Ligand Effects on Heats of Protonation of Multihydrido-Transition Metal Complexes of Osmium and Iridium

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Titration calorimetry has been used to determine heats of protonation (ΔH_{HM}) of the metal in $(H)_2Os(PR_3)_4$ (PR_3 = $PPhMe_2$, PPh_2Me, $PPh(OEt)_2$, $P(OEt)_3$), $(H)_4Os(PR_3)_3$ (PR_3 = $PPhMe_2$, PPh_2Me), $HIr(CO)(PPh_3)_3$, and $CpIr(ER_3)(H)_2$ (ER_3 = PPh_3, $AsPh_3$, $P(OPh)_3$) complexes with CF_3SO_3H in 1,2-dichloroethane solvent at 25.0 °C. For the $(H)_2Os(PR_3)_4$ complexes, the basicity ($-\Delta H_{HM}$) increases from 34.2 to 43.3 kcal/mol in the order $P(OEt)_3 < PPh(OEt)_2 < PPh_2Me < PPhMe_2$. The basicity ($-\Delta H_{HM}$) of the metal in $(H)_4Os(PR_3)_3$ (PR_3 = $PPhMe_2$, PPh_2Me) increases by ~15 kcal/mol when two hydride ligands are replaced by a PR_3 ligand to give $(H)_2Os(PR_3)_4$. Replacement of the two hydride ligands in $CpIr(PPh_3)(H)_2$ by a CO ligand to give $CpIr(PPh_3)(CO)$ results in a 10.4 kcal/mol increase in the basicity ($-\Delta H_{HM}$) of the metal. The basicities of the $CpIr(ER_3)(H)_2$ complexes increase in the order $P(OPh)_3 \ll AsPh_3 \approx PPh_3$. Comparisons of the basicities of $CpIr(PPh_3)(CO)$ and $(PPh_3)_2(H)Ir(PPh_3)(CO)$ complexes show that replacement of Cp by the isoelectronic $(PR_3)_2(H)$ ligand set increases the basicity of the metal. In other complexes, the replacement of Cp* by $(PR_3)_2(H)$ also increases the metal basicity, but the effect varies greatly.

Introduction

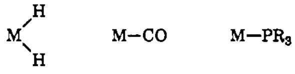
Many quantitative correlations of ligand parameters with spectroscopic, electrochemical, and kinetic properties of transition metal complexes have been reported.[1,2] In this research group, correlations have been observed between the basicities of phosphine (PR_3) ligands as measured by their heats of protonation (ΔH_{HP}) with CF_3SO_3H in 1,2-dichloroethane (DCE) solution (eq 1)[3] and the heats of protonation (ΔH_{HM}) of their transition metal complexes (eq 2). Such correlations were demonstrated in studies

$$PR_3 + CF_3SO_3H \xrightarrow[25.0\,°C]{DCE} HPR_3^+CF_3SO_3^-;\ \Delta H_{HP} \quad (1)$$

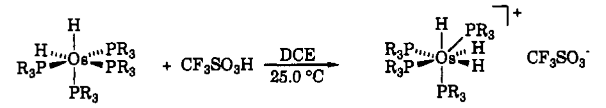
$$ML_n + CF_3SO_3H \xrightarrow[25.0\,°C]{DCE} HML_n^+CF_3SO_3^-;\ \Delta H_{HM} \quad (2)$$

of $Fe(CO)_3(PR_3)_2$,[4] $CpIr(PR_3)(CO)$,[4] $W(CO)_3(PR_3)_3$,[5] $Fe(CO)_3(\overset{\frown}{P\ P})$,[6] and $M(CO)_2(\overset{\frown}{P\ P})_2$ (M = Cr, Mo, W),[7] where $\overset{\frown}{P\ P}$ is a bidentate phosphine. Also, the effects of methyl-substituted

Chart I



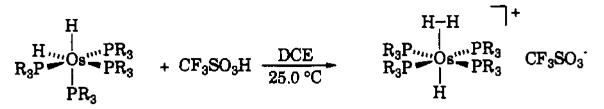
cyclopentadienyl ligands on the basicity of the metal in $(\eta^5\text{-}C_5Me_xH_{5-x})Ir(1,5\text{-cyclooctadiene})$[8] have been determined previously. In this report, we extend our studies of the effects of phosphorus-donor ligands on metal basicity (ΔH_{HM}) to the $(H)_2Os(PR_3)_4$ series of complexes, where PR_3 = $P(OEt)_3$, $PPh(OEt)_2$, PPh_2Me, and $PPhMe_2$ (eqs 3 and 4).



(3)

1 (PR_3 = $PPhMe_2$)
2 (PR_3 = PPh_2Me)

1H⁺, **2H⁺**

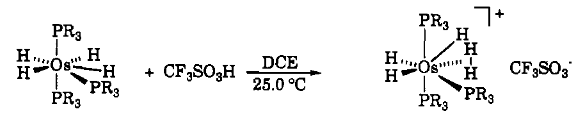


(4)

3 (PR_3 = $PPh(OEt)_2$)
4 (PR_3 = $P(OEt)_3$)

3H⁺, **4H⁺**

Also, we compare the donor ability of two hydride ligands with the donor ability of CO and PR_3 (Chart I). There are many examples of isoelectronic pairs of complexes that are related by the replacement of $(H)_2$ ligands by a CO or PR_3 ligand. In the present study, we compare basicities (ΔH_{HM}, eq 5) of $(H)_4Os(PR_3)_3$, where PR_3 = $PPhMe_2$ and PPh_2Me, with those (eq 3) of $(H)_2Os(PR_3)_4$, which contain one more PR_3 but two fewer hydride ligands. Also, we examine the effects of $(H)_2$ and CO on the basicities of the metal in $CpIr(PPh_3)(H)_2$ (eq 6) and the isoelectronic $CpIr(PPh_3)(CO)$ complex. In considering whether $(H)_2$ would make the metal more or less basic than the analogous



(5)

5 (R = $PPhMe_2$)
6 (R = PPh_2Me)

5H⁺, **6H⁺**

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[1] (a) Feltham, R. D.; Brant, P. *J. Am. Chem. Soc.* **1982**, *104*, 641. (b) Chatt, J. *Coord. Chem. Rev.* **1982**, *43*, 337. (c) Timney, J. A. *Inorg. Chem.* **1979**, *18*, 2502. (d) Bursten, B. E.; Green, M. R. *Prog. Inorg. Chem.* **1988**, *36*, 393. (e) Duff, C. M.; Heath, G. A. *Inorg. Chem.* **1991**, *30*, 2528. (f) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271. (g) Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650. (h) Prock, A.; Giering, W. P.; Green, J. E.; Meirowitz, R. E.; Hoffman, S. L.; Woska, D. C.; Wilson, M.; Chang, R.; Chen, J.; Magnuson, R. H.; Eriks, K. *Organometallics* **1991**, *10*, 3479. (i) Araghizadeh, F.; Branan, D. M.; Hoffman, N. W.; Jones, J. H.; McElroy, E. A.; Miller, N. C.; Ramage, D. L.; Salazar, A. B.; Young, S. H. *Inorg. Chem.* **1988**, *27*, 3752. (j) Morris, R. J. *Inorg. Chem.* **1992**, *31*, 1471. (k) Poë, A. J. *Pure Appl. Chem.* **1988**, *60*, 1209. (l) Heath, G. A.; Humphrey, D. G. *J. Chem. Soc., Chem. Commun.* **1991**, 1668.

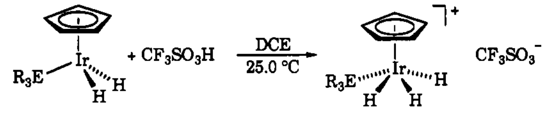
[2] (a) Kristjánsdóttir, S. S.; Norton, J. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, in press. (b) Kristjánsdóttir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983. (c) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257. (d) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (e) Tilset, M. *J. Am. Chem. Soc.* **1992**, *114*, 2740–2741. (f) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618. (g) Ryan, O. B.; Tilset, M.; Parker, V. D. *Organometallics* **1991**, *10*, 298. (h) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (i) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161.

[3] Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681.

[4] Sowa, J. R., Jr.; Zanotti, V.; Facchin, G.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 9185.

[5] Sowa, J. R., Jr.; Zanotti, V.; Angelici, R. J. *Inorg. Chem.* **1993**, *32*, 848.

0020-1669/93/1332-3282$04.00/0



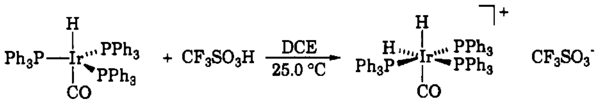
(6)

7 ($ER_3 = PPh_3$)
8 ($ER_3 = AsPh_3$)
9 ($ER_3 = P(OPh)_3$)

7H$^+$-9H$^+$

CO or PR_3 complex, we note that the hydride ligand in $CpOs(PPh_3)_2H$ makes the Os 23.2 kcal/mol more basic than the corresponding iodide complex $CpOs(PPh_3)_2I$.[9] So, as compared with a halide ligand, the hydride is a very strong donor. This suggests that dihydride complexes may be very basic as compared with the analogous CO and PR_3 complexes. On the other hand, the formal oxidation state of the metal in the dihydride is +2 units higher than in the CO or PR_3 complexes, which should make the dihydride complex less basic. Further complicating this comparison are differences in the geometries of the $(H)_2$ and CO or PR_3 complexes because there is one more ligand (two H's) in the $(H)_2$ complexes. The ΔH_{HM} measurements of reactions 3, 5, and 6 clarify the effects of $(H)_2$, CO, and PR_3 ligands on the basicities of the metals in these complexes.

We also sought to compare the effects of the η^5-cyclopentadienyl (Cp) ligand and the isoelectronic $(PR_3)_2(H)$ ligand set (Chart II) on the basicity of a metal. Again, there are many analogous CpM and $(PR_3)_2(H)$ complexes; we have chosen to compare ΔH_{HM} for $CpIr(PPh_3)(CO)$ with that for $(PPh_3)_2(H)Ir(PPh_3)(CO)$ (eq 7). In this comparison, the oxidation state of the metal is the same (+1) but the nature of the ligands is quite different.



(7)

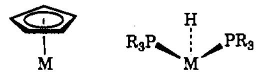
10

10H$^+$

Experimental Section

All preparative reactions and solvent purifications were carried out under an Ar atmosphere using standard Schlenk techniques. The complexes $(H)_2Os(PPhMe_2)_4$ (**1**),[10] $(H)_2Os(PPh_2Me)_4$ (**2**),[10] $(H)_2Os[PPh(OEt)_2]_4$ (**3**),[11] $(H)_2Os[P(OEt)_3]_4$ (**4**),[11] $(H)_4Os(PPhMe_2)_3$ (**5**),[12] $(H)_4Os(PPh_2Me)_3$ (**6**),[12] $CpIr(PPh_3)(H)_2$ (**7**),[13] $CpIr(AsPh_3)(H)_2$ (**8**),[13] and $CpIr[P(OPh)_3](H)_2$ (**9**)[13] were prepared as previously described. The complex $HIr(CO)(PPh_3)_3$ (**10**) was used as received from Strem Chemicals, Inc. Deuterated solvents (CD_2Cl_2 and $CDCl_3$) were stored over molecular sieves in air. 1,2-Dichloroethane (99.8%, HPLC grade) was purchased from Aldrich and distilled from P_4O_{10} immediately before use. CF_3SO_3H was purchased from 3M Co. and purified by fractional distillation under an argon atmosphere.[3] The ^1H NMR spectra were recorded in either CD_2Cl_2 or $CDCl_3$ using a Nicolet NT 300-MHz or a Varian VXR 300-MHz spectrometer with TMS (δ = 0.00 ppm) as the internal standard. T_1 values were measured from +25 to −85 °C using the standard inversion recovery sequence 180°–τ–90°.[14] The T_1(min) value is the minimum value of T_1 determined from a T_1 vs temperature plot. The $^{31}P\{^1H\}$ NMR spectra were recorded in CD_2Cl_2 on a Varian VXR 300-MHz spectrometer using 85% phosphoric acid (δ = 0.00 ppm) as the external standard.

Chart II



Calorimetric titrations were performed under an Ar atmosphere using a Tronac Model 458 isoperibol calorimeter as originally described[3] and then modified.[4] A 2-min titration period was used for all complexes and was preceded and followed by heat capacity calibrations. During the titration period approximately 0.8 mL of a 0.1 M CF_3SO_3H solution (standardized to a precision of ±0.0002 M) in DCE solvent was added at a constant rate to 50 mL of a 1.7 mM solution of the metal complex (5–10% excess) in DCE at 25.0 °C.

The ΔH_{HM} values were measured using two different standardized acid solutions and are reported as the average of at least four titrations and as many as six. The heat of dilution (ΔH_{dil}) of the acid in DCE (−0.2 kcal/mol)[4] was used to correct the reaction enthalpies.

Protonation Reactions. Compounds **1–10** were protonated for NMR characterization by dissolving ~5 mg of the complex in 0.5 mL of CD_2Cl_2 (or $CDCl_3$) in an NMR tube under an Ar atmosphere at room temperature. To the solution was added 1 equiv of CF_3SO_3H by microliter syringe through a rubber septum; this resulted in the quantitative formation of complexes **1H$^+$–10H$^+$**. Solutions of the protonated complexes are stable as long as they are kept under argon. Complexes **3H$^+$BF$_4^-$**,[11] **4H$^+$BPh$_4^-$**,[11] **5H$^+$BPh$_4^-$**,[11] **7H$^+$BF$_4^-$**,[13] **8H$^+$BF$_4^-$**,[13] **9H$^+$BF$_4^-$**,[13] and **10H$^+$SiF$_5^-$** [16] have been previously isolated and characterized; their ^1H NMR spectra are very similar to those of the same complexes that we prepared by protonation with CF_3SO_3H. Due to the air sensitivity of **1H$^+$**, **2H$^+$**, and **6H$^+$**, no attempts were made to isolate these complexes. The ^1H NMR spectra of all the protonated complexes are given below.

$[(H)_3Os(PPhMe_2)_4]^+CF_3SO_3^-$ (1H$^+$CF$_3$SO$_3^-$): ^1H NMR (CD_2Cl_2) δ 7.1–7.3 (m, 20H, Ph), 1.45 (br s, 24H, CH_3), −7.77 (quintet, $^2J_{PH}$ = 9.9 Hz, 3H, Os–H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −32.7 (s).

$[(H)_3Os(PPh_2Me)_4]^+CF_3SO_3^-$ (2H$^+$CF$_3$SO$_3^-$): ^1H NMR (CD_2Cl_2) δ 7.1–7.3 (m, 40H, Ph), 0.93 (br s, 12H, CH_3), −6.82 (quintet, $^2J_{PH}$ = 9.2 Hz, 3H, Os–H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −19.5 (s).

$[(H_2)(H)Os[PPh(OEt)_2]_4]^+CF_3SO_3^-$ (3H$^+$CF$_3$SO$_3^-$): ^1H NMR (CD_2Cl_2) δ 7.32–7.58 (m, 20H, Ph), 3.44 (m, 8H, CH_2), 3.22 (m, 8H, CH_2), 1.05 (t, $^2J_{HH}$ = 7.2 Hz, 24H, CH_3), −6.80 (br s, 3H, Os–H).

$[(H_2)(H)Os[P(OEt)_3]_4]^+CF_3SO_3^-$ (4H$^+$CF$_3$SO$_3^-$): ^1H NMR ($CDCl_3$) δ 3.9 (m, 24H, CH_2), 1.3 (t, $^2J_{HH}$ = 6.2 Hz, 36H, CH_3), −8.23 (br s, 3H, Os–H).

$[(H_2)(H)_3Os(PPhMe_2)_3]^+CF_3SO_3^-$ (5H$^+$CF$_3$SO$_3^-$): ^1H NMR (CD_2Cl_2) δ 7.1–7.4 (m, 15H, Ph), 1.78 (br s, 18H, CH_3), −9.68 (br s, 5H, Os–H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −33.4 (s).

$[(H_2)(H)_3Os(PPh_2Me)_3]^+CF_3SO_3^-$ (6H$^+$CF$_3$SO$_3^-$): ^1H NMR (CD_2Cl_2) δ 7.1–7.3 (m, 30H, Ph), 1.93 (br s, 9H, CH_3), −6.24 (br s, 2H, Os–(H_2)), −10.96 (br s, 3H, Os–$(H)_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −13.4 (s).

$[CpIr(PPh_3)(H)_3]^+CF_3SO_3^-$ (7H$^+$CF$_3$SO$_3^-$): ^1H NMR (CD_2Cl_2) δ 7.3–7.6 (m, 15H, Ph), 5.92 (s, 5H, Cp), −12.39 (d, $^2J_{PH}$ = 7.9 Hz, 3H, Ir–$(H)_3$).

$[CpIr(AsPh_3)(H)_3]^+CF_3SO_3^-$ (8H$^+$CF$_3$SO$_3^-$): ^1H NMR (CD_2Cl_2) δ 7.3–7.6 (m, 15H, Ph), 5.98 (s, 5H, Cp), −12.69 (s, 3H, Ir–$(H)_3$).

$[CpIr[P(OPh)_3](H)_3]^+CF_3SO_3^-$ (9H$^+$CF$_3$SO$_3^-$): ^1H NMR (CD_2Cl_2) δ 7.2–7.5 (m, 15H, Ph), 5.50 (s, 5H, Cp), −12.48 (d, $^2J_{PH}$ = 8.5 Hz, 3H, Ir–$(H)_3$).

$[(H)_2Ir(CO)(PPh_3)_3]^+CF_3SO_3^-$ (10H$^+$CF$_3$SO$_3^-$): ^1H NMR (CD_2Cl_2) δ 6.8–7.5 (m, 45H, Ph), −9.52 (m, 1H, Ir–H), −11.4 (dtd, $^2J_{PH}$ = 114 Hz, $^2J_{PH}$ = 19.2 Hz, $^2J_{HH}$ = 4.8 Hz, 1H, Ir–H).

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(6) Sowa, J. R., Jr.; Zanotti, V.; Facchin, G.; Angelici, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 160.

(7) Sowa, J. R., Jr.; Bonanno, J. B.; Zanotti, V.; Angelici, R. J. *Inorg. Chem.* **1992**, *31*, 1370.

(8) Sowa, J. R., Jr.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2537.

(9) (a) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 8296. (b) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.*, in press.

(10) (a) Bell, B.; Chatt, J.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1973**, 997. (b) Bruno, J. W.; Huffman, J. C.; Green, M. A.; Zubkowski, J. D.; Hatfield, W. E.; Caulton, K. G. *Organometallics* **1990**, *9*, 2556.

(11) (a) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Chem. Soc., Dalton Trans.* **1989**, 2353. (b) Amendola, P.; Antoniutti, S.; Albertin, G.; Bordignon, E. *Inorg. Chem.* **1990**, *29*, 318.

(12) Douglas, P. G.; Shaw, B. L. *J. Chem. Soc. A* **1970**, 334.

(13) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909.

(14) (a) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (b) Cotton, F. A.; Luck, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5757. (c) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 2181. (d) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (e) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173.

(15) (a) Johnson, T. J.; Huffman, K. G.; Caulton, K. G.; Jackson, S. A.; Eisenstein, O. *Organometallics* **1989**, *8*, 2073. (b) Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 1663.

(16) (a) Siedle, A. R.; Newmark, R. A.; Howells, R. D. *Inorg. Chem.* **1988**, *27*, 2473. (b) Bird, P.; Harrod, J. F.; Than, K. A. *J. Am. Chem. Soc.* **1974**, *96*, 1222.

The low-temperature spectra (see Results) were recorded in CD_2Cl_2 solvent.

Results

Characterization of *cis*-$(H)_2Os(PR_3)_4$ (1–4) and $H_3Os(PR_3)_4^+$ ($1H^+$–$4H^+$). Complexes **1–4** have previously[10–12] been identified by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy as having *cis*-octahedral structures (eqs 3 and 4). Bordignon et al.[11] assigned $(H)(H_2)Os[P(OEt)_3]_4^+$ (**4H$^+$**) a *trans*-octahedral geometry (eq 4) on the basis of its ^1H and $^{31}P\{^1H\}$ NMR spectra; $(H)(H_2)Os(PPh(OEt)_2)_4^+$ (**3H$^+$**) was assigned,[11] on the basis of the low-temperature $^{31}P\{^1H\}$ and ^1H NMR spectra, a distorted *trans*-octahedral structure (eq 4) with two of the *trans* PR_3 ligands bent slightly toward the η^2-dihydrogen (H_2) ligand and the other two *trans* PR_3 ligands bent slightly toward the hydride (H) ligand.

The structure of the related $(H)_3Os(PPh_3)_4^+$ complex, determined by X-ray crystallography,[17] has a distorted tetrahedral arrangement of phosphines (eq 3), while the hydrides, which were not located, were proposed to be capping three of the faces. Siedle et al.[17] noted that $(H)_3Os(PPh_3)_4^+$ is fluxional at room temperature as evidenced by a quintet for the hydride resonance in the ^1H NMR spectrum and a singlet in the $^{31}P\{^1H\}$ NMR spectrum; at −70 °C there is a broad singlet for the hydride in the ^1H NMR spectrum and two broad singlets in the $^{31}P\{^1H\}$ NMR spectrum.[17] At room temperature $(H)_3Os(PPh_2Me)_4^+$ (**2H$^+$**) is also fluxional, as indicated by a quintet for the hydride ligands in the ^1H NMR spectrum and a singlet in the $^{31}P\{^1H\}$ NMR spectrum. The fluxionality of **2H$^+$** is slowed at −75 °C, as suggested by a broad singlet for the hydride in the ^1H NMR spectrum and two broad singlets at −13.8 and −25.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The T_1(min) value (159 ms (−45 °C)) for the hydride peak in **2H$^+$** is consistent with a classical trihydride structure.[14] The T_1(min) value along with the similarities in the low-temperature $^{31}P\{^1H\}$ and ^1H NMR spectra of **2H$^+$** and $(H)_3Os(PPh_3)_4^+$ suggests that $(H)_3Os(PPh_2Me)_4^+$ (**2H$^+$**) also has a structure similar to that drawn in eq 3.

The hydride signal in the ^1H NMR spectrum of the less sterically crowded complex $(H)_3Os(PPhMe_2)_4^+$ (**1H$^+$**) occurs as a quintet at room temperature but as a broad singlet at −75 °C. The T_1(min) value (177 ms at −60 °C) for the hydride resonance is consistent with the trihydride structure.[14] Since only a singlet is observed in the $^{31}P\{^1H\}$ NMR spectrum from +20 to −75 °C, it is not possible to establish the geometry. Therefore, it is possible that **1H$^+$** has either a geometry similar to that drawn in eq 3 or a *trans*-octahedral geometry in which the phosphines are equivalent in the equatorial plane and the hydride ligands are fluxional. On the basis of the structure of $(H)_3Os(PPh_3)_4^+$, it seems likely that **1H$^+$** also has a structure similar to that shown in eq 3.

Characterization of $(H)_4Os(PR_3)_3$ (5, 6) and $(H)_5Os(PR_3)_3^+$ ($5H^+$, $6H^+$). Hart and co-workers[18] using neutron diffraction showed that $(H)_4Os(PPhMe_2)_3$ (**5**) has a pentagonal bipyramidal geometry with four hydrides and a $PPhMe_2$ ligand in the equatorial positions (eq 5) and the other two phosphines in the apical positions. The room-temperature ^1H NMR spectra of $(H)_4Os(PPhMe_2)_3$ (**5**) and $(H)_4Os(PPh_2Me)_3$ (**6**) indicate that they are both fluxional, as suggested by the hydride resonances of both complexes being split into quintets. At lower temperatures (0 to −75 °C) each complex exhibits a broad singlet for the hydride resonance. In the $^{31}P\{^1H\}$ NMR spectra of **5** and **6** from +20 to −70 °C only a singlet is observed; this too indicates that the complexes are fluxional over this temperature range. Because of the fluxionality of **5** and **6**, it is not possible to establish their structures by NMR spectroscopy in this temperature region; however, it seems likely that **6** has the pentagonal bipyramidal structure established for $H_4Os(PPhMe_2)_3$ (**5**, eq 5).

Structures of the protonated products **5H$^+$** and **6H$^+$** or related derivatives have not been established by X-ray or neutron diffraction. In the ^1H NMR spectrum of $(H_2)(H)_3Os(PPhMe_2)_3^+$ (**5H$^+$**) at room temperature, the broad hydride singlet indicates that the compound is fluxional; the singlet in the $^{31}P\{^1H\}$ NMR spectrum supports this conclusion. The hydride peak remains a broad singlet even at −75 °C in the ^1H NMR spectrum; however, the $^{31}P\{^1H\}$ NMR spectrum of **5H$^+$** at −75 °C exhibits a triplet at −18.8 ppm ($^2J_{PP}$ = 19.5 Hz) and a doublet at −23.4 ppm ($^2J_{PP}$ = 19.5 Hz). This doublet and triplet suggest that the phosphines are arranged in a manner similar to that drawn for **5** (eq 5). Caulton et al.[15a] report the T_1(min) for **5H$^+$** to be 68 ms (−70 °C) and assign it the $(H_2)(H)_3Os(PPhMe_2)_3^+$ structure.[19]

In the $^{31}P\{^1H\}$ NMR spectrum of $(H_2)(H)_3Os(PPh_2Me)_3^+$ (**6H$^+$**), a singlet is observed at −4.41 ppm at 25 °C, while at −75 °C a doublet at −1.8 ppm ($^2J_{PP}$ = 32.7 Hz) and a broad singlet at −12.5 ppm are observed. Two hydride signals for $(H_2)(H)_3Os(PPh_2Me)_3^+$ (**6H$^+$**) are observed in the ^1H NMR spectrum at −6.24 and −10.96 ppm; the integrals of these peaks are in a 2:3 ratio from +20 to −70 °C. The hydride peak at −6.24 ppm in the ^1H NMR spectrum has a T_1(min) value of 30 ms (−55 °C), which is consistent with the dihydrogen (η^2-H_2) assignment; the hydride peak at −10.96 ppm has a T_1(min) value of 70 ms (−55 °C). Therefore, the structure of **6H$^+$** is suggested to be similar to that drawn in eq 5.[19]

Characterization of $CpIr(ER_3)(H)_2$ (7–9) and $CpIr(ER_3)(H)_3^+$ ($7H^+$–$9H^+$). Complexes **7–9** have the three-legged piano-stool structure (eq 6), as suggested by ^1H NMR spectroscopy.[13] A neutron diffraction study of $[CpIr(PMe_3)(H)_3]BF_4$ indicates that it is a normal trihydride complex;[13,20] therefore, it is likely that complexes **7H$^+$–9H$^+$** also adopt the four-legged piano stool structure (eq 6) containing classical hydride ligands [T_1: $CpIr(PPh_3)(H)_3^+$, 200 ms (minimum not observed, 210 K, 500 MHz); $CpIr(AsPh_3)(H)_3^+$, 210 ms (minimum not observed, 210 K, 500 MHz)].[20]

Characterization of $(H)Ir(CO)(PPh_3)_3$ (10) and $(H)_2Ir(CO)(PPh_3)_3^+$ ($10H^+$). The structures of both **10**[21] and **10H$^+$**[,16b] have been established by X-ray crystallography. In the structure of **10**, the hydride and CO ligands are in the axial positions of a trigonal bipyramid, as shown in eq 7; **10H$^+$** has the *cis,mer*-$(H)_2Ir(CO)(PPh_3)_3^+$ structure, also shown in eq 7.

Calorimetric Studies. The heats of protonation (ΔH_{HM}) obtained from titrations of complexes **1–10** with CF_3SO_3H in 1,2-dichloroethane (DCE) solvent at 25.0 °C are presented in Table I. Plots of temperature vs amount of acid added were linear, which indicates that the complexes are protonated rapidly and quantitatively. There was no decomposition of either the neutral or the protonated species during the titration, as suggested by the normal pre- and posttitration baseline slopes for all of the compounds. It is possible to deprotonate compounds **4H$^+$–9H$^+$** with 1 equiv of 1,3-diphenylguanidine (ΔH_{HN} = −37.2 kcal/mol);[3] however, only compounds **7–9** can be easily purified by eluting the sample on a short neutral alumina column with CH_2Cl_2. The osmium compounds **4–6** were separated from the protonated 1,3-diphenylguanidine by extracting the complexes with 3 × 2 mL of benzene and then recrystallizing them in a minimum amount of methanol solvent at −20 °C. Compounds **1H$^+$–3H$^+$** and **10H$^+$** do not deprotonate with 1,3-diphenylguanidine; this

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(17) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *Inorg. Chem.* **1986**, *25*, 3412.

(18) Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 7557.

(19) T_1(min) values have commonly been used to determine whether dihydrogen or dihydride ligands exist in a compound.[14] However, more recently it was determined[14e] that this method is not reliable. In fact, many early polyhydrides have been misidentified using the T_1(min) criterion alone.[14e] Therefore, we are not able to definitively assign the structure of **6H$^+$**.

(20) Heinekey, D. M.; Payne, N. G.; Schulte, G. K. *J. Am. Chem. Soc.* **1988**, *110*, 2303.

(21) La Placa, S. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1963**, *85*, 3500.

Table I. Enthalpies of Protonation (ΔH_{HM}) of $(H)_2Os(PR_3)_4$, $(H)_4Os(PR_3)_3$, $(H)Ir(CO)(PPh_3)_3$, and $CpIr(ER_3)(H)_2$ Complexes

metal complex	$-\Delta H_{HM}$,[a,b] kcal/mol
cis-$(H)_2Os(PPhMe_2)_4$ (**1**)	43.3 (±0.3)
cis-$(H)_2Os(PPh_2Me)_4$ (**2**)	38.8 (±0.2)
cis-$(H)_2Os(PPh(OEt)_2)_4$ (**3**)	37.2 (±0.2)
cis-$(H)_2Os(P(OEt)_3)_4$ (**4**)	34.2 (±0.2)
$(H)_4Os(PPhMe_2)_3$ (**5**)	27.7 (±0.1)
$(H)_4Os(PPh_2Me)_3$ (**6**)	23.9 (±0.3)
$CpIr(PPh_3)(H)_2$ (**7**)	19.7 (±0.2)
$CpIr(AsPh_3)(H)_2$ (**8**)	19.4 (±0.1)
$CpIr[P(OPh)_3](H)_2$ (**9**)	11.9 (±0.2)
$(H)Ir(CO)(PPh_3)_3$ (**10**)	38.8 (±0.4)
$CpIr(PPh_3)(CO)$	30.1 (±0.2)[c]

[a] For protonation with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C. [b] Numbers in parentheses are average deviations from the mean of at least four titrations. [c] Reference 4.

was expected since diphenylguanidine is a weaker base than compounds **1**–**3** and **10**.

The low dielectric constant (ϵ = 10.46)[22] for DCE means that the protonated products occur as ion pairs. It has been estimated that dissociation of these ion pairs, autoprotolysis, and dimerization of CF_3SO_3H contribute little to the measured ΔH_{HM} values.[3,7,9b] Thus, we attribute trends and differences in the ΔH_{HM} values to the properties of the reactant and product complexes.

Discussion

Comparison of Basicities (ΔH_{HM}) of Complexes with Isoelectronic Ligand Sets: $(H)_2$, CO, and PR_3. As noted in the Introduction, one focus of these studies was to determine the effect of the 2-electron ligand sets $(H)_2$, CO, and PR_3 on the basicities of transition metal complexes. A comparison of ΔH_{HM} values (Table I) for $(H)_4Os(PPhMe_2)_3$ (**5**) (−27.7 kcal/mol) and $(H)_2Os(PPhMe_2)_4$ (**1**) (−43.3 kcal/mol) shows that replacement of two hydride ligands in $(H)_4Os(PPhMe_2)_3$ (eq 4) by one $PPhMe_2$ ligand to give $(H)_2Os(PPhMe_2)_4$ (eq 3) increases the basicity of Os by 15.6 kcal/mol. A slightly smaller increase (14.9 kcal/mol) in basicity occurs when two hydrides in $(H)_4Os(PPh_2Me)_3$ are replaced by one PPh_2Me to give $(H)_2Os(PPh_2Me)_4$. This smaller increase is consistent with PPh_2Me ($\Delta H_{HP} = -24.7$ kcal/mol)[3] being a weaker donor ligand than $PPhMe_2$ ($\Delta H_{HP} = -28.4$ kcal/mol).[3] To illustrate the magnitude of the increase in basicity of the metal (ΔH_{HM}) when $(H)_2$ is replaced by $PPhMe_2$, the equilibrium constant (K_{eq}) for eq 8 can be estimated from ΔH_{HM}

$$(H_2)(H)_3Os(PPhMe_2)_3^+ + (H)_2Os(PPhMe_2)_4 \overset{K_{eq}}{\rightleftharpoons} (H)_4Os(PPhMe_2)_3 + (H)_3Os(PPhMe_2)_4^+ \quad (8)$$

$\cong \Delta G° = -RT \ln K_{eq}$ (assuming $\Delta S° \cong 0$ eu, which is a reasonable approximation for protonation of similar neutral complexes).[4] Thus, a 15.6 kcal/mol increase in the basicity of the metal means that $(H)_2Os(PPhMe_2)_4$ is approximately 2.7×10^{11} times more basic than $(H)_4Os(PPhMe_2)_3$.

If the $(H)_2$ ligand set in $CpIr(PPh_3)(H)_2$ ($\Delta H_{HM} = -19.7$ kcal/mol) is substituted by a CO to give $CpIr(PPh_3)(CO)$ ($\Delta H_{HM} = -30.1$ kcal/mol),[4] the basicity of the metal is increased by 10.4 kcal/mol. In terms of a K_{eq} equilibrium constant ($\Delta S° \cong 0$; $\Delta H_{HM} \cong \Delta G° = -RT \ln K_{eq}$), $CpIr(PPh_3)(CO)$ is 4.2×10^7 times more basic than $CpIr(PPh_3)(H)_2$. Thus, the basicity of the metal increases with the isoelectronic ligand sets in the following order: $(H)_2 < CO < PR_3$.

These results indicate that the higher oxidation state, by +2 units, in $M(H)_2$ complexes as compared with that of M(CO) is responsible for the 10.4 kcal/mol (or 4.2 x 10^7 times for K_{eq}) lower basicity of $CpIr(Ph_3)(H)_2$ as compared with $CpIr(PPh_3)$(CO). On the other hand, the 4.2×10^7 factor is small compared to the change in basicity of a metal complex which undergoes a 1-electron oxidation. For example,[23] a 1-electron oxidation of $CpW(CO)_3H$ (pK_a = 16.1) to $CpW(CO)_3H^+$ (pK_a = −3.0) increases the acidity of the hydride ligand by a factor of 10^{19}. Thus, although the metal in $CpIr(PPh_3)(CO)$ is formally oxidized by +2 units in $CpIr(PPh_3)(H)_2$, the Ir basicity changes much less than the W does in a +1 oxidation of $CpW(CO)_3H$.

Effect of PR_3 Ligands on the Basicities (ΔH_{HM}) of $(H)_2Os(PR_3)_4$ and $(H)_4Os(PR_3)_3$ Complexes. Replacement of the PPh_2Me ligands in $(H)_2Os(PPh_2Me)_4$ (**2**) by $PPhMe_2$ increases the basicity (ΔH_{HM}, eq 3) of Os by 4.5 kcal/mol; thus, on average each $PPhMe_2$ ligand increases the basicity of the metal center by 1.1 kcal/mol (4.5/4) over a PPh_2Me ligand. Replacement of the PPh_2Me ligands in $(H)_4Os(PPh_2Me)_3$ (**6**) by $PPhMe_2$ to give $(H)_4Os(PPhMe_2)_3$ (**5**) increases the basicity (eq 5) of the metal by 3.8 kcal/mol, or by 1.3 kcal/mol per PR_3 ligand. Thus, it appears that in both $(H)_2Os(PR_3)_4$ and $(H)_4Os(PR_3)_3$ the replacement of one PPh_2Me by $PPhMe_2$ increases the basicity (ΔH_{HM}) of the metal by ~1.2 kcal/mol. In other systems, the replacement of PPh_2Me by $PPhMe_2$ increases the metal basicity by 0.8 kcal/mol per PR_3 in $W(CO)_3(PR_3)_3$,[5] by 0.9 kcal/mol in $CpIr(PR_3)(CO)$,[4] by 1.8 kcal/mol per PR_3 in $Fe(CO)_3(PR_3)_2$,[4] and by 3.1 kcal/mol per PR_3 in $CpOs(PR_3)_2Br$.[9b] Thus, the effect of replacing PPh_2Me by $PPhMe_2$ on metal basicity depends significantly on the metal and other ligands in the complex.

The basicities ($-\Delta H_{HM}$) of the $(H)_2Os(PR_3)_4$ complexes (eqs 3 and 4) increase with PR_3 in the order $P(OEt)_3$ (34.2 kcal/mol) < $PPh(OEt)_2$ (37.2 kcal/mol) < PPh_2Me (38.8 kcal/mol) < $PPhMe_2$ (43.3 kcal/mol). This is the same trend as observed for χ values for these ligands obtained from ν(CO) frequencies for $Ni(CO)_3(PR_3)$ complexes.[24]

Basicities (ΔH_{HM}) of $CpIr(ER_3)(H)_2$ Complexes. It was determined that the heats of protonation (ΔH_{HM}, eq 6) of the $CpIr(ER_3)(H)_2$ complexes increase in the order $P(OPh)_3$ (−11.9 kcal/mol) < $AsPh_3$ (−19.4 kcal/mol) ~PPh_3 (−19.7 kcal/mol). The $CpIr(PPh_3)(H)_2$ complex has essentially the same basicity as $CpIr(AsPh_3)(H)_2$, which suggests that the PPh_3 and $AsPh_3$ ligands have similar donor properties. This is in sharp contrast to the free ligand (ER_3) basicities as measured by the gas-phase heats of adduct formation of BH_3 with ER_3 [PPh_3 (−36.6 kcal/mol) is 10.0 kcal/mol more basic than $AsPh_3$ (−26.6 kcal/mol)],[25] the pK_b values [PPh_3 (8.57) is 2.03 units more basic than $AsPh_3$ (10.60)],[26] and the heat of protonation of the phosphorus atom in $(Ph)_2PCH_2CH_2P(Ph)_2(H)^+$ ($\Delta H_{HP} = -20.2$ kcal/mol), which is 12.0 kcal/mol more basic than that of the As atom in $(Ph)_2AsCH_2CH_2P(Ph)_2(H)^+$ ($\Delta H_{HAs} = -8.2$ kcal/mol).[27] Despite the large differences in PPh_3 and $AsPh_3$ basicities, other complexes containing these ligands also have similar basicities. Thus, *cis*-$Mo(CO)_2(dppe)_2$ ($\Delta H_{HM} = -27.4$ kcal/mol; dppe = $Ph_2PCH_2CH_2PPh_2$) is only 3.6 kcal/mol (1.8 kcal/mol per As donor) more basic than *cis*-$Mo(CO)_2(arphos)_2$ ($\Delta H_{HM} = -23.8$ kcal/mol; arphos = $Ph_2AsCH_2CH_2PPh_2$),[7] and $Fe(CO)_3(dppe)$ (ΔH_{HM} = −23.2 kcal/mol) is only 0.6 kcal/mol more basic than $Fe(CO)_3(arphos)$ ($\Delta H_{HM} = -22.6$ kcal/mol).[6] Therefore, it appears that arsenic-donor ligands are better donors in metal complexes than one would expect on the basis of the basicities of the free arsine ligands.

When PPh_3 in $CpIr(PPh_3)(H)_2$ is substituted by $P(OPh)_3$ to give $CpIr[P(OPh)_3](H)_2$, the basicity of the metal decreases by 7.8 kcal/mol. This large difference in basicities is illustrated by

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(22) *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1985.

(23) Ryan, O. B.; Tilset, M.; Parker, V. D. *Organometallics* **1991**, *10*, 298.

(24) (a) Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (c) Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29.

(25) Durand, M.; Jovany, C.; Jugie, G.; Elegant, L.; Gal, J.-F. *J. Chem. Soc., Dalton Trans.* **1977**, 57.

(26) Kolling, O. W.; Mawdsley, E. A. *Inorg. Chem.* **1970**, *9*, 408.

(27) Sowa, J. R., Jr.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 3534.

Table II. Effect of Cp′ and $(PR_3)_2(H)$ Isoelectronic Ligand Sets on Metal Basicity

less basic compound	$\Delta\Delta H_{HM}$/ligand set,[a] kcal/mol	more basic compound
$\mathit{Cp}\mathrm{Ir(PPh_3)(CO)}$[b]	8.7	$\mathit{(PPh_3)_2(H)}\mathrm{Ir(PPh_3)(CO)}$
$\mathit{(PPh_2Me)_2(H)}\mathrm{Os(PPh_2Me)_2H}$	0.4	$\mathit{Cp}\mathrm{Os(PPh_2Me)_2H}$[e]
$\mathrm{Cp^*Ru}\mathit{Cp^*}$[c]	16.2	$\mathrm{Cp^*Ru}\mathit{(PPh_3)_2H}$[f]
$\mathit{Cp^*}\mathrm{Os}\mathit{Cp^*}$[d]	8.4	$\mathit{(PPhMe_2)_2(H)}\mathrm{Os}\mathit{(PPhMe_2)_2H}$
$\mathit{Cp^*}\mathrm{Os}\mathit{Cp^*}$[d]	6.1	$\mathit{(PPh_2Me)_2(H)}\mathrm{Os}\mathit{(PPh_2Me)_2H}$
$\mathit{Cp^*}\mathrm{Os}\mathit{Cp^*}$[d]	5.3	$\mathit{(PPh(OEt)_2)_2(H)}\mathrm{Os}\mathit{(PPh(OEt)_2)_2}$
$\mathit{Cp^*}\mathrm{Os}\mathit{Cp^*}$[d]	3.8	$\mathit{(P(OEt)_3)_2(H)}\mathrm{Os}\mathit{(P(OEt)_3)_2H}$

[a] Italic ligands are the Cp′ and $(PR_3)_2(H)$ sets that are being compared. [$\Delta\Delta H_{HM} = \Delta H_{HM}$(less basic compound) − ΔH_{HM}(more basic compound)]/(number of ligand sets). [b] $\Delta H_{HM} = -30.1$ (±0.2) kcal/mol.[4] [c] $\Delta H_{HM} = -19.0$ (±0.1) kcal/mol.[7] [d] $\Delta H_{HM} = -26.6$ (±0.2) kcal/mol.[7] [e] $\Delta H_{HM} = -39.2$ (±0.3) kcal/mol.[9] [f] $\Delta H_{HM} = -35.2$ (±0.2) kcal/mol.[9b]

the K_{eq} in eq 9. Assuming $\Delta S° \cong 0$ eu, the equilibrium constant

$$\underset{\mathbf{9H^+}}{\mathrm{CpIr[P(OPh)_3](H)_3^+}} + \underset{\mathbf{7}}{\mathrm{CpIr(PPh_3)(H)_2}} \overset{K_{eq}}{\rightleftharpoons} \underset{\mathbf{9}}{\mathrm{CpIr[P(OPh)_3](H)_2}} + \underset{\mathbf{7H^+}}{\mathrm{CpIr(PPh_3)(H)_3^+}} \quad (9)$$

for eq 9 is 5.3 x 10^5. Norton and co-workers observed a similar difference (10^4) between the basicities of $Co(CO)_3(PPh_3)^-$ and $Co(CO)_3[P(OPh)_3]^-$,[2c] whose protonated forms have pK_a values in acetonitrile of 15.4 and 11.4, respectively. The large decrease in basicity when a PPh_3 ligand is substituted by $P(OPh)_3$ is consistent with the lower pK_a value of free $P(OPh)_3$ (−2.01)[24a] as compared with that of PPh_3 (2.73).[24a]

Comparisons of Basicities (ΔH_{HM}) of Complexes with the Isoelectronic Cp and $(PR_3)_2(H)$ Ligand Sets. Both the Cp ligand and the $(PR_3)_2(H)$ group of ligands contribute five (using the neutral-ligand formalism) electrons to a metal center; two examples of analogous Cp and $(PR_3)_2H$ complexes are $CpIr(PPh_3)(CO)$ and $(PPh_3)_2(H)Ir(PPh_3)(CO)$ (**10**). With the goal of predicting basicities of related complexes, we asked if there is a quantitative and predictable difference between Cp compounds and their $(PR_3)_2(H)$ analogs. In the comparisons listed in Table II, where the formal oxidation state of the metal is the same, substitution of the Cp ligand in $CpIr(PPh_3)(CO)$ ($\Delta H_{HM} = -30.1$ kcal/mol)[4] with $(PPh_3)_2(H)$ to give $(PPh_3)_2(H)Ir(PPh_3)(CO)$ ($\Delta H_{HM} = -38.8$ kcal/mol) increases the basicity of iridium by 8.7 kcal/mol. Since PPh_2Me is more basic than PPh_3, it is expected that substitution of the Cp ligand by the $(PPh_2Me)_2(H)$ group would result in an even greater increase in basicity; however, when the Cp ligand in $CpOs(PPh_2Me)_2H$ ($\Delta H_{HM} = -39.2 \pm 0.3$ kcal/mol)[9] is replaced by the $(PPh_2Me)_2(H)$ group to give $(PPh_2Me)_2(H)Os(PPh_2Me)_2(H)$ ($\Delta H_{HM} = -38.8 \pm 0.2$ kcal/mol), the basicity of the metal center is unchanged within experimental error. Thus, replacement of Cp by $(PR_3)_2(H)$ affects the metal basicity differently in the Ir and Os systems.

When a Cp* ligand (Cp* = C_5Me_5), which is more basic than Cp (Cp = C_5H_5), in Cp^*_2Ru ($\Delta H_{HM} = -19.0$ kcal/mol)[7] is replaced by the $(PPh_3)_2(H)$ group to give $Cp^*Ru(PPh_3)_2(H)$ ($\Delta H_{HM} = -35.2$ kcal/mol), the basicity of the metal increases by 16.2 kcal/mol. In the Cp^*_2Os complex ($\Delta H_{HM} = -26.6$ kcal/mol),[7] replacement of two Cp* ligands by two $(PPhMe_2)_2(H)$ groups to give $(PPhMe_2)_2(H)Os(PPhMe_2)_2(H)$ ($\Delta H_{HM} = -43.3$ kcal/mol) increases the basicity of the metal center by 16.7 kcal/mol; therefore, each $(PPhMe_2)_2(H)$ group increases the basicity by 8.4 kcal/mol. As the basicities of the phosphines in $(PR_3)_2(H)Os(PR_3)_2(H)$ decrease, the basicity of the metal also decreases; thus, the substitution of each Cp* ligand in Cp^*_2Os by different $(PR_3)_2(H)$ ligand sets to give $(PR_3)_2(H)Os(PR_3)_2H$ causes the metal basicity to increase by 3.8 kcal/mol ($PR_3 = P(OEt)_3$) to 8.4 kcal/mol ($PR_3 = PPhMe_2$) (Table II). These studies indicate that the replacement of Cp or Cp* by $(PR_3)_2(H)$ usually increases the basicity of the metal, but the magnitude of the increase is not reliably predictable.

Conclusions

Comparisons of $(H)_4Os(PR_3)_3$ vs $(H)_2Os(PR_3)_4$ and $CpIr(PPh_3)(H)_2$ vs $CpIr(PPh_3)(CO)$ establish that the basicity (ΔH_{HM}) of the metal increases with its isoelectronic ligands in the order $(H)_2 < CO < PR_3$. Despite the strong donor ability of an H^- ligand as compared with a halide (X^-), two H ligands reduce the basicity of the metal more than a CO ligand. When a Cp or Cp* ligand is replaced with an isoelectronic $(PR_3)_2(H)$ ligand set, the basicity (ΔH_{HM}) of the metal usually increases, but the magnitude of the increase depends greatly on the ligands and the metal. In the series of complexes $(H)_2Os(PR_3)_4$, the basicity of the metal increases with PR_3 in the order $P(OEt)_3 < PPh(OEt)_2 < PPh_2Me < PPhMe_2$. For the $CpIr(ER_3)(H)_2$ complexes, the basicity of the metal increases with the ER_3 ligand as follows: $P(OPh)_3 \ll AsPh_3 \approx PPh_3$. It is surprising that the basicities of the $AsPh_3$ and PPh_3 complexes are nearly the same despite the fact that PPh_3 is a much stronger σ-donor than $AsPh_3$.

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