Reaction of the Protonic Acids, $HCo(PF_3)_4$ and $HCo(CO)_4$, with *NN*-Dimethyl(trimethylsilyl)amine to form Silylammonium Compounds

By RONALD E. HIGHSMITH,† JEAN R. BERGERUD, and ALAN G. MACDIARMID*

(*John Harrison Laboratory of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania Philadelphia, Pennsylvania* 19104)

Summary $HCo(PF_3)_4$ and $HCo(CO)_4$ react with Me_2NSiMe_3 to form $[Me_2N(H)SiMe_3]^+[Co(PF_3)_4]^-$ and $[Me_2N(H)SiMe_3]^+[Co(CO)_4]^-$, respectively; the last compound is also formed from the reaction of Me_2NH with $Me_3SiCo(CO)_4$.

ONE of the major ways in which carbon and silicon amines differ is in their reaction with protonic acids, the former yielding ammonium compounds, the latter undergoing rapid Si–N bond cleavage.[1] No definitive evidence has yet been obtained for the formation of a silicon ammonium compound, stable at room temperature, from the reaction of a silicon amine with a protonic acid, although it has been suggested that Cl_3SiNMe_2 might form a hydrochloride.[2] Aylett and Emsley[3] have reported that H_3SiNMe_2 and HCl form an adduct, which may be the silyl ammonium compound, $[Me_2NH(SiH_3)]^+HCl_2^-$, at $-96°$ and that it decomposes rapidly to SiH_3Cl and $[Me_2NH_2]^+Cl^-$ at $-46°$.

We report that, contrary to a previous suggestion,[4] Me_3SiNMe_2 reacts quantitatively and instantly below 0° with a slight excess of $HCo(PF_3)_4$ to yield a white solid $Me_3SiNMe_2 \cdot HCo(PF_3)_4$ (1 : 1). This substance appears to be the ammonium compound, $[Me_3SiN(H)Me_2]^+[Co(PF_3)_4]^-$, (I). It has a very strong, broad absorption in the PF stretching region (Nujol mull) at 800 cm^{-1} which is identical with that obtained from the 1 : 1 adduct, presumably $[Me_2NH_2]^+$-$[Co(PF_3)_4]^-$, formed from Me_2NH and $HCo(PF_3)_4$. A very strong band at 820 cm^{-1} has previously been reported for the $Co(PF_3)_4^-$ ion.[5] I.r. bands in the NH and NMe regions and the ^1H n.m.r. spectrum in CD_3CN, (Me_4Si internal standard) were also consistent with this formulation: $\delta(Me_3Si)$ in Me_3SiNMe_2, $+2{\cdot}9$; in (I), $-24{\cdot}0$ Hz; $\delta(Me_2N)$ in Me_3SiNMe_2, $-141{\cdot}6$; in (I), $-191{\cdot}0$; in $[Me_2NH_2]^+Cl^-$, $-156{\cdot}6$ Hz. The Me_2N peak was a singlet in Me_3SiNMe_2 but a doublet (J_{HNCH} 4·6 Hz) in (I).

---

† Present address: Research and Development Division of the Carborundum Company, Niagara Falls, New York 14302.

Compound (I) is slightly volatile in the vacuum system at room temperature and sublimes readily, without decomposition, *in vacuo* at approximately 80°. Heating under a variety of conditions produced no $Me_3SiCo(PF_3)_4$.

When Me_3SiNMe_2 and $HCo(CO)_4$ were mixed at low temperatures a rapid reaction occurred to give a white, solid 1:1 adduct, formulated as $[Me_3SiN(H)Me_2]^+[Co(CO)_4]^-$, (II). This compound could not be obtained in an analytically pure state since it tended to darken rapidly at room temperature, presumably because of slight reversible dissociation to $HCo(CO)_4$ which then spontaneously decomposed. A very strong, broad ν_{CO} band in its i.r. spectrum (Nujol mull) at 1880 cm^{-1} showed the presence of the $Co(CO)_4^-$ ion.[6] The ^1H n.m.r. spectrum in CD_3CN was consistent with the ammonium salt formulation: $\delta(Me_3Si)$ $-25{\cdot}6$; $\delta(Me_2N)$ $-192{\cdot}8$, J_{HNCH} 4·3 Hz).

It was found that (II) could also be formed from $Me_3SiCo(CO)_4$ and Me_2NH. We have reported previously[7] that when $Me_3SiCo(CO)_4$ was treated with a slight deficit of Me_2NH, a 19% yield of Me_3SiNMe_2, based on Me_2NH employed, was obtained according to reaction (1). The

$$Me_3SiCo(CO)_4 + Me_2NH \rightarrow Me_3SiNMe_2 + HCo(CO)_4 \quad (1)$$

remainder of the reactants formed a white solid which was assumed to consist of $[Me_2NH_2]^+[Co(CO)_4]^-$, formed from a secondary reaction of the Me_2NH with the $HCo(CO)_4$ liberated, together with "$Me_3SiCo(CO)_4{\cdot}xMe_2NH$." A re-examination of this reaction [reaction (2)] shows that the white solid has an i.r. and ^1H n.m.r. spectrum essentially identical with that of $[Me_3SiN(H)Me_2]^+[Co(CO)_4]^-$. A side reaction occurs simultaneously according to equation (I) to give Me_3SiNMe_2. The extent to which this reaction occurs can be diminished by using a relatively smaller amount of amine. The reaction between $Me_3SiCo(CO)_4$ and Me_2NH as given by equation (2) is analogous to the reaction we recently observed between $Me_3SiCo(CO)_4$ and Me_3N[6] to give $[Me_3SiNMe_3]^+[Co(CO)_4]^-$ [reaction (3)].

$$Me_3SiCo(CO)_4 + Me_2NH \longrightarrow [Me_3SiN(H)Me_2]^+[Co(CO)_4]^- \quad (2)$$

$$Me_3SiCo(CO)_4 + Me_3N \longrightarrow [Me_3SiNMe_3]^+[Co(CO)_4]^- \quad (3)$$

This research was supported in part by the Advanced Research Projects Agency, Office of the U.S. Secretary of Defense, in the form of a fellowship to R.E.H., and by the National Science Foundation in the form of a grant to J.R.B.

(*Received, October 26th,* 1970; *Com.* 1853.)

[1] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp. 346,347.
[2] R. Cass and G. E. Coates, *J. Chem. Soc.*, 1952, 2347.
[3] B. J. Aylett and J. Emsley, *J. Chem. Soc. (A)*, 1967, 652.
[4] D. J. Cardin and M. F. Lappert, *Chem. Comm.*, 1966, 506.
[5] Th. Kruck, *Angew. Chem. Internat. Edn.*, 1967, **6**, 53.
[6] J. F. Bald, jun., and A. G. MacDiarmid, *J. Organometallic Chem.*, 1970, **22**, C22.
[7] Y. L. Baay and A. G. MacDiarmid, *Inorg. Chem.*, 1969, **8**, 987.