Journal of Organometallic Chemistry, 249 (1983) 55–61
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

HIGHLY HINDERED IODOTRIS- AND TETRAKIS-(PENTACARBONYLMETAL)SILANE DERIVATIVES CONTAINING MANGANESE AND RHENIUM *

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(Received January 31st, 1983)

Summary

The preparation of the highly hindered derivatives $ISi[M'(CO)_5]_3$ and $Si[M'(CO)_5]_4$ ($M' = Mn$, Re) by prolonged reaction of SiI_4 with $NaM'(CO)_5$ is described, together with their IR and mass spectra. The mono-iodo compounds undergo thermolysis or photolysis with loss of $M'_2(CO)_{10}$ and CO to yield cluster derivatives $(OC)_4M'[\mu\text{-}Si(I)M'(CO)_5]_2M'(CO)_4$. There is also evidence that they undergo metathetical reactions, although the presence of conducting ionic species $\{Si[M'(CO)_5]_3\}^+\ I^-$ in solution could not be demonstrated. The possibility of "multiple-cogwheel" rotation is discussed.

Introduction

The heavier Main Group IV elements (M) are known to form a number of open derivatives with transition (M′) groups involving three or four M–M′ bonds but no M′–M′ bonds [1], e.g. $M[Co(CO)_4]_4$ (M = Ge, Sn, Pb); $XSn[M'(CO)_5]_3$ (M′ = Mn, Re); and $Sn[Fe(CO)_2Cp]_4$. By contrast, silicon compounds with three or four Si–M′ bonds have been described only when additional M′–M′ bonds are present giving rise to clusters, and moreover when at least two of the M′ atoms are Co or Ir [2,3], e.g. $(OC)_4CoSiCo_3(CO)_9$; $MeSi[Mo(CO)_2Cp][Co_2(CO)_6]$; $MeSi[Fe(CO)_2Cp][Co_2(CO)_7]$ and $MeSiIr_3(CO)_9$. It therefore appeared that silicon was too large to form such open derivatives without excessive steric crowding.

We now describe the preparation of a set of open tris- and tetrakis-(pentacarbonylmetal)silane derivatives by slow reaction of the appropriate pentacarbonylmetallates with iodosilanes.

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* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June, 1983 [B.J.A. recalls with gratitude his training as a research student at Cambridge, 1951-54].

0022-328X/83/$03.00

Results and discussion

Preparation

The slow reaction of SiI_4 with an excess of $NaM'(CO)_5$ (M' = Mn, Re) as a slurry in isopentane at 25°C led successively to tri- and tetra-substituted products (eq. 1).

$$SiI_4 + nM'(CO)_5^- \rightarrow \underset{(I-IV)}{I_{4-n}Si[M'(CO)_5]_n} + nI^- \qquad (1)$$

(I, M' = Mn, $n = 3$; II, M' = Re, $n = 3$;
III, M' = Mn, $n = 4$; IV, M' = Re, $n = 4$)

The reaction times needed to form the rhenium-containing products were about twice those for manganese, being approximately: I, 36 h; II, 72 h; III, 14 days; IV, 27 days. This is reverse of the order expected on electronic grounds for a reaction involving nucleophilic attack by $M'(CO)_5^-$ at silicon [2], since $Re(CO)_5^-$ is normally a stronger nucleophile than $Mn(CO)_5^-$ [4]. Thus steric effects appear to predominate: $Re(CO)_5^-$ is larger than $Mn(CO)_5^-$ and both are much larger than I^-, so that, as observed, the reaction becomes more difficult with increasing pentacarbonylmetal substitution.

Unsuccessful routes to I included the reaction of $I_2Si[Mn(CO)_5]_2$ [5] in ether solution with: (i) $NaMn(CO)_5$, and (ii) $HMn(CO)_5$ and pyridine. In both cases, coloured ionic adducts appeared to be formed. However, the reaction of $I_2Si[Re(CO)_5]_2$ [5] with $NaRe(CO)_5$ in isopentane led as expected to reasonable yields of II.

The silicon-metal products were separated by fractional crystallization from hydrocarbon solvents as lemon-yellow (I and III) or pale yellow (II and IV) solids. They sublime slowly in a high vacuum in the temperature range 50–80°C, although some decomposition occurs, especially in the case of the iodo derivatives I and II (see below).

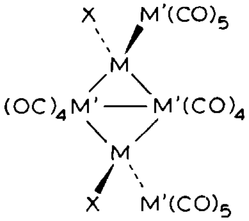
The compounds are sparingly soluble in aliphatic hydrocarbons, but decompose slowly when dissolved in benzene, chloromethanes, and ethers. Freshly-prepared solutions were non-conducting, affording no evidence for dissociation into substituted silicenium $\{Si[M'(CO)_5]_3\}^+$ and I^- ions. When pure, the crystalline solid compounds are stable in air for short periods, but solutions are rapidly oxidised. Compounds I and II reacted slowly with an equimolar amount of $HgCl_2$ in cyclohexane, giving a precipitate of dark yellow or red HgI_2 and a solution from which colourless solids containing Cl but not I could be isolated: their IR spectra were consistent with those expected for $ClSi[M'(CO)_5]_3$ (M' = Mn, Re), but they were not further investigated.

Thermolysis and photolysis

Preliminary mass spectral observations of compounds I and II showed ions containing $I_2Si_2M'_4$ (M' = Mn, Re) groupings, and it was suspected that these arose from thermolysis of the mono-iodo compounds during injection (see below). Consequently, II was heated for 8 h at 80°C, yielding $Re_2(CO)_{10}$, CO, and yellow $I_2Si_2Re_4(CO)_{18}$ according to equation 2.

$$\underset{(II)}{2ISi[Re(CO)_5]_3} \rightarrow \underset{(Va)}{I_2Si_2Re_4(CO)_{18}} + 2CO + Re_2(CO)_{10} \qquad (2)$$

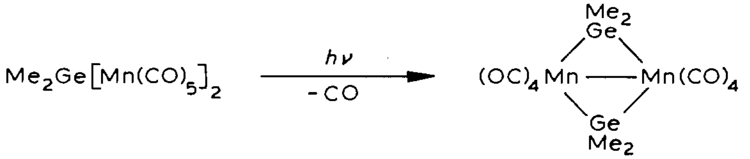
A similar reaction occurred when II was photolysed in cyclohexane solution with a powerful UV source. Compound Va is clearly analogous to a range of germanium and tin compounds (Vb) (shown to favour the *trans* form depicted), which were prepared and characterized by Haupt and his co-workers [6]; in one instance, they showed that thermolysis of $BrSn[Mn(CO)_5]_3$ yielded Vb (X = Br, M = Sn, M′ = Mn).



(V)

(Va: X = I, M = Si, M′ = Re;
Vb: X = halogen, M = Ge, Sn, M′ = Mn, Re;
Vc: X = I, M = Si, M′ = Mn;
Vd: X = $M'(CO)_5$, M = Si, M′ = Mn, Re)

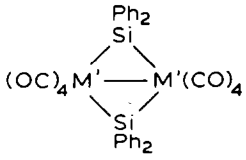
Loss of CO from two adjacent $M'(CO)_5$ groups in a molecule, leading to formation of M′–M′ bonds, is well-documented, e.g. [7] (eq. 3).



(3)

(VI)

Similar processes are probably involved in the formation of VII by heating together Ph_2SiH_2 and $M'_2(CO)_{10}$ [2,8].



(VII, M′ = Mn, Re)

It is now seen that molecules with three adjacent $M'(CO)_5$ groups form the same planar $M_2M'_2$ cluster unit, no doubt in a bimolecular process, by loss of CO and relatively volatile $M'_2(CO)_{10}$.

The manganese compound I behaved in a qualitatively similar way to II on thermolysis or photolysis, but more than two moles of CO were evolved, suggesting that the expected product Vc is unstable towards loss of CO. Furthermore, compounds III and IV both lost $M'_2(CO)_{10}$ and CO on moderate heating, consistent with the formation of Vd, although this could not be isolated in a pure form. It is noteworthy that the mass spectra of heated III and IV both showed peaks attributable to $M_2M'_6$ species and more highly condensed products (see below).

Infrared spectra

Table 1 shows that the silicon compounds of general formula $XSi[M'(CO)_5]_3$ have IR spectra in the ν(CO) region which are generally similar to those of three of their tin analogues [9]. A full vibrational analysis of such large molecules is difficult, particularly because a number of different conformations may arise by rotation of $M'(CO)_5$ groups about Si–M′ bonds; this rotation is expected to become much more difficult as X becomes larger. Thompson and Graham have suggested [9] that the numbers of IR-active modes for $XSn[M'(CO)_5]_3$ species are eight and nine for two conformations of C_{3v} symmetry, but ten for one of C_3. Certainly the large numbers of bands observed in the present study provides further evidence for coupling of the vibrational modes belonging to separate $M'(CO)_5$ groups via the central silicon atom, as has been discussed for $H_2Si[M'(CO)_5]_2$ [10].

Some guide to possible conformations is given by the results of X-ray crystal structure determinations on $ClSn[Mn(CO)_5]_3$ [11] and $BrSn[Mn(CO)_5]_3$ [12], which indicate probable molecular point group symmetries of C_3 and C_1, respectively. It is interesting that the more hindered molecule apparently possesses lower symmetry, although it cannot be assumed that these conformations are maintained in solution.

In the case of the tetrakis compounds III and IV, no direct comparisons are possible, because no other Main Group IV-centred derivatives $M[M'(CO)_5]_4$ have been reported. The closest parallels are with some tetrakis(tetracarbonylcobalt) compounds $M[Co(CO)_4]_4$ (M = Ge, Sn, Pb), for which four or five ν(CO) bands have been reported [13–15]. In the case of the tin compound, Patmore and Graham [13] suggested that a conformation of C_{3v} symmetry was sterically more attractive than either of two possible T_d conformations. As shown in Table 1, both III and IV show a large number of bands in the ν(CO) region, indicating that the overall symmetry is again less than T_d. Examination of ball-and-spoke models constructed to scale using reasonable Si–M′ bond lengths [2] and $M'(CO)_5$ dimensions suggests that a T_d conformation is extremely hindered, and that D_2 and C_1 represent respectively the likely maximum and minimum symmetries.

It is also apparent that, because of the interpenetration of $M'(CO)_5$ groups in III and IV, rotation of any one group about the Si–M′ bond is only possible as part of a concerted rotation of all four groups. Thus this molecule offers an intriguing picture

TABLE 1

ν(CO) FREQUENCIES OF TRIS- AND TETRAKIS-(PENTACARBONYLMETAL) DERIVATIVES

Compound	ν(CO) frequencies (cyclohexane solution, cm^{-1})	Ref.
$ISi[Mn(CO)_5]_3$ (I)	2118m 2096vs 2059s 2042vs 2018vs 1996vs 1978s	this work
$ISn[Mn(CO)_5]_3$	2093m 2080vs 2044s 2037s 2029s 2020vs 2005vs 1989s	[9]
$ISi[Re(CO)_5]_3$ (II)	2098s 2074s 2045vs 2028vs 2018vs 1988vs 1972s 1960m	this work
$ClSi[Mn(CO)_5]_3$ [a]	2078sh 2050vs 2018vs 2006s 1990s 1982vs 1958w	this work
$ClSn[Mn(CO)_5]_3$	2093w 2080vs 2037s 2030sh 2020vs 2005vs 1989s	[9]
$ClSi[Re(CO)_5]_3$ [a]	2078s 2060sh 2046s 2028sh 2020vs 2005sh 1986vs 1975vs	this work
$ClSn[Re(CO)_5]_3$	2117w 2101s 2044s 2034m 2026vs 2013s 2006s 1992vs	[9]
$Si[Mn(CO)_5]_4$ (III)	2097m 2075sh 2060sh 2045vs 2018vs 1998sh 1981vs 1958w	this work
$Si[Re(CO)_5]_4$ (IV)	2092m 2064s 2050m 2036vs 2018sh 2006vs 1983s 1972vs 1961sh	this work

[a] Products from metathetical reaction of corresponding iodo derivatives with $HgCl_2$.

of a "multiple-cogwheel" system. Conformation of this by NMR techniques has so far been frustrated by the compounds' limited solubility.

The cluster compounds $I_2Si_2M'_4(CO)_{18}$ (Va, M' = Re; Vc, M' = Mn) show respectively nine and eight bands assigned to $\nu(CO)$. The spectra are very similar to those reported by Haupt [6] for a range of compounds Vb, for which approximate C_{2h} symmetry is proposed.

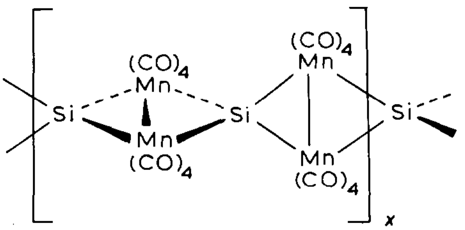
Mass spectra

All the compounds reported here had to be heated to temperatures in the range 100–150°C in order to introduce them at a suitable rate into the mass spectrometer. Consequently, some decomposition occurred, and the observed fragments were in some cases a useful guide to the nature of the thermolysis products.

Compound I gave no molecular ion under these conditions, but strong peaks due to fragments such as $ISiMn(CO)_n{}^+$, $SiMn_2(CO)_n{}^+$, and $SiMn(CO)_n{}^+$; there were also peaks clearly due to disproportionation products, such as $I_2SiMn_2(CO)_n{}^+$, $I_3SiMn(CO)_n{}^+$, and $SiMn(CO)_n{}^{m+}$ ($m = 1, 2$). Another set of strong peaks could be assigned to $I_4Si_2Mn_4(CO)_n{}^{2+}$ ions, known to be present in the mass spectrum of $I_2Si[Mn(CO)_5]_2$ [5], and possibly involving a Mn_4 tetrahedral cluster. Ions reasonably derived from Vc by loss of CO, e.g. $I_2Si_2Mn_4(CO)_7{}^+$, were present but weak.

In the case of the rhenium compound II, identification of species containing two, three or four Re atoms was aided by the characteristic isotope patterns observed. Again, series of peaks due to fragments $ISiRe(CO)_n{}^+$, $SiRe_2(CO)_n$ and $SiRe(CO)_n{}^+$ were prominent, but there was little evidence of disproportionation products. Consistent with this, no $I_4Si_2Re_4(CO)_n{}^{m+}$ species were observed. Instead, a few examples of ions $I_2Si_2Re_2(CO)_n{}^+$ and $I_2Si_2Re_4(CO)_nC^{2+}$ (reasonably derived from Va) were present: it has been noted previously that rhenium compounds show a greater tendency to form carbido ions than their manganese analogues [10].

The spectra of the tetrakis compounds were rather simpler. Compound III exhibited a doubly-charged molecular ion $SiMn_4(CO)_{20}{}^{2+}$ at $m/e = 404$ and the expected series of decarbonylated and fragment species $SiMn_4(CO)_n{}^+$, $SiMn_3(CO)_n{}^+$, and $SiMn_2(CO)_n{}^+$, also a few carbido species such as $SiMn_4(CO)_nC^+$. Ions no doubt derived from the condensation products (Va, M' = Mn), e.g. $Si_2Mn_6(CO)_n{}^{2+}$, and related oligomeric species, e.g. $Si_3Mn_8(CO)_n{}^{2+}$, were also observed. It is tempting to suppose that the final product of such condensation would be a linear cluster polymer VIII.



(VIII)

The rhenium analogue IV gave similar series of the ions $SiRe_4(CO)_n{}^+$ and $SiRe_3(CO)_n{}^+$, together with plentiful carbido species $SiRe_4(CO)_nC^+$ and $SiRe_3(CO)_nC^+$. In complete contrast to III, however, ions derived from condensed species were entirely absent. This may reflect a reluctance to break relatively strong Si–Re bonds: measurements of appearance potentials have led to estimates of 300 kJ mol^{-1} (M′ = Re) as against 240 kJ mol^{-1} (M′ = Mn) for D(Si–M′) in $Me_3SiM'(CO)_5$ [16].

Experimental

All manipulations were carried out in a high-vacuum system, in demountable vessels attached to it, or in a nitrogen-filled dry-box. The CO content of products was determined by displacement with bromine and direct measurement with a Toepler pump [17]; Mn and Re were determined by atomic absorption spectrometry, and halogens gravimetrically as AgX. IR spectra were recorded on a Perkin–Elmer 457 instrument, and mass spectra (70 eV) were obtained using an augmented A.E.I. (Kratos) MS902 spectrometer at Queen Mary College as part of the University of London Intercollegiate Research Service.

SiI_4 was either a commercial sample (Strem) or made by reaction of $SiPh_4$ with HI under pressure at 85°C [5]. Solvents were degassed and then dried using sodium benzophenone ketyl (hydrocarbons, ethers) or calcium hydride (chloromethanes, pyridine).

Preparation of iodotris(pentacarbonylrhenium)silane (II)

SiI_4 (460 mg, 0.9 mmol), $NaRe(CO)_5$ (1.39 g, 4.0 mmol), and isopentane (80 ml) were introduced into an all-glass reaction vessel fitted with sintered filters, capillary openers and seal-off points, as previously described [10]. The mixture was shaken at room temperature for 72 h, after which the resulting yellow solution was filtered off, the remaining off-white solid was repeatedly extracted with isopentane, and the combined filtrate was evaporated to dryness. The resulting yellow solid was recrystallised from cyclohexane in an all-glass sealed apparatus, yielding 590 mg (32% yield) of yellow crystals (Found: I, 11.2; CO, 36.8; Re, 48.1. $ISi[Re(CO)_5]_3$ calcd.: I, 11.2; CO, 37.1; Re, 49.2%). The manganese analogue I was prepared similarly, but with a reaction time of 36 h, in 56% yield.

Preparation of tetrakis(pentacarbonylrhenium)silane (IV)

SiI_4 (290 mg, 0.54 mmol), $NaRe(CO)_5$ (776 mg, 2.2 mmol) and isopentane (30 ml) were allowed to react in the same apparatus as before for 27 days at room temperature. After a similar process of extraction and recrystallization, 150 mg (50% yield) of pale yellow microcrystals were obtained (Found: CO, 42.2. $Si[Re(CO)_5]_4$ calcd.: CO, 42.0%). The manganese analogue III was obtained in 50% yield, using a similar procedure, after 14 days.

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