

Facile cleavage of Si–Si or Si–Ge bonds in the reactions of disilanes or germylsilanes with cobalt carbonyl

J. Scott McIndoe, Brian K. Nicholson *

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

Received 10 August 1998

Abstract

The disilane $(\text{Ph}_2\text{HSi})_2$ reacted at room temperature with $\text{Co}_2(\text{CO})_8$ to yield $\text{Co}(\text{SiPh}_3)(\text{CO})_4$ as a major product. Corresponding monosilyl derivatives were formed also when other disilanes $\text{Ph}_3\text{SiSiR}_2\text{H}$ ($\text{R}_2 = \text{Ph}_2, \text{PhMe}, \text{Me}_2, \text{Et}_2$), $\text{Me}_3\text{SiSiPh}_2\text{H}$ and $\text{PhMe}_2\text{SiSiPhMeH}$ were reacted with $\text{Co}_2(\text{CO})_8$ under the same conditions. A mechanism based on silyl–silylene intermediates is proposed. The germylsilanes $\text{Ph}_3\text{GeSiR}_2\text{H}$ ($\text{R} = \text{Ph}, \text{Et}$) with $\text{Co}_2(\text{CO})_8$ also gave $\text{Co}(\text{SiPh}_3)(\text{CO})_4$ by selective elimination of $:\text{GePh}_2$ which was trapped by $\text{Co}_2(\text{CO})_8$ as $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$. Crystal structures of $\text{Co}(\text{SiPh}_3)(\text{CO})_4$ and $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$ are presented. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cobalt; Carbonyl; Triphenylsilyl complexes; Silylene; Germylene

1. Introduction

Since Pannell and co-workers reported the de-oligomerisation of $\text{Fe}(\text{SiMe}_2\text{SiMe}_3)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ to $\text{Fe}(\text{SiMe}_3)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ in 1974 [1], there has been sustained interest in the chemistry of the silicon–silicon bond in transition metal-substituted oligosilanes [2]. The mechanism of the photodeoligomerisation was proposed [3] to occur via a series of equilibrating silyl(silylene) intermediates formed upon photoelimination of a CO ligand followed by a 1,2-silyl shift; a series of 1,3-migrations led to scrambling of the silicon substituents. Finally (photo)expulsion of the silylene fragment gave the mono-silyl product. Subsequent work, mainly from the laboratories of Pannell and Ogino, has supported this general mechanism and has included labelling [4], mixing of silicon substituents [5], direct observation of the intermediate at low temperature [6], intramolecular stabilisation of bis(silylene) complexes [7], trapping of the silyl(silylene) intermediate using a

base [8], trapping of the expelled silylene [9], and the recent isolation of a true intermediate in the photochemical silylene-elimination/isomerisation process [10]. A stable stannyl/stannylene complex of manganese has also been characterised fully [11]. This mechanism has been adopted for other systems including closely-related indenyl complexes $\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{CO})_2$ [12], the analogous $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ examples, and polysilyl complexes involving tungsten [13], palladium and platinum [14], rhodium [15], iridium [15], and nickel [16]. For most of these systems relatively vigorous conditions, usually UV-irradiation, has been necessary to effect the elimination reactions.

So far no examples of similar behaviour have been clearly defined for cobalt complexes. Kerber and Pakkanen reacted $(\text{Me}_2\text{HSi})_2$ with $\text{Co}_2(\text{CO})_8$ and isolated $(\mu_2\text{-Me}_2\text{Si})_2\text{Co}_2(\text{CO})_6$ in 15% yield [17]. A variety of other products were seen in the reaction but could not be identified positively [17]. A mechanism was proposed based on the intermediacy of complexes with terminal silylene ligands. One difficulty is that methyl-substituted silicon-cobalt complexes are known to be thermally labile and air-sensitive; $\text{Co}(\text{SiMe}_3)(\text{CO})_4$ is best handled

* Corresponding author. Fax: +64-7-8384219.

E-mail address: b.nicholson@waikato.ac.nz (B.K. Nicholson)

on a high-vacuum line [18], while $[\text{Me}_2\{(\text{OC})_4\text{Co}\}\text{Si}\}_2\text{O}$ was described by Greene and Curtis [19] as extremely thermolabile and it decomposed slowly even at -78°C under a nitrogen atmosphere. However, corresponding phenyl species such as $\text{Co}(\text{SiPh}_3)(\text{CO})_4$ are more amenable to study, although even these do not survive normal chromatographic separation.

This present paper describes some reactions of phenyl-substituted polysilane compounds with $\text{Co}_2(\text{CO})_8$ under mild conditions. Mixed germlyl-silyl substrates were investigated also.

2. Experimental

2.1. General

All manipulations were carried out in an oxygen-free N_2 atmosphere with rigorously dried solvents. Reactions were conducted either in Schlenk flasks or in sealed glass ampoules. Starting silicon compounds Ph_3SiCl , Ph_2SiHCl and PhMeSiHCl were purchased from Petrarch and used as supplied. $\text{Co}_2(\text{CO})_8$ was freshly sublimed before use. Me_2SiHCl was prepared using a published method, while Et_2SiHCl was prepared similarly to the published synthesis of $i\text{Pr}_2\text{SiHCl}$

Table 1
Atomic coordinates and equivalent isotropic displacement parameters for $\text{Ph}_3\text{SiCo}(\text{CO})_4$

	x	y	z	U_{eq}
Co(1)	0.7339(1)	0.6381(1)	0.8122(1)	0.034(1)
Si(1)	0.6254(1)	0.7929(1)	0.6875(1)	0.030(1)
O(1)	0.8707(2)	0.4442(2)	0.9626(2)	0.069(1)
O(2)	0.6803(2)	0.8533(2)	0.9936(2)	0.063(1)
O(3)	0.4892(2)	0.4956(2)	0.8409(2)	0.054(1)
O(4)	0.9943(2)	0.6289(2)	0.5696(2)	0.055(1)
C(1)	0.8180(3)	0.5182(3)	0.9044(3)	0.046(1)
C(2)	0.6989(3)	0.7713(3)	0.9223(3)	0.042(1)
C(3)	0.5852(3)	0.5522(2)	0.8265(2)	0.040(1)
C(4)	0.8913(3)	0.6338(2)	0.6625(3)	0.040(1)
C(11)	0.6826(2)	0.9591(2)	0.6860(2)	0.031(1)
C(12)	0.8252(3)	0.9798(3)	0.6620(3)	0.051(1)
C(13)	0.8643(3)	1.1040(3)	0.6586(3)	0.058(1)
C(14)	0.7604(3)	1.2119(3)	0.6795(3)	0.052(1)
C(15)	0.6177(3)	1.1950(3)	0.7028(3)	0.056(1)
C(16)	0.5794(3)	1.0704(2)	0.7064(3)	0.044(1)
C(21)	0.4202(2)	0.8111(2)	0.7600(2)	0.034(1)
C(22)	0.3392(3)	0.8039(2)	0.6778(3)	0.044(1)
C(23)	0.1880(3)	0.8233(3)	0.7283(4)	0.061(1)
C(24)	0.1146(3)	0.8508(3)	0.8606(4)	0.063(1)
C(25)	0.1914(3)	0.8584(3)	0.9439(3)	0.057(1)
C(26)	0.3430(3)	0.8384(3)	0.8946(3)	0.047(1)
C(31)	0.6859(2)	0.7381(2)	0.5102(2)	0.035(1)
C(32)	0.7432(3)	0.8245(3)	0.4040(2)	0.043(1)
C(33)	0.7915(3)	0.7864(3)	0.2722(3)	0.059(1)
C(34)	0.7828(3)	0.6608(4)	0.2444(3)	0.064(1)
C(35)	0.7263(4)	0.5734(3)	0.3459(3)	0.065(1)
C(36)	0.6776(3)	0.6111(3)	0.4787(3)	0.052(1)

[20]. The disilane starting materials were from treatment of R_3SiHCl with R_3SiLi , adapting published methods [21]. $\text{Me}_3\text{SiPh}_2\text{SiH}$ was prepared by acid hydrolysis of $\text{Me}_3\text{SiPh}_2\text{SiLi}$. Several literature routes to $(\text{Ph}_2\text{HSi})_2$ have been published [22], but we used rapid stirring of Ph_2SiHCl with lithium metal in THF for three days.

2.2. Instrumentation.

Infrared spectra were recorded on a Digilab FTS-40 FTIR spectrophotometer. NMR spectroscopy was performed using a Bruker AC300P Multinuclear FT spectrometer. Elemental analysis was performed by the Campbell Microanalytical Laboratory, University of Otago. Melting points were measured on a Reichart Thermopan melting point apparatus and are uncorrected.

2.3. Reactions

2.3.1. Reaction of $(\text{Ph}_2\text{HSi})_2$ with $\text{Co}_2(\text{CO})_8$

To a Schlenk flask was added $(\text{Ph}_2\text{HSi})_2$ (0.200 g, 0.55 mmol), $\text{Co}_2(\text{CO})_8$ (0.187 g, 0.55 mmol) and petroleum spirits (10 ml), and the mixture was left to stir for 2 days. An IR spectrum of the crude mixture showed the presence of $\text{Co}_2(\text{CO})_8$ ($\sim 40\%$), $\text{Co}_4(\text{CO})_{12}$ ($\sim 10\%$), $\text{CoH}(\text{CO})_4$ ($\sim 5\%$) and the remainder $\text{Co}(\text{SiPh}_3)(\text{CO})_4$ with peaks at 2095 (m), 2034 (m) and 2006 (vs) cm^{-1} . Prolonged pumping under high vacuum removed the $\text{CoH}(\text{CO})_4$ and the remaining species were separated by fractional crystallisation. Transparent crystals of $\text{Co}(\text{SiPh}_3)(\text{CO})_4$ (32 mg, 0.086 mmol, 16%) were hand separated in a glove box from black $\text{Co}_4(\text{CO})_{12}$ and orange $\text{Co}_2(\text{CO})_8$. Data for $\text{Co}(\text{SiPh}_3)(\text{CO})_4$: m.p. $158\text{--}160^\circ\text{C}$. IR $\nu(\text{CO})$: (petroleum spirits, cm^{-1}) 2095 (m), 2034 (m), 2006 (vs); (CH_2Cl_2 , cm^{-1}) 2096 (m), 2036 (m), 2002 (vs). NMR (CDCl_3) ^1H : δ 7.58, 7.38 (m, C_6H_5); ^{13}C : δ 198.8 (CO), 138.3 (*ipso*), 135.5 (*ortho*), 129.6 (*para*), 128.0 (*meta*) (C_6H_5).

2.3.2. Reaction of Ph_3SiH with $\text{Co}_2(\text{CO})_8$

Ph_3SiH (0.177 g, 0.680 mmol), $\text{Co}_2(\text{CO})_8$ (0.166 g, 0.340 mmol) and petroleum spirits (10 ml) were added to a Schlenk flask and allowed to react overnight. The pale brown solution was cooled to -20°C to give white crystals of $\text{Co}(\text{SiPh}_3)(\text{CO})_4$ (0.153 g, 0.412 mmol, 61%), spectroscopically identical to that synthesised indirectly.

2.3.3. Reaction of $\text{Ph}_3\text{SiSiPh}_2\text{H}$ with $\text{Co}_2(\text{CO})_8$

The reaction between $\text{Ph}_3\text{SiSiPh}_2\text{H}$ (0.100 g, 0.226 mmol) and $\text{Co}_2(\text{CO})_8$ (0.039 g, 0.113 mmol) in petroleum spirits (10 ml) proceeded slowly over 3 days. After this time, the main carbonyl-containing com-

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$

	x	y	z	U_{eq}
Ge(1)	0.1284(1)	0.1552(1)	0.4108(1)	0.024(1)
Co(1)	0.2282(1)	0.2312(1)	0.4205(1)	0.030(1)
Co(2)	0.0340(1)	0.2425(1)	0.4029(1)	0.030(1)
Ge(2)	0.1196(1)	0.6656(1)	0.4183(1)	0.027(1)
Co(3)	0.1073(1)	0.5786(1)	0.5794(1)	0.033(1)
Co(4)	0.1384(1)	0.5893(1)	0.2505(1)	0.033(1)
C(1)	0.3011(2)	0.2868(2)	0.4265(3)	0.039(1)
C(2)	0.2606(2)	0.1368(2)	0.3676(3)	0.036(1)
C(3)	0.2127(2)	0.2342(2)	0.5612(3)	0.041(1)
C(4)	0.1949(2)	0.3057(2)	0.3306(3)	0.040(1)
C(5)	-0.0351(2)	0.3075(2)	0.4068(3)	0.038(1)
C(6)	-0.0040(1)	0.1427(2)	0.4145(3)	0.035(1)
C(7)	0.0690(2)	0.2964(2)	0.5113(3)	0.040(1)
C(8)	0.0532(2)	0.2651(2)	0.2651(3)	0.040(1)
C(9)	0.1000(2)	0.5161(2)	0.6984(3)	0.041(1)
C(10)	0.1219(2)	0.6755(3)	0.6457(3)	0.044(1)
C(11)	0.1680(2)	0.5148(2)	0.5263(3)	0.042(1)
C(12)	0.0284(2)	0.5626(3)	0.5372(3)	0.047(1)
C(13)	0.1537(2)	0.5364(2)	0.1260(3)	0.047(1)
C(14)	0.2178(2)	0.5826(2)	0.2963(3)	0.043(1)
C(15)	0.0814(2)	0.5165(2)	0.2953(3)	0.041(1)
C(16)	0.1142(2)	0.6848(3)	0.1890(3)	0.046(1)
O(1)	0.3468(1)	0.3219(2)	0.4277(3)	0.057(1)
O(2)	0.2841(1)	0.0790(2)	0.3331(2)	0.049(1)
O(3)	0.2061(2)	0.2362(2)	0.6503(2)	0.064(1)
O(4)	0.1784(2)	0.3557(2)	0.2732(3)	0.061(1)
O(5)	-0.0770(1)	0.3495(2)	0.4111(3)	0.056(1)
O(6)	-0.0294(1)	0.0807(1)	0.4189(3)	0.047(1)
O(7)	0.0878(1)	0.3335(2)	0.5811(3)	0.060(1)
O(8)	0.0613(2)	0.2794(2)	0.1784(2)	0.060(1)
O(9)	0.0958(2)	0.4755(2)	0.7715(2)	0.058(1)
O(10)	0.1311(2)	0.7354(2)	0.6928(3)	0.060(1)
O(11)	0.2064(2)	0.4709(2)	0.4978(3)	0.061(1)
O(12)	-0.0222(2)	0.5504(2)	0.5158(3)	0.072(1)
O(13)	0.1636(2)	0.5057(2)	0.0472(3)	0.074(1)
O(14)	0.2684(1)	0.5775(2)	0.3207(3)	0.063(1)
O(15)	0.0454(2)	0.4681(2)	0.3191(3)	0.061(1)
O(16)	0.0986(2)	0.7429(2)	0.1441(2)	0.070(1)
C(21)	0.1250(2)	0.0767(2)	0.5308(3)	0.029(1)
C(22)	0.0828(2)	0.0820(2)	0.6141(3)	0.035(1)
C(23)	0.0811(2)	0.0219(2)	0.6929(3)	0.043(1)
C(24)	0.1222(2)	-0.0442(3)	0.6908(3)	0.044(1)
C(25)	0.1650(2)	-0.0505(2)	0.6094(3)	0.042(1)
C(26)	0.1663(2)	0.0097(2)	0.5306(3)	0.036(1)
C(31)	0.1277(2)	0.0833(2)	0.2838(3)	0.031(1)
C(32)	0.1569(2)	0.1067(2)	0.1897(3)	0.041(1)
C(33)	0.1555(2)	0.0530(3)	0.1022(3)	0.057(1)
C(34)	0.1242(2)	-0.0222(3)	0.1090(4)	0.063(2)
C(35)	0.0944(2)	-0.0452(3)	0.2003(4)	0.056(1)
C(36)	0.0962(2)	0.0069(2)	0.2888(3)	0.040(1)
C(41)	0.0450(1)	0.7355(2)	0.4068(3)	0.032(1)
C(42)	-0.0061(2)	0.7138(2)	0.3444(3)	0.041(1)
C(43)	-0.0589(2)	0.7633(3)	0.3430(3)	0.052(1)
C(44)	-0.0612(2)	0.8352(3)	0.4028(4)	0.056(1)
C(45)	-0.0117(2)	0.8583(2)	0.4650(3)	0.051(1)
C(46)	0.0416(2)	0.8092(2)	0.4670(3)	0.039(1)
C(51)	0.1907(2)	0.7422(2)	0.4311(3)	0.032(1)
C(52)	0.1929(2)	0.8108(2)	0.3625(3)	0.039(1)
C(53)	0.2456(2)	0.8612(2)	0.3579(3)	0.049(1)
C(54)	0.2965(2)	0.8436(2)	0.4214(4)	0.053(1)
C(55)	0.2946(2)	0.7767(3)	0.4912(4)	0.051(1)
C(56)	0.2417(2)	0.7264(2)	0.4958(3)	0.040(1)

pounds were $\text{Co}_2(\text{CO})_8$ ($\sim 50\%$), $\text{Co}_4(\text{CO})_{12}$ ($\sim 5\%$) and $\text{Co}(\text{SiPh}_3)(\text{CO})_4$ ($\sim 40\%$).

2.3.4. Reaction of $\text{Ph}_3\text{SiSiPhMeH}$ with $\text{Co}_2(\text{CO})_8$

$\text{Ph}_3\text{SiSiPhMeH}$ (0.262 g, 0.700 mmol), $\text{Co}_2(\text{CO})_8$ (0.118 g, 0.345 mmol) and petroleum spirits (~ 1 ml) were sealed in a small ampoule and left to react in the dark. After 2 months, crystals of $\text{Co}(\text{SiPh}_3)(\text{CO})_4$ (15 mg, 0.035 mmol, 5%) had precipitated. The solution IR showed mainly $\text{Co}(\text{SiPh}_3)(\text{CO})_4$, with small ($\sim 10\%$) amounts of $\text{Co}_2(\text{CO})_8$ present. A reaction in a sealed NMR tube between $\text{Co}_2(\text{CO})_8$ (31 mg, 0.091 mmol) and $\text{Ph}_3\text{SiSiPhMeH}$ (69 mg, 0.18 mmol) in C_6D_6 also showed mainly $\text{Co}(\text{SiPh}_3)(\text{CO})_4$ as product (by ^{13}C -NMR), with a complex methyl region (three peaks in the ^1H SiMe region, at δ 1.08, 1.03 and 0.56).

2.3.5. Reaction of $\text{Ph}_3\text{SiSiMe}_2\text{H}$ with $\text{Co}_2(\text{CO})_8$

$\text{Ph}_3\text{SiSiMe}_2\text{H}$ (16.9 mg, 0.0531 mmol) and $\text{Co}_2(\text{CO})_8$ (9.0 mg, 0.026 mmol) in petroleum spirits (5 ml) were stirred in a Schlenk flask overnight. The $\nu(\text{CO})$ IR spectrum showed some $\text{Co}_2(\text{CO})_8$ ($\sim 20\%$) and broad peaks at 2094 (m), 2032 (m) and 2002 (vs) cm^{-1} ($\sim 80\%$). Attempted purification of this solution was unsuccessful. An NMR study of the reaction between $\text{Co}_2(\text{CO})_8$ (22 mg, 0.064 mmol) and $\text{Ph}_3\text{SiSiMe}_2\text{H}$ (43 mg, 0.13 mmol) in C_6D_6 showed a mixture of products, with at least five peaks in the ^1H SiMe region, at δ 1.08, 1.03, 0.76, 0.51 and 0.29.

2.3.6. Reaction of $\text{Ph}_3\text{SiSiEt}_2\text{H}$ with $\text{Co}_2(\text{CO})_8$

$\text{Ph}_3\text{SiSiEt}_2\text{H}$ (0.343 g, 0.991 mmol) and $\text{Co}_2(\text{CO})_8$ (0.170 g, 0.497 mmol) in petroleum spirits (10 ml) were stirred in a Schlenk flask overnight. The $\nu(\text{CO})$ IR spectrum showed some $\text{Co}_2(\text{CO})_8$ ($\sim 20\%$) and broad peaks at 2093 (m), 2031 (m) and 1999 (vs) cm^{-1} ($\sim 80\%$). Attempted purification of this solution was unsuccessful.

2.3.7. Reaction of $\text{Me}_3\text{SiSiPh}_2\text{H}$ with $\text{Co}_2(\text{CO})_8$

$\text{Co}_2(\text{CO})_8$ (0.227 g, 0.663 mmol) was added to a Schlenk flask containing $\text{Me}_3\text{SiSiPh}_2\text{H}$ (~ 1 ml, excess) in petroleum spirits (~ 10 ml) and the mixture allowed to stir overnight. The $\nu(\text{CO})$ IR spectrum of the resulting solution showed peaks due to a small amount of $\text{Co}_2(\text{CO})_8$ ($\sim 5\%$) and peaks at 2091 (m), 2030 (m), 2001 (s) and 1997 (s) cm^{-1} . Attempted purification of this solution was unsuccessful. An NMR-scale study of the same reaction showed a complex mixture of products, with at least eight peaks in the ^1H SiMe region, at δ 1.08, 1.03, 0.76, 0.63, 0.50, 0.28, 0.21 and 0.13.

2.3.8. Reaction of $\text{PhMe}_2\text{SiSiPhMeH}$ with $\text{Co}_2(\text{CO})_8$

$\text{PhMe}_2\text{SiSiPhMeH}$ (0.309 g, 1.21 mmol), $\text{Co}_2(\text{CO})_8$ (0.207 g, 0.605 mmol) and petroleum spirits (~ 10 ml) were added to a Schlenk flask and allowed to stir

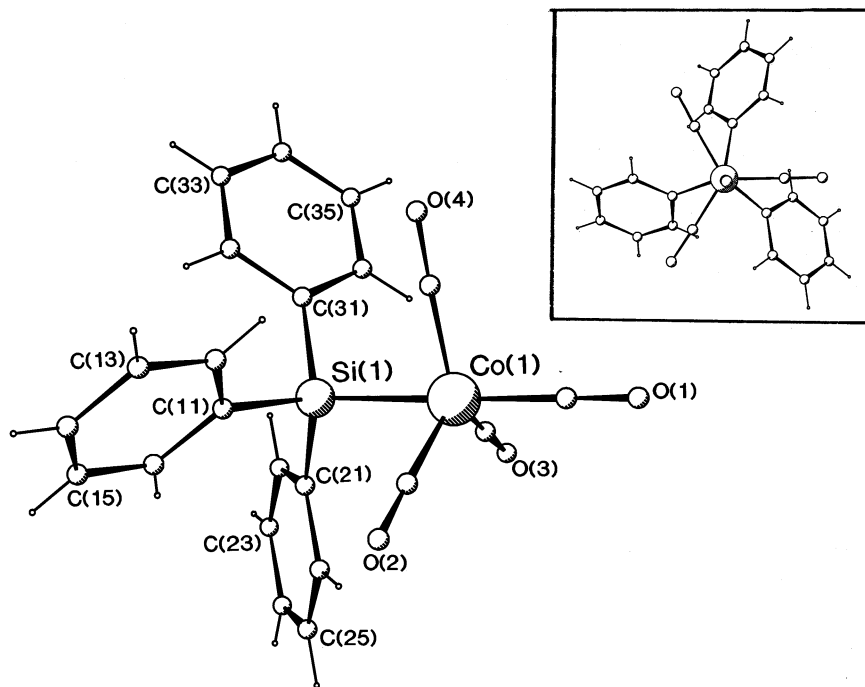


Fig. 1. Two views of the structure of $\text{Co}(\text{SiPh}_3)(\text{CO})_4$, a general view and (inset) a view along the Co–Si vector. Bond parameters include: $\text{Co}(1)\text{--Si}(1)$ 2.3810(7), $\text{Co}(1)\text{--C}(1)$ 1.813(3), $\text{Co}(1)\text{--C}_{\text{eq}}$ (av) 1.787(3), $\text{Si}(1)\text{--C}$ (av) 1.880(2) Å; $\text{Co}(1)\text{--Si}(1)\text{--C}$ (av) 110.65°, $\text{Si}(1)\text{--Co}(1)\text{--C}(1)$ 178.91(8), $\text{Si}(1)\text{--Co}(1)\text{--C}_{\text{eq}}$ (av) 83.86(8)°.

overnight. The $\nu(\text{CO})$ IR spectrum of the resulting clear orange/brown solution showed peaks due to $\text{Co}_2(\text{CO})_8$ (~20%) and broad peaks at 2092 (m), 2030 (m) and 1999 (vs) cm^{-1} indicating a mixture of products. Attempted purification of this solution was unsuccessful.

2.3.9. Reaction of $\text{Ph}_3\text{GeSiPh}_2\text{H}$ with $\text{Co}_2(\text{CO})_8$

$\text{Ph}_3\text{GeSiPh}_2\text{H}$ (0.100 g, 0.206 mmol) was added to a Schlenk flask containing $\text{Co}_2(\text{CO})_8$ (35 mg, 0.10 mmol) and toluene (10 ml). The reaction was stirred overnight. The $\nu(\text{CO})$ IR spectrum of the resulting clear yellow solution showed peaks at 2091 (m), 2033 (m) and 2002 (vs) cm^{-1} as well as peaks due to $\text{CoH}(\text{CO})_4$ at 2054 and 2030 cm^{-1} , and a large number of smaller peaks. The solution was reduced in volume to ~2 ml, petroleum spirits (~5 ml) added and left at -20°C to crystallise. A pale yellow powder was produced, which could be partially dissolved in petroleum spirits to give a spectrum identical to that of $\text{Co}(\text{SiPh}_3)(\text{CO})_4$. The remaining yellow powder dissolved in toluene to give a spectrum with peaks at 2100 (w), 2084 (s), 2033 (m), 2023 (s), 2015 (s) and 2000 (m) cm^{-1} . This species was later identified as $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$. No evidence for $\text{Co}(\text{GePh}_3)(\text{CO})_4$ species was seen.

2.3.10. Reaction of $\text{Ph}_3\text{GeSiEt}_2\text{H}$ with $\text{Co}_2(\text{CO})_8$

$\text{Ph}_3\text{GeSiEt}_2\text{H}$ (0.214 g, 0.548 mmol), $\text{Co}_2(\text{CO})_8$ (94 mg, 0.27 mmol) and petroleum spirits (~0.5 ml) were sealed in a mini-ampoule and left to react in the dark for 3 weeks. After this time, the ampoule contained a

bright yellow solution, some small black cubic crystals ($\text{Co}_4(\text{CO})_{12}$) and several large, pale yellow prisms, shown spectroscopically and by an X-ray crystal structure analysis to be $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$ (19 mg, 0.033 mmol, 18%). The solution showed peaks at 2091 (m), 2030 (m), 2002 (vs) and 1995 (s) cm^{-1} , consistent with $\text{PhEt}_2\text{SiCo}(\text{CO})_4$. Data for $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$: mp 140 °C (dec.). IR $\nu(\text{CO})$: (petroleum spirits, cm^{-1}) 2100 (w), 2084 (s), 2033 (m), 2023 (s), 2015 (s), 2000 (m).

2.4. X-ray crystallography

Unit cell parameters and intensity data were collected using a Siemens SMART CCD diffractometer, using standard collection procedures, with monochromatic Mo-K_α X-rays (0.71073 Å) at 203 K. Corrections for absorption and other effects was carried out with SADABS [23], all other calculations used the SHELX97 programs [24]. The structures were solved by direct methods, and developed routinely with refinement based on F^2 . All non-hydrogen atoms were assigned anisotropic temperature factors, and hydrogen atoms were included in calculated positions. Refined coordinates are given in Tables 1 and 2, while selected bond parameters are in the captions to Figs. 1 and 2.

2.4.1. Crystal data for $\text{Co}(\text{SiPh}_3)(\text{CO})_4$

$\text{C}_{22}\text{H}_{15}\text{CoO}_4\text{Si}$, M_r 430.38, triclinic, $P\bar{1}$, $a = 9.8742(5)$, $b = 10.3120(5)$, $c = 10.6963(5)$ Å, $\alpha = 85.687(1)$, $\beta = 69.236(1)$, $\gamma = 81.629(1)^\circ$, $V = 1007.21(8)$ Å³, $D_{\text{calc.}} =$

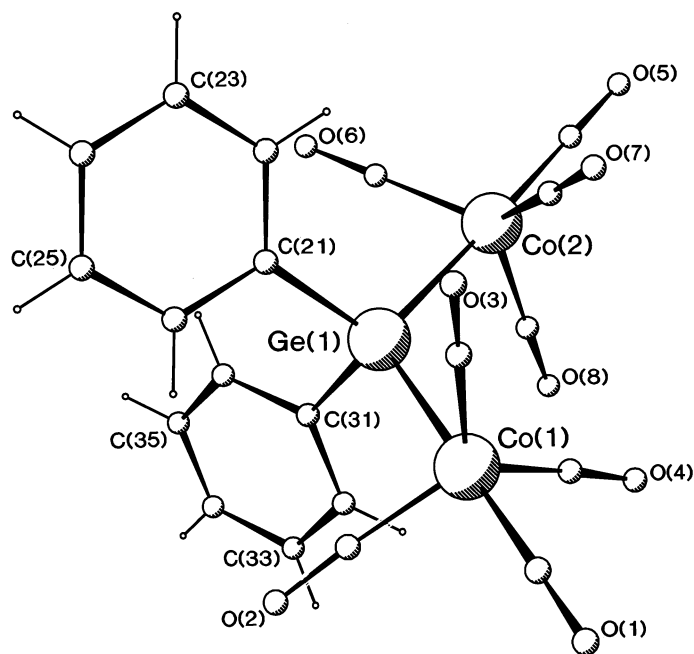


Fig. 2. The structure of one of the independent molecules of $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$ in the crystal. Bond parameters include: Ge(1)–Co(1) 2.4708(5), Ge(1)–Co(2) 2.4674(5), Ge(2)–Co(4) 2.4742(6), Ge(2)–Co(3) 2.4749(6), Ge–C (av) 1.967(4), Co–C_{ax} (av) 1.810(4), Co–C_{eq} (av) 1.790 Å; Co(1)–Ge(1)–Ge(2) 116.06(2), Co(3)–Ge(2)–Co(4) 116.18, C(21)–Ge(1)–C(31) 104.5(1), C(41)–Ge(2)–C(51) 106.7(1), Ge–Co–C_{ax} (av) 178.1(2), Ge–Co–C_{eq} (av) 85.3(2)°.

1.420 g cm⁻³, $Z = 2$, $F(000) = 440$, $\mu(\text{Mo-K}\alpha)$ 0.921 mm⁻¹, $T_{\text{max}} 0.9272$, $T_{\text{min}} 0.7104$, crystal size 0.41 × 0.14 × 0.11 mm³.

A total of 9726 reflections, 4444 unique ($R_{\text{int}} 0.0263$) was collected $2^\circ < \theta < 28^\circ$. Final $R_1 0.0391$ (3451 data with $I > 2\sigma(I)$), 0.0614 (all data), $wR_2 0.0866$, goodness-of-fit 1.073, final $\Delta e +0.331/-0.257$.

2.4.2. Crystal data for $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$

$\text{C}_{20}\text{H}_{10}\text{Co}_2\text{GeO}_8$, $M_r 568.73$, orthorhombic, $Pna2_1$, $a = 21.5209(2)$, $b = 15.9964(2)$, $c = 12.5992(2)$ Å, $V = 4337.4(1)$ Å³, $D_{\text{calc.}} = 1.742$ g cm⁻³, $Z = 8$, $F(000) = 2240$, $\mu(\text{Mo-K}\alpha)$ 2.932 mm⁻¹, $T_{\text{max}} 0.4967$, $T_{\text{min}} 0.3877$, crystal size 0.52 × 0.48 × 0.44 mm³.

A total of 24258 reflections, 9342 unique ($R_{\text{int}} 0.0198$) was collected $2^\circ < \theta < 28^\circ$. Final $R_1 0.0258$ (8744 data with $I > 2\sigma(I)$), 0.0306 (all data), $wR_2 0.0603$, goodness-of-fit 1.016, final $\Delta e +0.288/-0.430$, absolute structure parameter 0.156(9).

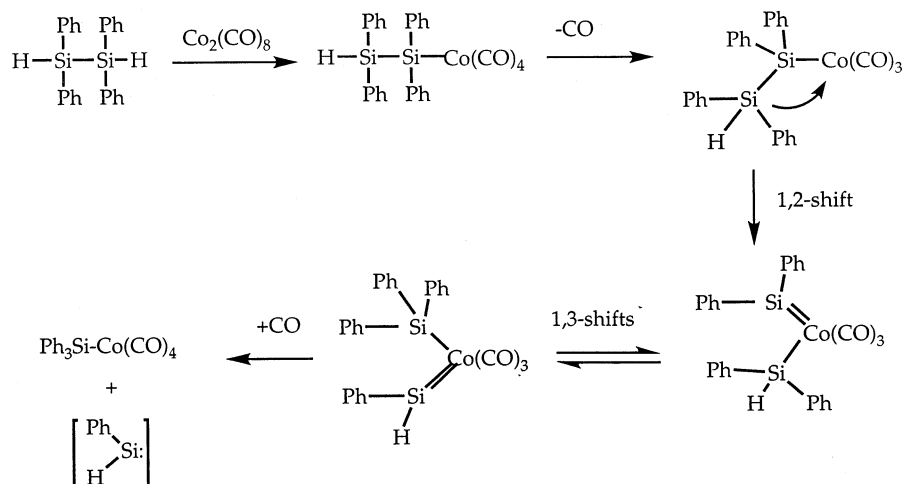
3. Results and discussion

3.1. Reactions

Instead of paralleling the reactivity observed by Kerber and Pakkanen for $(\text{Me}_2\text{HSi})_2$, when $(\text{Ph}_2\text{HSi})_2$ reacted with $\text{Co}_2(\text{CO})_8$ the only isolated compound containing a Co–Si bond was $\text{Co}(\text{SiPh}_3)(\text{CO})_4$. This was characterised fully by an X-ray crystal structure

determination, and by comparison with the product from Ph_3SiH with $\text{Co}_2(\text{CO})_8$, a known reaction [25]. Although IR evidence suggests that $\text{Co}(\text{SiPh}_3)(\text{CO})_4$ was the major product in the crude reaction mixture, the isolated yield was not high because of the difficulty of separating it from the byproducts formed by the presumed PhSiH species eliminated. This unexpected rearrangement can be explained by analogy with the previous photochemically induced processes for the $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ silyl complexes, as outlined in Scheme 1. The initial reaction of the Si–H bond with $\text{Co}_2(\text{CO})_8$ in the usual manner [25] by elimination of H_2 [or $\text{HCo}(\text{CO})_4$] and formation of a Si–Co bond will give $\text{HPh}_2\text{SiSiPh}_2\text{Co}(\text{CO})_4$. Loss of CO from the cobalt centre is then followed by a 1,2-silyl migration to give a silyl/silylene intermediate which undergoes redistribution of the substituents on the silicon atoms by a series of 1,3-shifts until the silylene fragment is replaced by CO to generate the stable complex $\text{Co}(\text{SiPh}_3)(\text{CO})_4$. The second Si–H bond in the starting silane may also be converted to a Si– $\text{Co}(\text{CO})_4$ group before rearrangement, but in this case some $(\mu_2\text{-Ph}_2\text{Si})_2\text{Co}_2(\text{CO})_6$ might have been expected to be formed, but no CO vibrations assignable to this species were observed in infrared spectra. The difference between the $(\text{R}_2\text{HSi})_2$ systems ($\text{R} = \text{Me}, \text{Ph}$) is presumably the relative rates of the Si–H/ $\text{Co}_2(\text{CO})_8$ reaction and the silyl/silylene rearrangement process for the two cases.

What is remarkable with this reaction, in contrast to previous examples, is the fact that it occurs sponta-



Scheme 1.

neously at room temperature without the need for photochemical initiation, presumably because of the higher lability of CO ligands of the $\text{Co}(\text{CO})_4$ group. This means that creation of a vacant coordination site, crucial for the 1,2-silyl migration to occur, is more readily accomplished for the cobalt system.

Further reactions showed the generality of the transformation. The mono-hydro disilanes $\text{Ph}_3\text{SiSiR}_2\text{H}$ ($\text{R}_2 = \text{Ph}_2, \text{PhMe}, \text{Me}_2, \text{Et}_2$), $\text{Me}_3\text{SiSiPh}_2\text{H}$ and $\text{PhMe}_2\text{-SiSiPhMeH}$ were also reacted with $\text{Co}_2(\text{CO})_8$. All appeared to form mono-silyl complexes $\text{Co}(\text{SiR}_n\text{-R}'_{3-n})(\text{CO})_4$ though these were generally not separated from each other, or from the products arising from the eliminated silylene fragment. Evidence for mixtures was apparent in the $\nu(\text{CO})$ IR spectra which showed marked broadening of the peaks of the characteristic pattern as well as small shifts in position. ^1H - and ^{13}C -NMR spectra also revealed the presence of a range of products, typically showing three to eight signals in the SiMe region.

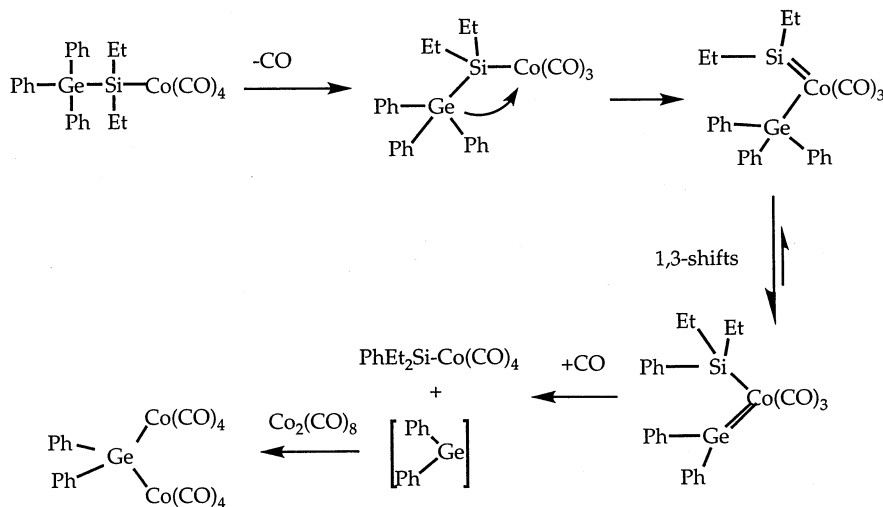
In an attempt to monitor the course of the reaction, and detect possible intermediates the reaction of $(\text{Ph}_2\text{HSi})_2$ with $\text{Co}_2(\text{CO})_8$ was carried out in C_6D_6 in a sealed NMR tube. Unfortunately, attempts to follow reactions in their early stages (0–1 h) were thwarted by extreme broadening of the peaks. This observation suggests the presence of paramagnetic compounds, consistent with the proposal of Markó and co-workers [26] that the reaction between hydrosilanes and $\text{Co}_2(\text{CO})_8$ implicates $\cdot\text{Co}(\text{CO})_4$ and/or $\cdot\text{Co}(\text{CO})_3$ radicals rather than $\text{CoH}(\text{CO})_4$ as proposed originally.

Detection of the eliminated silylene fragment has been achieved with other systems by trapping it with either $\text{HSi}(\text{SiMe}_3)_3$ or with alkynes; unfortunately for the cobalt carbonyl reactions the use of these reagents is precluded since they both react with $\text{Co}_2(\text{CO})_8$ themselves under the same conditions. However evidence for the validity of the mechanism outlined in Scheme 1

came from the reaction of the germylsilanes $\text{Ph}_3\text{GeSiPh}_2\text{H}$ and $\text{Ph}_3\text{GeSiEt}_2\text{H}$ with $\text{Co}_2(\text{CO})_8$. In both cases the product mixture was bright yellow in colour and the $\nu(\text{CO})$ IR evidence showed characteristic peaks assignable to $\text{Co}(\text{SiR}_3)(\text{CO})_4$ species. The presence of some $\text{Co}(\text{GeR}_3)(\text{CO})_4$ cannot be excluded since it would give a similar pattern, but most of the germanium was associated with other peaks which were assigned to the yellow germylene complex $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$, which was isolated and structurally characterised. Scheme 2 suggests a possible reaction route to these products for the example involving $\text{Ph}_3\text{GeSiEt}_2\text{H}$. Initial formation of $\text{Co}(\text{SiEt}_2\text{GePh}_3)(\text{CO})_4$ would occur, and a 1,2-germyl shift would give a germyl/silylene intermediate which equilibrates with a silyl/germylene version. The latter is likely to be the preferred form based on the greater stability of Ge(II) compared with Si(II). Trapping of the eliminated germylene fragment by insertion into the Co–Co bond of $\text{Co}_2(\text{CO})_8$ (a known reaction for GeI_2 for example) would give $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$. The exclusive elimination of $:\text{GePh}_2$, leaving $\text{PhEt}_2\text{SiCo}(\text{CO})_4$ is expected, since $:\text{GeR}_2$ species are considerably more stable than the analogous $:\text{SiR}_2$ species, and the Ph groups stabilise the germylene more than Et ones. The same selectivity was found by Pannell and Sharma [27] in the $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ system when germylsilanes were used.

3.2. Structural determinations

The crystal structure of $\text{Co}(\text{SiPh}_3)(\text{CO})_4$ was determined as part of the definite characterisation, and because there were no previous determinations of a simple tri-alkyl or -aryl complex of this type, although $\text{Co}(\text{SiH}_3)(\text{CO})_4$, $\text{Co}(\text{SiF}_3)(\text{CO})_4$ and $\text{Co}(\text{SiCl}_3)(\text{CO})_4$ have been described [28–30]. The compound is isomorphous with $\text{Fe}(\text{PPh}_3)(\text{CO})_4$ [31]. The structure is shown in Fig. 1. It conforms closely to C_3 symmetry,



Scheme 2.

although this is not required crystallographically. The Si–Co bond length, 2.3810(7) Å is equal to the longest known, 2.381(4) Å for $\text{Co}(\text{SiH}_3)(\text{CO})_4$. The equatorial CO ligands are tilted towards the silyl substituent by 6° , the well-known umbrella effect which is understood theoretically [32]

The structure of the known [33] complex $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$ is shown in Fig. 2, and is the first for a simple R_2GeM_2 species. There are two independent molecules in the asymmetric unit, but these do not differ in any meaningful way. The average Ge–Co bond length of 2.47 Å is longer than in $\text{Co}(\text{GeCl}_3)(\text{CO})_4$ (2.310 Å) [34], but similar to those in $\text{Co}(\text{GeMeNpPh})(\text{CO})_4$ (Np = 1-naphthyl) (2.458 Å) [35] and 3,4-dimethyl-1,1-bis(tetracarbonylcobaltio)-1-germacyclopent-3-ene (2.460 Å) [36] Steric crowding at the Ge centre in $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$ is indicated by the opened Co–Ge–Co angle of 116° .

Acknowledgements

The University of Waikato is acknowledged for financial support and a postgraduate scholarship (to J.S.M.). We thank Associate Professor Cliff Rickard and Allen Oliver, University of Auckland, for X-ray data sets.

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