Science Foundation for support as well as the Johnson Matthey Research Centre, England for the loan of $PdCl_2$.

Registry No. **1a** (M = Pd), 38897-83-5; **1a** (M = Pt), 30053-58-8; **1b**, 42489-94-1; **1c**, 41944-80-3; **1d**, 41904-61-4; **1e**, 124379-82-4; **1f** (M = Pd), 124356-96-3; **1f** (M = Pt), 124356-97-4; **1g**, 124356-98-5; **1h**, 124356-99-6; **1i**, 74129-88-7; **2a** (X = Cl) (isomer I), 124357-00-2; **2a** (X = Cl) (isomer II), 124440-02-4; **2a** (X = I) (isomer I), 124357-21-7; **2a** (X = I) (isomer II), 124439-49-2; **2a** (M = Pt, X = Cl), 124379-84-6; **2b** (isomer I), 124439-40-3; **2b** (isomer II), 124439-41-4; **2c** (isomer I), 124357-01-3; **2c** (isomer II), 124439-42-5; **2d** (isomer I), 124440-01-3; **2d** (isomer II), 124357-19-3; **2e** (isomer I), 124357-02-4; **2e** (isomer II), 124440-03-5; **2f** (isomer I), 124357-03-5; **2f** (isomer II), 124439-43-6; **2g** (isomer I), 124357-04-6; **2g** (isomer II), 124439-44-7; **2h** (isomer I), 124357-05-7; **2h** (isomer II), 124439-46-9; **3a**, 124357-06-8; **3b**, 41871-86-7; **3c**, 124357-07-9; **3d** (isomer I), 124357-08-0; **3d** (isomer II), 124439-45-8; **3e**, 124357-09-1; **3f**, 124357-10-4; **3g**, 124357-11-5; **3h** (isomer I), 124357-12-6; **3h** (isomer II), 124439-48-1; **3i** (isomer I), 124357-13-7; **3i** (isomer II), 124439-47-0; **3k**, 124357-20-6; **3l**, 124357-14-8; **4a**, 124357-15-9; **4b**, 124357-16-0; **4c**, 124357-18-2; **5a**, 124379-83-5; **5b**, 124399-59-3; $PdCl_2$, 7647-10-1; $PdCl_2(PhCN)_2$, 14220-64-5; $PtCl_2$, 10025-65-7.

Supplementary Material Available: Positional parameters and their estimated standard deviations (Table S1), general temperature factor expressions (Table S2), bond distances (Table S3), and bond angles (Table S4) (6 pages); observed and calculated structure factors (Table S5) (18 pages). Ordering information is given on any current masthead page.

Formation of Cationic MPt Heterobimetallic μ-Phosphido μ-Hydrido Complexes

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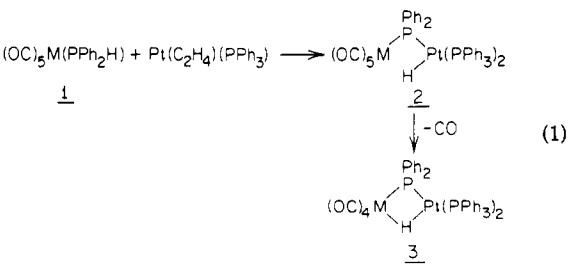
The cationic secondary phosphine complexes $[CpM(CO)(L)(PR_2H)]^+X^-$ (M = Ru, $PR_2H = PPh_2H$, $PPhH_2$, L = CO; M = Fe, $PR_2H = PPh_2H$, L = CO, MeC≡CMe, C_2H_4; M = Mn $PR_2H = PCy_2H$, PPr_2H, L = NO; $X^- = BF_4^-$, PF_6^-) and $[(\eta^7\text{-}C_7H_7)(CO)_2Mo(PCy_2H)]PF_6$, prepared by following literature procedures for the synthesis of their PPh_3 analogues, react with $Pt(C_2H_4)(PPh_3)_2$ to give $[Cp(L)M(\mu\text{-}PR_2)(\mu\text{-}H)Pt(PPh_3)_2]X$ and $[(\eta^7\text{-}C_7H_7)(CO)Mo(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PPh_3)_2]X$ as the final products. The reactions proceed by one or both, of two possible reaction pathways. One pathway involves the initial oxidative addition of a P–H bond to the Pt(0) complex to give $[Cp(CO)LM(\mu\text{-}PR_2)PtH(PPh_3)_2]X$ followed by PPh_3 loss from Pt and CO transfer from M to Pt (via a bridging CO). The rate of this CO-transfer step is sterically driven, in a manner similar to that observed for ortho-metalation reactions, with observed relative rates being as follows: $\mu\text{-}PPh_2 \gg \mu\text{-}PPhH$; $\mu\text{-}PCy_2 > \mu\text{-}PPr_2$; $\mu\text{-}PPh_2 \gg \mu\text{-}AsPh_2$; Cr > Mo > W; Fe > Ru; Mn ≫ Re; $\eta^5\text{-}C_5H_4Me > \eta^5\text{-}C_5H_5$. The more acidic (P–H) secondary phosphine complexes react with Pt(0) complexes by a route that involves deprotonation of the coordinated secondary phosphine to give a phosphidometal complex, which then substitutes a ligand from Pt(0) followed by CO transfer to Pt. Reprotonation of the resultant complex gives $[Cp(L)M(H)(\mu\text{-}PR_2)Pt(CO)(PR_3)]^+$ ($PR_3 = PPh_3$). Several complexes of this type ($PR_3 = PCy_3$) were prepared and studied from the reaction of $[CpM(CO)(L)(PR_2H)]^+$ with $Pt(C_2H_4)_2(PCy_3)$. The deprotonation pathway provides for faster Pt-assisted CO labilization/loss than the P–H oxidative-addition route. The $^1J_{^{195}Pt\text{-}^{31}P_\mu}$ coupling constants for a series of bimetallic μ-phosphido μ-hydrido complexes of the type $[M](\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2^+$ are shown to be much more sensitive to structural changes than the $^1J_{^{195}Pt\text{-}^{31}P}$ values of the PPh_3 trans to P_μ. While a plot of individual $^1J_{^{195}Pt\text{-}^{31}P}$ vs $^1J_{^{195}Pt\text{-}^1H}$ values gives relatively poor correlations, a plot of $\sum{}^1J_{^{195}Pt\text{-}^{31}P}$ (all three ^{31}P nuclei) vs $^1J_{^{195}Pt\text{-}^1H}$ is considerably improved suggesting an overall self-compensating effect for distortions/structural changes in individual Pt–P bonds as [M] is varied. For these structurally very similar complexes $^2J_{^{31}P_\mu\text{-}^{31}P}$(trans) varies almost linearly with $^1J_{^{195}Pt\text{-}^{31}P_\mu} + {}^1J_{^{195}Pt\text{-}^{31}P}$(trans to P_μ).

Introduction

Oxidative addition of the P–H bond of a secondary phosphine complex to zerovalent complexes of platinum provides easy access to singly bridged μ-phosphido heterobimetallic hydrides.[1-5] For example the metal carbonyl complexes $M(CO)_5(PPh_2H)$ (**1**; M = Cr, Mo, W) oxidatively add to $Pt(C_2H_4)(PPh_3)_2$ to give the μ-phosphido bimetallic $(OC)_5M(\mu\text{-}PPh_2)PtH(PPh_3)_2$ (**2**).[1] This complex loses CO under very mild conditions (for a group VI carbonyl)[6] to give the μ-phosphido μ-hydrido complex $(OC)_4M(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2$ (**3**; eq 1). While the net result of



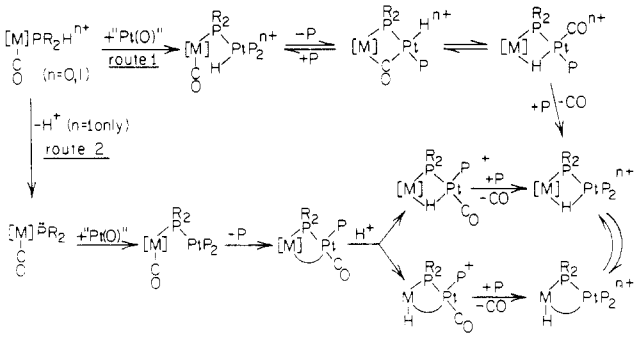
(1)

this reaction is effectively a substitution of CO at M by H, the reaction proceeds by a platinum-assisted process involving PPh_3 dissociation and a CO transfer, via a μ-CO intermediate, from M to Pt as outlined in Scheme I, route 1. Both the rate and the nature of the reaction of secondary phosphine complexes with Pt(0) systems are sen-

(1) Powell, J.; Gregg, M. R.; Sawyer, J. F. *Inorg. Chem. 1989, 28*, 4451.
(2) Powell, J.; Sawyer, J. F.; Stainer, M. V. R. *Inorg. Chem.* **1989**, *28*, 4461.
(3) Powell, J.; Sawyer, J. F.; Smith, S. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1312.
(4) Powell, J.; Gregg, M. R.; Sawyer, J. . *J. Chem. Soc., Chem. Commun.* **1987**, 1029.
(5) Schwald, J.; Peringer, P. *J. Organomet. Chem.* **1987**, *323*, C51.
(6) Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligott, P. J. *Organometallics* **1984**, *3*, 134.

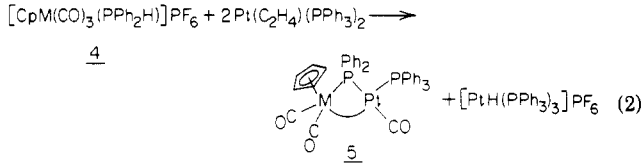
0276-7333/90/2309-0387$02.50/0

Scheme I. Generalized Reaction Pathways for Pt-Assisted CO Loss and the Formation of μ-Phosphido μ-Hydrido MPt Bimetallic Complexes from the Reactions of (Secondary phosphine)metal Carbonyl Complexes ([M](CO)(PR$_2$H)$^{n+}$) with Pt(O) Complexes[a]

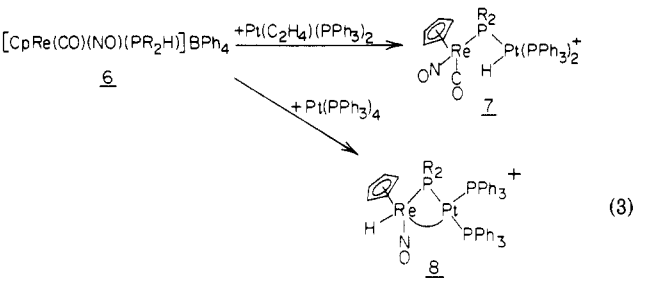


[a] Route 1 involves initial oxidative addition of the P–H bond across Pt(0). Route 2 involves deprotonation of the secondary phosphine to give the phosphide [M](CO)PR$_2$ followed by phosphide substitution of a ligand from the Pt(0) compound as the initial steps of bimetallic complex formation. These reaction pathways have been established from *previous studies*[1-4] of a range of phosphido-hydrido-MPt systems. It should be noted that very few of the proposed intermediates have been observed in the current study with the secondary phosphine complexes **9–12**. However, the structures, relative distributions, and interconversions of the *initially* formed MPt products are *consistent* with the two reaction routes outlined in the scheme.

sitive to the acidity of the P–H bond.[2] Thus, substitution of a carbonyl ligand by a donor phosphine (e.g. to give M(CO)$_4$(PR$_3$)(PR$_2$H)) or replacement of PPh$_2$H with PCy$_2$H in M(CO)$_5$(PR$_2$H) results in a less acidic P–H bond and markedly retards the oxidative-addition step.[1] In contrast, the P–H bond in cationic secondary phosphine complexes may be more acidic, which leads to an increased reactivity and the observation of a second reaction pathway (Scheme I, route 2). One such example is the complex [CpM(CO)$_3$(PPh$_2$H)]PF$_6$ (**4**; M = Mo, W), which reacts almost exclusively via route 2 to give initially the neutral complex Cp(OC)$_2$M(μ-PPh$_2$)Pt(CO)(PPh$_3$) (**5**; eq 2).[3]



Subsequent formation of [Cp(OC)$_2$M(μ-PPh$_2$)(μ-H)Pt(PPh$_3$)$_2$]$^+$ involves protonation followed by CO displacement by PPh$_3$. The protonation is M dependent, occurring at the metal–metal bond for **5** (M = Mo) to give [Cp(OC)$_2$Mo(μ-PPh$_2$)(μ-H)Pt(CO)(PPh$_3$)]$^+$, while for the tungsten analogue protonation occurs primarily at W to give [Cp(OC)$_2$HW(μ-PPh$_2$)Pt(CO)(PPh$_3$)]$^+$ (existing in a dynamic equilibrium with a minor amount of [Cp(OC)$_2$W(μ-PPh$_2$)(μ-H)Pt(CO)(PPh$_3$)]$^+$). The cationic complexes [CpRe(NO)(CO)(PR$_2$H)]BPh$_4$ (**6**; R = Cy, Ph, Pr) react with Pt(C$_2$H$_4$)(PPh$_3$) predominantly via route 1 to give [Cp(OC)(ON)Re(μ-PR$_2$)PtH(PPh$_3$)$_2$]$^+$ (**7**) as relatively stable solution species (losing CO very slowly at 20 °C (days); eq 3).[2] Reaction with the more basic complex Pt(PPh$_3$)$_4$ procedes predominantly via route 2 with rapid CO loss to give the μ-phosphido terminal rhenium hydride [Cp(ON)HRe(μ-PR$_2$)Pt(PPh$_3$)$_2$]$^+$ (**8**; eq 3). This terminal rhenium hydride is the kinetic product of the reaction and undergoes an unusual Cl$^-$-catalyzed rearrangement to the thermodynamically preferred isomer [Cp(ON)Re(μ-



(3)

PR$_2$)(μ-H)Pt(PPh$_3$)$_2$]$^+$. The interconversion of terminal and bridged isomers may be slow (e.g. the RePt system[2]) or very fast (e.g. [Cp(OC)$_2$W(H)(μ-PPh$_2$)Pt(CO)PPh$_3$]$^+$[3] and (OC)$_3$Fe(H)(μ-PR$_2$)Pt(PPh$_3$)$_2$;[4] $\Delta G^{\ddagger} < 5$ kcal mol^{-1}, estimated from NMR studies). These previously reported studies[1-4] have established *two* reaction routes whereby the secondary phosphine complex [M](CO)(PR$_2$H)$^{n+}$ (n = 0, 1) can react with zerovalent platinum complexes to give the μ-hydrido compounds [M](μ-PR$_2$)(μ-H)Pt(PR$_3$)$_2$ as *final* products (Scheme I). We have extended these studies to other cationic secondary phosphine complexes and herein we report on the chemistry associated with the complexes [CpM(CO)$_2$(PR$_2$H)]X (**9a**, M = Ru, PR$_2$H = PPh$_2$H, X = BF$_4$; **9b**, M = Ru, PR$_2$H = PPhH$_2$, X = BF$_4$; **10a**, M = Fe, PR$_2$H = PPh$_2$H, X = PF$_6$), [CpFe(CO)(MeC≡CMe)(PPh$_2$H)]PF$_6$ (**10b**), [CpFe(CO)(C$_2$H$_4$)(PPh$_2$H)]PF$_6$ (**10c**), [(η^5-C$_5$H$_4$R′)Mn(CO)(NO)(PR$_2$H)]PF$_6$ (**11a**, R′ = Me, PR$_2$H = PCy$_2$H; **11b**, R′ = Me, PR$_2$H = PPr$_2$H; **11c**, R′ = H, PR$_2$H = PCy$_2$H; **11d**, R′ = H, PR$_2$H = PPr$_2$H), and [(η^7-C$_7$H$_7$)Mo(CO)$_2$(PCy$_2$H)]PF$_6$ (**12**) and their reactions with Pt(0) complexes.

Results

Due to the high reactivity of P–H bonds, synthetic routes to generating [M]PR$_2$H complexes usually require mild reaction conditions. The cationic secondary phosphine complexes **9–12** were prepared according to eq 4–7 by following procedures previously developed for the synthesis of tertiary phosphine complexes.[6-8] Analytical and spectroscopic data are given in Table I.

$$\mathrm{CpM(CO)_2I + PR_2H + AgBF_4 \rightarrow [CpM(CO)_2(PR_2H)]BF_4 + AgI} \quad (4)$$

9a: M = Ru; R = Ph
9b: M = Ru; R$_2$ = PhH
10a: M = Fe; R = Ph

$$\mathrm{CpFe(CO)I(PPh_2H) + L + AgPF_6 \rightarrow [CpFe(CO)(L)(PPh_2H)]PF_6} \quad (5)$$

10b, L = MeC≡CMe
10c, L = H$_2$C=CH$_2$

$$\mathrm{[(\eta^5\text{-}C_5H_4R')Mn(CO)_2(NO)]PF_6 + PR_2H + Et_3N \rightarrow [(\eta^5\text{-}C_5H_4R')Mn(CO)(NO)(PR_2H)]PF_6} \quad (6)$$

11a: R′ = Me; R = Cy
11b: R′ = Me; R = Pr
11c: R′ = H; R = Cy
11d: R′ = H; R = Pr

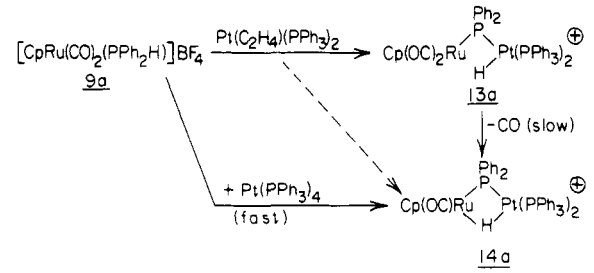
$$\mathrm{[(\eta^7\text{-}C_7H_7)Mo(CO)_3]PF_6 + PCy_2H \xrightarrow{50\ ^\circ C} [(C_7H_7)Mo(CO)_2(PCy_2H)]PF_6} \quad (7)$$

12

Reactions of [CpM(CO)$_2$(PR$_2$H)]BF$_4$ with Pt(0) Complexes. [CpRu(CO)$_2$(PPh$_2$H)]BF$_4$ (**9a**) reacts with Pt(C$_2$H$_4$)(PPh$_3$)$_2$ in CH$_2$Cl$_2$ to produce the cis terminal platinum hydride [Cp(OC)$_2$Ru(μ-PPh$_2$)PtH(PPh$_3$)$_2$]BF$_4$ (**13a**) as the major product (Scheme I, route 1) together

(7) James, T. A.; McCleverty, J. A. *J. Chem. Soc. A* **1970**, 850.
(8) Isaacs, E. E.; Graham, W. A. G. *J. Organomet. Chem.* **1975**, *90*, 319.

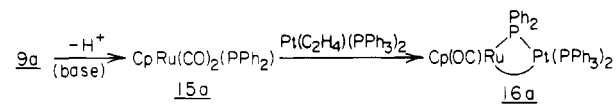
with a small amount of the hydrido-bridged $[Cp(OC)Ru(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]BF_4$ (**14a**; eq 8). Since the ter-



(8)

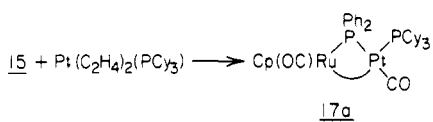
minal hydride **13a** loses CO to give the bridging hydride **14a** very slowly ($t_{1/2}$ for CO loss ca. 60 h at 20 °C), it is clear that **13a** is not an intermediate for the formation of the initially observed **14a**. A probable route to the initially produced **14a** is the deprotonation pathway (Scheme I, route 2). Consistent with this, the amount of **14a** formed on mixing $[CpRu(CO)_2(PPh_2H)]BF_4$ (**9a**) with $Pt(C_2H_4)(PPh_3)_2$ is *concentration dependent*, with dilute solutions resulting in the formation of **13a** only (IR monitoring of ν_{CO} region). A similar concentration effect has been noted and commented on for the reaction of $[CpRe(CO)(NO)(PPh_2H)]BF_4$ with $Pt(C_2H_4)(PPh_3)_2$.[2] The reaction of $[CpRu(CO)_2(PPh_2H)]BF_4$ (**9a**) with the more basic complex $Pt(PPh_3)_4$ results in the *rapid* formation of the hydride-bridged $[Cp(OC)Ru(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]BF_4$ (**14a**) as the sole product (i.e. Scheme I, route 2). (Complex characterization is discussed later; spectroscopic data are given in Table II.)

The complex $[CpRu(CO)_2(PPh_2H)]BF_4$ (**9a**) is readily deprotonated by Proton Sponge to give the very oxygen sensitive phosphido complex $CpRu(CO)_2PPh_2$ (**15a**; prepared in situ). Reaction of **15a** with $Pt(C_2H_4)(PPh_3)_2$ in toluene gives the neutral bimetallic complex $Cp(OC)Ru(\mu\text{-}PPh_2)Pt(PPh_3)_2$ (**16a**; eq 9). This complex is



(9)

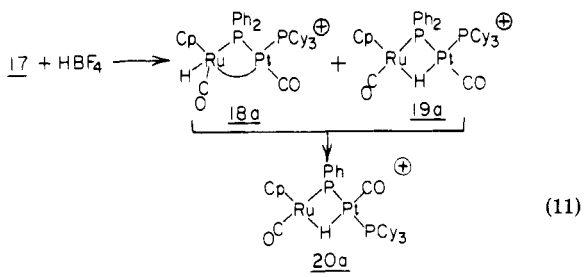
structurally similar to the previously reported $Cp(OC)_2M(\mu\text{-}PPh_2)Pt(PPh_3)_2$ (**5**; M = Mo, W).[3] Protonation of $Cp(OC)Ru(\mu\text{-}PPh_2)Pt(PPh_3)_2$ (**16a**; HBF_4 in CH_2Cl_2) leads to the bridged hydrido cation **14a**. The reaction of $CpRu(CO)_2PPh_2$ (**15a**) with $Pt(C_2H_4)_2(PCy_3)$ gives the neutral bimetallic complex $Cp(OC)Ru(\mu\text{-}PPh_2)Pt(CO)(PCy_3)$ (**17a**; eq 10). Protonation of **17a** with HBF_4 in



(10)

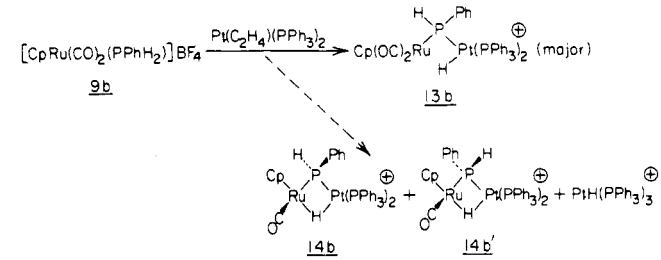
CD_2Cl_2 (NMR monitoring) gives initially an equilibrium mixture of the isomeric terminal hydrido cation $[Cp(OC)(H)Ru(\mu\text{-}PPh_2)Pt(CO)(PCy_3)]^+$ (**18a**) and the hydrido-bridged cation $[Cp(OC)Ru(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(CO)(PCy_3)]^+$ (**19a**). These slowly rearrange (ca. 10 h, 20 °C) to the hydrido-bridged cation **20** (eq 11). The primary phosphine complex $[CpRu(CO)_2(PPhH_2)]BF_4$ (**9b**) reacts with $Pt(C_2H_4)(PPh_3)_2$ to give *mainly* the terminal hydride $[Cp(OC)_2Ru(\mu\text{-}PhH)PtH(PPh_3)_2]^+$ (cation of **13b**; Scheme I, route 1) together with small amounts of $[PtH(PPh_3)_3]^+$[9]

(9) Dingle, T. W.; Dixon, K. *Inorg. Chem.* **1974**, *13*, 847.



(11)

and the diastereotopic hydrido-bridged isomers $[Cp(OC)Ru(\mu\text{-}PPhH)(\mu\text{-}H)Pt(PPh_3)_2]^+$ (cation of **14b** and **14b′**; Scheme I, route 2; eq 12). The ratio of **14b** to **14b′**



(12)

is ca. 1:1. The cis terminal hydride **13b** is rather inert to CO loss. Conversion of the terminal hydride **13b** to the bridged hydrides **14b** and **14b′** required ca. 40 h of reflux in THF with **14b** and **14b′** being formed in a ca. 2:1 ratio. (Which is the major isomer is not known, though on steric grounds **14b′** may be the preferred isomer.) The reaction of $[CpRu(CO)_2(PPhH_2)]BF_4$ (**9b**) with $Pt(PPh_3)_4$ surprisingly gave mainly the cis terminal Pt hydride **13b**, in contrast to the case for **9a**, which reacts with $Pt(PPh_3)_4$ to give mainly the hydrido-bridged cation **14a**.

The reactions of $[CpFe(CO)_2(PPh_2H)]PF_6$ (**10a**) with $Pt(C_2H_4)(PPh_3)_2$ and $Pt(PPh_3)_4$ are very similar to those of the ruthenium analogue **9a**. Noticeable differences are as follows: (i) the conversion of $[Cp(OC)_2Fe(\mu\text{-}PPh_2)PtH(PPh_3)_2]PF_6$ (**21**) to $[Cp(OC)Fe(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]PF_6$, (**22**; CO loss complete within 2 h) is faster than for the ruthenium system (**13a** → **14a**; eq 8); (ii) a considerable amount of $[PtH(PPh_3)_3]PF_6$ is formed; (iii) attempts to isolate neutral FePt bimetallics structurally similar to $Cp(OC)Ru(\mu\text{-}PPh_2)Pt(PPh_3)_2$ (**16a**) were not successful. The structurally similar $[CpFe(CO)(MeC{\equiv}CMe)(PPh_2H)]PF_6$ (**10b**) reacted with $Pt(C_2H_4)(PPh_{32}$ to give $[Cp(OC)Fe(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]PF_6$ (**22**) as the major product (reaction complete within 20 min). In preparative reactions $[Cp(OC)Fe(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]PF_6$ (**22**) was more easily isolated from **10b** than from **10a**. The ethylene-containing $[CpFe(CO)(C_2H_4)(PPh_2H)]PF_6$ (**10c**) reacted with $Pt(C_2H_4)(PPh_3)_2$ to give $[Cp(OC)(C_2H_4)Fe(\mu\text{-}PPh_2)PtH(PPh_3)_2]PF_6$ (**23**) as a relatively long-lived solution species that, over a period of ca. 3 h, lost C_2H_4 to give **22**. These observations raise the *possibility* of acetylene and ethylene transfer from Fe to Pt via but-2-yne or C_2H_4 bridging structures. (N.B. While C_2H_4 is not a good bridging ligand, it should be noted that an intramolecular transfer of a PPh_3 ligand (likely not a good bridge ligand) between adjacent Pt atoms has been recently observed in the complex $[Pt_3(CO)(PPh_3)(dppm)_3]^{2+}$.[10]) The reaction of $[CpFe(CO)_2(PPh_2H)]PF_6$ with $Pt(C_2H_4)_2(PCy_3)$ gave the complex $[Cp(OC)Fe(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(CO)(PCy_3)]PF_6$ (**24**), structurally analogous to **20a** (eq 11).

(10) Bradford, A. M.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 792.

Table I. Analytical and IR Data (ν_{CO} Region) for the Secondary Phosphine Complexes

compd no.	compd	anal. calcd (found) C	H	N	IR (CH_2Cl_2 soln) ν_{CO} (ν_{NO}), cm^{-1}	
9a	$[CpRu(CO)_2(PPh_2H)]BF_4$	46.09 (45.98)	3.26 (3.28)		2072	2021
9b	$[CpRu(CO)_2(PPhH_2)]BF_4$	37.41 (37.14)	2.64 (2.50)		2073	2026
10a	$[CpFe(CO)_2(PPh_2H)]PF_6$	31.37 (31.58)	3.92 (4.06)		2062	2016
10b	$[CpFe(CO)(MeC{\equiv}CMe)(PPh_2H)]PF_6$				1992	
10c	$[CpFe(CO)(C_2H_4)(PPh_2H)]PF_6$				1999	
11a	$[(\eta^2\text{-}C_5H_4Me)Mn(CO)(NO)(PCy_2H)]PF_6$	42.63 (42.52)	5.65 (5.65)	2.62 (2.61)	2034	(1792)
11b	$[(\eta^5\text{-}C_5H_4Me)Mn(CO)(NO)(Pr_2H)]PF_6$	34.30 (34.17)	4.87 (4.86)	3.08 (3.06)	2036	(1794)
11c	$[CpMn(CO)(NO)(PCy_2H)]PF_6$	41.47 (41.36)	5.41 (5.39)	2.69 (2.69)	2038	(1798)
11d	$[CpMn(CO)(NO)(PPr_2H)]PF_6$	32.67 (32.06)	4.57 (4.48)	3.18 (3.17)	2039	(1800)
12	$[(\eta^7\text{-}C_7H_7)Mo(CO)_2(PCy_2H)]PF_6$	43.02 (42.80)	5.16 (5.25)		2019	1977
15a	$[CpRu(CO)_2(PPh_2)]$				2024	1969
15b	$[CpRu(CO)_2(PPhH)]$				2025	1970
	$[CpFe(CO)_2(PPh_2)]$				2011	1960

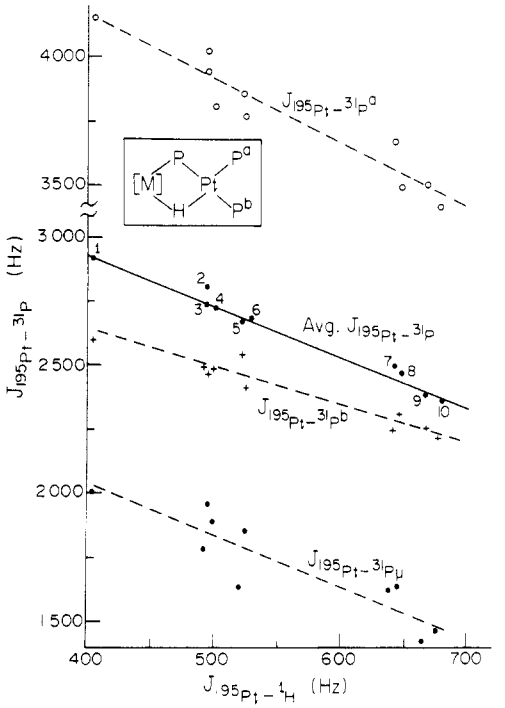
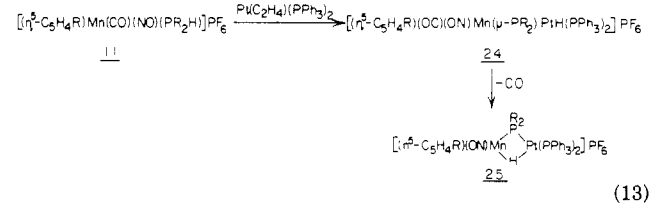


Figure 1. Plot of individual $^1J_{^{195}Pt-^{31}P}$ data and $\sum^1J_{^{195}Pt-^{31}P}$ for all three ^{31}P nuclei vs $J_{^{195}Pt-^1,_H}$ for the series of complexes $[M](\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2$, where [M] = $Cp(NO)Re^+$ (1), $Cp(CO)Ru^+$ (2), $Cp(CO)_2W^+$ (3), $Cp(CO)_2Mo^+$ (4), $(CO)_4Re^+$ (5), $Cp(CO)Fe^+$ (6), $(CO)_3BrRe$ (7), $(CO)_4Cr$ (8), $(CO)_4W$ (9), $(CO)_4Mo$ (10).

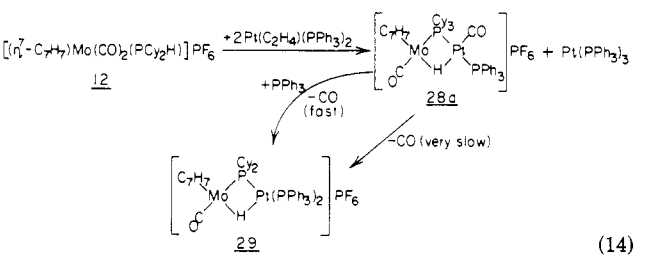
The reaction of $[(\eta^5\text{-}C_5H_4R')Mn(CO)(NO)(PR_2H)]PF_6$ (11) with $Pt(C_2H_4)(PPh_3)_2$ proceeds as outlined in eq 13. For the dipropylphosphine species **11b** (R′ = Me)



(13)

and **11d** (R′ = H) the cis platinum hydride $[(\eta^5\text{-}C_5H_4R')(OC)(ON)Mn(\mu\text{-}PPr_2)PtH(PPh_3)_2]PF_6$ (**25**) is readily formed (less than 5 min). Subsequent CO loss and formation of the bridged hydride (i.e. route 1, Scheme I) is relatively slow and at 20 °C takes ca. 24 h (**25b** → **26b**; R′ = Me) and ca. 48 h (**25d** → **26d** ; R′ = H). The dicyclohexylphosphine complexes $[(\eta^5\text{-}C_5H_4R')Mn(CO)(NO)(PCy_2H)]PF_6$, (**11a**, R′ = Me; **11c**, R′ = H) oxidatively add to $Pt(C_2H_4)(PPh_3)_2$ more slowly than the PPr_2H analogues since cis platinum hydrides (i.e. **25a** and **25c**) are not observed spectroscopically. However, CO loss and formation of the hydride-bridged $[(\eta^5\text{-}C_5H_4R')(ON)Mn(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PPh_3)_2]PF_6$ (**26a** and **26c**) is considerably more rapid than for the $\mu\text{-}PPr_2$ systems, being essentially complete within 5 h (20 °C). The reaction of $[(\eta^5\text{-}C_5H_4R')Mn(CO)(NO)(PR_2H)]PF_6$ (**11**) with $Pt(C_2H_4)_2(PCy_3)$ proceeded smoothly and quantitatively to give the complexes $[(\eta^5\text{-}C_5H_4Me)(ON)Mn(\mu\text{-}PR_2)(\mu\text{-}H)Pt(CO)(PCy_3)]PF_6$ (**27**). The reaction of $[(\eta^5\text{-}C_5H_4R')Mn(CO)(NO)(PR_2H)]PF_6$ (**11**) with $Pt(PPh_3)_4$ was monitored by IR spectroscopy (ν_{CO} region). The reaction proceeded to give the bridged hydrides **26** as the major final product. Several intermediate species were observed, including small amounts of the cis platinum hydride **25** together with other absorptions tentatively identified as neutral MnPt species. However, the $^{31}P\{^1H\}$ NMR spectra of these reaction mixtures were complex, and a clear structural assignment of the resonances to intermediate species was not achieved.

The reaction of $[(\eta^7\text{-}C_7H_7)Mo(CO)_2(PCy_2H)]PF_6$ (12) with $Pt(C_2H_4)(PPh_3)_2$ occurs as shown in eq 14 to give the hydrido-bridged platinum carbonyl $[(\eta^7\text{-}C_7H_7)(CO)Mo(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(CO)(PR_3)]PF_6$, (**28a**; R = Ph). The



(14)

tricyclohexylphosphine analogue **28b** (R = Cy) is readily obtained from the reaction of **12** with $Pt(C_2H_4)_2(PCy_3)$. Addition of PPh_3 to **28a** rapidly displaces CO to give $[(\eta^7\text{-}C_7H_7)(CO)Mo(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PPh_3)_2]PF_6$ (**29**).

Characterization of Complexes 13–29. The ^1H and $^{31}P\{^1H\}$ NMR and IR spectra provide ready structural characterization, and the relevant data for all the new bimetallic complexes described herein are listed in Table II. The relative magnitudes of $^1J_{^{195}Pt-^1H}$ and $^2J_{^{31}P(\text{trans to H})-^1H}$ for the hydride ligand are diagnostic of the bonding mode,[11,12] being >800 and ca. 165 Hz, respectively, for the platinum terminal hydrides, 400–600 and ca. 55–80 Hz, respectively, for bridged hydrides and 15 and ca. 0 Hz, respectively, for the ruthenium terminal hydride **18a**. Spin–spin coupling of the platinum hydrido ligand and ^{31}P(cis ligands) is typically 10–25 Hz.[11,12] The $^{31}P\{^1H\}$ NMR

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(12) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251.

Table II. ^1H (Hydrido Region) and $^{31}P\{^1H\}$ NMR (CD_2Cl_2) and IR (ν_{CO} Region) (CH_2Cl_2) Data for the Phosphido-bridged MPt Bimetallic Compounds[a]

compd no.	compd or compd cation	δ_H	$^1J_{195Pt-1H}$	$^2J_{31P-1H}$	δ_{P_μ}	δ_P^a	δ_P^b	$J_{195Pt-31P_\mu}$	$J_{195Pt-31P^a}$	$J_{195Pt-31P^b}$	$J_{31P^a-31P^b}$	$J_{31P_\mu-31P^b}$	ν_{CO}^b
13a	$[Cp(CO)_2Ru(\mu\text{-}PPh_2)PtH(PPh_3)_2]^+$	−5.78	805	166, 29, 18	−11	24	20	2205	2171	2552	18	328	17	2042, 1991
13b	$[Cp(CO)_2Ru(\mu\text{-}PPhH)PtH(PPh_3)_2]^+$	−4.60	894	166, 22, 18	−45	27	16.5	2077	2038	2568	20	320	20	2046, 1996
14a	$[Cp(CO)Ru(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]^+$	−9.11	494	74, 24, 16	167	21	13	1959	4018	2455	9	235	23	1968
14b	$[Cp(CO)Ru(\mu\text{-}PPhH)(\mu\text{-}H)Pt(PPh_3)_2]^+$	−9.09	486	74, 21, 16	127	20	13.5	1742	3950	2563	8	227	20	1968
14b′	$[Cp(CO)Ru(\mu\text{-}PPhH)(\mu\text{-}H)Pt(PPh_3)_2]^+$ (minor)	−9.29	484	74, 20, 16	126.5	19	14.5	1740	3916	2570	8	227	20	1968
16a	$[Cp(CO)Ru(\mu\text{-}PPh_2)Pt(PPh_3)_2]$				160	21	31	2619	3212	3220	17	244	10	1874
17a	$[Cp(CO)Ru(\mu\text{-}PPh_2)Pt(CO)(PCy_3)]$				142	47	...	2767	3396	...	12	...	...	not recorded
18a	$[Cp(CO)HRu(\mu\text{-}PPh_2)Pt(CO)(PCy_3)]^+$	−7.73	15	16, 0	191	51	...	2955	3514	...	5	...	...	
19a	$[Cp(CO)Ru(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(CO)(PCy_3)]^+$ (cis P)	−8.91	438	59, 16	161	38	...	2391	3226	...	5	...	...	
20a	$[Cp(CO)Ru(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(CO)(PCy_3)]^+$ (trans P)	−9.66	580	16, 14	172	...	37	1367	...	2321	...	170	...	2082,[c] 1988
21	$[Cp(CO)_2Fe(\mu\text{-}PPh_2)PtH(PPh_3)_2]^+$	−5.87	804	165, 28, 18										2033,[c] 1988
22	$[Cp(CO)Fe(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]^+$	−13.08	525	80, 28, 18	175	25	13	1851	3768	2408	15	224	22	1962
23	$[Cp(CO)(C_2H_4)Fe(\mu\text{-}PPh_2)PtH(PPh_3)_2]^+$	−5.32	810	166, 25, 18										
24	$[Cp(CO)Fe(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(CO)(PCy_3)]^+$	−13.35	600	23, 17	179	...	40	1261	...	2330	...	158	...	2084,[c] 1978
25b	$[(MeCp)(CO)(NO)Mn(\mu\text{-}PPr_2)PtH(PPh_3)_2]^+$	−6.00	880	166, 22, 16				not recorded						
25d	$[Cp(CO)(NO)Mn(\mu\text{-}PPr_2)PtH(PPh_3)_2]^+$	−6.18	872	164, 20, 18				not recorded						
26a	$[(MeCp)(NO)Mn(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PPh_3)_2]^+$	−10.2	548	82, 30, 30	218	29	16	1663	3780	2200	19	190	20	1718[d]
26b	$[(MeCp)(NO)Mn(\mu\text{-}PPr_2)(\mu\text{-}H)Pt(PPh_3)_2]^+$	−9.8	552	82, 30, 30	202	18	14	1615	3383	2216	20	200	20	
26c	$[Cp(NO)Mn(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PPh_3)_2]^+$	−10.3	550	82, 30, 30	184	29	14	1654	3799	2321	19	194	20	1721[d]
					217	27.5	13	1645	3768	2232	20	187	20	1724[d]
26d	$[Cp(NO)Mn(\mu\text{-}PPr_2)(\mu\text{-}H)Pt(PPh_3)_2]^+$	−9.9	551	82, 30, 30	202	17	12	nr[e]	nr	nr	20	190	20	
27a	$[(MeCp)(NO)Mn(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(CO)(PCy_3)]^+$	−11.4	636	23, 23	183	27	13	1670	3744	2304	20	195	20	1727[d]
27b	$[(MeCp)(NO)Mn(\mu\text{-}PPr_2)(\mu\text{-}H)Pt(CO)(PCy_3)]^+$	−11.1	637	24, 24	223	...	38	1117	...	2285	...	137	...	2076,[c] 1734[d]
28a	$[(\eta^7\text{-}C_7H_7)(CO)Mo(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(CO)(PPh_3)]^+$	−7.9	695	21, 14	190	...	38	1113	...	2308	...	139	...	2079,[c] 1740[d]
28b	$[(\eta^7\text{-}C_7H_7)(CO)Mo(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(CO)(PCy_3)]^+$	−8.6	692	16, 16				not recorded						2083,[c] 1926
29	$[(\eta^7\text{-}C_7H_7)(CO)Mo(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PPh_3)_2]^+$	−9.1	614	94, 24, 19	162	20	14	not recorded 1465		2064	15	190	...	2074,[c] 1947 1926

[a] All δ values in ppm and J values in Hz. P^a = cis to P_μ; P^b = trans to P_μ. [b] All ν values in cm^{-1}. [c] CO bonded to Pt. [d] ν_{NO}. [e] nr = not resolved.

data fully support the structures given, with δ_{P_μ} for M(μ-PR_2)(μ-H)Pt and M(μ-PR_2)Pt systems occurring well downfield from the PR_3 resonances while in singly bridged M(μ-PR_2)Pt systems (e.g. **13**) δ_{P_μ} occurs upfield of the PR_3 resonances, consistent with previous literature correlations.[13,14] An unusual situation arises with the ^1H and $^{31}P\{^1H\}$ NMR spectra of the complexes $[(\eta^5\text{-}C_5H_4R)(ON)Mn(PCy_2)(\mu\text{-}H)Pt(PPh_3)_2]PF_6$ (**26a**, R = Me; **26c**, R = H). On close inspections the hydrido signal can be seen to be composed of two overlapping resonance patterns in the ratio ca. 2:1 (**26a**) and ca. 6:1 (**26b**) with essentially identical coupling constants and with a chemical shift difference of <0.01 ppm. The presence of two isomeric forms in solution is more apparent in the $^{31}P\{^1H\}$ NMR spectra, where the difference in the two δ_{P_μ} resonances, Δ_{P_μ}, is ca. 15 ppm, $\Delta_P(PPh_3$ cis to $P_\mu)$ is ca. 10 ppm and $\Delta_P(PPh_3$ *trans* to $P_\mu)$ is ca. 2 ppm (Table II). Since this effect is not observed in the other structurally similar bridged hydrides **26**, it may be that this isomerization is a consequence of severe crowding involving $\eta^5\text{-}C_5H_4R$, μ-PCy_2, and the PPh_3 ligand on Pt cis to μ-PCy_2. Though its exact nature is not clear, it may be that steric strain is relieved by a puckering of the $MP_\mu H_\mu Pt$ ring, which would lead to diastereomers associated with asymmetric Mn and P_μ centers. An alternative possibility would involve specific orientations of the cyclohexyl substituents.

Discussion

Studies of the reaction of the secondary phosphine complexes **9–12** with Pt(0) tertiary phosphine systems provide further credence for the generality of the two mechanistic pathways for Pt-assisted CO loss from 18-electron metal centers as outlined in Scheme I.[1,2] For the pathway involving oxidative addition of the P–H bond across Pt to give initially the cis terminal hydrido platinum(II) derivative $[M](CO)(\mu\text{-}PR_2)PtHP_2^{n+}$ (Scheme I, route 1; usually observed for reactions with $Pt(C_2H_4)(PPh_3)_2$) *the rate of subsequent CO loss is found to be rather sensitive to a range of structural features.* From the above and other studies[1,2] the following qualitative structural effects on rate are observed: μ-PPh_2 ≫ μ-PPhH;[5] μ-PCy_2 > μ-P^nPr_2; Cr > Mo > W; Fe > Ru; Mn ≫ Re; $\eta^5\text{-}C_5H_4Me > \eta^5\text{-}C_5H_5$; μ-$PPh_2$ ≫ μ-$AsPh_2$;[15] $n = 0$ ≫ $n = +1$. These observations are understandable if the ease of formation of the bridging carbonyl species [M](μ-PR_2)(μ-CO)PtH(P) (four-atom-ring formation; Scheme I, route 1) contributes significantly to the overall reaction rate. An explanation/rationalization invokes the Thorp–Ingold effect[16] (a reorganizational entropy effect), whereby sterically demanding *gem* substituents (e.g. the R groups on μ-PR_2 in [M](μ-PR_2)PtH(PPh_3)$_2$) promote the formation of the four-atom ring in [M](μ-PR_2)(μ-CO)PtH(PPh_3). The decreases in relative rates associated with structural changes, as outlined above, are consistent with a decrease in steric repulsions between adjacent ligands. Alternatively it may be stated that the extent/degree to which the adjacent Pt influences the chemistry at [M] (Scheme I) is sterically forced. A similar explanation has been proposed to account for the sensitivity of ortho-metalation reactions of $PPhR_2$ complexes to the size (steric bulk) of the R groups.[17] The decrease in the rate of CO loss as one goes

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(14) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.
(15) Powell, J.; Phillips, J. Unpublished results.
(16) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Interscience: New York, 1965; p 191.
(17) Shaw, B. L. *J. Am. Chem. Soc.* **1975**, *97*, 3856.

from neutral to positively charged systems could well reflect the lower trans effect of the hydrido ligand in a $PtHP_3^+$ system vis à vis that in a neutral $PtHP_3$ system[18] and, hence, an increased ΔG^* for substitution of PPh_3 trans to H in the formation of $[M](\mu\text{-}PR_2)(\mu\text{-}CO)PtH(PPh_3)^+$. Besides CO labilization the mechanistic features of Scheme I, route 1, also allow for halide,[19] carbene,[20] probably acetylene, and possibly olefin transfer from 18-electron metal centers to an adjacent 16-electron Pt center. Features favoring the initial protonation pathway (Scheme I, route 2) are acidic P–H bonds and basic Pt(0) complexes. Consequently, this route is more probable for cationic systems and for PPh_2H complexes vs PCy_2H or P-*n*-Pr_2H complexes and is facilitated by the presence of proton bases (e.g. Proton Sponge) and basic Pt complexes ($Pt(PPh_3)_4 > Pt(C_2H_4)(PPh_3)_2$).

Correlation of $^1J_{^{195}Pt-^1H}$, $^1J_{^{195}Pt-^{31}P}$, and $^2J_{^{31}P-^{31}P}$ Data for Systems of the Type $[M](\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2$. The possibility of a correlation between $^1J_{^{195}Pt-^{31}P}$ data and Pt–P bond distances in Pt^{II}–phosphine complexes has been the subject of several investigations.[21,22] While both parameters are expected to be sensitive to s orbital character of the bond, several molecular variables contribute to the magnitude of $^1J_{^{195}Pt-^{31}P}$[23] and the correlations are, in the main, rather poor. In contrast we have recently observed a good correlation for $^1J_{^{195}Pt-^{31}P}$/P–Pt bond length data for the PtP_3 fragment in the closely related cations $[Cp(ON)Re(\mu\text{-}PR_2)(\mu\text{-}H)Pt(PPh_3)_2]^+$ (R = Ph, Cy) and $[Cp(ON)HRe(\mu\text{-}PCy_2)Pt(PPh_3)_2]^+$.[2] Particularly noteworthy were the observations that the P_μ–Pt bond lengths were significantly shorter than Pt–PPh_3 bond lengths in comparable coordination sites and that for the same bond length $^1J_{^{195}Pt-^{31}P_\mu}$ is less than 50% of the value for $^1J_{^{195}Pt-^{31}PPh_3}$. This suggested a lower phosphorus s orbital contribution to the P_μ–Pt bond, possibly reflective of ring strain effects (N.B. Re–P_μ–Pt ≈ 77°). Consistent with this argument is the decrease in the trans $^2J_{^{31}P-^{31}P}$ coupling from ca. 325 Hz in $[Cp(OC)_2Ru(\mu\text{-}PR_2)PtH(PPh_3)_2]BF_4$ (**13**) to ca. 230 Hz in $[Cp(OC)Ru(\mu\text{-}PR_2)(\mu\text{-}H)Pt(PPh_3)_2]BF_4$ (**14**). With respect to ring strain arguments it is interesting to note that $^1J_{^{31}P-^1H}$ for the μ-PPhH ligand increases from 334 Hz in $[Cp(OC)_2Ru(\mu\text{-}PPhH)PtH(PPh_3)_2]BF_4$ (**13b**) to 392 Hz in $[Cp(OC)_2Ru(\mu\text{-}PPhH)(\mu\text{-}H)Pt(PPh_3)_2]BF_4$ (**14b**), suggestive of an increase in s character in the P–H bond in the ring-strained structure **14b**. Similar, though smaller, changes in $^1J_{^{31}P-^1H}$ for the hypophosphite anion $H_2PO_2^-$ in the presence of added cations have been interpreted in terms of increases in $^1J_{^{31}P-^1H}$ being linked with $H_2PO_2^-$–M^+ association and a decrease in O–P–O upon chelation of M^+ by the anion.[24]

We have explored possible correlations involving coupling constant data for a range of structurally similar complexes containing the $[M](\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2$ unit (Figure 1). For these systems the basic coordination unit at Pt is essentially constant, only small variations associated with changes in [M] are being studied, and coupling constant data are available for all four donor atom–Pt interactions (not the case in previous studies). In Figure

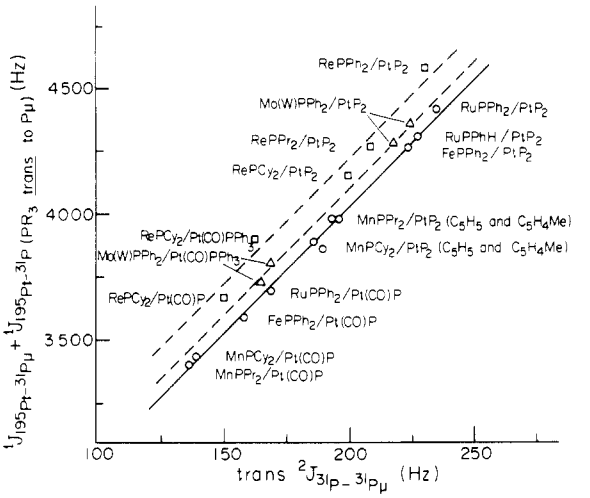

Figure 2. Plot of $\sum^1J_{^{195}Pt-^{31}P}$ for P_μ and the PR_3 ligand trans to P_μ vs the trans $^2J_{^{31}P-^{31}P}$ coupling constant for the structurally similar cations $[M](\mu\text{-}PR_2)(\mu\text{-}H)Pt(PPh_3)_2^+$ (PtP_2 systems) and $[M](\mu\text{-}PR_2)(\mu\text{-}H)Pt(CO)(PCy_3)^+$ (Pt(CO)P systems): (○) [M] = [Cp(CO)M] (M = Fe, Ru), [Cp(NO)Mn]; (□) [M] = [Cp(NO)Re]; (△) [M] = $[Cp(CO)_2M]$ (M = Mo, W). Labeling of points is according to the MPR_2/Pt system.

1, individual and average values of all three $^1J_{^{195}Pt-^{31}P}$ couplings for a series of $[M](\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2$ systems are plotted against the one-bond coupling constant to the fourth ligand, $^1J_{^{195}Pt-^1H}$(hydride). In mononuclear Pt(II) hydrides, changes in $J_{^{195}Pt-^1H}$ correlate mainly with changes in the trans ligand (NMR trans influence[18]). In contrast, in the bimetallic systems (Figure 1) (i) all three $^1J_{^{195}Pt-^{31}P}$ couplings vary considerably as $^1J_{^{195}Pt-^1H}$ varies, (ii) $^1J_{^{195}Pt-^{31}P_\mu}$(cis to H) exhibits the largest percentage variation, and (iii) while the correlation of $^1J_{^{195}Pt-^{31}P}$ with $^1J_{^{195}Pt-^1H}$ is rather poor for individual coupling constants, a much improved result is obtained when the average of all three $^1J_{^{195}Pt-^{31}P}$ values is used. These observations suggest that individual Pt–P bonds are easily distorted but that there is an internal self-compensating effect such that the net effect, as measured/reflected by the average $^1J_{^{195}Pt-^{31}P}$ value, correlates well with changes in the Pt–H bond as measured/reflected by $^1J_{^{195}Pt-^1H}$. We have recently shown that distortions in Pt(II) phosphine complexes, as reflected by P–Pt–P bond angle data, can be successfully rationalized in terms of P–Pt bond bending[25] and suggest that similar distortions may contribute to the relatively poor correlations for individual $^1J_{^{195}Pt-^{31}P}$ values (Figure 1). Particularly noticeable is the sensitivity of $^1J_{^{195}Pt-^{31}P_\mu}$ and $^2J_{^{31}P_\mu-^{31}P_{trans}}$ to changes in [M] or changes in ligands on Pt. The sensitivity of $^1J_{^{195}Pt-^{31}P_\mu}$ to changes in [M] and to replacement of the PPh_3 trans to H by a CO ligand is considerably greater in both absolute and percentage terms when compared to the effect of these changes on $^1J_{^{195}Pt-^{31}P}$ for the PR_3 ligand trans to P_μ (see Table II). The decrease in $^1J_{^{195}Pt-^{31}P_\mu}$ on replacing the PPh_3 (cis to P_μ) with CO is also reflected in the $^2J_{^{31}P_\mu-^{31}P}$ couplings to PR_3 trans to P_μ, which decrease markedly from ca. 200–235 to 140–170 Hz. Figure 2 is a plot of $^2J_{^{31}P_\mu-^{31}P}$(trans) vs $\sum[^1J_{^{195}Pt-^{31}P_\mu} + {}^1J_{^{195}Pt-^{31}P_{trans}}]$ for a range of structurally similar complexes containing the *trans*-$[M](\mu\text{-}PR_2)(\mu\text{-}H)PtL(PR_3)$ unit. A reasonably linear correlation is observed for a range of Fe, Mn, and Ru complexes with slight variation for Re and Mo/W systems. This correlation is understandable if the major variation is to be found in the P_μ s-oorbital contribution to the P_μ–Pt bond.

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Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of dry N_2 or argon, with use of dry and degassed solvents. IR spectra (CH_2Cl_2 solution) were recorded on a Nicolet 10DX spectrometer. ^1H and $^{31}P\{^1H\}$ NMR spectra (CD_2Cl_2 solution) were obtained on a Varian XL200 spectrometer, and chemical shifts were referenced to tetramethylsilane and 85% H_3PO_4, respectively. Microanalyses were carried out by Canadian Microanalytical Laboratories of Vancouver, Canada.

Starting Materials. $[CpRu(CO)_2I]$,[26] $[CpFe(CO)_2I]$,[27] $[(\eta^5\text{-}C_5H_4R')Mn(CO)_2(NO)]PF_6$ (R' = CH_3, H),[28] $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]PF_6$,[29] $Pt(C_2H_4)(PPh_3)_2$,[30] and $Pt(C_2H_4)_2(PCy_3)$[31] were prepared by following the appropriate literature procedure. PPh_2H, $PPhH_2$, and PCy_2H were purchased from either Pressure Chemical Co. or Strem Chemical Inc.

$[CpRu(CO)_2(PPh_2H)]BF_4$ (9a). $AgBF_4$ (0.514 g) was added to a solution of $CpRu(CO)_2I$ (0.412 g, 1.18 mmol) and PPh_2H (0.25 mL) in CH_2Cl_2 (10 mL) and the reaction mixture stirred overnight. The reaction mixture was checked for completion by IR spectroscopy. (If $CpRu(CO)_2I$ was still present, more $AgBF_4$ was added and the reaction mixture stirred for several more hours.) The reaction mixture was filtered through Celite several times and pumped to dryness and the residue recrystallized three times from CH_2Cl_2/diethyl ether to give **9a** as a white crystalline product (35% yield). A similar procedure gave **9b** (30% yield). The low yields were due to the difficulty of obtaining the complexes free of $AgBF_4$ contamination.

$[CpFe(CO)_2(PPh_2H)]PF_6$ (10a) was prepared (50% yield) with use of $AgPF_6$, and by a similar procedure $[CpFe(CO)(MeC{\equiv}CMe)(PPh_2H)]PF_6$ and $CpFe(CO)(C_2H_4)(PPh_2H)]PF_6$ (**10c**) were prepared (ca. 40% yield) from $CpFeI(CO)(PPh_2H)$, $AgPF_6$, and either $MeC{\equiv}CMe$ or $H_2C{=}CH_2$ by following the method of Reger et al.[6] for the synthesis of $[CpFe(CO)(MeC{\equiv}CMe)(PPh_3)]PF_6$ and $[CpFe(CO)(C_2H_4)(PPh_3)]PF_6$.

$[(\eta^5\text{-}C_5H_4Me)Mn(CO)(NO)(PCy_2H)]PF_6$ (11a). Et_3N (~0.2 mL) was added to a solution of $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(NO)]PF_6$ (1.02 g) and PCy_2H (0.70 mL) in acetone (30 mL). The reaction mixture was stirred for 30 min, ethanol (70 mL) added, and the volume reduced under vacuum to 35 mL. When the mixture was cooled, **11a** was obtained as orange crystals (60% yield). Complexes **11b–d** were similarly prepared in 40–60% yields.

$[(\eta^7\text{-}C_7H_7)Mo(CO)_2(PCy_2H)]PF_6$ (12). To a suspension of $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]PF_6$ (1.49 g) in 95% ethanol (150 mL) at 50 °C was slowly added a solution of PCy_2H (0.80 mL, 1.02 equiv) in 95% ethanol (60 mL) (addition time 1–2 h). The reaction mixture was cooled and left in the freezer overnight. Filtration of the resultant orange crystals gave **12** (57% yield).

$[Cp(OC)Ru(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]BF_4$ (14a). $[CpRu(CO)_2(PPh_2H)]BF_4$ (0.202 g) and $Pt(C_2H_4)(PPh_3)_2$ (0.325 g) were refluxed in THF for 3 h. When the solution was cooled and the volume reduced under vacuum, **14a** precipitated as a bright yellow powder (0.416 g, 85% yield). Anal. Calcd (found) for $C_{54}H_{46}BF_4OP_3PtRu$: C, 54.64 (54.42); H, 3.88 (3.66).

$[Cp(OC)Fe(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3]BF_4$ (22). $Pt(C_2H_4)(PPh_3)_2$ (0.311 g) was added to a CH_2Cl_2 solution (3 mL) of $[CpFe(CO)(MeC{\equiv}CMe)(PPh_2H)]BF_4$ (0.197 g). After the mixture stood at room temperature for 1 h, a few drops of pentane were added to precipitate trace amounts of $CpFeCl(CO)(PPh_3)$ as green crystals. After filtration, diethyl ether (2 mL) was added to the filtrate and the solution cooled to −20 °C. The complex **22** slowly crystallized as red prisms (0.180 g, 38%). Anal. Calcd (found) for $C_{54}H_{46}BF_4FeOP_3Pt$: C, 56.84 (56.31); H, 4.03 (4.06).

$[Cp(OC)Fe(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(CO)(PCy_3)]PF_6$ (24). $Pt(C_2H_4)_2(PCy_3)$ (0.203 g) was added to a CH_2Cl_2 solution (2 mL) of $[CpFe(CO)_2(PPh_2H)]PF_6$ (0.194 g). After 3 h addition of hexane (5 mL) precipitated **24** as a red-purple powder (0.306 g, 80% yield). Anal. Calcd (found) for $C_{37}H_{49}F_6FeO_2P_3Pt$: C, 45.21 (45.71); H, 4.98 (5.41).

$[(\eta^5\text{-}C_5H_4Me)(ON)Mn(\mu\text{-}P\text{-}n\text{-}Pr_2)(\mu\text{-}H)Pt(PPh_3)_2]PF_6$ (25). $Pt(C_2H_4)(PPh_3)_2$ (0.224 g) was added to $[(\eta^5\text{-}C_5H_4Me)Mn(CO)(NO)(P\text{-}n\text{-}Pr_2H)]PF_6$ (0.128 g) in CH_2Cl_2 (15 mL) and the solution allowed to stand overnight. The volume was reduced under vacuum, hexane added, and the solution cooled to −20 °C. The complex **25** was obtained as purple air-sensitive crystals (0.215 g, 67% yield). Anal. Calcd (found) for $C_{48}H_{52}F_6MnNOP_4Pt$: C, 50.26 (49.85); H, 4.54 (4.21); N, 1.22 (1.10).

$[(\eta^7\text{-}C_7H_7)(OC)Mo(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PPh_3)_2]PF_6$ (27). $[(\eta^7\text{-}C_7H_7)Mo(CO)_2(PCy_2H)]PF_6$ (0.158 g) and $Pt(C_2H_4)(PPh_3)_2$ (0.403 g, 2 equiv) were stirred in CH_2Cl_2 (15 mL) for 15 min, at which stage solution IR spectroscopy (ν_{CO} region) indicated that all the starting Mo complex had gone and that $[(\eta^7\text{-}C_7H_7)(OC)Mo(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(CO)(PPh_3)]PF_6$ and $Pt(PPh_3)_3$ were the major solution species. Triphenylphosphine (0.080 g, 1.1 equiv) was added and the solution stirred for a further 30 min. Removal of the solvent gave a yellow-green residue, which after several recrystallizations from CH_2Cl_2/hexane gave **27** as a yellow powder (0.125 g, 36% yield). Anal. Calcd (found) for $C_{56}H_{60}F_6MoOP_4Pt$: C, 52.60 (52.24); H, 4.73 (4.42).

$[(\eta^7\text{-}C_7H_7)(OC)Mo(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(CO)(PCy_3)]PF_6$ (26b). $[(\eta^7\text{-}C_7H_7)Mo(CO)_2(PCy_2H)]PF_6$ (0.120 g) and $Pt(C_2H_4)_2(PCy_3)$ (0.110 g, 1.02 equiv) were stirred in CH_2Cl_2 (20 mL) for 5 h. The solvent was removed (vacuum) and the residue recrystallized from CH_2Cl_2/hexane to give green crystals of **26b** (0.132 g, 65% yield). Anal. Calcd (found) for $C_{39}H_{63}F_6MoO_2P_3Pt$: C, 44.11 (43.02); H, 5.98 (5.82).

The other MPt bimetallic complexes described in this paper were characterized spectroscopically (Tables I and II). The complex $Cp(OC)\overline{Ru(\mu\text{-}PPh_2)}\overline{Pt(PPh_3)_2}$ (**16a**) could be precipitated from CH_2Cl_2 solution by the addition of hexane as an orange air-sensitive solid. Attempts to recrystallize **16a** for elemental analysis resulted in considerable decomposition and were not successful. **16a** is structurally similar to the more stable complex $Cp(OC)_2\overline{W(\mu\text{-}PPh_2)}\overline{Pt(PPh_3)_2}$.[3]

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