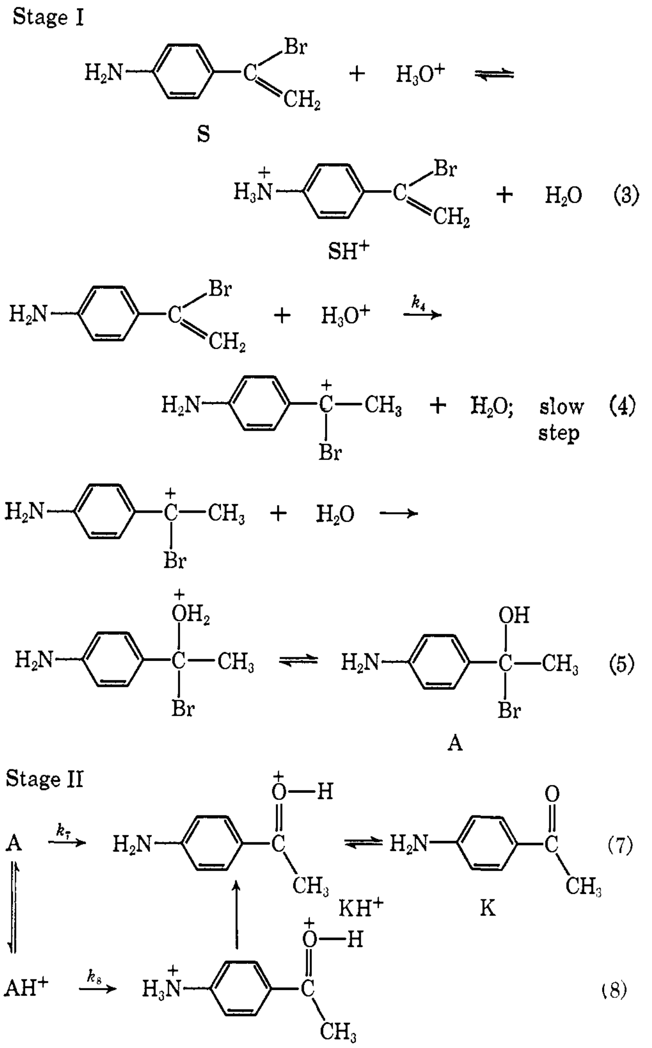
relatively slight increase, 60%, in $k_{\mathrm{obsd}}{}^{\mathrm{I}}$ between 0.1 and 2.4 M $HClO_4$ is attributable to a medium effect, as found for hydration of unsubstituted *p*-aminostyrene.[3] In the intermediate pH range, the unsimplified rate eq 9 applies, since the ground state consists of both S and SH^+, in equilibrium.

Also in agreement with the assigned mechanism for stage I is the finding of general catalysis in acetic acid (pH 5) and hydrogen phthalate (pH 6) buffers.[2,3] Values of k_4 at 50° and $\mu = 0.1$ M for H_3O^+ and HOAc are 1.4 and 1.3 $\times$ 10^{-4} l. mol^{-1} sec^{-1}, respectively. Based on the kinetic data $K_{\mathrm{SH^+}}{}^{\mathrm{c}}$, at 50° and $\mu = 0.1$ M, has the value 10^{-2}.



$$k_{\mathrm{obsd}}{}^{\mathrm{I}} = \frac{[S]}{[S] + [SH^+]}k_4[H_3O^+] =$$

$$\frac{[SH^+]}{[S] + [SH^+]}K_{\mathrm{SH^+}}{}^{\mathrm{c}}k_4 \quad (9)$$

$$\text{when } [SH^+] \ll [S],\ k_{\mathrm{obsd}}{}^{\mathrm{I}} = k_4[H_3O^+] \quad (9a)$$

$$\text{when } [SH^+] \gg [S],\ k_{\mathrm{obsd}}{}^{\mathrm{I}} = K_{\mathrm{SH^+}}{}^{\mathrm{c}}k_4 \quad (9b)$$

$$k_{\mathrm{obsd}}{}^{\mathrm{II}} = \frac{1}{[A] + [AH^+]}(k_7[A] + k_8[AH^+]) \quad (10)$$

As regards stage II, a reasonable mechanism is given by eq 7 and 8 (rate eq 10). The constancy of the first-order rate constant, $k_{\mathrm{obsd}}{}^{\mathrm{II}}$, in the media of higher acidity is attributed to the failure of reaction 7 to compete with reaction 8, due to a low relative concentration of free *p*-aminophenyl-1-aminoethanol (*i.e.*, $[AH^+] >>> [A]$ and eq 10 reduces to $k_{\mathrm{obsd}}{}^{\mathrm{II}} = k_8$). Values of $k_{\mathrm{obsd}}{}^{\mathrm{II}}$ have not been measured below 10^{-3} M H_3O^+ due to the overlap with stage I at lower acidity. However, as the acidity of the medium is reduced, solvolysis of free amine A should contribute, and since $k_7 > k_8$, $k_{\mathrm{obsd}}{}^{\mathrm{II}}$ should increase and then reach the limiting value k_7 when the ground state is essentially all A. The inferential extension of the behavior of $k_{\mathrm{obsd}}{}^{\mathrm{II}}$ in solutions of lower acidity is represented by the dashed portion of the line of Figure 1. The qualitative aspect of the dashed portion is consistent with the observation that at 50°, stage II competes with stage I at around pH 4.5, and is not seen in the solutions of lowest acidity. The specific position of the dashed portion of the line is based on the working hypothesis that k_7/k_8 is 100 and $K_{\mathrm{AH^+}}{}^{\mathrm{c}}$ is 10^{-5}.[4] In any event, for solvolysis of AH^+ to contribute significantly when $[H_3O^+]$ is as low as 10^{-3} M requires that the NH_2 *vs.* NH_3^+ substituent effect (k_7/k_8) be small in comparison to, for example, benzyl halide solvolysis. This is perhaps not surprising for a transition state having protonated ketone character, thereby reducing the demand placed upon the *para* substituent.

As a final point of interest, at 50° in 0.1 M $HClO_4$, $k_{\mathrm{obsd}}{}^{\mathrm{I}}$ (for the net change: $SH^+ + H_2O \rightarrow tr^+$) is 560 times as great as k_{obsd} for the hydration of unsubstituted *p*-aminostyrene. The large activating effect of the α-bromo substituent may in part be a reflection of the response of substituent polarizability to the high electron demand placed upon the substituent.[5]

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[4] The value of $K_{\mathrm{AH^+}}$ has not been determined. However, the intermediate is a significantly stronger base than α-bromo-*p*-aminostyrene, based on a comparison of the effect of acidity on the spectra of the intermediate and the styrene at the same concentration.

[5] (a) W. M. Schubert, J. M. Craven, and H. Steadly, *J. Amer. Chem. Soc.*, 81, 2695 (1959); (b) W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, 17, 199 (1962).

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Synthesis and Structure of $(C_5H_5CoCO)_2(GeCl_2)_2Fe(CO)_4$. A Novel Metal–Metal Heterocycle

Sir:

Organometallic derivatives of silicon and its congeners are well known to form cyclic compounds $(R_2M)_n$; in the case of tin, n ranges from 4 to 9.[1] In contrast, simple cyclic metal–metal bonded structures of transition metals have been observed only with three-membered rings, as in $Os_3(CO)_{12}$[2] or $[MnFe_2(CO)_{12}]^-$.[3] Larger numbers of transition metal atoms seem to adopt a more highly condensed cluster arrangement wherein the number of metal–metal bonds is greater than the number of metal atoms present,[4] as in $Rh_4(CO)_{12}$[5] and

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[1] H. Gilman, W. H. Atwell, and F. K. Cartledge, *Advan. Organometal. Chem.*, 4, 1 (1966).

[2] E. R. Corey and L. F. Dahl, *Inorg. Chem.*, 1, 521 (1962).

[3] U. Anders and W. A. G. Graham, *Chem. Commun.*, 292 (1966).

[4] On this definition, the anion $[Re_4(CO)_{16}]^{2-}$ would be regarded as a cluster, as it was in fact termed by the discoverers: R. Bau, B. Fontal, H. D. Kaesz, and M. R. Churchill, *J. Amer. Chem. Soc.*, 89, 6374 (1967).

[5] C. H. Wei, G. R. Wilkes, and L. F. Dahl, *ibid.*, 89, 4792 (1967).

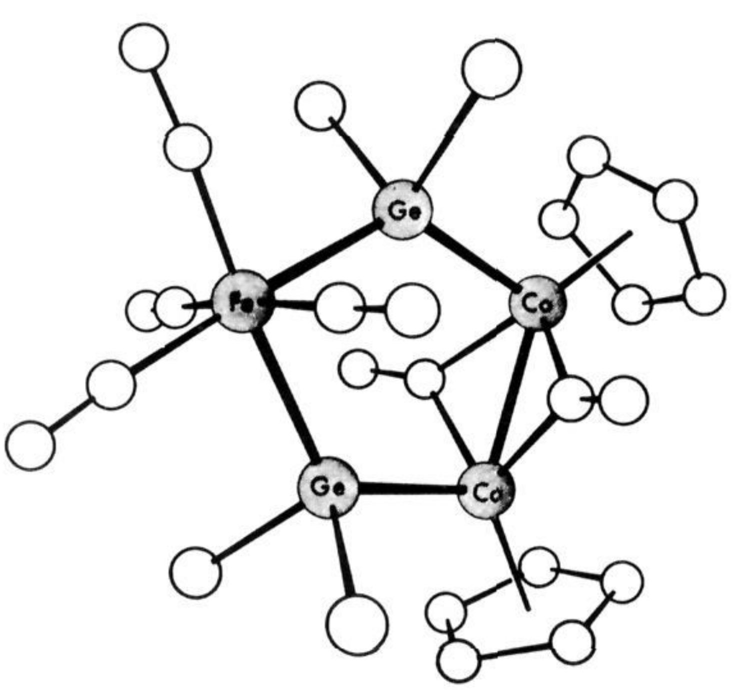


Figure 1. The molecular structure of $(C_5H_5CoCO)_2(GeCl_2)_2Fe(CO)_4$. Maximum deviation from the plane through the five-membered ring is 0.026 Å. Some important bond lengths (with rms deviations taken over all bonds of the same type) are Fe–Ge = 2.433 (0.008); Ge–Co = 2.340 (0.006); Co–Co = 2.436 (0.012); Ge–Cl = 2.215 (0.019); Co–C (C_5H_5) = 2.12 (0.04). Some bond angles are Ge–Fe–Ge, 89.1°; Fe–Ge–Co, 123.4°; Ge–Co–Co, 102.1°; Cl–Ge–Cl, 99°; Co–CO–Co, 81°.

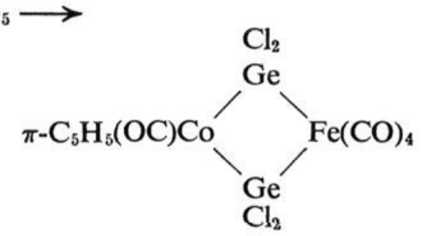
$Rh_6(CO)_{16}$.[6] Among organometallic compounds containing both main and transition group elements, three- and four-membered rings are established, as in $(C_6H_5)_2GeFe_2(CO)_8$[7] and $[R_2SnFe(CO)_4]_2$.[8] We report here the first five-membered ring in this mixed-metal class.

The investigation originated in a more complete study of the *ring-closure process* first recognized in the reaction[9]

$$cis\text{-}(OC)_4Fe(GeX_3)_2 + Fe(CO)_5 \longrightarrow [X_2GeFe(CO_4)]_2$$

It was, by analogy, anticipated that the following reaction would afford a product of structure **1**. Accord-

$$\pi\text{-}C_5H_5(OC)Co(GeCl_3)_2 + Fe(CO)_5 \longrightarrow$$



$$\pi\text{-}C_5H_5(OC)Co\begin{matrix} Cl_2 \\ Ge \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ Ge \\ Cl_2 \end{matrix}Fe(CO)_4$$

1

ingly, $\pi\text{-}C_5H_5(OC)Co(GeCl_3)_2$[10] (0.3 g, 0.6 mmole) and $Fe(CO)_5$ (2.1 g, 11 mmoles) were heated under nitrogen for 2 hr without solvent in a bath at 110°. The residue was washed with petroleum ether (bp 30–60°) to remove excess $Fe(CO)_5$, and then extracted with dichloromethane. Addition of petroleum ether to the extract afforded the dark green crystalline product, leaving $[Cl_2GeFe(CO)_4]_2$ in solution. Two recrystallizations from dichloromethane–petroleum ether gave the analytically pure product in 40% yield. In the crystalline state, the compound is stable for many months to light and air. The nmr spectrum showed a sharp cyclopentadienyl resonance at τ 4.48 $(CDCl_3)$, and infrared bands in the carbonyl stretching region at 2107 vs, 2063 m, 2046 vs, 1854 vw, and 1822 s cm^{-1} (dichloromethane solution). The bridging carbonyl bands ruled out structure **1**, and analysis (C, H, O, Cl) and mass spectrometry (molecular ion at *m/e* 758) established the molecular formula as $(C_5H_5CoCO)_2(GeCl_2)_2Fe(CO)_4$. The spectroscopic data, taken with the diamagnetism of the compound, seemed to be consistent only with a cyclic structure; this has now been confirmed by a single-crystal X-ray structure determination.

The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with eight molecules per unit cell. Three-dimensional intensity data were collected on a Pailred diffractometer. The structure was solved by Patterson and Fourier methods, and at the present stage of refinement the *R* factor is 8.2%, all atoms having isotropic temperature factors.

There are no significant differences in geometry between the two independent molecules at this point. Both exhibit symmetry that closely approximates C_{2v}-mm if the individual atoms of the cyclopentadienyl groups are not considered. The structure of the molecule is shown in Figure 1, and selected bond lengths and angles are given in the caption.

The iron–germanium bond length may be compared with 2.398 ± 0.004 Å in $[(CH_3)_2Ge]_3Fe_2(CO)_6$[11] and 2.357 ± 0.004 Å in $Cl_2Ge[C_5H_5Fe(CO)_2]_2$.[12] In the latter structure, the Fe–Ge–Fe angle of 128° is noteworthy, for it shows the preferred situation in a strainless molecule having germanium bonded to two transition metals. The angle is 5° smaller in the present structure, but is large enough to compensate for the more typically octahedral angles at iron and cobalt in making possible the planar five-membered ring. A striking feature of bis(transition metal)germanium structures is the angular adaptability of germanium. Angles as low as 70° have been observed where forced by the exigencies of bonding in the molecule.[11]

Several other examples of this type of reaction have been investigated, and have led to the isolation of stable compounds having other five-membered rings: Co–Ge–Co–Ge–Co and Co–Sn–Co–Sn–Co.[13] The compound $(C_5H_5CoCOSnCl_2)_3 \cdot C_6H_6$, believed to contain a six-membered ring, has also been obtained.[14,14a] It may be concluded that an interesting route has been opened to cyclic mixed-metal compounds, although at this stage the products are not entirely predictable.

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[8] R. B. King and F. G. A. Stone, *ibid.*, **82**, 3833 (1960).

[9] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 1208 (1968).

[10] R. Kummer and W. A. G. Graham, *ibid.*, **7**, 523 (1968).

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[12] M. A. Bush and P. Woodward, *J. Chem. Soc., A*, 1833 (1967).

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[14a] NOTE ADDED IN PROOF. Anisotropic refinement is continuing and final atomic parameters, when available, will be deposited with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.