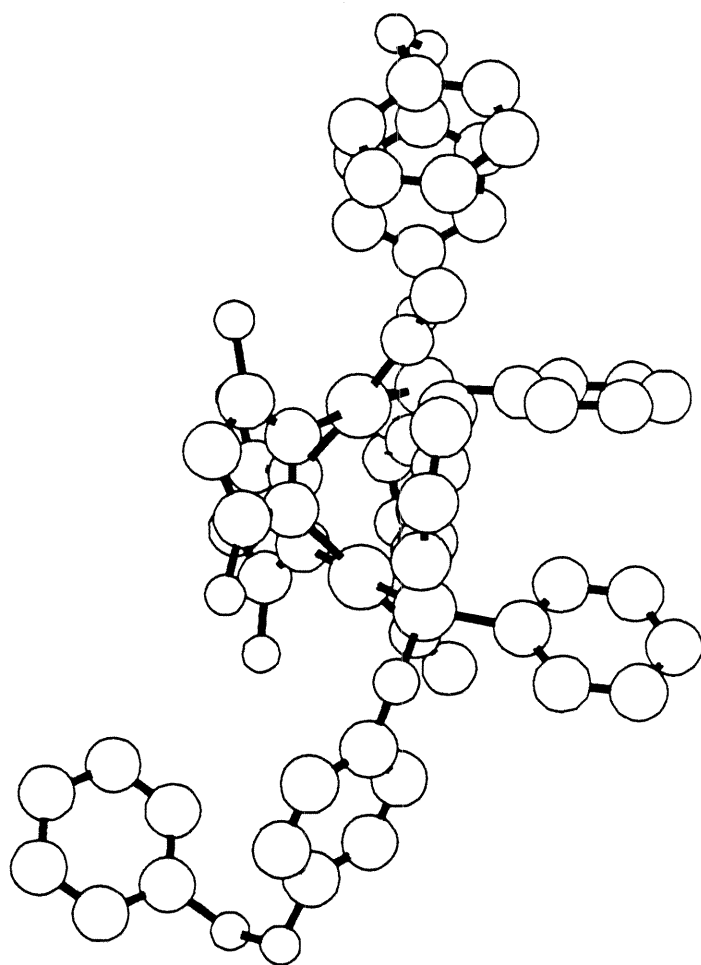
a
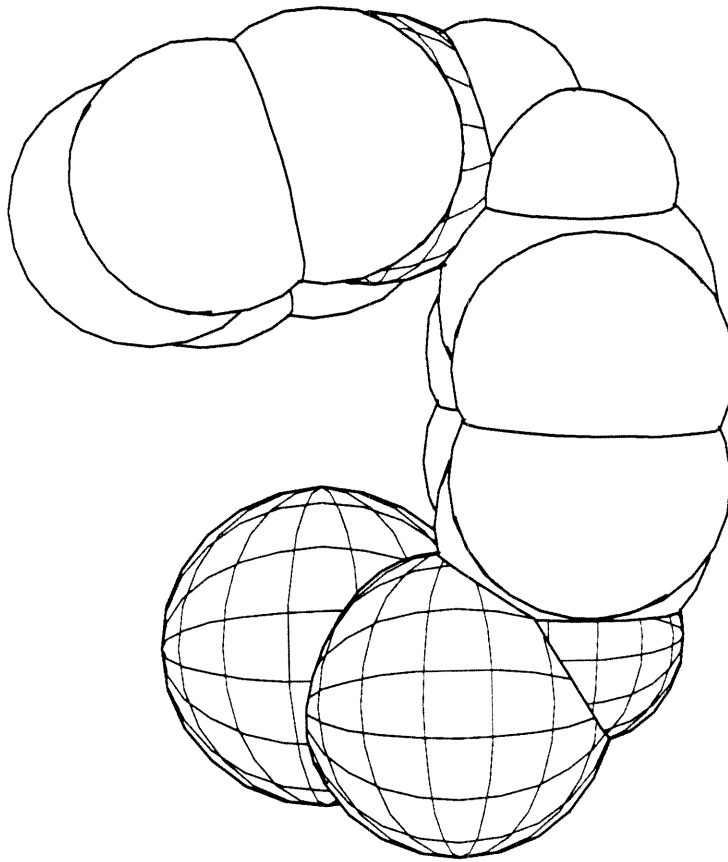
b

Figure 3.9. (a) Stretched conformation of $[Ir_2]-(CH_2)_3-py^+$ ($n = 3$). (b) Detailed view.
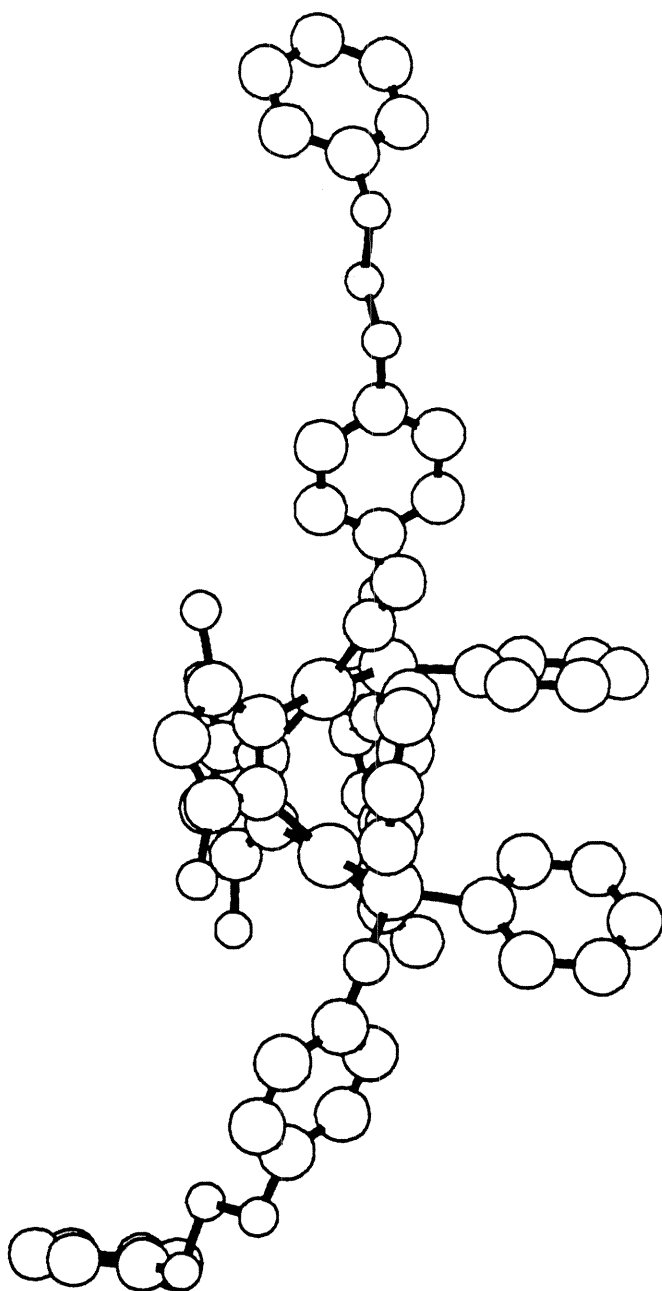
a
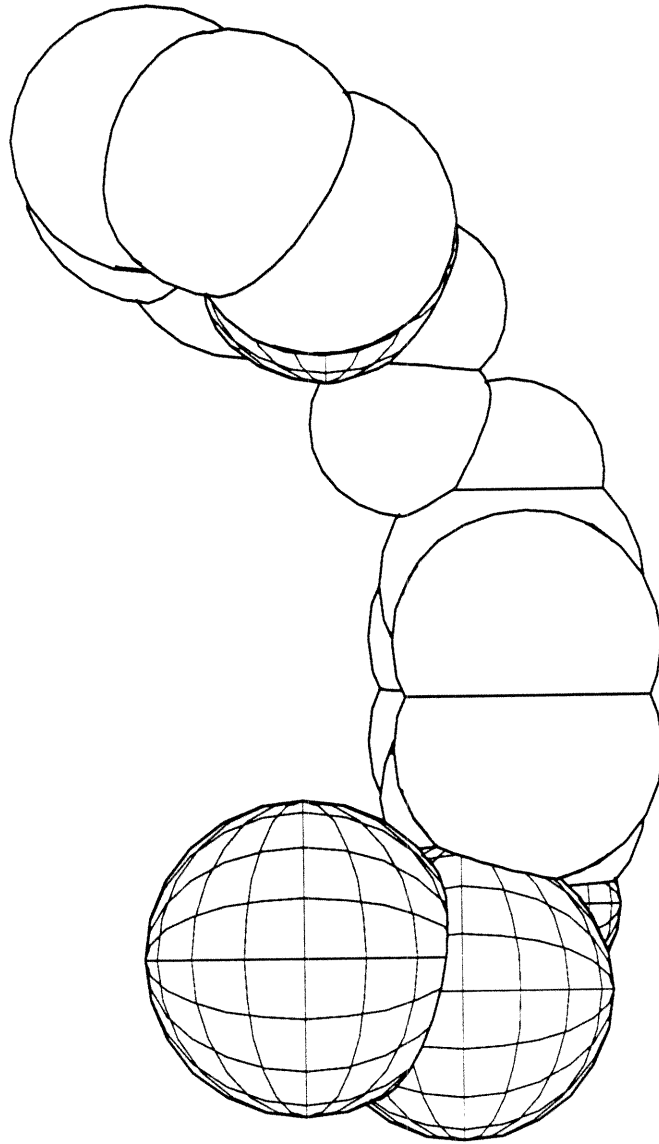
b

Figure 3.10. (a) Folded conformation of $[Ir_2]\text{-}(CH_2)_3\text{-py}^+$ ($n = 3$). (b) Detailed view.
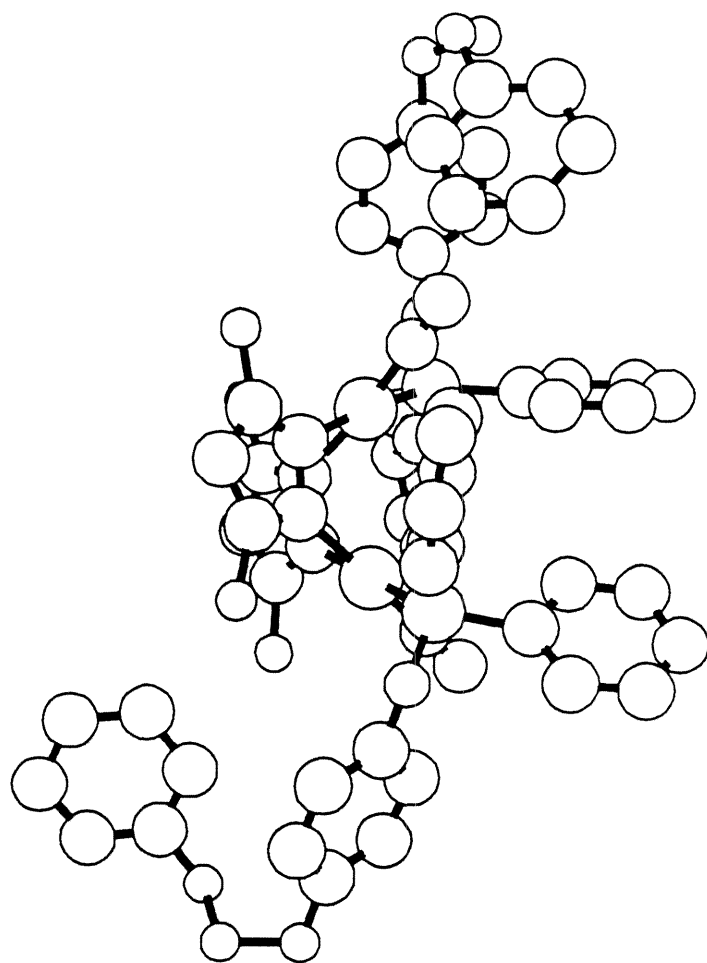
a
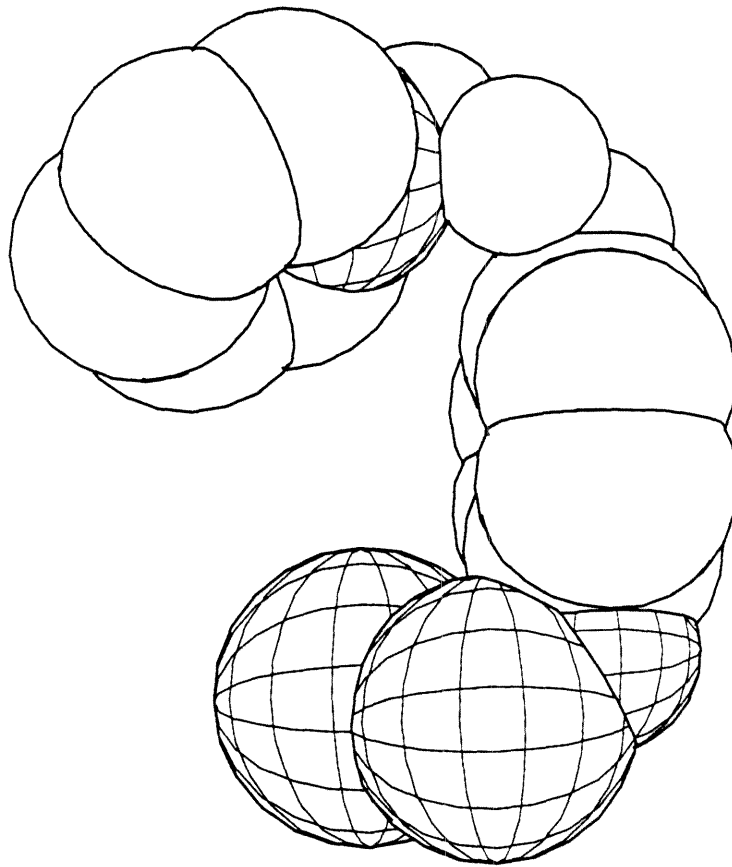
b

The structures of the two extreme conformations (stretched and folded) for the $n = 3$ complex are shown in Figures 3.9a and b, and 3.10a and b. The difference in values of r (see Table 3.5) between the stretched and folded conformations for this complex are much larger than in the previous three complexes ($n = 0$, 1 and 2).

The pronounced dependence of the calculated pyridinium and methylene chain geometries on n has been demonstrated in Figures 3.5-3.10. The results, shown in Table 3.5, reveal interesting dependencies of angles and distances on the value of n. In the folded conformations of $n = 0$ and 1 complexes, θ values are greater than 90°, while for complexes with $n = 2$ and 3, θ values are less than 90°. In the folded conformations the value of r increases as n increases while the values of θ decrease. In the stretched conformations θ alternates between 180° and 110° for all complexes: for $n = 0$ and 2, $\theta = 180°$; and for $n = 1$ and 3, $\theta = 110°$. An attempt to correlate these structural parameters to observed electron-transfer rates will be described in Chapter 5.

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Chapter 4

Steady-State Spectroscopy and
Electrochemistry

INTRODUCTION

Having chemically and structurally characterized the series of donor-spacer-acceptor complexes, $[Ir(\mu\text{-pz}^*)(CO)(Ph_2PO\text{-}C_6H_4\text{-}(CH_2)_n\text{-py}^+\text{-R})]_2(PF_6^-)_2$ (n = 0, 1, 2 or 3), an investigation of their photophysical properties is now presented. It was demonstrated in the previous chapter that the nature of the spacer has pronounced effects on the orientation of the pyridinium acceptor relative to the Ir_2 donor. The spacer-acceptor unit also plays an important role in determining the photophysical properties of the $Ir_2\text{-py}^+$ donor-acceptor complexes. For example, the quantum yields of emission from the $d^8\text{-}d^8$ iridium donor-acceptor complexes are all attenuated relative to an appropriate model complex. The source of this emission quenching is electron transfer, originating from the metal-localized excited states (singlet and triplet) of the iridium chromophore and terminating at the pyridinium cation. The result is the formation of an excited charge-transfer state with an electron deficient metal center and a neutral pyridinium radical. An important goal of the spectroscopic studies described in this chapter is to quantify the effects that each spacer-acceptor group (n = 0, 1, 2, and 3) has on the photophysical properties of these $d^8\text{-}d^8$ excited states.

In this chapter, results from steady-state absorption and emission studies were used to determine Ir_2 singlet and triplet excited-state energies, and results from ground-state electrochemical studies were used to calculate energies of the $Ir_2^+\text{-py}^\bullet$ charge-transfer states for each donor-acceptor complex. These calculations were combined to yield driving forces for each electron-transfer step. Fluorescence and phosphorescence quantum yield measurements were obtained for the series of $Ir_2\text{-py}^+$ donor-acceptor complexes, revealing the extent of electron-transfer quenching of the iridium $d^8\text{-}d^8$ singlet and triplet excited-states.

BACKGROUND

Research in our laboratories have established the rich reactivity of d^8-d^8 transition

metal complexes toward C-X and C-H bond activation,[1-3] and outer and inner-sphere

electron transfer.[4-7] Spectroscopic studies of these complexes have indicated that the

electronic structure of these complexes can be represented by the MO diagram shown in

Figure 4.1.[8-10] The interaction between two square planar d^8 fragments in these molecules

forces an interaction between the d_{z^2} and p_z orbitals of each monomer fragment forming $d\sigma$

and $p\sigma$ dimer MOs. Filling the molecular orbitals with $16e^-$ for each monomer leaves the

$d\sigma^*$ level as the HOMO and the $p\sigma$ level as the LUMO. The lowest electronic excited states

in these complexes are generated by promoting a $d\sigma^*$ electron into the vacant $p\sigma$ orbital,

which forms a $d\sigma^*p\sigma$ state in either a singlet or triplet spin state. These excited states,

$^1(d\sigma^*p\sigma)$ and $^3(d\sigma^*p\sigma)$, can then decay by radiative and nonradiative pathways, at

characteristic rates, back to the ground state, $(d\sigma^*)^2$. This model will be used as a basis for

understanding the electronic absorption and emission spectra of the iridium donor-acceptor

complexes presented here.

EXPERIMENTAL

Materials:

Acetonitrile (Burdick & Jackson) was used as received for UV-vis experiments; for

emission measurements this solvent was degassed with three freeze-pump-thaw cycles on a

high-vacuum line ($<10^{-5}$ torr), dried, and stored under vacuum over activated 3Å sieves.

Dichloromethane and acetonitrile were freshly distilled from calcium hydride and syringe-

degassed before use for electrochemical experiments. Tetra-n-butylammonium

hexafluorophosphate (TBAH) was recrystallized 2 times from 95% ethanol.

Figure 4.1. Molecular orbital diagram for the interaction of two square planar d^8 metal ions, showing HOMO and LUMO for d^8-d^8 metal dimers.

d^8 monomer d^8- d^8 dimer
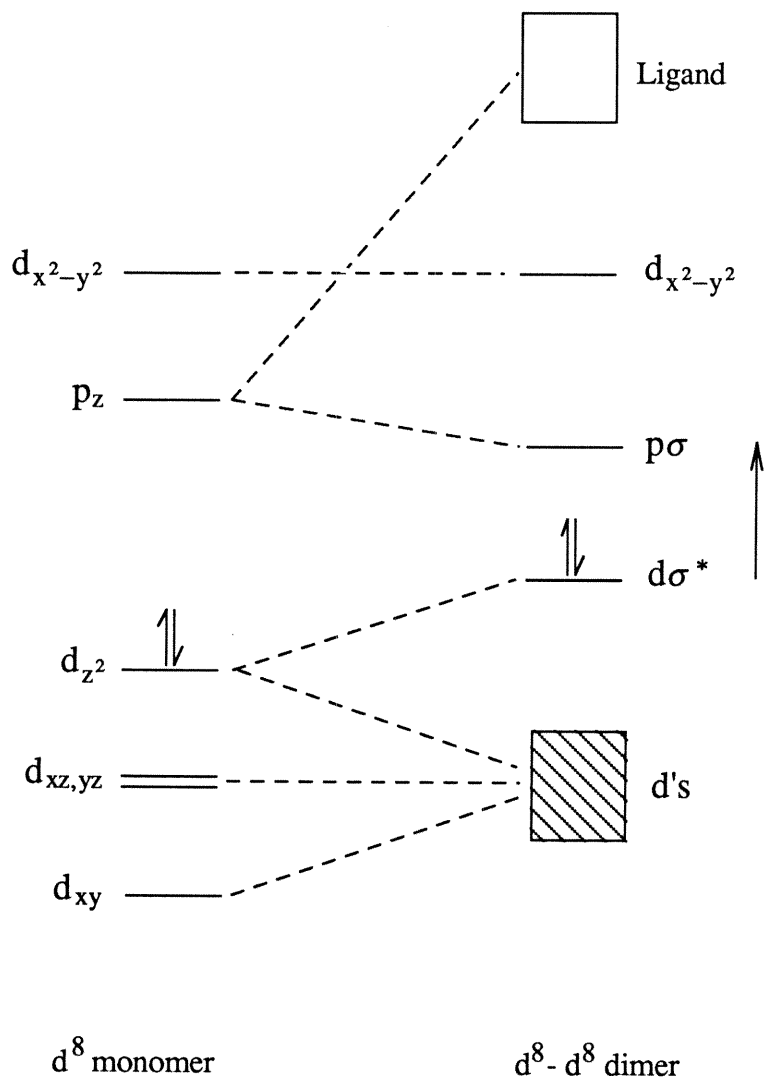
Electronic Absorption Spectroscopy:

Electronic absorption spectra were measured on one of three spectrophotometers: Cary 14 , converted to computer operation by On-Line Instruments Systems Inc.; Shimadzu UV-260; or Hewlett Packard 8450A Diode Array. Samples were prepared in high-precision 1 cm quartz cells, fitted with a Kontes needle valve, and either freeze-pump-thawed or bubble deoxygenated with argon.

Electronic Emission Spectroscopy:

Electronic emission spectra were obtained on an emission spectrometer constructed at Caltech, which has been described previously.[10,11] Measurements were made on freeze-pump-thawed acetonitrile solutions in 1 cm non-precision quartz cells. The samples were excited with the 436 nm line of an Oriel 200 Watt Hg/Xe lamp. This line was selected with a SPEX 1620 monochrometer and filtered with an Oriel 436 nm interference filter to remove stray excitation light. The luminescence from the sample was collimated, focused, and then filtered with a Corning 3387 sharp-cut filter to remove stray excitation before being directed into a SPEX 1870 monochrometer. Detection of the signal was achieved using a Hamamatsu R955 PMT. The signal from the PMT was amplified with an EG&G PAR 182A lock-in amplifier and plotted on a Soltec 3314 chart recorder. The data was digitized and corrected for PMT response. Room temperature quantum yields were determined by the optically dilute solution method described by Crosby and Demas.[12] Integrated emission intensities were determined by calculating the areas under Gaussian curves that best fit the data. The quantum yield standard was [Ru(bpy)$_3$]Cl$_2$ in water ($\Phi = 0.042$, $\lambda_{ex} = 436$ nm).[13] The absorbance of the samples and reference at 436 nm were adjusted so that they were equivalent within experimental error and less than or equal to 0.2.

Electronic Excitation Spectroscopy:

Electronic excitation spectra of optically dilute solutions (in CH$_3$CN) were recorded

using an instrument built at Brookhaven National Laboratories. Singlet and triplet spectra were obtained by detection at 560 and 750 nm, respectively. Excitation was controlled by an electronic feed-back circuit that kept the excitation source constant and eliminated the necessity to correct for excitation fluctuations.

Electrochemistry:

Electrochemical measurements were conducted using a Princeton Applied Research (PAR) model 173 potentiostat/galvanostat, a model 175 universal programmer, and a model 179 digital coulometer. Cyclic voltammograms were plotted on a Houston Instruments Omnigraphic 2000 x,y recorder. All electrochemical studies were conducted in acetonitrile (dried over 3Å sieves) using a standard one-compartment cell[14] with a Pt disk electrode as working electrode (surface area approximately 1.3 mm^2), coiled Pt wire or mesh as counter electrode, and aqueous saturated sodium calomel electrode (SSCE) as reference electrode. The ferrocene/ferrocenium couple was used as an internal reference redox system. The use of aqueous SSCE as a reference electrode introduces an unknown and irreproducible liquid junction potential, E_j. Therefore, all potentials were referenced to the ferrocene/ferrocenium couple (0.302 vs. SSCE) and reported versus SSCE. Supporting electrolyte in all cases was 0.1 M tetra-n-butyl ammonium hexafluoro-phosphate (TBAH).

RESULTS and DISCUSSION

Absorption Spectra: Electronic absorption spectra of the model complexes, $[Ir(\mu\text{-pz*})(CO)(Ph_2PO\text{-}C_6H_4\text{-}Y)]_2$ (Y is poor electron acceptors, CH_3 or $CH_2\text{-}Quin^+PF_6^-$), and donor-acceptor complexes, $[Ir(\mu\text{-pz*})(CO)(Ph_2PO\text{-}C_6H_4\text{-}(CH_2)_n\text{-}py^+\text{-}R)]_2(PF_6^-)_2$, all show identical features at nearly equivalent frequencies, indicating the dominance of the spectra by the photophysical properties of the $d^8\text{-}d^8$ iridium core (see Background section

of this chapter). The spectra in acetonitrile solution show two intense bands with maxima

at approximately 22,000 cm^{-1} (λ = 460 nm, ε = ~10,000 M^{-1} cm^{-1}) and 28,000 cm^{-1}

(λ = 350 nm, ε = ~5,000 M^{-1} cm^{-1}). Table 4.1 summarizes the absorption data for the

iridium complexes. Figure 4.2 shows the absorption spectrum of the model complex,

[Ir$_2$]-CH$_3$, which was typical of absorption spectra for all the iridium d^8-d^8 complexes.

The band at 22,000 cm^{-1} is assigned, by analogy to similar d^8-d^8 metal complexes,[10] to a

fully allowed S$_0\rightarrow$S$_1$(d$\sigma^*\rightarrow$pσ) electronic transition. The corresponding absorption into

the triplet manifold (S$_0\rightarrow$T$_1$) was not observed at room temperature due to its low

extinction coefficient.[10] The band at 28,000 cm^{-1} has been tentatively assigned to

(d$_{xz}$,d$_{yz}\rightarrow$p$_z$) transitions also by analogy to similar d^8-d^8 metal complexes. More research

into the precise nature of this and other higher energy bands is still necessary to

unequivocally assign them to specific electronic transitions.

Table 4.1. Absorption Data for the Iridium Donor-Acceptor Complexes

Compounds [a]	S$_0\rightarrow$S$_1$		Band II [c]	
	cm^{-1}	nm	cm^{-1}	nm
[Ir$_2$]-CH$_3$	21,800	458	28,400	353
[Ir$_2$]-CH$_2$-Quin$^+$ [b]	21,700	460	28,200	355
[Ir$_2$]-py$^+$	21,700	460	28,200	355
[Ir$_2$]-CH$_2$-py$^+$	21,700	461	28,300	354
[Ir$_2$]-CH$_2$-py$^+$-tB	21,700	462	28,400	353
[Ir$_2$]-CH$_2$-py$^+$-Am [b]	21,700	460	28,200	355
[Ir$_2$]-(CH$_2$)$_2$-py$^+$	21,800	460	28,200	354
[Ir$_2$]-3-(CH$_2$)$_2$-py$^+$ [b]	21,700	460	28,200	355
[Ir$_2$]-(CH$_2$)$_3$-py$^+$ [b]	21,700	460	28,200	355

[a] All measurements were conducted in CH$_3$CN solutions.
[b] These data have an error of ±2 nm.
[c] This band is referred to in the text as the higher energy transition.

Figure 4.2. Absorption spectrum of [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-CH$_3$)]$_2$. The band at 460 nm is assigned to the S$_0 \rightarrow$S$_1$(d$\sigma^* \rightarrow$pσ) electronic transition.
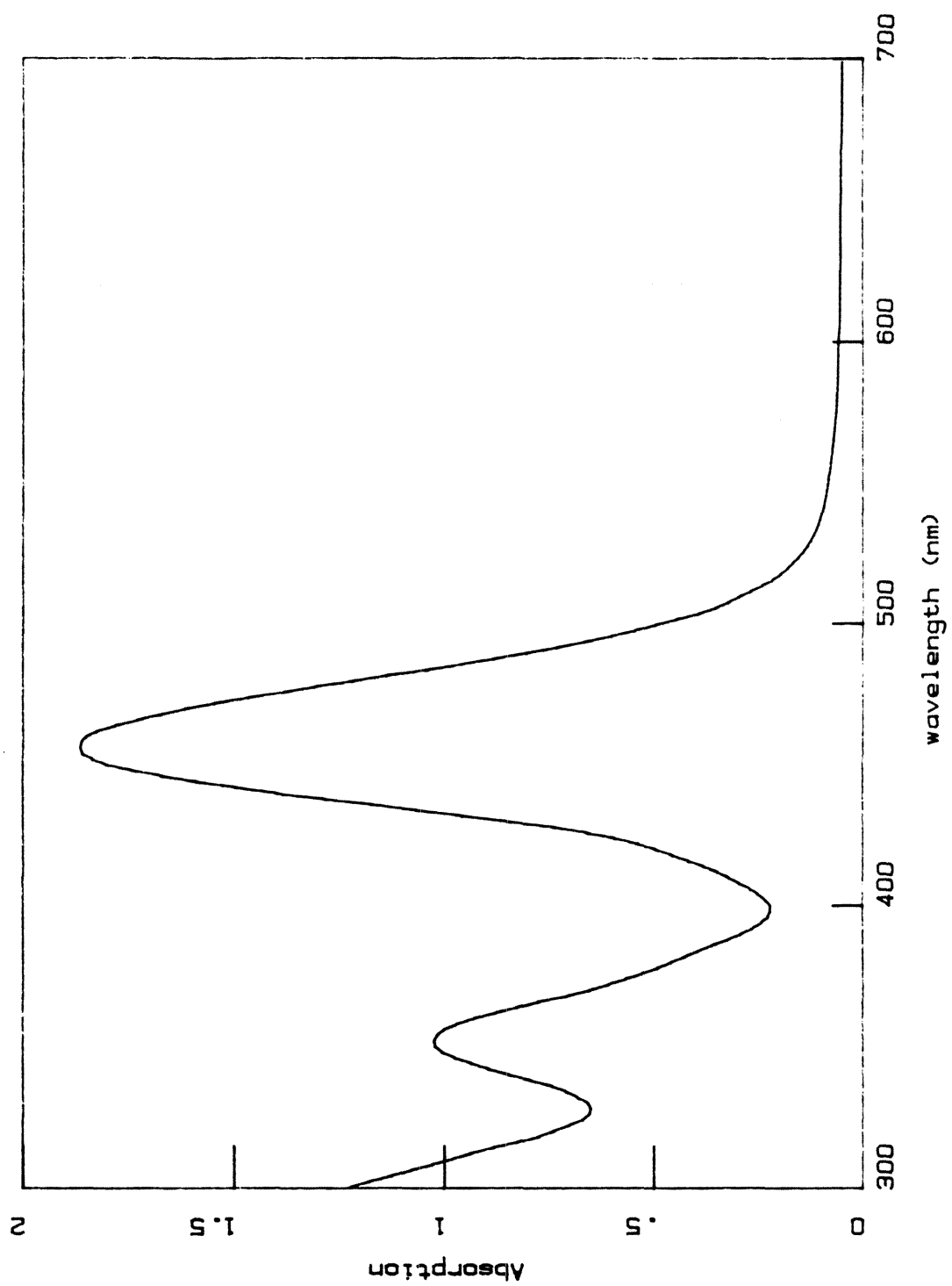
Excitation Spectra: Singlet and triplet excitation spectra were obtained by detection of emission at 560 nm and 750 nm, respectively. These wavelengths correspond to emission maxima for fluorescence and phosphorescence of the iridium complexes. Tables 4.2 and 4.3 summarize excitation data for two model complexes and one donor-acceptor complex. Figures 4.3a and b show singlet and triplet excitation spectra for the model complex, $[Ir_2]$-CH_3. The features of these spectra are similar to those of the absorption spectra described above. The $S_0{\to}S_1$ transitions appear in both singlet and triplet excitation spectra at wavelengths comparable to those in the absorption spectra. The high energy band at ~370 nm is weaker in the singlet excitation spectra, presumably due to diminished intersystem crossing to the singlet manifold from these higher lying excited-states (or possibly enhanced intersystem crossing to the triplet manifold). This point was not further investigated and is left for more extensive studies in the future.

Table 4.2. Singlet Excitation Data

Compounds	$S_0{\to}S_1$ cm^{-1}	nm
$[Ir_2]$-CH_3	21,300	471
$[Ir_2]$-CH_2-$Quin^+$	20,900	479
$[Ir_2]$-$(CH_2)_3$-py^+	21,200	472

Table 4.3. Triplet Excitation Data

Compounds	$S_0{\to}S_1$ cm^{-1}	nm	Band II cm^{-1}	nm
$[Ir_2]$-CH_3	21,200	471	27,400	365
$[Ir_2]$-CH_2-$Quin^+$	20,900	478	26,900	372
$[Ir_2]$-$(CH_2)_3$-py^+	21,200	471	27,400	365

Figure 4.3. (a) Singlet excitation spectrum of [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-CH$_3$)]$_2$, at room temperature in CH$_3$CN solution, showing band corresponding to S$_0$→S$_1$ transition at 470 nm. (b) Triplet excitation spectrum of [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-CH$_3$)]$_2$, at room temperature in CH$_3$CN solution, showing band corresponding to S$_0$→S$_1$ transition at 470 nm and a higher energy band at 365 nm.

a
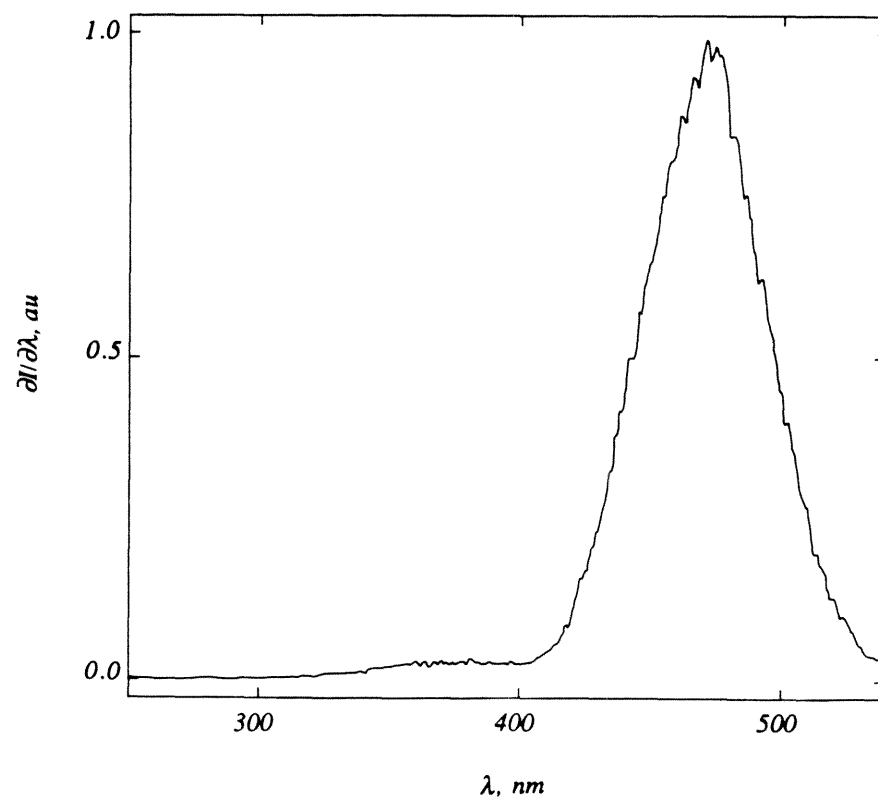
b
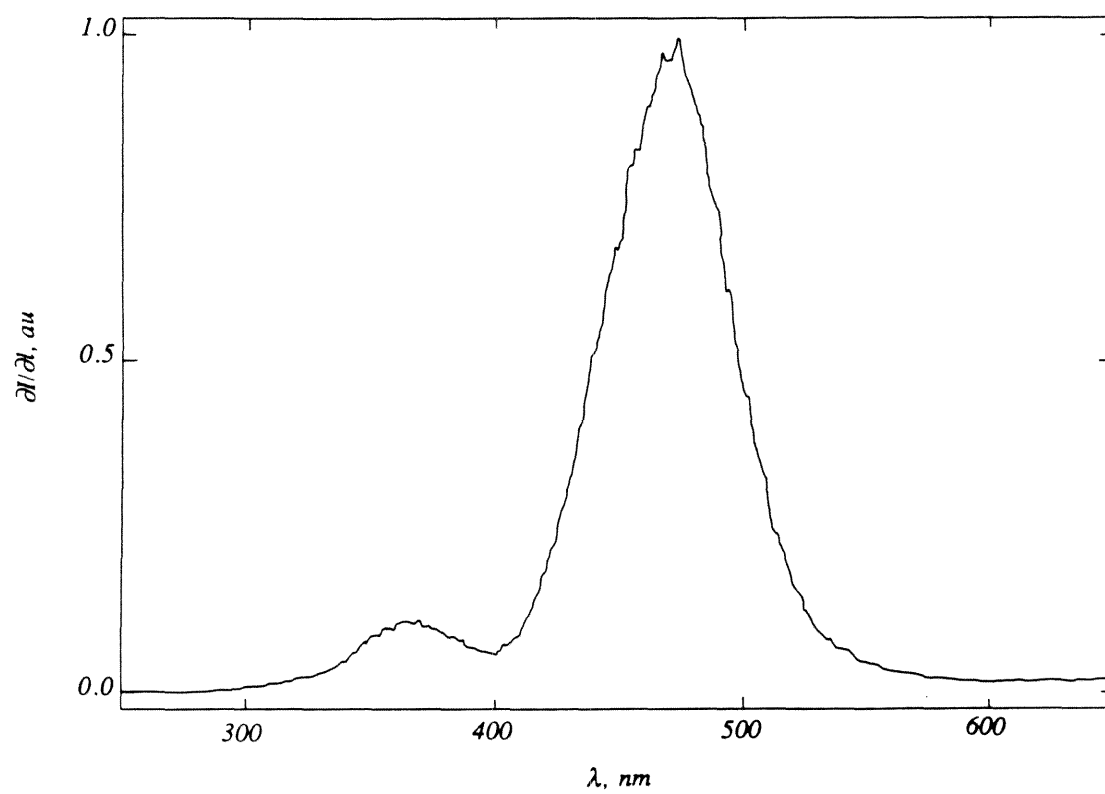
Emission Spectra: Electronic emission spectra of the model compounds, $[Ir(\mu\text{-}pz^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}CH_3)]_2$ and $[Ir(\mu\text{-}pz^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}CH_2\text{-}Quin^+)]_2$, at room temperature in acetonitrile solution show two emission bands in the spectral region between 11,000 and 22,000 cm^{-1} (450 and 900 nm) with maxima at approximately 17,500 cm^{-1} (570 nm) and 13,500 cm^{-1} (750 nm). The steady-state emission spectrum of $[Ir_2]\text{-}CH_3$ is given in Figures 4.4. The absorption and emission spectra for $[Ir_2]\text{-}CH_3$ are combined in Figure 4.5. These bands are assigned to $S_1{\rightarrow}S_0(p\sigma{\rightarrow}d\sigma^*)$ and $T_1{\rightarrow}S_0(p\sigma{\rightarrow}d\sigma^*)$ electronic transitions, respectively, by analogy to emission features observed for similar $d^8\text{-}d^8$ chromophores.[10] The emission spectra of all the donor-acceptor complexes also show two emission bands at nearly the same energies as the model complexes, however, they exhibit diminished emission intensities compared to the model complexes. Table 4.4 summarizes the emission data for the series of $Ir_2\text{-}py^+$ complexes, and Figure 4.6 shows the emission spectrum of the donor-acceptor complex, $[Ir_2]\text{-}(CH_2)_3\text{-}py^+$, demonstrating the decrease in emission intensities upon incorporation of the pyridinium acceptor into the molecule. The fluorescence and phosphorescence quenching is attributed to excited-state electron transfer, culminating in formation of an excited charge-transfer state. This deactivation pathway has been thoroughly characterized in similar $d^8\text{-}d^8$ iridium donor-acceptor complexes, where other possible mechanisms have been ruled out by energy and intensity considerations.[10] Table 4.5 lists the fluorescence and phosphorescence quantum yields. The dramatic effect of the number of methylene groups in the bridge between the donor group ($d^8\text{-}d^8$ iridium center) and the acceptor group (pyridinium cation) is apparent on inspection of the data in Table 4.5. The fluorescence of the donor-acceptor complex, $[Ir_2]\text{-}py^+$, is 96% quenched as compared to model complexes ($[Ir_2]\text{-}CH_3$ and $[Ir_2]\text{-}CH_2\text{-}Quin^+$), however, only 52% of the fluorescence is quenched in $[Ir_2]\text{-}CH_2\text{-}py^+$. In the next chapter, these results will be combined with excited-state lifetime data, yielding singlet and triplet electron-transfer rates, and the origin of these differences will also be discussed in Chapter 5.

Table 4.4. Emission Data for the Iridium Donor-Acceptor Complexes

Compounds [a]	$S_1 \rightarrow S_0$		$T_1 \rightarrow S_0$	
	cm^{-1}	nm	cm^{-1}	nm
$[Ir_2]$-CH_3	17,200	583	13,300	754
$[Ir_2]$-CH_2-$Quin^+$	17,200	583	13,200	758
$[Ir_2]$-py^+	18,300	547	—[b]	—[b]
$[Ir_2]$-CH_2-py^+	17,500	572	13,400	749
$[Ir_2]$-CH_2-py^+-Am	17,300	577	13,300	750
$[Ir_2]$-$(CH_2)_2$-py^+	17,800	563	13,900	720
$[Ir_2]$-3-$(CH_2)_2$-py^+	17,900	558	13,700	729
$[Ir_2]$-$(CH_2)_3$-py^+	17,400	576	13,700	732

[a] All measurements were conducted in CH_3CN solution.

[b] Signal intensity too low to observe.

Table 4.5. Quantum Yields for Fluorescence and Phosphorescence in Ir_2-py^+ Complexes

Compounds	Quantum Yields [a]	
	Φ_f ($\times 10^3$)	Φ_{ph} ($\times 10^3$)
$[Ir_2]$-CH_3	1.0	12
$[Ir_2]$-CH_2-$Quin^+$	1.2	17
$[Ir_2]$-py^+	0.039	—[b]
$[Ir_2]$-CH_2-py^+	0.53	4.3
$[Ir_2]$-CH_2-py^+-Am	0.69	11
$[Ir_2]$-$(CH_2)_2$-py^+	0.19	0.045
$[Ir_2]$-3-$(CH_2)_2$-py^+	0.093	0.021
$[Ir_2]$-$(CH_2)_3$-py^+	0.76	0.25

[a] These values are associated with error of ±30%.

[b] Emission too weak to measure.

Figure 4.4. Emission spectrum of $[Ir(\mu\text{-pz}^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}CH_3)]_2$ showing $S_1{\rightarrow}S_0$ transition at 17,200 cm^{-1} and $T_1{\rightarrow}S_0$ transition at 13,300 cm^{-1}.

Corrected Emission Intensity

wavenumber (cm-1)
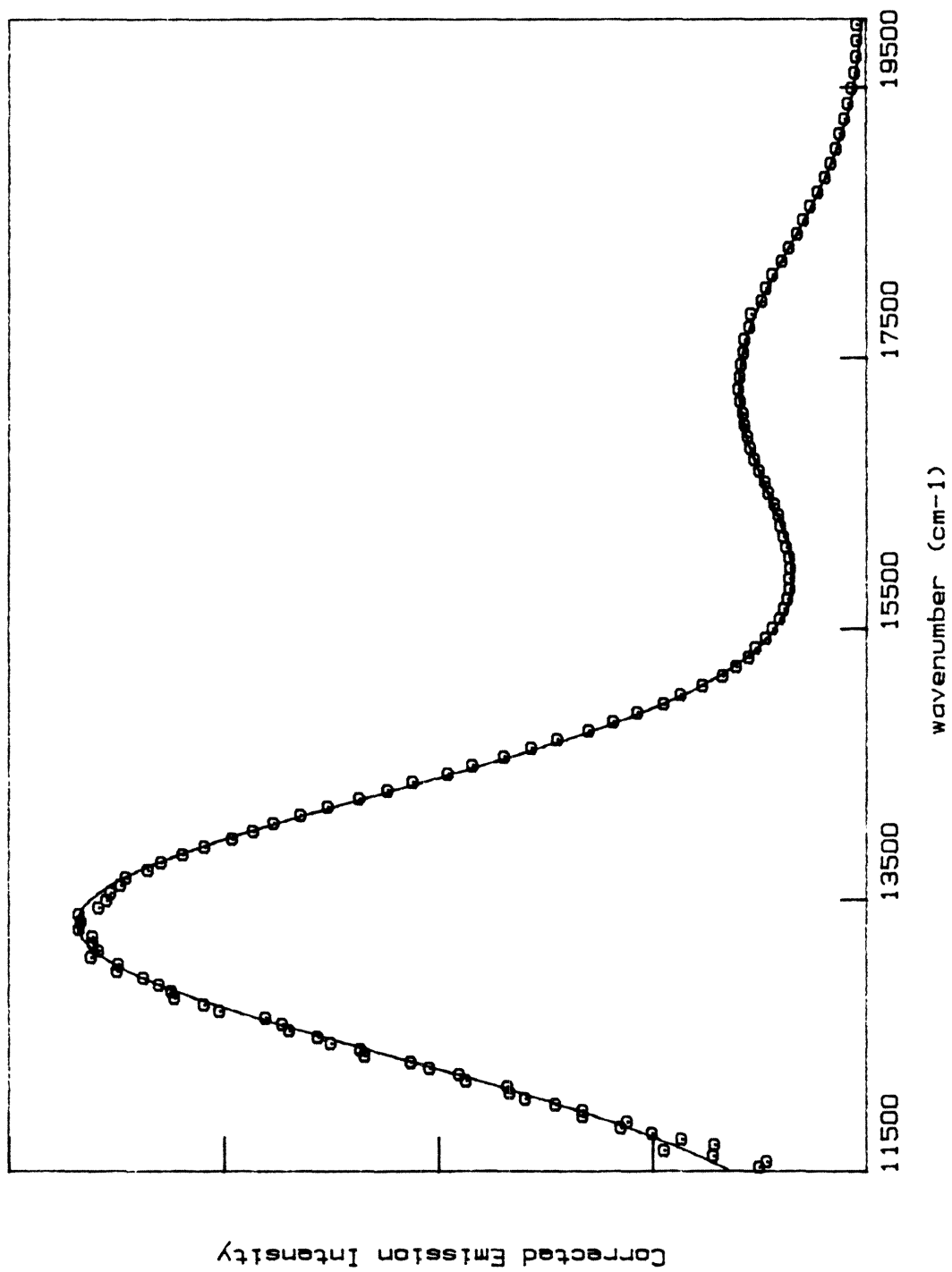
Figure 4.5. Absorption spectrum (— – —) of [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-CH$_3$)]$_2$ and emission spectrum (— · —) generated by excitation into 460 nm band.
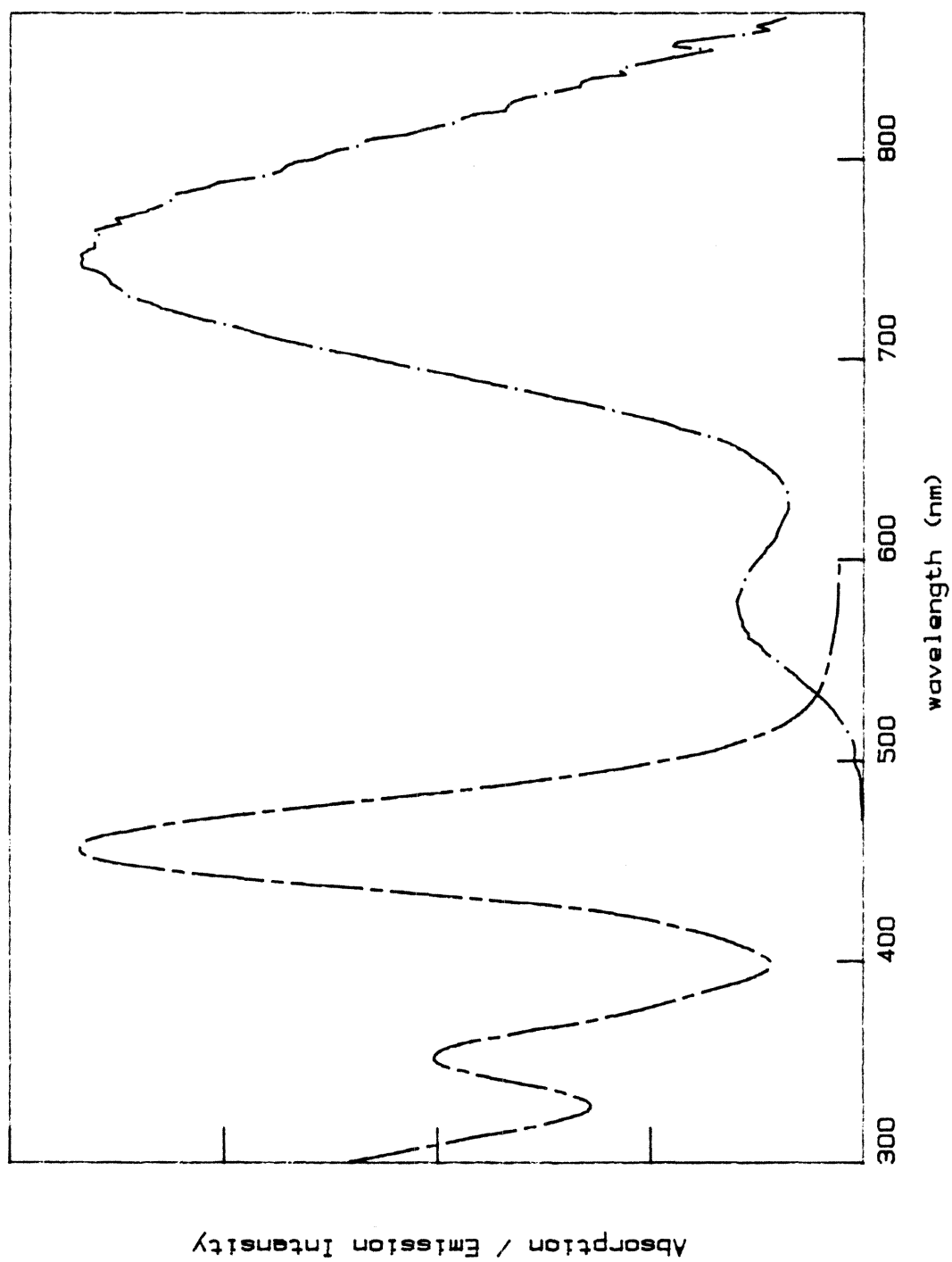
Figure 4.6. Emission spectrum of $[Ir(\mu\text{-}pz^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}(CH_2)_3\text{-}py^+)]_2$ showing $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ transition, at decreased intensity compared to the model complexes. The emission intensity scale is 8 times that of the spectrum in Figure 4.4.

Corrected Emission Intensity

wavenumber (cm-1)
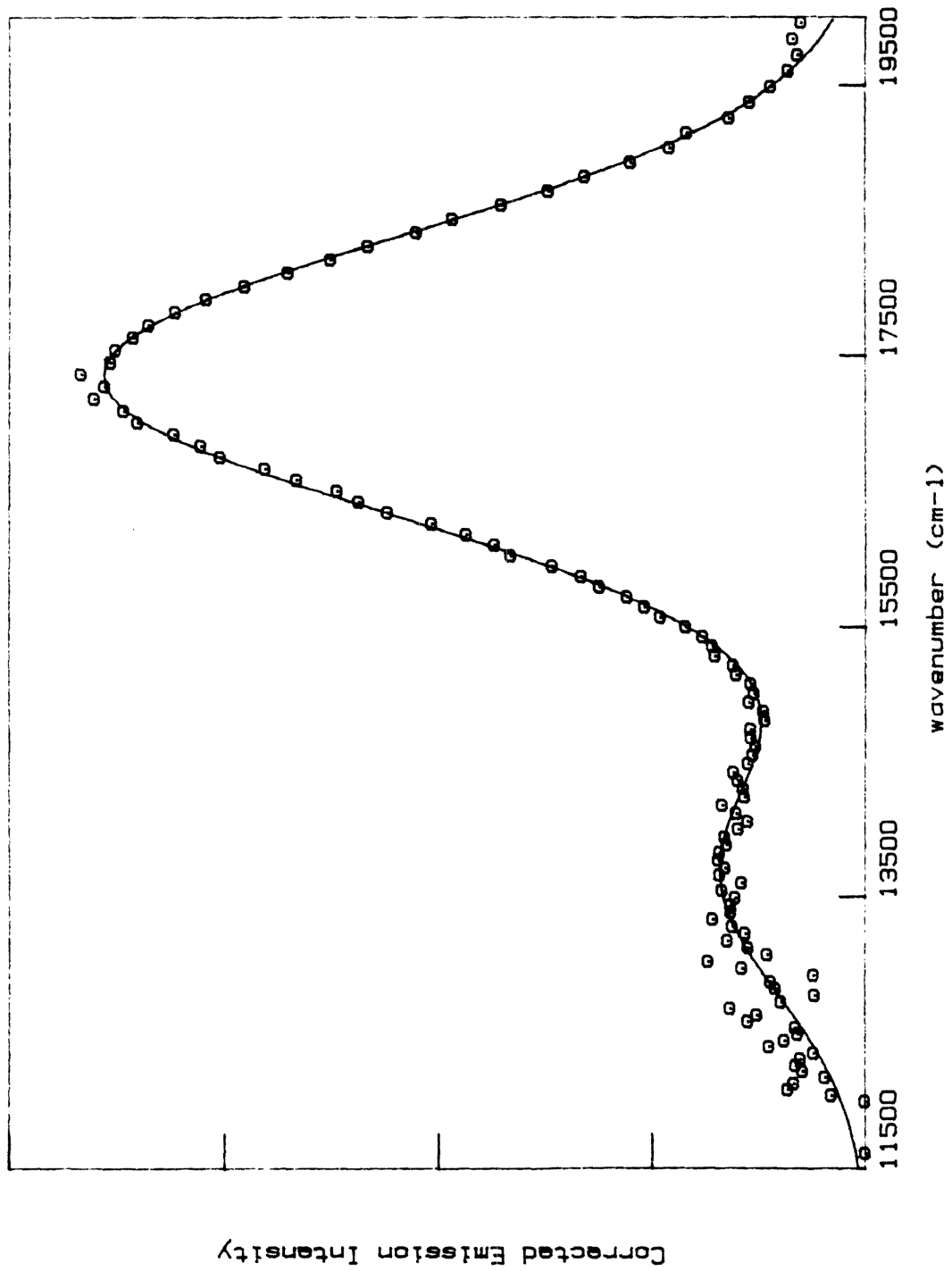
Electrochemistry:

Electrochemical studies were conducted on the series of phenol-pyridinium complexes, $HO\text{-}C_6H_4\text{-}(CH_2)_n\text{-}py^+\text{-}R$, and $Ir_2\text{-}py^+$ donor-acceptor complexes. The one-electron reduction of the pyridinium cation in the former complexes was irreversible on the time scale of the cyclic voltammetry experiment (up to 20 V/s scan rate), with the exception of $HO\text{-}C_6H_4\text{-}CH_2\text{-}py^+\text{-}Am$ (Am = 4-C(O)NH$_2$) which showed a reversible (py$^+$/py$^\bullet$) couple. The cathodic peak potentials, E_{pc}, (and half-wave potential for $HO\text{-}C_6H_4\text{-}CH_2\text{-}py^+\text{-}Am$) are summarized in Table 4.6.

Table 4.6. Cathodic Peak Potentials of $py^+ + e^- \rightarrow py^\bullet$ Reaction in Phenol-Pyridinium Complexes

Compounds	E_{pc}
$HO\text{-}C_6H_4\text{-}py^+$	-1.19
$HO\text{-}C_6H_4\text{-}CH_2\text{-}py^+$	-1.33
$HO\text{-}C_6H_4\text{-}CH_2\text{-}py^+\text{-}tB$	-1.56
$HO\text{-}C_6H_4\text{-}CH_2\text{-}py^+\text{-}Am$ [a]	-0.93
$HO\text{-}C_6H_4\text{-}(CH_2)_2\text{-}py^+$	-1.42
$HO\text{-}C_6H_4\text{-}3\text{-}(CH_2)_2\text{-}py^+$	-1.40
$HO\text{-}C_6H_4\text{-}(CH_2)_3\text{-}py^+$	-1.40

[a] This couple was reversible, $E_{1/2}$ is given.

Figure 4.7 shows a cyclic voltammogram (CV) of $HO\text{-}C_6H_4\text{-}(CH_2)_2\text{-}py^+$, which is representative of the irreversible (py$^+$/py$^\bullet$) couples for the phenol-pyridinium complexes. The wave at -1.4 V vs. SSCE corresponds to the one-electron reduction of py$^+$. The wave at ~-0.2 V has not been definitively assigned, but is only observed after initial negative scans through the reduction wave, indicating the oxidation of a species formed as a consequence of reducing the pyridinium cation to its radical (see below).

Figure 4.7. Cyclic voltammogram of HO-C$_6$H$_4$-(CH$_2$)$_2$-py$^+$, in 0.1 M TBAH CH$_3$CN solution, showing the irreversible wave at -1.4 V vs. SSCE corresponding to reduction of the pyridinium cation. Scan rate was 200 mV/s.

2.5 μA

V vs. SSCE
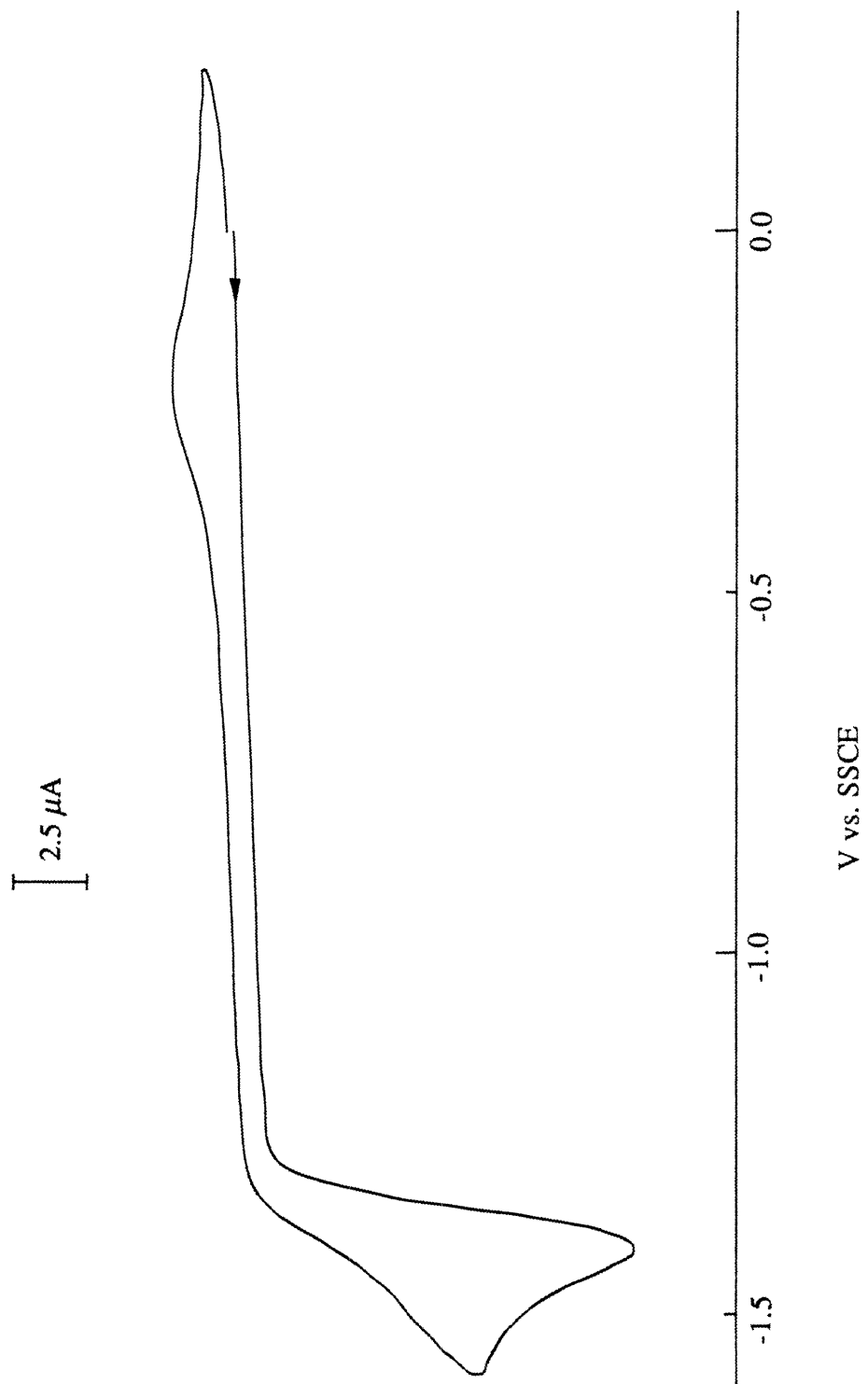
The irreversible behavior of the pyridinium reduction is due to the rapid dimerization of the pyridinium radical to form bipyridine complexes,[15] represented by the eqs 4.1 and 4.2.

$$py^+ + e^- \rightarrow py^\bullet \qquad (4.1)$$

$$2py^\bullet \rightarrow py_2 \qquad (4.2)$$

The process in which an electrochemical reduction is followed by a second-order chemical reaction (EC_2 mechanism) has been treated theoretically.([14],p. 451-461.) The equations that relate the cathodic peak potentials (E_{pc}) to their corresponding half-wave potentials ($E_{1/2}$) are given below:

$$E_{1/2} = E_{pc} + \frac{RT}{nF}\, 0.902 - \frac{RT}{3nF}\, \ln(2k_f C_o RT/3nFv) \qquad (4.3)$$

$$E_{1/2} = E_{pc} + 0.058 - 0.008563\, \ln(k_f C_o/v), \qquad (4.4)$$

where k_f is the rate of the following second-order chemical reaction, C_o is the concentration, and v is the CV scan rate. These equations, however, break down at large k_f (more specifically, when $|E_{1/2} - E_p| \geq \sim 60$ mV). Since the rates of dimerization are nearly diffusion limited ($\sim 10^8$ M^{-1} s^{-1}), eq 4.4 cannot be applied to the present electrochemical experiments. The experimental values for E_{pc} were, therefore, not converted to $E_{1/2}$ values as has previously been done.[10] The errors associated with using E_{pc} values in calculating driving forces will be discussed in the next section of this chapter.

The complex HO-C_6H_4-CH_2-py^+-Am exhibited reversible electrochemical behavior which has been attributed to the stability of the radical $py^\bullet$-Am in acetonitrile solution. The electron-withdrawing 4-amide group is the origin of this stability (4-cyanopyridiniums also exhibit reversible reduction waves). The CV of HO-C_6H_4-CH_2-py^+-Am, showing the

reversible pyridinium reduction, is given in Figure 4.8.

The CVs of the Ir_2-py^+ donor-acceptor complexes exhibit the same irreversible waves between -1.6 and -0.9 V vs. SSCE, corresponding to the familiar one-electron reduction of the pyridinium cation. The E_{pc} values for the iridium complexes were the same as those given in Table 4.6, within experimental error, indicating that there is virtually no effect of the phosphine or iridium dimer on the isolated electrochemical reactions of the pyridinium cation. The one-electron oxidation of the d^8-d^8 dimers to form their corresponding d^8-d^7 species was observed in methylene chloride solution as a reversible wave at $E_{1/2} = 0.31$ V vs. SSCE. An irreversible wave at ~-0.7 V was also observed (as of yet unassigned). The wave was, however, only observed when the initial scan direction was positive (forming Ir_2^+ species) and was not observed when the initial potential sweep was negative. CVs of the model complex, $[Ir_2]$-CH_3, where the initial scans were positive (Figure 4.9a) or negative (Figure 4.9b) demonstrate the behavior of this irreversible cathodic wave.

In acetonitrile solution, however, the (Ir_2/Ir_2^+) couple is not reversible, presumably due to coordination of acetonitrile solvent molecule(s) to the oxidized iridium species. In Figure 4.10 a typical CV of the donor-acceptor complex, $[Ir_2]$-CH_2-py^+, in acetonitrile is shown. This CV is simply a combination of the oxidation wave corresponding to the (Ir_2/Ir_2^+) couple (seen in the CV of $[Ir_2]$-CH_3 in Figure 4.9) and the reduction wave corresponding to the $(py^+/py^{\bullet})$ couple (seen in the CV of the phenol-pyridinium complexes, HO-C_6H_4-$(CH_2)_n$-py^+-R in Figures 4.7 and 4.8).

These electrochemical data, in combination with spectroscopic data, are now used to calculate driving forces for all three electron-transfer reactions in the series of donor-acceptor complexes: (1) singlet excited-state electron transfer, $^1ET = {}^1Ir_2^*$-$py^+ \rightarrow Ir_2^+$-$py^{\bullet}$; (2) triplet excited-state electron transfer, $^3ET = {}^3Ir_2^*$-$py^+ \rightarrow Ir_2^+$-$py^{\bullet}$; (3) and thermal back electron transfer, $ET^b = Ir_2^+$-$py^{\bullet} \rightarrow Ir_2$-$py^+$.

The approximate energetics of the charge-transfer complexes, Ir_2^+-$py^{\bullet}$, were obtained by summing the half-wave potential for one-electron oxidation of the iridium dimer and the

Figure 4.8. Cyclic voltammogram of HO-C_6H_4-CH_2-py$^+$-Am, in 0.1 M TBAH CH_3CN solution, showing the reversible wave at -0.9 V vs. SSCE corresponding to reduction of the pyridinium cation. Scan rate was 200 mV/s.

0.5 μA

-1.0   -0.5
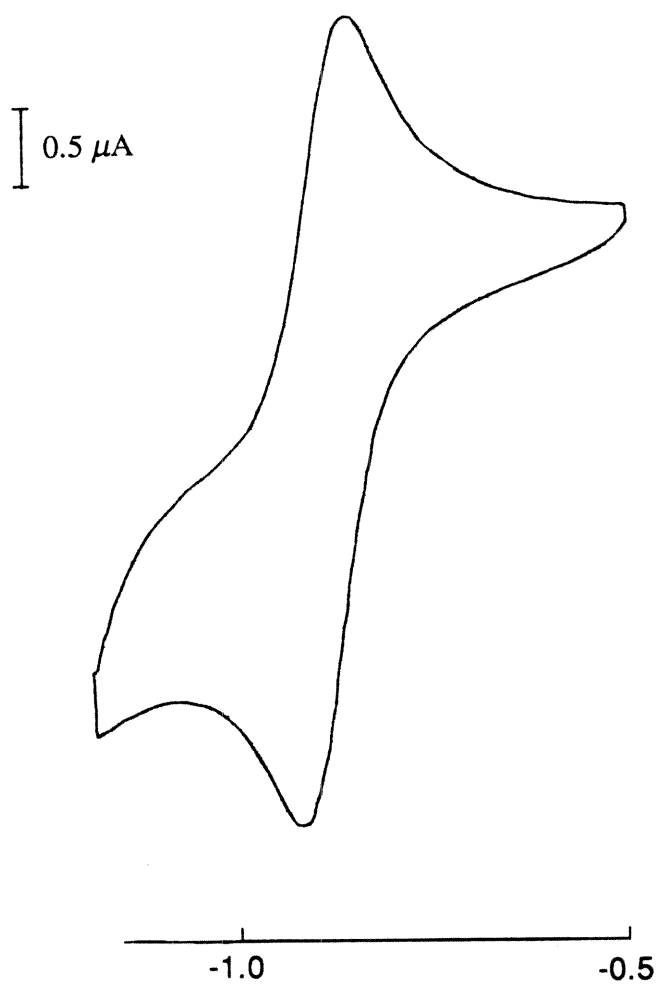
Figure 4.9. (a) Cyclic voltammogram of model complex, [Ir(μ-pz*)(CO)(Ph$_2$P-O-
C$_6$H$_4$-CH$_3$)]$_2$, in 0.1 M TBAH CH$_2$Cl$_2$ solution, showing the reversible wave at 0.3 V vs.
SSCE corresponding to the (Ir$_2$/Ir$_2$$^+$) redox couple. The initial scan direction was anodic,
and the scan rate was 500 mV/s. (b) Same as Figure a, except initial scan direction was
cathodic.

0.5 μA

+

+

-1.0   -0.5   0.0   0.5   1.0

V vs. SSCE

Figure 4.10. Cyclic voltammogram of donor-acceptor complex, $[\text{Ir}(\mu\text{-pz}^*)(\text{CO})(\text{Ph}_2\text{P-}$ $\text{O-C}_6\text{H}_4\text{-CH}_2\text{-py}^+)]_2$, in 0.1 M TBAH CH_3CN solution, showing irreversible one-electron oxidation of Ir_2 at 0.3 V vs. SSCE and one-electron reduction of py^+ at -1.3 V. Scan rate was 20 V/s.

peak potentials of the one-electron reductions of the pyridinium acceptor. Thus, the driving

forces for ET^b in the donor-acceptor complexes can be given by eq 4.5.[16] The driving

forces for the two excited state electron-transfer reactions (^1ET, ^3ET) are logically

expressed by eqs 4.6 and 4.7.

$$-\Delta G°(ET^b) = E_{1/2}(Ir_2/Ir_2^+) - E_{1/2}(py^+/py^\bullet) \qquad (4.5)$$

$$-\Delta G°(^1ET) = E_{00}(S_1) + \Delta G°(ET^b) \qquad (4.6)$$

$$-\Delta G°(^3ET) = E_{00}(T_1) + E_{1/2}(py^+/py^\bullet) - E_{1/2}(Ir_2/Ir_2^+) \qquad (4.7)$$

The results of these calculations are given in Table 4.7, and in Figure 4.11 in the form of a

state diagram. In the next chapter, the driving forces presented here will be employed in

calculations aimed at elucidating electronic-couplings for the electron-transfer reactions

described above.

Table 4.7. Driving Forces for ^1ET, ^3ET, and ET^b Reactions[a]

compounds	$-\Delta G° (^1ET)^b$	$-\Delta G° (^3ET)^b$	$-\Delta G° (ET^b)^b$
$[Ir_2]$-py$^+$	0.90	0.40	1.50
$[Ir_2]$-CH$_2$-py$^+$	0.76	0.26	1.64
$[Ir_2]$-CH$_2$-py$^+$-tB	0.53	0.03	1.87
$[Ir_2]$-CH$_2$-py$^+$-Am	1.16	0.66	1.24
$[Ir_2]$-(CH$_2$)$_2$-py$^+$	0.67	0.17	1.73
$[Ir_2]$-3-(CH$_2$)$_2$-py$^+$	0.69	0.19	1.71
$[Ir_2]$-(CH$_2$)$_3$-py$^+$	0.69	0.19	1.71

[a] $E_{00}(S_1) = 2.40 \pm 0.05$ eV, $E_{00}(T_1) = 1.90 \pm 0.03$ eV.

[b] Driving forces are associated with an error of 0.1 eV.

Figure 4.11. State diagram for donor-acceptor system, constructed from the spectroscopic and electrochemical data found in Tables 4.1, 4.2, 4.3 and 4.6.

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16. The error associated with the calculated driving forces is ±100mV due to the irreversible py$^+$/py$^\bullet$ couple.

Chapter 5

Time-Resolved Experiments

INTRODUCTION

The steady-state spectroscopic results presented in Chapter 4 demonstrated that emission quenching in the series of Ir_2-py^+ donor-spacer-acceptor complexes was a direct consequence of electron transfer from both the singlet and triplet excited states of the d^8-d^8 iridium donor. It was also established that the extent of quenching depended dramatically on the number of methylene groups in the bridge separating the donor and pyridinium acceptor. In this chapter, excited-state and thermal back electron-transfer rates were measured for the series of complexes by employing time-resolved experiments. Figure 5.1 summarizes the three distinct reactions under investigation: (1) singlet excited-state electron transfer, $^1Ir_2^* \rightarrow py^+$ (^{1}ET); (2) triplet excited-state electron transfer, $^3Ir_2^* \rightarrow py^+$ (^{3}ET); and (3) thermal back electron transfer from $py^{\bullet} \rightarrow Ir_2^+$ (ET^b). An expression that correlates the electron-transfer rates to the number of methylene groups in the bridge is presented in this chapter. The issue of through-space versus through-bond mechanisms of electron transfer is also discussed. The evidence presented in this chapter suggests for the first time that electron transfer in linked donor-acceptor complexes can occur via different mechanisms, depending on the initial spin state of the donor.

EXPERIMENTAL

General Procedures:

Samples of the iridium donor-acceptor complexes were prepared in acetonitrile solution and placed in sealed quartz cells. For picosecond experiments, the samples were flowed at rates rapid enough to ensure that a fresh portion of sample was irradiated with each laser shot. Acetonitrile was dried over activated 3Å Linde sieves for a minimum of 3 days, and freeze-pumped-thawed 4 times before being vacuum distilled into the quartz cells holding the samples.

Figure 5.1. A state diagram, showing approximate energy levels of the metal localized and charge-transfer excited states, and summarizing photoinduced (^{1}ET, ^{3}ET) and thermal back (ET^b) electron-transfer reactions.

Picosecond Experiments:

Transient absorption and emission experiments on the picosecond time-scale were conducted using the same laser source.

Laser source: Figure 5.2 shows the layout of the optical table which was common to both transient absorption and emission experiments. A train of 25 ps (FWHM) pulses was generated in an active/passive mode-locked Nd:YAG laser cavity. A saturable absorber was positioned near the back mirror (passive) and an acousto-optic mode-lock was placed near the front mirror (active). A Pockel cell pulse extractor was used to select one peak from the train of picosecond pulses. The beam was then amplified at Amp1, passed through apertures and amplified a second time at Amp2. The beam was then split into two beams: 20% was sent through a third amplifier, Amp3, and the remaining 80% was directed to a second optical table with no further amplification. In both experiments the former beam became the excitation source, and the latter beam became either the trigger pulse in the emission experiment or the probe and reference beams in the transient absorption experiment.

Transient Absorption Experiment: This experiment was conducted by using the pump-probe method for detecting changes in absorption after laser excitation.[1,2] The schematic in Figure 5.3 shows the setup used in this experiment. The excitation beam was generated by frequency doubling the beam from Amp2 and sending it directly to the sample. The probe beam was generated in the following manner: the beam from Amp3 was frequency doubled and tripled, filtered with a 350 nm sharp cut-off filter, passed through a prism and directed to a double-pass movable track. The beam was then passed through a 10 cm cell containing an 80:20 mixture of D_2O/H_2O which generated continuum light. The beam was then passed through a 1:1 beam splitter. One of the beams, which was used as the probe beam, was sent directly to the sample and the other was allowed to bypass the sample and was used as a reference beam. The probe beam, which was delayed

Figure 5.2. Schematic diagram of Nd:YAG laser source used to generate 25 ps (FWHM) laser pulses.

back mirror

Nd:YAG rod

front mirror

pulse extractor

Amp 1

Amp 2

Amp 3

80%

20%

excitaiton beam

Figure 5.3. Layout of transient absorption experiment showing excitation, probe, and reference beams.

relative to the excitation beam by adjusting the position of the double-pass movable track, was passed through one of two slits of a monochrometer. The reference beam was passed through the other slit and both beams were detected using one photomultiplier tube for each. 200 laser shots were used for each delay time and wavelength. 100 ratios of the probe and reference beams were measured without sample excitation and another 100 ratios were measured with sample excitation. The log of the ratio of these ratios is equal to Δ Absorbance. Data were transferred to a PDP 11/23 computer and analyzed using software developed at Brookhaven National Laboratories.

Emission Experiment: In this experiment, the beam from Amp3 was frequency doubled and tripled, then sent through an IR filter where about 20% of the beam was reflected and used as a timing pulse. The remaining 80% was focused into a 10 cm cell containing methanol which generated raman shifted Stokes and anti-Stokes emission at ~630 and ~460 nm. The anti-Stokes emission was separated from the Stokes and fundamental emission by passing the beam through a prism. The trigger pulse was generated from filtered leakage of intensity from Amp2. The trigger pulse, timing pulse and picosecond excitation pulse at 460 nm were directed to a third optical table. The excitation beam was made to pass through a 460 nm narrow-band-pass filter, focused, and vertically polarized before exciting the sample. Emission from the sample was directed into a spectrometer at magic angle polarization (57.74°), eliminating artifacts arising from solute rotation. The signal (spectrally confined to 250 nm) was then focused into the 400 μm slit of a Hamamatsu Temporal Disperser C1587. The data was transmitted from a High Speed Streak Unit M1952 to a monitor via a high resolution video camera. Data were transferred to a PDP11/23 computer and analyzed using software developed at BNL.

Nanosecond Experiment:

A laser system built at Caltech that has been previously described,[3] was used for determining phosphorescence lifetimes. The excitation source was a Quanta Ray DCR-1

Q-switched Nd:YAG laser, which was frequency doubled and tripled with a Quanta Ray HG-1 harmonic generator (KDP). Doubled (532 nm) and tripled (~355 nm) 8 ns (FWHM) laser pulses were separated from the YAG fundamental (1064 nm) using a Quanta Ray PHS-1 prism harmonic separator. Light emitted from the sample was collimated at 90° from the excitation beam, and focused through a Corning 3483 sharp cut-off filter onto the entrance slit of a MacPherson monochrometer. Luminescence was detected using a Hamamatsu R955 photomultiplier tube, and the signal was amplified with a LeCroy VV101ATM amplifier. Signals were digitized with a Biomation 6500 waveform recorder and transferred to a Digital PDP11/103-L computer. The data were analyzed on a Compaq 386 PC using OLIS software.

RESULTS

Figure 5.4 shows transient difference spectra immediately following (0-20 ps) and 90 ps after 355 nm laser irradiation for the $n = 2$ donor-acceptor complex, $[Ir(\mu\text{-}pz^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}(CH_2)_2\text{-}py^+)]_2$ ($[Ir_2]\text{-}(CH_2)_2\text{-}py^+$). Two main features are apparent in the spectra: a bleach centered around 460 nm which corresponds to the position of the ground-state $S_0 \rightarrow S_1$ absorption, and a broad positive absorption feature at around 400 nm which was logically assigned to absorption by the singlet and triplet ($d\sigma^*p\sigma$) excited states.[4] The kinetics of these features obtained by detection at 460 nm and 405 nm are given in Figures 5.5 and 5.6. Both show biexponential behavior with lifetimes of 120±20 ps and 2.4±0.2 ns for the positive absorption region, and 190±30 ps and 2.5±0.2 ns for the bleach region. Independent time-resolved emission measurements conducted on $[Ir_2]\text{-}(CH_2)_2\text{-}py^+$ (presented in the next section) revealed triplet and singlet lifetimes of 1.7 ns and 36 ps, respectively. The transient species in the absorption experiments are, therefore, assigned to the triplet excited state ($\tau = \sim 2$ ns) and a species ($\tau = \sim 150$ ps) which

Figure 5.4. Transient difference spectra of $[Ir(pz^*)(CO)(Ph_2P-O-C_6H_4-(CH_2)_2-py^+)]_2$ at 0 ps (o) and 90 ps (•) after laser excitation. The spectra show the decay of the bleach and absorption regions.

Figure 5.5. Kinetics of bleach obtained by excitation at 355 nm and detection at 460 nm of [Ir(pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-(CH$_2$)$_2$-py$^+$)]$_2$ donor-acceptor complex. Biexponential fit to the data yielded τ_1 = 2.5 ns and τ_2 = 190 ps.

Figure 5.6. Kinetics of absorption feature obtained by excitation at 355 nm and detection at 405 nm of $[Ir(pz^*)(CO)(Ph_2P-O-C_6H_4-(CH_2)_2-py^+)]_2$ donor-acceptor complex. Biexponential fit to the data yielded $\tau_1 = 2.4$ ns and $\tau_2 = 120$ ps.

does *not* correspond to the singlet or triplet excited state. This species has been identified, by analogy to transient absorption experiments conducted on similar donor-acceptor complexes,[4] as the charge-transfer complex. Similar results were obtained for the $n = 1$ complex, $[Ir_2]\text{-}CH_2\text{-}py^+$, which revealed a charge transfer state lifetime, τ_{CT}, of about an order of magnitude longer than was found for $[Ir_2]\text{-}(CH_2)_2\text{-}py^+$. These results are summarized in Table 5.1.

Time-resolved emission experiments, conducted on the series of donor-acceptor complexes, $[Ir(\mu\text{-}pz^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}(CH_2)_n\text{-}py^+\text{-}R)]_2$, and on two model complexes,$[Ir(\mu\text{-}pz^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}Y)]_2$ (Y was either CH_3 or $CH_2\text{-}Quin^+$, both of which are extremely poor electron acceptors), were employed to measure singlet and triplet excited-state lifetimes. Either of two emission experiments was used depending on the lifetime of the complexes. A Streak Camera experiment was utilized in obtaining the

Table 5.1. Fluorescence, Phosphorescence, and Charge-Transfer State Lifetimes of Model and Donor-Acceptor Complexes

Compounds	τ_f (ps)	τ_p (ns)	τ_{CT} (ns)
$[Ir_2]\text{-}CH_3$	—[a]	640 ± 50 [d,e]	—[a]
$[Ir_2]\text{-}CH_2\text{-}Quin^+$	124 ± 7 [c]	1000 ± 100 [e]	—[a]
$[Ir_2]\text{-}py^+$	—[b]	360 ± 40 [d]	—[a]
$[Ir_2]\text{-}CH_2\text{-}py^+$	—[a]	660 ± 50 [d]	1.8 ± 0.2 [f]
$[Ir_2]\text{-}CH_2\text{-}py^+\text{-}tB$	93 ± 6 [c]	740 ± 110 [e]	—[a]
$[Ir_2]\text{-}CH_2\text{-}py^+\text{-}Am$	—[a]	680 ± 50 [d]	—[a]
$[Ir_2]\text{-}(CH_2)_2\text{-}py^+$	36 ± 3 [c]	1.7 ± 0.1 [c]	0.15 ± 0.02 [f]
$[Ir_2]\text{-}3\text{-}(CH_2)_2\text{-}py^+$	19 ± 1 [c]	1.8 ± 0.2 [c]	—[a]
$[Ir_2]\text{-}(CH_2)_3\text{-}py^+$	74 ± 6 [c]	20 ± 2 [e]	—[a]

[a] These lifetimes were not measured.

[b] The lifetime of this complex was too short to measure.

[c] Obtained from Streak Camera experiment.

[d] Obtained from nanosecond emission experiment, Caltech.

[e] Obtained from picosecond emission experiment, Brookhaven National Laboratories.

[f] Obtained from picosecond transient absorption experiment, Brookhaven National Laboratories.

singlet lifetimes of $[Ir_2]$-$(CH_2)_2$-Quin$^+$, $[Ir_2]$-CH_2-py$^+$-tB, $[Ir_2]$-$(CH_2)_2$-py$^+$,

$[Ir_2]$-3-$(CH_2)_2$-py$^+$, and $[Ir_2]$-$(CH_2)_3$-py$^+$ donor-acceptor complexes, as well as the short

triplet lifetimes of $[Ir_2]$-$(CH_2)_2$-py$^+$ and $[Ir_2]$-3-$(CH_2)_2$-py$^+$. Figure 5.7 shows

spectral/kinetic data for the $n = 3$ complex, $[Ir_2]$-$(CH_2)_3$-py$^+$. This time-resolved emission

spectrum in the range between 440 and 580 nm showed the expected maximum at ~550 nm

(refer to Table 4.4. Emission Data) which decayed with a lifetime of 74 ps over the entire

emission band (470-570 nm). Figure 5.8 shows the kinetic data accumulated from the

most intense spectral window (520-580 nm). The data for this compound and the

complexes mentioned above were all fit to monoexponential intensity functions, the results

of which are given in Table 5.1.

The triplet lifetimes of the $[Ir_2]$-CH_3, $[Ir_2]$-CH_2-Quin$^+$, $[Ir_2]$-CH_2-py$^+$-tB, and

$[Ir_2]$-$(CH_2)_3$-py$^+$ complexes were obtained using standard emission experiments (laser

excitation at 460 or 355 nm, and detection of emission at 750 nm using a PMT).

Figure 5.9 shows representative kinetic data for the model complex, $[Ir_2]$-$(CH_2)_2$-Quin$^+$,

($\tau = 1.0\ \mu s$). The data for all compounds were fit satisfactorily to monoexponential

intensity functions and are summarized in Table 5.1.

The excited-state electron-transfer rates were calculated from the lifetime data by using

eq 5.1. The factor of 1/2 in the equation is required by the 2:1 acceptor/donor

$$k_{ET} = 1/2\left(\frac{1}{\tau} - \frac{1}{\tau^\circ}\right) \tag{5.1}$$

stoichiometry in these complexes. τ_0 is the intrinsic singlet or triplet lifetime of the

unquenched complexes, *i.e.*, the lifetime of the model complex, and τ is the singlet or

triplet lifetimes of the donor-acceptor complex. This equation is valid because the radiative

and nonradiative rate constants, intrinsic to the d^8-d^8 chromophore, are unperturbed by the

pyridinium cation (this situation was established from the spectroscopic data presented in

Chapter 4). In cases where lifetime data were not available, emission quantum yields were

Figure 5.7. Kinetic/spectral data obtained from Streak Camera experiment for [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-(CH$_2$)$_3$-py$^+$)]$_2$.

Figure 5.8. Kinetics of [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-(CH$_2$)$_3$-py$^+$)]$_2$, τ_f = 74 ps, λ_{ex} = 460 nm, data collected between 520 and 580 nm. The dashed line is the best fit to the data, and the dotted line is the instrument response function.

Figure 5.9. Kinetics of [Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-CH$_2$-Quin$^+$)]$_2$, τ_{ph} = 1.0 μs, λ_{ex} = 460 nm, λ_{em} = 750 nm, obtained from nanosecond emission experiment.

TIME, μs

Y-axis

employed to determine singlet and triplet electron-transfer rates using eqs 5.2 and 5.3,

respectively. Φ_f^o and Φ_p^o are the fluorescence and phosphorescence quantum yields for the

model complex and Φ_f and Φ_p are the corresponding quantum yields for the donor-acceptor

complex. Thermal back electron-transfer rates were calculated using eq 5.4, where $k_{ET}b$ is

simply the inverse of the charge-transfer state lifetime, τ_{CT}.

$$\frac{\Phi_f^o}{\Phi_f} = 1 + 2k_{^1ET}\tau_f^o \tag{5.2}$$

$$\frac{\left(\dfrac{\Phi_f^o}{\Phi_f}\right)}{\left(\dfrac{\Phi_p^o}{\Phi_p}\right)} = 1 + 2k_{^3ET}\tau_p^o \tag{5.3}$$

$$k_{ET^b} = 1/\tau_{CT} \tag{5.4}$$

The results of these calculations are summarized in Tables 5.2 and 5.3. The driving forces

for each reaction, calculated in Chapter 4, are also given. In the next section these ET rates

will be discussed in light of the structural parameters presented in Chapter 3. A discussion

of the effects of the initial spin-state of the donor on ET rates will also be given.

DISCUSSION

A previous study conducted in our laboratory on the donor-acceptor complexes,

$[Ir(pz^*)(CO)(Ph_2P\text{-}O\text{-}(CH_2)_2\text{-}py^+\text{-}R)]_2$, has demonstrated the effects of driving force on

electron-transfer rates.[5] The ^1ET, ^3ET, and ET^b rates were fit to classical Marcus theory

with the same set of parameters: $\lambda = 1.0$ eV and $H_{DA} = 24$ cm^{-1}. These results are applied

to the present investigation in an effort to extract electronic coupling matrix elements. This

was accomplished by first assuming that the nuclear reorganization energies (mainly due to

Table 5.2. Singlet and Triplet Excited-State Electron-Transfer Rates for Donor-Acceptor Complexes

Compounds	^{1}ET		^{3}ET	
	-$\Delta G°$(eV) [a]	k_{ET} (s^{-1})	-$\Delta G°$(eV) [a]	k_{ET} (s^{-1})
[Ir$_2$]-py$^+$	0.90	1.0±0.3 × 10^{11} [b]	0.40	8.9±1.8 × 10^5
[Ir$_2$]-CH$_2$-py$^+$	0.76	3.6±0.9 × 10^9 [b]	0.26	2.5±0.5 × 10^5
[Ir$_2$]-CH$_2$-py$^+$-tB	0.53	1.3±0.1 × 10^9	0.03	1.8±0.4 × 10^5
[Ir$_2$]-CH$_2$-py$^+$-Am	1.16	1.8±0.5 × 10^9 [b]	0.66	2.4±0.5 × 10^5
[Ir$_2$]-(CH$_2$)$_2$-py$^+$	0.67	1.4±0.1 × 10^{10}	0.17	1.6±1.4 × 10^8
[Ir$_2$]-3-(CH$_2$)$_2$-py$^+$	0.69	3.1±0.2 × 10^{10}	0.19	1.6±1.3 × 10^8
[Ir$_2$]-(CH$_2$)$_3$-py$^+$	0.69	2.7±0.3 × 10^9	0.19	2.1±0.3 × 10^7

[a] Driving forces are associated with an error of ±0.1 eV.

[b] Obtained from quantum yield measurements using eq 5.3 since triplet lifetimes were not available.

Table 5.3. Thermal Back Electron-Transfer Rates for Two Donor-Acceptor Complexes [a]

Compounds	-$\Delta G°$(eV)	k_{ET} (s^{-1})
[Ir$_2$]-CH$_2$-py$^+$	1.50	5.6±0.6 × 10^8
[Ir$_2$]-(CH$_2$)$_2$-py$^+$	1.73	6.7±1.9 × 10^9

[a] the back electron-transfer rates for the remaining Ir$_2$-py$^+$ complexes were not measured.

solvent reorganization with little contribution from internal modes[4]) in both systems are similar. This assumption is valid because the same solvent (CH$_3$CN) was used, and the approximate donor-acceptor separations are comparable. The values of H_{DA} for electron transfer in [Ir(pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-(CH$_2$)$_n$-py$^+$)]$_2$ were then calculated by solving the Marcus expression for electron-transfer rates,[6] imputing a value for λ of ~1.0 eV. These calculations were conducted on the four classes of donor-acceptor complexes (n = 0, 1, 2, and 3) for ^{1}ET, ^{3}ET, and ET[b] reactions. We will refer to electronic couplings associated

with singlet and triplet excited-state electron transfer as $^1H_{DA}$ and $^3H_{DA}$, respectively, and the electronic couplings associated with the thermal back electron transfer as $^bH_{DA}$. In Figures 5.10a-d, the results of these calculations are shown in the form of four separate Marcus curves for the $n = 0, 1, 2$, and 3 complexes. The results are also summarized in Table 5.4.

It is apparent from the calculations of H_{DA} for ^1ET, ^3ET and ET^b in the series of donor-acceptor complexes that: (1) in complexes with $n = 0$ and 1, $^1H_{DA} >> ^3H_{DA}$; (2) in complexes with $n = 2$ and 3, $^1H_{DA} = ^3H_{DA}$; and (3) in the two complexes where k_{ET^b} were measured, $^1H_{DA} = ^bH_{DA}$.

Table 5.4. Electronic Coupling Matrix Elements for ^1ET, ^3ET and ET^b in the Donor-Acceptor Complexes

Compounds	n	$^1H_{DA}$ (cm^{-1})	$^3H_{DA}$ (cm^{-1})	$^bH_{DA}$ (cm^{-1})
[Ir$_2$]-py$^+$	0	21	0.4	— [a]
[Ir$_2$]-CH$_2$-py$^+$-R	1	5	<0.3	5
[Ir$_2$]-(CH$_2$)$_2$-py$^+$	2	26	26	26
[Ir$_2$]-(CH$_2$)$_3$-py$^+$	3	7	7	— [a]

[a] Back electron-transfer rates were not measured for these complexes.

In an effort to understand these observations, the singlet ET reactions (along with the thermal back ET reactions) will first be discussed followed by a discussion of the triplet ET reactions. Once we have established the possible explanations for the electronic couplings observed for each excited-stated ET reaction, the results from the donor-acceptor complex, [Ir$_2$]-3-(CH$_2$)$_2$-py$^+$, which has in its bridge a 1,3-disubstituted phenylene group, will be discussed. This complex will serve to further substantiate our theoretical models concerning electron transfer from singlet and triplet excited states.

Figure 5.10. (a) Fit of ^{1}ET (○) rate for [Ir$_2$]-py$^+$ (n = 0) to Marcus theory (eq 1.2). (b) Fit of ^{1}ET (○) and ET^b (▲) rates for [Ir$_2$]-CH$_2$-py$^+$ (n = 1). (c) Fit of ^{1}ET (○), ^{3}ET (□), and ET^b (▲) rates for [Ir$_2$]-(CH$_2$)$_2$-py$^+$ (n = 2). (d) Fit of ^{1}ET (○) and ^{3}ET (□) rates for [Ir$_2$]-(CH$_2$)$_2$-py$^+$ (n = 3).

c

$H_{DA} = 26\ cm^{-1}$

$\lambda = 1.10\ eV$

d

$H_{DA} = 7\ cm^{-1}$

$\lambda = 1.05\ eV$

Singlet Electron Transfer:

Even though the through-bond edge-to-edge Ir_2 to py^+ distance in $[Ir_2]-CH_2-py^+$ is

~1.5 Å shorter than that of $[Ir_2]-(CH_2)_2-py^+$ (refer to Table 3.5. Structural Parameters), the

$^1H_{DA}$ in the former is about five times smaller. This strongly suggests that the principal

pathway for the electron transfer from the singlet excited state of the iridium dimer is

through the bonds of the hydrocarbon bridge.[7] We will therefore discuss the singlet

electronic couplings in terms of through-bond mechanisms only. Through-bond (TB)

interactions are the result of mutual mixing of orbitals via the intervening σ (or π)

framework. Model calculations[7-9] and experimental results[10-15] have led to several

important generalizations concerning orbital interactions through n methylene groups: (1)

The extent of orbital interactions through n methylene groups ($n - 1 = m$ bonds), for a

given value of n, depends on the geometry of the σ relay and is maximized for an all-trans

arrangement of σ bonds; (2) ET rates, in a series of donor-acceptor complexes with all trans

bridges (n must be even), decay exponentially with an increasing number of intervening

σ-bonds. Oliver *et al.*[16] recently observed this behavior in molecules possessing

1,4-dimethoxynaphthalene donors attached via rigid hydrocarbon spacers (norbornyl

groups) to 1,1-dicyanoethylene acceptors. Their hydrocarbon spacers had either an

all-*trans* arrangement of single bonds or a single σ-*cis* kink in the chain. In each case the

all-*trans* isomer gave the faster rate by about a factor of 10. Similar results were also

obtained by Wasielewski *et al.*[17] in rigid porphyrin-quinone complexes, shown in

Figure 5.11. The all-*trans* isomer exhibited a singlet ET rate approximately two times

faster than the cisoid isomer. These examples demonstrate that through-bond coupling of

donor and acceptor through saturated bridges plays an important role in determining ET

rates, and furthermore, *trans* donor-acceptor configurations result in enhanced ET rates

over cisoid configurations.

A discussion of the experimentally determined singlet electronic coupling matrix

elements ($^1H_{DA}$) for the four classes of Ir_2-py^+ donor-acceptor complexes (n = 0, 1, 2,

all-*trans*   cisoid

▬▬▬ = –C₆H₅ or –C₆H₄–

▬▬▬ = $-C_6H_5$ or $-C_6H_4-$

■Q■ = quinone

P = porphyrin

Figure 5.11. Edge-view of porphyrin-quinone complexes.

and 3) will therefore be presented in light of through-bond electron-transfer mechanisms. The discussion that follows hinges on the assumption that in these complexes, photoinduced electron transfer from the singlet excited state of the Ir_2 donor occurs via the *stretched* conformations (stretched and folded conformations are discussed in Chapter 3). In the stretched conformation, gauche interactions between the aromatic rings (phenylene and pyridinium groups) are minimized, implying that it is the lowest energy conformation in solution. Therefore, during the short lifetime of the Ir_2 singlet excited state (~100 ps), the most populated structure found in solution would be the stretched conformation.

Through-Bond Electron Transfer Mediated by *One* Methylene Group: The orbital interactions in complexes where π systems are separated by one methylene group can be modelled by the π-orbital overlap in norbornadiene.[18] The π MOs in this complex are known from photoelectron (PE) spectroscopy to interact predominantly through space.[19] Therefore, in the $n = 1$ donor-acceptor complex, $[Ir_2]$-CH_2-py^+, only through-*space* interactions between the phenylene and pyridinium groups are expected to play a role in

coupling $^1Ir_2^*$ and py^+. Since it has already been established that solely through-*bond* interactions couple $^1Ir_2^*$ and py^+, the value of $^1H_{DA}$ is predicted to be extremely small. The experimentally determined $^1H_{DA}$ of 5 cm^{-1} for $[Ir_2]$-CH_2-py^+ is therefore not surprising.

Electron Transfer through *Two* Methylene Groups: The orbital interactions in complexes where π systems are separated by two methylene groups can be modelled by compound **1** shown in Figure 5.12. From PE spectroscopy, the difference in vertical

1   **2**

Figure 5.12. Structure of molecules which exhibit strong π through-bond interactions (**1**) and diminished through-bond interactions (**2**)

ionization potential, $\Delta I_v(\pi)$, for the π_- and π_+ MO levels can be calculated.[18] Large values of $\Delta I_v(\pi)$ have been shown to imply efficient through-bond orbital interactions.[20] $\Delta I_v(\pi)$ in this molecule was found to be 1.16 eV. This value can be compared to 0.78 eV for the *syn*-isomer, **2**, where the reduced $\Delta I_v(\pi)$ is due to the presence of competing through-space interactions, which are of course absent in the **1**.

The results from this model predict that $^1H_{DA}$ for $[Ir_2]$-$(CH_2)_2$-py^+ ($n = 2$) should be much larger than for $[Ir_2]$-CH_2-py^+ ($n = 1$), due to enhanced through-bond coupling in the former complex. This was experimentally observed: $^1H_{DA}(1) = 5$ cm^{-1} and $^1H_{DA}(2) = 26$ cm^{-1}.

Electron Transfer through *Three* Methylene Groups: The orbital interactions in complexes where π systems are separated by three methylene groups can be modelled by the compound shown in Figure 5.13. $\Delta I_v(\pi)$ in this compound was found to be only 0.87 eV[21] as compared to 1.16 eV for compound 1 in Figure 5.12. The diminished through-bond orbital interaction in this compound can been attributed to the trans effect for electron transfer. The relatively small value of $^1H_{DA}$ (7 cm^{-1}) for [Ir$_2$]-(CH$_2$)$_3$-py$^+$ is therefore not surprising.

Figure 5.13. Structure of model compound for p orbital interactions through three methylene groups.

The experimental values of $^1H_{DA}$ (given in Table 5.4) for the series of donor-acceptor complexes are adequately explained by invoking through-bond interactions in the stretched conformations of the Ir$_2$-py$^+$ donor-acceptor complexes. The result, which indicates that electronic coupling in the $n = 2$ donor-acceptor complex is the most efficient of the series, can be attributed to the trans effect for electron transfer. The values of $^bH_{DA}$ for the $n = 1$ and 2 complexes are equivalent to the corresponding values of $^1H_{DA}$. A satisfactory explanation for this is not presented; however, this result implies that thermal back electron-transfer in these complexes occurs from a charge-transfer state exhibiting singlet character.

The $n = 0$ complex, [Ir$_2$]-py$^+$, was not modelled in the preceding discussion,

however, its large value of $^1H_{DA}$ (21 cm^{-1}) implies that the p-orbitals at the point of attachment of the pyridinium and phenylene rings interact strongly. This point is discussed in more detail in the next section, where electronic couplings for triplet electron-transfer reactions are considered.

Triplet Electron Transfer:

The results presented in Table 5.4 show that $^3H_{DA}$ values for the $n = 0$ and $n = 1$ donor-acceptor complexes are considerably smaller than for the $n = 2$ and $n = 3$ complexes, and furthermore, the $^3H_{DA}$ for the $n = 2$ complex is larger than for the $n = 3$ complex. These results imply that the through-bond mechanism (which plays an important role in determining values of $^1H_{DA}$) does not play an important role in $^3H_{DA}$. Therefore the $^3H_{DA}$s will be discussed in terms of through-space (TS) interactions. TS interactions, as the term implies, result from direct spatial overlap of two interacting (basis) orbitals.[7-9]

Evidence that through-space interactions can lead to such strong couplings of π systems ($^3H_{DA}(2) = 26$ cm^{-1}) is available in a system comprised of xanthene and related dyes dissolved in the non-polar solvents anthracene, phenanthrene, and 1-chloronaphthalene.[22] In this system of interacting aromatic rings a determination of the pure through-space electron-exchange matrix element, H_{DA}, was possible. A value of 35 cm^{-1} for H_{DA} was obtained by fitting the charge-transfer data to the Marcus expression for electron transfer. This system clearly demonstrates that through-space coupling of face-to-face aromatic groups can be considerable. It is, however, not clear what the precise structural requirements are for large through-space interactions to persist, and more precisely, what role, if any, the number of intervening methylene groups play in determining the extent of through-space coupling.

Studies of the charge-transfer quenching of benzophenone phosphorescence (^3ET) by olefins shed some light on these questions.[23] In this system, the benzophenone and olefin were separated by n methylene groups ($n = 1$–21). It was observed that there was a

sudden increase in $k_{ET}(n)$ for chains of length $n = 8$ and another significant jump for $n = 9$, as seen in the data presented in Table 5.5. Space-filling models indicated that only chains of at least eight CH_2 groups permit the terminal $-CH=CH_2$ group to come within van der Waals contact of the ketone carbonyl. The suggestion was made, from these results, that a close approach between the alkene and the ketone carbonyl group was necessary for quenching of the ketone triplet to occur. The diminished ET rates at large values of n (18 and 21) are most likely due to the decreased probability of the donor and acceptor meeting in a favorable conformation.

Table 5.5. Triplet Electron-Transfer Rates in a series of Benzophenone-Alkene Complexes

n	$k_{ET} \times 10^{-4}$ (s^{-1})
1	0
2	0
4	1.0
6	1.3
8	23.5
9	54.1
10-15	63.6 ± 10 [a]
18	36.3
21	30.2

[a] Average of rates for $n = 10$-15.

When our results are considered in light of the above observations, a correlation of the number of methylene groups in the bridge to $^3H_{DA}$ arises. If through-space coupling is primarily responsible for the observed values of $^3H_{DA}$, then the through-space interactions in $[Ir_2]$-$(CH_2)_2$-py^+ ($n = 2$) are the largest of the series followed by the $n = 3$ complex, and then the $n = 0$ and $n = 1$ complexes which presumably have diminished TS interactions.

In an attempt to quantify the dependence of $^3H_{DA}$ on n, the assumption will therefore

be made that the origin of the coupling between the donor and acceptor is specifically the TS interaction between the pyridinium ring and the phenylene ring in the *folded* conformation. Furthermore, since the structures of the folded conformations for the series of complexes (see Figures 3.5-3.10) reveal that the most important interaction between the two aromatic rings is between the C4 atom of the phenylene ring and the N atom of the pyridinium ring, only the TS interaction between the corresponding p-orbitals on C4 and N will be considered. The electron accepting molecular orbital (LUMO) of the pyridinium acceptor has p-character on the N atom,[24] warranting consideration of the interactions of the 2p-orbitals on the C4 and N atoms.

Since electron densities usually fall off exponentially as the distance between the electron and the nucleus is increased, the orbital overlap between C4 and N is also expected to fall off exponentially as their separation, r, increases.[25, 26] If the assumption is made that electron transfer occurs via electronic coupling between the p-orbitals of C4 and N, then the electron-transfer rates would also be expected to fall off exponentially with r. The exponential dependence of electron-transfer rates on r has been demonstrated in many donor-acceptor systems[11-15, 25, 27-33] and can be expressed by eq 5.1, where A is a

$$k_{ET} = A \exp(-\beta \cdot r), \qquad (5.1)$$

preexpontential constant and β is a measure of the steepness of a log k_{ET} vs r plot. However, eq 5.1 neglects stereoelectronic details of the p-orbital overlap. The introduction of angular terms into the equation will take into account the asymmetry of the p-orbitals. This is accomplished by considering the angular dependence on the overlap between the 2p-orbitals on C4 and N.

The overlap between two 2p-orbitals, S_{12}, whose axes lie in parallel planes at a distance r is a function of the overlap integral of parallel 2p orbitals, $S_{\pi\pi}$, and the cant angle, γ, which is defined in Figure 5.14a.[34] $S_{\pi\pi}$ is a function of the effective nuclear

charge, Z, usually taken to be 3.09, and decays exponentially with r, as described above. Eq 5.2 reflects the dependence of S_{12} on $S_{\pi\pi}$ and γ. When the p-orbitals are also slanted towards one another at the angle θ, as defined in Figure 5.14b, the expression for S_{12} (which is now resolved into σ and π type overlaps) is given by eqs 5.3 and 5.4, where $S_{12}(\sigma)$ and $S_{12}(\pi)$ are the σ and π contributions to the total overlap. The values of $S_{\sigma\sigma}$ and $S_{\pi\pi}$ were obtained from Kopineck's compilation.[35] It was established in Chapter 1 that the electron-transfer rates are proportional to the square of the electronic coupling or, in this case the direct orbital overlap (eq 5.5).

$$S_{12} = S_{\pi\pi} \cos\gamma \tag{5.2}$$

$$S_{12} = S_{\sigma\sigma} \cos^2\theta + S_{\pi\pi} \sin^2\theta \cos\gamma \tag{5.3}$$

$$S_{12} = S_{12}(\sigma) + S_{12}(\pi) \tag{5.4}$$

$$k_{ET} \propto S_{12}^2 \tag{5.5}$$

Figure 5.14. (a) Definition of γ and r. (b) Definition of C4, N, and θ.

Before the validity of eq 5.5 is tested, we must consider the statistical distributions in solution of the folded conformations. If we assume that only a finite number of low energy conformations exist in solution and that the energy associated with each possible conformation is approximately the same, then a statistical factor, P, can be introduced into eq 5.5, which is the number of conformations in the folded form divided by the total number of possible conformations. For example, in the $n = 2$ complex there are three possible low energy conformations, shown in Figures 5.15: two folded (a and b) and one

a   b   c

Figure 5.15. Newman projections of the three low energy conformations for n = 2 donor-acceptor complex, (a) and (b) represent the folded conformations, and (c) represents the stretched conformation.

stretched (c). Therefore, P in this case is 2/3. The value of P decreases rapidly as n increases, expressing the fact that at large n the probability of finding the pyridinium ring eclipsed over the phenylene ring is severely diminished (as in bimolecular reactions). P can now be incorporated into eq 5.5 yielding the final expression, eqs 5.7, which relates

electron-transfer rates to the statistical and angular terms of eqs 5.2-5.6.

$$k_{ET} \propto P\, S_{12}^2 \qquad\qquad (5.6)$$

$$k_{ET} \propto I_T^{\,2} \qquad\qquad (5.7)$$

The parameters in eqs 5.1, 5.3, and 5.6 (r, γ, θ, P, $S_{\sigma\sigma}$, and $S_{\pi\pi}$) are given in Table 5.6 for the series of donor-acceptor complexes. Included in the table are the parameters for the analogous $n = 4$ complex, which were not prepared in this study, but can lead to predictions concerning future studies.

Table 5.6. Structural and Electronic Parameters for Donor-Acceptor Complexes

Compounds	n	r (Å)	γ	θ	P	$S_{\sigma\sigma}$	$S_{\pi\pi}$
$[Ir_2]$-py$^+$	0	1.4	42	90	1	0.32	0.27
$[Ir_2]$-CH$_2$-py$^+$	1	2.4	0	55	1	0.17	0.046
$[Ir_2]$-(CH$_2$)$_2$-py$^+$	2	3.1	0	25	.67	0.085	0.015
$[Ir_2]$-(CH$_2$)$_3$-py$^+$	3	3.7	0	20	.11	0.056	0.0074
$[Ir_2]$-(CH$_2$)$_4$-py$^+$	*4*	*4.0*	*0*	*8.5*	*.07*	*0.038*	*0.0038*

Assuming that $k_{ET}(n)$ is proportional to the square of the statistically adjusted C4-N p-orbital overlap, $I_T^{\,2}(n)$, experimental values of $^3H_{DA}^{\,2}(n)$ can be compared to the calculated values of $I_T^{\,2}(n)$. If the calculated orbital overlaps parallel the experimental results for every n, we would conclude that the p-orbital overlap between C4 and N is responsible for the coupling between the $^3Ir_2^*$ donor and the py$^+$ acceptor. However, if the calculated $I_T^{\,2}(n)$ values did not correlate with the experimental values of $^3H_{DA}^{\,2}(n)$, an alternate analysis would have to be considered. The answers to these questions can be found in Table 5.7. The first column of the table contains the calculated values of $I_T^{\,2}$, the second column is the

Table 5.7. Calculated Orbital Overlaps $(I_T{}^2)$ and Experimental Matrix Elements $(H_{DA}{}^2)$

Compounds	Calculated $I_T{}^2 \times 10^4$	Normalized $I_T{}^2$	Found $^3H_{DA}{}^2$ (cm^{-2})
$[Ir_2]$-py$^+$	400	10,000	0.2
$[Ir_2]$-CH_2-py$^+$	60	2,000	<0.1
$[Ir_2]$-$(CH_2)_2$-py$^+$	30	900	900
$[Ir_2]$-$(CH_2)_3$-py$^+$	0.4	10	50
$[Ir_2]$-$(CH_2)_4$-py$^+$	0.08	2	—

same data normalized to match $^3H_{DA}{}^2(2)$, and the third column contains the experimental $^3H_{DA}{}^2$ values. The normalized values of $I_T{}^2(n)$, for all n, do not compare favorably to the experimental $^3H_{DA}{}^2(n)$ values: $I_T{}^2(1)$ is twice $I_T{}^2(2)$ which was not observed experimentally $(^3H_{DA}{}^2(2) >> {}^3H_{DA}{}^2(1))$; the largest orbital overlap is $I_T{}^2(0)$ which is also not consistent with experiment. Clearly, the C4-N p-orbital overlap is not responsible for the observed coupling in this series of Ir_2-py$^+$ donor-acceptor complexes. The calculations must therefore be reanalyzed in a search for the origin of $^3H_{DA}(n)$.

It was demonstrated in eq 5.4 that σ and π terms contribute to the total orbital overlap. Table 5.8 summarizes the results of separating $I_T{}^2$ into $I_\sigma{}^2$ and $I_\pi{}^2$ components. $I_\sigma{}^2$ and $I_\pi{}^2$ represent σ and π type p-orbital overlaps. These two types of orbital overlaps show dramatically different dependences on n. For example, $I_\pi{}^2(n)$ values predict (as did $I_T{}^2(n)$ values) that $^3H_{DA}{}^2(0)$ should be the largest of the series followed by $H_{DA}{}^2(1)$ and then $^3H_{DA}{}^2(2)$. However, $I_\sigma{}^2(n)$ values predict that $^3H_{DA}{}^2(2)$ should be the largest followed by $^3H_{DA}{}^2(1)$. The σ contribution to the total overlap also predicts that $^3H_{DA}{}^2(0)$ should be very small. A comparison of the normalized values of $I_\sigma{}^2(n)$ with $^3H_{DA}{}^2(n)$ for all n reveals the relatively good agreement of the σ-type p-orbital overlaps with the matrix elements for ^{3}ET: $I_\sigma{}^2(2) > I_\sigma{}^2(1) > I_\sigma{}^2(3) >> I_\sigma{}^2(0)$ compared to $^3H_{DA}{}^2(2) > {}^3H_{DA}{}^2(3) >> {}^3H_{DA}{}^2(0) > {}^3H_{DA}{}^2(1)$.

Table 5.8. Calculated σ and π Orbital Overlaps (I_σ^2 and I_π^2) and Experimental Matrix Elements (H_{DA}^2)

Compounds	Calculated		Normalized [a]		Found
	$I_\pi^2 \times 10^4$	$I_\sigma^2 \times 10^4$	I_π^2	I_σ^2	$^3H_{DA}^2$
$[Ir_2]$-py$^+$	400	0	2×10^7	0	0.2
$[Ir_2]$-CH$_2$-py$^+$	6	20	3×10^5	450	<0.1
$[Ir_2]$-(CH$_2$)$_2$-py$^+$	0.02	40	900	900	900
$[Ir_2]$-(CH$_2$)$_3$-py$^+$	~0	2	~0	45	50
$[Ir_2]$-(CH$_2$)$_4$-py$^+$	*~0*	*1*	*~0*	*20*	*20 [b]*

$$I_\sigma^2 = P\, S_{12}^2(\sigma)$$

$$I_\pi^2 = P\, S_{12}^2(\pi)$$

[a] These values are normalized to $^3H_{DA}^2$ for $n = 2$ complex.

[b] Predicted value based on normalized I_σ^2 value.

The theoretical prediction that through-space coupling is maximized when the number of intervening methylene groups is 2 has also been confirmed in a study of X-C$_6$H$_4$-(CH$_2$)$_n$-py$^+$-Y complexes, where n = 1, 2, or 3, X = H, OMe and Y = 3-CN, 4-CN.[36] The intensities of charge-transfer transitions in these complexes, which is a measure of the coupling between the redox sites, were found to strongly depend on the methylene chain length with the n = 2 compounds exhibiting by far the most intense CT bands compared to n = 1 and 3 compounds.

Although the trend of $^3H_{DA}^2(n)$ values is approximately predicted by the $I_\sigma^2(n)$ values, there are discrepancies between the magnitudes of these values. Two major disagreements between $I_\sigma^2(n)$ and $^3H_{DA}^2(n)$ arise when we assume that the value of $I_\sigma^2(1)$ accurately describes the through-space interaction between the phenylene and pyridinium rings: (1) the unusually small calculated value for $I_\sigma^2(0)$; and (2) the unusually small calculated values of $I_\sigma^2(2)$ and $I_\sigma^2(3)$.

The small value of $I_\sigma^2(0)$ can be adjusted to more closely match its associated $^3H_{DA}^2$ by simply invoking a small contribution of π-type orbital overlap in this complex. Since

$I_\pi^2(0)$ is much larger than the other $I_\pi^2(n)$ values, this would only serve to increase the calculated orbital overlap in the $n = 0$ complex with no appreciable effect on the other complexes.

The unusually small values of $I_\pi^2(2)$ and $I_\pi^2(3)$ can be attributed to two problems associated with their calculations. First, in considering the conformations that would lead to efficient overlap of the p-orbitals on C4 and N, high energy conformations were neglected, and only low energy staggered configurations were considered. From molecular mechanics calculations (described in Chapter 3) it was apparent that high energy eclipsed conformations exhibited potentially large values of p-orbital overlaps. Consideration of these high energy conformations would almost certainly increase the calculated orbital overlaps. It should be noted that for complexes with $n = 0$ and $n = 1$, such high energy structures need not be considered due to the rigid nature of these bridges. The second possible shortcoming in the calculations is the neglect of the overlap of the remaining p-orbitals of the rings aside from the C4 and N orbitals. If the contribution of all p-orbitals on the phenylene and pyridinium rings are considered in calculating the through-space coupling in these donor-acceptor complexes, a factor of up to 5^2 can be added to the $I_\sigma^2(2)$ and $I_\sigma^2(3)$ values. Again, this correction would not apply to $n = 0$ and 1 complexes because the large plane angle between the two rings precludes additional p-orbital overlap above that of the C4 and N p-orbitals.

We have demonstrated that there are three factors that contribute to $^3H_{DA}$, the electronic coupling between $^3Ir_2^*$ and py^+: (1) the relative orientation and (2) separation between donor and acceptor, and (3) a statistical factor that measures the probability of the donor and acceptor to interact favorably in solution. The conditions for large coupling between the donor and acceptor groups are short distances, relative orientations leading to σ-type p-orbital overlaps (*i.e.*, plane angles between the phenylene and pyridinium rings approaching 0°), and large statistical factors the make contact between donor and acceptor highly probable (*i.e.*, short bridges). When two methylene groups bridge the phenylene

and pyridinium rings, the effect of these three factors appears to be balanced, resulting in the maximum electronic coupling between donor and acceptor. Although the relative orientation in complexes with three methylene groups is more favorable, the distance is longer and statistical factors are unfavorable, thus the result is diminished donor-acceptor coupling. When one methylene group separates donor and acceptor, the beneficial effect of a short through-space separation and a large statistical factor are outweighed by an unfavorable orientation.

Singlet and Triplet Electron Transfer:

The electron transfer results from $[Ir(\mu\text{-pz}^*)(CO)(Ph_2P\text{-}O\text{-}C_6H_4\text{-}3\text{-}(CH_3)_2\text{-py}^+)]_2$ ($[Ir_2]\text{-}3\text{-}(CH_2)_2\text{-py}^+$), which remain to be discussed, will serve to bridge the two separate discussions of singlet and triplet electron transfer. Recalling the structure of this $n = 2$ donor-acceptor complex reveals the unique nature of its bridge: the phenylene group is 1,3-disubstituted rather than the familiar 1,4-substitution. The ^{1}ET and ^{3}ET rates in this complex are compared to those of the similar $n = 2$ complex, $[Ir_2]\text{-}(CH_2)_2\text{-py}^+$, with the results given in Table 5.9.

Table 5.9. Singlet and Triplet Excited-State Electron-Transfer Rates for Selected Donor-Acceptor Complexes

Compounds	^{1}ET		^{3}ET	
	$-\Delta G°(eV)$	k_{ET} (s^{-1})	$-\Delta G°(eV)$	k_{ET} (s^{-1})
$[Ir_2]\text{-}(CH_2)_2\text{-py}^+$	0.67	$1.4\pm0.1 \times 10^{10}$	0.17	$1.6\pm1.4 \times 10^8$
$[Ir_2]\text{-}3\text{-}(CH_2)_2\text{-py}^+$	0.69	$3.1\pm0.2 \times 10^{10}$	0.19	$1.6\pm1.3 \times 10^8$

The ^{3}ET rates in these complexes are identical within experimental error, while the ^{1}ET rates differ by a factor of more than two. These results are consistent with a through-bond mechanism dominating in the ^{1}ET reactions and a through-space mechanism dominating in

the ^{3}ET reactions, in agreement with the discussions of the previous sections.

We have established that in the series of Ir_2-py$^+$ donor-acceptor complexes, triplet electron transfer occurs via a folded conformation of the bridge, where through-space interactions between the phenylene and pyridinium rings are maximized. If this is the case, we would expect ^{3}ET rates in the two complexes to be similar, since the point of attachment of the hydrocarbon chain to the phenylene ring (3- or 4-position) does not affect the distance, orientation, or statistical factor of the folded conformation. The experimental results corroborate this hypothesis.

We have also established that in the series of Ir_2-py$^+$ donor-acceptor complexes, singlet electron transfer occurs via a stretched conformation of the bridge, where through-bond interactions between the phenylene and pyridinium rings are maximized. In this case, the point of attachment of the hydrocarbon chain to the phenylene ring does have an effect on the electron-transfer pathway. Namely, the electron-transfer pathway in $[Ir_2]$-3-$(CH_2)_2$-py$^+$, across the phenylene group, is shorter than in $[Ir_2]$-$(CH_2)_2$-py$^+$, giving rise to a slightly faster ^{1}ET rate in the former complex.

For the donor-acceptor complex, $[Ir_2]$-3-$(CH_2)_2$-py$^+$, the ^{1}ET rate is consistent with a through-bond mechanism, while ^{3}ET rate is consistently a through-space mechanism, exclusively.

CONCLUSIONS

The series of iridium donor-acceptor complexes presented in this thesis is the first example of an ET system that exhibits different electronic coupling matrix elements depending on the spin state of the excited donor. The ^{1}ET and ^{3}ET rates for the series of Ir_2-py$^+$ donor-acceptor complexes have been correlated separately to the number of intervening methylene groups in the bridge. The ^{1}ET rates in the series, $[Ir_2]$-$(CH_2)_n$-py$^+$

($n = 0, 1, 2,$ and 3), follow a trend consistent with through-bond mechanisms, where $^1H_{DA}(2) \approx {}^1H_{DA}(0) \gg {}^1H_{DA}(3) \approx {}^1H_{DA}(1)$. However, the ^{3}ET rates in the series follow a trend consistent with through-space mechanisms, where $^3H_{DA}(2) \gg {}^3H_{DA}(3) \gg {}^3H_{DA}(0) \approx {}^3H_{DA}(1)$. The ET^b rates appeared to parallel the ^{1}ET rates: $^1H_{DA}(2,3) = {}^bH_{DA}(2,3)$. Future investigations will be aimed at understanding the back electron-transfer rates in more detail, with the goal of discovering the structural parameters that lead to smaller values of $^bH_{DA}$. Theoretical work aimed at elucidating the origin of the observed differences in $^3H_{DA}$ and $^1H_{DA}$ is currently in progress. Below is a brief summary of our current understanding of this theoretical problem:

This two-electron system can be represented by three orthogonal molecular orbitals, D, D*, and A, shown in Figure 5.16 (a one-electron treatment of the problem cannot distinguish between singlet and triplet ET). The simplest approximation of the initial and final states (neglecting normalization) for singlet ET is:

$$\Psi_I^S = |\Phi_D \, \Phi_{D^*}|^S = [\phi_D(1)\phi_{D^*}(2) + \phi_D(2)\phi_{D^*}(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$
$$\Psi_F^S = |\Phi_D \, \Phi_A|^S = [\phi_D(1)\phi_A(2) + \phi_D(2)\phi_A(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)],$$

and similarly for triplet ET,

$$\Psi_I^T = |\Phi_D \, \Phi_{D^*}|^T = [\phi_D(1)\phi_{D^*}(2) - \phi_D(2)\phi_{D^*}(1)]\alpha(1)\alpha(2)$$
$$\Psi_F^T = |\Phi_D \, \Phi_A|^T = [\phi_D(1)\phi_A(2) - \phi_D(2)\phi_A(1)]\alpha(1)\alpha(2).$$

For either singlet or triplet ET, the initial and final states must have the same spin wave function for H_{DA} to be nonzero. The Hamiltonian of the system is therefore given by:

$$H = T_1 + T_2 + [(V_{1D} + V_{1A}) + (V_{2D} + V_{2A})] + V_{12},$$

where T is the kinetic energy operator; V_{1D}, V_{1A}, V_{2D}, and V_{2A} are the one-electron interactions between molecular potential wells and the two

electrons, and V_{12} is the electron-electron repulsion. Since the system has been defined in terms of only two states, H_{DA} is equal to $\langle \Psi_I | H | Y_F \rangle$. Similarly, $H_{DA}^S = \langle \Psi_I^S | H | \Psi_F^S \rangle$ and $H_{DA}^T = \langle \Psi_I^T | H | \Psi_F^T \rangle$. The only difference between H_{DA}^S and H_{DA}^T is the sign of the two-electron matrix element, $\langle \Psi_I | V_{12} | Y_F \rangle$, which enters with a (+) sign for singlets and a (-) sign for triplets because of the different signs in the spatial parts of Ψ^S and Ψ^T. This may account for the smaller value of H_{DA}^T (referred to as $^3H_{DA}$ in the main text) in these donor-acceptor complexes. Theoretical work along these lines is in progress.[37]

Figure 5.16. Schematic of initial and final states for singlet and triplet electron transfer in a two-electron system, showing the orthogonal molecular orbitals, D, D*, and A.

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Appendix Supplementary material for the X-ray crystal structure determination of
[Ir(μ-pz*)(CO)(Ph$_2$P-O-C$_6$H$_4$-CH$_3$)]$_2$

Table A.1. Crystal and Intensity Collection Data

Formula: $Ir_2C_{50}H_{48}N_4O_4P_2 \cdot CH_2Cl_2$ Formula weight: 1300.28

Crystal color: Orange/red   Habit: Irregular

Space group: $P2_1/c$ (#14)

$a = 18.677(2)$Å

$b = 13.817(1)$Å $\beta = 101.37(1)°$

$c = 20.225(3)$Å

$V = 5116.8(10)$Å^3

$\rho_{calc} = 1.688$ g cm^{-3}

$\mu = 57.28$ cm^{-1} $(\mu r_{max} = 5.70)$ Transmission coeff. $= 0.39 - 0.54$

     ω scan

$\lambda = 0.7107$Å   Graphite monochromator

2θ range: $3°-45°$ Octants collected: $\pm h, k, \pm l$

$T = 293°$K

Number of reflections measured: 14173

Number of independent reflections: 6662

Number with $F_o^2 > 0$: 6470

Number with $F_o^2 > 3\sigma(F_o^2)$: 5547

Number of reflections used in refinement: 6662

Goodness of fit for merging data: 1.02

Final R-index: 0.0316 for 6470 reflections with $F_o^2 > 0$

Final R-index: 0.0235 for 5547 reflections with $F_o^2 > 3\sigma(F_o^2)$

Final goodness of fit: 1.46 for 588 parameters and 6662 reflections

Table A.2. Final Non-Hydrogen Coordinates and Displacement Parameters

x, y, z and $U_{eq}{}^a \times 10^4$

Atom	x	y	z	U_{eq}
Ir1	2540(.1)	593(.1)	8324(.1)	370
Ir2	2248(.1)	2833(.2)	8783(.1)	384
P1	2457(1)	−576(1)	9062(1)	438(3)
P2	3275(1)	3689(1)	9024(1)	444(3)
NP1A	2567(2)	1700(3)	7636(2)	408(10)
NP1B	2361(2)	2607(3)	7798(2)	407(11)
NP2A	1458(2)	1024(3)	8281(2)	430(11)
NP2B	1346(2)	1941(3)	8505(2)	444(11)
O1	4071(2)	45(3)	8293(2)	776(13)
O2	1901(3)	3201(3)	10135(2)	835(14)
O3	2176(2)	−1645(3)	8786(2)	576(10)
O4	3235(2)	4862(2)	9105(2)	560(10)
C1	3466(3)	257(4)	8308(3)	553(15)
C2	2050(3)	3056(4)	9611(3)	576(16)
CP1A	2700(3)	1753(4)	7005(3)	526(15)
CP1B	2360(3)	3200(4)	7278(3)	518(15)
CP1C	2577(3)	2681(4)	6771(3)	572(17)
CP1D	2934(4)	880(5)	6668(3)	884(22)
CP1E	2126(4)	4232(4)	7305(3)	733(20)
CP2A	811(3)	579(4)	8120(3)	547(16)

Atom	x	y	z	U_{eq}
CP2B	631(3)	2048(5)	8470(3)	593(17)
CP2C	281(3)	1204(5)	8231(3)	700(20)
CP2D	745(4)	−424(5)	7848(4)	842(21)
CP2E	318(4)	2971(5)	8673(4)	899(22)
CS1A	2366(3)	−2126(4)	8231(3)	506(14)
CS1B	1825(3)	−2647(4)	7831(3)	580(16)
CS1C	1987(3)	−3147(4)	7288(3)	663(18)
CS1D	2668(3)	−3135(4)	7136(3)	607(16)
CS1E	3199(3)	−2608(5)	7550(4)	728(19)
CS1F	3057(3)	−2108(4)	8100(3)	618(17)
CS1G	2830(4)	−3656(5)	6525(4)	895(21)
CS2A	2791(3)	5284(4)	9511(3)	522(15)
CS2B	3087(4)	5539(4)	10151(3)	659(17)
CS2C	2653(5)	5975(5)	10548(4)	863(24)
CS2D	1932(5)	6133(5)	10304(5)	898(25)
CS2E	1649(5)	5887(6)	9652(5)	1078(28)
CS2F	2078(4)	5465(5)	9249(4)	876(22)
CS2G	1439(6)	6555(6)	10748(6)	1621(39)
CA1A	3285(3)	−854(4)	9670(3)	492(14)
CA1B	3455(4)	−1792(4)	9904(3)	654(17)

Atom	x	y	z	U_{eq}
CA1C	4075(4)	−1951(5)	10400(4)	833(22)
CA1D	4508(4)	−1209(7)	10666(4)	882(24)
CA1E	4345(4)	−292(6)	10445(4)	833(22)
CA1F	3739(3)	−111(5)	9947(3)	652(17)
CA2A	3914(3)	3350(4)	9793(3)	475(13)
CA2B	4586(3)	3813(5)	9961(3)	669(17)
CA2C	5068(3)	3585(5)	10544(3)	748(19)
CA2D	4890(4)	2900(6)	10971(3)	807(21)
CA2E	4233(4)	2420(6)	10808(3)	847(22)
CA2F	3758(3)	2641(4)	10213(3)	641(17)
CB2A	3859(3)	3707(4)	8405(2)	470(14)
CB2B	4139(3)	2829(4)	8237(3)	561(15)
CB2C	4623(3)	2792(5)	7798(3)	686(17)
CB2D	4817(4)	3639(6)	7520(3)	791(20)
CB2E	4531(4)	4502(5)	7673(4)	835(21)
CB2F	4055(4)	4555(4)	8117(3)	692(18)
CB1A	1804(3)	−385(4)	9609(3)	443(13)
CB1B	1787(3)	525(4)	9900(3)	599(16)
CB1C	1326(3)	710(5)	10341(3)	660(17)
CB1D	882(3)	−5(6)	10491(3)	704(19)

Atom	x	y	z	U_{eq}
CB1E	891(3)	−890(5)	10210(4)	744(19)
CB1F	1348(3)	−1096(4)	9770(3)	611(16)
Cl1	210(2)	2650(2)	6341(2)	1670(12)
Cl2	491(2)	716(3)	6059(2)	2264(18)
C3	790(5)	1722(7)	6512(5)	1322(35)

a $U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*)(\vec{a}_i \cdot \vec{a}_j)]$

Table A.3. Anisotropic Displacement Parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir1	353(1)	387(1)	373(1)	13(1)	78(1)	20(1)
Ir2	436(1)	408(1)	322(1)	25(1)	106(1)	−3(1)
P1	432(8)	404(8)	485(8)	−11(7)	111(6)	27(7)
P2	563(9)	405(8)	379(8)	−9(7)	131(7)	−11(6)
NP1A	470(26)	397(25)	393(25)	6(21)	176(20)	−42(20)
NP1B	523(27)	432(26)	260(23)	3(21)	64(19)	17(19)
NP2A	352(25)	467(27)	466(26)	−27(21)	69(20)	42(21)
NP2B	375(26)	507(29)	465(26)	61(21)	116(20)	25(21)
O1	483(26)	901(33)	995(35)	168(24)	269(24)	83(27)
O2	1046(37)	1044(37)	509(27)	−55(29)	379(26)	−147(25)
O3	724(27)	434(21)	616(24)	−95(20)	242(21)	−43(20)
O4	775(27)	380(21)	577(24)	−37(20)	262(21)	−24(18)
C1	595(40)	520(36)	583(38)	15(30)	214(31)	89(28)
C2	543(37)	573(39)	604(40)	−26(29)	90(31)	−48(31)
CP1A	667(39)	559(37)	363(31)	65(30)	126(27)	−63(28)
CP1B	628(38)	541(36)	363(31)	5(29)	41(27)	40(28)
CP1C	804(44)	634(40)	290(30)	31(33)	140(28)	73(29)
CP1D	1361(66)	843(52)	534(41)	250(45)	397(42)	−36(36)
CP1E	1087(55)	523(40)	560(40)	128(36)	94(36)	120(30)
CP2A	388(33)	620(38)	598(37)	−72(31)	10(27)	70(31)
CP2B	395(35)	766(44)	647(39)	138(33)	172(28)	107(34)
CP2C	347(34)	890(50)	855(47)	−81(36)	101(32)	129(40)
CP2D	672(45)	750(49)	1021(55)	−187(37)	−36(39)	47(41)
CP2E	677(47)	963(55)	1116(58)	245(41)	319(42)	16(46)
CS1A	567(38)	462(33)	483(33)	8(29)	87(28)	34(28)
CS1B	480(36)	619(39)	677(40)	−125(30)	200(30)	−59(32)
CS1C	627(43)	641(42)	720(44)	−149(33)	129(33)	−210(34)
CS1D	673(43)	556(39)	631(40)	−107(32)	220(33)	−66(31)
CS1E	571(41)	748(45)	926(51)	−36(35)	297(37)	−123(40)
CS1F	443(36)	612(39)	815(45)	−78(30)	163(31)	−192(35)
CS1G	1069(59)	934(55)	777(48)	−208(45)	411(43)	−222(41)
CS2A	656(41)	369(32)	577(38)	88(28)	212(32)	36(28)
CS2B	877(47)	530(37)	582(41)	16(35)	176(35)	−46(32)
CS2C	1532(78)	485(40)	706(48)	71(47)	547(53)	−7(34)
CS2D	1134(68)	467(42)	1312(75)	130(45)	772(62)	−10(46)
CS2E	871(59)	907(62)	1468(83)	239(47)	261(58)	−239(58)
CS2F	846(55)	779(51)	959(55)	213(43)	74(44)	−166(43)
CS2G	2221(113)	831(62)	2346(116)	137(67)	1753(101)	−174(69)
CA1A	497(34)	491(36)	512(34)	43(28)	161(27)	51(27)
CA1B	809(47)	553(39)	626(40)	111(34)	208(35)	101(32)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
CA1C	886(56)	862(56)	733(49)	403(45)	117(42)	281(42)
CA1D	585(46)	1177(69)	834(53)	196(46)	17(38)	262(51)
CA1E	549(42)	1002(58)	846(51)	−202(39)	−109(36)	177(43)
CA1F	510(38)	647(41)	751(44)	−12(33)	4(32)	111(35)
CA2A	530(35)	464(32)	437(32)	−32(28)	108(26)	−45(27)
CA2B	704(43)	671(43)	581(39)	−138(35)	4(33)	64(33)
CA2C	621(43)	937(52)	649(42)	−156(37)	32(35)	9(38)
CA2D	708(47)	1128(59)	522(39)	−20(44)	−30(34)	103(40)
CA2E	767(49)	1121(60)	603(43)	−78(44)	11(36)	323(40)
CA2F	629(40)	714(43)	571(38)	−145(33)	94(31)	121(33)
CB2A	533(34)	501(35)	384(30)	−55(28)	110(26)	−1(26)
CB2B	606(38)	563(37)	539(35)	−47(31)	171(30)	−10(30)
CB2C	605(40)	831(48)	665(42)	95(36)	233(33)	−24(37)
CB2D	817(51)	960(55)	680(44)	−131(44)	354(38)	−89(41)
CB2E	1067(57)	804(52)	762(48)	−281(44)	493(43)	38(39)
CB2F	931(50)	564(41)	674(42)	−87(35)	387(38)	−7(32)
CB1A	423(31)	492(35)	416(31)	−13(26)	85(24)	23(25)
CB1B	673(40)	595(39)	555(37)	−74(33)	185(31)	−23(31)
CB1C	727(43)	739(45)	561(38)	95(36)	245(33)	−64(33)
CB1D	568(41)	944(54)	663(43)	100(39)	274(33)	92(40)
CB1E	617(42)	777(49)	948(52)	−90(36)	419(39)	65(40)
CB1F	636(40)	503(36)	743(42)	−81(31)	253(33)	37(32)
Cl1	1416(26)	1199(23)	2500(40)	452(19)	645(24)	384(23)
Cl2	2275(44)	1424(31)	2913(55)	305(29)	70(36)	−425(31)
C3	924(68)	1156(77)	1732(99)	−41(59)	−110(62)	392(72)

$U_{i,j}$ values have been multiplied by 10^4

The form of the displacement factor is:

$$\exp -2\pi^2 (U_{11}h^2a^{*^2} + U_{22}k^2b^{*^2} + U_{33}\ell^2c^{*^2} + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)$$

Table A.4. Assigned Hydrogen Parameters

x, y and $z \times 10^4$

Atom	x	y	z	B
HB1F	1349	−1724	9579	5.8
HB1E	577	−1380	10318	7.0
HB1D	565	120	10796	6.7
HB1C	1318	1332	10538	6.3
HB1B	2095	1025	9795	5.7
HB2F	3865	5161	8223	6.6
HB2E	4661	5078	7469	7.9
HB2D	5151	3623	7222	7.5
HB2C	4818	2190	7690	6.5
HB2B	3996	2246	8425	5.3
HA2F	3312	2293	10094	6.1
HA2E	4107	1940	11101	8.0
HA2D	5219	2755	11380	7.6
HA2C	5527	3903	10651	7.1
HA2B	4713	4295	9669	6.3
HA1F	3634	533	9794	6.2
HA1E	4651	229	10634	7.9
HA1D	4926	−1328	11008	8.4
HA1C	4196	−2591	10554	7.9
HA1B	3150	−2319	9725	6.2
HP2C	−229	1080	8158	6.6
HP1C	2632	2919	6343	5.4
HS1E	3677	−2588	7454	6.9
HS1F	3434	−1756	8384	5.8
HS1B	1346	−2665	7925	5.5
HS1C	1613	−3512	7011	6.3
HS2B	3589	5419	10329	6.2
HS2C	2863	6166	10996	8.2
HS2E	1148	6008	9473	10.2
HS2F	1877	5303	8794	8.3
HP1DA	3388	1016	6546	8.4
HP1DB	2572	745	6279	8.4
HP1DC	2981	356	6976	8.4
HP1EA	2544	4630	7344	6.9
HP1EB	1903	4307	7685	6.9
HP1EC	1787	4371	6901	6.9
HP2DA	871	−860	8215	8.0
HP2DB	1067	−491	7543	8.0
HP2DC	253	−523	7623	8.0

Atom	x	y	z	B
HP2EA	500	3489	8448	8.5
HP2EB	465	3039	9147	8.5
HP2EC	−199	2936	8548	8.5
HS1GA	3335	−3818	6613	8.5
HS1GB	2718	−3234	6150	8.5
HS1GC	2540	−4221	6455	8.5
HS2GA	1682	6500	11203	15.4
HS2GB	996	6201	10669	15.4
HS2GC	1350	7215	10627	15.4
H3A	852	1572	6978	12.5
H3B	1246	1909	6411	12.5

Table A.5. Complete Distances and Angles

	Distance(Å)		Distance(Å)
Ir1 – Ir2	3.307(1)	CS2A – CS2B	1.350(8)
Ir1 – C1	1.797(6)	CS2B – CS2C	1.385(10)
Ir2 – C2	1.810(6)	CS2C – CS2D	1.358(12)
Ir1 – P1	2.224(1)	CS2D – CS2E	1.362(13)
Ir2 – P2	2.224(1)	CS2E – CS2F	1.380(12)
Ir1 – NP1A	2.075(4)	CS2A – CS2F	1.356(9)
Ir2 – NP1B	2.068(4)	CS2D – CS2G	1.524(14)
Ir1 – NP2A	2.091(4)	CA1A – CA1B	1.395(8)
Ir2 – NP2B	2.073(4)	CA1A – CA1F	1.378(8)
C1 – O1	1.174(7)	CA1B – CA1C	1.393(10)
C2 – O2	1.165(7)	CA1C – CA1D	1.351(11)
P1 – O3	1.629(4)	CA1D – CA1E	1.358(11)
P1 – CA1A	1.817(5)	CA1E – CA1F	1.382(9)
P1 – CB1A	1.820(5)	CA2A – CA2B	1.390(8)
O3 – CS1A	1.410(6)	CA2A – CA2F	1.365(8)
P2 – O4	1.633(4)	CA2B – CA2C	1.371(9)
P2 – CA2A	1.826(5)	CA2C – CA2D	1.365(10)
P2 – CB2A	1.815(5)	CA2D – CA2E	1.378(10)
O4 – CS2A	1.404(7)	CA2E – CA2F	1.380(9)
NP1A – NP1B	1.370(6)	CB2A – CB2B	1.389(8)
NP1A – CP1A	1.349(7)	CB2A – CB2F	1.388(8)
NP1B – CP1B	1.334(7)	CB2B – CB2C	1.388(8)
CP1A – CP1C	1.371(8)	CB2C – CB2D	1.377(9)
CP1A – CP1D	1.493(9)	CB2D – CB2E	1.366(10)
CP1B – CP1C	1.377(8)	CB2E – CB2F	1.386(10)
CP1B – CP1E	1.494(8)	CB1A – CB1B	1.392(8)
NP2A – NP2B	1.376(6)	CB1A – CB1F	1.382(8)
NP2A – CP2A	1.337(7)	CB1B – CB1C	1.378(9)
NP2B – CP2B	1.332(7)	CB1C – CB1D	1.362(9)
CP2A – CP2C	1.365(9)	CB1D – CB1E	1.350(10)
CP2A – CP2D	1.488(9)	CB1E – CB1F	1.378(9)
CP2B – CP2C	1.377(9)	C3 – CL1	1.670(10)
CP2B – CP2E	1.493(9)	C3 – CL2	1.697(11)
CS1A – CS1B	1.368(8)	CP1C – HP1C	0.950
CS1B – CS1C	1.380(8)	CP1D – HP1DA	0.947
CS1C – CS1D	1.365(9)	CP1D – HP1DB	0.948
CS1D – CS1E	1.374(9)	CP1D – HP1DC	0.948
CS1E – CS1F	1.379(9)	CP1E – HP1EA	0.946
CS1A – CS1F	1.368(8)	CP1E – HP1EB	0.949
CS1D – CS1G	1.512(9)	CP1E – HP1EC	0.949

	Distance(Å)
CP2C – HP2C	0.950
CP2D – HP2DA	0.948
CP2D – HP2DB	0.947
CP2D – HP2DC	0.950
CP2E – HP2EA	0.947
CP2E – HP2EB	0.948
CP2E – HP2EC	0.950
CS1B – HS1B	0.950
CS1C – HS1C	0.950
CS1E – HS1E	0.950
CS1F – HS1F	0.950
CS1G – HS1GA	0.951
CS1G – HS1GB	0.947
CS1G – HS1GC	0.944
CS2B – HS2B	0.950
CS2C – HS2C	0.950
CS2E – HS2E	0.950
CS2F – HS2F	0.950
CS2G – HS2GA	0.945
CS2G – HS2GB	0.948
CS2G – HS2GC	0.951
CA1B – HA1B	0.950
CA1C – HA1C	0.950
CA1D – HA1D	0.950
CA1E – HA1E	0.950
CA1F – HA1F	0.950
CB1B – HB1B	0.950
CB1C – HB1C	0.950
CB1D – HB1D	0.950
CB1E – HB1E	0.950
CB1F – HB1F	0.950
CA2B – HA2B	0.950
CA2C – HA2C	0.950
CA2D – HA2D	0.950
CA2E – HA2E	0.950
CA2F – HA2F	0.950
CB2B – HB2B	0.950
CB2C – HB2C	0.950
CB2D – HB2D	0.950
CB2E – HB2E	0.950

	Distance(Å)
CB2F – HB2F	0.950
C3 – H3A	0.950
C3 – H3B	0.950

	Angle(°)			Angle(°)
NP1A – Ir1 – NP2A	85.1(2)	Ir2 – P2 – CA2A	116.2(2)
NP1A – Ir1 – C1	91.6(2)	Ir2 – P2 – CB2A	117.8(2)
P1 – Ir1 – C1	91.0(2)	CB2A – P2 – CA2A	102.1(2)
P1 – Ir1 – NP2A	92.3(1)	CA2B – CA2A –P2	119.9(4)
NP2A – Ir1 – C1	176.3(2)	CA2F – CA2A –P2	122.0(4)
P1 – Ir1 – NP1A	177.4(1)	CB2B – CB2A –P2	117.5(4)
NP1B – Ir2 – NP2B	83.1(2)	CB2F – CB2A –P2	123.0(4)
NP2B – Ir2 – C2	92.9(2)	CA2A – P2 – O4	101.8(2)
P2 – Ir2 – C2	91.8(2)	CB2A – P2 – O4	95.8(2)
P2 – Ir2 – NP1B	92.5(1)	CS2A – O4 – P2	121.0(3)
NP1B – Ir2 – C2	174.1(2)	CS2B – CS2A – O4	119.5(5)
P2 – Ir2 – NP2B	174.2(1)	CS2F – CS2A – O4	119.6(5)
Ir1 – NP1A –NP1B	117.9(3)	Ir1 – NP1A –CP1A	135.1(3)
Ir1 – NP2A –NP2B	117.2(3)	CP1A – NP1A –NP1B	106.8(4)
Ir2 – NP1B –NP1A	117.1(3)	CP1B – NP1B –NP1A	109.3(4)
Ir2 – NP2B –NP2A	118.0(3)	Ir2 – NP1B –CP1B	133.0(3)
NP1A – Ir1 – Ir2	61.7(1)	CP1C – CP1A –NP1A	109.2(5)
NP2A – Ir1 – Ir2	62.2(1)	CP1D – CP1A –NP1A	120.8(5)
P1 – Ir1 – Ir2	117.0(1)	CP1D – CP1A –CP1C	130.0(5)
C1 – Ir1 – Ir2	117.4(2)	CP1C – CP1B –NP1B	108.2(5)
NP1B – Ir2 – Ir1	62.3(1)	CP1E – CP1B –NP1B	120.8(5)
NP2B – Ir2 – Ir1	62.5(1)	CP1E – CP1B –CP1C	130.9(5)
P2 – Ir2 – Ir1	112.1(1)	CP1B – CP1C –CP1A	106.5(5)
C2 – Ir2 – Ir1	119.6(2)	Ir1 – NP2A –CP2A	134.3(4)
O1 – C1 – Ir1	179.3(5)	CP2A – NP2A –NP2B	108.4(4)
O2 – C2 – Ir2	178.0(5)	CP2B – NP2B –NP2A	107.4(4)
Ir1 – P1 – O3	119.3(1)	Ir2 – NP2B –CP2B	134.5(4)
Ir1 – P1 – CA1A	116.5(2)	CP2C – CP2A –NP2A	108.6(5)
Ir1 – P1 – CB1A	116.4(2)	CP2D – CP2A –NP2A	121.6(5)
CB1A – P1 – CA1A	101.7(2)	CP2D – CP2A –CP2C	129.7(6)
CA1B – CA1A –P1	122.2(4)	CP2C – CP2B –NP2B	109.1(5)
CA1F – CA1A –P1	119.4(4)	CP2E – CP2B –NP2B	121.5(5)
CB1B – CB1A –P1	117.6(4)	CP2E – CP2B –CP2C	129.5(6)
CB1F – CB1A –P1	124.0(4)	CP2B – CP2C –CP2A	106.5(5)
CA1A – P1 – O3	102.4(2)	CS1F – CS1A – CS1B	120.7(5)
CB1A – P1 – O3	97.5(2)	CS1C – CS1B – CS1A	118.7(5)
CS1A – O3 – P1	125.9(3)	CS1D – CS1C – CS1B	122.3(6)
CS1B – CS1A – O3	116.5(5)	CS1E – CS1D – CS1C	117.5(6)
CS1F – CS1A – O3	122.7(5)	CS1G – CS1D – CS1C	121.6(6)
Ir2 – P2 – O4	119.7(1)	CS1G – CS1D – CS1E	120.9(6)

	Angle(°)			Angle(°)
CS1F – CS1E – CS1D	121.8(6)		HP1DB – CP1D – HP1DA	110.6
CS1E – CS1F – CS1A	119.0(6)		HP1DC – CP1D – HP1DA	110.6
CS2F – CS2A – CS2B	120.8(6)		HP1DC – CP1D – HP1DB	110.7
CS2C – CS2B – CS2A	119.6(6)		HP1EA – CP1E – CP1B	108.4
CS2D – CS2C – CS2B	120.6(7)		HP1EB – CP1E – CP1B	108.2
CS2E – CS2D – CS2C	118.7(8)		HP1EC – CP1E – CP1B	108.2
CS2G – CS2D – CS2C	121.2(8)		HP1EB – CP1E – HP1EA	110.8
CS2G – CS2D – CS2E	120.1(8)		HP1EC – CP1E – HP1EA	110.8
CS2F – CS2E – CS2D	121.2(8)		HP1EC – CP1E – HP1EB	110.4
CS2E – CS2F – CS2A	119.1(7)		HS1E – CS1E – CS1D	119.1
CA1F – CA1A –CA1B	118.3(5)		HS1E – CS1E – CS1F	119.1
CA1C – CA1B –CA1A	119.5(6)		HS1C – CS1C – CS1B	118.8
CA1D – CA1C –CA1B	121.0(7)		HS1C – CS1C – CS1D	118.8
CA1E – CA1D –CA1C	120.0(7)		HS1B – CS1B – CS1A	120.7
CA1F – CA1E –CA1D	120.4(7)		HS1B – CS1B – CS1C	120.7
CA1E – CA1F –CA1A	120.8(6)		HP2C – CP2C –CP2A	126.8
CA2F – CA2A –CA2B	118.1(5)		HP2C – CP2C –CP2B	126.8
CA2C – CA2B –CA2A	120.8(6)		HP2DA – CP2D – CP2A	108.2
CA2D – CA2C –CA2B	120.2(6)		HP2DB – CP2D – CP2A	108.3
CA2E – CA2D –CA2C	119.9(6)		HP2DC – CP2D – CP2A	108.3
CA2F – CA2E –CA2D	119.5(6)		HP2DB – CP2D – HP2DA	110.8
CA2E – CA2F –CA2A	121.4(6)		HP2DC – CP2D – HP2DA	110.6
CB2F – CB2A –CB2B	119.5(5)		HP2DC – CP2D – HP2DB	110.7
CB2C – CB2B –CB2A	120.8(5)		HP2EA – CP2E – CP2B	108.4
CB2D – CB2C –CB2B	119.2(6)		HP2EB – CP2E – CP2B	108.2
CB2E – CB2D –CB2C	120.2(7)		HP2EC – CP2E – CP2B	108.4
CB2F – CB2E –CB2D	121.5(7)		HP2EB – CP2E – HP2EA	110.6
CB2E – CB2F –CB2A	118.9(6)		HP2EC – CP2E – HP2EA	110.7
CB1F – CB1A –CB1B	118.4(5)		HP2EC – CP2E – HP2EB	110.5
CB1C – CB1B –CB1A	120.7(5)		HS1F – CS1F – CS1A	120.5
CB1D – CB1C –CB1B	119.7(6)		HS1F – CS1F – CS1E	120.5
CB1E – CB1D –CB1C	120.3(6)		HS1GA – CS1G – CS1D	108.1
CB1F – CB1E –CB1D	121.3(6)		HS1GB – CS1G – CS1D	108.1
CB1E – CB1F –CB1A	119.6(6)		HS1GC – CS1G – CS1D	108.3
Cl2 – C3 – Cl1	112.8(6)		HS1GB – CS1G – HS1GA	110.4
HP1C – CP1C –CP1A	126.7		HS1GC – CS1G – HS1GA	110.7
HP1C – CP1C –CP1B	126.7		HS1GC – CS1G – HS1GB	111.2
HP1DA – CP1D – CP1A	108.3		HS2B – CS2B – CS2A	120.2
HP1DB – CP1D – CP1A	108.3		HS2B – CS2B – CS2C	120.2
HP1DC – CP1D – CP1A	108.3		HS2C – CS2C – CS2B	119.7

		Angle(°)			Angle(°)
HS2C – CS2C – CS2D	119.7		HB2F – CB2F –CB2E	120.6
HS2E – CS2E – CS2D	119.4		HB1B – CB1B –CB1A	119.6
HS2E – CS2E – CS2F	119.4		HB1B – CB1B –CB1C	119.6
HS2F – CS2F – CS2A	120.5		HB1C – CB1C –CB1B	120.2
HS2F – CS2F – CS2E	120.5		HB1C – CB1C –CB1D	120.2
HS2GA – CS2G – CS2D	108.3		HB1D – CB1D –CB1C	119.9
HS2GB – CS2G – CS2D	108.2		HB1D – CB1D –CB1E	119.9
HS2GC – CS2G – CS2D	108.1		HB1E – CB1E –CB1D	119.3
HS2GB – CS2G – HS2GA	111.1		HB1E – CB1E –CB1F	119.3
HS2GC – CS2G – HS2GA	110.7		HB1F – CB1F –CB1A	120.2
HS2GC – CS2G – HS2GB	110.4		HB1F – CB1F –CB1E	120.2
HA1B – CA1B –CA1A	120.3		H3A – C3 – Cl1	108.6
HA1B – CA1B –CA1C	120.3		H3B – C3 – Cl1	108.6
HA1C – CA1C –CA1B	119.5		H3A – C3 – Cl2	108.7
HA1C – CA1C –CA1D	119.5		H3B – C3 – Cl2	108.7
HA1D – CA1D –CA1C	120.0		H3B – C3 – H3A	109.4
HA1D – CA1D –CA1E	120.0			
HA1E – CA1E –CA1D	119.8			
HA1E – CA1E –CA1F	119.8			
HA1F – CA1F –CA1A	119.6			
HA1F – CA1F –CA1E	119.6			
HA2B – CA2B –CA2A	119.6			
HA2B – CA2B –CA2C	119.6			
HA2C – CA2C –CA2B	119.9			
HA2C – CA2C –CA2D	119.9			
HA2D – CA2D –CA2C	120.1			
HA2D – CA2D –CA2E	120.1			
HA2E – CA2E –CA2D	120.3			
HA2E – CA2E –CA2F	120.3			
HA2F – CA2F –CA2A	119.3			
HA2F – CA2F –CA2E	119.3			
HB2B – CB2B –CB2A	119.6			
HB2B – CB2B –CB2C	119.6			
HB2C – CB2C –CB2B	120.4			
HB2C – CB2C –CB2D	120.4			
HB2D – CB2D –CB2C	119.9			
HB2D – CB2D –CB2E	119.9			
HB2E – CB2E –CB2D	119.3			
HB2E – CB2E –CB2F	119.3			
HB2F – CB2F –CB2A	120.6			

Table A.6. Observed and Calculated Structure Factors

The columns contain, in order, ℓ, $10F_{obs}$, $10F_{calc}$ and $10\left(\frac{F_{obs}^2 - F_{calc}^2}{\sigma F_{obs}^2}\right)$. A minus sign preceding F_{obs} indicates that F_{obs}^2 is negative.

```
          -6   0   l                0   0   l
-20  0  l           2  186   53  38      2  552  432 143
 4  651  597  26    4 2275 2258   8      4 2877 2935 -23
 6  730  721   5    6  344  354  -7      6 2873 2871   0
                    8  844  899 -48      8 1017 1033 -13
-19  0  l          10  505  443  35     10  349  337   6
 2  251  227   7   12  926  932  -3     12  517  530  -8
 4  985  996  -6   14 2513 2529  -6     14 1750 1749   0
 6  985  963  13   16  213  174   8     16  273  115  30
 8  379  405  -9   18 2102 2099   1     18 1543 1530   7
10 1610 1616  -3   20  842  810  19     20 1347 1289  35

-18  0  l          -5   0   l            1   0   l
 2  602  614  -6    2 2295 2302  -3      2 5518 5551  -6
 4  624  608   9    4 1149 1099  39      4 3601 3742 -45
 6 1024 1016   5    6 1871 1846  14      6 1963 2040 -44
 8 1585 1614 -17    8 1101 1076  18      8 1756 1719  21
10  122   98   3   10  575  625 -40     10  263  276  -5
12 1578 1565   7   12 1808 1836 -15     12  201  215  -5
                   14  223  240  -4     14  315  273  13
-17  0  l          16 2494 2499  -2     16 1473 1460   7
 2  112   70   5   18  764  752   8     18  804  801   1
 4  846  832   9   20 1783 1767   8     20  665  644  11
 6 1208 1200   4
 8  128  149  -3   -4   0   l            2   0   l
10 1943 1955  -6    2 1317 1319  -1      0 5869 5876  -1
12  423  450 -11    4 4288 4379 -24      2 1589 1423 107
14 1058 1071  -8    6 1295 1313 -13      4 2652 2653   0
                    8 1312 1355 -32      6 2367 2393 -11
-16  0  l          10 1134 1162 -20      8  748  751  -2
 2  341  334   3   12  140  124   4     10  652  663  -8
 4  819  826  -5   14 2197 2240 -19     12  412  385  13
 6  435  399  18   16  418  426  -3     14  570  550  10
 8 1566 1602 -22   18 2297 2298   0     16  245  158  19
10  518  459  31   20  899  851  30     18 1071 1052  13
12 1714 1736 -12                        20 1362 1325  22
14 1202 1183  12   -3   0   l
16  956  923  20    2 4115 4226 -30      3   0   l
                    4  545  488  53      0 1041 1010  28
-15  0  l           6 1494 1549 -38      2 5216 5183   6
 2  106   51   4    8  320  274  26      4 1884 1836  27
 4  194  208  -3   10  471  469   0      6 3215 3268 -19
 6 1353 1345   4   12 1951 2017 -34      8 1703 1729 -15
 8  344  330   4   14  342  348  -2     10  203   72  28
10 1843 1891 -26   16 2295 2308  -5     12  616  621  -2
12  956  937  12   18  622  592  17     14  193  111  27
14 1554 1569  -8   20 1357 1338  11     16  810  781  20
16 1304 1309  -3                        18  902  873  19
                   -2   0   l           20  345  287  17
-14  0  l           2 1388 1383   4
 2  223  170  13    4 2460 2519 -27      4   0   l
 4  561  570  -5    6 1180 1211 -25
 6  126   90   4    8 1027 1045 -15      0 5254 5357 -20
 8 1967 1986  -9   10  919  885  27      2 4579 4554   6
10 1038 1071 -19   12  180  120  14      4 3323 3230  31
12 2122 2122   0   14 2376 2362   6      6 1734 1705  17
14 1605 1635 -18   16  356  331  10      8  470  465   2
16  999  993   4   18 1806 1821  -8     10 1716 1705   6
18 1074 1045  18   20 1255 1211  27     12  251   41  37
                                        14  127   73   6
-13  0  l          -1   0   l           16  527  535  -4
 2  816  812   3    2 5728 5710   3     18  648  652  -2
 4  227  155  19    4  407  359  42     20 1268 1246  13
 6 1517 1485  18    6 2942 3035 -36
 8  829  778  30    8  494  380  72      5   0   l
10 2400 2419  -8   10  133   67  14
12 1501 1499   0   12 1924 1975 -27      0 1970 1846  66
14 1759 1739  11   14  209   52  27      2 3211 3179  11
16 1645 1638   4   16 1987 1986   0      4 3604 3552  16
18  493  473   9   18  921  891  21      6 1239 1228   8
                   20 1102 1080  14      8 2555 2647 -39
-12  0  l                               10  296   49  48
 2  958  925  23                        12  998  983   9
 4  224  234  -3                        14  164   29  13
 6  314  272  15
 8 2012 2063 -25
10 1281 1300 -11
12 2291 2320 -12
14 2016 2058 -21
16  904  878  17
18 1339 1334   2

-11  0  l
 2 1429 1398  19
 4  868  864   3
 6 1076 1069   4
 8  544  584 -25
10 2007 2026  -9
12 1551 1597 -26
14 2223 2244  -9
16 1803 1833 -17
18  224  177  10
20 1132 1091  25

-10  0  l
 2  966  976  -7
 4  643  645  -1
 6  803  788  11
 8 1662 1657   2
10 1048 1070 -15
12 2516 2544 -11
14 1784 1827 -22
16  756  778 -15
18 1718 1747 -16
20  202  236  -7

-9  0  l
 2 1554 1514  24
 4  407  397   5
 6 1403 1457 -36
 8  681  688  -5
10 1661 1709 -28
12 1696 1731 -19
14 1702 1732 -16
16 2099 2105  -3
18  236  143  22
20 1533 1515  11

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 2  854  823  26
 4  989 1014 -21
 6  261  274  -6
 8 1874 1854  11
10 1235 1267 -21
12 1506 1541 -21
14 2306 2356 -22
16  312  240  18
18 1838 1825   7
20  524  544  -9

-7  0  l
 2 2499 2492   3
 4  964  980 -13
 6  452  458  -4
 8 1073 1077  -2
10 1966 1992 -13
12 1977 2042 -33
14  885  894  -5
16 2216 2204   5
18  540  512  15
20 1618 1603   9
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16  406  368  17          0 1561 1565  -2          7  641  631   5          1  207  175   7
18  949  924  16          2 2519 2469  20          8  928  919   5          2  380  379   0
                          4  750  721  17          9  330  365 -11          3 1321 1305  10
      6   0   1           6 2075 2019  26         10  132  220 -16          4  401  415  -5
                          8  681  698  -8                                   5  827  833  -3
 0 3929 3983 -15         10 1317 1289  18             -18   1   1           6 1021 1009   7
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 1 1689  1707  -11
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14  640   614   16
15  166    98   10
16  365   371   -2
17  458   439    8

     -11   6   1

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13  332   357  -10
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17  270   194   22

     -10   6   1

 1 1820  1813    4
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10  420   445  -13        6  1115 1110    3           -3   7   l             10   683   665   11
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9  2008 1992    7        4  1170 1179   -6        18   225   209    4        7  2344 2398  -25
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                         13  1467 1439   16        5  1792 1782    5       16   135   204  -14
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12  261  259   0        11  560  547   8         9  584  580   2         8  331  305   8
13 1472 1438  21        12  122  122   0        10  495  487   3         9  935  973 -29
14  499  524 -13        13 1228 1226   1        11   71   21   3        10  301  276   9
15  921  900  13        14  198  196   0        12  259  234   8        11  717  730  -9
16 -134   10  -9        15  989  961  18        13  341  325   6        12  174  199  -6
                        16   65   52   0        14  220  126  22        13   15   36   0
    -6  9  l            17  638  603  18        15  578  527  28        14  113   50   7
                                                16  222  268 -13        15  134  168  -6
 1 1762 1754   4            -2  9  l
 2  520  515   2                                     2  9  l                 6  9  l
 3 1035 1022   8         1 2450 2454  -1
 4  274  258   5         2  340  354  -6         0  879  885  -4         0  280  250   9
 5  642  626  10         3 2172 2203 -15         1 1866 1861   2         1  533  552 -10
 6 -180   70 -23         4  248  223   8         2  535  555 -12         2  745  741   2
 7   98  175 -13         5  924  913   7         3 2725 2719   2         3 2665 2691 -10
 8  301  272   9         6  265  230  13         4  482  470   6         4  152  124   4
 9  165  138   5         7  858  851   4         5  443  439   1         5  652  656  -2
10  305  305   0         8  248  228   6         6  329  305   9         6  490  491   0
11 1166 1145  14         9  304  292   5         7 1344 1344   0         7 1605 1597   4
12  640  639   1        10  116   44   7         8  410  380  12         8  444  459  -9
13  562  559   1        11  343  359  -8         9  282  252   9         9  941  941   0
14  153  183  -6        12   59   39   1        10  243  196  15        10  194  157   8
15 1288 1286   1        13  627  597  18        11  491  494  -1        11  518  531  -7
16  336  390 -19        14  175  160   3        12  -60   52  -4        12  -85   14  -4
17 1122 1090  19        15  945  966 -14        13   47   76  -2        13  475  457   9
                        16  -82  116 -11        14  399  346  23        14  137   82   7
    -5  9  l            17 1190 1185   3        15  376  373   1
                                                16  371  367   1             7  9  l
 1 1541 1526   8            -1  9  l
 2  587  582   3                                     3  9  l             0  525  453  37
 3 1165 1159   4         1 2669 2689  -8                                 1 2283 2319 -16
 4  360  350   4         2  250  222   9         0  734  714  13         2  227  188   9
 5 1125 1101  15         3 1335 1351 -10         1 2719 2756 -15         3  364  367  -1
 6  298  287   3         4  595  608  -8         2  568  570  -1         4  517  545 -13
 7   94  160 -10         5 1987 2001  -7         3  690  686   2         5 2046 2062  -7
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 9  491  488   1         7  239  261  -7         5 2089 2091  -1         7  885  901 -11
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12  294  259  14        10  418  376  17         8  363  366  -1        10  296  213  27
13 1294 1303  -5        11  370  334  18         9 1008 1011  -2        11  906  877  20
14  353  383 -12        12  170  186  -4        10  190  181   2        12  -44   93  -7
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17  796  791   2        15  854  834  13        13  184  184   0             8  9  l
                        16  242  229   3        14  117  177 -13
    -4  9  l            17  393  428 -14        15  299  304  -1         0 -100   33  -6
                                                16  160  195  -7         1  242  190  13
 1 1941 1953  -6             0  9  l                                     2  510  507   1
 2  446  452  -3                                     4  9  l             3 2232 2257 -11
 3 1516 1497  11         1 1931 1956 -13                                 4  276  224  13
 4  315  264  18         2  482  473   5         0  503  502   0         5  517  536 -12
 5  659  668  -5         3 2329 2335  -2         1 1531 1556 -15         6  278  310 -12
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11  712  726  -9         9  332  305   9         7 1574 1581  -4        12  193  222  -6
12  314  305   3        10  269  258   3         8  407  403   1
13  677  686  -6        11  128   29  12         9  492  498  -3             9  9  l
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 0  261  263   0        1  579  575   2        5  127    7  12       12  287  226  19
 1 1963 1967  -2        2  110  161  -7        6  333  313   8       13  506  489   8
 2  135  124   2                               7  568  569   0       14  759  745   8
 3  313  370 -24           -14  10  1          8  769  755   9       15  607  609   0
 4  236  224   3                               9  100   40   5
 5 1833 1837  -2        1  154  150   0       10  843  833   6          -4  10  1
 6  621  617   2        2  750  735   9       11  720  682  24
 7  947  945   1        3  -36   73  -3       12  267  242   7        1  844  845   0
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12   98   96   0        8  204  189   3                              6 1348 1346   1
                                              1 -218   48 -25        7  355  352   1
      10  9  1             -13  10  1          2  840  808  19        8  926  904  13
                                              3  419  442  -9        9  205  192   4
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 3 1766 1790 -13        4  953  950   2        7   66  171 -16       13  495  513  -9
 4  511  496   8        5   82   61   2        8  857  833  16       14  161  114   7
 5  855  863  -5        6  227  177  11        9  670  654  10       15  799  780  11
 6  159  150   2        7  551  550   0       10  654  654   0       16  418  400   6
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11  263  272  -2           -12  10  1         15  622  576  24        2  700  688   7
                                                                     3 1339 1314  15
      11  9  1          1  197  251 -15          -7  10  1            4 1233 1216  10
                        2  988 1013 -16                              5  583  584   0
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 1 1324 1340 -11        4  283  286   0        2  822  802  12        7  844  842   1
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15  328   349   -7

          0  10  l                    0   896   894    1        9   941   947   -4        1    52   105   -4
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 0   651   639    5                   2   -30   129  -11       11   635   607   15        3   936   943   -3
 1  1810  1835  -13                   3    34    33    0                                  4  1273  1292  -11
 2   650   666  -10                   4   291   259   12        9  10  l                   5   547   556   -4
 3   842   824   12                   5  1279  1281   -1                                  6   128    32    8
 4  -106    49   -8                   6   610   614   -1        0   587   581    3        7   581   574    3
 5  1484  1448   21                   7   467   472   -3        1    76    43    2        8   923   934   -7
 6   609   629  -11                   8   740   772  -24        2   575   580   -2        9   517   504    6
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 8   879   873    3                  10   398   402   -1        4   219   221    0      -11  11  l
 9   399   331   33                  11   282   273    3        5   667   685  -12
10   245   227    6                  12  1176  1187   -7        6   180   163    3        1  1144  1146   -1
11   312   311    0                  13   280   275    1        7  1062  1072   -6        2  1260  1271   -7
12  1286  1273    8                  14   465   470   -2        8   176   103   14        3   450   441    4
13   157   185   -5                                            9   577   567    5        4   295   291    1
14   257   282   -7                    5  10  l               10   619   624   -2        5   894   904   -6
15   611   566   25                                                                      6  1245  1248   -1
                                      0   391   411  -10       10  10  l                  7   705   688   10
          1  10  l                    1   316   260   18                                  8   375   337   13
                                      2   777   795  -11        0   821   824   -2        9   229   263   -9
 0   218   204    4                   3  1577  1572    3        1  1035  1036    0       10   640   621   10
 1  1080  1071    5                   4   462   491  -13        2   312   330   -7
 2   477   483   -3                   5   544   548   -1        3   516   525   -5      -10  11  l
 3  1774  1785   -6                   6   457   480  -14        4   513   480   18
 4   800   785    9                   7  1037  1028    7        5  1017  1018    0        1   149   228  -17
 5   471   467    1                   8   338   342   -1        6   299   278    6        2   436   478  -19
 6   616   651  -20                   9   516   537  -12        7   520   530   -4        3  1195  1179   10
 7   845   820   15                  10   958   940   12        8   240   196   12        4  1384  1369    9
 8   391   381    4                  11   564   578   -8        9   662   677   -8        5   654   605   28
 9   -14    25    0                  12   262   196   18                                  6   102   182  -13
10  1038  1017   15                  13   276   281   -1       11  10  l                  7   570   555    8
11   315   305    4                                                                      8  1042  1029    8
12   143    56   11                    6  10  l                0   691   716  -16        9   872   860    7
13   280   206   22                                            1   193   203   -2       10   391   370    8
14  1024  1027   -2                   0   758   757    0        2   911   922   -7       11   249   215    9
15   203   186    3                   1  1342  1347   -3        3  1004  1021  -11
                                      2    93   140   -7        4   125    37    9       -9  11  l
          2  10  l                    3   441   432    4        5   610   636  -15
                                      4   310   288    6        6   284   319  -12        1  1066  1059    4
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 2    88   171  -13                   7   635   646   -7                                  4   216   201    3
 3   685   695   -6                   8   711   721   -7       12  10  l                  5   955   948    4
 4   178   151    5                   9   796   800   -2                                  6  1307  1318   -7
 5  1233  1219    8                  10   -61    32   -3        0  1023  1015    5        7   809   795    9
 6   600   585    8                  11   516   518    0        1   832   816   10        8   375   364    4
 7   -64   108  -11                  12   966   966    0        2   199   173    5        9   257   297  -12
 8   789   780    7                  13   401   392    3        3   469   497  -14       10   764   805  -26
 9   451   463   -7                                            4   636   664  -17       11   672   672    0
10   243   247   -1                    7  10  l                5   577   550   14       12   429   412    7
11   154    79   12                                            6   265   261    0
12  1286  1275    7                   0   487   515  -13                                 -8  11  l
13   131   110    3                   1   -86    77   -7       13  10  l
14   367   340    9                   2   681   654   14                                  1   286   266    6
15   399   387    4                   3  1587  1622  -22        0   477   468    4        2   616   626   -6
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                                      6   231   237   -2        3   648   646    1        5   589   580    5
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 1   847   836    7                   8   201   197    1                                  7   643   628    9
 2   710   699    6                   9   662   657    3       14  10  l                  8  1149  1163   -9
 3  1525  1501   13                  10   760   759    0                                  9   914   926   -8
 4   469   512  -22                  11   680   670    6        0   890   912  -13       10   578   577    0
 5   254   279   -8                  12   314   275   12        1   453   476  -10       11    55    61    0
 6   313   293    7                                            2   203   153   10       12   453   454    0
 7   903   895    4                    8  10  l                                         13   432   397   15
 8   382   361   11                                          -13  11  l
 9   378   402  -12                   0   822   844  -17                                 -7  11  l
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11   567   531   21                   2   137    45   15        2   953   924   18        1  1006  1011   -3
12   139    15   14                   3   637   653  -10        3  -151   109  -17        2  1225  1209   11
13    85     0    4                   4   408   367   19        4   371   381   -3        3   549   504   26
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                                      6   303   351  -19        6  1194  1204   -5        5   687   672   10
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                                                                                         8   689   655   21
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  9  299  210  31      3  196  231  -8     11  901  892    6      8  539  536    1
 10  864  862   1      4 1310 1312  -1     12  194   37   23      9  690  672   11
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  7  340  352  -4                           8  968  980   -8      8  -55  108   -8
  8 1099 1087   7      1  339  333   2      9  555  583  -16      9  209  158   13
  9 1010  984  18      2  754  780 -16     10  326  323    1
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                       8 1213 1228 -10                            3  509  512   -2
    -5  11  l          9  463  407  26      0  440  430    4      4  181   45   22
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  1  528  502  12     11 1000  997   2      2  337  283   18      6   67  137   -9
  2 1481 1462  10     12 1069 1052  11      3  136  176  -10      7   57    1    2
  3 1092 1098  -4     13  627  608  10      4  413  458  -26      8  343  333    4
  4  203  170   8     14   94   67   2      5  280  330  -21
  5  489  511 -12                           6  531  523    5        10  11  l
  6 1286 1266  13        0  11  l           7  191  137   15
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  8 1066 1078  -8      1  397  409  -4      9  919  930   -7      1  902  927  -17
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-224-

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