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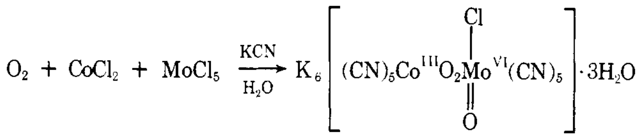
Reaction of Cyanocobaltate(II) and Cyanomolybdate(V) Ions with Molecular Oxygen. A Bimetallic Dioxygen Adduct

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.



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

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.

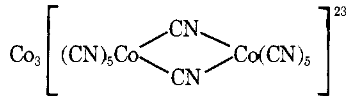
The presence of a peroxide ligand, suggested by the infrared absorption band at 893 cm^{-1},[4,9] was confirmed by a standard peroxidic titration in the presence of acetic acid, indicating one O-O moiety per molecule of **1**.[12] A thermal decomposition (100 °C) of **1** causing a loss of weight corresponding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

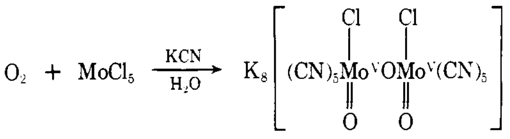
with absorption bands at 2085 and 2105 cm^{-1} has recently been reported by Halpern and coworkers,[9] a similar pattern for **1** should be expected to have absorption bands at higher wavenumbers.[17] In fact the anion $[Co^{III}(CN)_6]^{-3}$ has an absorption band at 2154 cm^{-1},[23] whereas a band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

$$O_2 + CoCl_2 \xrightarrow[H_2O]{KCN} \underset{\mathbf{3}}{K_6[(CN)_5CoO_2Co(CN)_5]\cdot H_2O} \qquad (2)$$

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]



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

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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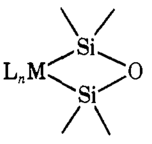
Catalysis of Siloxane Metathesis by Cyclometalladisiloxanes. Mechanistic Similarities to Olefin Metathesis Catalysis

Sir:

We wish to report that small-ring metallocycles of type I catalyze the disproportionation of 1,1,3,3-tetramethyldisiloxane (TMDS) into dimethylsilane and higher siloxane oligomers (eq 1).



I

$$(n+1)\mathrm{TMDS} \rightarrow \underset{\mathrm{E'D}_n\mathrm{E'}}{\mathrm{Me_2SiH(OSiMe_2)}_n\mathrm{OSiHMe_2}} + n\mathrm{Me_2SiH_2} \qquad (1)$$

In this reaction strong Si-O bonds are broken and re-formed at room temperature in a *neutral* milieu. To our knowledge, this represents the first observation of Si-O bond rearrangements under such mild conditions.[1,2]

Eaborn et al.[3] prepared the first complex of type I, $L_2Pt(SiMe_2OSiMe_2)$, by refluxing a benzene solution of TMDS with $L_2Pt(C_2H_4)$ ($L = Ph_3P$). We have prepared the palladium analogue from TMDS and L_2PdCl_2. The metallocycle, $L_2Pd(SiMe_2OSiMe_2)$, mp 142 °C dec, is obtained in 20-30% yield following purification by column chromatography over Florisil (^{1}H NMR δ 7.2 (15, Ph), 0.1 (6, Me)). The iridium metallocycle, $L_2Ir(CO)(H)(SiMe_2OSiMe_2)$ (II), was prepared by stirring a benzene solution of TMDS with Vaska's compound at room temperature for ~20 min. Complex II melts at 150 °C dec and exhibits ν_{CO} and ν_{IrH} bands at 1950 and 2030 cm^{-1}, respectively. The methyl resonances of II occur as two equally intense singlets at δ 0.2 and 0.4, showing that the methyl groups are in nonequivalent environments in solution.

Wilkinson's catalyst, L_3RhCl, also reacts readily with TMDS to give a pale yellow solution, from which a bright yellow powder can be isolated. This substance is thermally labile and rapidly darkens at room temperature under a nitrogen atmosphere. The powder decomposes at 135-140 °C and its ^{1}H NMR spectrum shows a phenyl multiplet at δ 7.2 (15) and a methyl singlet at 0.2 (6). No RhH peak is observed in the IR. The exact nature of this complex is not yet established, although the IR spectrum in the SiOSi region resembles those of the platinum and palladium metallocycles.

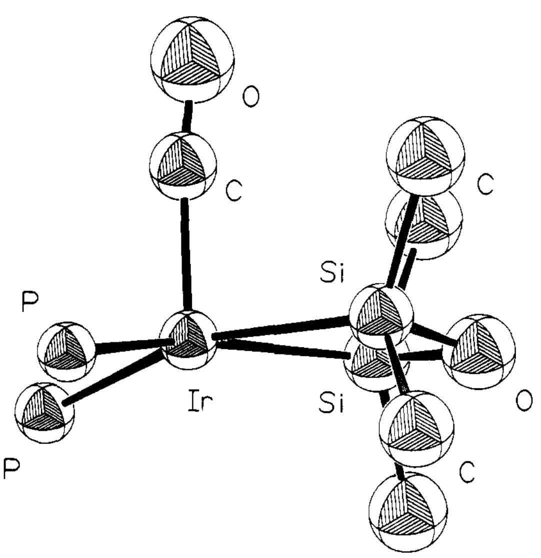


Figure 1. ORTEP drawing of the structure of hydrido-1,3-(1,1,3,3-tetramethyldisiloxanyl)carbonylbis(triphenylphosphine)iridium(III).

The molecular structure of the iridium metallocycle (II) has been determined by x-ray diffraction.[4] Figure 1 is an ORTEP drawing of the structure of the inner coordination sphere. The hydrogen presumably sits in the vacant coordination site below the basal plane. The IrSiOSi ring is folded along the Si···Si axis so that the displacements from the mean plane of the four atoms are Ir (−0.04), Si (+0.06), Si (+0.06), and O (−0.08) Å. The iridium is also displaced 0.26 Å out of the basal P_2Si_2 plane toward the carbonyl group. The Ir-Si bond distances are essentially identical at 2.40 Å and are just slightly longer than the Ir-P distance, 2.38 Å. Hence, the Ir-Si distances appear to be normal, since the covalent radii of P and Si are within 0.04 Å of each other, as judged by a variety of P-X and Si-X bond lengths.[5] The Si-O bond lengths are 1.67 and 1.70 Å and appear to be slightly longer than Si-O bonds in unstrained siloxanes (av Si-O $\simeq$ 1.63-1.65 Å).[5,6]

The angles associated with the IrSiOSi ring reflect the strain in this system. The internal angles are 99.6° (SiOSi), 97.5° (IrSiO), and 64.6° (SiIrSi). In an ideal octahedral complex, the SiIrSi angle would be 90°, so that the observed angle reflects the small bite angle of the SiOSi chelate. The SiOSi angle is also greatly compressed. In linear and higher cyclic siloxanes, the SiOSi angle falls in the 130-160° range.[5] The large SiOSi angle in siloxanes has been ascribed to the effects of (p-d) π bonding, so that a decrease of this angle may reflect some loss of (p-d) π back-donation from oxygen. This in turn would lead to a weakening (and lengthening) of the Si-O bond, as observed.

The catalytic effect of metallocycles I on excess TMDS is remarkable in that catalytic amounts of these metallocycles induce a disproportionation of TMDS into dimethylsilane and higher polysiloxanes, E'D$_n$E' (eq 1). In addition, the rhodium complex gives cyclic, D_3 and D_4, oligomers. The platinum and palladium metallocycles are poor catalysts for eq 1. The rates are low and the catalytic effect diminishes after a few turnovers. On the other hand, the iridium and rhodium catalysts seem to be indefinitely active, the reactions are clean and rapid