Because of the hydrolytic instability of trimethylchlorosilane, triphenylchlorosilane was used in a series of experiments. This compound is less sensitive to hydrolysis than trimethylchlorosilane and is reported[2,3] to be a slightly stronger acid. When triphenylchlorosilane was injected into a TPPO–benzene solution, very little heat was detected. If the equilibrium constant for the complex is as large as that reported by Graddon and Rana[2,3] for similar systems, the enthalpy change for complexation may be calculated to be about 0.3 kcal/mol.

The reproducible results obtained for triphenylchlorosilane suggests that there may be some interaction which generates heat for both the silicon and germanium derivatives. However, the quantiy of heat suggests that either the equilibrium constants are very small and/or that the complexation enthalpy is very small.

Thus, the large heats reported by Graddon and Rana, and attributed by them to interaction of the base at the chlorine of the chlorosilane, are almost certainly due to hydrolysis. If, as Graddon and Rana report, the equilibrium constant for the reaction of trimethylchlorosilane with pyridine in acetonitrile is greater than 10^6, the enthalpy change must be much less than the 13.3 kcal/mol reported (the equilibrium constant in cyclohexane should be even greater than in acetonitrile). Likewise, if the enthalpy of Graddon and Rana is correct, the equilibrium constant must be small (<20). On the basis of the present results it appears that there is little or no interaction between trimethylchlorosilane and bases such as pyridine.

NMR Spectroscopy. Complexation frequently alters the chemical shifts of NMR-active nuclei at the active sites of the acid and base. Zeldin, Mehta, and Vernon[4] have used the change in ^{31}P chemical shift of triphenylphosphine oxide to monitor the Lewis acidity of some group 14 halides. In our laboratory this procedure allowed the calculation of a value of 20 for the equilibrium constant for the interaction of trimethylchlorostannane with triphenylphosphine oxide in benzene. This value is in excellent agreement with that obtained calorimetrically (Table I) but different from the value of 100 ± 5 obtained by Zeldin, et al.[4] Trimethylchlorogermane produced no change in the ^{31}P shift of TPPO, in agreement with the calorimetric data that indicated a small or zero enthalpy change. The values obtained for trimethylchlorosilane were not reproducible (HCl should protonate TPPO and lead to a change in the ^{31}P shift).

Acknowledgment. We are indebted to the National Science Foundation, Research Corp. for a Cottrell College Science Grant, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. $(CH_3)_3SnCl$, 1066-45-1; $(CH_3)_3GeCl$, 1529-47-1; $(CH_3)_3SiCl$, 75-77-4; $(CH_3)_3CCl$, 507-20-0.

Tricarbonylbis(trichlorosilyl)nickel. An Unusual Carbonyl Complex of Nickel(II)

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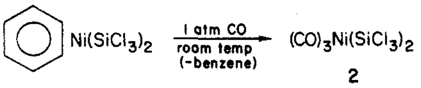
Displacement of η^6-arene by carbon monoxide in (η^6-benzene)bis(trichlorosilyl)nickel yields an unusual tricarbonyl derivative of nickel(II). The compound crystallizes with four molecules of $(SiCl_3)_2Ni(CO)_3$ per unit cell in space group $P2_1/c$ with lattice constants of a = 9.709 (8) Å, b = 22.65 (2) Å, c = 6.731 (5) Å, and β = 75.76 (5)°. The structure was determined from 1219 diffractometer data and refined to an R value of 5.9%. The molecular geometry is a slightly distorted trigonal bipyramid with three CO ligands in the equatorial plane and two trichlorosilyl ligands in the axial positions.

Introduction

Recently we reported that the facile displacement of η^6-arene by CO in $(\eta^6\text{-}C_6H_6)Ni(SiCl_3)_2$ (1) yielded an unusual carbonyl derivative of Ni(II).[2] The product 2 possesses very labile CO ligands and can be converted quantitatively back to 1 in excess benzene. This appears to be the first example of such reversible CO ⇄ arene complexation under such mild conditions.



1
red-orange solid

2
colorless solid
(volatile)

Complete characterization of 2 has been difficult due to its reactivity, and some confusion as to whether two or three carbonyl groups were attached in the solid state persisted until we were able to grow suitable crystals for X-ray structural elucidation. The unusual nature of 2 and the need to clarify its structure and bonding prompted us to determining the structure of this compound.

Experimental Section

Crystals were obtained by subliming the compound at room temperature in a vacuum sealed Pyrex tube. A colorless crystal of the compound with dimensions 1.00 × 0.40 × 0.33 mm was wedged in a thin-walled glass capillary under an argon atmosphere in a specially modified inert-atmosphere chamber. Preliminary Weisenberg and precession photographs led to the determination

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[1] (a) University of North Dakota. (b) Kansas State University.

[2] Groshens, T. J.; Klabunde, K. J. *J. Organomet. Chem.* **1983**, *259*, 337.

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Table I. Atomic Coordinates in $Ni(CO)_3(SiCl_3)_2$[a]

atom	10^4x	10^4y	10^4z
Ni	6701 (1)	1226.1 (6)	2547 (2)
Si$_1$	4278 (3)	1263 (2)	3301 (4)
Si$_2$	9133 (3)	1229 (2)	1775 (4)
Cl$_1$	3549 (3)	1338 (2)	712 (4)
Cl$_2$	3466 (3)	1962 (2)	5105 (6)
Cl$_3$	3343 (4)	527 (2)	4791 (6)
Cl$_4$	9999 (3)	1253 (2)	−1275 (5)
Cl$_5$	9897 (3)	1932 (2)	3012 (7)
Cl$_6$	9899 (3)	491 (2)	2850 (6)
C$_1$	6696 (13)	538 (6)	1132 (18)
C$_2$	6747 (12)	1916 (6)	1259 (19)
C$_3$	6684 (11)	1183 (5)	5197 (18)
O$_1$	6693 (10)	140 (5)	225 (16)
O$_2$	6775 (9)	2361 (4)	477 (16)
O$_3$	6656 (10)	1173 (5)	6871 (14)

[a] In this and subsequent tables standard deviations are given in parentheses for the least significant digits.

of space group $P2_1/c$ (No. 14).[3] Lattice constants determined on a Picker FACS-1 diffractometer with Mo Kα radiation at 25 °C were $a = 9.709$ (8) Å, $b = 22.65$ (2) Å, $c = 6.731$ (5) Å, and $\beta = 75.76$ (5)°. This unit cell with $Z = 4$ has a calculated density of 1.905 g/mL at 25 °C.

Intensity data were collected on the Picker diffractometer with Zr-filtered Mo Kα radiation. The takeoff angle was ~3°, and the incident bean collimator was 1.5 mm in diameter. Each peak was scanned 2.5° in 2θ at a rate of 1°/min with background counts of 20-s duration. A set of three standards were monitored every 100 data to check for crystal and instrument stability. The intensity of these standards decreased by 26% during the collection of data with $2\theta \leq 42.93°$. The crystal was recentered once during this time but the decay continued. More severe crystal decomposition occurred while attempting to collect higher angle data. The product of this decomposition was a thin film of liquid that eventually encompassed the crystal causing the crystal to float in the capillary and precluding further data collection. Thus only data in the range $2\theta \leq 42.93°$ were used in the structure determination. The intensity of the standards were fit to an equation of a straight line by the method of least squares, and the data were scaled accordingly.

The data were reduced as described previously,[4] and of the 1630 data collected some 1219 having $I > 3\sigma_I$ were judged observed and utilized in the structure determination. Patterson and Fourier[5] methods were used to locate all atoms that were then refined isotropically by full-matrix least squares[6] followed by fully anisotropic refinement. Anomalous dispersion corrections[7] were applied for the nickel, silicon, and chlorine atoms, and $1/\sigma^2$ weighting was used where σ was calculated from counting statistics. Absorption corrections were applied to the data in the final cycles of refinement. Transmission factors ranged from 0.665 to 0.559 Final refinement of the 136 parameters produced $R^6 = 5.9\%$ and $R_w = 7.4\%$. A final difference synthesis revealed the largest residual electron density of 0.75 e/Å^3 in the region of the Ni to C$_3$ bond. The coordinates from this final refinement are listed in Table I.

Results and Discussion

A drawing of one molecule of the compound as it exists in the crystal is shown in Figure 1 with thermal ellipsoids represented at 50% probability.[9] The structure consists of discrete molecules of $(SiCl_3)_2Ni(CO)_3$ having quasi D_{3h} symmetry. The three CO ligands form the equatorial plane while the two SiCl$_3$ ligands occupy the axial positions of the slightly distorted trigonal-bipyramid geometry. To our knowledge, this is the first example of a tricarbonyl complex of nickel(II).

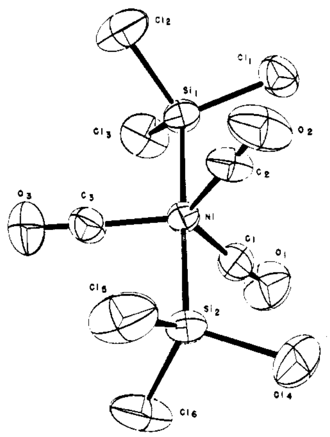

Figure 1. An ORTEP drawing of one molecule of $(SiCl_3)_2Ni(CO)_3$ as it exists in the crystal. Thermal ellipsoids are represented at 50% probability.

Table II. Bond Distances (Å) in $Ni(CO)_3(SiCl_3)_2$

Ni-Si$_1$	2.283 (3)	Si$_1$-Cl$_3$	2.040 (5)
Ni-Si$_2$	2.289 (3)	Si$_2$-Cl$_4$	2.019 (5)
Ni-C$_1$	1.83 (1)	Si$_2$-Cl$_5$	2.021 (5)
Ni-C$_2$	1.78 (1)	Si$_2$-Cl$_6$	2.035 (5)
Ni-C$_3$	1.78 (1)	C$_1$-O$_1$	1.09 (1)
Si$_1$-Cl$_1$	2.043 (4)	C$_2$-O$_2$	1.13 (1)
Si$_1$-Cl$_2$	2.032 (5)	C$_3$-O$_3$	1.12 (1)

Table III. Selected Bond Angles (deg) in $Ni(CO)_3(SiCl_3)_2$

Si$_1$-Ni-Si$_2$	177.7 (3)	Ni-C$_1$-O$_1$	177 (1)
Ni-Si$_1$-Cl$_1$	111.6 (2)	Ni-C$_2$-O$_2$	178 (1)
Ni-Si$_1$-Cl$_2$	112.9 (2)	Ni-C$_3$-O$_3$	178 (1)
Ni-Si$_1$-Cl$_3$	112.9 (2)	C$_1$-Ni-C$_2$	119.8 (5)
Ni-Si$_2$-Cl$_4$	112.3 (2)	C$_1$-Ni-C$_3$	118.3 (5)
Ni-Si$_2$-Cl$_5$	111.8 (2)	C$_2$-Ni-C$_3$	121.9 (5)
Ni-Si$_2$-Cl$_6$	111.3 (2)	Si$_1$-Ni-C$_1$	90.7 (4)
Cl$_1$-Si$_1$-Cl$_2$	106.3 (2)	Si$_1$-Ni-C$_2$	88.6 (4)
Cl$_1$-Si$_1$-Cl$_3$	106.3 (2)	Si$_1$-Ni-C$_3$	91.4 (3)
Cl$_2$-Si$_1$-Cl$_3$	106.4 (2)	Si$_2$-Ni-C$_1$	91.1 (4)
Cl$_4$-Si$_2$-Cl$_5$	107.1 (2)	Si$_2$-Ni-C$_2$	89.2 (4)
Cl$_4$-Si$_2$-Cl$_6$	106.6 (2)	Si$_2$-Ni-C$_3$	89.0 (3)
Cl$_5$-Si$_2$-Cl$_6$	107.3 (2)		

The observed bond distances are listed in Table II and the angles in Table III. These parameters reflect the closeness of the observed geometry to full D_{3h} symmetry although there is no crystallographic symmetry. Those atoms forming the equatorial plane (Ni, C$_1$, C$_2$, C$_3$, O$_1$, O$_2$, O$_3$) are planar within experimental error. In the axial direction there is a slight tilt of the two silicon atoms, away from C$_1$, resulting in an Si$_1$NiSi$_2$ angle of 177.7 (3)°.

The average Ni–C bond length of 1.80 (1) Å is similar to those reported in other nickel complexes containing nonbridging carbonyl ligands.[10-12] Similarly the average C–O bond length of 1.11 (1) Å and NiCO angle of 178 (2)° is not unusual.

Bond parameters within the trichlorosilyl ligand are similar to those reported in $Cl_3SiCo(CO)_4$.[13] The observed

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Ni–$SiCl_3$ length of 2.286 (4) Å is within the range of reported values for Ni–Si[14] bonds. However, few structural data are available for Ni–$SiCl_3$ bonds. Interestingly, recent results in our laboratory[15] on the structure of $[\eta^6\text{-}C_6H_3(CH_3)_3]Ni(SiCl_3)_2$ reveal a considerably shorter Ni–Si distance of 2.194 (2) Å. Trigonal-bipyramidal complexes have been the subject of many studies. Several authors, including Osborn,[16] Churchill,[17] Dartiguenave,[11] and coworkers, have noted that strong π-acceptor ligands tend to occupy equatorial sites. Additionally, Rossi and Hoffmann[19] have considered a unified molecular orbital treatment of five-coordinate complexes in general. They concluded for the d^8 case that good σ-donor ligands will prefer axial sites while good π-acceptors will prefer the equatorial sites. The observed equatorial position of the three CO ligands in the present structure can be attributed to the better π-accepting ability of CO. This is supported by the fact that the Ni–CO bonds are typically short while the Ni–$SiCl_3$ bonds are ~0.09 Å longer than those in $[\eta^6\text{-}C_6H_3(CH_3)_3]Ni(SiCl_3)_2$[15] (where considerable π-backbonding to $SiCl_3$ is expected).

Acknowledgement is made to the University of North Dakota for a contribution of computer time, and the National Science Foundation for program support (K.J.K.).

Registry No. 2, 93921-98-3.

Supplementary Material Available: Listings of anisotropic thermal parameters and structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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(14) See, for example: Von Werner, B.; Schuster, H. *Z. Anorg. Allg. Chem.* **1981**, *482*, 40–48. Herberich, G. E.; Thännessen, M.; Schmitz, D. *J. Organomet. Chem.* **1980**, *191*, 27–37.

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Communications

A General Route to Novel Dinuclear Iron Carbonyl Complexes Containing Alkanethiolate and Bridging Organic Ligands†

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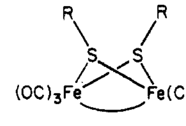
Summary: The reaction of $Fe_3(CO)_{12}$ with mercaptans (RSH, R = Et, Me_3C) in the presence of stoichiometric Et_3N in THF gives the reactive salt $[Et_3NH^+][(\mu\text{-}RS)(\mu\text{-}CO)Fe_2(CO)_6^-]$. Reactions of the latter with benzoyl and acetyl chloride, diphenylchlorophosphine, allyl chloride, and propargylic halides have been studied. New bridging ligands (μ-RC=O, μ-Ph_2P, μ-C_3H_6, μ-η^1,η^2-allenyl) were introduced between the iron atoms in all of these reactions. X-ray crystal structures of $(\mu\text{-}EtS)(\mu\text{-}C_3H_6)Fe_2(CO)_6$ and $(\mu\text{-}Me_3CS)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C{=}CH_2)Fe(CO)_6$ were determined.

Reactions of organic thiols with iron carbonyls have received much attention, and the first report on this subject was published by Hieber and Spacu in 1939.[1] In general, complexes of type 1 are formed in such reactions.[2]



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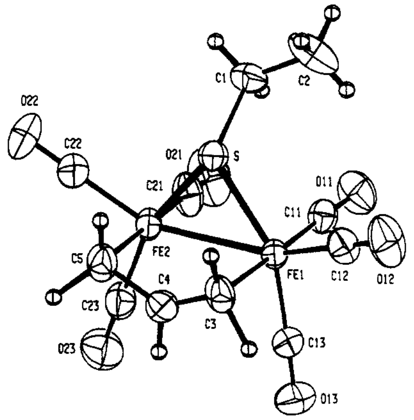

Figure 1. ORTEP diagram of **5** showing the 40% probability thermal ellipsoids and the atom labeling scheme. Hydrogen atoms are drawn as arbitrary spheres with B = 1.0 $Å^2$. Bond lengths (in Å) are as follows Fe(1)–Fe(2) = 2.675 (1), Fe(1)–S = 2.235 (2), Fe(1)–C(3) = 2.119 (5), Fe(1)···C(4) = 2.546 (4), Fe(2)–S = 2.251 (2), Fe(2)–C(5) = 2.139 (5), Fe(2)···C(4) = 2.445 (4), S–C(1) = 1.823 (5), C(1)–C(2) = 1.513 (9), C(3)–C(4) = 1.426 (8), C(4)–C(5) = 1.414 (8), Fe–CO(mean) = 1.784, C–O(mean) = 1.137.

In reactions of bulky thiols with $Fe_3(CO)_{12}$ trinuclear iron products $(\mu_3\text{-}RS)(\mu\text{-}H)Fe_3(CO)_9(2Fe\text{–}Fe)$, **2**, are formed instead.[2b,3] In related work, Takács and Markó carried out reactions of $Fe_3(CO)_{12}$ with sodium alkanethiolates, RSNa, in refluxing THF and obtained solutions containing $[Fe_3(CO)_9SR]^-$ anions which on acidification gave complexes of type **2**.[4] We report here a new mode of reaction

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† Dedicated to Professor G. Wilke on the occasion of his 60th birthday.

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