2150 *Organometallics* **1985**, *4*, 2150–2160

mp 158 °C. Anal. Calcd for $C_{24}H_{38}O_2Si$: C, 74.57; H, 9.91. Found: C, 74.95; H, 9.97.

α- and β-(3-(Dimethyl-*tert*-butylsiloxy)-17β-hydroxyestra-1,3,5(10)triene)tricarbonylchromium, 10 and 11. Monosilylated estradiol **9** (3.2 g, 8.3 mmol) and $Cr(CO)_6$ (3.7 g, 16 mmol) were heated under reflux in dibutyl ether (150 mL) during 8 h. After filtration and solvent removal, the residue was chromatographed on a silica gel (Merck 7734) column using ether/petroleum ether (1:1) as eluent. The first fraction was identified as **10** (1.27 g, 2.4 mmol; 29%), mp 220 °C. Anal. Calcd for $C_{27}H_{38}O_5CrSi$: C, 62.05; H, 7.33. Found: C, 61.82; H, 7.27. The second fraction was identified as **11** (1.8 g, 3.4 mmol; 41.5%), mp 179 °C. Anal. Calcd for $C_{27}H_{38}O_5CrSi$: C, 62.05; H, 7.33. Found: C, 62.00; H, 7.30.

α- and β-(3-(*tert*-Butyldimethylsiloxy)-17-hydroxyestra-1,3,5(10)-triene)dicarbonyl(thiocarbonyl)chromium, 12 and 13. Following the method of Jaouen et al.,[27] the $Cr(CO)_3$ complex **10** (0.52 g, 1.0 mmol) was photolysed in benzene/cyclooctene (150 mL/25 mL) and treated with triphenylphosphine (1 g) and CS_2 (25 mL). After removal of solvent, the residue was chromatographed on a silica gel (Merck 9385) column using ether/petroleum ether (3:2) as eluent. The yellow solid was identified as **12** (0.06 g, 0.11 mmol; 11%), mp 142 °C. The mass spectrum showed peaks at *m/z* 482 $[M - 2CO]^+$ and 386 $[M - Cr(CO)_2CS]^+$. The molecule **12** was identified by X-ray crystallography.[7] Likewise, **11** yielded **13** (35%), mp 125 °C. The mass spectrum showed peaks at *m/z* 482 $[M - 2CO]^+$, 438 $[M - 2CO - CS]^+$, and 386 $[M - Cr(CO)_2CS]^+$.

α- and β-(3,17β-Bis(dimethyl-*tert*-butylsiloxy)estra-1,3,5(10)-triene)tricarbonylchromium, 14 and 15. As with the corresponding benzyl analogues, the monosilylated estradiol complex **10** (7.5 g, 14 mmol) was treated with 50% NaH (6.72 g, 140 mmol) and t-$BuMe_2Cl$ (6.39 g, 43 mmol). The yellow solid obtained after chromatography (silica gel column (Merck 7734), using ether/petroleum ether (1:10) as eluent) was identified as **14** (8.7 g, 13.6 mmol; 96%), mp 255 °C. Calcd for $C_{33}H_{52}O_5CrSi_2$: C, 62.22; H, 8.23. Found: C, 62.32; H, 8.27. The mass spectrum showed peaks at *m/z* 636 $[M]^+$, 580 $[M - 2CO]^+$, 552 $[M - 3CO]^+$, and 500 $[M - Cr(CO)_3]^+$. Analogously, **15** was obtained from **11** (93%), mp 253 °C. Anal. Calcd for $C_{33}H_{52}O_5CrSi_2$: C, 62.22; H, 8.23. Found: C, 61.98; H, 8.40. The mass spectrum showed peaks at *m/z* 636 $[M]^+$, 580 $[M - 2CO]^+$, 552 $[M - 3CO]^+$, and 500 $[M - Cr(CO)_3]^+$.

3,17β-Bis(dimethyl-*tert*-butylsiloxy)estra-1,3,5(10)-triene, 16. The disilylated complex **14** (or **15**) (636 mg, 1.0 mmol) was dissolved in ether and exposed to sunlight during 3 h.[26] After filtration and evaporation of the solvent, the residual white solid was recrystallized from ether/petroleum ether and identified as **16** (425 mg, 0.85 mmol; 85%), mp 120 °C.

Acknowledgment. We thank the C.N.R.S. (France) and N.S.E.R.C. (Canada) for financial support.

Registry No. **1**, 50-28-2; **2**, 77109-92-3; **3**, 98757-31-4; **4**, 98688-30-3; **5**, 98757-32-5; **6**, 88729-93-5; **7**, 88765-18-8; **8**, 98688-31-4; **9**, 57441-02-8; **10**, 93036-14-7; **11**, 98757-33-6; **12**, 93173-93-4; **13**, 98757-34-7; **14**, 91795-23-2; **15**, 91841-08-6; **16**, 57711-41-8; $Cr(CO)_6$, 13007-92-6.

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(27) Jaouen, G.; Simonneaux, G. *Inorg. Synth.* **1979**, *XIX*, 197.

Intermolecular Formation of C–H Bonds: Application to the Synthesis of Heterobimetallic Complexes

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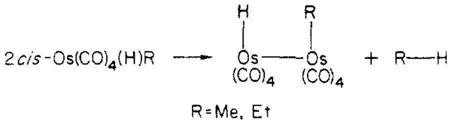
The reactions of various alkylmetal carbonyl complexes (e.g., $MeMn(CO)_5$, $EtRe(CO)_5$, $MeFe(CO)_2Cp$, $Me_2Os(CO)_4$) with various transition-metal hydrides (e.g., $HRe(CO)_5$, $H_2Os(CO)_4$, $HMn(CO)_5$, $HW(CO)_3Cp$) have been examined in solvents of different coordinating abilities. In coordinating solvents the metal-containing products are solvated dinuclear complexes; in noncoordinating solvents the metal-containing products are polynuclear hydrides, formed by the coordination of a second equivalent of the hydride reactant. The vacant coordination site is created on the metal that originally bears the alkyl ligand: in CH_3CN, $MeMn(CO)_5$ and $HRe(CO)_5$ give $(CH_3CN)Mn(CO)_4Re(CO)_5$, whereas $EtRe(CO)_5$ and $HMn(CO)_5$ give $(CH_3CN)Re(CO)_4Mn(CO)_5$. The organic products eliminated are generally aldehydes (although alkane elimination is also seen, particularly when the initial alkyl carbonyl complex is a dialkyl). The reaction is fastest in coordinating solvents and for the alkyl carbonyl complexes that most readily form acyls: $MeMn(CO)_5$ and those complexes of other metals (e.g., $EtRe(CO)_5$) that contain alkyl groups that migrate more readily than methyl. When heated in acetonitrile solution, $EtRe(CO)_5$, i-$BuRe(CO)_5$, and some other alkyl carbonyl complexes equilibrate with solvated acyl complexes such as *cis*-$RC(O)(CH_3CN)Re(CO)_4$; these solvated acyl complexes react rapidly at low temperatures with hydrides to eliminate aldehydes. In favorable cases, the reactions of alkyl carbonyls with transition-metal hydrides are synthetically attractive routes to heterobimetallic complexes.

The intermolecular formation of C–H bonds from alkyl carbonyl complexes and transition-metal hydrides has attracted the attention of several research groups. We have shown that alkane elimination from *cis*-$Os(CO)_4(H)R$ according to eq 1 is intermolecular, and have proposed that



$$2\,cis\text{-}Os(CO)_4(H)R \longrightarrow \underset{(CO)_4}{\overset{H}{Os}}-\underset{(CO)_4}{\overset{R}{Os}} + R-H \qquad (1)$$

R = Me, Et

the rate-determining step is the formation of a coordinatively unsaturated acyl intermediate from *cis*-$Os(CO)_4(H)R$.[1] Bergman and co-workers[2] have proposed that rate-determining formation of an acyl from $CpMo(CO)_3R$ precedes the formation of aldehydes in eq 2. Halpern and

$$CpMo(CO)_3R + CpMo(CO)_3H \rightarrow RCHO + {}^1/_2Cp_2Mo_2(CO)_6 + {}^1/_2Cp_2Mo_2(CO)_4 \qquad (2)$$

R = Me, Et

co-workers[3] have proposed that rate-determining formation

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(1) (a) Okrasinski, S. J.; Norton, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 295. (b) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (c) Carter, W. J.; Okrasinski, S. J.; Norton, J. R. *Organometallics* **1985**, *4*, 1376.

(2) (a) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415. (b) Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 5447.

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Table I. Reactions of Mn and Re Alkyl Carbonyl Complexes with Transition-Metal Hydrides

hydride	hydride/alkyl ratio	organic product	organometallic product(s)	derivative for characterization	yield of organometallic derivative
$MeMn(CO)_5$ (0.2 M) in CH_3CN at 25–30 °C[a]					
$HRe(CO)_5$	1:1	CH_3CHO	$Re(CO)_5Mn(CO)_4(CH_3CN)$	$Re(CO)_5Mn(CO)_4(PPh_3)$	95%[b]
$H_2Os(CO)_4$	1:2	CH_3CHO	$Os(CO)_4[Mn(CO)_4(CH_3CN)]_2$[d]	$Os(CO)_4[Mn(CO)_5]_2$	62%[c]
$HMoCp(CO)_3$	2:1	CH_3CHO	not identified[e]		
$HWCp(CO)_3$	1:1	CH_3CHO	$CpW(CO)_3Mn(CO)_4(CH_3CN)$[d]	$CpW(CO)_3Mn(CO)_5$	
$HGePh_3$	1:1	CH_3CHO	not identified		
$EtRe(CO)_5$ (0.2 M) in CH_3CN at 55–60 °C[f]					
$HRe(CO)_5$	1:1	EtCHO	$Re_2(CO)_9(CH_3CN)$	(same)	70%
$H_2Os(CO)_4$	2:1	EtCHO	$Os(CO)_4[Re_2(CO)_4(CH_3CN)]_2$[d]	$Os(CO)_4[Re(CO)_5]_2$	67%
$HMn(CO)_5$	1:1	EtCHO	$Mn(CO)_5Re(CO)_4(CH_3CN)$	$Mn(CO)_5Re(CO)_4(PPh_3)$	84%
$HWCp(CO)_3$	1:1	EtCHO	$CpW(CO)_3Re(CO)_4(CH_3CN)$[d]	$CpW(CO)_3Re(CO)_5$	56%
$HWCp(CO)_2PMe_3$	1:1	EtCHO	not identified	$CpW(CO)_2(PMe_3)Re(CO)_5$	56%
$HCrCp(CO)_3$	3:2	EtCHO	not identified	$CpCr(CO)_3Re(CO)_5$	
$MeMn(CO)_5$ (0.2 M) in C_6H_6 at 25 °C					
$HRe(CO)_5$	1:1	CH_3CHO	$HMnRe_2(CO)_{14}$	(same)	73%
$H_2Os(CO)_4$	1:2	CH_3CHO	$HMnOs_2(CO)_{12}$, $HMnOs_3(CO)_{16}$[g]	(same)	23%
$EtRe(CO)_5$ (0.2 M) in C_6H_6 at 60 °C					
$HRe(CO)_5$	1:1	EtCHO	$HRe_3(CO)_{14}$[g]	(same)	46%
$H_2Os(CO)_4$	1:2	EtCHO	$HReOs_2(CO)_{12}$, $HReOs_3(CO)_{16}$[g]	(same)	

[a] Organic yield quantitative. [b] Yield 64% in THF. [c] Yield 68% in THF. [d] Not isolated; observed spectroscopically and characterized by conversion to the derivative in the right-hand column. [e] $HMoCp(CO)_3$ decomposes to C_5H_6 and $Mo(CO)_3(CH_3CN)_3$ in CH_3CN: Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. [f] Organic yield >88%. [g] Several other heteronuclear cluster hydride complexes were formed in low yield, and homonuclear cluster hydrides (e.g., $H_2Os_3(CO)_{10}$, $H_2Re_2(CO)_8$) were present in small amounts.

Table II. Reactions of Other Alkyl Carbonyl Complexes with Transition-Metal Hydrides[a]

reactants	temp, °C	organic products	organometallic products
FpMe (0.25 M) + $HMn(CO)_5$ (1:1)[b]	55	CH_3CHO	$Mn_2(CO)_9(CH_3CN) + Fp_2$
FpMe (0.25 M) + $H_2Os(CO)_4$ (2:1)[b]	55	CH_3CHO	
FpMe (0.26 M) + $HRe(CO)_5$ (1:1)[b,c]	55	CH_3CHO	$Re_2(CO)_9(CH_3CN) + Fp_2$
FpEt (0.17 M) + $HRe(CO)_5$ (1:2)	47	EtCHO	$Re_2(CO)_9(CH_3CN) + Fp_2$
$Me_2Os(CO)_4$ (0.21 M) + $H_2Os(CO)_4$ (1:4)[d]	80	$CH_4 + CH_3CHO$ + EtOH (1:.4:.2)	
$Me_2Os(CO)_4$ (0.18 M) + $HRe(CO)_5$ (1:6)[b,d]	80	$CH_4 + CH_3CHO$ + EtOH (.8:.3:1)	
$Me_2Os(CO)_4$ (0.16 M) + $HRe(CO)_5$ (1:4)[b,c]	60	$CH_4 + CH_3CHO$ (1:1)	$OsRe_2(CO)_{13}(CH_3CN)$
$Et_2Os(CO)_4$ (0.15 M) + $HRe(CO)_5$ (1:2)	49	C_2H_6 + EtCHO (1:1)	$OsRe_2(CO)_{13}(CH_3CN)$
$EtOsRe(CO)_9$ (0.05 M) + $HRe(CO)_5$ (1:3)	50	EtCHO	$EtC(O)Os(CO)_3(CH_3CN)Re(CO)_5$
$Et(Cl)Os(CO)_4$ (0.06 M) + $HRe(CO)_5$ (1:1)	50	EtCHO	
$Me(Cl)Os(CO)_4$ (0.23 M) + $HRe(CO)_5$ (1:2)	50	CH_4 + a small amount of CH_3CHO	

[a] In CH_3CN unless otherwise noted; Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$. [b] Did not go to completion due to hydride decomposition. [c] Reaction was also run in C_6H_6; little reaction had occurred after 1 week at 60 °C. [d] In toluene.

of an acyl from $p\text{-}CH_3OC_6H_4CH_2Mn(CO)_5$ precedes the formation of aldehydes in eq 3. In all three cases the acyl intermediates have been proposed on the basis of kinetic evidence only; none of the acyls has been directly observed.

$$p\text{-}CH_3OC_6H_4CH_2Mn(CO)_5 + HMn(CO)_5 \xrightarrow[\text{acetonitrile}]{\text{acetone or}} p\text{-}CH_3OC_6H_4CH_2CHO + Mn_2(CO)_9(s) \quad (3)$$

In an effort to explore the generality of such elimination reactions when other evidence indicates that acyl intermediates should be available, we have carried out a systematic study of the reactions of alkyl carbonyl complexes with metal hydrides. The results are completely consistent with the involvement of acyl intermediates and also demonstrate the usefulness of these reactions for the synthesis of heterobismetallic complexes.

Results and Discussion

As shown in Tables I and II, the formation of aldehydes from transition-metal hydrides and alkyl carbonyl complexes is quite a general reaction. It proceeds in benzene, THF, and acetonitrile, with the rate increasing in that order: the reaction of 0.2 M $MeMn(CO)_5$ with 1 equiv of $HRe(CO)_5$ is complete in 35 min in CH_3CN and in 2.5 h in THF, but some $MeMn(CO)_5$ remains unreacted after 2.5 days in C_6H_6 (although—see below—the $HRe(CO)_5$ is consumed).

The solvent also affects the yield of aldehyde and the nature of the organometallic products. For example, under the conditions of Table I, $RM(CO)_5$ (R = Me, M = Mn and R = Et, M = Re) reacts rapidly (within 45 min at 30 °C if M = Mn and in 9 h at 60 °C if M = Re) with 1 equiv of $HRe(CO)_5$ in CH_3CN and gives quantitative yields of aldehydes. The organometallic products are $ReMn(CO)_9(CH_3CN)$ and $Re_2(CO)_9(CH_3CN)$—dinuclear species in which the carbonyl ligand incorporated into the aldehyde has been replaced by coordinated acetonitrile.

$$RM(CO)_5 + HRe(CO)_5 \xrightarrow{CH_3CN} RCHO + RM(CO)_9(CH_3CN) \quad (4)$$

Similar dinuclear or polynuclear acetonitrile solvates are observed in other reactions with acetonitrile as solvent, although they are difficult to isolate and have in some cases been characterized only by IR and by identification of the stable derivative formed upon treatment with CO or PPh_3. (However, dimanganese and dirhenium solvates are observed instead, along with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, when

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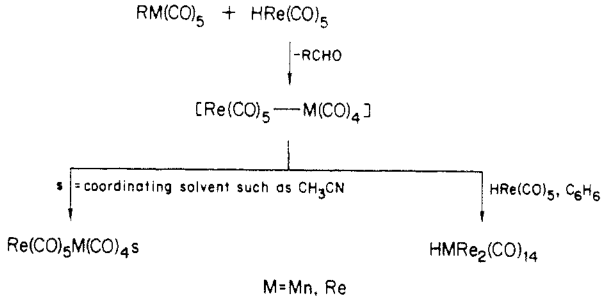
(3) (a) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. (b) Nappa, M. J.; Santi, R.; Diefenbach, S. P.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 619. (c) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34.

Scheme I

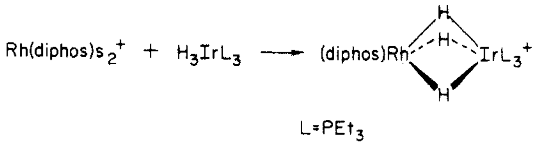


$(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ or $(\eta^5\text{-}C_5H_5)Fe(CO)_2Et$ is the alkyl carbonyl complex; heterobimetallic solvates are probably formed initially but disproportionate during the long reaction times required in these cases.[4,5]) THF solvates are apparently formed when THF is used as a solvent.[6]

In contrast, in the noncoordinating solvent C_6H_6 these reactions are much slower and do not convert all of the alkyl complex to aldehyde. (After 2 days the yield of aldehyde was 40–50% for M = Mn, and after 3 days the yield of aldehyde was 20–30% for M = Re.) However, all of the hydride (initially present in a 1:1 mole ratio with the starting alkyl) is consumed, with the extra equivalent of $HRe(CO)_5$ being incorporated into $HMnRe_2(CO)_{14}$ or $HRe_3(CO)_{14}$.

Polynuclear metal hydride complexes are the major organometallic products of all of the reactions in benzene in Table I. This change of the organometallic product with change in solvent is readily explained if the primary organometallic product is a coordinatively unsaturated dinuclear complex (as illustrated in Scheme I for reaction 4), which then either coordinates solvent or, in a noncoordinating solvent such as C_6H_6, reacts with an additional equivalent of the hydride complex.

In the latter case Scheme I implies that the hydride complex is itself a nucleophile, with the pair of electrons in the M–H bond becoming the pair of electrons in a three-center two-electron M(H)M bond. Such behavior on the part of transition-metal hydrides has been seen in numerous recent syntheses of hydride-bridged bimetallic complexes (reactions 5–10).[7-11] The relative reactivity of various anionic metal hydrides in the reduction of alkyl halides has been suggested as a measure of the relative nucleophilicity of these anionic metal hydrides (although the detailed mechanism of these reductions is not clear).[12]



(5)[7]

$Ph_3PAuCl + TlPF_6 + HCr(CO)_5^- \longrightarrow Ph_3PAu(\mu\text{-}H)Cr(CO)_5$ (6)[8a]

$Ph_3PAu(THF)^+ + H_3Ir(PPh_3)_3 \longrightarrow Ph_3PAu(\mu\text{-}H)IrH_2(PPh_3)_3^+$ (7)[8b]

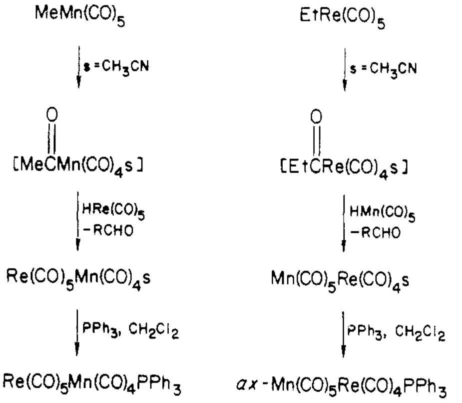
$Cu(MeCN)_4PF_6 + 2H_5Re(PMePh_2)_3 \longrightarrow [H_2(MePh_2P)_3Re(\mu\text{-}H)_3]_2Cu^+$ (8)[9]

$CpMo(CO)_3H + CpMo(CO)_3^+ \longrightarrow [Cp(CO)_3Mo(\mu\text{-}H)MoCp(CO)_3]^+$ (9)[10]

$Cp_2Ta(CO)H + (THF)ML_n \longrightarrow Cp_2Ta(CO)(\mu\text{-}H)ML_n$ (10)[11]

$ML_n = Cr(CO)_5, Mo(CO)_5, W(CO)_5, CpMn(CO)_2$

Scheme II



Aldehyde formation in CH_3CN is much faster with $EtRe(CO)_5$ than with $MeRe(CO)_5$: at 60 °C in CH_3CN the reaction of $EtRe(CO)_5$ with $HRe(CO)_5$ is complete in 10 h, whereas $MeRe(CO)_5$ shows only 11% reaction under the same conditions. This $MeRe(CO)_5$ result and the data in Tables I and II make it clear that the reactivity of methyl carbonyl complexes toward a given hydride (e.g., $HRe(CO)_5$) decreases substantially from $MeMn(CO)_5$ to $MeFe(CO)_2Cp$, $MeRe(CO)_5$, $Me_2Os(CO)_4$, and $Me(Cl)Os(CO)_4$.

These observations and the solvent effects on the rates of these aldehyde elimination reactions (C_6H_6 < THF < CH_3CN) are consistent with the rate-determining formation of acyl intermediates. Carbonyl insertion is both faster and more thermodynamically favorable for an ethyl group than for a methyl group (as is demonstrated most convincingly by the results for $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ in Me_2SO[13]). Carbonyl insertion in CH_3CN is known to be much faster for $MeMn(CO)_5$[14] than for $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$[15] and is expected to be very slow for third-row methyl carbonyl complexes such as $MeRe(CO)_5$ and $Me_2Os(CO)_4$.[16-18] Polar solvents are known to enhance the rate of carbonyl insertion; Bergman and co-workers[19] have shown that this enhancement is due to nucleophilic attack by solvent at the metal center.

The intermediacy of acyl complexes in dinuclear aldehyde elimination means that the aldehyde carbonyl must come from the metal that originally bears the alkyl ligand.

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[4] Although $(\eta^5\text{-}C_5H_5)Fe(CO)_2Mn(CO)_5$[5] can be formed from $[\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $Mn_2(CO)_{10}$ at room temperature, the equilibrium is unfavorable: Madach, T.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 2675. It is thus not surprising that an Fe–Mn solvate disproportionates after a prolonged period at 55 °C.

[5] King, R. B.; Treichel, P. M.; Stone, F. G. A. *Chem. Ind. (London)* **1961**, 747.

[6] Evidence for $Re(CO)_5Mn(CO)_4(THF)$ was obtained from the following experiment: $MeMn(CO)_5$ was allowed to react with an equimolar amount of $HRe(CO)_5$ in THF, and 1 equiv of PPh_3 was added after that reaction had finished. The organometallic product was $Re(CO)_5Mn(CO)_4PPh_3$.

[7] Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251 and references therein.

[8] (a) Green, M.; Orpen, A. G.; Salter, I. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2497. (b) Lehner, H.; Matt, D.; Pregosin, P. S.; Venanzi, L. M.; Albinati, A. *J. Am. Chem. Soc.* **1982**, *104*, 6825.

[9] Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 5137.

[10] Markham, J.; Cutler, A. *Organometallics* **1984**, *3*, 736.

[11] Leblanc, J. C.; Reynoud, J. F.; Moise, C. *J. Organomet. Chem.* **1983**, *244*, C24.

[12] (a) Kao, S. C.; Darensbourg, M. Y. *Organometallics* **1984**, *3*, 646. (b) Kao, S. C.; Darensbourg, M. Y.; Schenk, W. *Organometallics* **1984**, *3*, 871.

[13] Cotton, J. D.; Crisp, G. T.; Latif, L. *Inorg. Chim. Acta* **1981**, *47*, 171.

[14] Green, M.; Hancock, R. I.; Wood, D. C. *J. Chem. Soc. A* **1968**, 2718.

[15] Green, M.; Westlake, D. J. *J. Chem. Soc. A* **1971**, 367.

[16] (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

[17] An early report by Davison, McCleverty, and Willkinson[18] implies that $RRe(CO)_5$ complexes undergo carbonyl insertion very slowly.

[18] Davison, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133.

[19] Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.

This prediction is testable if the same heterobimetallic solvate is generated in two separate reactions, with the metal bearing the alkyl ligand and the metal bearing the hydride ligand reversed. As shown in Scheme II, treatment of $MeMn(CO)_5$ with $HRe(CO)_5$ in CH_3CN should yield $(CH_3CN)Mn(CO)_4Re(CO)_5$; treatment of $EtRe(CO)_5$ with $HMn(CO)_5$ in CH_3CN should yield the opposite regioisomer $(CH_3CN)Re(CO)_4Mn(CO)_5$.

The regiochemistry predicted in Scheme II is in fact observed. The $MeMn(CO)_5/HRe(CO)_5$ reaction and the $EtRe(CO)_5/HMn(CO)_5$ reaction give different isomers, with different IR spectra, of $MnRe(CO)_9$(acetonitrile); both isomers show the same parent ion in their mass spectrum. Treatment of each isomer with Ph_3P under mild conditions (1.5 equiv of Ph_3P at room temperature in CH_2Cl_2) gives, as shown in Scheme II, a different isomer of $MnRe(CO)_9(PPh_3)$. The two isomers of $MnRe(CO)_9(PPh_3)$ can be identified (by comparison of their IR and ^{31}P NMR spectra with those reported in the literature[20]) as *ax*-$(Ph_3P)Mn(CO)_4Re(CO)_5$ and *ax*-$(Ph_3P)Re(CO)_4Mn(CO)_5$, respectively. The fact that different regioisomers of $MnRe(CO)_9(PPh_3)$ are formed (or, more specifically, that treatment of the $MeMn(CO)_5/HRe(CO)_5$ product with Ph_3P gives *ax*-$(Ph_3P)Mn(CO)_4Re(CO)_5$, which is known[20a] to be the less stable regioisomer) shows that both aldehyde elimination and Ph_3P substitution of acetonitrile are occurring with kinetic control of regiochemistry; thus, barring the remote possibility that phosphine substitution occurs with clean *reversal* of regiochemistry, the regiochemistry shown in Scheme II for the $MnRe(CO)_9$(acetonitrile) isomers must be correct, and solvent is coordinated to the metal that originally bears the alkyl ligand.

The $MeMn(CO)_5/HRe(CO)_5$ system offers indirect kinetic evidence—similar to that found in the cases discussed in the Introduction—for the formation of an acyl intermediate in nonpolar solvents. At 25 °C in mesitylene the pseudo-first-order rate constant k_{11} for the disappearance of $MeMn(CO)_5$ according to eq 11 is 3.5 (1) × 10^{-6} s^{-1}—a

$$MeMn(CO)_5 + \text{excess } HRe(CO)_5 \xrightarrow[25\ °C]{\text{mesitylene}} CH_3CHO + HMnRe_2(CO)_{14} \quad (11)$$

value remarkably close to that (2.2 × 10^{-6} s^{-1}) reported[21] in 1964 by Mawby, Basolo, and Pearson for k_{12} (see Scheme III and eq 14) for the reaction of $MeMn(CO)_5$ with excess cyclohexylamine at the same temperature in the same solvent. As k_{12} is believed to be the rate of formation of the unsolvated acyl in Scheme III, the formation of the same unsolvated acyl must be rate-determining in reaction 11 (and in the corresponding reaction in benzene).

Direct Observation of Solvated Acyl Complexes in Acetonitrile. In addition to all of the *indirect* evidence implicating acyl intermediates in these aldehyde elimination reactions, *direct observation* of the *solvated* acyl intermediate has proven possible in some cases in acetonitrile. Above 40 °C, a solution of $EtRe(CO)_5$ in acetonitrile begins to show NMR (Figure 1) and IR (Figure 2) evidence for the presence of another species as well as $EtRe(CO)_5$. In the ^1H NMR the new species has a triplet at 0.82 ppm and a quartet at 2.64 ppm; in the IR it absorbs at 2092, 1986, 1940, and 1593 cm^{-1}. The new species thus has a propionyl ligand. The IR (2087, 1985, 1950, 1939 cm^{-1}) obtained when the acetonitrile is removed and the residue taken up in hexane (Figure 3) shows that the new species has a carbonyl region spectrum very similar to that of *cis*-$EtC(O)(Ph_3P)Re(CO)_4$. The fact that the new species contains coordinated acetonitrile[22,23] has been es-

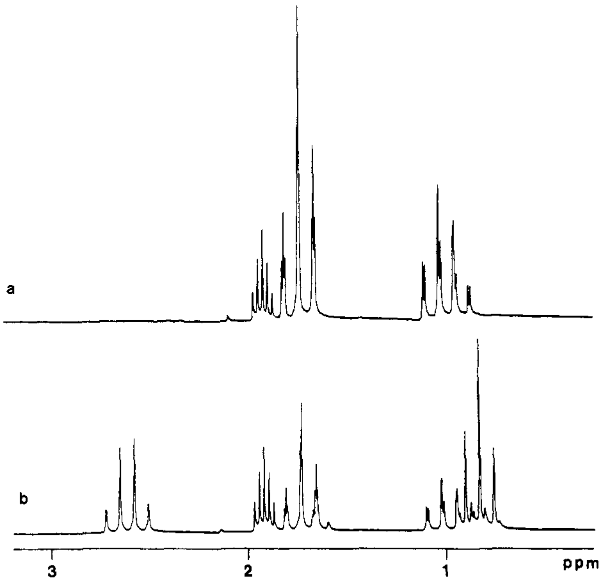


Figure 1. ^1H NMR spectra (99.60 MHz) of a solution of $EtRe(CO)_5$ in CD_3CN: (a) before reaction; (b) after 1.5 h at 69 °C.

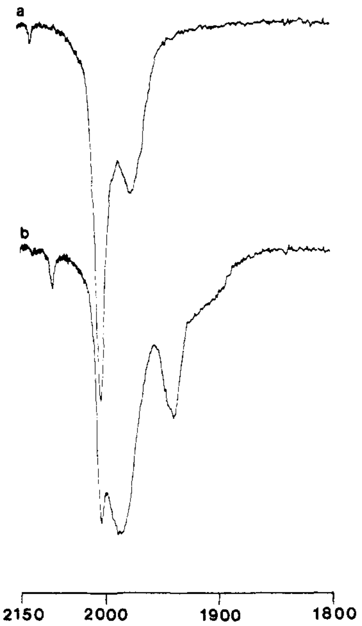
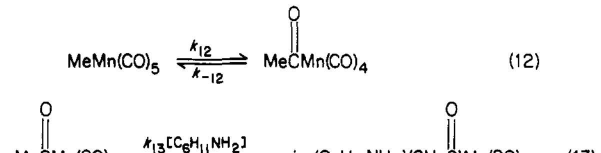


Figure 2. IR spectra of acetonitrile solutions of (a) $EtRe(CO)_5$ and (b) $EtRe(CO)_5$ and $EtC(O)(CH_3CN)Re(CO)_4$.

Scheme III



$$MeMn(CO)_5 \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} MeC(O)Mn(CO)_4 \quad (12)$$

$$MeC(O)Mn(CO)_4 \xrightarrow{k_{13}[C_6H_{11}NH_2]} cis\text{-}(C_6H_{11}NH_2)(CH_3C(O))Mn(CO)_4 \quad (13)$$

$$\frac{-d[MeMn(CO)_5]}{dt} = k_{12}k_{13}\frac{[MeMn(CO)_5][C_6H_{11}NH_2]}{k_{-12} + k_{13}[C_6H_{11}NH_2]} \quad (14)$$

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(20) (a) Fawcett, J. P.; Poë, A. J.; Twigg, M. V. *J. Organomet. Chem.* **1973**, *61*, 315. (b) Fawcett, J. P.; Poë, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2039. (c) Sonnenberger, D.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 3484.

(21) Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994. These workers obtained k_1 from plots of $1/k_{obsd}$ vs. $1/[L]$.

(22) The decrease in the equilibrium constant K_{15} with temperature[23] also shows that the new species—on the right-hand side of eq 15—must be solvated. Coordinated acetonitrile in $Re_2(CO)_9(CH_3CN)$ is also at δ 2.37 in CD_3CN.

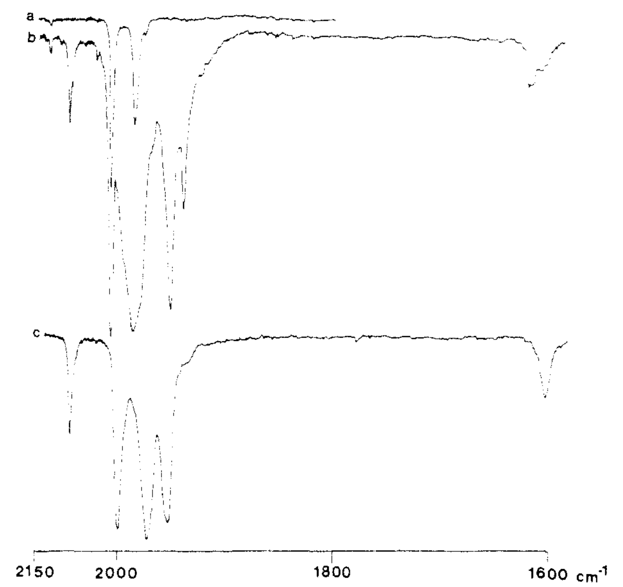
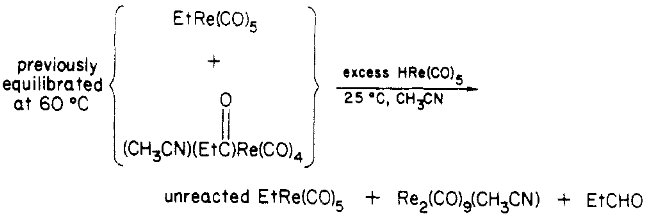
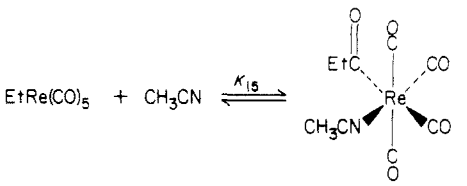


Figure 3. IR spectra of hexane solutions of (a) $EtRe(CO)_5$, (b) $EtRe(CO)_5$ and $EtC(O)(CH_3CN)Re(CO)_4$, and (c) $EtC(O)Re(CO)_4PPh_3$.

Scheme IV



tablished by ^1H NMR; if $EtRe(CO)_5$ is first heated to 59 °C in CD_3CN, addition of CH_3CN results in the appearance of a new peak at δ 2.37 with an intensity appropriate for coordinated CH_3CN.[22,23] The new species is therefore an acyl solvate with C_s symmetry and the structure shown in eq 15.

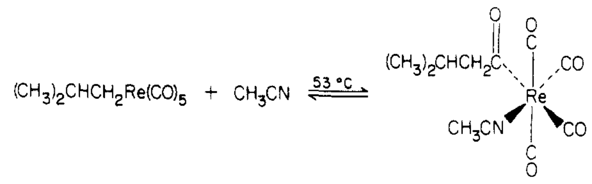


(15)

Although the solvate is unstable in hexane and cannot be isolated, as a component of the equilibrium mixture in acetonitrile it reacts readily with hydrides to give propionaldehyde and solvated dinuclear complexes. For example, after $EtRe(CO)_2$ and its solvate have been equilibrated at 60 °C and the mixture cooled to 25 °C (at which temperature $EtRe(CO)_5$ and the solvate no longer interconvert), addition of excess $HRe(CO)_5$ causes the solvate to disappear, leaving unreacted $EtRe(CO)_5$ and forming EtCHO and $Re_2(CO)_9(CH_3CN)$ (Scheme IV).

The agreement of the forward rate constant in reaction 15 with the observed rate constant for the disappearance of $EtRe(CO)_5$ in the presence of excess $HRe(CO)_5$ (both of which will be published[23] along with a detailed analysis of the mechanism of (acyl solvate)/(hydride) reactions such as that in Scheme IV) demonstrates that the solvated propionyl complex of reaction 15 is in fact an intermediate in the $EtRe(CO)_5/HRe(CO)_5$ reaction in CH_3CN.

A number of other alkyl carbonyl complexes similarly generate observable solvates. A solution of i-$BuRe(CO)_5$ in acetonitrile shows NMR and IR evidence for the formation of an isovaleroyl ligand at 53 °C, implying the formation of an acyl solvate (eq 16); i-$BuRe(CO)_5$ reacts with $HRe(CO)_5$ in CH_3CN to form i-BuCHO. Similarly, a solution of $Et_2Os(CO)_4$ shows NMR evidence (a propionyl resonance with diastereotopic methylene protons, and at least one new ethyl ligand resonance[24]) for the formation of one or more acyl solvates at 40 °C. Other ethylosmium carbonyl complexes ($ClEtOs(CO)_4$ and $EtOs(CO)_4Re(CO)_5$) also show evidence for the formation of acyl solvates in acetonitrile solution; $MeMn(CO)_5$, $(\eta^5$-$C_5H_5)Fe(CO)_2Et$, $(\eta^5$-$C_5H_5)W(CO)_3Et$, $Me_2Os(CO)_4$, and $ClMeOs(CO)_4$ do not show any evidence for the formation of such solvates in acetonitrile.



(16)

Elimination from Dialkyl Carbonyl Complexes. As shown in Table II, dialkyl carbonyl complexes also react with transition-metal hydrides, yielding trinuclear complexes such as $Re_2Os(CO)_{13}(CH_3CN)$ (from $Et_2Os(CO)_4$ and $HRe(CO)_5$). Alkanes as well as aldehydes are eliminated, in contrast with the exclusive formation of aldehydes generally seen (the only exception being the $ClMeOs(CO)_4/HRe(CO)_5$ system) with the monoalkyl carbonyl complexes in Tables I and II. The reaction of $Me_2Os(CO)_4$ with $H_2Os(CO)_4$ in toluene (for which preliminary results have been reported in benzene[1b,c,25]) gives methane as well as acetaldehyde, along with some ethanol; similar results are found with $Me_2Os(CO)_4$ and $HRe(CO)_5$ in toluene.

In acetonitrile, as described above, formation of an ethyl propionyl solvate[24] can be observed from $Et_2Os(CO)_4$; addition of 6 equiv of $HRe(CO)_5$ to a mixture of the solvate and $Et_2Os(CO)_4$ leads to the rapid (1.5 h at 18 °C) formation of ethane and propionaldehyde in a 4:1 ratio (reaction 17). The ethane formed in the $Et_2Os(CO)_4/HRe(CO)_5$ reaction is thus formed via the ethyl propionyl solvate.[24]

$$EtC(=O)(Et)(CH_3CN)Os(CO)_3 + \text{excess } HRe(CO)_5 \xrightarrow{CH_3CN} EtH + EtCHO \ (4:1) \quad (17)$$

The organometallic product of ethane elimination between the solvate and $HRe(CO)_5$ must retain one ethyl ligand, and such a compound can in fact be isolated (reaction 18) from the reaction of $Et_2Os(CO)_4$ with only 1 equiv of $HRe(CO)_5$; separate NMR experiments, as discussed above, show that $EtOs(CO)_4Re(CO)_5$ is in equilibrium with its own acyl solvate in acetonitrile and indeed that acyl solvate $EtC(=O)Os(CO)_3(CD_3CN)Re(CO)_5$ can be seen as a byproduct of reaction 18 when the latter is run in CD_3CN and monitored by NMR.

$$Et_2Os(CO)_4 + 1 \text{ equiv of } HRe(CO)_5 \xrightarrow[CH_3CN]{20\text{ h, }45\text{ °C}} C_2H_6 + EtOs(CO)_4Re(CO)_5 \quad (18)$$

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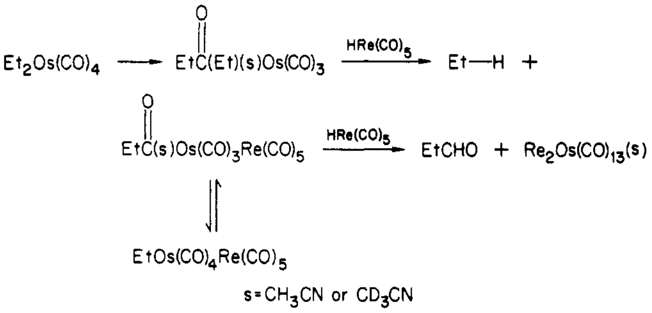
[23] Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.*, in press.

[24] Although the diastereotopic methylene protons in the ^1H NMR spectrum of the propionyl ligand suggest a structure with cis propionyl, ethyl, and acetonitrile ligands, the spectrum is too complex for unambiguous interpretation and other species may also be present.

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

Scheme V



The observations, along with the fact that (Table II) $EtOs(CO)_4Re(CO)_5$ forms *only propionaldehyde* (not ethane) with $HRe(CO)_5$, suggest the overall mechanism shown in Scheme V for the $Et_2Os(CO)_4/HRe(CO)_5$ reaction. $EtC(=O)(s)Os(CO)_3Re(CO)_5$ slowly reacts with $HRe(CO)_5$ to form propionaldehyde, but ethane is formed initially (and predominantly[26] when less than 2 equiv of $HRe(CO)_5$ are present) from the faster reaction of $EtC(=O)(Et)(s)Os(CO)_3$ with $HRe(CO)_5$.

Preferential ethane elimination from $EtC(=O)(Et)(s)Os(CO)_3/HRe(CO)_5$ is most readily explained if the ethane comes from the ethyl ligand rather than from the propionyl one. The reaction is analogous to the elimination of methane in reaction 19[27] and of p-$CH_3OC_6H_4CH_3$ in reaction 20;[3] interaction of a coordinatively unsaturated *alkyl*

$$CpCoMe_2 + CpCo(PPh_3)H_2 \xrightarrow{C_6D_6} 2CH_4 \quad (19)$$

$$p\text{-}CH_3OC_6H_4Mn(CO)_4 + HMn(CO)_5 \xrightarrow{C_6H_6} p\text{-}CH_3OC_6H_4CH_3 \quad (20)$$

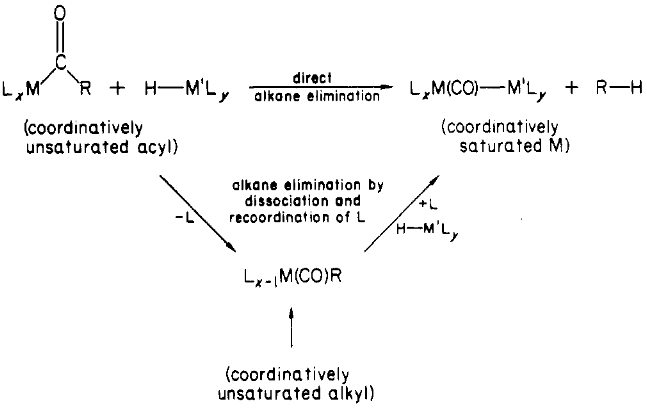
(in the Os case, an acetonitrile solvate) with a hydride gives alkane. Alkane elimination in the $R_2Os(CO)_4/HRe(CO)_5$ system can thus be explained without invoking direct alkane elimination from a metal hydride and a coordinatively unsaturated *acyl*—a step we have proposed[1] in the elimination of alkane between two molecules of $Os(CO)_4(H)R$ (reaction 1).

There remain, however, a number of cases in addition to $Os(CO)_4(H)R$ where such direct alkane elimination (as defined in Scheme VI) seems likely: the reaction of $Bu_4N[RhI_3(CO)Ac]$ with $Os(CO)_4H_2$,[1b,c] the reaction of $Ir(CO)Cl_2(AsPh_3)Ac$ with $Os(CO)_4H_2$,[1b,c] and the reaction of $ClMeOs(CO)_4$ with $HRe(CO)_5$ (Table II). The factors responsible for the occasional appearance of this reaction pattern remain unclear.

Conclusions

Dinuclear aldehyde (from treatment of monoalkyl carbonyls with transition-metal hydrides) and aldehyde/alkane (from treatment of dialkyl carbonyls with such hydrides) elimination is a general reaction when an acyl intermediate is accessible from the alkyl carbonyl complex. As acyl formation is encouraged by the presence of certain metals (e.g., Mn), by the use of alkyl groups which migrate readily (e.g., Et or *i*-Bu instead of Me), and by the use of coordinating, nucleophilic, solvents (e.g., CH_3CN), these same factors promote dinuclear elimination. As the yields in Table I show, the dinuclear elimination reaction with $MeMn(CO)_5$ or $EtRe(CO)_5$ in CH_3CN is a synthetically useful route to mixed-metal dinuclear and trinuclear complexes.

Scheme VI



Experimental Section

Deuterated solvents were dried over P_4O_{10} and vacuum distilled before use. Benzene, toluene, and THF were distilled under N_2 from Na/benzophenone, and CH_3CN was predried over molecular sieves and vacuum distilled from CaH_2.[28] Tetraglyme was predried over molecular sieves (4 Å) and vacuum distilled (<0.01 mmHg) from NaH before use.

Mass spectra were obtained with either a VG MM16 (70 eV) or an AEI MS902 (70 eV) mass spectrometer equipped with a direct inlet system. Spectra were recorded with and without the standards perfluorokerosene (*m/e* 805) or tris(perfluoroheptyl)-*s*-triazine (*m/e* 1185) in order to ensure that *m/e* values were accurate. All compounds (unless otherwise stated) exhibited parent ion envelopes with isotopic distributions which agreed with those calculated for the molecular formula.

Infrared spectra were obtained on either a Beckman IR-12 or a Perkin-Elmer 983 equipped with a data station. $Os_3(CO)_{12}$ and DCl were used as instrument calibrants, and wavenumber values are within 1 cm^{-1}.

Residual solvent proton shifts were used as secondary ^1H NMR chemical shift standards. ^{31}P spectra were obtained on a Nicolet NT150 (60 MHz, ^{31}P); chemical shifts were determined by the method of substitution and are reported with H_3PO_4 (85%) as chemical shift reference.

Reactions involving volatile organometallic complexes were (unless otherwise stated) carried out on a high vacuum line in standard reaction bulbs (a 25-mL bulb connected through a high-vacuum Teflon stopcock to an O-ring joint) or 5-mm NMR tubes sealed under vacuum. As many of the complexes below are only slowly decomposed by air and light, satisfactory separation of these compounds could be achieved by using preparative layer chromatography in the air. The standard conditions were 1-mm silica gel support with 30% CH_2Cl_2 in hexanes as the eluant.

Mononuclear osmium compounds were (unless stated otherwise) prepared from $Na_2Os(CO)_4$ as previously described.[25] $RFeCp(CO)_2$ (R = Me, Et),[29] $CpW(CO)_3Et$,[30] and $CpM(CO)_3H$ (M = Mo, W)[29] were prepared by literature procedures. $HGePh_3$ was a gift from Dr. K. M. Motyl.

Hydridopentacarbonylmanganese and hydridopentacarbonylrhenium were prepared by dissolving $Na[M(CO)_5]$[29] (M = Mn, Re) in tetraglyme and placing the solution under high vacuum for 2 h at room temperature to remove any residual THF, followed by acidification with 85% H_3PO_4 and drying with a small amount of P_4O_{10}. Similarly, **methylpentacarbonylmanganese and methylpentacarbonylrhenium** were prepared by adding 2 equiv of methyl tosylate to $Na[M(CO)_5]$ in tetraglyme. The system was then left under high vacuum overnight and the $MeM(CO)_5$ distilled into a −196 °C trap. ^1H NMR: for M = Mn,

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[26] The propionaldehyde seen as a minor product from 1:1 $Et_2Os(CO)_4/HRe(CO)_5$ and from $EtC(O)(Et)(s)Os(CO)_3/HRe(CO)_5$ probably arises from the slow reaction of the initial product $EtOs(CO)_4Re(CO)_5$ with $HRe(CO)_5$, and not directly from the reaction of $EtC(O)(Et)(s)Os(CO)_3$ with $HRe(CO)_5$. Note that when sufficient $HRe(CO)_5$ is present the alkane/aldehyde ratio is 1:1.

[27] Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2488.

[28] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals", 2nd ed.; Pergamon Press: Oxford, 1980.

[29] King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. I.

[30] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

δ −0.28 in C_6D_6, −0.14 in THF-d_8, and −0.17 in CD_3CN; for M = Re, δ −0.13 in CD_3CN. **Ethylpentacarbonylrhenium**[18] was prepared in the same way from $NaRe(CO)_5$ with excess ethyl tosylate in tetraglyme: IR (hexanes) 2124 (w), 2010 (vs), 1983 (m) cm^{-1}; ^1H NMR (CD_3CN) δ 1.73 (t, 3 H, *J* = 7.8 Hz), 0.98 (q, 2 H, *J* = 7.8 Hz). **Isobutylpentacarbonylrhenium** was prepared from isobutyl tosylate and $NaRe(CO)_5$ in tetraglyme in the same way. The reaction was very slow and required 6 days to give a 53% yield of product: IR (hexanes) 2119 (w), 2006 (vs), 1989 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.95 (m, 1 H, *J* = 6.4 Hz), 1.01 (d, 2 H, *J* = 6.5 Hz), 0.98 (d, 6 H, *J* = 6.4 Hz). The mass spectrum showed an appropriate parent ion at *m/e* 384 (^{187}Re).

***cis*-Chloromethyltetracarbonylosmium** was prepared by treatment of $Me(H)Os(CO)_4$ with CCl_4 as previously described for $Et(Cl)Os(CO)_4$.[25] $R(Cl)Os(CO)_4$ (R = Me, Et) was isolated from crude $R(H)Os(CO)_4$ reaction mixtures (containing $R_2Os(CO)_4$, $H_2Os(CO)_4$, and $R(H)Os(CO)_4$) by treatment of the latter with CCl_4. The volatile $R_2Os(CO)_4$ was removed along with the solvent, and the $R(Cl)Os(CO)_4$ was purified by sublimation (at room temperature to a −78 °C probe) from the nonvolatile $Cl_2Os(CO)_4$. *cis*-$Me(Cl)Os(CO)_4$: IR (hexanes) 2161 (w), 2082 (vs), 2031 (s) cm^{-1}; ^1H NMR (CD_3CN) δ 0.54.

Hydridocyclopentadienyldicarbonyl(trimethylphosphine)tungsten was prepared by the literature method[31] from a solution of 0.30 g (0.90 mmol) of $HWCp(CO)_3$ in 10 mL of THF with 0.095 g (1.23 mmol) of PMe_3. However, an IR spectrum showed that no reaction had occurred after 1 h, and the reaction was therefore initiated by opening the flask briefly to the air: ^1H NMR (CD_3CN, −21 °C) δ 5.39 (s), 5.16 (d, *J* = 0.98 Hz), 1.60 (dd, *J* = 9.6, 4.2 Hz), −7.96 (d, *J* = 67.4 Hz), −7.98 (d, *J* = 23.9 Hz).

Reaction of $MeMn(CO)_5$ and $HRe(CO)_5$ in CH_3CN. $MeMn(CO)_5$ (28.1 mg, 0.13 mmol), 0.55 mL of CD_3CN, and 49.0 mg (0.15 mmol) of $HRe(CO)_5$ were vacuum transferred into an NMR tube and the tube sealed. The NMR tube was thawed and rapidly placed in the instrument probe (ca. 30 °C). The initial spectrum (ca. 3 min into the reaction) showed that significant reaction had occurred (78% completion). The reaction was complete within 35 min (no $MeMn(CO)_5$ remained); the elimination product was CH_3CHO (100% yield by integration).

The organometallic product $(CO)_5ReMn(CO)_4(CD_3CN)$ was isolated by preparative layer chromatography on silica gel. Recrystallization from CH_2Cl_2/hexanes (ca. 1:3) at −25 °C gave pure $(CO)_5ReMn(CO)_4(CD_3CN)$ as yellow needles in 62% yield: IR (hexanes) 2104 (w), 2057 (w), 2047 (vw), 2027 (s), 2021 (s), 1994 (vs), 1978 (w), 1963 (m), 1954 (w), 1940 (m) cm^{-1}. The mass spectrum showed an appropriate parent ion at *m/e* 538 (^{187}Re). Anal. Calcd for $C_{11}D_3MnNO_9Re$: C, 24.59; D, 1.12. Found: C, 24.49; D, 1.32.[32]

In another reaction, 62 mg (0.30 mmol) of $MeMn(CO)_5$, 1.5 mL of CH_3CN, and 93.3 mg (0.29 mmol) of $HRe(CO)_5$ were distilled into a standard reaction bulb. After the mixture was stirred overnight at room temperature, the volatiles were removed under vacuum and the yellow residue was taken up in 3 mL of CH_2Cl_2. PPh_3 (151 mg) in 2 mL of CH_2Cl_2 was then added, and the reaction was stirred for 1 week in the dark at room temperature. The product *ax*-$Re(CO)_5Mn(CO)_4PPh_3$[20] was isolated via preparative layer chromatography in 95% yield: IR (hexanes) 2109 (m), 2006 (vs), 1970 (s), 1930 (s) cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 75.6 (s, very broad). The IR spectrum agreed with that reported, and the ^{31}P NMR spectrum agreed with that expected for the Mn-substituted positional isomer.[20]

In THF. $MeMn(CO)_5$ (22.5 mg, 0.11 mmol), 0.37 mL of THF-d_8, and 50.3 mg (0.15 mmol) of $HRe(CO)_5$ were sealed in an NMR tube. Upon thawing, the solution turned orange immediately. The initial spectrum showed that some reaction had occurred (40%). The reaction required 2.7 h to go to completion, with CH_3CHO being formed in 100% yield (by integration).

In another reaction, 25.2 mg (0.12 mmol) of $MeMn(CO)_5$, 0.6 mL of THF, and 41.3 mg (0.13 mmol) of $HRe(CO)_5$ were distilled into a standard reaction bulb and the reaction was stirred for 1 day at room temperature. PPh_3 (52 mg, 0.2 mmol) in 2 mL of CH_2Cl_2 was then added and the solution stirred for 2 days in the dark at room temperature. The product *ax*-$Re(CO)_5Mn(CO)_4PPh_3$[20] was isolated as before in 64% yield.

In C_6H_6. $MeMn(CO)_5$ (28.1 mg, 0.13 mmol), 0.5 mL of C_6D_6, and 55.6 mg (0.17 mmol) of $HRe(CO)_5$ were sealed in an NMR tube under vacuum. No color change was observed on thawing, and the initial spectrum showed only starting materials. The reaction was very slow, taking 44 h to go to completion (based on disappearance of $HRe(CO)_5$; see Results). The yield of CH_3CHO was 62%. In an analogous experiment in which the $HRe(CO)_5/MeMn(CO)_5$ ratio was 1.05 (0.20 mmol of $HRe(CO)_5$/0.19 mmol of $MeMn(CO)_5$), the yield of CH_3CHO was 47%.

In another experiment, 41.4 mg (0.20 mmol) of $MeMn(CO)_5$, 1.6 mL of C_6H_6, and 93.2 mg (0.29 mmol) of $HRe(CO)_5$ were distilled into a standard reaction bulb, which was kept in the dark for 5 days. At that time the room-temperature volatiles were removed under vacuum; the remaining red crystalline solid was washed with hexanes and vacuum dried overnight. The yield of $HMnRe_2(CO)_{14}$[33] was 85 mg or 73%. Spectroscopic data: IR (hexanes) 2146 (w), 2101 (m), 2093 (vw), 2049 (vs), 2020 (m, sh), 2015 (s), 2007 (w), 1993 (s), 1987 (m, sh), 1977 (s), 1966 (m), 1957 (w), 1929 (m) cm^{-1}, in agreement with that reported in cyclohexane;[33] ^1H NMR (C_6D_6) δ −19.23. Anal. Calcd for $C_{14}HMnO_{14}Re_2$: C, 20.48; H, 0.12. Found: C, 20.73; H, 0.13.

Reaction of $MeMn(CO)_5$ and $H_2Os(CO)_4$ in CH_3CN. $MeMn(CO)_5$ (20.2 mg, 0.10 mmol), 0.44 mL of CD_3CN, and 15.1 mg (0.05 mmol) of $H_2Os(CO)_4$ were sealed in an NMR tube under vacuum. The tube was thawed, giving an immediate yellow-red color. The first NMR spectrum showed that approximately 50% reaction had occurred. The reaction was complete in 70 min, giving 100% yield of CH_3CHO by integration. It proved impossible to obtain the organometallic product (presumably $Mn_2Os(CO)_{12}(CD_3CN)_2$) in a pure state due to its instability; in hexanes its IR spectrum showed absorbances due to $Mn_2Os(CO)_{14}$,[34] which increased with time, and other absorbances at 2115 (vw), 2072 (m), 2055 (s), 2008 (vs), 1976 (m), 1964 (vw), and 1944 (w) cm^{-1}. The mass spectrum of the organometallic product showed only $Mn_2Os(CO)_{14}$.[34]

In another experiment, 20.7 mg (0.10 mmol) of $MeMn(CO)_5$, 0.8 mL of CH_3CN, and 14.1 mg (0.05 mmol) of $H_2Os(CO)_4$ were reacted for 8 h at room temperature. The solvent was removed under vacuum and the yellow residue taken up in 4 mL of CH_2Cl_2. The solution was frozen and degassed (3×) and CO (2 atm) admitted. The reaction was stirred for 32 h in the dark at room temperature. At the end of that time 21.2 mg (62% yield) of $Mn_2Os(CO)_{14}$[34] was isolated via preparative layer chromatography: IR (hexanes) 2064 (s), 2018 (vs), 1985 (s) cm^{-1}, in agreement with that reported (solvent unspecified);[34] its mass spectrum showed an appropriate parent ion at *m/e* 694 (^{192}Os).

In THF. $MeMn(CO)_5$ (31.3 mg, 0.15 mmol), 0.6 mL of THF, and 25.5 mg (0.08 mmol) of $H_2Os(CO)_4$ were reacted overnight at room temperature. An IR spectrum at that time showed the presence of CH_3CHO. The solution was frozen and degassed (3×) and CO (2 atm) was admitted. The reaction was stirred overnight at room temperature. Preparative layer chromatography yielded 35 mg (68%) of $Mn_2Os(CO)_{14}$.[34]

In C_6H_6. $MeMn(CO)_5$ (25.5 mg, 0.12 mmol), 0.62 mL of C_6D_6, and 16.7 mg (0.06 mmol) of $H_2Os(CO)_4$ were sealed in an NMR tube. After 1.5 day at room temperature, 33% of the $MeMn(CO)_5$ was consumed (along with all of the $H_2Os(CO)_4$), giving CH_3CHO as the only organic product. Preparative layer chromatography of the red residue gave as major products $HMnOs_2(CO)_{12}$ (identified by its known IR)[35] (23% yield based on $H_2Os(CO)_4$) and an unidentified red complex; minor products were $H_2Os_3(CO)_{10}$[36] and $HMnOs_3(CO)_{16}$ (identified by its known IR).[35] $HMnOs_2(CO)_{12}$: ^1H NMR (C_6D_6) δ −22.88 (s); the mass spectrum showed

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an appropriate parent ion at *m/e* 776 (^{192}Os). Red complex: IR (hexanes) 2126 (w), 2080 (s), 2068 (m), 2044 (vs), 2020 (s), 2005 (s), 1988 (m), 1963 (s) cm^{-1}.

Reaction of $MeMn(CO)_5$ and $HMoCp(CO)_3$ in CH_3CN. $MeMn(CO)_5$ (17.6 mg, 0.08 mmol), 0.36 mL of CD_3CN, and 39.7 mg (0.16 mmol) of $HMoCp(CO)_3$ were sealed in an NMR tube under vacuum. The initial spectrum showed that approximately 60% reaction had occurred after 5 min. The reaction (disappearance of $MeMn(CO)_5$ and appearance of CH_3CHO) was complete within 40 min. At a much slower rate (in about 12 h), the $HMoCp(CO)_3$ disappeared and resonances (δ 2.95 (br, 2 H), 6.42 (br, 4 H)) assignable to cyclopentadiene grew in. No attempt to isolate the organometallic products was made.

Reaction of $MeMn(CO)_5$ and $HWCp(CO)_3$ in CH_3CN. $MeMn(CO)_5$ (32.5 mg, 0.16 mmol), 0.59 mL of CD_3CN, and 75.3 mg (0.22 mmol) of $HWCp(CO)_3$ were sealed in an NMR tube under vacuum. NMR monitoring of the reaction showed that it took 4 h to go to completion ($MeMn(CO)_5$ disappearance), and CH_3CHO was the only organic product. Attempts to isolate the organometallic product via preparative layer chromatography yielded only a mixture of $CpWMn(CO)_8$[37] (see below) and an unidentified complex, presumably $Mn(CO)_4(CD_3CN)WCp(CO)_3$. IR (hexanes) showed peaks at 2044 (w), 2013 (w), 2003 (m), 1988 (vs), 1963 (m), and 1945 (m) cm^{-1} in addition to those due to $CpWMn(CO)_8$.

Reaction of $MeMn(CO)_5$ and $HGePh_3$ in CH_3CN. Under N_2 flow, 0.61 mL of 0.19 M $HGePh_3$ (0.12 mmol) in CD_3CN was added via syringe to an NMR tube. The contents were frozen and degassed (2×) on a vacuum line, and 32 mg (0.15 mmol) of $MeMn(CO)_5$ was added by vacuum transfer. The initial NMR spectrum showed that approximately 40% reaction had occurred. All of the $HGePh_3$ (δ 5.58) was consumed after 50 min. The yield of CH_3CHO was 98% (based upon $HGePh_3$).

Reaction of $MeRe(CO)_5$ and $HRe(CO)_5$ in CH_3CN. Under N_2 flow, 0.49 mL of 0.13 M $CH_3Re(CO)_4$ (0.06 mmol) in CD_3CN was added via syringe to an NMR tube. The contents were frozen and degassed (3×) on a vacuum line, and 22 mg (0.07 mmol) of $HRe(CO)_5$ was added by vacuum transfer. The tube was sealed and heated to 60 °C. The reaction was very slow, giving only 11% reaction (the organic product was CH_3CHO) after 30 h at 60 °C.

Reaction of *i*-$BuRe(CO)_5$ and $HRe(CO)_5$ in CH_3CN. *i*-$BuRe(CO)_5$ (39.5 mg, 0.10 mmol), 0.40 mL of CD_3CN, and 42.1 mg (0.13 mmol) of $HRe(CO)_5$ were sealed in an NMR tube under vacuum. The reaction was heated to 46 °C and periodically an NMR spectrum was taken. After 30 h the reaction was 66% complete; the organic product was *i*-BuCHO (66% yield by integration).

Reaction of $EtRe(CO)_5$ and $HRe(CO)_5$ in CH_3CN. Under N_2 flow, 0.40 mL of 0.21 M $EtRe(CO)_5$ (0.08 mmol) in CD_3CN was added via syringe to an NMR tube. The contents were frozen and degassed (3×) on a vacuum line, and 34.6 mg (0.11 mmol) of $HRe(CO)_5$ was added by vacuum transfer. The tube was sealed and heated (60 °C) for a total of 27 h. At that time an NMR spectrum showed that the reaction was complete (all of the $EtRe(CO)_5$ had been consumed) and that the only organic product was EtCHO (88% yield by integration). In an identical experiment, 0.08 mmol of $EtRe(CO)_5$ reacted with 0.11 mmol of $HRe(CO)_5$ in 0.42 mL of CD_3CN. Close monitoring of the reaction by NMR spectroscopy showed that the reaction time was only 10 h.

The contents of the two NMR tubes were combined, and the product $Re_2(CO)_9(CD_3CN)$ (78 mg, 70% yield based on $EtRe(CO)_5$) was isolated by preparative layer chromatography: IR (hexanes) 2102 (w), 2046 (s), 2011 (m), 1999 (m, sh), 1988 (vs), 1963 (m), 1940 (m) cm^{-1}; the mass spectrum showed an appropriate parent ion at *m/e* 670 (^{187}Re). Anal. Calcd for $C_{11}D_3NO_9Re_2$: C, 19.76, D, 0.90; N, 2.09. Found: C, 19.81; D, 1.02; N, 1.93.[32] $Re_2(CO)_9(CH_3CN)$ has been synthesized from $Re_2(CO)_{10}$ + $ONMe_3$ in CH_3CN.[38]

In C_6H_6. $EtRe(CO)_5$ (37.9 mg, 0.11 mmol), 0.54 mL of C_6D_6, and 37.2 mg (0.11 mmol) of $HRe(CO)_5$ were sealed in an NMR tube under vacuum. NMR monitoring of the reaction showed that 27% of the $EtRe(CO)_5$ was converted to EtCHO after 3 days at 60 °C (the $HRe(CO)_5$ had been consumed). In another experiment, 42 mg (0.12 mmol) of $EtRe(CO)_5$, 1.0 mL of C_6H_6, and 137 mg (0.42 mmol) of $HRe(CO)_5$ were distilled into a standard reaction bulb and the reaction was heated to 60 °C for 5 days. The room-temperature volatiles were removed under vacuum, and the yellow residue was washed with hexanes (3 × 3 mL) and dried in vacuo. The yield of $HRe_3(CO)_{14}$ (identified by its known IR)[33] was 88 mg or 46%, based on $HRe(CO)_5$. Final purification was afforded by preparative layer chromatography, followed by crystallization from CH_2Cl_2/hexanes at −25 °C: ^{1}H NMR (C_6D_6) δ −15.42 (s). The mass spectrum showed an appropriate parent ion at *m/e* 954 (^{187}Re).

Reaction of $EtRe(CO)_5$ and $HMn(CO)_5$ in CH_3CN. Under N_2 flow, 0.42 mL of 0.21 M $EtRe(CO)_5$ (0.09 mmol) in CD_3CN was added via syringe to an NMR tube. The contents were frozen and degassed (3×) on a vacuum line, and 26 mg (0.13 mmol) of $HMn(CO)_5$ was added by vacuum transfer. NMR monitoring showed that the $EtRe(CO)_5$ was completely converted to EtCHO in 7 h at 60 °C. The product $Mn(CO)_5Re(CO)_4(CD_3CN)$ was isolated in 68% yield (32 mg) via preparative layer chromatography: IR (hexanes) 2098 (m), 2040 (s), 2003 (vs), 1994 (s), 1975 (m), 1957 (m), 1946 (m) cm^{-1}. The mass spectrum showed an appropriate parent ion at *m/e* 538 (^{187}Re). A sample of $Mn(CO)_5Re(CO)_4(CH_3CN)$ (see below) was analyzed: Anal. Calcd for $C_{11}H_3MnNO_9Re$: C, 24.73; H, 0.57; N, 2.62. Found: C, 25.25; H, 0.59; N, 2.47.

In another experiment, 78.9 mg (0.22 mmol) of $EtRe(CO)_5$, 0.92 mL of CH_3CN, and 50.4 mg (0.26 mmol) of $HMn(CO)_5$ were distilled into a standard reaction bulb and the reaction heated to 60 °C for 30 h. At that time, 84.6 mg (0.16 mmol, 73% yield) of $Mn(CO)_5Re(CO)_4(CH_3CN)$ was isolated as described above. Of this material 75 mg (0.14 mmol) was dissolved in 3 mL of CH_2Cl_2 and 88.3 mg (0.34 mmol) of PPh_3 was added. The reaction was extremely slow (analytical TLC showed starting material after 2 weeks). The reaction was stopped, and 52 mg (49%) of the product $Mn(CO)_5Re(CO)_4PPh_3$ along with 26 mg (35% recovery) of $Mn(CO)_5Re(CO)_4(CH_3CN)$ were isolated via preparative layer chromatography. For $Mn(CO)_5Re(CO)_4PPh_3$: IR (hexanes) 2096 (m), 2032 (m), 1990 (vs), 1971 (m), 1948 (m) cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 14.92 (s). Both spectra agreed with those reported.[20]

Reaction of $EtRe(CO)_5$ and $H_2Os(CO)_4$ in CH_3CN. Under N_2 flow, 0.43 mL of 0.21 M $EtRe(CO)_5$ (0.09 mmol) in CD_3CN was added via syringe to an NMR tube. The contents were frozen and degassed (3×) on a vacuum line, and 18 mg (0.06 mmol) of $H_2Os(CO)_4$ was added by vacuum transfer. ^{1}H NMR monitoring showed that the reaction was complete ($EtRe(CO)_5$ was consumed) in 8 h at 62 °C. The organic product was EtCHO (89% by integration). The tube was opened and the solvent removed in vacuo. The yellow residue was taken up in CH_2Cl_2 and the product precipitated by the addition of hexanes. The resulting material (presumably $Re_2Os(CO)_{12}(CD_3CN)_2$) proved to be unstable and was thus impossible to obtain pure: IR (hexanes) 2074 (m), 2047 (m), 2025 (w), 2013 (s), 2004 (vs), 1986 (m), 1972 (m), 1942 (m), 1933 (w) cm^{-1}; (CH_2Cl_2) 2108 (w), 2074 (m), 2055 (m), 2042 (m), 2012 (s), 1991 (vs), 1955 (m), 1918 (m), 1897 (m) cm^{-1}. The mass spectrum of this material showed only $Re_2Os(CO)_{14}$ (see below), with an appropriate parent ion at *m/e* 958 (^{187}Re, ^{192}Os).

In another experiment, $EtRe(CO)_5$ (50.1 mg, 0.15 mmol), 1 mL of CH_3CN, and 25 mg (0.08 mmol) of $H_2Os(CO)_4$ were distilled into a standard reaction bulb and heated to 60 °C overnight. The solvent was removed and the residue taken up in 2 mL of CH_2Cl_2, frozen, and degassed (3×); CO (2 atm) was then admitted. The reaction was stirred in the dark at room temperature for 2 days. The product $Re_2Os(CO)_{14}$ was isolated via preparative layer chromatography and identified by its known IR spectrum.[34] The yield was 98 mg or 67%, based upon $EtRe(CO)_5$. The mass spectrum showed an appropriate parent ion at *m/e* 958 (^{187}Re, ^{192}Os).

In C_6H_6. $EtRe(CO)_5$ (59.0 mg, 0.17 mmol), 1.4 mL of C_6H_6, and 25.1 mg (0.08 mmol) of $H_2Os(CO)_4$ were distilled into a standard reaction bulb and heated to 60 °C for 6 days. The room-temperature volatiles were removed, leaving a dark red-orange residue. Preparative layer chromatography yielded small

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amounts of the following compounds (in order of elution): $H_2Os_3(CO)_{10}$,[36] a red-orange complex (tentatively identified as $HReOs_3(CO)_{16}$), a yellow complex, and $HReOs_2(CO)_{12}$ (20 mg) (identified by its known IR).[35] For $HReOs_2(CO)_{12}$, ^1H NMR (C_6D_6) δ −19.31 (s); the mass spectrum showed an appropriate parent ion at *m/e* 908 (^{187}Re, ^{192}Os). The orange complex (IR (hexanes) 2129 (w), 2096 (w), 2081 (vs), 2064 (s), 2056 (vs), 2049 (s), 2046 (s), 2036 (m), 2024 (s), 2015 (s), 2003 (m), 1987 (w), 1979 (w), 1950 (m), 1931 (vw) cm^{-1}) showed an ion in the mass spectrum at *m/e* 1016 which appeared to be $H^{187}Re^{192}Os_3(CO)_9^+$.

Reaction of $EtRe(CO)_5$ and $HWCp(CO)_3$ in CH_3CN. $EtRe(CO)_5$ (32 mg, 0.09 mmol), 0.5 mL of CD_3CN, and 50 mg (0.15 mmol) of $HWCp(CO)_3$ were sealed in an NMR tube under vacuum. NMR monitoring showed that the conversion of $EtRe(CO)_5$ to EtCHO was complete in 8 h at 61 °C.

In another experiment, 100.5 mg (0.28 mmol) of $EtRe(CO)_5$, 1 mL of CH_3CN, and 114 mg (0.34 mmol) of $HWCp(CO)_3$ were placed in a standard reaction bulb and heated for 10 h at 61 °C. After solvent removal the orange-red residue was dissolved in 3 mL of CH_2Cl_2, frozen, and degassed (3×) and pressurized to 2 atm with CO. The reaction was stirred for 2 days in the dark at room temperature. Preparative layer chromatography yielded 74 mg (40% yield based on $EtRe(CO)_5$) of $CpWRe(CO)_8$ (identified by its known IR).[39] Also, 30 mg (16%) of an orange compound (probably $CpWRe(CO)_7(CH_3CN)$) was isolated. For $CpWRe(CO)_8$: ^1H NMR (C_6D_6) δ 4.50 (s); the mass spectrum showed an appropriate parent ion at *m/e* 662 (^{186}W, ^{187}Re). The orange compound (IR (hexanes) 2045 (s), 2030 (w), 2015 (vs), 1988 (m), 1982 (m), 1968 (s), 1948 (s) cm^{-1}) showed only $CpWRe(CO)_8$ when a mass spectrum was attempted.

Reaction of $EtRe(CO)_5$ and $HWCp(CO)_2PMe_3$ in CH_3CN. $EtRe(CO)_5$ (104 mg, 29 mmol), 5 mL of CH_3CN, and 86 mg (0.22 mmol) of $HWCp(CO)_2(PMe_3)$ were placed in a standard reaction bulb and heated for 18 h at 60 °C. The solvent was removed under vacuum and the resulting red-orange solid dissolved in 3 mL of Et_2O. The solution was frozen and degassed (3×), CO (2 atm) was added to the system, and the reaction was stirred for 3 weeks at room temperature. Chromatography (Chromatotron (Harrison Research, Palo Alto), 20% CH_2Cl_2 in hexanes, 1-mm silica gel) of the mixture gave the following complexes (in order of elution): $CpWRe(CO)_8$(20%),[39] $Cp_2W_2(CO)_6$ (3%), $CpW(CO)_2(PMe_3)Re(CO)_5$ (45%), and a complex (11%) which appeared to be an isomer of $CpW(CO)_2(PMe_3)Re(CO)_5$ with different stereochemistry about W. $CpW(CO)_2(PMe_3)Re(CO)_5$: IR (hexanes) 2073 (m), 1986 (s), 1980 (s), 1953 (s), 1935 (s), 1874 (m, br), 1845 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 4.76 (s, 5 H), 1.10 (d, J = 8.9 Hz, 9 H); the mass spectrum showed an appropriate parent ion at *m/e* 711 (^{186}W, ^{187}Re). For the $CpW(CO)_2(PMe_3)Re(CO)_5$ isomer: IR (hexanes) 2096 (s), 2027 (m), 2000 (s), 1985 (vs), 1963 (s), 1873 (m), 1812 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 4.51 (d, J = 1.95 Hz, 5 H), 1.17 (d, J = 9.5 Hz, 9 H).

Reaction of $EtRe(CO)_5$ and $HCrCp(CO)_3$ in CH_3CN. $EtRe(CO)_5$ (84 mg, 0.24 mmol), 2 mL of CH_3CN, and 75 mg (0.37 mmol) of $HCrCp(CO)_3$ were allowed to react for 18 h at 60 °C. ^1H NMR showed that the organic product was propionaldehyde. The solvent was removed, and the resulting brown residue was dissolved in 4 mL of Et_2O. The brown solution was frozen and degassed (3X), and CO (2 atm) was added to the system. The reaction was stirred for 4 weeks at 25 °C. The solvent was removed, and the residue was extracted with hexanes (8 × 5 mL). The resulting orange-brown solution was filtered through neutral alumina (Woelm, super active, 200 mesh), and the solvent was removed, leaving an orange-brown solid. Although the compound was too unstable during chromatography to permit purification for elemental analysis, its mass spectrum showed a parent ion at *m/e* 528 (^{52}Cr, ^{187}Re) appropriate for $CpCr(CO)_3Re(CO)_5$. IR (hexanes): 2114 (m), 2046 (m), 2013 (vs), 1983 (s), 1959 (m), 1900 (w), 1880 (m) cm^{-1}.

Reaction of $MeFeCp(CO)_2$ and $HRe(CO)_5$ in CH_3CN. Under N_2 flow, 0.43 mL of 0.25 M $MeFeCp(CO)_2$ (0.11 mmol) in CD_3CN was added via syringe to an NMR tube. The contents were frozen and degassed (3X) on a vacuum line, 37.5 mg (0.12 mmol) of $HRe(CO)_5$ was added by vacuum transfer, and the tube was sealed under vacuum. NMR monitoring showed that 50% of the $MeFeCp(CO)_2$ was converted to CH_3CHO after 2.5 days at 55 °C. TLC of the contents of the NMR tube showed that the organometallic products were $Cp_2Fe_2(CO)_4$ and $Re_2(CO)_9(CD_3CN)$.

Reaction of $MeFeCp(CO)_2$ and $HMn(CO)_5$ in CH_3CN. As described above, 0.40 mL of 0.25 M (0.10 mmol) $MeFeCp(CO)_2$ in CD_3CN and 23.3 mg (0.12 mmol) $HMn(CO)_5$ were left for 2.5 days at 55 °C. An NMR spectrum showed that CH_3CHO was formed in 53% yield. The organometallic products were $Cp_2Fe_2(CO)_4$ and $Mn_2(CO)_9(CD_3CN)$ (identified by its known IR).[38a]

Reaction of $MeFeCp(CO)_2$ and $H_2Os(CO)_4$ in CH_3CN. In a similar experiment, 0.41 mL of 0.25 M (0.10 mmol) $MeFeCp(CO)_2$ in CD_3CN and 16.1 mg (0.05 mmol) of $H_2Os(CO)_4$ were left for 3 days at 55 °C. The yield of CH_3CHO was 25%. No attempt to isolate the organometallic products was made.

Reaction of $EtFeCp(CO)_2$ and $HRe(CO)_5$ in CH_3CN. As described above, 0.60 mL of 0.17 M $EtFeCp(CO)_2$ (0.10 mmol) in CD_3CN was added to an NMR tube. The contents were frozen and degassed (3X), 56 mg (0.17 mmol) of $HRe(CO)_5$ was added, and the tube was sealed under vacuum. NMR monitoring showed that 88% of the $EtFeCp(CO)_2$ was converted to EtCHO after 16.5 h at 48 °C. An IR spectrum of the contents of the NMR tube showed the presence of $Cp_2Fe_2(CO)_4$ and $Re_2(CO)_9(CD_3CN)$.

Reaction of $Me_2Os(CO)_4$ and $H_2Os(CO)_4$ in Toluene. $Me_2Os(CO)_4$ (24.2 mg, 0.0728 mmol), 0.35 mL of C_7D_8, and 80.7 mg (0.265 mmol, 3.6 equiv) of $H_2Os(CO)_4$ were sealed in an NMR tube and heated at 80 °C for 7 weeks. An NMR spectrum showed that the $Me_2Os(CO)_4$ had been consumed and that CH_3CHO (22% based on $Me_2Os(CO)_4$), EtOH (8%), other volatile organic species (3%), $MeOs_2(CO)_8H$,[25] H_2, and CH_4 had been formed. The tube was then broken open on the vacuum line, and the volatile components (−196 °C) were collected via a Toepler pump. GC analysis indicated that 0.075 mmol of CH_4 (52% yield based upon $Me_2Os(CO)_4$) had been formed.

Reaction of $Me_2Os(CO)_4$ and $HRe(CO)_5$ in Toluene. $Me_2Os(CO)_4$ (20.4 mg, 0.0614 mmol), 0.35 mL of C_7D_8, and 118.4 mg (0.362 mmol, 5.9 equiv) of $HRe(CO)_5$ were sealed in an NMR tube and heated at 80 °C for 5 weeks. An NMR spectrum showed that the $HRe(CO)_5$ had been consumed and that CH_3CHO (15% based on $Me_2Os(CO)_4$), EtOH (50%), $MeOs_2(CO)_8H$,[25] H_2, and CH_4 had been formed. The tube was then broken open on the vacuum line, and the volatile components (−196 °C) were collected via a Toepler pump. GC analysis indicated that 0.05 mmol of CH_4 (39% yield based upon $Me_2Os(CO)_4$) had been formed.

Reaction of $Me_2Os(CO)_4$ and $HRe(CO)_5$ in CH_3CN. $Me_2Os(CO)_4$ (25.1 mg, 0.08 mmol), 0.5 mL of CD_3CN, and 105 mg (0.32 mmol) of $HRe(CO)_5$ were sealed in an NMR tube and heated at 60 °C for 10 days. An NMR spectrum showed that the $Me_2Os(CO)_4$ had been consumed and that CH_3CHO (42% based on $Me_2Os(CO)_4$) and CH_4 had been formed. The tube was then broken open on the vacuum line, and the volatile components (−196 °C) were collected via a Toepler pump. GC analysis indicated that 0.07 mmol of CH_4 (44% yield based upon $Me_2Os(CO)_4$) had been formed. Preparative layer chromatography of the nonvolatile residue gave, in order of elution, $Re_2(CO)_{10}$, $Re_2(CO)_9(CD_3CN)$, and a compound identified as $Re_2Os(CO)_{13}(CD_3CN)$ by mass spectrometry: *m/e* 974 (^{187}Re, ^{192}Os). The IR of $Re_2Os(CO)_{13}(CH_3CN)$ is given below.

Reaction of $Et_2Os(CO)_4$ and $HRe(CO)_5$ in CH_3CN. $Et_2Os(CO)_4$ (34 mg, 0.09 mmol), 0.6 mL of CD_3CN, and 84.5 mg (0.26 mmol, 2 equiv) of $HRe(CO)_5$ were distilled into an NMR tube. The tube was sealed under vacuum and heated to 40 °C for 20 h. An NMR spectrum showed that the $Et_2Os(CO)_4$ had been consumed. The tube was opened on a vacuum line, and the volatile (−120 °C) components were collected via a Toepler pump. GC analysis indicated that 0.10 mmol (55%) of ethane had been formed. In an analogous experiment, 41 mg (0.11 mmol) of $Et_2Os(CO)_4$, 0.54 mL of CD_3CN, and 39.8 mg (0.12 mmol) of $HRe(CO)_5$ were heated for 24 h at 50 °C. The tube was opened on a vacuum line, and the volatile (25 °C) components were vacuum transferred into another NMR tube. NMR analysis showed that the ethane/EtCHO ratio was 1.16.

In another experiment, 86.2 mg (0.24 mmol) of $Et_2Os(CO)_4$, 1.2 mL of CH_3CN, and 156.2 mg (0.48 mmol) of $HRe(CO)_5$ were heated (50 °C) in a standard reaction bulb for 30 h. The solvent

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was removed in vacuo and the resulting yellow solid washed (6X, 4 mL) with hexanes. The product $Re_2Os(CO)_{13}(CH_3CN)$ was isolated by dissolving the yellow solid in CH_2Cl_2 (0.6 mL) and precipitating it with hexanes: IR (C_6H_{12}) 2096 (w), 2068 (s), 2045 (s), 2035 (vs), 2023 (m), 2015 (m), 2002 (m), 1982 (m), 1965 (w); (CH_2Cl_2) 2114 (vw), 2077 (m), 2001 (vs), 1960 (m) cm^{-1}. The mass spectrum showed an appropriate parent ion at *m/e* 971 (^{187}Re, ^{192}Os).

In a separate reaction, $Et_2Os(CO)_4$ (39 mg, 0.11 mmol), 0.54 mL of CD_3CN, and 39.8 mg (0.12 mmol, 1 equiv) of $HRe(CO)_5$ were sealed under vacuum in an NMR tube. The reaction was heated to 49 °C for 25 h. An NMR spectrum showed ethane and EtCHO along with a resonance assignable to EtOs (δ 1.69 (t), 1.01 (q)) and two signals assignable to EtC(O)Os (δ 2.86 (q), 0.94 (t) and 2.72 (q), 0.77 (t)). The latter signals were due to $EtC(O)Os(CO)_3(CD_3CN)Re(CO)_5$ and $EtC(O)OsRe(CO)_9$, respectively (see below). The tube was broken open on the vacuum line and the volatiles distilled into an NMR tube. The ^1H NMR spectrum showed that the EtH/EtCHO ratio was 4.2.

In another experiment, 62.1 mg (0.17 mmol) of $Et_2Os(CO)_4$, 1.2 mL of CH_3CN, and 51.6 mg (0.16 mmol) of $HRe(CO)_5$ were heated to 45 °C for 20 h in a standard reaction bulb. After solvent removal the resulting off-white solid was placed under high vacuum overnight. Preparative layer chromatography yielded the following compounds (in order of elution): $EtOsRe(CO)_9$ (42%), a compound tentatively identified as $EtC(O)OsRe(CO)_9$ (10%) and a small amount of $Re_2Os(CO)_{13}(CH_3CN)$. For $EtOsRe(CO)_9$: IR (hexanes) 2124 (w), 2073 (s), 2036 (m), 2022 (vs), 2009 (s), 1994 (m), 1981 (s), 1966 (w), 1941 (vw) cm^{-1}; ^1H NMR (CD_3CN) δ 1.84 (t, J = 6.75 Hz, 3 H), 1.20 (q, J = 6.74 Hz, 2 H). The mass spectrum showed an appropriate parent ion at *m/e* 660 (^{187}Re, ^{192}Os). Anal. Calcd: C, 20.09; H, 0.77. Found: C, 20.60; H, 0.84.

For the compound tentatively identified as $EtC(O)OsRe(CO)_9$: IR (hexanes) 2130 (w), 2084 (m), 2050 (m), 2036 (m), 2022 (vs), 2014 (s), 1994 (m), 1982 (s), 1943 (w), 1636 (m) cm^{-1}; ^1H NMR (CD_3CN) δ 2.71 (q, J = 7.21 Hz, 2 H), 0.74 (t, J = 7.21 Hz, 3 H). The mass spectrum showed a peak at *m/e* 660 (^{187}Re, ^{192}Os) corresponding to $P^+ - 28$. Similarly, when purification by sublimation (60 °C, 10 μm) was attempted, $EtC(O)OsRe(CO)_9$ formed $EtOsRe(CO)_9$ by decarbonylation.

Reaction of $EtOsRe(CO)_9$ and $HRe(CO)_5$ in CH_3CN. $EtOsRe(CO)_9$ (14 mg, 0.02 mmol), 0.41 mL of CD_3CN, and 23 mg (0.07 mol) of $HRe(CO)_5$ were sealed in an NMR tube under vacuum. NMR monitoring showed that the $EtOsRe(CO)_9$ was rapidly (within 3 h at 46 °C) converted to an acyl species (presumably $EtC(O)Os(CO)_3(CD_3CN)Re(CO)_5$, see below). After 6 h at 46 °C only 10% formation of EtCHO had occurred, compared to 40% conversion to $EtC(O)Os(CO)_3(CD_3CN)Re(CO)_5$.

Reaction of $Me(Cl)Os(CO)_4$ and $HRe(CO)_5$ in CH_3CN. Under N_2 flow, 0.51 mL of 0.23 M $Me(Cl)Os(CO)_4$ (0.12 mmol) in CD_3CN was added via syringe to an NMR tube. The contents were frozen and degassed (3×) on a vacuum line, 65 mg (0.20 mmol) of $HRe(CO)_5$ was added by vacuum transfer, and the tube was sealed. NMR monitoring showed that the reaction was complete in 15 h at 50 °C. The organic products were CH_3CHO (5%) and a large but undetermined amount of CH_4.

Reaction of $Et(Cl)Os(CO)_4$ and $HRe(CO)_5$ in CH_3CN. $Et(Cl)Os(CO)_4$ (11 mg, 0.03 mmol), 0.5 mL of CD_3CN, and 15 mg (0.05 mmol) of $HRe(CO)_5$ were sealed in an NMR tube under vacuum. NMR monitoring showed that the reaction was complete in 8 h at 50 °C. The sole organic product was EtCHO. No attempt to isolate the organometallic products was made.

Formation of $EtC(O)(CH_3CN)Re(CO)_4$ in CH_3CN. $EtRe(CO)_5$ (34.7 mg, 0.10 mmol) and 0.43 mL of CD_3CN were sealed under vacuum in an NMR tube. Periodic NMR monitoring (the tube was heated to 60 °C, removed at appropriate time intervals, and an NMR spectrum—Figure 1—recorded) showed that the ethyl pattern of $EtRe(CO)_5$ decreased in intensity, with concurrent formation of new peaks assignable to a propionyl group (see below). The maximum concentration of product was reached in about 3 h at this temperature. Extended heating of this reaction led to decomposition of the solvate and the formation of new EtRe and EtC(O)Re signals.

In another experiment, 11 mg (0.03 mmol) of $EtRe(CO)_5$ and 3.2 mL of CH_3CN were placed in a standard reaction bulb at 60 °C; aliquots were removed and their IR spectra (Figure 2) recorded. The absorbances due to $EtRe(CO)_5$ diminished while the absorbances due to the solvate grew in.

In another experiment, 96 mg (0.27 mmol) of $EtRe(CO)_5$ and 1.2 mL of CH_3CN were heated for 5 h at 60 °C. The solvent was removed under vacuum and the resulting yellow oil extracted with 4 mL of hexanes and an IR spectrum recorded (Figure 3); the hexane solution decomposed rapidly at room temperature. For the solvate: IR (CH_3CN) 2092 (m), 1989 (vs), 1940 (s), 1600 (m); (hexanes) 2087 (m), 1985 (s), 1950 (s), 1939 (m), 1610 (m) cm^{-1}; ^1H NMR (CD_3CN) δ 2.64 (q, J = 7.2 Hz, 2 H), 0.80 (t, J = 7.2 Hz, 3 H).

Exchange of CH_3CN with Coordinated CD_3CN in $EtC(O)Re(CO)_4(CD_3CN)$. In an NMR tube, $EtRe(CO)_5$ in CD_3CN (0.42 mL, 0.21 M) was heated for 3.5 h at 59 °C. The tube was then attached to a vacuum line and frozen (−196 °C), CH_3CN (0.050 mL) was added, and the tube was sealed and thawed to 268 K. NMR monitoring before and after 40 min at room temperature showed a peak grow in at δ 2.37 which showed intensity (9% of free CH_3CN, δ 1.954 in CD_3CN) proportional to the mole fraction (10.6%) of CH_3CN in acetonitriles.

In a similar experiment, $EtRe(CO)_5$ in CD_3CN (0.43 mL, 0.21 M) was treated as above with CH_3CN (0.090 mL) and the tube sealed and warmed to 268 K. NMR monitoring before and after 40 min at room temperature showed a peak grow in at δ 2.37 which showed intensity (15% of free CH_3CN, δ 1.954 in CD_3CN) proportional to the mole fraction (17.3%) of CH_3CN in acetonitriles.

***cis*-Propionyltetracarbonyl(triphenylphosphine)rhenium.** In a standard reaction bulb, $EtRe(CO)_5$ (67.8 mg, 0.191 mmol), CH_3CN (1.0 mL), and PPh_3 (50.0 mg, 0.191 mmol) were combined, frozen, and degassed (3×). After 6 h at 64 °C, the solution was cooled slowly to −30 °C and the volume of solvent was reduced, and the yellow crystals and solution were cooled in an inert-atmosphere box to −25 °C. The liquid was decanted, and the resulting yellow crystals were washed with cold hexanes (4 × 2 mL) and pumped to dryness. The isolated yield of $EtC(O)Re(CO)_4PPh_3{\cdot}0.36(CH_3CN)$ (solvation determined by NMR) was 21.9 mg (0.035 mmol, 19%): IR (hexanes) 2087 (m), 2001 (s), 1972 (s), 1954 (s), 1602 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 7.6–7.5 (m, 6 H), 6.97–6.93 (m, 9 H), 2.63 (q, 2 H, J = 7.1 Hz), 0.86 (t, 3 H, J = 7.1 Hz), 0.59 (s, 1.1 H). Anal. Calcd for $C_{25.7}H_{21.1}N_{0.4}O_5PRe$: C, 48.85; H, 3.36. Found: C, 49.24; H, 3.43.

Formation of *i*-$BuC(O)(CH_3CN)Re(CO)_4$ in CH_3CN. *i*-$BuRe(CO)_5$ (44.2 mg, 0.12 mmol) and 0.51 mL of CD_3CN were sealed in an NMR tube under vacuum. The tube was heated to 53 °C and its NMR spectrum periodically recorded. The *i*-Bu (δ 1.00 (d), 0.98 (d); the methine proton was masked by solvent) signal for *i*-$BuRe(CO)_5$ decreased with time, while resonances assignable to an isovaleroyl group (reported below) increased. IR monitoring (0.02 mmol in 22 mL CH_3CN) also showed decreasing *i*-$BuRe(CO)_5$ absorbances with increasing *i*-$BuC(O)(CH_3CN)Re(CO)_4$ absorbances. For the solvate: IR (CH_3CN) 2091 (w), 1982 (s), 1939 (m), 1605 (m) cm^{-1}; ^1H NMR (CD_3CN) δ 2.53 (d, J = 6.4 Hz, 2 H), 2.07 (m, 1 H), 0.84 (d, J = 6.1 Hz, 6 H).

Reaction of $Et_2Os(CO)_4$ in CH_3CN. $Et_2Os(CO)_4$ (36.2 mg, 0.10 mmol) and 0.46 mL of CD_3CN were sealed under vacuum in an NMR tube and heated to 46 °C for 3 h. The resulting ^1H NMR (360 MHz) pattern was very complex and it proved impossible to make exact assignments. However, propionyl methyl signals (cf. $EtC(O)(CH_3CN)Re(CO)_4$) were observed at δ 0.807 (J = 7.25 Hz) and at δ 0.780 (J = 7.22 Hz) and a propionyl methylene signal was observed as a complex multiplet centered at δ 2.60; the 20-line pattern of the latter indicated that at least one propionyl ligand had diastereotopic methylene hydrogens. Similarly, new methyl triplets appeared at δ 1.639 (J = 7.88 Hz) and 1.617 (J = 7.87 Hz), and new methylene signals appeared at δ 1.05 and 0.90; the former showed the AB structure of diastereotopic hydrogens. There were thus EtOs resonances besides those of $Et_2Os(CO)_4$ (δ 1.687 (J = 7.78 Hz, t, 3 H), 0.971 (J = 7.78 Hz, q, 2 H)). ^{13}C NMR (CD_3CN): δ 242.55, 239.75 (acyls), 180.65, 180.36, 178.61, 177.59, 176.57, 174.02 (carbonyls), 55.37, 55.15 ($MC(O)CH_2CH_3$), 21.29, 21.15 (CH_3CH_2M), 8.82, 8.60 ($MC(O)CH_2CH_3$), 2.54, 0.06 (CH_3CH_2M). After 0.09 mmol of $Et_2Os(CO)_4$ in 3.2 mL of CH_3CN was heated for 7.5 h at 48–50 °C, IR showed absorbances at 2078 (m), 2067 (m), 2038 (m, $Et_2Os(CO)_4$), 2000 (s), 1977 (vs), 1966 (m, sh), and 1625 (m, br) cm^{-1}.

$ClEtOs(CO)_4$ in CH_3CN. $Et(Cl)Os(CO)_4$ (0.01 mmol) was dissolved in 2 mL of CH_3CN and heated to 50 °C; IR showed absorbances at 2102 (w), 2081 (m), 2042 (s, sh), 2036 (s), 1996 (w), 1962 (vs), and 1628 (m, br) cm^{-1}. All of the absorbances due to the $ClEtOs(CO)_4$ (2160 (w), 2078 (vs), 2032 (s)) had disappeared.

$EtOs(CO)_4Re(CO)_5$ in CH_3CN. $EtOsRe(CO)_9$ (12 mg, 0.02 mmol) and 0.43 mL CD_3CN were sealed in an NMR tube under vacuum. NMR monitoring of the reaction at −46 °C showed that new resonances grew in at δ 2.79 (m), 0.92 (t, J = 7.18 Hz), and 0.76 (t, J = 7.10 Hz).

Reaction of $EtRe(CO)_5$ and Its Propionyl Solvate with $HRe(CO)_5$ in CH_3CN. Under a stream of N_2, 0.54 mL of 0.042 M $EtRe(CO)_5$ in CD_3CN was syringed into an NMR tube; the tube was closed by a stopcock under 1 atm of N_2 and heated for 3 h at 60 °C. The tube was then attached to a vacuum line, frozen, and evacuated, and 127 mg (0.38 mmol) of $HRe(CO)_5$ was added by vacuum transfer. The tube was sealed under vacuum and warmed to room temperature, and the reaction was monitored by NMR. The $EtC(O)Re(CO)_4(CH_3CN)$ was rapidly consumed (within 1 h) with concurrent formation of EtCHO. The amount of $EtRe(CO)_5$ remained unchanged throughout the reaction.

Reaction of $Et_2Os(CO)_4$ and Its Propionyl Solvate with $HRe(CO)_5$ in CH_3CN. Under a stream of N_2, 0.46 mL of 0.035 M $Et_2Os(CO)_4$ (0.02 mmol) in CD_3CN was syringed into an NMR tube; the tube was closed by a stopcock under 1 atm of N_2 and heated for 5 h at 46 °C. The tube was attached to a vacuum line, frozen, and evacuated, and 31.4 mg (0.10 mmol) of $HRe(CO)_5$ was added by vacuum transfer. The tube was sealed and the reaction monitored by NMR. Ethane and EtCHO were formed within 1 h at 18 °C. No further changes occurred up to 2 h at 18 °C. Integration of the NMR spectrum showed that the EtH/EtCHO ratio was 4:1.

Kinetics of the Reaction of $MeMn(CO)_5$ with $HRe(CO)_5$ in Mesitylene. The rate was measured by monitoring the appearance of the IR absorption of $HMnRe_2(CO)_{14}$ at 2045 cm^{-1}. A solution of $MeMn(CO)_5$ (9×10^{-3} M) and 0.12 M $HRe(CO)_5$ was placed in a standard reaction bulb. The bulb was placed in a constant temperature bath set to 25.5 (± 0.1) °C, removed at appropriate intervals, and cooled in ice water to quench the reaction. Aliquots were then removed and their IR spectra recorded.

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Registry No. $Na[Mn(CO)_5]$, 13859-41-1; $Na[Re(CO)_5]$, 33634-75-2; $HMn(CO)_5$, 16972-33-1; $HRe(CO)_5$, 16457-30-0; $MeMn(CO)_5$, 13601-24-6; $MeRe(CO)_5$, 14524-92-6; $EtRe(CO)_5$, 75149-83-6; *i*-$BuRe(CO)_5$, 98688-78-9; $Me(H)Os(CO)_4$, 22639-03-8; *cis*-$Me(Cl)Os(CO)_4$, 66705-58-6; $HWCp(CO)_2PMe_3$, 98757-38-1; $HWCp(CO)_3$, 12128-26-6; $(CO)_5ReMn(CO)_4(CD_3CN)$, 98688-79-0; $(CO)_5ReMn(CO)_4(CH_3CN)$, 98688-80-3; *ax*-$Re(CO)_5Mn(CO)_4PPh_3$, 51320-29-7; $HMnRe_2(CO)_{14}$, 12276-95-8; $H_2OS(CO)_4$, 22372-70-9; $Mn_2Os(CO)_{12}(CD_3CN)_2$, 98688-81-4; $Mn_2Os(CO)_{14}$, 33292-90-9; $Mn_2Os(CO)_{12}(CH_3CN)_2$, 98688-82-5; $HMnOs_2(CO)_{12}$, 12560-43-9; $H_2Os_3(CO)_{10}$, 41766-80-7; $HMnOs_3(CO)_{16}$, 12566-57-3; $HMoCp(CO)_3$, 12176-06-6; $CpWMn(CO)_8$, 12085-49-3; $Mn(CO)_4(CD_3CN)WCp(CO)_3$, 98688-83-6; $HGePh_3$, 2816-43-5; $Re_2(CO)_9(CD_3CN)$, 98688-84-7; $HRe_3(CO)_{14}$, 12086-80-5; $Mn(CO)_5Re(CO)_4(CD_3CN)$, 98688-85-8; $Mn(CO)_5Re(CO)_4(CH_3CN)$, 98688-86-9; $Mn(CO)_5Re(CO)_4PPh_3$, 51320-28-6; $Re_2Os(CO)_{12}(CD_3CN)_2$, 98688-87-0; $Re_2Os(CO)_{14}$, 33153-70-7; $Re_2Os(CO)_{12}(CH_3CN)_2$, 98688-88-1; $HReOs_3(CO)_{16}$, 12566-58-4; $HReOs_2(CO)_{12}$, 12560-44-0; $CpWRe(CO)_7(CH_3CN)$, 98688-89-2; $CpWRe(CO)_8$, 12085-52-8; $Cp_2W_2(CO)_6$, 12091-65-5; $CpW(CO)_2(PMe_3)Re(CO)_5$, 98688-90-5; $HCrCp(CO)_3$, 36495-37-1; $CpCr(CO)_3Re(CO)_5$, 98688-91-6; $MeFeCp(CO)_2$, 12080-06-7; $Cp_2Fe_2(CO)_4$, 12154-95-9; $Mn_2(CO)_9(CD_3CN)$, 97315-01-0; $EtFeCp(CO)_2$, 32611-65-7; $Me_2Os(CO)_4$, 59599-35-8; $MeOs_2(CO)_8H$, 60442-71-9; $Re_2(CO)_{10}$, 14285-68-8; $Re_2Os(CO)_{13}(CD_3CN)$, 98688-92-7; $Et_2Os(CO)_4$, 98757-39-2; $Re_2Os(CO)_{13}(CH_3CN)$, 98688-93-8; $EtC(O)Os(CO)_3(CD_3CN)Re(CO)_5$, 98688-94-9; $EtC(O)OsRe(CO)_9$, 98688-95-0; $EtOsRe(CO)_9$, 98688-96-1; $Et(Cl)Os(CO)_4$, 68568-91-2; $EtC(O)(CH_3CN)Re(CO)_4$, 98688-97-2; $EtC(O)Re(CO)_4(CD_3CN)$, 98688-98-3; $EtC(O)Re(CO)_4PPh_3$, 98688-99-4; *i*-$BuC(O)(CH_3CN)Re(CO)_4$, 98689-00-0; $ClEtC(O)(CH_3CN)Os(CO)_3$, 98689-01-1; $EtC(O)(Et)(CD_3CN)Os(CO)_3$, 98689-02-2; CH_3CHO, 75-07-0; *i*-BuCHO, 590-86-3; EtCHO, 123-38-6; EtOH, 64-17-5; CH_4, 74-82-8; C_2H_6, 74-84-0; C, 7440-44-0; H_2, 1333-74-0.