

Chemistry of the Group IB Metals. IX* Preparation of a Complex Containing a Copper-Molybdenum Bond

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Abstract

The reaction between $\text{Cu}(\text{CO})[\text{HB}(\text{pz})_3]$ and $\text{MoH}_2(\text{C}_5\text{H}_5)_2$ affords $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{H})_2\text{Cu}[\text{HB}(\text{pz})_3]$, containing a Cu-Mo bond.

We have previously reported the synthesis,^{1,2} structure³ and some reactions^{2,4} of the copper(I) carbonyl derivative $\text{Cu}(\text{CO})[\text{HB}(\text{pz})_3]$ (pz = pyrazolyl, $\text{C}_3\text{H}_3\text{N}_2$), and have noted the pronounced tendency for replacement of the carbonyl group by other, stronger σ -donor ligands.

X-ray studies have suggested that the complex hydride $\text{MoH}_2(\text{C}_5\text{H}_5)_2$ contains a non-bonding electron pair in an orbital located in the plane containing the metal atom, and directed between the two, tilted rings.⁵ The basicity of this complex, and that of the tungsten analogue, has been demonstrated by their protonation,⁶ and adduct formation with BF_3 ⁷ or AlR_3 (R = Me, Et or Ph).^{8,9} In addition, the complexes $(\text{C}_5\text{H}_5)_2\text{M}(\text{H})_2\text{M}'(\text{CO})_5$ (M = Mo or W; M' = Cr, Mo or W), containing M-M' bonds, are formed in reactions between the hydrides and $\text{M}(\text{CO})_5(\text{thf})$.¹⁰ The donor power of the complex hydrides has been estimated as comparable to that of pyridine or PPh_3 .

We considered it likely that the reaction between the carbonyl and the dihydride would produce a complex containing a Mo→Cu bond. Previously, several complexes containing copper bonded to a transition metal moiety have been described, and have

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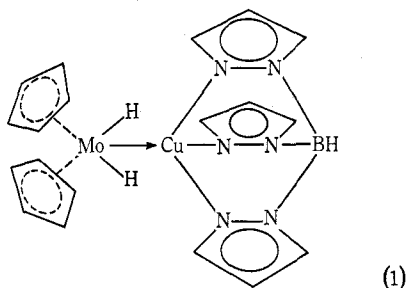
⁹ Storr, A., and Thomas, B. S., *Can. J. Chem.*, 1971, 49, 2504.

¹⁰ Deubzer, B., and Kaesz, H. D., *J. Am. Chem. Soc.*, 1968, 90, 3276.

tertiary phosphines or arsines attached to the copper.¹¹ More recently, the interaction of several carbonylmetal anions with copper(I) chloride has given complexes such as $\{\text{Cu}[\text{M}(\text{CO})_3(\text{C}_5\text{H}_5)_2]_2\}^-$ or $[\text{CuCo}(\text{CO})_3(\text{PBu}_3)]_n$,¹² while reactions of some rhodium(I) and iridium(I) complexes with copper(I) trifluoroacetate, triazimide or formamidine derivatives afforded complexes containing $\text{M}' \rightarrow \text{Cu}$ bonds ($\text{M}' = \text{Rh}$ or Ir).¹³

The addition of $\text{Cu}(\text{CO})[\text{HB}(\text{pz})_3]$ to a benzene solution of $\text{MoH}_2(\text{C}_5\text{H}_5)_2$ resulted in immediate effervescence, presumably of carbon monoxide, and a pale yellow product crystallized out within a few minutes. Analyses were consistent with the formula $(\text{C}_5\text{H}_5)_2\text{MoH}_2\text{Cu}[\text{HB}(\text{pz})_3]$, while the mass spectrum contained peaks arising from $[\text{Cu}_2\{\text{HB}(\text{pz})_3\}_2]^+$ and $[\text{MoH}_2(\text{C}_5\text{H}_5)_2]^+$ and their fragmentation products, ions containing molybdenum being relatively weak. The infrared spectrum contained a medium intensity $\nu(\text{BH})$ absorption at 2461 cm^{-1} , but did not show any bands which could be assigned to $\nu(\text{MoH})$ in the $1800\text{--}2200\text{ cm}^{-1}$ region. However, a broad band at 1598 cm^{-1} may result from some metal-hydrogen stretching mode, reduced by some interaction with electrons of the other metal-ligand moiety, in a similar manner to that postulated by Kaesz and his coworkers for the Group VI carbonyl complexes.¹⁰

The proton n.m.r. spectrum contained five signals, three assigned to the protons of the equivalent pyrazolyl groups at τ 2.38, 2.51 and 3.87, a sharp triplet at τ 5.14 for the cyclopentadienyl protons, and a high-field resonance at τ 18.98. The latter was a broad band, coupled to the cyclopentadienyl protons.



The most likely structure for this complex is (1), containing a dative molybdenum-to-copper bond. Attempts to detect a $\nu(\text{MoCu})$ vibration by laser Raman spectroscopy were unsuccessful, resulting only in decomposition of the complex. The equivalence of the pyrazolyl groups, shown in the proton n.m.r. spectrum, may arise either by rotation of the $\text{Cu}[\text{HB}(\text{pz})_3]$ moiety about the Mo-Cu axis, or by rotation of the pyrazolyl groups around the Cu-B axis, as described earlier for the complex $\text{Mo}(\text{CO})_2(\text{C}_3\text{H}_5)[\text{HB}(\text{pz})_3]$.¹⁴

The complex is very air-sensitive in solution, and decomposes slowly if kept in air, even as a solid. It can be kept for several weeks without decomposition under vacuum. It is another example of the growing family of complexes formed by donation of non-bonding electrons of one metal atom to a suitable second metal atom, with formation of a two-electron metal-metal bond, the first to be described for the Group IB metals.

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Experimental

Spectra were obtained on Perkin-Elmer 457 (infrared), Varian Associates HA100 (^1H n.m.r.) or AEI-GEC M3902 (mass) instruments. Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen in dry, redistilled solvents. Literature methods were used to prepare $\text{Cu}(\text{CO})[\text{HB}(\text{pz})_3]^2$ and $\text{MoH}_2(\text{C}_5\text{H}_5)_2$.¹⁵

Preparation of $(\text{C}_5\text{H}_5)_2\text{MoH}_2\text{Cu}[\text{HB}(\text{pz})_3]$

Solid $\text{Cu}(\text{CO})[\text{HB}(\text{pz})_3]$ (305 mg, 1 mmol) was added to a solution of $\text{MoH}_2(\text{C}_5\text{H}_5)_2$ (228 mg, 1 mmol) in benzene (20 ml). During the addition, gas was evolved from the solution. The reaction mixture was stirred for 15 min at room temperature, during which time a pale yellow precipitate was formed. On heating, the precipitate dissolved, but separated out again on cooling. Addition of light petroleum (b.p. 40–60°) to the mixture resulted in further deposition of bright yellow crystals of the complex, which were filtered off, and washed with light petroleum (total yield 440 mg, 87%). The compound decomposed slowly above 130° (sealed tube) (Found: C, 45.0; H, 4.4; Cu, 12.0; Mo, 18.7; N, 16.4. $\text{C}_{19}\text{H}_{22}\text{BCuMoN}_6$ requires C, 45.2; H, 4.4; Cu, 12.5; Mo, 19.1; N, 16.7%). Proton n.m.r. (CDCl_3): τ 2.38 d, 2.51 d (H 3 and H 5), 3.87 t (H 4), 5.14 t (C_5H_5 , $J_{\text{H,H}}$ 0.4 Hz), 18.98 m, br (MoH_2); relative intensities 3 : 3 : 3 : 10 : 2.

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