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Preliminary communication

Novel carbene complexes from triphenyl- and trimethyl-germylpentacarbonylmanganese

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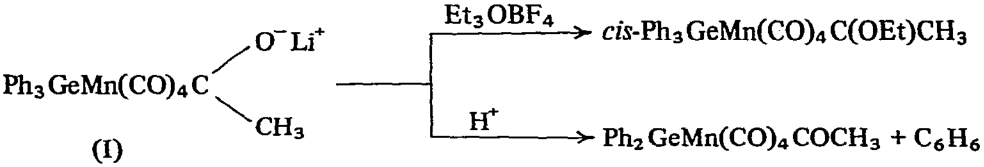
Although stable carbene complexes of transition metals have received much attention[1], there has been only one report of carbene derivatives of a transition metal having as ligand an element of the fourth main group, *viz.*, $Ph_3SnCo(CO)_3C(OC_2H_5)C_6H_5$, and its lead analog[2]. In the course of work to extend this area, we have encountered some unexpected results, which prompt this communication.

An ethereal solution of methyllithium reacts at room temperature with $Ph_3GeMn(CO)_5$ to form the lithium salt of the anion [*cis*-$Ph_3GeMn(CO)_4C(O)Me]^-$. This lithium salt (I) was not isolated, but the anion is readily obtained as its colorless, air stable tetraethylammonium salt* [ν(C≡O) 2023 m, 1938 vs, 1920 vs, 1904 s; ν(C–O$^-$) 1570 m; dichloromethane solution, all peaks broad].

A typical ethoxycarbene complex resulted when $Et_3O^+BF_4^-$ was added to I in water; *cis*-$Ph_3GeMn(CO)_4C(OEt)Me$* was recovered in 78% yield as a yellow solid [ν(C≡O) 2056 m, 1986 m, 1967 vs, 1962 s (sh) in cyclohexane] melting without decomposition at 107–108°, showing the molecular ion at *m/e* 544, and the expected NMR spectrum.

When dilute hydrochloric acid is added to I in water, a phenyl group is cleaved in a matter of seconds to precipitate a colorless solid having the formula* $Ph_2GeMn(CO)_4COCH_3$ (II). Spectroscopic data for II: molecular ion at *m/e* 438: ν(C≡O) 2059 m, 1992 m, 1975 vs, 1962 s, in cyclohexane; ^1H NMR (CD_2Cl_2) τ 2.53 (complex multiplet, C_6H_5), 7.19 (singlet, CH_3).



(II)

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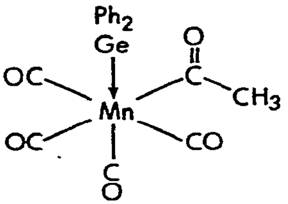
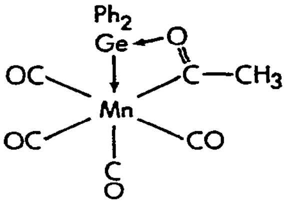
* Satisfactory elemental analyses were obtained for all new compounds.

Even more surprising is the similar rapid conversion of the trimethyl analog of I to the dimethyl analog of II with methane evolution. This remarkable ease of cleavage can perhaps be attributed to a four-center process, following initial formation of a hydroxycarbene complex. Phenyl cleavage leading to II also occurred when I reacted with methyl fluorosulfonate in water, but with this reagent a small yield of the methylmethoxycarbene complex also formed. It may be that $MeOSO_2F$ serves as a proton source rather than as a methylating agent in the formation of II*; the stability of the methylmethoxycarbene complex suggests that it is not the intermediate.

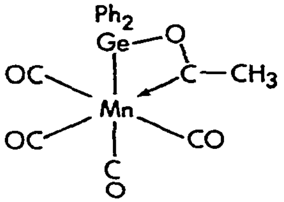
The structure of the novel product II must involve a *cis* geometry at manganese in view of the four observed carbonyl stretching bands. We have considered several possible formulations consistent with this fact as well as with the effective atomic number rule.



IIa



IIb



IIc

Formulation IIa implies a true germylene complex since it involves three-coordinate germanium. Unfortunately, this intriguing possibility must be rejected because an infrared band in the 1600 cm^{-1} region corresponding to a free acetyl group is not observed. Accordingly, we postulate an interaction between oxygen and germanium such as IIb or IIc, which may be viewed as potential canonical forms representing the actual structure.

A clear choice in favor of IIc as the most appropriate representation of the structure is made possible by ^{13}C NMR spectroscopy. The very soluble dimethyl analog of II exhibits a peak at -338.17 ppm relative to TMS, a chemical shift characteristic of carbene carbon atoms in transition metal carbene complexes[3]. Furthermore, this peak is well removed from the region (ca. -250 ppm) where an acetyl carbon bound to a transition metal is expected[4]. Infrared spectra of II and its dimethyl analog are complex, but we tentatively assign a band at 1110 cm^{-1} in the spectra of both compounds (KBr disc) as $\nu(C-O)$; this would also be consistent with the alkoxide structure IIc.

Accordingly, II and its dimethyl analog may be regarded as cyclic germoxycarbene derivatives of manganese, and are related to the siloxycarbene compound of Moser and Fischer[5], $(OC)_5CrC(OSiMe_3)Me$, inasmuch as a Group IV element other than carbon is bonded to the carbene oxygen. An X-ray crystallographic study will be necessary to confirm our suggested formulation, but efforts to obtain suitable crystals have been hampered by the instability of solutions of both products. Work is continuing on these and related derivatives.

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Added in proof. Reaction of I with Me_3OPF_6 results in formation of II and a small yield of methylmethoxycarbene. GLC analysis of the organic products of the reaction shows the presence of benzene, establishing that the trimethyloxonium salt acts both as a proton source and a methylating agent. The mechanism involved in the reaction of I with methylfluorosulphonate is presumably analogous.