Chapter 6

Dehydrogenation of Amine-Boranes with a Frustrated Lewis Pair

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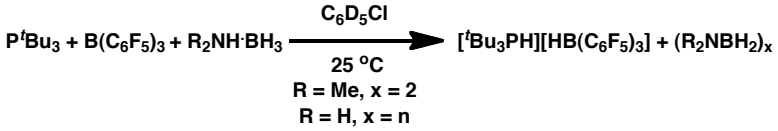
Chapter 6

Introduction

Amine-boranes are the subject of intense interest due to their potential application in hydrogen storage schemes.[1] A number of fast and efficient transition metal dehydrocoupling catalysts have been discovered,[2] and various coordination compounds relevant to the catalytic pathways have been isolated.[3] Progress has also been made in the challenging area of regeneration of spent ammonia-borane fuel.[4] Theoretical studies[5] of one amine-borane dehydrocoupling system employing N-heterocyclic carbenes (NHCs) as ligands[2a] suggested that the free NHC could heterolytically dehydrogenate NH_3•BH_3, yielding $(NH_2BH_2)_n$ and NHC–H_2, similar to the H_2 addition reactivity of Bertrand's carbenes.[6] Because the reactivity of these NHC species has been compared to that of bulky phosphine-borane "frustrated Lewis pairs" (FLPs), it occurred to us that FLPs might also be able to dehydrogenate amine-boranes.

FLPs — combinations of bulky Lewis acids and bases that are unable to form traditional Lewis acid-base pairs[7] — exhibit a number of unusual reactions,[8] including amine activation[9] and in particular the heterolytic cleavage of H_2,[10] which has been utilized for metal-free catalytic hydrogenation of bulky imines.[11] *De*hydrogenation reactions have only very recently been realized using FLPs; examples include self-dehydrogenation of an

NHC/$B(C_6F_5)_3$ FLP,[12] and unusual dehydrogenations of Ge species.[13] Mention of a phosphinoborane-catalyzed transfer hydrogenation from ammonia-borane to bulky imines[8a] was likely premature, as the reaction proceeds without any FLP participation.[14] Calculations suggested that FLP dehydrogenation of polarized substrates such as alcohols to aldehydes should be possible.[15] During this rapidly evolving period, we reported that the simple frustrated Lewis pair $P^tBu_3/B(C_6F_5)_3$ rapidly and cleanly dehydrogenates amine-boranes at room temperature, with concomitant formation of the phosphonium borohydride salt $[^tBu_3PH][HB(C_6F_5)_3]$ (Scheme 6.1). Closely following our publication, a theoretical treatment "predicted" that dehydrogenations of amine-boranes could be carred out by FLPs,[16] consistent with our findings.



Scheme 6.1

Results and Discussion

Initial experiments were carried out with $Me_2NH{\bullet}BH_3$, a common model for $NH_3{\bullet}BH_3$ which has desirable solubility properties and generally releases only a single equivalent of H_2. The frustrated Lewis pair $P^tBu_3/B(C_6F_5)_3$ was formed according to literature procedures in C_6D_5Cl,[10b] and no discernable reaction was observed by NMR. The preformed FLP (which was yellow in our hands; see Experimental Section) was added to a C_6D_5Cl solution of $Me_2NH{\bullet}BH_3$ at 25 °C, and the yellow color bleached to a clear colorless solution. ^1H, ^{31}P (Figure 6.1), ^{19}F, and ^{11}B (Figure 6.2) NMR experiments

confirmed that > 95% of the FLP-derived product was $[^tBu_3PH][HB(C_6F_5)_3]$.[10b] The major dehydrocoupling product was dimeric $(Me_2NBH_2)_2$, assigned by a diagnostic ^{11}B NMR resonance at δ 5.2 (t, $\mathcal{J}_{BH}$ = 112 Hz), and by signals in the ^1H NMR spectrum at δ 2.28 (s, Me_2N) and δ 2.83 (1:1:1:1 q, $\mathcal{J}_{BH}$ = 112 Hz, BH_2). Minor side products, including monomeric $Me_2N{=}BH_2$ (^{11}B NMR δ 37.6, t, $\mathcal{J}_{HB}$ = 127 Hz) and $HB(NMe_2)_2$ (^{11}B NMR δ 28.5, d, $\mathcal{J}_{HB}$ = 124 Hz), dissipated over time, leaving ~97% dimeric $(Me_2NBH_2)_2$ along with traces of $(BH_2)_2NMe_2(\mu\text{–}H)$ (**A**) and $H_3B{\bullet}NMe_2BH_2{\bullet}NHMe_2$ (**B**). The two boron resonances of $H_3B{\bullet}NMe_2BH_2{\bullet}NHMe_2$ are similar to $Me_2NH{\bullet}BH_3$ and the cyclic trimer $(Me_2NHBH_2)_3$. The latter species is unstable; the persistence of the resonances rule out the trimer. ^1H NMR data and the observed 1:1 ratio of ^{11}B NMR resonances both point to the double-adduct assignment. This product distribution is similar to that observed in metal-catalyzed dehydrocoupling of $Me_2NH{\bullet}BH_3$;[17] thermolysis of a $Me_2NH{\bullet}BH_3$ melt at 150 °C also affords $(Me_2NBH_2)_2$, along with trace impurities including $HB(NMe_2)_2$.[17b,18]

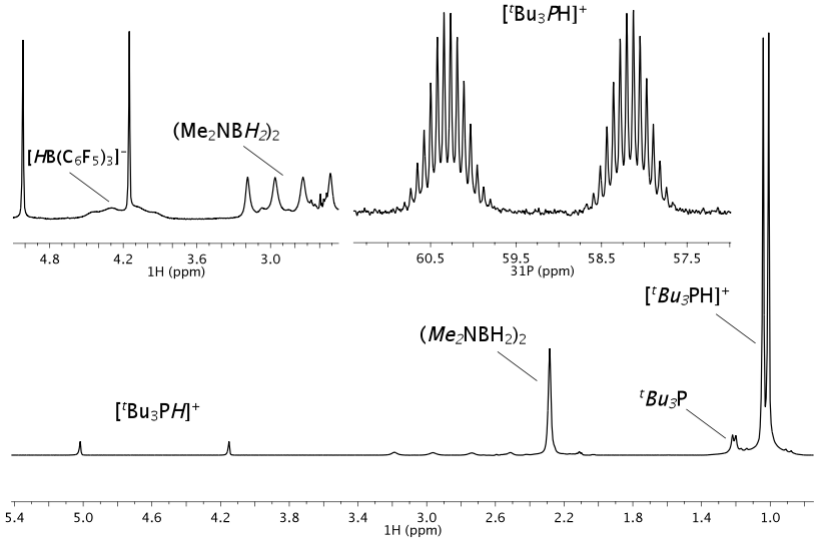


Figure 6.1. ^{1}H NMR spectrum after FLP-mediated dehydrocoupling of $Me_2NH{\bullet}BH_3$. Left inset is a blow-up of the borohydride ^{1}H NMR resonances; right inset is the ^{31}P NMR spectrum of $[^{t}Bu_3PH][HB(C_6F_5)_3]$.

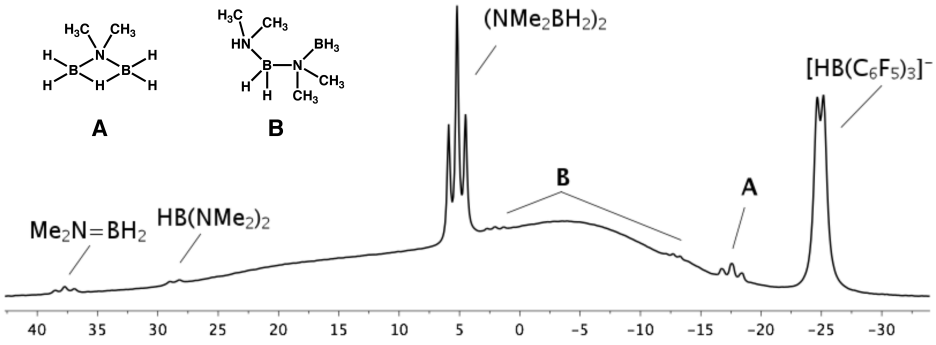


Figure 6.2. ^{11}B NMR spectrum shortly after FLP-mediated dehydrocoupling of $Me_2NH{\bullet}BH_3$. The underlying broad feature arises from borosilicate glass in the probe construction.

The order of reagent addition is important in the dehydrocoupling reaction. If $B(C_6F_5)_3$ and $Me_2NH{\bullet}BH_3$ are dissolved in C_6D_5Cl a few minutes prior to addition of $P^{t}Bu_3$, several products including only ~50% $(Me_2NBH_2)_2$ are produced. On the other hand, combining $P^{t}Bu_3$ and $Me_2NH{\bullet}BH_3$ in C_6D_5Cl, followed by addition of $B(C_6F_5)_3$ led to near-quantitive

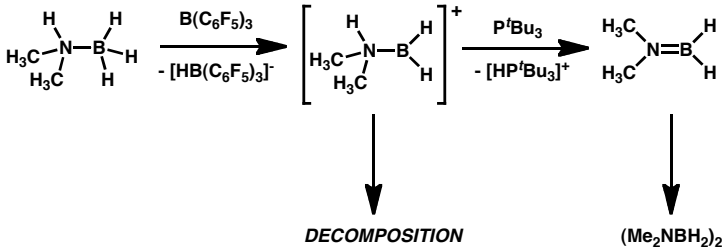
formation of [^{t}Bu$_3$PH][HB(C$_6$F$_5$)$_3$] and (Me$_2$NBH$_2$)$_2$, in essentially the same distribution as with prior formation of the FLP.

To explore the possibility of H_2 release and amine-borane regeneration, the mixture of [^{t}Bu$_3$PH][HB(C$_6$F$_5$)$_3$] and (Me$_2$NBH$_2$)$_2$ was heated between 90 and 130 °C. We hoped that regeneration might be driven by formation of more stable Lewis adducts P^{t}Bu$_3$•BH$_3$ and NH$_3$•B(C$_6$F$_5$)$_3$. Complete decomposition of the dimer to a variety of species was observed; only P^{t}Bu$_3$•BH$_3$ and [HB(C$_6$F$_5$)$_3$]$^-$ were readily identified by ^{11}B NMR,[19] leaving this experiment inconclusive. In isolation, (Me$_2$NBH$_2$)$_2$ is stable up to 450 °C in the gas phase[17b] and 130 °C in a melt.[18] Similarly, it has been reported that [^{t}Bu$_3$PH][HB(C$_6$F$_5$)$_3$] is stable to H_2 loss up to 150 °C.[10b]

The FLP system can dehydrogenate NH$_3$•BH$_3$ as well. Treatment of NH$_3$•BH$_3$ with P^{t}Bu$_3$/B(C$_6$F$_5$)$_3$ afforded once again [^{t}Bu$_3$PH][HB(C$_6$F$_5$)$_3$] as a principal product (85%, ^{31}P NMR; ~80%, ^{19}F NMR). The major dehydrocoupling product is consistent with branched-chain polyaminoborane ((NH$_2$BH$_2$)$_n$, broad ^{11}B NMR, δ –7.7, –14.4, –27.2) as observed upon thermolysis of NH$_3$•BH$_3$ in ionic liquids.[20] The other ^{11}B NMR signals correspond to [HB(C$_6$F$_5$)$_3$]$^-$ and two smaller peaks which could be Lewis adducts between P^{t}Bu$_3$ and boranes; two broad resonances in the ^{31}P NMR spectrum are consistent with this formulation. Apparently dehydrocoupling is more favorable than forming stable Lewis pairs, although in this case some of that competing pathway is observed. Lewis adduct formation has been observed when Me$_2$NH•BH$_3$ and P^{i}Pr$_3$ were heated to 85 °C for 1 hour (giving ^{i}Pr$_3$P•BH$_3$).[2c] Some insoluble colorless material was extracted with pyridine and shown to be unreacted NH$_3$•BH$_3$, consistent with some amount of deactivation of the FLP

(by strong Lewis adduct formation) before quantitative dehydrocoupling could take place. Neither the insoluble cyclic pentamer $(NH_2BH_2)_5$[2b,3d] nor long linear polymers[21] were detected, in contrast to a number of metal-catalyzed reactions. Treatment of NH_3•BH_3 with excess FLP did not lead to detectable amounts of borazine, suggesting that only one equivalent of H_2 could be released using this method.

$B(C_6F_5)_3$ by itself can *catalytically* dehydrogenate NH_3•BH_3,[22] but only at elevated temperatures; no significant amounts of product are observed under the present conditions without P^tBu_3. Importantly, $B(C_6F_5)_3$ by itself is unable to dehydrocouple Me_2NH•BH_3,[17b] leading us to conclude that the FLP is essential for rapid, ambient-condition dehydrocoupling. Initial attempts at catalytic H_2 release from Me_2NH•BH_3 under mild conditions using an FLP were met with disappointment. The FLP $B(p\text{-}C_6F_4H)_3/P(o\text{-tolyl})_3$ — which releases H_2 from $[(o\text{-tolyl})_3PH][HB(p\text{-}C_6F_4H)_3]$ under vacuum[10c] — did not give clean dehydrocoupling chemistry when allowed to react with Me_2NH•BH_3, precluding attempts to release H_2 from the phosphonium borohydride and turn over a cycle.



Scheme 6.2

The mechanism of heterolytic cleavage of H_2 by FLP's has not been fully elucidated, although a number of theoretical studies have been performed.[8a,23] DFT calculations suggest that a weak interaction holds the borane and phosphine in proximity; a molecule of

H_2 approaches the pair and is cleaved in a concerted fashion. Since the heterolytic dehydrogenation of amine-boranes constitutes a net transfer of H_2 and gives a similar product, one could invoke a similar mechanism. We prefer an alternative, stepwise mechanism in which $B(C_6F_5)_3$ first abstracts a hydride from $Me_2NH•BH_3$, followed by fast deprotonation of the resulting $[Me_2NHBH_2]^+$, affording the $Me_2N=BH_2$ unit that dimerizes to the final product (Scheme 6.2). In the absence of P^tBu_3, oligomerization of the cationic intermediate might take place (as suggested by Baker for the reaction of acid with $NH_3•BH_3$[22]) accounting for the multiple side products observed when $B(C_6F_5)_3$ is added first.

We have shown that frustrated Lewis pairs consisting of bulky tertiary phosphines and $B(C_6F_5)_3$ are capable of rapidly dehydrocoupling $Me_2NH•BH_3$ and $NH_3•BH_3$. While the current FLP systems could serve as H_2 storage compounds themselves,[10a] their weight % capacity is far from ideal. Using FLPs as a H_2 shuttle with lighter, non-frustrated amine-boranes as the terminal H_2 storage medium is perhaps more attractive. Recent advances in H_2 release from FLPs[10c,24] may open the door to catalytic dehydrocoupling, and indeed perhaps dehydrogenation of a wider variety of substrates.

Experimental Section

General Considerations

All air- and moisture-sensitive compounds were manipulated using standard vacuum line or Schlenk techniques, or in a glovebox under a nitrogen atmosphere. Under standard glovebox conditions, petroleum ether, diethyl ether, benzene, toluene, and tetrahydrofuran were used without purging, such that traces of those solvents were in the atmosphere, and could be found intermixed in the solvent bottles. The solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl, calcium hydride, or by the method of Grubbs.[25] NMR solvents were purchased from Cambridge Isotopes Laboratories, Inc. Chlorobenzene-d_5 was degassed by three freeze-pump-thaw cycles and dried by passage through a small column of activated alumina. Unless noted, other materials were used as received. P^tBu_3 and $B(C_6F_5)_3$ were purchased from Strem Chemicals, Inc., and $B(C_6F_5)_3$ was sublimed before use. $NH_3{\bullet}BH_3$, and $Me_2NH{\bullet}BH_3$ were purchased from Aldrich. ^1H, ^{31}P, ^{19}F, ^{11}B, and ^{13}C NMR spectra were recorded on Varian Mercury 300 MHz, or Varian INOVA 500 MHz spectrometers at room temperature, unless indicated otherwise. Chemical shifts are reported with respect to residual internal protio solvent for ^1H and ^{13}C spectra. Other nuclei were referenced to an external standard: 85% H_3PO_4 (^{31}P), 15% $BF_3{\bullet}Et_2O/CDCl_3$ (^{11}B), $CFCl_3$ (^{19}F), all at 0 ppm.

Experimental Procedures

Dehydrocoupling of $Me_2NH{\bullet}BH_3$ by $P^tBu_3/B(C_6F_5)_3$ Pair. A 10 mL vial was charged with 97 mg (0.19 mmol) $B(C_6F_5)_3$ 39 mg (0.19 mmol) P^tBu_3, and ~0.3 mL C_6D_5Cl.

Upon dissolution, the solution turned yellow. In a separate 10 mL vial, 11 mg (0.19 mmol) $Me_2NH•BH_3$ was dissolved in ~0.3 mL C_6D_5Cl with stirring. The yellow borane/phosphine solution was added to the stirring $Me_2NH•BH_3$ solution, and the mixture immediately lost the yellow color, giving a clear colorless solution. The reaction mixture was transferred to a J-Young Teflon-stoppered NMR tube, and multinuclear NMR experiments showed high conversion to $(Me_2NBH_2)_2$. After 24 hours the spectra were reacquired, showing the disappearance of some minor side products, giving ~97% pure $(Me_2NBH_2)_2$. **^{1}H NMR** (C_6D_5Cl, 500 MHz): δ 1.03 (d, $\mathcal{J}_{PH}$ = 15.7 Hz, 27H, $[HP^tBu_3]^+$), 1.14 (d, $\mathcal{J}_{PH}$ = 9.4 Hz, ~5% P^tBu_3 impurity), 2.28 (s, 6H, $(Me_2NBH_2)_2$), 2.85 (1:1:1:1 q, $\mathcal{J}_{BH}$ = 112.4 Hz, 2H, $(Me_2NBH_2)_2$), 4.2 (br 1:1:1:1 q, $\mathcal{J}_{BH}$ ~ 84 Hz, 1H, $[HB(C_6F_5)_3]^-$), 4.58 (d, $\mathcal{J}_{PH}$ = 433.1 Hz, 1H, $[HP^tBu_3]^+$). **^{31}P{^{1}H} NMR** (C_6D_5Cl, 202 MHz): δ 59.2 (s, 1P, $[HP^tBu_3]^+$), 62.4 (s, ~5% P^tBu_3 impurity). **^{31}P NMR** (C_6D_5Cl, 202 MHz): δ 59.2 (doublet of 14-line (*observed*, 28-line hypothetical) patterns, $\mathcal{J}_{PH}$ = 432.6, 15.7 Hz, 1P, $[HP^tBu_3]^+$), 62.4 (br s, ~5% P^tBu_3 impurity), **^{19}F NMR** (C_6D_5Cl, 282 MHz): δ –132.63 (br d, $\mathcal{J}_{FF}$ = 20.0 Hz, 6F, *o*-C_6F_5), –163.61 (br t, $\mathcal{J}_{FF}$ = 20.0 Hz, 3F, *p*-C_6F_5), –166.53 (br d, $\mathcal{J}_{FF}$ = 15.77 Hz, *m*-C_6F_5). **^{11}B NMR** (C_6D_5Cl, 160 MHz): δ –25.0 (d, $\mathcal{J}_{BH}$ = 84.3 Hz, $[HB(C_6F_5)_3]^-$), –17.6 (minor, dt, $\mathcal{J}_{BH}$ = 129 Hz, 31 Hz, $(BH_2)_2NMe_2(\mu–H)$), –12.85 (minor, q, $\mathcal{J}_{BH}$ = 92 Hz, $H_3B•NMe_2BH_2•NHMe_2$), 2.00 (minor, 116 MHz, $H_3B•NMe_2BH_2•NHMe_2$), –5.2 (t, $\mathcal{J}_{BH}$ = 112.7 Hz, $(Me_2NBH_2)_2$). **^{13}C{^{1}H} NMR** (C_6D_5Cl, 126 MHz): δ 29.11 (s, $P(C(CH_3)_3)_3$), 36.79 (d, $\mathcal{J}_{PC}$ = 27.0 Hz, $P(C(CH_3)_3)$), 51.54 (s, $(Me_2NBH_2)_2$), 136.83 (dm, $^1\mathcal{J}_{FC}$ = 245.4 Hz, $[HB(m\text{-}C_6F_5)_3]^-$), 138.12 (dm, $^1\mathcal{J}_{FC}$ = 244 Hz, $[HB(p\text{-}C_6F_5)_3]^-$), 148.71 (dm, $^1\mathcal{J}_{FC}$ = 236 Hz, $[HB(o\text{-}C_6F_5)_3]^-$).

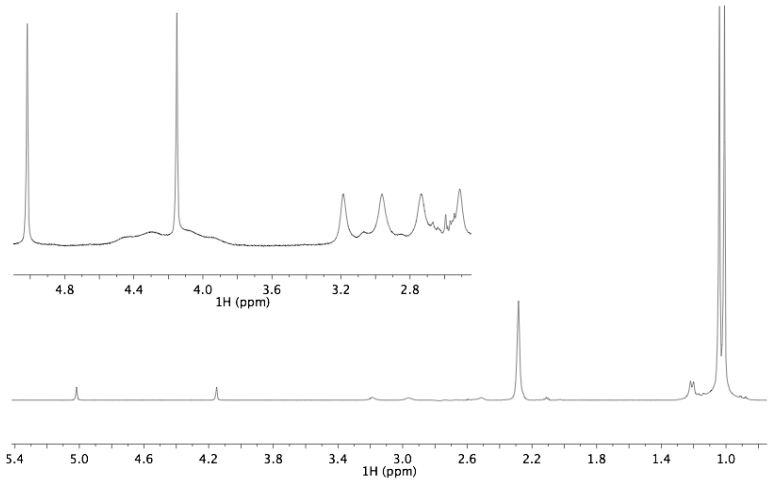


Figure 6.3. ^{1}H NMR of $(Me_2NBH_2)_2$ and $[^{t}Bu_3PH][HB(C_6F_5)_3]$ (with enlargement inset).

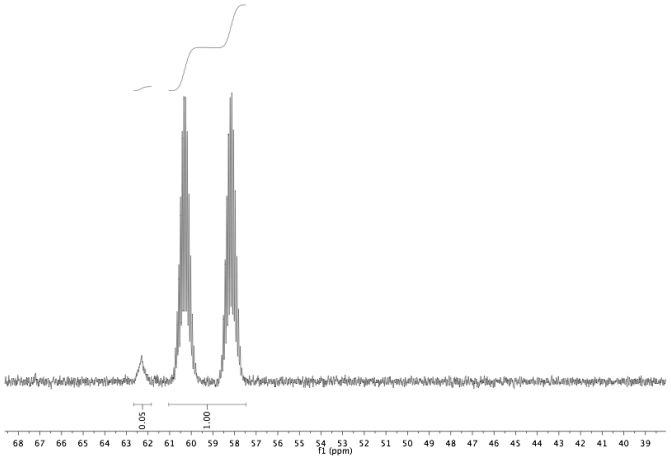


Figure 6.4. ^{31}P NMR of $(Me_2NBH_2)_2$ and $[^{t}Bu_3PH][HB(C_6F_5)_3]$.

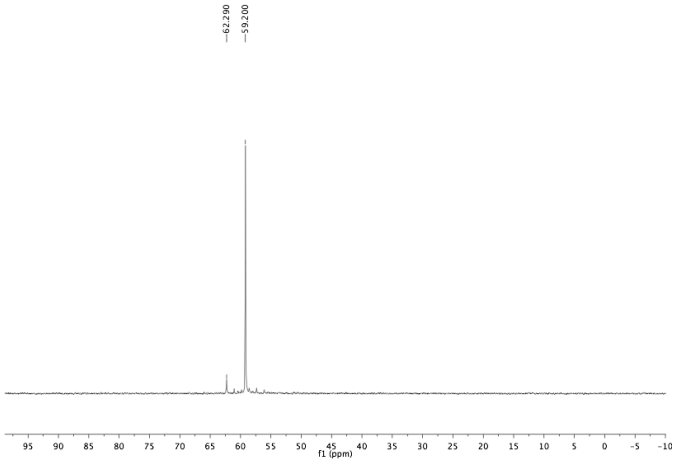


Figure 6.5. $^{31}P\{^{1}H\}$ NMR of $(Me_2NBH_2)_2$ and $[^tBu_3PH][HB(C_6F_5)_3]$.

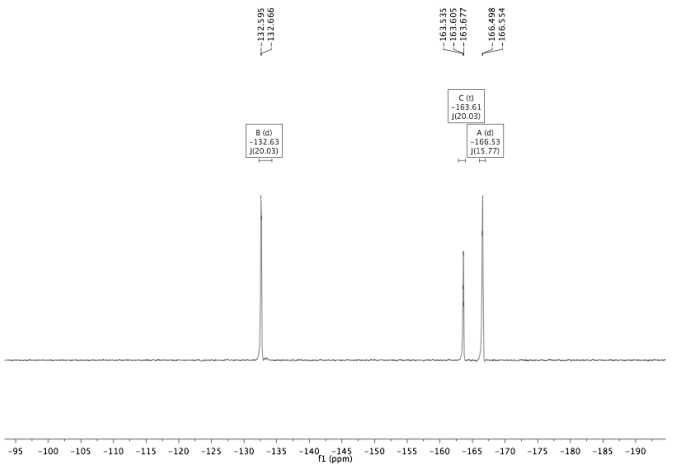


Figure 6.6. ^{19}F NMR of $(Me_2NBH_2)_2$ and $[^tBu_3PH][HB(C_6F_5)_3]$.

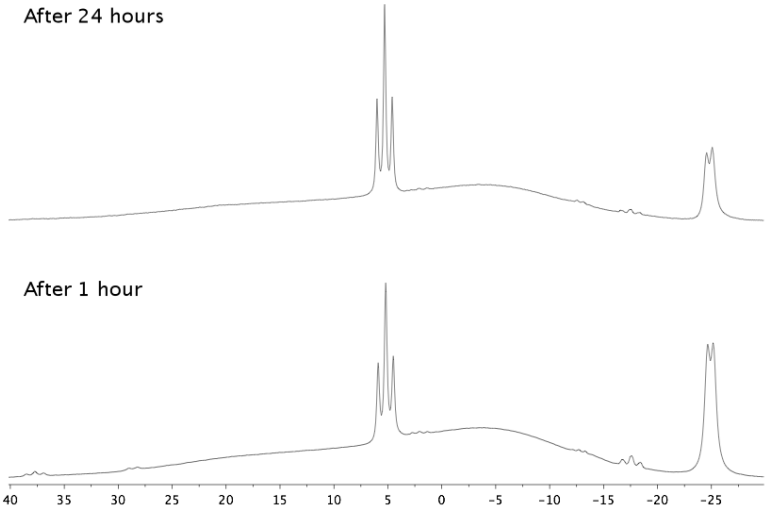


Figure 6.7. ^{11}B NMR of $(Me_2NBH_2)_2$ and $[^tBu_3PH][HB(C_6F_5)_3]$, at 1 and 24 hours.

Reaction of $Me_2NH•BH_3$ with $B(C_6F_5)_3$, followed by P^tBu_3. In a 10 mL vial, 6.7 mg (0.114 mmol) $Me_2NH•BH_3$ was dissolved in ~0.2 mL C_6D_5Cl. To the solution was added 58.2 mg (0.114 mmol) $B(C_6F_5)_3$ in ~0.4 mL C_6D_5Cl, and the mixture was mixed well and added to a J-Young Teflon-sealed NMR tube. Multinuclear NMR experiments showed a mixture of products, including a number of broad features in the ^{19}F and ^{11}B NMR spectra. A short while later, the tube was returned to the glovebox, and the contents poured into a vial containing 23.0 mg (0.114 mmol) P^tBu_3. The reaction mixture was returned to the NMR tube and shaken well, and further NMR experiments were undertaken. Multiple species were observed by NMR, including ~80% $[^tBu_3PH][HB(C_6F_5)_3]$, and only ~50% dimeric $(Me_2NBH_2)_2$.

Reaction of $Me_2NH•BH_3$with P^tBu_3, followed by $B(C_6F_5)_3$. A 10 mL vial was charged with 6.3 mg (0.107 mmol) $Me_2NH•BH_3$, 21.6 mg (0.107 mmol) P^tBu_3, and ~0.6 mL C_6D_5Cl. The colorless solution was mixed well, and then added to another vial charged

with solid 54.8 (0.107 mmol) $B(C_6F_5)_3$. The clear, colorless reaction mixture was transferred to a J-Young Teflon-sealed NMR tube, sealed, and assessed by multinuclear NMR. After 30 minutes, clean conversion to a product distribution similar to that of the preformed FLP was observed.

Dehydrocoupling of NH_3•BH_3 by $P^tBu_3/B(C_6F_5)_3$ Pair. A small vial was charged with 30 mg (0.15 mmol) P^tBu_3 and 76 mg (0.15 mmol) $B(C_6F_5)_3$ and ~0.6 mL C_6D_5Cl to give a yellow solution. A J-Young Teflon-sealed NMR tube was charged with 2.3 mg (0.075 mmol) NH_3•BH_3, and the phosphine/borane mixture was added to the tube. The NH_3•BH_3 slowly dissolved, and the yellow color slowly bleached to give a clear colorless solution, which was examined by multinuclear NMR spectroscopy. **^{1}H NMR** (C_6D_5Cl, 500 MHz): δ 1.03 (d, $\mathcal{J}_{PH}$ = 15.7 Hz), 1.15 (minor, d, $\mathcal{J}_{PH}$ = 12.2 Hz), 1.23 (minor, d, $\mathcal{J}_{PH}$ = 11.6 Hz), 4.1 (br, q $[HB(C_6F_5)_3]^-$). A number of additional broad peaks were observed, assigned to various polyaminoborane BH and NH resonances. **^{31}P NMR** (C_6D_5Cl, 121 MHz): δ 33.5 (minor, br), 35.9 (minor, br), 58.6 (doublet of multiplets, $\mathcal{J}_{PH}$ = 434.5 Hz, $[HP^tBu_3]^+$). **^{19}F NMR** (C_6D_5Cl, 282 MHz): δ –132.61 (br d, $\mathcal{J}_{FF}$ = 21.4 Hz, 6F, *o*-C_6F_5), –163.64 (br t, $\mathcal{J}_{FF}$ = 20.4 Hz, 3F, *p*-C_6F_5), –166.57 (br d, $\mathcal{J}_{FF}$ = 18.4 Hz, 6F, *m*-C_6F_5). A number of unidentified peaks were observed as well. **^{11}B NMR** (C_6D_5Cl, 160 MHz): δ –34.3 (br m, $^tBu_3P$•BH_3), –29.6 (t, $\mathcal{J}_{BH}$ = 78 Hz, unknown), –27.2 (br sh, $(NH_2BH_2)_n$), –25.1 (d, $\mathcal{J}_{BH}$ = 82.3, $[HB(C_6F_5)_3]^-$), -14.5 (br, $(NH_2BH_2)_n$), -7.7 (br, $(NH_2BH_2)_n$).

Thermolysis of $(Me_2NBH_2)_2$ / $[^tBu_3PH][HB(C_6F_5)_3]$ Mixture. A mixture of $(Me_2NBH_2)_2$ and $[^tBu_3PH][HB(C_6F_5)_3]$ in C_6D_5Cl, formed (including trace impurities) as

described above, was heated to either 90 °C or 130 °C in separate experiments. Both temperatures led to similar product mixtures, although at 90 °C the products grew in more slowly. Heating at 130 °C led to complete consumption of $(Me_2NBH_2)_2$ in a few hours. Along with $[HB(C_6F_5)_3]^-$, a number of other B–containing species are present, including $^tBu_3P{\bullet}BH_3$.

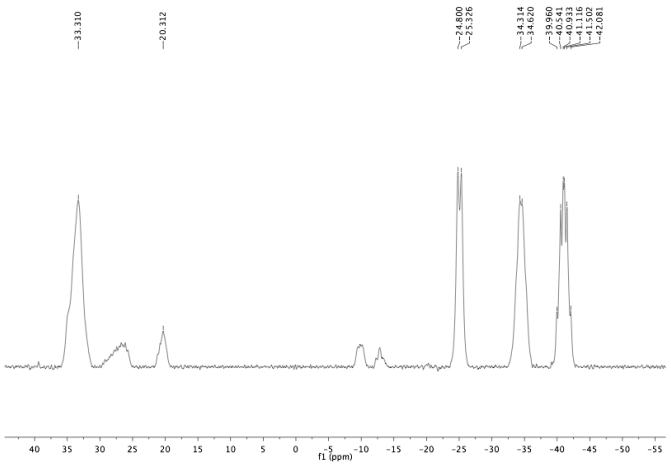


Figure 6.8. ^{11}B NMR after thermolysis of $(Me_2NBH_2)_2$ and $[^tBu_3PH][HB(C_6F_5)_3]$ (with linear prediction subtraction of borosilicate signals).

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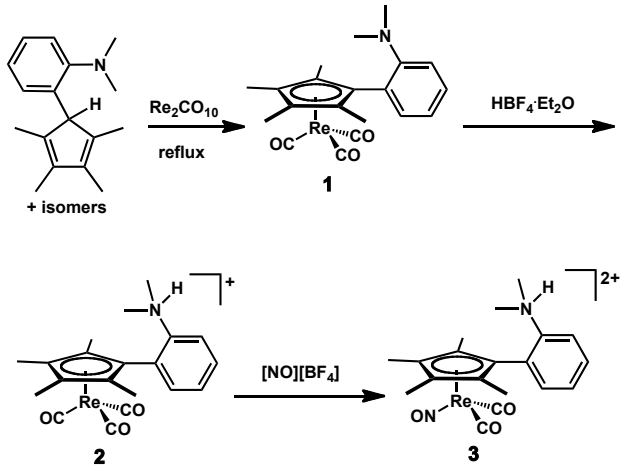
Appendix A

Investigations into Brønsted Acid-Assisted CO Reduction

Appendix A

Introduction

Chapters 3 and 4 detailed the role that Lewis acids can play in CO reduction chemistry. In theory, Brønsted acids could also aid in C–H or C–C bond formation; Shriver indeed reported that a slight excess of proton acid (of appropriate pK_a) accelerated migratory insertion by up to a factor of 10.[1] Other potential benefits include a) the ability of the acid to transfer protons to reduced CO species; or b) the ability of the conjugate base to help cleave dihydrogen in concert with a late transition metal.[2] Our initial studies, focused on ammonium-substituted cyclopentadienyl (Cp) ligands, are described here.



Scheme A.1

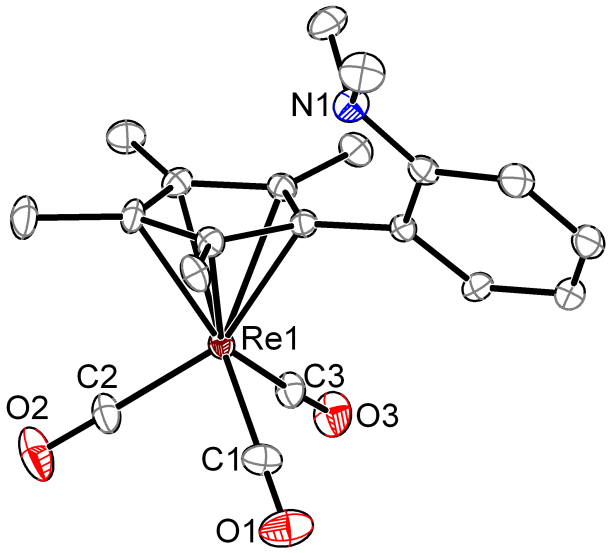


Figure A.1. Structural representation of **1**, ellipsoids at 50% probability. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Re1–C1 1.911(4), Re1–C3 1.917(3), Re1–C2 1.918(3), C1–Re1–C3 89.82(16), C1–Re1–C2 89.27(18), C3–Re1–C2 88.96(14).

Results and Discussion

Aniline-based Cp ligands were explored first; the ligand was synthesized according to literature procedures,[3] and metallated with Re_2CO_{10} under thermally forcing conditions to form ^{NAr}Cp*Re(CO)$_3$ (**1**, Scheme A.1). Crystals of **1** suitable for XRD were grown from cold hexanes, allowing structural characterization (Figure A.1). Protonation by HBF_4 provided cationic **2** (also structurally characterized, Figure A.2), which was treated with [NO][BF_4] to effect ligand exchange, yielding the desired dicationic nitrosyl complex, [^{HNAr}Cp*Re(CO)$_2$(NO)][BF_4]$_2$ (**3**). Despite being doubly charged, the CO stretching frequencies of **3** are essentially identical to that of [Cp*Re(CO)$_2$NO]$^+$.

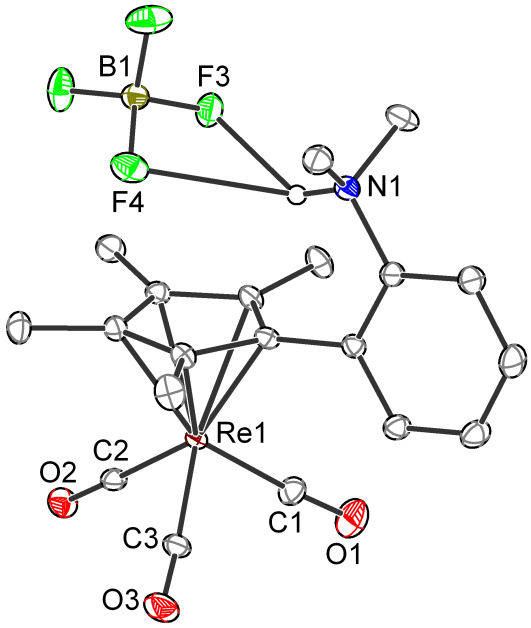
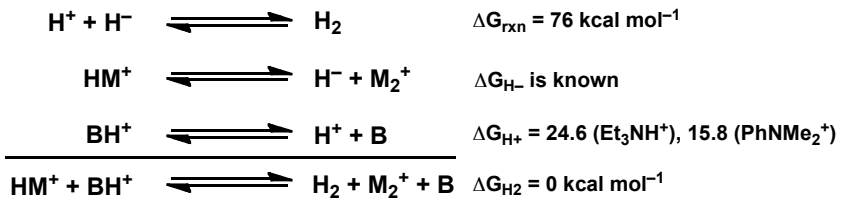


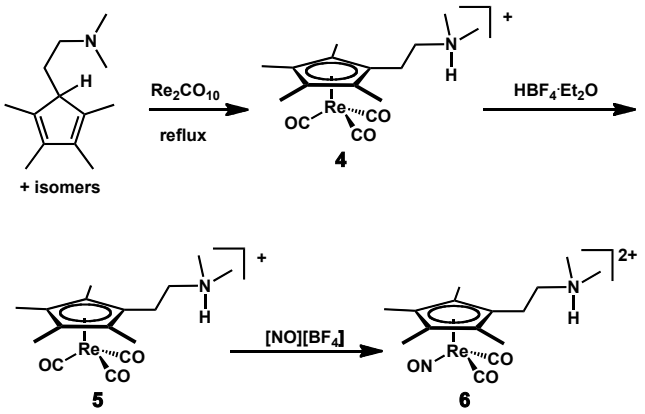
Figure A.2. Structural representation of **2**, ellipoids at 50% probability. Most hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Re1–C3 1.918(2) Re1–C2 1.923(2), Re1–C1 1.927(3), N1–F3 2.791(3), C3–Re1–C2 88.34(10), C3–Re1–C1 91.37(11), C2–Re1–C1 90.77(11).



Scheme A.2

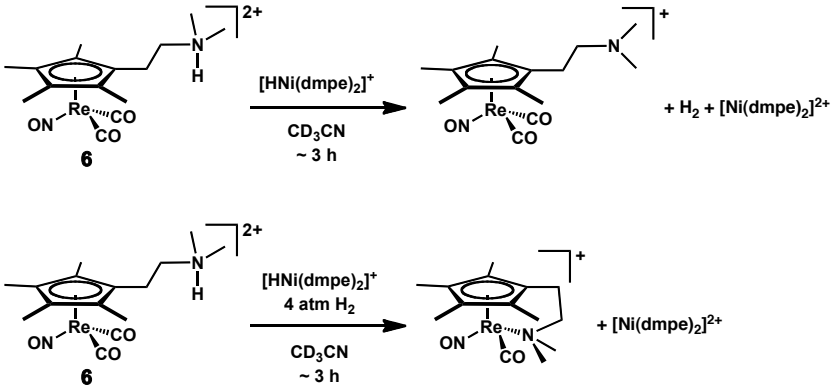
Treatment of **3** with the weak hydride $[HNi(depe)_2]^+$ (depe = bis(diethylphosphino)ethane.) resulted only in deprotonation of the pendent ammonium, evidenced by H_2 evolution and the formation of $[Ni(depe)_2]^{2+}$. Presumably, the anilinium group is too acidic to be used with late transition metal hydrides. Thermodynamic analysis according to Scheme A.2 (using pK_a of *N*,*N*-dimethylanilinium and triethylammonium) can put a lower bound on the hydricity required to avoid forming H_2. These calculations suggest that a hydride donor

with $\Delta G_{H^-} > 60$ kcal mol^{-1} will be required to avoid reaction with anilinium acids, while a hydride donor with $\Delta G_{H^-} > 51$ kcal mol^{-1} will be required to avoid reaction with trialkylammonium acids. Cp*Re(CO)(NO)(CHO) has $\Delta G_{H^-} = 52.6$ kcal mol^{-1}; a hydride with $\Delta G_{H^-} < 52.6$ kcal mol^{-1} is required to reduce it. If there is *no Brønsted acid assitance*, there is no hydride that can satisfy both requirements for a pendent anilinium group (ΔG_{H^-} larger than 60 kcal mol^{-1} but also smaller than 52.6 kcal mol^{-1}), consistent with the observed reactivity; a very small window, between 51 and 52.6 kcal mol^{-1} exists for trialkylammonium groups. This narrow window of opportunity might be widened if a large Brønsted acid assistance was engendered by the ammonium salts.



Scheme A.3

Based on the thermodynamic calculations, a new ligand containing an alkyl linker between the amine and cyclopentadienyl was targeted.[4] DuBois has observed that $[HNi(dmpe)_2]^+$ is able to reduce $[Cp^*Re(CO)_2(NO)]^+$ as well as remain stable in the presence of the $HNEt_3^+$ under H_2.[2a] We hoped that the less acidic protons of complex **6** (Scheme A.3), formed by the same route as the anilinium analogue, would be less susceptible to H_2 formation.



Scheme A.4

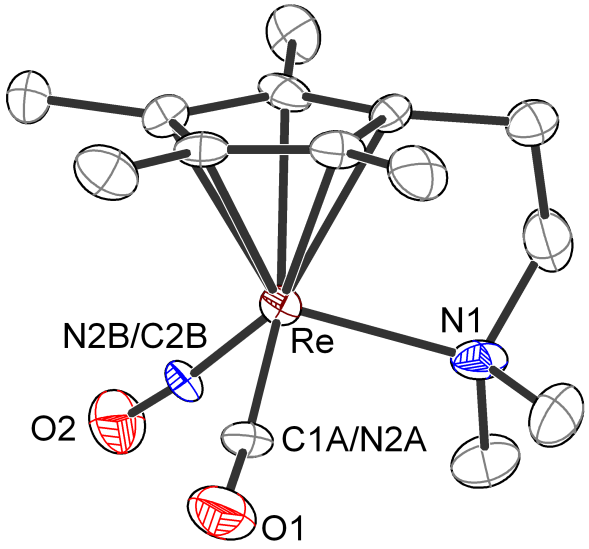
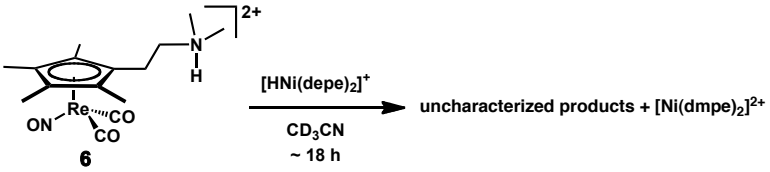


Figure A.3. Structural representation of **7**, ellipsoids at 50% probability. Hydrogen atoms and PF_6 counterion omitted for clarity. Selected bond distances (Å) and angles (°): Re–C1A/N2A 1.855(8), Re–N2B/C2B 1.838(8), Re–N1 2.186(7), C1A/N2A–Re–N2B/C2B 93.6(3), C1A/N2A–Re–N1 99.5(3), N2B/C2B–Re–N1 100.9(3).

Reaction of $[^{HNEt}Cp^*Re(CO)_2(NO)][BF_4]_2$ (**6**) in acetonitrile with $[HNi(dmpe)_2][PF_6]$ leads to clean deprotonation under N_2, as shown in Scheme A.4. The same reaction was carried out under 4 atm of H_2, which might disfavor H_2 formation. Indeed, treatment of **6** with $[HNi(dmpe)_2][PF_6]$ under 4 atm H_2 led to different reactivity (Scheme A.4), with the major product being a new Re-containing species, identified by ^1H NMR, IR, and XRD as **7**

(Figure A.3). Spectroscopic data are similar to a related complex.[5] It is not entirely clear how **7** is formed. No deprotonation is observed, although such a reaction cannot be ruled out. Additionally, compound **6** is stable in CD_3CN solutions for 48 hours, and does not spontaneously lose CO to form **7**. No sign of common reduced species, such as methane, methanol, or two-carbon species are visible by NMR spectroscopy.



Scheme A.5

Treatment of **6** with the weaker hydride donor $[HNi(depe)_2][PF_6]$ under N_2 does not result in any deprotonation; unknown products grew in over 18 hours. These products remain unidentified, but do not contain the signature downfield shifts of Re formyl or carbene species, nor the upfield shifts of Re hydrides. $[HNi(depe)_2][PF_6]$ and $[Cp^*Re(CO)_2(NO)][BF_4]$ do not obviously react over 48 hours.

Conclusions

Few encouraging signs of productive CO reduction were observed in these reactions, even when a relatively weak acid was employed. In cases where deprotonation was not observed, very little effect on reactivity could be ascribed to the Brønsted acid; in fact, this may be due in part to the necessity to use such weak acids. In light of these problems, this approach was abandoned in favor of Lewis acidic pendent groups, which retain their acidity without problematic elimination of H_2.

Experimental Section

General Considerations

All air- and moisture-sensitive compounds were manipulated using standard vacuum line or Schlenk techniques, or in a glovebox under a nitrogen atmosphere. The solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl, calcium hydride, or by the method of Grubbs.[6] All NMR solvents were purchased from Cambridge Isotopes Laboratories, Inc. Dichloromethane-*d*$_2$ (CD_2Cl_2) was freeze-pump-thaw degassed three times before being run through a small column of activated alumina. Acetonitrile-*d*$_3$ (CD_3CN) was degassed and vacuum transferred from CaH_2 prior to use. Unless noted, other materials were used as received. 1-(2-*N*,*N*-Dimethylaminophenyl)-2,3,4,5-tetramethylcyclopentadiene,[3] [2-(*N*,*N*-Dimethylamino)ethyl]tetramethylcyclopentadiene,[4] $[HNi(dmpe)_2][PF_6]$[7] and $[HNi(depe)_2][PF_6]$[8] were synthesized by literature methods. ^1H and ^{13}C NMR spectra were recorded on Varian Mercury 300 MHz, or Varian INOVA-500 or 600 MHz spectrometers at room temperature, unless indicated otherwise. Chemical shifts are reported with respect to residual internal protio solvent for ^1H and $^{13}C\{^1H\}$ spectra. Other nuclei were referenced to an external standard: H_3PO_4 (^{31}P), 15% BF_3•Et_2O/$CDCl_3$ (^{11}B), $CFCl_3$ (^{19}F), all at 0 ppm.

Synthetic Procedures

Preparation of 1. In air, a 10 mL Schlenk tube was charged with 1.41 g (5.83 mmol) of oily solid 1-(2-*N*,*N*-Dimethylaminophenyl)-2,3,4,5-tetramethylcyclopentadiene (as a mixture

of double bond isomers). The vessel was degassed by evacuation, and 1.0 g (1.53 mmol) solid Re_2CO_{10} was added under Ar counterflow. The tube was equipped with a reflux condenser, and the semisolid mixture was heated neat to 170 ºC. As it was heated the Re_2CO_{10} dissolved in the ligand to give an orange solution that bubbled vigorously during the reaction. The temperature was raised over 3 hours to 210 ºC, and heated overnight at 195 ºC. The reaction mixture was allowed to cool to room temperature, and ~15 mL cold hexanes was added, causing a white precipitate to form. The solids were collected on a frit, and washed with more cold hexanes. The solids gave 285 mg clean product; the filtrate was placed in a –25 ºC freezer, and white crystals grew. The crystals were collected on a frit and washed with cold hexanes to provide another 458 mg **1** (total, 743 mg, 95%). **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 2.04 (s, 6H, C_5Me_4R), 2.36 (s, 6H, C_5Me_4R), 2.52 (s, 6H, NMe_2), 6.9 (m, 2H, *Ar*NMe_2), 7.2 (m, 2H, *Ar*NMe_2). **IR** (CH_2Cl_2): ν_{CO}, 2008, 1910.

Preparation of 2. In air, a 20 mL scintillation vial was charged with 285.0 mg (0.558 mmol) **1**, and 10 mL untreated ("wet") Et_2O. To the stirring solution was added 85 μL (0.614 mmol) HBF_4•Et_2O by syringe dropwise. As the acid is added, fluffy white precipitates formed. The mixture was stirred 15 minutes after addition, at which point the white solids were collected on a frit, washed with additional Et_2O, and dried under vacuum to afford 281.6 (84%) **2**. **^{1}H NMR** (CD_2Cl_2, 300 MHz): δ 2.02 (s, 6H, C_5Me_4R), 2.28 (s, 6H, C_5Me_4R), 3.32 (d, $\mathcal{J}$ = 5.1 Hz, $HNMe_2Ar$), 7.5 (m, 3H, $HNMe_2Ar$), 7.7 (m, 1H, $HNMe_2Ar$), 8.5 (br, 1H, *H*NMe_2Ar). **^{19}F NMR** (282 MHz): –152.4. **IR** (CH_2Cl_2): ν_{CO}, 2014, 1921 cm^{-1}.

Preparation of 3. An oven-heated Schlenk flask was cooled under vacuum, and then charged with 183.0 mg (0.306 mmol) **2** and a magnetic stir bar under Ar counterflow. At 0 °C, ~10 mL CH_2Cl_2 was added by cannula, and 53.6 mg (0.459 mmol) $[NO][BF_4]$ (previously washed with CH_2Cl_2 and dried under vacuum) was added as a solid under counterflow. The reaction was allowed to stir overnight while the ice bath slowly warmed. Brown solids precipitated during this time. After ~10 hours, the solids were collected on a frit, and washed with THF (to quench and extract excess NO^+) until the filtrate ran colorless, leaving a yellow powder which was dried in vacuo to afford 138.4 mg (65%) **3**. **^{1}H NMR** (CD_3CN, 300 MHz): 2.16 (s, 6H, C5Me4R), 2.42 (s, 6H, C5Me4R), 3.29 (s, 6H, HNMe2Ar), 7.24 (dd, $\mathcal{J}$ = 1.3, 7.6 Hz, 1H, Ar), 7.68 (t, $\mathcal{J}$ = 7.7 Hz, 1H, Ar), 7.85-7.95 (m, 2H, Ar). **IR** (CH_3CN): ν_{CO}, 2100, 2050; ν_{NO}, 1811 cm^{-1}.

Preparation of 4. A Teflon-sealed pressure vessel was charged with 860 mg (4.45 mmol) ligand, and degassed under vacuum. Under counterflow, 829 mg (1.27 mmol) of Re_2CO_{10} was added as a solid. The vessel was sealed, and the components were heated neat to 200 °C, which prompted dissolution to a pale yellow solution, and vigorous bubbling. After 20 hours, the mixture was allowed to cool to room temperature. Both the product and the excess ligand were very soluble in hexanes, preventing facile separation. Crude **4**, containing a small amount of free ligand, was used in subsequent steps. **^{1}H NMR** (CD_2Cl_2, 300 MHz): δ 2.16 (s, 6H, C_5Me_4R), 2.17 (s, 6H, C_5Me_4R), 2.23 (s, 6H, $CpCH_2CH_2NMe_2$), 2.23-2.27 (m, 2H, $CpCH_2CH_2NMe_2$), 2.53-2.59 (m, 2H, $CpCH_2CH_2NMe_2$). **IR** (CH_2Cl_2): ν_{CO}, 2006, 1907 cm^{-1}.

Preparation of 5. In air, a Et_2O solution of 1.1 g (2.45 mmol) crude **4** was treated with 673 *m*L (4.9 mmol) HBF_4.Et_2O (added dropwise by syringe with stirring). Beige precipitates formed, which were collected and crystallized from CH_2Cl_2/Et_2O at –30 ºC, affording ~800 mg pure white crystalline **5**. **^{1}H NMR** (CD_2Cl_2, 300 MHz): δ 2.16 (s, 6H, C_5Me_4R), 2.21 (s, 6H, C_5Me_4R), 2.5 (m, 2H, $CpCH_2CH_2NHMe_2$), 3.01 (d, $\mathcal{J}$ = 5.1 Hz, 6H, $CpCH_2CH_2NHMe_2$), 3.04 (m, 2H, $CpCH_2CH_2NHMe_2$) 7.7 (br, 1H, $CpCH_2CH_2NHMe_2$). **^{19}F NMR** (CD_2Cl_2, 282 MHz): δ –151.6.

Preparation of 6. A Schlenk flask was charged with 224.3 mg (0.408 mmol) **5** and a stir bar. After degassing under vacuum, 30 mL CH_2Cl_2 was added by cannula. At 0 ºC, 110 mg (0.941 mmol) $[NO][BF_4]$ was added as a solid under counterflow. The mixture was stirred overnight, with the ice bath slowly warming to room temperature during this time. The solids were collected on a frit, and washed copiously with THF (to quench and extract excess NO^+) to provide a 118 mg (45%) yellow powder **6**. **^{1}H NMR** (CD_3CN, 300 MHz): δ 2.30 (s, 6H, C_5Me_4R), 2.36 (s, 6H, C_5Me_4R), 2.91 (d, J = 5.1 Hz, 6H, $CpCH_2CH_2NHMe_2$), 2.91-2.96 (m, 2H, $CpCH_2CH_2NHMe_2$), 3.09-3.14 (m, 2H, $CpCH_2CH_2NHMe_2$). **IR** (CH_3CN): ν_{CO}, 2098, 2041, ν_{NO}, 1798 cm^{-1}.

Treatment of 3 with $[HNi(depe)_2]^+$. A J-Young NMR tube was charged with 10.3 mg (0.015 mmol) **3**, 10.2 mg (0.0165 mmol) $[HNi(depe)_2][PF_6]$, and ~0.6 mL CD_3CN. Monitoring by NMR showed steady evolution of H_2 and formation of $[Ni(depe)_2]^{2+}$ and deprotonated **3** over 7 hours.

Treatment of 6 with $[HNi(dmpe)_2]^+$. A J-Young NMR tube was charged with 19.9 mg (0.0311 mmol) **6**, 15.7 mg (0.0311 mmol) $[HNi(dmpe)_2][PF_6]$, and ~0.6 mL CD_3CN. After 10 minutes, a ~ 1:1 mixture of $[Ni]^{2+}$:$[HNi]^+$ was observed, along with H_2 and deprotonated **6**. After 1 hour almost no Ni–H remained, and conversion was complete after ~8 hours.

Treatment of 6 with $[HNi(dmpe)_2]^+$ under H_2. A J-Young NMR tube was charged with a 200 μL solution of 10.2 mg (0.015 mmol) **6**, and frozen in an LN_2 cooled cold well in the glovebox. A layer of 200 μL CD_3CN was added, and frozen again. A final 200 μL CD_3CN solution of 8.9 mg (0.0176 mmol) $[HNi(dmpe)_2][PF_6]$ was added, and the tube frozen. The tube was removed from the glovebox and 4 atm H_2 were added (condensed at LN_2 temperature). The tube was thawed and shaken well just before insertion into the NMR probe. The first NMR showed minimal consumption of Re, but over 18 hours a new major Re product formed. No formyl or other discernible reduced CO products were observed. Crystals grown from THF/Et_2O vapor diffusion were suitable for XRD, and assigned the intramolecularly coordinated product **7**. **^{1}H NMR** (THF-d_8, 300 MHz): δ 1.98 (s, 3H), 2.52 (s, 3H), 2.45 (s, 3H), 2.55 (s, 3H), 2.7 (m, 1H), 2.9 (m, 1H) 3.31 (s, 3H), 3.55 (s, 3H), 3.91 (t, $\mathcal{J}$ = 6.3 Hz).

Treatment of 6 with $[HNi(depe)_2]^+$. A J-Young NMR tube was charged with 14.6 mg (0.0228 mmol) **6**, 14.1 mg (0.0228 mmol) $[HNi(depe)_2][PF_6]$, and ~0.6 mL CD_3CN. Monitoring over the first 2 hours showed no observable reaction, while over 10 hours new

asymmetric products grew in by NMR, with **7** appearing to be the major product. No formyl or other discernible reduced CO species were observed.

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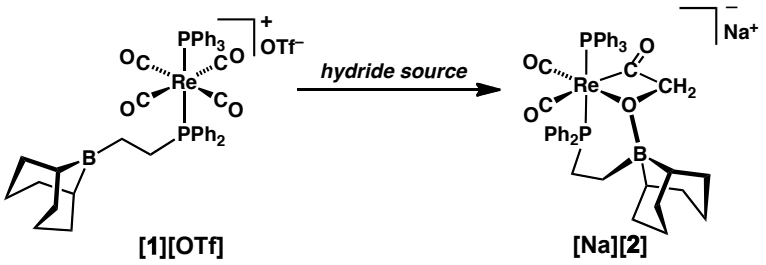
Appendix B

Crown Ether Alteration of Triethylborohydride Speciation

Appendix B

Introduction

Triethylborohydride reagents, often termed "Super-hydrides", are versatile main group reductants, used in a variety of organic and inorganic transformations.[1] In the course of our studies on metal carbonyl reduction (Chapter 3), we noticed subtle differences in reactivity between the Li, Na, and K salts of $[HBEt_3]^-$. Such variability could be due to different solvation or solubility effects, or the speciation of the borohydride in solution. To probe the role of speciation in reduction chemistry, reductions were performed with two discrete reagents: $KHBEt_3$ and the corresponding 18-crown-6 adduct, 18c6/$KHBEt_3$. Here we briefly compare the structure and reactivity of these reagents.



Scheme B.1

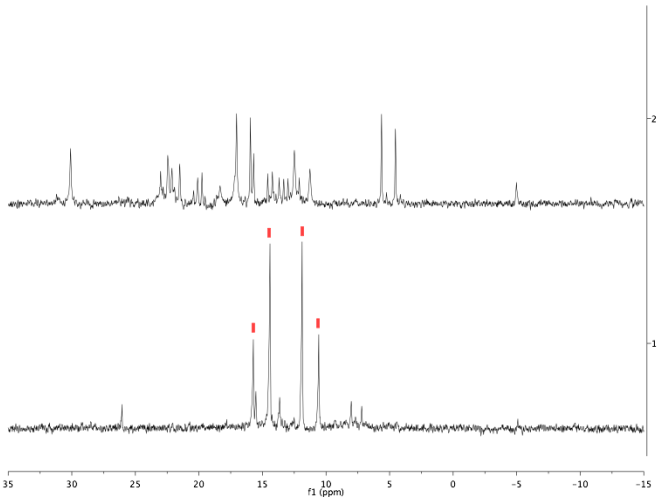


Figure B.1. $^{31}P\{^{1}H\}$ NMR spectra after reduction of [**1**][OTf] with $KHBEt_3$ (top) and 18c6/$KHBEt_3$ (bottom). Red squares indicate $[\mathbf{2}]^-$.

Results and Discussion

Reduction of *trans*-$[(Ph_2P(CH_2)_2B(C_8H_{14}))(PPh_3)Re(CO)_4][OTf]$ ([**1**][OTf]) with two equivalents $KHBEt_3$ (prepared from KH and BEt_3 following a literature procedure[2]) in C_6D_5Cl produced an intractable mixture of products. As an alternative to $KHBEt_3$, which is only sparingly soluble in C_6D_5Cl, 18c6/$KHBEt_3$ was prepared. Addition of the crown ether to a chlorobenzene suspension of $KHBEt_3$ led to incorporation of all solids into solution, and provided microcrystalline 18c6/$KHBEt_3$ upon removal of solvents *in vacuo*. Two equivalents of 18c6/$KHBEt_3$ was added as a solid to a stirring C_6D_5Cl solution of [**1**][OTf], and surprisingly afforded just one major product, containing a new C–C bond (Scheme B.1). Full details of characterization (including structural analysis) are provided in Chapter 3. The change in reactivity might be ascribed to changes in speciation, either in the hydride source itself, or in the K^+ salts of a product. Addition of 18c6 also increases the solubility of $KHBEt_3$ in C_6D_5Cl, which could play a role.

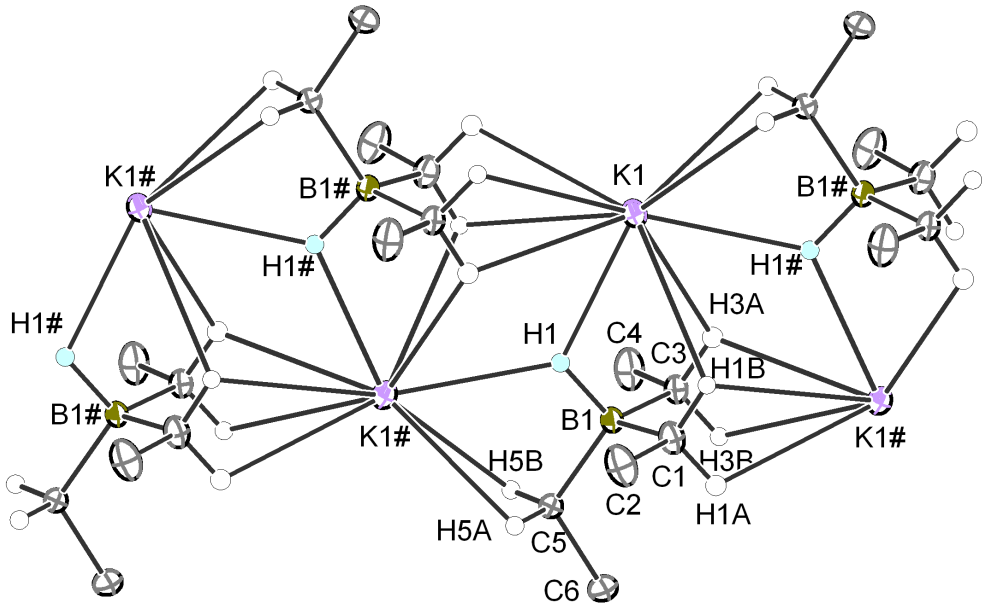


Figure B.2. Structural representation of $KHBEt_3$, ellipsoids at 50% probability.

Table B.1. Selected interatomic distances of $KHBEt_3$.

Atoms	Distance
K1–H1	2.544(9)
K1–H1#	2.70(1)
K1#–H1A	2.93(1)
K1–H1B	2.975(9)
K1#–H1B	2.966(9)
K1–H3A	2.74(1)
K1#–H3A	2.95(1)
K1#–H3B	2.959(9)
K1#–H5A	2.782(9)
K1#–H5B	2.758(9)
B1–H1	1.196(9)
B1–C1	1.642(1)
B1–C3	1.643(1)
B1–C5	1.640(1)
K1#–C1	3.5164(8)
K1–C1	3.3808(9)
K1–C3	3.3086(8)
K1#–C3	3.3896(8)
K1#–C5	3.0976(8)
K1#–B1	3.4627(9)
K1–B1	3.2038(8)

Differences in speciation of the borohydride reagents were investigated in the *solid state* by single crystal X-Ray diffraction. Structural characterization of polyhydridoborates is quite common, but this is not the case for trialkylmonohydridoborates. A few salts, all with solvent or ligand supporting the alkali cation, have been characterized in a variety of nuclearity and binding modes.[3] There are also a number of cases where $[HBR_3]^-$ interacts with transition metals in some fashion.[4] Crystals of $KHBEt_3$ were grown from concentrated toluene solutions at –35 °C. The crystals were packed in the space group P $2_12_12_1$ and all hydrogen atoms were located in the difference map and refined without constraint. The solid-state structure (Figure B.2) is firstly remarkable for containing only $KHBEt_3$ and no solvents or other ligands to bind K^+. Perhaps as a result, the crystal lattice is made up of a dense polymeric network with a number of unusual K^+ supporting interactions (Figure B.4). The core is built from an asymmetric bridging K_2–μ–H–BEt_3 moiety. Two different interactions between K and C–H bonds are present: two of the ethyl groups arrange themselves to donate 4 C–H bonds to K^+, while the other donates 2 C–H bonds to a different K^+. This unusual stabilization has been observed before for tetraalkylborate species interacting with alkali metal cations.[2,5] These cores string together into repeating units, forming long chains in the lattice. Interatomic distances and angles are summarized in Table B.1.

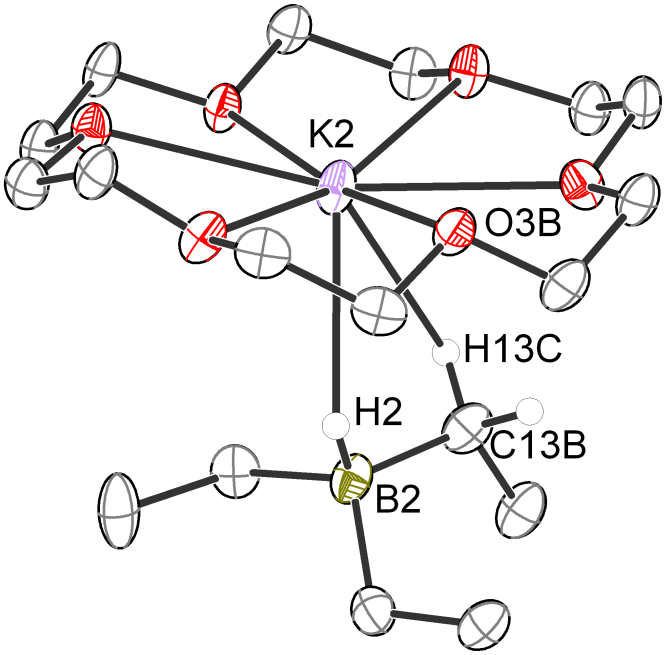


Figure B.3. Structural representation of 18c6/KHBEt$_3$, ellipsoids at 50% probability.

Table B.2. Selected interatomic distances of 18c6/KHBEt$_3$.

Atoms	Distance
K1–B1	3.568(3)
K1–C13A	3.254(3)
K2–B2	3.395(3)
K2–C13B	3.469(3)
K3–B3	3.494(3)
K3–C13C	3.378(3)
K4–B4	3.558(3)
K4–C13D	3.268(3)
B1–C13A	1.640(5)
B1–C15A	1.636(4)
B1–C17A	1.643(4)
K1–O1A	2.779(2)
K1–O2A	2.826(2)
K1–O3A	2.859(2)
K1–O4A	2.801(2)
K1–O5A	2.947(2)
K1–O6A	2.831(2)

Crystals of 18c6/KHBEt$_3$ were grown from concentrated chlorobenzene at −35 °C. The crystals were twinned, and as such the hydrogen atom positions were calculated. Nonetheless, the overall structure (Figure B.3) contrasts starkly with that of the crown-free borohydride: the solid state structure (space group P $2_1/c$) features a strictly monomeric core, with no bridging interactions between multiple K^+ ions (Figure B.4). The K^+ ion is sequestered in the crown ether, and is additionally stabilized by interaction with the $[HBEt_3]^-$ fragment, which is positioned to donate electron density from the B–H bond and a C–H bond of a methylene unit. The C–K and B–K distances differ significantly between the different molecules in the asymmetric unit, consistent with differing amounts of C–H or B–H donation in the independent molecules. Details of bond lengths and angles are provided in Table B.2.

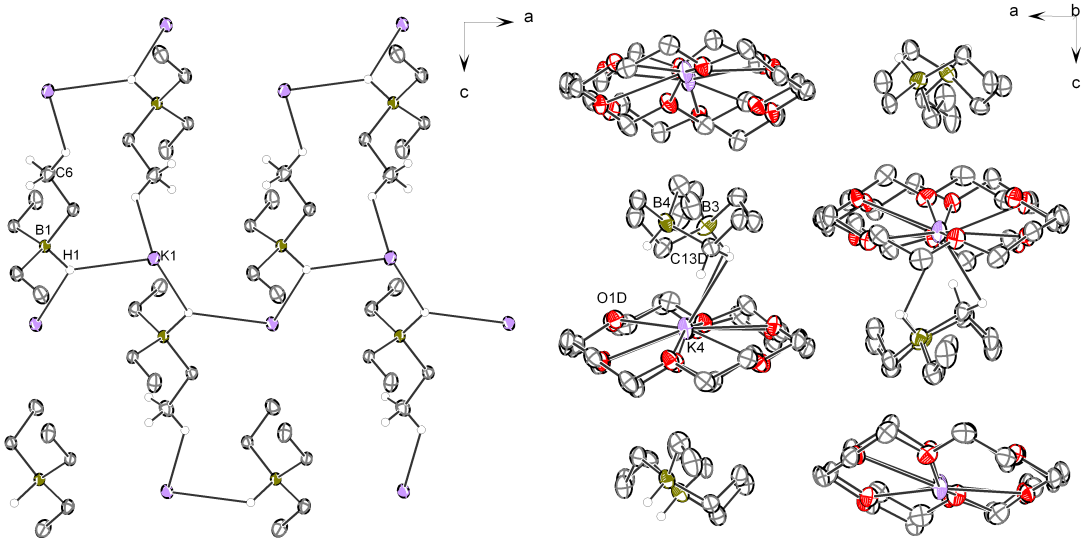


Figure B.4. Packing diagrams of KHBEt$_3$ (left) and 18c6/KHBEt$_3$ (right), both looking down the b axis. For clarity, hydrogen atoms are drawn isotropically, and only certain K–H interactions are drawn. The closest K–H interaction was drawn for each independent molecule in 18c6/KHBEt$_3$, showing the different binding modes.

Conclusions

While it would be foolhardy to suggest that the disparate solid state structures of $KHBEt_3$ and 18c6/$KHBEt_3$ are indicators of solution reactivity without a much more detailed study, the two different structures are interesting in their own right. Further, it seems plausible that monomeric 18c6/$KHBEt_3$ would be more easily dissolved than the dense polymer network of $KHBEt_3$ itself. Whether or not the origin lies in solubility or speciation differences, the crown ether adduct of 18c6/$KHBEt_3$ shows promising reactivity in one case relative to $KHBEt_3$, and may be of general interest as an alternative hydride source.

Experimental Section

General Considerations

All air- and moisture-sensitive compounds were manipulated using standard vacuum line or Schlenk techniques, or in a glovebox under a nitrogen atmosphere. The solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl, calcium hydride, or by the method of Grubbs.[6] All NMR solvents were purchased from Cambridge Isotopes Laboratories, Inc. Chlorobenzene-d_5 (C_6D_5Cl) was freeze-pump-thaw degassed three times before being run through a small column of activated alumina. Unless noted, other materials were used as received. ^1H and ^{13}C NMR spectra were recorded on Varian Mercury 300 MHz, or Varian INOVA-500 or 600 MHz spectrometers at room temperature, unless indicated otherwise. Chemical shifts are reported with respect to

residual internal protio solvent for ^{1}H and $^{13}C\{^{1}H\}$ spectra. Other nuclei were referenced to an external standard: 85% H_3PO_4 (^{31}P), 15% BF_3•Et_2O/$CDCl_3$ (^{11}B), $CFCl_3$ (^{19}F), all at 0 ppm.

Preparation of $KHBEt_3$. Following a literature procedure,[2] a scintillation vial was charged with 238.8 mg (5.95 mmol) KH and 7 mL toluene. To the stirring suspension was added 5.9 mL (5.9 mmol) BEt_3 (1.0 M in hexanes) slowly by syringe. The reaction mixture, which warmed slightly during the addition, was allowed to stir for 3 hours before filtration through a frit. Some solids remaining on the frit were extracted with 5 mL toluene, and the mixture was concentrated to about 4 mL before storage at –35 °C. Large colorless single crystals formed overnight; a few were retained for X-Ray structural analysis, while the bulk of the material was collected and dried under vacuum, yielding 480 mg (59%) $KHBEt_3$. **^{1}H NMR** (C_6D_5Cl, 300 Mhz): δ 0.17 (br, 6H, BCH_2CH_3), 0.97 (t, $\mathcal{J}$ = 7.5 Hz, 9H, BCH_2CH_3).

Preparation of 18-crown-6/$KHBEt_3$. To a stirring slurry of 204.7 mg (1.48 mmol) $KHBEt_3$ in 5 mL chlorobenzene was added 391.5 mg (1.48 mmol) of solid 18-crown-6. After stirring for 24 hours, there were still some undissolved solids, which went into solution upon addition of another 5 mL chlorobenzene. The mixture was filtered; 1 mL of filtrate was reserved for single crystal growth (at –35 °C), while the rest was placed under vacuum to remove the solvent to dryness, yielding 548 mg (92%) 18c6/$KHBEt_3$. **^{1}H NMR** (C_6D_5Cl, 300 MHz): δ 0.69 (br q, 6H, $HBCH_2CH_3$), 1.00 (br, 1H, $HBCH_2CH_3$), 1.37 (br t, 9H, $HBCH_2CH_3$), 3.26 (s, 24H, $–OCH_2CH_2O–$).

Reduction of *trans*-[($Ph_2P(CH_2)_2B(C_8H_{14})$)($PPh_3$)$Re(CO)_4$][OTf] with $KHBEt_3$. A small vial was charged with 13.5 mg (0.098 mmol) $KHBEt_3$, 51.0 mg (0.049 mmol) *trans*-[($Ph_2P(CH_2)_2B(C_8H_{14})$)($PPh_3$)$Re(CO)_4$][OTf], and a stir bar. With stirring, ~1 mL C_6D_5Cl was added, and the mixture was stirred overnight before being filtered into a J-Young NMR tube. A large number of resonances were observed by ^1H and ^{31}P NMR spectra.

Reduction of *trans*-[($Ph_2P(CH_2)_2B(C_8H_{14})$)($PPh_3$)$Re(CO)_4$][OTf] with 18c6/$KHBEt_3$. A J-Young NMR tube was charged with 34.7 mg (0.033 mmol) *trans*-[($Ph_2P(CH_2)_2B(C_8H_{14})$)($PPh_3$)$Re(CO)_4$][OTf], 26.7 mg (0.067 mmol) solid 18-crown-6/$KHBEt_3$, and ~0.6 mL C_6D_5Cl. The tube was shaken well, and darkened considerably. NMR spectroscopy revealed quite clean conversion to an asymmetric Re compound, which was identified (see Chapter 3) as a C–C coupled acyl anion.

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Chem. Soc. **1998**, *120*, 6047; (e) Drouin, S. D.; Amoroso, D.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2002**, *21*, 1042; (f) Dawson, D. M.; Meetsma, A.; Roedelof, J. B.; Teuben, J. H. *Inorg. Chim. Acta* **1997**, *259*, 237.

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Appendix C

NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist

Adapted in part from:
Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.
http://dx.doi.org/10.1021/om100106e

Appendix C

Introduction

Synthetic chemists rely heavily on NMR spectroscopy as a tool for product characterization and reaction monitoring. An essential reference tool was published in 1997 by Gottlieb, Kotlyar, and Nudelman: "NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities"[1] compiles the chemical shifts of a large number of contaminants commonly encountered in synthetic chemistry, allowing for easy identification of known impurities as well as providing a quick means of estimating the functionality and structure of unknown compounds in a variety of deuterated organic solvents. However, despite the utility of Gottlieb et al.'s work, the chemical shifts of impurities in a number of NMR solvents often used by organometallic chemists were not included. Tetrahydrofuran-d_8 (THF-d_8), toluene-d_8, dichloromethane-d_2 (CD_2Cl_2), chlorobenzene-d_5 (C_6D_5Cl), and 2,2,2-trifluoroethanol-d_3 (TFE-d_3) are commonplace in laboratories practicing inorganic syntheses. Therefore, we have expanded the spectral data compilation with the inclusion of chemical shifts of common impurities recorded in the deuterated solvents heavily employed in our organometallic laboratories. The chemical shifts of various gases (hydrogen, methane, ethane, propane, ethylene, propylene, and carbon dioxide), often encountered as reagents or products in organometallic reactions, along with organic compounds relevant to organometallic chemists (allyl acetate, benzaldehyde, carbon disulfide, carbon tetrachloride, 18-crown-6, cyclohexanone, diallyl carbonate, dimethyl carbonate, dimethyl malonate,

furan, Apiezon H grease, hexamethylbenzene, hexamethyldisiloxane, imidazole, pyrrole, and pyrrolidine) have also been added to this expanded list.

Results and Discussion

Chemical shifts for each of the impurities are reported in the tables below: ^{1}H and ^{13}C NMR spectral data of all substrates are presented in Tables C.1 and C.2, respectively. Notably, physically larger tables with bigger font sizes, containing all the data from Tables C.1–C.2 as well as the chemical shifts of additional organic compounds are provided in the Supporting Information. Unless noted otherwise, coupling constants (reported in Hz) and resonance multiplicities (abbreviated with the following: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad) were observed to be solvent-independent.

It was noted that the amount of gas dissolved in solution gave ^{1}H NMR signal integrations that were qualitatively comparable to the solutions made with the 3 μL additions of the liquid or solid contaminants. However, typically in order to observe signals for the gas samples by ^{13}C NMR spectroscopy, additional time for data collection was required. The solubility of each gas in D_2O was extremely limited, making ^{13}C detection impractical. Of all the gases, methane required the most number of transients in order to obtain an observable signal by ^{13}C NMR spectroscopy. In most cases, the ^{13}C chemical shift of methane was acquired through the use of gs-HMQC NMR spectroscopy to provide enhanced sensitivity. In order to reflect what would be observed in typical NMR-scale

experiments, ^{13}C detection was not pursued with isotopically enriched gases. A number of misreported values were discovered in the years since the original publication and in the preparation of this manuscript. These are detailed in the Supporting Information, and the values are now correctly listed in Tables C.1 and C.2.

Table C.1. ^{1}H NMR data[a]

	proton	mult	THF-d_8	CD_2Cl_2	$CDCl_3$	toluene-d_8	C_6D_6	C_6D_5Cl	$(CD_3)_2CO$	$(CD_3)_2SO$	CD_3CN	TFE-d_3	CD_3OD	D_2O
solvent residual signals			1.72 3.58	5.32	7.26	2.08 6.97 7.01 7.09	7.16	6.96 6.99 7.14	2.05	2.50	1.94	5.02 3.88	3.31	4.79
water	OH	s	2.46	1.52	1.56	0.43	0.40	1.03	2.84[b]	3.33[b]	2.13	3.66	4.87	-
acetic acid	CH_3	s	1.89	2.06	2.10	1.57	1.52	1.76	1.96	1.91	1.96	2.06	1.99	2.08
acetone	CH_3	s	2.05	2.12	2.17	1.57	1.55	1.77	2.09	2.09	2.08	2.19	2.15	2.22
acetonitrile	CH_3	s	1.95	1.97	2.10	0.69	0.58	1.21	2.05	2.07	1.96	1.95	2.03	2.06
benzene	CH	s	7.31	7.35	7.36	7.12	7.15	7.20	7.36	7.37	7.37	7.36	7.33	-
tert-butyl alcohol	CH_3	s	1.15	1.24	1.28	1.03	1.05	1.12	1.18	1.11	1.16	1.28	1.40	1.24
	OH	s	3.16	-	-	0.58	0.63	1.30	-	4.19	2.18	2.20	-	-
chloroform	CH	s	7.89	7.32	7.26	6.10	6.15	6.74	8.02	8.32	7.58	7.33	7.90	-
18-crown-6	CH_2	s	3.57	3.59	3.67	3.36	3.39	3.41	3.59	3.51	3.51	3.64	3.64	3.80
cyclohexane	CH_2	s	1.44	1.44	1.43	1.40	1.40	1.37	1.43	1.40	1.44	1.47	1.45	-
1,2-dichloroethane	CH_2	s	3.77	3.76	3.73	2.91	2.90	3.26	3.87	3.90	3.81	3.71	3.78	-
dichloromethane	CH_2	s	5.51	5.33	5.30	4.32	4.27	4.77	5.63	5.76	5.44	5.24	5.49	-
diethyl ether	CH_3	t, 7	1.12	1.15	1.21	1.10	1.11	1.10	1.11	1.09	1.12	1.20	1.18	1.17
	CH_2	q, 7	3.38	3.43	3.48	3.25	3.26	3.31	3.41	3.38	3.42	3.58	3.49	3.56
diglyme	CH_2	m	3.43	3.57	3.65	3.43	3.46	3.49	3.56	3.51	3.53	3.67	3.61	3.67
	CH_2	m	3.53	3.50	3.57	3.31	3.34	3.37	3.47	3.38	3.45	3.62	3.58	3.61
	OCH_3	s	3.28	3.33	3.39	3.12	3.11	3.16	3.28	3.24	3.29	3.41	3.35	3.37
1,2-dimethoxyethane	CH_3	s	3.28	3.34	3.40	3.12	3.12	3.17	3.28	3.24	3.28	3.40	3.35	3.37
	CH_2	s	3.43	3.49	3.55	3.31	3.33	3.37	3.46	3.43	3.45	3.61	3.52	3.60
dimethylformamide	CH	s	7.91	7.96	8.02	7.57	7.63	7.73	7.96	7.95	7.92	7.86	7.97	7.92
	CH_3	s	2.88	2.91	2.96	2.37	2.36	2.51	2.94	2.89	2.89	2.98	2.99	3.01
	CH_3	s	2.76	2.82	2.88	1.96	1.86	2.30	2.78	2.73	2.77	2.88	2.86	2.85
1,4-dioxane	CH_2	s	3.56	3.65	3.71	3.33	3.35	3.45	3.59	3.57	3.60	3.76	3.66	3.75
ethane	CH_3	s	0.85	0.85	0.87	0.81	0.80	0.79	0.83	0.82	0.85	0.85	0.85	0.82
ethanol	CH_3	t, 7	1.10	1.19	1.25	0.97	0.96	1.06	1.12	1.06	1.12	1.22	1.19	1.17
	CH_2	q, 7[c]	3.51	3.66	3.72	3.36	3.34	3.51	3.57	3.44	3.54	3.71	3.60	3.65
	OH	s[c,d]	3.30	1.33	1.32	0.83	0.50	1.39	3.39	4.63	2.47	-	-	-
ethyl acetate	CH_3CO	s	1.94	2.00	2.05	1.69	1.65	1.78	1.97	1.99	1.97	2.03	2.01	2.07
	CH_2CH_3	q, 7	4.04	4.08	4.12	3.87	3.89	3.96	4.05	4.03	4.06	4.14	4.09	4.14
	CH_2CH_3	t, 7	1.19	1.23	1.26	0.94	0.92	1.04	1.20	1.17	1.20	1.26	1.24	1.24
ethylene	CH_2	s	5.36	5.40	5.40	5.25	5.25	5.29	5.38	5.41	5.41	5.40	5.39	5.44
ethylene glycol	CH_2	s[e]	3.48	3.66	3.76	3.36	3.41	3.58	3.28	3.34	3.51	3.72	3.59	3.65
H grease	CH_3	m	0.85–0.91	0.84–0.90	0.84–0.87	0.89–0.96	0.90–0.98	0.86–0.92	0.90	0.82–0.88	-	0.88–0.94	0.86–0.93	-
	CH_2	br s	1.29	1.27	1.25	1.33	1.32	1.30	1.29	1.24	-	1.33	1.29	-
hexamethylbenzene	CH_3	s	2.18	2.20	2.24	2.10	2.13	2.10	2.17	2.14	2.19	2.24	2.19	-
hexamethyldisoloxane	CH_3	s	0.07	0.07	0.07	0.10	0.12	0.10	0.07	0.06	0.07	0.08	0.07	0.28
n-hexane	CH_3	t, 7	0.89	0.89	0.88	0.88	0.89	0.85	0.88	0.86	0.89	0.91	0.90	-
	CH_2	m	1.29	1.27	1.26	1.22	1.24	1.19	1.28	1.25	1.28	1.31	1.29	-
HMPA	CH_3	d, 9.5	2.58	2.60	2.65	2.42	2.40	2.47	2.59	2.53	2.57	2.63	2.64	2.61
hydrogen	H_2	s	4.55	4.59	4.62	4.50	4.47	4.49	4.54	4.61	4.57	4.53	4.56	-
imidazole	CH(2)	s	7.48	7.63	7.67	7.30	7.33	7.53	7.62	7.63	7.57	7.61	7.67	7.78
	CH(4,5)	s	6.94	7.07	7.10	6.86	6.90	7.01	7.04	7.01	7.01	7.03	7.05	7.14
methane	CH_4	s	0.19	0.21	0.22	0.17	0.16	0.15	0.17	0.20	0.20	0.18	0.20	0.18
methanol	CH_3	s[f]	3.27	3.42	3.49	3.03	3.07	3.25	3.31	3.16	3.28	3.44	3.34	3.34
	OH	s[d,f]	3.02	1.09	1.09	-	-	1.30	3.12	4.01	2.16	-	-	-
nitromethane	CH_3	s	4.31	4.31	4.33	3.01	2.94	3.59	4.43	4.42	4.31	4.28	4.34	4.40
n-pentane	CH_3	t, 7	0.89	0.89	0.88	0.87	0.87	0.84	0.88	0.86	0.89	0.90	0.90	-
	CH_2	m	1.31	1.30	1.27	1.25	1.23	1.23	1.27	1.27	1.29	1.33	1.29	-
propane	CH_3	t, 7.3	0.90	0.90	0.90	0.89	0.86	0.84	0.88	0.87	0.90	0.90	0.91	0.88
	CH_2	sept, 7.3	1.33	1.32	1.32	1.32	1.26	1.26	1.31	1.29	1.33	1.33	1.34	1.30
2-propanol	CH_3	d, 6	1.08	1.17	1.22	0.95	0.95	1.04	1.10	1.04	1.09	1.20	1.50	1.17
	CH	sept, 6	3.82	3.97	4.04	3.65	3.67	3.82	3.90	3.78	3.87	4.05	3.92	4.02
propylene	CH_3	dt, 6.4, 1.5	1.69	1.71	1.73	1.55	1.55	1.58	1.68	1.68	1.70	1.70	1.70	1.70
	CH_2(1)	dm, 10	4.89	4.93	4.94	4.92	4.95	4.91	4.90	4.94	4.93	4.93	4.91	4.95
	CH_2(2)	dm, 17	4.99	5.03	5.03	4.98	5.01	4.98	5.00	5.03	5.04	5.03	5.01	5.06
	CH	m	5.79	5.84	5.83	5.70	5.72	5.72	5.81	5.80	5.85	5.87	5.82	5.90
pyridine	CH(2,6)	m	8.54	8.59	8.62	8.47	8.53	8.51	8.58	8.58	8.57	8.45	8.53	8.52
	CH(3,5)	m	7.25	7.28	7.29	6.67	6.66	6.90	7.35	7.39	7.33	7.40	7.44	7.45
	CH(4)	m	7.65	7.68	7.68	6.99	6.98	7.25	7.76	7.79	7.73	7.82	7.85	7.87
pyrrole	NH	br t	9.96	8.69	8.40	7.71	7.80	8.61	10.02	10.75	9.27	-	-	-
	CH(2,5)	m	6.66	6.79	6.83	6.43	6.48	6.62	6.77	6.73	6.75	6.84	6.72	6.93
	CH(3,4)	m	6.02	6.19	6.26	6.27	6.37	6.27	6.07	6.01	6.10	6.24	6.08	6.26
pyrrolidine[g]	CH_2(2,5)	m	2.75	2.82	2.87	2.54	2.54	2.64	-	2.67	2.75	3.11	2.80	3.07
	CH_2(3,4)	m	1.59	1.67	1.68	1.36	1.33	1.43	-	1.55	1.61	1.93	1.72	1.87
silicone grease	CH_3	s	0.11	0.09	0.07	0.26	0.29	0.14	0.13	–0.06	0.08	0.16	0.10	-
tetrahydrofuran	CH_2(2,5)	m	3.62	3.69	3.76	3.54	3.57	3.59	3.63	3.60	3.64	3.78	3.71	3.74
	CH_2(3,4)	m	1.79	1.82	1.85	1.43	1.40	1.55	1.79	1.76	1.80	1.91	1.87	1.88
toluene	CH_3	s	2.31	2.34	2.36	2.11	2.11	2.16	2.32	2.30	2.33	2.33	2.32	-
	CH(2,4,6)	m	7.10	7.15	7.17	6.96–7.01	7.02	7.01–7.08	7.10–7.20	7.18	7.10–7.30	7.10–7.30	7.16	-
	CH(3,5)	m	7.19	7.24	7.25	7.09	7.13	7.10–7.17	7.10–7.20	7.25	7.10–7.30	7.10–7.30	7.16	-
triethylamine	CH_3	t, 7	0.97	0.99	1.03	0.95	0.96	0.93	0.96	0.93	0.96	1.31	1.05	0.99
	CH_2	q, 7	2.46	2.48	2.53	2.39	2.40	2.39	2.45	2.43	2.45	3.12	2.58	2.57

a) Except for the compounds in solutions 8–10, as well as the gas samples, hexamethylbenzene, and the corrected values mentioned in the Supporting Information, all data for the solvents $CDCl_3$, C_6D_6, $(CD_3)_2CO$, $(CD_3)_2SO$, CD_3CN, CD_3OD, and D_2O were previously reported[1]. b) A signal for HDO is also observed in $(CD_3)_2SO$ (3.30 ppm) and $(CD_3)_2CO$ (2.81 ppm), often seen as a 1:1:1 triplet ($^2\mathcal{J}_{H,D}$ = 1 Hz). c) In some solvents, the coupling interaction between the CH_3 and the OH protons may be observed ($\mathcal{J}$ = 5 Hz) d) Not all OH signals were observable. e) In CD_3CN, the OH proton was seen as a multiplet at 2.69 ppm, as well as extra coupling to the CH_2 resonance. f) In some solvents, the coupling interaction between the CH_3 and the OH protons may be observed ($\mathcal{J}$ = 5.5 Hz). g) Pyrrolidine was observed to react with $(CD_3)_2CO$.

Table C.2. ^{13}C NMR data[a]

	carbon	THF-d_8	CD_2Cl_2	$CDCl_3$	toluene-d_8	C_6D_6	C_6D_5Cl	$(CD_3)_2CO$	$(CD_3)_2SO$	CD_3CN	TFE-d_3	CD_3OD	D_2O
solvent signals		67.21	53.84	77.16	137.48	128.06	134.19	29.84	39.52	1.32	61.50	49.00	-
		25.31			128.87		129.26	206.26		118.26	126.28		
					127.96		128.25						
					125.13		125.96						
					20.43								
acetic acid	CO	171.69	175.85	175.99	175.30	175.82	175.67	172.31	171.93	173.21	177.96	175.11	177.21
	CH_3	20.13	20.91	20.81	20.27	20.37	20.40	20.51	20.95	20.73	20.91	20.56	21.03
acetone	CO	204.19	206.78	207.07	204.00	204.43	204.83	205.87	206.31	207.43	32.35	209.67	215.94
	CH_3	30.17	31.00	30.92	30.03	30.14	30.12	30.60	30.56	30.91	214.98	30.67	30.89
acetonitrile	CN	116.79	116.92	116.43	115.76	116.02	115.93	117.60	117.91	118.26	118.95	118.06	119.68
	CH_3	0.45	2.03	1.89	0.03	0.20	0.63	1.12	1.03	1.79	1.00	0.85	1.47
benzene	CH	128.84	128.68	128.37	128.57	128.62	128.38	129.15	128.30	129.32	129.84	129.34	-
tert-butyl alcohol	$(CH_3)_3\boldsymbol{C}$	67.50	69.11	69.15	68.12	68.19	68.19	68.13	66.88	68.74	72.35	69.40	70.36
	$(\boldsymbol{C}H_3)_3C$	30.57	31.46	31.25	30.49	30.47	31.13	30.72	30.38	30.68	31.07	30.91	30.29
carbon dioxide	CO_2	125.69	125.26	124.99	124.86	124.76	126.08	125.81	124.21	125.89	126.92	126.31	-
carbon disulfide	CS_2	193.37	192.95	192.83	192.71	192.69	192.49	193.58	192.63	193.60	196.26	193.82	197.25
carbon tetrachloride	CCl_4	96.89	96.52	96.34	96.57	96.44	96.38	96.65	95.44	96.68	97.74	97.21	96.73
chloroform	CH	79.24	77.99	77.36	77.89	77.79	77.67	79.19	79.16	79.17	78.83	79.44	-
18-crown-6	CH_2	71.34	70.47	70.55	70.86	70.59	70.55	71.25	69.85	71.22	70.80	71.47	70.14
cyclohexane	CH_2	27.58	27.38	26.94	27.31	27.23	26.99	27.51	26.33	27.63	28.34	27.96	-
1,2-dichloroethane	CH_2	44.64	44.35	43.50	43.40	43.59	43.60	45.25	45.02	45.54	45.28	45.11	-
dichloromethane	CH_2	54.67	54.24	53.52	53.47	53.46	53.54	54.95	54.84	55.32	54.46	54.78	-
diethyl ether	CH_3	15.49	15.44	15.20	15.47	15.46	15.35	15.78	15.12	15.63	15.33	15.46	14.77
	CH_2	66.14	64.67	65.91	65.94	65.94	65.79	66.12	62.05	66.32	67.55	66.88	66.42
diglyme	CH_3	58.72	58.95	59.01	58.62	58.66	58.42	58.77	57.98	58.90	59.40	59.06	58.67
	CH_2	71.17	70.70	70.51	70.92	70.87	70.56	71.03	69.54	70.99	73.05	71.33	70.05
	CH_2	72.72	72.25	71.90	72.39	72.35	72.07	72.63	71.25	72.63	71.33	72.92	71.63
1,2-dimethoxyethane	CH_3	58.72	59.02	59.08	58.63	58.68	58.31	58.45	58.03	58.89	59.52	59.06	58.67
	CH_2	72.58	72.24	71.84	72.25	72.21	71.81	72.47	71.17	72.47	72.87	72.72	71.49
dimethylformamide	CH	161.96	162.57	162.62	161.93	162.13	162.01	162.79	162.29	163.31	166.01	164.73	165.53
	CH_3	35.65	36.56	36.50	35.22	35.25	35.45	36.15	35.73	36.57	37.76	36.89	37.54
	CH_3	30.70	31.39	31.45	30.64	30.72	30.71	31.03	30.73	31.32	30.96	31.61	32.03
1,4-dioxane	CH_2	67.65	67.47	67.14	67.17	67.16	66.95	67.60	66.36	67.72	68.52	68.11	67.19
ethane	CH_3	6.79	6.91	6.89	6.94	6.96	6.91	6.88	6.61	6.99	7.01	6.98	-
ethanol	CH_3	18.90	18.69	18.41	18.78	18.72	18.55	18.89	18.51	18.80	18.11	18.40	17.47
	CH_2	57.60	58.57	58.28	57.81	57.86	57.63	57.72	56.07	57.96	59.68	58.26	58.05
ethyl acetate	$\boldsymbol{C}H_3CO$	20.45	21.15	21.04	20.46	20.56	20.50	20.83	20.68	21.16	21.18	20.88	21.15
	CO	170.32	171.24	171.36	170.02	170.44	170.20	170.96	170.31	171.68	175.55	172.89	175.26
	CH_2	60.30	60.63	60.49	60.08	60.21	60.06	60.56	59.74	60.98	62.70	61.50	62.32
	CH_3	14.37	14.37	14.19	14.23	14.19	14.07	14.50	14.40	14.54	14.36	14.49	13.92
ethylene	CH_2	123.09	123.20	123.13	122.92	122.96	122.95	123.47	123.52	123.69	124.08	123.46	-
ethylene glycol	CH_2	64.35	64.08	63.79	64.29	64.34	64.03	64.26	62.76	64.22	64.87	64.30	63.17
H grease	CH_2	30.45	30.14	29.71	30.31	30.22	30.11	-	-	-	-	-	-
hexamethylbenzene	C	131.88	132.09	132.21	131.72	131.79	131.54	132.22	131.10	132.61	134.04	132.53	-
	CH_3	16.71	16.93	16.98	16.84	16.95	16.68	16.86	16.60	16.94	17.04	16.90	-
hexamethyldisiloxane	CH_3	1.83	1.96	1.97	1.99	2.05	1.92	2.01	1.96	2.07	2.09	1.99	2.31
n-hexane	CH_3	14.22	14.28	14.14	14.34	14.32	14.18	14.34	13.88	14.43	14.63	14.45	-
	CH_2(2,5)	23.33	23.07	22.70	23.12	23.04	22.86	23.28	22.05	23.40	24.06	23.68	-
	CH_2(3,4)	32.34	32.01	31.64	32.06	31.96	31.77	32.30	30.95	32.36	33.17	32.73	-
HMPA[b]	CH_3	36.89	36.99	36.87	36.80	36.88	36.64	37.04	36.42	37.10	37.21	37.00	36.46
imidazole	CH(2)	135.72	135.76	135.38	135.57	135.76	135.50	135.89	135.15	136.33	136.58	136.31	136.65
	CH(4,5)	122.20	122.16	122.00	122.13	122.16	121.96	122.31	121.55	122.78	122.93	122.60	122.43
methane	CH_4	–4.90	–4.33	–4.63	–4.34	–4.29	–4.33	–5.33	–4.01	–4.61	–5.88	–4.90	-
methanol	CH_3	49.64	50.45	50.41	49.90	49.97	49.66	49.77	48.59	49.90	50.67	49.86	49.50[c]
nitromethane	CH_3	62.49	63.03	62.50	61.14	61.16	61.68	63.21	63.28	63.66	63.17	63.08	63.22
n-pentane	CH_3	14.18	14.24	14.08	14.27	14.25	14.10	14.29	13.28	14.37	14.54	14.39	-
	CH_2(2,4)	23.00	22.77	22.38	22.79	22.72	22.54	22.98	21.70	23.08	23.75	23.38	-
	CH_2(3)	34.87	34.57	34.16	34.54	34.45	34.26	34.83	33.48	34.89	35.76	35.30	-
propane	CH_3	16.60	16.63	16.63	16.65	16.66	16.56	16.68	16.34	16.73	16.93	16.80	-
	CH_2	16.82	16.63	16.37	16.63	16.60	16.48	16.78	15.67	16.91	17.46	17.19	-
2-propanol	CH_3	25.70	25.43	25.14	25.24	25.18	25.14	25.67	25.43	25.55	25.21	25.27	24.38
	CH	66.14	64.67	64.50	64.12	64.23	64.18	63.85	64.92	64.30	66.69	64.71	64.88
propylene	CH_3	19.27	19.47	19.50	19.32	19.38	19.32	19.42	19.20	19.48	19.63	19.50	-
	CH_2	115.74	115.70	115.74	115.89	115.92	115.86	116.03	116.07	116.12	116.38	116.04	-
	CH	134.02	134.21	133.91	133.61	133.69	133.57	134.34	133.55	134.78	136.00	134.61	-
pyridine	CH(2,6)	150.57	150.27	149.90	150.25	150.27	149.93	150.67	149.58	150.76	149.76	150.07	149.18
	CH(3,5)	124.08	124.06	123.75	123.46	123.58	123.49	124.57	123.84	127.76	126.27	125.53	125.12
	CH(4)	135.99	136.16	135.96	135.17	135.28	135.32	136.56	136.05	136.89	139.62	138.35	138.27
pyrrole	CH(2,5)	118.03	117.93	117.77	117.61	117.78	117.65	117.98	117.32	118.47	119.61	118.28	119.06
	CH(3,4)	107.74	108.02	107.98	108.15	108.21	108.03	108.04	107.07	108.31	108.85	108.11	107.83
pyrrolidine[d]	CH(2,5)	45.82	47.02	46.93	47.12	46.86	46.75	-	46.51	47.57	47.43	47.23	46.83
	CH(3,4)	26.17	25.83	25.56	25.75	25.65	25.59	-	25.26	26.34	25.73	26.29	25.86
silicone grease	CH_3	1.20	1.22	1.19	1.37	1.38	1.09	1.40	-	-	2.87	2.10	-
tetrahydrofuran	CH_2(2,5)	68.03	68.16	67.97	67.75	67.80	67.64	68.07	67.03	68.33	69.53	68.83	68.68
	CH_2(3,4)	26.19	25.98	25.62	25.79	25.72	25.68	26.15	25.14	26.27	26.69	26.48	25.67
toluene	CH_3	21.29	21.53	21.46	21.37	21.10	21.23	21.46	20.99	21.50	21.62	21.50	-
	C(1)	138.24	138.36	137.89	137.84	137.91	137.65	138.48	137.35	138.90	139.92	138.85	-
	CH(2,6)	129.47	129.35	129.07	129.33	129.33	129.12	129.76	128.88	129.94	130.58	129.91	-
	CH(3,5)	128.71	128.54	128.26	128.51	128.56	128.31	129.03	128.18	129.23	129.79	129.20	-
	CH(4)	125.84	125.62	125.33	125.66	125.68	125.43	126.12	125.29	126.28	126.82	126.29	-
triethylamine	CH_3	12.51	12.12	11.61	12.39	12.35	11.87	12.49	11.74	12.38	9.51	11.09	9.07
	CH_2	47.18	46.75	46.25	46.82	46.77	46.36	47.07	45.74	47.10	48.45	46.96	47.19

a) Except for the compounds in solutions 8–10, as well as the gas samples, hexamethylbenzene, and the corrected values mentioned in the Supporting Information, all data for the solvents $CDCl_3$, C_6D_6, $(CD_3)_2CO$, $(CD_3)_2SO$, CD_3CN, CD_3OD, and D_2O were previously reported[1]. b) Phosphorus coupling was observed ($^2J_{PC}$ = 3 Hz). c) Internal reference; see text. d) Pyrrolidine was observed to react with $(CD_3)_2CO$.

Experimental Section

All deuterated solvents were obtained commercially through Cambridge Isotope Laboratories, Inc. NMR spectra were recorded at 298 K using 300, 500, or 600 MHz spectrometers (^{13}C frequencies of 75.5, 126, or 151 MHz, respectively). Adopting the previously reported strategy,[1] standard solutions of mixtures of specific impurities were used to reduce the number of necessary individual NMR experiments. The combinations of organic compounds were chosen in a way in which intermolecular interactions and resonance convolution would be minimized. Unless otherwise stated, the standard solutions were prepared with qualitatively equal molar amounts of the following compounds: solution 1 – acetone, dimethylformamide, ethanol, toluene; solution 2 – benzene, dimethylsulfoxide, ethyl acetate, methanol; solution 3 – acetic acid, chloroform, diethyl ether, 2-propanol, tetrahydrofuran; solution 4 – acetonitrile, dichloromethane, 1,4-dioxane, *n*-hexane, hexamethylphosphoramide (HMPA); solution 5 – 1,2-dichloroethane, *n*-pentane, pyridine, hexamethylbenzene; solution 6 – *tert*-butyl alcohol, 2,6-di-*tert*-butyl-4-methylphenol (BHT), cyclohexane, 1,2-dimethoxyethane, nitromethane, poly(dimethylsiloxane) (silicone grease), triethylamine; solution 7 – diglyme, dimethylacetamide, ethylene glycol, ethyl methyl ketone; solution 8 – allyl acetate, 2,6-di-*tert*-butyl-4-methoxyphenol (BHA), and long-chain, linear aliphatic hydrocarbons from pump oil (VWR brand vacuum pump oil #19); solution 9 – benzaldehyde, carbon disulfide, carbon tetrachloride, cyclohexanone, dimethyl malonate, furan, Apiezon H grease (H grease); solution 10 – 18-crown-6, diallyl carbonate, dimethyl carbonate, hexamethyldisoloxane, imidazole, pyrrole, pyrrolidine. The components of solution 10 were stable together in dilute solution but unstable when neat

mixtures were prepared. In general it was observed that the nitrogen containing compounds and possibly 18-crown-6 either catalyzed the hydrolysis of the carbonates, reacted directly with them, or both. Therefore, for the purpose of storage, the solution was partitioned into two sub-solutions: 10A – 18-crown-6, imidazole, pyrrole, and pyrrolidine; 10B – diallyl carbonate, dimethyl carbonate, and hexamethyldisiloxane. These sub-solutions were stable for long periods as neat mixtures and were combined to form solution 10 by adding equal portions to an NMR tube containing the desired deuterated solvent. In the case of TFE-d_3, nitromethane was omitted from standard 6 and run separately since the protons of CH_3NO_2 exchange with deuterium from TFE-d_3 in the presence of triethylamine. In the case of $(CD_3)_2CO$, pyrrolidine was omitted from solution 10 since the two compounds were observed to react with each other. The gases used in this study included hydrogen, methane, ethane, propane, ethylene, propylene, and carbon dioxide.

Before examining the various standard contaminant solutions by ^{1}H NMR spectroscopy, solvent signals from residual proteo impurity and chemical shifts for H_2O for each NMR solvent were referenced against tetramethylsilane (TMS, δ = 0 ppm) and reported. Note that the chemical shift of H_2O can shift widely based on a number of factors such as temperature and concentration.[1] Before collecting ^{13}C NMR spectral data, solvent signals were recorded with reference to the signal of a TMS internal standard. For D_2O, ^{1}H NMR spectra were referenced to the methyl signal (δ = 0 ppm) of sodium-3-(trimethylsilyl) propanesulfonate,[2] and ^{13}C NMR spectra were referenced to the signal for the methyl group of methanol (one drop, added as an internal standard) which was set to 49.50 ppm.[1]

In a typical experiment for collecting ^{1}H NMR spectral data, a 3 μL sample of a standard contaminant solution was added to a NMR tube containing approximately 0.4 mL of a deuterated solvent. For ^{13}C NMR spectral data collection, an approximately 50 μL sample of the standard contaminant solution was added. When there was any uncertainty on the assignment of a resonance, the solution was spiked with an additional 1–2 μL of the impurity in question to accurately identify its chemical shift. In cases where the chemical shifts of resonances were highly dependent on the concentration of the impurities present, ambiguous resonances were instead resolved via gradient-selected heteronuclear single-quantum coherence (gs-HSQC) and gradient-selected heteronuclear multiple-quantum coherence (gs-HMQC) NMR spectroscopies. For the experiments involving gases, a J. Young NMR tube containing approximately 0.4 mL of NMR solvent was first degassed with three freeze-pump-thaw cycles. Using a vacuum line equipped with a gas manifold, 1 atm of the desired gas was added to the tube. Each gas was run separately, degassing between each set of gas sample.

References

1. Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.
2. Harris, R. K.; Becker, E. D.; De Menezes, S. M. C.; Granger, P.; Hoffman, R. E.; Zilm, K. W. *Pure Appl. Chem.* **2008**, *80*, 59.

Appendix D

Crystallographic Tables

Appendix D

Special Refinement Details for All Structures

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Additional details are provided at the end of the crystal data and structure refinement tables for each structure.

Chapter 2 Crystallographic Tables

[PN]Cu(PPh$_3$)$_2$ (2, ajmm03).

Table 1. Crystal data and structure refinement for ajmm03.

Empirical formula	C54 H53 Cu N P3	
Formula weight	872.42	
Temperature	100(2) K	
Wavelength	0.71073 α	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.764(2) Å	a= 90°.
	b = 18.894(4) Å	b= 98.135(13)°.
	c = 22.199(4) Å	g = 90°.
Volume	4469.0(14) Å^3	
Z	4	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	0.634 mm^{-1}	
Crystal size	0.407 x 0.241 x 0.222 mm^3	
Theta range for data collection	1.85 to 36.01°.	
Index ranges	-16<=h<=17, -30<=k<=24, -36<=l<=32	
Completeness to theta = 36.01°	86.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18249 / 0 / 536	
Goodness-of-fit on F^2	1.309	
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.0704	
R indices (all data)	R1 = 0.0878, wR2 = 0.0757	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for ajmm03. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	6584(1)	2629(1)	5930(1)	12(1)
P(2)	7325(1)	1788(1)	6662(1)	13(1)
P(1)	8081(1)	3309(1)	5545(1)	13(1)
P(3)	4995(1)	2201(1)	5202(1)	13(1)
C(22)	10822(2)	2672(1)	7885(1)	23(1)
C(32)	6515(2)	1691(1)	7830(1)	21(1)
N(1)	6311(1)	3545(1)	6417(1)	13(1)
C(1)	9725(1)	3082(1)	5460(1)	16(1)
C(44)	3364(2)	2993(1)	4302(1)	20(1)
C(21)	9718(2)	3059(1)	7771(1)	20(1)
C(19)	8725(1)	2100(1)	7158(1)	15(1)
C(3)	10384(1)	2762(1)	6053(1)	20(1)
C(39)	7096(2)	1702(1)	3858(1)	25(1)
C(7)	7279(1)	4029(1)	6502(1)	13(1)
C(18)	4542(1)	3123(1)	6884(1)	15(1)
C(45)	2517(2)	3539(1)	4137(1)	22(1)

C(50)	4423(2)	778(1)	5418(1)	21(1)
C(31)	6297(1)	1516(1)	7214(1)	14(1)
C(13)	5201(1)	3687(1)	6657(1)	13(1)
C(48)	3420(1)	3325(1)	5347(1)	16(1)
C(14)	4620(1)	4355(1)	6635(1)	17(1)
C(37)	5473(2)	1836(1)	4505(1)	16(1)
C(43)	3830(1)	2875(1)	4913(1)	15(1)
C(25)	7828(1)	937(1)	6381(1)	16(1)
C(30)	7839(2)	306(1)	6709(1)	23(1)
C(10)	9445(2)	4918(1)	6722(1)	20(1)
C(2)	9830(2)	2595(1)	4918(1)	20(1)
C(6)	6317(2)	4221(1)	4913(1)	22(1)
C(26)	8252(2)	928(1)	5817(1)	20(1)
C(38)	6706(2)	1929(1)	4398(1)	18(1)
C(17)	3366(2)	3223(1)	7061(1)	20(1)
C(15)	3453(2)	4452(1)	6820(1)	20(1)
C(46)	2133(2)	3981(1)	4570(1)	19(1)
C(27)	8694(2)	308(1)	5588(1)	28(1)
C(51)	3728(2)	233(1)	5632(1)	27(1)
C(47)	2583(2)	3870(1)	5177(1)	19(1)
C(8)	8264(1)	3986(1)	6133(1)	14(1)
C(16)	2805(2)	3884(1)	7032(1)	22(1)
C(33)	5640(2)	1511(1)	8212(1)	25(1)
C(12)	7430(1)	4543(1)	6975(1)	16(1)
C(34)	4563(2)	1145(1)	7988(1)	22(1)
C(9)	9316(2)	4430(1)	6254(1)	17(1)
C(20)	8684(2)	2779(1)	7408(1)	16(1)
C(41)	5019(2)	1267(1)	3522(1)	28(1)
C(5)	8478(2)	4286(1)	4596(1)	22(1)
C(53)	2207(2)	1068(1)	5866(1)	31(1)
C(54)	2892(2)	1612(1)	5651(1)	26(1)
C(24)	9837(2)	1712(1)	7279(1)	18(1)
C(29)	8269(2)	-316(1)	6473(1)	31(1)
C(49)	4011(1)	1477(1)	5425(1)	15(1)
C(42)	4635(2)	1487(1)	4061(1)	22(1)
C(35)	4342(2)	968(1)	7379(1)	24(1)
C(11)	8483(2)	4967(1)	7082(1)	19(1)
C(36)	5198(2)	1155(1)	6995(1)	22(1)
C(23)	10882(2)	2001(1)	7635(1)	23(1)
C(4)	7505(2)	3803(1)	4832(1)	17(1)
C(40)	6245(2)	1381(1)	3418(1)	28(1)
C(28)	8695(2)	-315(1)	5916(1)	31(1)
C(52)	2625(2)	378(1)	5858(1)	26(1)

[PN]Cu(PMe$_3$)$_2$ (3, ajmm08).

Table 1. Crystal data and structure refinement for ajmm08.

Empirical formula	$C_{24}H_{41}CuNP_3$	
Formula weight	500.03	
Temperature	100(2) K	
Wavelength	0.71073 α	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.9195(4) Å	a= 90°.
	b = 16.3588(7) Å	b= 90°.
	c = 16.5646(7) A	g = 90°.
Volume	2687.96(19) Å^3	
Z	4	
Density (calculated)	1.236 Mg/m^3	
Absorption coefficient	1.002 mm^{-1}	
Crystal size	0.444 x 0.148 x 0.130 mm^3	
Theta range for data collection	1.75 to 38.21°.	
Index ranges	-14<=h<=17, -27<=k<=27, -20<=l<=28	
Completeness to theta = 38.21°	91.1 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12091 / 0 / 272	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.0615	
R indices (all data)	R1 = 0.0734, wR2 = 0.0660	
Absolute structure parameter	-0.025(7)	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for ajmm08. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5897(2)	5983(1)	8325(1)	14(1)
C(2)	5086(2)	6749(1)	8545(1)	20(1)
C(3)	5428(2)	5648(1)	7508(1)	21(1)
C(4)	6906(2)	4379(1)	8818(1)	15(1)
C(5)	8337(2)	4694(1)	8662(1)	20(1)
C(6)	6941(2)	3707(1)	9465(1)	20(1)
C(7)	5923(2)	5272(1)	10757(1)	12(1)
C(8)	6423(2)	5611(1)	10024(1)	12(1)
C(9)	7399(2)	6232(1)	10038(1)	14(1)
C(10)	7886(2)	6537(1)	10761(1)	17(1)
C(11)	7386(2)	6225(1)	11482(1)	17(1)
C(12)	6431(2)	5611(1)	11484(1)	15(1)
C(13)	4795(2)	4091(1)	11304(1)	14(1)
C(14)	5854(2)	3817(1)	11808(1)	15(1)
C(15)	5663(2)	3192(1)	12360(1)	18(1)
C(16)	4432(2)	2803(1)	12441(1)	21(1)
C(17)	3375(2)	3058(1)	11948(1)	20(1)
C(18)	3554(2)	3682(1)	11391(1)	18(1)
C(19)	3176(2)	6591(1)	10694(1)	24(1)

C(20)	1240(2)	6370(1)	9444(1)	23(1)
C(21)	1124(2)	5426(1)	10879(1)	29(1)
C(22)	2075(2)	4013(1)	8083(1)	29(1)
C(23)	1129(2)	3307(1)	9541(1)	22(1)
C(24)	3594(2)	2793(1)	8885(1)	32(1)
Cu	3714(1)	4775(1)	9688(1)	13(1)
N	4924(1)	4683(1)	10714(1)	13(1)
P(1)	5679(1)	5191(1)	9112(1)	11(1)
P(2)	2660(1)	3730(1)	9093(1)	17(1)
P(3)	2325(1)	5785(1)	10123(1)	16(1)

$[^{Me}PN]Cu(PPh_3)_2$ (7, ajmm15).

Table 1. Crystal data and structure refinement for ajmm15.

Empirical formula	$C_{59}H_{65}CuNOP_3$	
Formula weight	960.57	
Temperature	100(2) K	
Wavelength	0.71073 α	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.099(4) Å	a= 90°.
	b = 21.513(7) Å	b= 103.72(3)°.
	c = 21.933(6) Å	g = 90°.
Volume	5088(3) $Å^3$	
Z	4	
Density (calculated)	1.254 Mg/m^3	
Absorption coefficient	0.565 mm^{-1}	
Crystal size	0.407 x 0.1184 x 0.111 mm^3	
Theta range for data collection	1.89 to 28.31∞.	
Index ranges	-14<=h<=13, -27<=k<=28, -25<=l<=28	
Completeness to theta = 28.31°	87.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11108 / 0 / 593	
Goodness-of-fit on F^2	1.589	
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.0938	
R indices (all data)	R1 = 0.0732, wR2 = 0.0974	

Special Refinement Details

A diethyl ether molecule of crystallization was present in the lattice.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ajmm15. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu	2313(1)	4290(1)	2852(1)	13(1)
P(1)	1103(1)	4639(1)	3515(1)	12(1)
P(2)	1318(1)	3637(1)	2031(1)	13(1)
P(3)	3479(1)	5035(1)	2486(1)	12(1)
C(1)	2644(2)	5733(1)	2130(1)	14(1)
C(2)	1663(3)	5944(1)	2361(1)	22(1)
C(3)	475(3)	2850(1)	2836(1)	20(1)
C(4)	2117(2)	3027(1)	1681(1)	14(1)
C(5)	2378(2)	3600(1)	4039(1)	13(1)
C(6)	695(2)	3268(1)	4775(1)	19(1)
C(7)	6032(3)	6242(1)	3567(1)	25(1)
C(8)	5571(2)	4981(1)	3484(1)	16(1)
C(9)	-1114(2)	3127(1)	1924(1)	20(1)
N	3084(2)	3737(1)	3621(1)	12(1)
C(10)	-579(2)	4823(1)	3366(1)	17(1)
C(11)	1761(3)	2915(1)	4811(1)	18(1)
C(12)	6550(2)	5213(1)	3941(1)	19(1)

C(13)	-889(3)	5455(1)	3054(1)	24(1)
C(14)	4164(2)	4752(1)	1854(1)	13(1)
C(15)	4821(2)	3395(1)	3220(1)	16(1)
C(16)	5148(3)	4236(1)	901(1)	29(1)
C(17)	3294(2)	3137(1)	1589(1)	17(1)
C(18)	5058(2)	6015(1)	3101(1)	20(1)
C(19)	2377(3)	6620(1)	1437(1)	25(1)
C(20)	6402(2)	3413(1)	4394(1)	22(1)
C(21)	5155(2)	3542(1)	4330(1)	17(1)
C(22)	5854(3)	4261(1)	1510(1)	27(1)
C(23)	4809(2)	5379(1)	3058(1)	13(1)
C(24)	6773(2)	5842(1)	3989(1)	22(1)
C(25)	121(2)	3171(1)	2267(1)	16(1)
C(26)	-370(3)	2499(1)	3053(2)	27(1)
C(28)	5370(2)	4518(1)	1985(1)	21(1)
C(29)	-1599(3)	2461(1)	2711(2)	29(1)
C(30)	3950(3)	4463(1)	769(1)	24(1)
C(31)	1391(3)	6825(1)	1666(2)	31(1)
C(32)	1134(2)	5415(1)	4576(1)	19(1)
C(33)	-1951(3)	2775(1)	2148(1)	24(1)
C(34)	4327(2)	3544(1)	3735(1)	13(1)
C(35)	6874(3)	3276(1)	3880(2)	25(1)
C(36)	2184(3)	2001(1)	1234(1)	25(1)
C(37)	486(2)	3789(1)	4389(1)	16(1)
C(38)	-1343(2)	4309(1)	2971(1)	22(1)
C(39)	1563(3)	2447(1)	1503(1)	20(1)
C(40)	1821(2)	5277(1)	4063(1)	16(1)
C(41)	2996(2)	6081(1)	1662(1)	19(1)
C(42)	1297(2)	3962(1)	4028(1)	13(1)
C(43)	1037(3)	6491(1)	2136(2)	31(1)
O	3095(2)	3882(1)	9373(1)	51(1)
C(45)	10(3)	3798(1)	754(1)	25(1)
C(46)	2585(2)	3082(1)	4453(1)	14(1)
C(47)	406(2)	4056(1)	1345(1)	17(1)
C(48)	3187(2)	5132(1)	4351(1)	19(1)
C(49)	28(3)	4657(1)	1444(1)	24(1)
C(50)	3461(2)	4712(1)	1242(1)	18(1)
C(51)	3348(3)	2119(1)	1145(1)	24(1)
C(52)	-717(3)	4997(2)	969(2)	37(1)
C(53)	3904(3)	2689(1)	1318(1)	21(1)
C(54)	6064(2)	3269(1)	3291(1)	21(1)
C(59)	2015(3)	2346(1)	5235(2)	28(1)
C(55)	3907(3)	3999(2)	8960(2)	44(1)
C(57)	1749(4)	3247(2)	9743(2)	56(1)
C(58)	2620(4)	3278(2)	9330(2)	60(1)
C(56)	3193(3)	4130(2)	8313(2)	50(1)
C(60)	-1103(3)	4732(2)	384(2)	43(1)
C(61)	-740(3)	4141(2)	271(2)	40(1)

$[^{CF3}PN]Cu(PPh_3)_2$ (8, ajmm12).

Table 1. Crystal data and structure refinement for ajmm12.

Empirical formula	$C_{59}H_{62}CuF_3NOP_3$	
Formula weight	1014.55	
Temperature	100(2) K	
Wavelength	0.71073 α	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.101(16) Å	a= 90°.
	b = 21.70(5) Å	b= 103.11(7)°.
	c = 22.30(4) Å	g = 90°.
Volume	5231(17) Å^3	
Z	4	
Density (calculated)	1.288 Mg/m^3	
Absorption coefficient	0.561 mm^{-1}	
Crystal size	0.296 x 0.0518 x 0.037 mm^3	
Theta range for data collection	1.88 to 28.30°.	
Index ranges	-14<=h<=14, -28<=k<=28, -29<=l<=28	
Completeness to theta = 28.30°	91.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11900 / 0 / 619	
Goodness-of-fit on F^2	1.320	
Final R indices [I>2sigma(I)]	R1 = 0.0617, wR2 = 0.1007	
R indices (all data)	R1 = 0.1176, wR2 = 0.1078	

Special Refinement Details

A highly disordered molecule of diethyl ether was cocrystallized with **8**.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for ajmm12. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	7353(1)	4340(1)	2853(1)	14(1)
P(2)	8523(1)	5077(1)	2481(1)	13(1)
P(3)	6334(1)	3682(1)	2053(1)	15(1)
P(1)	6114(1)	4696(1)	3505(1)	13(1)
N(1)	8107(3)	3795(1)	3621(1)	15(1)
C(50)	7696(3)	5779(2)	2137(2)	17(1)
F(3)	6316(3)	1918(1)	4906(1)	63(1)
F(2)	8102(2)	2258(1)	5355(1)	58(1)
C(14)	9339(3)	3583(1)	3729(2)	12(1)
F(1)	6532(2)	2490(1)	5704(1)	46(1)
C(15)	10165(3)	3574(2)	4316(2)	18(1)
C(55)	6776(3)	6014(2)	2406(2)	22(1)
C(33)	4966(3)	3874(2)	809(2)	24(1)
C(10)	6715(3)	2984(2)	4776(2)	16(1)
C(13)	6916(4)	2422(2)	5175(2)	26(1)
C(31)	8310(3)	3177(2)	1607(2)	17(1)
C(21)	5525(3)	2879(2)	2845(2)	20(1)

C(38)	9218(3)	4791(2)	1856(2)	16(1)
C(26)	7114(3)	3076(2)	1688(2)	15(1)
C(20)	5155(3)	3207(2)	2293(2)	17(1)
C(19)	9832(3)	3425(2)	3222(2)	17(1)
C(3)	3686(3)	4370(2)	2957(2)	25(1)
C(22)	4703(4)	2508(2)	3064(2)	28(1)
C(11)	7569(3)	3139(2)	4436(1)	14(1)
C(1)	4439(3)	4879(2)	3349(2)	19(1)
C(51)	7983(4)	6099(2)	1648(2)	26(1)
C(52)	7346(4)	6636(2)	1429(2)	34(1)
C(7)	6287(3)	4015(2)	4004(1)	14(1)
C(16)	11403(3)	3421(2)	4378(2)	22(1)
C(36)	4408(4)	5093(2)	1047(2)	30(1)
C(8)	5430(3)	3838(2)	4351(2)	16(1)
C(23)	3474(4)	2468(2)	2736(2)	28(1)
C(32)	5422(3)	4122(2)	1398(2)	17(1)
C(24)	3098(3)	2789(2)	2188(2)	23(1)
C(34)	4227(4)	4237(2)	347(2)	33(1)
C(25)	3926(3)	3161(2)	1965(2)	18(1)
C(37)	5139(3)	4739(2)	1505(2)	23(1)
C(45)	10582(3)	5015(2)	3472(2)	18(1)
C(28)	7155(4)	2066(2)	1215(2)	27(1)
C(44)	9846(3)	5410(2)	3042(2)	14(1)
C(41)	10206(4)	4263(2)	914(2)	29(1)
C(54)	6154(4)	6559(2)	2187(2)	36(1)
C(42)	10912(3)	4307(2)	1505(2)	30(1)
C(39)	8491(3)	4734(2)	1252(2)	20(1)
C(49)	10116(3)	6044(2)	3084(2)	22(1)
C(40)	8988(3)	4479(2)	785(2)	26(1)
C(43)	10422(3)	4567(2)	1976(2)	24(1)
C(12)	7377(3)	3657(2)	4022(1)	13(1)
C(18)	11066(3)	3279(2)	3289(2)	21(1)
C(30)	8919(3)	2728(2)	1336(2)	23(1)
C(2)	4142(3)	5510(2)	3042(2)	23(1)
C(9)	5626(3)	3323(2)	4734(2)	19(1)
C(29)	8348(4)	2178(2)	1138(2)	26(1)
C(27)	6543(3)	2514(2)	1491(2)	22(1)
C(53)	6437(4)	6868(2)	1702(2)	38(1)
C(35)	3955(4)	4840(2)	469(2)	34(1)
C(17)	11871(3)	3281(2)	3866(2)	25(1)
C(5)	6124(3)	5444(2)	4572(2)	19(1)
C(4)	6819(3)	5320(2)	4059(2)	16(1)
C(6)	8191(3)	5171(2)	4345(2)	21(1)
C(47)	11800(4)	5870(2)	3968(2)	26(1)
C(48)	11083(3)	6273(2)	3541(2)	26(1)
C(46)	11558(3)	5242(2)	3930(2)	20(1)
O(1)	7864(4)	3820(2)	9440(2)	87(1)
C(56)	6505(9)	3217(3)	9751(3)	160(5)
C(58)	8785(6)	3964(3)	8951(3)	80(2)
C(57)	7548(8)	3295(3)	9352(5)	228(8)
C(59)	8178(6)	4097(3)	8370(4)	110(3)

[PN]Ag(PPh$_3$)$_2$ (9, ajmm05).

Table 1. Crystal data and structure refinement for ajmm05.

Empirical formula	C54 H53 Ag N P3	
Formula weight	916.75	
Temperature	100(2) K	
Wavelength	0.71073 α	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.8189(5) Å	a= 90°.
	b = 19.1162(8) Å	b= 97.2540(10)°.
	c = 22.2135(9) Å	g = 90°.
Volume	4557.3(3) Å^3	
Z	4	
Density (calculated)	1.336 Mg/m^3	
Absorption coefficient	0.585 mm^{-1}	
Crystal size	0.370 x 0.222 x 0.185 mm^3	
Theta range for data collection	1.41 to 35.99°.	
Index ranges	-16<=h<=17, -31<=k<=31, -35<=l<=30	
Completeness to theta = 35.99°	90.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19574 / 0 / 536	
Goodness-of-fit on F^2	1.446	
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0629	
R indices (all data)	R1 = 0.0585, wR2 = 0.0662	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for ajmm05. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ag(1)	1581(1)	7437(1)	858(1)	12(1)
C(1)	2604(1)	6150(1)	-209(1)	16(1)
C(2)	3553(1)	5639(1)	-417(1)	21(1)
C(3)	1368(1)	5784(1)	-141(1)	21(1)
C(4)	4775(1)	6879(1)	419(1)	15(1)
C(5)	5384(1)	7215(1)	1008(1)	21(1)
C(6)	4821(1)	7371(1)	-124(1)	20(1)
C(7)	2308(1)	5924(1)	1470(1)	13(1)
C(8)	3296(1)	5978(1)	1101(1)	13(1)
C(9)	4357(1)	5552(1)	1219(1)	16(1)
C(10)	4492(1)	5067(1)	1687(1)	19(1)
C(11)	3528(1)	5003(1)	2047(1)	18(1)
C(12)	2468(1)	5412(1)	1943(1)	15(1)
C(13)	224(1)	6250(1)	1628(1)	13(1)
C(14)	-354(1)	5587(1)	1616(1)	16(1)
C(15)	-1536(1)	5501(1)	1785(1)	21(1)
C(16)	-2206(1)	6071(1)	1969(1)	23(1)
C(17)	-1645(1)	6723(1)	1991(1)	20(1)
C(18)	-457(1)	6815(1)	1831(1)	16(1)
C(19)	3702(1)	7936(1)	2151(1)	14(1)
C(20)	3624(1)	7249(1)	2360(1)	16(1)

C(21)	4651(1)	6931(1)	2691(1)	19(1)
C(22)	5773(1)	7289(1)	2804(1)	21(1)
C(23)	5865(1)	7968(1)	2587(1)	21(1)
C(24)	4836(1)	8293(1)	2268(1)	18(1)
C(25)	1268(1)	8515(1)	2222(1)	14(1)
C(26)	1460(1)	8346(1)	2836(1)	20(1)
C(27)	553(2)	8494(1)	3210(1)	25(1)
C(28)	-546(1)	8822(1)	2977(1)	22(1)
C(29)	-745(2)	8995(1)	2365(1)	25(1)
C(30)	147(1)	8836(1)	1991(1)	22(1)
C(31)	2866(1)	9134(1)	1427(1)	16(1)
C(32)	2898(2)	9739(1)	1783(1)	24(1)
C(33)	3344(2)	10361(1)	1569(1)	32(1)
C(34)	3760(2)	10388(1)	1005(1)	33(1)
C(35)	3729(2)	9794(1)	648(1)	30(1)
C(36)	3268(1)	9170(1)	857(1)	22(1)
C(37)	-1124(1)	8581(1)	346(1)	14(1)
C(38)	-2251(1)	8431(1)	556(1)	24(1)
C(39)	-2932(2)	8951(1)	807(1)	30(1)
C(40)	-2492(2)	9630(1)	842(1)	26(1)
C(41)	-1381(2)	9788(1)	629(1)	24(1)
C(42)	-692(1)	9271(1)	387(1)	20(1)
C(43)	373(1)	8229(1)	-592(1)	16(1)
C(44)	1591(1)	8089(1)	-698(1)	19(1)
C(45)	2019(2)	8302(1)	-1235(1)	26(1)
C(46)	1227(2)	8651(1)	-1670(1)	29(1)
C(47)	16(2)	8808(1)	-1568(1)	28(1)
C(48)	-411(2)	8603(1)	-1030(1)	22(1)
C(49)	-1245(1)	7189(1)	-158(1)	13(1)
C(50)	-1474(1)	6694(1)	275(1)	17(1)
C(51)	-2254(1)	6128(1)	123(1)	20(1)
C(52)	-2819(1)	6050(1)	-470(1)	19(1)
C(53)	-2620(1)	6543(1)	-900(1)	22(1)
C(54)	-1831(1)	7113(1)	-750(1)	20(1)
N(1)	1333(1)	6388(1)	1397(1)	13(1)
P(1)	3152(1)	6636(1)	503(1)	12(1)
P(2)	-137(1)	7882(1)	102(1)	13(1)
P(3)	2339(1)	8287(1)	1680(1)	13(1)

$[PN]_2Zn$ (10, ajmm06).

Table 1. Crystal data and structure refinement for ajmm06.

Empirical formula	$C_{36}H_{46}N_2P_2Zn$	
Formula weight	634.06	
Temperature	100(2) K	
Wavelength	0.71073 α	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 21.074(14) Å	a= 90°.
	b = 8.729(6) Å	b= 110.905(14)°.
	c = 19.086(13) Å	g = 90°.
Volume	3280(4) $Å^3$	
Z	4	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	0.873 mm^{-1}	
Crystal size	0.259 x 0.244 x 0.152 mm^3	
Theta range for data collection	2.07 to 38.26°.	
Index ranges	-27<=h<=36, -15<=k<=14, -31<=l<=30	
Completeness to theta = 38.26°	88.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8084 / 0 / 190	
Goodness-of-fit on F^2	1.390	
Final R indices [I>2sigma(I)]	R1 = 0.0451, wR2 = 0.0713	
R indices (all data)	R1 = 0.0791, wR2 = 0.0752	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ajmm06. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn	0	206(1)	2500	11(1)
P	968(1)	-1117(1)	2455(1)	12(1)
N	22(1)	1322(1)	1613(1)	13(1)
C(8)	1072(1)	29(1)	1719(1)	13(1)
C(7)	566(1)	1162(1)	1377(1)	12(1)
C(5)	1706(1)	-1854(2)	3928(1)	21(1)
C(1)	770(1)	-3103(1)	2100(1)	16(1)
C(18)	-836(1)	3175(1)	1591(1)	16(1)
C(9)	1647(1)	-86(2)	1510(1)	16(1)
C(13)	-548(1)	2204(1)	1202(1)	13(1)
C(4)	1799(1)	-1180(1)	3232(1)	16(1)
C(10)	1738(1)	876(2)	980(1)	19(1)
C(17)	-1438(1)	3952(2)	1217(1)	19(1)
C(15)	-1486(1)	2822(2)	65(1)	20(1)
C(11)	1252(1)	1982(2)	650(1)	18(1)
C(6)	2119(1)	402(2)	3414(1)	22(1)
C(16)	-1764(1)	3791(2)	453(1)	20(1)
C(2)	146(1)	-3078(2)	1375(1)	23(1)
C(14)	-890(1)	2032(2)	428(1)	17(1)
C(12)	678(1)	2128(1)	838(1)	16(1)
C(3)	1353(1)	-3965(2)	1979(1)	23(1)

Chapter 3 Crystallographic Tables

[($Ph_2P(CH_2)_2B(C_8H_{14})_2Re(CO)_4$][$BF_4$] ([1-$E_2$][$BF_4$], ajmm22).

Table 1. Crystal data and structure refinement for AJMM22 (CCDC 677279).

Empirical formula	$[C_{48}H_{56}B_2O_4P_2Re]^+ BF_4^- \bullet 2(CH_2Cl_2)$	
Formula weight	1223.35	
Crystallization Solvent	Dichloromethane	
Crystal Habit	Plate	
Crystal size	0.36 x 0.34 x 0.01 mm^3	
Crystal color	Colorless	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 13.5643(10) Å	a= 71.725(4)°
	b = 14.4026(10) Å	b= 70.883(4)°
	c = 14.6998(11) Å	g = 89.203(5)°
Volume	2563.9(3) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.585 Mg/m^3	
q range for data collection	1.77 to 41.25°	
Completeness to θ = 41.25°	89.6 %	
Index ranges	$-24 \le h \le 23$, $-25 \le k \le 26$, $-25 \le l \le 26$	
Absorption coefficient	2.699 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	30749 / 0 / 616	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	2.971	
Final R indices [I>2s(I), 18556 reflections]	R1 = 0.0515, *w*R2 = 0.0876	
R indices (all data)	R1 = 0.1091, *w*R2 = 0.0895	

Special Refinement Details

The asymmetric unit is composed of two half-molecules each sitting on inequivalent centers of symmetry with the net effect of one molecule per asymmetric unit..

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM22 (CCDC 677279). U(eq) is defined a the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	10000	10000	0	13(1)
P(1A)	9410(1)	8612(1)	-369(1)	16(1)
O(1A)	7658(2)	10358(2)	891(2)	29(1)
O(2A)	9660(2)	8687(2)	2246(2)	25(1)
B(1A)	6923(4)	6673(3)	2056(4)	35(1)
C(1A)	8513(3)	10252(2)	535(2)	19(1)
C(2A)	9815(3)	9148(2)	1425(2)	18(1)
C(3A)	9362(2)	9000(2)	-1651(2)	17(1)
C(4A)	8524(3)	9484(2)	-1838(3)	24(1)

C(5A)	8497(3)	9851(2)	-2819(3)	29(1)
C(6A)	9294(3)	9732(2)	-3615(3)	27(1)
C(7A)	10131(3)	9266(2)	-3446(3)	23(1)
C(8A)	10186(3)	8901(2)	-2472(2)	18(1)
C(9A)	10175(2)	7560(2)	-270(2)	16(1)
C(10A)	10087(2)	6887(2)	-755(2)	19(1)
C(11A)	10641(3)	6063(2)	-639(3)	24(1)
C(12A)	11252(3)	5889(2)	-25(3)	27(1)
C(13A)	11315(3)	6532(2)	486(3)	25(1)
C(14A)	10782(3)	7379(2)	344(3)	21(1)
C(15A)	8088(3)	8019(2)	378(3)	28(1)
C(16A)	7882(3)	7491(3)	1484(3)	36(1)
C(17A)	6697(3)	5862(3)	1625(3)	41(1)
C(18A)	5558(3)	5849(3)	1638(3)	52(1)
C(19A)	4721(3)	5798(3)	2679(3)	49(1)
C(20A)	5030(3)	6474(3)	3165(3)	39(1)
C(21A)	6174(3)	6495(2)	3140(3)	34(1)
C(22A)	6448(4)	5549(3)	3786(4)	50(1)
C(23A)	6399(3)	4678(3)	3455(3)	41(1)
C(24A)	6902(3)	4857(3)	2321(3)	45(1)
Re(2)	0	5000	5000	10(1)
P(1B)	455(1)	3608(1)	4386(1)	12(1)
O(1B)	2363(2)	5777(2)	4294(2)	24(1)
O(2B)	363(2)	3913(2)	7056(2)	25(1)
B(1B)	2833(3)	2080(2)	5251(3)	19(1)
C(1B)	1509(3)	5514(2)	4519(2)	16(1)
C(2B)	187(2)	4279(2)	6329(3)	17(1)
C(3B)	1444(2)	3820(2)	3132(2)	14(1)
C(4B)	1663(2)	3029(2)	2755(2)	19(1)
C(5B)	2445(3)	3140(2)	1848(3)	23(1)
C(6B)	3038(3)	4033(2)	1291(3)	24(1)
C(7B)	2827(2)	4823(2)	1642(2)	21(1)
C(8B)	2035(2)	4720(2)	2550(2)	17(1)
C(9B)	-677(2)	3011(2)	4307(2)	13(1)
C(10B)	-878(2)	3258(2)	3400(2)	17(1)
C(11B)	-1778(2)	2842(2)	3370(3)	21(1)
C(12B)	-2482(3)	2193(2)	4242(3)	22(1)
C(13B)	-2295(2)	1960(2)	5149(3)	21(1)
C(14B)	-1400(2)	2356(2)	5186(2)	17(1)
C(15B)	969(2)	2611(2)	5180(2)	16(1)
C(16B)	2057(2)	2905(2)	5154(2)	20(1)
C(17B)	2524(3)	970(2)	5480(3)	26(1)
C(18B)	3062(3)	279(2)	6164(3)	34(1)
C(19B)	3753(3)	829(2)	6492(3)	33(1)
C(20B)	4559(3)	1596(2)	5587(3)	32(1)
C(21B)	4036(3)	2327(2)	4915(3)	25(1)
C(22B)	4373(3)	2267(3)	3808(3)	38(1)
C(23B)	4064(3)	1234(3)	3820(3)	46(1)
C(24B)	2914(3)	903(3)	4380(3)	37(1)
B(1)	7655(3)	2185(3)	8024(3)	23(1)
F(1)	7060(2)	2850(2)	8432(2)	42(1)
F(2)	7838(2)	1458(1)	8807(2)	36(1)
F(3)	7110(2)	1765(1)	7578(2)	33(1)
F(4)	8595(2)	2676(2)	7315(2)	43(1)

C(31)	5116(4)	1279(5)	9345(4)	82(2)
Cl(1)	4201(1)	1321(1)	10528(1)	89(1)
Cl(2)	4463(1)	881(1)	8654(1)	71(1)
C(32)	6273(3)	2170(3)	1048(3)	46(1)
Cl(3)	6928(1)	2019(1)	1956(1)	43(1)
Cl(4)	5642(1)	3196(1)	921(1)	64(1)

$(Ph_2P(CH_2)_2B(C_8H_{14}))_2Re(CO)_3(CHO)$ (2-E$_2$, ajmm24).

Table 1. Crystal data and structure refinement for AJMM24 (CCDC 681294).

Empirical formula	$C_{96}H_{114}B_4O_8P_4Re_2 \bullet 2(CH_2Cl_2)$	
Formula weight	2105.24	
Crystallization Solvent	Dichloromethane/toluene	
Crystal Habit	Fragment	
Crystal size	0.20 x 0.20 x 0.14 mm^3	
Crystal color	Colorless	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 11.2518(5) Å	a= 88.406(3)°
	b = 13.3609(6) Å	b= 74.156(3)°
	c = 16.3588(7) Å	g = 80.300(3)°
Volume	2331.60(18) Å^3	
Z	1	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.499 Mg/m^3	
q range for data collection	1.91 to 54.57°	
Completeness to θ = 54.57°	94.9 %	
Index ranges	$-25 \le h \le 25$, $-26 \le k \le 30$, $-37 \le l \le 35$	
Absorption coefficient	2.832 mm^{-1}	
Absorption correction	None	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	55878 / 0 / 541	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	1.248	
Final R indices [I>2s(I), 43261 reflections]	R1 = 0.0351, *w*R2 = 0.0668	
R indices (all data)	R1 = 0.0521, *w*R2 = 0.0681	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for AJMM24 (CCDC 681294). U(eq) is defined a the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	6790(1)	2417(1)	3610(1)	8(1)
P(1)	7415(1)	2189(1)	2080(1)	10(1)
P(2)	6137(1)	2705(1)	5142(1)	9(1)
O(1)	4568(1)	1241(1)	3682(1)	25(1)
O(2)	8618(1)	425(1)	3732(1)	22(1)
O(3)	8738(1)	3848(1)	3524(1)	20(1)
O(4)	4334(1)	3805(1)	3688(1)	14(1)
B(1)	7675(2)	5155(1)	1063(1)	23(1)
B(2)	6634(1)	5262(1)	6530(1)	11(1)
C(1)	5373(1)	1664(1)	3670(1)	15(1)
C(2)	7950(1)	1163(1)	3691(1)	13(1)
C(3)	8046(1)	3298(1)	3544(1)	12(1)
C(4)	5498(1)	3744(1)	3535(1)	11(1)
C(5)	7114(1)	3317(1)	1454(1)	15(1)
C(6)	7749(1)	4188(1)	1630(1)	19(1)
C(7)	7326(2)	6265(1)	1415(1)	42(1)
C(8)	8218(3)	6959(2)	843(1)	54(1)

C(9)	9118(2)	6407(1)	50(1)	28(1)
C(10)	8483(2)	5860(2)	-445(1)	36(1)
C(11)	7673(2)	5112(1)	93(1)	31(1)
C(12)	6292(2)	5416(2)	118(1)	39(1)
C(13)	5725(2)	6461(2)	526(2)	43(1)
C(14)	5916(2)	6573(2)	1395(1)	44(1)
C(15)	6374(1)	3954(1)	5441(1)	12(1)
C(16)	6202(1)	4194(1)	6379(1)	12(1)
C(17)	6631(1)	5481(1)	7502(1)	14(1)
C(18)	7620(1)	4669(1)	7735(1)	16(1)
C(19)	8948(1)	4584(1)	7122(1)	18(1)
C(20)	8990(1)	4606(1)	6174(1)	17(1)
C(21)	8002(1)	5422(1)	5944(1)	13(1)
C(22)	8218(1)	6518(1)	6044(1)	17(1)
C(23)	7988(1)	6893(1)	6963(1)	20(1)
C(24)	6826(1)	6583(1)	7601(1)	17(1)
C(25)	6650(1)	1251(1)	1715(1)	15(1)
C(26)	6901(1)	245(1)	1968(1)	22(1)
C(27)	6322(2)	-499(1)	1744(1)	32(1)
C(28)	5475(2)	-249(2)	1260(1)	40(1)
C(29)	5217(2)	742(2)	1007(1)	34(1)
C(30)	5805(1)	1498(1)	1232(1)	23(1)
C(31)	9071(1)	1708(1)	1569(1)	11(1)
C(32)	10007(1)	1752(1)	1969(1)	14(1)
C(33)	11264(1)	1405(1)	1549(1)	17(1)
C(34)	11587(1)	1007(1)	728(1)	16(1)
C(35)	10666(1)	966(1)	324(1)	16(1)
C(36)	9413(1)	1316(1)	736(1)	13(1)
C(37)	4496(1)	2631(1)	5628(1)	12(1)
C(38)	4084(1)	1695(1)	5668(1)	20(1)
C(39)	2816(1)	1636(1)	5979(1)	27(1)
C(40)	1945(1)	2508(1)	6236(1)	26(1)
C(41)	2334(1)	3446(1)	6194(1)	21(1)
C(42)	3605(1)	3504(1)	5889(1)	16(1)
C(43)	7010(1)	1846(1)	5741(1)	13(1)
C(44)	6449(1)	1325(1)	6454(1)	23(1)
C(45)	7183(2)	662(2)	6869(1)	32(1)
C(46)	8484(1)	532(1)	6583(1)	28(1)
C(47)	9052(1)	1068(1)	5883(1)	22(1)
C(48)	8319(1)	1719(1)	5467(1)	17(1)
C(51)	1371(2)	7903(2)	1742(1)	38(1)
Cl(1)	8(1)	8813(1)	1843(1)	33(1)
Cl(2)	2624(1)	8196(1)	905(1)	48(1)

[Na][($Ph_2P(CH_2)_2B(C8H_{14})2Re(CO)_2(=C(O–)CH_2O–)$] ([Na][3-$E_2$], ajmm29).

Table 1. Crystal data and structure refinement for AJMM29 (CCDC 687691).

Empirical formula	$C_{48}H_{58}B_2O_4P_2Re \bullet Na3.52(C_4H_8O)0.48(C_4H_{10}O)$	
Formula weight	1281.12	
Crystallization Solvent	THF/diethylether	
Crystal Habit	Plate	
Crystal size	0.33 x 0.31 x 0.09 mm^3	
Crystal color	Pale yellow	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 11.5211(5) Å	a= 81.125(2)°
	b = 12.3378(5) Å	b= 81.140(2)°
	c = 23.1407(8) Å	g = 67.210(2)°
Volume	2980.1(2) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.428 Mg/m^3	
q range for data collection	1.93 to 52.54°	
Completeness to θ = 52.54°	89.3 %	
Index ranges	$-23 \le h \le 24$, $-26 \le k \le 26$, $-48 \le l \le 49$	
Absorption coefficient	2.154 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	62112 / 15 / 833	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	1.696	
Final R indices [I>2s(I), 47581 reflections]	R1 = 0.0440, *w*R2 = 0.0574	
R indices (all data)	R1 = 0.0691, *w*R2 = 0.0590	

Special Refinement Details

Ligands to Na are disordered. The three equatorial ligands are disordered THF with each exhibiting different types of disorder, refined without restraints. The axial ligand is a mixture of THF and diethylethher, distances and angle in the diethylether were restrained.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM29 (CCDC 687691). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Re(1)	6928(1)	4885(1)	6946(1)	13(1)	1
P(1)	8846(1)	5303(1)	6769(1)	14(1)	1
P(2)	5094(1)	4335(1)	7119(1)	15(1)	1
O(1)	7765(1)	3353(1)	5896(1)	26(1)	1
O(2)	8312(1)	2796(1)	7793(1)	27(1)	1
O(3)	6370(1)	6749(1)	7894(1)	19(1)	1
O(4)	5632(1)	6594(1)	6529(1)	15(1)	1
B(1)	7422(1)	6220(1)	8342(1)	18(1)	1
B(2)	4525(1)	6892(1)	6133(1)	15(1)	1
C(1)	7444(1)	3927(1)	6280(1)	18(1)	1
C(2)	7795(1)	3598(1)	7454(1)	19(1)	1
C(3)	5314(1)	7177(1)	7049(1)	18(1)	1

C(4)	6238(1)	6309(1)	7458(1)	16(1)	1
C(5)	6190(1)	8197(1)	8808(1)	23(1)	1
C(6)	5543(1)	7602(1)	9313(1)	28(1)	1
C(7)	5612(1)	6385(1)	9197(1)	26(1)	1
C(8)	6911(1)	5571(1)	8929(1)	22(1)	1
C(9)	7934(1)	5127(1)	9361(1)	29(1)	1
C(10)	8332(1)	6099(1)	9517(1)	32(1)	1
C(11)	8493(1)	6994(1)	8998(1)	26(1)	1
C(12)	7502(1)	7391(1)	8553(1)	20(1)	1
C(13)	8740(1)	5373(1)	8008(1)	20(1)	1
C(14)	9130(1)	5894(1)	7393(1)	19(1)	1
C(15)	10237(1)	3959(1)	6650(1)	19(1)	1
C(16)	11074(1)	3396(1)	7073(1)	31(1)	1
C(17)	12121(2)	2362(1)	6962(1)	48(1)	1
C(18)	12320(2)	1884(1)	6440(1)	46(1)	1
C(19)	11491(1)	2433(1)	6018(1)	37(1)	1
C(20)	10452(1)	3466(1)	6120(1)	28(1)	1
C(21)	9138(1)	6361(1)	6176(1)	18(1)	1
C(22)	8171(1)	7464(1)	6093(1)	23(1)	1
C(23)	8367(1)	8355(1)	5690(1)	28(1)	1
C(24)	9528(1)	8139(1)	5357(1)	31(1)	1
C(25)	10489(1)	7044(1)	5430(1)	32(1)	1
C(26)	10304(1)	6159(1)	5842(1)	26(1)	1
C(27)	6213(1)	6822(1)	5238(1)	21(1)	1
C(28)	5785(1)	8176(1)	5159(1)	22(1)	1
C(29)	4940(1)	8799(1)	5686(1)	21(1)	1
C(30)	3908(1)	8320(1)	5969(1)	18(1)	1
C(31)	2860(1)	8613(1)	5561(1)	20(1)	1
C(32)	3272(1)	7958(1)	5006(1)	21(1)	1
C(33)	4121(1)	6640(1)	5107(1)	20(1)	1
C(34)	5171(1)	6356(1)	5513(1)	16(1)	1
C(35)	3498(1)	6336(1)	6486(1)	17(1)	1
C(36)	3990(1)	4979(1)	6560(1)	18(1)	1
C(37)	4092(1)	4632(1)	7814(1)	21(1)	1
C(38)	2822(1)	4783(2)	7872(1)	39(1)	1
C(39)	2112(1)	4928(2)	8413(1)	56(1)	1
C(40)	2647(2)	4921(2)	8906(1)	45(1)	1
C(41)	3902(2)	4776(2)	8856(1)	44(1)	1
C(42)	4623(1)	4644(2)	8312(1)	34(1)	1
C(43)	5460(1)	2743(1)	7137(1)	18(1)	1
C(44)	5530(1)	2233(1)	6631(1)	27(1)	1
C(45)	5810(1)	1027(1)	6651(1)	32(1)	1
C(46)	6021(1)	312(1)	7173(1)	28(1)	1
C(47)	5968(2)	804(1)	7679(1)	36(1)	1
C(48)	5687(1)	2010(1)	7660(1)	31(1)	1
Na(1)	10115(1)	1207(1)	8119(1)	49(1)	1
O(5A)	8748(1)	1072(1)	8978(1)	44(1)	1
C(51A)	8097(2)	2137(2)	9251(1)	70(1)	1
C(52A)	7024(5)	2081(5)	9577(3)	53(2)	0.412(9)
C(52B)	6702(3)	2371(3)	9267(2)	51(1)	0.588(9)
C(53A)	6623(2)	1261(2)	9263(1)	62(1)	1
C(54A)	7851(2)	563(2)	8936(1)	64(1)	1
O(6A)	9848(1)	323(1)	7362(1)	46(1)	1
C(55A)	9232(1)	1009(1)	6855(1)	30(1)	1

C(56A)	9443(10)	198(8)	6393(5)	36(2)	0.355(6)
C(57A)	9645(7)	-971(9)	6769(4)	33(2)	0.355(6)
C(58A)	9625(5)	-709(3)	7434(2)	31(1)	0.355(6)
C(56B)	9669(7)	145(5)	6399(2)	45(1)	0.645(6)
C(57B)	9945(6)	-1055(5)	6757(3)	56(2)	0.645(6)
C(58B)	10438(4)	-952(2)	7208(2)	51(1)	0.645(6)
O(7A)	11431(2)	2058(2)	8590(1)	45(1)	0.510(3)
C(59A)	12796(3)	1614(3)	8451(2)	48(1)	0.510(3)
C(60A)	13317(5)	1454(6)	9042(3)	70(2)	0.510(3)
C(61A)	12264(6)	1439(5)	9494(2)	68(2)	0.510(3)
C(62A)	11149(4)	2231(4)	9201(2)	61(1)	0.510(3)
O(7B)	11194(2)	1624(2)	8788(1)	35(1)	0.490(3)
C(59B)	11667(3)	2568(3)	8728(2)	42(1)	0.490(3)
C(60B)	12967(4)	1995(4)	8933(2)	46(1)	0.490(3)
C(61B)	12889(6)	1040(4)	9374(4)	62(2)	0.490(3)
C(62B)	11702(4)	864(4)	9297(2)	54(1)	0.490(3)
O(8A)	11421(2)	-939(2)	8409(1)	30(1)	0.518(3)
C(64A)	13159(3)	-537(3)	7869(1)	39(1)	0.518(3)
C(65A)	12764(3)	-1443(3)	8263(2)	36(1)	0.518(3)
C(66A)	10893(3)	-1775(2)	8690(1)	34(1)	0.518(3)
C(67A)	11075(3)	-2070(3)	9338(1)	44(1)	0.518(3)
O(8B)	11616(3)	-412(3)	8376(2)	53(1)	0.482(3)
C(64B)	11700(5)	-989(3)	8935(2)	66(1)	0.482(3)
C(65B)	11960(4)	-2256(4)	8884(2)	59(1)	0.482(3)
C(66B)	12596(4)	-2435(3)	8258(2)	53(1)	0.482(3)
C(67B)	12599(4)	-1208(4)	7988(3)	55(1)	0.482(3)

[Na][($Ph_2P(CH_2)_2B(C8H_{14})2Re(CO)_2(=C(O–)CH_2O–)$] ([Na][3-$E_2$], ajmm29).

Table 1. Crystal data and structure refinement for AJMM23 (CCDC 687834).

Empirical formula	$C_{48}H_{58}B_2O_4P_2Re \bullet Na(C_4H_{10}O)_3$	
Formula weight	1214.05	
Crystallization Solvent	Diethylether	
Crystal Habit	Plate	
Crystal size	0.21 x 0.15 x 0.04 mm^3	
Crystal color	Colorless	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 11.5493(10) Å	a= 90.795(5)°
	b = 12.2399(10) Å	b= 100.549(5)°
	c = 22.961(2) Å	g = 113.895(5)°
Volume	2903.4(4) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.389 Mg/m^3	
q range for data collection	1.81 to 32.08°	
Completeness to θ = 32.08°	98.0 %	
Index ranges	$-17 \le h \le 17, -18 \le k \le 18, -34 \le l \le 34$	
Absorption coefficient	2.206 mm^{-1}	
Absorption correction	None	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	19892 / 0 / 664	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	2.715	
Final R indices [I>2s(I), 16074 reflections]	R1 = 0.0756, *w*R2 = 0.1263	
R indices (all data)	R1 = 0.0950, *w*R2 = 0.1273	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM23 (CCDC 687834). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	1459(1)	9357(1)	8040(1)	12(1)
P(1)	3392(1)	8986(1)	8216(1)	16(1)
P(2)	-381(1)	9865(1)	7864(1)	14(1)
O(1)	2529(4)	11181(4)	9174(2)	30(1)
O(2)	2788(4)	11247(3)	7262(2)	26(1)
O(3)	671(3)	7100(3)	7071(2)	19(1)
O(4)	203(3)	7775(3)	8441(2)	15(1)
B(1)	1614(6)	7498(5)	6608(3)	20(1)
B(2)	-824(6)	7631(5)	8842(3)	17(1)
C(1)	2106(5)	10498(5)	8751(2)	19(1)
C(2)	2291(5)	10519(4)	7566(2)	17(1)
C(3)	-249(5)	6987(4)	7906(2)	17(1)
C(4)	625(5)	7711(4)	7507(2)	16(1)
C(5)	218(5)	5282(5)	6116(3)	26(1)
C(6)	-572(6)	5715(5)	5640(3)	31(2)
C(7)	-457(6)	6989(5)	5792(3)	32(2)
C(8)	922(6)	7927(5)	6041(3)	26(1)
C(9)	1826(7)	8236(6)	5586(3)	39(2)
C(10)	2153(7)	7208(6)	5389(3)	39(2)
C(11)	2472(6)	6503(5)	5896(3)	31(2)

C(12)	1633(5)	6235(4)	6362(2)	21(1)
C(13)	3034(6)	8463(5)	6955(3)	25(1)
C(14)	3517(5)	8153(5)	7568(2)	21(1)
C(15)	4855(5)	10376(4)	8365(2)	20(1)
C(16)	5647(5)	10762(5)	7953(3)	27(1)
C(17)	6789(6)	11820(5)	8092(3)	38(2)
C(18)	7115(6)	12469(5)	8634(3)	39(2)
C(19)	6330(6)	12090(5)	9040(3)	37(2)
C(20)	5204(5)	11064(5)	8910(3)	29(1)
C(21)	3780(5)	8115(5)	8795(2)	21(1)
C(22)	2824(6)	7013(5)	8866(3)	28(1)
C(23)	3078(6)	6237(5)	9258(3)	30(1)
C(24)	4313(6)	6562(5)	9577(3)	32(1)
C(25)	5275(6)	7637(6)	9528(3)	33(2)
C(26)	5025(6)	8418(5)	9128(3)	29(1)
C(27)	1077(6)	8032(5)	9744(3)	25(1)
C(28)	619(6)	6692(5)	9808(3)	26(1)
C(29)	-373(6)	5850(4)	9264(2)	25(1)
C(30)	-1447(6)	6249(4)	8987(2)	23(1)
C(31)	-2421(5)	6093(4)	9401(2)	22(1)
C(32)	-1853(6)	6958(4)	9975(2)	25(1)
C(33)	-970(6)	8259(4)	9890(2)	23(1)
C(34)	-16(5)	8407(4)	9479(2)	20(1)
C(35)	-1892(5)	8079(4)	8492(2)	18(1)
C(36)	-1361(5)	9441(4)	8428(2)	17(1)
C(37)	-1562(5)	9293(4)	7155(2)	18(1)
C(38)	-2821(6)	9100(7)	7085(3)	49(2)
C(39)	-3658(7)	8750(7)	6528(4)	55(2)
C(40)	-3248(8)	8578(7)	6047(4)	50(2)
C(41)	-1948(9)	8788(8)	6105(3)	65(3)
C(42)	-1130(8)	9122(7)	6647(3)	49(2)
C(43)	25(5)	11474(4)	7842(2)	19(1)
C(44)	108(5)	12183(4)	8341(3)	21(1)
C(45)	425(5)	13409(5)	8319(3)	27(1)
C(46)	672(6)	13929(5)	7805(3)	31(2)
C(47)	637(7)	13245(5)	7310(3)	37(2)
C(48)	308(6)	12028(5)	7329(3)	28(1)
Na(1)	4314(3)	12807(2)	6918(1)	51(1)
O(5)	3270(6)	13093(5)	6011(2)	64(2)
C(51)	1252(9)	11370(8)	5738(4)	84(3)
C(52)	1946(8)	12645(8)	5994(4)	63(2)
C(53)	3603(9)	13430(10)	5445(4)	85(4)
C(54)	5083(10)	14067(12)	5552(6)	142(6)
O(6)	4629(4)	14189(4)	7665(2)	39(1)
C(55)	3887(8)	13719(7)	8596(4)	64(2)
C(56)	4830(7)	13762(6)	8244(3)	46(2)
C(57)	4725(8)	15375(6)	7708(4)	64(3)
C(58)	4849(9)	15826(7)	7122(4)	73(3)
O(7)	5918(5)	12434(5)	6604(3)	64(2)
C(59)	7436(8)	14348(7)	7012(4)	64(3)
C(60)	7220(8)	13215(7)	6656(4)	62(2)
C(61)	5575(12)	11190(7)	6356(5)	106(5)
C(62)	5316(9)	11160(7)	5763(4)	101(5)

$(PPh_3)_2Re(CO)_3(CHOBEt_3)$ (2-Ph_2•BEt_3, ajmm59).

Table 1. Crystal data and structure refinement for AJMM59 (CCDC 770577).

Empirical formula	$C_{46}H_{46}BO_4P_2Re \bullet C_7H_8$	
Formula weight	1013.91	
Crystallization Solvent	Toluene	
Crystal Habit	Fragment	
Crystal size	0.19 x 0.19 x 0.06 mm^3	
Crystal color	Colorless	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 14.9591(6) Å	
	b = 25.5104(9) Å	b= 105.268(2)°
	c = 25.5702(10) Å	
Volume	9413.5(6) $Å^3$	
Z	8	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Density (calculated)	1.431 Mg/m^3	
q range for data collection	1.43 to 28.89°	
Completeness to θ = 28.89°	99.7 %	
Index ranges	$-20 \le h \le 19$, $-34 \le k \le 34$, $-34 \le l \le 34$	
Absorption coefficient	2.694 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	24722 / 0 / 1107	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	1.689	
Final R indices [I>2s(I), 19590 reflections]	R1 = 0.0325, *w*R2 = 0.0499	
R indices (all data)	R1 = 0.0491, *w*R2 = 0.0515	

Special Refinement Details

The crystal contains two molecules per asymmetric unit with each molecule accompanied by a toluene solvent of crystallization.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM59 (CCDC 770577). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	7124(1)	3019(1)	6560(1)	11(1)
P(1A)	6635(1)	3000(1)	5580(1)	12(1)
P(2A)	7612(1)	3088(1)	7539(1)	12(1)
O(1A)	5428(1)	3758(1)	6516(1)	27(1)
O(2A)	5743(1)	2118(1)	6612(1)	27(1)
O(3A)	8837(1)	2319(1)	6568(1)	25(1)
O(4A)	7461(1)	4169(1)	6408(1)	22(1)
B(1A)	7928(2)	4762(1)	6421(1)	24(1)
C(1A)	6040(2)	3494(1)	6536(1)	17(1)
C(2A)	6289(2)	2433(1)	6597(1)	17(1)
C(3A)	8206(2)	2577(1)	6566(1)	16(1)
C(4A)	7863(2)	3735(1)	6522(1)	16(1)
C(5A)	5554(2)	3360(1)	5322(1)	14(1)
C(6A)	4727(2)	3120(1)	5339(1)	17(1)

C(7A)	3900(2)	3399(1)	5209(1)	22(1)
C(8A)	3892(2)	3918(1)	5060(1)	24(1)
C(9A)	4711(2)	4163(1)	5041(1)	26(1)
C(10A)	5543(2)	3887(1)	5177(1)	21(1)
C(11A)	6350(2)	2354(1)	5256(1)	13(1)
C(12A)	6665(2)	1891(1)	5538(1)	18(1)
C(13A)	6488(2)	1409(1)	5274(1)	21(1)
C(14A)	6011(2)	1387(1)	4735(1)	21(1)
C(15A)	5689(2)	1842(1)	4454(1)	21(1)
C(16A)	5849(2)	2324(1)	4713(1)	18(1)
C(17A)	7415(2)	3268(1)	5199(1)	15(1)
C(18A)	7090(2)	3396(1)	4652(1)	20(1)
C(19A)	7684(2)	3579(1)	4362(1)	23(1)
C(20A)	8621(2)	3634(1)	4611(1)	24(1)
C(21A)	8958(2)	3507(1)	5155(1)	22(1)
C(22A)	8357(2)	3324(1)	5446(1)	19(1)
C(23A)	6733(2)	3411(1)	7803(1)	14(1)
C(24A)	6128(2)	3119(1)	8023(1)	21(1)
C(25A)	5396(2)	3365(1)	8166(1)	27(1)
C(26A)	5272(2)	3900(1)	8100(1)	27(1)
C(27A)	5860(2)	4192(1)	7879(1)	23(1)
C(28A)	6581(2)	3948(1)	7725(1)	18(1)
C(29A)	7845(2)	2483(1)	7938(1)	14(1)
C(30A)	7750(2)	1987(1)	7706(1)	19(1)
C(31A)	7897(2)	1539(1)	8031(1)	23(1)
C(32A)	8146(2)	1584(1)	8587(1)	26(1)
C(33A)	8261(2)	2079(1)	8824(1)	28(1)
C(34A)	8118(2)	2522(1)	8500(1)	21(1)
C(35A)	8698(2)	3442(1)	7831(1)	13(1)
C(36A)	9491(2)	3258(1)	7696(1)	19(1)
C(37A)	10345(2)	3490(1)	7911(1)	20(1)
C(38A)	10427(2)	3911(1)	8259(1)	19(1)
C(39A)	9655(2)	4098(1)	8399(1)	18(1)
C(40A)	8795(2)	3862(1)	8191(1)	17(1)
C(41A)	7402(2)	5005(1)	5840(1)	32(1)
C(42A)	7752(2)	4829(1)	5355(1)	40(1)
C(43A)	9032(2)	4718(1)	6505(1)	26(1)
C(44A)	9641(2)	4657(1)	7089(1)	32(1)
C(45A)	7626(2)	5029(1)	6922(1)	25(1)
C(46A)	6579(2)	5109(1)	6839(1)	35(1)
Re(2)	2064(1)	2200(1)	6557(1)	11(1)
P(1B)	2583(1)	2086(1)	7530(1)	13(1)
P(2B)	1582(1)	2198(1)	5576(1)	13(1)
O(1B)	353(1)	1475(1)	6524(1)	21(1)
O(2B)	699(1)	3115(1)	6601(1)	27(1)
O(3B)	3781(1)	2906(1)	6575(1)	26(1)
O(4B)	2468(1)	1055(1)	6413(1)	17(1)
B(1B)	2982(2)	491(1)	6395(1)	19(1)
C(1B)	983(2)	1729(1)	6539(1)	16(1)
C(2B)	1235(2)	2791(1)	6591(1)	16(1)
C(3B)	3151(2)	2649(1)	6569(1)	16(1)
C(4B)	2818(2)	1501(1)	6518(1)	14(1)
C(5B)	1712(2)	1755(1)	7800(1)	15(1)
C(6B)	1178(2)	2033(1)	8079(1)	20(1)

C(7B)	450(2)	1789(1)	8224(1)	28(1)
C(8B)	255(2)	1266(1)	8102(1)	29(1)
C(9B)	785(2)	985(1)	7826(1)	25(1)
C(10B)	1497(2)	1231(1)	7669(1)	19(1)
C(11B)	2885(2)	2662(1)	7965(1)	16(1)
C(12B)	2711(2)	3168(1)	7758(1)	17(1)
C(13B)	2912(2)	3601(1)	8107(1)	22(1)
C(14B)	3294(2)	3526(1)	8654(1)	28(1)
C(15B)	3486(2)	3024(1)	8860(1)	31(1)
C(16B)	3283(2)	2596(1)	8518(1)	24(1)
C(17B)	3649(2)	1694(1)	7764(1)	14(1)
C(18B)	4433(2)	1880(1)	7627(1)	18(1)
C(19B)	5262(2)	1604(1)	7778(1)	20(1)
C(20B)	5314(2)	1139(1)	8060(1)	20(1)
C(21B)	4536(2)	952(1)	8200(1)	20(1)
C(22B)	3711(2)	1233(1)	8059(1)	16(1)
C(23B)	492(2)	1844(1)	5344(1)	14(1)
C(24B)	-330(2)	2104(1)	5342(1)	18(1)
C(25B)	-1158(2)	1829(1)	5249(1)	22(1)
C(26B)	-1172(2)	1295(1)	5158(1)	25(1)
C(27B)	-357(2)	1033(1)	5159(1)	24(1)
C(28B)	471(2)	1305(1)	5259(1)	19(1)
C(29B)	1349(2)	2829(1)	5221(1)	18(1)
C(30B)	1647(2)	3300(1)	5486(1)	19(1)
C(31B)	1530(2)	3772(1)	5197(1)	25(1)
C(32B)	1123(2)	3771(1)	4645(1)	29(1)
C(33B)	816(2)	3305(1)	4378(1)	31(1)
C(34B)	924(2)	2838(1)	4667(1)	25(1)
C(35B)	2340(2)	1892(1)	5204(1)	14(1)
C(36B)	3297(2)	1898(1)	5424(1)	18(1)
C(37B)	3886(2)	1691(1)	5138(1)	21(1)
C(38B)	3529(2)	1470(1)	4634(1)	20(1)
C(39B)	2576(2)	1465(1)	4408(1)	18(1)
C(40B)	1994(2)	1676(1)	4692(1)	17(1)
C(41B)	2552(2)	133(1)	6793(1)	30(1)
C(42B)	1498(2)	61(1)	6637(2)	48(1)
C(43B)	4092(2)	552(1)	6633(1)	22(1)
C(44B)	4659(2)	798(1)	6281(1)	35(1)
C(45B)	2637(2)	345(1)	5760(1)	26(1)
C(46B)	2988(2)	-192(1)	5623(1)	32(1)
C(51C)	3286(3)	4895(1)	6250(1)	40(1)
C(52C)	3653(3)	4505(2)	6610(2)	57(1)
C(53C)	3078(3)	4230(2)	6838(2)	66(1)
C(54C)	2135(3)	4323(1)	6713(2)	51(1)
C(55C)	1764(3)	4725(2)	6363(2)	63(1)
C(56C)	2353(2)	5017(1)	6116(2)	36(1)
C(57C)	3948(3)	5197(2)	5981(2)	58(1)
C(51D)	8396(2)	91(1)	6036(1)	30(1)
C(52D)	8814(2)	506(1)	6354(1)	34(1)
C(53D)	8349(2)	795(1)	6659(1)	41(1)
C(54D)	7460(2)	671(1)	6657(2)	41(1)
C(55D)	7024(2)	254(1)	6335(2)	47(1)
C(56D)	7494(2)	-28(1)	6033(2)	41(1)
C(57D)	8903(2)	-226(1)	5708(1)	38(1)

$[(Ph_2PCH_2B(C_8H_{14}))_2Re(CO)_4][B(C_6F_5)_4]$ ($[1\text{-}M_2][B(C_6F_5)_4]$, ajmm43).

Table 1. Crystal data and structure refinement for AJMM43 (CCDC 768445).

Empirical formula	$[C_{46}H_{52}B_2O_4P_2Re]^+ [C_{24}BF_{20}]^- \bullet C_2H_4Cl_2$
Formula weight	1716.64
Crystallization Solvent	Dichloroethane
Crystal Habit	Block
Crystal size	0.26 x 0.21 x 0.14 mm^3
Crystal color	Colorless
Data Collection Temperature	100(2) K
Unit cell dimensions	a = 16.0785(8) Å
	b = 19.3393(9) Å b= 90.578(2)°
	c = 22.2924(10) Å
Volume	6931.4(6) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	P $2_1/n$
Density (calculated)	1.645 Mg/m^3
q range for data collection	1.88 to 36.56°
Completeness to θ = 36.56°	86.5 %
Index ranges	$-23 \le h \le 25$, $-28 \le k \le 31$, $-36 \le l \le 36$
Absorption coefficient	1.980 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	29574 / 117 / 983
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.971
Final R indices [I>2s(I), 24164 reflections]	R1 = 0.0371, *w*R2 = 0.0708
R indices (all data)	R1 = 0.0515, *w*R2 = 0.0713

Special Refinement Details

One of the borabicylcononane ligands is disordered by a rotation around the B-C bond. Both the minor (34%) and major (66%) components were restrained to the same geometry as the ordered ligand. The minor component was refined as isotropic and the major component was refined as anisotropic but was restrained to simulate isotropic behavior. The dichloroethane solvent of crystallization was also disordered with both orientations apparently sharing one common Cl site and the ethyl portion flipped about the approximated Cl-Cl vector. The minor component (34%) was refined isotropically and the major component (66%) anisotropically; no geometry restraints were imposed.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM43 (CCDC 768445). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Re(1)	2798(1)	8597(1)	5895(1)	13(1)	1
P(1)	3164(1)	7812(1)	5075(1)	14(1)	1
P(2)	2388(1)	9494(1)	6610(1)	15(1)	1
O(1)	1562(1)	7577(1)	6497(1)	32(1)	1
O(2)	4156(1)	7916(1)	6715(1)	32(1)	1
O(3)	4159(1)	9649(1)	5463(1)	24(1)	1
O(4)	1352(1)	9123(1)	5055(1)	26(1)	1
C(1)	2001(2)	7949(1)	6260(1)	20(1)	1
C(2)	3671(2)	8176(1)	6416(1)	20(1)	1

C(3)	3657(1)	9272(1)	5597(1)	18(1)	1
C(4)	1890(2)	8953(1)	5354(1)	18(1)	1
C(5)	3959(1)	8200(1)	4603(1)	16(1)	1
C(6)	4795(2)	8171(1)	4779(1)	21(1)	1
C(7)	5397(2)	8484(1)	4428(1)	25(1)	1
C(8)	5168(2)	8832(1)	3905(1)	23(1)	1
C(9)	4346(2)	8871(1)	3735(1)	21(1)	1
C(10)	3740(1)	8558(1)	4082(1)	18(1)	1
C(11)	3604(1)	6976(1)	5276(1)	17(1)	1
C(12)	4053(2)	6603(1)	4856(1)	23(1)	1
C(13)	4347(2)	5948(1)	4994(1)	30(1)	1
C(14)	4203(2)	5660(1)	5547(1)	30(1)	1
C(15)	3752(2)	6020(1)	5970(1)	27(1)	1
C(16)	3452(2)	6676(1)	5835(1)	21(1)	1
C(17)	2338(1)	7574(1)	4547(1)	17(1)	1
B(1)	1715(2)	6994(1)	4782(1)	20(1)	1
C(18)	1820(2)	6227(1)	4641(1)	22(1)	1
C(19)	1479(2)	5736(1)	5122(1)	28(1)	1
C(20)	1114(2)	6114(1)	5649(1)	36(1)	1
C(21)	493(2)	6662(1)	5487(1)	35(1)	1
C(22)	802(2)	7180(1)	5011(1)	27(1)	1
C(23)	325(2)	7122(1)	4421(1)	32(1)	1
C(24)	400(2)	6407(1)	4123(1)	31(1)	1
C(25)	1282(2)	6187(1)	4040(1)	26(1)	1
C(26)	1853(2)	10193(1)	6209(1)	19(1)	1
C(27)	2319(2)	10675(1)	5892(1)	29(1)	1
C(28)	1918(2)	11175(1)	5544(1)	44(1)	1
C(29)	1061(2)	11200(2)	5516(1)	48(1)	1
C(30)	597(2)	10723(1)	5832(1)	41(1)	1
C(31)	998(2)	10221(1)	6176(1)	30(1)	1
C(32)	3189(1)	9960(1)	7028(1)	17(1)	1
C(33)	3993(1)	9706(1)	7101(1)	19(1)	1
C(34)	4576(2)	10061(1)	7449(1)	24(1)	1
C(35)	4362(2)	10676(1)	7724(1)	26(1)	1
C(36)	3564(2)	10934(1)	7651(1)	30(1)	1
C(37)	2977(2)	10583(1)	7308(1)	25(1)	1
C(38)	1655(1)	9232(1)	7183(1)	21(1)	1
B(2A)	1942(2)	8780(1)	7730(1)	33(1)	0.343(3)
C(39A)	1781(4)	8026(2)	7893(3)	49(2)	0.343(3)
C(40A)	2547(6)	7591(4)	8063(5)	206(13)	0.343(3)
C(41A)	3094(7)	7905(5)	8543(5)	94(4)	0.343(3)
C(42A)	3304(5)	8645(5)	8422(6)	138(8)	0.343(3)
C(43A)	2553(4)	9095(3)	8233(3)	70(4)	0.343(3)
C(44A)	1947(6)	9212(4)	8740(4)	79(5)	0.343(3)
C(45A)	1432(6)	8581(4)	8935(3)	57(3)	0.343(3)
C(46A)	1167(5)	8106(5)	8443(3)	62(4)	0.343(3)
B(2B)	1942(2)	8780(1)	7730(1)	33(1)	0.657(3)
C(39B)	2744(2)	8403(2)	7893(1)	40(1)	0.657(3)
C(40B)	2638(3)	7641(2)	8069(2)	49(2)	0.657(3)
C(41B)	1926(3)	7481(3)	8478(3)	78(2)	0.657(3)
C(42B)	1118(3)	7809(2)	8301(3)	106(3)	0.657(3)
C(43B)	1169(2)	8586(2)	8145(2)	67(2)	0.657(3)
C(44B)	1400(3)	9042(3)	8674(2)	86(2)	0.657(3)
C(45B)	2319(3)	9066(4)	8871(2)	87(2)	0.657(3)

C(46B)	2998(4)	8869(3)	8453(2)	119(3)	0.657(3)
B(3)	1787(2)	9973(1)	2479(1)	15(1)	1
F(1)	3560(1)	9472(1)	2231(1)	24(1)	1
F(2)	4116(1)	9041(1)	1195(1)	37(1)	1
F(3)	3114(1)	9010(1)	203(1)	34(1)	1
F(4)	1507(1)	9459(1)	289(1)	30(1)	1
F(5)	930(1)	9927(1)	1332(1)	23(1)	1
F(6)	1818(1)	11156(1)	1547(1)	28(1)	1
F(7)	1180(1)	12389(1)	1707(1)	52(1)	1
F(8)	301(1)	12706(1)	2710(1)	60(1)	1
F(9)	53(1)	11699(1)	3553(1)	38(1)	1
F(10)	712(1)	10455(1)	3413(1)	23(1)	1
F(11)	2398(1)	8626(1)	2828(1)	25(1)	1
F(12)	1543(1)	7470(1)	2988(1)	37(1)	1
F(13)	-151(1)	7466(1)	2871(1)	39(1)	1
F(14)	-951(1)	8658(1)	2550(1)	34(1)	1
F(15)	-109(1)	9815(1)	2374(1)	23(1)	1
F(16)	3208(1)	10879(1)	2361(1)	23(1)	1
F(17)	4266(1)	11296(1)	3213(1)	32(1)	1
F(18)	4083(1)	10859(1)	4366(1)	38(1)	1
F(19)	2839(1)	9957(1)	4632(1)	33(1)	1
F(20)	1838(1)	9474(1)	3793(1)	24(1)	1
C(51)	2216(1)	9753(1)	1837(1)	15(1)	1
C(52)	3014(1)	9500(1)	1766(1)	18(1)	1
C(53)	3326(2)	9261(1)	1227(1)	23(1)	1
C(54)	2824(2)	9256(1)	727(1)	24(1)	1
C(55)	2016(2)	9484(1)	769(1)	21(1)	1
C(56)	1729(1)	9723(1)	1317(1)	18(1)	1
C(57)	1287(1)	10718(1)	2465(1)	16(1)	1
C(58)	1379(2)	11250(1)	2054(1)	22(1)	1
C(59)	1058(2)	11906(1)	2127(1)	33(1)	1
C(60)	615(2)	12066(1)	2631(1)	36(1)	1
C(61)	490(2)	11560(1)	3053(1)	27(1)	1
C(62)	827(1)	10915(1)	2965(1)	19(1)	1
C(63)	1189(1)	9295(1)	2616(1)	16(1)	1
C(64)	1562(2)	8663(1)	2763(1)	19(1)	1
C(65)	1129(2)	8057(1)	2849(1)	26(1)	1
C(66)	282(2)	8050(1)	2787(1)	27(1)	1
C(67)	-122(2)	8653(1)	2627(1)	24(1)	1
C(68)	340(1)	9252(1)	2541(1)	19(1)	1
C(69)	2470(1)	10140(1)	3019(1)	15(1)	1
C(70)	3104(1)	10614(1)	2918(1)	18(1)	1
C(71)	3652(2)	10848(1)	3352(1)	22(1)	1
C(72)	3566(2)	10626(1)	3934(1)	25(1)	1
C(73)	2940(2)	10175(1)	4062(1)	22(1)	1
C(74)	2421(1)	9936(1)	3614(1)	18(1)	1
Cl(2)	4306(1)	3070(1)	3839(1)	69(1)	1
Cl(1C)	1876(1)	2234(1)	4081(1)	79(1)	0.661(6)
C(81C)	3264(3)	2757(2)	3663(2)	40(1)	0.661(6)
C(82C)	2941(3)	2492(3)	4239(2)	51(2)	0.661(6)
Cl(1D)	1869(11)	2162(9)	4066(7)	371(11)	0.339(6)
C(81D)	2810(6)	2554(4)	3677(3)	28(2)	0.339(6)
C(82D)	3473(5)	2678(3)	4170(3)	17(2)	0.339(6)

[(Ph$_2$PCH$_2$B(C$_8$H$_{14}$))Re(CO)$_5$][OTf] ([1-M$_1$][OTf] ajmm45).

Table 1. Crystal data and structure refinement for AJMM45 (CCDC 779779).

Empirical formula	$[C_{26}H_{26}BO_5PRe]^+ [CF_3O_3S]^-$	
Formula weight	795.52	
Crystallization Solvent	Dichloromethane/pentane	
Crystal Habit	Block	
Crystal size	0.25 x 0.21 x 0.09 mm^3	
Crystal color	Colorless	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 17.3374(4) Å	a= 85.9010(10)°
	b = 17.3374(4) Å	b= 85.9010(10)°
	c = 17.3374(4) Å	g = 85.9010(10)°
Volume	5173.2(2) Å^3	
Z	6	
Crystal system	Rhombohedral	
Space group	R -3	
Density (calculated)	1.532 Mg/m^3	
Completeness to θ = 37.73°	94.6 %	
Index ranges	-26 ≤ h ≤ 29, -26 ≤ k ≤ 29, -29 ≤ l ≤ 28	
Absorption coefficient	3.687 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	17454 / 0 / 440	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	2.593	
Final R indices [I>2s(I), 14238 reflections]	R1 = 0.0328, *w*R2 = 0.0541	
R indices (all data)	R1 = 0.0432, *w*R2 = 0.0547	

Special Refinement Details

SQUEEZE[1] was used to model disordered solvent. A void near the origin, volume = 867 Å^3, presumably filled with dichloromethane and pentane, was accounted for by 309e$^-$. The two phenyl rings are disordered by rotation around the P-C bond. Each was constrained to a regular hexagon.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for AJMM45 (CCDC 779779). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Re(1)	3232(1)	6057(1)	3009(1)	17(1)	1
P(1)	2116(1)	7035(1)	2933(1)	21(1)	1
O(1)	4341(1)	7337(1)	2316(1)	30(1)	1
O(2)	3122(1)	5574(1)	1315(1)	54(1)	1
O(3)	2062(1)	4807(1)	3598(1)	36(1)	1
O(4)	3517(1)	6401(1)	4718(1)	25(1)	1
O(5)	4600(1)	4831(1)	3254(1)	32(1)	1
B(1)	1369(1)	8316(1)	3775(1)	26(1)	1
C(1)	3949(1)	6880(1)	2576(1)	23(1)	1
C(2)	3150(1)	5762(1)	1925(1)	33(1)	1
C(3)	2478(1)	5264(1)	3401(1)	25(1)	1
C(4)	3381(1)	6309(1)	4107(1)	19(1)	1
C(5)	4110(1)	5280(1)	3138(1)	23(1)	1

C(6)	1948(1)	7581(1)	3792(1)	21(1)	1
C(7)	565(1)	8436(1)	3415(2)	42(1)	1
C(8)	-15(1)	8347(2)	4147(2)	65(1)	1
C(9)	112(2)	8870(2)	4812(2)	58(1)	1
C(10)	952(2)	8899(1)	4976(2)	47(1)	1
C(11)	1511(1)	9008(1)	4265(2)	40(1)	1
C(12)	1401(2)	9784(2)	3810(2)	66(1)	1
C(13)	705(3)	9912(2)	3372(2)	92(1)	1
C(14)	487(2)	9224(2)	2974(2)	82(1)	1
C(15A)	2407(2)	7761(3)	2119(2)	18(1)	0.358(2)
C(16A)	2512(2)	7539(2)	1362(2)	23(1)	0.358(2)
C(17A)	2777(3)	8059(2)	772(2)	33(1)	0.358(2)
C(18A)	2938(3)	8801(2)	939(3)	42(2)	0.358(2)
C(19A)	2834(3)	9023(2)	1696(3)	50(3)	0.358(2)
C(20A)	2569(3)	8503(3)	2286(2)	22(2)	0.358(2)
C(15B)	2139(2)	7789(2)	2172(2)	44(1)	0.642(2)
C(16B)	1668(2)	7839(2)	1552(2)	91(2)	0.642(2)
C(17B)	1739(2)	8435(3)	976(2)	150(4)	0.642(2)
C(18B)	2281(3)	8981(3)	1020(3)	197(6)	0.642(2)
C(19B)	2752(2)	8931(2)	1640(3)	110(4)	0.642(2)
C(20B)	2681(2)	8335(3)	2216(2)	56(2)	0.642(2)
C(21A)	1213(2)	6700(2)	2709(2)	13(1)	0.358(2)
C(22A)	860(3)	6242(3)	3304(2)	22(1)	0.358(2)
C(23A)	154(3)	5941(3)	3204(2)	30(2)	0.358(2)
C(24A)	-197(2)	6098(3)	2509(3)	33(2)	0.358(2)
C(25A)	156(2)	6556(3)	1914(2)	38(2)	0.358(2)
C(26A)	862(2)	6857(2)	2014(2)	29(1)	0.358(2)
C(21B)	1232(1)	6507(2)	2854(1)	23(1)	0.642(2)
C(22B)	663(2)	6437(2)	3457(1)	23(1)	0.642(2)
C(23B)	44(1)	5985(2)	3390(1)	30(1)	0.642(2)
C(24B)	-7(1)	5603(2)	2719(2)	57(2)	0.642(2)
C(25B)	562(1)	5673(2)	2115(2)	73(2)	0.642(2)
C(26B)	1181(1)	6125(2)	2183(1)	57(2)	0.642(2)
C(41)	5806(1)	618(2)	6182(1)	39(1)	1
F(1)	5360(1)	140(1)	5898(1)	56(1)	1
F(2)	6539(1)	330(1)	6074(1)	63(1)	1
F(3)	5645(1)	607(1)	6949(1)	74(1)	1
O(6)	4878(1)	1820(1)	5966(1)	30(1)	1
O(7)	6232(1)	2010(1)	6106(1)	41(1)	1
O(8)	5849(1)	1512(1)	4933(1)	35(1)	1
S(1)	5677(1)	1604(1)	5746(1)	23(1)	1

$[(Ph_2P(CH_2)_2B(C_8H_{14}))_2Re(CO)_4]_2$-*m*-$(OH)_2$ (8, ajmm42).

Table 1. Crystal data and structure refinement for AJMM42 (CCDC 768183).

Empirical formula	$C_{96}H_{112}B_4O_{10}P_4Re_2 \bullet 0.42(C_5H_{12}) \bullet 2.58(C_6H_6)$
Formula weight	2197.16
Crystallization Solvent	Benzene/pentane/heptane
Crystal Habit	Fragment
Crystal size	0.21 x 0.15 x 0.11 mm^3
Crystal color	Colorless
Data Collection Temperature	100(2) K
Unit cell dimensions	a = 15.2592(6) Å
	b = 27.8836(12) Å b= 98.936(2)°
	c = 25.0134(11) Å
Volume	10513.6(8) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	P $2_1/n$
Density (calculated)	1.388 Mg/m^3
Completeness to θ = 29.89°	90.2 %
Index ranges	$-20 \le h \le 21$, $-38 \le k \le 33$, $-35 \le l \le 33$
Absorption coefficient	2.419 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	27378 / 0 / 1186
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.100
Final R indices [I>2s(I), 22663 reflections]	R1 = 0.0332, *w*R2 = 0.0504
R indices (all data)	R1 = 0.0463, *w*R2 = 0.0510

Special Refinement Details

There are three sites containing solvent, two contain benzene only. The third site is a mixture of benzene and pentane. The benzene in this site was restrained to an ideal hexagon and the pentane had no restraints applied.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM42 (CCDC 768183). U(eq) is defined at he trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Re(1)	3351(1)	6419(1)	3945(1)	18(1)	1
Re(2)	1546(1)	9026(1)	3821(1)	18(1)	1
P(1)	2306(1)	6227(1)	4561(1)	22(1)	1
P(2)	4392(1)	6613(1)	3323(1)	17(1)	1
P(3)	2982(1)	9387(1)	4179(1)	17(1)	1
P(4)	35(1)	8764(1)	3472(1)	19(1)	1
O(1)	2618(1)	7471(1)	3852(1)	27(1)	1
O(2)	1979(1)	5996(1)	3004(1)	36(1)	1
O(3)	4127(2)	5380(1)	4058(1)	53(1)	1
O(4)	4834(1)	6591(1)	4936(1)	38(1)	1
O(5)	2442(1)	8370(1)	3043(1)	34(1)	1
O(6)	1234(1)	9841(1)	2955(1)	43(1)	1
O(7)	768(1)	9657(1)	4675(1)	34(1)	1
O(8)	1735(1)	8140(1)	4603(1)	29(1)	1

O(9)	5530(1)	8237(1)	4024(1)	21(1)	1
O(10)	-578(1)	7075(1)	3694(1)	25(1)	1
B(1)	-251(2)	6957(1)	4324(1)	32(1)	1
B(2)	5355(2)	8071(1)	3406(1)	21(1)	1
B(3)	5026(2)	8335(1)	4530(1)	18(1)	1
B(4)	-247(2)	7267(1)	3158(1)	26(1)	1
C(1)	2868(2)	7081(1)	3875(1)	21(1)	1
C(2)	2462(2)	6173(1)	3340(1)	23(1)	1
C(3)	3836(2)	5755(1)	4014(1)	32(1)	1
C(4)	4286(2)	6560(1)	4572(1)	25(1)	1
C(5)	2110(2)	8611(1)	3318(1)	24(1)	1
C(6)	1354(2)	9549(1)	3272(1)	27(1)	1
C(7)	1039(2)	9426(1)	4362(1)	23(1)	1
C(8)	1682(2)	8468(1)	4329(1)	22(1)	1
C(9)	1124(2)	6332(1)	4312(1)	26(1)	1
C(10)	821(2)	6857(1)	4386(1)	32(1)	1
C(11)	-506(2)	7402(1)	4694(1)	36(1)	1
C(12)	-1501(2)	7532(1)	4516(1)	41(1)	1
C(13)	-2151(2)	7112(1)	4532(1)	45(1)	1
C(14)	-1849(2)	6638(1)	4332(1)	41(1)	1
C(15)	-852(2)	6522(1)	4487(1)	34(1)	1
C(16)	-604(2)	6407(1)	5091(1)	42(1)	1
C(17)	-695(2)	6825(1)	5487(1)	46(1)	1
C(18)	-293(2)	7291(1)	5299(1)	42(1)	1
C(19)	2415(2)	6521(1)	5216(1)	22(1)	1
C(20)	2811(2)	6963(1)	5322(1)	27(1)	1
C(21)	2725(2)	7211(1)	5793(1)	36(1)	1
C(22)	2228(2)	7021(1)	6156(1)	37(1)	1
C(23)	1836(2)	6581(1)	6056(1)	36(1)	1
C(24)	1932(2)	6325(1)	5598(1)	29(1)	1
C(25)	2413(2)	5596(1)	4742(1)	29(1)	1
C(26)	1850(2)	5254(1)	4466(1)	43(1)	1
C(27)	1991(3)	4771(1)	4583(2)	62(1)	1
C(28)	2685(3)	4629(1)	4970(2)	68(1)	1
C(29)	3245(3)	4966(1)	5251(1)	59(1)	1
C(30)	3105(2)	5448(1)	5131(1)	40(1)	1
C(31)	5154(2)	6118(1)	3261(1)	18(1)	1
C(32)	4868(2)	5716(1)	2951(1)	26(1)	1
C(33)	5433(2)	5328(1)	2928(1)	32(1)	1
C(34)	6283(2)	5342(1)	3204(1)	36(1)	1
C(35)	6571(2)	5735(1)	3508(1)	36(1)	1
C(36)	6011(2)	6121(1)	3539(1)	26(1)	1
C(37)	3940(2)	6757(1)	2623(1)	17(1)	1
C(38)	4509(2)	6746(1)	2235(1)	23(1)	1
C(39)	4234(2)	6919(1)	1719(1)	28(1)	1
C(40)	3396(2)	7106(1)	1578(1)	28(1)	1
C(41)	2820(2)	7115(1)	1956(1)	28(1)	1
C(42)	3099(2)	6944(1)	2476(1)	21(1)	1
C(43)	5113(2)	7129(1)	3512(1)	19(1)	1
C(44)	4678(2)	7618(1)	3362(1)	20(1)	1
C(45)	6330(2)	7968(1)	3242(1)	21(1)	1
C(46)	6211(2)	7810(1)	2646(1)	26(1)	1
C(47)	5720(2)	8169(1)	2249(1)	32(1)	1
C(48)	4889(2)	8380(1)	2423(1)	28(1)	1

C(49)	4982(2)	8525(1)	3026(1)	23(1)	1
C(50)	5575(2)	8966(1)	3173(1)	28(1)	1
C(51)	6558(2)	8886(1)	3130(1)	32(1)	1
C(52)	6937(2)	8406(1)	3356(1)	28(1)	1
C(53)	3067(2)	9976(1)	3872(1)	20(1)	1
C(54)	3631(2)	10061(1)	3496(1)	28(1)	1
C(55)	3607(2)	10497(1)	3228(1)	41(1)	1
C(56)	3026(2)	10849(1)	3328(1)	41(1)	1
C(57)	2467(2)	10776(1)	3704(1)	32(1)	1
C(58)	2499(2)	10344(1)	3977(1)	26(1)	1
C(59)	3198(2)	9512(1)	4904(1)	17(1)	1
C(60)	3782(2)	9876(1)	5104(1)	21(1)	1
C(61)	4029(2)	9939(1)	5653(1)	25(1)	1
C(62)	3706(2)	9638(1)	6018(1)	27(1)	1
C(63)	3117(2)	9282(1)	5828(1)	25(1)	1
C(64)	2859(2)	9220(1)	5275(1)	21(1)	1
C(65)	3979(2)	9061(1)	4085(1)	19(1)	1
C(66)	4042(2)	8552(1)	4317(1)	18(1)	1
C(67)	5689(2)	8682(1)	4923(1)	20(1)	1
C(68)	6612(2)	8449(1)	5084(1)	25(1)	1
C(69)	6605(2)	7945(1)	5321(1)	29(1)	1
C(70)	5897(2)	7615(1)	5015(1)	30(1)	1
C(71)	4974(2)	7845(1)	4875(1)	24(1)	1
C(72)	4563(2)	7957(1)	5388(1)	34(1)	1
C(73)	4978(2)	8381(1)	5732(1)	34(1)	1
C(74)	5250(2)	8808(1)	5417(1)	26(1)	1
C(75)	-745(2)	9096(1)	3815(1)	20(1)	1
C(76)	-939(2)	9570(1)	3684(1)	27(1)	1
C(77)	-1470(2)	9839(1)	3972(1)	32(1)	1
C(78)	-1807(2)	9631(1)	4396(1)	32(1)	1
C(79)	-1629(2)	9166(1)	4531(1)	30(1)	1
C(80)	-1098(2)	8890(1)	4242(1)	25(1)	1
C(81)	-370(2)	8867(1)	2757(1)	21(1)	1
C(82)	193(2)	8834(1)	2367(1)	34(1)	1
C(83)	-151(2)	8851(1)	1821(1)	49(1)	1
C(84)	-1041(2)	8921(1)	1657(1)	43(1)	1
C(85)	-1600(2)	8966(1)	2034(1)	35(1)	1
C(86)	-1268(2)	8935(1)	2579(1)	26(1)	1
C(87)	-246(2)	8140(1)	3558(1)	23(1)	1
C(88)	288(2)	7771(1)	3293(1)	24(1)	1
C(89)	332(2)	6858(1)	2912(1)	32(1)	1
C(90)	600(2)	7049(1)	2387(1)	48(1)	1
C(91)	-165(2)	7237(1)	1969(1)	58(1)	1
C(92)	-899(2)	7522(1)	2196(1)	50(1)	1
C(93)	-1144(2)	7323(1)	2721(1)	34(1)	1
C(94)	-1661(2)	6851(1)	2642(1)	44(1)	1
C(95)	-1115(2)	6417(1)	2495(1)	51(1)	1
C(96)	-186(2)	6381(1)	2836(1)	40(1)	1
C(1A)	4461(4)	4097(1)	8574(2)	79(2)	1
C(2A)	4850(3)	4023(1)	9124(2)	68(1)	1
C(3A)	4537(2)	3656(1)	9404(1)	47(1)	1
C(4A)	3877(2)	3369(1)	9159(1)	50(1)	1
C(5A)	3503(2)	3437(2)	8637(2)	67(1)	1
C(6A)	3777(3)	3795(2)	8348(2)	76(2)	1

C(1B)	5504(4)	9619(2)	1710(2)	112(2)	1
C(2B)	5879(4)	10047(2)	1840(2)	118(2)	1
C(3B)	6038(3)	10324(2)	1417(2)	85(1)	1
C(4B)	5860(3)	10161(2)	878(2)	70(1)	1
C(5B)	5489(3)	9742(2)	774(2)	70(1)	1
C(6B)	5311(3)	9460(2)	1188(2)	80(1)	1
C(1D)	2608(3)	9009(2)	1920(2)	80(2)	0.576(4)
C(2D)	2073(3)	9345(2)	1616(2)	91(3)	0.576(4)
C(3D)	1598(3)	9217(2)	1116(2)	77(2)	0.576(4)
C(4D)	1659(3)	8754(2)	921(2)	84(3)	0.576(4)
C(5D)	2195(4)	8418(2)	1226(3)	122(4)	0.576(4)
C(6D)	2670(4)	8545(2)	1725(3)	224(9)	0.576(4)
C(1E)	2819(7)	9773(4)	2014(4)	100(4)	0.424(4)
C(2E)	2863(9)	9309(5)	2064(5)	134(5)	0.424(4)
C(3E)	2415(7)	8966(3)	1574(4)	72(3)	0.424(4)
C(4E)	2387(8)	8491(3)	1677(3)	63(3)	0.424(4)
C(5E)	1818(7)	8244(4)	1151(4)	78(3)	0.424(4)

Dinuclear alkyl-dioxycarbene Compound 11 (ajmm55).

Table 1. Crystal data and structure refinement for AJMM55 (CCDC 776949).

Empirical formula	$C_{44}H_{39}BO_{10}P_2Re_2$	
Formula weight	1172.90	
Crystallization Solvent	Dichloromethane/Toluene	
Crystal Habit	Fragment	
Crystal size	0.10 x 0.09 x 0.03 mm^3	
Crystal color	Colorless	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 15.776(2) Å	a= 90°
	b = 16.5631(19) Å	b= 90.322(5)°
	c = 16.523(2) Å	g = 90°
Volume	4317.5(9) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Density (calculated)	1.804 Mg/m^3	
q range for data collection	1.74 to 26.41°	
Completeness to θ = 26.41°	98.1 %	
Absorption coefficient	5.733 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	8714 / 12 / 532	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	1.229	
Final R indices [I>2s(I), 4950 reflections]	R1 = 0.0658, *w*R2 = 0.0941	
R indices (all data)	R1 = 0.1423, *w*R2 = 0.1068	

Special Refinement Details

This is a small and weakly diffracting crystal. Restraints were placed on the ADP's of atoms C19 and C25 keep them fro going non-positive definite during refinement.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM55 (CCDC 776949). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	6728(1)	10615(1)	6770(1)	21(1)
Re(2)	8595(1)	8846(1)	4369(1)	28(1)
P(1)	6569(2)	9536(2)	7797(2)	20(1)
P(2)	7988(2)	9338(2)	3095(2)	29(1)
O(1)	6538(6)	12008(5)	8023(6)	62(3)
O(2)	7207(6)	11874(5)	5452(6)	46(3)
O(3)	4811(5)	10761(4)	6286(5)	36(2)
O(4)	8691(5)	10374(5)	6954(6)	45(3)
O(5)	10382(6)	8206(5)	3971(6)	53(3)
O(6)	7907(7)	7114(6)	4256(9)	127(7)
O(7)	9235(6)	10617(5)	4576(6)	52(3)
O(8)	8780(6)	8647(5)	6239(6)	61(3)
O(9)	7154(5)	9938(5)	5168(5)	34(2)
O(10)	6547(5)	8952(4)	5845(4)	26(2)
B(1)	6062(9)	8448(7)	6519(7)	19(3)

C(1)	6614(8)	11473(6)	7575(7)	27(3)
C(2)	7002(7)	11407(6)	5905(8)	27(3)
C(3)	5511(9)	10700(6)	6504(7)	27(3)
C(4)	7953(8)	10470(5)	6924(7)	25(3)
C(5)	9707(9)	8442(7)	4122(9)	45(4)
C(6)	8134(9)	7765(8)	4258(11)	65(5)
C(7)	9012(7)	9962(7)	4505(7)	28(3)
C(8)	8731(9)	8691(8)	5502(10)	54(5)
C(9)	6805(8)	9664(6)	5844(8)	28(3)
C(10)	6109(8)	7521(6)	6157(7)	33(4)
C(11)	5660(8)	6965(6)	6777(8)	35(4)
C(12)	4756(8)	7167(6)	6937(8)	41(4)
C(13)	4603(8)	8095(6)	7114(7)	31(3)
C(14)	5080(7)	8665(6)	6546(7)	24(3)
C(15)	4727(7)	8673(6)	5681(7)	33(3)
C(16)	4828(8)	7863(6)	5212(7)	34(4)
C(17)	5723(8)	7487(6)	5325(7)	33(4)
C(18)	6616(7)	8539(5)	7342(6)	25(3)
C(19)	7416(7)	9570(5)	8567(6)	14(3)
C(20)	7834(7)	8879(6)	8815(7)	33(3)
C(21)	8437(8)	8908(6)	9417(7)	39(4)
C(22)	8617(8)	9630(7)	9789(7)	41(4)
C(23)	8202(8)	10301(7)	9565(8)	38(4)
C(24)	7588(7)	10304(6)	8970(7)	29(3)
C(25)	5636(8)	9544(6)	8428(7)	26(3)
C(26)	5538(8)	8953(7)	9006(8)	34(3)
C(27)	4833(10)	8904(8)	9496(8)	50(4)
C(28)	4180(8)	9472(8)	9400(8)	42(4)
C(29)	4266(9)	10083(8)	8839(8)	45(4)
C(30)	5009(7)	10135(6)	8354(7)	26(3)
C(31)	7207(8)	9927(6)	3665(7)	33(3)
C(32)	7266(9)	9368(8)	4477(8)	46(4)
C(33)	7386(8)	8673(7)	2419(8)	33(3)
C(34)	6677(8)	8288(6)	2681(8)	38(4)
C(35)	6200(9)	7779(7)	2177(9)	43(4)
C(36)	6494(10)	7686(7)	1391(9)	52(5)
C(37)	7190(9)	8081(8)	1094(9)	52(4)
C(38)	7642(8)	8576(7)	1608(8)	45(4)
C(39)	8573(8)	10016(6)	2455(7)	27(3)
C(40)	8175(8)	10578(7)	1988(7)	38(4)
C(41)	8648(9)	11142(7)	1534(9)	44(4)
C(42)	9510(10)	11073(7)	1523(8)	54(4)
C(43)	9907(9)	10476(7)	1954(8)	46(4)
C(44)	9439(8)	9965(7)	2429(7)	32(3)

[Na][($Ph_2PCH_2B(C_8H_{14})$)$Re(CO)_3(C(O)CH_2O–)$] ([Na][3-M_1], ajmm64).

Table 1. Crystal data and structure refinement for AJMM64 (CCDC 781654).

Empirical formula	$[C_{26}H_{28}BO_5PRe]^+ [Na]^- \bullet 3(C_4H_8O)$	
Formula weight	887.77	
Crystallization Solvent	Pentane/deuterobenzene	
Crystal Habit	Fragment	
Crystal size	0.17 x 0.11 x 0.02 mm^3	
Crystal color	Colorless	
Data Collection Temperature	100(2) K	
q range for 9975 reflections used in lattice determination	2.24 to 25.40°	
Unit cell dimensions	a = 11.6537(4) Å	a= 90°
	b = 27.6665(9) Å	b= 96.479(2)°
	c = 12.1243(4) Å	g = 90°
Volume	3884.1(2) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Density (calculated)	1.518 Mg/m^3	
q range for data collection	1.84 to 27.72°	
Completeness to θ = 27.72°	89.9 %	
Index ranges	$-14 \le h \le 14$, $-35 \le k \le 34$, $-14 \le l \le 15$	
Absorption coefficient	3.230 mm^{-1}	
Absorption correction	Gaussian	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	8198 / 0 / 451	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	1.487	
Final R indices [I>2s(I), 6185 reflections]	R1 = 0.0401, *w*R2 = 0.0514	
R indices (all data)	R1 = 0.0624, *w*R2 = 0.0528	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM64 (CCDC 781654). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	2791(1)	3559(1)	2115(1)	16(1)
P(1)	3896(1)	4127(1)	1068(1)	14(1)
Na(1)	6474(2)	2740(1)	4390(1)	28(1)
O(1)	1769(3)	2847(1)	3710(3)	39(1)
O(2)	2932(3)	2714(1)	519(3)	32(1)
O(3)	356(3)	3808(1)	909(3)	31(1)
O(4)	3087(2)	4161(1)	3308(2)	16(1)
O(5)	5107(3)	3232(1)	3579(3)	29(1)
O(6)	7883(3)	3244(1)	3973(3)	35(1)
O(7)	5498(3)	2672(1)	5948(3)	39(1)
O(8)	6166(3)	2145(1)	3094(3)	66(1)
B(1)	3159(4)	4696(2)	2878(4)	15(1)
C(1)	2111(4)	3126(2)	3114(4)	28(1)
C(2)	2868(4)	3046(2)	1151(4)	25(1)
C(3)	1287(4)	3731(1)	1342(4)	21(1)
C(4)	4114(4)	3962(2)	3914(3)	22(1)

C(5)	4310(3)	3501(2)	3262(3)	19(1)
C(6)	3635(4)	5059(1)	3874(3)	16(1)
C(7)	2884(4)	5004(2)	4840(3)	20(1)
C(8)	1586(4)	5083(2)	4518(3)	23(1)
C(9)	1113(3)	4826(2)	3438(3)	18(1)
C(10)	1866(3)	4871(1)	2473(3)	14(1)
C(11)	1898(4)	5386(1)	1999(3)	19(1)
C(12)	2526(3)	5761(1)	2784(3)	20(1)
C(13)	3662(4)	5577(1)	3419(3)	20(1)
C(14)	4076(3)	4670(1)	1916(3)	15(1)
C(15)	3261(3)	4327(1)	-311(3)	13(1)
C(16)	2177(4)	4546(1)	-425(3)	16(1)
C(17)	1664(4)	4705(1)	-1441(3)	19(1)
C(18)	2232(4)	4646(2)	-2375(4)	22(1)
C(19)	3298(4)	4432(2)	-2281(4)	23(1)
C(20)	3820(4)	4275(1)	-1255(3)	17(1)
C(21)	5324(4)	3922(1)	788(3)	14(1)
C(22)	5499(4)	3443(1)	507(3)	21(1)
C(23)	6553(4)	3286(2)	234(4)	27(1)
C(24)	7467(4)	3602(2)	256(3)	23(1)
C(25)	7316(4)	4077(2)	540(3)	19(1)
C(26)	6256(4)	4236(2)	794(3)	16(1)
C(27)	7608(4)	3720(2)	3542(4)	35(1)
C(28)	8725(4)	3963(2)	3369(4)	30(1)
C(29)	9603(4)	3680(2)	4144(4)	37(1)
C(30)	9110(4)	3180(2)	4022(4)	40(2)
C(31)	5637(5)	3052(2)	6746(5)	58(2)
C(32)	4576(5)	3049(2)	7340(5)	62(2)
C(33)	3673(5)	2842(2)	6483(5)	64(2)
C(34)	4357(4)	2492(2)	5885(4)	41(2)
C(35)	5277(5)	2215(2)	2158(5)	71(2)
C(36)	4400(4)	1870(2)	2359(5)	62(2)
C(37)	5149(5)	1438(2)	2794(5)	81(2)
C(38)	6281(5)	1633(2)	3192(4)	46(2)

[Na][(PPh$_3$)(Ph$_2$P(CH$_2$)$_2$B(C$_8$H$_{14}$))Re(CO)$_2$(C(O)CH$_2$O–)] ([Na][3-E$_1$Ph$_1$], ajmm48).

Table 1. Crystal data and structure refinement for AJMM48 (CCDC 770346).

Empirical formula	$C_{56}H_{69}BNaO_7P_2Re$	
Formula weight	1136.05	
Crystallization Solvent	THF	
Crystal Habit	Block	
Crystal size	0.21 x 0.21 x 0.19 mm^3	
Crystal color	Colorless	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 10.8404(4) Å	a= 80.396(2)°
	b = 12.8132(5) Å	b= 81.298(2)°
	c = 20.4220(7) Å	g = 65.477(2)°
Volume	2533.91(16) Å^3	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.489 Mg/m^3	
q range for data collection	1.76 to 49.89°	
Completeness to θ = 49.89°	99.1 %	
Index ranges	-22 ≤ h ≤ 23, -27 ≤ k ≤ 27, -43 ≤ l ≤ 43	
Absorption coefficient	2.522 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	52421 / 0 / 613	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	1.289	
Final R indices [I>2s(I), 46790 reflections]	R1 = 0.0233, *w*R2 = 0.0399	
R indices (all data)	R1 = 0.0299, *w*R2 = 0.0407	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for AJMM48 (CCDC 770346). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	8307(1)	6674(1)	7744(1)	7(1)
P(1)	7623(1)	8394(1)	8269(1)	8(1)
P(2)	9031(1)	4829(1)	7327(1)	9(1)
Na(1)	3113(1)	7110(1)	7741(1)	13(1)
O(1)	11150(1)	6783(1)	7445(1)	18(1)
O(2)	9054(1)	5179(1)	9071(1)	18(1)
O(3)	5224(1)	6857(1)	7982(1)	13(1)
O(4)	7378(1)	7816(1)	6833(1)	9(1)
O(5)	3119(1)	5810(1)	8669(1)	18(1)
O(6)	2139(1)	9100(1)	7554(1)	19(1)
O(7)	3896(1)	6686(1)	6674(1)	19(1)
B(1)	7315(1)	9051(1)	6539(1)	9(1)
C(1)	10099(1)	6714(1)	7553(1)	10(1)
C(2)	8763(1)	5760(1)	8564(1)	11(1)
C(3)	6222(1)	7019(1)	7677(1)	10(1)
C(4)	6080(1)	7737(1)	7000(1)	11(1)

C(5)	8843(1)	8917(1)	6232(1)	10(1)
C(6)	9418(1)	8040(1)	5717(1)	13(1)
C(7)	8496(1)	8255(1)	5161(1)	16(1)
C(8)	6963(1)	8648(1)	5384(1)	14(1)
C(9)	6403(1)	9529(1)	5898(1)	11(1)
C(10)	6374(1)	10723(1)	5594(1)	15(1)
C(11)	7782(1)	10771(1)	5416(1)	16(1)
C(12)	8802(1)	10121(1)	5942(1)	14(1)
C(13)	8738(1)	8276(1)	8895(1)	10(1)
C(14)	9801(1)	8649(1)	8728(1)	16(1)
C(15)	10657(1)	8537(1)	9204(1)	21(1)
C(16)	10472(1)	8040(1)	9850(1)	21(1)
C(17)	9435(1)	7646(1)	10018(1)	20(1)
C(18)	8570(1)	7771(1)	9546(1)	15(1)
C(19)	5961(1)	8921(1)	8758(1)	11(1)
C(20)	5198(1)	10097(1)	8810(1)	16(1)
C(21)	3978(1)	10465(1)	9217(1)	20(1)
C(22)	3508(1)	9664(1)	9583(1)	19(1)
C(23)	4251(1)	8495(1)	9531(1)	17(1)
C(24)	5466(1)	8123(1)	9115(1)	13(1)
C(25)	7630(1)	9636(1)	7691(1)	11(1)
C(26)	6693(1)	9905(1)	7134(1)	12(1)
C(27)	8493(1)	3781(1)	7891(1)	12(1)
C(28)	7111(1)	4128(1)	8108(1)	23(1)
C(29)	6616(1)	3343(1)	8480(1)	27(1)
C(30)	7496(1)	2210(1)	8652(1)	20(1)
C(31)	8873(1)	1863(1)	8452(1)	21(1)
C(32)	9369(1)	2643(1)	8071(1)	18(1)
C(33)	10893(1)	4065(1)	7220(1)	12(1)
C(34)	11640(1)	3749(1)	7775(1)	16(1)
C(35)	13057(1)	3230(1)	7701(1)	21(1)
C(36)	13752(1)	3021(1)	7072(1)	22(1)
C(37)	13021(1)	3328(1)	6520(1)	21(1)
C(38)	11603(1)	3848(1)	6589(1)	17(1)
C(39)	8597(1)	4655(1)	6532(1)	12(1)
C(40)	8334(1)	5571(1)	6025(1)	14(1)
C(41)	8168(1)	5424(1)	5385(1)	19(1)
C(42)	8268(1)	4361(1)	5254(1)	21(1)
C(43)	8502(1)	3453(1)	5761(1)	21(1)
C(44)	8661(1)	3594(1)	6400(1)	17(1)
C(45)	2028(1)	5445(1)	8908(1)	16(1)
C(46)	2625(1)	4435(1)	9432(1)	20(1)
C(47)	3577(1)	4779(1)	9749(1)	25(1)
C(48)	3777(1)	5741(1)	9244(1)	19(1)
C(49)	2669(1)	9827(1)	7775(1)	17(1)
C(50)	2770(1)	10683(1)	7168(1)	17(1)
C(51)	2026(1)	10499(1)	6643(1)	22(1)
C(52)	1276(1)	9796(1)	7044(1)	19(1)
C(53)	3458(1)	7300(1)	6042(1)	25(1)
C(54)	4344(1)	6510(1)	5526(1)	26(1)
C(55)	4605(1)	5322(1)	5901(1)	29(1)
C(56)	4708(1)	5485(1)	6603(1)	30(1)

$(PPh_3)(Ph_2P(CH_2)_2B(C_8H_{14}))Re(CO)_2(C(OCH_3)CH_2O–)$ (13, ajmm50).

Table 1. Crystal data and structure refinement for AJMM50 (CCDC 738920).

Empirical formula	$C_{45}H_{48}BO_4P_2Re \bullet ½ (C_6H_5Cl)$	
Formula weight	968.06	
Crystallization Solvent	Chlorobenzene	
Crystal Habit	Block	
Crystal size	0.27 x 0.22 x 0.19 mm^3	
Crystal color	Yellow	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 11.4898(4) Å	a= 80.831(2)°
	b = 13.5141(5) Å	b= 84.498(2)°
	c = 15.1385(5) Å	g = 64.883(2)°
Volume	2100.11(13) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.531 Mg/m^3	
q range for data collection	1.68 to 53.10°	
Completeness to θ = 53.10°	94.1 %	
Index ranges	$-24 \le h \le 25, -23 \le k \le 30, -34 \le l \le 34$	
Absorption coefficient	3.045 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	47162 / 0 / 540	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	1.413	
Final R indices [I>2s(I), 40639 reflections]	R1 = 0.0243, *w*R2 = 0.0396	
R indices (all data)	R1 = 0.0350, *w*R2 = 0.0405	

Special Refinement Details

The crystal contains chlorobenzene as a solvent of crystallization and occupies a site near a center of symmetry, occupancy = ½. Additionally, the chlorine position is disordered over two sites in a 4:1 ratio and was modeled as such. The benzene ring was constrained to an ideal hexagon and aside from riding hydrogen atoms no other restraints were applied.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM50 (CCDC 738920). U(eq) is defined at he trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Re(1)	3818(1)	4048(1)	2615(1)	8(1)	1
P(1)	1838(1)	5510(1)	2043(1)	9(1)	1
P(2)	5815(1)	2700(1)	3303(1)	10(1)	1
O(1)	2332(1)	2840(1)	3843(1)	22(1)	1
O(2)	3809(1)	5574(1)	3901(1)	18(1)	1
O(3)	3967(1)	3220(1)	1424(1)	10(1)	1
O(4)	5521(1)	4971(1)	1244(1)	16(1)	1
B(1)	2861(1)	3221(1)	867(1)	11(1)	1
C(1)	2856(1)	3308(1)	3407(1)	13(1)	1
C(2)	3813(1)	4965(1)	3427(1)	12(1)	1
C(3)	4807(1)	3665(1)	932(1)	13(1)	1
C(4)	4853(1)	4404(1)	1554(1)	11(1)	1

C(5)	5552(1)	5752(1)	1794(1)	20(1)	1
C(6)	1032(1)	5184(1)	1219(1)	12(1)	1
C(7)	1918(1)	4499(1)	507(1)	13(1)	1
C(8)	2129(1)	2560(1)	1504(1)	12(1)	1
C(9)	3102(1)	1418(1)	1905(1)	15(1)	1
C(10)	4032(1)	708(1)	1221(1)	16(1)	1
C(11)	4531(1)	1331(1)	445(1)	14(1)	1
C(12)	3552(1)	2479(1)	63(1)	12(1)	1
C(13)	2529(1)	2420(1)	-491(1)	16(1)	1
C(14)	1607(1)	1997(1)	70(1)	18(1)	1
C(15)	1101(1)	2504(1)	945(1)	17(1)	1
C(16)	1993(1)	6766(1)	1508(1)	13(1)	1
C(17)	2210(1)	7422(1)	2046(1)	21(1)	1
C(18)	2326(1)	8386(1)	1662(1)	28(1)	1
C(19)	2215(1)	8708(1)	746(1)	30(1)	1
C(20)	1984(1)	8073(1)	208(1)	28(1)	1
C(21)	1880(1)	7100(1)	589(1)	19(1)	1
C(22)	533(1)	6112(1)	2854(1)	11(1)	1
C(23)	664(1)	5815(1)	3776(1)	15(1)	1
C(24)	-351(1)	6322(1)	4364(1)	18(1)	1
C(25)	-1518(1)	7117(1)	4036(1)	19(1)	1
C(26)	-1660(1)	7410(1)	3118(1)	19(1)	1
C(27)	-647(1)	6921(1)	2532(1)	16(1)	1
C(28)	6906(1)	3366(1)	3347(1)	13(1)	1
C(29)	6885(1)	3922(1)	4051(1)	15(1)	1
C(30)	7661(1)	4494(1)	4011(1)	20(1)	1
C(31)	8474(1)	4503(1)	3278(1)	22(1)	1
C(32)	8511(1)	3942(1)	2577(1)	24(1)	1
C(33)	7728(1)	3382(1)	2604(1)	19(1)	1
C(34)	5597(1)	2133(1)	4461(1)	14(1)	1
C(35)	6026(1)	995(1)	4709(1)	21(1)	1
C(36)	5828(1)	574(1)	5588(1)	27(1)	1
C(37)	5227(1)	1275(1)	6224(1)	28(1)	1
C(38)	4786(1)	2409(1)	5984(1)	24(1)	1
C(39)	4948(1)	2834(1)	5103(1)	18(1)	1
C(40)	6902(1)	1480(1)	2803(1)	14(1)	1
C(41)	8198(1)	936(1)	3042(1)	24(1)	1
C(42)	9042(1)	60(1)	2612(1)	28(1)	1
C(43)	8622(1)	-298(1)	1945(1)	22(1)	1
C(44)	7334(1)	208(1)	1731(1)	19(1)	1
C(45)	6476(1)	1096(1)	2157(1)	15(1)	1
Cl(1A)	-1382(2)	11699(1)	5630(1)	84(1)	0.403(1)
Cl(1B)	766(3)	11349(3)	4151(3)	42(1)	0.097(1)
C(1A)	-512(2)	10429(1)	5294(1)	41(1)	0.50
C(2A)	-870(1)	9578(2)	5640(1)	44(1)	0.50
C(3A)	-192(2)	8536(1)	5380(1)	45(1)	0.50
C(4A)	843(2)	8345(1)	4772(1)	43(1)	0.50
C(5A)	1200(1)	9195(2)	4426(1)	48(1)	0.50
C(6A)	523(2)	10237(1)	4686(1)	46(1)	0.50

Chapter 4 Crystallographic Tables

$[(Ph_2P(CH_2)_2B(C_8H_{14}))_2Re(CO)_4][BF_4]\bullet(THF)_2$ ($1\bullet(THF)_2$, ajmm49).

Table 1. Crystal data and structure refinement for AJMM49 (CCDC 759590).

Empirical formula	$[C_{56}H_{72}B_2O_6P_2Re]^+ [BF_4]^-$	
Formula weight	1197.71	
Crystallization Solvent	THF/pentane	
Crystal Habit	Block	
Crystal size	0.27 x 0.26 x 0.19 mm^3	
Crystal color	Colorless	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 9.7744(4) Å	a= 92.554(2)°
	b = 10.3565(4) Å	b= 104.359(2)°
	c = 14.9063(6) Å	g = 105.481(2)°
Volume	1398.82(10) $Å^3$	
Z	1	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.422 Mg/m^3	
θ range for data collection	2.25 to 49.35°	
Completeness to θ = 49.35°	98.4 %	
Index ranges	$-20 \le h \le 20$, $-21 \le k \le 22$, $-31 \le l \le 31$	
Absorption coefficient	2.290 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	28016 / 0 / 349	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	2.373	
Final R indices [I>2s(I), 27766 reflections]	R1 = 0.0306, *w*R2 = 0.0591	
R indices (all data)	R1 = 0.0311, *w*R2 = 0.0592	

Special Refinement Details

The tetrafluoroborate anion is disordered about a center of symmetry and is modeled with no restraints. The Re atom sits at a center of symmetry.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM49 (CCDC 759590). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	5000	5000	5000	13(1)
P(1)	5234(1)	5965(1)	3568(1)	16(1)
O(1)	6268(3)	2696(2)	4500(1)	104(1)
O(2)	1977(2)	2936(2)	3964(1)	80(1)
O(3)	5825(1)	2594(1)	1400(1)	33(1)
B(1)	4152(2)	2772(1)	1366(1)	30(1)
C(1)	5863(2)	3567(2)	4688(1)	45(1)
C(2)	3049(2)	3719(2)	4344(1)	39(1)
C(3)	6713(1)	7536(1)	3723(1)	24(1)
C(4)	8039(2)	7563(2)	3540(1)	49(1)

C(5)	9140(2)	8784(3)	3654(2)	70(1)
C(6)	8929(2)	9963(2)	3955(2)	62(1)
C(7)	7643(2)	9945(2)	4146(2)	59(1)
C(8)	6519(2)	8735(1)	4027(1)	43(1)
C(9)	3681(1)	6478(1)	2901(1)	27(1)
C(10)	3824(2)	7153(1)	2124(1)	43(1)
C(11)	2671(3)	7590(2)	1618(1)	63(1)
C(12)	1402(3)	7403(2)	1881(2)	79(1)
C(13)	1255(2)	6749(3)	2632(3)	84(1)
C(14)	2381(2)	6273(2)	3151(2)	50(1)
C(15)	5560(1)	4868(1)	2699(1)	25(1)
C(16)	4300(2)	3546(1)	2373(1)	30(1)
C(17)	3042(2)	1260(1)	1156(1)	34(1)
C(18)	1497(2)	1378(1)	1146(1)	38(1)
C(19)	934(2)	2314(1)	459(1)	40(1)
C(20)	2098(2)	3651(1)	439(1)	36(1)
C(21)	3655(2)	3537(1)	473(1)	31(1)
C(22)	3698(2)	2794(1)	-437(1)	36(1)
C(23)	2852(2)	1283(1)	-620(1)	41(1)
C(24)	3088(2)	523(1)	245(1)	39(1)
C(25)	7013(2)	3608(1)	1165(1)	38(1)
C(26)	8428(2)	3638(2)	1909(1)	49(1)
C(27)	8097(2)	2189(2)	2134(1)	47(1)
C(28)	6472(2)	1819(1)	2106(1)	41(1)
B(2)	9772(3)	4397(4)	4887(3)	36(1)
F(1)	8569(3)	4842(3)	4623(3)	80(1)
F(2)	9290(4)	3035(3)	4893(4)	121(2)
F(3)	10636(4)	4693(6)	4351(4)	145(2)
F(4)	10567(5)	4993(3)	5779(2)	93(1)

Appendix A Crystallographic Tables

$(C_5Me_4ArNMe_2)Re(CO)_3$ (1, ajmm16)

Table 1. Crystal data and structure refinement for AJMM16 (CCDC 650764).

Empirical formula	$C_{20}H_{22}NO_3Re$	
Formula weight	510.59	
Crystallization Solvent	Hexanes	
Crystal Habit	Block	
Crystal size	0.33 x 0.22 x 0.16 mm^3	
Crystal color	Colorless	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 7.9326(2) Å	
	b = 8.3019(2) Å	b= 96.9710(10)°
	c = 14.6614(4) Å	
Volume	958.40(4) $Å^3$	
Z	2	
Crystal system	Monoclinic	
Space group	$P2_1$	
Density (calculated)	1.769 Mg/m^3	
θ range for data collection	2.59 to 47.28°	
Completeness to θ = 47.28°	91.0 %	
Index ranges	$-16 \le h \le 16$, $-15 \le k \le 16$, $-28 \le l \le 28$	
Absorption coefficient	6.357 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	12762 / 1 / 232	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	1.293	
Final R indices [I>2s(I), 11217 reflections]	R1 = 0.0368, *w*R2 = 0.0765	
R indices (all data)	R1 = 0.0445, *w*R2 = 0.0783	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM16 (CCDC 650764). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	5225(1)	-1475(1)	8099(1)	14(1)
O(1)	2530(4)	-1825(5)	6424(2)	37(1)
O(2)	4378(5)	-4882(4)	8726(3)	37(1)
O(3)	2572(4)	-81(4)	9246(2)	29(1)
N(1)	9292(4)	1775(4)	6432(2)	20(1)
C(1)	3532(4)	-1695(5)	7062(3)	23(1)
C(2)	4683(5)	-3599(4)	8488(3)	22(1)
C(3)	3545(4)	-626(4)	8804(2)	19(1)
C(4)	6977(3)	461(4)	7585(2)	14(1)
C(5)	7522(4)	-1111(3)	7286(2)	16(1)
C(6)	8091(4)	-2027(4)	8088(2)	18(1)
C(7)	7897(4)	-1053(4)	8879(2)	17(1)
C(8)	7214(4)	474(4)	8566(2)	15(1)

C(9)	7634(4)	-1643(5)	6310(2)	19(1)
C(10)	8868(5)	-3681(5)	8093(3)	27(1)
C(11)	8513(4)	-1430(11)	9860(2)	23(1)
C(12)	6976(5)	1896(4)	9170(3)	21(1)
C(13)	6501(4)	1867(4)	6973(2)	15(1)
C(14)	4940(4)	2630(4)	6973(3)	21(1)
C(15)	4454(5)	3919(4)	6401(3)	25(1)
C(16)	5550(5)	4444(5)	5791(3)	26(1)
C(17)	7131(4)	3734(6)	5795(2)	23(1)
C(18)	7660(4)	2469(4)	6400(2)	17(1)
C(19)	10394(4)	2022(5)	7295(3)	25(1)
C(20)	10207(5)	2047(6)	5642(3)	29(1)

[(C5Me4ArNHMe2)Re(CO)3][BF4] (2, ajmm17).

Table 1. Crystal data and structure refinement for AJMM17 (CCDC 650764).

Empirical formula	$[C_{20}H_{23}NO_3Re]^+ [BF_4]^-$
Formula weight	598.40
Crystallization Solvent	Dichloromethane
Crystal Habit	Plate
Crystal size	0.33 x 0.29 x 0.07 mm^3
Crystal color	Colorless
Data Collection Temperature	100(2) K
Unit cell dimensions	a = 11.9180(3) Å b = 14.8020(4) Å c = 12.3664(3) Å
Volume	2181.56(10) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	$Pca2_1$
Density (calculated)	1.822 Mg/m^3
θ range for data collection	2.19 to 47.16°
Completeness to θ = 47.16°	94.2 %
Index ranges	$-24 \le h \le 24$, $-30 \le k \le 21$, $-25 \le l \le 22$
Absorption coefficient	5.624 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Refinement method	Full matrix least-squares on F^2
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.124
Final R indices [I>2s(I), 13046 reflections]	R1 = 0.0334, *w*R2 = 0.0640
R indices (all data)	R1 = 0.0514, *w*R2 = 0.0690

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM17 (CCDC 650764). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	4851(1)	3842(1)	1191(1)	10(1)
O(1)	5974(3)	3784(2)	-1051(2)	33(1)
O(2)	2830(2)	4908(1)	323(2)	20(1)
O(3)	5942(2)	5646(1)	1821(2)	29(1)
N(1)	6507(2)	1002(1)	3011(2)	16(1)
C(1)	5546(2)	3836(2)	-216(2)	19(1)
C(2)	3593(2)	4510(2)	632(2)	14(1)
C(3)	5547(2)	4973(2)	1544(2)	17(1)
C(4)	5739(2)	2668(2)	2038(2)	12(1)
C(5)	4807(2)	2294(2)	1413(2)	14(1)
C(6)	3797(2)	2655(2)	1860(2)	14(1)
C(7)	4073(2)	3244(2)	2749(2)	14(1)
C(8)	5272(2)	3244(2)	2860(2)	14(1)
C(9)	4897(2)	1603(2)	531(2)	19(1)
C(10)	2620(2)	2393(2)	1535(2)	20(1)
C(11)	3260(2)	3686(2)	3503(2)	20(1)
C(12)	5926(3)	3724(2)	3718(3)	23(1)
C(13)	6947(2)	2397(2)	1978(2)	13(1)
C(14)	7760(2)	2958(2)	1502(2)	16(1)

C(15)	8888(2)	2712(2)	1501(2)	20(1)
C(16)	9227(2)	1906(2)	1958(3)	24(1)
C(17)	8441(2)	1335(2)	2431(3)	22(1)
C(18)	7319(2)	1597(2)	2446(2)	16(1)
C(19)	6743(2)	952(2)	4203(2)	21(1)
C(20)	6455(2)	70(2)	2519(2)	21(1)
B(1)	3795(2)	1078(2)	4207(3)	18(1)
F(1)	3944(2)	347(1)	4895(2)	34(1)
F(2)	2667(2)	1298(1)	4129(2)	29(1)
F(3)	4182(1)	819(1)	3165(1)	24(1)
F(4)	4435(2)	1806(1)	4551(2)	26(1)

[(η^6-$C_5Me_4ArNMe_2$)$Re(CO)_2$][BF_4] (7, ajmm20).

Table 1. Crystal data and structure refinement for (AJMM20) (CCDC 796319).

Empirical formula	$[C_{14}H_{22}N_2O_2Re]^+ [PF_6]^-$	
Formula weight	581.51	
Crystallization Solvent	Not given	
Crystal Habit	Needle	
Crystal size	0.21 x 0.03 x 0.03 mm^3	
Crystal color	Orange	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 8.7993(6) Å	a= 90°
	b = 8.7993(6) Å	b= 90°
	c = 23.6102(19) Å	g = 90°
Volume	1828.1(2) $Å^3$	
Z	4	
Crystal system	Tetragonal	
Space group	P 4_3	
Density (calculated)	2.113 Mg/m^3	
θ range for data collection	2.31 to 27.48°	
Absorption coefficient	6.804 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Geometric positions	
Refinement method	Full matrix least-squares on F^2	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	1.340	
Final R indices [I>2s(I), 3549 reflections]	R1 = 0.0379, *w*R2 = 0.0662	
R indices (all data)	R1 = 0.0509, *w*R2 = 0.0686	
Type of weighting scheme used	Sigma	
Weighting scheme used	$w=1/s^2(Fo^2)$	

Special Refinement Details

We were not able to distinguish between carbonyl and nitrosyl positions so the corresponding carbon and nitrogen atoms were refined as a 50:50 mixture.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM20 (CCDC 796319). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	4264(1)	934(1)	7501(1)	22(1)
O(1)	7383(7)	523(7)	6984(3)	45(2)
O(2)	3103(7)	3116(7)	6628(3)	40(2)
N(1)	4780(7)	2430(7)	8215(3)	26(2)
C(1A)	6185(9)	792(8)	7181(4)	29(2)
N(2A)	6185(9)	792(8)	7181(4)	29(2)
C(2B)	3591(8)	2316(8)	6974(3)	25(2)
N(2B)	3591(8)	2316(8)	6974(3)	25(2)
C(3)	3161(8)	-310(8)	8239(3)	20(2)

C(4)	2026(9)	-34(8)	7825(4)	24(2)
C(5)	2452(8)	-828(8)	7319(3)	24(2)
C(6)	3839(7)	-1597(7)	7434(4)	21(2)
C(7)	4311(9)	-1302(9)	7993(4)	25(2)
C(8)	511(9)	741(9)	7925(4)	30(2)
C(9)	1519(9)	-925(9)	6785(4)	31(2)
C(10)	4655(9)	-2685(10)	7033(4)	34(2)
C(11)	5679(9)	-1947(10)	8300(4)	36(2)
C(12)	3316(9)	515(8)	8791(4)	26(2)
C(13)	3611(11)	2177(10)	8668(4)	45(2)
C(14)	4830(13)	4049(9)	8074(4)	54(3)
C(15)	6316(10)	2096(11)	8461(4)	50(3)
P(1)	-268(3)	5430(3)	7807(1)	42(1)
F(1)	-1134(6)	4012(6)	7571(4)	64(2)
F(2)	1105(7)	5139(12)	7416(5)	102(3)
F(3)	395(9)	4470(7)	8298(3)	98(3)
F(4)	-1070(10)	6465(10)	7369(5)	138(4)
F(5)	476(10)	6872(7)	8050(3)	106(3)
F(6)	-1688(8)	5700(9)	8198(3)	100(3)

Appendix B Crystallographic Tables

$KHBEt_3$ (ajmm38).

Table 1. Crystal data and structure refinement for AJMM38 (CCDC 796321).

Empirical formula	$[C_6H_{16}B]^- K^+$	
Formula weight	138.10	
Crystallization Solvent	Toluene	
Crystal Habit	Block	
Crystal size	0.19 x 0.11 x 0.11 mm^3	
Crystal color	Colorless	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 7.4674(5) Å	a= 90°
	b = 7.6679(6) Å	b= 90°
	c = 14.8055(11) Å	g = 90°
Volume	847.75(11) $Å^3$	
Z	4	
Crystal system	Orthorhombic	
Space group	$P\ 2_12_12_1$	
Density (calculated)	1.082 Mg/m^3	
θ range for data collection	2.75 to 34.95°	
Completeness to θ = 34.95°	98.0 %	
Index ranges	$-11 \le h \le 10, -12 \le k \le 11, -23 \le l \le 23$	
Reflections collected	30389	
Independent reflections	3592 [R_{int}= 0.0800]	
Absorption coefficient	0.536 mm^{-1}	
Absorption correction	None	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Difference Fourier map	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	3592 / 0 / 137	
Treatment of hydrogen atoms	Unrestrained	
Goodness-of-fit on F^2	1.286	
Final R indices [I>2s(I), 3241 reflections]	R1 = 0.0238, *w*R2 = 0.0439	
R indices (all data)	R1 = 0.0289, *w*R2 = 0.0445	
Type of weighting scheme used	Sigma	
Weighting scheme used	$w=1/s^2(Fo^2)$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for AJMM38 (CCDC 796321). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
K(1)	2231(1)	6266(1)	5707(1)	17(1)
B(1)	2627(1)	8873(1)	4027(1)	13(1)
C(1)	1429(1)	10264(1)	4615(1)	18(1)
C(2)	2467(1)	11737(1)	5076(1)	26(1)
C(3)	1319(1)	7365(1)	3595(1)	14(1)
C(4)	2246(2)	5955(1)	3036(1)	25(1)
C(5)	3825(1)	9836(1)	3244(1)	15(1)
C(6)	2754(2)	10701(1)	2485(1)	24(1)

18c6/KHBEt3 (ajmm34)

Table 1. Crystal data and structure refinement for AJMM34 (CCDC 796320).

Empirical formula	$[C_{12}H_{24}KO_6]^+ [C_6H_{16}B]^-$	
Formula weight	402.41	
Crystallization Solvent	Chlorobenzene	
Crystal Habit	Block	
Crystal size	0.26 x 0.25 x s0.23 mm^3	
Crystal color	Colorless	
Data Collection Temperature	100(2) K	
Unit cell dimensions	a = 15.2147(8) Å	a= 90°
	b = 38.660(2) Å	b= 90.331(3)°
	c = 15.5890(9) Å	g = 90°
Volume	9169.3(9) $Å^3$	
Z	16	
Crystal system	Monoclinic	
Space group	P $2_1/c$	
Density (calculated)	1.166 Mg/m^3	
θ range for data collection	1.31 to 30.31°	
Completeness to θ = 30.31°	93.1 %	
Index ranges	$-21 \le h \le 21$, $-54 \le k \le 30$, $-21 \le l \le 21$	
Reflections collected	104729	
Independent reflections	25606 [R_{int}= 0.0801]	
Absorption coefficient	0.259 mm^{-1}	
Absorption correction	None	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Geometric positions	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	25606 / 0 / 950	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	1.579	
Final R indices [I>2s(I), 15131 reflections]	R1 = 0.0621, *w*R2 = 0.0888	
R indices (all data)	R1 = 0.1169, *w*R2 = 0.0955	
Type of weighting scheme used	Sigma	
Weighting scheme used	$w=1/s^2(Fo^2)$	

Special Refinement Details

This crystal is a twin that mimics orthorhombic. The twin law employed was -1 0 0 0 -1 0 0 0 1 with a batch scale factor of 0.389.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AJMM34 (CCDC 796320). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
K(1)	2538(1)	2629(1)	3988(1)	27(1)
O(1A)	4171(1)	2812(1)	3342(1)	27(1)
O(2A)	3936(2)	2152(1)	4160(1)	29(1)
O(3A)	2208(2)	1903(1)	4119(1)	31(1)
O(4A)	810(1)	2382(1)	4078(1)	27(1)

O(5A)	1058(2)	3042(1)	3319(1)	30(1)
O(6A)	2784(2)	3304(1)	3331(1)	30(1)
B(1)	2940(3)	3003(1)	6046(2)	24(1)
C(1A)	4854(2)	2623(1)	3778(2)	33(1)
C(2A)	4692(2)	2245(1)	3681(2)	33(1)
C(3A)	3735(2)	1793(1)	4060(2)	32(1)
C(4A)	2900(2)	1714(1)	4519(2)	36(1)
C(5A)	1377(2)	1830(1)	4476(2)	36(1)
C(6A)	686(2)	2019(1)	3968(2)	32(1)
C(7A)	123(2)	2572(1)	3658(2)	37(1)
C(8A)	281(2)	2950(1)	3777(2)	35(1)
C(9A)	1236(2)	3402(1)	3373(2)	33(1)
C(10A)	2064(3)	3474(1)	2901(2)	37(1)
C(11A)	3588(2)	3354(1)	2897(2)	34(1)
C(12A)	4309(2)	3174(1)	3385(2)	34(1)
C(13A)	2071(2)	3156(1)	5548(2)	28(1)
C(14A)	1522(2)	3413(1)	6075(2)	32(1)
C(15A)	3517(2)	3310(1)	6498(2)	28(1)
C(16A)	3805(2)	3596(1)	5890(2)	32(1)
C(17A)	2686(2)	2707(1)	6760(2)	33(1)
C(18A)	2416(3)	2358(1)	6379(2)	45(1)
K(2)	2523(1)	134(1)	3935(1)	26(1)
O(1B)	2331(1)	-591(1)	4178(1)	25(1)
O(2B)	863(1)	-150(1)	4088(1)	27(1)
O(3B)	1004(1)	522(1)	3340(1)	28(1)
O(4B)	2735(1)	792(1)	3251(1)	28(1)
O(5B)	4172(1)	342(1)	3308(1)	25(1)
O(6B)	4006(1)	-281(1)	4252(1)	24(1)
B(2)	2350(2)	502(1)	5904(2)	26(1)
C(1B)	1484(2)	-692(1)	4459(2)	29(1)
C(2B)	800(2)	-510(1)	3921(2)	30(1)
C(3B)	126(2)	39(1)	3752(2)	30(1)
C(4B)	291(2)	416(1)	3876(2)	30(1)
C(5B)	1209(2)	878(1)	3463(2)	31(1)
C(6B)	1981(2)	968(1)	2916(2)	30(1)
C(7B)	3504(2)	852(1)	2764(2)	29(1)
C(8B)	4277(2)	708(1)	3245(2)	28(1)
C(9B)	4896(2)	184(1)	3757(2)	26(1)
C(10B)	4761(2)	-198(1)	3765(2)	25(1)
C(11B)	3872(2)	-648(1)	4291(2)	27(1)
C(12B)	3022(2)	-719(1)	4720(2)	28(1)
C(13B)	3083(2)	750(1)	5462(2)	30(1)
C(14B)	3628(2)	978(1)	6081(2)	34(1)
C(15B)	2857(2)	174(1)	6387(2)	29(1)
C(16B)	2264(2)	-89(1)	6800(2)	42(1)
C(17B)	1724(2)	716(1)	6552(2)	29(1)
C(18B)	1272(2)	1037(1)	6153(2)	32(1)
K(3)	2506(1)	9853(1)	9095(1)	27(1)
O(1C)	4160(1)	10159(1)	9082(1)	27(1)
O(2C)	3980(1)	9475(1)	8435(1)	26(1)
O(3C)	2260(1)	9186(1)	8436(1)	28(1)
O(4C)	831(1)	9647(1)	8433(1)	28(1)

O(5C)	992(1)	10302(1)	9216(1)	26(1)
O(6C)	2669(2)	10589(1)	9098(1)	29(1)
B(3)	2873(3)	9482(1)	11109(2)	30(1)
C(1C)	4866(2)	9967(1)	8714(2)	31(1)
C(2C)	4726(2)	9590(1)	8910(2)	27(1)
C(3C)	3798(2)	9119(1)	8577(2)	30(1)
C(4C)	3004(2)	9019(1)	8068(2)	30(1)
C(5C)	1471(2)	9120(1)	7964(2)	30(1)
C(6C)	717(2)	9281(1)	8425(2)	31(1)
C(7C)	101(2)	9817(1)	8799(2)	34(1)
C(8C)	234(2)	10202(1)	8732(2)	32(1)
C(9C)	1129(2)	10668(1)	9152(2)	31(1)
C(10C)	1995(2)	10757(1)	9561(2)	30(1)
C(11C)	3524(2)	10707(1)	9337(2)	30(1)
C(12C)	4186(2)	10514(1)	8840(2)	32(1)
C(13C)	2013(2)	9288(1)	10672(2)	32(1)
C(14C)	1465(2)	9065(1)	11286(2)	37(1)
C(15C)	2617(2)	9805(1)	11740(2)	40(1)
C(16C)	2373(2)	10134(1)	11292(2)	48(1)
C(17C)	3476(2)	9211(1)	11664(2)	33(1)
C(18C)	3800(2)	8892(1)	11193(2)	37(1)
K(4)	2442(1)	7637(1)	4108(1)	26(1)
O(1D)	1064(1)	7145(1)	4280(1)	26(1)
O(2D)	780(1)	7807(1)	3463(1)	25(1)
O(3D)	2132(1)	8311(1)	3492(1)	30(1)
O(4D)	3871(2)	8070(1)	3450(1)	30(1)
O(5D)	4189(1)	7405(1)	4171(1)	28(1)
O(6D)	2803(2)	6915(1)	4216(1)	29(1)
B(4)	2073(3)	8002(1)	6171(2)	26(1)
C(1D)	302(2)	7233(1)	3784(2)	28(1)
C(2D)	112(2)	7612(1)	3884(2)	33(1)
C(3D)	612(2)	8169(1)	3537(2)	30(1)
C(4D)	1310(2)	8361(1)	3065(2)	34(1)
C(5D)	2818(2)	8497(1)	3078(2)	31(1)
C(6D)	3668(2)	8428(1)	3526(2)	31(1)
C(7D)	4668(2)	7979(1)	3883(2)	34(1)
C(8D)	4843(2)	7601(1)	3743(2)	36(1)
C(9D)	4313(2)	7043(1)	4039(2)	32(1)
C(10D)	3659(2)	6845(1)	4555(2)	31(1)
C(11D)	2134(2)	6717(1)	4628(2)	31(1)
C(12D)	1288(2)	6790(1)	4179(2)	32(1)
C(13D)	2940(2)	8155(1)	5695(2)	28(1)
C(14D)	3512(2)	8404(1)	6245(2)	34(1)
C(15D)	2329(2)	7699(1)	6884(2)	37(1)
C(16D)	2563(3)	7352(1)	6505(2)	48(1)
C(17D)	1506(2)	8306(1)	6612(2)	28(1)
C(18D)	1225(2)	8600(1)	6017(2)	32(1)

1. van der Sluis, P.; Spek, A. L. *Acta Crystallogr A* **1990**, *46*, 194.