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GENERATION OF GROUP VI BINUCLEAR METAL CARBONYL DIANIONS BY ION-PAIR EXTRACTION

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Summary

Ion-pair extraction has been used to provide a new synthetic route to binuclear dianions of the type $M_2(CO)_{10}^{2-}$ (M = Cr, Mo, W) from the corresponding μ-hydrido anions; yields are good to excellent (62–90%). ^{13}C NMR data for the binuclear dianions and μ-hydrides are reported and compared to that for the hydrido anions, $HM(CO)_5^-$. Efforts to prepare μ-methylene complexes by reactions of the binuclear dianions with dihaloalkanes resulted only in formation of haloanions, $M(CO)_5X^-$.

Introduction

During the past twenty years, a number of synthetic methods have been reported for the Group VI binuclear metal carbonyl dianions, $M_2(CO)_{10}^{2-}$. The older methods have generally employed alkali metal reductions [1] but a very recent method [2] described the preparation of magnesium salts of the dianions. All of these require cation exchange reactions before the more stable quaternary ammonium or PPN salts can be obtained. Although several of these methods are very effective in generating the dianions, the highly moisture-sensitive nature of the reductions requires the use of special handling techniques. We believe that the inconvenience in preparing these dianions is responsible, at least in part, for the limited synthetic uses which have been made of them [1h,3]. We have therefore sought to develop convenient syntheses of the quaternary ammonium salts of $M_2(CO)_{10}^{2-}$ in order to facilitate their use.

Results and discussion

Having effectively used ion-pair extraction techniques for the synthesis of quaternary ammonium salts of Group VI hydrido anions, $HM(CO)_5^-$ and μ-H-$M_2(CO)_{10}^-$ (M = Cr, W) [4], we have sought to develop a similar method for the binuclear dianions, $M_2(CO)_{10}^{2-}$ (M = Cr, Mo, W). Tetraethylammonium salts of

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these binuclear dianions were first prepared by Hayter [1c], but the yields were poor (35–50%). Since Hayter had noted (without elaboration) that deprotonation of the μ-hydrido anions led to the binuclear dianions, it seemed to us that deprotonations of the μ-hydrides under the strongly basic conditions of liquid–solid phase transfer catalysis by KOH/Et_4NHSO_4 might provide convenient preparative methods for the dianions. Samples of the μ-hydrides were prepared by our previously published methods [4,5] and treated with base as described in the Experimental section [6]; good to excellent yields of the binuclear dianions were obtained in all cases. As with our related syntheses of $HM(CO)_5^-$ [4], a small quantity of water is necessary to promote the phase transfer reaction; this must be carefully controlled since water does cause conversion of the dianions to the μ-hydrides. IR spectra of the reaction mixtures showed no evidence of bands which could be attributed to mononuclear dianions [1f], although small quantities of the hydrido anion $[HM(CO)_5^-]$ and acetamide were evident. The μ-hydrides are thermally quite stable and are not highly sensitive to air or moisture; thus they provide excellent "shelf" reagents for the synthesis of the dianions. The quaternary ammonium salts of the dianions can be stored for long periods of time (> 6 months) at low temperature (−20°C) in Schlenk vessels under nitrogen.

The ^{13}C NMR spectral data (carbonyls only) for the binuclear dianions and the μ-hydrides are summarized in Table 1. As with the hydrido anions, $HM(CO)_5^-$ [7], the *trans*-CO ligands in the μ-hydrido anions appear downfield from the corresponding *cis* ligands. With the binuclear dianions, this effect is reversed. With all three groups, the magnitude of δ follows the order Cr > Mo > W. With both $W_2(CO)_{10}^{2-}$ and μ-H-$W_2(CO)_{10}^-$ the *cis*-CO ligands are observed as a pair of doublets due to unequal coupling to the two tungsten atoms; we have not determined the magnitude of the J values.

As indicated above, few synthetic uses have been made of the binuclear dianions. The possibility that their behavior might parallel that of $Fe_2(CO)_8^{2-}$ led us to try reactions between $M_2(CO)_{10}^{2-}$ (M = Cr, W) and CH_2X_2 (X = Br, I) in hopes of preparing μ-methylene complexes [8]. Under the conditions tried, with either stoichiometric quantities of CH_2X_2 or excess reagent and at 0°C or ambient temperature, the only product observed was the haloanion, $M(CO)_5X^-$ (identified by spectral comparisons with authentic samples). The reactions are thus similar to one reported by Hayter [1c] in which $Cr_2(CO)_{10}^{2-}$ reacted with C_3F_7I to yield $Cr(CO)_5I^-$ exclusively. With a few exceptions, the binuclear dianions suffer metal–metal bond cleavage in reactions with electrophiles. Since the dianions are

TABLE 1

^{13}C NMR CHEMICAL SHIFTS [a] FOR $(Et_4N)_2[M_2(CO)_{10}]$ [b]

Anion	δ_{trans}	δ_{cis}
$Cr_2(CO)_{10}^{2-}$	242.18	242.79
$Mo_2(CO)_{10}^{2-}$	230.57	235.47
$W_2(CO)_{10}^{2-}$	219.45	223.15
μ-H-$Cr_2(CO)_{10}^-$	226.90	221.83
μ-H-$Mo_2(CO)_{10}^-$	213.79	210.13
μ-H-$W_2(CO)_{10}^-$	201.90	199.70

[a] Spectra were determined at 20°C in CD_3CN solution. [b] Carbonyl carbons only.

isoelectronic with $Mn_2(CO)_{10}$ and appear to have very weak metal–metal bonds [3], reactions with CH_2X_2 may result from halogen abstraction by $M(CO)_5^-$ or electron transfer from $M_2(CO)_{10}^{2-}$ followed by fragmentation rather than nucleophilic displacement leading to μ-CH_2-$M_2(CO)_{10}$.

Experimental

All reactions were carried out under an atmosphere of prepurified nitrogen. THF was dried over KOH, distilled and then stored over molecular sieves; CH_3CN was distilled from P_2O_5 and stored over molecular sieves under nitrogen. Hexane was treated with concentrated H_2SO_4 and distilled before use. Acetone was reagent grade and was dried over molecular sieves. Tetraethylammonium hydrogen sulfate was prepared as described previously [4]. Flake KOH (MCB) was powdered in a mortar under nitrogen (glovebag).

Infrared spectra were recorded on Perkin–Elmer 283 or 599B spectrophotometers and were calibrated against polystyrene film. ^{13}C NMR spectra were obtained on a Varian XL-300 spectrometer; peak positions are given in parts per million downfield (+) or upfield (−) from Me_4Si. Elemental analysis was performed by Galbraith Laboratories.

Preparation of $(Et_4N)_2[Cr_2(CO)_{10}]$. A mixture containing 1.00 g (1.92 mmol) of Et_4N^+ μ-H-$Cr_2(CO)_{10}^-$ [4], 1.08 g (19.3 mmol) powdered flake KOH, 0.44 g (1.94 mmol) Et_4N^+ HSO_4^- and 125 ml CH_3CN was placed in a three-necked flask fitted with a mechanical stirrer, a Claisen adapter containing a nitrogen inlet tube and a condenser with a gas outlet tube. Water, 0.5 ml, was then added to the mixture and the system was flushed with nitrogen and then heated to 70°C for 3.5 h. As evidenced by the IR spectrum of the solution, the reaction was complete after this time.

The mixture was then cooled to room temperature, filtered through celite under nitrogen into a Schlenk vessel and concentrated to dryness under vacuum. The resulting residue was triturated under N_2 with 40 ml of acetone (to remove dissolved potassium and quaternary ammonium salts) and again dried under vacuum. The residue was then triturated (under N_2) four times with small portions of a 10/1.5 mixture of THF/hexane (to remove $HCr(CO)_5^-$, acetamide and any residual $HCr_2(CO)_{10}^-$) followed by drying under vacuum. The residual product, 1.10 g (90%), had the following spectral properties: IR ν(CO)(CH_3CN) 2060 (vw), 1912 (m), 1885 (vs) and 1786 (m) cm^{-1} (lit. [1c] (KBr) 2050 (vw), 1960 (m) 1930 (vs) 1870 (s) and 1740 (m) cm^{-1}). After recrystallization from acetone/ether, the product had the following elemental analysis: Found: C, 48.34; H, 6.16; N, 4.35. $C_{26}H_{40}O_{10}N_2Cr_2$ calcd.: C, 48.45; H, 6.25; N, 4.35.

Preparation of $(Et_4N)_2[Mo_2(CO)_{10}]$. In the manner described above, 1.00 g (1.65 mmol) of Et_4N^+ μ-H-$Mo_2(CO)_{10}^-$ [5], 0.39 g (1.65 mmol) of Et_4N^+ HSO_4^-, 0.46 g (8.25 mmol) of powdered KOH and 125 ml of CH_3CN were mixed together under nitrogen followed by 0.5 ml H_2O. The resulting mixture was heated to 60°C for 3.5 h; an IR spectrum indicated that conversion to product was complete after this time. The product, 0.75 g (62%), was isolated as described above for the corresponding tungsten complex; the IR spectrum of the product showed the following carbonyl bands (CH_3CN): 1930 (m), 1890 (vs) and 1787 (m) cm^{-1} (lit. [1c] (KBr) 2035 (w), 2010 (w), 1930 (s), 1885 (vs), 1825 (s) 1800 (s) and 1740 (s) cm^{-1}).

Preparation of $(Et_4N)_2[W_2(CO)_{10}]$. In the manner described above for the chromium complex, 1.00 g (1.28 mmol) of Et_4N^+ μ-H-$W_2(CO)_{10}^-$ [4], 0.72 g (12.8 mmol) of powdered KOH, 0.92 g (1.28 mmol) of Et_4N^+ HSO_4^- and 125 ml of CH_3CN were mixed together under nitrogen followed by 0.5 ml H_2O. The mixture was heated to 70°C for 45 min, after which an IR spectrum indicated complete conversion of the μ-hydride. The product, 1.06 g (91%), was isolated as described above; its IR spectrum showed the following carbonyl bands (CH_3CN): 1940 (m), 1880 (vs) and 1790 (m) cm^{-1} (lit. [1c] (KBr): 2020 (vw), 1965 (sh), 1935 (s), 1890 (vs), 1825 (s), 1800 (s) and 1740 (s) cm^{-1}).

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