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Photochemical decarbonylation of $Ph_2Ge[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ and analogous compounds

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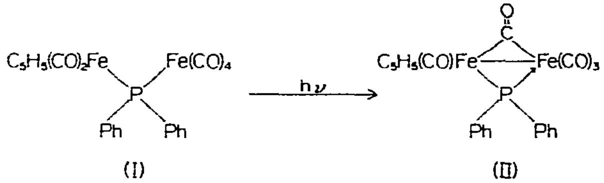
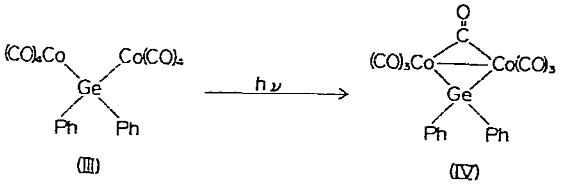
Several novel transition metal complexes have recently been described in which two metal atoms are joined by a metal–metal bond, a bridging carbonyl group, and a bridging phosphido group[1,2]. In particular it has been found that $(\pi\text{-}C_5H_5)Fe_2(CO)_6PPh_2$ (I) can be photochemically converted to $(\pi\text{-}C_5H_5)Fe_2(CO)_5PPh_2$ (II).



(1)



(2)

Furthermore there has also been considerable recent interest in carbonyl-bridged metal dimers in which one or more of the bridging ligands have been replaced by R_2M (M = C, Si, Ge, Sn; R = organic group, halogen)[3–10]. We now report that such derivatives are accessible via a photochemical route analogous to (1). For example, $Ph_2Ge[Co(CO)_4]_2$ (III) is completely converted to $Ph_2GeCo_2(CO)_7$ (IV) within one-half hour at room temperature in hexane. This decarbonylation reaction did not occur under the conditions previously used to prepare (III)[11].

A solution of $Ph_2Ge[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$[12] (V) (ca. 0.03 *M*) in dry, degassed benzene was irradiated, under nitrogen in a Pyrex flask, at 25° with a 100 Watt floodlamp*

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*Ultra-Violet Products, Inc.

for 45 min. Solvent was removed and the resulting red-violet solid washed with 20 ml portions of hexane until the washings were free of unreacted (V). In this way we obtained a violet, air-stable compound, in yields of 60–70%, which was characterized by elemental analysis, NMR and infrared spectroscopy as $Ph_2GeFe_2(CO)_3(\pi\text{-}C_5H_5)_2$ (VI). This formulation was confirmed by the mass spectrum which shows the molecular ion (*m/e* 554 for ^{74}Ge and ^{56}Fe isotopes) and ions corresponding to the stepwise loss of three carbonyl groups. A structure based on $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$[13], in which one bridging carbonyl has been replaced by Ph_2Ge, is suggested for this derivative on the basis of its infrared spectrum which indicates the presence of both terminal and bridging carbonyl groups.

Similar irradiation of a solution containing $Ph_2Si[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$[14] gave, in addition to $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, a violet compound believed to be $Ph_2SiFe_2(CO)_3(\pi\text{-}C_5H_5)_2$ on the basis of its infrared spectrum [ν(CO) at 1784 cm^{-1}]. Attempts to obtain a pure sample of this compound have thus far been unsuccessful. The complex, $Ph_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$[15] (VII), however, yielded $Ph_2SnFe_2(CO)_3(\pi\text{-}C_5H_5)_2$ (VIII), identified by elemental analysis and its solid-state spectrum (KBr disc) which was very similar to that of (VI). Whereas (VI) is stable to air for several weeks, (VIII) is completely decomposed within hours and is very unstable in solution. This enhanced stability of (VI) may be associated with the more favoured steric requirements of germanium in complexes of this type[16].

The infrared spectrum of (VI) in cyclohexane shows three, rather than the expected two, terminal carbonyl bands and a strong absorption at 1781 cm^{-1}, thus indicating the presence in solution of distinct isomers of (VI). This possibility is given further support by the observation that in more polar solvents the bridging ν(CO) band is asymmetric, suggesting that it is due to the coincidence of two vibrations. Since both compounds (VI) and (VIII) could adopt structures in which the cyclopentadienyl groups are *cis* or *trans* to the $Fe\cdot\mu(CO)\cdot\mu(Ph_2M)\cdot Fe$ ring, we propose that it is the presence of such isomers which gives rise to the observed spectrum of (VI).

The NMR spectrum of (VI) is consistent with the existence of *cis* and *trans* isomers*. Thus in CCl_4, at 25°, (VI) exhibits two peaks at τ 5.31 and 5.47 due to the cyclopentadienyl protons. In this respect the spectrum is similar to the low-temperature NMR spectrum of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ where both *cis*- and *trans*-$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ are

TABLE 1

ANALYTICAL DATA

Compound	Analyses, found (calcd.) (%)		
	C	H	O
(VI)	54.62 (54.33)	3.71 (3.65)	9.13 (8.68)
(VIII)	50.09 (50.14)	3.61 (3.37)	7.43 (8.02)

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*In all solvents tried, (VI) was observed to slowly undergo irreversible changes, and we have as yet been unable to entirely exclude the possibility that the observed NMR spectrum is due in part to decomposition products. Consequently although the spectrum supports the suggestion of isomerism, it cannot be said to prove it.

TABLE 2

INFRARED DATA

Compound		ν(CO) (cm^{-1})
(V)	cyclohexane	2016 (3.0), 2006 (7.5), 1997 (3.0), 1987 (10.0), 1964 (2.1), 1953 (8.6), 1938 (9.8)
(VII)	cyclohexane	2010 (3.0), 1999 (7.0), 1992 (2.7), 1982 (10.0), 1960 (2.2), 1949 (8.8), 1934 (7.8)
(VI)	cyclohexane	1985 (2.0), 1950 (1.7), 1937 (10.0), 1781 (7.1)
(VI)	KBr disc	2003 w, 1974 sh, 1956 m, 1936 s, 1932 s, 1916 vs, 1881 w, 1757 vs, 1747 sh
(VIII)	KBr disc	2001 w, 1965 sh, 1948 m, 1932 s, 1927 s, 1911 vs, 1876 w, 1751 vs, 1743 sh

discernible[17]. It therefore appears that (VI) is a mixture of *cis* and *trans* isomers at room temperature and that these species do not rapidly interconvert.

The proposed isomers of (VI) are presumably formed from different rotational isomers of (V). Although the reported spectrum of (V) shows four terminal carbonyl absorptions[18], we have observed three additional weaker bands indicating restricted rotation about the Ge–Fe bonds as recently proposed for $Cl_2Ge[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$[19]. Thus in going from (V) to (VI), elimination of CO from the different rotamers of (V) could occur in such a way that the iron–iron bond forms with the cyclopentadienyl groups in either *cis* or *trans* positions. Similarly, (VII) shows seven terminal ν(CO) bands rather than the reported four[20] and it is therefore possible that (VIII) also is a mixture of isomers. The similarity in the solid-state spectra of (VI) and (VIII) supports this suggestion, but the instability of (VIII) in solution has so far prohibited further studies.

Analytical data and IR spectra are given in Tables 1 and 2, respectively.

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