Synthesis and Characterization of Dihydrogen and Dihydride Complexes of $[CpMH_2(diphosphine)]^+$ (M = Fe, Os)

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Protonation of CpFeH(P-P) (P-P = dppe, dppp) with HBF_4 produced the molecular dihydrogen complexes $[CpFe(H_2)(P\text{-}P)]BF_4$. Protonation of CpOsH(P-P) (P-P = dppm, dppe, dppp) with HBF_4 at −78 °C gave a mixture of *cis*-$[CpOsH_2(P\text{-}P)]BF_4$ and *trans*-$[CpOsH_2(P\text{-}P)]BF_4$. Depending on the size of the chelating rings, the thermodynamically stable structures of the protonated products at room temperature may be exclusively *trans*-$[CpOsH_2(P\text{-}P)]BF_4$ or a mixture of *cis*-$[CpOsH_2(P\text{-}P)]BF_4$ and *trans*-$[CpOsH_2(P\text{-}P)]BF_4$. At room temperature in dichloromethane solutions, $[CpOsH_2(dppm)]BF_4$ exists as a mixture of *cis* and *trans* isomers in a ratio of 10:1, $[CpOsH_2(dppe)]BF_4$ exists as a mixture of *cis* and *trans* isomers in a ratio of 1:70, and $[CpOsH_2(dppp)]BF_4$ adopts only *trans* geometry.

Introduction

Complexes of the formula $[(\eta^5\text{-}C_5R_5)MH_2(L)(L')]^+$ (M = Fe,[1−3] Ru,[4−8] Os;[9−12] (L)(L′) = $(CO)_2$, $(CO)(PR_3)$, $(PR_3)_2$) have attracted considerable attention recently for their structural, chemical, and physical properties. Previous study on ruthenium complexes shows that $[(\eta^5\text{-}C_5R_5)RuH_2(L)(L')]^+$ can adopt either the dihydride form *trans*-$[(\eta^5\text{-}C_5R_5)RuH_2(L)(L')]^+$ or the dihydrogen form $[(\eta^5\text{-}C_5R_5)Ru(H_2)(L)(L')]^+$, depending on the ligands used. The dihydrogen form is adopted by the CO-containing complexes $[(\eta^5\text{-}C_5R_5)Ru(H_2)(CO)(PR_3)]^+$ and $[(\eta^5\text{-}C_5Me_5)Ru(H_2)(CO)_2]^+$. The dihydride form is usually observed for the monophosphine complexes $[(\eta^5\text{-}C_5R_5)RuH_2(PR_3)_2]^+$. Analogous complexes with chelating diphosphines can adopt either the dihydride form $[(\eta^5\text{-}C_5R_5)MH_2(P\text{-}P)]^+$ or the dihydrogen form $[(\eta^5\text{-}C_5R_5)M(H_2)(P\text{-}P)]^+$ or a mixture of both, depending on the size of the chelating ring and C_5R_5. For example, Simpson *et al*. reported that protonation of CpRuH(dppm), CpRuH(dppe), and CpRuH(dppp) produced $[CpRu(H_2)(dppm)]^+$, $[CpRu(H_2)(dppe)]^+$/$[CpRuH_2(dppe)]^+$, and $[CpRuH_2(dppp)]^+$, respectively.[5b] It is also interesting to note that although Cp*RuH(dppm)[8b−d] and CpRuH(dmpe)[7c] are more electron rich than $CpRuH(PPh_3)_2$,[9] the protonated products of these monohydride complexes are $[Cp^*Ru(H_2)(dppm)]^+$/$[Cp^*RuH_2(dppm)]^+$, $[CpRu(H_2)(dmpe)]^+$/$[CpRuH_2(dmpe)]^+$, and $[CpRuH_2(PPh_3)_2]^+$, respectively. It appears that the presence of some chelating ligands favors the dihydrogen form.

Compared to ruthenium, the chemistry of the iron and osmium homologs is still underdeveloped. The reported iron complexes of the formula $[CpFeH_2(L)(L')]^+$ include *trans*-$[(C_5R_5)FeH_2(dippe)]BPh_4$ (dippe = $(i\text{-}Pr)_2PCH_2CH_2P(i\text{-}Pr)_2$; R = H, Me),[1] $[Cp^*Fe(H_2)(dppe)]BF_4$ (which isomerized to *trans*-$[Cp^*FeH_2(dppe)]BF_4$ on warming),[2] and $[CpFe(H_2)(CO)(PR_3)]BAr'_4$ (PR_3 = PEt_3, PPh_3, Ar′ = 3,5-$(CF_3)_2C_6H_3$).[3] The reported osmium complexes of the formula $[CpOsH_2(L)(L')]^+$ include $[Cp^*Os(H_2)(CO)_2]^+$/$[Cp^*OsH_2(CO)_2]^+$, *trans*-$[CpOsH_2(CO)(P(i\text{-}Pr)_3)]BF_4$, and *trans*-$[CpOsH_2(PR_3)_2]^+$ ($(PR_3)_2$ = $(PPh_3)_2$, $(Ph_2PMe)_2$, $(PPh_3)(P(OEt)_3)$).[9−12] To compare the structures and properties of iron and osmium homologs with those of ruthenium, and to study the effect of chelating ring size on the structure and properties of $[CpMH_2(P\text{-}P)]^+$, we have studied the protonation reactions of CpMH(diphosphine) (M = Fe, Os).

Experimental Section

Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^1H and $^{31}P\{^1H\}$ NMR spectra were collected

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(1) Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1994,** *13*, 3330.
(2) Hamon, P.; Toupet, L.; Hamon, J. R.; Lapinte, C. *Organometallics* **1992**, *11*, 1429.
(3) Scharrer, E.; Chang, S.; Brookhart, M. *Organometallics* **1995**, *14*, 5686.
(4) (a) Brammer, F. R.; Klooster, W. T.; Lemke, F. R. *Organometallics* **1996**, *15*, 1721. (b) Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980.
(5) (a) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1986**, 506. (b) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675.
(6) Wilczewski, T. *J. Organomet. Chem.* **1989**, *361*, 219.
(7) (a) Chinn, M. S. Heinekey, D. M. *J. Am. Chem. Soc.* **1987,** *109*, 5865. (b) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824. (c) Chinn, M. S. Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.
(8) (a) Jia, G. Morris, R. H. *Inorg. Chem.* **1990**, *29*, 583. (b) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (c) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161. (d) Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994,** *116*, 7677.
(9) Wilczewski, J. *J. Organomet. Chem.* **1986,** *317*, 307.
(10) Esteruelas, N.; Gomez, A. V.; Lopez, A. M.; Oro, L. A. *Organometallics* **1996**, *15*, 878.
(11) (a) Rottink, M. R.; Angelici, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 7267. (b) Rottink, M. R.; Angelici, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 8296.
(12) Bullock, R. M.; Song, J. S.; Szalda, D. J. *Organometallics* **1996,** *15*, 2504.

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on a JEOL EX-400 spectrometer (400 MHz) or a Bruker ARX-300 spectrometer (300 MHz). ^{1}H NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4.

All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium−benzophenone (hexane, diethyl ether, THF), sodium (benzene), or calcium hydride (dichloromethane). The complexes CpFeCl(dppe),[13] CpFeH(dppe),[14] CpOsBr(dppm),[15] CpOsBr(dppe),[15] and CpOsBr(dppp)[11a] were prepared according to literature methods. The procedure for CpFeCl(dppe)[12] was also used to prepare CpFeCl(dppp). All other reagents were used as purchased from Aldrich or Strem.

CpFeH(dppp). A mixture of CpFeCl(dppp) (0.50 g, 0.88 mmol) and $NaBH_4$ (0.50 g, 14 mmol) in THF (50 mL) was stirred for 2 h to give a cloudy yellow solution. The solvent of the reaction mixture was evaporated to give a brown residue. The residue was extracted with hexane, and the insoluble material was removed by filtration to give a yellow solution. The solvent of the extract was evaporated to give an orange yellow solid. Yield: 0.26 g, 55%. ^{31}P{^{1}H} NMR (C_6D6): δ 75.1 (s). ^{1}H NMR (C_6D_6): −15.75 (t, J(PH) = 70.1 Hz, 1 H, FeH), 1.23−2.38 (m, 6 H, CH_2), 4.11 (s, 5 H, Cp), 7.07−7.79 (m, 20 H, Ph). Anal. Calcd for $C_{32}H_{32}P_2Fe$: C, 71.92; H, 6.04. Found: C, 71.83; H, 5.96.

[CpFe(H_2)(dppe)]BF_4. HBF_4·Et_2O was added to a solution of CpFeH(dppe) in CD_2Cl_2 in an NMR tube. The color of the solution changed immediately from yellow to light brown. NMR spectra were collected immediately. ^{31}P{^{1}H}NMR (CD_2Cl_2): δ 94.5 (s). ^{1}H NMR (CD_2Cl_2): δ 7.0−8.0 (m, Ph), 4.5 (s, Cp), 2.8−1.2 (m, dppe), −12.5 (br, Fe(H_2)). T_1 (ms, 300 MHz): 17 (298 K), 13 (280 K), 5 (240), 5 (230 K), 7 (220 K). A T_1(min) value of 5 ms (at 235 K) was estimated from a plot of T_1 vs temperature.

[CpFe(HD)(dppe)]BF_4. This compound was prepared in an NMR tube in CD_2Cl_2 by the reaction of CpFeH(dppe) with DBF_4. DBF_4 was prepared in situ by mixing HBF_4·Et_2O and D_2O in a ratio of 1:3 (v:v). ^{1}H NMR (CD_2Cl_2): δ −12.5 (tt, J(PH) = 6.8 Hz, J(HD) = 30.7 Hz, Fe(HD)).

[CpFe(H_2)(dppp)]BF_4. The procedure for [CpFe(H_2)(dppe)]BF_4 was followed exactly. ^{31}P{^{1}H}NMR (CD_2Cl_2): δ 54.8 (s). ^{1}H NMR (CD_2Cl_2): δ 7.8−7.4 (m, Ph), 4.6 (s, Cp), 3.0−1.2 (m, CH_2), −12.0 (br, Fe(H_2)). T_1 (ms, 300 MHz): 18 (298 K), 10 (250 K), 7 (230 K), 7 (210 K), 9 (190 K). A T_1(min) value of 7 ms (at 220 K) was estimated from a plot of T_1 vs temperature.

[CpFe(HD)(dppp)]BF_4. This compound was prepared in an NMR tube in CD_2Cl_2 by the reaction of CpFeH(dppp) with DBF_4. DBF_4 was prepared in situ by mixing HBF_4·Et_2O and D_2O in a ratio of 1:3 (v:v). ^{1}H NMR (CD_2Cl_2): δ −12.0 (t, J(HD) = 29.0 Hz, Fe(HD)).

[CpFe(η^2-dppe)(η^1-dppe)]BPh_4. A mixture of CpFeCl(dppe)·$CHCl_3$ (135 mg, 0.200 mmol), dppe (159 mg, 0.400 mmol), and $NaBPh_4$ (137 mg, 0.400 mmol) in 20 mL of CH_2Cl_2 was stirred at room temperature for 2 h. The insoluble material was remove by filtration to give an orange red solution. The solvent was then removed completely. The residue was washed with hexane, benzene, and water and then extracted with CH_2Cl_2. The solvent of the extract was removed completely to give a brownish yellow solid. Yield: 212 mg, 86%. ^{31}P{^{1}H}NMR (CD_2Cl_2): δ 86.7 (d, J(PP) = 45.2 Hz); 49.9 (dt, J(PP) = 30.6, 45.0 Hz); −13.88 (d, J(PP) = 30.6 Hz). ^{1}H NMR (CD_2Cl_2): δ 7.42−6.59 (m, 60 H, Ph), 4.45 (s, 5 H, Cp), 2.43 (m, 2 H, CH_2), 2.09 (m, 2 H, CH_2), 1.80 (m, 2 H, CH_2), 1.40 (m, 2 H, CH_2). Anal. Calcd for $C_{81}H_{73}BP_4Fe$: C, 78.65; H, 5.95. Found: C, 78.50; H, 5.94.

[CpFe(dppe)(μ-dppe)CpFe(dppe)](BPh_4)$_2$. A mixture of CpFeCl(dppe)·$CHCl_3$ (135 mg, 0.200 mmol), dppe (39.8 mg, 0.100 mmol), and $NaBPh_4$ (130 mg, 0.38 mmol) in 20 mL of CH_2Cl_2 was stirred at room temperature for 3 h. The insoluble material was remove by filtration to give a red solution. The solvent was then removed completely. The residue was washed with methanol and water. The crude product was purified by column chromatography on silica gel with CH_2Cl_2 as the eluent. Yield: 125 mg, 60%. ^{31}P{^{1}H}NMR (CD_2Cl_2): δ 88.5 (d, J(PP) = 43.3 Hz, η^2-dppe)); 51.5−50.61 (m, μ-dppe). ^{1}H NMR (CD_2Cl_2): δ 7.60−6.87 (m, 100 H, PPh_2, BPh_4), 4.11 (s, 10 H, Cp), 2.28 (m, 4 H, CH_2), 1.59 (m, 4 H, CH_2), 1.20 (m, 4 H, CH_2). Anal. Calcd for $C_{136}H_{122}B_2P_6Fe_2$: C, 78.70; H, 5.92. Found: C, 78.58; H, 6.11.

CpOsBr(PPh_3)$_2$. An ampule of osmium tetraoxide (1 g, 3.93 mmol) was broken in a flask containing hydrobromic acid (48%, 40 mL), and the red solution was refluxed for 2 h. The solution was reduced to 5 mL and added to a stirred, boiling solution of triphenylphosphine (6.3 g, 24 mmol) in methanol (180 mL) to give a red precipitate. The solid was collected by filtration, washed with methanol and benzene, and dried under vacuum to give 4.0 g of red powder. A mixture of the red solid (0.85 g), Zn (3.00 g, 45.9 mmol), and 0.9 mL of cyclopentadiene in 50 mL of EtOH was stirred at room temperature for 12 h to give a yellow solution with some yellow fine precipitate. The unreacted zinc metal was separated, and the yellow solid was collected by filtration and washed with hexane. The crude product was purified by column chromatography on silica gel with benzene as the eluent. The benzene was removed to give 0.58 g of yellow powder. ^{31}P{^{1}H} NMR (C_6D_6): δ −5.7 (s). ^{1}H NMR (C_6D_6): δ 7.67−7.02 (m, 30 H, Ph), 4.45 (s, 5 H, Cp). Anal. Calcd for $C_{41}H_{35}BrP_2Os$: C, 57.28; H, 4.10; Br, 9.29. Found: C, 57.27; H, 4.19; Br, 9.09.

CpOsH(dppm). A mixture of CpOsBr(dppm) (0.50 g, 0.69 mmol) and Na (0.10 g, 4.3 mmol) in 80 mL of methanol was refluxed for 4 days to give a pale yellow solution. The volume of the solution was reduced, and a yellow powder precipitated out. The solid was collected by filtration, washed with methanol, and dried under vacuum. Yield: 0.34, 75%. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −35.4 (s). ^{1}H NMR (CD_2Cl_2): δ −14.79 (t, J(PH) = 24.5 Hz, 1 H, OsH), 4.32 (dt, J(PH) = 11.1 Hz, J(HH) = 14.7 Hz, 1 H, CH_2), 6.26 (dtd, J(PH) = 10.0 Hz, J(HH) = 14.7 Hz, J(HH) = 2.5 Hz, 1 H, CH_2), 4.87 (s, 5 H, Cp), 7.3−7.7 (m, 20 H, Ph). Anal. Calcd for $C_{30}H_{28}P_2Os$: C,56.24; H, 4.41. Found: C, 56.42; H, 4.62.

[CpOsH_2(dppm)]BF_4. To a solution of CpOsH(dppm) (0.20 g, 0.31 mmol) in 30 mL of Et_2O was added 0.1 mL of HBF_4·Et_2O. The reaction mixture was stirred for 30 min to give a white solid. The solid was collected by filtration, washed with Et_2O, and dried under vacuum. Yield: 0.16 g, 70%. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −47.3 (s, *cis*-OsH_2), −36.1 (s, *trans*-OsH_2). ^{1}H NMR (CD_2Cl_2): δ −11.42 (t, J(PH) = 6.5 Hz, *cis*-OsH_2), −10.76 (t, J(PH) = 31.8 Hz, *trans*-OsH_2), 5.01 (dt, J(PH) = 12.0 Hz, J(HH) = 15.8 Hz, CH_2, *cis*-OsH_2), 6.19 (dt, J(PH) = 11.7 Hz, J(HH) = 15.8 Hz, CH_2, *cis*-OsH_2), 5.27 (s, Cp, *cis*-OsH_2), 5.53 (m, CH_2, *trans*-OsH_2), 5.68 (s, Cp, *trans*-OsH_2), 7.3−7.8 (m, Ph), *cis*-OsH_2/*trans*-OsH_2 = 10:1. T_1 (ms, 300 MHz, *cis*-OsH_2): 228 (270 K), 192 (250), 160 (230), 149 (210 K), 149 (200 K), 182 (190 K). T_1 (ms, 300 MHz, *trans*-OsH_2): 1210 (270 K), 1160 (250 K), 881 (230 K), 613 (210 K), 779 (200 K), 832 (190 K). Anal. Calcd for $C_{30}H_{29}BF_4P_2Os$: C, 49.46; H, 4.01. Found: C, 49.49; H, 3.86.

[CpOsHD(dppm)]BF_4. This compound was prepared according to the same protocol, except that DBF_4 was used instead of HBF_4·Et_2O. DBF_4 was prepared in situ by mixing HBF_4·Et_2O and D_2O in a ratio of 1:3 (v:v). ^{1}H NMR (CD_2Cl_2): δ −11.48 (tt, J(PH) = 6.5 Hz, J(HD) = 3.0 Hz, *cis*-Os(HD)), −10.77 (t, J(PH) = 31.5 Hz, *trans*-Os(HD)). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −47.3 (s, *cis*-Os(HD), 298 K), −35.7 (s, *trans*-Os(HD), 298 K); −48.2 (s, *cis*-Os(HD), 190 K), −36.2 (s, *trans*-Os(HD), 190 K).

(13) Adams, R. D.; Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1979,** *101,* 7232.
(14) Mays, M. J.; Sears, P. L. *J. Chem. Soc., Dalton Trans.* **1973**, 1873.
(15) Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979,** *32,* 1003.

CpOsH(dppe). A mixture of CpOsBr(dppe) (0.50 g, 0.68 mmol) and Na (0.10 g, 4.3 mmol) in 80 mL of methanol was refluxed for 4 h to give a pale yellow solution. The volume of the solution was reduced, and a yellow powder precipitated out. The solid was collected by filtration, washed with methanol, and dried under vacuum. Yield: 0.38 g, 85%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 50.3 (s). ^1H NMR (CD_2Cl_2): δ −16.60 (t, J(PH) = 27.3 Hz, 1 H, OsH), 2.02 (m, 2 H, CH_2), 2.40 (m, 2 H, CH_2), 4.56 (s, 5 H, Cp), 7.3−7.8 (m, 20 H, Ph). Anal. Calcd for $C_{31}H_{30}P_2Os$: C, 56.87; H, 4.62. Found: C, 56.69; H, 4.75.

[$CpOsH_2$(dppe)]BF_4. The procedure for [$CpOsH_2$(dppm)]BF_4 was followed exactly, substituting CpOsH(dppe) for CpOsH(dppm). Yield: 0.16 g, 70%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 24.9 (s, *trans*-OsH_2), 45.6 (s, *cis*-OsH_2). ^1H NMR (CD_2Cl_2): δ −13.1 (t, J(PH) = 32.5 Hz, *trans*-OsH_2), −12.53 (t, J(PH) = 7.6 Hz, *cis*-OsH_2), 2.58 (m, CH_2), 4.95 (s, Cp of *cis*-OsH_2), 5.56 (s, Cp of *trans*-OsH_2), 7.5 (m, Ph). *cis*-OsH_2/*trans*-OsH_2 = 1:70. Anal. Calcd for $C_{31}H_{31}BF_4P_2Os$: C, 50.14; H, 4.21. Found: C, 50.20; H, 4.30.

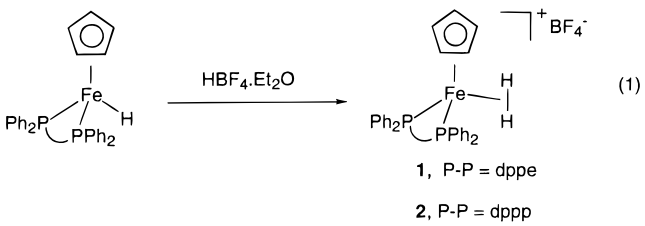
CpOsH(dppp). A mixture of CpOsBr(dppp) (0.50 g, 0.67 mmol) and Na (0.10 g, 4.3 mmol) in 80 mL of methanol was refluxed for 4 h to give a pale yellow solution. The volume of the solution was reduced, and a yellow powder precipitated out. The solid was collected by filtration, washed with methanol, and dried under vacuum. Yield: 0.36 g, 80%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 1.2 (s). ^1H NMR (CD_2Cl_2): δ −15.85 (t, J(PH) = 28.2 Hz, 1 H, OsH), 1.5−3.3 (m, 6 H, CH_2), 4.50 (s, 5 H, Cp), 7.2−7.5 (m, 20 H, Ph). Anal. Calcd for $C_{32}H_{32}P_2Os$: C, 57.47; H, 4.82. Found: C, 57.19; H, 5.04.

[$CpOsH_2$(dppp)]BF_4. The procedure for [$CpOsH_2$(dppm)]BF_4 was followed exactly, substituting CpOsH(dppp) for CpOsH(dppm). Yield: 0.18 g, 78%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −14.3 (s, *cis*-OsH_2), −0.7 (s, *trans*-OsH_2). ^1H NMR (CD_2Cl_2): δ −12.80 (t, J(PH) = 31.7 Hz, *trans*-OsH_2), −12.22 (t, J(PH) = 6.8, *cis*-OsH_2), 1.94 (m, CH_2), 2.88 (m, CH_2), 5.07 (s, Cp, *cis*-OsH_2), 5.17 (s, Cp, *trans*-OsH_2), 7.5 (m, Ph). *cis*-OsH_2/*trans*-OsH_2 = 1:3, if the protonation was carried out at −78 °C. Anal. Calcd for $C_{32}H_{33}BF_4P_2Os$: C, 50.80; H, 4.40. Found: C, 51.00; H, 4.16.

Protonation at Low Temperature. Appropriate amounts of CpMH(P-P) and CD_2Cl_2 were loaded into an NMR tube under inert atmosphere. The NMR tube was capped with a rubber septum and cooled to −78 °C. HBF_4·Et_2O was added via a microsyringe. The NMR tube was quickly inverted to ensure complete mixing and then placed in an NMR probe precooled to 200 K. ^1H and ^{31}P NMR spectra were collected.

Results and Discussion

Characterization of [$CpFe(H_2)$(diphosphine)]BF_4 Complexes. The molecular dihydrogen complexes [$CpFe(H_2)$(diphosphine)]BF_4 (diphosphine = dppe (**1**), dppp (**2**)) were prepared by protonation of the corresponding hydride complexes in CD_2Cl_2 with HBF_4·Et_2O (eq 1). Due to their low stability, these complexes could

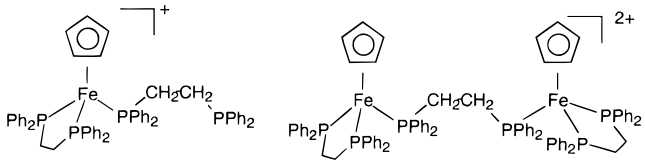


(1)

not be isolated as solids in analytically pure form and so were characterized in situ. The starting hydride complexes CpFeH(dppe)[14] and CpFeH(dppp) were prepared by the reaction of $NaBH_4$ with the corresponding chloride complexes CpFeCl(diphosphine).

Protonation of CpFeH(dppe) with HBF_4·Et_2O at room temperature in CD_2Cl_2 produced [$CpFe(H_2)$(dppe)]BF_4, **1**. The ^{31}P NMR spectrum of the dihydrogen complex showed a singlet at 94.5 ppm for the dppe ligand. The ^1H NMR spectrum of the dihydrogen complex showed a broad hydride signal at −12.5 ppm. The existence of the η^2-H_2 moiety in [$CpFe(H_2)$(dppe)]BF_4 was confirmed by the variable-temperature T_1 measurements and the observation of a large ^1J(HD) value for the corresponding isotopomer [CpFe(HD)(dppe)]BF_4. The variable-temperature T_1 measurements gave a T_1(min) of 5 ms (300 MHz) for the broad hydride signal at −12.5 ppm at *ca.* 235 K. Acidification of CpFeH(dppe) with 1 equiv of DBF_4 gave the η^2-HD isotopomer, [CpFe(HD)(dppe)]BF_4. The HD signal in the ^1H NMR spectrum in CD_2Cl_2 was observed as a 1:1:1 triplet (^1J(HD) = 30.7 Hz) of 1:2:1 triplets (^2J(PH) = 6.8 Hz) at −12.5 ppm, after nulling the η^2-H_2 peak. The observations of small T_1(min) (5 ms, 300 MHz) and large ^1J(HD) (30.7 Hz) clearly indicate that the molecular dihydrogen complex **1** was produced in the protonation reaction.[16] Small ^2J(P−H) coupling constants have been observed for a few η^2-HD complexes.[17]

The molecular dihydrogen complex **1** is thermally unstable in solution, and it decomposed at room temperature after 1 day. Loss of H_2 was also observed in attempts to isolate it. Among the decomposed products, two were identified as [$CpFe(\eta^2$-dppe)$(\eta^1$-dppe)]$^+$, **3**, and



[{$CpFe(\eta^2$-dppe)}$_2(\mu$-dppe)]$^{2+}$, **4**, by comparing the NMR spectra of [$CpFe(\eta^2$-dppe)$(\eta^1$-dppe)]BPh_4 and [{$CpFe(\eta^2$-dppe)}$_2(\mu$-dppe)]$(BPh_4)_2$. Complexes [$CpFe(\eta^2$-dppe)$(\eta^1$-dppe)]BPh_4 and [{$CpFe(\eta^2$-dppe)}$_2(\mu$-dppe)]$(BPh_4)_2$ could be easily prepared by reactions of CpFeCl(dppe) with 1 and 0.5 equiv of dppe in the presence of excess $NaBPh_4$, respectively. They were characterized by ^{31}P and ^1H NMR spectroscopy and elemental analysis.

Protonation of CpFeH(dppp) with HBF_4·Et_2O at room temperature in CD_2Cl_2 produced the dihydrogen complex [$CpFe(H_2)$(dppp)]BF_4, **2**. The molecular dihydrogen complex **2** is also unstable in solution, and it decomposed at room temperature after 1 day. The ^{31}P NMR spectrum of **2** in CD_2Cl_2 showed a singlet at 54.8 ppm for the dppp ligand, and the ^1H NMR spectrum showed

(16) (a) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 789. (b) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (c) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (e) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (f) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 289.

(17) (a) Schlaf, M.; Lough, A. L.; Maltby, P. A.; Morris, R. H. *Organometallics*, **1996**, *15*, 2270. (b) Chin, B.; Lough, A. J.; Morris, R. H.; Schweitzer, C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278. (c) Bianchini, C.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Romerosa, A.; Rossi, R.; Vacca, A. *Organometallics* **1995**, *14*, 3203. (d) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 2181. (e) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1986**, 506. (f) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675. (g) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (h) Joshi, A. M.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1785. (i) Mudalige, D. C.; Rettig, S. J.; James, B. R.; Cullen, W. R. *J. Chem. Soc., Chem. Commun.* **1993**, 830.

a broad hydride signal at −12.0 ppm assignable to $Fe(H_2)$. The classification of **2** as a dihydrogen complex is based on variable-temperature T_1 measurements and the observation of large ^1J(HD) coupling constants for the HD isotopomer. The variable-temperature T_1 measurements gave a T_1(min) of 7 ms for the broad hydride signal at *ca.* 220 K (300 MHz). The η^2-HD isotopomer, $[CpFe(HD)(dppp)]BF_4$, prepared by acidification of CpFeH(dppe) with DBF_4, showed a 1:1:1 triplet (^1J(HD) = 29.0 Hz) centered at δ −12.0 ppm in the ^{1}H NMR spectrum after nulling the η^2-H_2 peak. Unlike $[CpFe(HD)(dppe)]BF_4$, the ^2J(P−H) coupling was not resolved for $[CpFe(HD)(dppp)]BF_4$.

The fact that only dihydrogen complexes $[CpFe(H_2)(dppe)]^+$ and $[CpFe(H_2)(dppp)]^+$ were observed in solution is in sharp contrast to the protonation reactions of CpRuH(dppe) and CpRuH(dppp), which produced $[CpRu(H_2)(dppe)]^+$/*trans*-$[CpRuH_2(dppe)]^+$ and *trans*-$[CpRuH_2(dppp)]^+$, respectively.[5b] This observation is consistent with the general periodic trend in the relative stability of dihydrogen and dihydride forms.[16,18] There are a few reported analogous iron complexes. The unstable dihydrogen complexes $[CpFe(H_2)(CO)(PR_3)]BAr'_4$ (PR_3 = PEt_3, PPh_3, Ar′ = 3,5-$(CF_3)_2C_6H_3$) were reported by Brookhart *et al.* recently.[3] It was reported by Lapinte *et al.* that protonation of the more electron rich complex Cp*FeH(dppe) at low temperature leads to the initial formation of $[Cp^*Fe(H_2)(dppe)]BF_4$, which isomerizes to *trans*-$[Cp^*FeH_2(dppe)]BF_4$ on warming.[2] Reactions of $(C_5R_5)FeCl(dippe)$ (dippe = $(i\text{-Pr})_2PCH_2CH_2P(i\text{-Pr})_2$; R = H, Me) with hydrogen in the presence of $NaBPh_4$ produced the dihydride complexes *trans*-$[(C_5R_5)FeH_2(dippe)]BPh_4$.[1]

Preparation of Monohydrido Osmium Complexes. To prepare $[CpOsH_2(P\text{-}P)]^+$, we require the hydride complexes CpOsH(P-P). These monohydrido complexes were prepared according to eq 2.

$$CpOsBr(P\text{-}P) + NaOMe \longrightarrow CpOsH(P\text{-}P) + NaBr + \text{"}OCH_2\text{"} \quad (2)$$

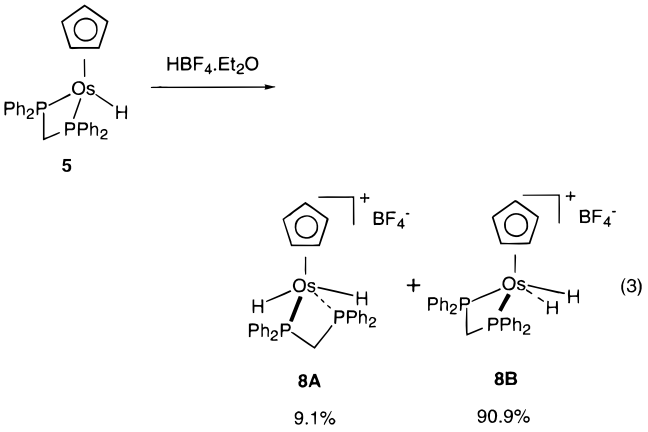
5, P-P = dppm; **6**, P-P = dppe

7, P-P = dppp

The complexes CpOsBr(P-P) were prepared by the reactions of $CpOsBr(PPh_3)_2$ with appropriate diphosphines as reported previously.[11a,15] To prepare the starting material $CpOsBr(PPh_3)_2$, we initially attempted to use the method developed by Bruce *et al.*, which involves the one-pot reaction of H_2OsBr_6, PPh_3, and cyclopentadiene in MeOH.[19] However, the desired complex $CpOsBr(PPh_3)_2$ could not *always* be obtained in high yield in our hands, and often a significant amount of an insoluble red solid was obtained. The same red material could also be obtained by simply refluxing H_2OsBr_6 with excess PPh_3 in MeOH. Elemental analysis of the red solid indicated that its composition is close to that of $OsBr_4(PPh_3)_2$.[20] We found that the red material could be easily converted to $CpOsBr(PPh_3)_2$ by its reaction with cyclopentadiene in MeOH in the presence of Zn. Reaction of the green compound $OsBr_2(PPh_3)_3$ with cyclopentadiene to give $CpOsBr(PPh_3)_2$ has been reported previously.[21]

The bromide complexes CpOsBr(P-P) were converted into the new hydride complexes CpOsH(P-P) (P-P = dppm (**5**), dppe (**6**), and dppp (**7**)) by refluxing a mixture of CpOsBr(P-P) and NaOMe in methanol (eq 2). It is interesting to note that the time required to complete the reaction is dependent on the diphosphines. It takes several days refluxing in methanol to completely convert CpOsBr(dppm) to CpOsH(dppm) and only about 4 h for the dppe and dppp analogs. The hydride complexes CpOsH(P-P) are pale yellow solids and were characterized by ^{1}H and ^{31}P NMR spectroscopic data and elemental analysis. In particular, the ^{1}H NMR spectra of the monohydride complexes displayed the characteristic hydride signals as a triplet due to coupling to the two equivalent phosphorus atoms.

Preparation and Characterization of $[CpOsH_2(dppm)]BF_4$. Protonation of CpOsH(dppm) with $HBF_4\cdot Et_2O$ at room temperature produced a white powder analyzed as $[CpOsH_2(dppm)]BF_4$. NMR spectroscopic data indicate that the product consists of a mixture of two hydride species in a ratio of 10:1. The minor hydride species can be formulated as *trans*-$[CpOsH_2(dppm)]BF_4$, **8A**, and the major one *cis*-$[CpOsH_2(dppm)]BF_4$, **8B** (eq 3).



In the ^{31}P NMR spectrum of the protonated product in CD_2Cl_2, the dppm signals were observed as singlets at −47.3 ppm for *cis*-$[CpOsH_2(dppm)]BF_4$ and at −36.1 ppm for *trans*-$[CpOsH_2(dppm)]BF_4$. In the ^{1}H NMR spectrum (in CD_2Cl_2), the hydride signal for *trans*-$[CpOsH_2(dppm)]BF_4$ was observed at −10.76 ppm with ^2J(PH) = 31.8 Hz. The ^2J(PH) coupling constant of 31.8 Hz is very similar to those observed for *trans*-$[CpOsH_2(LL')]^+$ ((LL′) = $(PPh_3)_2$, $(PPh_2Me)_2$, $(PPh_3)(P(OMe)_3)$, $(CO)(P(i\text{-}Pr_3))$).[9−11] The hydride signal for *cis*-$[CpOsH_2(dppm)]BF_4$ was observed at −11.42 ppm with ^2J(PH) of 6.5 Hz. Consistent with the structure assignments, two methylene proton signals were observed at 5.01 and 6.19 ppm for *cis*-$[CpOsH_2(dppm)]BF_4$, and only one methylene proton signal was observed at 5.53 ppm for *trans*-$[CpOsH_2(dppm)]BF_4$ in the ^{1}H NMR spectrum in CD_2Cl_2.

The ^2J(PH) coupling constant of 6.5 Hz observed for the hydride signal of *cis*-$[CpOsH_2(dppm)]BF_4$ (at −11.42 ppm) is smaller than those normally observed for

(18) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1994**, *135/136*, 845 and references therein.

(19) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977,** *30*, 1601.

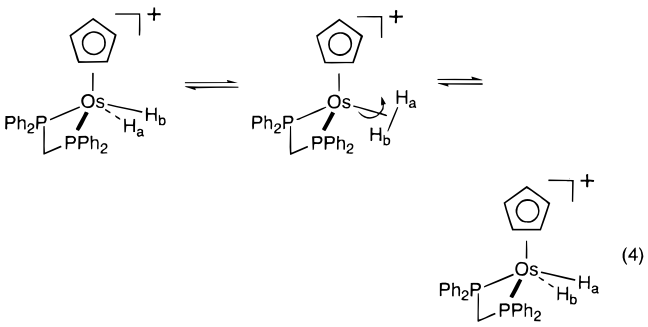
(20) A number of complexes of the formula $OsX_4(PR_3)_2$ (X = Cl, Br) have been reported. See for example: (a) Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2379. (b) Chatt, J.; Leigh, F. G. J.; Paske, R. J. *J. Chem. Soc. A* **1969**, 2239. (c) Chatt, J.; Mingos, D. M. P.; Paske, R. J. *J. Chem. Soc. A* **1968**, 2636.

(21) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2376.

$CpOsH(PR_3)_2$ or $[CpOsH_2(PR_3)_2]^+$ and is close to those observed for molecular dihydrogen complexes.[16,17] Thus there is a possibility that *cis*-$[CpOsH_2(dppm)]BF_4$ contains a dihydrogen ligand. To clarify the structure of $[CpOsH_2(dppm)]BF_4$, we have measured the T_1 values for the hydride signals and J(HD) coupling constants for the HD isotopomers $[CpOsHD(dppm)]BF_4$. The variable T_1 measurements at 300 MHz gave T_1(min) of *ca.* 150 ms for the hydride signal of *cis*-$[CpOsH_2(dppm)]BF_4$ at −11.42 ppm and *ca.* 610 ms for that of *trans*-$[CpOsH_2(dppm)]BF_4$ at −10.76 ppm. Although the T_1(min) value for *cis*-$[CpOsH_2(dppm)]BF_4$ (150 ms) is significantly smaller than that for *trans*-$[CpOsH_2(dppm)]BF_4$ (610 ms), the T_1(min) value of 150 ms is too large for molecular dihydrogen complexes. Molecular dihydrogen complexes usually have T_1(min) values less than 50 ms at 250 MHz.[16]

We have prepared the HD isotopomers $[CpOsHD(dppm)]^+$ by protonation of CpOsH(dppm) with DBF_4. In the ^{1}H NMR spectrum of the isotopomers in CD_2Cl_2, the hydride signal of *cis*-$[CpOsHD(dppm)]BF_4$ appeared at −11.48 ppm with J(HD) = 3.0 Hz and ^2J(PH) = 6.5 Hz. The J(HD) coupling was not resolved for the hydride signal at −10.77 ppm due to *trans*-$[CpOsHD(dppm)]BF_4$. The J(HD) value of 3.0 Hz is too small for η^2-HD complexes, which usually give ^1J(HD) larger than 20 Hz.[16] The observations of long T_1(min) (>150 ms) and small J(HD) for the HD isotopomers support the classic dihydride formulation for both isomers of $[CpOsH_2(dppm)]^+$. However, the alternative formulation of *cis*-$[CpOsH_2(dppm)]^+$ as the elongated dihydrogen complex $[CpOs(H\cdot\cdot H)(dppm)]^+$ cannot be ruled out completely, especially in view of the observations of only one hydride signal and small ^2J(PH) and J(HD) values. The observation of a J(HD) of 3.0 Hz for *cis*-$[CpOsHD(dppm)]BF_4$ implies that there will be *ca.* 18 Hz coupling for the two hydride ligands in *cis*-$[CpOsH_2(dppm)]BF_4$ when contribution from quantum mechanical exchange is not considered. ^2J(HH) coupling constants for classic polyhydride complexes are usually less than 15 Hz.[22] However, unusually large J(HD) coupling constants have been observed for some metal hydride complexes that can undergo quantum mechanical exchange.[23] It is also noted that the isotopomers of several osmium complexes with elongated dihydrogen ligands also have small J(HD) coupling constants,[24] for example, $[Os(HD)(NH_3)_4(acetone)]^+$ (J(HD) = 4.0 Hz) and $[Os(HD)(NH_3)_4(D_2O)]^+$ (J(HD) = 8.1 Hz).

The two phosphorus atoms and the two hydrides in *cis*-$[CpOsH_2(dppm)]^+$ are chemical equivalent but are magnetically inequivalent. Thus a triplet signal is not normally expected in the ^{1}H NMR for the two hydride ligands of *cis*-$[CpOsH_2(dppm)]BF_4$. However, the hydride signal of *cis*-$[CpOsH_2(dppm)]BF_4$ was observed as a triplet in the temperature range 298−230 K. The observation of a triplet hydride signal for *cis*-$[CpOsH_2(dppm)]BF_4$ is likely due to fast exchange of the two hydrides, which could involve the dihydrogen intermediate shown in eq 4. Similar mechanism has been



(4)

proposed for H/H exchange in $ReH_2(CO)(NO)(PR_3)_2$ (PR_3 = PCy_3, $P(i\text{-}Pr)_3$, PMe_3, $P(O\text{-}i\text{-}Pr)_3$).[25] Consistent with the existence of the exchange process, a singlet dppm signal was observed in the ^{31}P NMR spectra of both *cis*-$[CpOsHD(dppm)]^+$ and *cis*-$[CpOsH_2(dppm)]^+$ in the temperature range 298−190 K.

The small ^2J(PH) coupling constant (6.5 Hz) observed for *cis*-$[CpOsH_2(dppm)]BF_4$ could be related to the exchange process and/or the fact that ^2J(PH) are angular dependent and can have both positive and negative values. Very small ^2J(P−H) values have been reported previously for classic hydride complexes. For example, only about 3 Hz is observed for some $RhH(CO)_2(P_2)$ complexes (P_2 = diphosphites)[26] and ^2J(PH) of 0 Hz have been noted for complexes like $CpRuH_3(PR_3)$.[27] Caulton *et al.* have noted that ^2J(PH) coupling constants are usually small when the P−M−H angles are in the range 90−140° and change signs at *ca.* 75−80°.[28] The small ^2J(PH) (6.5 Hz) observed for *cis*-$[CpOsH_2(dppm)_2]BF_4$ could be related to P−Os−H angles in this complex. Alternatively, the small coupling constant could be due to the average of $^2J(PH)_{cis}$ and $^2J(PH)_{trans}$, which are of opposite signs, involving the process shown in eq 4.

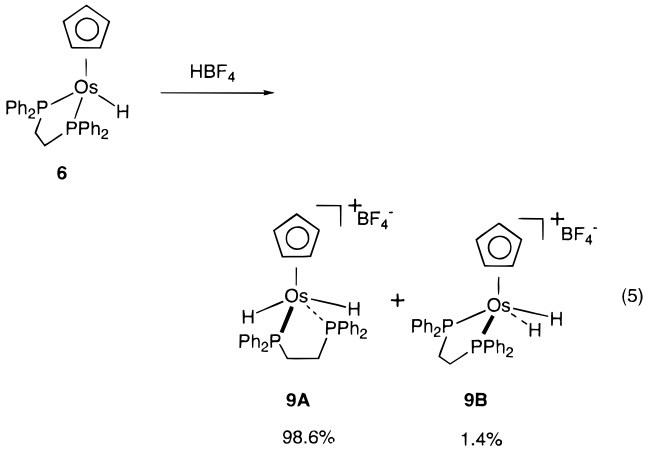
Formation of the dihydride complex $[CpOsH_2(dppm)]^+$ from the protonation reaction of CpOsH(dppm) is not surprising, as even the less electron rich CO-containing complex *trans*-$[CpOsH_2(CO)(P(i\text{-}Pr)_3)]^+$ is a classic dihydride complex.[10] In contrast, protonation of $CpRuH(CO)(PR_3)$[7a,d] and CpRuH(dppm)[5b] at room temperature gave the molecular dihydrogen complexes $[CpRu(H_2)(CO)(PR_3)]BF_4$ and $[CpRu(H_2)dppm)]BF_4$, respectively. Protonation of the more electron-rich ruthenium complex Cp*RuH(dppm) with HBF_4 led to a mixture of *trans*-$[Cp^*RuH_2(dppm)]BF_4$ and $[Cp^*Ru(H_2)(dppm)]BF_4$ in a ratio of 1:2 in solution.[8b−d]

The observation that *cis*-$[CpOsH_2(dppm)]^+$ is more stable than *trans*-$[CpOsH_2(dppm)]^+$ is rather unusual, as dihydride complexes of the type $[(\eta^5\text{-}C_5R_5)MH_2(PR_3)_2]^x$ usually adopt *trans* geometry.[1,2,4,5b,6,7c,9,11,29] The large size of osmium and the small bite angle of dppm are the most likely factors contributing to the stability of *cis*-$[CpOsH_2(dppm)]^+$.

Protonation Reactions of CpOsH(P-P) (P-P = dppe and dppp) at Room Temperature. Protona-

(22) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983,** *12*, 415.
(23) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990,** *112*, 909 and references therein.
(24) (a) Li, Z. W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946. (b) Li, Z. W.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 9506. (c) Hasegawa, T.; Koetzle, T. J. Li, Z.; Parkin, S.; McMullan, R.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352. (d) Bacskay, G. B.; Bytheway, I.; Hush, N. S. *J. Am. Chem. Soc.* **1996,** *118*, 3755.
(25) Bakhmutov, V.; Burgi, T.; Burger, P.; Ruppli, U.; Berke, H. *Organometallics* **1994,** *13*, 4203.
(26) See for example: Buisman, G. H. B.; Vos, E. J.; Kamer, P. C. J.; von Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **1995**, 409 and references therein.
(27) Arliguie, T.; Boreder, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308.
(28) Gusev, D. G.; Kuhlman, R.; Rambo, J. R.; Berke, H.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1995,** *117*, 281.
(29) See for example: (a) Jones, W. D.; Maguire, J. A. *Organometallics* **1987,** *6*, 1301. (b) Herrmann, W. A.; Theiler, H. G.; Herdtweck, E.; Kiprof, P. *J. Organomet. Chem.* **1989,** *367*, 291.

tion of CpOsH(dppe) with $HBF_4 \cdot Et_2O$ at room temperature produced a mixture of *trans*-$[CpOsH_2(dppe)]BF_4$, **9A**, and *cis*-$[CpOsH_2(dppe)]BF_4$, **9B**, in a ratio of 70:1 (eq 5). In the ^1H NMR spectrum in CD_2Cl_2, *trans*-



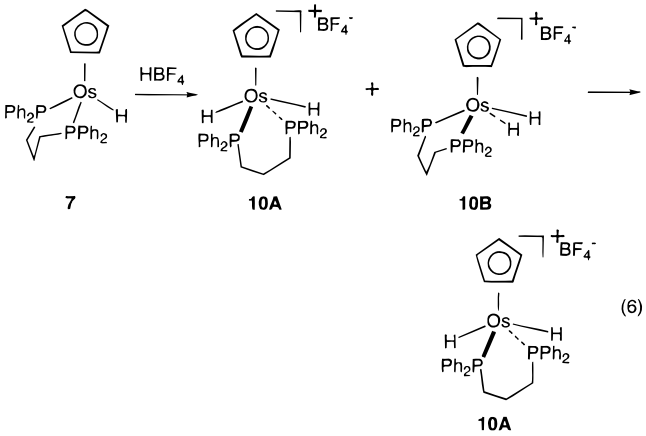
(5)

$[CpOsH_2(dppe)]BF_4$ displayed a triplet hydride signal at −13.11 ppm with $^2J(PH)$ of 32.5 Hz, and *cis*-$[CpOsH_2(dppe)]BF_4$ displayed a triplet hydride signal at −12.53 ppm with $^2J(PH)$ of only 7.6 Hz. These coupling constants are similar to those observed for the isomers of $[CpOsH_2(dppm)]BF_4$.

For comparison, it has been reported that protonation of CpRuH(dppe) produced a mixture of $[CpRu(H_2)(dppe)]^+$ and *trans*-$[CpRuH_2(dppe)]^+$ in a ratio of 2:1.[5b] Reaction of $[Cp^*Ru(dppe)]^+$ with H_2 only led to the formation of *trans*-$[Cp^*RuH_2(dppe)]^+$.[30] The existence of a small amount of *cis*-$[CpOsH_2(dppe)]^+$ in equilibrium with *trans*-$[CpOsH_2(dppe)]^+$ in solution (not observed for ruthenium complexes) could be attributed to the relatively large size of osmium. As expected, the ratio of *cis* to *trans* isomers of $[CpOsH_2(P\text{-}P)]^+$ increases from 1:70 for $[CpOsH_2(dppe)]^+$ to 9:1 for $[CpOsH_2(dppm)]^+$, as dppm has a smaller bite angle.

The observation of *cis*-$[CpOsH_2(dppe)]^+$ in solution at room temperature promoted us to prepare $[CpOsH_2(dppp)]^+$, which contains a more flexible diphosphine, in order to see if *cis*-$[CpOsH_2(dppp)]^+$ is also a thermodynamically stable complex. When CpOsH(dppp) in Et_2O was protonated with $HBF_4 \cdot Et_2O$ at room temperature, a white powder of $[CpOsH_2(dppp)]BF_4$, **10**, was produced. The NMR spectra collected immediately after dissolving the powder in CD_2Cl_2 showed signals of both *trans*-$[CpOsH_2(dppp)]BF_4$ (**10A**, major) and *cis*-$[CpOsH_2(dppp)]BF_4$ (**10B**, trace) (eq 6). However *cis*-$[CpOsH_2(dppp)]BF_4$ is unstable and isomerized to *trans*-$[CpOsH_2(dppp)]BF_4$ in solution within 10 min, as confirmed by the disappearance of the signals of *cis*-$[CpOsH_2(dppp)]BF_4$ in NMR experiments. Complexes **10A**,**B** show ^1H NMR data similar to those of **8** and **9**.

Protonation Reactions at Low Temperature. The observation of *cis*-$[CpOsH_2(dppp)]BF_4$ isomerizing to *trans*-$[CpOsH_2(dppp)]BF_4$ at room temperature raises the question of the sites of protonation for the monohydride complexes. In principle, both the metal center and hydride can be protonated to give the initial protonation products, which can then isomerize to the final thermodynamic products. It has been reported



(6)

that protonation of $(C_5R_5)RuH(L_2)$ (R = H, Me; L = phosphine) at low temperature appears always to give the molecular dihydrogen complexes $[(C_5R_5)Ru(H_2)(L_2)]^+$ which may isomerize into thermodynamically more stable dihydrido complexes $[(C_5R_5)RuH_2(L_2)]^+$.[7c,8c] Protonation of Cp*FeH(dppe) at −80 °C also initially produced the molecular dihydrogen complex $[Cp^*Fe(H_2)(dppe)]^+$, which converted to the dihydride complex *trans*-$[Cp^*FeH_2(dppe)]^+$ upon warming.[2] However, Brookhart and his co-worker recently reported that protonation of CpFeH(CO)(PEt_3) with $H(OEt_2)BAr'_4$ at −78 °C in CD_2Cl_2 containing water initially produced the dihydride complex *trans*-$[CpFeH_2(CO)(PEt_3)]^+$, which isomerized into the molecular dihydrogen complex $[CpFeH_2(CO)(PEt_3)]^+$ upon being warmed to −20 °C.[3]

We have studied the protonation reactions of CpFeH(P-P) (P-P = dppe, dppp) and CpOsH(P-P) (P-P = dppm, dppe, and dppp) at low temperature to determine the initial kinetic protonation products. Protonation of CpFeH(P-P) (P-P = dppe, dppp) at −78 °C produced the dihydrogen complexes $[CpFe(H_2)(P\text{-}P)]^+$, as observed at room temperature.

Protonation of CpOsH(dppm) with HBF_4 at −78 °C produced a mixture of *cis*-$[CpOsH_2(dppm)]BF_4$ and *trans*-$[CpOsH_2(dppm)]BF_4$ in a ratio of 24:1. When the solution was warmed to room temperature, the ratio of *cis*-$[CpOsH_2(dppm)]BF_4$ to *trans*-$[CpOsH_2(dppm)]BF_4$ changed to 10:1. Protonation of CpOsH(dppe) with HBF_4 at −78 °C produced *cis*-$[CpOsH_2(dppe)]BF_4$ and *trans*-$[CpOsH_2(dppe)]BF_4$ in a ratio of 1:3. When the solution was warmed to room temperature, the ratio of *cis*-$[CpOsH_2(dppe)]BF_4$ to *trans*-$[CpOsH_2(dppe)]BF_4$ changed to 1:70. Protonation of CpOsH(dppp) with HBF_4 at −78 °C produced a mixture of *cis*-$[CpOsH_2(dppp)]BF_4$ and *trans*-$[CpOsH_2(dppp)]BF_4$ in a ratio of 1:3. *cis*-$[CpOsH_2(dppp)]BF_4$ is unstable and isomerized to *trans*-$[CpOsH_2(dppp)]BF_4$ on warming to room temperature. Since more *cis* isomers were observed when the protonation was carried out at low temperature, it is likely that the Os−H was preferentially protonated in the reaction of HBF_4 with CpOsH(P-P), at least at low temperature.

Conclusion. This study on the protonation reactions of CpMH(P-P) (M = Fe, Os), together with previous studies on ruthenium complexes, shows that the thermodynamically stable structures of $[CpMH_2(P\text{-}P)]^+$ are dependent on the size of the chelating rings and metals. The molecular dihydrogen form is more stable for the iron complexes $[CpFe(H_2)(P\text{-}P)]BF_4$ (P-P = dppe, dppp). Analogous ruthenium complexes can adopt either the

(30) Kirchner, K.; Mauthner, K.; Mereiter, K.; Schmid, R. *J. Chem. Soc., Chem. Commun.* **1993**, 893.

dihydride form *trans*-[(η^5-C_5R_5)RuH_2(P-P)]$^+$ or the dihydrogen form [(η^5-C_5R_5)Ru(H_2)(P-P)]$^+$ or a mixture of both, depending on the size of the chelating rings and C_5R_5. Due to its electron-rich nature, the dihydride form is more stable for the osmium analogs [$CpOsH_2$-(P-P)]$^+$. These observations support the general trend in relative stability of dihydrogen and dihydride forms.[16,18]

Depending on the size of the chelating rings, the thermodynamically stable structures of $CpOsH_2$(P-P)]-BF_4 at room temperature may be exclusively *trans*-[$CpOsH_2$(P-P)]BF_4 or a mixture of *cis*-[$CpOsH_2$(P-P)]BF_4 and *trans*-[$CpOsH_2$(P-P)]BF_4. At room temperature in dichloromethane solution, [$CpOsH_2$(dppm)]BF_4 exists as a mixture of *cis* and *trans* isomers in a ratio of 10:1, [$CpOsH_2$(dppe)]BF_4 exists as a mixture of *cis* and *trans* isomers in a ratio of 1:70, and [$CpOsH_2$(dppp)]BF_4 adopts only *trans* geometry. The isolation and observation of *cis*-[$CpOsH_2$(P-P)]$^+$ (P-P = dppm, dppe) is rather unusual, as dihydride complexes of the type [(η^5-C_5R_5)-$MH_2(PR_3)_2$]^x usually adopt *trans* geometry.[1,2,4,5b,6,7c,9,11,29] The relatively large size of osmium and small bite angles of dppm and dppe are the most likely factors contributing to the stability of *cis*-[$CpOsH_2$(P-P)]$^+$.

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