Cobalt to Oxygen Migration of the Trimethylsilyl Group in Trimethylsilylcobalt Tetracarbonyl

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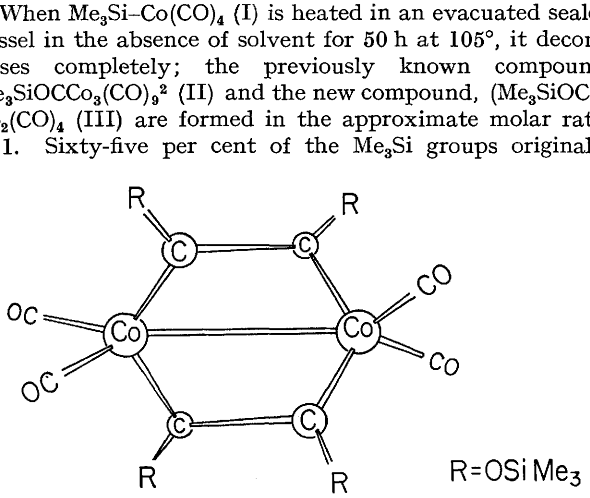
Summary When $Me_3Si–Co(CO)_4$ is heated at 105° for 50 h, migration of the Me_3Si group from cobalt to oxygen takes place to give $Me_3SiOCCo_3(CO)_9$ and $(Me_3SiOC)_4Co_2(CO)_4$; the former compound is also formed in high yields within an hour at room temperature by the reaction of $Me_3Si–Co(CO)_4$ with tetrahydrofuran.

WE have previously suggested[1] that the greater thermal stability of $Me_3Si–M(CO)_x$ compounds, as compared to their carbon analogues, may be caused by the small tendency of silicon to form an intermediate or transition state during decomposition involving $(p–p)\pi$ bonds between carbon and silicon. We have therefore investigated the controlled thermal decomposition of an alkylsilyl transition-metal carbonyl in order to determine whether its decomposition products are analogous to those obtained for related carbon compounds.

When $Me_3Si-Co(CO)_4$ (I) is heated in an evacuated sealed vessel in the absence of solvent for 50 h at 105°, it decomposes completely; the previously known compound, $Me_3SiOCCo_3(CO)_9$[2] (II) and the new compound, $(Me_3SiOC)_4Co_2(CO)_4$ (III) are formed in the approximate molar ratio 2:1. Sixty-five per cent of the Me_3Si groups originally present in $Me_3Si-Co(CO)_4$ appear as analytically pure (II) and (III), both compounds being characterized by elemental analysis. The actual yields of (II) and (III) are larger than this figure implies, since material was always lost during the complex chromatographic and sublimation purification procedures. No sign of any other reaction products apart from some CO and traces of $(Me_3Si)_2O$ was observed. Heating at 105° for 50 h does not convert (II) into (III) or (III) into (II); hence one compound is not the precursor of the other in the thermal rearrangement process. No evidence for the formation of $(Me_2SiCH_2)_x$ and $HCo(CO)_4$, both of which might have been expected if (I) had decomposed by a β-H-elimination process such as that commonly found for related types of carbon compounds,[1,3] was observed.



FIGURE

It was surprising to find that (I) reacts completely with THF in a few minutes at room temperature to give, after 1 h, high yields of (II) together with *cis*- and *trans*-$Me_3SiOCH{=}CHEt$ and *cis*- and *trans*-$Me_3SiOCH{=}CHCH_2CH_2CH_2OSiMe_3$. It has been reported that reaction of a silyl halide with a transition-metal carbonyl anion in THF frequently yields not the expected silyl transition-metal carbonyl derivative, but disiloxanes.[3] The present study suggests that in certain cases the expected product or intermediate might have reacted rapidly with the THF solvent.

Compound (III) shows only a single sharp ^1H n.m.r. absorption at τ 9·68. The i.r. spectrum (Nujol) displays terminal metal carbonyl bands at 2075s, 2023s, 2008vs, and 1961s cm^{-1}. No bridging carbonyl absorptions are observed. The mass spectrum shows a reasonably strong (7·4% normalized against *m/e* 75, 100%) parent ion† (*m/e* 634) and other ions due to the consecutive loss of four carbonyls. It is believed that the structure of (III) may be similar to that of $(Bu^tC{\equiv}CBu^t)_2Fe_2(CO)_4$ (IV),[4] in which the iron and four carbonyl groups are coplanar with both acetylenes lying in a plane normal to this plane. This compound apparently contains an Fe–Fe double bond. It is believed that (III) may be considered as being derived from $(Me_3SiOC{\equiv}COSiMe_3)_2CO_2(CO)_4$, in which no Co–Co double bond character need be suggested. However, the four bands observed in the i.r. spectrum of (III) in the CO stretching region apparently result from a symmetry no higher than C_2.[5] This is consistent with a structure such as that shown in the Figure in which a twisting of the molecular framework from that observed in (IV) has taken place presumably to accommodate an expected Co–Co bond length of approximately 2·5—2·7 Å,[6] as compared to the very short Fe–Fe bond length of 2·215 Å found in (IV).[4]

We have shown previously[6a] that a strong attractive interaction may exist between the silicon and the equatorial carbonyl groups in a compound such as (I). It is interesting to find that under appropriate conditions the Me_3Si group migrates from the cobalt atom to the oxygen of a carbonyl group. Thermodynamically, this must be related to the large Si–O bond energy.

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† A weak (P + CO) peak, intensity 0·7%, was also observed. Spectra were continuously recorded until the sample was depleted; the intensity of this ion decreased to zero while the spectrum of (III) could still be observed. Consequently, this (P + CO) ion is apparently caused by a small amount of impurity in the sample.

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