Phosphorus Abstraction Reactions Related to Hydrodesulfurization: Formation of $Cp'_2Mo_2Co_2S_3(CO)_2(\mu_3\text{-}PR)$ from $Cp'_2Mo_2Co_2S_3(CO)_4$ and Phosphines

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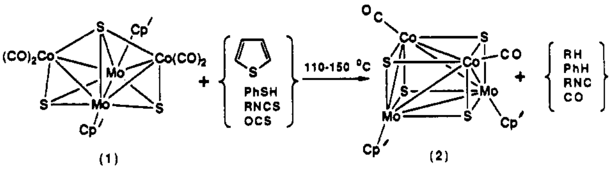
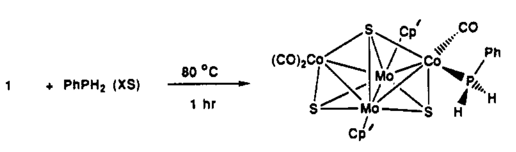
Summary: The cluster $Cp'_2Mo_2Co_2S_3(CO)_4$ (**1**) ($Cp' = C_5H_4Me$) abstracts the phosphinidene group R–P at 80 °C from phenylphosphine to form the cubane-like cluster $Cp'_2Mo_2Co_2S_3(CO)_2(\mu_3\text{-}PPh)$ (**4**) probably via the phosphine adduct $Cp'_2Mo_2Co_2S_3(CO)_3(PH_2Ph)$ (**3**). This is analogous to the desulfurization of thiols and thiophene by **1**. Further reaction with the phosphine leads to the phosphine-substituted cubane $Cp'_2Mo_2Co_2(CO)(PH_2Ph)S_3(\mu_3\text{-}PPh)$ (**5**). Reactions of **1** with diphenylphosphine are faster and form the monophosphine adduct as well as the cis and trans diadducts. Further reaction at 110 °C with an excess of the phosphine does not give a clean reaction; however, some benzene is observed to form. Crystal data for **4**: space group $Pc2_1n$, $Z = 4$, $a = 10.210\ (2)$ Å, $b = 12.767\ (3)$ Å, $c = 18.097\ (4)$ Å, $\alpha = \beta = \delta = 90.000°$, $V = 2358.8\ (7)$ Å^3, $R = 5.84$, $R_w = 4.93$ based on 1995 reflections with $F_o \geq 0.6\sigma(F)$.

Hydrodesulfurization (HDS) and related "hydrotreating" processes, e.g., hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO), are of increasing importance in fossil fuel refining.[1] The most common industrial hydrotreating catalysts are based on Mo/Co/S species supported on alumina.[2] We recently reported that discrete Mo/Co/S clusters, e.g., $Cp'_2Mo_2Co_2S_3(CO)_4$ (1) ($Cp' = C_5H_4Me$) produce the same active site as commercial catalysts when supported on alumina and sulfided in the conventional manner.[3] Cluster 1 has also been shown to abstract sulfur from organic and inorganic sulfur compounds, e.g., thiophene, thiophenol, RNCS, and OCS, under relatively mild conditions (one or both carbonyl groups on 2 are displaced during the reaction when X = RNC, eq 1).[4]



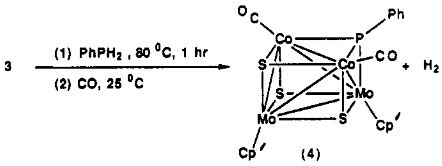
(1) (2) (1)

We now report that cluster 1 also abstracts the phosphinidene group R–P, isoelectronic with sulfur, from organic phosphines probably via intermediate phosphine adducts. Thus, 1 reacts with excess $PhPH_2$ in refluxing benzene (1 h) to give the phenylphosphine adduct 3[5] (eq 2). Adduct 3, in the presence of $PhPH_2$ (to inhibit dis-



(3) (2)

sociation of the phosphine), reacts further (80 °C, 2 h), presumably with loss of H_2 and CO, to give a mixture of the phenylphosphinidene cluster $Cp'_2Mo_2S_2(CO)_2S_3(PPh)$, 4 (eq 3), and the phosphine adduct of 4, $Cp'_2Mo_2Co_2(CO)(PH_2Ph)S_3(PPh)$ (5). The latter is converted to 4 by stirring the reaction mixture under CO.



(4) (3)

Complex 3 exhibits two ABCD multiplets[5] (δ 5.43–4.62) due to the inequivalent, diastereotopic Cp′ groups and two singlets for the Cp′-*Me* groups at δ 1.92 and 1.85. The P–H protons are also diastereotopic and appear at δ 4.99 ($J_{P\text{-}H}$ = 314 Hz) and δ 4.98 ($J_{P\text{-}H}$ = 324 Hz, $J_{H\text{-}H}$ = 6.84 Hz). Cluster 4 contains a plane of symmetry, so the chemically distinct Cp′ groups show two A_2B_2 pattern[6] (δ 5.24–4.84) for the ring protons and two singlets for the methyl protons (δ 1.79, 1.60).

Continued heating of the reaction mixture containing 4 and excess $PhPH_2$, or reaction of isolated 4 and $PhPH_2$, in refluxing benzene, leads to the green/brown phosphine-substituted cubane 5. Substitution of one carbonyl by the phosphine destroys the mirror plane in 4, and the Cp′ resonances again exhibit the ABCD pattern charac-

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(5) Complex **3** was obtained in 65% yield from the reaction of **1** (0.42 mmol) with $PhPH_2$ (1.36 mmol) in toluene at room temperature for 8 days. The brown product was isolated by chromatography over alumina (3:1 toluene:hexane eluant). ^1H NMR (C_6D_6): δ 7.55 (m, 2 H, PhH), 7.03 (m, 3 H, PhH), 5.43 (m, 2 H), 5.30 (m, 1 H), 5.15 (m, 1 H), 5.11 (m, 2 H), 4.80 (m, 1 H), 4.62 (m, 1 H) 2ABCD pattern for CpH, 4.99 (dd, J_{HH} = 6.8 Hz, J_{PH} = 314 Hz, 1 H, PH), 4.98 (dd, J_{HH} = 6.8 Hz, J_{PH} = 324 Hz, 1 H, PH), 1.93 (s, 3 H, $CpCH_3$), 1.85 (s, 3 H, $CpCH_3$). ^{31}P NMR (C_6D_6): δ −36.8 ppm. IR (toluene): ν(CO) 1990 (s), 1942 (s, br) cm^{-1}. Anal. Calcd for $C_{21}H_{21}Co_2Mo_2O_3PS_3$: C, 33.26; H, 2.79. Found: C, 31.24; H, 2.63. Instability of the phenylphosphine adducts with respect to loss of ligand resulted in poor microanalysis results.

(6) Cluster **4** may also be prepared directly from **1** and $PhPH_2$. A solution of cluster **1** (0.30 g, 0.44 mmol) and $PhPH_2$ (0.3 mL, 2.7 mmol) in 50 mL of benzene was refluxed for 5 h. Solvent and excess phosphine were removed under vacuum, and the brown solid was dissolved in benzene. This solution was stirred under CO for 2 h (to convert the phosphine adduct of **4**, compound **5** (observed by IR spectroscopy) to the dicarbonyl). Flash chromatography gave 0.15 g (47%) of dark green crystals after recrystallization from CH_2Cl_2/hexane. ^1H NMR (C_6D_6): δ 7.52 (m, 2 H, PhH), 6.95 (m, 3 H, PhH), 5.25 (t, *J* = 2.3 Hz, 2 H), 5.02 (t, *J* = 2.3 Hz, 2 H), 5.00 (t, *J* = 2.3 Hz, 2 H), 4.84 (t, J = 2.3 Hz, 2 H), $2A_2B_2$ pattern for CpH, 1.79 (s, 3 H, $CpCH_3$), 1.60 (s, 3 H, $CpCH_3$). ^{31}P NMR (C_6D_6): δ 451.5 ppm. IR (benzene): ν(CO) 1968 (ms), 1952 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{19}Co_2Mo_2O_2PS_3$: C, 33.01; H, 2.63. Found: C, 33.12; H, 2.55.

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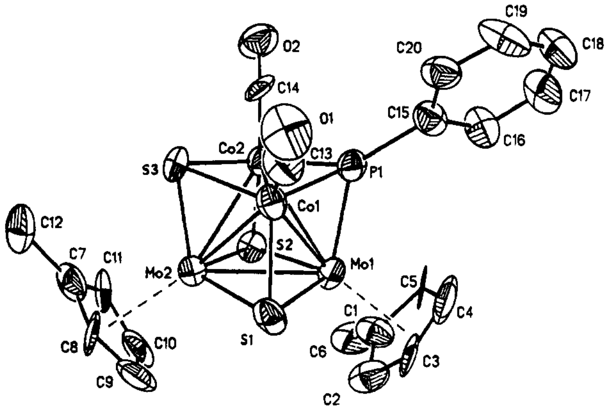
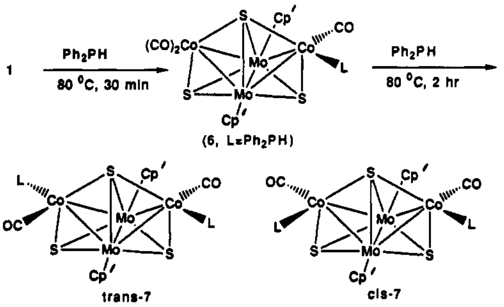


Figure 1. ORTEP plot of $Cp'_2Mo_2Co_2S_3(PPh)(CO)_2$ (4).

teristic of a diastereotopic environment.[7]

Substitution reactions on 1 by Ph_2PH are faster than with $PhPH_2$. After 8 h at ambient temperature or after 30 min in refluxing benzene, formation of the monoadduct $Cp'_2Mo_2Co_2S_3(CO)_3(PHPh_2)$ (6) is complete,[8] and after 3 h in refluxing benzene, a mixture of the cis and trans diadduct 7 is formed (eq 4).[9]



(4)

As with complexes 3 and 5, 6 exhibits two ABCD multiplets (δ 5.42–4.77) and two singlets for the Cp–Me groups (δ 1.92 and 1.87). The P–H proton appears as a doublet at δ 5.89 with $J_{P-H} = 320$ Hz. Although the cis and trans diadducts 7 cannot be separated by chromatography, their NMR spectra are quite distinct; the cis adduct has C_s symmetry and thus shows two A_2B_2 patterns for the Cp hydrogens (δ 5.57–4.68) and two singlets for the Cp–Me groups (δ 2.05 and 1.91). The trans adduct, however, has C_2 symmetry and shows an ABCD pattern for CpH (δ 5.54–4.86) and one singlet for the Cp–Me groups (δ 2.00).

Refluxing a toluene solution of a mixture of *cis-* and *trans*-7 with excess Ph_2PH does not result in a clean abstraction of a phosphinidene group to give cluster 4. Some benzene was observed to form, however, indicating that some C–P bond breaking does occur. It is possible that competing reactions, e.g., sulfur abstraction from 1 or 4 by the excess phosphine, are responsible for the complexity of this reaction.

The cubane-like structure[10] of 4 (Figure 1) is very similar to that of 2[11] with one μ_3-S ligand replaced by the μ_3-PR group. The Co–P bonds in 4 appear to be anomalously short (2.152 (5) and 2.158 (5) Å) when compared to the Co–S distances (2.22 ± 0.01 Å in 2 and 4), since the covalent radius of phosphorus is expected to be ca. 0.06 Å larger than that of sulfur.

Formation of phosphinidene clusters from phenylphosphine has been observed before, with the H atoms often ending up as hydride ligands[12] rather than being lost as H_2.[13] In some cases, intermediate species containing μ_2-RPH ligands are observed.[13] Cleavage of P–O and P–C bonds has also been observed in the synthesis of μ_3-RP clusters.[12] The isoelectronic/isolobal set of clusters, $Fe_2(\mu_3\text{-}X)(\mu_3\text{-}Y)(CO)_9$ (X, Y = S, PR), are also known.[14]

The similarity between the desulfurization of thiols by 1 and the reaction of 1 with $PhPH_2$ and Ph_2PH suggests the first step in the desulfurization process is a carbonyl replacement. Further work is being done to elucidate the mechanism of the desulfurization and phosphorus abstraction reactions exhibited by complex 1.

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Supplementary Material Available: Tables listing X-ray data, atomic positional parameters, thermal parameters, bond distances, bond angles, and H-atom coordinates (11 pages); a table of F_o and F_c (8 pages). Ordering information is given on any current masthead page.

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(7) Complex 5: ^1H NMR (C_6D_6): δ 7.53 (m, 4 H, PhH), 7.00 (m, 6 H, PhH), 6.30 (m, $J_{PH} \sim 315$ Hz, 2 H, PH_2), 5.41 (m, 2 H), 5.16 (m, 2 H), 5.12 (m, 2 H), 5.02 (m, 2 H) 2ABCD pattern for CpH, 1.93 (s, 3 H, $CpCH_3$), 1.79 (s, 3 H, $CpCH_3$). IR (toluene): ν(CO) 1947 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{28}Co_2Mo_2OP_2S_3$: C, 37.05; H, 3.23. Found: C, 32.90; H, 2.94. Instability with respect to loss of ligand resulted in poor microanalysis results.

(8) Cluster 1 (0.150 g, 0.22 mmol) was dissolved in 30 mL of toluene. Ph_2PH (0.3 mL, 1.6 mmol) was added and the solution stirred overnight. Chromatography down a 25-cm column of alumina with 3:1 toluene/hexane eluted a dark brown band of $Cp'_2Mo_2Co_2S_3(CO)_3(Ph_2PH)$ (6) (0.11 g, 60% yield) followed by a small brown band of $Cp'_2Mo_2Co_2S_3(CO)_2(Ph_2PH)_2$. A small green band was not eluted. ^1H NMR (C_6D_6): δ 7.5 (m, 4 H, PhH), 7.05 (m, 6 H, PhH), 5.42 (m, 2 H), 5.35 (m, 1 H), 5.25 (m, 1 H), 5.09 (m, 1 H), 5.06 (m, 1 H), 4.89 (m, 1 H), 4.77 (m, 1 H) 2ABCD pattern for CpH, 5.89, (d, $J_{PH} = 320$ Hz, 1 H, PH), 1.92 (s, 3 H, $CpCH_3$), 1.87 (s, 3 H, $CpCH_3$). IR (toluene): ν(CO) 1988 (s), 1941 (s, br) cm^{-1}. Anal. Calcd for $C_{27}H_{25}Co_2Mo_2O_3PS_3$: C, 38.87; H, 3.02. Found: C, 39.34; H, 3.17.

(9) A solution of cluster 1 (0.129 g, 0.19 mmol) and Ph_2PH (0.17 mL, 0.96 mmol) in 30 mL of benzene was refluxed under a slow stream of N_2 for 3 h. Chromatography down a 20-cm column on alumina with 4:1 benzene/hexane eluted a dark brown band of a 2:1 mixture of *trans*- and *cis*-$Cp'_2Mo_2Co_2S_3(CO)_2(Ph_2PH)_2$ (0.11 g, 58% yield). A small green band could not be eluted. ^1H NMR (C_6D_6): *cis*-$Cp'_2Mo_2Co_2S_3(CO)_2(Ph_2PH)_2$ δ 7.75 (m, 8 H, PhH), 7.05 (m, 12 H, PhH), 6.06 (d, $J_{PH} = 317$ Hz, 2 H, PH), 5.57 (t, $J = 2.3$ Hz, 2 H), 5.25 (t, $J = 2.3$ Hz, 2 H), 5.21 (t, $J = 2$ Hz, 2 H), 4.68 (t, $J = 2$ Hz, 2 H) $2A_2B_2$ pattern for CpH, 2.01 (s, 3 H, $CpCH_3$), 1.91 (s, 3 H, $CpCH_3$); *trans*-$Cp'_2Mo_2Co_2S_3(CO)_2(Ph_2PH)_2$ δ 7.75 (m, 8 H, PhH), 7.05 (m, 12 H, PhH), 6.05 (d, $J_{PH} = 317$ Hz, 2 H, PH), 5.54 (m, 2 H), 5.34 (m, 2 H), 5.06 (m, 2 H), 4.86 (m, 2 H) ABCD pattern for CpH, 2.00 (s, 6 H, $CpCH_3$). IR of mixture (toluene): ν(CO) 1933 (sh), 1917 (s) cm^{-1}. Anal. Calcd for $C_{38}H_{36}Co_2Mo_2O_2P_2S_3$: C, 45.98; H, 3.65. Found: C, 46.04; H, 3.92.

(10) Crystal data: orthorhombic, $Pc2_1n$ (alternate setting of $Pna2_1$, No. 33), $a = 10.210$ (2) Å, $b = 12.767$ (3) Å, $c = 18.097$ (4) Å, $\alpha = \beta = \delta = 90.000°$, T = ambient, $V = 2358.8$ (7) Å^3, $Z = 4$, $R = 0.0584$, $R_w = 0.0493$. See supplementary material for complete crystallographic data.

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