

$[\text{HM}_2(\text{CO})_{10}]^-$ (M = Cr, Mo, W): Protonated Covalent Metal–Metal Bonds

By UDO ANDERS and W. A. G. GRAHAM

(*Department of Chemistry, University of Alberta, Edmonton, Alberta*)

THE special properties of a hydrogen atom bonded to a transition metal have attracted considerable attention during the past several years.¹ Recently, an X-ray-crystallographic determination² of the structure of $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}_2\text{H}(\text{Me}_2\text{P})(\text{CO})_4]$ provided evidence for a three-centre metal–hydrogen–metal bond in this molecule. We now describe a convenient synthesis of the anions $[\text{HM}_2(\text{CO})_{10}]^-$

(M = Cr, Mo, W), and some observations which suggest a similar novel metal–hydrogen bonding in these species.

Sodium or tetra-alkylammonium salts of the anions $[\text{HM}_2(\text{CO})_{10}]^-$ can be rapidly and simply prepared by treating the hexacarbonyls of the sub-Group VI metals with sodium borohydride or tetra-alkylammonium borohydride in diglyme at

¹ J. Chatt, *Proc. Chem. Soc.*, 1962, 318.

² R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 1965, **87**, 2576.

temperatures from 60–150°. The salts, *e.g.*, $[\text{Et}_4\text{N}][\text{HCr}_2(\text{CO})_{10}]$ were characterized by a complete elemental analysis. Previously, these anions were obtained³ by a rather difficult route involving the use of liquid ammonia as a solvent, and no spectroscopic evidence as to their structure was provided.

Proton n.m.r. and infrared-spectroscopic studies suggest a structure for the anions in which the proton is equivalently bonded to the two metal atoms, *viz.*, $[(\text{OC})_5\text{M}(\text{H})\text{M}(\text{CO})_5]^-$. The high-resolution infrared spectrum of $[\text{HW}_2(\text{CO})_{10}]^-$ in the carbonyl region shows three bands centred at 2040(m), 1932(vs), and 1876(s) cm^{-1} , in accord with a structure of D_{4d} symmetry, like that of $\text{Re}_2(\text{CO})_{10}$, which also has three principal carbonyl stretching absorptions.⁴ The proton resonance spectra for the anions $[\text{HCr}_2(\text{CO})_{10}]^-$ and $[\text{HMo}_2(\text{CO})_{10}]^-$ show a single sharp band at τ 16.7 and 22.2, respectively. The anion $[\text{HW}_2(\text{CO})_{10}]^-$ shows a triplet centered at τ 22.5, with a proton-tungsten (¹⁸³W, $I=1/2$, 14.3%) coupling constant of 41.3 c./sec. The

relative band intensities of the triplet components are in accord with equivalent association of the proton with the two tungsten nuclei.⁵ A further noteworthy feature is the long relaxation time for the high-field proton; a value of approximately *two minutes* was measured for the molybdenum anion $[(\text{OC})_5\text{Mo}(\text{H})\text{Mo}(\text{CO})_5]^-$. This long relaxation time may be diagnostic for this type of three-centre bonding.

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Added in proof: Very shortly after submission of this communication, Dr. R. G. Hayter (Shell Development Co., Emeryville, California) reported similar results in a paper presented at the Second International Symposium on Organometallic Chemistry, Madison, Wisconsin. Dr. Hayter reported n.m.r. absorption for $[\text{HCr}_2(\text{CO})_{10}]^-$ at τ 29.17; we now confirm his finding and conclude that the τ 16.7 line also observed in our preparations is due to an impurity, perhaps $[\text{HCr}(\text{CO})_5]^-$.

³ H. Behrens and J. Vogl, *Chem. Ber.*, 1963, **96**, 2220; and references cited therein.

⁴ N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 1964, **3**, 1123.

⁵ A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3653.