123°.[24a] Furthermore, similar $Os_3(CO)_{10}(\mu\text{-}X)_2$ compounds are known in which the dibridged Os–Os separation is as great as 3.29 Å.[20h] Thus there must be some residual metal–metal interaction in 4 and 6 that hold the metals as close together as they are. These structural data also indicate that a continuum of M–CH_2–M angles and metal–metal distances exist between the strictly metal–metal nonbonded[24] and unambiguously metal–metal bonded[22] μ-CH_2 complexes.

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Registry No. 1, 77208-32-3; 2, 96897-74-4; 3, 96897-75-5; 4, 96897-76-6; 5, 96897-77-7; 6, 96897-78-8; [PPN]Cl, 21050-13-5; [PPN]Br, 20545-30-6; [PPN]I, 38011-33-5; [PPN]NO_2, 38011-35-7; [PPN]N_3, 38011-36-8; Os, 7440-04-2.

Supplementary Material Available: Tables of anisotropic thermal parameters, complete lists of bond angles and bond lengths, calculated positions of hydrogen atoms, and the structure factors for 4 and 6 (65 pages). Ordering information is given on any current masthead page.

Binuclear Tungsten–Rhenium Alkyl–Acyl and Alkyl–Carbene Complexes. Crystal and Molecular Structure of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3CH_3$

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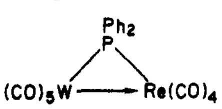
Reaction of $(CO)_5\overline{W(\mu\text{-}PPh_2)Re}(CO)_4$ with PPh_2H gives $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4(PPh_2H)$ which upon thermolysis yields $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3H$, 3. Abstraction of hydride from 3 with BuLi gives the anion $[(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3]^-$, 4. Treatment of the latter with CH_3I, $EtOSO_2CF_3$, phosgene, and PhC(O)Br leads to formation of the new complexes $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3X$ with X = CH_3 (5), Et (6), Cl (7), PhC(O) (8), and Br (9). Complex 5 has been crystallographically characterized: $P2_1/c$, a = 9.766 (3) Å, b = 19.659 (4) Å, c = 17.212 (4) Å, β = 103.06 (3)°, V = 3219 (2) Å^3, Z = 4, R_F = 0.047, R_{wF} = 0.047, 3693 reflections with $F_o \geq 2.5\sigma(F_o)$. Both the W and Re centers have octahedral coordination geometries with the W ligated by four CO's and two μ-PPh_2 ligands and Re by three CO's, two μ-PPh_2 ligands, and the methyl ligand. The W–Re bond distance of 3.015 (1) Å implies a single metal–metal bond between these atoms. Treatment of complexes 5 and 6 with RLi and then $EtOSO_2CF_3$ reagents gives first formation of acyl and then Fischer-type carbene ligands on tungsten. No interaction of the organic ligands on the different metals occurs in these binuclear alkyl–acyl and alkyl–carbene complexes.

In an earlier publication we described the preparation and derivative chemistry of the *monophosphido-bridged* WRe complex 1.[1] Complex 1 contains a weak donor–acceptor bond which is easily displaced by better donor ligands and which provides easy access to an open coordination site for deinsertion reactions of formyl and acyl ligands.[1] Other work in these laboratories has shown that such metal–metal bond cleavage does not occur nearly so readily in *bis(phosphido)-bridged* heterobinuclear complexes.[2,3] We thus sought a corresponding WRe(μ-PPh_2)$_2$ complex with which to compare the derivative chemistry of complex 1, and a suitable species 3 has been found to derive in good yield by the reactions of eq 1. Complex 3 has proven to be a versatile precursor to a number of unusual binuclear alkyl, acyl, alkyl–acyl, and alkyl–carbene complexes and these are described herein. Binuclear complexes such as these with organic ligands on adjacent



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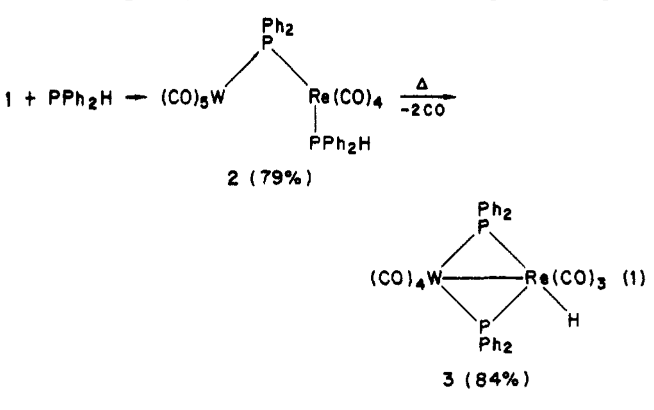

2 (79%)

3 (84%)

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(1) Mercer, W. C.; Whittle, R. R.; Burkhardt, E. W.; Geoffroy, G. L. *Organometallics* 1985, *4*, 68.

(2) Breen, M. J.; Shulman, P. M.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* 1984, *3*, 782–793.

(3) Morrison, E. D.; Harley, A. D.; Marcelli, M. A.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* 1984, *3*, 1407–1413.

0276-7333/85/2304-1418$01.50/0

metals are of interest because the possibility exists for unusual interaction of these ligands with each other across the metal–metal bond.

Experimental Section

$(CO)_5\overline{W(\mu\text{-}PPh_2)Re}(CO)_4$, 1, was prepared as described in ref 1. PPh_2H (Strem Chemical Co.), CH_3Li, *n*-BuLi, PhLi, $Li[BHEt_3]$, CH_3I, $CH_3C(O)Cl$ (Aldrich Chemical Co.), and EtOTf (Alfa-Ventron Co.; OTf = OSO_2CF_3) were purchased and used as received; PhC(O)Br (97%, Aldrich) was purchased and purified by literature procedures before use.[4] All manipulations were performed in standard Schlenk glassware under prepurified N_2. Solvents were dried by stirring over Na/benzophenone (THF, Et_2O, hexanes, benzene, toluene) or BaO (CH_2Cl_2) followed by distillation under N_2. Instruments used in this study have been previously described.[1] IR spectra were recorded on an IBM FT/IR-32 spectrometer. This instrument gives difference spectra in absorption units only; spectra recorded in the absorption mode will be noted as such ("abs"). All other IR data are from transmission spectra. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Preparation of $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4PPh_2H$, 2. Diphenylphosphine (0.065 mL, 0.374 mmol) was added via syringe to a benzene (50 mL) solution of 1 (0.301 g, 0.373 mmol). The solution was refluxed for 25 min during which time the yellow color lightened considerably. The solvent was evaporated to a minimum and loaded onto a preparative scale SiO_2 TLC plate. Elution with 30% CH_2Cl_2/hexane gave three yellow bands: unreacted 1 (10%), a small amount (<1%) of an unidentified product, and 2. Complex 2 was removed from the support and recrystallized from CH_2Cl_2/hexane (0.295 g, 0.297 mmol, 79% yield): IR: (hexane, abs) ν_{CO} 2099 w, 2062 w, 2016 m, 2006 s, 1968 m, 1930 s, 1923 vs cm^{-1}; ^{31}P NMR (25 °C, benzene-d_6) δ −3.1 (dd, PPh_2H, J_{P-H} = 391 Hz, J_{P-P} = 13.7 Hz), −73.9 (d, μ-PPh_2, J_{P-W} = 188 Hz); MS, m/z 965 (M^+ − CO) and fragment ions corresponding to loss of eight CO's. anal. Calcd for $C_{33}H_{21}O_9P_2ReW$: C, 39.88, H, 2.11, Found: C, 39.89, H, 2.14.

Preparation of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3H$, 3. Complex 2 (0.295 g, 0.297 mmol) was dissolved in toluene (50 mL) and refluxed for 45 min followed by cooling to room temperature. Solvent evaporation gave 3 as an orange microcrystalline solid in 84% yield (0.234 g, 0.250 mmol): IR (hexane, abs) ν_{CO} 2039 s, 2004 m, 1979 vs, 1959 s, 1948 sh, 1937 m cm^{-1}; ^1H NMR (25 °C, benzene-d_6) δ −4.80 (dd, Re–*H*, J_{P-H}, J_{P-H} = 4.07 Hz, 79.2 Hz); $^{31}P\{^1H\}$ (25 °C benzene-d_6) δ 181.5 (d, μ-PPh_2, J_{P-P} = 25.0 Hz, J_{P-W} = 161.1 Hz), 176.8 (d, μ-PPh_2, J_{P-W} = 160.5 Hz); MS, m/z 937 (M^+) and fragment ions corresponding to the loss of seven CO's. Anal. Calcd for $C_{31}H_{21}O_7P_2ReW$: C, 39.70; H, 2.24. Found: C, 39.65; H, 2.24.

Preparation of $[Li(Et_2O)_x][(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3]$, 4. Complex 3 (0.100 g, 0.107 mmol) was dissolved in Et_2O (10 mL) and cooled to −78 °C in a 2-propanol/dry ice bath. CH_3Li (1.2 M, 0.098 mL) was added via syringe. The solution immediately turned from orange to red, and a dark red precipitate of 4 formed over a 15-min period. Filtration gave 4 (0.099 g, 0.091 mmol, 75% yield) as a dark red microcrystalline solid. Although this material was satisfactory for use in the following syntheses, an acceptable elemental analysis was not obtained in several attempts, perhaps because of varying amounts of Et_2O solvate present. 4: IR (THF, abs) ν_{CO} 1982 sh, 1975 m, 1921 vs, 1900 m, 1881 m, 1848 w cm^{-1}; $^{31}\{^1H\}$ NMR (25 °C, acetone-d_6) δ 152.1 (s, μ-PPh_2, J_{P-W} = 122.0 Hz).

Preparation of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3CH_3$, 5. Excess CH_3I (1.0 mL, 16 mmol) was added to a dark red THF (40 mL) solution of 4, prepared by adding CH_3Li (1.2 M, 0.500 mL) to 3 (0.506 g, 0.540 mmol). The solution changed color to light orange over 30 min. The THF was removed in vacuo, the oily residue was dissolved in toluene (25 mL), the salts were removed via filtration, and the residue was recrystallized from Et_2O to give orange microcrystalline 5 (0.414 g, 0.435 mmol) in 80% yield: IR (THF) ν_{CO} 2035 s, 1995 m, 1970 vs, 1954 sh, 1925 m cm^{-1}; ^1H NMR (25 °C, benzene-d_6) δ 0.108 (d, Re–CH_3, J_{P-H} = 4.5 Hz); $^{31}P\{^1H\}$ (25 °C, benzene-d_6) δ 177.8 (d, μ-PPh_2, J_{P-P} = 19.4 Hz, J_{P-W} = 172 Hz), 147.8 (d, μ-PPh_2, J_{P-W} = 147 Hz); MS, m/z 951 (M^+) and fragment ions corresponding to loss of seven CO's. Anal. Calcd for $C_{32}H_{23}O_7P_2ReW$: C, 40.38; H, 2.42. Found: C, 40.35; H, 2.61.

Preparation of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3Et$, 6. EtOTf (0.068 mL, 0.535 mmol) was added to a slurry of 4 (0.501 g, 0.535 mmol) in Et_2O (30 mL) via syringe. The solution changed color from red to orange over a 20-min period. The salts were extracted into H_2O (30 mL) via syringe, and the ether layer was dried over anhydrous $MgSO_4$. Removal of the ether in vacuo yielded orange microcrystalline 6 (0.387 g, 0.401 mmol) in 75% yield: IR (THF) ν_{CO} 2035 s, 1997 m, 1970 vs, 1956 sh, 1923 m cm^{-1}; ^1H NMR (25 °C, benzene-d_6) δ 2.14 (dt, Re–CH_2CH_3, J_{H-H} = 7.4 Hz, J_{P-H} = 1.2 Hz), 2.80 (pseudoquintet, Re–CH_2CH_3, J_{H-H}, J_{P-H} = 7.4 Hz); $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6) δ 176.6 (d, μ-PPh_2, J_{P-P} = 20.3 Hz, J_{P-W} = 175 Hz), 143.7 (d, μ-PPh_2, J_{P-W} = 144 Hz); MS, m/z 965 (M^+) and fragment ions corresponding to loss of seven CO's and one C_2H_5. Anal. Calcd for $C_{33}H_{25}O_7P_2ReW$: C, 41.04; H, 2.59. Found: C, 40.60; H, 2.78.

Preparation of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3Cl$, 7. Phosgene (0.234 mL, 0.537 M in toluene) was added via syringe to a dark red THF (20 mL) solution of 4, prepared by adding CH_3Li (1.2 M, 0.100 mL) to 3 (0.102 g, 0.109 mmol). The solution turned orange immediately. The solvent was removed in vacuo, and the oily orange residue was dissolved in a minimum of CH_2Cl_2 and loaded onto a preparative scale SiO_2 chromatography plate. Elution with 20% CH_2Cl_2/hexane gave two orange bands of 3 and 7 and a large amount of a brown material which did not elute. Evaporation of solvent from the second orange band gave 7 (0.025 g, 0.025 mmol) in 24% yield. 7: IR (CH_2Cl_2) ν_{CO} 2045 vs, 2005 m, 1981 s, 1966 vs, 1933 w cm^{-1}; $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6) δ 177.9 (s, μ-PPh_2, J_{P-W} = 190 Hz); MS, m/z 944 (M^+ − 1 CO) and fragment ions corresponding to loss of six CO's.

Preparation of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3\{C(O)Ph\}$, 8, and $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3Br$, 9. Benzoyl bromide (0.015 mL, 0.127 mmol) was added via syringe to a dark red slurry of 4, prepared by adding CH_3Li (1.2 M, 0.103 mL) to 3 (0.116 g, 0.124 mmol) in Et_2O (50 mL). The solution turned orange and became homogeneous over a 1-h period. The solvent was removed in vacuo and the resultant orange oil was chromatographed (20% CH_2Cl_2/hexane, SiO_2) yielding two orange bands of 8 and 9, in that order. Slow evaporation of solvent from these fractions yielded pure 8 (0.059 g, 45%) and pure 9 (0.058 g, 47%). 8: IR (hexane) ν_{CO} 2047 s, 2006 m, 1978 s, 1968 vs, 1935 w, 1598 w cm^{-1}; $^{31}P\{^1H\}$ NMR (25 °C, acetone-d_6) δ 166 (d, μ-PPh_2, J_{P-P} = 15 Hz, J_{P-W} = 168 Hz), 144 (d, μ-PPh_2, J_{P-P} = 15 Hz, J_{P-W} = 176 Hz); MS, m/z 1041 (M^+) and fragment ions corresponding to successive loss of eight CO's. Anal. Calcd for $C_{38}H_{25}O_8P_2ReW$: C, 43.80; H, 2.40. Found: C, 44.00; H, 2.42. 9: IR (hexane) ν_{CO} 2046 vs, 2004 m, 1980 s, 1968 vs, 1935 cm^{-1}; $^{31}P\{^1H\}$ NMR (25 °C, acetone-d_6) δ 201 (s, μ-PPh_2, J_{P-W} = 192 Hz); MS, m/z 988 (M^+ − 1 CO) and fragment ions corresponding to successive loss of six CO's. Anal. Calcd for $C_{31}H_{20}BrO_7P_2ReW$: C, 36.61; H, 1.97. Found: C, 36.81, H, 2.20.

Reaction of 5 and 6 with $Li[BHEt_3]$. $Li[BHEt_3]$ (0.054 mL, 0.054 mmol) was added via syringe to THF (~30 mL) solutions of 5 (0.050 g, 0.054 mmol) and 6 (0.054 g, 0.056 mmol) at 22 °C. IR monitoring revealed the presence of formyl complexes in both cases: 5, ν_{CHO} 1622 cm^{-1}; 6, ν_{CHO} 1599 cm^{-1}. These complexes decomposed over a period of ~4 h at 22 °C. $^{31}P\{^1H\}$ NMR spectra of these solutions showed the presence of a complex mixture of products, but no attempts were made to isolate and characterize these.

Reaction of 5 with CH_3Li. CH_3Li (0.048 mL, 0.058 mmol) was added via syringe to a Et_2O (50 mL) solution of 5 (0.050 g, 0.053 mmol) at 22 °C. NMR (^{31}P, ^{13}C) *monitoring of this reaction* mixture revealed the presence of two isomers **10a** and **10b** of the acetyl complex $[\{C(O)CH_3\}(CO)_3\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3CH_3]^-$, formed in a 1:1 ratio, but no attempt was made to isolate these: IR (THF) ν_{CO} 2020 w, 1985 m, 1960 s, 1935 vs, 1869 m, 1595 wm,

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(4) Oakwood, T. S.; Weiserer, C. A. "Organic Syntheses"; Wiley: New York, 1955; Coll. Vol. 3, p 112.

1575 w cm^{-1}; ^{1}H NMR (25 °C, THF-d_8) δ 7.2 (m, Ph's), δ 2.78 (br d, C(O)CH_3, J_{H-P} = 12.5 Hz), 0.68 (d, Re–CH_3, J_{H-P} = 5.5 Hz); $^{31}P\{^1H\}$ NMR (25 °C, THF-d_8) δ 163.7 (d, μ-PPh$_2$, J_{P-P} = 17 Hz, J_{P-W} = 170 Hz), 102.6 (d, μ-PPh$_2$, J_{P-P} = 17 Hz, J_{P-W} = 162 Hz), 137.4 (d, μ-PPh$_2$, J_{P-P} = 14 Hz, J_{P-W} = 185 Hz), 135.9 (d, μ-PPh$_2$, J_{P-P} = 14 Hz, J_{P-W} = 181 Hz); $^{13}C\{^1H\}$ NMR (25 °C, THF-d_8) δ 281 (d, C(O)CH$_3$, J_{C-P} = 20 Hz), 278 (d, C(O)CH$_3$, J_{C-P} = 40 Hz), –42 (s, Re–CH$_3$), –44 (s, Re–CH$_3$).

Reaction of 6 with PhLi. PhLi (0.052 mL, 0.126 mmol) was added via syringe to a Et$_2$O (30 mL) solution of **6** (0.120 g, 0.126 mmol) at 22 °C. Spectroscopic monitoring of this reaction mixture showed the rapid formation of two isomeric benzoyl complexes $[\{C(O)Ph\}(CO)_3\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3Et]^-$, **11a** and **11b**, in a 1:1 ratio but no attempt was made to isolate these: IR (THF) ν_{CO} 2035 m, 1985 m, 1970 s, 1960 s, 1935 vs, 1871 m, 1597 w, 1557 w cm^{-1}; $^{31}P\{^1H\}$ NMR (25 °C, THF-d_8) δ 164.4 (d, μ-PPh$_2$, J_{P-P} = 17 Hz, J_{P-W} = 158 Hz), 102.4 (d, μ-PPh$_2$, J_{P-P} = 17 Hz, J_{P-W} = 165 Hz), 137.5 (d, μ-PPh$_2$, J_{P-P} = 13.5 Hz, J_{P-W} = 248 Hz), 135 d, μ-PPh$_2$, J_{P-P} = 13.5 Hz, J_{P-W} = 165 Hz); $^{13}C\{_1H\}$ (25 °C, THF-d_8) δ 287 (t, C(O)CH$_3$, J_{C-P} = 15 Hz), 286 (d, C(O)CH$_3$, J_{C-P} = 5 Hz), –22.8 (t, Re–CH$_2$CH$_3$, J_{C-P} = 6.2 Hz), –25.4 (dd, Re–CH$_2$CH$_3$, J_{C-P} = 3.1 Hz, 7.2 Hz), 27 (d, Re–CH$_2$$CH_3$, J_{C-P} = 6.9 Hz), 23.0 (d, Re–CH$_2$$CH_3$, J_{C-P} = 6.3 Hz).

Preparation of $\{C(OEt)CH_3\}(CO)_3\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3CH_3$, 12a and 12b. EtOTf (0.007 mL, 0.053 mmol) was added to a solution of **10a** and **10b**, prepared as above by adding CH$_3$Li (0.048 mL, 0.058 mmol) to a Et$_2$O (50 mL) solution of **5** (0.050 g, 0.053 mmol) via syringe. The solution was stirred for 12 h. Solvent was removed in vacuo and the resultant red oil chromatographed on SiO$_2$ (20% CH$_2$Cl$_2$/hexane). The one major band which eluted yielded an orange powder upon solvent evaporation, and this was recrystallized from CH$_2$Cl$_2$/hexane to give a 1:1 mixture of isomers **12a** and **12b** as an orange microcrystalline solid in 70% yield (0.037 g, 0.037 mmol): IR (Et$_2$O) ν_{CO} 2040 w, 1985 m, 1964 s, 1956 s, 1935 vs cm^{-1}; ^{1}H NMR (25 °C, benzene-d_6) δ 7.2 (m, Ph's), 3.3 (q, 2 H, OCH_2CH$_3$, J_{H-H} = 7.2 Hz), 2.7 (s, 3 H, CH_3), 1.17 (t, 3 H, OCH$_2$CH_3, J_{H-H} = 7 Hz), 0.26 (d, 3 H, Re–CH_3, J_{P-H} = 4.8 Hz); $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6) 172 (d, μ-PPh$_2$, J_{P-P} = 14.5 Hz, J_{P-W} = 134 Hz), 108 (d, μ-PPh$_2$, J_{P-P} = 14.5 Hz, J_{P-W} = 140 Hz), 145.2 (d, μ-PPh$_2$, J_{P-P} = 12 Hz, J_{P-W} = 119 Hz), 140 (d, μ-PPh$_2$, J_{P-P} = 12 Hz, J_{P-W} = 230 Hz); MS, m/z 996 (M$^+$) and fragment ions corresponding to loss of seven CO's, two CH$_3$'s, and one C$_2$H$_5$. Anal. Calcd for $C_{35}H_{31}O_7P_2ReW$: C, 42.17; H, 3.11. Found: C, 42.35; H, 3.06.

Preparation of $\{C(OEt)Ph\}(CO)_3\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3Et$, 13a and 13b. EtOTf (0.016 mL, 0.126 mmol) was added via syringe to a solution of **11a** and **11b**, prepared by adding PhLi (0.052 mL, 0.126 mmol) to a Et$_2$O (50 mL) solution of **6** (0.120 g, 0.126 mmol). The solution was stirred for 12 h, the solvent was removed in vacuo, and the resultant red oil was chromatographed on SiO$_2$ (20% CH$_2$Cl$_2$/hexane). The one major band that moved yielded an orange powder which was recrystallized from CH$_2$Cl$_2$/hexane to give a 1:1 mixture of isomers **13a** and **13b** as an orange microcrystalline product in 68% yield (0.092 g, 0.086 mmol): IR (hexane) ν_{CO} 2049 m, 2010 m, 1997 m, 1983 m, 1958 vs, 1949 sh cm^{-1}; ^{1}H NMR (25 °C, benzene-d_6) δ 7.2 (m, Ph's), δ 3.48 (m, OCH_2CH$_3$), 2.8 (m, ReCH_2CH$_3$), 2.3 (m, ReCH$_2$CH_3), 1.29 (m, OCH$_2$CH_3); $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6) δ 168 (d, μ-PPh$_2$, J_{P-P} = 12 Hz, J_{P-W} = 136 Hz), 105 (d, μ-PPh$_2$, J_{P-P} = 12 Hz, J_{P-W} = 199 Hz), 137.8 (d, μ-PPh$_2$, J_{P-P} = 9.2 Hz, J_{P-W} = 200 Hz), 136.9 (d, μ-PPh$_2$, J_{P-P} = 9.4 Hz, J_{P-W} = 150 Hz); $^{13}C\{^1H\}$ NMR (25 °C, THF-d_8) δ 299.7 (m, W–C(OEt)Ph), 298.0 (t, W–C(OEt)Ph, J_{P-C} = 8.5 Hz), 22.7 (s, Re–CH$_2$$CH_3$), 22.4 (s, Re–CH$_2$$CH_3$), –22.5 (t, Re–$CH_2CH_3$, J_{P-C} = 6.1 Hz), –24.3 (t, Re–CH$_3$, J_{P-C} = 1.2 Hz); MS, m/z 1071 (M$^+$) and fragment ions corresponding to loss of seven CO's and two C$_2$H$_5$'s. Anal. Cald for $C_{41}H_{35}O_7P_2ReW$: C, 45.94; H, 3.27. Found: C, 46.15; H, 3.53.

Table I. Crystallographic Data for the X-ray Diffraction Study of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3CH_3$, 5

Crystal Parameters	
cryst system: monoclinic	β = 103.06 (3)°
space group $P2_1/c$	V = 3219 (2) Å^3
a = 9.766 (3) Å	Z = 4
b = 19.659 (4) Å	ρ(calcd) = 1.96 g cm^{-3}
c = 17.212 (4) Å	μ = 79.0 cm^{-1}
Measurement of Intensity Data	
diffractometer	Nicolet R3
radiation	Mo Kα (λ = 0.71073 Å)
monochromator	graphite crystal
scan type	$2\theta/\theta$
std refltns	3 std/97 data (no decay)
data limits	$4° \leqslant 2\theta \leqslant 45°$
unique data	4211 (4534 collected)
unique data with $F_o \geqslant 2.5\sigma(F_o)$	3693
R_F	0.047
R_{wF}	0.047
GOF	1.520

Reaction of 6 with PPh$_3$. Triphenylphosphine (0.015 g, 0.057 mmol) and **6** (0.055 g, 0.057 mmol) were dissolved in toluene and refluxed for 1 h. The solution was then cooled and the solvent removed in vacuo to give an oily orange residue. Chromatography (20% CH$_2$Cl$_2$/hexane, SiO$_2$) yielded two orange bands. Evaporation of solvent from these bands and recrystallization from CH$_2$Cl$_2$/hexane yielded $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_2(PPh_3)H$, **14**, in 45% yield (0.030 g, 0.026 mmol) from the first band and $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3\{C(O)Et\}$ (**15**) in 25% yield (0.014 g, 0.014 mmol) from the second. Complex **14** was never obtained analytically pure, but its spectroscopic data are consistent with its formulation. **14**: IR (hexane) ν_{CO} 2056 w, 2045 m, 2018 m, 1999 m, 1950 vs, 1889 w cm^{-1}; ^{1}H NMR (25 °C, benzene-d_6) δ 7.2 (m, Ph's), –4.2 (dd, Re–H, J_{P-H} = 48, 16, 10 Hz); $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6) δ 174.8 (dd, μ-PPh$_2$, J_{P-P} = 23.5, 79.5 Hz, J_{P-W} = 248 Hz), 148.7 (pseudotriplet, μ-PPh$_2$, J_{P-P} = 23.9 Hz, J_{P-W} = 130.5 Hz), 15.6 (dd, Re–PPh$_3$, J_{P-P} = 25, 79.5 Hz); MS, m/z 1143 (M$^+$ – 1 CO) and fragment ions corresponding to loss of five CO's. **15**: IR (hexane) ν_{CO} 2072 w, 2037 s, 2008 m, 1972 vs, 1960 s, 1927 m, 1573 vw cm^{-1}; ^{1}H NMR (25 °C, acetone-d_6) δ 7.2 (m, Ph's), 2.16 (q, 2 H, C(O)CH_2CH$_3$, J_{H-H} = 7.4 Hz), 1.5 (t, 3 H, C(O)-CH$_2$CH_3), J_{H-H} = 7.4 Hz); $^{31}P\{^1H\}$ NMR (25 °C, acetone-d_6) δ 181.8 (d, μ-PPh$_2$, J_{P-P} = 18.7 Hz, J_{P-W} = 172 Hz), 151.2 (d, μ-PPh$_2$, J_{P-P} = 18.7 Hz, J_{P-W} = 150 Hz); MS, m/z 965 (M$^+$ – 1 CO) and fragment ions correspnding to the loss of seven CO's and one C$_2$H$_5$. anal. Calcd for $C_{34}H_{25}O_8P_2ReW$: C, 41.09; H, 2.52. Found: C, 41.03. H, 2.85.

Thermolysis of 6. Complex **6** (0.050 g, 0.052 mmol) was dissolved in toluene (20 mL) and refluxed for 1.25 h. Chromatography (20% CH$_2$Cl$_2$/hexane, SiO$_2$) yielded orange bands of **3** in 30% yield (0.015 g, 0.016 mmol) and **15** in 22% yield (0.011 g, 0.011 mmol) in that order.

X-ray Diffraction Study of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3CH_3$, 5. Crystals of **5** were grown by slow diffusion of n-heptane into a saturated CH$_2$Cl$_2$ solution of **5**. Diffraction data were collected as previously described[5] with pertinent crystal and intensity data given in Table I. All data were converted to $|F_o|$ values following correction for absorption (empirical ψ-scan technique, max/min transmission 0.211/0.122) and for Lp effects. Systematic absences uniquely defined the monoclinic space group $P2_1/c$.

A learned profile procedure was used in the initial data processing to improve the precision in the measurement of weak reflections. The structure was solved by locating the W and Re atoms from a Patterson map. A difference map phased on these atoms revealed the locations of all remaining non-hydrogen atoms. The hydrogen atoms of the phenyl rings were placed in calculated positions (d(C–H) = 0.96 Å), and the rings themselves were treated as rigid bodies. All non-hydrogen atoms were refined anisotropically. Disorder exists in the location of the C(8) methyl and C(6)–O(6) carbonyl groups, which occupy sites related by the approximate mirror plane defined by the metal atoms and the (2), (4), and (5) carbonyl groups. Refinement of the site occupancy factors (sof) for C(8), C(6), and O(6) as a single variable in the sites shown in Figure 1 gave a sof of 70%; this value was fixed during further refinement. The 30% minority positions for C(6) and O(6) were located as the top two peaks in the final difference map: C(6)*, x/a = 0.0402, y/b = 0.685, z/c = 0.848; 1.44 e Å^{-3};

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[5] Fultz, W. C.; Rheingold, A. L.; Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 860–863.

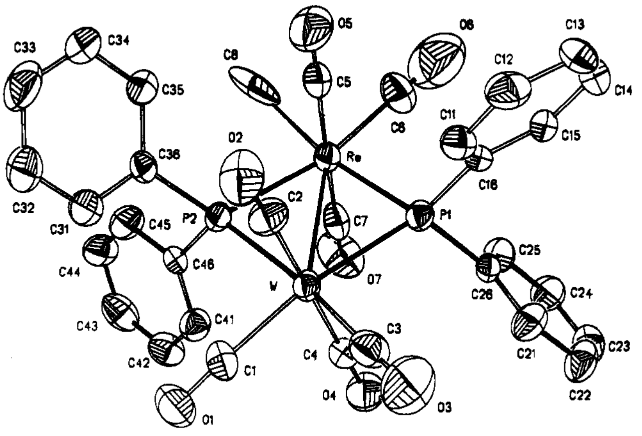


Figure 1. An ORTEP drawing of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3CH_3$, 5.

Table II. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³) for 5

atom	x	y	z	U^a
Re^b	18340 (5)	64893 (2)	79055 (3)	40 (0)
W^b	36128 (5)	69327 (2)	67754 (3)	38 (0)
P(1)	3500 (3)	5807 (2)	7399 (2)	38 (1)
P(2)	1855 (3)	7592 (2)	7295 (2)	37 (1)
O(1)	4403 (12)	8364 (5)	6164 (7)	89 (5)
O(2)	1141 (12)	6745 (5)	5243 (6)	85 (5)
O(3)	5583 (15)	6226 (7)	5744 (8)	120 (7)
O(4)	6308 (10)	7120 (5)	8182 (6)	79 (4)
O(5)	−515 (11)	5913 (6)	6534 (6)	87 (5)
O(6)^c	1226 (18)	5236 (11)	8792 (11)	173 (11)
O(7)	3995 (14)	7047 (6)	9396 (6)	100 (6)
C(1)	4076 (15)	7846 (7)	6360 (8)	54 (5)
C(2)	2026 (14)	6803 (7)	5831 (8)	55 (5)
C(3)	4896 (15)	6490 (7)	6117 (8)	61 (6)
C(4)	5307 (13)	7061 (6)	7693 (7)	48 (5)
C(5)	371 (13)	6132 (6)	7031 (7)	53 (5)
C(6)^c	1419 (21)	5690 (9)	8544 (12)	82 (8)
C(7)	3217 (15)	6841 (6)	8844 (7)	55 (5)
C(8)^c	−11 (20)	7018 (9)	8558 (9)	114 (9)
C(11)	2347 (8)	5039 (3)	6020 (4)	48 (5)
C(12)	1867 (8)	4441 (3)	5612 (4)	62 (6)
C(13)	1937 (8)	3827 (3)	6027 (4)	64 (6)
C(14)	2487 (8)	3812 (3)	6849 (4)	62 (6)
C(15)	2967 (8)	4410 (3)	7256 (4)	48 (5)
C(16)	2897 (8)	5024 (3)	6841 (4)	38 (4)
C(21)	6226 (8)	6308 (4)	7752 (4)	60 (5)
C(22)	7471 (8)	5069 (4)	8242 (4)	68 (6)
C(23)	7595 (8)	5023 (4)	9064 (4)	67 (6)
C(24)	6476 (8)	5216 (4)	9395 (4)	63 (6)
C(25)	5232 (8)	5455 (4)	8905 (4)	52 (5)
C(26)	5107 (8)	5501 (4)	8083 (4)	39 (4)
C(31)	471 (8)	8390 (4)	6034 (5)	63 (6)
C(32)	−677 (8)	8593 (4)	5439 (5)	82 (7)
C(33)	−1991 (8)	8295 (4)	5390 (5)	91 (8)
C(34)	−2156 (8)	7795 (4)	5937 (5)	95 (8)
C(35)	−1008 (8)	7592 (4)	6532 (5)	75 (7)
C(36)	305 (8)	7889 (4)	6580 (5)	43 (4)
C(41)	3731 (7)	8501 (4)	8271 (5)	53 (5)
C(42)	4062 (7)	9047 (4)	8799 (5)	62 (6)
C(43)	2990 (7)	9429 (4)	9000 (5)	72 (7)
C(44)	1588 (7)	9267 (4)	8674 (5)	64 (6)
C(45)	1257 (7)	8721 (4)	8147 (5)	61 (6)
C(46)	2329 (7)	8338 (4)	7946 (5)	42 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Atomic coordinates for these atoms (×10⁵). [c] 70% occupancy (see text).

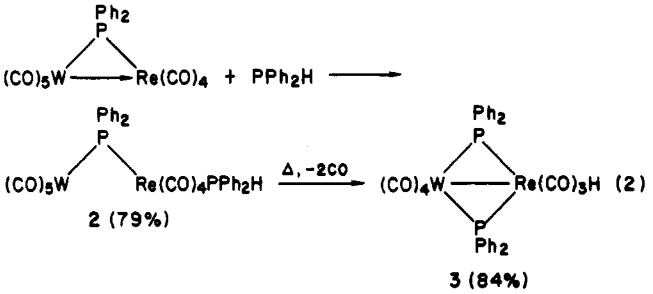
Table III. Selected Bond Lengths (Å) and Angles (deg) in $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3CH_3$, 5

Bond Lengths			
W–Re	2.015 (1)	W–C(2)	1.992 (12)
Re–P(1)	2.418 (3)	W–C(3)	2.063 (15)
Re–P(2)	2.410 (3)	W–C(4)	2.029 (11)
Re–C(5)	1.956 (11)	C(1)–O(1)	1.141 (18)
Re–C(6)	2.011 (19)	C(2)–O(2)	1.179 (15)
Re–C(7)	1.982 (12)	Cβ–O(3)	1.151 (21)
Re–C(8)	2.550 (20)	C(4)–O(4)	1.142 (14)
W–P(1)	2.473 (3)	C(5)–O(5)	1.154 (15)
W–P(2)	2.474 (3)	C(6)–O(6)	1.025 (28)
W–C(1)	2.021 (14)	C(7)–O(7)	1.148 (16)
Bond Angles			
Re–W–P(1)	51.1 (1)	W–Re–P(1)	52.8 (1)
Re–W–P(2)	50.9 (1)	W–Re–P(2)	52.8 (1)
Re–W–C(1)	133.8 (4)	W–Re–C(5)	92.0 (4)
Re–W–C(2)	92.0 (4)	W–Re–C(6)	142.7 (6)
Re–W–C(3)	138.0 (4)	W–Re–C(7)	92.3 (4)
Re–W–C(4)	91.2 (4)	W–Re–C(8)	137.2 (4)
P(1)–W–P(2)	102.1 (1)	P(1)–Re–P(2)	105.6 (1)
P(1)–W–C(1)	169.7 (4)	P(1)–Re–C(5)	87.6 (4)
P(1)–W–C(2)	97.9 (4)	P(1)–Re–C(6)	89.9 (6)
P(1)–W–C(3)	87.3 (4)	P(1)–Re–C(7)	95.6 (4)
P(1)–W–C(4)	83.2 (3)	P(1)–Re–C(8)	170.0 (4)
P(2)–W–C(1)	83.8 (4)	P(2)–Re–C(6)	93.7 (4)
P(2)–W–C(2)	83.5 (4)	P(2)–Re–C(6)	164.5 (6)
P(2)–W–C(3)	167.7 (4)	P(2)–Re–C(7)	88.3 (4)
P(2)–W–C(4)	99.5 (4)	P(2)–Re–C(8)	84.4 (4)
C(1)–W–C(2)	91.2 (5)	C(5)–Re–C(6)	86.4 (6)
C(1)–W–C(3)	88.2 (6)	C(5)–Re–C(7)	175.7 (6)
C(1)–W–C(4)	87.5 (5)	C(5)–Re–C(8)	91.1 (5)
C(2)–W–C(3)	87.4 (5)	C(6)–Re–C(7)	90.7 (6)
C(2)–W–C(4)	176.6 (6)	C(6)–Re–C(8)	80.1 (7)
C(3)—W–C(4)	89.4 (5)	C(7)–Re–C(8)	85.3 (5)

0.72 Å from C(8) and 1.27 Å from O(6)*; O(6)*, $x/a = -0.029$, $y/b = 0.729$, $z/c = 0.875$; 1.61 e Å^{-3}; 2.00 Å from Re and 0.58 Å from C(8). The minority location for C(8)* could not be determined. The disorder is reflected in the large thermal parameters for C(6), O(6), and C(8) and probably accounts for the anomolously short C(6)–O(6) bond distance given in Table III. No other features in the final difference map had chemical significance; all remaining peaks were <0.5 e Å^{-3}. The final positional parameters are given in Table II and selected bond distances and angles in Table III.

Results

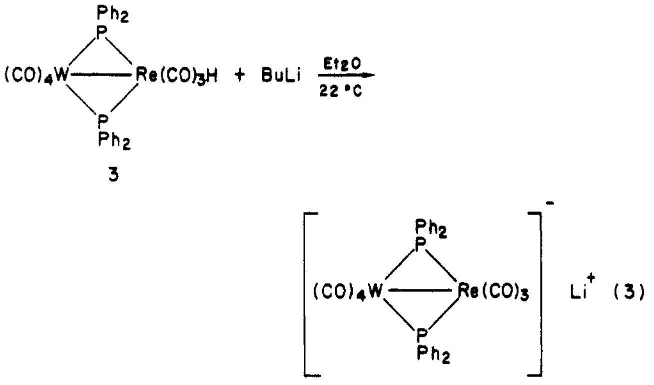
Synthesis and Spectroscopic Characterization of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3X$ (X = H, CH_3, Et, C(O)Ph, Cl, Br). The weak donor–acceptor bond of complex 1 was earlier shown to be easily displaced by tertiary phosphines.[1] This works equally well with the secondary phosphine PPh_2H to give complex 2 in good yield (eq 2). Bonding of the PPh_2H ligand to Re and not W is indicated by the absence of ^{183}W satellites on the ^{31}P NMR resonance (δ −3.17) for this ligand. Complex 2 then provides a convenient entry into *bis(phosphido)* W–Re chemistry via thermolysis which induces CO loss and migration of hydrogen from phosphorus to Re (eq 2). The pathway by which this latter reaction occurs is not clear. Carbonyl ligands are lost from both metals and the hydride ligand coordinates to Re, although the usual oxidative addition of a P–H bond to a metal would have logically placed the hydride on W.

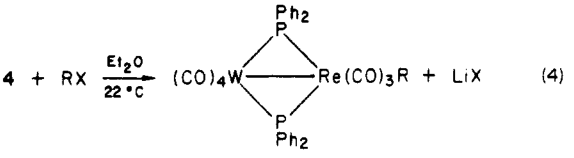


2 (79%)

3 (84%)

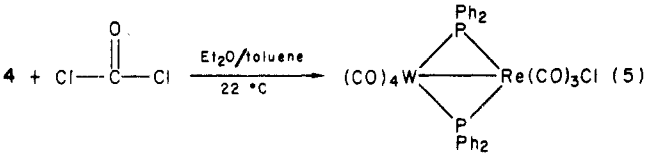
Complex 3 is readily deprotonated by strong base to generate the anion 4 (eq 3). Complex 4 in turn reacts with CH_3I, EtOTf, and $C_6H_5C(O)Br$ to yield the alkyl and benzoyl complexes 5, 6, and 8 (eq 4). Reaction of 4 with





5, R = CH3 (80%)
6, R = C2H5 (75%)
8, R = C(O)C6H5 (45%)

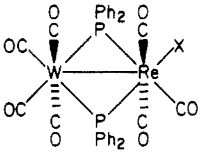
benzoyl bromide also gave $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3Br$, **9**, in 47% yield. An analogous chloride derivative $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3Cl$, **7**, arises from the reaction of **4** with phosgene (eq 5). An intermediate chloroformyl complex may be formed in this reaction as such species would give the observed product **7** by CO loss and chloride migration to Re.



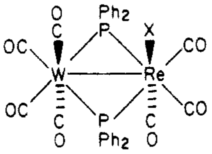
7 (24%)

Spectroscopic data for all the new complexes reported herein are given in the Experimental Section. Each of the bis(phosphido)-bridged complexes **3–9** shows downfield ^{31}P NMR resonances which are consistent with the presence of metal–metal bonds in these compounds as required by the 18-electron rule and shown by the crystal structure of **5** (see below). Literature data indicate that μ-PPh$_2$ ligands which bridge two metals joined by a metal–metal bond generally appear downfield (δ 300 → δ 50) whereas upfield (δ 50 → δ −300) resonances are usually observed for compounds in which this ligand bridges two metals not joined by a metal–metal bond.[6] However, there are exceptions to this correlation,[7] and caution must be exercised in its use. The ^1H NMR resonance at δ −4.8 for the hydride ligand in **3** (X = H) does not show ^{183}W satellites which implies its location on Re and not W.

Complexes **3**, **5**, **6**, and **8** show two well-separated ^{31}P NMR resonances which indicate the presence of two *inequivalent* phosphido bridges as in structure I. This structure was confirmed for the X = CH_3 complex **5** by an X-ray diffraction study (see below). In contrast, complexes **7** and **9** exhibit single downfield ^{31}P NMR resonances which imply the presence of *equivalent* μ-PPh$_2$ ligands. The structure II drawn below with the halide ligand cis to both μ-PPh$_2$ ligands is thus indicated for these compounds.

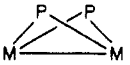


I (X = H, CH$_3$, Et, C(O)Ph)



II (X = Cl, Br)

Crystal and Molecular Structure of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3CH_3$, 5. The molecular structure and labeling scheme for complex **5** are shown in Figure 1. The W and Re atoms are bridged by two μ-PPh$_2$ ligands with the W further coordinated by four CO's and the Re by three CO's and a methyl ligand. As clearly illustrated in Figure 1, each metal in **5** has an octahedral coordination geometry if we neglect the metal–metal vector. The central WRe(μ-P)$_2$ core of the molecule is essentially planar with a [W–P(1)–Re]–[W–P(2)–Re] dihedral angle of 1.5 (1)°. This coordination geometry is characteristic of bis(phosphido)-bridged binuclear complexes in which one of the metals has a strong preference for an octahedral coordination geometry and in which there is a need to satisfy the 18-electron rule through metal–metal interaction.[2,3,7c,8] The alternative bent structure III is strongly disfavored



III

because of steric interactions between the substituents on the phosphorus atoms as well as between the "axial" ligands on the metals. This steric repulsion is relieved somewhat when a "metal–metal bond" is not required by the 18-electron rule since larger M–P–M angles can be adopted and the metals move further apart. Nevertheless, the planar $M_2(\mu\text{-}P)_2$ core still appears preferred because of the residual interaction between the phosphorus atom substituents.[7c,8a,d] It should be recalled that this situation reverses for d^8 metals which adopt five-coordinate geometries where the bent M_2P_2 core is found in compounds with a formal metal–metal bond whereas a planar core is adopted for non-metal–metal bonded compounds.[9]

A formal metal–metal bond in **5** is required by the 18-electron rule, and the W–Re distance of 3.015 (1) Å falls within the 2.867 (1)–3.155 (1) Å range associated with W–Re single bonds in other crystallographically characterized compounds of these metals: $[ReW(\mu\text{-}CHC_6H_4Me\text{-}4)(CO)_9]^-$, 3.033 (1) Å;[10] $ReW\{\mu\text{-}C(O)\text{-}CH_2C_6H_4Me\text{-}4\}(CO)_6(\mu\text{-}dppm)\{P(OMe)_3\}$, 3.155 (1) Å;[10] $ReW_2(\mu\text{-}Br)(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_4Cp_2$, 2.867 (1) and 2.912

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(6) (a) Peterson, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, *19*, 186–191. (b) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163–193. (c) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *204*, C27–C32.

(7) (a) Jones, R. A.; Wright, J. C.; Atwood, J. C.; Hunter, W. e. *Organometallics* **1983**, *2*, 470–472. (b) Rosen, R. A.; Hoke, J. B.; Whittle, R. R.; Geoffroy, G. L.; Hutchinson, J. P.; Zubieta, J. A. *Organometallics* **1984**, *3*, 846–855. (c) Targos, T. S.; Rosen, R. P.; Whittle, R. R.; Geoffroy, G. L. *Inorg. Chem.* **1985**, *24*, 1375.

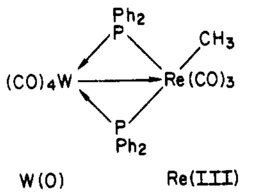
(8) (a) Vahrenkamp, H. *Chem. Ber.* **1978**, *111*, 3472–3483. (b) Linck, M. H.; Nassimbeni, L. R. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 1105–1113. (c) Vahrenkamp, H.; Keller, E. *Chem. Ber.* **1979**, *112*, 1991. (d) Baker, R. T.; Tulip, T. H.; Wreford, S. S. *Inorg. Chem.*, in press.

(9) Ginsburg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550–6562.

(10) Jeffrey, J. C.; Orpen, A. G.; Robinson, W. T.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 396.

(1) Å;[11] $ReW_2(\mu\text{-}Br)(\mu\text{-}O)(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_3Cp_2$, 3.004 (1) and 2.871 (1) Å.[11] The metal–metal bond in **5** is 0.096 Å shorter than that in $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4$ for which a donor–acceptor metal–metal bond was implied.[1] This shortening could be caused by the steric constraints of the two μ-PPh_2 groups but is probably reflective of a stronger metal–metal interaction. In support of the latter, no reactions of **5** or any of the related compounds described herein have been observed in which the metal–metal bond has been broken.

An important question in such μ-PPh_2 complexes concerns the *formal* oxidation states of the metals present. In this case there is a total of three negatively charged ligands (two PPh_2, CH_3) which implies a total metal oxidation state of +3. Of the possible structures, that drawn in IV with W(0) and Re(III) oxidation states appears most reasonable. An appropriate model for the W center is *cis*-$W(CO)_4(PPh_3)_2$, and Re(III) is a reasonable oxidation state for this metal.[12] The W–P and Re–P bond distances in **5** support this model, and an instructive comparison is with those determined for $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4$, **1**,[1] where W(0) and Re(I) oxidation states are clearly indicated. In compound **1**, the W–P and Re–P distances are respecively 2.499 (2) and 2.407 (2) Å.[1] In complex **5**, the W–P distances (Table III) average 2.473 Å and the Re–P distances average 2.414 Å, not dramatically different from those of **1**. The shorter W–P distance does imply some degree of oxidation of W in **5**, but it cannot be large.

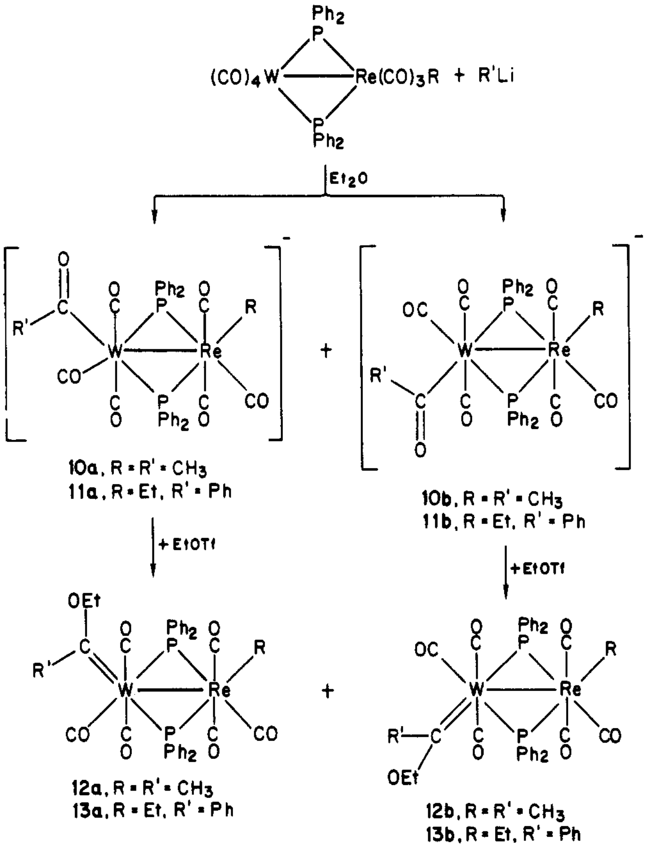


IV

Binuclear Alkyl–Acyl and Alkyl–Carbene Complexes. When the alkyl complexes **5** (R = CH_3) and **6** (R = Et) were reacted with CH_3Li and PhLi, air-sensitive but thermally stable isomeric acyl–alkyl complexes resulted (Scheme I). These in turn gave air and thermally stable carbene–alkyl isomeric complexes upon reaction with EtOTf.

Both ^{13}C and ^{31}P NMR spectra indicate that two isomers of each compound are formed which differ according to the relative cis or trans disposition of the organic ligands across the W–Re bond. The product mixture shows two sets of two ^{31}P NMR resonances for the μ-PPh_2 ligands and two sets of ^{13}C NMR resonances which can be assigned to the acyl or carbene ligands in the two isomers. For example, the reaction of **6** (R = Et) with PhLi followed by addition of EtOTf gave two isomers of air and thermally stable **13**, but these proved inseparable by chromatography. The ^{13}C NMR spectrum showed two equal intensity resonances at δ 299.7 and 298.0 for the two different carbene ligands as well as two separate sets of resonances due to two different Et ligands (see Experimental Section). The ^{31}P NMR spectrum showed resonances at δ 168 (d) and 105 (d) due to one isomer and δ 137.8 (d) and 136.9 (d) due to the second isomer. The widely different ^{31}P NMR chemical shifts ($\Delta\delta$ = 63 ppm) for the two μ-PPh_2 ligands in the first isomer **13a** imply significantly different electronic environments for these ligands. The only ligand arrangement which would create this significant electronic difference is where one μ-PPh_2 is trans to *both* the alkyl and carbene ligands as in **13a**. In contrast, the two μ-PPh_2 ligands of the second isomer **13b** have similar chemical shifts ($\Delta\delta$ = 0.9 ppm) implying similar electronic environments. We thus formulate this isomer as having the carbene ligand on W cis to the μ-PPh_2 ligand which the Et ligand is trans to in **13b**. Consistent with this interpretation is the fact that the two μ-PPh_2 ligands in **13b** show ^{31}P NMR resonances (δ 137.8 and 136.9) almost exactly midway between the two widely different resonances for **13a** (average δ 136.5).

Scheme I



It should be noted that we have no unambiguous proof that the acyl and carbene ligands in **12** and **13** are located on W since the ^{13}C NMR spectra of these products were not sufficiently resolved to detect ^{183}W satellites. We also have not succeeded in obtaining suitable crystals for an X-ray diffraction study. Nevertheless, we fell confident of our structural assignments based on (1) the consistency of the above spectral interpretation, (2) the fact that similar W-bound acyl and carbene ligands form upon analogous reactions with $(CO)_4W(\mu\text{-}PPh_2)_2IrH(CO)PPh_3$,[2a] and (3) the total lack of any evidence for interaction between the two different organic ligands. If both ligands were bound to Re, alkyl–acyl and alkyl–carbene coupling would likely occur.

Reaction of Complex 6 with PPh_3. Complex **6** reacts with PPh_3 at elevated temperatures (110 °C) to yield $(CO)_4W(\mu\text{-}PPh_2)_2Re(CO)_2(PPh_3)H$, **14**, along with the propionyl complex **15** and unreacted **6** (eq 6). These complexes apparently arise through the competing reaction pathways shown in Scheme II. Carbon monoxide loss from **6** followed by β-H elimination and substitution of PPh_3 for ethylene would give **14** whereas **15** can form via Et migration to CO followed by addition of the CO released

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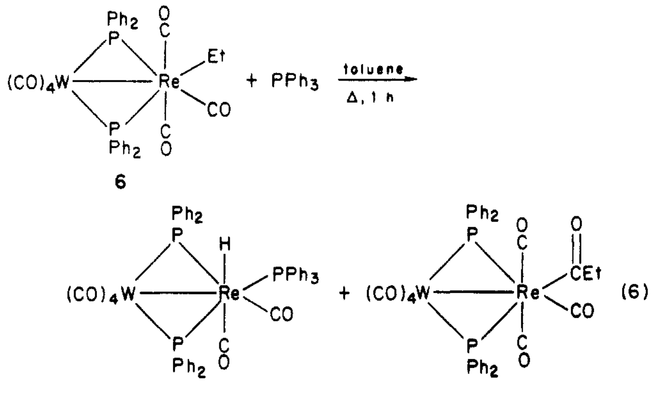
[11] Carriedo, G. A.; Jeffrey, J. C.; Stone, F. G. A., *J. Chem. Soc., Dalton Trans.* **1984**, 1597–1603.

[12] Cotton, F. A., Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 883 ff.



6

14 (45%)

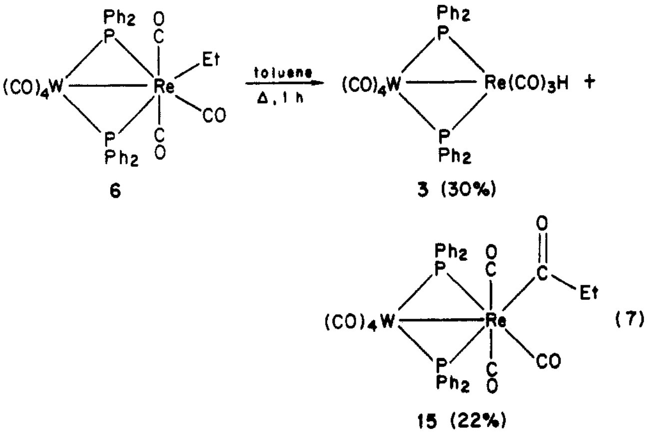
15 (25%)

(6)

in formation of 14. Surprisingly, we saw no evidence for a complex similar to 15 in which PPh_3, instead of CO, had added.

The spectroscopic data for 14 and 15 indicate their assigned structures. The ^{31}P NMR spectrum of 14 shows three inequivalent phosphorus ligands and coupling constants which indicate that the PPh_3 ligand is cis to one μ-PPh_2 ligand and trans to the other. Neither the hydride ^1H NMR resonance (δ -4.2 (ddd)) nor the PPh_3 ^{31}P NMR resonance (δ 15.6) show ^{183}W satellites, consistent with the location of these ligands on Re. The ^{31}P NMR spectrum of 15 shows two downfield resonances at δ 181.8 and 151.2 similar to those of the starting ethyl complex 6, implying similar structures. The IR spectrum of 15 has a characteristic acyl absorption at 1573 cm^{-1}.

Thermolysis of Complex 6. When complex 6 was refluxed in toluene for 1 h, compounds 3 and 15 were formed (eq 7). These presumably arise via competing migratory insertion and β-hydride elimination pathways as in Scheme II.



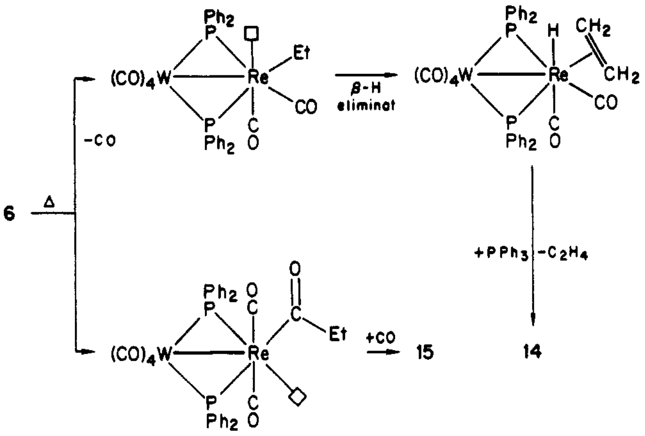
6

3 (30%)

15 (22%)

(7)

Scheme II



6

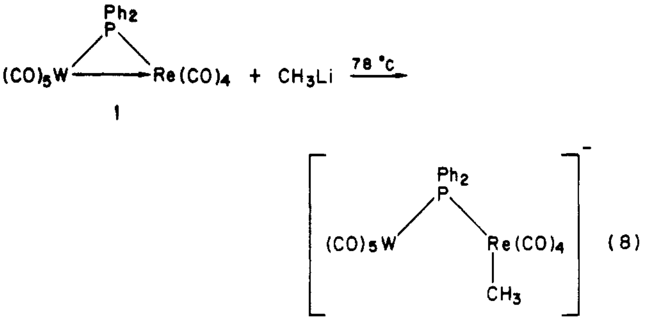
15

14

Discussion

The *bis(phosphido)-bridged* complex $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Re}(CO)_3H$, 3, was prepared in this study by the reaction of the *mono(phosphido)-bridged* complex 1 with PPh_2H, followed by heating to induce CO loss and migration of hydrogen from phosphorus to Re (eq 2). Such reaction should prove to be a general method to prepare bis(phosphido)-bridged complexes from mono(phosphido)-bridged precursors and should yield many new examples of such compounds.

Our reasons for preparing complex 3 was to compare its chemistry with 1 which contains a single phosphido bridge. The chemistry of 1 is dominated by cleavage of the weak donor-acceptor metal-metal bond which opens a coordination site for further reactivity.[1] For example, it was not possible to prepare acyl derivatives of 1 since displacement of the W-Re bond occurred at low temperature to directly form alkyl complexes (eq 8).[2] In contrast, complex 3 with two phosphido bridges readily forms acyl derivatives 8 and 15 which were sufficiently stable to isolate and characterize. Indeed, in none of the reactions examined for this class of bis(phosphido)-bridged W-Re compounds have we seen evidence for W-Re bond cleavage. Although, this could be a consequence of less flexibility in the $WReP_2$ core of the molecule, it probably is not since an analogous W-Os complex, $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Os}(CO)_3$, undergoes relatively easy cleavage of the W-Os bond upon treatment with PR_3 ligands to give complexes of the type $(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_3(PR_3)$.[13] Rather, it probably reflects a significant electronic difference between 1 and 3 since the oxidation states of the metals in these two complexes must differ. In complex 1, a W(0)-Re(I) formulation is clearly indicated whereas in complex 3, a W(0)-Re(III) oxidation state assignment appears most reasonable.



1

(8)

The stability of the binuclear alkyl-acyl and alkyl-carbene complexes 10-13 is also noteworthy. Although coupling of these ligands across the W-Re bond to give ketones in the former case and a different alkyl complex in the latter might have been anticipated, neither occurred. This is presumably because it is necessary for one of the ligands to migrate so as to place both ligands on the same metal in some intermediate complex for such coupling reactions to occur. However, the metals in these complexes are coordinatively saturated with no easy path for ligand transfer. In order to observe such coupling of organic ligands on adjacent metals, it will probably be necessary to employ binuclear complexes which are either coordinatively unsaturated or which have ultralabile ligands so as to easily open coordinative sites for ligand transfer.

Another unique aspect of the chemistry of this series of compounds is the ease with which Re-bound acyl ligands

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[13] Rosenberg, S.; Whittle, R. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* 1984, *106*, 5934-5940.

form by apparent alkyl migration to CO. Such a transformation does not readily occur for mononuclear $(CO)_5ReR$ complexes[14] but in this study the acyl derivative **15** readily forms upon either thermolysis or treatment of the ethyl complex **6** with PPh_3 (eq 6 and 7). We do not presently understand the basis for this effect, whether it is a consequence of the ligand environment of Re or whether it is facilitated by the presence of the tungsten center, but that will be the basis for a future study in this series.

Acknowledgment. The National Science Foundation (CHE8201160) is gratefully acknowledged for support of this research and for contributing funds toward purchase of the diffractometer at the University of Delaware.

Registry No. **1**, 92763-15-0; **2**, 96665-99-5; **3**, 96666-00-1; **4**, 96666-01-2; **5**, 96666-02-3; **6**, 96666-03-4; **7**, 96666-04-5; **8**, 96666-05-6; **9**, 96666-06-7; **10a**, 96666-07-8; **10b**, 96744-22-8; **11a**, 96666-08-9; **11b**, 96744-23-9; **12a**, 96688-69-6; **12b**, 96744-98-8; **13a**, 96666-09-0; **13b**, 96744-24-0; **14**, 96688-70-9; **15**, 96666-10-3; diphenylphosphine, 829-85-6; benzoyl bromide, 618-32-6.

Supplementary Material Available: Tables of structure factors, complete bond lengths and angles, thermal parameters, and calculated hydrogen atom positions for **5** (26 pages). Ordering information is given on any current masthead page.

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(14) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; p 274.

Ferrocenyl Sulfides. Preparation and Reactivity as Bidentate Chelating Ligands

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A series of ferrocenyl sulfide derivatives, $Fe(C_5H_4SR)_2$, where R = Me, *i*-Pr, I-Bu, Ph, and $PhCH_2$, have been prepared by lithiation of ferrocene followed by reaction with the appropriate disulfide. The complexes were characterized by ^1H and ^{13}C NMR, mass spectra, and infrared spectroscopy. The ferrocenyl sulfide derivatives readily chelate palladium and platinum halides to form [3]ferrocenophane complexes $Fe(C_5H_4SR)_2MX_2$ (R = Me, *i*-Pr, *i*-Bu, Ph, $PhCH_2$; M = Pd, Pt; X = Cl, Br). ^1H, ^{13}C, and ^{195}Pt NMR spectra were obtained where possible, and infrared, ultraviolet–visible and cyclic voltammetry data of the complexes are presented. The structure of $Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$ (**6**) was determined by single-crystal X-ray diffraction measurements. Compound **6** crystallizes in the orthorhombic space group *Pbca* with lattice parameters $a = 22.168\ (11)$ Å, $b = 11.855\ (7)$ Å, $c = 16.131\ (6)$ Å, $M_r = 539.69$, $\rho(\text{calcd}) = 1.691\ \text{cm}^{-3}$, and $Z = 8$. Least-squares refinement gave a final R value of 0.046 for 3689 observed reflections. The dihedral angle between the $Fe\text{–}S_1\text{–}S_2$ plane and the $S_1\text{–}Pd\text{–}S_2$ plane is 104.6°. The molecule **6** is fluxional in solution where the palladium atom flips from one side of the $Fe\text{–}S_1\text{–}S_2$ plane to the other.

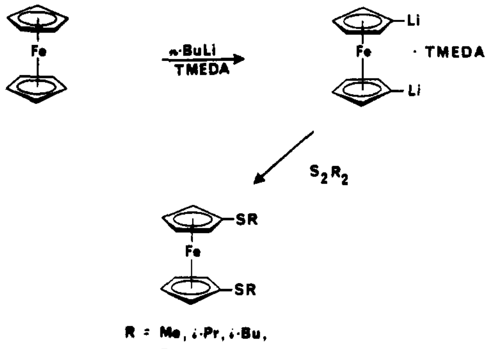
Introduction

Symmetrically 1,1′-disubstituted ferrocene complexes $Fe(C_5H_4R)$, where R is a potential donor such as phosphine or arsine, have generated much interest as rigid chelating ligands.[1] In particular Ni and Pd complexes of $Fe(C_5H_4PPh_2)_2$ exhibit high catalytic activity for selective cross-coupling reactions[2] whereas the analogous rhodium complexes of $Fe(C_5H_4PR_2)_2$, R = aryl, are reported to be highly selective hydroformylation catalysts.[3] In addition, chiral (ferrocenylphosphine)rhodium complexes have been shown to be highly selective catalysts in asymmetric hydrogenation.[4] Recently Seyferth[5] reported that ferrocenylphosphine oligomers are effective ligands in the cobalt catalyzed-hydroformylation of 1-hexene.

In order to extend the utility of ferrocene as a chelating ligand, we investigated the preparation and reactivity of ferrocenyl sulfide complexes. (Methylthio)ferrocene has previously been prepared from either ferrocenesulfonic acid[6] or thiocyanatoferrocene,[7] and ferrocenyl methyl sulfides have been obtained from ferrocene and mercaptans.[8]

Elschenbroich[9] recently prepared 1,1′-bis((methylthio)benzene)chromium by lithiation of bis(benzene)chromium followed by subsequent reaction with methyl disulfide. A similar approach was used in the synthesis

Scheme I



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† Present address: Imperial College, London.

(1) Cullen, W. R.; Woollins, J. D. *Coord. Chem. Rev.* **1981**, *39*, 1–30.

(2) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669–679. Hayashi, T.; Konishi, M.; Yokota, K.-I.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1981**, 313–314.

(3) Hughes, O. H.; Unruh, J. D. *J. Mol. Catal.* **1981**, *12*, 71–83. Unruh, J. D.; Christenson, J. R. *J. Mol. Catal.* **1982**, *14*, 19–34. Unruh, J. D. *Chem. Abstr.* **1900**, *90*, 203 487; US Patent 2834742.

(4) Hayashi, T.; Kumada, M. *Acc. Chem. Res.* **1982**, *15*, 395–401 and references therein.