Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Synthesis of silylammonium and silylphosphosnium compounds by the reaction of amines and phosphines with silylcobalt tetracarbonyls

JAMES F. BALD, Jr. and ALAN G. MacDIARMID

The John Harrison Laboratory of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104 (U.S.A.)

(Received June 12th, 1969; in revised form January 16th, 1970)

It has been reported[1] that $H_3Si{-}Co(CO)_4$ reacts with bases such as trimethylamine and pyridine to give species such as $[H_3SiB_2]^+[Co(CO)_4]^-$, ($B = NMe_3$, C_5H_5N). In marked contrast, phosphines have been reported to react with $R_3Si{-}Co(CO)_4$ with elimination of carbon monoxide to give *trans*-$R_3Si{-}Co(CO)_3PR'_3$ [$R = H$ and $R' = Ph$[2]; $R = Cl$ or Et and $R' = Et$[3]].

We have found that NMe_3 undergoes instant reaction with a deficiency of $Me_3Si{-}Co(CO)_4$ in cyclohexane, at room temperature, to give a white precipitate, $[Me_3SiNMe_3]^+[Co(CO)_4]^-$. The carbonyl stretching frequencies in the infrared spectra of $R_3Si{-}Co(CO)_4$ and the $Co(CO)_4^-$ ion are very strong and have very different characteristic frequencies (Table 1). It has been pointed out by Aylett[4] that the carbonyl stretching frequency provides an excellent "internal probe" to show whether or not the $Co(CO)_4^-$ ion is present in a given species. The data in Table 1 suggest most strongly that the formulation of this species as an ammonium salt is indeed correct, since the ν(CO) values for $Na^+[Co(CO)_4]^-$, $[Me_3NH]^+[Co(CO)_4]^-$, and $[Me_3SiNMe_3]^+[Co(CO)_4]^-$ are almost identical. A comparison of that portion of the infrared spectrum arising from the $[Me_3SiNMe_3]^+$ ion with the spectra of several substituted ammonium ions[5] and related compounds[6,7], is also consistent with this formulation.

It was particularly interesting to note that no reaction occurred between $Cl_3Si{-}Co(CO)_4$ and NMe_3 under conditions identical to those used for the $Me_3Si{-}Co(CO)_4/NMe_3$ reaction, or even when a solution of $Cl_3Si{-}Co(CO)_4$ in neat NMe_3 was held at room temperature for one hour. This observation is consistent with recent studies which report that Cl_3SiI and NMe_3 do not react[8]. If the general type of compound formed from $R_3Si{-}Co(CO)_4$ and NMe_3 is indeed $[R_3SiNMe_3]^+[Co(CO)_4]^-$, then if R is an electronegative group (such as Cl) the compound would be expected to have a lower stability than when $R = Me$. It has been pointed out previously[9] that the presence of electronegative groups in a cation of this type will tend to decrease its stability; however, stabilization of cationic species containing electronegative groups is expected to be favored by the coordination of more than one molecule of base to the silicon[10].

In the present investigation it was found that, in certain cases, phosphines underwent a reaction with $R_3Si{-}Co(CO)_4$ analogous to that observed with tertiary amines.

TABLE 1

CARBONYL STRETCHING VIBRATIONS (ν(CO)) IN SELECTED COBALT TETRACARBONYL DERIVATIVES [a]

Compound	Observed (cm^{-1})	Conditions
$Na^+[Co(CO)_4]^-$	1883, 1861 (sh) [b]	THF soln.[15]
$[Me_3NH]^+[Co(CO)_4]^-$ [c]	1882	Nujol mull
$H_3Si{-}Co(CO)_4$	2105, 2050, 2025	Gas[2]
$[H_3Si(NMe_3)_2]^+[Co(CO)_4]^-$	1870	Nujol mull[2]
$[H_3Sipy_2]^+[Co(CO)_4]^-$	1882	Nujol mull[2]
$[H_3Sidipy]^+[Co(CO)_4]^-$	1870	Nujol mull[2]
$Me_3Si{-}Co(CO)_4$	2100, 2041, 2009	Gas[16]
$Cl_3Si{-}Co(CO)_4$ [d]	2118, 2062, 2037	$C_{16}H_{34}$ soln.[3]
$Et_3Si{-}Co(CO)_4$	2089, 2025, 1995	$C_{16}H_{34}$ soln.[3]
$[Me_3SiNMe_3]^+[Co(CO)_4]^-$ [c]	1895 [e]	CH_3CN soln.
$[Me_3SiNMe_3]^+[Co(CO)_4]^-$ [c]	1882	Nujol mull
$[Me_3SiPMe_3]^+[Co(CO)_4]^-$ [c]	1885	Nujol mull
$[Me_3SiPEt_3]^+[Co(CO)_4]^-$ [c]	1875	Nujol mull
$[Et_3SiPEt_3]^+[Co(CO)_4]^-$ [c]	1885	Nujol mull
$Et_3Si{-}Co(CO)_3PEt_3$	1952	$C_{16}H_{34}$ soln.[3]
$Cl_3Si{-}Co(CO)_3PMe_3$	1988	C_7H_{16} soln.
$Cl_3Si{-}Co(CO)_3PEt_3$	1986	$C_{16}H_{34}$ soln.[3]
$Me_3Si{-}Co(CO)_3PPh_3$	1939	Nujol mull

[a] All measurements in this study, unless stated to the contrary, were made with a Perkin–Elmer model 521 double-beam spectrophotometer. [b] sh = shoulder. [c] Using standard vacuum system techniques the stoichiometries obtained for these adducts were: Me_3N / $HCo(CO)_4$ = 1.00 / 0.99; Me_3N / $Me_3Si{-}Co(CO)_4$ = 1.00 / 1.00; Me_3P / $Me_3Si{-}Co(CO)_4$ = 1.00 / 1.00; Et_3P / $Et_3Si{-}Co(CO)_4$ = 1.00 / 0.99. A commercial elemental analysis of $[Et_3PSiMe_3]^+[Co(CO)_4]^-$ was obtained (Found: C, 42.96; H, 6.68. $C_{13}H_{24}O_4PSiCo$ calcd.: C, 43.09; H, 6.68%.) [d] Gas phase data are very similar[16]. [e] Spectrum recorded with a Perkin–Elmer 137B Infracord spectrophotometer.

Thus PMe_3 reacted instantly with a deficiency of $Me_3Si{-}Co(CO)_4$ in hexane at room temperature to give a white precipitate of $[Me_3SiPMe_3]^+[Co(CO)_4]^-$. A similar reaction occurred between PEt_3 and $Me_3Si{-}Co(CO)_4$ or $Et_3Si{-}Co(CO)_4$. This is believed to be the first synthesis of compounds which apparently involve simple phosphonium ions containing an R_3Si— group attached directly to phosphorus. The close similarity of ν(CO) values for the several $[Co(CO)_4]^-$ species (Table 1) and for these phosphine derivatives strongly supports this formulation★. The ^1H NMR spectrum of $[Me_3SiPMe_3]^+[Co(CO)_4]$ [11] in CH_2Cl_2 was also consistent with this formulation: $\delta(Me_3Si) = 9.39\ \tau$, $\delta(Me_3P) = 8.21\ \tau$; $J(PH) = 11.6$ Hz. In $[Me_4P]^+I^-$ [12], $\tau = 7.53$; $J(PH) = 14.4$ Hz. In Me_3P [12], $\tau = 9.11$; $J(PH) = 2.7$ Hz.

★It has been reported previously that $Et_3Si{-}Co(CO)_4$ and PEt_3 react to give *trans*-$Et_3Si{-}Co(CO)_3PEt_3$ [3]. Why a different product is obtained in the present study is not clear; however, specific experimental details were not given for the synthesis of $Et_3Si{-}Co(CO)_3PEt_3$. The difference may be related to the fact that in the present study it was found that $[Et_3SiPEt_3]^+[Co(CO)_4]^-$ is extremely sensitive to traces of water (which may have been present in the previously reported synthesis) and as little as 1 mg of water brought about complex decomposition of approximately 500 mg of $[Et_3SiPEt_3]^+[Co(CO)_4]^-$.

It was interesting to find that when either the phosphorus or the silicon was bonded to electronegative groups, then no phosphonium compound was formed. This is exactly analogous to what was noted for the amine system. Thus, no silylphosphonium compound formation was noted when $Me_3Si{-}Co(CO)_4$ was mixed with PF_3[13], PCl_3 or PPh_3, or when $Cl_3Si{-}Co(CO)_4$ was mixed with PF_3[14], PMe_3 or PEt_3. Either no reaction was observed, or a slow replacement of CO by PR_3 took place with, or without, irradiation by ultraviolet light to give *trans*-$R_3Si{-}Co(CO)_3PR_3$. Thus UV irradiation of cyclohexane solutions of $Me_3Si{-}Co(CO)_4$ and PPh_3, or $Cl_3Si{-}Co(CO)_4$ and PF_3 yielded *trans*-$Me_3Si{-}Co(CO)_3PPh_3$ and $Cl_3Si{-}Co(CO)_3PF_3$[14], respectively. Trimethylphosphine and PEt_3 reacted with $Cl_3Si{-}Co(CO)_4$, in the absence of ultraviolet light, during 2–3 hours at room temperature to give *trans*-$Cl_3Si{-}Co(CO)_3PMe_3$ and *trans*-$Cl_3Si{-}Co(CO)_3PEt_3$, respectively. For the latter compound this simply represents a confirmation of its earlier synthesis[3].

ACKNOWLEDGEMENT

This research is based on portions of a thesis to be submitted by James F. Bald Jr., to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. It was supported by the Advanced Research Projects Agency, Office of the Department of Defense.

REFERENCES

1 B.J. Aylett and J.M. Campbell, *Chem. Commun.*, (1967) 159.
2 B.J. Aylett and J.M. Campbell, *Inorg. Nucl. Chem. Lett.*, 3 (1967) 137.
3 O. Kahn and M. Bigorgne, *J. Organometal. Chem.*, 10 (1967) 137.
4 B.J. Aylett, *Advan. Inorg. Chem. Radiochem.*, 11 (1968) 249.
5 E.A.V. Ebsworth and N. Sheppard, *Spectrochim. Acta*, 13 (1969) 261.
6 H.J. Campbell-Ferguson and E.A.V. Ebsworth, *J. Chem. Soc., A*, (1967) 705.
7 I.R. Beattie and F. Parrett, *J. Chem. Soc., A*, (1966) 1784.
8 I.R. Beattie, T. Gilson and G.A. Ozin, *J. Chem. Soc., A*, (1968) 1092.
9 A.G. MacDiarmid, *Quart. Rev.*, 10 (1956) 208.
10 G.A. Ozin, *Chem. Commun.*, (1969) 104.
11 W.I. Ingle and A.G. MacDiarmid, unpublished observations (1969).
12 J.B. Hendrickson, M.L. Maddox, J.J. Sims and H.D. Kaesz, *Tetrahedron*, 20 (1964) 449.
13 Y.L. Baay and A.G. MacDiarmid, *Inorg. Chem.*, 8 (1969) 986.
14 R.E. Highsmith, J.R. Bergerud and A.G. MacDiarmid, unpublished observation (1969).
15 W.F. Edgell, M.T. Yang and N. Koizumi, *J. Amer. Chem. Soc.*, 87 (1965) 2563.
16 A.P. Hagen and A.G. MacDiarmid, *Inorg. Chem.*, 6 (1967) 686; *ibid.*, 6 (1967) 1941.