Metalation of Bis(cyclopentadienyl)metal Hydrides by *n*-Butyllithium in the Presence of Pentamethyldiethylenetriamine. Synthesis of Bis(cyclopentadienyl)rhenium Alkyls and the Mixed Metal Complexes: $(\eta^5\text{-}C_5H_5)_2M(\mu\text{-}CO)_2Re(CO)(\eta^5\text{-}C_5H_5)$ (M = Mo, W)[1a-c]

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Abstract: *n*-Butyllithium in the presence of pentamethyldiethylenetriamine (PMDT) in a 1:1 ratio has been found to metalate the metal (M = Re and Mo) atom of bis(cyclopentadienyl) transition metal hydrides in hexane. The complex $Cp_2ReLi\cdot PMDT$ (I) is pale yellow, air sensitive, and soluble in aromatic solvents. Compound I has been used to synthesize the previously unreported bis(cyclopentadienyl)rhenium alkyls of methyl, ethyl, *n*-propyl, and allyl. Triphenylcarbenium tetrafluoroborate has been reacted with selected $Cp_2Re\text{-}R$ compounds giving cationic rhenium species. Compound I also reacts with $CpM(CO)_3Cl$ (M = Mo, W) with transfer of a cyclopentadienyl ring from the rhenium atom to the molybdenum or tungsten atom resulting in $Cp_2M(\mu\text{-}CO)_2Re(CO)Cp$. The molybdenum-rhenium complex has been characterized by single-crystal X-ray diffraction and has been shown to contain a metal-metal single bond that is asymmetrically bridged by two "semibridging" carbonyls. These carbonyl groups in the tungsten derivative exhibit an extremely low stretching frequency (1650 cm^{-1}, Nujol; 1690 cm^{-1}, THF) for a dibridging carbonyl. The structural results for the molybdenum-rhenium complex revealed a statistically elongated C-O (bridge) bond, thus implying substantial reduction of the carbon-oxygen bond order of the bridging carbonyl group by the metal fragments.

Introduction

Bis(cyclopentadienyl)rhenium hydride has received little attention in the literature since its original synthesis by Green and Wilkinson in 1958.[2] At that time, they reported its reaction with HCl to yield $[Cp_2ReH_2]Cl$ along with its reaction with carbon monoxide (200 atm/100 °C) to yield a cyclopentadienylcyclopentadienedicarbonylrhenium olefin complex, $Cp(\eta^2\text{-}C_5H_6)Re(CO)_2$. Reaction of Cp_2ReH with halogens leads to $[Cp_2ReX_2]^+$ (X = Cl, Br, I)[3] while dimethyl acetylenedicarboxylate and methyl propiolate insert into the rhenium-hydride bond.[4] It had been reported in 1965 that Cp_2ReH in ether reacts with 2.5-3.0 equiv of *n*-butyllithium to give a white compound.[5] This white compound was reacted with D_2O and $HgCl_2$ to give $(C_5H_4D)_2ReH$ and $(\eta^5\text{-}ClHgC_5H_4)_2ReH$, respectively. Those reaction products suggested that metalation occurred at the cyclopentadienyl rings forming the intermediate, $(C_5H_4Li)_2ReH$, whose insolubility in aromatic solvents precluded the recording of an NMR spectrum. Also Kaesz[6] reported in 1971 that the cyclopentadienyl ring of Cp_2ReH is attacked when reacted with $CH_3Mn(CO)_5$, producing $Cp(H)Re(\eta^5{:}\eta^1\text{-}C_5H_4)Mn(CO)_4$. The above reactions show that both the rhenium-hydride bond and the cyclopentadienyl ring are susceptible to attack under appropriate conditions.

In contrast to the Cp_2ReH case, treatment of Cp_2MH_2 (M = Mo, W) in toluene with either an equimolar quantity of or an excess of *n*-butyllithium in hexane at 60 °C produced a complex in which the lithium atom is bonded to a molybdenum or tungsten atom, the cyclopentadienyl ring being untouched.[7] An X-ray crystal structure of the Mo-Li complex was determined.[8] However, NMR data for those intermediates could not be recorded since they are insoluble in aliphatic and aromatic solvents and react with most other solvents.

Our research group has been interested in the metalation reactions of *n*-butyllithium in the presence of various tertiary polyamines.[9] These amines chelate the lithium atom and greatly modify the reactivity and properties of organolithium compounds. It has also been our experience that chelating organolithium complexes with tertiary polyamines greatly increases their solubility. This is especially true of the tridentate base PMDT (1,1,4,7,7-pentamethyldiethylenetriamine) when compared to TMED (*N,N,N′,N′*-tetramethylethylenediamine), which is most frequently employed as the chelating agent. Recently, the superiority of *n*-butyllithium·PMDT as a metalating agent for ferrocene has been demonstrated.[9a] The dilithiated ferrocene derivative contains lithium atoms in two types of environments. In light of the differences observed for the metalation reactions of Cp_2ReH and Cp_2MoH_2, as well as our interest in synthesizing soluble cyclopentadienyl lithio complexes, we decided to study the effect of the base PMDT upon the reaction of the bis(cyclopentadienyl)metal hydrides Cp_2ReH and Cp_2MoH_2 with *n*-butyllithium. These results and the versatility of the lithium reagents in preparing new complexes are now presented.

Experimental Section

Preparations. All manipulations were carried out under an inert atmosphere using either Schlenk-ware techniques or a Vacuum Atmospheres glovebox. Aromatic, hydrocarbon, and ether solvents were distilled from sodium-benzophenone ketyl under N_2. Chloroform was deoxygenated by N_2 purge. 1,1,4,7,7-Pentamethyldiethylenetriamine was purchased from Eastman Organic Chemicals and deoxygenated by N_2 purge. $MoCl_5$ was a gift from the Climax Molybdenum Co. $ReCl_5$ was purchased from Ventron Corp., Alfa Division.

Elemental analyses were performed by the microanalytical facilities at the University of Illinois, School of Chemical Sciences. NMR spectra were recorded either on Varian HA-100 or EM-390 spectrometers at 100 or 90 MHz, respectively. Chemical shifts are reported in τ (Me_4Si = 10.0). Infrared spectra were recorded on a Perkin-Elmer 467 spectrophotometer. Mass spectra were recorded at the University of Illinois Mass Spectrometry Center.[10] Electron impact mass spectra (10 eV) were recorded on a Varian-MAT CH-5 spectrometer, while the field desorption spectra were recorded on a Varian-MAT-731 spectrometer operating in the low-resolution mode. Relative intensities of mass spectral peaks are given in parentheses following peak data.

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1. Preparation of Bis(cyclopentadienyl)metal Hydrides. All of the bis(cyclopentadienyl)metal hydrides were prepared by the method of Green, Pratt, and Wilkinson.[2] Purity of products was checked by elemental analysis, NMR, and mass spectroscopy.

2. Preparation of Bis(cyclopentadienyl)(1,1,4,7,7-pentamethyldiethylenetriaminelithio)rhenium (I). The base 1,1,4,7,7-pentamethyldiethylenetriamine (PMDT), (0.06 mL, 0.35 mmol) was syringed into a solution of 0.10 g (0.32 mmol) of Cp_2ReH in 30 mL 0.34 mmol) was then added at room temperature. A pale yellow precipitate formed immediately. This was isolated by filtration, washed with hexane, and dried. The precipitate darkens immediately when exposed to *trace* amounts of oxygen. It is very soluble in benzene and toluene: yield 0.13 g (87%); NMR (C_6D_6) τ 5.82 (s, 10 H, C_5H_5), 8.02, 8.07 (s, s, 15 H, CH_3), 8.22 (s, 8 H, CH_2CH_2).

3. Preparation of Bis(cyclopentadienyl)hydrido(1,1,4,7,7-pentamethyldiethylenetriaminelithio)molybdenum (II). 1,1,4,7,7-Pentamethyldiethylenetriamine (0.08 mL, 0.47 mmol) was added to a solution of 0.10 g (0.44 mmol) of Cp_2MoH_2 in 30 mL of hexane. The solution was cooled to −78 °C and a slight excess of 2.4 M (0.19 mL, 0.46 mmol) *n*-butyllithium in hexane was added. The stirred mixture was allowed to warm slowly to room temperature. After filtration, the yellow-orange precipitate was washed with hexane and dried: NMR (C_6D_6) τ 5.87 (d, J = 1.1 Hz, 10 H, C_5H_5), 8.02, 8.04 (s, s, 15 H, CH_3), 8.21 (s, 8 H, CH_2CH_2), 18.32 (m, 1 H, Mo–H); IR 1671 cm^{-1} (m, br, Mo–H).

4. Preparation of Bis(cyclopentadienyl)rhenium Deuteride. Deuterium oxide (2 mL) was syringed into a suspension of 0.13 g (0.26 mmol) of I in 35 mL of hexane. The mixture was stirred for 30 min to give a yellow hexane layer and a colorless D_2O layer. After separation of the two layers in a pressure-equalizing dropping funnel, the solvent was removed from the hexane layer, leaving a yellow residue which on sublimation (80 °C) gave 0.07 g (80%) of yellow crystals: NMR (C_6D_6) τ 5.82 (s); mass spectrum *m/e* 319.1 (100) $^{187}M^+$, 317.1 (69.3) $^{185}M^+$, $^{187}M^+ - D$.

5. Preparation of Bis(cyclopentadienyl)molybdenum Hydridodeuteride. This compound was prepared in an analogous manner to the bis(cyclopentadienyl)rhenium deuteride using 0.15 g (0.37 mmol) of $Cp_2MoH(Li{\cdot}PMDT)$: yield 0.080 g (94%); NMR (C_6D_6) τ 5.66 (s, 10 H, C_5H_5), 18.86 (m, 1 H, Mo–H). Mass spectrum: *m/e* 233.0 (3.3) $^{100}M^+$; 230.9 (20.9) $^{100}M^+ - D$, $^{98}M^+$; 229.9 (49.4) $^{100}M^+ - HD$, $^{98}M^+ - H$, $^{97}M^+$; 228.9 (41.4) $^{98}M^+ - D$, $^{97}M^+ - H$. $^{96}M^+$; 227.9 (100.0) $^{98}M^+ - HD$, $^{97}M^+ - D$, $^{96}M^+ - H$.

6. Preparation of Bis(cyclopentadienyl)methylrhenium. Methyl chloride (1–2 mL) was condensed into a reaction vessel containing 0.13 g (0.26 mmol) of I suspended in 30 mL of hexane at −78 °C. The mixture was stirred for 1 h at −78 °C and 10 h at room temperature. An orange solution with a white precipitate resulted. Removal of the solvent left a brown residue, which on sublimation at 50–55 °C yielded 0.055 g (65%) of orange crystals. The product is extremely soluble in aliphatic and aromatic hydrocarbons. Anal. Calcd for $C_{11}H_{13}Re$: C, 39.88; H, 3.93. Found: C, 39.19; H, 3.77. NMR (C_6D_6): τ 6.04 (s, 10 H, C_5H_5), 9.27 (s, 3 H, CH_3). Mass spectrum: *m/e* 332.1 (100.0) $^{187}M^+$, 330.1 (91.5) $^{185}M^+$, 317.0 (87.3) $^{187}M^+ - CH_3$.

7. Preparation of Bis(cyclopentadienyl)ethylrhenium. A large excess of ethyl bromide (0.2 mL) was added to a suspension of 0.13 g (0.26 mmol) of I in 30 mL of hexane at 0 °C. An orange solution resulted immediately. The mixture was stirred for 12 h as it warmed to room temperature. The solvent was removed under vacuum, leaving an orange-brown residue which, when sublimed at 55 °C, gave 0.06 g of orange crystals. From the NMR spectrum, it was shown that the product consisted of >90% $Cp_2ReCH_2CH_3$ and the rest a Cp_2ReH impurity. An analytically pure sample can be obtained by column chromatography on deactivated alumina, but extensive decomposition results. Decomposition or no separation also results if silica gel, Florisil, or Teflon powder is used in place of alumina. Ethyl chloride can be used in place of ethyl bromide, but yields a higher percentage of Cp_2ReH in the product. Anal. Calcd for $C_{12}H_{15}Re$: C, 41.71; H, 4.35. Found: C, 42.35; H, 4.52. NMR (C_6D_6): τ 6.07 (s, 10 H, C_5H_5), 8.37 (m, 5 H, CH_2CH_3). Mass spectrum: *m/e* 346.1 (29.3) $^{187}M^+$, 344.1 (19.4) $^{185}M^+$, 318.1 (100.1) $^{187}M^+ - CH_2CH_2$, 317.1 (36.3) $^{187}M^+ - CH_2CH_3$, 316.1 (61.0) $^{185}M^+ - CH_2CH_2$, 315.1 (17.4) $^{185}M^+ - CH_2CH_3$.

8. Preparation of Bis(cyclopentadienyl)(*n*-propyl)rhenium. A large excess of *n*-propyl bromide (0.2 mL) was added to a suspension of 0.13 g (0.26 mmol) of I in 30 mL of hexane at 0 °C. An orange solution with a white precipitate gradually formed after a few hours. The mixture was stirred a total of 12 h as the reaction flask warmed to room temperature. The solvent was removed under vacuum leaving an orange-brown residue. Sublimation of this residue between 50 and 55 °C yielded 0.07 g of orange crystals. The NMR spectrum showed ~6% Cp_2ReH impurity. Purification by fractional crystallization from pentane resulted in the following analysis (column chromatography can also be used to obtain a pure sample but extensive decomposition results). Anal. Calcd for $C_{13}H_{17}Re$: C, 43.45; H, 4.74. Found: C, 42.90; H, 4.52. NMR (C_6D_6): τ 6.07 (s, 10 H, C_5H_5), 8.53 (m, 4 H, CH_2CH_2), 9.02 (m, 3 H, CH_3). Mass spectrum: *m/e* 360.0 (8.4) $^{187}M^+$, 358.0 (5.7) $^{185}M^+$, 317.8 (100) $^{187}M^+ - CH_2CHCH_3$, 316.8 (28.1) $^{187}M^+ - CH_2CH_2CH_3$, 315.8 (61.9) $^{185}M^+ - CH_2CHCH_3$, 314.8 (13.5) $^{185}M^+ - CH_2CH_2CH_3$.

9. Preparation of Allylbis(cyclopentadienyl)rhenium. A similar procedure as for the synthesis of $Cp_2ReCH_2CH_2CH_3$ was followed employing allyl bromide, yielding upon sublimation 0.040 g (43%) of the product. Anal. Calcd for $C_{13}H_{15}Re$: C, 43.70, H, 4.20. Found: C, 43.43; H, 4.32. NMR ($Cp_2ReCH(A)_2CH(D){=}CH(B)H(C)$) ($C_6D_6$): τ 3.93 (m, J_{BD} = 9.8, J_{CD} = 16.6 Hz, 1 H(D), 5.52, 5.68, 5.79 (m, J_{BC} = 2.6 Hz. 2 H(**B**.C)). 6.14 (s, 10 H, C_5H_5), 7.85 (dq, J_{AD} = 8.4 Hz, 2 H, $CH(A)_2$). Coupling constants were obtained by decoupling the methylene protons. Mass spectrum: *m/e* 358.0 (36.2) $^{187}M^+$, 356 (19.9) $^{185}M^+$, 317.0 (100.0) $^{187}M^+ - CH_2CHCH_2$, 315.0 (64.0) $^{185}M^+ - CH_2CHCH_2$. IR(XC=C, cm^{-1}): 1608 s (Nujol).

10. Preparation of Bis(cyclopentadienyl)ethylenerhenium Tetrafluoroborate. To a solution of $Cp_2ReCH_2CH_3$ (0.16 g, 0.46 mmol) in 20 mL of chloroform was added a solution of $(C_6H_5)_3C^+BF_4^-$ (0.15 g, 0.46 mmol) in 35 mL of chloroform. Upon mixing of the solutions at room temperature via syringe, the solution turned a maroon color and within 1 h a maroon precipitate appeared. The solvent was removed under vacuum, leaving white and maroon solids. The mixture was extracted with diethyl ether to remove the organic products. The resulting purple solid was dissolved in acetone. Upon addition of diethyl ether a precipitate formed and the solution was filtered. Upon standing, deep maroon crystals formed from the filtrate, yield before recrystallization 41%. Anal. Calcd for $C_{12}H_{14}BF_4Re$: C, 33.42; H, 3.27. Found: C, 33.13; H, 2.93. Field desorption mass spectrum: *m/e* 343 $^{185}M^+$, 345 $^{187}M^+$. NMR ($(CD_3)_2CO$): τ 4.57 (s, 10 H, C_5H_5), 7.63 (s, 4 H, CH_2CH_2).

11. Preparation of Bis(cyclopentadienyl)molybdenumdi(μ-carbonyl)cyclopentadienylcarbonylrhenium (III). A solution of 0.13 g (0.26 mmol) of I in 8–10 mL of toluene was slowly added to a suspension of 0.08 g (0.29 mmol) of $CpMo(CO)_3Cl$[11] in 70 mL of hexane. The mixture turned orange-brown and was stirred for 12 h. Filtration and drying under vacuum gave an orange-brown powder, which was insoluble in benzene. The precipitate was dissolved in THF and filtered to give a dark red solution. Crystallization by slow evaporation of THF gave 0.11 g (75%) of dark red needles. Anal. Calcd for $C_{18}H_{15}O_3ReMo$: C, 38.50; H, 2.67; Mo, 17.11. Found: C, 38.40; H, 2.83; Mo, 17.02. NMR ($(CD_3)_2CO$): τ 4.70 (s), 5.27 (s), 5.32 (s), IR (γ CO, cm^{-1}): 1876 vs, 1789 m, 1724 s, 1678 vs (Nujol); 1899 vs, 1718 s (THF). Field desorption mass spectrum: *m/e* 556–567.

12. Preparation of Bis(cyclopentadienyl)tungstendi(μ-carbonyl)cyclopentadienylcarbonylrhenium. To a suspension of 0.11 g (0.33 mmol) of $CpW(CO)_3Cl$ in 70 mL of hexane was added a solution of 0.13 g (0.26 mmol) of I in 8–10 mL of toluene. After 10 min, a pinkish-brown precipitate was noticeable. The mixture was stirred for 12 h and filtered to give a pinkish-brown precipitate. The precipitate was extracted with THF (40 mL) and filtered. Removal of the THF under vacuum gave an orange-brown powder. Yield was 0.09 g (53%). Anal. Calcd for $C_{18}H_{15}O_3ReW$: C, 33.28; H, 2.31; W, 28.35. Found: C, 32.80; H, 2.50; W, 28.04. IR (γ CO, cm^{-1}): 1863 vs, 1773 vs, 1684 sh, 1650 vs (Nujol); 1892 s, 1690 s (THF). Field desorption mass spectrum: *m/e* 646–654.

X-ray Diffraction Study of $CpRe(CO)(\mu\text{-}CO)_2MoCp_2$ (III). A single crystal of III with dimensions 0.04 × 0.12 × 0.45 mm was selected and mounted along its long dimension in a thin-walled glass capillary under argon. Preliminary film data indicated the space group $P2_1/c$. The lattice parameters were determined by a least-squares treatment of 26 automatically centered independent reflections to be a = 7.975 (3) Å, b = 13.824 (7) Å, c = 14.728 (8) Å, β = 107.36 (3)°. Data were collected on a Picker FACS 1 automatic diffractometer using Mo Kα radiation with a graphite monochromator and a θ-2θ scan technique with a scan rate of 1°/min and 10-s background counts at each end of the scan. A scan width of 2.0° and a takeoff angle of 1.0° were

Table I. Positional and Thermal Parameters of Nonhydrogen Atoms of $Cp_2Mo(\mu\text{-}CO)_2Re(CO)Cp$

atom	x^a	y	z	$U_{11}{}^b$	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re	0.4143(1)	0.2485(1)	0.3267(0)	0.0338(2)	0.0373(3)	0.0313(2)	0.0031(3)	0.0071(2)	−0.0039(4)
Mo	0.1305(1)	0.1029(1)	0.2658(1)	0.0386(6)	0.0314(6)	0.0273(6)	0.0031(6)	0.0021(5)	−0.0043(6)
C1	0.1678(12)	0.2523(11)	0.3323(7)	0.036(6)	0.032(6)	0.022(6)	0.008(8)	0.006(5)	−0.003(9)
O1	0.0664(10)	0.2976(6)	0.3579(6)	0.048(6)	0.046(6)	0.067(6)	−0.001(5)	0.023(5)	0.012(5)
C2	0.4172(17)	0.1248(9)	0.2594(9)	0.059(10)	0.050(9)	0.037(8)	−0.001(7)	0.001(7)	0.018(8)
O2	0.4989(12)	0.0704(6)	0.2250(7)	0.061(6)	0.061(7)	0.114(9)	−0.007(7)	0.038(7)	0.014(6)
C3	0.3545(16)	0.3203(9)	0.2063(9)	0.037(8)	0.040(8)	0.075(10)	−0.043(8)	0.019(8)	−0.002(7)
O3	0.3258(14)	0.3636(7)	0.1374(6)	0.126(9)	0.0949(9)	0.044(6)	0.046(6)	0.022(7)	0.006(8)
C4	0.0754(33)	−0.0361(12)	0.3217(10)	0.190(23)	0.034(10)	0.021(9)	0.003(7)	0.008(12)	−0.072(13)
C5	0.0196(25)	0.0291(15)	0.3715(14)	0.089(14)	0.087(16)	0.076(15)	0.023(11)	0.039(12)	−0.012(13)
C6	0.1544(39)	0.0699(16)	0.4237(15)	0.0291(39)	0.055(13)	0.023(10)	0.022(9)	−0.017(20)	−0.057(22)
C7	0.3050(33)	0.0321(21)	0.4124(20)	0.159(26)	0.140(31)	0.103(22)	0.070(20)	−0.651(21)	−0.111(23)
C8	0.2493(29)	−0.0297(16)	0.3482(16)	0.087(14)	0.099(18)	0.134(21)	0.094(15)	0.071(15)	0.0639(13)
C9	−0.1124(24)	0.0640(13)	0.1472(12)	0.085(14)	0.066(14)	0.061(13)	0.023(11)	−0.008(11)	−0.033(12)
C10	−0.1284(20)	0.1581(13)	0.1642(10)	0.047(10)	0.079(13)	0.058(10)	−0.014(10)	−0.013(9)	0.0371(10)
C11	−0.0045(18)	0.2048(9)	0.1379(9)	0.048(10)	0.038(8)	0.042(9)	0.003(7)	0.005(7)	−0.001(7)
C12	0.0909(20)	0.142(15)	0.1067(9)	0.065(11)	0.137(17)	0.019(8)	0.001(10)	−0.004(8)	−0.033(13)
C13	0.0233(25)	0.0474(11)	0.1132(10)	0.120(16)	0.044(10)	0.025(9)	−0.014(8)	−0.019 (10)	0.014(12)
C14	0.5306(19)	0.2572(19)	0.4903(8)	0.055(10)	0.146(17)	0.021(7)	−0.007(14)	−0.009(7)	−0.044(16)
C15	0.6527(20)	0.2094(11)	0.4595(12)	0.043(10)	0.058(10)	0.084(14)	−0.024(,10)	−0.032(10)	0.004(9)
C16	0.7089(17)	0.2783(15)	0.4011(10)	0.046(9)	0.123(18)	0.043(9)	−0.002(11)	0.021(7)	−0.018(11)
C17	0.6055(25)	0.3621(14)	0.4078(12)	0.097(16)	0.093(15)	0.064(13)	0.031(12)	−0.031(12)	−0.081(13)
C18	0.4989(22)	0.3511(14)	0.4595(12)	0.067(12)	0.074(14)	0.063(12)	−0.014(10)	−0.003(10)	−0.005(12)

[a] Estimated standard deviations in the least significant figures are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table II. Selected Bond Distances (Å) in $Cp_2Mo(\mu\text{-}CO)_2Re(CO)Cp$

atoms	distance	atoms	distance
Mo-Re	2.959(1)	C1-O1	1.171(15)
Re-C1	1.993(10)	C2-O2	1.201(18)
Re-C2	1.981(13)	C3-O3	1.141(16)
Re-C3	1.962(13)	C14-C15	1.361(26)
Re-C14	2.309(12)	C15-C16	1.442(26)
Re-C15	2.344(14)	C16-C17	1.442(28)
Re-C16	2.311(13)	C17-C18	1.311(29)
Re-C17	2.263(18)	C18-C14	1.374(32)
Re-C18	2.345(17)	C4-C5	1.321(30)
Mo-C1	2.267(14)	C5-C6	1.252(30)
Mo-C2	2.337(14)	C6-C7	1.365(42)
Mo-C4	2.188(18)	C7-C8	1.253(35)
Mo-C5	2.253(23)	C8-C4	1.326(34)
Mo-C6	2.321(23)	C9-C10	1.338(25)
Mo-C7	2.398(25)	C10-C11	1.332(23)
Mo-C8	2.246(21)	C11-C12	1.324(24)
Mo-C9	2.248(16)	C12-C13	1.430(26)
Mo-C10	2.286(14)	C13-C9	1.342(29)
Mo-C11	2.339(12)	Re-centroid (C14-C18)	1.995
Mo-C12	2.331(14)	Mo-centroid (C4-C8)	1.994
Mo-C13	2.283(14)	Mo-centroid (C9-C13)	1.993

Table III. Selected Bond Angles (deg) in $Cp_2Mo(\mu\text{-}CO)_2Re(CO)Cp$

Re-C1-O1	144.4(1.0)	Mo-C1-O1	127.8(0.8)
Re-C2-O2	147.2(1.1)	Mo-C2-O2	126.7(0.9)
Re-C3-O3	177.4(1.1)	Mo-Re-C1	49.9(0.4)
Re-C1-Mo	87.8(0.5)	Mo-Re-C2	52.0(0.4)
Re-C2-Mo	86.1(0.5)	Mo-Re-C3	96.5(0.3)
C1-Re-C3	92.8(0.5)	C2-Re-C3	91.1(0.5)
C2-Re-C1	101.8(0.6)		

employed for data collection. Three standard reflections which were monitored after every 50 reflections exhibited a small systematic decrease in intensity of about 6-8%. The data were corrected accordingly.

A full form of data (hkl to $\bar{h}kl$) was measured to a 2θ value of 50° giving 3333 reflections, of which 2483 unique reflections were judged observed. A semiempirical absorption correction (μ = 82.26 cm^{-1}) was employed which gave good agreement with four intense reflections as observed at several different values of ϕ.

The structure was solved using the SHELX program package[12] and plotting programs described previously.[13] The rhenium and molybdenum atoms were located by means of a Patterson map. Subsequent Fourier and difference Fourier maps revealed the locations of all remaining nonhydrogen atoms. Several cycles of least-squares anisotropic refinement of the metal atoms and isotropic refinement of the carbon and oxygen atoms gave $R_1 = 0.080$ ($R_1 = \sigma|F_o - F_c|/\sigma(F_o)$; $R_2 = 0.079(\sigma(w[F_o - F_c]^2)^{1/2}/\sigma(w(F_o)^2))$. Automatic generation of hydrogen atoms 1.08 Å from the carbon atom, followed by anisotropic refinement of all nonhydrogen atoms, resulted in final R factors of $R_1 = 0.066$, $R_2 = 0.024$. Final positional and thermal parameters are given in Table I. Selected bond distances and angles are given in Tables II and III, respectively. Idealized hydrogen atom positions (Table IV) and tables of $|F_o|$ and $|F_c|$ are available as supplementary material.[14]

Results

Synthesis and Properties of $Cp_2ReLiPMDT$. Metalation of Cp_2ReH in hexane by n-butyllithium in the presence of PMDT results in the formation of the amine-chelated compound $Cp_2Re\text{-}Li{\cdot}PMDT$ (I) in 87% yield. This pale yellow compound dissolves in aromatic solvents, yielding a yellow solution. The ^1H NMR spectrum at ambient temperature exhibits signals due only to the cyclopentadienyl rings (singlet) and the PMDT base. The PMDT moiety shows three resonances; based on the integration, the signals could be assigned to the methyl group on the middle nitrogen atom, the methyl groups on the terminal nitrogen atoms, and the methylene protons, respectively. There are no other signals observed below τ 40. The infrared spectrum shows no bands in the terminal metal hydride region, 1500-2100 cm^{-1}; the complex Cp_2ReH exhibits hydride bands at 2037 and 2000 cm^{-1} in Nujol. Treatment of I with D_2O yields $Cp_2Re\text{-}D$ with a small $Cp_2Re\text{-}H$ impurity in some cases.

Compound I reacts with CO and CO_2 in hexane to yield small amounts of $CpRe(CO)_3$ and brown precipitates whose IR spectra show bands due to terminal carbonyls and cyclopentadienyl rings. The nature of these precipitates is now being investigated.

Reaction of Cp_2MoH_2 with n-Butyllithium in the Presence of PMDT. Treatment of a solution of Cp_2MoH_2 in hexane with *n*-butyllithium in the presence of PMDT at −78 °C yields a yellow-orange precipitate that is soluble in aromatic solvents. The NMR spectrum shows a nonbridging hydride resonance, a doublet for the cyclopentadienyl rings, which collapses to a singlet upon decoupling of the hydride, and the protons on the PMDT base. The PMDT moiety for this complex shows three peaks almost identical with those observed in I. Also in support of the presence of a Mo-H bond, a medium broad band at 1671 cm^{-1} is observed in the infrared spectrum. These results are consistent with the structure $Cp_2MoH(Li{\cdot}PMDT)$.

Synthesis and Reactions of Cp_2Re Alkyls. Compound I has been found to be a useful reagent for the synthesis of the previously unknown Cp_2Re alkyls by reaction with the alkyl halides. The alkyl bromides gave a substantially smaller percentage of Cp_2ReH impurity than the alkyl chlorides.

Bis(cyclopentadienyl)ethylrhenium has been found to be thermally stable. No decomposition or formation of Cp_2ReH is observed upon heating in benzene to 70 °C. The complexes $Cp_2ReCH_2CH_3$ and $Cp_2ReCH_2CH_2CH_3$ exhibit second-order NMR spectra in the alkyl region as presented in the Experimental Section. Instead of the normal triplet-quartet spectrum, the ethyl group in $Cp_2ReCH_2CH_3$ exhibits a complex multiplet centered at τ 8.37. A second-order spectrum for the propyl group in $Cp_2ReCH_2CH_2CH_3$ was also observed. The allyl ligand in Cp_2Re allyl has been found to act as a σ donor. The NMR spectrum of $Cp_2ReCH_2CHCH_2$ exhibits the A_2BCD spectrum observed for other such σ-allyl species[15] and the IR spectrum shows a strong band at 1608 cm^{-1}, indicative of σ-allyl complexes.[16]

Although $Cp_2ReCH_2CH_3$ and $Cp_2ReCH_2CH_2CH_3$ do not undergo β-hydride elimination when heated, their mass spectra show a base peak corresponding to $(Cp_2ReH)^+$, indicating that under mass spectral conditions β-hydride elimination has occurred. Photochemical irradiation of $Cp_2ReCH_2CH_2CH_3$ for 10 h in hexane also produced no β-hydride elimination or decomposition. The ion $(Cp_2Re)^+$ was observed as the base peak for Cp_2ReCH_3 and Cp_2Re (σ-allyl) where no β-hydride elimination is possible.

Triphenylcarbenium tetrafluoroborate abstracts a methyl hydride ion from $Cp_2ReCH_2CH_3$ yielding $Cp_2ReCH_2CH_2^+$. This compound, when reacted with I, produces a complex whose mass spectrum shows peaks corresponding to $Cp_2ReCH_2CH_2ReCp_2$, $Cp_2ReCH_2ReCp_2$, and $Cp_2ReReCp_2$. This complex and further reactions of the Cp_2Re alkyls with triphenylcarbenium ion as well as with Magic Methyl, protonating agents such as HPF_6, and trimethylaluminum will be discussed in a forthcoming paper.[17]

Synthesis of Bimetallic Species. The reaction of I with $CpM(CO)_3Cl$ (M = Mo, W) yields new mixed-metal bimetallic species in which exchange of a cyclopentadienyl ring from the rhenium atom to the molybdenum or tungsten atom is observed. A field desorption mass spectrum of $Cp(CO)Re(\mu\text{-}CO)_2MoCp_2$ (III) yielded a molecular ion at *m/e* 556-567 with the isotopic pattern expected for a Re-Mo complex. An electron impact mass spectrum for this complex shows only $CpRe(CO)_3$ with subsequent loss of carbon monoxide and Cp_2Mo. The lowest carbonyl frequency of the Re-Mo complex is observed at the extreme low end of the bridging carbonyl frequency range. This is explained by the crystal structure analysis of the compound, which revealed two semibridging[18] carbonyls (Figure 1). The NMR is indicative of three nonequivalent cyclopentadienyl rings, with three singlets at τ 4.70, 5.27, and 5.32 in acetone-d_6. The bridging carbonyls are asymmetrically bridged favoring the Re atom. The bond distances between the Re atom and the carbon atoms of the bridging carbonyls are approximately 0.3 Å smaller than the corresponding Mo bond distances. The carbon-oxygen distance in the bridging carbonyls is also observed to be statistically longer than the carbon-oxygen distance in the terminal carbonyl. Prolonged heating of the Re-Mo complex results in the loss of the bridging carbonyl frequency as observed from infrared spectroscopy.

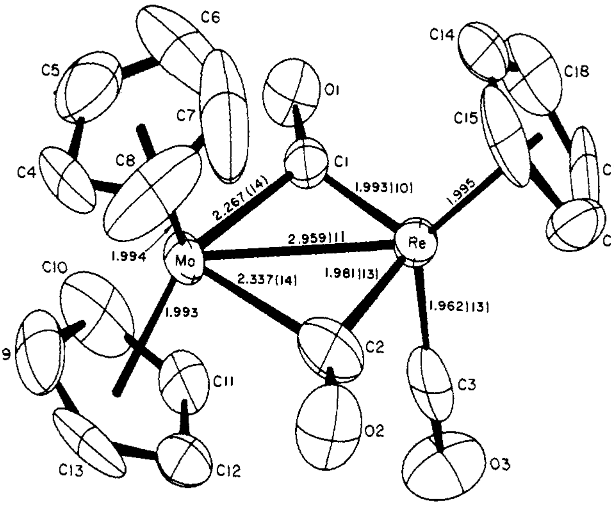

Figure 1. ORTEP plot of the $Cp_2Mo(\mu\text{-}CO)_2Re(CO)Cp$ molecule. Hydrogen atoms have been omitted. Other atoms are drawn at the 50% probability level for thermal vibration. The labeling scheme is shown.

The product of I with $CpW(CO)_3Cl$ is an orange-brown powder that is much less soluble in THF than the Mo analogue. The infrared spectrum of this compound shows similar but even lower stretching frequencies (Nujol, 1863 vs, 1773 vs, 1684 sh, 1650 vs; THF, 1892 s, 1690 cm^{-1} s), indicative of bridging carbonyls. The molecular ion of the complex, $(Cp(CO)Re(\mu\text{-}CO)_2WCp_2)$ (IV), is observed in the field desorption mass spectrum at *m/e* 646-654 with the correct isotopic pattern for a Re-W complex.

Discussion

The use of *n*-butyllithium in the presence of PMDT for metalation reactions allows one to form electron-rich transition metal compounds. These amine-chelated species are characteristically more reactive than the unchelated compounds[19] and usually demonstrate enhanced solubility toward organic solvents. The increased solubility greatly simplifies characterization problems that have been encountered in the past.[5] Compound I appears to be best viewed as a monomeric molecule with a Re-Li covalent bond with enhanced ionic character due to the tridentate amine coordination to the lithium atom.

Compound II also appears to be monomeric involving a Mo-Li covalent bond with a PMDT moiety coordinatively satisfying the Li atom. This monomeric nature is in contrast to the tetrameric nature of the Mo-Li compound found by Green in the absence of PMDT.[7] It should be noted that the reaction of *n*-butyllithium with Cp_2ReH or Cp_2MoH_2 in the presence of TMED produced only insoluble precipitates which could not be unequivocally characterized. The presence of the tridentate base PMDT reduces the possibility of forming lithium-bridged oligomers, as opposed to the bidentate base TMED.

Compound II can be reacted with D_2O to yield Cp_2MoHD. The use of large excesses of PMDT and *n*-butyllithium followed by deuteration never produced Cp_2MoD_2. Reaction of II with CO_2 and CO yields $Cp_2Mo(CO)$ as previously reported.[7] Reaction of *n*-butyllithium with Cp_2TaH_3 and PMDT leads to inconclusive results at the present time.

The reactions of I are summarized in Figure 2. The bis(cyclopentadienyl)rhenium alkyls of methyl, ethyl, *n*-propyl and allyl synthesized by use of the Re-Li reagent demonstrate the

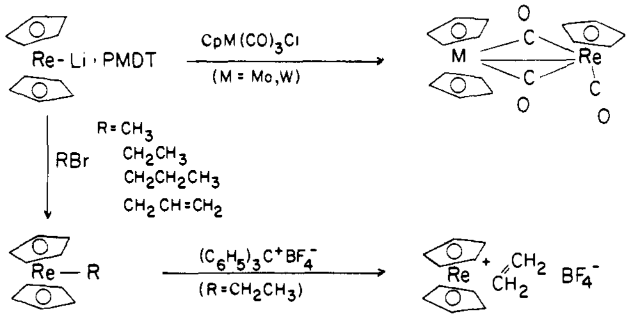

Figure 2. Reactions of Cp_2Re--Li·PMDT.

expected stability of an electronically saturated transition metal compound. Decomposition or β-hydride elimination does not occur easily in these compounds, either by prolonged heating or by UV irradiation. So far, the preparation of the isopropyl derivative has been unsuccessful.

The NMR spectra demonstrate that the chemical shifts of the protons on the carbon atom β to the rhenium are shifted downfield, causing the second-order spectrum to be observed for $Cp_2ReCH_2CH_3$ and $Cp_2ReCH_2CH_2CH_3$. Downfield shift of protons on carbon atoms β to a bis(cyclopentadienyl) transition metal fragment has been observed before,[20] and is most likely due to the deshielding effect of the metal atom.

The abstraction of a hydride ion from $Cp_2ReCH_2CH_3$ to yield $Cp_2Re(CH_2{=}CH_2)^+BF_4^-$ indicates that there is a possible wealth of electrophilic chemistry to be investigated in the Cp_2Re monoalkyls.

The mixed metal Re-Mo complex is an interesting case in which ligand scrambling has occurred. The transfer of a cyclopentadienyl ring from one metal to another is relatively rare, but has been reported for reactive transition metal compounds such as nickelocene and the cyclopentadienyliron dicarbonyl dimer.[21,22] The two bridging carbonyls in the structure of III are excellent examples of "semibridging" carbonyls as described by Cotton.[18] The molecular structure of III revealed that the bridging carbonyls truly favor the rhenium atom and the molecule seems best viewed as a $CpRe(CO)_3$ fragment and a molybdocene fragment. The long Mo-Re bond of 2.959 Å is stabilized by the two semibridging carbonyls. The carbon-oxygen bond lengths in the two bridging carbonyls show a significant increase over the carbon-oxygen bond length in the terminal carbonyl. If we assume that the bridging carbonyl groups are chemically equivalent, and that, although their thermal motion in the solid state differs, the carbon-oxygen bond lengths are not altered by crystal packing forces, the bridging carbonyl bond lengths can be averaged to give $d_{\mathrm{CO(br)}} = 1.186\ (8)$ Å.[23] The difference between this value and the $d_{\mathrm{CO(term)}}$ value of 1.140 (12) Å is 0.046 (14) Å or 3.2 σ_{diff} so that the difference in the bridging and terminal bond lengths is statistically significant at the 99.9% level.[23] These semibridging carbonyls show extremely low stretching frequencies for dibridging carbonyls, values of 1690 and 1718 cm^{-1} in THF solution for the IV and III, respectively. These frequencies are reflected in the elongated C-O bond length observed for the bridging carbonyls as compared to the terminal carbonyl. We consider these carbonyls to be activated, since the carbonyl band in the infrared spectrum is within the region where organic aldehydes and ketones characteristically fall. The average of 1.186 (8) Å observed for the bridging carbonyl is actually closer to the accepted value of 1.23 (1) Å for a carbon-oxygen double bond in aldehydes and ketones than it is to the 1.14 Å carbon-oxygen triple bond of the terminal carbonyl. This again implies a significant weakening of the carbon-oxygen bond. The weakening of the carbon-oxygen bond in the bridging carbonyls is most likely due to the basicity of the molybdocene fragment. Following the analysis of Cotton,[18] the Re-Mo bond is viewed in terms of a donation of a lone pair of electrons from the Re to an empty orbital on the Mo. This added electron density from the Re coupled with the electron-donating properties of the cyclopentadienyl rings allows the molybdocene fragment to act as an unusually strong electron donor to the π^* orbitals of the bridging carbonyls, thus causing the elongated nature of the carbon-oxygen bonds. The infrared stretching frequency of these semibridging carbonyl groups in the tungsten derivative is among the lowest carbonyl stretching frequencies yet observed for dibridging carbonyls.[24]

The loss of the bridging carbonyl frequencies in the infrared spectra of complexes III and IV with prolonged heating is not without precedent. Wrighton[25] has observed decarbonylation of $[CpM(CO)_3]_2$ (M = Mo, W, Cr) with heating to form metal-metal multiple bonds. The decarbonylation reactions and reactivity of III and IV are currently under investigation. The activation of the carbonyl ligand by two different transition metals leads one to believe that other small molecules such as N_2 or CN^- could also be activated or reduced in a similar fashion.

Conclusion

We have shown that the use of the tridentate amine, pentamethyldiethylenetriamine, in conjunction with *n*-butyllithium facilitates the metalation of bis(cyclopentadienyl) transition metal hydrides at the metal. These electron-rich complexes can be used in the synthesis of bis(cyclopentadienyl) metal alkyls and mixed metal complexes. The coordination of the semibridging carbonyls by two different transition metals suggests the possibility of activating other unsaturated molecules by the cooperative bonding to two different transition metals.

Acknowledgment. We would like to express our thanks to the National Science Foundation for support of this work under Grants DMR-72-23999 and CHE-77-24964.

Supplementary Material Available: Idealized positions of hydrogen atoms and a complete listing of structure factor tables (15 pages). Ordering information is given on any current masthead page.

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A Dimeric Naphthyl Hydride Derivative of Zirconocene. Synthesis, Structure, and Chemical Properties

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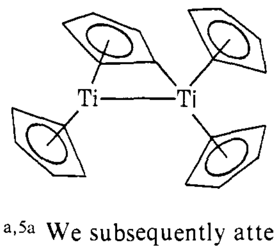
Abstract: Reduction of bis(η-cyclopentadienyl)zirconium dichloride with potassium naphthalene, at low temperatures in tetrahydrofuran, yields μ-(2-η^1:1-2-η^2-naphthyl)-hydrido-bis[bis(η-cyclopentadienyl)zirconium](*Zr–Zr*), $(\eta\text{-}C_5H_5)_2\overline{Zr(C_{10}H_7)(H)Zr}(\eta\text{-}C_5H_5)_2$ (hereinafter labeled I). The compound was characterized by a combination of chemical methods and X-ray crystallography. Crystals of I are orthorhombic, of space group *Pbca* (centrosymmetric), cell parameters $a = 1.9243$ (8), $b = 2.0507$ (6), and $c = 1.1931$ (8) nm, and contain eight molecules of $(C_5H_5)_4Zr_2(C_{10}H_7)(H)$ per unit cell. Key structural parameters follow: D(Zr–Zr) = 0.3307 (2), mean D(Zr–C_5H_5, centroid) = 0.255 (3), D(Zr–η^1-naphthyl, carbon) = 0.229 (1) nm. The hydrido ligand in I was not located by the X-ray work, but its presence was inferred from ^{1}NMR spectra in THF-d_8, which show a singlet at $\delta_{(CH_3)_4Si}$ -9.3. Reaction of I with excess CH_3I yields 1 mol CH_4/Zr_2 unit, which is in accordance with the monohydride structure. With HCl in THF, dicyclopentadienylzirconium dichloride, hydrogen, naphthalene, and a mixture of partially hydrogenated and hydrochlorinated naphthalenes are formed. Reaction of the complex with H_2 in THF yields naphthalene and dicyclopentadienylzirconium dihydride. In toluene and THF solutions, I is a catalyst for the hydrogenation of cyclohexene to cyclohexane.

Introduction

Low-valent bis(η-cyclopentadienyl)titanium[1] and bis(η-pentamethylcyclopentadienyl)titanium[2] and zirconium compounds[3] display unusual reactivity toward N_2, H_2, and CO, as well as interesting stoichiometric[4] and catalytic[5] reactions with olefins. The remarkable chemical reactivity of group 4B metallocenes toward small unsaturated molecules may be ascribed in part to the carbene-like character[6] of 14-electron, metal d^2, $(\eta\text{-}C_5H_5)_2M$ or $(\eta\text{-}C_5R_5)_2M$ species, where M is Ti, Zr, and Hf. Bis(η-pentamethylcyclopentadienyl)titanium, $[\eta\text{-}C_5(CH_3)_5]_2Ti$,[2a] has been prepared as a yellow-orange, crystalline solid from its dinitrogen derivative $[\eta\text{-}C_5(CH_3)_5]_4Ti_2N_2$. Bis($\eta$-pentamethylcyclopentadienyl)zirconium, $[\eta\text{-}C_5(CH_3)_5]_2Zr$, has not been isolated as a discrete compound, but is believed to be an intermediate in the decomposition of $[\eta\text{-}C_5(CH_3)_5]_4Zr_2(N_2)_3$.[3a] A characteristic property of low-valent titanium and zirconium metallocenes is the facile interaction of the metal with ligand hydrogens resulting in the formation of complex metal hydrides. Thus in solution, $[\eta\text{-}C_5(CH_3)_5]_2Ti$ rearranges reversibly to the tautomeric hydride, $[\eta\text{-}C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiH$, and the effect is even more pronounced in the corresponding zirconium system.[2a,3a] With bis(η-cyclopentadienyl)titanium and -zirconium species, the rearrangement to complex metal hydrides is apparently irreversible. Titanocene, $(\eta\text{-}C_5H_5)_2Ti$, and zirconocene, $(\eta\text{-}C_5H_5)_2Zr$, are not known.[1,8] Reduction of $(\eta\text{-}C_5H_5)_2TiCl_2$ at ambient temperatures yields the fulvalene-bridged cyclopentadienyltitanium hydride complex: $\mu\text{-}(\eta^5{:}\eta^5\text{-}C_{10}H_8)\text{-}\mu(H)_2\text{-}[(\eta\text{-}C_5H_5)_2Ti]_2$ (II).[7] In an attempt to minimize the rearrangement of possible intermediate $(\eta\text{-}C_5H_5)_2Ti$ species, we reduced $(\eta\text{-}C_5H_5)_2TiCl_2$ at low temperatures and isolated the $\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_3Ti_2$ complex (III), which proved to be highly reactive toward N_2, H_2, and olefins.[1a,5a] We subsequently attempted the preparation of a similar zirconium complex (which we hoped might be even more reactive toward N_2, H_2, etc.) by reduction of $(\eta\text{-}C_5H_5)_2ZrCl_2$ with potassium naphthalene at low temperatures in tetrahydrofuran. A naphthyl hydride derivative of bis[bis(η-cyclopentadienyl)zirconium](*Zr–Zr*) was obtained. This paper describes the synthesis, molecular structure, and basic chemical properties of μ-(2-η^1:1-2-η^2-naphthyl)-hydrido-bis[bis(η-cyclopentadienyl)zirconium](*Zr–Zr*), $(\eta\text{-}C_5H_5)_2\overline{Zr(C_{10}H_7)(H)Zr}(\eta\text{-}C_5H_5)_2$ (I).



Results and Discussion

Preparation of $(\eta\text{-}C_5H_5)_2\overline{Zr(C_{10}H_7)(H)Zr}(\eta\text{-}C_5H_5)_2$ (I). Watt and Drummond[8] reported in 1966 that reduction of $(\eta\text{-}C_5H_5)_2ZrCl_2$ with sodium naphthalene yields a purple-black material assigned the formula $(C_5H_5)_2Zr$ on the basis of an infrared spectrum (which showed no apparent metal hydride absorptions) and elemental analyses. When Brintzinger and Bercaw[7a] later demonstrated that the "$(C_5H_5)_2Ti$" commonly

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