

Preliminary communication

NOVEL SPECIES IN THE ELECTROCHEMICAL REDUCTION OF A METAL—METAL BOND BRIDGED BY A BIDENTATE FLUOROPHOSPHINE

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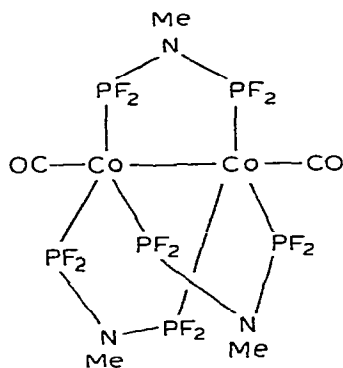
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Summary

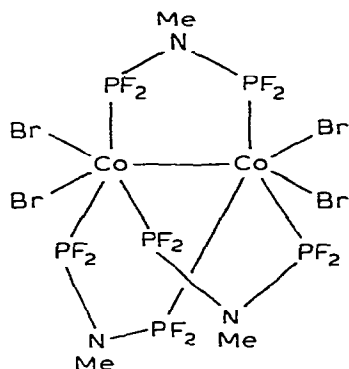
The purple bridged bimetallic complex $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ undergoes successive chemically and electrochemically reversible one-electron reductions to the corresponding green radical anion and pale-yellow dianion. The radical anion is relatively unreactive towards oxygen and methyl iodide. The dianion is not only reactive towards oxygen and methyl iodide but also captures small positively charged species (e.g. Li^+ and H^+) with significant alteration of its chemical properties.

The reaction of $\text{Co}_2(\text{CO})_8$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$ gives the complex $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ (I) containing a cobalt—cobalt bond bridged by three $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands [1, 2]. The $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2$ structural unit in this complex is of high stability as indicated by its remaining intact upon reaction with bromine to give a tetrabromide $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2\text{Br}_4$ (II) [3]. We have now found that electrochemical reduction of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ gives successively the corresponding radical anion and dianion as stable species. The radical anion is of interest in representing an unusual mixed oxidation state cobalt derivative. The dianion is the first example of a bimetallic analogue of the well-known $\text{Co}(\text{CO})_4^-$ where the cobalt atoms are held in close proximity by the three strong $\text{CH}_3\text{N}(\text{PF}_2)_2$ bridges. Some preliminary electrochemical evidence is also presented for an unusual ability of the dianion $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2^{2-}$ to capture small positively charged species (Li^+ and H^+) with significant alteration of its chemical properties.

Polarography of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ (I : $\nu(\text{CO})$ 2003 cm^{-1}) results in two well-defined reduction steps at -0.59 and -1.07 V vs. SCE using dichloromethane as the solvent and $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{PF}_6]$ as the supporting electrolyte.



(I)



(II)

Cyclic voltammetry as well as thin layer linear potential sweep voltammetry shows that both steps are chemically and electrochemically reversible. Coulometry indicates that each step is a one-electron reduction.

Controlled potential electrolysis at -0.7 V vs. SCE in dichloromethane using $[(n-C_4H_9)_4N][PF_6]$ or $[(C_6H_5)_3PNP(C_6H_5)_3][PF_6]$ as the supporting electrolyte at a platinum electrode generates the dark green radical anion apparently free of the other oxidation states. This radical anion is relatively stable towards air oxidation. However, it could not be isolated in the chemically pure states because of similar solubility of the salts $[(C_6H_5)_3PNP(C_6H_5)_3][PF_6]$ and $[(C_6H_5)_3PNP(C_6H_5)_3][CH_3N(PF_2)_2]_3Co_2(CO)_2$. Its unambiguous characterization is based on the following observations: (1) A single $\nu(CO)$ frequency at 1940 cm^{-1} (CH_2Cl_2) exhibiting the expected lowering relative to the corresponding neutral complex in accord with the presence of the negative charge; (2) A complex multiline ESR spectrum centered at $g = 2.0257$ indicating a free radical; (3) Electrochemical reoxidation to the original $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ indicating retention of the fundamental structural unit.

Controlled potential electrolysis of 1 at -1.3 V vs. SCE in dichloromethane using $[(C_6H_5)_3PNP(C_6H_5)_3][PF_6]$ as the supporting electrolyte at a platinum electrode results eventually in reduction to the pale yellow dianion. The dianion, in contrast to the radical anion, is very oxygen sensitive and rapidly becomes green upon exposure to air through reoxidation to the radical anion. The characterization of the dianion depends upon the following observations: (1) A single $\nu(CO)$ frequency at 1877 cm^{-1} (CH_2Cl_2) which is lower than that of the radical anion in accord with the additional negative charge in the dianion; (2) The lack of an ESR signal in the sample of pure pale yellow dianion compared with the appearance of the ESR signal of the radical anion (see above) when the dianion is allowed to oxidize spontaneously in air to the radical anion; (3) Electrochemical demonstration of reoxidation of the dianion to the radical anion and to the neutral species again indicating preservation of the $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ unit.

The reactivities of the radical anion and dianion towards methyl iodide have been compared. Treatment of the radical anion with excess methyl iodide does not appear to result in any change, as indicated both by retention of the characteristic 1940 cm^{-1} $\nu(CO)$ frequency and the same polarogram. However, treatment of the dianion with methyl iodide results in the generation of a new system exhibiting a changed polarogram (a one electron oxidation wave at $+0.3$

V vs. SCE) and new $\nu(\text{CO})$ frequencies at 1710 and 1635 cm^{-1} . These observations, including the evaluation of the height of the mercury oxidation wave in the presence of iodide in the polarogram at ~ -0.3 V, suggest that the dianion reacts with one methyl iodide molecule with liberation of iodide and formation of a new bimetallic anion. However, attempts to isolate and to identify this methylated monoanion have so far failed.

All the above studies have used supporting electrolytes containing large cations such as tetrabutylammonium and bis(triphenylphosphine)iminium. The results are different when relatively small cations such Li^+ and H^+ are added to the solution. Thus, reduction of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ in tetrahydrofuran using $[\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte gives in presence of small amount of Li^+ , the same successive stages of reduction to the radical anion and dianion. However, reoxidation of the dianion results in direct conversion to the neutral species in a two-electron at -0.15 V vs. SCE process without the intermediate formation of the radical anion. To explain these observations we postulate that a small positively charged lithium ion can be held in a bridging position between the two negatively charged cobalt sites in the dianion. This trapped lithium ion "holds" the system in the dianion oxidation state so that oxidation of the dianion can only proceed at much more positive potentials which already are sufficient for complete oxidation to the neutral species. A similar effect is observed when water, which presumably functions as a proton source is added to the tetrahydrofuran solution.

These studies suggest that reduction of the strongly bridged bimetallic system $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ [1] exhibits many interesting features not present in the reduction of unbridged or weakly bridged (i.e. only by CO) bimetallic systems such as $\text{Co}_2(\text{CO})_8$. The relative reactivities of the radical anion and dianion of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ [1] with methyl iodide indicate, as expected, a considerably higher nucleophilicity of the dianion relative to the radical anion, an effect of potential value in synthetic organometallic chemistry in the design of methods for the synthesis of transition metal complexes exhibiting novel structural features. In any case the dianion $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2^{2-}$ is clearly an interesting organometallic reagent, having two nucleophilic sites held at a well-defined distance because of the rigidity of the three $\text{CH}_3\text{N}(\text{PF}_2)_2$ bridges. Attempts to isolate and fully characterize these new bimetallic anionic systems and studies of their synthetic applications are in progress.

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