

## Reaction of the Protonic Acids, $\text{HCo}(\text{PF}_3)_4$ and $\text{HCo}(\text{CO})_4$ , with *NN*-Dimethyl(trimethylsilyl)amine to form Silylammonium Compounds

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**Summary**  $\text{HCo}(\text{PF}_3)_4$  and  $\text{HCo}(\text{CO})_4$  react with  $\text{Me}_2\text{NSiMe}_3$  to form  $[\text{Me}_2\text{N}(\text{H})\text{SiMe}_3]^+[\text{Co}(\text{PF}_3)_4]^-$  and  $[\text{Me}_2\text{N}(\text{H})\text{SiMe}_3]^+[\text{Co}(\text{CO})_4]^-$ , respectively; the last compound is also formed from the reaction of  $\text{Me}_2\text{NH}$  with  $\text{Me}_3\text{SiCo}(\text{CO})_4$ .

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.<sup>1</sup> 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  $\text{Cl}_3\text{SiNMe}_2$  might form a hydrochloride.<sup>2</sup> Aylett and Emsley<sup>3</sup> have reported that  $\text{H}_3\text{SiNMe}_2$  and  $\text{HCl}$  form an adduct, which may be the silyl ammonium compound,  $[\text{Me}_2\text{NH}(\text{SiH}_3)]^+\text{HCl}_2^-$ , at  $-96^\circ$  and that it decomposes rapidly to  $\text{SiH}_3\text{Cl}$  and  $[\text{Me}_2\text{NH}_2]^+\text{Cl}^-$  at  $-46^\circ$ .

We report that, contrary to a previous suggestion,<sup>4</sup>  $\text{Me}_3\text{SiNMe}_2$  reacts quantitatively and instantly below  $0^\circ$  with a slight excess of  $\text{HCo}(\text{PF}_3)_4$  to yield a white solid  $\text{Me}_3\text{SiNMe}_2 \cdot \text{HCo}(\text{PF}_3)_4$  (1:1). This substance appears to be the ammonium compound,  $[\text{Me}_3\text{SiN}(\text{H})\text{Me}_2]^+[\text{Co}(\text{PF}_3)_4]^-$ , (I). It has a very strong, broad absorption in the PF stretching region (Nujol mull) at  $800\text{ cm}^{-1}$  which is identical with that obtained from the 1:1 adduct, presumably  $[\text{Me}_2\text{NH}_2]^+[\text{Co}(\text{PF}_3)_4]^-$ , formed from  $\text{Me}_2\text{NH}$  and  $\text{HCo}(\text{PF}_3)_4$ . A very strong band at  $820\text{ cm}^{-1}$  has previously been reported for the  $\text{Co}(\text{PF}_3)_4^-$  ion.<sup>5</sup> I.r. bands in the NH and NMe regions and the  $^1\text{H}$  n.m.r. spectrum in  $\text{CD}_3\text{CN}$ , ( $\text{Me}_4\text{Si}$  internal standard) were also consistent with this formulation:  $\delta(\text{Me}_3\text{Si})$  in  $\text{Me}_3\text{SiNMe}_2$ , +2.9; in (I), -24.0 Hz;  $\delta(\text{Me}_2\text{N})$  in  $\text{Me}_3\text{SiNMe}_2$ , -141.6; in (I), -191.0; in  $[\text{Me}_2\text{NH}_2]^+\text{Cl}^-$ , -156.6 Hz. The  $\text{Me}_2\text{N}$  peak was a singlet in  $\text{Me}_3\text{SiNMe}_2$  but a doublet ( $J_{\text{HNCH}}$  4.6 Hz) in (I).

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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  $\text{Me}_3\text{SiCo}(\text{PF}_3)_4$ .

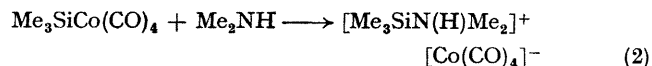
When  $\text{Me}_3\text{SiNMe}_2$  and  $\text{HCo}(\text{CO})_4$  were mixed at low temperatures a rapid reaction occurred to give a white, solid 1:1 adduct, formulated as  $[\text{Me}_3\text{SiN}(\text{H})\text{Me}_2]^+[\text{Co}(\text{CO})_4]^-$ , (II). This compound could not be obtained in an analytically pure state since it tended to darken rapidly at room temperature, presumably because of slight reversible dissociation to  $\text{HCo}(\text{CO})_4$  which then spontaneously decomposed. A very strong, broad  $\nu_{\text{CO}}$  band in its i.r. spectrum (Nujol mull) at  $1880\text{ cm}^{-1}$  showed the presence of the  $\text{Co}(\text{CO})_4^-$  ion.<sup>6</sup> The  $^1\text{H}$  n.m.r. spectrum in  $\text{CD}_3\text{CN}$  was consistent with the ammonium salt formulation:  $\delta(\text{Me}_3\text{Si}) -25.6$ ;  $\delta(\text{Me}_2\text{N}) -192.8$ ,  $J_{\text{HNCH}} 4.3\text{ Hz}$ .

It was found that (II) could also be formed from  $\text{Me}_3\text{SiCo}(\text{CO})_4$  and  $\text{Me}_2\text{NH}$ . We have reported previously<sup>7</sup> that when  $\text{Me}_3\text{SiCo}(\text{CO})_4$  was treated with a slight deficit of  $\text{Me}_2\text{NH}$ , a 19% yield of  $\text{Me}_3\text{SiNMe}_2$ , based on  $\text{Me}_2\text{NH}$  employed, was obtained according to reaction (1). The

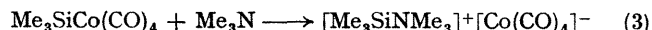


remainder of the reactants formed a white solid which was assumed to consist of  $[\text{Me}_2\text{NH}_2]^+[\text{Co}(\text{CO})_4]^-$ , formed from a

secondary reaction of the  $\text{Me}_2\text{NH}$  with the  $\text{HCo}(\text{CO})_4$  liberated, together with " $\text{Me}_3\text{SiCo}(\text{CO})_4 \cdot \text{Me}_2\text{NH}$ ." A re-examination of this reaction [reaction (2)] shows that the white solid has an i.r. and  $^1\text{H}$  n.m.r. spectrum essentially identical with that of  $[\text{Me}_3\text{SiN}(\text{H})\text{Me}_2]^+[\text{Co}(\text{CO})_4]^-$ . A



side reaction occurs simultaneously according to equation (1) to give  $\text{Me}_3\text{SiNMe}_2$ . The extent to which this reaction occurs can be diminished by using a relatively smaller amount of amine. The reaction between  $\text{Me}_3\text{SiCo}(\text{CO})_4$  and  $\text{Me}_2\text{NH}$  as given by equation (2) is analogous to the reaction we recently observed between  $\text{Me}_3\text{SiCo}(\text{CO})_4$  and  $\text{Me}_3\text{N}$ <sup>6</sup> to give  $[\text{Me}_3\text{SiNMe}_3]^+[\text{Co}(\text{CO})_4]^-$  [reaction (3)].



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