Appendix A

Compound Numbers by Chapter: A Handy Guide

Appendix A

Chapter 2 Compounds

1 $(CO)_5Cr\{(OMe)(p\text{-}CF_3\text{-}C_6H_4)\}$

2 $(CO)_5Cr\{(OMe)(p\text{-}OMe\text{-}C_6H_4)\}$

3 $(CO)_5Cr\{(OMe)(p\text{-}NMe_2\text{-}C_6H_4)\}$

4 (*E*/*Z*)-1,2-dimethoxy-1,2-bis(4-methoxyphenyl)ethane

5 $Cp(CO)(NO)Cr\{C(OMe)(C_6H_5)\}$

6 $Cp(CO)(NO)Cr\{C(OMe)(p\text{-}CF_3\text{-}C_6H_4)\}$

7 $(triphos)(PPh_3)Pd$

8 $(triphos)(PPh_3)Pt$

9 $Cl_2Pt\{C(OMe)Me\}_2$

10 $Br_2Pt\{C(OMe)Me\}_2$

11 $Cl_2Pt\{C(O^iPr)Me\}_2$

12 (*E*/*Z*)-2,3-dimethoxybut-2-ene

13 (*E*/*Z)*-2,3-diisopropoxybut-2-ene

14 *cis*-dichlorobis(triphenylphosphine)platinum(II)

15 2,3-dimethoxybut-1-ene **15**

16 *cis*-dibromobis(triphenylphosphine)platinum(II)

17 2,3-diisopropoxybut-1-ene

18 Cl(py)Pt(COMe){C(OMe)Me}

19 Br(py)Pt(COMe){C(OMe)Me}

20 Cl(py)Pt(COMe){C(O^iPr)Me}

21 dichloride(but-2-yl)platinum(II) intermediate

22 $[Cl_2Pt(COMe)\{C(OMe)(Me)\}]nBu_4NCl$

Chapter 3 Compounds

1 2-(3,5-di-*t*-butyl-2-(methoxymethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (boronic ester)

2 2-bromo-6-(3,5-di-*t*-butyl-2-(methoxymethoxy)phenyl)pyridine (monoarylated pyridine)

3 6,6'-(pyridine-2,6-diyl)bis(2,4-di-*tert*-butylphenol) (Bis-arylated pyridine)

4 2-bromo-*N*-(1-phenylethyl)aniline

5 2,4-di-*t*-butyl-6-(6-(2-((1-phenylethyl)amino)phenyl)pyridin-2-yl)phenol (NNO)

6 (**5**)$ZrBn_2$

7 (**5**)$HfBn_2$

8 (**5**)$TiCl_2$

9 (**5**)$TiBn_2$

10 ^{Bn}NNO

11 ^{Ad}NNO

12 2-bromo-*N*-methoxyethylaniline

13 ^{MeOEt}NNO

14 (**10**)$ZrBn_2$

15 (**10**)$TiCl_2$

16 (**11**)$TiCl_2$

17 (**13**)$ZrBn_2$

18 2,4-di-*t*-butyl-6-(6-(*o*-tolyl)pyridin-2-yl)phenol **(**CNO)

19 (**18**)$TiBn_2$

20 2,4-di-*t*-butyl-6-(6-(3,5-di-*t*-butylphenyl)pyridin-2-yl)phenol (ArNO)

21 2,4-di-*t*-butyl-6-(6-(((1-phenylethyl)amino)-methyl)pyridin-2-yl)phenol **(**amido(pyridine)phenoxide)

22 (**21**)$TiBn_2$

23 (**21**)$HfBn_2$

24 (**21**)$TiCl_2$

Chapter 4 Compounds

1 3-admantyl-2-hydroxy-5-methylbenzaldehyde

2 2-(2'-methoxyphenyl)aniline

3 phenoxy–imine ligand

4 (**3**)$TiCl_3$

Appendix B

Comparison of ^{13}C NMR Data of Polypropylene from (NNO)$TiCl_2$ (**8**) and Reported ^{13}C NMR Data for Regioirregular Propylene

Appendix B

Analysis of Polypropylene Regiospecificity by ^{13}C NMR Spectroscopy

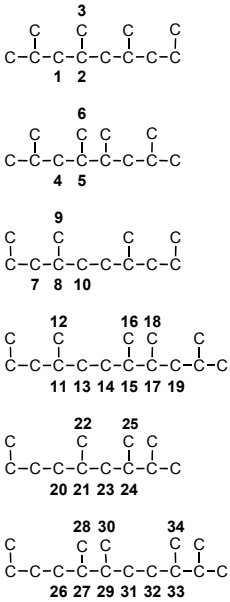
The following table compares peaks observed in the ^{13}C spectra of polypropylene (PP) from (NNO)$TiCl_2$ (Chapter 3, **8**) with known literature values. The ^{13}C chemical shifts of PP from (NNO)$TiCl_2$ are listed in the column "Expt'l Data." The column to the right of the experimental data shows a range of chemical shifts reported in the literature and the corresponding type of insertion. The number in bold (1-44) corresponds to a carbon atom in the chemdraws to the right of the table, which show all of the possible sequences obtained from 1,2-, 2,1- and 3,1-insertion modes. The S, T and P in parentheses next to the bold carbon numbers indicate secondary, tertiary, and primary carbons, respectively, and the number range indicates the chemical shift range reported in the references listed at the top of the table. Finally, the colored blocks (orange, pink, and blue) represent the chemical shift ranges for secondary (orange), tertiary (pink), and primary (blue) carbons in polypropylene as reported in the literature. These color blocks show that chemical shift range for secondary and tertiary carbons overlap in the region of ~32-40 ppm in ^{13}C NMR spectroscopy.

This table allows for three important observations: 1) The methyl region of the ^{13}C spectra is well separated from the methine and methylene regions. 2) Since the data for PP from complex **8** has peaks in the overlapping region for secondary and tertiary carbons, we are not able to assign methylene and

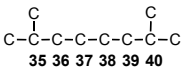
methine carbons by ^{13}C NMR data alone. 3) We observe peaks very close to the reported regions for 3,1-insertions (which overlap regions for 2,1-insertions), so we cannot rule out 3,1-insertions from our ^{13}C NMR data.

Expt'l Data	*Macromolecules* **1992**, *25,* 4876				*Makromol. Chem.* **1989**, *190,* 1931	
	2,1-insertions				**3,1-insertion**	**n-propyl end group**
46.49 46.01 45.94	**1** (S) (45.7-47.7)	**7** (S) (45.7-46.5)	Secondary (methylene)			
45.49						
45.39						
43.01	**4, 19, 23** (S) (43.3 - 44.1)					
42.82 42.72 42.65						
41.67 41.39 41.29 41.13	**4** (S) (40.9 - 42.3)					
40.83						**42** (S) (39.59-40.8)
38.11	**15, 27, 29, 33** (T) (36.8-39.1)			Tertiary (methine)	**36, 39** (S) (37.62-38.51)	
37.23 37.06 36.76						
36.65						
36.48	**13** (T) (36.5)					
35.16	**5, 24** (T), **10, 13, 20** (S) (35.4-35.6)					
34.10	**5, 17, 24** (T), **10, 20** (S) (34.2-34.8)					
33.82						
33.58 33.25	**31** (S) (33.4)					
32.99						
32.88	**14, 16** (S) (32.6)					
32.06 31.97						
31.16	**8, 11, 21** (T), **32** (S) (31.1-31.3)					
30.90					**35, 40** (T) (30.8-30.92)	
30.84						**41** (T) (30.3-30.8)
30.69 30.57						
30.07						
28.67 28.60 28.25	**2** (T) (28.3-28.4)					
28.07						
28.00					***37, 38*** *(S) (27.57-27.83)*	
21.35 21.16		**3** (P) (20.1-20.7)		Primary (methyl)		
21.00 20.69 20.57 20.43 20.29	**9, 12, 22** (P) (20.1-20.9)					
19.65						**43** (S) (19.73-20.3)
17.06 16.71 16.63	**6, 25, 34** (P) (16.6-17.2)					
15.19						
15.12 14.69	**6, 16, 18, 25, 28, 30** (P) (14.7-15.1)					
14.50						
14.23 14.12						**44** (P) (14.3-14.51)

2,1-insertion modes



3,1-insertion



n-propyl end group

Secondary Carbon (methylene) = S
Tertiary Carbon (methine) = T
Primary Carbon (methyl) = P