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ORGANOMETALLIC COMPOUNDS HAVING METAL—METAL BONDS

XXIII*. HYDRIDO(TRIPHENYLGERMANIUM)TETRACARBONYLIRON AND ITS CONJUGATE BASE

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Summary

Reaction of Ph_3GeLi with $[Et_4N][HFe_3(CO)_{11}]$ affords the new carbonylferrate salt $[Et_4N][Ph_3GeFe(CO)_4]$ and the same reaction provides an alternative route to the known silicon and tin analogs. Protonation of $[Et_4N][Ph_3GeFe(CO)_4]$ with HCl in ether—THF forms the air-sensitive, thermally rather unstable *cis*-$Ph_3GeFeH(CO)_4$. The latter protonates chloride ions in dichloromethane.

Introduction

A convenient and general synthetic route to silyl hydrides of transition metals involves the photochemical reaction of metal carbonyls with silicon—hydrogen bonds [1]. This reaction has been most fully investigated in the case of iron pentacarbonyl [2,3], as indicated in eqn. 1. Tetracarbonyliron compounds of this class show acidic properties [4], are fluctional [3], and in analogy with the determined structure of $Ph_3SiFeH(CO)_4$ [5], may be expected to have considerably distorted octahedral structures.

$$R_3SiH + Fe(CO)_5 \xrightarrow{h\nu} R_3SiFeH(CO)_4 + CO \qquad (1)$$

$(R_3 = Ph_3, Me_3, Cl_3, Me_2Cl, MeCl_2, PhCl_2, PhMe_2, PhMeCl)$

It seemed desirable, in view of these interesting properties, to prepare and examine the germanium and tin analogs of the silyliron hydrides. Surprisingly, Ph_3GeH did not react with $Fe(CO)_5$ as in eqn. 1 [6], and the present work describes an alternative route to $Ph_3GeFeH(CO)_4$ via its conjugate base anion $[Ph_3GeFe(CO)_4]^-$.

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[*] Part XXII, reference 10.

Results and discussion

[$Ph_3GeFe(CO)_4$]$^-$ and related anions

The triphenylgermyltetracarbonylferrate anion has not been reported, although the corresponding silicon [7] and tin [8] anions have been prepared by reaction of Ph_3SiLi and Ph_3SnLi with $Fe(CO)_5$. We report here a variation of this reaction (eqn. 2), which is suitable for the preparation of all three anions. The use of the trinuclear iron anion in the reaction was an inadvertent discovery, stemming from the fact that reactions reported [9] to produce the intended starting material, $[IFe(CO)_4]^-$, led in our hands to $[HFe_3(CO)_{11}]^-$.

$$Ph_3MLi + [Et_4N][HFe_3(CO)_{11}] \xrightarrow{THF} [Et_4N][Ph_3MFe(CO)_4] + \ldots \qquad (2)$$

(M = Si, Ge, Sn)

The salts $[Et_4N][Ph_3MFe(CO)_4]$ are colorless, and soluble in dichloromethane, acetone and tetrahydrofuran. The solids are stable in air for long periods, but decompose in solution over several hours. For the anticipated C_{3v} structure of the anions, three IR carbonyl stretching bands are predicted ($2A_1 + E$); three bands are observed in THF solution, with a fourth appearing as a shoulder in this solvent. An incipient shoulder in dichloromethane solutions of $[Et_4N][Ph_3SiFe(CO)_4]$ has been attributed to ion pairing [4], which reduces the symmetry of the anion. The shoulder near 1870 cm^{-1} for all three ions in THF is much better resolved in that solvent than in CH_2Cl_2 [4], a solvent effect observed also in the anions $[Ph_3MM'(CO)_5]^-$ (M'= Cr,Mo,W) [10].

The neutral hydride cis-$Ph_3GeHFe(CO)_4$

Reaction of ethereal hydrogen chloride with $[Et_4N][Ph_3GeFe(CO)_4]$ in THF at 0° afforded colorless, air sensitive $Ph_3GeFeH(CO)_4$. The compound is also thermally rather unstable, and IR spectra of its solutions in n-hexane exhibit bands due to $Fe(CO)_5$ within a few minutes at room temperature. The four carbonyl stretching bands are almost identical in position and pattern to those of $Ph_3SiFeH(CO)_4$ [2], so both compounds have a *cis*-octahedral geometry.

Addition of excess Et_4NCl to a dichloromethane solution of $Ph_3GeFeH(CO)_4$ converts the latter completely to $[Ph_3GeFe(CO)_4]^-$, as shown by infrared spectroscopy. An equilibrium is thus involved, as shown in eqn. 3. The result

$$[Et_4N]^+ + [Ph_3GeFe(CO)_4]^- + HCl \rightleftharpoons Ph_3GeFeH(CO)_4 + [Et_4N]^+ + Cl^- \qquad (3)$$

in dichloromethane, in which all compounds are soluble, suggests that $Ph_3GeFeH(CO)_4$ is a stronger acid than HCl in that solvent. This would be reasonable, in view of the strongly acidic character of related silyliron compounds [4]. The fact that the reaction proceeds to the right in THF is presumably a result of the very low solubility of Et_4NCl in THF.

One noteworthy difference in the chemistry of the triphenylgermyl- and triphenylsilyl-iron hydrides is in their behavior towards THF. Since it is prepared in THF, $Ph_3GeFeH(CO)_4$ obviously undergoes no irreversible reaction with THF. In contrast, $Ph_3SiFeH(CO)_4$ reacts very rapidly with THF forming

$[HFe_3(CO)_{11}]^-$ and hexaphenyldisiloxane, in a reaction which is not yet fully understood [3].

The reaction of $[Et_4N][Ph_3SnFe(CO)_4]$ with HCl in THF was complex, as judged from the changes in the infrared spectrum, and was not pursued. It seems probable that phenyl—tin bond cleavage was occurring, as it did under similar conditions with $[Ph_3SnW(CO)_5]^-$ [10].

Experimental

Preparation of $[Et_4N][HFe_3(CO)_{11}]$

A mixture of $[Et_3NH][HFe_3(CO)_{11}]$ (22.0 g, 38.0 mmol, prepared by the published method [11]) and Et_4NCl (8.0 g, 49.3 mmol) was stirred for 0.5 h in dichloromethane. Solvent was removed at reduced pressure using a rotary evaporator. The deep red crystalline residue was washed with several portions of water and dried under vacuum overnight. Recrystallization from methanol afforded the pure tetraethylammonium salt (found:C, 37.32; H, 3.49; N, 2.43. $C_{19}H_{21}Fe_3NO_{11}$ calcd.: C, 37.60; H, 3.49; N, 2.31). The NMR spectrum in CD_3CN showed conclusively that replacement of $[Et_3NH]^+$ ions was complete, since the closely spaced triplets due to $^3J(N—CH_2—\underline{H}_3)$ were regular and sharply resolved. It was shown that the presence of a few percent of $[Et_3NH]^+$ drastically perturbed this highly characteristic pattern.

Preparation of $[Et_4N][Ph_3GeFe(CO)_4]$

Excess lithium metal (6 cm of 3.2 mm diameter wire, ca. 37 mmol) in the form of fresh clippings was stirred with a solution of Ph_3GeCl (3.1 g, 9.1 mmol) in THF (18 ml), for several hours. The solution was withdrawn by syringe (leaving excess lithium behind) and added to a magnetically stirred solution of $[Et_4N][HFe_3(CO)_{11}]$ (2.2 g, 3.6 mmol) in 100 ml THF. After 10 min, infrared bands of $[HFe_3(CO)_{11}]^-$ had disappeared. Solvent was then removed under vacuum and the solid residue was washed with several portions of water until the washings were free of a red coloration. The brown residue was dried overnight under vacuum, dissolved in the minimum amount of THF, and passed through a column packed with a 5 cm thickness of Celite over 5 cm of alumina. Further THF (100 ml) was passed through the column, and ca. 300 ml ether was added to the THF eluate to precipitate a cream-coloured solid. Recrystallization from THF—ether afforded the colorless crystalline product (1.9 g, 86% yield based on eqn. 2) m.p. 196-200°. (Found: C, 59.25, H, 6.12; N, 2.63. $C_{30}H_{35}FeGeNO_4$ calcd.: C, 59.85; H, 5.86; N, 2.53.) IR ν (CO) cm^{-1} in THF: 1994 m, 1906 m, 1887 s, 1873 m (sh).

A similar procedure afforded $[Et_4N][Ph_3SiFe(CO)_4]$ as colorless crystals, m.p. 205-209° (dec.) in 82% yield. (Found: C, 65.70; H, 6.64; N, 2.36. $C_{30}H_{35}FeNO_4Si$ calcd.: C, 64.63; H, 6.33; N, 2.51.) IR ν (CO) in THF: 1994 m, 1907 m, 1881 s, 1869 m (sh). (lit. [7] 2007, 1906, 1880, cm^{-1} in THF).

Likewise, $[Et_4N][Ph_3SnFe(CO)_4]$ was prepared in 75% yield as colorless crystals, m.p. 158-160° (dec.). (Found: C, 55.29; H, 5.57; N, 2.40. $C_{30}H_{35}FeNO_4Sn$ calcd.: C, 55.59; H, 5.44; N, 2.16.) IR ν (CO) cm^{-1}, in THF: 1992 m, 1905 m, 1883 s, 1869 m(sh).

Preparation of cis-$Ph_3GeFeH(CO)_4$

Gaseous HCl was passed into ether for ca. 30 min and the molarity of the resulting solution determined by titration in water. A portion of this solution (1.5 ml, 4.0 mmol HCl) was added to $[Et_4N][Ph_3GeFe(CO)_4]$ (2.0 g, 3.6 mmol) in 25 ml THF at 0° in a flask connected to a vacuum system. The flask was briefly evacuated and the solution stirred under closed vacuum for 20 min, as a white precipitate (Et_4NCl) formed. Solvents were distilled off at 0° and iso-pentane was distilled into the flask. The nearly colorless iso-pentane extract was filtered and solvent removed in vacuum affording 1.0 g (59%) of crude product. The analytical sample was obtained from a second preparation by cooling the iso-pentane extract to —78°. (Found: C, 55.80; H, 4.06. $C_{22}H_{16}$-$FeGeO_4$ calcd.: C, 55.93; H, 3.41.) IR ν (CO), cm^{-1} in n-hexane: 2097 m, 2036 m, 2027 s, 2022 s, an additional weak band at 2000 cm^{-1} is always present, and is attributed to $Fe(CO)_5$ formed as a decomposition product.

Mass spectrometry (direct introduction of solid sample at 80°) showed ions of the series $[Ph_3GeFeH(CO)_n]^+$ (n = 1-4) with the extremely weak molecular ion (n = 4, m/e 474) as the highest peak. Fragments due to the loss of a phenyl group were present in low abundance. The mass spectrum at 135° was complex, and in addition to those noted above, showed mainly ions of the series $[Ph_5Ge_2Fe_2(CO)_n]^+$ (n = 0-6).

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