For **5**: 44%; ^1H NMR (C_6D_6) δ 7.695 (d, 12 H, J = 8.4 Hz), 6.68 (d, 12 H, J = 8.4 Hz), 3.25 (s, 18 H), −9.89 (t, 2 H). Anal. Calcd for $C_{47}H_{49}O_6P_2Re$: C, 58.9; H, 5.2; P, 6.5. Found: C, 58.4; H, 4.9; P, 6.4.

For **1**: ^1H NMR (C_6D_6) δ 7.2 (m, 30 H), 4.27 (s, 5 H), −9.95 (t, 2 H).

Ferricinium Oxidation of $CpRe(PPh_3)_2H_2$ (1). A. In Acetonitrile. Compound **1** (0.428 g, 0.500 mmol) was dissolved in 20 mL of acetonitrile. Ferricinium hexafluorophosphate (0.166 g, 0.500 mmol) was added, giving an orange solution. The reaction mixture was chilled, precipitating a gold crystalline solid which was collected by filtration. The mother liquors were concentrated to half-volume which precipitated a second crop of the gold crystals. Combined yield was 0.198 g (43%) of $[CpRe(PPh_3)_2(NCCH_3)H]^+[PF_6]^-$ (**7**).

Anal. Calcd for $C_{43}H_{39}NP_2Re{\cdot}PF_6$: C, 53.6; H, 4.1; N, 1.5; P, 9.7. Found: C, 53.5; H, 4.1; N, 1.0; P, 9.2.

The mother liquors were diluted with 15 mL of ether. The resulting solution was chilled, precipitating a white crystalline solid. The solid was collected by filtration and dried to give 0.202 g (45%) of $[CpRe(PPh_3)_2H_3]^+[PF_6]^-$ (**8**).

Anal. Calcd for $C_{41}H_{38}P_2Re{\cdot}PF_6$: C, 53.3; H, 4.1; P, 10.1. Found: C, 53.0; H, 4.4; P, 10.0.

The mother liquors were allowed to stand 24 h, precipitating dark red crystals which were collected by filtration to give 0.022 g (6%) of $[CpRe(NCCH_3)_4]^{2+}2[PF_6]^-$ (**8**).

Anal. Calcd for $C_{13}H_{17}N_4Re{\cdot}2PF_6$: C, 22.1; H, 2.4; N, 7.9. Found: C, 22.5; H, 2.8; N, 7.9.

B. In Acetonitrile-d_3. Complex **1** (0.086 g, 0.10 mmol) was dissolved in 5 mL of acetonitrile-d_3. The ferricinium hexafluorophosphate (0.033 g, 0.10 mmol) was added and the resulting mixture stirred at ambient temperature for 3 min. Aliquots were then examined by ^1H NMR.

C. In Dichloromethane. Complex **1** (0.214 g, 0.250 mmol) was dissolved in 10 mL of dichloromethane. Ferricinium hexafluorophosphate (0.083 g, 0.25 mmol) was added and the resulting solution stirred for 5 min at ambient temperature. The reaction mixture was concentrated to 5 mL and 15 mL of ether was added. The resulting solution was chilled, precipitating a white solid. The solid was collected by filtration to give 0.127 g (55%) of **8**.

Preparation of 8 from 1. To a slurry of **1** (0.17 g, 0.20 mmol) in 15 mL of ether was added a drop of 60% aqueous HPF_6. A white solid precipitated immediately which was collected by filtration and washed with ether (6 × 10 mL). The ^1H NMR spectrum of the product was identical with that of **8**: (CD_3CN) δ 7.5–7.3 (m, 30 H), 4.68 (s, 5 H), −5.97 (t, 3 H, J = 30.1 Hz).

The tetrafluoroborate salt was prepared similarly with 50% aqueous HBF_4. Anal. Calcd for $C_{41}H_{38}P_2Re{\cdot}BF_4{\cdot}H_2O$: C, 55.7; H, 4.6; P, 7.0. Found: C, 56.0; H, 4.7; P, 6.7.

Ferricinium Oxidation of $CpRe[P(p\text{-}FC_6H_4)_3]_2H_2$ (4) in Acetonitrile-d_3. Complex **4** (0.090 g, 0.10 mmol) was dissolved in 2 mL of acetonitrile-d_3. Ferricinium hexafluorophosphate (0.033 g, 0.10 mmol) was added and the reaction mixture examined by ^1H NMR.

Acknowledgment. The authors thank Catherine Franke for her expertise in conducting the flow cell experiments and Alex Wernberg for helpful and stimulating discussions.

Supplementary Material Available: Table of fractional atomic coordinates (3 pages). Ordering information is available on any current masthead page.

Equilibria Studies Involving Ligand Coordination to "Open Titanocenes": Phosphine and Pentadienyl Cone Angle Influences and the Existence of These Electron-Deficient Molecules

Lothar Stahl and Richard D. Ernst*

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.

Received November 25, 1986

Abstract: A series of phosphine adducts of bis(2,4-dimethylpentadienyl)titanium has been prepared, having the formulas $Ti(2,4\text{-}C_7H_{11})_2L$, for which L = $P(C_2H_5)_3$, $P(OC_2H_5)_3$, $P(OCH_3)_3$, $P(CH_3)_2(C_6H_5)$, and $P(CH_3)_3$. In solution these 16-electron adducts reversibly dissociate the phosphine or phosphite ligands, with respective ΔH values being 10.0, 10.6, 11.4, 12.9, and 14.5 kcal/mol, with the ΔS values falling in the range of 27.4–34.1 eu. Except for the seemingly weak binding by phosphites, these data can be rationalized in terms of reported ligand cone angles, and it is suggested that the cone angles for $P(OMe)_3$ and a few related ligands should be revised, in some cases quite significantly. In addition, the $P(C_2H_5)_3$ adducts of $Ti(3\text{-}C_6H_9)_2$ and $Ti(C_5H_7)_2$ have been prepared (C_6H_9 = methylpentadienyl; C_5H_7 = pentadienyl). Similar studies indicate significantly enhanced phosphine binding, with ΔH and ΔS values being 14.6 kcal/mol and 34.8 eu for the former compound. For the latter complex, no detectable dissociation could be observed up to 60 °C, at which point decomposition took place. This information suggests that nonbonded repulsions between eclipsing pentadienyl methyl groups disfavor the formation of the ligand adducts, and hence they are to a large extent responsible for the isolability of the 14-electron "open titanocene", $Ti(2,4\text{-}C_7H_{11})_2$.

Of all the metallocenes, titanocene has exhibited perhaps the most intriguing chemistry, which includes applications in catalysis and organic synthesis.[1] Unlike the other $M(C_5H_5)_2$ complexes from vanadium to nickel, $Ti(C_5H_5)_2$ is known to be extremely unstable, and all attempts to isolate this material have failed. In fact, a myriad of other materials have been isolated, including nitrogen adducts like $[Ti(C_5Me_5)_2]_2N_2$, and a variety of complexes containing ligands such as hydride, fulvalene, etc. Even $Ti(C_5(CH_3)_5)_2$ is unstable, existing in equilibrium with a Ti(IV) complex which decomposes at room temperature.[1d] Recently we reported the synthesis and characterization of an "open titanocene", bis(2,4-dimethylpentadienyl)titanium, which contrasts markedly with "titanocenes" in being quite stable thermally despite its 14-electron configuration.[2,3] Furthermore, this green compound does not form

---

(1) (a) Pez, G. P.; Armor, J. N. In *Advances in Organometallic Chemistry*; West, R., Stone, F. G. A., Eds.; Academic: New York, 1981; Vol. 19, p 1. (b) Bottrill, M.; Gavens, P. D.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, pp 281–329. (c) Bottrill, M.; Gavens, P. D.; Kelland, J. W.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, pp 331–474. (d) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087. (e) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *Ibid.* **1978**, *100*, 3611. (f) Stille, J. R.; Grubbs, R. H. *Ibid.* **1983**, *105*, 1664. (g) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733.

(2) (a) Liu, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 3737. (b) Ernst, R. D.; Liu, J.-Z.; Wilson, D. R. *J. Organomet. Chem.* **1983**, *250*, 257.

0002-7863/87/1509-5673$01.50/0

a nitrogen adduct, and treatment with CO or PF_3 was found to lead only to mono(ligand) adducts possessing 16-electron configurations.[2] The addition of triethylphosphine, generally a much better ligand than nitrogen, did not lead to detectable adduct formation at room temperature. Subsequently, however, we found that when such solutions were cooled, a deep brownish color developed, and the analogous mono(ligand) adducts could be isolated.[4] As similar behavior was exhibited by a number of phosphine ligands, this therefore provided a good opportunity to study the equilibria for the formation of these adducts, which has yielded some valuable data regarding the ligand preferences exhibited by the "open titanocenes". This information has now provided key insight into the factors which favor the existence of the 14-electron "open titanocenes", and it also indicates that substantial revision of some phosphine cone angle values is necessary. In particular, while it has been quite universally accepted that phosphite ligands possess nearly the smallest of cone angles,[5] this now appears not to be the case, so that previous indications of strong phosphite binding in various nickel complexes can best be attributed to electronic, rather than steric, influences. As phosphite ligands have found applications in important catalytic processes,[6] this information should allow for a better understanding of the role of these ligands in such processes.

Experimental Section

All operations involving organometallics were carried out under a nitrogen atmosphere in prepurified Schlenk apparatus or in a glovebox. Nonaqueous solvents were thoroughly dried and deoxygenated in a manner appropriate to each and were distilled immediately before use. Mass spectra were recorded on a VG Micromass 7070 double focussing mass spectrometer with a VE Data System 2000. Except for the parent fragment, peaks are only quoted if their relative intensities are at least 10% of the intensity of the strongest peak. NMR spectra were recorded on Varian XL-300 spectrometers. ^{31}P NMR spectra are referenced to external H_3PO_4, while ^1H NMR spectra were referenced either to C_6D_5H (7.15 ppm) or $CD_3C_6D_4H$ (6.98 ppm). Similarly, ^{13}C NMR spectra were referenced to either C_6D_6 (128.0 ppm) or $CD_3C_6D_5$ (137.5 ppm). Infrared spectra were recorded with Perkin-Elmer 298 or 1500 FT spectrophotometers. Mulls were prepared in a glovebox with dry, degassed Nujol. Elemental analyses were performed by Dornis and Kolbe or MicAnal Laboratories. Melting points are uncorrected.

Trimethylphosphine and triethylphosphine were prepared according to published procedures.[7] Triethylphosphine was also purchased from Aldrich and used without further purification. Dimethylphenylphosphine (Strem) and trimethylphosphite (Aldrich) were also purchased commercially and were used as received. $TiCl_4$ was used as received from Alfa and converted to $TiCl_4(THF)_2$ by a published procedure.[8] Both 1,3-pentadiene and 3-methyl-1,3-pentadiene were obtained from Aldrich, while 2,4-dimethyl-1,3-pentadiene was prepared according to a published procedure.[9] After deoxygenation by a series of freeze-thaw degas cycles, these could be converted to their potassium salts by published procedures.[10] Except for $K(2,4\text{-}C_7H_{11})$, these salts were stored at −20 °C.

(Triethylphosphine)bis(2,4-dimethylpentadienyl)titanium [$Ti(2,4\text{-}C_7H_{11})_2(PEt_3)$]. Procedure A. To a stirred solution of 0.51 g (2.2 mmol) of bis(2,4-dimethylpentadienyl)titanium[10c] in 50 mL of pentane is added by syringe 1.30 mL (8.8 mmol) of triethylphosphine (Aldrich), resulting in a reddish-brown solution. Occasionally some red solid may precipitate at this point. The solution volume is reduced to 20 mL, the stirring bar is removed, and the flask is placed in a −20 °C freezer. After 3 days, 0.75 g (2.1 mmol) of dark red crystals of the title compound are isolated. The yield is 95% based on bis(2,4-dimethylpentadienyl)titanium.

Procedure B. A 250-mL three-necked flask equipped with magnetic stirring bar and nitrogen inlet is charged with 1.34 g (4.0 mmol) of $TiCl_4(THF)_2$, 50 mL of THF, and 0.12 g (5.0 mmol) of granular magnesium (Fisher). The flask is then fitted with a water-cooled reflux condenser, and the solution is refluxed under nitrogen for 1 h. During the reflux period the solution turns from bright yellow to black. The reaction mixture is allowed to cool to room temperature, and the reflux condenser is replaced with a pressure equalizing dropping funnel which was charged with 1.21 g (9.0 mmol) of potassium 2,4-dimethylpentadienide. After the flask is cooled to −78 °C, 1.13 mL (8.0 mmol) of triethylphosphine is added to the mixture. The potassium reagent is then dissolved in 50 mL of THF and added dropwise to the stirred solution over a period of 10 min. Upon completion of the addition the reaction mixture is allowed to warm up slowly to room temperature and is then stirred for an additional 4 h. While cold the solution is red but it turns green on warming. The THF is removed under reduced pressure to give a black-red residue. This residue is extracted with 400 mL of pentane, and the pentane extracts are filtered through a Celite pad on a coarse frit. The green pentane solution is concentrated to 30 mL in vacuo and cooled to −20 °C for 4 days. Dark red crystals (1.14 g, 3.20 mmol, mp 141–142 °C dec) are isolated, corresponding to an 80% yield based on $TiCl_4(THF)_2$.

Anal. Calcd for $C_{20}H_{37}PTi$: C, 67.40; H, 10.47. Found: C, 67.49; H, 10.40. Complete infrared data (Nujol mull): 3066 (m), 3030 (sh), 3022 (sh), 1439 (sh), 1408 (sh), 1282 (vw), 1255 (w), 1023 (vs), 1010 (sh), 1001 (sh), 992 (s), 865 (m), 841 (s), 823 (ms), 810 (ms), 777 (w), 749 (s), 723 (w), 696 (s), 641 (w), 608 (w) cm^{-1}.

^1H NMR (toluene-d_8, −50 °C): δ 4.10 (s, 2 H), 2.09 (d, 4 H, $J = 4.4$ Hz), 1.71 (s, 12 H), 1.40 (m, 6 H), 0.93 (m, 9 H), 0.86 (d, 4 H, $J = 4.5$ Hz). ^{13}C NMR (toluene-d_8, −30 °C): δ 118.9 (s), 97.4 (d, $J = 156$ Hz), 56.6 (t, $J = 159$ Hz), 30.5 (q, $J = 128$ Hz), 17.5 (t, $J = 125$ Hz), 8.1 (q, $J = 124$ Hz). ^{31}P NMR (THF, −20 °C): δ 42.3.

Mass spectrum (EI, 17 eV), *m/e* (relative intensity): 55 (21), 61 (13), 62 (64), 67 (29), 79 (26), 81 (16), 90 (100), 94 (21), 95 (55), 96 (18), 103 (16), 118 (66), 238 (11).

(Trimethylphosphine)bis(2,4-dimethylpentadienyl)titanium [$Ti(2,4\text{-}C_7H_{11})_2(PMe_3)$]. Procedure A. This compound is synthesized in a manner strictly analogous to that of the triethylphosphine adduct. To a stirred solution of 0.60 g (2.5 mmol) of bis(2,4-dimethylpentadienyl)titanium in 50 mL of pentane is added 0.38 g (5.0 mmol) of trimethylphosphine. The solution turns instantly from green to dark red, and some product may precipitate. The stirring bar is removed and the flask cooled to −20 °C. After 5 days, 0.75 g (2.4 mmol) of dark red crystals of the title compound are isolated. This corresponds to a yield of 96% based on bis(2,4-dimethylpentadienyl)titanium.

Procedure B. The synthesis follows the instructions given for the triethylphosphine adduct. In a typical reaction 8.0 mmol (2.7 g) of $TiCl_4(THF)_2$ in 50 mL of THF are reduced with 0.24 g (10 mmol) of granular magnesium (Fisher). The solution is then cooled to −78 °C and approximately 1.2 g (16 mmol) of trimethylphosphine is then added to the stirred "$TiCl_2$" solution. This is followed by the dropwise addition of 1.34 g (10.0 mmol) of potassium 2,4-dimethylpentadienide in 50 mL of THF. Upon completion of the addition, the mixture is allowed to warm slowly to room temperature, after which workup follows procedure B given for the PEt_3 adduct above, except that all volumes must be doubled. This leads to 2.06 g (6.56 mmol) of dark red crystals (mp 134–135 °C dec), corresponding to an 82% yield based on $TiCl_4(THF)_2$. The compound may be stored for long periods at −20 °C under a nitrogen atmosphere without noticeable decomposition.

Anal. Calcd for $C_{17}H_{31}PTi$: C, 64.97; H, 9.94. Found: C, 64.94; H, 9.89. Complete infrared data (Nujol mull): 3087 (mw), 3055 (mw), 3027 (mw), 1467 (vs), 1436 (vs), 1401 (s), 1298 (m), 1276 (vs), 1194

---

(3) (a) Catalytic applications for the "open metallocenes" of titanium, vanadium, and chromium have also been developed.[3b,c] (b) Smith, P. D.; Hsieh, E. U.S. Patent 4587227, 1986. (c) Freeman, J. W.; Wilson, D. R.; Ernst, R. D.; Smith, P. D.; Klendworth, D. D.; McDaniel, M. P. *J. Polym. Sci.* **1987**, *25A*, 2063.

(4) (a) Similar behavior is exhibited by the analogous vanadium, but not chromium, complexes.[4b] (b) Newbound, T. D.; Ernst, R. D., unpublished results.

(5) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransitionmetal Chemistry*; University Science Books: Mill Valley, CA, 1980. (c) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, 1984. (d) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole Publishers: Monterey, CA, 1985. (e) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole Publishers: Monterey, CA, 1985. (f) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986. (g) Nolan, S. P.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *290*, 365. (h) Socol, S. M.; Verkade, J. G. *Inorg. Chem.* **1984**, *23*, 3487.

(6) (a) Tolman, C. A.; Faller, J. W. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983. (b) Parshall, G. W. *Homogeneous Catalysis, The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; Wiley-Interscience: New York, 1980. (c) Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* **1979**, *12*, 324. (d) Masters, C. *Homogeneous Transition-metal Catalysis—a Gentle Art*; Chapman and Hall: London, 1981.

(7) (a) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met-Org. Chem.* **1974**, *4*, 149. (b) Markham, R. T.; Dietz, E. A., Jr.; Martin, D. R. *Inorg. Synth.* **1976**, *16*, 153.

(8) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

(9) Jitkow, O. N.; Bogert, M. T. *J. Am. Chem. Soc.* **1941**, *63*, 1979.

(10) (a) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036. (b) Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* **1976**, *59*, 453. (c) Wilson, D. R.; Stahl, L.; Ernst, R. D. *Organomet. Synth.* **1986**, *3*, 136.

(w), 1022 (vs), 1006 (s), 995 (vs), 948 (vs), 932 (s), 869 (ms), 834 (vs), 813 (vs), 711 (s), 665 (s) cm^{-1}.

^{1}H NMR (toluene-d_8, 27 °C): δ 4.31 (s, 2 H), 2.11 (br s, 4 H), 1.67 (br s, 12 H), 1.12 (br s, 9 H), 0.66 (br s, 4 H). ^{13}C NMR (toluene-d_8, 0 °C): δ 118.1 (s), 98.9 (d, J = 162 Hz), 56.2 (t, J = 157 Hz), 30.1 (q, J = 120 Hz), 19.6 (q, J = 124 Hz). ^{31}P NMR (THF-d_8, 27 °C): δ 23.3.

Mass spectrum (EI, 17 eV): 59 (16), 61 (36), 76 (59), 81 (14), 95 (12), 96 (14), 140 (75), 141 (12), 232 (22), 233 (14), 234 (100), 235 (25), 236 (20), 237 (13), 238 (94), 239 (19).

(Dimethylphenylphosphine)bis(2,4-dimethylpentadienyl)titanium [Ti(2,4-C_7H_{11})$_2$(PMe$_2$C$_6$H$_5$)]. Procedure A. Following the procedure outlined for the triethylphosphine adduct, 0.55 g (4.0 mmol) of dimethylphenylphosphine is added by syringe to a stirred solution of 0.48 g (2.0 mmol) of bis(2,4-dimethylpentadienyl)titanium in 50 mL of pentane. An instant color change from emerald-green to red is observed and occasionally some product precipitates at this point. The solution volume is reduced to 30 mL, the stir bar is removed, and the flask is placed in a −20 °C freezer for 4 days. Dark red crystals (0.72 g, 1.90 mmol) of the title compound are isolated, corresponding to a 95% yield with respect to bis(2,4-dimethylpentadienyl)titanium.

Procedure B. The synthesis of this compound again follows that described for the triethylphosphine adduct. A solution of "TiCl$_2$" is prepared by reducing 1.07 g (3.2 mmol) of TiCl$_4$(THF)$_2$ with 4.0 mmol (0.10 g) of granular magnesium in 50 mL of THF under reflux for 1 h. The resulting black solution is cooled to −78 °C and 1.2 mL (7.0 mmol) of dimethylphenylphosphine (Strem) and 0.91 g (7.0 mmol) of potassium 2,4-dimethylpentadienide in 50 mL of THF are added in this order. The ensuing dark red solution is allowed to warm up slowly and then is stirred for an additional 4 h. Removal of the solvent in vacuo gives a red-black solid which is extracted with several 50-mL portions of pentane. The red pentane solution is filtered through a Celite pad and concentrated to 50 mL under reduced pressure. After 5 days at −20 °C, 0.95 g (2.5 mmol) of dark red product is isolated (mp 125–126 °C). The yield is 78% based on TiCl$_4$(THF)$_2$.

Anal. Calcd for $C_{22}H_{33}PTi$: C, 70.21; H, 8.84. Found: C, 70.18; H, 8.80. Complete infrared data (Nujol mull): 3062 (w), 3041 (w), 3024 (sh), 1437 (sh), 1431 (w), 1425 (w), 1411 (w), 1398 (w), 1289 (mw), 1272 (m), 1258 (m), 1021 (vs), 993 (s), 985 (m), 939 (s), 909 (ms), 899 (vs), 865 (m), 853 (m), 842 (ms), 818 (s), 797 (sh), 741 (vs), 709 (ms), 693 (vs), 664 (ms), 610 (sh) cm^{-1}.

^{1}H NMR (toluene-d_8, −10 °C): δ 7.31 (br s, 2 H, aromatic), 7.13 (br s, 2 H, aromatic), 7.05 (s, 1 H, aromatic), 4.26 (s, 2 H), 2.32 (s, 4 H), 1.65 (s, 12 H), 1.41 (d, 6 H, J(P–H) = 4.1 Hz), 0.50 (d of d, 4 H, J(P–H) = 10 Hz, J(H–H) = 4.5 Hz). ^{13}C NMR (toluene-d_8, −10 °C): δ 118.4 (s), 98.8 (d, J = 161 Hz), 57.5 (t, J = 150 Hz), 30.0 (q, J = 127 Hz), 18.1 (q, J = 132 Hz). ^{31}P NMR (toluene-d_8, 0 °C); δ 41.2.

(Trimethylphosphite)bis(2,4-dimethylpentadienyl)titanium [Ti(2,4-C_7H_{11})$_2$(P(OMe)$_3$)]. In a 250-mL two-necked flask equipped with nitrogen inlet and magnetic stirring bar, 0.48 g (2.0 mmol) of bis(2,4-dimethylpentadienyl)titanium is dissolved in 50 mL of pentane. By syringe 0.50 g (4.0 mmol) of trimethylphosphite (Aldrich) is added to the stirred solution leading to an instantaneous color change from emerald-green to orange. (In case a white solid precipitates at this point the solution must be filtered before continuing.) The solution volume is reduced to 25 mL in vacuo and the flask cooled to −98 °C. After 3 days, 0.67 g (1.84 mmol) of golden-orange crystals (mp 80–81 °C dec) are isolated. The yield is 92% based on bis(2,4-dimethylpentadienyl)titanium. An analogous procedure may be used to isolate the corresponding P(OEt)$_3$ adduct.[11]

Anal. Calcd for $C_{17}H_{31}O_3PTi$: C, 56.36; H, 8.56. Found: C, 56.39; H, 8.58. Complete infrared data (Nujol mull): 3090 (sh), 3063 (mw), 1482 (sh), 1278 (w), 1257 (mw), 1078 (s), 1055 (sh), 1017 (vs), 988 (sh), 872 (w), 862 (m), 840 (ms), 802 (ms), 746 (s), 716 (vs), 695 (sh).

^{1}H NMR (toluene-d_8, −50 °C): δ 4.35 (s, 2 H), 3.44 (d, 9 H, J(P–H) = 9.2 Hz), 2.67 (s, 4 H), 1.68 (s, 12 H), 1.03 (d of d, 4 H, J(P–H) = 10 Hz, J(H–H) = 4 Hz). ^{13}C NMR (toluene-d_8, −20 °C): 117.1 (s), 98.2 (d, J = 155 Hz), 56.8 (t, J = 156 Hz), 51.1 (q, J = 146 Hz), 30.1 (q, J = 124 Hz). ^{31}P NMR (THF, 0 °C): δ 215.3.

Mass spectrum (EI, 17 eV): 81 (11), 93 (94), 94 (30), 95 (16), 96 (16), 109 (69), 124 (100), 140 (52), 232 (15), 234 (62), 235 (14), 236 (12), 238 (80), 239 (14).

(Triethylphosphine)bis(3-methylpentadienyl)titanium [Ti(3-C_6H_9)$_2$(PEt$_3$)]. This compound is synthesized in a manner similar to that used for the 2,4-dimethylpentadienyl analogue. A 250-mL three-necked flask is charged with 0.67 g (2.0 mmol) of TiCl$_4$(THF)$_2$, 0.053 g (2.2 mmol) of granular magnesium (Fisher), and 50 mL of THF. After refluxing the solution under nitrogen for 1 h the flask is cooled to −78 °C and the reflux condenser is replaced with a dropping funnel. By syringe, 0.59 mL (4.0 mmol) of triethylphosphine is added to the mixture. A solution of 0.60 g (5.0 mmol) of potassium 3-methylpentadienide in 50 mL of THF is prepared in the dropping funnel and this solution is added dropwise to the stirred "titanium dichloride" solution. The reaction mixture is allowed to warm up slowly to room temperature and then is stirred for an additional 4 h to ensure completion of the reaction. Removal of the solvent under reduced pressure leaves a red-black solid residue which is extracted with several 50-mL portions of pentane. The combined reddish extracts are filtered through a Celite pad and then concentrated to 30 mL in vacuo. After 4 days at −20 °C, 160 mg (0.50 mmol) of dark red crystals (mp 101–102 °C) are isolated. The yield is 25% based on TiCl$_4$(THF)$_2$. The compound is thermally less stable than the 2,4-dimethylpentadienyl analogue.

Anal. Calcd for $C_{18}H_{33}PTi$: C, 65.85; H, 10.13. Found: C, 65.57; H, 10.39. Complete infrared data (Nujol mull): 3078 (m), 1500 (m), 1232 (m), 1210 (ms), 1161 (s), 1027 (vs), 819 (vs), 766 (ms), 746 (ms), 723 (m), 696 (s), 640 (vw), 612 (vw) cm^{-1}.

^{1}H NMR (C_6D_6, 20 °C): δ 4.52 (t, 4 H, J = 11.6 Hz), 2.48 (d of d, 4 H, J = 11.3, 2.8 Hz), 1.81 (s, 6 H), 1.50 (br, 6 H, (PEt$_3$)), 0.92 (br m, 9 H (PEt$_3$)), 0.84 (d, 4 H, J = 11.4 Hz). ^{13}C NMR (C_6D_6, 10 °C): δ 110.8 (s), 106.6 (d, J = 154 Hz), 55.4 (t, J = 157 Hz), 27.7 (q, J = 126 Hz), 19.3 (t, J = 126 Hz), 8.4 (q, J = 126 Hz). ^{31}P NMR (C_6D_6, 10 °C): δ 44.7.

(Triethylphosphine)bis(pentadienyl)titanium [Ti(C_5H_7)$_2$(PEt$_3$)]. The synthesis of this compound follows that given for the 3-methylpentadienyl compound. In a 250-mL three-necked flask, 1.0 g (3.0 mmol) of TiCl$_4$(THF)$_2$ in 50 mL of THF is reduced under reflux by 0.096 g (4.0 mmol) of granular magnesium to give a black "TiCl$_2$" solution. The flask is cooled to −78 °C and 0.89 mL (6.0 mmol) of triethylphosphine and 0.85 g (8.0 mol) of potassium pentadienide dissolved in 50 mL of THF are added in this order. The reaction mixture is allowed to warm slowly to room temperature and is then stirred for approximately 4 h. Removal of the solvent under vacuum gives a red-black solid. This residue is extracted with 200 mL of pentane and the resulting red pentane solution is filtered through a pad of Celite. The volume of the solution is reduced to 30 mL and cooled to −20 °C for 4 days. Approximately 0.18 g (0.60 mmol) of dark red, crystalline product (mp 122 °C dec) is isolated corresponding to a 20% yield based on TiCl$_4$(THF)$_2$. The thermal stability of this compound is even less than that of the 3-methylpentadienyl analogue.

Anal. Calcd for $C_{16}H_{29}PTi$: C, 64.00; H, 9.73. Found: C, 62.03; H, 9.76. Complete infrared data (Nujol mull): 3079 (mw), 3068 (mw), 3053 (mw), 1498 (m), 1485 (ms), 1427 (m), 1369 (m), 1261 (s), 1219 (ms), 1034 (vs), 939 (w), 913 (m), 833 (sh), 813 (vs), 800 (s), 772 (ms), 751 (ms), 698 (s), 667 (vs), 659 (w), 648 (w), 616 (w) cm^{-1}.

^{1}H NMR (C_6D_6, 21 °C): δ 4.63 (q, 4 H, J = 9 Hz), 4.19 (t, 2 H, J = 9 Hz), 2.50 (d of d, 4 H, J = 11, 1.5 Hz), 1.47 (m, 6 H (PEt$_3$)), 0.89 (m, 9 H (PEt$_3$)), 0.79 (d of d of d, 4 H, J(P–H) = 14 Hz, J(H–H) = 11, 3.5 Hz). ^{13}C NMR (C_6D_6, 21 °C): δ 108.4 (d, J = 157 Hz), 98.4 (d, J = 157 Hz), 57.1 (t, J = 155 Hz), 19.7 (t, J = 126 Hz), 8.2 (q, J = 126 Hz). ^{31}P NMR (C_6D_6, 21 °C): δ 44.4.

Thermodynamic Studies of Lewis Base Adducts of Various Bis(pentadienyl)titanium Compounds. For a typical experiment a high-quality 5-mm NMR tube (Wilmad) was flame attached to a Schlenk-line adapter. A calibration mark corresponding to 0.80 mL was then etched onto the side of the tube. The apparatus was transferred to a glovebox where an accurately weighed solid sample of the corresponding Lewis base adduct was placed inside the NMR tube. The amount of sample was chosen so as to give solutions of approximately 0.06 to 0.10 molarity. Upon transfer of the apparatus to a Schlenk-line the sample was dissolved in freshly distilled THF which was added to the calibration mark by microsyringe. Following addition of the THF the lower part of the NMR tube was cooled to −196 °C and a partial vacuum was applied. With the sample frozen, the NMR tube was flame-sealed and detached from the adapter. After the sample had warmed up to room temperature, it was checked for visible signs of decomposition and stored at −20 °C. For the competitive experiments, a nearly identical procedure was followed. Two solutions having similar concentrations (0.06–0.10 M) of the PF$_3$ adduct[2b] were prepared, containing also 10–20 equiv of PMe$_3$. One sample was studied at various temperatures, while the second was examined at room temperature as a control.

The proton-decoupled ^{31}P NMR data were obtained on a Varian SC-300 or an XL-300 NMR spectrometer at a frequency of 121.4210 MHz. The spectra were acquired with the instrument in an "unlocked" condition so that nondeuteriated THF could be used as solvent. Before data acquisition the field homogeneity was adjusted with a phosphorus standard (such as P(OCH$_3$)$_3$) in deuteriated THF. Following a 90° flip angle calibration the pulse width was set to give a 30° flip angle (generally 5–9 μs). The acquisition time was approximately 0.6–1.0 s with a 50-s pulse delay. This delay time corresponds to about 3T$_1$–5T$_1$ which

---

[11] Stahl, L.; Thomson, M. A.; Ernst, R. D., unpublished results.

is necessary for accurate intensity measurements to be made.[12] The spectra were acquired with use of either ^1H broadband or WALTZ-16 (both gated) decoupling, i.e., the decoupler was "on" only during the acquisition time to give decoupled spectra with suppressed NOE.[12] The spectra were not digitally filtered, i.e., the FID was not multiplied with a suitable exponential for sensitivity enhancement. While this results in a decreased signal-to-noise ratio, such a function may affect the integrations of peaks in a nonlinear way and, therefore, give erroneous intensities for integrated peaks. Generally 100–200 transients were necessary to give sufficiently good signal/noise ratios, after which the peaks were integrated and the integral heights measured with a ruler. The probe temperatures during data acquisition fluctuated by no more than ±0.2 deg. The displayed temperatures were corrected with methanol and ethylene glycol for standard temperature calibration techniques.[13]

From the known molarity of the sample and the integrated intensities of the two peaks for "free" and coordinated Lewis bases, the equilibrium constants were easily determined. The pertinent thermodynamic parameters were obtained by plotting ln K vs. $1/T$ with the slope of the line corresponding to $-\Delta H/R$ and the intercept at the y axis to $\Delta S/R$. The lines were derived from least-squares computations, as were the standard deviations for the enthalpy and entropy of adduct formation.

The reported standard deviations are strictly mathematical and reflect the deviation of the data points about the least-squares line. They are not meant to reflect uncertainties in sample preparation, integration, or temperature control. However, for one compound, (triethylphosphine)bis(2,4-dimethylpentadienyl)titanium, data were obtained from two independently prepared samples, and suggest that additional sources of error are probably minor. No corrections were applied for the temperature-induced volume changes of the samples, which should also be minor over the relatively small temperature ranges studied.

Results

Phosphine adducts of the bright green "open titanocene", $Ti(2,4-C_7H_{11})_2$, may readily be prepared in high yield by either reaction 1 or 2, although the reversibility of the reaction generally requires the product mixture to be cooled somewhat in order for adduct formation to be nearly complete (vide infra). The $P(OMe)_3$

$$Ti(2,4-C_7H_{11})_2 + L \rightarrow Ti(2,4-C_7H_{11})_2(L) \qquad (1)$$

$$L = PMe_3,\ PMe_2(C_6H_5),\ P(OMe)_3,\ P(OEt)_3,\ PEt_3$$

$$\text{"}TiCl_2(THF)_2\text{"} + 2K(2,4-C_7H_{11}) + L \rightarrow Ti(2,4-C_7H_{11})_2(L) \qquad (2)$$

$$L = PMe_3,\ PMe_2(C_6H_5),\ PEt_3$$

and $P(OEt)_3$ adducts may also be prepared as in reaction 1, as had the previously reported monocarbonyl and PF_3 adducts.[2b] Simple dissolution of the above reddish-brown PEt_3 adduct in organic solvents leads to a bright green solution, indicating nearly complete phosphine dissociation, while the dissolution of the PMe_3 complex leads to a deep reddish solution, suggesting little if any dissociation. For the $PMe_2(C_6H_5)$, $P(OMe)_3$, and $P(OEt)_3$ adducts, intermediate degrees of dissociation result, and qualitatively one can clearly observe that the $PMe_2(C_6H_5)$ binding is stronger than that of PEt_3, while $P(OEt)_3$ seems roughly comparable to $P(OMe)_3$ and PEt_3. Hence, the favorability for binding seems to fall in the order $PF_3 > PMe_3 > PMe_2(C_6H_5) > P(OMe)_3 > PEt_3$, which agrees with the results of more quantitative equilibria studies (vide infra).

Since neither $Ti(C_5H_7)_2$ nor $Ti(3-C_6H_9)_2$ has been isolated, both $Ti(C_5H_7)_2(PEt_3)$ and $Ti(3-C_6H_9)_2(PEt_3)$ had to be prepared by a variation of reaction 2, in which KC_5H_7 or $K(3-C_6H_9)$, respectively, replaces $K(2,4-C_7H_{11})$. Unlike $Ti(2,4-C_7H_{11})_2(PEt_3)$ which dissociates nearly completely in solution at room temperature, solutions of $Ti(C_5H_7)_2(PEt_3)$ and $Ti(3-C_6H_9)_2(PEt_3)$ are deep red, indicating substantially stronger phosphine binding. As with the previous adducts, these complexes are very air- and moisture-sensitive. In addition, however, they are also far more thermally sensitive and must be stored cold. Spectroscopic data, particularly ^1H and ^{13}C NMR spectroscopy, indicates that the expected, symmetrical syn-eclipsed configurations have been adopted for all complexes, i.e., I–III. Such configurations have been crystallographically demonstrated for several $M(2,4-C_7H_{11})_2(L)$ complexes ($M = Ti, V$; $L = PF_3$[14] and $M = Zr, Nb$; $L = PEt_3$[15]), as well as for $V(3-C_6H_9)_2(CO)$ and $V(2,4-C_7H_{11})_2(CO)$,[16] although both $Mo(2,4-C_7H_{11})_2(PEt_3)$[15] and $W(2,4-C_7H_{11})_2(PEt_3)$[17] have been observed to adopt unsymmetric configurations in which one η^5-2,4-dimethylpentadienyl ligand is present in the unusual sickle (S) geometry.

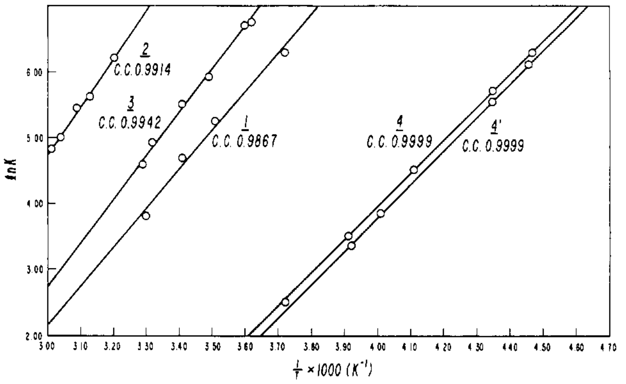
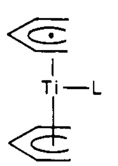
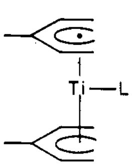


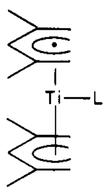
Figure 1. Plots of ln K vs. T^{-1} for the formation of representative ligand adducts of $Ti(2,4-C_7H_{11})_2$. Correlation coefficients are designated by CC. The adducts are as follows: (1) $P(OMe)_3$; (2) PMe_3; (3) $PMe_2(C_6H_5)$; (4 and 4′) PEt_3.



I



II



III

In order to obtain thermodynamic parameters for the dissociation of the phosphine adducts, variable-temperature ^{31}P NMR spectra were recorded for each compound in the appropriate temperature range. Equilibrium constants were determined by integration of the phosphorus resonances for both the free and the coordinated phosphines and from the known total concentration of phosphine species, x. Under conditions of the experiments, the concentration of the free "open titanocene" is equal to the concentration of the free phosphine (as in reaction 3). It is important to note that to obtain accurate phosphorus integrations, the spectra strictly speaking must be obtained by using gated proton decoupling techniques. Runs without such decoupling, however, indicated little variation in results for at least the phosphine ligands.

$$\underset{x-y}{Ti(2,4-C_7H_{11})_2L} \rightleftarrows \underset{y}{Ti(2,4-C_7H_{11})_2} + \underset{y}{L} \qquad (3)$$

Except for $Ti(C_5H_7)_2(PEt_3)$, all complexes did indeed demonstrate reversible phosphine dissociation. Pertinent equilibria parameters are listed in Table I, while the pertinent plots of log K vs. $1/T$ are provided in Figure 1, along with their correlation coefficients. Standard deviations for the thermodynamic parameters given in Table I were obtained strictly mathematically, i.e., no adjustment for systematic errors is included. However, to judge the overall reliability of the thermodynamic parameters, three measurements on $Ti(2,4-C_7H_{11})_2(PEt_3)$ were carried out. Two of these involved duplicate runs on the same sample, while the third involved an independent sample. The respective ΔH values

---

(12) (a) Stanislawski, D. A.; Van Wazer, J. R. *Anal. Chem.* **1980**, *52*, 96. (b) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979.

(13) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227.

(14) (a) Ernst, R. D. *Struct. Bond. (Berlin)* **1984**, *57*, 1. (b) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56.

(15) Stahl, L.; Hutchinson, J. P.; Wilson, D. R.; Ernst, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 5016.

(16) Rheingold, A. L., private communication.

(17) Ziegler, M. L., private communication.

Table I. Equilibrium Parameters for Ligand Dissociation from Open Titanocene Complexes

compound	1000/T	-ln K
$Ti(2,4-C_7H_{11})_2P(CH_3)_3$	3.20	6.20
	3.13	5.62
	3.09	5.45
	3.04	4.97
	3.01	4.82
ΔH = 14.5 ± 0.8 kcal/mol; ΔS = 34.1 ± 2.4 eu		
$Ti(2,4-C_7H_{11})_2P(CH_3)_2(C_6H_5)$	3.62	6.75
	3.60	6.70
	3.49	5.86
	3.41	5.49
	3.32	4.90
	3.29	4.57
ΔH = 12.9 ± 0.5 kcal/mol; ΔS = 33.3 ± 1.9 eu		
$Ti(2,4-C_7H_{11})_2P(OCH_3)_3$	3.72	6.28
	3.51	5.24
	3.41	4.68
	3.30	3.87
ΔH = 11.4 ± 0.9 kcal/mol; ΔS = 30.1 ± 3.2 eu		
$Ti(2,4-C_7H_{11})_2P(OC_2H_5)_3$	3.45	4.62
	3.56	5.35
	3.71	6.12
	3.86	6.84
ΔH = 10.6 ± 0.6 kcal/mol; ΔS = 27.4 ± 2.1 eu		
$Ti(2,4-C_7H_{11})_2P(C_2H_5)_3$	4.47	6.28
	4.35	5.68
	4.11	4.50
	3.91	3.48
	3.72	2.50
ΔH = 10.0 ± 0.1 kcal/mol; ΔS = 32.2 ± 0.3 eu		
$Ti(3-C_6H_9)_2P(C_2H_5)_3$	3.33	6.99
	3.24	6.28
	3.14	5.59
ΔH = 14.6 ± 0.7 kcal/mol; ΔS = 34.8 ± 2.4 eu		

Table II. Equilibrium Parameters for the $Ti(2,4-C_7H_{11})_2(PF_3)$ + $PMe_3 \rightleftarrows Ti(2,4-C_7H_{11})_2(PMe_3) + PF_3$ Competitive Reaction

1000/T	-ln K
3.33	6.27
3.43	6.47
3.51	6.59
3.70	6.82
ΔH = 2.9 ± 0.2 kcal/mol; ΔS = −2.9 ± 0.8 eu	

for these three runs are 9.9 ± 0.1, 10.1 ± 0.1, and 10.0 ± 0.1 kcal/mol, while the respective ΔS values are 32.4 ± 1.5, 32.8 ± 1.4, and 32.2 ± 1.2 eu. From the reproducibility of these results, it would appear that the overall reliabilities of the ΔH and ΔS values have been reasonably well estimated mathematically. As PF_3 binding appeared to be stronger than that of any of the other ligands, its binding was determined indirectly through a competition with PMe_3. Combining the data for Tables I and II leads to ΔH and ΔS values for PF_3 dissociation of 17.4 ± 0.8 kcal/mol and 31.2 ± 2.5 eu, respectively.

Another estimate of the reliability of the data may be obtained by comparing the various ΔS values determined for each of the complexes. As can be seen in Table I, the ΔS values for dissociation fall in the relatively narrow range of 27.4–34.8 eu, suggesting that the data do indeed reflect a similar process for each of these complexes. A value of 32.5 eu seems to be a reasonable overall average for ΔS, and in fact, only one value of the seven determined deviates from this by more than one standard deviation. This again suggests that the systematic contributions to the reported standard deviations are likely to be small.

As can be seen in Table I, the ΔH values for the phosphine binding in the 2,4-dimethylpentadienyl complexes follow exactly the qualitative color observations (which reflect ΔG) for these species upon dissolution (vide supra). Thus, the order of binding is clearly $PF_3 > PMe_3 > PMe_2(C_6H_5) > P(OMe)_3 > PEt_3$, with $P(OEt)_3$ being similar to the latter two ligands. An even more dramatic effect is brought about by the presence or absence of methyl groups on the pentadienyl ligands—while $Ti(2,4-C_7H_{11})_2(PEt_3)$ dissociates very readily (ΔH = 10.0 kcal/mol), $Ti(3-C_6H_9)_2(PEt_3)$ does so much less readily, and it is actually quite comparable to $Ti(2,4-C_7H_{11})_2(PMe_3)$ (14.6 vs. 14.5 kcal/mol, respectively). For $Ti(C_5H_7)_2(PEt_3)$, no dissociation could be detected up to ca. 60 °C, at which the decomposition rate became too rapid to allow for useful data to be obtained. Hence, it can be seen that the addition of methyl groups to the pentadienyl ligands tends to promote ligand dissociation, thereby favoring the existence of the 14-electron "open titanocene".

Table III. Comparison of Phosphine Cone Angles with ΔH(dissociation) for the $Ti(2,4-C_7H_{11})_2(L)$ Complexes

L	ΔH	TCA[a]	RCA[b]
PF_3	17.4	104°	104°
$P(CH_3)_3$	14.5	118°	118°
$P(CH_3)_2(C_6H_5)$	12.9	122°	122°
$P(OCH_3)_3$	11.4	107°	128°
$P(OC_2H_5)_3$	10.6	109°	134°
$P(C_2H_5)_3$	10.0	132°	137°

[a] Tolman cone angle. [b] Revised cone angle.

Discussion

The data provided in Table I clearly demonstrate the reversibility of (16 electron) adduct formation by the 14-electron "open titanocene" $Ti(2,4-C_7H_{11})_2$. Previously, a PF_3 adduct had also been reported, although its binding is significantly stronger.[2b] With this reasonably diverse group of phosphines and phosphites, one would hope to be able to reach some meaningful conclusions regarding adduct formation by the "open titanocene", which clearly differs markedly from $Ti(C_5H_5)_2$ as well as $Ti(C_5Me_5)_2$, which will even form adducts with N_2. Certainly the most important factor related to phosphine ligand coordination is the ligand cone angle, a measure of steric influences proposed by Tolman.[5a,18] Indeed, one can note a significant correlation between the ΔH values for dissociation and the cone angles for the given phosphine and phosphite ligands (Table III). A significant departure from this trend, however, may be seen for the phosphites, which seem to bind anomalously weakly for their reported cone angles of 107–109°. While one might try to explain this as an electronic influence, this would seem somewhat difficult to do, as both the relatively good donor PMe_3 and the good acceptor PF_3 bind quite strongly, while it is the intermediate $P(OMe)_3$ which binds weakest.[19] In fact, it actually does appear that even the $P(OMe)_3$ data can be understood in terms of a predominantly steric effect. It seems that the cone angles for the phosphites and PEt_3 should be revised for at least these and related adducts, as the configurations they adopt do not match those used in the initial cone angle estimations. Thus, several $M(2,4-C_7H_{11})_2(PEt_3)$ complexes (M = Zr, Nb, Mo, W)[15,17], as well as $V(C_5H_5)(C_5H_7)(PEt_3)$,[20] $Ti(C_5H_5)_2(CO)(PEt_3)$,[21] and $Zr(C_5H_5)_2(CO)(P(OMe)_3)$,[22] all have their phosphine or phosphite ligands present in configuration IV, while configuration V was the original (and at that time certainly reasonable) configuration chosen for cone angle estimation. In fact, about 40 other structures involving $P(OMe)_3$ ligands have

---

[18] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953, 2956.

[19] (a) By analogy to the situation observed for Fischer vs. Schrock carbene complexes,[19b] one could try to invoke some multiple P–O bonding, which might prevent M–P multiple bonding, but this explanation does not appear to fit in the present situation. (b) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

[20] Gedridge, R. W.; Hutchinson, J. P.; Ernst, R. D., manuscript in preparation.

[21] Edwards, B. H.; Rogers, R. D.; Sikora, D. J.; Atwood, J. L.; Rausch, M. D. *J. Am. Chem. Soc.* **1983**, *105*, 416.

[22] Erker, G.; Dorf, U.; Krüger, C.; Angermund, K. *J. Organomet. Chem.* **1986**, *301*, 299.

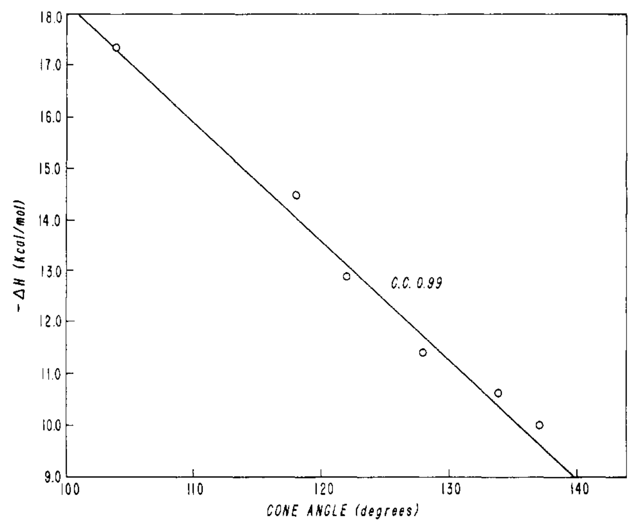
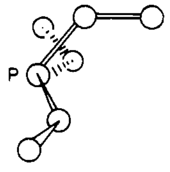
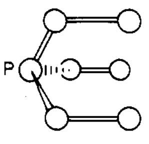


Figure 2. Dependence of the ΔH values for adduct formation on the ligand cone angles.

been determined, and while the $P(OMe)_3$ group has been found to adopt five different configurations, that of V has not been observed.[23] Using configuration IV for $P(OMe)_3$, $P(OEt)_3$, and PEt_3 leads to revised cone angles of 128, 134, and 137°, respectively. The phosphite ligands are clearly affected most, as in the original assumed configuration, oxygen atom lone pairs rather than C–H bonds were directed to the periphery of the cone. As can be seen in Table III and Figure 2, the use of the revised cone angle values for the phosphites and PEt_3 leads to excellent agreement with the ΔH values (correlation coefficient = 0.99).[24] Thus, it appears at least for phosphine ligands that the relative binding to the already sterically crowded "open titanocene" is determined predominantly by steric considerations. In retrospect, one would have to expect that cone angle effects would tend to dominate more in such a sterically crowded complex than in the less crowded nickel complexes initially employed by Tolman.[25] Interestingly, the above considerations suggest that $Ti(2,4\text{-}C_7H_{11})_2$ should form a much more strongly bound adduct with a rigidly fixed phosphite such as $P(OCH_2)_3CR$ as compared to $P(OMe)_3$. This expectation has, in fact, been verified.[26]



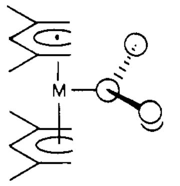
IV



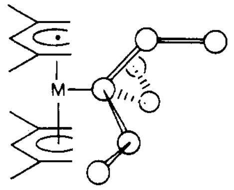
V

It can be noted that in the observed conformation IV, one ethyl or methoxy group does remain pointed back, as had been expected in the original cone angle estimation. It would appear that the other two groups are prevented from pointing back by the CH_3–CH_3 interactions which would ensue.[27] Hence, if these arguments are correct, the original cone angles estimated for such ligands as PX_2Et, $PX_2(OMe)$, or $PX_2(NHMe)$ (X = Me, F, etc.) should still be valid, while those for such ligands as PEt_2X, $P(OMe)_2X$, and possibly $P(NHMe)_2X$ (X = H, F, Me, Et, OMe, etc.) would need revision. Of course, some phosphine ligand conformations may vary from complex to complex, and in such cases due allowances would need to be made.

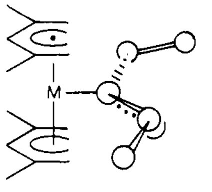
In addition to affecting the tendency for their adducts to dissociate, it actually appears that phosphine ligands with methyl groups in each of their three β positions (i.e., phosphines with three attached CH_2CH_3 or OCH_3 groups) prefer to adopt a different orientation in their bis(pentadienyl)metal complexes compared to that adopted by PF_3 or PMe_3. In $Ti(2,4\text{-}C_7H_{11})_2(PF_3)$, $V(2,4\text{-}C_7H_{11})_2(PF_3)$, and $Ti(2,4\text{-}C_7H_{11})_2(PMe_3)$,[17] the phosphine ligands each have one substituent lying midway between the two pentadienyl ligand planes, as in VI, while in the $M(2,4\text{-}C_7H_{11})_2(PEt_3)$ (M = Zr, Nb, Mo, W)[15,17] and even $V(C_5H_5)(C_5H_7)(PEt_3)$[20] structures, one of the ethyl groups is situated by the open edge of a pentadienyl ligand, as in VII. It would appear that placement of three OCH_3 or C_2H_5 groups on the phosphine in a structure such as VI might bring about repulsions between the two equivalent phosphine or phosphite groups (not the one midway between the pentadienyl planes) and the terminal pentadienyl CH_2 groups toward which they are directed. If this is indeed correct, one might expect an "open titanocene" adduct of PEt_2F (or $P(OMe)_2F$) to adopt a structure such as VIII, although other alternatives might exist as well. Also apparent from the data in Table I is the fact that incorporation of methyl groups onto the pentadienyl ligands brings about a weakening of the phosphine binding. The most likely explanation for this effect would involve the CH_3–CH_3 repulsions which are generated on the adoption of eclipsed structures (II or III). Structural studies on adducts such as $Ti(2,4\text{-}C_7H_{11})_2(PF_3)$ indicate that the methyl groups are well within the expected van der Waals separation of 4.0 Å (ca. 3.2–3.3 Å).[28] Furthermore, in the eclipsed structure the methyl groups are prohibited by these contacts from bending as far below their ligand planes (toward the metal atom) as they otherwise would (by ca. 9° for 2 and 4 substituents[14]) in order to improve overlap between the ligand and metal d orbitals.[29] Thus, in the $M(2,4\text{-}C_7H_{11})_2(PF_3)$ (M = Ti, V) structures, the methyl substituents are tilted out of the ligand planes by averages of less than 4°. However, it has been observed that methyl substituents in the 3 position have a much lesser tendency to bend below the ligand plane than their 2 and 4 counterparts;[30] hence,



VI



VII



VIII

---

[23] (a) In fact, in no structure does one even observe just two methoxy groups bent straight back. (b) Bart, J. C. J.; Favini, G.; Todeschini, R. *Phosphorus Sulfur* 1983, *17*, 205. (c) Michael, G.; Kaub, J.; Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 502.

[24] Use of the Tolman cone angles leads to a correlation coefficient of 0.21.

[25] (a) It seems quite possible that in Tolman's Ni(0) systems, electronic effects might dominate at small cone angles (prior to reaching a "steric threshold"[25b]), favoring the π-acceptors, e.g., $PF_3 > P(OMe)_3 > PMe_3$, until steric crowding increased and became dominant. Note that for our titanium adducts, an excellent correlation with steric size is obtained for relatively small phosphines and phosphites, having widely differing electronic properties. Extension to larger cone angle analogues should only serve to reduce the electronic effects, which appear small as it is. (b) Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650. (c) Cotton, J. D.; Markwell, R. D. *Ibid.* **1985**, *4*, 937.

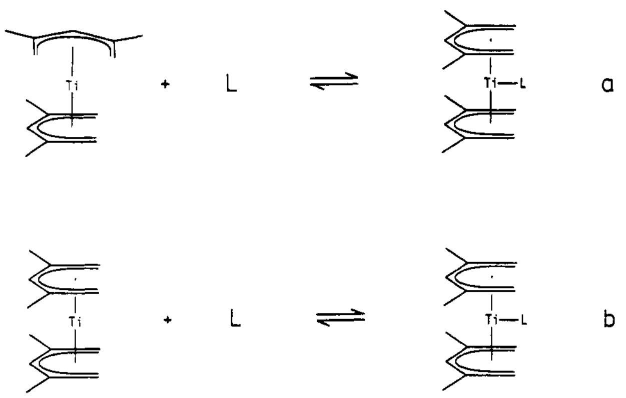
[26] Freeman, J. W.; Diver, S.; Ernst, R. D., unpublished results.

[27] (a) Even with O–P–O angles of 109.5°, the C_{3v} form of $P(OCH_3)_3$ would have CH_3—CH_3 contacts of only 3.2 Å, compared to the van der Waals separation of 4.0 Å. In reality, O–P–O angles in coordinated phosphites are generally ca. 103°.[23b] (b) Pauling, L. *The Nature of the Chemical Bond*; 3rd. ed.; Cornell University Press: Ithaca, NY, 1960.

[28] Wilson, D. R.; Ernst, R. D., unpublished results.

[29] Haaland, A. *Acc. Chem. Res.* **1979**, *12*, 415.

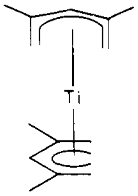
Scheme I



dissociation should not be aided quite as much by a 3-methyl substituent as by a single 2- or 4-methyl substituent, so that $Ti(3\text{-}C_6H_9)_2(PEt_3)$ would be expected to be more similar to $Ti(C_5H_7)_2(PEt_3)$ than to $Ti(2,4\text{-}C_7H_{11})_2(PEt_3)$. With this in mind, it would appear that a likely upper bound on the ΔH of dissociation for $Ti(C_5H_7)_2(PEt_3)$ would be 19.1 kcal/mol. On the assumption that at least a 5% dissociation would have been observable, a lower bound of 16.4 kcal/mol can be estimated (with ΔS = 32.5 eu). However, methylation of the 2, 3, or 4 positions of a pentadienyl ligand does bring about one other effect, a contraction of the particular C–C(Me)–C bond angle,[14] and hence contraction of the pentadienyl ligand. This effect is generally ca. 4°, and it seems comparable for either 2-, 3-, or 4-methylation.[14,30] The overall effect is rather slight, however, and it does not appear to be nearly as important as the eclipsing CH_3–CH_3 interactions.[31]

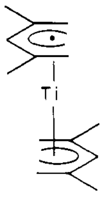
While the above considerations clearly implicate steric factors in the dissociation of the phosphine adducts of the "open titanocenes", they do not entirely explain why the pentadienyl complexes as a general group have a greater favorability relative to titanocene moieties (even $Ti(C_5Me_5)_2$) for adopting the electron-deficient 14- and 16-electron complexes. To understand this difference, it is helpful to estimate cone angles for the pentadienyl ligands, as well as for C_5Me_5. Using space-filling models and the general procedure described by Tolman,[5a] we have estimated the cone angle for C_5Me_5 as 167°, and those for C_5H_7, $3\text{-}C_6H_9$, and $2,4\text{-}C_7H_{11}$ as ca. 180–182° (cf., 136° for C_5H_5). These angles apply for a constant metal–carbon bond distance of ca. 2.36 Å and will vary accordingly for larger or smaller metals. However, there is one further complication. While metal–carbon bond distances for pentadienyl and cyclopentadienyl complexes have been found to be quite comparable for chromium,[32] manganese,[30a] iron,[14,33] ruthenium,[30b] and cobalt,[34] it has been found for vanadium that the metal–pentadienyl bonding is significantly enhanced relative to metal–cyclopentadienyl bonding (ca. 2.21 vs. 2.29 Å, respectively).[20,32] It seems certain that such a difference will also occur for titanium as well. If a correction for the shortened metal–carbon bond distance is applied, the values for the above pentadienyl cone angles jump to ca. 190–192°. Thus, the fact that the pentadienyl ligands are more sterically demanding than C_5Me_5 (at least in titanium and vanadium complexes) is a result not only of the larger girth of the bonded portion of the pentadienyl ligand and of the resulting shortening of the metal–ligand plane distance but also of the further metal–pentadienyl shortening which preferentially takes place for these metals.[35]

Some final comments need to be made about the ΔH values. In effect these are actual metal–ligand bond energies, although some degree of caution must be employed in their interpretation as a result of the adoption of differing orientations of the two pentadienyl ligands in an "open titanocene" and in the various base adducts. A variety of considerations, particularly an MO[36] study and conformational trends in $M(2,4\text{-}C_7H_{11})_2$ complexes (M = Fe, Cr, V),[32] indicate that $Ti(2,4\text{-}C_7H_{11})_2$ should exist in the ideally staggered conformation IX. In this conformation the two ends of a given pentadienyl ligand become nonequivalent, and

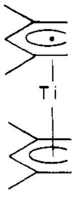


IX

variable-temperature NMR studies indicate a barrier of 15.3 kcal/mol for the ligand oscillation process which reestablishes the equivalence.[14b,37] One might expect that this process would involve X rather than XI as the symmetric intermediate, and that XI should be even higher in energy than X.[37a] However, recent MO calculations suggest that XI is actually much lower in energy than X.[36] Thus while process a in Scheme I does involve the observed ΔH values, that for process b is underestimated by at least 15.3 kcal/mol. An important consequence of this is that despite the fairly low $Ti(2,4\text{-}C_7H_{11})_2$–(L) bond energies, there is a substantial energy barrier to the exchange of free and coordinated ligand.[38] As a result, in the ^{31}P NMR spectra one sees two signals which can be used to derive the thermodynamic parameters after integration. In other situations, a single resonance may be observed, which is in a weighted-average position of the free and coordinated ligand. With some approximations, thermodynamic parameters may still be derived, although they seem to be somewhat less accurate, and much larger ranges of ΔS have been reported.[39] Hence, the "open titanocenes" seem in many respects ideal for



X



XI

---

(30) (a) Böhm, M. C.; Ernst, R. D.; Gleiter, R.; Wilson, D. R. *Inorg. Chem.* **1983**, *22*, 3815. (b) Stahl, L.; Ernst, R. D. *Organometallics* **1983**, *2*, 1229.

(31) As a result of this contraction, the ligand plane should move slightly further from the metal atom, and therefore away from the phosphorus atom as well. However, the open edge (C1—C5) of the pentadienyl ligand also becomes pinched slightly, which will tend to cancel the first effect. Neither of these should be particularly significant relative to the CH_3—CH_3 interactions themselves. It should be noted that the lack of methyl groups in I could lead to a tilting of the pentadienyl ligands.

(32) Campana, C. F.; Ernst, R. D.; Wilson, D. R.; Liu, J.-Z. *Inorg. Chem.* **1984**, *23*, 2732.

(33) (a) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1983**, *2*, 1220. (b) Han, J.-C.; Hutchinson, J. P.; Ernst, R. D. *J. Organomet. Chem.* **1987**, *321*, 389.

(34) Ernst, R. D.; Ma, H.; Sergeson, G.; Zahn, T.; Ziegler, M. L. *Organometallics* **1987**, *6*, 848.

(35) In addition, Tolman has noted the possibility of C_5Me_5 ligands meshing together, which effectively reduces the areas they occupy.[5a] Such meshing is a common feature of $M(C_5Me_5)_2L_n$ complexes, but it has no analogue in $M(2,4\text{-}C_7H_{11})_2L_n$ complexes due to their (generally) syn-eclipsed conformations.

(36) Gleiter, R., personal communication.

(37) (a) Note, however, that recently the solid compound $Ti(2,4\text{-}(t\text{-}C_4H_9)C_5H_5)_2$ has been prepared and found to possess a similar barrier.[37b] If an intermediate analogous to XI is indeed involved, one might have expected a much higher barrier due to the presence of two eclipsing *tert*-butyl interactions. (b) Wilson, D. R.; Stahl, L.; Ernst, R. D., unpublished results.

(38) It is possible that some interaction between the open titanocenes and an incoming ligand could take place prior to the point at which the syn-eclipsed conformation is reached, thereby lowering the barrier. As these complexes are sterically very crowded even without the additional ligands, it is unlikely that this is very significant, however. Note that the barrier to ligand coordination arising from the twisting of pentadienyl ligands in the open metallocenes is akin to the analogous barrier in metallocenes arising from the tilting of the two cyclopentadienyl ligand planes toward one another.

(39) (a) Beatty, R. P.; Datta, S.; Wreford, S. S. *Inorg. Chem.* **1979**, *18*, 3139. (b) Joedicke, I. B.; Studer, H. V.; Yoke, J. T. *Ibid.* **1976**, *15*, 1352.

thermodynamic studies and the estimation of ligand cone angle effects.

Summary

Thermodynamic parameters have been obtained for the binding of PMe_3, $PMe_2(C_6H_5)$, $P(OMe)_3$, $P(OEt)_3$, and PEt_3 to $Ti(2,4\text{-}C_7H_{11})_2$, as well as for PEt_3 to $Ti(3\text{-}C_6H_9)_2$. The much stronger binding of PEt_3 to $Ti(3\text{-}C_6H_9)_2$ as compared to $Ti(2,4\text{-}C_7H_{11})_2$ suggests that the binding is greatly inhibited by the presence of intramolecular CH_3–CH_3 interactions which are generated on the adoption of syn-eclipsed bis(pentadienyl)–metal configurations. These CH_3–CH_3 interactions therefore seem to be a key in allowing for the existence of the 14-electron "open titanocene", $Ti(2,4\text{-}C_7H_{11})_2$. For $Ti(2,4\text{-}C_7H_{11})_2$, the binding by phosphines may be correlated entirely with steric effects, although revisions of particularly the phosphite cone angles are required. It may be that further structural studies will aid in providing slightly better estimates of some other phosphine cone angles;[40] nevertheless, it is important to note that even with these relatively minor revisions of Tolman's early models, it is still quite clear that phosphine cone angles play an important, if not dominant, role in the binding of these ligands to metals, in accord with Tolman's conclusions. The crowded "open titanocene" adducts even provide an example of complexes in which the steric factor seems overwhelming.

Acknowledgment. R.D.E. expresses his appreciation for generous support of this research from the National Science Foundation and from the donors of the Petroleum Research Fund, administered by the American Chemical Society. We are grateful to Dr. Chad Tolman and Prof. John Verkade for very helpful discussions. The NMR and mass spectrometers were obtained through NSF and DOE instrumentation grants and with the support of the University of Utah Institutional Funds Committee.

---

(40) (a) Socol, S. M.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1984**, *23*, 88. (b) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *25*, L41.

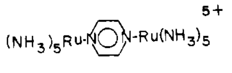
Mixed-Valent Cations of Dinuclear Chromium Aryl Complexes: Electrochemical, Spectroscopic, and Structural Considerations[⊥]

Norman Van Order, Jr.,[†] William E. Geiger,*[†] Thomas E. Bitterwolf,[‡] and Arnold L. Rheingold[§]

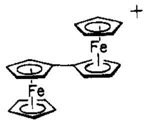
Contribution from the Departments of Chemistry, University of Vermont, Burlington, Vermont 05405, U.S. Naval Academy, Annapolis, Maryland 21402, and University of Delaware, Newark, Delaware 19716. *Received December 19, 1986*

Abstract: The oxidation of a series of six dinuclear chromium carbonyl complexes linked by a biphenyl ligand and/or a diphosphino- (or arsino-) methane moiety has been studied by electrochemistry, infrared spectroscopy, electron spin resonance spectroscopy, and X-ray crystallography. Comparison is made with four mononuclear analogues. Each dinuclear complex shows two successive one-electron oxidations, with the separation of $E°$ values varying from a low of 160 mV for $[(\text{benzene})Cr(CO)_2]_2(\mu\text{-dppm})$ (**11**, dppm = (diphenylphosphino)methane) to a high of 550 mV for $(\text{biphenyl})[Cr(CO)_2]_2(\mu\text{-dmpm})$ (**10**, dmpm = (dimethylphosphino)methane). The monocation derived from $(\text{biphenyl})[Cr(CO)_2(PPh_3)]_2$ ($\mathbf{7}^+$) displays IR and ESR spectra indicative of a charge- and spin-localized mixed-valent complex. Complexes $\mathbf{8}^+$–$\mathbf{10}^+$ with both a biphenyl and diphosphino- or arsinomethane linkage are valence-delocalized, judging from IR and ESR spectra. Neutral $(\text{biphenyl})[Cr(CO)_2]_2(\mu\text{-dppm})$ (**8**) has a severe twisting of the phenyl rings, the torsion angle being 50.8°. However, the torsion angle relaxes to 3.7° in the monocation $\mathbf{8}^+$. Neutral **8** crystallizes in the space group $P1$ with $a = 9.606$ (3) Å, $b = 13.530$ (3) Å, $c = 18.774$ (8) Å, $\alpha = 76.57$ (3)°, $\beta = 78.88$ (3)°, $\gamma = 70.04$ (3)°, and $Z = 2$. Cationic $\mathbf{8}^+[PF_6]^-$ crystallizes in the space group $C2/c$ with $a = 34.353$ (9) Å, $b = 11.185$ (2) Å, $c = 31.011$ (9) Å, $\beta = 126.18$ (2)°, and $Z = 8$.

Shortly after the appearance of the first modern theoretical treatments of mixed valency,[1,2] two important classes of mixed-valent compounds were reported. One of these originated with the pyrazine-bridged bis(pentammineruthenium) complex, A, $[(H_3N)_5Ru]_2(\mu\text{-}C_6H_4N_2)^{5+}$, containing formal Ru(II) and Ru(III).[3] The other was based on the biferrocenium ion, B, containing formal Fe(II) and Fe(III).[4] For nearly two decades parallel investigations have proceeded on both classes of compounds and their analogues to probe the factors influencing charge delocalization in dinuclear complexes. These efforts have been sustained by ancillary interest in excited-state charge transfer, low-dimensional conductivity, and other chemical and physical properties of mixed-valent compounds and lattices.[5a] Recently, enhancement of reactivity through cooperative metal effects has also received attention for these types of molecules.[5b,c] Partly because of the synthetic flexibility in designing bridging ligands



A



B

[⊥] Structural Consequences of Electron-Transfer Reactions, Part 15. For Part 14 see ref 49.

[†] University of Vermont.

[‡] U.S. Naval Academy

[§] University of Delaware.

(1) Allen, G. C.; Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 357.

(2) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(3) (a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988; (b) Ford, P.; Rudd, D. F. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.

(4) (a) Cowan, D. O.; Kaufman, F. *J. Am. Chem. Soc.* **1970**, *92*, 219. (b) Cowan, D. O.; LeVanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1.

(5) (a) Brown, D. B., Ed. *Mixed Valence Compounds*; D. Reidel: Boston, 1980. (b) Bitterwolf, T. E. *J. Organomet. Chem.* **1980**, *252*, 305. (c) MacLaughlin, S. A.; Murray, R. A.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1985**, *4*, 796.

0002-7863/87/1509-5680$01.50/0