

Correspondence to: Professor B K Nicholson
Chemistry Department
University of Waikato
Private Bag 3105
Hamilton
New Zealand
Email: b.nicholson@waikato.ac.nz
Fax: 64 7 838 4219

Anomalous reaction of an aryl silane with $\text{Co}_2(\text{CO})_8$; characterisation of $\text{Me}_2\text{NC}_6\text{H}_4\text{Si}[\text{Co}(\text{CO})_4][\text{OCCo}_3(\text{CO})_9]_2$.

Gwion J. Harfoot, and Brian K Nicholson*.

Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand.

Synopsis

Reaction of $\text{Me}_2\text{NC}_6\text{H}_4\text{SiH}_3$ with $\text{Co}_2(\text{CO})_8$ gives

$\text{Me}_2\text{NC}_6\text{H}_4\text{Si}[\text{Co}(\text{CO})_4][\text{OCCo}_3(\text{CO})_9]_2$ with a mixture of Si-Co and Si-O bonds.

Abstract.

Reaction of $\text{Me}_2\text{NC}_6\text{H}_4\text{SiH}_3$ with $\text{Co}_2(\text{CO})_8$ gave $\text{Me}_2\text{NC}_6\text{H}_4\text{Si}[\text{Co}(\text{CO})_4][\text{OCCo}_3(\text{CO})_9]_2$ which was shown to have one $-\text{Co}(\text{CO})_4$ group and two $-\text{OCCo}_3(\text{CO})_9$ cluster units bonded to the silicon atom.

1. Introduction.

The reaction of organosilanes with $\text{Co}_2(\text{CO})_8$ has long been known to give products with Si-Co bonds [1]. Thus Cl_3SiH gives $\text{Cl}_3\text{SiCo}(\text{CO})_4$ [2], SiH_4 gives $\text{Si}[\text{Co}_2(\text{CO})_7]_2$ [3], and PhSiH_3 results in $\text{PhSi}[\text{Co}(\text{CO})_4][\text{Co}_2(\text{CO})_7]$ which decarbonylates to the *closo*-cluster $\text{PhSiCo}_3(\text{CO})_9$ [4]. Reaction of silicon hydrides to give Si-Co bonds is involved in the hydrosilation of alkenes, catalysed by $\text{Co}_2(\text{CO})_8$ [5].

We have recently examined the reactions of primary silanes RSiH_3 with $\text{Co}_4(\text{CO})_{12}$, which for $\text{R} = \text{Me}, \text{Ph}, p\text{-MeOC}_6\text{H}_4$ or $\text{MeO}(\text{CH}_2)_3\text{-}$ give the *pseudo*-octahedral clusters $\text{Co}_4(\mu_4\text{-SiR})_2(\text{CO})_{11}$ [6,7]. However when $\text{R} = p\text{-Me}_2\text{NC}_6\text{H}_4$ the yields of the Si_2Co_4 cluster were low, giving by-products that from their intense purple colour and infrared spectra appeared to be of the type $\text{X-ECO}_3(\text{CO})_9$ ($\text{E} = \text{Si}$ or C), but which could not be further identified [7]. To see if there was a more specific route to these by-products we reacted $p\text{-Me}_2\text{NC}_6\text{H}_4\text{SiH}_3$ with $\text{Co}_2(\text{CO})_8$ and now report that a completely different reaction takes place.

2. Experimental Section

2.1 General

Reactions were carried out under nitrogen, using standard Schlenk techniques. $p\text{-Me}_2\text{NC}_6\text{H}_4\text{SiCl}_3$ was prepared by combining the Grignard reagent from $p\text{-Me}_2\text{NC}_6\text{H}_4\text{Br}$ with excess SiCl_4 , and reducing the chloride with LiAlH_4 gave the silane [8].

Electrospray mass spectra were recorded on a VG Platform II spectrometer, operated as detailed elsewhere [9] and IR on a Digilab FTS-40 instrument.

2.2 Reaction of $p\text{-Me}_2\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{SiH}_3$ with $\text{Co}_2(\text{CO})_8$.

$p\text{-Me}_2\text{NC}_6\text{H}_4\text{SiH}_3$ (0.25 g, 1.67 mmol) and $\text{Co}_2(\text{CO})_8$ (0.93 g, 2.71 mmol) were dissolved in toluene (20 mL) in a Schlenk flask. The mixture was stirred at 45-55°C for 4 hours, by which time it was a deep purple-red. Solvent was removed *in vacuo*, and the residue chromatographed on a silica column, eluting with petroleum spirits: CH_2Cl_2 (4:1). Four bands were collected: (i) unreacted $\text{Co}_2(\text{CO})_8$; (ii) brown $\text{Co}_4(\text{CO})_{12}$; (iii) a purple band characterised below; and (iv) orange $\text{Co}_4(\mu_4\text{-SiC}_6\text{H}_4\text{NMe}_2)_2(\text{CO})_{11}$ identified by IR spectra [7]. Total recovery of material was low because significant decomposition accompanied the chromatography.

The purple band was evaporated to give 0.050 g of microcrystalline solid, ν_{CO} (petroleum spirit, cm^{-1}) 2109m, 2100m, 2071w,sh, 2060s, 2053s, 2041m, 2033s, 2020m, 2011m, 2005m, 1866m. This could not be further separated but ESI-MS indicated strongly that there were two components in this band: ESI-MS (MeOH) m/z 1234 $[\text{M}_A+\text{H}]^+$, 1206 $[\text{M}_A+\text{H}-\text{CO}]^+$, and 1368 $[\text{M}_B+\text{H}]^+$, 1340 $[\text{M}_B+\text{H}-\text{CO}]^+$. Recrystallisation from CH_2Cl_2 :petroleum spirits yielded a few black crystals of the $M_r=1233$ component which was fully characterised by an X-ray structure determination. The $M_r=1367$ component has not yet been identified, since insufficient pure material could be obtained for elemental analysis or NMR studies.

2.4 X-ray crystallography

2.4.1 Structure of $\text{Me}_2\text{NC}_6\text{H}_4\text{Si}[\text{Co}(\text{CO})_4][\text{OCCo}_3(\text{CO})_9]_2$

Intensely purple-black crystals of **1** were obtained as described above. Data were collected on a Bruker CCD diffractometer.

Crystal data: C₃₂H₁₀Co₇NO₂₄Si, M = 1233.02, orthorhombic, a = 23.454(7), b = 9.672(3), c = 18.810(5) Å, U 4267(2) Å³, T 163 K, space group Pca2₁, Z = 4, μ(Mo-K_α) = 2.77 mm⁻¹, 52177 reflections collected, 7295 unique (R_{int} 0.035) used after correction for absorption (T_{max, min} 1.000, 0.864). Crystal dimensions 0.86 x 0.36 x 0.20 mm³.

Refinement on F² gave R₁ 0.0208 [6876 data with I > 2σ (I)] and wR₂ 0.0487 (all data).

The hydrogen atoms were included in calculated positions.

The structure of **1** is illustrated in Figure 1, with selected bond parameters included in the caption to the figure.

Crystallography was carried out with the SHELX programs [10].

3 Results and discussion

The reaction between Me₂NC₆H₄SiH₃ and Co₂(CO)₈ in toluene is clearly different from that of other RSiH₃ since the solution turns distinctly purple, in contrast to the more usual orange-brown. Work-up required chromatographic separation, which led to extensive decomposition on the column so material recovery was relatively low. A small amount of orange Co₄(μ₄-SiC₆H₄NMe₂)₂(CO)₁₁ was identified by comparison with an authentic sample, possibly formed from reaction of the silane with the Co₄(CO)₁₂ generated in the reaction mixture [7]. There was no indication of Me₂NC₆H₄Si[Co(CO)₄][Co₂(CO)₇] which might have been expected by analogy with the reaction of PhSiH₃ [4].

The only new material that could be isolated by chromatography was an intense-purple material. The complexity of the carbonyl-region infrared spectrum indicated there was a mixture of at least two components but these could not be further separated. ESI-MS gave two sets of clean signals representing two parent ions with daughter ions arising

from CO loss. The major ions can be assigned as $[M+H]^+$ species under the conditions used, so the two compounds correspond to molecular masses of 1233 and 1367 respectively. This was confirmed for the lighter species by an X-ray structure determination. No further information could be gathered for the second component which remains unidentified, since a pure sample could not be obtained by crystallisation.

The X-ray structure determination of **1** is shown in the Figure. The $\text{Me}_2\text{NC}_6\text{H}_4\text{Si}$ group is attached to a $\text{Co}(\text{CO})_4$ moiety by a Si-Co bond, and to two $-\text{OCCO}_3(\text{CO})_9$ clusters via the oxygen atoms. This generates a very crowded molecule as shown by an intramolecular O(19)...O(32) distance of 2.86 Å, significantly less than the usual *ca* 3 Å for non-bonded O...O contacts in metal carbonyls. Surprisingly, the O(10)-Si-O(20) angle is $97.7(1)^\circ$, much more acute than the idealised 109° , despite it being between the two largest groups. However interactions between the two $-\text{OCCO}_3(\text{CO})_9$ cluster units are accommodated by the high flexibility of the C-O-Si linkages. In other molecules of the type $\text{XOCCO}_3(\text{CO})_9$, the X-O-C angle varies between 118° (X = a small group such as Me or Et [11]), to over 170° when X is large as in $\text{Cp}_2\text{Zr}[\text{OCCO}_3(\text{CO})_9]_2$ [12]. In the silicon complex **1** these angles are 153° .

The $\text{Co}(\text{CO})_4$ group has a Co-Si bond length of 2.284(8) Å, in the middle of the range from 2.226(5) Å for $\text{F}_3\text{SiCo}(\text{CO})_4$ [13] to 2.381(7) Å for $\text{H}_3\text{SiCo}(\text{CO})_4$ [14].

There is an interesting parallel between $\text{Me}_2\text{NC}_6\text{H}_4\text{Si}[\text{Co}(\text{CO})_4][\text{OCCO}_3(\text{CO})_9]_2$ and $\text{CpTi}[\text{Co}(\text{CO})_4][\text{OCCO}_3(\text{CO})_9]_2$ [12], with similar overall structures. The larger size of the organic group in the titanium example is accommodated by the larger metal atom and longer distances to the other substituents, compared with those in the silicon example. However these are not uniformly changed. If the Ti-O vs Si-O distances (1.829 vs 1.656

Å) are used to calculate the difference in radii between the two metals, the resulting figure of 0.17 Å is much smaller than the difference of 0.33 Å between the Ti-Co and Si-Co bonds (2.613 and 2.284 Å respectively). This suggests the $\text{Co}(\text{CO})_4$ group is much less strongly bonded to Ti than to Si.

The infrared spectrum for **1** can be assigned on the basis of characteristic patterns for the $-\text{Co}(\text{CO})_4$ and $-\text{OCCO}_3(\text{CO})_9$ groups [15], the bands at 2010, 2011, and 2005 cm^{-1} arising from the former and those at 2109, 2053, 2041 and 2033 cm^{-1} from the latter. This leaves distinctive bands at 2060, 2020 and 1866 cm^{-1} for the second component of the crude reaction product with M_r 1367, but further characterisation was not achieved.

There have been several reports of compounds formed which incorporate $\text{OCCO}_3(\text{CO})_9$ groups generated from $\text{Co}_2(\text{CO})_8$. The usual requirements for this are a Lewis-acidic, oxophilic centre which ends up attaches to the oxygen atom (e.g. Li^+ , Et_3NBCl_2 , $\text{Cp}_2(\text{Cl})\text{Hf}$, $(\text{acac})_3\text{Zr}$ or Cl_3Si [16]). In some cases where a basic solvent is used, a route involving base-induced disproportionation of $\text{Co}_2(\text{CO})_8$ to give $\text{Co}(\text{II})$ and $\text{Co}(\text{CO})_4^-$, and subsequent reaction of $\text{Co}(\text{CO})_4^-$ with $\text{Co}_2(\text{CO})_8$ to give $[\text{OCCO}_3(\text{CO})_9]^-$, which then acts as a nucleophile, provides a rationale for cluster formation. However there are cases where $\text{OCCO}_3(\text{CO})_9$ groups are formed where this process is unlikely, such as the isolation of $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{SiOCCO}_3(\text{CO})_9$ from the reaction of the parent silatrane with $\text{Co}_2(\text{CO})_8$ [17], and of $\text{Ph}_2\text{Si}[\text{Co}(\text{CO})_4][\text{OCCO}_3(\text{CO})_9]$ from Ph_2SiH_2 in non-polar solvents [15]. It is therefore not clear which factors divert the reaction of silanes with $\text{Co}_2(\text{CO})_8$ from the normal H_2 elimination reaction leading to Si-Co bonds. For $\text{Me}_2\text{NC}_6\text{H}_4\text{SiH}_3$, the amine functional group may be sufficiently basic to induce the disproportionation of $\text{Co}_2(\text{CO})_8$, initiating that pathway to **1** with $\text{OCCO}_3(\text{CO})_9$ groups

attached to the oxophilic Si atom, but other factors are also possible. Despite over thirty years of study, these apparently simple reactions are not yet fully understood.

4. Supplementary material.

Crystallographic data for the structural analysis of **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no 198997. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Rd., Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

Acknowledgements

We thank Dr Jan Wikaira and Professor Ward Robinson, University of Canterbury, for collection of X-ray intensity data. The William Georgetti Trust is thanked for a scholarship for GJH.

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Caption to figure.

Figure 1. The structure of the $\text{Me}_2\text{NC}_6\text{H}_4\text{Si}[\text{Co}(\text{CO})_4][\text{OCCo}_3(\text{CO})_9]_2$ (**1**). Parameters include bond lengths (Å): Si(1)-Co(30) 2.2841(8), Si(1)-O(10) 1.652(2), Si(1)-O(20) 1.660(2), Si(1)-C(1) 1.827(3), C(10)-O(10) 1.316(3), C(20)-O(20) 1.321(3), Co-Co bonds 2.469 (av); bond angles (degrees) O(10)-Si(1)-O(20) 97.7(1), C(1)-Si(1)-Co(30) 116.9(1), C(10)-O(10)-Si(1) 153.9(2), C(20)-O(20)-Si(1) 151.8(2).