A Radical-Chain Mechanism for Dinuclear C–H Bond Formation

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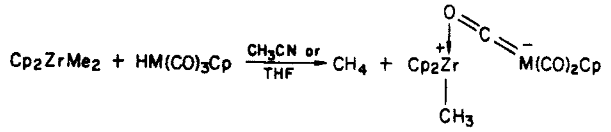
Abstract: Both the formation of $(Ph_3PAu)_2Os(CO)_4$ from Ph_3PAuCH_3 and $H_2Os(CO)_4$ and the formation of $(Ph_3PAu)Mn(CO)_5$ from Ph_3PAuCH_3 and $HMn(CO)_5$ occur by radical-chain mechanisms. The chain carriers are $\cdot Mn(CO)_5$ and $\cdot Os(H)(CO)_4$, respectively, arising from hydrogen atom abstraction from the initial hydrides. Photolysis of a small amount of the appropriate dimer ($Mn_2(CO)_{10}$ or $H_2Os_2(CO)_8$) generates the chain carrier and thus initiates the reaction. No such reaction occurs between Ph_3PAuCH_3 and $HRe(CO)_5$, even in the presence of substantial amounts of $\cdot Re(CO)_5$. The formation of $H_2Os(CO)_3PPh_3$ from Ph_3P and $H_2Os(CO)_4$ also occurs by a radical-chain mechanism with $\cdot Os(H)(CO)_4$ as the chain carrier, and the reactions of Ph_3PAuCH_3 and Ph_3P with $H_2Os(CO)_4$ can be simultaneously initiated.

After concluding that the reaction of Cp_2ZrMe_2 with $HM(CO)_3Cp$ (M = Cr, Mo, W) (reaction 1) proceeded by a proton-transfer mechanism,[1] our attention was attracted by the briefly reported (without specification of solvent or reaction conditions)[2] reaction of $(Ph_3P)AuMe$ with $HMn(CO)_5$ (reaction 2). Although Stone and co-workers used $HMn(CO)_5$ in the course of a study of the reaction of $(Ph_3P)AuCH_3$ with strong acids, they noted that $HMn(CO)_5$ contained "only weakly protonic hydrogen",[2] and we considered a proton-transfer mechanism unlikely for reaction 2 for a variety of reasons. While $HMn(CO)_5$ is in fact an organometallic acid of moderate strength (its pK_a in acetonitrile is 15.2, in between that of $HMo(CO)_3Cp$ and that of $HW(CO)_3Cp$[3]), the Au–CH_3 bond is much less polar than the Zr–CH_3 bond in reaction 1; the Pauling electronegativity of Au (2.4) is approximately equal to that of C (2.5), while that of Zr is much less (1.4).[4] We have therefore investigated the mechanism of the reaction of $(Ph_3P)AuCH_3$ with $HMn(CO)_5$ and with other carbonyl hydrides. We now report that these reactions proceed (if they proceed at all) by *radical-chain* mechanisms and are the first example of the operation of such mechanisms in intermolecular C–H bond-forming reactions.[5-7]

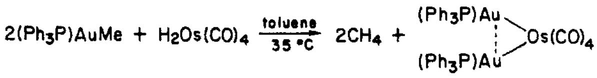


(1)

$$(Ph_3P)AuMe + HMn(CO)_5 \rightarrow \underset{\mathbf{1}}{(Ph_3P)AuMn(CO)_5} \quad (2)$$

Results

Preliminary investigation confirmed that $(Ph_3P)AuMe$ and $HMn(CO)_5$, in C_6D_6 at room temperature, gave the known (from the reaction of $Mn(CO)_5^-$ and Ph_3PAuCl)[8] dinuclear mixed-metal complex $(Ph_3P)AuMn(CO)_5$ (**1**). Use of $H_2Os(CO)_4$ in place of $HMn(CO)_5$, in toluene at 35 °C, gave (reaction 3) methane and the trinuclear mixed-metal complex **2**, also previously prepared by an alternate route ($[Os(CO)_4]^{2-}$ and 2 equiv of Ph_3PAuCl).[9]



(3)

2

The recently reported[10] X-ray structure of **2** shows an unmistakable Au–Au interaction, with an Au–Au distance of 2.929 (1) Å; similar structures, with somewhat longer Au–Au distances, have been reported for the iron analogues of **2**, $(Ph_3PAu)_2Fe(CO)_4$[11] and $[(Ph_2PCH_2CH_2PPh_2)Au_2Fe(CO)_4]_2$.[12]

No toluene was found when reaction 3 was carried out in benzene (which would have formed some toluene if attacked by methyl radicals[13]), suggesting that the reaction either did not proceed by Au–C bond homolysis or that the resulting methyl radicals abstracted hydrogen atoms from $H_2Os(CO)_4$ more rapidly than they attacked benzene. In any case, the known[14] mechanism of decomposition of Ph_3PAuCH_3 in decalin at 100 °C (rate-limiting loss of Ph_3P followed by rapid reaction with another molecule of Ph_3PAuCH_3) made facile Au–C bond homolysis at 35 °C extremely unlikely.

Our initial measurements of the kinetics of reaction 3, however, gave inconsistent results. Under pseudo-first-order conditions, with $[Ph_3PAuCH_3] = 0.074$ M, the rate of disappearance of $H_2Os(CO)_4$ varied from 1.3×10^{-4} to $<6.0 \times 10^{-6}$ s^{-1}. Slower rates were observed when the reaction was carried out under argon than when it was carried out under nitrogen, an observation which suggested that the rate of the reaction was quite sensitive to small amounts of oxygen (argon, being heavier than nitrogen, is presumably more effective at excluding oxygen).

These results suggested that reaction 3 was occurring by a radical-chain mechanism induced by traces of oxygen.[15-18] Indeed,

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[1] (a) Edidin, R. T.; Longato, B.; Martin, B. D.; Matchett, S. A.; Norton, J. R. In "Organometallic Compounds: Synthesis, Structure, Theory"; Shapiro, B. L., Ed.; Texas A & M University Press: College Station, 1983; pp 260–80. (b) Edidin, R. T.; Sullivan, J. M.; Norton, J. R., unpublished results.

[2] Mitchell, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 102.

[3] (a) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (b) Jordan, R. F.; Norton, J. R. *ACS Symp. Ser.* **1982**, *No. 198*, 403. (c) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, in press.

[4] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell Press: Ithaca, NY, 1960; p 92.

[5] A radical mechanism has been demonstrated for the elimination of p-$CH_3OC_6H_4CH_3$ from *cis*-p-$CH_3OC_6H_4CH_2Mn(CO)_4L$ and *cis*-$HMn(CO)_4L$ in nondonor solvents, but the mechanism involves Mn–C bond homolysis rather than a chain process.[6] Similarly, Bergman and Jones[7] have proposed that the formation of toluene from $CpMo(CO)_3CH_2C_6H_5$ and $HMo(CO)_3Cp$ occurs by Mo–C bond homolysis. Homolysis is doubtless more likely when, as in these two cases, benzyl radicals are formed.

[6] (a) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. (b) Nappa, M. J.; Santi, R.; Diefenbach, S. P.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 619. (c) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34.

[7] Jones, W. D.; Bergman, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 5447.

[8] Coffey, C. E.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1964**, 1741.

[9] George, R. D.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 972.

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[11] (a) Lauher, J. W.; Wald, K., unpublished results quoted by: Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237. (b) Day, V., unpublished results.

[12] Briant, C. E.; Hall, K. P.; Mingos, D. M. P. *Chem. Commun.* **1983**, 843.

[13] (a) Hay, J. M. "Reactive Free Radicals"; Academic Press: New York, 1974; pp 22–23 and 116–117 and refernces therein. (b) Williams, G. H. "Homlytic Aromatic Substitution"; Pergamon Press: New York, 1960. (c) Corbett, G. E.; Williams, G. H. *J. Chem. Soc.* **1964**, 3437.

[14] Tamaki, A.; Kochi, J. K. *J. Organomet. Chem.* **1973**, *61*, 441.

[15] The effectiveness of small amounts of oxygen at initiating the radical-chain reactions involving M–H bonds is well-established for tertiary phosphine substitution on $HRe(CO)_5$[16] and on *cis*-$H(CH_3)Os(CO)_4$[17] and for the reaction of tin hydrides with alkyl halides.[18]

[16] Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527 and references therein.

[17] Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. *Inorg. Chem.* **1982**, *21*, 3955.

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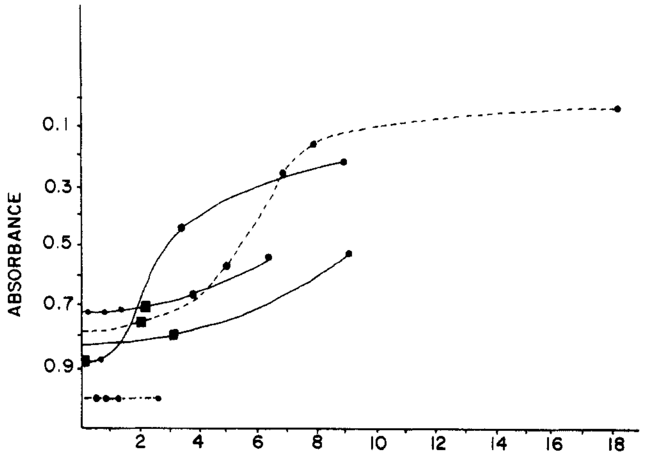
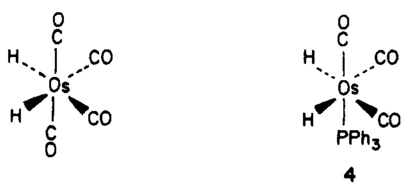


Figure 1. Absorbance (in 0.1-mm cells) at 2049 cm^{-1} due to $H_2Os(CO)_4$ (about 1.5 × 10^{-3} M) in the presence of 0.074 M Ph_3PAuCH_3. In toluene under nitrogen (—), in benzene under nitrogen (- - -), and in toluene under argon (–●–●–). AIBN was added when shown by ■.

when a solution of Ph_3PAuCH_3 and $H_2Os(CO)_4$ in toluene was repeatedly frozen and degassed on a high vacuum line, and when the solution was sampled under argon with careful exclusion of air, no detectable reaction occurred at 35 °C. Addition of AIBN (10%–15% mole fraction of $H_2Os(CO)_4$) to carefully deoxygenated reaction mixtures resulted in a noticeable increase in the rate of the reaction, even at 35 °C (as shown in Figure 1). As AIBN is not a very efficient initiator at 35 °C,[19] these reaction profiles suggested that reaction 3 was not only a radical-chain reaction but a very efficient one.

The most plausible chain carrier was the osmium-centered radical $H\dot{O}s(CO)_4$ (**3**). Facile radical-chain substitution involving initial hydrogen atom abstraction and substitution on the resulting 17-electron species had already been established for other osmium hydrides, e.g., $H(CH_3)Os(CO)_4$[17] and $HOs(CO)_4Os(CO)_4CH_3$,[20] and such processes were familiar from the pioneering work of Brown and his research group on $HRe(CO)_5$[16,21] and $CpM(CO)_3H$ (M = Mo and W).[21,22] We therefore examined Ph_3P substitution on $H_2Os(CO)_4$ (reaction 4), which seemed likely, by analogy with the mechanism established[16,21] for Ph_3P substitution on $HRe(CO)_5$, to proceed by a radical-chain mechanism involving **3** as the chain carrier.

$$H_2Os(CO)_4 + Ph_3P \xrightarrow{C_6H_6} H_2Os(CO)_3PPh_3 + CO \qquad (4)$$



4

There had been an early report[23] that reaction 4 gave **4** in 4 h at 80 °C in heptane; NMR and IR evidence unambiguously showed that **4** had the structure shown. The relatively mild conditions reported offered additional evidence against the only plausible nonradical mechanism, carbonyl dissociation; at 125.8 °C in mesitylene, the rate constant for carbonyl dissociation was known[24] to be 6.1 × 10^{-5} s^{-1}.

Addition of a small amount of AIBN to a benzene solution of 10:1 $Ph_3P/H_2Os(CO)_4$ permitted reaction 4 to occur at a reasonable rate even at 35 °C. Furthermore, the induction period observed when AIBN was not initially present, and the sudden acceleration of rate observed when it was added (Figure 2), provided clear evidence that a radical-chain mechanism was operating.

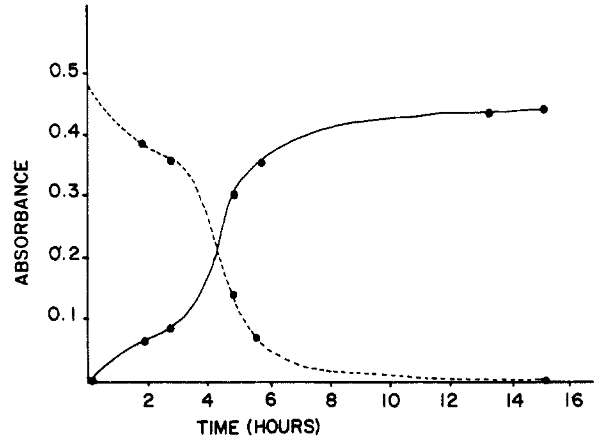


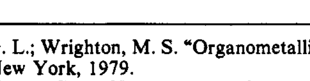
Figure 2. Absorbance (in 0.1-mm cells) at 2071 cm^{-1} due to $H_2Os(CO)_4$ (- - -), and absorbance at 2081 cm^{-1} due to $H_2Os(CO)_3PPh_3$ (**4**) (—), arising from a 10:1 $Ph_3P/H_2Os(CO)_4$ solution in benzene at 35 °C.

Reaction 4 thus occurred under conditions similar to those for reaction 3, an observation which suggested that they shared similar radical-chain mechanisms. We therefore carried out the experiment shown as reaction 5. Both NMR and IR showed that the

$$\left.\begin{matrix} Ph_3PAuCH_3 \\ + \\ Ph_3P \end{matrix}\right| \xrightarrow[C_6H_6,\ 35\ ^\circ C,\ AIBN]{H_2Os(CO)_4} \left|\begin{matrix} (Ph_3PAu)_2Os(CO)_4\ \mathbf{(2)} \\ + \\ H_2Os(CO)_3PPh_3\ \mathbf{(4)} \end{matrix}\right. \qquad (5)$$

formation of **2** paralleled the formation of **4** and, therefore, that reactions 3 and 4 proceeded via a common chain carrier.

In order to determine whether or not the chain carrier was indeed $H\dot{O}s(CO)_4$, we decided to generate the latter by photolysis of $H_2Os_2(CO)_8$. The primary photoprocess upon visible irradiation (300–500 nm) of such metal–metal-bonded dimers is metal–metal bond homolysis, yielding two metal-centered radicals.[25] For example, $Re_2(CO)_{10}$ has a UV absorption at 313 nm (ϵ = 1.55 × 10^4 M^{-1} cm^{-1}) which arises from a $\sigma \rightarrow \sigma^*$ transition;[26,27] photolysis at 313 or 366 nm generates $\cdot Re(CO)_5$.[27] Time-resolved IR spectroscopy has recently allowed direct observation of $\cdot Mn(CO)_5$ (along with some $Mn_2(CO)_9$) after flash photolysis of $Mn_2(CO)_{10}$.[28] Irradiation of $H_2Os_2(CO)_8$, which shows a UV absorption at 286 nm with ϵ = 4.37 × 10^3 M^{-1} cm^{-1},[29] must therefore generate $H\dot{O}s(CO)_4$ according to eq 6.

 (6)

$$\underset{(OC)_4}{\overset{H}{Os}} - \underset{(OC)_4}{\overset{H}{Os}} \xrightarrow{h\nu} 2H\dot{O}s(CO)_4 \qquad (6)$$

Irradiation of solutions containing such metal–metal-bonded dimers (e.g., $Re_2(CO)_{10}$,[16] $[CpW(CO)_3]_2$[22]) was known to initiate a number of radical-chain reactions (e.g., $Ph_3P + HRe(CO)_5 \rightarrow HRe(CO)_4PPh_3$,[16] $Ph_3P + CpW(CO)_3H \rightarrow CpW(CO)_2(PPh_3)H$[22]). We therefore irradiated with Pyrex-filtered light a benzene solution of $H_2Os(CO)_4$, $H_2Os_2(CO)_8$ (10% of $H_2Os(CO)_4$), and excess Ph_3PAuCH_3. (No reaction occurred under

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(29) $H_2Os(CO)_4$, which lacks the Os–Os bond, shows λ_{max} at 225 nm and no significant absorption above 280 nm.

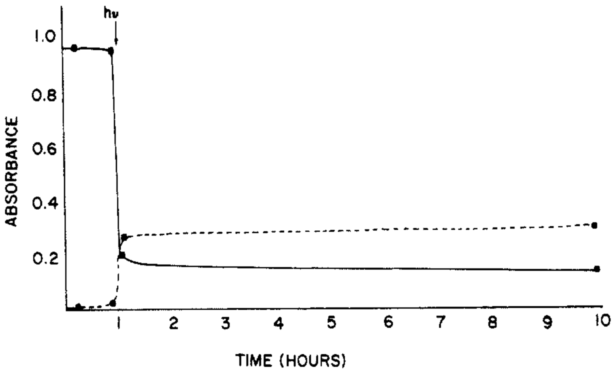


Figure 3. Absorbance (in 0.1-mm cells) at 2049 cm^{-1} due to $H_2Os(CO)_4$ (—), and absorbance at 2035 cm^{-1} due to $(Ph_3PAu)_2Os(CO)_4$ (**2**) (- - -), arising from a solution originally 0.032 M in Ph_3PAuCH_3, 1.4×10^{-3} M in $H_2Os(CO)_4$, and 1.1×10^{-4} M in $H_2Os_2(CO)_8$. The solution was briefly (3 min) irradiated after 1 h as shown.

the same conditions without $H_2Os_2(CO)_8$.) As illustrated in Figure 3, 3 min of irradiation converted 80% of the starting material to product, although the same solution had shown virtually no reaction during an hour prior to irradiation. This dramatic increase

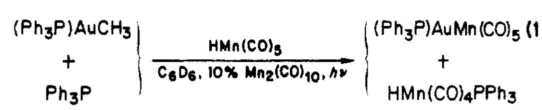
$$2(Ph_3P)AuMe + H_2Os(CO)_4 \xrightarrow[10\%\ H_2Os_2(CO)_8]{h\nu} CH_4 + \underset{\mathbf{2}}{(Ph_3PAu)_2Os(CO)_4} \quad (7)$$

in rate (the rate of the $H_2Os_2(CO)_8/h\nu$ reaction was at least 100 times faster than the maximum rate observed for reaction 3 under any other conditions) confirmed that $\dot{H}Os(CO)_4$, or some species derived from it,[30,31] was the chain carrier for reaction 3, and therefore for reaction 4 as well.

Radical-Chain Reactions of Ph_3PAuCH_3 with Other Hydrides. In the absence of initiator and with careful exclusion of air, reaction 2 (Ph_3PAuCH_3/$HMn(CO)_5$) occurred very slowly at ambient temperature (<5% in 22 h). However, photolysis for 3 min in the presence of 10% $Mn_2(CO)_{10}$ (known[25-28] to give rise to $\cdot Mn(CO)_5$ radicals) caused the reaction to go to 53% completion. Photolysis of a 1:1:1 mixture of $HMn(CO)_5$, Ph_3PAuCH_3, and PPh_3 containing 10% $Mn_2(CO)_{10}$ (an experiment similar to

$$(Ph_3P)AuCH_3 + HMn(CO)_5 \xrightarrow[10\%\ Mn_2(CO)_{10}]{h\nu} CH_4 + \underset{\mathbf{1}}{(Ph_3P)AuMn(CO)_5} \quad (8)$$

reaction 5, but with photochemical rather than thermal initiation) showed the simultaneous formation of **1** and $HMn(CO)_4PPh_3$.



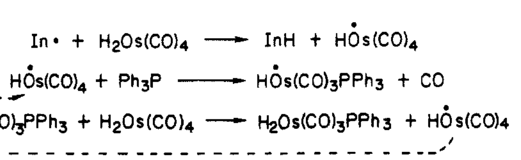
$$\left.\begin{matrix}(Ph_3P)AuCH_3\\ +\\ Ph_3P\end{matrix}\right| \xrightarrow[C_6D_6,\ 10\%\ Mn_2(CO)_{10},\ h\nu]{HMn(CO)_5} \left|\begin{matrix}(Ph_3P)AuMn(CO)_5\ (\mathbf{1})\\ +\\ HMn(CO)_4PPh_3\end{matrix}\right. \quad (9)$$

In view of the established[16] radical-chain nature (with $\cdot Mn(CO)_5$ as the chain carrier) of $Ph_3P + HMn(CO)_5 \rightarrow HMn(CO)_4PPh_3$, this result implied that reaction 2 proceeded by a radical-chain mechanism with $\cdot Mn(CO)_5$ as the chain carrier. The fact that the $HMn(CO)_4PPh_3$/**1** ratio at the end of experiment 9 (which had contained insufficient $HMn(CO)_5$ to react completely with both substrates) was 9:1 suggested that $\cdot Mn(CO)_5$ was more reactive toward Ph_3P than toward $(Ph_3P)AuCH_3$.

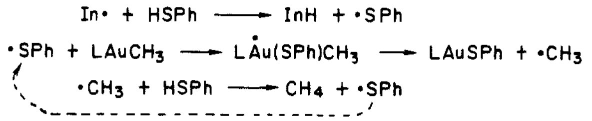
To our surprise, $HRe(CO)_5$ proved completely unreactive toward Ph_3PAuCH_3, despite the fact that the expected product **5** had been prepared from $[Re(CO)_5]^-$ and Ph_3PAuCl.[32] No

$$(Ph_3P)AuCH_3 + HRe(CO)_5 \not\rightarrow CH_4 + \underset{\mathbf{5}}{(Ph_3P)AuRe(CO)_5} \quad (10)$$

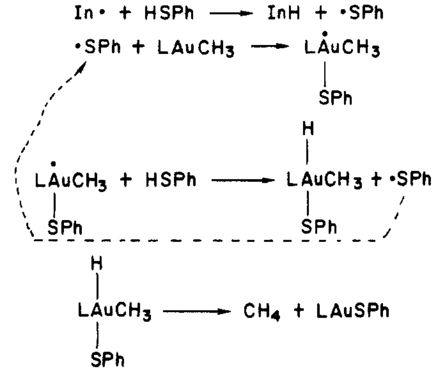
Scheme I



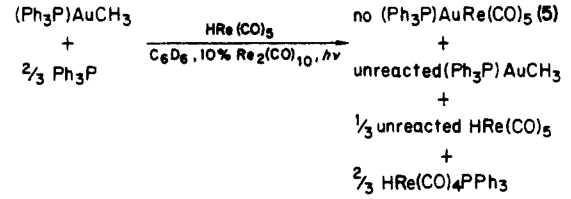
Scheme II



Scheme III



amount of added AIBN (even a stoichiometric amount at 90 °C!) would initiate the reaction, and photolysis in the presence of added $Re_2(CO)_{10}$ also had no effect. Photolysis in the presence of $^2/_3$ of an equivalent of Ph_3P gave immediate formation of $HRe(CO)_4PPh_3$—demonstrating that $\cdot Re(CO)_5$ radicals had been generated—but left the Ph_3PAuCH_3 unchanged.



$$\begin{matrix}(Ph_3P)AuCH_3\\ +\\ ^2/_3\ Ph_3P\end{matrix} \xrightarrow[C_6D_6,\ 10\%\ Re_2(CO)_{10},\ h\nu]{HRe(CO)_5} \begin{matrix}\text{no } (Ph_3P)AuRe(CO)_5\ (\mathbf{5})\\ +\\ \text{unreacted}(Ph_3P)AuCH_3\\ +\\ ^1/_3\ \text{unreacted } HRe(CO)_5\\ +\\ ^2/_3\ HRe(CO)_4PPh_3\end{matrix} \quad (11)$$

Discussion

Radical-chain mechanisms are well-estalbished for phosphine substitution on metal carbonyl hydrides, particularly $HRe(CO)_5$,[16,21] and it is hardly surprising to find one operating for phosphine substitution on the closely related $H_2Os(CO)_4$. Assuming that the chain carrier is $\dot{H}Os(CO)_4$ itself,[30] reaction 4 must proceed by the mechanism in Scheme I, parallel to the known mechanism for $Ph_3P + HRe(CO)_5 \rightarrow HRe(CO)_4PPh_3$ with $\cdot Re(CO)_5$ as a chain carrier. In view of the good evidence[30,31] that the reaction of $\cdot Re(CO)_5$ and Ph_3P is associative, it is likely that the reaction of $\dot{H}Os(CO)_4$ with Ph_3P is associative.

In contrast, there is no known mechanism which immediately suggests a parallel mechanism for reactions 2 and 3. A radical-chain process has, however, been proposed for another reaction of LAuMe (reaction 12).[33] One mechanism suggested, Scheme

$$LAuCH_3 + HSPh \rightarrow LAuSPh + CH_4 \quad (12)$$
$$(L = Me_3P,\ MePh_2P,\ \text{and}\ Ph_3P)$$

II, involves displacement of a methyl radical from $LAuCH_3$ by attack of $\cdot SPh$, either by a concerted or a stepwise S_H2 mechanism. The other mechanism suggested, Scheme III, involves hydrogen atom abstraction by a gold-centered radical after $\cdot SPh$ attack on

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(30) In view of the evidence showing that neither $\cdot Mn(CO)_5$[28] nor $\cdot Re(CO)_5$[31] readily dissociates CO, it seems likely that the chain carrier for reactions 3 and 4 is $\dot{H}Os(CO)_4$ itself.

(31) Fox, A.; Malito, J.; Poë, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1052.

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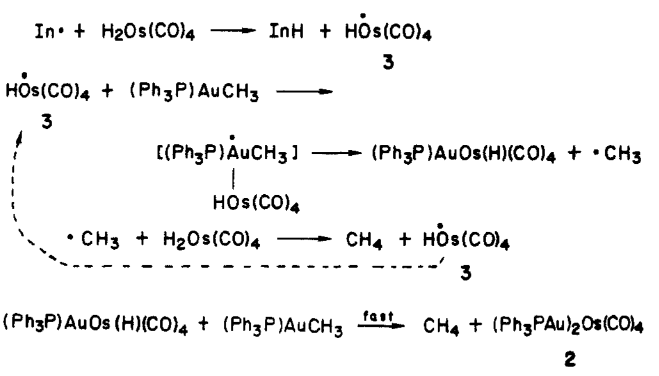
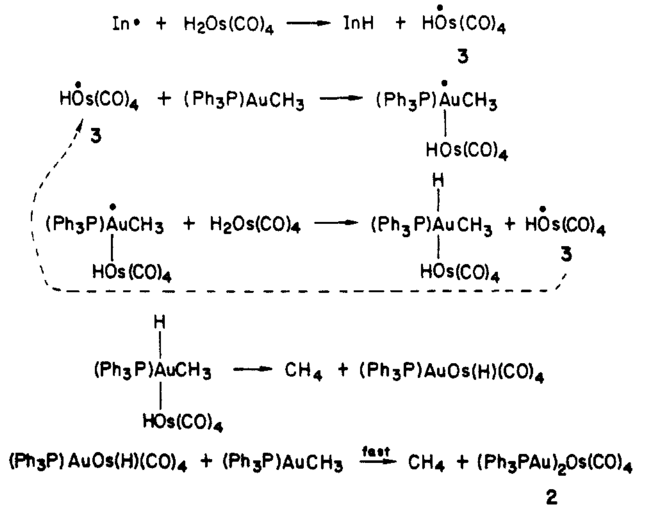
(33) Johnson, A.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1975**, 115.

Scheme IV



Scheme V



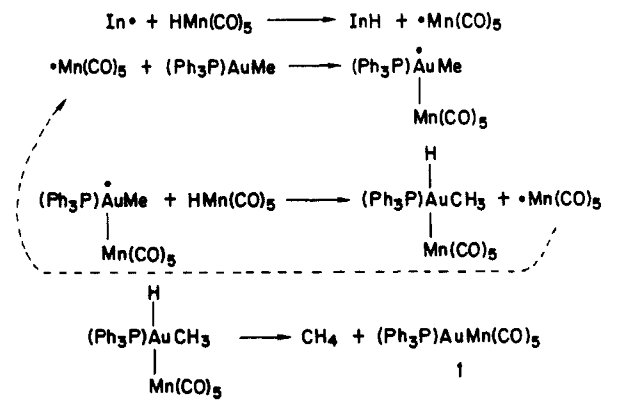
$LAuCH_3$; the resulting gold(III) hydridomethyl complex then eliminates methane, leaving LAuSPh.

If one replaces HSPh by $H_2Os(CO)_4$ and ·SPh by $H\dot{O}s(CO)_4$, Schemes II and III give rise to Schemes IV and V for reacion 3. As in Scheme II, the second step of Scheme IV may be either a concerted or a stepwise S_H2 reaction.

Both Schemes IV and V involve the same chain carrier, **3**, as Scheme I—as required by the results of the coinitiation experiment. In both Schemes IV and V, the second hydrogen in $H_2Os(CO)_4$ must react rapidly with a second $(Ph_3P)AuCH_3$ in order to account for the fact that no spectroscopically observable intermediate builds up. It is reasonable to suppose that this second methane elimination ($Ph_3PAuOs(H)(CO)_4 + Ph_3PAuCH_3 \rightarrow CH_4 + (Ph_3PAu)_2Os(CO)_4$) also occurs by a radical-chain mechanism, but it is not at all clear why it is faster than the first methane elimination. An Au–Au interaction, of the sort seen in the X-ray structure of the product **2**, may be involved. In any case, the structural and electronic analogy between H and Ph_3PAu[34] makes it reasonable for hydrogen atom abstraction from the presumed intermediate $Ph_3PAuOs(H)(CO)_4$ to be as fast as abstraction from $H_2Os(CO)_4$.

Scheme V may be regarded as a radical-chain oxidative addition of an H–Os bond of $H_2Os(CO)_4$ across the Au in Ph_3PAuCH_3. As such, it finds precedent in the well-established[35] radical-chain oxidative additions of alkyl halides to complexes containing low-valent transition metals. However, the result of the H–Os addition in Scheme V, and the H–S addition proposed by Puddephatt[33] in Scheme III, is the formation of an Au–H bond. Such bonds are generally believed to be weak (no mononuclear gold hydrides are known, although hydride bridges between gold and other metals have recently been reported[36]), and thus their formation by H· transfer from H–Os and H–S bonds is an unattractive feature of Schemes III and V.

Scheme VI



Of course, Schemes II and IV have their own unattractive feature, the formation of methyl radicals from LAuMe and ·SPh or $H\dot{O}s(CO)_4$ in an S_H2 reaction; the results given above (no formation of toluene in benzene) offer no evidence in support of the presence of methyl radicals in reaction 3.[37,38] Given the present lack of reliable thermochemical information for organometallic systems, it is not possible to make a definitive choice between Schemes IV and V—or between these and any other radical-chain mechanism involving $H\dot{O}s(CO)_4$. On balance, we prefer Scheme V—the simplest explanation for our observations, and the one best supported by analogy. Its corollary for reaction 2, Scheme VI, offers a relatively straightforward explanation of the fact that $HRe(CO)_5$ does not react and $HMn(CO)_5$ does. It is generally believed[39–41] that the Re–H bond is stronger than the Mn–H one, and it is possible that the Re–H bond is stronger than the Os–H one. (Rhenium shows an exceptional ability to form stable polyhydrides, e.g., ReH_9^{2-},[42] and $HRe(CO)_5$ is a weaker acid than $H_2Os(CO)_4$.[3c]) An Re-to-Au H· transfer may thus be endothermic when the corresponding Mn-to-Au and Os-to-Au transfers are exothermic.

Overall, it is clear that reactions 2 and 3 proceed by radical-chain mechanisms and that the chain carriers are $\cdot Mn(CO)_5$ and $H\dot{O}s(CO)_4$, respectively. Such radical-chain mechanisms for intermolecular C–H bond formation, while not previously reported, are likely to prove common, particularly when the alkyl complex can readily undergo oxidative addition. The formation of $M_2Pt(CO)_{12}$ in reaction 13[43] is almost certainly another example.

$$Me_2Pt(cyclooctadiene) + 2HM(CO)_5 \xrightarrow{CO} 2CH_4 + M_2Pt(CO)_{12} \quad (13)$$

Experimental Section

General. IR spectra were obtained on a Beckman IR-12 spectrometer. NMR kinetics measurements were made on a JEOL FX-100 FT spectrometer. UV-visible spectra were obtained on either a Cary 17 spectrophotometer or a Varian 620 spectrophotometer. Unless otherwise

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[37] In reaction 12, Puddephatt[33] observed some Me(*t*-Bu)NO by EPR when *t*-BuNO was added, but on a variety of grounds, principally the failure of added *t*-BuNO to affect the rate, he favored Scheme III over Scheme II.

[38] It is quite possible that methyl radicals are formed in reaction 3 (i.e., Scheme IV) but are trapped so effectively by $H_2Os(CO)_4$ that their lifetime is too short for reaction with solvent.

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specified, all operations were carried out under a nitrogen atmosphere by using standard vacuum-line or inert atmosphere techniques. Nitrogen was purified by passage through BTS catalyst (BASF) and 3-Å molecular sieves.

Toluene was distilled under nitrogen from sodium and benzophenone. Benzene used for kinetics and benzene-d_6 used for NMR studies were dried over P_4O_{10}, frozen, and degassed at least 3 times and transferred under vacuum either directly into a kinetics vial or into a storage vessel.

Infrared extinction coefficients for carbonyl bands of $H_2Os(CO)_4$, $H_2Os(CO)_3PPh_3$ (**4**), and *cis*-$[PPh_3Au]_2Os(CO)_4$ (**2**), determined from the absorbance of solutions of known concentration, were as follows: $H_2Os(CO)_4$, 6.1 × 10^2 (2049 cm^{-1}); **4**, 2.4 × 10^2 (2081 cm^{-1}), 2.9 × 10^2 (2023 cm^{-1}); **2**, 2.8 × 10^2 (2035 cm^{-1}) cm^{-1} M^{-1}.

Compounds. The compounds $H_2Os(CO)_4$,[17] PPh_3AuCH_3,[44] and $HMn(CO)_5$[45] (M = Mn and Re) were prepared by published methods. Triphenylphosphinemethylgold(I) was recrystallized at least twice from CH_2Cl_2/hexane immediately before each kinetics run. $H_2Os(CO)_4$ was purified on a vacuum line by passage through a U-tube packed with P_4O_{10} interspersed among glass beads and was stored under vacuum at −30 °C.

Preparation of $H_2Os_2(CO)_8$. A 24-cm long vacuum line reaction bulb was charged with $H_2Os(CO)_4$ (132.3 mg, 0.435 mmol) and was placed under 10 mmHg CO pressure. A 1-in. span in the middle of the bulb was heated with nichrome wire, while the lower half of the bulb was immersed in ice water. After 20 min, droplets of a clear viscous liquid (presumably $H_2Os_2(CO)_8$) appeared on the cold portion of the surface directly below the nichrome heating coil. The process was continued for 12 h, after which a copious amount of viscous liquid and yellow solid appeared to be present. Ambient temperature volatiles were removed in vacuo, and under nitrogen, the remaining materials were dissolved in 6 mL of hexane. The resultant solution was transferred to a 25-mL round-bottom flask, the solvent was removed in vacuo, and the $H_2Os_2(CO)_8$ remaining was purified by bulb-to-bulb evaporative distillation at 40 °C: yield (based on $H_2Os(CO)_4$) 21%. The infrared spectrum was consistent with that reported in the literature.[46] The UV spectrum in decane showed a peak at 286 nm, ϵ = 4.37 × 10^3 cm^{-1} M^{-1}, and one at 231 nm, ϵ = 3.45 × 10^3 cm^{-1} M^{-1}.

Kinetics of Ph_3PAuCH_3 + $H_2Os(CO)_4$. General. All kinetic and other studies of the Ph_3PAuCH_3/$H_2Os(CO)_4$ system were performed at 35 °C. Calcium fluoride (1 mm) or KBr (0.1 mm) cells used for infrared measurements were purged with nitrogen or argon prior to each measurement. The carbonyl stretches at 2071 and 2049 cm^{-1} of the reactant *cis*-$H_2Os(CO)_4$ were easily monitored, as was that of the product, **2**, which falls at 2035 cm^{-1}. All reactions were carried out in a 25-mL vacuum-line reaction bulb equipped with a Teflon stopcock.

In a typical run, a bulb was charged with Ph_3PAuCH_3 (0.074 M) and toluene, the solution was frozen and degassed several times, and $H_2Os(CO)_4$ (3 × 10^{-3} to 10^{-2} M) was transferred in under vacuum. The reaction mixture was sampled by quenching the solution at 0 °C and removing an aliquot by syringe under a heavy flow of nitrogen or argon. The product *cis*-$[PPh_3Au]_2Os(CO)_4$, **2**, was identified by its IR, reported in the literature.[9] Apparent rate constants varied from 1.3 × 10^{-4} to <6.0 × 10^{-6} s^{-1} (no detectable reaction).

Ph_3PAuCH_3 + $H_2Os(CO)_4$ with Added Initiator (AIBN). A solution of Ph_3PAuCH_3 (0.074–0.073 M) and $H_2Os(CO)_4$ (about 1.5 × 10^{-3} M) was prepared as above, and some initial data points were taken. AIBN (approximately 15 mol % of the $H_2Os(CO)_4$) was then added either as a solid or as an aliquot (i.e., 0.1 mL of a 0.015 M solution in toluene or benzene) under a heavy stream of nitrogen. Monitoring at 2049 cm^{-1} was then continued as described above. The results are shown in Figure 1. After initiation, the apparent rate constant was about 7 × 10^{-5} s^{-1}.

PPh_3 Substitution of $H_2Os(CO)_4$. *cis*-Dihydridotetracarbonylosmium(II), (0.88 mg, 2.90 × 10^{-3} mmol) was transferred in vacuo to a standard vacuum-line reaction bulb containing PPh_3 (7.8 mg, 2.98 × 10^{-2} mmol), AIBN (1.0 mg, 6.0 × 10^{-3} mmol), and benzene (2 mL) and the resultant solution frozen and degassed several times. The reaction was then sampled at appropriate intervals. Spectroscopic data for the product $H_2Os(CO)_4PPh_3$ (**4**) agreed with that given in the literature.[23] Infrared carbonyl bands of the disubstituted product $H_2Os(CO)_2(PPh_3)_2$, expected at 2014 (vs) and 1990 cm^{-1} (vs),[47] were not observed.

Ph_3PAuCH_3/PPh_3 Simultaneous Reaction with *cis*-$H_2Os(CO)_4$ (IR Study). A standard vacuum-line reaction bulb was charged with Ph_3PAuCH_3 (2.3 mg, 4.85 × 10^{-3} mmol), PPh_3 (1.4 mg, 5.34 × 10^{-3} mmol), AIBN (0.1 mg, 6.7 × 10^{-4} mmol), *cis*-$H_2Os(CO)_4$ (1.46 mg, 4.80 × 10^{-3} mmol), and benzene (4 mL). The resultant solution was frozen and degassed several times. After 3 days, **4** was identified by the appearance of its infrared bands at 2081 and 2023 cm^{-1}.[23] The other product, **2**, was similarly identified by its infrared carbonyl band at 2035 cm^{-1}.[9] The ratio of products, calculated from the relative absorbances of the 2081-cm^{-1} band of $H_2Os(CO)_3PPh_3$ and the 2035-cm^{-1} band of *cis*-$[PPh_3Au]_2Os(CO)_4$, was found to be 60:40 for **4**:**2**.

Ph_3PAuCH_3/PPh_3 Competition for *cis*-$H_2Os(CO)_4$ (NMR Study). An NMR tube was charged with Ph_3PAuCH_3 (23 mg, 4.85 × 10^{-2} mmol), PPh_3 (12.5 mg, 4.77 × 10^{-2} mmol), and AIBN (1.1 mg, 6.55 × 10^{-3} mmol). Benzene-d_6 (0.3 mL) and *cis*-$H_2Os(CO)_4$ (15 mg, 4.93 × 10^{-2} mmol) were transferred in under vacuum, and the tube was sealed. The initial spectrum showed a small amount of reaction (<5%) between PPh_3, Ph_3PAuCH_3, and *cis*-$H_2Os(CO)_4$. The tube was heated at 35 °C for 2 h after which a decrease in all reactants was observed. A peak at δ 0.18 due to methane was now present, in addition to a doublet at δ −7.51 (J = 24 Hz) due to $H_2Os(CO)_3PPh_3$ (indicating an all-cis geometry).[23] The ratio of products, calculated from the decrease in the integral of the Ph_3PAuCH_3 methyl peak and the increase in the integral for the $H_2Os(CO)_4PPh_3$ doublet, was found to be 62:38 for **4**:**2**, in good agreement with that found in the analogous IR experiment (above).

Initiation of $H_2Os(CO)_4$ + Ph_3PAuCH_3 by $H_2Os_2(CO)_8$ Photolysis. A standard vacuum-line reaction bulb was charged with Ph_3PAuCH_3 (30 mg, 6.33 × 10^{-2} mmol), *cis*-$H_2Os(CO)_4$ (0.85 mg, 2.80 × 10^{-3} mmol), $H_2Os_2(CO)_8$ (0.13 mg, 2.16 × 10^{-4} mmol), and benzene (2 mL). The resultant solution was shielded from light during the initial reaction and IR sampling period and then irradiated with a 450-W mercury lamp (Pyrex-filtered light) for 3 min, resulting in a golden-yellow solution (as expected for **2**). Infrared measurements were resumed immediately after irradiation. The extent of product formation after photolysis (80% conversion to product) was determined from the intensity of the product peak at 2035 cm^{-1}. The concentrations of $H_2Os(CO)_4$ and **2** as a function of time are shown in Figure 3. A similar reaction without $H_2Os_2(CO)_8$ (28 mg of Ph_3PAuCH_3 and 1.88 mg of *cis*-$H_2Os(CO)_4$ in 1.9 mL of toluene) showed no reaction when photolyzed for 5 min in the same apparatus.

Attempted Initiation of $HRe(CO)_5$ + Ph_3PAuCH_3 with AIBN. In a typical experiment, a NMR tube was charged with Ph_3PAuCH_3 (about 0.04 mmol) and AIBN, and under vacuum, solvent and $HRe(CO)_5$ (about 0.04 mmol) were transferred into the tube. No evidence of reaction was seen after 36 h, nor was it possible to induce thermal initiation by heating a stoichiometric amount of AIBN and reactants to 90 °C.

Reaction of Ph_3PAuCH_3, PPh_3, and $HRe(CO)_5$ Initiated by Photolysis of $Re_2(CO)_{10}$. An NMR tube containing Ph_3PAuCH_3 (25 mg, 5.27 × 10^{-2} mmol), $HRe(CO)_5$ (17.4 mg, 5.32 × 10^{-2} mmol), $Re_2(CO)_{10}$ (3 mg, 4.60 × 10^{-3} mmol), and benzene-d_6 (0.3 mL) was prepared under vacuum, and the NMR spectrum (δ 10 to −10) before and after photolysis (3 min, 450-W UV broad-band lamp, Pyrex-filtered) showed only starting materials. Triphenylphosphine (9.0 mg, 3.72 × 10^{-2} mmol) was then added under nitrogen to the contents of the tube. The methyl peak of Ph_3PAuCH_3 now appeared as a singlet at δ 1.10 (due to rapid exchange between free phosphine and the phosphine on Ph_3PAuCH_3). After photolysis, the methyl doublet of Ph_3PAuCH_3 (δ 1.10, J_{PH} = 8 Hz)[44] had now reappeared, the doublet (δ −4.96, J_{PH} = 22 Hz) due to $HRe(CO)_4PPh_3$[48] was present in addition to the singlet of $HRe(CO)_5$ (δ −5.60).

Reaction of $HMn(CO)_5$ + Ph_3PAuCH_3. An NMR tube containing Ph_3PAuCH_3 (28 mg, 5.91 × 10^{-2} mmol), $HMn(CO)_5$ (15.6 mg, 0.0796 mmol), and benzene-d_6 (0.3 mL) was prepared and sealed under vacuum. The reaction was maintained at ambient temperature and monitored by ^1H NMR over a 22-h period. At this time, very little $(CO)_5MnAuPPh_3$ (**1**) had formed (<5% by NMR integration) and a small amount of starting material decomposition had occurred.

Reaction of $HMn(CO)_5$ + Ph_3PAuCH_3 Initiated by Photolysis of $Mn_2(CO)_{10}$. An NMR tube containing $HMn(CO)_5$ (12 mg, 6.12 × 10^{-2} mmol), Ph_3PAuCH_3 (27 mg, 5.70 × 10^{-2} mmol), $Mn_2(CO)_{10}$ (2 mg, 5.13 × 10^{-3} mmol), and benzene-d_6 (0.3 mL) was prepared and sealed under vacuum. The ^1H NMR spectrum (δ 10 to −10) before photolysis showed only starting materials. Photolysis for 3 min with a 450-W broad-band UV lamp (Pyrex-filtered) resulted in the formation of $(CO)_5MnAuPPh_3$ (53%) as determined by the decrease in NMR resonances due to Ph_3PAuCH_3 (δ 1.10, d, J_{PH} = 9 Hz) and $HMn(CO)_5$ (δ −7.42, s) relative to the phenyl region. A peak at δ 0.18 due to methane was also present. The presence of $(CO)_5MnAuPPh_3$ (**1**) was verified by an IR (CCl_4: 1962 (s), 2057 (s) cm^{-1}) in agreement with that reported in the literature.[8]

Photolysis of $HMn(CO)_5$ + Ph_3PAuCH_3 + PPh_3 in the Presence of 10% $Mn_2(CO)_{10}$. An NMR tube containing $HMn(CO)_5$ (6 mg, 3.06 × 10^{-2} mmol), Ph_3PAuCH_3 (15 mg, 3.16 × 10^{-2} mmol), PPh_3 (7.2 mg, 2.75

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× 10^{-2} mmol), $Mn_2(CO)_{10}$ (2 mg, 5.13 × 10^{-3} mmol), and 0.2 mL of benzene-d_6 was prepared and sealed under vacuum. The initial NMR prior to photolysis showed that some reaction (about 63%) had occurred between $HMn(CO)_5$ and PPh_3 to give $HMn(CO)_4PPh_3$ (δ –6.9, d, J_{PH} = 35 Hz).[49] The tube, shielded from light during the initial reaction period, was then photolyzed for 2 min (see above for details). A decrease in both Ph_3PAuCH_3 methyl and $HMn(CO)_5$ hydride integrals relative to the phenyl region integration (which should remain constant) was observed; the **1**/$HMn(CO)_4PPh_3$ ratio thereby indicated was 1:9. A small peak at δ 0.18 due to methane was also now present. The product $HMn(CO)_4PPh_3$ was identified by its infrared spectrum in the carbonyl region (CCl_4, 1962 s, 2057 s).[49]

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Registry No. 1, 14692-78-5; **2**, 99747-68-9; **4**, 99782-58-8; $H_2Os_2(CO)_8$, 25685-05-6; $H_2Os(CO)_4$, 22372-70-9; Ph_3PAuCH_3, 23108-72-7; *cis*-$H_2Os(CO)_4$, 18972-42-4; $HRe(CO)_5$, 16457-30-0; $Re_2(CO)_{10}$, 14285-68-8; $HRe(CO)_4PPh_3$, 25838-69-1; $HMn(CO)_5$, 16972-33-1; $Mn_2(CO)_{10}$, 10170-69-1.

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Experimental Characterization of an Electron-Rich ($\sigma^2\pi^4\delta^2\delta^{*2}$) Metal–Metal Triple Bond. Synthesis, Reactivity, and Photoelectron Spectral Studies of Trimethylphosphine Complexes of Dirhenium(II)

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Abstract: The reaction of $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl or Br) with PMe_3 gives high yields of the triply bonded complexes $Re_2X_4(PMe_3)_4$. These compounds are oxidized by $NOPF_6$ to give paramagnetic $[Re_2X_4(PMe_3)_4]PF_6$, and the chloro derivative reacts with $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2PNHPPh_2$ (dppa) to give $Re_2Cl_4(PMe_3)_2$(dppm) and $Re_2Cl_4(PMe_3)_2$(dppa), respectively. NMR spectroscopy (^1H and $^{31}P\{^1H\}$) shows that the latter complexes possess fairly symmetrical structures in which the PMe_3 ligands are in cis dispositions with respect to the bridging dppm and dppa ligands. The volatility of $Re_2Cl_4(PMe_3)_4$ has permitted the measurement of its gas-phase photoelectron spectrum which accords with this compound possessing a $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration. The δ* ionization band is slightly narrower than the δ ionization band and occurs at about 0.9 eV lower binding energy. The π ionization gives evidence of spin–orbit splitting as expected for the heavy-atom rhenium character. An ionization assigned to removal of an electron from the valence σ orbital is observed at a binding energy 1 eV higher than the π ionization. Comparison of these ionizations with those of the corresponding $W_2Cl_4(PMe_3)_4$ ($\sigma^2\pi^4\delta^2$) complex is especially informative. In particular, these observations support a strong interaction between the valence σ density on one metal atom and the core density on the neighboring metal atom in these complexes.

Complexes with close metal–metal interactions offer special opportunities to investigate the factors that influence metal–metal bonding, electronic structure, and reactivity.[2] Quadruply bonded complexes, which are derived from d^4–d^4 metal interactions and have the $\sigma^2\pi^4\delta^2$ configuration, are especially interesting because they provide occupied orbitals with each symmetry type of metal–metal interaction—σ, π, and δ. Also interesting are species which are related by either the addition or removal of electrons from the $\sigma^2\pi^4\delta^2$ configuration. In particular, "electron-poor" metal–metal triple bonds derived from d^3–d^3 complexes with $\sigma^2\pi^4$ configurations, and "electron-rich" metal–metal triple bonds derived from d^5–d^5 complexes with $\sigma^2\pi^4\delta^2\delta^{*2}$ configurations,[2] serve to expand our knowledge of the range of metal–metal interactions.

Valence photoelectron spectroscopy (PES) has proven to be extremely valuable in providing insight into the electronic interactions in metal–metal bonds, particularly for the quadruple[3-7] and electron-poor triple[8,9] metal–metal bonds. Nonetheless, important questions remain concerning the nature of the δ-ionized

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