Δ-$Na_8HW_9PO_{34}$. Fifty grams of $Na_8W_9PO_{34}$ hydrate was heated at 140–150 °C (340 torr) for 2 h and then for 1 h at 1 torr to obtain Δ-$Na_8HW_9PO_{34}$ (46 g) with the infrared spectrum shown in Figure 6b and the ^{31}P MAS described in the text. This product reacted with cobalt(II) nitrate to form $(H_2O)_2Co_4W_{18}P_2O_{68}{}^{10-}$ as described by Finke.[8] The conversion of W_9P to Δ-W_9P is somewat erratic; the conditions described above give the most consistent results. In some thermolyses, particularly if the entire thermolysis was conducted at 1 torr, a product with distinctly different infrared and solid-state ^{31}P MAS NMR spectra was obtained. This product has not yet been identified.

Reaction of Δ-W_9P with $PhSnCl_3$. Phenyltin trichloride was added dropwise with stirring to a fresh solution of Δ-W_9P (10 g) in water (75 mL) until the pH dropped to 5.5. The mixture was filtered. Trimethylamine hydrochloride (5 g) was added to the filtrate, precipitating 6.7 g of a white solid. Infrared analysis suggested this was a mixture containing $[(CH_3)_3NH]_5(PhSn)_2W_{10}PO_{38}$ and $[(CH_3)_3NH]_4PhSnW_{11}PO_{39}$.[2] This was confirmed by comparison of the ^{31}P NMR spectrum in dimethyl sulfoxide with the spectra of the authentic salts in the same solvent. Two of the four major lines, at −7.33 ($^2J_{P-Sn}$ = 26 Hz) and −8.60 ppm ($^2J_{P-Sn}$ = 24 Hz) are identical with the lines found (−7.33 ($^2J_{P-Sn}$ = 24 Hz), −8.69 ppm, ($^2J_{P-Sn}$ = 24 Hz)) in dimethyl sulfoxide for the trimethylammonium salts of the two isomers of $(PhSn)_2W_{10}PO_{38}{}^{5-}$ described in footnote 15.[28] A third major line in the spectrum is at −8.15 ppm ($^2J_{P-Sn}$ = 20 Hz) and may represent a third isomer of $(PhSn)_2W_{10}PO_{38}{}^{5-}$. The fourth major line is at −11.26 ppm ($^2J_{P-Sn}$ = 22 Hz), which agrees with the values found for $[(CH_3)_3NH]_4PhSnW_{11}PO_{39}$ in dimethyl sulfoxide.

Reaction of Δ-W_9P with $CpFe(CO)_2SnCl_3$. A solution of $CpFe(CO)_2SnCl_3$ (5 g) in tetrahydrofuran (20 mL) was added to 10 g of Δ-W_9P in water (150 mL) rapidly with stirring. Stirring was continued for 15 min; the solution was filtered. Ten grams of $(CH_3)_3NHCl$ was added to the filtrate to precipitate 6.7 g of a yellow solid. The infrared spectrum and the ^{31}P NMR spectrum showed this to be a mixture of $CpFe(CO)_2SnW_{11}PO_{39}{}^{4-}$ and 1,5-$[CpFe(CO)_2Sn]_2W_{10}PO_{38}{}^{5-}$.[3,5]

Acknowledgment. Fine technical assistance was given by J. H. McCartney, R. F. Carver, and G. Watunya. We are grateful to R. G. Finke and M. W. Droege for correspondence regarding the W_9P/Δ-W_9P problem.

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[28] It is noteworthy that, although the chemical shifts of the lithium salts in water are the same as those of the trimethylammonium salts in dimethyl sulfoxide, the phosphorus–tin coupling constants are different. This has been confirmed by several different measurements of the spectra of authentic salts.

Alkyl, Aryl, Acyl, Formyl, and Hydride Derivatives of Phosphido-Bridged WRe Complexes. Crystal and Molecular Structure of $(CO)_5\overline{W(\mu\text{-}PPh_2)Re}(CO)_4$[†]

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Received July 2, 1984

The new heterobimetallic phosphido-bridged complex $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_5$, **2**, has been prepared by reaction of $Li[W(CO)_5PPh_2]$ with $Re(CO)_5Br$. This complex loses CO upon workup to yield $(CO)_5\overline{W(\mu\text{-}PPh_2)Re}(CO)_4$, **3**. These new complexes have been characterized spectroscopically, and $(CO)_5\overline{W(\mu\text{-}PPh_2)Re}(CO)_4$ has been characterized by a complete single-crystal X-ray diffraction study. The latter crystallizes in the space group $P\bar{1}$ with a = 8.609 (1) Å, b = 9.292 (2) Å, c = 18.376 (3) Å, α = 75.37 (1)°, β = 77.50 (1)°, γ = 63.38 (1)°, V = 2525 (2) Å^3, and Z = 2. The structure refined to R = 0.0386 and R_w = 0.0434 for the 3204 reflections with $I \geq 2\sigma(I)$. The μ-PPh_2 ligand bridges the W and Re atoms with W further coordinated by five CO's and Re by four. The W–Re bond length of 3.111 (1) Å together with the geometries about each metal imply a single donor–acceptor bond between these two atoms. Complex **3** reacts with CH_3CN and $PMePh_2$ to displace the metal–metal bond to give $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4(CH_3CN)$ and $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4PMePh_2$, **4**. Hydride, alkyl, and aryl complexes result from reaction of **3** with $Li[BHEt_3]$, CH_3Li, and PhLi, respectively, with these ligands attached to Re. Reaction of **4** with $Li[BHEt_3]$ and CH_3Li yields the formyl complex $Li[(CO)_5W(\mu\text{-}PPh_2)Re(CO)_3(PMePh_2)(CHO)]$ and the acetyl complex $Li[(CO)_5W(\mu\text{-}PPh_2)Re(CO)_3(PMePh_2)\{C(O)CH_3\}]$, respectively.

One of the consequences of assembling diverse metal centers into heterobinuclear and polynuclear complexes is that the resultant metal–metal bonds are usually not purely covalent but can have significant donor–acceptor character.[1,2] On an orbital basis this simply means that the metal-localized orbitals that overlap to form the metal–metal bonding and antibonding orbitals are of different initial energies. Hence, the bonding MO will be closer in energy to one of the initial metal orbitals, and thus the electron density in that MO will be more localized on one metal than the other (Scheme I). A similar situation arises for the usual donor–acceptor mode of ligand–metal binding with electron density localized on the ligand. For heterometallic complexes, an important question concerns the strength of these donor–acceptor bonds and the particular chemistry that may result as a consequence of their presence.

[†] In memory of Earl L. Muetterties, a brilliant and dedicated chemist.

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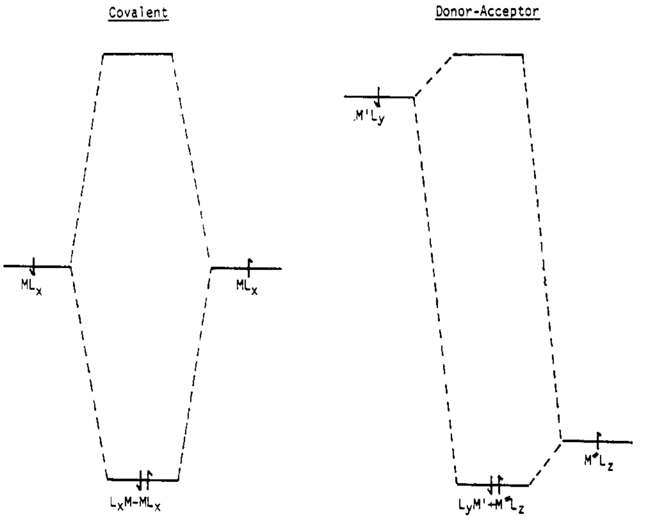
0276-7333/85/2304-0068$01.50/0

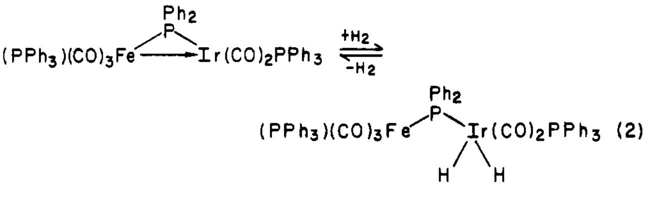
Scheme I



Other work has shown that these bonds are relatively weak and can be cleaved by a variety of nucleophiles.[3] For example, in the complex $(PEt_3)_2(CO)Rh{-}Co(CO)_4$, 1, weakly coordinating solvents such as CH_3CN readily displace the donor $[Co(CO)_4]^-$ from the acceptor Rh^+ center (eq 1), and kinetic studies showed that this second-order

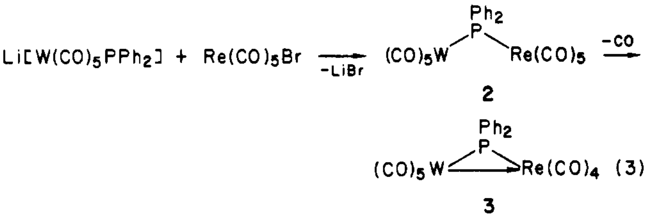
$$(PEt_3)_2(CO)Rh{-}Co(CO)_4 + S \rightleftharpoons [(PEt_3)_2(CO)Rh{-}S]^+ + [Co(CO)_4]^- \quad (1)$$

reaction occurs with a rate constant of $k = 1.7 \times 10^4\ M^{-1}\ s^{-1}$.[4] When the metals in a donor–acceptor complex are supported by a bridging ligand, which can be another metal in a polynuclear complex or a bridging main-group ligand such as μ-PR_2, μ-SR, etc., cleavage of the metal–metal bond can yield products in which the metal nuclearity has not changed as the reaction of eq 2 illustrates.[5]



(2)

We have been interested in the preparation and chemistry of binuclear and polynuclear alkyl, formyl, and acyl complexes[6] and have been particularly concerned with the effect of a donor–acceptor metal–metal bond on the stability and reactivity of such species. We report herein a series of WRe complexes and various reactions that address this point. The starting material for these investigations is $(CO)_5\overline{W(\mu\text{-}PPh_2)Re}(CO)_4$, 3, which was prepared by the reactions shown in eq 3. Complex 3 has been crystallographically characterized, and its structure clearly shows the presence of a donor–acceptor metal–metal bond.



(3)

Experimental Section

$W(CO)_5PPh_2H$[7] and $Re(CO)_5Br$[8] were prepared by literature procedures. PPh_2H, $PMePh_2$ (Strem), $Li[BEt_3H]$, *n*-BuLi, CH_3Li, and PhLi (Aldrich) were purchased and used without further purification. 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) or BaO (CH_2Cl_2) followed by distillation under N_2. NMR spectra were recorded on Bruker WP200, Bruker WM360, or JEOL PS100 FT-NMR spectrometers. $Cr(acac)_3$ (~1%) was added to each ^{13}C NMR sample as a shiftless relaxation agent.[9] ^{31}P NMR chemical shifts are relative to external H_3PO_4 with downfield chemical shifts reported as positive. Electron-impact mass spectra were recorded on an AEI-MS9 mass spectrometer operated in the electron-impact mode with a source voltage of 70 eV and probe temperatures in the 100–200 °C range. IR spectra were recorded on Perkin-Elmer 580 and IBM FT/IR-32 spectrometers. The latter gives difference spectra in absorption units (abs) only; spectra recorded in the absorption mode will be noted as such. All other IR data are from transmission spectra.

Preparation of $(CO)_5\overline{W(\mu\text{-}PPh_2)Re}(CO)_4$, 3. A solution of $Li[W(CO)_5PPh_2]$, prepared by adding *n*-BuLi (1.6 M, 1.17 mL, 1.87 mmol) to a stirred THF (50 mL) solution of $W(CO)_5PPh_2H$ (0.952 g, 1.87 mmol), was added dropwise to a stirred slurry of $Re(CO)_5Br$ (0.780 g, 1.92 mmol) in 50 mL of THF. The resultant light red solution was stirred for 12 h at 22 °C. The THF was removed in vacuo, and the residue was extracted into hexane by repeated washings. The hexane extracts were filtered through Celite 545 to remove suspended salts, and the solvent was removed in vacuo to leave yellow microcrystalline 3 in 66% yield (1.00 g, 1.24 mmol). Careful monitoring of the reaction by $^{31}P\{^1H\}$ NMR spectroscopy revealed the initial formation of $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_5$, 2, in near quantitative yield. Complex 2 proved too unstable to isolate and yielded 3 upon workup. Recrystallization of 3 from hexane at −20 °C gave analytically pure material. 2: $^{31}P\{^1H\}$ (25 °C, THF-d_8) δ −56.8 (s, μ-PPh_2, $J_{P-W} = 186$ Hz). 3: IR ν_{CO} (hexane) 2101 (w), 2062 (s), 2004 (vs), 1996 (sh), 1983 (s), 1963 (m), 1925 (w, br) cm^{-1}; $^{31}P\{^1H\}$ (25 °C, benzene-d_6) δ 110.4 (s, μ-PPh_2, $J_{P-W} = 142$ Hz); $^{13}C\{^1H\}$ (25 °C, benzene-d_6) δ 204.4 (d, $J_{P-C} = 11$ Hz, $J_{P-W} = 200$ Hz, 1 CO), 203 (d, $J_{P-C} = 3.7$ Hz,

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J_{P-W} = 186 Hz, 4 CO), 200.2 (d, J_{P-C} = 32 Hz, 1 CO), 196.9 (s br, 1 CO), 195 (d, J_{P-C} = 8.5 Hz, 2 CO); *m/z* 807 (M^+) and fragment ions corresponding to successive loss of nine CO's. Anal. Calcd for $C_{21}H_{10}O_9PReW$ (**3**): C, 31.18; H, 1.24. Found: C, 30.91; H, 1.22.

Preparation of $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4(PMePh_2)$, 4. To a stirred benzene (15-mL) solution of **3** (1.00 g, 1.24 mmol) was added $PMePh_2$ (0.235 mL, 1.3 mmol) followed by 15-min reflux and then cooling to 22 °C. To the resultant orange solution was added 1 g of SiO_2, and the solvent was removed in vacuo. The SiO_2 supported complex was placed on top of 3 × 32 cm SiO_2 chromatography column. Elution with 1:9 CH_2Cl_2/hexane gave a light yellow band of **4** that yielded a light yellow solid **4** (0.900 g, 0.894 mmol, 72%) upon solvent evaporation. Recrystallization from CH_2Cl_2/hexane gave analytically pure material. **4**: IR ν_{CO} (hexane, abs) 2095 (w), 2062 (w), 2017 (m), 2000 (s), 1971 (m), 1931 (vs), 1923 (vs) cm^{-1}; $^{31}P\{^1H\}$ (25 °C, benzene-d_6) δ −16.4 (d, *P*MePh$_2$, J_{P-P} = 18 Hz), −74.1 (d, μ-*P*Ph$_2$, J_{P-P} = 18 Hz, J_{P-W} = 191.3 Hz); *m/z* 1007 (M^+) and fragment ions corresponding to successive loss of nine CO's. Anal. Calcd for $C_{34}H_{23}O_9P_2ReW$: C, 40.51; H, 2.29. Found: C, 40.52; H, 2.44.

Preparation of $(CO)_5W(\mu\text{-}PPh_2)Re(CH_3CN)(CO)_4$, 5. Complex **3** (0.100 g, 0.124 mmol) was dissolved in CH_3CN (20 mL). The initial yellow color lightened within 5 min to a very pale yellow. Evaporation of solvent in vacuo gave yellow microcrystalline **5** in 90% yield (0.0952 g, 0.112 mmol). **5**: IR ν_{CO} (CH_3CN, abs) 2107 (w), 2062 (w), 2010 (s), 1964 (m), 1923 (vs), 1900 (sh) cm^{-1}; $^{31}P\{^1H\}$ (25 °C, benzene-d_6) δ −61.1 (s, μ-*P*Ph$_2$, J_{P-W} = 188 Hz); ^1H (25 °C, acetone-d_6) δ 2.86 (br s, C*H*$_3$CN, 3 H). Anal. Calcd for $C_{23}H_{13}NO_9PReW$: C, 32.54; H, 1.53. Found: C, 32.88; H, 1.65.

Preparation of $[Li(THF)_2][(CO)_5W(\mu\text{-}PPh_2)ReH(CO)_4]$, 6. $Li[BEt_3H]$ (1.0 M, 0.12 mL, 0.12 mmol) was added via syringe to a stirred THF (10 mL) solution of **3** (0.100 g, 0.124 mmol) maintained at −78 °C by a liquid N_2/2-propanol slush bath. The solution was slowly warmed to room temperature over the course of 2 h followed by solvent evaporation in vacuo. This left a yellow oil that gave a yellow powder of **6** upon trituration with hexane (0.030 g, 0.031 mmol, 25%). **6**: IR ν_{CO} (THF, abs) 2064 (w), 2051 (w), 1981 (m), 1964 (s), 1956 (s), 1923 (s), 1915 (s), 1881 (m), 1833 (w) cm^{-1}; ^1H (25 °C, THF-d_8) δ 7.2 (m, Ph), −3.93 (d, ReH, J_{P-H} = 17 Hz); $^{31}P\{phenyl\}$ (25 °C, THF-d_8) δ −73.6 (d, μ-*P*Ph$_2$, J_{P-H} = 17 Hz, J_{P-W} = 181 Hz). Anal. Calcd for $C_{29}H_{27}LiO_{11}PReW$: C, 36.29; H, 2.81. Found: C, 36.63; H, 3.21. Careful NMR (^1H, $^{31}P\{^1H\}$, ^{13}C) monitoring of the reaction at −78 °C showed the initial formation of two formyl complexes (**7a** and **7b**) that are thermally unstable above −20 °C and that decompose to form **6**. **7a**: ^{13}C (−78 °C, THF-d_8) δ 284.7 (s, CHO), 214.6 (d, CO, J_{C-P} = 26 Hz), 208.6 (d, CO, J_{C-P} = 6 Hz), 195.9 (d, CO, J_{C-P} = 6 Hz), 194.2 (d, CO, J_{C-P} = 8 Hz), 135.9 (d, Ph, J_{C-P} = 54 Hz), 127.6 (s, Ph), 127.0 (d, Ph, J_{C-P} = 40 Hz); ^1H (−78 °C, THF-d_8) δ 13.6 (s, C*H*O), 7.2 (m, Ph); $^{31}P\{^1H\}$ (−78 °C, THF-d_8) δ 115.7 (s, μ-*P*Ph$_2$, J_{P-W} = 135.7 Hz). **7b**: ^1H (−78 °C, THF-d_8) δ 15.73 (s, C*H*O).

Preparation of $[Li(Et_2O)_2][(CO)_5W(\mu\text{-}PPh_2)Re(CHO)(CO)_3(PMePh_2)]$, 8. $Li[BEt_3H]$ (1.0 M, 0.100 mL, 0.100 mmol) was added via syringe to a Et_2O (20 mL) solution of **4** (0.100 g, 0.100 mmol) at 22 °C. The solution became slightly darker yellow in color, and the IR spectrum showed a formyl ν_{CO} at 1548 cm^{-1} attributed to **8**. Slow removal of the Et_2O at −50 °C led to the deposition of yellow microcrystalline **8** (0.075 g, 0.064 mmol, 64% yield): IR ν_{CO} (THF) 2060 (m), 2010 (s), 1930 (vs), 1885 (sh), 1548 (w) cm^{-1}; $^{31}P\{^1H\}$ δ −5.7 (d, *P*MePh$_2$, J_{P-P} = 23 Hz), −58.1 (d, μ-*P*Ph$_2$, J_{P-W} = 178 Hz); ^1H δ 14.3 (dd, C*H*O, J_{P-H} = 6.5, 7.0 Hz), 7.2 (m, Ph), 1.5 (d, PC*H*$_3$Ph$_2$, J_{P-H} = 9.0 Hz). Anal. Calcd for $C_{42}H_{44}LiO_{11}P_2ReW$: C, 43.34; H, 3.78. Found: C, 43.69; H, 3.45.

Reaction of 3 with CH_3Li. CH_3Li (1.8 M, 0.069 mL, 0.124 mmol) was added dropwise to a stirred yellow THF (15 mL) solution of **3** (0.100 g, 0.124 mmol) at 22 °C to immediately give a red-orange solution of $Li[(CO)_5W(\mu\text{-}PPh_2)Re(CH_3)(CO)_4]$, **9**. $^{31}P\{^1H\}$ NMR integration showed the yield of **9** to be ~75%, but this species was too unstable to isolate and it was characterized in solution. **9**: IR ν_{CO} (THF) 2050 (w), 2002 (w), 1960 (m), 1921 (s), 1885 (m) cm^{-1}; ^1H (25 °C, THF-d_8) δ 7.2 (m, Ph), −0.74 (d, C*H*$_3$, J_{P-H} = 6.6 Hz); $^{31}P\{^1H\}$ (25 °C, THF-d_8) δ −63.3 (s, μ-*P*Ph$_2$, J_{P-W} = 179 Hz).

Reaction of 3 with PhLi. PhLi (2.0 M, 0.124 mL, 0.248 mmol) was added via syringe to a yellow THF (15 mL) solution of **3** (0.100 g, 0.124 mmol) at 22 °C to immediately give an orange solution of $Li[(CO)_5W(\mu\text{-}PPh_2)Re(C_6H_5)(CO)_4]$, **10**. $^{31}P\{^1H\}$ NMR integration showed the yield of **10** to be ~45%, but this species proved too unstable to isolate. **10**: IR ν_{CO} (THF, abs) 2070 (w), 2056 (w), 1991 (sh), 1975 (vs), 1927 (s), 1873 (s) cm^{-1}; $^{31}P\{^1H\}$ (25 °C, THF-d_8) δ −61.4 (s, (μ-*P*Ph$_2$, J_{P-W} = 175 Hz).

Table I. Crystallographic Data for the X-ray Diffraction Study of $(CO)_5\overline{W(\mu\text{-}PPh_2)Re}(CO)_4$, 3

Crystal Parameters

cryst system: triclinic
space group $P\bar{1}$
a = 8.609 (1) Å
b = 9.292 (2) Å
c = 18.376 (3) Å
α = 75.37 (1)°
β = 77.50 (1)°
γ = 63.38 (1)°

V = 2525 (2) Å^3
Z = 2
ρ(calcd) = 2.26 g cm^{-3}
abs coeff μ = 96.18 cm^{-1}
T = 21 °C

Measurement of Intensity Data

diffractometer: Enraf-Nonius CAD4
radiation: Mo Kα (λ = 0.710 73 Å)
monochromator: graphite crystal
scan type: θ-2θ
scan speed: variable, 1.0-5.0° min^{-1}
scan width: (0.9 + 0.347 tanθ)°
std reflns: 3 measured every 2.0 h
data limits: 3.0 < 2θ < 47.0
reflns measd: $+h, \pm k, \pm l$
reflns collected: 3738
unique data with $I \geqslant 2\sigma(I)$: 3204
aniso decay corr: 0.995-1.320
R = 0.0386
R_w = 0.0434

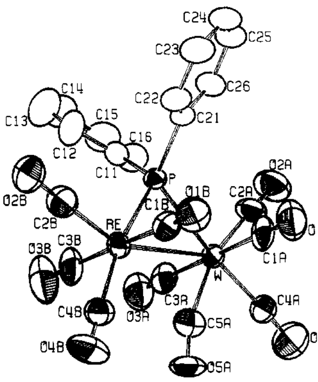

Figure 1. An ORTEP drawing of complex 3.

Reaction of 4 with CH_3Li. CH_3Li (1.8 M, 0.117 mL, 0.210 mmol) was added via syringe to a THF (10 mL) solution of **4** (0.106 g, 0.105 mmol), maintained at −78 °C in a liquid N_2/2-propanol slush bath. The color immediately changed from light yellow to orange as the acetyl derivative $Li[(CO)_5W(\mu\text{-}PPh_2)Re(CO)_3(PMePh_2)\{C(O)Me\}]$, **11**, formed. This species decomposed upon warmup to 22 °C and was not isolated in pure form. **11**: IR ν_{CO} (Et_2O) 2058 (m), 2008 (w), 1977 (w), 1935 (vs), 1905 (s), 1860 (m), 1580 (w) cm^{-1}; ^1H (25 °C, THF-d_8) δ 7.2 (m, Ph), 2.1 (s, C(O)C*H*$_3$), 1.55 (d, PC*H*$_3$Ph$_2$, J_{H-P} = 4 Hz); $^{31}P\{^1H\}$ (25 °C, THF-d_8) δ −3.55 (d, *P*MePh$_2$, J_{P-P} = 23 Hz), −51.0 (d, μ-*P*Ph$_2$, J_{P-W} = 170 Hz).

X-ray Structure Determination of $(CO)_5\overline{W(\mu\text{-}PPh_2)Re}(CO)_4$, 3. Orange crystals of **3** were grown from a saturated benzene solution. An irregularly shaped crystal of dimensions 0.21 mm × 0.35 mm × 0.38 mm was mounted on a glass fiber, fixed into an aluminum pin, and mounted onto a eucentric goniometer. Diffraction data were collected as previously described[10] with pertinent crystal and intensity data given in Table I. Psi scan data were collected and used to apply empirical absorption corrections (corr, 0.648–0.998; trans, 42.0–99.7%). The structure

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(10) Horrocks, W. D.; Ishley, J. N.; Whittle, R. R. *Inorg. Chem.* **1982**, *21*, 3265.

Table II. Atomic and Positional Parameters and Their Estimated Standard Deviations for $(CO)_5\overline{W(\mu\text{-}PPh_2)Re}(CO)_4$, 3

atom	x	y	z	B,[a] Å^2
Re	−0.18400 (5)	0.26920 (5)	0.63406 (3)	2.74 (1)
W	0.19730 (5)	0.01080 (5)	0.65325 (3)	2.52 (1)
P	−0.0403 (3)	0.1618 (3)	0.7470 (2)	2.25 (6)
O1A	0.059 (1)	−0.269 (1)	0.6919 (7)	5.8 (3)
O1B	−0.322 (1)	−0.002 (1)	0.6633 (6)	4.7 (2)
O2A	0.441 (1)	−0.171 (1)	0.7839 (6)	6.8 (4)
O2B	−0.538 (1)	0.501 (1)	0.7039 (7)	6.3 (3)
O3A	0.328 (1)	0.292 (1)	0.6111 (6)	5.3 (3)
O3B	−0.063 (1)	0.555 (1)	0.5945 (8)	7.4 (4)
O4A	0.533 (2)	−0.195 (1)	0.5554 (7)	7.5 (4)
O4B	−0.295 (2)	0.362 (1)	0.4732 (6)	7.4 (4)
O5A	0.110 (1)	0.098 (1)	0.4823 (5)	5.0 (3)
C1A	0.108 (1)	−0.168 (1)	0.6777 (8)	3.8 (3)
C1B	−0.267 (1)	0.094 (1)	0.6530 (7)	3.3 (3)
C2A	0.350 (2)	−0.105 (2)	0.7377 (7)	3.9 (3)
C2B	−0.408 (2)	0.416 (2)	0.6764 (8)	4.2 (3)
C3A	0.278 (1)	0.192 (1)	0.6275 (8)	3.5 (3)
C3B	−0.105 (2)	0.450 (2)	0.6103 (9)	4.6 (4)
C4A	0.410 (2)	−0.122 (2)	0.5923 (8)	3.8 (3)
C4B	−0.253 (2)	0.329 (2)	0.5307 (8)	4.0 (3)
C5A	0.110 (2)	0.087 (2)	0.5457 (8)	4.3 (3)
C11	−0.004 (1)	0.298 (1)	0.7910 (6)	2.8 (3)
C12	−0.148 (2)	0.428 (2)	0.8161 (9)	4.8 (4)
C13	−0.124 (2)	0.528 (2)	0.8528 (9)	6.6 (4)
C14	0.036 (2)	0.503 (2)	0.8655 (9)	5.5 (4)
C15	0.180 (2)	0.379 (2)	0.8390 (8)	5.1 (4)
C16	0.160 (2)	0.270 (2)	0.8028 (8)	4.2 (3)
C21	−0.124 (1)	0.048 (1)	0.8316 (6)	2.5 (3)
C22	−0.284 (2)	0.045 (1)	0.8369 (7)	3.6 (3)
C23	−0.343 (2)	−0.040 (2)	0.9015 (8)	4.5 (4)
C24	−0.244 (2)	−0.122 (2)	0.9593 (8)	5.1 (4)
C25	−0.084 (2)	−0.118 (2)	0.9546 (7)	4.5 (4)
C26	−0.023 (2)	−0.036 (2)	0.8900 (7)	3.8 (3)
C1	0.410 (2)	0.556 (2)	0.938 (1)	6.7 (5)
C2	0.399 (2)	0.667 (2)	0.980 (1)	6.3 (5)
C3	0.493 (2)	0.607 (2)	1.0427 (9)	5.9 (4)

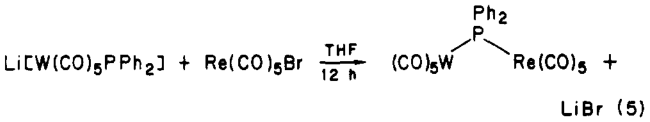
[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)$.

was solved by locating the W and Re atoms from a Patterson map. These atoms cannot be crystallographically distinguished but were assigned as indicated in Figure 1 on the basis of the ^{13}C NMR spectrum of 3 which clearly showed that five carbonyls were bound to W and only four to Re, as evidenced by the presence or absence of ^{183}W–^{13}C coupling. A difference map phased on the heavy atoms revealed the locations of all remaining non-hydrogen atoms. The hydrogen atoms of the phenyl rings were placed at their calculated positions (C–H = 0.97 Å) and assigned isotropic temperature factors of B = 5.0 Å^2. In the final cycle of least-squares refinement, 325 parameters were varied, including the overall scale factor, positional parameters for all non-hydrogen atoms, anisotropic thermal parameters for the metal, phosphorus, oxygen, and carbonyl carbon atoms, and isotropic thermal parameters for the phenyl carbon atoms. The structure converged to $R = 0.0386$ and $R_w = 0.0434$, defined as $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma(F_o)^2$. In the last cycle of refinement the maximum shift per error was 0.01. A final difference map showed the largest peak to be less than 0.30 times the height of a carbon atom and located 1 Å away from Re. The final error of an observation of unit weight was 3.32. Final positional and thermal parameters are listed in Table II, relevant bond distances and angles are given in Table III, and tables in the supplementary material give the derived positions of the hydrogen atoms, anisotropic temperature factors, and the structure factors.

Results

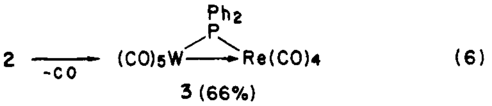
Syntheses. The new WRe complex 2 forms from the sequence of reactions 4 and 5. In this "bridge-assisted"

$$W(CO)_5PPh_2H + BuLi \rightarrow Li[W(CO)_5PPh_2] + BuH \quad (4)$$



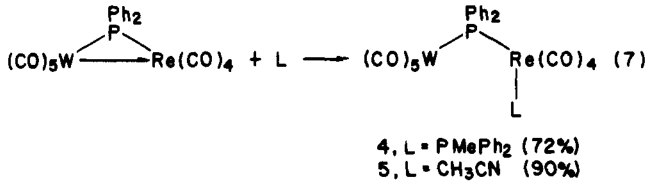
(5)

synthetic reaction,[1b] the nucleophilic phosphido ligand of $[W(CO)_5PPh_2]^-$ displaces the bromide from Re and brings the metals together in the binuclear product. Infrared and ^{31}P NMR spectroscopic data indicate reaction 5 to be nearly quantitative. However, complex 2 readily loses CO, and upon workup only the metal–metal bonded complex 3 can be isolated (eq 6). Surprisingly, this reaction cannot be easily reversed since no detectable reaction occurred when 3 was stirred under 100 psig of CO pressure for 12 h.



(6)

Complex 3 has a weak donor–acceptor metal–metal bond that can be readily displaced by better donor ligands. For example, addition of $PMePh_2$ and CH_3CN to solutions of 3 gives the addition products 4 and 5 in good yields (eq 7). Complexes 3 to 5 are all air-stable compounds, both in solution and in the solid state.



(7)

Spectroscopic Characterization. Spectroscopic data for all the new complexes reported herein are given in the Experimental Section. The instability of complex 2 has precluded its complete characterization although its clean loss of CO to give fully characterized 3 (eq 6) implies that the formulation given is correct. Its upfield μ-PPh_2 ^{31}P NMR resonance at δ −56.8 is consistent with the absence of a metal–metal bond, as required by the 18-electron rule if each metal has five CO's. Literature data indicate that μ-PPh_2 ligands which bridge two metals joined by a metal–metal bond appear downfield (δ 300–δ 50) whereas upfield (δ 50 → δ −300) resonances are observed for compounds in which this ligand bridges two metals not joined by a metal–metal bond.[11]

An ORTEP drawing of complex 3 is shown in Figure 1, and its spectral data are consistent with the determined structure. Since W and Re cannot be crystallographically distinguished, the metal assignments of Figure 1 were deduced from the ^{13}C NMR spectrum of 3 which showed that the carbonyl resonances with ^{183}W satellites had a relative intensity of 5 whereas the resonances without ^{183}W satellites had a relative intensity of 4. Thus, the metal with five CO's attached must be W. The downfield position of the μ-PPh_2 resonance at δ 110.4 is consistent with the presence of a W–Re bond as found (W–Re 3.111 (1) Å) in the structure determination.

Complexes 4 and 5 both show upfield ^{31}P NMR resonances due to the bridging μ-PPh_2 groups, consistent with their synthesis in which the added donor ligand has displaced the W–Re bond. Bonding of the $PMePh_2$ ligand

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[11] (a) Petersen, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, *19*, 186. (b) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 1963. (c) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *204*, C27. (d) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

Table III. Selected Bond Distances (Å) and Angles (deg) in $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4$, 3

Bond Distances

W-Re	3.111 (1)	W-C5A	2.106 (9)
Re-P	2.407 (2)	C1B-O1B	1.145 (8)
Re-C1B	1.982 (8)	C2B-O2B	1.139 (9)
Re-C2B	1.929 (9)	C3B-O3B	1.132 (9)
Re-C3B	2.004 (9)	C4B-O4B	1.117 (9)
Re-C4B	1.983 (8)	C1A-O1A	1.143 (9)
Re-C5A	2.772 (9)	C2A-O2A	1.141 (9)
W-P	2.499 (2)	C3A-O3A	1.138 (8)
W-C1A	2.041 (8)	C4A-O4A	1.146 (9)
W-C2A	2.016 (7)	C5A-O5A	1.142 (9)
W-C3A	2.011 (7)		
W-C4A	1.980 (7)		

Bond Angles

W-P-Re	78.68 (5)	C2B-Re-W	150.1 (3)
W-Re-P	51.97 (4)	C3B-Re-W	90.6 (2)
P-W-Re	49.34 (4)	C4B-Re-W	116.0 (2)
P-W-C1A	90.2 (2)	Re-C1B-O1B	177.3 (7)
P-W-C2A	88.0 (2)	Re-C2B-O2B	177.6 (8)
P-W-C3A	89.4 (2)	Re-C3B-O3B	177.6 (9)
P-W-C4A	170.7 (2)	Re-C4B-O4B	178.5 (8)
P-W-C5A	109.9 (2)	C2A-W-C5A	162.0 (3)
C1A-W-C2A	90.5 (3)	C3A-W-C4A	89.6 (3)
C1A-W-C3A	178.1 (3)	C3A-W-C5A	88.6 (3)
C1A-W-C4A	91.3 (3)	C4A-W-C5A	79.3 (3)
C1A-W-C5A	90.0 (3)	W-C1A-O1A	179.5 (5)
C2A-W-C3A	91.3 (3)	W-C2A-O2A	178.0 (7)
C2A-W-C4A	82.8 (3)	W-C3A-O3A	177.6 (7)
C1B-Re-C2B	91.0 (3)	W-C4A-O4A	177.8 (7)
C1B-Re-C3B	177.2 (2)	W-C5A-O5A	160.5 (8)
C1B-Re-C4B	87.1 (3)	P-Re-C1B	93.5 (2)
C2B-Re-C3B	88.7 (3)	P-Re-C2B	98.1 (3)
C2B-Re-C4B	94.0 (3)	P-Re-C3B	89.2 (3)
C3B-Re-C4B	90.2 (4)	P-Re-C4B	167.9 (2)
C1B-Re-W	91.1 (2)		

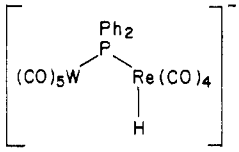
to Re rather than W is indicated by the absence of ^{183}W satellites on the ^{31}P NMR resonance of this ligand. Although we cannot be sure that the CH_3CN ligand in **5** is likewise bound to Re, the similarity of the IR and ^{31}P NMR data for the two compounds argue for similar structures. The ν_{CN} stretch of the coordinated CH_3CN ligand was too weak to observe, but the ^1H NMR spectrum of **5** showed a broad singlet of relative intensity 3 at δ 2.86 that is attributed to this ligand. Complex **5** can be isolated in pure form and does not readily lose CH_3CN upon solvent evaporation nor upon dissolution in a weakly coordinating solvent such as THF.

Crystal and Molecular Structure of $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4$, 3. An ORTEP drawing of complex **3** is shown in Figure 1. The W and Re atoms are bridged by the μ-PPh_2 ligand with the W further coordinated by five CO's and the Re by four. Carbonyl C5A-O5A on W is slightly bent in the direction of Re with a W-C5A-O5A angle of 160.5 (8)°. Although this could be viewed as indicative of a semibridging CO between W and Re, the long Re-C5A distance of 2.772 (9) Å suggests that this is probably not the case. The unusual bending is likely due to crystal packing with perhaps a very weak interaction with Re.

The W-Re distance of 3.111 (1) Å falls within the range 2.950 (1)-3.155 (1) Å associated with the W-Re single bond in the other crystallographically characterized compounds of these metals.[12] We prefer to formulate the metal-metal bonding in **3** as a donor-acceptor bond from a W(0) center to Re(I), as indicated in eq 6, similar to descriptions given earlier for $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)$,[5] $FeCo(\mu\text{-}AsMe_2)_2(CO)_7$,[3n] $(CO)_4Mo(\mu\text{-}SMe)_2Ti(C_5H_5)_2$,[3o] and related molecules. If we neglect the W-Re vector for the moment, Figure 1 shows that the tungsten center has an octahedral arrangement of six ligands, the μ-PPh_2 and five CO's, with the rhenium center having a square-pyramidal arrangement of four CO's and the μ-PPh_2 ligand. The W atom can be viewed as occupying the sixth coordination site of Re by electron pair donation from a filled t_{2g} orbital on tungsten to this empty coordination position, much as a PR_3 ligand would donate an electron pair to such a metal. Consistent with this view is the observation that the W-Re vector bisects an edge of the tungsten octahedron, precisely where one of the filled t_{2g} orbitals lies. Also consistent with the donor-acceptor bond between the two metals is the easy displacement of the W atom from Re by better electron donor ligands such as CH_3CN and $PMePh_2$.

An analysis of the IR spectrum of **2** should help resolve the question of metal oxidation states in this complex since ν_{CO} stretching frequencies are sensitive indicators of electron density at the metal centers. Although an unambiguous assignment of the IR bands in **2** is not possible, due to the complexity of the spectrum, we suggest that the 2101 (w), 2004 (vs), 1996 (sh), and 1963 (m) cm^{-1} bands correspond to the rhenium carbonyls since these compare favorably to the 2100 (s), 2015 (s), 1998 (vs), and 1940 (s) cm^{-1} bands reported for the Re(I) complex $ReBr(CO)_4(PPh_3)$.[13] The remaining bands of **2** at 2062 (s), 1983 (s), and 1925 (w, br) cm^{-1} are assigned to the tungsten carbonyls and compare in position to the 2074 (w), 2024 (vw), 1950 (vs), and 1912 (w, br) cm^{-1} bands of the W(0) complex $W(CO)_5(PPh_2H)$. Thus, although not conclusive, the IR spectrum of **2** is consistent with the W(0)-Re(I) formulation.

Generation of Formyl Complexes and Their Derivatives from 3 and 4. Reaction of **3** with $Li[BEt_3H]$ at -78 °C yields two unstable formyl complexes as evidenced by the appearance of two ^1H NMR resonances in the -78 °C reaction mixture at δ 15.73 and 13.60. The relative intensities of these vary from experiment to experiment but generally fall within the range 9:1 to 2:5. These formyl species are unstable and decompose at temperatures >-20 °C to form the hydride complex **6**. In one



6

reaction of $Li[BEt_3H]$ with ^{13}CO-enriched **3** only the δ 13.60 formyl resonance was observed. The ^{13}C NMR spectrum of this sample showed a single formyl signal at δ 284.7 without ^{183}W satellites, indicating that the formyl ligand is bound to Re. The ^{31}P NMR spectrum of this sample showed a downfield resonance at δ 115.7, implying the presence of a W-Re bond in this formyl complex.[11] Thus, although the instability of the two formyl complexes that derive from **3** has precluded their definitive characterization, the spectral data for the complex with the δ 13.60 formyl resonance are consistent with the structure drawn below (**7a**). No data was obtained that would reveal the structure of the δ 15.73 formyl complex, but a rea-

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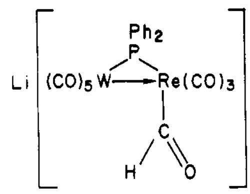
(12) (a) Kreissl, F. R.; Friedrich, P.; Lindner, T. L., Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 314. (b) Jeffrey, J. C.; Orpen, A. G.; Robinson, W. T.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 396.

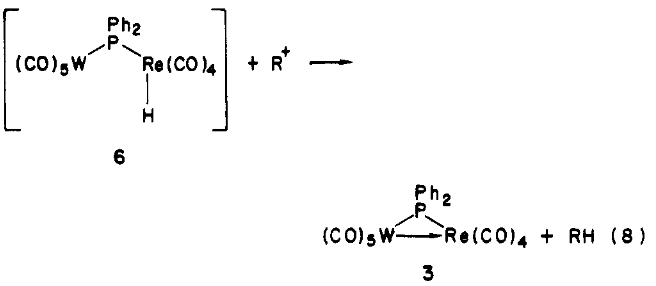
(13) Jolly, P. W.; Stone, F. G. A. *J. Chem. Soc.* **1965**, 5259.

sonable possibility would have the formyl ligand bound to W.

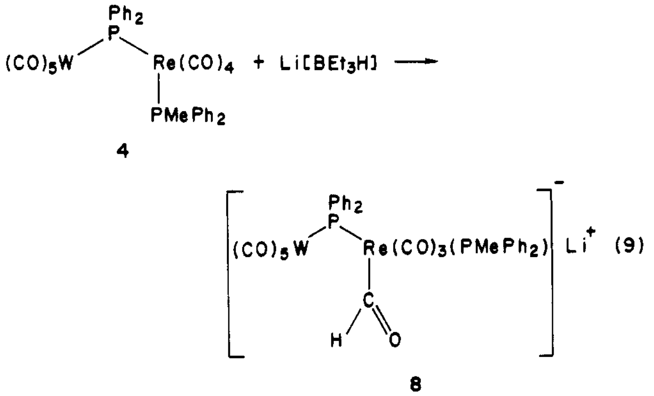


7a

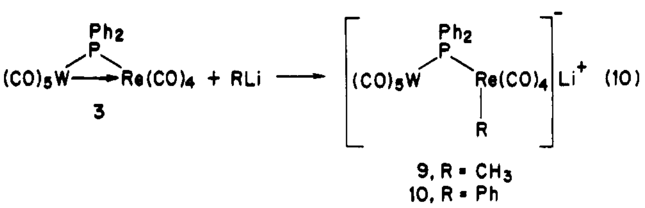
The hydride complex **6** was isolated as a yellow microcrystalline solid. It shows an upfield μ-PPh$_2$ ^{31}P NMR resonance at δ −73.6, implying the absence of a W–Re bond[11] and a hydride ^{1}H NMR resonance at δ −3.93 (d) without ^{183}W satellites. The latter indicates the hydride is bound to Re and not W, consistent with the structure drawn above. We attempted to derivatize **6** by reaction with a series of electrophiles but were not successful. Treatment of **6** with HBF$_4$, [Me$_3$O]BF$_4$, CH$_3$OTf, CH$_3$C(O)Cl, and CH$_3$I gave regeneration of **3** in near quantitative yield in each case (eq 8).



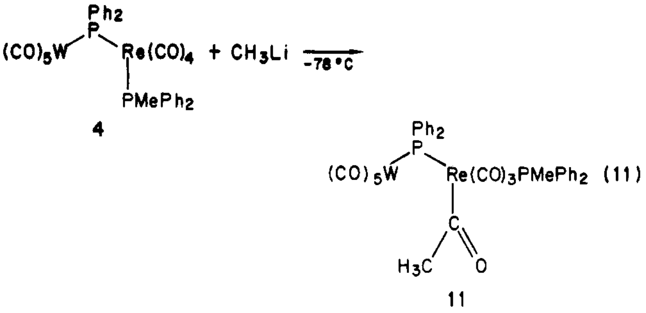
As indicated above, the main route of decomposition of the formyl complexes formed from **3** is deinsertion in which the hydride displaces the weak W–Re bond. We reasoned that the lack of a metal–metal bond in **4** should block this decay path and lead to more stable formyl derivatives. This is indeed the case. When Li[BEt$_3$H] was added to a THF solution of **4** at −78 °C, the relatively stable formyl complex **9** was formed (eq 9). This complex persists in room-temperature solutions for several hours and can be isolated as a pure solid. At 50 °C, complex **8** decomposes with a half-life of 30 min to give **6** and free PMePh$_2$. The ^{31}P NMR spectrum of **8** shows separate resonances for the PMePh$_2$ and μ-PPh$_2$ ligands with the upfield (δ −58.1 (d)) position of the latter implying the absence of a W–Re bond, consistent with the structure drawn in eq 9. Complex **8** shows the expected ν_{CO} stretch at 1548 cm^{-1} and a formyl ^{1}H NMR resonance at δ 14.3 (dd). Attempted derivatization of **8** with HBF$_4$ or CH$_3$OTf led only to regeneration of **4**.



Reaction of Complexes 3 and 4 with RLi Reagents. When complex **3** was treated with CH$_3$Li or PhLi in THF at room temperature, the corresponding methyl and phenyl complexes were produced (eq 10). Neither **9** nor **10** were sufficiently stable to isolate, but they were spectroscopically characterized. The ^{1}H NMR resonance of the methyl group of **9** appears at δ −0.74 (d) without ^{183}W satellites, implying its presence on Re, and the upfield μ-PPh$_2$ ^{31}P NMR resonance at δ −63.3 indicates the absence of a metal–metal bond. Complex **10** shows a similar ^{31}P{^{1}H} NMR spectrum with a μ-PPh$_2$ resonance at δ −61.4. Complexes **9** and **10** apparently arise through nucleophilic attack of RLi at the Re center, although they could form via rapid deinsertion of unstable intermediate acyl complexes, concomitant with metal–metal bond cleavage. Attempted derivatization of **9** and **10** by reaction with HBF$_4$ and [Me$_3$O]BF$_4$ led only to regeneration of the starting complex **3**.

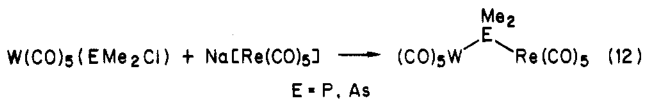


Reaction of complex **4** with CH$_3$Li at −78 °C initially gives an acetyl complex, **11** (eq 11) as evidenced by the appearance of an IR band at 1580 cm^{-1}. Examination of this reaction by variable-temperature ^{31}P NMR showed that **11** was the only product formed at −39 °C. However, upon warmup to 0 °C deinsertion occurs to give primarily the anionic methyl complex **9** and free PMePh$_2$. Complex **11** was spectroscopically characterized. It shows an upfield ^{31}P{^{1}H} NMR resonance at δ −51.0 (d) due to the μ-PPh$_2$ ligand and a separate resonance at δ −3.6 (d) attributed to the Re-bound PMePh$_2$ ligand. Its ^{1}H NMR spectrum shows a resonance at δ 2.1 without ^{183}W satellites, assigned to the Re-bound acetyl ligand.



Discussion

The synthesis of **2** and **3** provide further evidence for the broad applicability of the "bridge-assisted synthetic method"[1b] for the preparation of heteronuclear transition-metal complexes. Vahrenkamp and co-workers[14] have carried out a similar bridge-assisted synthesis (eq 12) in which the products were formulated as WRe(μ-EMe$_2$)(CO)$_{10}$ (E = P, As), analogous to **2**, without a metal–metal bond. Their complexes were characterized by IR, ^{1}H NMR, and C, H analytical data. However, the IR spectra of their products (e.g., WRe(μ-PMe$_2$)(CO)$_{10}$, ν_{CO} 2100 (w),



$$\mathrm{W(CO)_5(EMe_2Cl) + Na[Re(CO)_5] \longrightarrow (CO)_5W\overset{EMe_2}{\frown}Re(CO)_5 \quad (12)}$$

E = P, As

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[14] Ehrl, W.; Vahrenkamp, H. *Chem. Ber.* 1971, *104*, 3261.

2060 (m), 1995 (vs), 1978 (m), 1962 (vs), 1949 (s)) are similar to the spectrum of **3** and as these authors noted, C, H analyses will not unambiguously distinguish $(CO)_9$ and $(CO)_{10}$ formulations. We suspect Vahrenkamp's compounds are $(CO)_9$ derivatives analogous to **3**, a conclusion which could be verified by the ^{31}P NMR chemical shift position of the μ-PMe_2 ligand in $WRe(\mu\text{-}PMe_2)(CO)_x$, but this data was not reported.

The donor–acceptor W–Re bond in **3** is relatively weak as it is readily cleaved by better donor ligands such as CH_3CN and $PMePh_2$ to form **4** and **5**. Both of these ligands appear to bond irreversibly, thus prohibiting the metal–metal bond from reforming. This easy generation of an open coordination site on Re from W–Re bond cleavage in **3** also provides a low-energy decomposition pathway for the formyl derivatives of **3**. The latter are not stable above −20 °C as they readily undergo deinsertion concomitant with W–Re bond cleavage to form the hydride complex **6**. Also, reaction of **3** with RLi reagents led directly to the methyl and phenyl complexes **9** and **10**. Such easy cleavage of donor–acceptor bonds to open coordination sites will likely limit the formyl and acyl derivative chemistry of such compounds. To circumvent this problem, we first displaced the W–Re bond by adding $PMePh_2$ to **3** to form complex **4**. This latter complex then gave more stable formyl and acyl derivatives.

The relative thermal stabilities of the formyl complex **8** and the isoelectronic acetyl complex **11** are somewhat surprising. Recall that **11** undergoes deinsertion at lower temperatures than does **8**. Previous studies[15,16] have shown that deinsertion of a formyl ligand is kinetically and thermodynamically favored over deinsertion of an acetyl ligand. The decomposition of **8** and **11** presumably occurs via initial phosphine loss to open a coordination site. Apparently, loss of phosphine from the acetyl complex **11** is more favored than loss of $PMePh_2$ from the formyl complex **8**, and hence the former undergoes more rapid deinsertion.

An interesting aspect of the chemistry of these W–Re complexes is the domination of the reactivity by the rhenium center. In the case of nucleophilic attack at metal-bound carbonyls by RLi and $Li[BHEt_3]$ reagents, this is probably due to the higher oxidation state of rhenium in the complex. Recall that in the donor–acceptor formulation, the oxidation states were W(0) and Re(I). This would render the carbonyls bound to rhenium more electrophilic and more susceptible to nucleophilic attack. Even when a basic phosphine ligand is bound to Re as in **4**, nucleophilic addition to the rhenium bound carbonyls is still preferred, suggesting that the increased electron density at the rhenium center due to phosphine binding is not sufficient to counter the oxidation state difference.

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Registry No. **2**, 92763-14-9; **3**, 92763-15-0; **4**, 92763-16-1; **5**, 92763-17-2; **6**, 92763-19-4; **7a**, 92763-20-7; **8**, 92786-71-5; **9**, 92763-21-8; **10**, 92763-22-9; **11**, 92763-23-0; $Li[W(CO)_5PPh_2]$, 92763-24-1; $Re(CO)_5Br$, 14220-21-4; $Li[BEt_3H]$, 22560-16-3; Re, 7440-15-5; W, 7440-33-7.

Supplementary Material Available: Tables of anisotropic temperature factors, calculated hydrogen atom positions, and structure factors (22 pages). Ordering information is given on any current masthead page.

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A General Route to Tri-*tert*-butoxytungsten Alkylidyne Complexes. Scission of Acetylenes by Ditungsten Hexa-*tert*-butoxide[†1]

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Alkylidyne complexes of the type $W(CX)(OCMe_3)_3$ can be prepared by reacting $W_2(OCMe_3)_6$ with $XC{\equiv}CX$ or $RC{\equiv}CX$ (R = Me or Et; X = Me, Et, Pr, CMe_3, Ph, $CH{=}CH_2$, CH_2NR_2, CH_2OMe, CH_2OSiMe_3, $CH(OEt)_2$, CO_2Me, CH_2CO_2Me, C(O)Me, $SCMe_3$, or H). Several others have been prepared by reacting $W(CMe)(OCMe_3)_3$ with $XC{\equiv}CX$ or $RC{\equiv}CX$ (X = $SiMe_3$, NEt_2, CH_2CN, $C{\equiv}CEt$, or CN). In one case a diacetylene ($EtC{\equiv}CC{\equiv}CEt$) reacts with $W_2(OCMe_3)_6$ to give $[(Me_3CO)_3W{\equiv}C]_2$. Approximately half of the compounds can be isolated only as adducts, $W(CX)(OCMe_3)_3(B)$, where B = pyridine or quinuclidine. By analogy with WC_3 tungstenacyclobutadiene and "tungstenatetrahedrane" (η^3-cyclopropenyl) complexes it is proposed that alkylidyne complexes can form only from a molecule having a planar 1,3-W_2C_2 core and that added nitrogenous base can play a direct role in the scission reaction. Derivatized alkylidyne complexes that contain electron donors react most rapidly with 3-heptyne; those that contain electron acceptors directly attached to the α-carbon do not react with 3-heptyne to any significant extent at 25 °C. We conclude that the W≡C bond behaves as if it were polarized $W(+){\equiv}C(-)$.

Introduction

$W(CCMe_3)(OCMe_3)_3$ is a remarkably effective catalyst for the metathesis of dialkylacetylenes (eq 1).[2] Its synthesis consists of first preparing $W(CCMe_3)(CH_2CMe_3)_3$ from $W(OMe)_3Cl_3$ and 6 equiv of Me_3CCH_2MgCl, treating $W(CCMe_3)(CH_2CMe_3)_3$ with 3 equiv of HCl in the presence of dimethoxyethane to give $W(CCMe_3)$(1,2-dimethoxyethane)Cl_3, and reacting $W(CCMe_3)(dme)Cl_3$ with 3 equiv

$$RC{\equiv}CR + R'C{\equiv}CR' \rightleftarrows 2RC{\equiv}CR' \qquad (1)$$

[†] This paper is dedicated to the memory of Earl Muetterties.

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