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Preliminary communication

Pentacarbonylrhenium(μ-hydrido)pentacarbonylchromium and related compounds

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Few compounds are known in which a single hydrogen atom forms the only bridge between two transition metals. They are $[HM_2(CO)_{10}]^-$ (M = Cr, Mo, W)[1,2], $HRe_2Mn(CO)_{14}$[3,4], $HRe_3(CO)_{14}$* and $HRe_2(CO)_9SiRCl_2$[5]. X-ray diffraction results show that only $[HCr_2(CO)_{10}]^-$ and its isomorphous Mo and W analogs have linear metal–hydrogen–metal linkages. We report here the synthesis of members of the series $HM'M(CO)_{10}$ (M = Cr, Mo, W; M' = Mn, Re) which possess this rare structural characteristic. Moreover, they provide the first examples in which transition metals of different periodic groups are bridged by a hydrogen atom only.

A sample[6] of $Et_4N^+[ReCr(CO)_{10}]^-$ was stirred as a slurry in n-pentane over 85% phosphoric acid for 2 days. The pentane layer was cooled to −78° to give a yellow solid consisting of $HReCr(CO)_{10}$, $HRe_3(CO)_{14}$, and $Cr(CO)_6$, with the first predominating. Owing to decomposition in solution, $HReCr(CO)_{10}$ could not be purified by crystallization, but fractional sublimation in an evacuated tube resulted in a very low yield of beautifully formed orange crystals. The mass spectrum of these crystals exhibited all peaks of the series $[HReCr(CO)_n]^+$ (n = 0–10) and there was no hydrogen loss from the molecular ion.

Crystals of $HReCr(CO)_{10}$ are triclinic, space group $P\bar{1}$; $a = 9.689(4)$, $b = 8.970(5)$, $c = 9.357(5)$ Å, $\alpha = 115.85(4)°$, $\beta = 90.77(4)°$, $\gamma = 98.80(3)°$; $Z = 2$. Data collection (Mo-K_α radiation, Picker automatic diffractometer) yielded 2405 reflections having $F \geqslant 3\sigma(F)$. Our initial model refined well except that the Cr temperature factor became negative. We then changed to a model in which the Re site scattering factor was 80% of that for Re and 20% of that for Cr; similarly, the chromium site was considered 80% Cr and 20% Re. This model converged with $R = 0.058$, major population 79.1% with anisotropic thermal parameters for the two heavy atoms. The structure is shown in Fig. 1. The Re site to Cr site distance is 3.435(1) Å, leaving no doubt as to the bridging position of hydrogen, even though the latter could not be crystallographically located. The two metal pentacarbonyl groups adopt an eclipsed conformation, and imply a linear Re–H–Cr bond because the least squares

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*Unpublished X-ray results of R.P. White, Jr., T.E. Block and L.F. Dahl, quoted in reference 2.

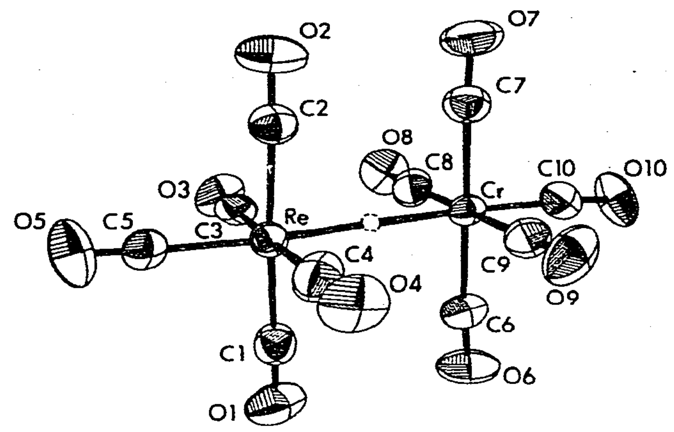

Fig. 1. The molecular structure of disordered (OC)$_5$ReHCr(CO)$_5$, showing 50% probability thermal ellipsoids. The Re site to Cr site distance is 3.435(1) Å. Hydrogen was not located, but is considered to be colinear with the metal atoms and is shown arbitrarily at the mid-point.

planes containing equatorial CO groups are within 2.5° of being parallel.

Although all hydrogen-bridged metal—metal distances exceed those expected in a direct metal—metal bond, it is noteworthy that they fall into a "long" group and a "short" group. The HReCr(CO)$_{10}$ structure belongs to the "long" group, together with [(OC)$_5$CrHCr(CO)$_5$]$^-$ (3.41 Å[1,2]) and HMnRe$_2$(CO)$_{10}$ (3.392 Å[3,4]); all members of this group have the eclipsed pattern of radial carbonyls. Known structures having the "short" bridged distance are HRe$_3$(CO)$_{12}$ (3.295 Å[2]), HRe$_2$(CO)$_9$SiCl$_3$ (3.274 Å[5]), and HW$_2$(CO)$_9$NO (3.329 Å[7]), all of which have the staggered arrangement of radial carbonyls.

Protonation of [ReW(CO)$_{10}$]$^-$ at 0° under conditions similar to those used for the chromium compound afforded HReW(CO)$_{10}$. This compound is much more stable in solution, and could be obtained as a microcrystalline yellow solid, free of carbonyl-containing impurities, by crystallization of the pentane extract at —80°. It was characterized by mass spectrometry and analysis and exhibited a broad, very weak NMR signal at τ 24.4 in C$_6$D$_6$ (τ 24.2 in CD$_2$Cl$_2$). The infrared spectrum showed six carbonyl stretching bands at 2141, 2070, 2038, 2014, 1942, and 1936 cm^{-1} (cyclohexane), as expected for D_{4h} symmetry.

Other members of the HMM′(CO)$_{10}$ series which we have investigated are less stable, and it appears that some will not be isolable. Protonation of [MnW(CO)$_{10}$]$^-$ afforded HMnW(CO)$_{10}$ (identified by mass spectrometry) together with HMn(CO)$_5$ and W(CO)$_6$ as decomposition products in solution, but sealed tube sublimation of the impure solid resulted only in Mn$_2$(CO)$_{10}$ and W(CO)$_6$. Protonation of [ReMo(CO)$_{10}$]$^-$ gave HRe(CO)$_5$, Mo(CO)$_6$, and small amounts of HRe$_3$(CO)$_{14}$, while [MnCr(CO)$_{10}$]$^-$ yielded Cr(CO)$_6$, HMn(CO)$_5$, and an as yet uncharacterized product.

The compounds reported here are among the simplest metal carbonyl systems to contain a hydrogen bridge. The most suitable compound for further study, in view of its greater stability, is HReW(CO)$_{10}$, and work on its chemistry is in progress.

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REFERENCES

1 U. Anders and W.A.G. Graham, *Chem. Commun.*, (1965) 499; R.G. Hayter, *J. Amer. Chem. Soc.*, 88 (1966) 4376.

2 L.B. Handy, P.M. Treichel, L.F. Dahl and R.G. Hayter, *J. Amer. Chem. Soc.*, 88 (1966) 366; L.B. Handy, J.K. Ruff and L.F. Dahl, *ibid.*, 92 (1970) 7312.

3 W. Fellman and H.D. Kaesz, *Inorg. Nuclear Chem. Letters*, 2 (1966) 63.

4 H.D. Kaesz, R. Bau and M.R. Churchill, *J. Amer. Chem. Soc.*, 89 (1967) 2775; M.R. Churchill and R. Bau, *Inorg. Chem.*, 6 (1967) 2086.

5 J.K. Hoyano and W.A.G. Graham, *Inorg. Chem.*, 11 (1972) 1265; L.Y.Y. Chan and W.A.G. Graham, to be submitted for publication.

6 U. Anders and W.A.G. Graham, *J. Amer. Chem. Soc.*, 89 (1967) 539.

7 R. Bau, personal communication, 1972.