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Synthesis and Reactivity Studies of Phosphido-Bridged Heterobimetallic Cr–Os and Fe–Os Formyl Complexes

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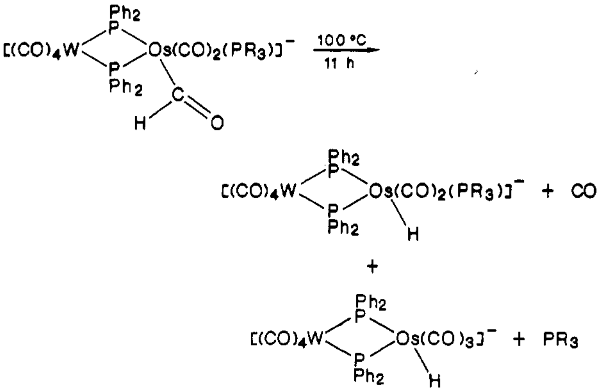
The new bimetallic complexes $(CO)_3\overline{Fe(\mu\text{-}PPh_2)_2Os}(CO)_3$ (1), $(CO)_4\overline{Cr(\mu\text{-}PPh_2)_2Os}(CO)_3$ (2), and $(CO)_4Cr(\mu\text{-}PPh_2)_2Os(CO)_3(PMePh_2)$ (3) have been prepared and spectroscopically characterized. Stable bimetallic formyl complexes $[(CO)_3\overline{Fe(\mu\text{-}PPh_2)_2Os}(CO)_2(CHO)]^-$ (4) and $[(CO)_4Cr(\mu\text{-}PPh_2)_2Os(CO)_2(PMePh_2)(CHO)]^-$ (5) derive from 1 and 3 upon treatment with $Li[BHEt_3]$. Formyl complex 5 exists in two isomeric forms which appear to be geometrical isomers with the formyl ligand located in different coordination positions in the Os octahedral coordination sphere. Formyl complex 4 is unusual in that it is one of the few examples of a stable formyl complex with a metal–metal bond, and reasons for its unusual stability are discussed. Formyl complex 5 reacts with $[(CH_3)_3O]BF_4$ to give $(CO)_4\overline{Cr(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CH(OMe))Os}(CO)_2(PMePh_2)$ (8) containing the μ-$PPh_2CH(OMe)$ ligand which derives from coupling of phosphide and methoxycarbene ligands, the latter being formed by methylation of the formyl oxygen.

In the course of our studies directed toward the preparation and reactions of binuclear and polynuclear formyl complexes, we prepared the bimetallic formyl derivatives $[(CO)_4W(\mu\text{-}PPh_2)_2Os(CHO)(CO)_2(PR_3)]^-$ which were unusually stable.[1] For example, the $PMePh_2$ derivative required ~11 h at 110 °C for complete conversion to the corresponding hydride complex (eq 1). This unusual stability was attributed to the absence of a metal–metal bond in the initial formyl complex as well as to the inertness of the osmium center toward ligand loss. In other work, we have shown that the presence of metal–metal bonds can markedly limit the stability of formyl and acyl derivatives since metal–metal bond cleavage provides an easy access to the open coordination site needed for deinsertion.[2]



(1)

We describe herein the preparation and properties of bimetallic Fe–Os and Cr–Os formyl complexes similar to the W–Os formyl complex in eq 1, all with the formyl ligand bound to Os. These allow an assessment of the effect of the nature of the adjacent metal on the stability of the Os–formyl, and the Fe–Os complex has given an example of a stable formyl complex which has a metal–metal bond. The unusual stability of this derivative is rationalized on the basis of the overall geometry of the $M_2(\mu\text{-}PPh_2)_2$ core and the relative Fe–Os bond strength.

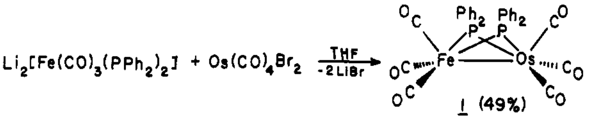
Table I. ^{31}P and ^1H NMR Data at 22 °C[a]

compd	$\delta(P_\mu)$	$\delta(P_{Os})$	$J_{P_\mu-P_\mu}$	$J_{P_\mu-P_M}$	$\delta(H)$	$J_{^1H-^{31}P}$
1	81.5 (s)					
2	197.4 (s)					
3	−79.6 (dd) −89.5 (d)	−27.0 (d)	10.3	88.6		
4[b]	107.0 (d) 72.4 (d)		72.8		14.9 (dd)	18.8 24.5
5a	−69.6 (dd) −96.0 (dd)	−18.9 (dd)	45.0	107.3 11.4	15.3 (dd)	4.9 24.9
5b	−70.2 (m) −90.1 (dd)	−16.8 (dd)	7.3	135.0 11.4	15.4 (m)	
6	−91.7 (s)				−3.2 (t)	15
7	−88.3 (dd) −89.0 (dd)	−11.0 (dd)	6.5	141.9 12.5	−3.6 (ddd)	10, 18 24
8	41.0 (dd) 111.6 (d)	−2.7 (d)	7.4	 10.2		

[a] Solvents used: C_6D_6 (**1**, **2**, **8**), CD_2Cl_2 (**3**), THF-d_8 (**4**–**6**), and $(CD_3)_2SO$ (**7**). *J* values in Hz. [b] ^{31}P, −80 °C; ^1H, −100 °C.

Results

Preparation and Characterization of $(CO)_3\overline{Fe(\mu\text{-}PPh_2)_2Os}(CO)_3$ (1) $(CO)_4\overline{Cr(\mu\text{-}PPh_2)_2Os}(CO)_3$ (2) and $(CO)_4Cr(\mu\text{-}PPh_2)_2Os(CO)_3PMePh_2$ (3). The title complexes 1 and 2 were prepared by using the bridge-assisted synthetic routes[3] outlined in eq 2 and 3 which are analogous to the synthesis of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Os}(CO)_3$ reported earlier.[1] Both complexes 1 and 2 were isolated in pure form and have been spectroscopically characterized. NMR data (^{31}P, ^1H) for these and all the new compounds described herein are summarized in Table I. Both 1 and 2 show single downfield resonances in their $^{31}P\{^1H\}$ NMR spectra assigned to equivalent μ-PPh_2 ligands. The downfield positions imply the presence of a metal-metal



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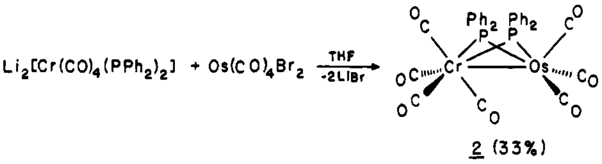

(3)

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[1] Rosenberg, S.; Whittle, R. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 5934.

[2] Mercer, W. C.; Whittle, R. R.; Burkhardt, E. W.; Geoffroy, G. L. *Organometallics* **1985**, *4*, 68.

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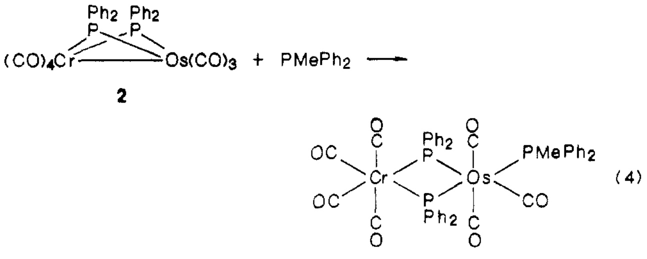
bond in each complex,[4] as required to achieve satisfactory 18-electron counts at each metal. The IR spectrum of **1** is similar in pattern to the IR spectrum of the crystallographically characterized and isoelectronic diiron complex $(CO)_3Fe(\mu\text{-}PPh_2)_2Fe(CO)_3$ (ν_{co} (hexane) 2055 (m), 2018 (vs), 1994 (m), 1966 (s), 1957 (w) cm^{-1} [5].) The latter complex has a square-pyramidal ligand geometry about Fe,[6] and similar ligand arrangements are implied for the two metal centers in **1**. The geometries of the complexes described herein appear to be important in determining the stability of the formyl derivatives (vide infra), and thus special attention will be given throughout this paper to this subject.

Complex **2** appears to be completely analogous to its W analogue, $(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_3$, which was described in ref 1. Although the structure of **2** has not been determined, we expect the $CrOs(\mu\text{-}PPh_2)_2$ core to be bent with respective octahedral and square-pyramidal geometries about the Cr and Os centers, as drawn in eq 3. Such a coordination geometry has been established for the isoelectronic complex $(CO)_4Cr(\mu\text{-}AsMe_2)_2Fe(CO)_3$.[7]

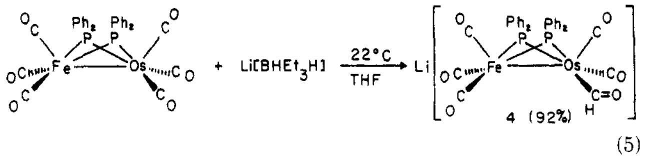
Like $(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_3$,[1] complex **2** reacts with $PMePh_2$ to give a derivative in which the metal-metal bond has been displaced and the phosphine has added to osmium (eq 4). Complex **3** is analogous to its W–Os analogue (eq 1), and its ^{31}P NMR data (Table I) indicate that the terminal PPh_2Me ligand is cis to one μ-PPh_2 ligand and trans to the other as shown in eq 4. Although the structure of **3** has not been determined, the $CrOs(\mu\text{-}PPh_2)_2$ core should be planar with octahedrally coordinated metals as typically found for other $M_2(\mu\text{-}ER_2)_2L_8$[8] complexes.


2

3 (89%)

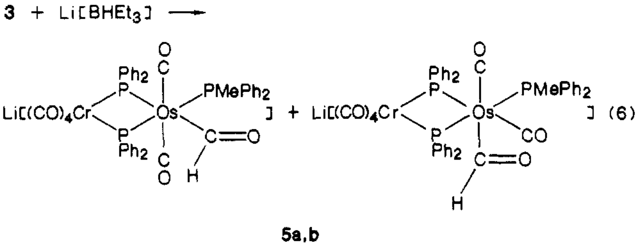
(4)

Synthesis of an Fe–Os Formyl Complex from 1. Complex **1** cleanly reacts with $Li[BEt_3H]$ at 22 °C to give formyl complex **4** in high yield (eq 5). Complex **4** can be isolated as a solid containing two THF molecules per formula unit, and the presence of the formyl ligand is indicated by an IR formyl vibration at 1545 cm^{-1}. Its −80 °C $^{31}P\{^1H\}$ NMR spectrum shows two doublets at δ 107.0 and 72.4 with J_{P-P} = 72.4 Hz assigned to nonequivalent μ-PPh_2 groups. This spectrum is invariant over the −80 → 0 °C temperature range, but is broad but still resolved at 22 °C. The ^1H NMR spectrum of **4** at −100 °C shows a doublet of doublets at δ 14.9 (J_{H-P} = 18.5, 24.5 Hz) which appears as a broad triplet at 22 °C. No resonance was apparent in any of the spectra in the upfield metal hydride region other than that at δ −3.2 due to its deinsertion product **6**; see below. The spectroscopic data indicate the presence of some sort of fluxional process at or near room temperature, but the thermal instability of the complex (see below) has prevented an in-depth study of this phenomenon.


4 (92%)

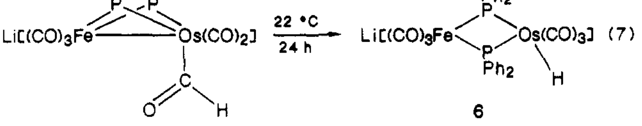
(5)

Synthesis of Isomeric Cr–Os Formyl Complexes from 3. The metal–metal bonded Cr–Os complex **2** reacts with $Li[BHEt_3]$ at −78 °C to give a mixture of hydride containing products, but no evidence for a formyl complex was obtained. In contrast, complex **3** without a metal–metal bond cleanly reacts with $Li[BEt_3H]$ at 22 °C to afford two isomers of formyl complex **5** in high yield (eq 6). This mixture of isomers was isolated as a solid containing 1.5 THF molecules per formula unit. The available spectral data do not indicate to which metal, Cr or Os, the formyl ligand is bound, but the reactivity data discussed below indicate that both isomers have the formyl ligand bound to Os. Also, isomeric Os–formyl complexes were formed upon treatment of the isoelectronic W–Os complex with $[BHEt_3]^-$.[1] The two isomers show their respective ^1H NMR formyl resonances at δ 15.30 (dd) and 15.35 (dd) (Table I) in a 3:1 intensity ratio. Resonances for both isomers were also apparent in the ^{31}P NMR spectrum (Table I), and these show that the phosphido ligands are nonequivalent in both isomers. Also, the presence of one large and one small P_μ–P_{Os} coupling constant in each isomer implies that the $PMePh_2$ ligand is cis to one μ-PPh_2 ligand and trans to the other in both. Although the structures of the two formyl isomers **5a,b** are not known with certainty, those drawn in eq 8 appear most consistent with the spectral data. Isomeric structures similar to these were indicated for the analogous W–Os formyl complexes.[1]


5a,b

(6)

Thermal Stabilities of Complexes 4 and 5. While formyl complex **4** can be prepared and isolated at 22 °C, when allowed to stand in solution at 22 °C for 24 h or when heated it deinserts to give the hydride complex **6** (eq 7).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6

(7)

No attempt was made to isolate **6**, but instead it was spectroscopically characterized in solution. Complex **6** shows a hydride resonance in its ^1H NMR spectrum at δ −3.2 (t, J_{H-P} = 15 Hz) and a $^{31}P\{^1H\}$ resonance at δ −97.1 assigned to the two equivalent μ-PPh_2 ligands. In order for the μ-PPh_2 ligands to be equivalent, the hydride must be cis to both phosphorus nuclei, as also indicated by the small P–H coupling. The related hydride complex

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(4) (a) Petersen, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, *19*, 186. (b) Carty, A. J.; Maclaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *204*, C27. (c) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (d) Johannsen, G.; Stetzer, O. *Chem. Ber.* **1977**, *110*, 3438. (e) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163.

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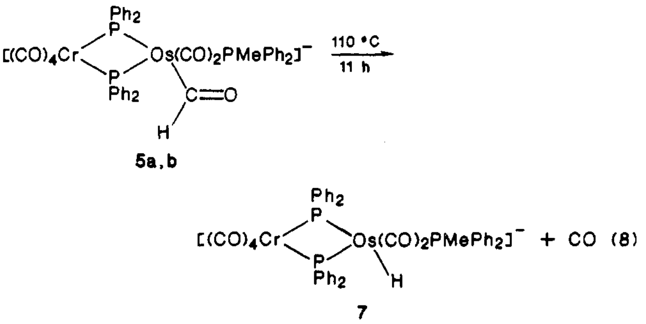
(8) Vahrenkamp, H. *Chem. Ber.* **1978**, *111*, 3472.

$[(CO)_3Fe(\mu\text{-}PPh_2)_2Fe(CO)_2H]^-$,[9] which differs from **6** only by replacement of Fe by Os, shows a ^1H NMR hydride resonance at δ −20.3 (t). The 17 ppm chemical shift difference between the hydride resonance for **6** and that of $[(CO)_3Fe(\mu\text{-}PPh_2)_2Fe(CO)_3H]^-$ is consistent with the location of the hydride ligand in **6** on Os. The $FeOs(\mu\text{-}P)_2$ core of **6** should be planar as found in the isoelectronic complex $[Fe_2(\mu\text{-}PPh_2)_2(CO)_6]^{2-}$.[6] As the $FeOs(\mu\text{-}PPh_2)_2$ core changes from bent to planar in going from **1** to **6**, the coordination geometry about Fe should change from square pyramidal to trigonal bipyramidal as occurs in the isoelectronic transition from $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$ to $Fe_2(\mu\text{-}PPh_2)_2(CO)_6{}^{2-}$.[6]

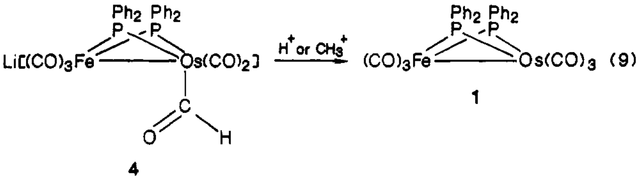
When the 3:1 mixture of formyl complexes **5a** and **5b** is heated at 67 °C for 1 h, no decomposition or change in the **5a**/**5b** ratio occurs. However, when heated at 110 °C for 11 h, the formyl mixture decomposes cleanly to give the hydride complex **7** as the only detectable product (eq 8). Spectral data for complex **7** (Table I) imply that it is structurally analogous to the corresponding W–Os complex $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(H)(CO)_2PMePh_2]$.[1] Its hydride resonance at δ −3.6 (ddd) shows coupling to all three phosphorus nuclei indicating its presence on osmium. The isolation of an Os hydride complex upon decomposition of the **5a**/**5b** formyl mixture is consistent with the formyl ligand being located on Os in both isomers. Interestingly, decomposition of **5a,b** occurs only with CO loss. The analogous W–Os formyl complex decomposes under the same conditions to give a 3:1 mixture of products resulting from competitive $PMePh_2$ and CO loss (eq 1).[1] The reasons for this reactivity difference are unknown, but the reaction illustrates an interesting example of how changing one metal in a bimetallic complex can influence the reactivity at an adjacent metal center.



5a,b

7

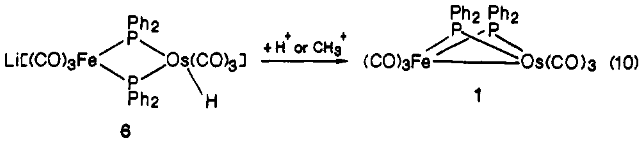
Protonation and Methylation of 4 and 6. Attempts to protonate as prepared formyl complex **4** with 20% H_3PO_4 or alkylate it with $[(CH_3)_3O]BF_4$ resulted only in net hydride loss and quantitative regeneration of **1** (eq 9).



4

1

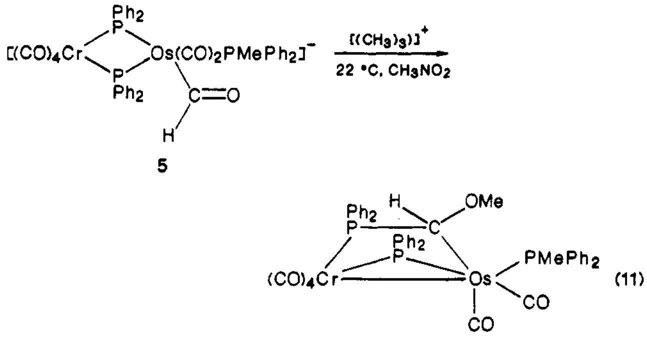
Hydride complex **6** also reacts with 20% H_3PO_4 and $[(CH_3)_3O]BF_4$ to generate complex **1** via net hydride loss (eq 10). This reaction probably occurs via H^+ or $CH_3{}^+$ addition to Os followed by coupling with the hydride ligand to release H_2 or CH_4.



6

1

Carbene–Phosphide Coupling from Reaction of 5 with [(CH₃)₃O]BF₄. Treatment of formyl complex **5** with $[(CH_3)_3O]BF_4$ in CH_3NO_2 at 22 °C results in formation of complex **8** (eq 11). Complex **8** can be isolated in modest yield (34%) and has been characterized spectroscopically (Table I). It is analogous to the structurally characterized complex $(CO)_4W(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CHOMe)Os(CO)_2(PMePh_2)$ prepared by an analogous methylation of the corresponding W–Os formyl complex.[1] Complex **8** possesses a bridging $\eta^2(P,C)\text{-}\mu\text{-}PPh_2CH(OMe)$ ligand formed by coupling of a $\mu\text{-}PPh_2$ ligand with a methoxymethylene ligand, the latter generated by methylation of the formyl oxygen. The ^{31}P NMR spectrum of complex **8** shows a $\mu\text{-}PPh_2$ resonance at δ 111.4 (d) with the downfield position implying the presence of a metal-metal bond.[4] The $\mu\text{-}PPh_2CH(OMe)$ and $PMePh_2$ ligands show characteristic resonances at δ 41.0 (dd) and −2.7 (d), respectively.[1] The absence of coupling between the $\mu\text{-}PPh_2$ and $PMePh_2$ ligands and the small 7.4-Hz coupling between the $\mu\text{-}PPh_2CH(OMe)$ and $PMePh_2$ ligands (Table I) imply the cis location of the $PMePh_2$ ligand relative to both bridging ligands as found in its structurally characterized W–Os analogue.[1]

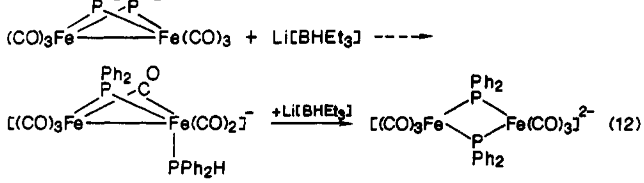


5

8

Discussion

Whether or not a formyl complex results from reaction of phosphido-bridged compounds with $Li[BHR_3]$ reagents depends markedly on the metals involved and the nature of the metal–metal bonding. For example, when Wojcicki and co-workers[9,10a] treated the Fe_2, Mo_2, and W_2 complexes shown in eq 12 and 13 with $Li[BHR_3]$ reagents, stable formyl complexes were not produced but rather the observed products involved either net hydride addition to phosphorus or net reduction of the complex. More recently, these workers have demonstrated that a formyl complex initially forms in the reaction of eq 14 but that it rapidly decomposes to give first a hydride complex and then the isolated $[Fe_2(\mu\text{-}PPh_2)_2(CO)_6PPh_2H]^-$ complex.[10b] An unstable formyl complex was also detected by ^1H NMR spectroscopy when $W_2(\mu\text{-}PPh_2)_2(CO)_8$ was treated with



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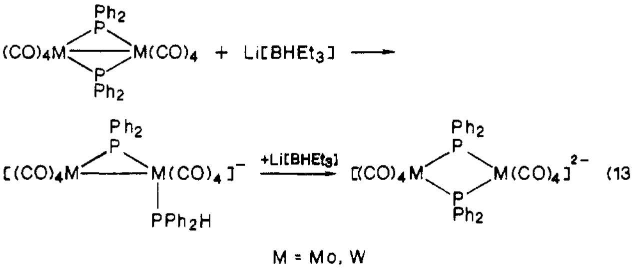
[9] Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1983**, *105*, 4826.

[10] (a) Shyu, S.-G.; Wojcicki, A. *Organometallics* **1984**, *3*, 809. (b) Shyu, S.-G.; Wojcicki, A. *Organometallics* **1985**, *4*, 1457.

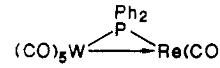


(13)

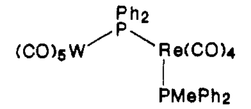
Li[BHEt$_3$] at 78 °C.[11] Likewise, our metal–metal bonded Cr–Os complex **2** did not give a stable formyl derivative. In contrast to the above results, stable formyl complexes do form when (CO)$_4$W(μ-PPh$_2$)$_2$Os(CO)$_3$PMePh$_2$,[1] and, as described herein, the Fe–Os and Cr–Os complexes **1** and **3** are allowed to react with Li[BHEt$_3$].

One important factor which appears to affect the stability of binuclear and polynuclear formyl complexes is the extent and nature of the metal–metal bonding. Weak metal–metal bonds destabilize polynuclear formyl complexes since metal–metal bond cleavage provides an easy access to open coordination sites needed for deinsertion of the formyl ligand. This has been well illustrated by the many attempts to prepare formyl-substituted clusters which rarely lead to the desired formyl product but usually to a hydride cluster.[12,13] A likely decomposition process for formyl-substituted clusters involves opening of a coordination site by metal–metal bond cleavage, followed by deinsertion of the formyl ligand, loss of CO, and reformation of the metal–metal bond to give μ-H products (Scheme I). Indeed, the only well-characterized cluster formyls which are sufficiently stable at room temperature to study are [Os$_3$(CO)$_{11}$(CHO)]$^-$[13] and [Fe$_3$(μ_3-NPh)$_2$(CO)$_8$(CHO)]$^-$.[14] The stability of the former reflects the relatively strong Os–Os bonds,[15] whereas the latter is apparently stable because of the rigidity of the metal framework imposed by the capping μ_3-NPh ligands.

An illustration of the effect of the metal–metal bonding on the stability of binuclear formyl complexes comes from our earlier study of the two W–Re complexes **9** and **10**.[2]

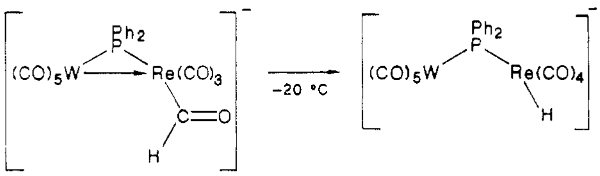


9



10

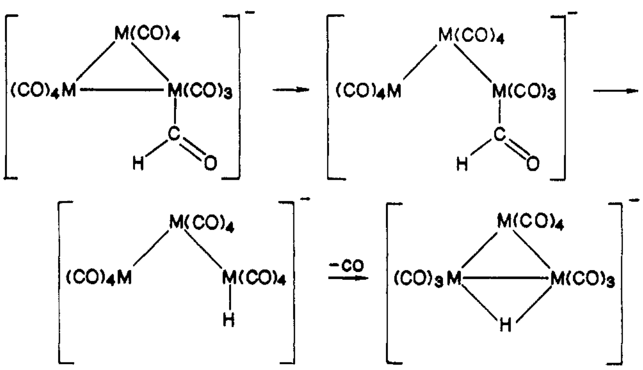
Complex **9** with a weak donor–acceptor W→Re bond gave an unstable formyl complex at −78 °C which decomposed upon warmup to −20 °C by cleavage of the W→Re bond and deinsertion of the formyl (eq 14). In contrast, complex



(14)

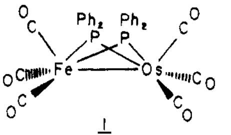
10 in which the metal–metal bond was previously displaced

Scheme I



by the PMePh$_2$ ligand gave a formyl complex which was stable enough to isolate as a crystalline solid and which required heating to 50 °C to induce deinsertion accompanied by PMePh$_2$ loss.[2]

Stable formyl complexes also did not result upon treatment of the metal–metal bonded complexes (CO)$_4$W(μ-PPh$_2$)$_2$Os(CO)$_3$[1] and, as reported herein, (CO)$_4$Cr(μ-PPh$_2$)$_2$Os(CO)$_3$ (**2**) with [BHEt$_3$]$^-$ reagents. It was thus most surprising when the metal–metal bonded Fe–Os complex **1** gave the stable formyl derivative **4**. Indeed, *substituting an Fe(CO)$_3$ unit in 1 for the Cr(CO)$_4$ fragment in 2, with no other chemical change, markedly influences the stability of the formyl ligand on the adjacent Os center.* We suggest that the reason for this stability difference lies in the nature of the metal–metal bonding in the formyl complexes which is a reflection of the metal–metal bonding in the parent compounds **1** and **2**. As pointed out by Vahrenkamp and Keller[7] in their



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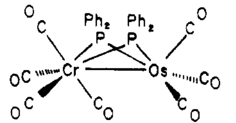

2

structural studies of Cr$_2$(μ-AsMe$_2$)$_2$(CO)$_8$, CrFe(μ-AsMe$_2$)$_2$(CO)$_7$, and Fe$_2$(μ-AsMe$_2$)$_2$(CO)$_6$ and by Collman, Dahl, et al.[6] in their study of Fe$_2$(μ-PPh$_2$)$_2$(CO)$_6$, the metal–metal bond lengths and the overall core geometries of these types of complexes are determined by the geometrical requirements of the ligand arrangements about the individual metal centers. The two Fe$_2$ complexes which are isoelectronic with **1** have been shown to have square-pyramidal coordination geometries at each metal with a bent, covalent metal–metal bond filling the sixth coordination site on each metal. In contrast, compound **2** presumably has a structure analogous to that determined for CrFe(μ-AsMe$_2$)$_2$(CO)$_7$ with an octahedral coordination geometry at the Cr center and a square-pyramidal geometry at Os. In this complex the metal–metal bond appears better described as a donor–acceptor bond between Cr(0) and Os(+II) centers.

As expected, reactivity studies indicate that the donor–acceptor metal–metal bonds are weaker than the covalent metal–metal bonds. For example, the metal–metal bonds and bent inner core geometries are retained when the (CO)$_3$Fe(μ-ER$_2$)$_2$Fe(CO)$_3$ complexes analogous to **1** react with phosphines to yield substituted M$_2$(μ-E)$_2$(CO)$_5$L derivatives.[16-18] These reactions also require forcing

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conditions, and for example, $Fe_2(\mu\text{-}PPh_2)_2(CO)_6$ has to be irradiated or heated above 140 °C to induce PR_3 substitution. In contrast, $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Os}(CO)_3$[1] and, as described herein, complex **2** react with phosphines under relatively mild thermal conditions to give products in which the metal–metal bonds have been displaced by the PR_3 ligands. The greater strength of the metal–metal bonds in complexes of type **1** presumably accounts for the much greater stability of its formyl derivative compared to the stability of the formyl derivatives of **2** and its W–Os analogue where the weak metal–metal bonds readily give an open coordination site for deinsertion.

Experimental Section

$Fe(CO)_3(PPh_2H)_2$ and $Cr(CO)_4(PPh_2H)_2$ were prepared by the literature methods,[19,20] with $Cr(CO)_4(NBD)$ (NBD = norbornadiene) generated via the method of King et al. for $W(CO)_4(NBD)$.[21] $Os(CO)_4Br_2$ was synthesized by a modification of the procedure of Calderazzo,[22] using 1700 psi of 3:1 CO/H_2 pressure and heating at 165 °C for 48 h. $PMePh_2$ (Strem), MeLi, *n*-BuLi, $[(CH_3)_3O]BF_4$, and $LiBEt_3H$ (Aldrich) were used as received without further purification. Unless otherwise specified, all operations were performed under a prepurified N_2 atmosphere using rigorously dried and deoxygenated solvents and standard Schlenk techniques. NMR spectra were recorded on a Bruker WP200 FT NMR spectrometer; other instruments have been previously described.[23] Field desorption (FD) mass spectra were recorded by Robert Hale at the Tennessee Eastman Co., Kingsport, TN. Elemental analyses were performed by Schwarzkoff Microanalytical Laboratories, Woodside, NY.

Synthesis of $(CO)_3\overline{Fe(\mu\text{-}PPh_2)_2Os}(CO)_3$ (1). To a solution of $Fe(CO)_3(PPh_2H)_2$ (337 mg, 0.658 mmol) in 10 mL of THF in a 10-mL Schlenk flask was added *n*-BuLi (820 μL of a 1.6 M hexane solution). This solution was stirred for 5 min to generate $Li_2[Fe(CO)_3(PPh_2)_2]$ in situ. The resultant brown solution was added via cannula to a solution of $Os(CO)_4Br_2$ (300 mg, 0.649 mmol) in 20 mL of THF in a 50-mL Schlenk flask. This red solution was heated at reflux for 1 h, cooled, and rotary evaporated in air leaving a red oil. The oil was dissolved in a minimum of CH_2Cl_2 and loaded onto three 25-g SiO_2 plates. Elution with hexane afforded a small yellow band followed by a large yellow band. The large yellow band was removed from the SiO_2 by CH_2Cl_2 extraction. Removal of solvent by rotary evaporation afforded complex **1** as an air-stable, microcrystalline, yellow solid in 49% yield (250 mg, 0.319 mmol). **1**: MS, *m/e* (EI) 784 (M^+), 756 ($M^+ - CO$), 728 ($M^+ - 2CO$), 700 ($M^+ - 3CO$), 672 ($M^+ - 4CO$), 644 ($M^+ - 5CO$), 616 ($M^+ - 6CO$); IR (hexane) ν_{CO} 2065 (m), 2030 (vs), 2003 (m), 1975 (s), 1963 (w) cm^{-1}. Anal. Calcd for $C_{30}H_{20}FeO_6OsP_2$: C, 45.90; H, 2.55. Found: C, 45.77; H, 3.04.

Synthesis of $(CO)_4\overline{Cr(\mu\text{-}PPh_2)_2Os}(CO)_3$ (2). To a solution of $Cr(CO)_4(PPh_2H)_2$ (1.955 g, 3.65 mmol) in 75 mL of THF in a 200-mL Schlenk flask was added MeLi (2.8 mL of a 1.2 M THF solution). This solution was stirred for 5 min to generate $Li_2[Cr(CO)_4(PPh_2)_2]$ in situ. The resultant orange solution was added via cannula to a solution of $Os(CO)_4Br_2$ (1.55 g, 3.35 mmol) in 75 mL of THF. This red solution was heated at reflux for 1 h, cooled, and rotary evaporated in air leaving a red oil. The oil was dissolved in a minimum of CH_2Cl_2 and adsorbed onto 3 g of SiO_2 by rotary evaporation. This silica was loaded midway down a 12 ft × 3/4 in. glass SiO_2 chromatography column. Elution with hexane afforded two small yellow fractions followed by an orange fraction of **2**. Complex **2** was isolated as an orange, air-stable microcrystalline solid in 33% yield (880 mg, 1.09 mmol) by solvent removal from this fraction. **2**: MS, *m/e* (FD) 808 (M^+); IR (hexane) ν_{CO} 2026 (m), 2006 (s), 1952 (vs), 1940 (msh) cm^{-1}. Anal. Calcd for $C_{31}H_{20}CrO_7OsP_2$: C, 46.03; H, 2.47. Found: C, 46.26; H, 2.92.

Synthesis of $(CO)_4Cr(\mu\text{-}PPh_2)_2Os(CO)_3(PMePh_2)$ (3). Compound **2** (561 mg, 0.694 mmol) was dissolved in 30 mL of acetone in air in a 400-mL beaker. This was placed in the back of a fume hood, and $PMePh_2$ (200 μL, 1.0 mmol) was added. After evaporation of the acetone, the residue was suspended in 25 mL of acetone and again allowed to evaporate in the fume hood. This procedure was repeated four times, and then the orange residue was collected on a medium porosity frit and washed with 10 mL of hexane (10×) and dried in vacuo for 12 h. This afforded **3** as an air-stable, orange powder in 89% yield (660 mg, 0.619 mmol). **3**: MS, *m/e* (FD) 1008 (M^+); IR (CH_2Cl_2) ν_{CO} 2101 (w), 2027 (s), 2017 (msh), 1989 (s), 1890 (ssh), 1875 (s), 1846 (s) cm^{-1}. Anal. Calcd for $C_{44}H_{33}CrO_7OsP_3\cdot(CH_3)_2CO$: C, 52.91; H, 3.66. Found: C, 53.23; H, 3.88.

Synthesis of $[Li(THF)_2][(CO)_3\overline{Fe(\mu\text{-}PPh_2)Os}(CHO)(CO)_2]$ (4). $Li[BEt_3H]$ (500 μL of a 1 M THF solution) was added to a stirred solution of **1** (300 mg, 0.382 mmol) in 10 mL of THF at 22 °C in a 50-mL Schlenk flask. This yellow solution was stirred for 15 min and then transferred to a 60-mL Schlenk fritted funnel containing 40 mL of hexane. This resulted in the immediate precipitation of a yellow solid. The liquids were filtered, and the yellow solid was washed with 20 mL of hexane (2×). The solid was dried in vacuo for 2 h to give **4** as an air-sensitive yellow solid in 92% yield (332 mg, 0.355 mmol). **4**: IR (THF) ν_{CO} 2010 (vs), 1970 (vs), 1935 (msh), 1920 (s), 1903 (m), ν_{CHO} 1545 (w) cm^{-1}. Anal. Calcd for $C_{38}H_{36}FeLiO_8OsP_2$: C, 48.71; H, 3.95. Found: C, 48.71; H, 3.35.

Synthesis of $[Li(THF)_{1.5}][(CO)_4Cr(\mu\text{-}PPh_2)_2Os(CO)_2(PMePh_2)(CHO)]$ (5). $Li[BEt_3H]$ (1300 μL of a 1 M THF solution) was added to a stirred suspension of **3** (431 mg, 0.427 mmol) in 75 mL of THF at 22 °C. All the solid dissolved within 5 min to give a clear orange solution. Hexane (10 mL) was layered on top of the THF, and this mixture was placed in a freezer overnight. The orange powder that deposited was collected in a Schlenk frit under N_2, washed with 20 mL of hexane (2×), and dried in vacuo for 1 h. This afforded complex **5** in 56% yield (269 mg, 0.239 mmol). **5**: IR (THF) ν_{CO} 1977 (s), 1962 (s), 1877 (ssh), 1864 (s), 1833 (m), ν_{CHO} 130 (w) cm^{-1}. Anal. Calcd for $C_{50}H_{46}CrLiO_{8.5}OsP_3$: C, 53.38; H, 4.49. Found: C, 53.23; H, 4.22.

Thermal Decomposition of 4. A solution of **4** in 10 mL of THF, generated from **1** (100 mg, 0.116 mmol) and $Li[BEt_3H]$ (170 μL of a 1 M THF solution), was allowed to stir at 22 °C for 24 h. This orange solution was then reduced in vacuo to an orange oil and redissolved in 1 g of THF-d_8. ^{31}P and ^1H NMR spectra of this orange solution showed the presence $Li[(CO)_3\overline{Fe(\mu\text{-}PPh_2)_2Os}(H)(CO)_3]$ (**6**) as the only organometallic product.

Thermal Decomposition of 5. A solution of **5** in THF, generated in situ from **2** (70 mg, 0.069 mmol) and $Li[BEt_3H]$ (100 μL of a 1 M THF solution), was reduced in vacuo to a yellow oil. This oil was dissolved in 1 mL of $(CD_3)_2SO$ in a 5-mm NMR tube. This NMR tube was heated at 110 °C for 11 h, and the ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded. The only product formed was $Li[(CO)_4\overline{Cr(\mu\text{-}PPh_2)_2Os}(H)(CO)_2(PMePh_2)]$ (**7**) identified by its ^1H and ^{31}P NMR spectra.

Reaction of 4 with 20% H_3PO_4. To a solution of **4** in 10 mL of THF, generated in situ from **1** (112 mg, 0.143 mmol) and $Li[BEt_3H]$ (200 μL of a 1 M THF solution) was added excess 20% H_3PO_4. After the mixture was stirred for 30 min, the THF was removed in vacuo and the water decanted. The residue was dissolved in a minimum of CH_2Cl_2 and loaded onto a 25-g SiO_2 plate. Elution with hexane gave only a yellow fraction of complex **1** (by IR). This fraction was removed from the SiO_2 by CH_2Cl_2 extraction. Removal of solvent afforded complex **1** in 91% yield (102 mg, 0.130 mmol).

Reaction of 4 with $[(CH_3)_3O]BF_4$. A solution of **4** in 10 mL of THF, generated in situ from **1** (102 mg, 0.130 mmol) and $Li[BEt_3H]$ (150 μL of a 1 M THF solution), was transferred to a 50-mL Schlenk flask containing $[(CH_3)_3O]BF_4$ (23 mg, 0.155 mmol). After the mixture was stirred for 15 min, the solvent was removed in vacuo. Chromatography in the manner described for complex **1** afforded as the only product complex **1** in 92% yield (94 mg, 0.120 mmol).

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Reaction of 6 with 20% H_3PO_4 and $[(CH_3)_3O]BF_4$. Solutions of 1 in THF were treated with $Li[BEt_3H]$ and allowed to stand for 24 h to generate 6 in situ. Procedures identical with those used for the reactions of 4 with the title reagents were used with 6, but complex 1 was isolated as the only product in 90–94% yields following the reactions.

Synthesis of $(CO)_4Cr(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CH(OMe))Os(CO)_2(PMePh_2)$ (8). A solution of 5 in 10 mL of THF, generated from 3 (223 mg, 0.221 mmol) and $Li[BEt_3H]$ (500 μL of a 1 M THF solution), was reduced in vacuo to a yellow oil and redissolved in 25 mL of CH_3NO_2. This orange solution was transferred via cannula to a 100-mL Schlenk flask containing $[(CH_3)_3O]BF_4$ (120 mg, 0.80 mmol). The solution turned red immediately and was stirred for 45 min. The CH_3NO_2 was removed in vacuo and the residue dissolved in a minimum of CH_2Cl_2 and loaded onto two SiO_2 chromatography plates (25 g). Elution with 20% acetone/hexane afforded an orange band of complex 8 on each. Complex 8 was isolated as an orange band of complex 8 on each. Complex 8 was isolated as an orange, air-stable, microcrystalline solid in 34% yield (81 mg, 0.075 mmol) by solvent removal from these fractions. 8: IR (CH_2Cl_2) ν_{CO} 2026 (s), 1993 (vs), 1950 (s), 1900 (m) cm^{-1}. Anal. Calcd for $C_{45}H_{36}CrO_7OsP\cdot(CH_3)CO$: C, 53.28; H, 3.88. Found: C, 53.53; H, 3.69.

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A Comparison of the Reactivities toward Oxidative Addition of the Dimethylplatinum(II) Units in Mononuclear and Binuclear Complexes with Bis(diimine) Ligands

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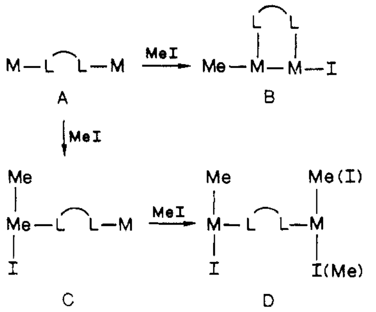
A study of the reactivity toward oxidative addition of methyl iodide of some mononuclear and binuclear dimethylplatinum(II) complexes with the binucleating bis(diimine) ligands 2,2′-bipyrimidine (bipym), 2,3-bis(2-pyridyl)pyrazine (pypz), and bis(2-pyridinal)ethylenediimine (pyen) has been made. In this series of binucleating ligands, the metals are held progressively further apart and the coordination planes of the two metal centers vary from rigidly coplanar to slightly and almost completely flexible with respect to one another. In all cases, the binuclear complexes react more slowly than the mononuclear complexes. This is believed to be primarily an electronic effect for the bipym and pypz complexes, but steric effects may dominate for the pyen complexes. The effect is greatest for the bipym complexes in which, as deduced from the UV–visible spectra, there is strongest conjugation between the two diimine donor units. However, there is no correlation between the reactivity to oxidative addition and the energy of a metal-to-ligand charge-transfer band in the UV–visible spectra, and reasons for this are discussed. Within the series of mixed oxidation state complexes $[Me_2RXPt(\mu\text{-bipym})PtMe_2]$, the trend in reactivity of the platinum(II) center to oxidative addition depends primarily on steric effects of R and X, giving the reactivity series R, X = Me, Cl > Me, Br > Me, I > *i*-Pr, I. Several of the μ-pypz complexes undergo a novel disproportionation reaction. For example, the complexes $[Me_3IPt(\mu\text{-pypz})PtMe_n]$, $n = 2$ or 4, disproportionate readily to the corresponding symmetrical complexes $[Me_3IPt(\mu\text{-pypz})PtIMe_3]$ and $[Me_nPt(\mu\text{-pypz})PtMe_n]$. Evidence, from variable-temperature ^1H NMR spectroscopy, is presented that the μ-pypz complexes adopt a twisted structure but are fluxional, with a planar transition state between two equivalent but less symmetrical twisted forms.

Introduction

Binuclear complexes can exhibit patterns of organometallic reactivity which are significantly different from those of mononuclear complexes. For bridged binuclear complexes, oxidative addition reactions with alkyl halides can occur to yield three types of products,[1] and each of these reactions can be reversible or irreversible (eq 1, L–L = bridging ligand, M = metal complex).[2-4]



(1)

Complexes of general type B are formed by binuclear oxidative addition, in which the oxidation state of each metal center increases by one unit,[5-7] complexes C by oxidative addition at a single metal center, and complexes D by double oxidative addition.[3,4,8] In principle, complexes D could be formed from either B or C, but only formation from C appears to be known in alkyl halide additions.[1-7] Two isomers of D are often possible, as illustrated in eq 1.

In systems which react along the pathway A ⇌ C ⇌ D, it appears that the first oxidative addition occurs more

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