ORGANOMETALLICS

Reactions of molybdenum cobalt clusters Cp'2Mo2Co2S3(CO)4 with nucleophiles: carbonyl substitution via cleavage of a cobalt-sulfur bond. Preparation and x-ray structure of Cp'2Mo2Co2S3(CO)4(PMe3)

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Organometallics, **1992**, 11 (6), 1984-1986• DOI: 10.1021/om00042a003 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Reactions of $Cp'_2Mo_2Co_2S_3(CO)_4$ with Nucleophiles: Carbonyl Substitution via Cleavage of a Cobalt–Sulfur Bond. Preparation and X-ray Structure of $Cp'_2Mo_2Co_2S_3(CO)_4(PMe_3)$

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Received November 25, 1991

Summary: **The cluster $Cp'_2Mo_2Co_2S_3(CO)_4$ (1; Cp′ = C_5H_4Me) reacts with trimethylphosphine to form the adduct $Cp'_2Mo_2Co_2S_3(CO)_4(PMe_3)$ (2a), in which a Co–S bond has been cleaved. Methyl isocyanide forms a similar adduct, $Cp'_2Mo_2Co_2S_3(CO)_4(MeNC)$ (2b), at <0 °C but loses CO to form the carbonyl-substituted cluster $Cp'_2Mo_2Co_2S_3(CO)_3(MeNC)$ (3) at higher temperatures. Reaction of 1 with CO at high pressure (1450 psi) was shown to give reversibly the pentacarbonyl cluster $Cp'_2Mo_2Co_2S_3(CO)_5$ (2c). Crystal data for 2a: space group *Pn*; $Z = 4$; $a = 7.089$ (1) Å, $b = 18.669$ (6) Å, $c = 18.469$ (4) Å, $\beta = 90.84$ (2)°, $T = -100$ °C, $V = 2448$ (1) Å^3, $R = 0.0404$, $R_w = 0.0500$ based on 4739 reflections with $F_o \geq 5\sigma(F)$.**

Carbonyl substitution reactions on mononuclear transition-metal carbonyl species have been extensively studied.[1] Three general mechanisms can be used to classify these reactions:[2] dissociative, interchange (or concerted), and associative, of which the dissociative mechanism is most common. Most carbonyl substitution reactions on metal carbonyl clusters also proceed via a dissociative mechanism; however, there are many examples of associative mechanisms mediated by metal–metal bond breaking.[3] The attack of nucleophiles on metal carbonyl clusters to give edge-opened clusters is well-known.[4]

Metal–heteroatom bonds are generally stronger than metal–metal bonds;[5,6] for this reason, nucleophilic attack on heteroatom–metal carbonyl clusters to cleave metal–heteroatom bonds is rare.[7-10] Carbonyl substitution reactions with metal–heteroatom bond breaking are sparsely reported in the literature,[11-14] and in a few cases, metal–heteroatom bond breaking occurs prior to adduct formation of the cluster with the nucleophile.[15,16] In this communication we report an example of a carbonyl substitution reaction in which the intermediate displays metal–heteroatom bond breaking.

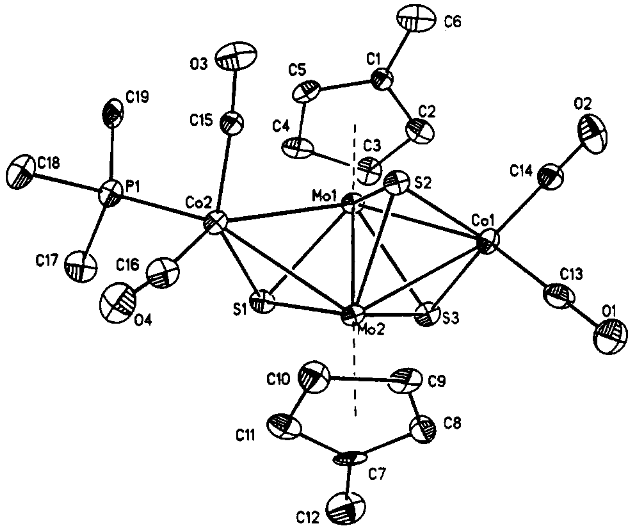

Figure 1. ORTEP plot of one independent molecule of $Cp'_2Mo_2Co_2S_3(CO)_4(PMe_3)$ (**2a**).

Carbonyl substitution by aryl phosphines on $Cp'_2Mo_2Co_2S_3(CO)_4$ (1; Cp′ = C_5H_4Me) was reported in an earlier communication.[17] Reaction of 1 with PMe_3 at 0 °C does not give substitution products but instead allows for the isolation of the dark red, unsubstituted adduct $Cp'_2Mo_2Co_2S_3(CO)_4(PMe_3)$ (**2a**).[18] An X-ray crystal structure determination obtained at low temperature[19]

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(18) $Cp'_2Mo_2Co_2S_3(CO)_4$ (1; 0.138 g, 0.20 mmol) was dissolved in 25 mL of CH_2Cl_2 and cooled to 0 °C. PMe_3 (0.024 mL, 0.23 mmol) was added with vigorous stirring; the solution immediately became dark red-brown. Addition of hexane (10 mL), followed by concentration of 5 mL and cooling to −20 °C, gave dark red needles of $Cp'_2Mo_2Co_2S_3(CO)_4(PMe_3)$ (**2a**; 0.038 g, 85% yield). ^1H NMR (C_6D_6): δ 5.06 (m, 2 H), 4.95 (m, 2 H), 4.83 (m, 2 H), 4.80 (m, 2 H) ABCD pattern for CpH, 1.88 (s, 6 H, $CpCH_3$), 0.91 (d, $J_{PH} = 8.4$ Hz, 9 H, $P(CH_3)_3$). IR (C_6H_6): ν(CO) 1990 (s), 1956 (ms, br), 1941 (ms), 1921 (m, br) cm^{-1}. Due to the facile loss of Me_3P from **2a**, even in the solid state, a satisfactory elemental analysis could not be obtained.

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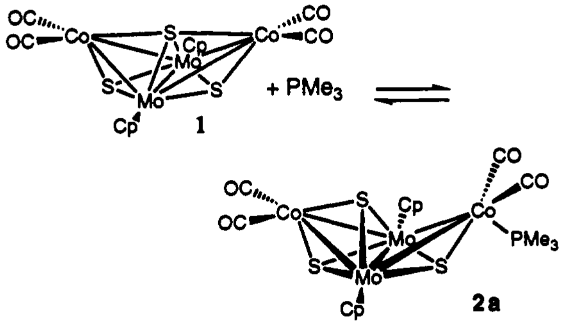
shows the phosphine attached to one of the Co atoms and cleavage of the Co–(μ_4-S) bond to that Co atom (Figure 1). The average nonbonded Co–S distance for the two independent molecules is 3.16 Å. The only significant difference between the two independent molecules is the orientation of the $Co(CO)_2(PMe_3)$ unit; in molecule 1, the P1–Co2–S1–(Mo1/Mo2 midpoint) torsion angle is 151.8 (1)°, while the corresponding torsion angle in molecule 2 is 162.1 (1)°. This difference is consistent with a facile rotation of the $Co(CO)_2(PMe_3)$ unit. The proton NMR spectrum is consistent with the solid-state structure, displaying one ABCD pattern for the cyclopentadienyl ring protons (δ 5.06–4.80) and one resonance for the methyl group (δ 1.88). This pattern necessitates the presence of a mirror plant through the Co atoms but not through the Mo atoms. The solution IR spectrum shows four ν_{CO} bands; the somewhat broader peaks at 1956 and 1921 cm^{-1} are assigned to the symmetric and antisymmetric stretching modes, respectively, of the carbonyl ligands on the Co atom ligated by the phosphine. The broadness is attributed to the distribution of isomers formed by rotation of the $Co(CO)_2(PMe_3)$ unit with respect to the rest of the molecule. The bands at 1990 and 1941 cm^{-1} are assigned to the symmetric and antisymmetric stretching modes, respectively, of the carbonyl ligands on the other Co atom.

Compound **2a** is unstable with respect to loss of PMe_3 such that, in solution at ambient temperature, **2a** reverts to 1 in a few hours. In the solid state, this reaction requires several days at room temperature.

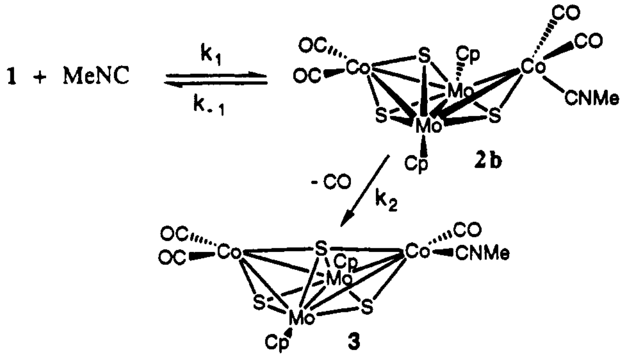


(1)

The reaction of 1 (0.03 mmol) with MeNC (0.02 mmol) was followed by NMR spectroscopy.[20] At −20 °C, 1 and the adduct $Cp'_2Mo_2Co_2S_3(CO)_4(MeNC)$ (**2b**) were observed in a 3:2 ratio. As found for **2a**, an ABCD pattern for the Cp′ ring protons (δ 5.30–5.01) and a singlet for the Cp′ methyl protons (δ 2.07) were recorded. The IR spectrum shows two broader stretches at 2003 and 1958 cm^{-1}, corresponding to the symmetric and antisymmetric stretching modes, respectively, of the carbonyl ligands on the Co atom ligated by the isocyanide. As expected on the basis of the π-accepting character of the isocyanide ligand, these frequencies are at higher energy than the corresponding ones in **2a**. The bands assigned to the symmetric and antisymmetric stretches for the carbonyl ligands on the other Co atom appear at 1984 and 1940 cm^{-1}, respectively. These frequencies are very similar to those in **2a**. The ν_{CN} band in **2b** appears at 2170 cm^{-1}.

At about 5 °C, the monosubstituted adduct $Cp'_2Mo_2Co_2S_3(CO)_3(MeNC)$ (**3**) began to form. The NMR spectrum showed the expected 2 ABCD pattern for the Cp′ ring protons (δ 5.6–5.2). The resonances of the Cp′ methyl protons, however, were coincident and only one singlet was observed at δ 2.12. The infrared spectrum in the carbonyl region was very similar to that of the mono(arylphosphine) adducts[17] (1994 (s) and 1950 (s, br) cm^{-1}) with the ν_{CN} band appearing at 2135 (m, br) cm^{-1}.

The behavior of 1 with different nucleophiles may be understood with respect to the kinetic acheme shown in eq 2. The steady-state concentration of intermediate 2 is given by $K[1][L]/(1 + k_2/k_{-1})$, where L is the nucleophile and $K = k_1/k_{-1}$. With less basic arylphosphines, K is small with respect to $1 + k_2/k_{-1}$ and detectable concentrations of 2 do not form. With Me_3P and MeNC, K is large with respect to $1 + k_2/k_{-1}$ at low temperature, but the temperature dependences of the k_i values are different for the two adducts **2a** and **2b**. In the former case, k_{-1} increases faster with increasing temperature than either k_1 or k_2 and the adduct decomposes back to starting materials. In the case of **2b**, it is k_2 that shows the greatest increase with temperature and CO substitution is observed. These different behaviors presumably arise from the different donor/acceptor properties of the various ligands. Trimethylphosphine is a strong σ-donor and causes a strengthening of the Co–CO bonds; therefore, the phosphine is preferentially displaced. The π-acceptor quality of the isocyanide ligand decreases the Co–CO bond strength, thus promoting loss of a carbonyl.



(2)

The reactivity of 1 with CO was investigated by NMR and IR spectroscopy.[21] At 1450 psi of CO, 40% of 1 is converted to $Cp'_2Mo_2Co_2S_3(CO)_5$ (**2c**; $K_p \approx 6.8 \times 10^{-3}$ atm^{-1} for reaction 3). Removal of CO allows **2c** to completely revert to 1.

The NMR spectrum of **2c** shows the expected ABCD pattern (δ 4.90–4.65) for the Cp′ ring protons and a singlet

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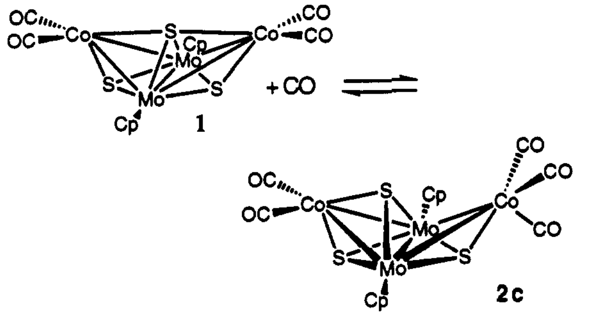
[19] Crystal data: monoclinic, *Pn* (No. 7), $a = 7.089$ (1) Å, $b = 18.669$ (6) Å, $c = 18.469$ (4) Å, $\beta = 90.84$ (2)°, $T = -100$ °C, $V = 2448$ (1) Å^3, $Z = 4$, $R = 0.0404$, $R_w = 0.0500$. See the supplementary material for complete crystallographic data.

[20] $Cp'_2Mo_2Co_2S_3(CO)_4$ (1; approximately 20 mg, 0.03 mmol) was dissolved in 0.7 mL of a 1:1 $CDCl_3/CCl_4$ mixture in an NMR tube and cooled to −65 °C. MeNC (1.0 μL, 0.02 mmol) was added and the tube placed into the NMR spectrometer at −20 °C. NMR spectra were recorded as the temperature was allowed to rise. The reaction was also followed by infrared spectroscopy: a solution of 1 (7.7×10^{-3} M) and MeNC (8.0×10^{-3} M) in toluene at −94 °C was syringed into an infrared solution cell cooled to −78 °C. Spectra were then collected as the temperature was allowed to rise. $Cp'_2Mo_2Co_2S_3(CO)_4(MeNC)$ (**2b**): ^1H NMR ($CDCl_3/CCl_4$) δ 5.30 (m, 2 H), 5.05 (m, 4 H), 5.01 (m, 2 H), ABCD pattern for Cp *H*, 3.51 (s, 3 H, $CNCH_3$), 2.07 (s, 6 H, $CpCH_3$); IR (toluene) ν(CN) 2170 (w, br) cm^{-1}, ν(CO) 2003 (mw, br), 1984 (s), 1958 (m, br), 1940 (m) cm^{-1}. $Cp'_2Mo_2Co_2S_3(CO)_3(MeNC)$ (**3**): ^1H NMR ($CDCl_3/CCl_4$) δ 5.59 (m, 4 H), 5.24 (m, 4 H) 2 ABCD pattern for Cp′ *H*, 3.48 (s, 3 H, $CNCH_3$), 2.12 (s, 6 H, $CpCH_3$); IR ($CDCl_3/CCl_4$) ν(CN) 2135 (m, br) cm^{-1}, ν(CO) 1994 (s), 1950 (s, br) cm^{-1}. These spectroscopic properties are nearly identical with those of the corresponding *tert*-butyl isocyanide complex $Cp'_2Mo_2Co_2S_3(CO)_3(^tBuNC)$, which was isolated and characterized by satisfactory elemental analysis.

[21] 1 was loaded into a high-pressure sapphire NMR tube and dissolved in toluene-d_8. The reaction with CO was monitored as the pressure of CO was increased to 1450 psi, at which point 40% of 1 was converted to $Cp'_2Mo_2Co_2S_3(CO)_5$ (**2c**). Removal of CO showed complete converstion of **2c** back to 1. The reaction was also investigated by infrared spectroscopy with an internal reflectance cell under 800 psi of CO. $Cp'_2Mo_2Co_2S_3(CO)_5$ (**2c**): ^1H NMR (toluene-d_8) δ 4.90 (m, 2 H), 4.77 (m, 2 H), 4.69 (m, 2 H), 4.65 (m, 2 H) ABCD pattern for Cp′ *H*, 1.76 (s, 6 H, $CpCH_3$); IR (C_6H_6) ν(CO) 2040 (m), 1987 (s), 1958 (s, br), 1940 (sh) cm^{-1}.



(3)

(δ 1.76) for the methyl protons. The infrared spectrum, obtained with an internal reflectance cell, shows two ν_{CO} bands at 2040 (m) and 1958 (s, br) cm^{-1}, which may be assigned to the Co(CO)$_3$ fragment. The two peaks at 1987 (s) and 1940 (sh) cm^{-1} are assigned to the Co(CO)$_2$ group. The formation of **2c** may account for the lack of desulfurization catalysis when **1** is heated with thiols at 150 °C under 1000 psi of CO.[22]

While Co–S bond breaking clearly occurs in the course of these carbonyl substitution reactions, kinetic studies are necessary to determine if this occurs prior to nucleophilic attack in a preequilibrium step or if Co–S bond breakage is initiated by the nucleophile. These studies are currently underway; preliminary results indicate that the conversion of **2** to **3** is also reversible.

The electronic unsaturation of cluster **1**, and consequently the weaker Co–(μ_4-S) bond,[23] accounts for its unusual reactivity toward nucleophiles. Cluster **1** has 60 valence shell electrons (VSE) but only 5 M–M bonds (rather than the 6 M–M bonds usually present in 60-VSE clusters). Addition of a nucleophile to **1** converts it into an electronically saturated, 62-VSE, 5-M-M-bonded cluster. Although this type of reaction should be general, the sparse number of unsaturated clusters limits the known examples.[3e,i,12,13,24]

Acknowledgment. M.D.C. thanks the National Science Foundation (Grant No. CHE-8619864) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The high-pressure NMR and IR experiments carried out at TAMU were sponsored by NSF grant CHE-8817873 to D. J. Darensbourg. We thank Prof. Darensbourg for the generous use of this equipment.

Supplementary Material Available: Tables listing X-ray data, atomic positional parameters, thermal parameters, bond distances, bond angles, and H atom coordinates (18 pages). Ordering information is given on any current masthead page.

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Carbon Dioxide Chemistry of the Trinuclear Complex [Ni$_3$(μ_3-CNMe)(μ_3-I)(dppm)$_3$][PF$_6$]. Electrocatalytic Reduction of Carbon Dioxide

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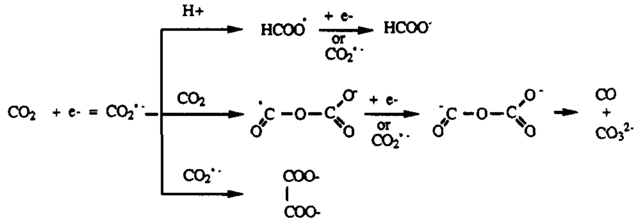
Received April 3, 1992

Summary: The triangular nickel complex [Ni$_3$(μ_3-CNMe)(μ_3-I)(dppm)$_3$][PF$_6$] (1) is an electrocatalyst for the reduction of CO$_2$. Complex 1 exhibits a reversible single-electron reduction at $E_{1/2}$ = −1.09 V vs Ag/AgCl. In the presence of CO$_2$, 1 reduces CO$_2$ by an apparent EC′ electrochemical mechanism. The reduction products correspond to the reductive disproportionation of CO$_2$ to CO and CO$_3^{2-}$. Isotope labeling studies with ^{13}CO$_2$ indicate that ^{13}CO$_2^{\bullet-}$ disproportionation produces only ^{13}CO and ^{13}CO$_3^{2-}$. In the presence of an H$^+$ donor, only HCO$_2^-$ is observed.

The reduction of carbon dioxide has been investigated by chemical,[1-18] electrochemical,[19-25] and photochemical[26-30] means. The direct reduction of carbon dioxide at most electrode surfaces is impeded by large overpotentials for

Scheme I



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