Communications to the Editor

Supported Cyclopentadienyl Metal Carbonyl Complexes. 1. Mononuclear Iron(II) and Cobalt(I) Derivatives Stabilized by Attachment to a Polystyrene Support

Sir:

The increase in reactivity of organometallic catalysts, which is observed when these compounds are attached to a polymer matrix, has been interpreted in terms of a stabilization of coordinatively unsaturated, mononuclear reaction centers against aggregation by metal-metal bond formation, which would compete with substrate activation in homogeneous solutions.[1-3] In order to verify directly whether attachment to a polymer support does in fact suppress such a formation of di- and polynuclear clusters, we have initiated a study of reaction intermediates with polymer-supported cyclopentadienyl metal carbonyl compounds, for which such structural data are readily obtainable, even on a polymer support, by IR spectroscopy. We wish to report mutually complementary observations of this kind concerning cyclopentadienyliron(II) dicarbonyl hydride and cyclopentadienylcobalt(I) dicarbonyl derivatives covalently bound to a cross-linked polystyrene support.

Treatment of a $(C_5H_5)CH_2$-substituted polystyrene-divinylbenzene (18%) copolymer (obtained via chloromethylation of the polymer as described by Grubbs et al.[2,3]) with an amount of $Fe_2(CO)_9$ equivalent to its C_5H_5 content in refluxing tetrahydrofuran[4] yields a tan-colored product which contains 1-3 wt % iron.[5] Upon heating in a vacuum manifold to temperatures above 180 °C, this material loses 2.0 ± 0.05 mmol of CO and 0.4 ± 0.05 mmol of H_2/mmol of Fe present. In its IR spectrum, two sharp $\nu(CO)$ bands are observable at 1960 and 2040 cm^{-1}; this is in close agreement with $\nu(CO)$ bands reported for $C_5H_5Fe(CO)_2H$ in solution.[6] No μ-CO bands are present in the region between 1900 and 1600 cm^{-1}, neither in the original product nor in material obtained by partial thermal elimination of CO and H_2.

From these spectral and thermolysis data we have to conclude that the reaction of $Fe_2(CO)_9$ with the polymer-linked cyclopentadiene

$$\textcircled{\scriptsize PS}\text{-}CH_2\text{-}C_5H_5$$

1

yields an iron carbonyl hydride

$$\textcircled{\scriptsize PS}\text{-}CH_2\text{-}C_5H_4Fe(CO)_2H$$

2

At room temperature, under exclusion of light and air, **2** remains unchanged for months, as judged by its IR spectrum. Quite in contrast to this, homogeneously dissolved $C_5H_5Fe(CO)_2H$ has been observed to be a highly unstable species, which is rapidly transformed, under loss of H_2, to dinuclear $(C_5H_5)_2Fe_2(CO)_4$.[7-9] The absence of any μ-CO absorptions, typical of such a dinuclear particle, from the polymer-supported iron compound substantiates the view that attachment to a cross-linked polymer can suppress any metal-metal interactions and that the unusual stability of the polymer-supported iron hydride species is a consequence of their mutual isolation by the polymer network.

Similar observations concern the photoreactions of cobalt cyclopentadienyl dicarbonyl attached to a cross-linked polystyrene

$$\textcircled{\scriptsize PS}\text{-}CH_2\text{-}C_5H_4Co(CO)_2$$

3

This substance is obtained, as an umber-colored material with a Co content of 4-6% by treatment of **1** with $Co_2(CO)_8$ in refluxing methylene chloride. It is characterized by loss of 1.95 ± 0.05 mmol of CO/mmol of Co present (at 160 °C) and by an IR spectrum with two strong, terminal CO absorptions at 1960 and 2020 cm^{-1}, virtually identical with those of $C_5H_5Co(CO)_2$ in frequency and relative intensity. If protected by an argon atmosphere and kept in the dark, the material remains unchanged for several weeks as judged by its IR spectrum.

When **3** is irradiated in petroleum ether suspension at ambient temperature with an unfiltered medium-pressure Hg or Xe lamp, one observes a steady decrease and final disappearance of the absorptions at 1960 and 2020 cm^{-1}, indicating the photodissociation of the CO ligands. No trace of any μ-CO bands is observed at wavelengths below 1900 cm^{-1}, be it as an intermediate or in the final photolysis product. These data clearly indicate the absence of any CO-bridged, di- or polynuclear species. In contrast to this, photolysis of $C_5H_5Co(CO)_2$ in homogeneous solution leads to a succession of di- and trinuclear clusters such as $(C_5H_5)_2Co_2(CO)_2$, $(C_5H_5)_2Co_2(CO)_3$, and $(C_5H_5)_3Co_3(CO)_3$, characterized by IR absorptions around 1970, 1800, and 1670 cm^{-1}.[10,11] Mononuclear intermediates or reaction products are not stable in homogeneous solutions at ambient temperature, except for very dilute solutions in aromatic solvents, where stable species such as $C_5H_5Co(AR)$ and $C_5H_5Co(AR)_2$, with AR = benzene or toluene, are obtained in addition to the polynuclear carbonyl clusters.[12] These data are in accord with the view that the unsaturated cobalt centers generated by photolysis of **3** interact—in the absence of adjacent metal centers—with aromatic rings of the polymer support to form species of the kind

$$\textcircled{\scriptsize PS}\text{-}CH_2\text{-}C_5H_4Co(C_6H_5\text{-}\textcircled{\scriptsize PS})_n \quad (n = 1 \text{ or } 2)$$

duplicating in this manner the behavior of the corresponding homogeneous reaction system at the limit of extreme dilution.

Catalytic properties of **2** and **3** are presently under investigation in our laboratory.

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$C_5H_4CH_2$-substituted polymer suspended in a solution of $Fe(CO)_5$ in toluene.
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(13) On leave from Donegani Institute, Novara, Italy.

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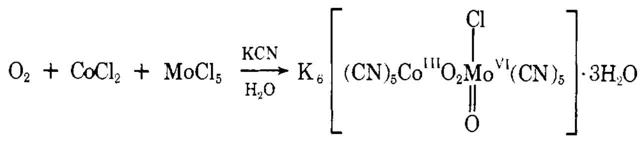
Reaction of Cyanocobaltate(II) and Cyanomolybdate(V) Ions with Molecular Oxygen. A Bimetallic Dioxygen Adduct

Sir:

The ability of cobalt(II) complex ions to bind molecular oxygen to form peroxide and superoxide compounds is well established.[1-4] These adducts are characterized by a wide variety of structure and reactivity.[5-9] In the course of a study on bimetallic catalysis in autoxidation reactions[10] we became involved in an investigation of the interaction of metal couples in the presence of oxygen. This led to the discovery of a new type of dioxygen adduct containing two different metals. Thus $CoCl_2$ and $MoCl_5$ in the presence of excess KCN react with O_2 to give a stable adduct according to eq 1.



$$O_2 + CoCl_2 + MoCl_5 \xrightarrow[H_2O]{KCN} K_6\left[(CN)_5Co^{III}O_2\overset{\overset{Cl}{|}}{\underset{\underset{O}{\|}}{Mo}}{}^{VI}(CN)_5\right]\cdot 3H_2O \tag{1}$$

1

Passing a stream of O_2 through a cold aqueous solution (60 mL) of KCN (0.128 mol, 8.4 g) containing $MoCl_5$ (0.008 mol, 2.2 g) and $CoCl_2$ (0.008 mol, 1.04 g) for 1 h resulted in a dark green solution. Addition of precooled ethanol precipitated immediately a light green solid which was filtered, washed with *n*-pentane, and dried under vacuum:[11] IR (KBr) 3500, 1650 (H_2O), 2155, 2128, 2100 (-CN), 918 (Mo=O), 893 (OO), 840 (MoO or CoO), 414 (CoC≡N?), 396 (MoC≡N), 327 (MoCl). Anal. Calcd for $C_{10}H_6CoK_6MoClN_{10}O_6$: C, 15.3; H, 0.77; Co, 7.5; K, 29.8; Mo, 12.2; Cl, 4.5; N, 17.8; O, 12.2. Found: C, 15.3; H, 0.75; Co, 8.2; K, 31.1; Mo, 11.8; Cl, 5.3; N, 17.6.

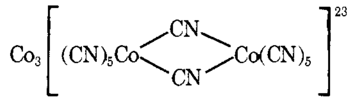
The presence of a peroxide ligand, suggested by the infrared absorption band at 893 cm^{-1},[4,9] was confirmed by a standard peroxidic titration in the presence of acetic acid, indicating one O-O moiety per molecule of **1**.[12] A thermal decomposition (100 °C) of **1** causing a loss of weight corresponding to ½ of O-O per molecule[14] was further evidence for a peroxide group.

The presence of an intense and sharp absorption band at 918 cm^{-1} indicates a Mo=O group; this is in accord with similar bands reported in the literature.[15] Sharp absorption bands at 2155, 2128, and 2100 cm^{-1} are assigned to cobalt and molybdenum cyano groups.[16-22] Although an unusual cyanide bridging structure for the cobalt dioxygen adduct **2**

$$(CN)_2(PMePh)_3CoNCCo(PMe_2Ph)_2(CN)O_2$$

2

with absorption bands at 2085 and 2105 cm^{-1} has recently been reported by Halpern and coworkers,[9] a similar pattern for **1** should be expected to have absorption bands at higher wavenumbers.[17] In fact the anion $[Co^{III}(CN)_6]^{-3}$ has an absorption band at 2154 cm^{-1},[23] whereas a band at 2183 cm^{-1} has been assigned to a μ-CN group

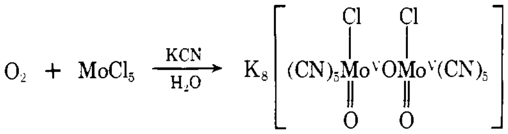


Furthermore, the brown dioxygen adduct **3**, obtained with cobalt alone[5] under identical experimental conditions (eq 2)

$$O_2 + CoCl_2 \xrightarrow[H_2O]{KCN} K_6[(CN)_5CoO_2Co(CN)_5]\cdot H_2O \tag{2}$$

3

as used to obtain **1**, and known to lack a cyano bridging structure has absorption bands at 2080, 2100, 2130, and 2160 cm^{-1} assigned to cyano groups. Most of the experimental evidence presented above supports the formulation given for **1**; a doubt, however, persisted as to whether **1** was a mixture of **3** and a molybdenum compound. Duplicating the experimental procedure in the absence of $CoCl_2$ resulted in a sky-blue solid (**4**) lacking any peroxidic function and having the following infrared characteristics[24] (KBr): 2115, 2100 (-CN), 1400, 1315 (MoO), 915 (Mo=O?), 828-840 (MoOMo?), 380 (MoCN), 329, 295 (MoCl). Anal. Calcd for $C_{10}K_8Mo_2Cl_2N_{10}O_3$: C, 13.59; K, 35.40; Mo, 21.72; Cl, 8.02; N, 15.84. Found: C, 13.75; K, 35.90; Mo, 22.30; Cl, 8.23; N, 15.98. These results suggest formulation 3.[25]



$$O_2 + MoCl_5 \xrightarrow[H_2O]{KCN} K_8\left[(CN)_5\overset{\overset{Cl}{|}}{\underset{\underset{O}{\|}}{Mo}}{}^{V}O\overset{\overset{Cl}{|}}{\underset{\underset{O}{\|}}{Mo}}{}^{V}(CN)_5\right] \tag{3}$$

4

The presence of Mo-Cl in **4** was a good indication that the same pattern rather than Co-Cl was present in **1**. Additional support for **1** being a single compound was given by the fact that a synthetic mixture of **3** and **4** did not give **1** upon recrystallization, whereas **1** could be recrystallized without altering significantly its composition. It must be noted that **1** is not obtained when molybdenum(VI) species are used; furthermore the use of deficient amount of cyanide ion also prevents its formation. Compound **1** constitutes, on one hand, the first example of a dioxygen adduct containing two different metals, and on the other the first peroxidic molybdenum species obtained directly with molecular oxygen.[27,28] We are presently pursuing the study of this and related compounds.

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