had found that glycylleucyltyrosine amide is cleaved more rapidly by α-chymotrypsin and has a lower K_m value than peptides containing residues smaller than leucine in the second position. Our observation can be explained either by lack of space for the leucyl side chain in the γ-chymotrypsin crystal or by low solubility of the inhibitor. No peptide chloromethyl ketones have been found which inhibit α-chymotrypsin crystals although PMSF gives complete inhibition under the conditions of our experiments. We found it surprising that Ac-PheCH$_2$Cl and CHO-PheCH$_2$Cl would not react with α-chymotrypsin crystals since the Cambridge laboratory has obtained a Fourier difference map of the enzyme inhibited with formyltryptophan.[11] Possibly small peptide chloromethyl ketones are able to bind to α-chymotrypsin crystals and yet are unable to react due to geometric restraints imposed by the α-chymotrypsin dimer structure; crystallographic experiments designed to test this hypothesis are in process.

For the first crystallographic analysis we have chosen the inhibitor Ac-Ala-PheCH$_2$Cl because of its close structural resemblance to natural peptide substrates. Precession photographs of γ-chymotrypsin crystals (0.5 mm × 0.3 mm) inhibited with Ac-Ala-PheCH$_2$Cl in pure 2.4 *M* phosphate at pH 5.6 for 2–5 weeks (83% inhibition) were obtained with a Buerger camera using Cu Kα radiation and 15° precession. Control photographs of uninhibited crystals were obtained for comparison. The cell parameters are as follows: uninhibited $a = b = 70.1$ Å, $c = 97.4$ Å; inhibited $a = b = 69.3$ Å, $c = 98.4$ Å. A collaborative study with David R. Davies and David Segal of the National Institutes of Health on the difference Fourier maps of γ-chymotrypsin inhibited with Ac-Ala-PheCH$_2$Cl and related halomethyl ketones is in progress.

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(11) D. M. Blow, personal communication.

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On the Identity of the Anion of Mercury Cobalt Carbonyl. Characterization of a Complex Anion, $Hg[Co(CO)_4]_3^-$

Sir:

In a recent paper Vizi-Orosz, Papp, and Marko[1] described the formation of an anion of mercury cobalt carbonyl, $\{Hg[Co(CO)_4]_2\}^-$, by reaction of $Hg[Co(CO)_4]_2$ with sodium amalgam or with $NaCo(CO)_4$. While the presence of such an anionic intermediate in the sodium reduction of $Hg[Co(CO)_4]_2$ to $Co(CO)_4^-$ did not seem unreasonable to us, the "reduction" of $Hg[Co(CO)_4]_2$ to $Hg[Co(CO)_4]_2^-$ by $Co(CO)_4^-$ appeared to be quite unusual and worthy of further investigation.

The infrared spectrum of a deep orange-brown solution of equimolar quantities of $Hg[Co(CO)_4]_2$ and $NaCo(CO)_4$ in THF, prepared and observed under an argon atmosphere, showed very strong absorptions at 2036 and 1986–1958 (broad) cm^{-1}.[2] In addition there were weak absorptions at 2068, 1895 (sh), and 1862 cm^{-1}. The first of these may be attributed to unreacted $Hg[Co(CO)_4]_2$, while the latter two are characteristic of $Co(CO)_4^-$ in THF.[3] A 1:1 stoichiometry was indicated for the reaction by infrared analysis of various mixtures of $Hg[Co(CO)_4]_2$ and $Co(CO)_4^-$. If $Hg[Co(CO)_4]_2$ were actually reduced by $Co(CO)_4^-$, a substantial quantity of $Co_2(CO)_8$ should have been found as the oxidized species.

$$Hg[Co(CO)_4]_2 + Co(CO)_4^- \longrightarrow Hg[Co(CO)_4]_2^- + Co(CO)_4 \tag{1}$$

$$Co(CO)_4 \longrightarrow {}^1/_2Co_2(CO)_8 \tag{2}$$

No evidence of $Co_2(CO)_8$ was obtained. Furthermore solutions prepared as above or with stoichiometric quantities of sodium amalgam and $Hg[Co(CO)_4]_2$ exhibit no esr signal and are diamagnetic when examined by the nmr technique of Evans.[4]

The identity of the dark-colored species in these solutions responsible for the observed spectrum has been shown to be $Hg[Co(CO)_4]_3^-$. This anion has been isolated as the tris(1,10-phenanthroline)iron(II), tetraphenylarsonium and tetramethylammonium salts. In addition to the analytical results[5] a number of other observations on these derivatives lead us to believe we have isolated $Hg[Co(CO)_4]_3^-$ and to question the existence of $Hg[Co(CO)_4]_2^-$ under these conditions. The first of these, $[Fe(1,10\text{-phen})_3][HgCo_3(CO)_{12}]_2$ (**1**), obtained only as a red powder by Markó and coworkers,[1] crystallizes with a monoclinic lattice in the space group P2$_1$/c. The unit cell parameters, $a = 14.41 \pm 0.02$ Å, $b = 27.34 \pm 0.05$ Å, $c = 17.94 \pm 0.06$ Å, and $\beta = 72°\,40' \pm 5'$, with the observed density of 2.00 g/cc, give an observed molecular weight of 2038 for the molecule assuming that it occupies the general positions of the unit cell. The calculated molecular weights of $[Fe(1,10\text{-phen})_3][HgCo_3(CO)_{12}]_2$ and $[Fe(1,10\text{-phen})_3][HgCo_2(CO)_8]_2$ are 2023 and 1681, respectively.

Treatment of the diamagnetic $(CH_3)_4N^+Hg[Co(CO)_4]_3^-$ (**2**) with excess triphenylphosphine in methanol resulted in rapid precipitation of 98% of the expected quantity of $Hg[Co(CO)_3P(C_6H_5)_3]_2$.[6] The infrared spectrum of the resulting light yellow solution contained only the carbonyl absorptions corresponding to $Co(CO)_4^-$. This anion was precipitated as the insoluble $[Ni(1,10\text{-phen})_3][Co(CO)_4]_2$[7] in 90% yield by addition of an aqueous solution of $[Ni(1,10\text{-phen})_3]Cl_2$ to the aqueous extracts of the residue left on evaporation of the methanol. These results, summarized in the following scheme, are consistent only with a $Co(CO)_4$/Hg ratio of 3:1.

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(1) A. Vizi-Orosz, L. Papp, and L. Markó, *Inorg. Chim. Acta*, 3, 103 (1969).

(2) These values may be compared with 2035 and 1969 cm^{-1} reported for $[Hg[Co(CO)_4]_2]^-$ in ref 1.

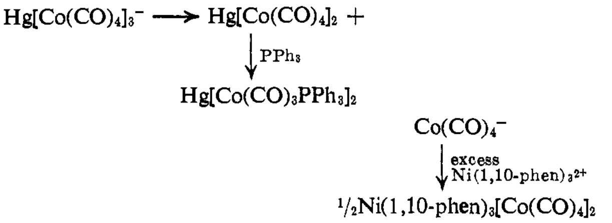
(3) W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Amer. Chem. Soc.*, 87, 2563 (1965).

(4) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(5) *Anal.* Calcd for $[Fe(C_{12}H_8N_2)_3][HgCo_3(CO)_{12}]_2$: C, 35.4; H, 1.18; N, 4.13; Hg, 19.8. Found: C, 35.4; H, 1.40; N, 4.15; Hg, 19.4. Calcd for $[As(C_6H_5)_4][HgCo_3(CO)_{12}]$: C, 39.4; H, 1.86; Hg, 18.8. Found: C, 39.2; H, 1.89; Hg, 18.9. Calcd for $[(CH_3)_4N][HgCo_3(CO)_{12}]$: C, 24.4; H, 1.54; N, 1.78; Co, 22.4; Hg, 25.5. Found: C, 24.3; H, 1.64; N, 1.80; Co, 22.8; Hg, 27.2.

(6) W. Hieber and R. Breu, *Chem. Ber.*, **90**, 1259 (1967).

(7) W. Hieber and H. Schulten, *Z. Anorg. Allg. Chem.*, 232, 17 (1937).



$$\begin{tikzcd} \mathrm{Hg[Co(CO)_4]_3^-} \arrow[r] & \mathrm{Hg[Co(CO)_4]_2} + \arrow[d, "\mathrm{PPh_3}"] & \mathrm{Co(CO)_4^-} \arrow[d, "\mathrm{excess\ Ni(1,10\text{-}phen)_3^{2+}}"] \\ & \mathrm{Hg[Co(CO)_3PPh_3]_2} & \mathrm{{}^1/_2Ni(1,10\text{-}phen)_3[Co(CO)_4]_2} \end{tikzcd} \qquad (3)$$

The infrared spectrum of **2** in THF, as observed in a sealed Fluorite cell, showed strong bands at 2039 and 1963 $\mathrm{cm^{-1}}$ for the complex, in addition to weak bands at 2069 and 1996 (sh) $\mathrm{cm^{-1}}$ from $\mathrm{Hg[Co(CO)_4]_2}$ and at 1887 $\mathrm{cm^{-1}}$ for $\mathrm{Co(CO)_4^-}$. In Nujol mulls of **1** only the absorptions attributable to the complex are observed. These spectra together with those of the THF reaction mixture confirm the reversible nature of the complex ion formation.[8] The approximately 30-$\mathrm{cm^{-1}}$

$$\mathrm{Hg[Co(CO)_4]_2} + \mathrm{Co(CO)_4^-} \rightleftarrows \mathrm{Hg[Co(CO)_4]_3^-} \qquad (4)$$

shift to lower energies on going from $\mathrm{In[Co(CO)_4]_3}$[9] to $\mathrm{Hg[Co(CO)_4]_3^-}$ is similar to that observed[10] between $\mathrm{Co_4(CO)_{12}}$ and $\mathrm{FeCo_3(CO)_{12}^-}$. Absorptions at 130 $\mathrm{cm^{-1}}$ in the far-infrared and Raman and at 100 $\mathrm{cm^{-1}}$ in the Raman spectra of $\mathrm{Hg[Co(CO)_4]_3^-}$ can be attributed respectively to the antisymmetric and symmetric HgCo stretching vibrations of the $\mathrm{HgCo_3}$ moiety. The reduction of the energies of the HgCo modes on going from $\mathrm{HgCo_2(CO)_8}$[11] to $\mathrm{HgCo_3(CO)_{12}^-}$ is expected for the increase in coordination number. Analogous shifts are observed in mercuric halides upon formation[12] of $\mathrm{HgX_3^-}$ from $\mathrm{HgX_2}$.

Mercury(II) complexes of the type $\mathrm{HgX_3^-}$ have been characterized with halides,[13] pseudohalides,[13] main group elements,[14] transition metals and halides,[15] and carbon,[16] but not previously with transition metals alone. A related cadmium(II) halide–metal carbonyl complex has been described.[17] The most likely structure for $\mathrm{Hg[Co(CO)_4]_3^-}$ would involve a planar arrangement of the four metal atoms. With the carbonyl groups staggered an ion of C_{3h} symmetry would result, for which seven infrared active carbonyl stretching vibrations would be expected. In an elegant study of the vibrational spectrum of $\mathrm{Hg[Co(CO)_4]_2}$, Bor[18] recently showed that coupling of the stretching vibrations of CO ligands on different cobalt atoms was quite small except for that of the *trans*-axial groups acting through a linear sequence of bonds. Since no linear arrangement of ligands exists in the proposed structure of $\mathrm{Hg[Co(CO)_4]_3^-}$, it is reasonable to expect that local symmetry will adequately describe the carbonyl stretching vibrations. For C_{3v} local symmetry three infrared-active bands are predicted. That only two of these are observed is probably a result of broadening due to the polar solvent necessary to dissolve the complex. An X-ray structure determination is currently in progress to provide more complete structural information.

The susceptibility of $\mathrm{Hg[Co(CO)_4]_2}$ to nucleophilic attack by halide ions has recently been reported in these letters.[19] Attack of halides on $\mathrm{Hg[Co(CO)_4]_3^-}$, like that on $\mathrm{Hg[Co(CO)_4]_2}$, leads to displacement of $\mathrm{Co(CO)_4^-}$. In a similar reaction, equimolar amounts of $\mathrm{(Ph_3PCH_2Ph)^+X^-}$ ($X = \mathrm{Cl, I}$) and $\mathrm{Hg[Co(CO)_4]_2}$ lead to the formation of new species, $\mathrm{(Ph_3PCH_2Ph)^+\{XHg[Co(CO)_4]_2\}^-}$, for which satisfactory elemental analyses have been obtained. The infrared spectrum of the chloride complex in $\mathrm{CH_2Cl_2}$ exhibits bands at 2052 m and 1983 vs $\mathrm{cm^{-1}}$ in addition to a weak band at 2070 $\mathrm{cm^{-1}}$ attributable to $\mathrm{Hg[Co(CO)_4]_2}$. The shifts of the CO stretching peaks to lower frequencies indicate the $\mathrm{Co(CO)_4}$ groups bear a fractional negative charge.

We are presently extending our study of complex anions to other transition metal carbonyl groups as well as to other main group elements. Preliminary studies have demonstrated the existence of such complexes as $\mathrm{Hg[Fe(CO)_2C_5H_5]_3^-}$, $\mathrm{Cd[W(CO)_3C_5H_5]_3^-}$, and $\mathrm{In[Co(CO)_4]_4^-}$. Other derivatives of gallium, indium, and thallium such as $\mathrm{Br_2In[Co(CO)_4]_2^-}$ and $\mathrm{Tl[Fe(CO)_2C_5H_5]_2^+}$ have been independently observed.[20]

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[8] Preliminary investigations on the zinc and cadmium analogs of the complex ion indicate that the equilibrium (eq 4) is shifted toward the right in noncoordinating solvents; only infrared absorptions due to the complex were observed.

[9] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1586 (1966).

[10] P. Chini, L. Colli, and M. Peraldo, *Gazz. Chim. Ital.*, **90**, 1005 (1960).

[11] H. Stammreich, K. Kawai, O. Sala, and P. Krumholz, *J. Chem. Phys.*, **35**, 2175 (1961).

[12] D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968.

[13] D. Grdenic, *Quart. Rev.* (London), **19**, 303 (1965).

[14] T. F. Schaaf and J. P. Oliver, *J. Amer. Chem. Soc.*, **91**, 4327 (1969).

[15] K. Edgar, B. F. G. Johnson, J. Lewis, and S. B. Wild, *J. Chem. Soc., A*, 2851 (1968).

[16] L. M. Seitz and S. D. Hall, *J. Organometal. Chem.*, **15**, P7 (1968).

[17] J. K. Ruff, *Inorg. Chem.*, **7**, 1499 (1968).

[18] G. Bor, *Inorg. Chim. Acta*, **3**, 196 (1969).

[19] J. M. Burlitch, *J. Amer. Chem. Soc.*, **91**, 4563 (1969).

[20] W. A. G. Graham, private communication to J. M. B.

[21] Author to whom communications should be addressed.

[22] National Defense Education Act, Title IV, Fellow, 1966–1969.

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Stereochemistry of the Oxidation of the *cis*- and *trans*-1-Amino-2,3-diphenylaziridines

Sir:

The thermal fragmentation of episulfones,[1] nitrosoaziridines,[2] and ethyleneazamines[3] has been observed to be stereospecific in contrast to the nonstereospecific decomposition of episulfoxides[4] and contrary to the initial conclusions of Woodward and Hoffmann based

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[1] (a) N. P. Neureiter and F. G. Bordwell, *J. Amer. Chem. Soc.*, **85**, 1209 (1963); (b) N. P. Neureiter, *ibid.*, **88**, 558 (1966); (c) L. A. Carpino and L. V. McAdams, III, *ibid.*, **87**, 5804 (1965); (d) N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966); (e) F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *J. Amer. Chem. Soc.*, **90**, 429 (1968).

[2] R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964).

[3] J. P. Freeman and W. H. Graham, *J. Amer. Chem. Soc.*, **89**, 1761 (1967).

[4] G. E. Hartzell and J. N. Paige, *J. Org. Chem.*, **32**, 459 (1967).