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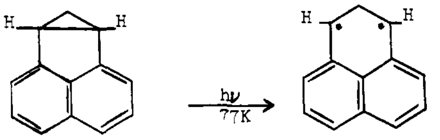

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## Redox Properties of Small Metallocarborane Clusters: Electrochemistry of Cobalt Triple-Decker Sandwich Compounds

*Sir:*

Following the reports of Werner and Salzer in 1972[1] on the synthesis of the tris($\eta^5$-cyclopentadienyl)dinickel cation, $Cp_3Ni_2^+$, there has been considerable interest in so-called "triple-decker sandwich" compounds, partly due to the attractive possibility of building extended, electron-delocalized, organometallic chains.[2,3] The oxidation-reduction properties of these molecules, as well as the physical properties of their radical ions, are of obvious interest in attempting to understand the nature of the metal-metal interaction in these compounds and the degree to which delocalization may occur.

**Table I.** Reduction and Oxidation Potentials of Cobalt Carboranes in $CH_3CN$

| compound | $E_{1/2}$[a,b] red$_1$ | red$_2$ | ox$_1$ | ox$_2$ |
|---|---|---|---|---|
| (**1**) 1,7,2,3-$Cp_2Co_2C_2B_3H_5$ | −1.44 | −2.23 | +0.51 | +1.72[c] |
| (**2**) 1,7,2,4-$Cp_2Co_2C_2B_3H_5$ | −1.35 | −2.30 | +0.89 | [e] |
| (**3**) 1,2,3-$CpCoC_2B_4H_6$ | −1.62 | −2.50 | +1.52[d] | |
| (**4**) 1,2,4-$CpCoC_2B_4H_6$ | −1.43 | [e] | +1.70[d] | |
| $Cp_2Co^+$ [f] | −0.94 | −1.88 | [e] | |

[a] Volts vs. saturated calomel electrode. [b] Each process is a reversible, one-electron step, unless otherwise noted. [c] Irreversible wave in $CH_3CN$. [d] Reversible in $CH_2Cl_2$, irreversible in $CH_3CN$. [e] Not observed within available electrochemical window (+2.0 to −2.8 V). [f] Geiger, W. E. *J. Am. Chem. Soc.*, **1974**, *96*, 2632.

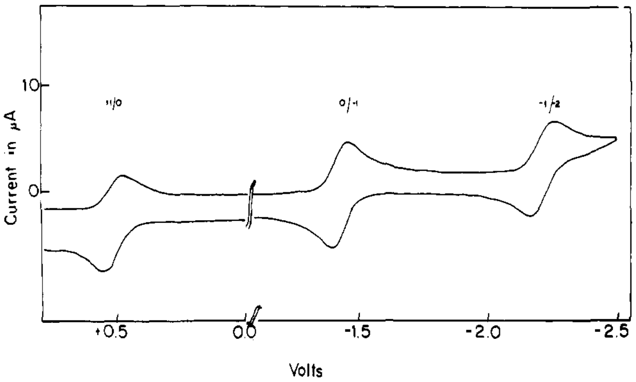
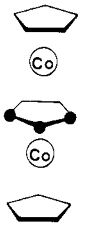
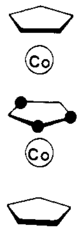


**Figure 1.** Cyclic voltammogram of an acetonitrile solution containing 2 × $10^{-4}$ M of **1** and 0.1 M $Bu_4NPF_6$ at a platinum bead electrode. Scan rate 0.20 V/s.

We wish to report electrochemical data on the dicobalt species (**1** and **2**)[3-5] which show that the triple-decker compounds are part of a *five-membered* electron-transfer series, at least four of which are stable. For comparison purposes, we include data on the monocobalt species[6] **3** and **4**, $CpCoC_2B_4H_6$.



(1)



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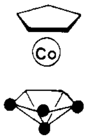
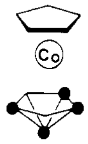


(3)



(4)

● = BH

The triple-deckers **1** and **2** undergo a series of generally reversible one-electron oxidations and reductions in nonaqueous solvents[7] (Table I). A typical cyclic voltammogram (CV) is shown in the figure for 1,7,2,3-$Cp_2Co_2C_2B_3H_5$ (**1**). With the exceptions designated, each redox step is a diffusion-controlled, reversible, one-electron process. These conclusions were reached on the basis of dc polarography[8] (diffusion current constants, compared to $Cp_2Co^+$, and slope of polarographic wave), cyclic voltammetry[9] (current function dependence on scan rate, anodic-to-cathodic current ratio, anodic-to-cathodic peak potential difference), and thin-layer coulometry, and will be elaborated on in a subsequent forum.

The electron-transfer reactions of the dicobalt triple deckers are typified by a five-membered electron-transfer series in which each process except the second oxidation step is completely reversible in slow (<50 mV/s) cyclic voltammetry scans. This behavior is in marked contrast to that of the neutral

$$? \leftarrow 1^{2+} \rightleftharpoons 1^{+} \rightleftharpoons Cp_2Co_2C_2B_3H_5^{0} \rightleftharpoons 1^{-} \rightleftharpoons 1^{2-}$$

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monocobalt compounds (e.g., **3**), which have two or more voltammetric waves, but only one (the reduction to the monoanion) is reversible in acetonitrile. In **3**, for example, reduction of the monoanion occurs in a one-electron step at −2.50 V, but the resulting dianion is extremely unstable and the wave is irreversible even at rather high (10 V/s) scan rates.

The greatly enhanced stability of the dicobalt dianions is most likely due to the ability of the cluster to spread the negative charge over both metals. This kinetic stability could occur if the anions have a delocalized electronic structure, or if there is charge isolation on the cobalts (e.g., two formally Co(II)'s in the dianions). Our electrochemical results strongly favor the delocalized electronic structure, for if there were strictly isolated cobalt reduction sites, or very weak electronic coupling, we would expect to find either a single two-electron wave, or two closely spaced one-electron waves.[10] Although the electrochemical data cannot offer a quantitative description of the lowest unoccupied molecular orbital (LUMO) of the triple deckers, it seems clear that there is significant charge delocalization in the anions. This is consistent with the results of a molecular orbital treatment of this class of compounds by Lauher and co-workers,[11] in which it was shown that there is significant mixing of the metal and central ligand $\sigma$ orbitals, and that the LUMO for **1** is weakly *bonding* between the metals.

The stable ions generated in our electrochemical experiments contain from 29 to 32 valence electrons ($\mathbf{1}^+$ to $\mathbf{1}^{2-}$), if the usual conventions for electron counting are followed. The LUMO orbital for neutral **1** (30 electrons) is actually a degenerate ($e_1'$) set which is fully occupied in the 34-electron $Cp_3Ni_2^+$. This orbital is high in metal character and nonbonding with respect to the central ring.[11] Since the highest occupied orbital (HOMO) of **1** is also a nonbonding metal orbital,[11] it is not surprising that the several redox steps do not seem to affect the metal-ligand bonding in any catastrophic way. It does not seem that the degree of occupancy of the $e_1'$ set is critical to the stability of triple deckers. We note in this regard that Siebert and co-workers have recently isolated neutral triple deckers with various metals, containing 30 to 33 electrons.[12]

The above discussion employed a model in which the triple deckers were viewed as delocalized, multi-metal, $\pi$-complexes. A popular alternative model would view **1–4** as cluster compounds derived from the pentagonal-bipyramidal structure of $C_2B_5H_7$ by replacement of one or two BH vertices by $CpCo^{2+}$. The similarity of $CpCo^{2+}$ and BH bonding in molecular clusters has been pointed out previously,[13-15] and the neutral cobalt clusters retain the closo shape with $2n + 2$ framework electrons.[16] Taken in this context, the apparent absence of major structural changes in going to the $Cp_2Co_2C_2B_3H_5^{2-}$ dianions might be surprising because electron-counting rules predict a nido structure for a $2n + 4$ electron species.[16] Comparing these seven-vertex dicobalt clusters with smaller clusters, we note that when the closo tetrahedral cluster $Co_3(CO)_9CR$ is reduced,[17] an extremely unstable dianion is produced, and, similarly, reduction beyond the monoanion stage has proved fatal for other metal clusters as well.[18,19]

Since Hawthorne and co-workers have reported extensively on the electrochemical properties of large metallocarboranes,[20] clusters of this general type may provide a model system to investigate the effects of size and stoichiometry on the redox properties of molecular clusters. We will comment on these aspects in more detail in a subsequent paper.

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## Mapping of Cocaine and Cinnamoylcocaine in Whole Coca Plant Tissues by MIKES

*Sir:*

Methodology is presented which allows the distribution of organic compounds in plant tissue to be mapped accurately on a dimensional scale as small as 1 mm³. Individual tissue specimens are examined so that averaging over a population is avoided; no sample preparation or prefractionation is needed, and total analysis time is only a few minutes per sample. In addition to demonstrating this organic mapping capability, we show that different parts of a plant as well as plants from different regions can be differentiated on the basis of alkaloid content. The data presented are for *Erythroxylum coca* Lam., and they have immediate analytical implications for chemotaxonomy and plant physiology; however, the approach used is likely to be more generally applicable.

Analysis is by MIKES (mass-analyzed ion kinetic energy spectrometry), i.e., by sequential two-stage mass spectrometry with dissociation of selected ions in the interanalyzer region and mass analysis of the resulting fragments in the second analyzer. The direct (nonchromatographic) analysis of individual trace organic constituents of complex mixtures is thus possible.[1-4] The present experiments employ direct probe vaporization, chemical ionization, and collision-induced dissociation. Cocaine (benzoylmethylecgonine) and cinnamoylco-

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