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Bridging Ligands in Organometallic Chemistry. 2. Synthesis and Reactivity of the Green Dimer of Molybdenocene Containing a Bridging Fulvalene Ligand

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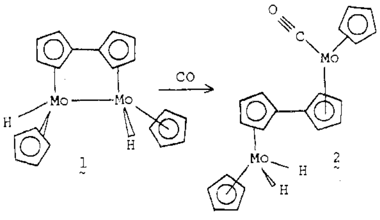
Current interest in the reactivity of coordinatively unsaturated metallocenes[1] and our interest in analogous dinuclear derivatives[2] have led us to explore synthetic routes to complexes of the early transition metals.

The reactive molybdenocene[3] monomer, with 16 valence electrons, is a postulated intermediate in a number of reaction systems that yield addition and oxidative-addition products. Thomas[4] reported that the reduction of $(C_5H_5)_2MoCl_2$ with sodium amalgam in tetrahydrofuran yields a red-brown polymeric material $[(C_5H_5)_2Mo]_x$, with no bridging ligands. Green[5] recently reported that $[(C_5H_5)_2MoHLi]_4$ reacts with nitrous oxide in toluene to yield two moderately stable, yellow isomeric dimers of molybdenocene containing η^5-C_5H_5 and hydride ligands, and a bridging $\eta^1{:}\eta^5$-C_5H_4 ligand that presumably is formed by the oxidative addition of a ring C–H bond to the intermediate molybdenocene monomer. These complexes undergo a reductive coupling in toluene at 50 °C to yield a green dimer $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)MoH]_2$(*Mo–Mo*) (**1**), containing a bridging fulvalene ligand.



This report describes a distinctly different synthesis of **1** and our initial reaction studies involving the addition of carbon monoxide and deprotonation with *n*-butyllithium.

Experimental Section

Reagent grade tetrahydrofuran (THF) was predried over CaH_2. Toluene, diethyl ether, heptane, and THF were purified by distillation from sodium–benzophenone ketyl and stored under argon. Previously reported procedures were used to prepare $(CH_3CO_2)_4Mo_2$[6] and $Na(DME)C_5H_5$.[2a] All other chemicals were reagent grade and were used without further purification.

Air-sensitive solids were stored and manipulated in a Vacuum Atmospheres glovebox with a modified dry train. Deoxygenated solvents and air-sensitive solutions were transferred under argon via 18-gauge stainless steel cannulae. All reactions were carried out under an atmosphere of argon using standard inert-atmosphere and Schlenk-tube techniques. Fischer-Porter bottles and attendant stainless steel fittings were obtained from Fischer & Porter Co., Lab-Crest Scientific Div., Warminster, Pa.

Infrared spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer as Nujol or halocarbon mulls and calibrated with polystyrene. Variable-temperature proton NMR spectra at 100 MHz were obtained with a Varian Associates Model XL-100 spectrometer and at 180 MHz with the multinuclear departmental instrument operating in the pulsed Fourier-transform mode. Elemental analyses were performed by the microanalytical laboratory of the University of California, Berkeley, Calif. and Spang Microanalytical Laboratory, Eagle Harbor, Mich.

Dicyclopentadienyl(fulvalene)dihydridodimolybdenum $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)MoH]_2$(*Mo–Mo*). A solution of $Na(DME)C_5H_5$ (7.46 g, 42.0 mmol) in THF (250 mL) was added dropwise to a stirred suspension of $(CH_3CO_2)_4Mo_2$ (4.28 g, 10.0 mmol) in THF (300 mL) over a period of 2 h. During the addition, the yellow color of the reaction mixture changed to yield a dark red-brown solution and a suspension of light-colored sodium acetate. After the mixture was stirred at room temperature for 20 h, the color of the solution darkened to a brown-green. The reaction mixture was filtered and the light-colored material collected was extracted with THF (2 × 25 mL) and then discarded. The combined green filtrate was concentrated in vacuo and the resulting dark solid was extracted with hot toluene (200 mL) and filtered. The remaining solid was washed with toluene (2 × 10 mL) and discarded. The clear, dark green filtrate was stirred at 60 °C for 1 h and then the volume was reduced in vacuo to yield small dark green crystals. The product was isolated by cooling the solution to 0 °C and removing the solvent via a cannula. The material was washed with diethyl ether (3 × 25 mL) in a similar manner and dried in vacuo to yield 2.5 g (55%) of crystalline product. Analytically pure material was obtained by sublimation at 155 °C (10^{-4} mm). The compound melts and decomposes at 203 °C under vacuum. Anal. Calcd for $C_{20}H_{20}Mo_2$: C, 53.11; H, 4.46; Mo, 42.43. Found: C, 53.19; H, 4.32; Mo, 42.18. Infrared: 3100 (sh), 3090 (m), 1803 (m) (br), 1555 (w), 1422 (m), 1292 (w), 1107 (m), 1032 (m), 1018 (w), 1009 (m), 988 (m), 902 (sh), 898 (m) (br), 833 (m), 821 (w), 780 (w), 748 (sh), 744 (s), 597 (w), 555 (m) (br) cm^{-1}. ^1H NMR (toluene-d_8, 180 MHz): δ 4.37 (s, 5 H), 3.85 (t, 2 H, J = 2.2 Hz), 3.28 (t, J = 2.2 Hz), −10.01 (s, 1 H).

(Fulvalene)(carbonylcyclopentadienyl)molybdenum(cyclopentadienyldihydrido)molybdenum, $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Mo(CO)][(\eta^5\text{-}C_5H_5)Mo(H)_2]$. In a drybox, $(C_{10}H_8)[(C_5H_5)MoH]_2$ (2.48 g, 5.5 mmol) was placed in a 6-oz borosilicate glass Fischer-Porter bottle equipped with a magnetic stir bar. The bottle was sealed and removed from the drybox, and toluene (100 mL) was added. The system was then purged with carbon monoxide and pressurized to 220 psi. Over a period of 13 h, the dark green solution lightened and light green crystalline material deposited. After the reaction system was vented to atmospheric pressure and passed into a drybox, the precipitate was separated by filtration, washed with toluene (2 × 3 mL), and dried in vacuo to yield 0.30 g of light green product. The volume of the green filtrate was reduced under vacuum at 40 °C until the solution became cloudy. Cooling to −20 °C yielded green crystals which were collected by filtration, washed with cold toluene (10 mL), and dried in vacuo to give an additional 1.10 g of product (53% combined yield). Anal. Calcd for $C_{21}H_{20}Mo_2O$: C, 52.52; H, 4.20. Found: C, 52.31; H, 4.21. Infrared: 3125 (w), 3105 (sh), 3085 (m), 3065 (m), 3050 (sh), 1900 (s) (1910 (s) in THF solution), 1850 (w), 1820 (m), 1805 (m), 1540 (w), 1430 (w), 1365 (w), 1194 (w), 1104 (m), 1100 (m), 1076 (w), 1064 (w), 1047 (w), 1030 (m), 1000 (m) (br), 982 (w), 917 (sh), 906 (m) (br), 886 (w), 841 (m), 831 (sh), 827 (m), 768 (s), 689 (m), 676 (w), 616 (m), 490 (s), 484 (sh), 466 (s) cm^{-1}. ^1H NMR (toluene-d_8, 180 MHz): δ 4.37 (m, 2 H), 4.33 (m, 2 H), 4.30 (s, 5 H, br), 4.23 (m, 2 H), 4.15 (s, 5 H), 4.11 (m, 2 H), −8.38 (s, 2 H, br).

Dibenzyldicyclopentadienyl(fulvalene)dimolybdenum, $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Mo(CH_2C_6H_5)]_2$(*Mo–Mo*). A solution of $(C_{10}H_8)[(C_5H_5)MoH]_2$ (0.25 g, 0.55 mmol) in dry, oxygen-free toluene (25 mL) was treated dropwise with butyllithium (2.6 M in hexane, 0.45 mL, 1.17 mmol, 6% excess) to yield a suspension of yellow-green $(C_{10}H_8)(C_5H_5)_2Mo_2(Li)_2$. This was stirred for 15 min and benzyl bromide (0.20 mL, 0.29 g, 1.7 mmol, 54% excess) was added, causing the color to change to yellow-green and solid material to deposit. This suspension was filtered immediately to give a light green solid (0.20 g) and a yellow-green solution. The volume of the filtrate was reduced under vacuum to ca. 5 mL and dropwise addition of heptane (50 mL) caused a yellow-green solid to precipitate. This was collected by filtration, washed with heptane, and dried to give 0.12 g (35%) of

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moderately pure product. An analytical sample was obtained by recrystallization from hot toluene. Anal. Calcd for $C_{34}H_{32}Mo_2$: C, 64.56; H, 5.10. Found: C, 64.75; H, 5.24. Infrared: 3127 (m), 3112 (sh), 3090 (w), 3064 (w), 3015 (w), 3003 (w), 2985 (w), 2960 (m), 2928 (m), 1593 (m), 1487 (m), 1447 (w), 1428 (w), 1418 (w), 1384 (w), 1363 (w), 1293 (m), 1260 (w), 1202 (m), 1181 (m), 1160 (w), 1111 (m), 1048 (w), 1033 (m), 1028 (m), 1013 (m), 993 (m), 938 (w), 907 (s), 896 (m), 851 (m), 848 (m), 836 (s), 827 (sh), 799 (m), 782 (m), 775 (m), 747 (s), 721 (w), 699 (s), 679 (w), 613 (w), 597 (w), 583 (w), 550 (m), 530 (m) cm^{-1}. ^1H NMR (THF-d_8, 180 MHz): δ 6.87 (m, 4 H), 6.61 (m, 6 H), 4.58 (s, 10 H), 4.42 (m, 2 H), 3.87 (m, 2 H), 3.49 (m, 2 H), 2.83 (m, 2 H), 1.22 (d, 2 H, $J = 10.3$ Hz), −0.51 (d, 2 H, $J = 10.3$ Hz).

Results and Discussion

Prior to the report of Green[5] and co-workers, we independently[2b,c] synthesized **1** in high yield by the straightforward substitution reaction of molybdenum(II) acetate with 4 equiv of sodium cyclopentadienide in tetrahydrofuran at 24 °C. Thus far we have not detected any precursor oxidative-addition products with bridging $\eta^1{:}\eta^5$-C_5H_4 ligands, which may form and rapidly couple in this reaction at some intermediate stage of acetate ligand substitution. While **1** is air sensitive in solution and as a solid, it is thermally stable to loss of hydrogen on sublimation under vacuum at 160 °C.

The infrared spectrum of **1** exhibits a broad, low-intensity band (ν(M–H) = 1803 cm^{-1}, Nujol mull) that supports the formulation of terminal[7] molybdenum hydride ligands. The ^1H NMR spectrum of **1** exhibits a widely spaced pair of symmetrical triplets for the bridging $\eta^5{:}\eta^5$-fulvalene ligand, a sharp cyclopentadienyl resonance at lower field and a broader molybdenum hydride resonance at high field. Homonuclear spin decoupling of the fulvalene protons confirms the assignment of an AA′BB′ spin system in which the cross-ring coupling constants are approximately equal and small relative to the chemical shift difference between protons α and β to the bridge. The formulation of a metal–metal single bond allows a closed-shell configuration for each molybdenum and is supported by the relatively large chemical shift difference of the fulvalene protons in related complexes of molybdenum.[2a] While the pseudotetrahedral geometry about molybdenum depicted for **1** is *not* supported by the simple spectrum observed, variable-temperature studies indicate that **1** is stereochemically nonrigid with changes in the high temperature limiting 100-MHz NMR spectrum becoming evident at −90 °C. The facile intraconversion of diasteromers of **1**, in the dissymmetric trans configuration depicted, is thought to occur via a symmetric bridged dihydride transition state. In the absence of any preferred bonding requirements of the fulvalene ligand, either a coplanar or twisted disposition of bridged five-membered rings seems feasible for the ground state of **1**, from an inspection of molecular models. Alternatively, **1** may have a cis configuration of C_s point-group symmetry with a planar fulvalene ligand as has been proposed[2b] for the doubly bridged $(C_{10}H_8)_2Mo_2(CO)$ and found crystallographically[8] for $[(\eta^5{:}\eta^5\text{-}C_{10}H_8)_2V_2(CH_3CN)_2]^{2+}$.

The addition of carbon monoxide at 20 atm to **1** in toluene at 25 °C results in transfer of a hydride ligand and rupture of the Mo–Mo bond to yield **2**. The infrared spectrum of **2** exhibits one sharp terminal metal–carbonyl stretch and symmetric and asymmetric stretching modes of a metal dihydride moiety.[9] The ^1H NMR spectrum of **2** shown in Figure 1 exhibits a sharp singlet and a narrow multiplet at lower field for the two η^5-C_5H_5 ligands and a pair of triplets and a more closely spaced pair of multiplets at lower field for the $\eta^5{:}\eta^5$-$C_{10}H_8$ ligand. Spin-decoupling experiments confirm the assignment of two uncoupled AA′BB′ spin systems. The high-field metal–hydride resonance exhibits a small unresolved splitting that decoupling experiments confirm is from coupling to protons of one η^5-C_5H_5 ring and one ring of the $\eta^5{:}\eta^5$-$C_{10}H_8$ ligand. This clearly establishes that the three sets of resonances at low field are those of the molybdenocenium dihydride[9b] moiety. All proton resonances in **2** are more shielded than those of the analogous molybdenocene complexes, and this is consistent with a tentative assignment of the higher and lower field triplets in each set, to protons α and β to the bridge.

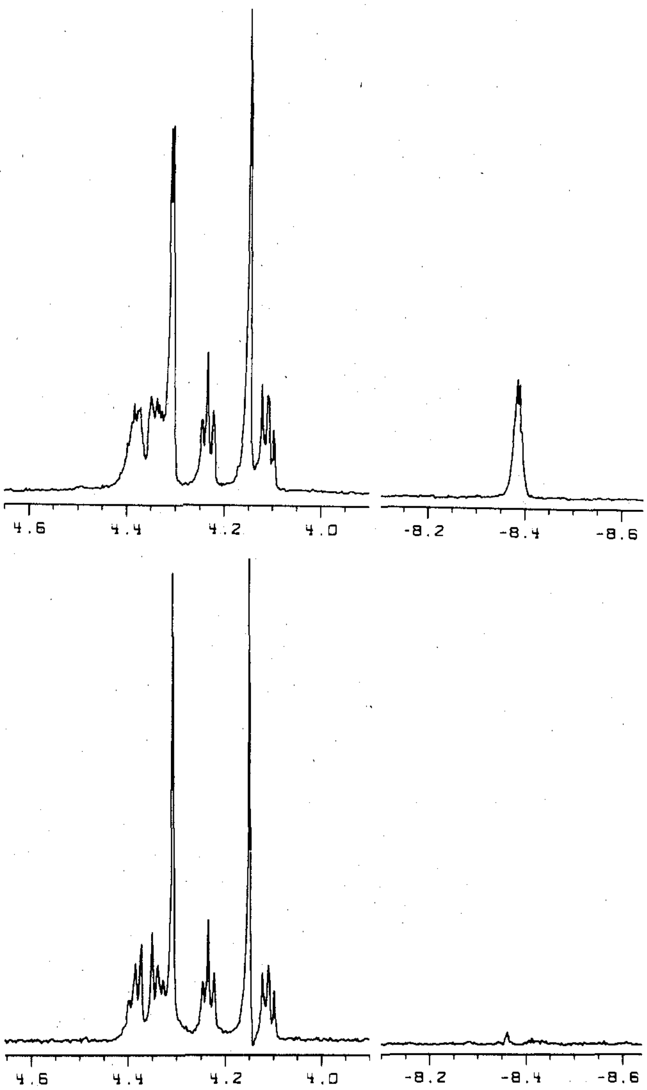

Figure 1. The 180-MHz ^1H NMR spectra of **2** in toluene-d_8. The lower spectrum is spin decoupled from the molybdenum hydride resonance at δ −8.38.

Reaction of **1** with 2 equiv of *n*-butyllithium in toluene yields a very reactive yellow-green dilithio complex $(C_5H_5)_2(C_{10}H_8)Mo_2(Li)_2$ (**3**). This complex is insoluble in aliphatic and aromatic solvents and reacts with various other solvents, including tetrahydrofuran, to give uncharacterized products that are only initially soluble. The infrared spectrum of **3** exhibits no molybdenum–hydride stretch, suggesting a covalent and perhaps associated Mo–Li structure as was found[10] for $[(C_5H_5)_2Mo(H)Li]_4$. This is further supported by protonation reactions of **3** to regenerate **1** and alkylation reactions that yield stereochemically rigid dialkyl complexes of structure **1**. One isomer of the dibenzyl complex was isolated and characterized. Its ^1H NMR spectrum exhibits four widely spaced multiplets of a completely coupled ABCD spin system for both rings of the $\eta^5{:}\eta^5$-$C_{10}H_8$ ligand. The diastereotopically nonequivalent methylene protons exhibit a widely spaced pair of doublets of an AB spin system. The analogous (trimethylsilyl)methyl complex was obtained as a mixture of cis and trans isomers, each of whose spectrum is qualitatively similar to the dibenzyl complex.

Reactivity studies of **3** as a nucleophile and a reducing agent as well as addition and photolysis reactions of **1** and **2** are in progress.

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Registry No. **1**, 63630-86-4; **2**, 67350-79-2; (η^5:η^5-$C_{10}H_8$)[(η^5-C_5H_5)Mo($CH_2C_6H_5$)]$_2$, 67328-64-7; $(CH_3CO_2)_4Mo_2$, 14221-06-8.

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Synthesis, Characterization, and Structure of the Complex (η^3-*cyclo*-Triphosphorus)(tris(2-diphenylphosphinoethyl)amine)cobalt

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Recently we have described the first examples of metal complexes with the cyclic unit δ-P_3 acting as a η^3 ligand.[1] These compounds are obtained by direct action of white phosphorus on cobalt(II) and nickel(II) hydrated salts in the presence of the tri(tertiary phosphine) 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$, triphos, and have formulas [(triphos)M-μ(η^3-P_3)-M(triphos)]Y_2 (M = Co, Ni; Y = BF_4, BPh_4) and [(η^3-P_3)Co(triphos)]. In all these complexes each metal atom is coordinated by six phosphorus atoms, three belonging to the triphos ligand and three to the δ-P_3 unit.

With the aim of obtaining other δ-P_3 metal complexes we have tried to use another tripod ligand, the potentially tetradentate tri(tertiary phosphine) tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$, np$_3$. From the reaction of $Co(BF_4)_2\cdot 6H_2O$ with np$_3$ and white phosphorus in tetrahydrofuran–ethanol solution, a new (*cyclo*-triphosphorus)cobalt complex was obtained. This compound, having formula [(η^3-P_3)Co(np$_3$)]$\cdot 0.5C_4H_8O$ was characterized by the usual methods. Its structure was elucidated by means of a three-dimensional X-ray diffraction analysis.

Experimental Section

Reagents. All solvents were of reagent grade quality and were used without further purification. The ligand np$_3$ was prepared by the method previously described.[2]

Preparation of the [(η^3-P_3)Co(np$_3$)]$\cdot$0.5C_4H_8O Complex. The reaction was carried out under dry nitrogen. One millimole of $Co(BF_4)_2\cdot 6H_2O$ in 10 mL of ethanol was added to 1 mmol of np$_3$ in 15 mL of THF. Then a THF solution of white phosphorus P_4 (1 mmol in 15 mL of THF) was added slowly, with stirring, at room temperature. Gentle heating of the resulting solution (ca. 50 °C for ca. 0.5 h) precipitated bright red crystals. They were filtered off and washed with THF, ethanol, and finally petroleum ether before being dried. Anal. Calcd. for $C_{44}H_{46}CoNO_{0.5}P_6$: C, 62.79; H, 5.51; Co, 7.00; N, 1.66; P, 22.08. Found: C, 61.70; H, 6.01; Co, 6.70; N, 1.43; P, 20.80. The analytical data are slightly lower than those in agreement with the structural results. This disagreement can be attributed to the presence of impurities which we could not eliminate by recrystallization on account of the low solubility of the compound.

Physical Measurements. Magnetic and spectrophotometric measurements were carried out using methods already described.[3]

Collection of X-ray Data. The crystals, quite stable in air, are rhombohedral, space group $R\bar{3}$, with a = 28.950 (6) Å, c = 26.896 (6) Å (hexagonal cell), Z = 18, D_{calcd} = 1.29 g cm^{-3}, and D_{measd} = 1.30 g cm^{-3}. The crystal used for data collection was a rhombohedron having edges of about 0.3 mm. Cell parameters were determined by least-squares refinement of 20 reflections centered on a four-circle Philips PW1100 automatic diffractometer at about 22 °C, using Mo Kα radiation (λ 0.7107 Å). The intensity data were measured in the range 6° $\leq 2\theta \leq$ 40° using Mo Kα radiation monochromatized by a flat graphite crystal. The method used was the θ–ω scan technique: scans of 0.7° in 10 s were taken across the peaks (background was counted for 5 s on each side of the peak). Three standard reflections were measured every 120 min: no systematic loss of intensity was noticed during the collection. The standard deviations on the intensities were calculated by the expression $\sigma(I) = [P - 0.25(B_1 + B_2)(T_p/T_b) + (0.03I)^2]^{1/2}$,[4] where P is the peak count, B_1 and B_2 are the background counts, T_p and T_b are the count times on the peak and background, respectively, and I is the intensity itself.

The 2320 reflections having $I \geq 3\sigma(I)$ were considered observed and were used in the structure analysis. An absorption correction (μ = 6.39 cm^{-1}) was applied by a numerical method.[5] The intensities were corrected for Lorentz and polarization effects. The Lp factor for the graphite monochromator is 4.64. Atomic scattering factors for cobalt, phosphorus, oxygen, nitrogen, and carbon atoms were taken from ref 6 (all in the neutral state); those for hydrogen atoms were taken from ref 7 (in the neutral state).

Solution and Refinement of the Structure. The positions of the cobalt and phosphorus atoms were obtained from a three-dimensional Patterson synthesis. Two three-dimensional Fourier syntheses showed the positions of all nonhydrogen atoms of the structure. The atoms of the tetrahydrofuran molecule gave peaks lower in magnitude than those of the carbon atoms of the np$_3$ ligand. A population parameter of 0.5 will be assigned to these atoms on the basis of a least-squares refinement. Refinement was performed with the full-matrix least-squares program of Busing and Levy, adapted by Stewart.[8] The minimized function was $\sum w(|F_o| - |F_c|)^2$, where w is the weight assigned to the F_o values, according to the expression $w = 1/\sigma^2(F_o)$. Anisotropic temperature factors were assigned only to cobalt and phosphorus atoms; isotropic temperature factors were used for the lighter atoms. The hydrogen atoms of the np$_3$ ligand were introduced in calculated positions (C–H = 0.95 Å) with temperature factors $B_H = 1 + B_{C(attached)}$. The carbon atoms of the phenyl groups were refined