phosphoryl oxygen, it is hydrogen bonded to the phosphoryl-bound alcohol group of another molecule. This dissymmetry may account for distortion of the 1,3,2-dioxaphosphepane ring in **9**.

Conclusions. The tricyclic phosphorus compounds **4a–e** and their derivatives do not equilibrate to form detectable quantities of pentacoordinate phosphorus species. Although nucleophilic attack of the pendant alcoholic oxygen on phosphorus is not favored, such attack at a neighboring OC carbon in **4a–e** is catalyzed by protonic acids, giving rise to isomeric phosphonates **5a–e** via an unusual Arbuzov-like rearrangement. Solution ^{1}H and ^{13}C NMR of **4a–e** and their derivatives are consistent with the postulate that hydrogen bonding occurs between the oxygen of the pendant alcohol and a hydrogen on a neighboring OC carbon. The relatively low Lewis basicity of phosphite esters of types **3** and **4a–e** is a conformational effect rather than the result of strain.

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Supplementary Material Available: Tables of positional parameters, hydrogen atom parameters, and anisotropic thermal parameters for **2d**, **5c**, **9**, **11c**, and **11d**, bond distances for **2d** and **11c**, bond angles for **2d**, **9**, and **11c**, high-resolution mass spectral data, and ^{1}H and ^{13}C NMR data (61 pages); tables of calculated and observed structure factors (32 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Heterobimetallic Complexes with Bridging Acyl Groups: $(CO)_4Fe(\mu\text{-}C(R)O)M(CO)_4$ (R = Ph, Me; M = Re, Mn)

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The reaction of $[(CO)_4Fe(C(O)R)][NMe_4]$ (**1a**, R = Ph; **1b**, R = Me) and $[(CO)_4ReBr]_2$ (**2**) in THF at 0 °C results in the formation of $(CO)_4Fe(\mu\text{-}C(R)O)Re(CO)_4$ (**4a**, R = Ph; **4b**, R = Me) in yields of 40–46%. The analogous derivative of manganese from **1a** and $[(CO)_4MnBr]_2$ (**3**) proved to be thermally unstable. The structures of **4a** and **4b** were determined by single-crystal X-ray diffraction analysis. Compound **4a** crystallizes in a triclinic space group $P\bar{1}$ with $Z = 4$. The cell dimensions are $a = 15.674$ (1) Å, $b = 14.986$ (1) Å, $c = 7.768$ (1) Å, $\alpha = 107.90$ (1)°, $\beta = 90.02$ (1)°, and $\gamma = 70.98$ (1)°. The final structure was refined to $R_F = 3.3\%$ and $R_{wF} = 4.9\%$ on 5297 reflections with $I > 3\sigma(I)$. Compound **4b** was also found to be triclinic, space group $P\bar{1}$ with $Z = 2$ and $a = 8.177$ (1) Å, $b = 9.869$ (1) Å, $c = 9.212$ (1) Å, $\alpha = 106.59$ (1)°, $\beta = 108.18$ (1)°, and $\gamma = 76.38$ (1)°. The structure was refined to $R_F = 1.6\%$ and $R_{wF} = 2.4\%$ on 2235 reflections with $I > 3\sigma(I)$. The Fe–Re distances are 2.841 (1) Å in **4a** and 2.861 (1) Å in **4b**. These rather long bond distances as well as the thermal instability of the manganese analogue reflect a weakening of the M–M′ bond over those observed in phosphide-bridged analogues.

Introduction

Bimetallic heterogeneous catalysts have been shown to possess improved activity, selectivity, and stability over the corresponding homometallic systems.[1a] As a consequence, the physical and chemical properties of bimetallic and mixed-metal polynuclear transition-metal complexes became of interest;[1b,c] heteronuclear compounds may polarize and activate substrates differently from analogous homometallic systems and thus lead to enhanced chemical and/or catalytic properties under homogeneous conditions. Due to prevalence of heterolytic (ionic) cleavage of complexes with dissimilar metals, emphasis has been placed on the presence of bridging ligands. Extensive studies have appeared on diorganophosphide-bridged bimetallic complexes. Acyl groups have been also been observed as bridging ligands and would exert different electronic effects on the bridged metal atoms. However, this group of complexes has been the subject of relatively fewer studies.[2] In this paper we report the synthesis and characterization of some heterometallic acyl-bridged compounds by interaction of iron acyl metalates with electrophilic complexes of manganese or rhenium.

Results

The syntheses undertaken in this study are summarized in eqs 1 and 2. The reaction is followed by the disappearance of the

$$\underset{\textbf{1a},\ R = Ph;\ \textbf{1b},\ R = Me}{[(CO)_4Fe(C(O)R)][NMe_4]} + \underset{\textbf{2}}{[(CO)_4ReBr]_2} \xrightarrow{THF/0\ ^\circ C} \underset{\substack{\textbf{4a},\ R = Ph;\ \textbf{4b},\ R = Me\\ \text{yields 46 or 40\%}}}{(CO)_4Fe\{\mu\text{-}C(R)O\}Re(CO)_4} \quad (1)$$

$$\textbf{1a} + \underset{\textbf{3}}{[(CO)_4MnBr]_2} \xrightarrow{PhMe/25\ ^\circ C} \underset{\substack{\textbf{5a}\\ \text{yield ca. 20\%}\\ \text{(thermally unstable)}}}{(CO)_4Fe\{\mu\text{-}C(Ph)O\}Mn(CO)_4} \quad (2)$$

bands corresponding to **2** or **3** in the IR spectrum. The IR absorptions in the CO stretching region and the NMR spectra for **4a**, **4b**, and **5** are collected in Table I. The bridging acyl groups in these compounds are identified through their characteristic IR absorbances at 1470–1525 cm^{-1}. There is a larger difference in the acyl stretching absorption between the phenyl and methyl derivatives compared to the corresponding iron dimers $(OC)_3Fe\{\mu\text{-}C(R){=}O\}_2Fe(CO)_3$ (ν(bridging acyl) = 1497 cm^{-1} for R = CH_3 and 1536 cm^{-1} for R = Ph).[2a] The ^{13}C NMR resonances for the acyl carbon of the bridging acyl groups appear at a typical[2] low-field position, 280–300 ppm. Two singlets of unequal peak height are observed in the carbonyl region of the ^{13}C NMR spectrum for **4a**. The one at lower peak height (189.7 ppm) is assigned to the four CO groups on Re on the basis of two ob-

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Table I. NMR and IR Spectral Data for **4a**, **4b**, and **5**

	4a	**4b**	**5**
^{1}H NMR^a	7.2–7.6 (m) ($C_6\mathit{H}_5$)	2.43 (s) ($C\mathit{H}_3$)	7.0–7.5 (m) ($C_6\mathit{H}_5$)
^{13}C NMR^a	126.6, 128.6, 134.2, 147.4 (C_6H_5) 189.7, 201.8 ($\mathit{C}O$) 286.9 (μ-C(R)O)	51.4 ($\mathit{C}H_3$) 189.4, 201.5, 210.4 ($\mathit{C}O$) 296.3 (μ-C(R)O)	126.1, 128.4, 133.5, 146.3 (C_6H_5) 210.3, 214.1 ($\mathit{C}O$) 278.7 (μ-C(R)O)
IR^b	2102 (m), 2053 (s), 2007 (vs), 1985 (s), 1949 (s), 1919 (vw), 1471 (w)	2104 (w), 2056 (s), 2016 (s), 2007 (vs), 1986 (m), 1955 (s), 1523 (w)	2093 (m), 2045 (s), 2016 (vs), 2009 (vs), 1981 (s), 1953 (w), 1498 (w)

[a] In $CDCl_3$ solution; residue $CHCl_3$ peak as reference. Values in ppm. [b] **4a** in tetrachloroethylene solution; **4b** and **5** in hexane solution. Values in cm^{-1}.

servations. First, there is a tendency for the ^{13}C signal to be broadened by the quadrupolar nucleus of rhenium.[3] Second, there is a similar peak of lower height at the same chemical shift in the spectrum of **4b** (189.4 ppm) deriving from the fact that the immediate environment around the rhenium atom is unchanged in these two derivatives.

The resonance of the carbonyl groups around rhenium in **4a** persists as a singlet at −50 °C, implying a rapid equilibration. By contrast, the signal of the carbonyl carbons around iron in **4a** (201.8 ppm at room temperature) collapses at −15 °C and is replaced by peaks at 210.5 and 208.4 ppm at −50 °C. In **4b**, two peaks can already been seen at room temperature (at 210.4 ppm and 201.5 ppm) for the carbonyl groups around iron.

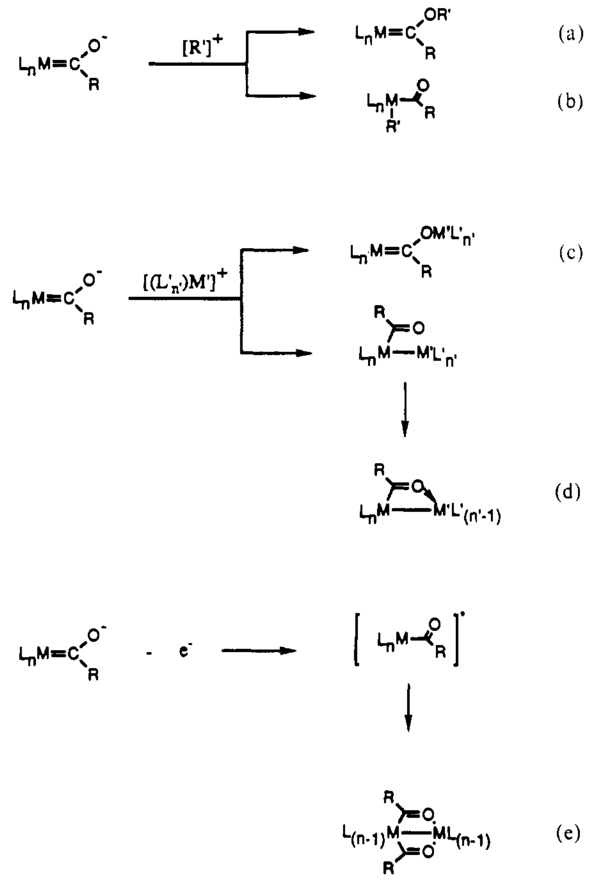
Compounds **4a** and **4b** were further characterized by single-crystal X-ray diffraction studies, which are presented below.

Discussion

The alkylation of acylmetalates may occur on oxygen (to give the corresponding Fischer carbene (eq a of Scheme I))[4] or on the metal (eq b of Scheme I) depending on the properties of the alkylating reagents and the reaction medium.[5] The different reactivities may be interpreted on the basis of the hard–soft acid–base rule.[5] In addition, electron-transfer reactions may take place leading to acyl-bridged homometallic complexes. The first example of this was in the reaction of tetracarbonyliron acylate with trityl chloride in a mixture of ethanol and diether ether; the bis(acyl)-bridged dimer $(OC)_3Fe\{\mu\text{-}C(Ph){=}O\}_2Fe(CO)_3$) is observed.[2a] In later work[2g] it was demonstrated that treatment of $[Li]_2[Ru_3\{C(O)Me\}_2(CO)_{10}]$ with $[Me_3O][SbCl_6]$ leads to oxidation of the ruthenium acylate; the acyl-bridged ruthenium *dimer* $(OC)_3Ru\{\mu\text{-}C(Me){=}O\}_2Ru(CO)_3$ is obtained.

Metal-centered electrophiles also show these three different types of behavior toward acylmetalates. If the metal center is oxophilic like Ti, Zr, etc., a metal-centered electrophile binds preferentially at the oxygen of the acyl group giving a metallo-Fischer carbene complex (eq d of Scheme I).[7] Other examples of this reaction have been reported by Beck[2h] and Cutler[2j] and their co-workers. On the other hand, if the metal of the acylmetalate is a relatively soft Lewis acid, the electrophile may form a metal–metal-bonded complex; subsequent loss of a σ-donating ligand on the adjacent metal leads to an acyl-bridged complex, (eq e of Scheme I). An example of the last reaction type was reported about 10 years ago: when $[(CO)_4Fe(C(O)NMe_2)][C(NMe_2)_3]$ is treated with $NiCl_2$, an acyl-bridged bimetallic complex is obtained.[2d] In this work we have found that the reaction of an acyltetracarbonylmetalate with electrophilic manganese or rhenium complexes gives acyl-bridged heterometallic products

Scheme I. Reactions of Acylmetalates



Scheme II. Proposed Pathways for the Formation of Acyl Bridging Complexes

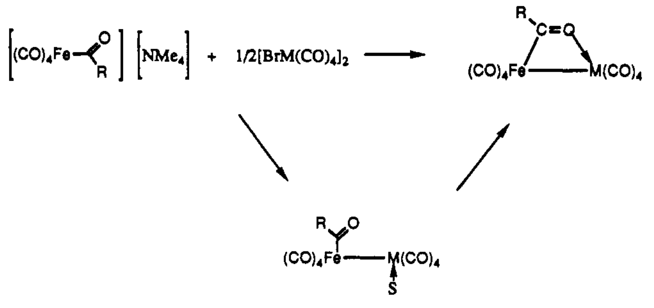


Table II. Selected Interatomic Distances (Å) for **4a**

Re(1)–C(11)	1.924 (7)	C(11)–O(11)	1.146 (9)
Re(1)–C(12)	2.004 (7)	C(12)–O(12)	1.121 (8)
Re(1)–C(13)	2.009 (7)	C(13)–O(13)	1.127 (9)
Re(1)–C(14)	1.929 (7)	C(14)–O(14)	1.149 (8)
Fe(1)–C(31)	1.807 (6)	C(31)–O(31)	1.130 (8)
Fe(1)–C(32)	1.811 (7)	C(32)–O(32)	1.138 (8)
Fe(1)–C(33)	2.002 (6)	C(33)–O(33)	1.252 (7)
Fe(1)–C(34)	1.819 (6)	C(34)–O(34)	1.119 (7)
Fe(1)–C(35)	1.811 (7)	C(35)–O(35)	1.152 (9)
Re(1)–Fe(1)	2.843 (1)	Re(2)–Fe(2)	2.840 (1)
Re(1)–O(33)	2.153 (4)		

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Table III. Selected Bond Angles (deg) for **4a**

Re(1)–Fe(1)–C(33)	69.47 (17)	Fe(1)–Re(1)–C(13)	87.14 (19)
Fe(1)–C(33)–O(33)	114.41 (43)	C(33)–Fe(1)–C(31)	83.20 (26)
Re(1)–O(33)–C(33)	110.58 (38)	C(33)–Fe(1)–C(34)	83.39 (24)
O(33)–Re(1)–C(12)	90.67 (23)	Re(1)–Fe(1)–C(31)	92.72 (20)
O(33)–Re(1)–C(13)	92.65 (22)	Re(1)–Fe(1)–C(34)	82.18 (19)
Fe(1)–Re(1)–C(12)	95.38 (18)		

Table IV. Selected Interatomic Distances (Å) for **4b**

Fe–C(11)	1.979 (4)	C(11)–O(11)	1.245 (5)
Fe–C(12)	1.801 (5)	C(12)–O(12)	1.138 (5)
Fe–C(13)	1.805 (5)	C(13)–O(13)	1.147 (5)
Fe–C(14)	1.837 (5)	C(14)–O(14)	1.125 (6)
Fe–C(15)	1.815 (5)	C(15)–O(15)	1.132 (6)
Re–C(21)	1.999 (5)	C(21)–O(21)	1.132 (6)
Re–C(22)	2.002 (5)	C(22)–O(22)	1.134 (6)
Re–C(23)	1.920 (5)	C(23)–O(23)	1.150 (6)
Re–C(24)	1.917 (4)	C(24)–O(24)	1.150 (5)
Fe–Re	2.861 (1)	Re–O(11)	2.164 (3)

Table V. Selected Bond Angles (deg) for **4b**

Re–Fe–C(11)	68.38 (12)	C(11)–Fe–C(13)	85.04 (17)
Fe–C(11)–O(11)	117.63 (28)	Re–Fe–C(12)	84.02 (13)
Fe–C(11)–C(20)	125.75 (30)	Re–Fe–C(13)	84.24 (13)
C(20)–C(11)–O(11)	116.61 (36)	O(11)–Re–C(21)	91.25 (14)
C(11)–O(11)–Re	108.40 (25)	O(11)–Re–C(22)	92.29 (14)
O(11)–Re–Fe	65.59 (08)	Fe–Re–C(21)	94.50 (12)
C(11)–Fe–C(12)	87.83 (17)	Fe–Re–C(22)	93.08 (12)

shown in eqs 1 and 2. These are new examples of eq e of Scheme I.

By comparison, the treatment of metal acylates with other electrophiles has led to the oxidation (and coupling) reactions f and g.[6]

$$[(CO)_4Fe(C(O)Ph)][NMe_4] + BrMn(CO)_5 \rightarrow (OC)_3Fe\{\mu\text{-}C(Ph){=}O\}_2Fe(CO)_3 + Mn_2(CO)_{10} \quad \text{(f)}$$

$$[(CO)_4Fe(C(O)Ph)][NMe_4] + L_2(CO)_3WI_2 \rightarrow (OC)_3Fe\{\mu\text{-}C(Ph){=}O\}_2Fe(CO)_3 + [NMe_4][L_2(CO)_3WI_2] \quad L_2 = (MeCN)_2,\ \text{dppe} \quad \text{(g)}$$

Assuming comparable oxidation potentials in the electrophiles, these experiments show that an easily removable ligand is essential to the formation of bridging acyl compounds. Acylmetalates may not be strong enough to displace ligands like carbon monoxide or phosphines, permitting the electron-transfer product to form.

We propose that the acyl-bridged bimetallic compounds are formed through the M-M′-bonded intermediates shown in Scheme II. We employed halide-bridged complexes as starting materials with the speculation that one coordination site is automatically available when the halide bridge is split and/or when the halide is displaced. This kind of reaction mode is similar to that of the syntheses of allyl compounds,[8] with the acylmetalates serving as "metalloallylic" anions.

Crystal Structures of $(CO)_4Fe(\mu\text{-}C(R)O)Re(CO)_4$ (4a, R = Ph; 4b, R = Me). The ORTEP drawings are shown in Figures 1 and 2; packing diagrams are given in the supplementary material. Selected bond distances and angles are listed in Tables II–V. The two structures are remarkably similar, with rhenium, iron, and the bridging acyl approximately sitting in the same plane. This can be seen by comparing the bond angles of Fe(1)–Re(1)–C(12)/C(13) with O(33)–Re(1)–C(12)/C(13) and Re(1)–Fe(1)–C(31)/C(34) with C(33)–Fe(1)–C(31)/C(34) in Table III. They are all close to 90°, meaning the coplanar arrangement of atoms Fe(1), Re(1), C(33), and O(33). The same argument is also held for **4b**. The rhenium to iron distances are 2.841 (1) Å (average) in **4a** and 2.861 (1) Å in **4b**, respectively. These are very close to the expected value 2.86 Å for a Re–Fe single-bond distance obtained by taking half each of the Re–Re distance in $Re_2(CO)_{10}$ (3.04 Å)[9] and the unbridged Fe–Fe separation in $Fe_3(CO)_{12}$ (2.68 Å).[10] This indicates a weak bridging property of the acyl groups. However, the bridging acyl group does exert different electronic effects on the two metals centers. Generally, an acyl group withdraws electron density from the carbon-linked metal center and donates electron density to the oxygen-bound metal center. While the distance of iron to carbonyl carbons coplanar with the benzoyl group (Fe–C(32)/C(35) = 1.811 Å, average) is about the same value as that of iron to those perpendicular to the Fe(μ-C(Ph)O)Re plane (Fe–C(31)/C(34) = 1.813 Å, average) in **4a** possibly due to the conjugation of the phenyl group, the difference between the distances of Fe to the coplanar carbonyl carbons (Fe–C(14)/C(15) = 1.826 Å, average) and the perpendicular carbonyl carbons (Fe–C(12)/C(13) = 1.804 Å, average) in **4b** is significant (see Tables II and V and Figures 1 and 2). Both the benzoyl group in **4a** and acetyl group in **4b** exert similar electron-donating effects on rhenium centers, with rhenium to coplanar carbonyl carbon distances being shortened by a factor of 0.96 compared with that of rhenium to perpendicular carbonyl carbon (**4a**, Re–C(coplanar)/Re–C(perpendicular) = 1.927/2.007 Å; **4b**, Re–C(coplanar)/Re–C(perpendicular) = 1.919/2.001 Å).

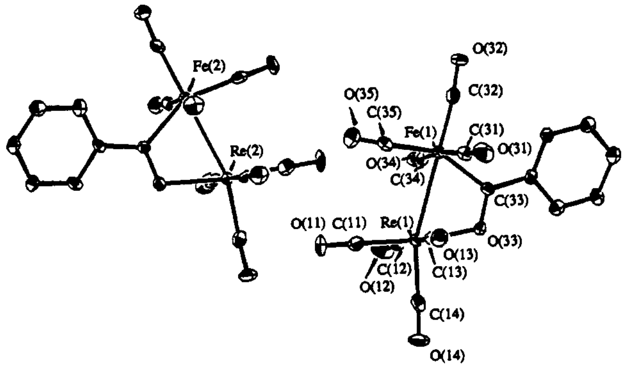


Figure 1. ORTEP projections of **4a** (thermal ellipsoids at 50% probability).

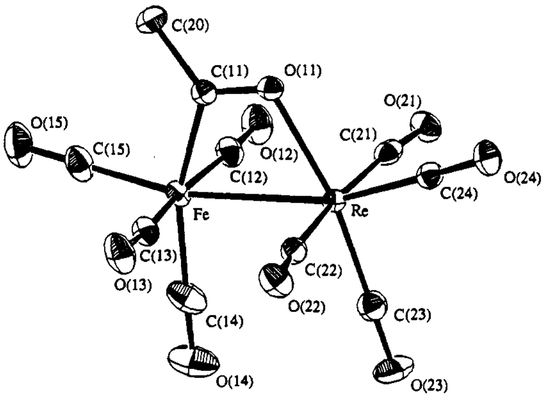
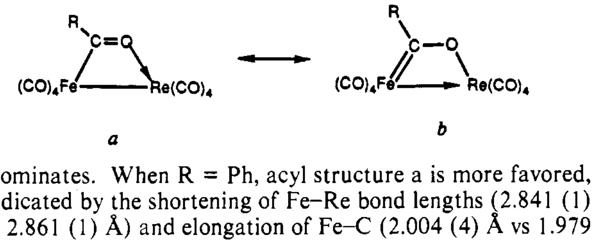


Figure 2. ORTEP projection of **4b** (thermal ellipsoids at 50% probability).

The actual bonding of these compounds is best represented by the two resonance structures a and b in which the acyl forms



predominates. When R = Ph, acyl structure a is more favored, as indicated by the shortening of Fe–Re bond lengths (2.841 (1) Å vs 2.861 (1) Å) and elongation of Fe–C (2.004 (4) Å vs 1.979

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Table VI. Abbreviated Crystal and Refinement Data for **4a** and **4b**[a]

compd	**4a**	**4b**
formula	$ReFeC_{15}O_9H_5$	$ReFeC_{10}O_9H_3$
fw	571.25	267.13
space group	$P\bar{1}$	$P\bar{1}$
a/Å	15.674 (1)	8.177 (1)
b/Å	14.986 (1)	9.869 (1)
c/Å	7.768 (1)	9.212 (1)
α/deg	107.90 (1)	106.59 (1)
β/deg	90.02 (1)	108.18 (1)
γ/deg	70.98 (1)	76.38 (1)
V/Å^3	1631.43	668.11
Z	4	2
ρ_{calc}/g cm^{-3}	1.40	1.33
goodness of fit	2.0998	1.0353
R^c	3.3	1.6
$R_w{}^d$	4.9	2.4

[a] Radiation source, Mo Kα with 0.71070 Å; T = 110 K. [b] GOF = $[\sum w(|F_o| - |F_c|)^2/N_o - N_v)]^{1/2}$, where $w = 1/[\sigma(|F_o|)]^2$. [c] $R = \sum||F_o| - |F_c||/|F_o|$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/|F_o|/\sum w|F_o|^2]^{1/2}$.

(4) Å) and Re–O bond lengths (2.153 (4) Å and 2.164 (3) Å). The C–O bond lengths are almost the same, i.e. 1.252 (7) Å for **4a** and 1.245 (5) Å for **4b**. This is because of the delocalization of phenyl group electrons to the acyl carbon, C–O, as suggested by the fact that the phenyl ring is sitting almost totally in the least-squares plane consisting of the "Fe{μ-C(Ph)O}Re" moiety.

Experimental Section

Starting materials $[(CO)_4Fe(C(O)R)][NMe_4]$,[2a,11] $[(CO)_4ReBr]_2$,[12] $[(CO)_4MnBr]_2$[13] were prepared according to literature methods. Others were used as received. THF (tetrahydrofuran), toluene, and *n*-hexane were dried by distillation from K–benzophenone ketyl under N_2. All reactions were conducted under an atmosphere of dry N_2 or Ar by using standard Schlenk techniques or in a glovebox.

^1H NMR and ^{13}C NMR spectra were recorded on either a Bruker AM200, Bruker AM360, or Bruker 500 spectrometer using deuterated solvents as locks. The chemical shifts were reported relative to the residue peaks of the deuterated solvents. IR spectra were obtained on a Nicolet MX-1 IR spectrometer using an NaCl solution IR cell.

Preparation of $(CO)_4Fe(\mu\text{-}C(Ph)O)Re(CO)_4$ (4a). A THF solution of $[(CO)_4Fe(C(O)Ph)][NMe_4]$ (**1a**) (0.70 g in 20 mL of THF) was added slowly to a stirring THF suspension of $[(CO)_4ReBr]_2$ (**2**) (0.75 g in 50 mL) at −20 °C. After addition of **1**, the mixture was slowly warmed to 0 °C. Then it was stirred at this temperature for another 3 h, affording a red solution. The volatile material was removed at 0 °C and the residue extracted with two 50-mL aliquots of hexane at room temperature. Slow evaporation of the hexane gave yellow crystals. These were washed with two 3-mL aliquots of cold hexane (−20 °C). Yield: 0.52 g (45.5% based on **2**). Anal. Calc for $C_{15}H_5FeReO_9$: C, 31.54; H, 0.88; Fe, 9.77. Found: C, 31.50; H, 0.88; Fe, 9.34.

Preparation of $(CO)_4Fe(\mu\text{-}C(Me)O)Re(CO)_4$ (4b). A THF solution of $[(CO)_4Fe(C(O)Me)][NMe_4]$ (**1b**) (0.6 g in 50 mL of THF) was added slowly to a stirred THF suspension of $[(CO)_4ReBr]_2$ (**2**) (0.75 g in 30 mL of THF) at −20 °C. After addition of **1b**, the mixture was slowly warmed to 0 °C and then stirred for 2 h at this temperature, changing slowly from an initial yellow/orange to a red solution. The volatile materials were removed at 0 °C and the residue extracted with two 50-mL aliquots of hexane. Slow evaporation of solvent gave pale yellow crystals, which were washed with two 3-mL aliquots of cold hexane (−20 °C). Yield: 0.40 g (40% based on **2**). Anal. Calc for $C_{10}H_3FeReO_9$: C, 23.64; H, 0.60. Found: C, 23.66; H, 0.65.

Preparation of $(CO)_4Fe(\mu\text{-}C(Ph)O)Mn(CO)_4$ (5). A quantity of 0.70 g (2.0 mmol) of **1a** and 0.494 g (1.0 mmol) of $[(CO)_4MnBr]_2$ (**3**) were suspended in toluene (50 mL). The mixture was stirred under N_2 overnight at room temperature, turning from yellow to dark red. The precipitate of $[Me_4N]Br$ was filtered away and the solvent removed under pump vacuum. The residue was extracted with two 50-mL aliquots of hexane, affording a red solution, which is then condensed to one-fifth of its original volume and cooled to −78 °C; an amorphous orange solid was obtained, which slowly darkened at room temperature under N_2. Spectral data confirm the identity of this compound. Yield: 0.21 g (24% based on **3**).

X-ray Data Collection and Structure Determination of 4a and 4b. Yellow, slightly air-sensitive crystals of **4a** and **4b** were grown from their saturated hexane solutions at −20 °C. Crystals of **4a** and **4b** each suitable for structure analysis were glued to the tips of glass fibers and mounted and centered on a Picker four-circle automated diffractometer equipped with a scintillation counter and graphite monochromator and modified at The University of California, Los Angeles, CA, by Prof. C. E. Strouse for operation under control of a VAX 11/750 computer.

The 2θ, ω, χ, and ϕ settings of the Mo Kα peaks of reflections (**4a**, 43 reflections, 2θ = 9–20°; **4b**, 37 reflections, 2θ = 10–21°) were determined. These values were used in a least-squares refinement of cell and orientation parameters. Abbreviated refined unit cell parameters and specifics related to collection and refinement of data are given in Table VI. The complete summary of the crystal and refinement data is found in the supplementary material. The intensities of three standard reflections (**4a**, (032), $(4\bar{3}1)$, (650); **4b**, $(1\bar{1}\bar{2})$, $(3\bar{2}0)$, $(34\bar{1})$) were recorded after every 97 intensity measurements throughout the data collection to monitor crystal and diffractometer stability. The variations in the standards indicate a slow decay to about 98.6% of the original values in 70.3 h with a mean fluctuation of 4.7% for **4a** and to 98.9% of the original values in 28.6 h with a mean fluctuation of 4.1% for **4b**. A survey of the complete data set reveals no systematic absences for all the reflections for both **4a** and **4b**. $P\bar{1}$ was arbitrarily chosen as the space group between the two primary groups, which was turned out later to be the right choice. Scattering factors for neutral rhenium, oxygen, and carbon atoms were taken from Table 2.2A of ref 14, while those for hydrogen were from Stewart et al.[15] Both real (f') and imaginary (f'') components of anomalous dispersion were included for rhenium by using the values in Table 2.3.1 of ref 14. Reasonable positions for the metal atoms were obtained by Patterson method in both **4a** and **4b**. Full-matrix least-squares refinement on the metals with isotropic temperature factors followed by difference Fourier syntheses in each case revealed the positions of all non-hydrogen atoms. Least-squares refinement, first with anisotropic thermal parameters for all the metal atoms and then with anisotropic thermal parameters for all non-hydrogen atoms, afforded the R factors shown in Table VI. Hydrogen atoms were not located for **4a**. Three hydrogen atoms of the methyl group in **4b** were located on a difference electron density map. Neither the positions nor the temperature factors were refined for the hydrogen atoms. These parameters, however, were used in the calculation of the final structure factors and residual electron density. The final atomic positional parameters, final thermal parameters, and the packing diagrams of **4a** and **4b** are found in the supplementary material.

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Supplementary Material Available: Packing diagrams of **4a** (Figure A) and **4b** (Figure B), $^{13}C\{^1H\}$ NMR spectra of compounds **4a**, **4b**, and **5** (Figures C–E), bond distances and bond angles for **4a** (Tables A and B) and **4b** (Tables C and D), final atomic parameters for **4a** (Table E) and **4b** (Table F), final thermal parameters for **4a** (Table G) and **4b** (Table H), and completed crystal and refinement data for **4a** and **4b** (Table I) (26 pages); listings of observed and calculated structure factors for **4a** and **4b** (35 pages). Ordering information is given on any current masthead page.

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