a reaction which involves loss of the carbocyclic ring, is less clear.[13] However, some indication that interceptible, highly unsaturated (or THF-solvated) metal species are involved is provided by the following experiment. Slow addition of **8** to a mixture of Na-Hg in THF containing 1.2 M $(C_6H_5)_3P$ gave a solution which contained only small amounts of **9** and **10**, but much larger quantities of $NaCo(CO)_2(P(C_6H_5)_3)_2$ (**13**)[14] and $NaCo(CO)_3(P(C_6H_5)_3)$ (**14**).[15] Control experiments showed that (a) **9** is inert to substitution[16] by $P(C_6H_5)_3$ under these reaction conditions; (b) η^5-$C_5H_5Co(CO)((C_6H_5)_3P)$ is formed only slowly from **8** and $(C_6H_5)_3P$ at these temperatures, and in any case gives neither **13** nor **14** when reduced with Na-Hg in THF in the presence of excess phosphine.[17,18]

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(8) The magnetic moment of **10**, measured using either the Gouy balance method or the procedure of Evans,[9] is 1.70 ± 0.10 μ_B (corrected for ligand diamagnetism).
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(11) We have obtained preliminary results on both the reduction of **10** and its reaction with alkylating agents. Although it is stable to 1% Na–Hg in THF, under more severe reducing conditions (Na dispersion in THF or Na in HMPT over a period of 24 h) **10** is converted in high yield to sodium cyclopentadienide and unidentified metallic products. Methyl iodide and *n*-propyl bromide react at least an order of magnitude more rapidly with **10** than with $Co(CO)_4^-$; characterization of the products of these reactions is in progress and will be reported in a full paper.
(12) Electrochemical experiments were carried out in acetonitrile under a nitrogen atmosphere at a mercury-drop electrode. Tetraethylammonium perchlorate was the supporting electrolyte and silver–silver perchlorate reference was used.
(13) Control experiments have demonstrated that under the conditions of the reduction of **8** in THF or HMPT, the sodium cyclopentadienide NMR resonance is severely broadened and is therefore difficult to observe. Apparently electron exchange between Na^+Cp^- and **10** (or some other paramagnetic species) occurs rapidly on the NMR time scale in these solvents. In acetonitrile, however, the Na^+Cp^- signal (only slightly broadened) may be observed in the NMR during reduction; Na^+Cp^- is therefore a product of the initial reduction reaction and is apparently produced in yields comparable to $NaCo(CO)_4$. We assume that the ring is extruded as cyclopentadienide in THF and HMPT as well. We have considered the possible intermediacy of cobaltocene in this reaction; however, although there is precedent for the formation of cobaltocene from **8** under certain conditions,[13a] it apparently is not converted to Cp^- by reduction;[13b] (a) D. Sellmann, *Z. Naturforsch. B*, **25**, 1482 (1970); (b) W. E. Geiger, Jr., *J. Am. Chem. Soc.*, **96**, 2632 (1974).
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(17) η^5-$C_5H_5Co(CO)[P(C_6H_5)_3]$ is reduced more slowly than **8** to give $(C_6H_5)_3P$ and a dark, insoluble (probably polymeric) complex. Interestingly, however, exposure of this material to carbon monoxide in THF immediately forms **9** and **10** in a ratio similar to that observed on direct reduction of **8**.
(18) (a) Reduction of η^5-$C_5H_5Rh(CO)_2$ with Na–Hg in THF has been reported[18b] to also produce a product having an ir band near 1890 cm^{-1}. However, this material is apparently not the known[18c] $NaRh(CO)_4$, since it has been assigned the rhodium hydride structure $Na^+[\eta^5$-$C_5H_5Rh(H)(CO)]^-$; (b) R. Hill and S. A. R. Knox, *J. Organomet. Chem.*, **84**, C31 (1975); (c) P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 21 (1969).
(19) National Institutes of Health Postdoctoral Fellow, 1975–present.
(20) National Institutes of Health Postdoctoral Fellow, 1974–present.
(21) Camille and Henry Dreyfus Teacher–Scholar Grant Awardee, 1970–1975.

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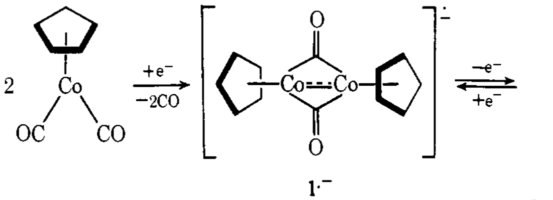
Crystal and Molecular Structure, Spectroscopic Properties, and Redox Behavior of $[\eta^5\text{-}C_5H_5CoCO]_2{\cdot}^-$, a "Mixed-Valence" Organometallic Radical Anion Having a High Degree of Intramolecular Delocalization and Cobalt in Formal Oxidation State +0.5

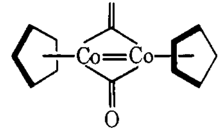
Sir:

We wish to report the structure, ESR and electronic spectra, and redox behavior of the paramagnetic title compound ($\mathbf{1}{\cdot}^-$). This material can be considered a formal cobalt(I)-cobalt(0) "mixed-valence" transition metal complex[1] having a high degree of interaction or delocalization between the two intramolecular metal atoms; each cobalt is in formal oxidation state +0.5. It is one of the very few examples of a complex having cobalt-cobalt multiple bond character (in this case a bond order of ca. 1.5), and it is easily oxidized to a neutral complex which presumably has a complete cobalt-cobalt double bond.

The bis(triphenylphosphine)iminium salt of radical anion $\mathbf{1}{\cdot}^-$, prepared by Na-Hg reduction of η^5-$C_5H_5Co(CO)_2$ as described in the accompanying communication,[2] crystallizes in the triclinic system with the following crystal data: a = 11.279 (3), b = 17.593 (5), c = 10.428 (1) Å; α = 101.59 (3), β = 93.52 (6), γ = 91.69 (2)°; space group $P\bar{1}$; Z = 2. The density, 1.37 (2) g cm^{-3} at 23°, measured by flotation in aqueous KBr, corresponds to ρ_{calcd} = 1.385 g cm^{-3}. Single-crystal x-ray diffraction data were collected on a Datex-automated General Electric diffractometer using monochromatic Mo Kα radiation at room temperature; the structure was determined using 2871 reflections with intensities $I \geq 3\sigma(I)$, and phased by both heavy atom techniques and direct methods (MULTAN). A three-dimensional electron density map revealed the locations of all 55 nonhydrogen atoms in the asymmetric unit. Refinement was carried out using group parameters for the phenyl rings of the PPN^+ cation (rigid body approximation); positions of the 40 hydrogen atoms were calculated and were not refined. Anisotropic full-matrix least-squares refinement



$\mathbf{1}{\cdot}^-$



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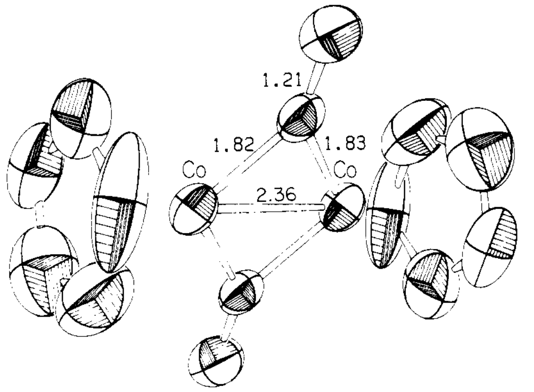

Figure 1. ORTEP drawing of the molecular structure of $[\eta^5\text{-}C_5H_5CoCO]_2{\cdot}^-$, determined by x-ray diffraction on the bis(triphenylphosphine)iminium salt. Bond lengths are given in angstrom units.

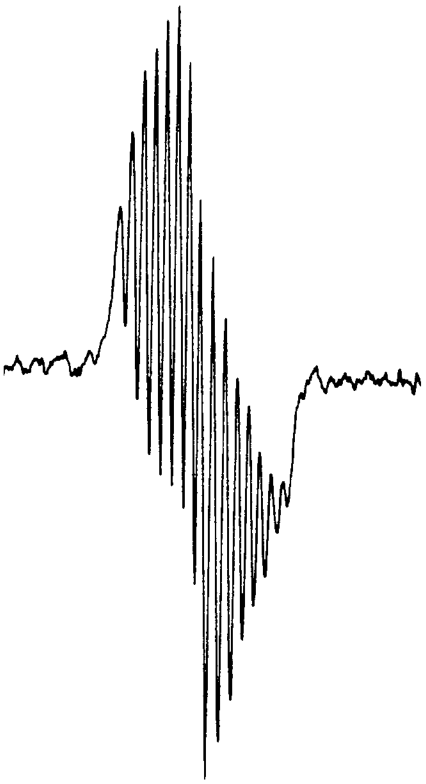

Figure 2. ESR spectrum of $[\eta^5\text{-}C_5H_5CoCO]_2{\cdot}^-PPN^+$.

(phenyl groups refined isotropically) of F converged to a final $R = 0.073$.

An ORTEP drawing of the final structure of the radical anion is shown in Figure 1. A complete list of bond distances and angles follows this article in the microfilm edition of the journal; however, the most important structural characteristics are: (a) the cobalt–cobalt bond lies on a crystallographic center of inversion and is perpendicular to the planes of the two C_5H_5 rings; (b) the cobalt atoms and bridging carbonyl groups are essentially coplanar, *unlike* those of dicobalt octacarbonyl,[3] in which the dihedral angle between the two Co-Co bridging carbonyl planes is 127°; (c) the cobalt-cobalt bond distance is 2.36 Å. Comparison of the Co-Co distance in $\mathbf{1}{\cdot}^-$ with the single bond length in[3] $Co_2(CO)_8$ (2.52 Å), the double bond in[4] η^5-cyclopentadienyliron nitrosyl dimer (2.33 Å), and the triple bond in[5] $(\eta^5\text{-}C_5Me_5)_2Cr_2(CO)_4$ (2.28 Å) is consistent with a judgment made on the basis of the 18-electron rule[6] that the bond order in $\mathbf{1}{\cdot}^-$ is ca. 1.5. That is, it should be thought of as the delocalized "radical anion" of the corresponding neutral

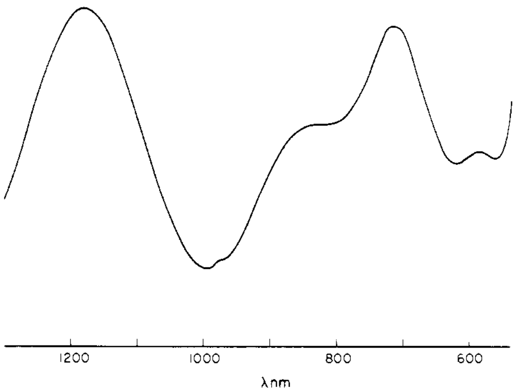

Figure 3. Electronic absorption spectrum of $[\eta^5\text{-}C_5H_5CoCO]_2{\cdot}^-PPN^+$.

(and presumably doubly bonded) $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2$ (**1**). This picture is supported by the ESR spectrum of $\mathbf{1}{\cdot}^-$. As shown in Figure 2, in THF solution at 25°, a symmetrical 15-line spectrum is observed, centered at roughly 3100 G with $a_0 = 50$ G. This indicates that (at least on the ESR time scale) the unpaired electron is shared equally by both cobalt atoms ($I = 7/2$) (the hyperfine splitting due to the hydrogens is apparently too small to be observed under our conditions). The ESR spectra of the sodium and PPN^+ salts of **1** are completely identical.

The conception of $\mathbf{1}{\cdot}^-$ as the radical anion of **1** also suggests that it should be easily converted to **1** by oxidation. This inference was confirmed both chemically and electrochemically. Addition of a number of oxidizing agents (e.g., O_2, chloranil, $FeCl_3$) to a THF solution of $\mathbf{1}{\cdot}^-$ at room temperature converted the complex immediately to a mixture of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and a material having a single ir band at 1790 cm^{-1}. Removal of the mononuclear dicarbonyl by vacuum transfer, followed by sublimation of the residue, gave pure **1** as a dark green solid. This material has properties identical with those recently described by Lee and Brintzinger,[7] who reported its formation during low-temperature irradiation of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and Na-Hg reduction of $(\eta^5\text{-}C_5H_5)Co(CO)I_2$. Rapid-scan cyclic voltammetry (acetonitrile solution) confirmed the reversibility of the $\mathbf{1} \rightleftharpoons \mathbf{1}{\cdot}^-$ reaction; $\mathbf{1}{\cdot}^-$ is oxidized reversibly at a potential of -1.05 V vs. the Ag|AgClO$_4$ electrode.[8]

Consideration of $\mathbf{1}{\cdot}^-$ as a mixed-valence complex[1] suggests that it may be important in the study of potentially conducting organometallic materials. Many such species show electronic transitions in the near-infrared;[1c,9] $\mathbf{1}{\cdot}^-$, too, exhibits a near-ir absorption. Both the sodium and PPN^+ salts of $\mathbf{1}{\cdot}^-$ exhibit near-ir bands at 1190 nm ($\epsilon \simeq 50$), in addition to absorptions in the uv including one at 375 nm ($\epsilon \simeq 5000$). The low near-ir extinction coefficient is perhaps due to the high degree of mixing between the +1 and 0 valence states. In crystals of $[\mathbf{1}{\cdot}^-PPN^+]$, the cations prevent close approach of the counteranions, making this salt a poor candidate for conductivity. However, other derivatives of $\mathbf{1}{\cdot}^-$(e.g., $\mathbf{1}{\cdot}^-\ TTF^+$)[10] may be more promising; attempts to prepare such materials are in progress.

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Hans Brintzinger for disclosing experimental results prior to publication.

Supplementary Material Available: Five tables, listing interatomic distances and angles, fractional coordinates, and intensity data (22 pages). Ordering information is given on any current masthead page.

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(7) W.-S. Lee and H. Brintzinger, manuscript submitted for publication. We find the neutral complex **1** to be very air sensitive; in the absence of air, it decomposes at a moderate rate at high concentration in solution, but appears to be stable at room temperature in the solid state. It does not react with weak ligands such as CH_3CN or THF but is converted rapidly to η^5-$C_5H_5Co(CO)L$ in the presence of ligands such as $(C_6H_5)_3P$ or CO.

(8) (a) For details of the electrochemical experiments, see ref 12 in the accompanying communication;[2] (b) an interesting series of paramagnetic, cationic iron dimers having Fe in formal oxidation state +1.5 $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2[Ph_2P(CH_2)_nPPh_2]^+$ has been prepared and studied recently.[8c,d] These complexes are analogous to $\mathbf{1}\cdot^-$ in the sense that they contain delocalized adjacent-valent metal atoms; they differ in charge, ligands, and metal–metal bond order (0.5 instead of 1.5); (c) J. A. Ferguson and T. J. Meyer, *Inorg. Chem.*, **11**, 631 (1972); (d) R. J. Haines and A. L. DuPreez, *ibid.*, **11**, 330 (1972).

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(11) National Institutes of Health Postdoctoral Fellow, 1974–present.

(12) National Institutes of Health Postdoctoral Fellow, 1975–present.

(13) Camille and Henry Dreyfus Teacher-Scholar Grant Awardee, 1970–1975.

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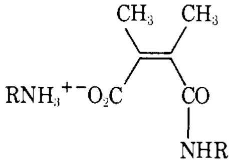
Cooperative Catalysis of the Cleavage of an Amide by Carboxylate and Phenolic Groups in a Carboxypeptidase A Model

Sir:

The enzyme carboxypeptidase A catalyzes the hydrolysis of *N*-acylamino acids and also of the related esters, *O*-acylhydroxy acids, at comparable rates.[1] For both classes of substrates catalytic functions are apparently performed by a Zn^{2+} and a γ carboxylate of glutamate 270. In addition, tyrosine 248 has often been assigned a catalytic role, at least with peptide substrates. It is agreed that the phenolic hydroxyl of Tyr-248 can be within a catalytically useful distance of a bound substrate, and x-ray structure work[2] shows that it can be hydrogen bonded to the leaving group nitrogen in a peptide substrate. However, various modification studies[3] suggest that Tyr-248 plays no role in the hydrolysis of esters, and according to some interpretations[4] may not even be involved in the peptidase activity of the enzyme.

As part of our general program of exploring the chemistry of carboxypeptidase A and various model systems for its action,[5] we have investigated the question of whether the hydrolysis of an amide, catalyzed by a neighboring carboxylate ion, can also be assisted by a phenolic hydroxyl in an appropriate position to protonate the leaving amino group. We find that such bifunctional catalysis is indeed significant, but only under special conditions related to those within the enzyme itself. Perhaps more striking, we find that our reactions undergo a change of mechanism on approach to physiological pH conditions which is directly related to the principal ambiguity in the mechanism of action of carboxypeptidase A.

The compounds of interest, **1–5**, were all prepared by reaction of 2 equiv of the appropriate benzylamine with 2,3-dimethylmaleic anhydride in ether–dimethoxyethane at room temperature for 12 h. Depending on the reaction conditions (vide infra) these compounds underwent cleavage of the amide group to afford either dimethylmaleic anhydride or dimethylmaleic acid. In all cases the kinetics were followed at 250 nm for at least two–three half-lives, and they obeyed a good first-order rate law. In the important pH region corresponding to neutrality, there was no catalysis by buffer, and the identity of the reaction product was confirmed by isolation.



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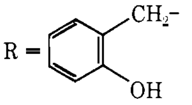

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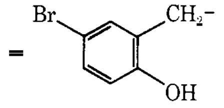

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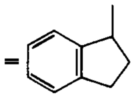

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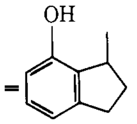

In aqueous solution, all these compounds showed essentially the same behavior as has been described by Kirby[6] for simple *N*-alkyldimethylmaleamic acids. That is, the free carboxylic acid underwent rapid cyclization to produce the dimethylmaleic anhydride, while the corresponding carboxylate ion showed a negligible rate of reaction. Thus, in all aqueous pH ranges compounds **1–5** had similar rates and gave no evidence for catalysis by the phenolic hydroxyl. The situation was different in a nonaqueous medium.

The interior of many enzymes is at least partially nonaqueous in character, and catalytic hydrogen bonding effects do not have to compete with hydrogen bonds involving water. Thus, we have also examined the amide cleavage reactions of compounds **1–5** in CH_3CN containing 1 M H_2O as a model for such a medium. The data are listed in Table I. Of course, the definition of "pH" in such a medium is a problem,[7] so our systems were examined simply in terms of the buffer ratio of HOAc/KOAc. With a 10:1 ratio of HOAc/KOAc, corresponding to an acidic medium, all the compounds underwent a cyclization to produce dimethyl-