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THE PHOTOCHEMICAL SYNTHESIS OF $(Et_4N)[Mn_2(CO)_6(\mu\text{-}Cl)_3]$

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Summary

The title compound can be prepared photochemically from three different starting materials. Infrared and electronic spectral data are reported. Preliminary information on the bromo analogue is also presented.

Thermal preparations of tribridged hexacarbonyldimetal compounds have been reported in the past few years. The species $M_2(CO)_6(\mu\text{-}OH)_3^{3-}$ (M = Mo, W) were prepared by the direct action of KOH on $M(CO)_6$ [1-3]. Complexes of formula $Re_2(CO)_6(\mu\text{-}X)_3^-$ (X = OH, OMe, OEt, i-PrO, H) have also been synthesized, using either $Re(CO)_5Br$ or ReH_9^{2-} as the starting materials [4,5]; a photochemical preparation was also described but no details were reported [4]. The preparation of $Re_2(CO)_5(NO)(\mu\text{-}Cl)_3$ has been accomplished by the action of NO on $Re_2(CO)_8Cl_2$ in CCl_4 at 50°C [6]. Several manganese derivatives have been prepared by the action of NaN_3 on $Mn(CO)_5Br$ to yield $[Mn_2(CO)_6(\mu\text{-}N_3)_x(\mu\text{-}NCO)_{3-x}]^-$ (x = 0-3) [7]. A series of Group VI complexes of general formula $[M_2(CO)_6(\mu\text{-}X)_3]^{3-}$ (M = Cr, Mo, W; X = halogen, OH, SCN, N_3, OEt) have also been reported [8].

The photochemistry of $Mn_2(CO)_{10}$ has so far been limited to the producttion of axially- or equatorially-substituted Lewis base complexes and to reactions which result in the cleavage of the Mn—Mn bond [9]. In this paper we report the photochemical preparation of the first tribridged halide derivative of manganese carbonyl, $Mn_2(CO)_6(\mu\text{-}Cl)_3^-$, starting with $Mn_2(CO)_{10}$. Infrared and UV-visible spectral data of this complex are presented along with a discussion of possible intermediates in its formation. Work on the related bromo complex is also reported.

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Experimental

Et_4NCl was obtained commercially and used without further purification. $Mn_2(CO)_{10}$ was prepared by the method of King [10]. All solvents were reagent grade and used without further purification. The infrared spectra in CH_2Cl_2 (KBr cells) were obtained on a Beckman IR-9 spectrophotometer which had been calibrated against polystyrene. The electronic spectrum of the chloro derivative was obtained in CH_3CN and was recorded on a Cary-14 spectrophotometer.

$Et_4N[Mn_2(CO)_6(\mu\text{-}Cl)_3]$. $Mn_2(CO)_{10}$ (0.65 g) and Et_4NCl (0.40 g) were dissolved in 20 ml $CHCl_3$ (purged with nitrogen immediately prior to use) in a 100 ml flask and irradiated for 4 h under a nitrogen atmosphere with a Hanovia high pressure quartz mercury vapor lamp at room temperature. Et_2O was added to produce a white precipitate until the first appearance of a yellow precipitate. After filtration, excess Et_2O was added to the yellow-organe filtrate to give a yellow precipitate which was recrystallized twice from acetone/Et_2O. The yield is 19% based on $Mn_2(CO)_{10}$. [Analysis Found: C, 32.97; H, 3.79; Cl, 20.19; Mn, 21.78; N, 3.13. $Mn_2C_{14}NO_6H_{20}Cl_3$ calcd.: C, 32.68; H, 3.89; Cl, 20.67; Mn, 21.38; N, 2.72%.]

The synthesis was also attempted in CH_2Cl_2 and diglyme with yields of ca. 10 and 1% respectively. The product was not obtained in the absence of Et_4NCl. In all cases a mixture of the $Mn_2(CO)_6(\mu\text{-}Cl)_3^-$ and a product indentified as axially-substituted $Mn_2(CO)_9Cl^-$ [11] could be obtained; the reported preparation has been optimized for $Mn_2(CO)_6(\mu\text{-}Cl)_3^-$.

The bromo derivative was prepared similarly except that the solvent used was $CHBr_3$. It is difficult to purify and it has not yet been possible to separate it from other carbonyl containing complexes. It has been identified by its two bands in the infrared spectrum which are always present in the same intensity ratio irregardless of the nature of the impurities.

Results and discussion

The infrared spectrum of the complexes in the carbonyl stretching region shows only two bands (2029s and 1928vs cm^{-1} for X = Cl; 2025s and 1936vs cm^{-1} for X = Br). This is consistent with a complex $Mn_2(CO)_6(\mu\text{-}X)_3^-$ of D_{3h} symmetry; the bands are assigned as the A''_2 (ca. 2027 cm^{-1}) and E' (ca. 1932 cm^{-1}) modes. While it is also consistent with the formulation $[XMn(CO)_4(\mu\text{-}X)\text{-}Mn(CO)_4X]^-$ in which all halides on the same manganese atom are *trans* to each other, it is highly unlikely in view of the preference of manganese(I) carbonyls bound to halogens for a *cis*-configuration [12,13]. It was also not possible to obtain, by suitable choice of solvent, the infrared spectrum reported by Abel and Butler [13] for the metal—metal bonded complexes $Mn_2(CO)_8X_2^{2-}$ which also shows two peaks in the same region. The electronic spectrum for $Mn_2(CO)_6\text{-}(\mu\text{-}Cl)_3^-$ shows only bands at 26730 cm^{-1} (ϵ = 2720) and 46930 cm^{-1} (ϵ = 41500).

The chloro complex is stable in ethanol solution for periods up to 1 h. The solid may be stored indefinitely at 5°C and for 2 weeks at room temperature without signs of decomposition. It is soluble in common polar organic solvents and is somewhat soluble in water. Upon irradiation for 0.5 h in CH_2Cl_2 solution there is very little change in the infrared spectrum. The complex is apparently far more stable to oxygen than the Group VI analogues [8]. The bromo derivative is of comparable stability.

The mechanisms involved in the photochemistry of $Mn_2(CO)_{10}$, both in halogenated and non-halogenated solvents, have received some discussion [14-17]. In particular, Bamford [14] has examined not only $Mn_2(CO)_{10}$, but also the photochemical behavior of $Mn(CO)_5X$ and $[Mn(CO)_4X]_2$ (X = Cl, Br). In the present case the dependence of product upon solvent may possibly be related to the ability of the solvent to contribute halogen to the complex. This is illustrated by the larger yield of $Mn_2(CO)_6(\mu\text{-}Cl)_3^-$ in $CHCl_3$ than in diglyme; the ratio of the bridged species to $Mn_2(CO)_9Cl^-$ is larger in the former solvent. Also, in $CHCl_3$ the relative amount of $Mn_2(CO)_9Cl^-$ produced is inversely proprtionate to the length of irradiation. Irradiation of pure $Mn_2(CO)_9Cl^-$ [11] in $CHCl_3$ in the presence of Et_4NCl also produced $Mn_2(CO)_6(\mu\text{-}Cl)_3^-$, indicating that the axially substituted manganese(0) species is a possible intermediate in the synthesis of the tribridged manganese(I) complex. However, we have found that irradiation of $Mn_2(CO)_8Cl_2$ in $CHCl_3$ in the presence of Et_4NCl produces the title compound; $Mn_2(CO)_8Cl_2$ is a possible product upon irradiation of $Mn_2(CO)_{10}$ in a halogenated solvent [14]. Photochemical reaction of $Mn(CO)_5Br$ and *cis*-$Mn(CO)_4Br_2^-$ in CH_2Cl_2 lead to rapid decomposition with products void of infrared peaks in the carbonyl region.

Further work is in progress to help elucidate the details of this interesting photochemical reaction. We also note that irradiation of $Mn_2(CO)_{10}$ in the presence of numerous other anions (e.g., N_3^-, OAc^-, SCN^-) gives complexes with infrared spectra showing only two bands in the carbonyl stretching region [11].

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