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Synthesis, Characterization, and Reactivity of a Chromium Tricarbonyl Complex of Phenylsilatrane: Molecular Structure of $[C_6H_5Si(OCH_2CH_2)_3N]Cr(CO)_3$

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Summary: The new compound $[C_6H_5Si(OCH_2CH_2)_3N]$-$Cr(CO)_3$ has been prepared and characterized by elemental analysis, IR, ^1H NMR, and ^{13}C NMR spectroscopy, and X-ray diffraction. $[C_6H_5Si(OCH_2CH_2)_3N]Cr(CO)_3$ crystallizes in the orthorhombic space group *Pbca*, with $a = 12.078$ (2) Å, $b = 12.347$ (1) Å, $c = 21.917$ (3) Å, and $Z = 8$. The molecule possesses the usual silatrane skeleton containing a five-coordinated silicon atom. The N–Si distance (2.108 (5) Å) is somewhat shorter than that in phenylsilatrane. This is the first case where the crystal structure of the silatrane derivative, which acts as a π-coordinating ligand to transition metals, has been determined. This compound is a versatile starting material for a wide range of complexes, in particular for those of the general formula $[C_6H_5Si(OCH_2CH_2)_3N]Cr(CO)_2L$ (L = PPh_3, $P(CH_2CH_2CN)_3$, and $AsPh_3$) and $\{[C_6H_5Si(OCH_2CH_2)_3]Cr(CO)_2\}_2(\mu$-L-L) (L-L = dppe).

The silatranes (silatrane = 2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane) have been studied in detail by various physical methods.[1] However, there have been no reports on the use of arylsilatranes as π-coordinating ligands to transition metals. We report in this note the synthesis of $[C_6H_5Si(OCH_2CH_2)_3N]Cr(CO)_3$ (1) and its characterization by IR, ^1H NMR, ^{13}C NMR, and mass spectrometry and X-ray diffraction. We also report substitution reactions of 1 with several ligands.

Experimental Section

All chemicals were of reagent grade from commercial sources and were used without purification. All solvents were dried prior to use. Chemical analysis was performed at the Chemical Analytic Center, College of Engineering, Seoul National University. ^1H NMR and ^{13}C NMR spectra were measured on either a Bruker AC80 or Varian XL-200 spectrometer. All infrared spectra were recorded on a Perkin-Elmer 782 spectrometer using KBr pellets. Mass spectra were recorded on a VG ZAB-E double-focusing mass spectrometer.

Preparation of 1. Phenylsilatrane (3.02 g, 12 mmol) was added to $Cr(CO)_6$ (2.64 g, 12 mmol) in Decalin (100 mL). The mixture was heated at reflux temperature for 6 h. During the course of the reaction, the solution became dark greenish yellow. After it had been cooled to room temperature, the reaction mixture was filtered. The dark greenish yellow precipitate was washed several times with acetone until no yellow color was retained in the precipitate. After removal of the solvent, a yellow crystalline solid was obtained (2.84 g, 61%). Single crystals of 1 suitable for X-ray crystallographic analysis were grown by evaporation of a saturated acetone solution of the complex at 5 °C. IR: ν(CO) 1960, 1880 cm^{-1}. ^1H NMR (acetone-d_6): δ 3.12 (NCH_2, t, $J = 5.8$ Hz), 3.93 (OCH_2, t, $J = 5.8$ Hz), 7.26 (Ph, m), 7.78 (Ph, m) ppm. ^{13}C NMR (acetone-d_6 and $CDCl_3$): δ 51.25 (NCH_2), 57.51 (OCH_2), 92.60, 93.86, 100.61, 134.07 (Ph), 234.54 (CO) ppm. EI-MS: m/z 387 (M^+), 303 ($M^+ - 3CO$), 251 ($M^+ - Cr(CO)_3$), 174 ($M^+ - C_6H_5Cr(CO)_3$). Anal. Calcd for $C_{15}H_{17}CrNO_6Si$: C, 46.51; H, 4.42; N, 3.61. Found: C, 46.35; H, 4.17; N, 3.59.

Preparation of $[C_6H_5Si(OCH_2CH_2)_3N]Cr(CO)_2PPh_3$. A solution of 1 (0.387 g, 1 mmol) and PPh_3 (1.048 g, 4 mmol) in THF was irradiated with a UV lamp at 40–45 °C for 1 h. The solvent was removed under vacuum, and the residue was washed with hexane to remove any unreacted PPh_3. Workup involved dissolution of the residue in benzene, centrifugation, and decantation of the supernatant liquid. Filtration yielded the title compound (0.400 g): IR: ν(CO) 1880, 1820 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.04 (t), 3.80 (t), 7.29–7.58 (Ph, m) ppm. Anal. Calcd for $C_{32}H_{32}CrNO_5PSi$: C, 61.33; H, 5.14; N, 2.23. Found: C, 61.61; H, 5.01; N, 2.32.

Preparation of $[C_6H_5Si(OCH_2CH_2)_3N]Cr(CO)_2P(CH_2CH_2CN)_3$. A solution of 1 (0.194 g, 0.5 mmol) and $P(CH_2CH_2CN)_3$ (0.406 g, 2.0 mmol) in THF (25 mL) was irradiated with a UV lamp at 40–45 °C for 30 min. The solvent was removed under vacuum, and the residue was column chromatographed on silica gel (10:1 CH_2Cl_2–THF as eluant) to give the title compound as a yellow-orange solid in 60% yield (0.167 g). TLC: R_f 0.31 (10:1 CH_2Cl_2–THF). IR: ν(CO) 1870, 1810 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.10 (m), 2.62 (m), 3.02 (t), 3.85 (t), 7.25–7.50 (m) ppm. Anal. Calcd for $C_{23}H_{29}CrN_4O_5PSi$: C, 49.99; H, 5.29; N, 10.14. Found: C, 49.15; H, 5.43; N, 9.85.

Preparation of $[C_6H_5Si(OCH_2CH_2)_3N]Cr(CO)_2AsPh_3$. A solution of 1 (0.194 g, 0.5 mmol) and $AsPh_3$ (0.612 g, 2.0 mmol) in THF (30 mL) was irradiated with a UV lamp at 40–45 °C for 40 min. The reaction mixture turned red. The solvent was removed under vacuum, and the residue was washed with hexane to remove any unreacted $AsPh_3$. Workup involved dissolution of the residue in benzene, centrifugation, and decantation of the supernatant liquid. Filtration yields the title compound (0.191 g). IR: ν(CO) 1875, 1815 cm^{-1}. ^1H NMR (CDMO-d_6): δ 2.90 (m), 3.70 (m), 7.37 (m) ppm. Anal. Calcd for $C_{32}H_{32}AsCrNO_5Si$: C, 57.74; H, 4.85; N, 2.10. Found: C, 57.75; H, 4.51; N, 2.35.

Preparation of $\{[C_6H_5Si(OCH_2CH_2)_3N]Cr(CO)_2\}_2(\mu$-$Ph_2PCH_2CH_2PPh_2)$. A solution of 1 (0.194 g, 0.5 mmol) and dppe (0.797 g, 2 mmol) was irradiated with a UV lamp at 40–45 °C for 40 min. The reaction mixture turned red. The solvent was removed under vacuum, and the residue was column chromatographed on silica gel (1:1 THF–Et_2O as eluant) to give the title compound as a yellow-orange solid in 65% yield. TLC: R_f 0.21 (1:1 THF–Et_2O). IR: ν(CO) 1865, 1810 cm^{-1}. ^1H NMR (benzene-d_6): δ 1.96 (t), 2.63 ($-CH_2-$, s), 3.45 (t), 6.8–7.7 (Ph, m) ppm. ^{31}P NMR (benzene-d_6): δ 89.08 (d, $J = 39.7$ Hz) ppm. Anal. Calcd for $C_{54}H_{58}Cr_2N_2O_{10}P_2Si_2$: C, 58.06; H, 5.23; N, 2.51. Found: C, 58.11; H, 5.57; N, 2.96.

Crystallographic Analysis of Complex 1. All the crystallographic data were obtained on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.70930$ Å, $\lambda(K\alpha_2) = 0.71359$ Å) at ambient temperature (23 ± 2 °C). The crystal of 1 was glued to the interior of a thin-walled glass capillary. A preliminary diffractometric investigation indicated that 1 belongs to the space group *Pbca*.[2] The

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Table I. Crystal Data and Experimental Details for $[N(CH_2CH_2O)_3SiC_6H_5]Cr(CO)_3$

formula	$SiCrO_6NC_{15}H_{17}$
fw	387.38
cryst syst	orthorhombic
space group	*Pbca*
a, *b*, *c*, Å	12.078 (2), 12.347 (1), 21.917 (3)
V, Å	3268.3 (7)
Z	8
d_{calcd}, g cm^{-3}	1.574
cryst size, mm	0.2 × 0.3 × 0.4
μ, cm^{-1}	7.41
radiation	Mo Kα (λ = 0.71073 Å)
scan method	ω–2θ
2θ range, deg	$2 < 2\theta < 50$
no. of rflns measd	3384
no. of rflns obsd, $I > 3\sigma(I)$	1438
no. of params refined	219
overdetermn ratio	11.15
$R = (\sum\lvert F_o - F_c\rvert)/\sum F_o$	0.042
$R_G = (\sum\lvert F_o - F_c\rvert^2/\sum F_o^2)^{1/2}$	0.047

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for $[N(CH_2CH_2O)_3SiC_6H_5]Cr(CO)_3$[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq},[b] Å^2
Cr	0.2263 (1)	0.1468 (1)	0.3119 (0)	0.0319 (0)
Si	0.2422 (2)	0.2121 (1)	0.4848 (1)	0.0298 (1)
C(11)	0.2978 (5)	0.1866 (5)	0.4047 (3)	0.0315 (4)
C(12)	0.3239 (5)	0.2694 (6)	0.3638 (3)	0.0363 (4)
C(13)	0.3764 (6)	0.2497 (7)	0.3074 (3)	0.0460 (5)
C(14)	0.4073 (6)	0.1454 (8)	0.2923 (3)	0.0524 (6)
C(15)	0.3828 (6)	0.0593 (7)	0.3316 (3)	0.0481 (5)
C(16)	0.3290 (6)	0.0792 (6)	0.3865 (3)	0.0398 (4)
C(1)	0.0977 (7)	0.0920 (7)	0.3441 (3)	0.0466 (5)
O(1)	0.0147 (5)	0.0586 (6)	0.3605 (3)	0.0781 (6)
C(2)	0.1983 (6)	0.0617 (6)	0.2457 (3)	0.0455 (4)
O(2)	0.1790 (5)	0.0079 (5)	0.2040 (2)	0.0742 (4)
C(3)	0.1460 (6)	0.2562 (7)	0.2764 (4)	0.0480 (5)
O(3)	0.0962 (6)	0.3250 (5)	0.2536 (3)	0.0837 (5)
O(4)	0.1872 (4)	0.3320 (4)	0.4714 (2)	0.0432 (3)
O(5)	0.3685 (4)	0.2031 (4)	0.5147 (2)	0.0448 (3)
O(6)	0.1594 (4)	0.1055 (4)	0.4881 (2)	0.0415 (3)
N	0.1909 (5)	0.2386 (5)	0.5755 (2)	0.0335 (3)
C(4)	0.1435 (7)	0.3984 (6)	0.5190 (3)	0.0520 (5)
C(5)	0.1090 (6)	0.3266 (6)	0.5712 (3)	0.0482 (5)
C(6)	0.3864 (6)	0.2028 (7)	0.5784 (3)	0.0536 (6)
C(7)	0.2940 (6)	0.2660 (7)	0.6085 (3)	0.0519 (5)
C(8)	0.0869 (7)	0.0876 (6)	0.5380 (3)	0.0471 (5)
C(9)	0.1394 (7)	0.1356 (7)	0.5948 (3)	0.0483 (5)

[a] Estimated standard deviations are given in parentheses. [b] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

lattice constants were determined by the least-squares refinement of the diffraction geometry for 25 intense reflections having $12 < \theta_{Mo\,K\alpha} < 16°$. Crystal parameters for the complex and information on the procedure used for data collection and structure refinement are given in Table I. The structure was solved with use of the conventional heavy-atom method and difference Fourier techniques and was refined by means of a full-matrix least-squares procedure with SHELX-76, a system of computer programs for X-ray structure determination by G. M. Sheldrick.[3] The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the difference Fourier map and idealized with a 1.08-Å distance for the C–H bond. The final atomic parameters are given in Tables II and III.

Table III. Positional Parameters and Isotropic Thermal Parameters of Hydrogen Atoms for $[N(CH_2CH_2O)_3SiC_6H_5]Cr(CO)_3$[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*, Å^2
H(12)	0.3030 (5)	0.3517 (6)	0.3758 (3)	0.0573 (100)
H(13)	0.3924 (6)	0.3157 (8)	0.2763 (3)	0.0573 (100)
H(14)	0.4505 (6)	0.1302 (6)	0.2500 (3)	0.0573 (100)
H(15)	0.4055 (7)	−0.0224 (6)	0.3193 (3)	0.0573 (100)
H(16)	0.3102 (6)	0.0120 (6)	0.4164 (3)	0.0573 (100)
H(41)	0.2092 (6)	0.4530 (7)	0.5345 (3)	0.0678 (73)
H(42)	0.0755 (6)	0.4445 (7)	0.5025 (3)	0.0678 (73)
H(51)	0.0278 (7)	0.2937 (6)	0.5621 (3)	0.0678 (73)
H(52)	0.1071 (7)	0.3724 (7)	0.6132 (3)	0.0678 (73)
H(61)	0.3867 (6)	0.1206 (7)	0.5951 (3)	0.0678 (73)
H(62)	0.4650 (6)	0.2406 (7)	0.5885 (3)	0.0678 (73)
H(71)	0.3101 (6)	0.3519 (7)	0.6054 (3)	0.0678 (73)
H(72)	0.2869 (6)	0.2430 (7)	0.6559 (3)	0.0678 (73)
H(81)	0.0082 (7)	0.1263 (6)	0.5293 (3)	0.0678 (73)
H(82)	0.0744 (7)	0.0017 (6)	0.5443 (3)	0.0678 (73)
H(91)	0.2013 (7)	0.0812 (7)	0.6128 (3)	0.0678 (73)
H(92)	0.0770 (7)	0.1504 (7)	0.6291 (3)	0.0678 (73)

[a] Estimated standard deviations are given in parentheses.

Table IV. Bond Distances and Bond Angles for $[N(CH_2CH_2O)_3SiC_6H_5]Cr(CO)_3$[a]

Bond Distances (Å)			
Cr–C(1)	1.836 (8)	C(13)–C(14)	1.382 (11)
Cr–C(2)	1.824 (8)	C(14)–C(15)	1.400 (11)
Cr–C(3)	1.836 (9)	C(11)–C(16)	1.435 (9)
Cr–C(11)	2.264 (7)	C(15)–C(16)	1.390 (10)
Cr–C(12)	2.230 (7)	O(1)–C(1)	1.142 (9)
Cr–C(13)	2.216 (8)	O(2)–C(2)	1.154 (8)
Cr–C(14)	2.228 (7)	O(3)–C(3)	1.154 (9)
Cr–C(15)	2.220 (8)	O(4)–C(4)	1.420 (8)
Cr–C(16)	2.216 (7)	O(5)–C(6)	1.413 (8)
Si–C(11)	1.907 (6)	O(6)–C(8)	1.418 (8)
Si–O(4)	1.649 (5)	N–C(5)	1.473 (9)
Si–O(5)	1.664 (5)	N–C(7)	1.479 (8)
Si–O(6)	1.655 (5)	N–C(9)	1.478 (9)
Si–N	2.108 (5)	C(4)–C(5)	1.511 (10)
C(11)–C(12)	1.396 (9)	C(6)–C(7)	1.513 (10)
C(12)–C(13)	1.410 (9)	C(8)–C(9)	1.517 (9)

Bond Angles (deg)			
C(1)–Cr–C(2)	86.3 (3)	C(11)–C(16)–C(15)	121.7 (7)
C(1)–Cr–C(3)	89.2 (4)	Cr–C(1)–O(1)	175.6 (7)
C(2)–Cr–C(3)	89.3 (3)	Cr–C(2)–O(2)	179.0 (7)
O(4)–Si–C(11)	97.2 (3)	Cr–C(3)–O(3)	179.4 (8)
O(5)–Si–C(11)	91.6 (3)	Si–O(4)–C(4)	122.0 (4)
O(6)–Si–C(11)	97.0 (3)	Si–O(5)–C(6)	121.9 (4)
O(4)–Si–O(5)	120.0 (3)	Si–O(6)–C(8)	122.1 (4)
O(4)–Si–O(6)	118.6 (3)	Si–N–C(5)	104.5 (4)
O(5)–Si–O(6)	118.9 (3)	Si–N–C(7)	104.4 (4)
N–Si–C(11)	176.4 (3)	Si–N–C(9)	105.0 (4)
N–Si–O(4)	84.9 (2)	C(5)–N–C(7)	115.4 (6)
N–Si–O(5)	84.8 (2)	C(5)–N–C(9)	111.8 (6)
N–Si–O(6)	84.5 (2)	C(7)–N–C(9)	114.3 (6)
Si–C(11)–C(12)	123.4 (5)	C(4)–C(5)–N	106.7 (6)
Si–C(11)–C(16)	120.0 (5)	C(6)–C(7)–N	106.8 (6)
C(12)–C(11)–C(16)	116.1 (6)	C(8)–C(9)–N	106.2 (5)
C(11)–C(12)–C(13)	122.5 (7)	C(5)–C(4)–O(4)	108.8 (6)
C(12)–C(13)–C(14)	119.5 (7)	C(7)–C(6)–O(5)	108.8 (6)
C(13)–C(14)–C(15)	120.1 (7)	C(9)–C(8)–O(6)	108.3 (6)
C(14)–C(15)–C(16)	119.9 (8)		

[a] Estimated standard deviations are given in parentheses.

Results and Discussion

Crystal Structure of Complex 1. The molecular geometry and labeling scheme for complex 1 is shown in Figure 1. The bond distances and angles are tabulated in Table IV. Complex 1 possesses the usual skeleton containing a five-coordinate silicon atom. The N–Si–C(11) angle is 176.40°, and the arrangement of the O(4), O(5), and O(6) atoms is planar, while the Si atom is displaced from the center of the O_3 plane toward the C(11) atom. The stereochemistry of the Si atom is distorted trigonal bipyramidal. Introduction of $Cr(CO)_3$ into the phenylsilatrane does not affect the silatrane cycle geometry very much. However, the N–Si bond is shortened in this case by 0.08 Å, to 2.108 (5) Å, and the Si–C(phenyl) bond (1.907

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(2) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(3) Sheldrick, G. M. SHELX 76: Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

Table V. Geometrical Data Characterizing the Stereochemistry of Silicon in Silatranes $\mathrm{RSi(OCH_2CH_2)_3N}$

R	R-Si-O, deg	C(16)-C(11)-C(12), deg	*d*(Si-N), Å	*d*(Si-O), Å	ref
α-C_6H_5	97	115.9	2.193 (5)	1.66	4
β-C_6H_5	97	116.13	2.156 (4)	1.65	5
γ-C_6H_5	96	116.6 (5)	2.132 (4)	1.65	6
$C_6H_5Cr(CO)_3$	97.2 (3) [C(11)-Si-O(4)] 91.6 (3) [C(11)-Si-O(5)] 97.0 (3) [C(11)-Si-O(6)]	116.1 (6)	2.108 (5)	1.65	this work
$ClCH_2$	96		2.120	1.64	7
CH_3	93		2.175 (4)	1.67	8
m-$NO_2C_6H_4$	96		2.116 (8)	1.66	9

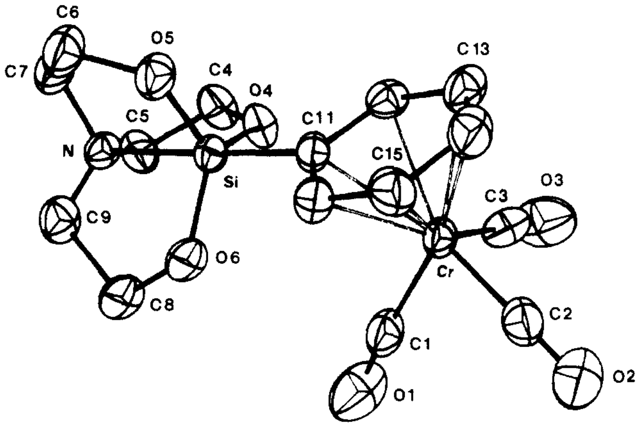

Figure 1. Diagram of the $[N(CH_2CH_2O)_3SiC_6H_5]Cr(CO)_3$ molecule with the atom numbering.

(6) Å) in lengthened by 0.03 Å.[4] The effect of the introduction of $Cr(CO)_3$ into the phenylsilatrane is very similar to the introduction of a *m*-nitro group into the phenylsilatrane or the introduction of a chlorine atom into the methyl group of 1-methylsilatrane (Table V). The equatorial O-Si bond lengths in 1 (1.649 (5)-1.664 (5) Å, average 1.656 Å) are very close to the values in α, β, and γ crystalline modifications of silatrane. The C(11)-Si-O(4) and C(11)-Si-O(6) bond angles (97.2 (3) and 97.0 (3)°, respectively) are very close to the values in α, β, and γ crystalline modifications of phenylsilatrane (97, 97, and 96°, respectively), but the C(11)-Si-O(5) bond angles are decreased to 91.6 (3)°. The C(16)-C(11)-C(12) bond angle at the ipso carbon of the phenyl ring in 1 is 116.1 (6)°, which is very close to the value for the β-phenylsilatrane (116.13 (65)°).[5] The dihedral angles between the phenyl ring and the planes of four coplanar atoms in chelate rings are 44.8, 100.4, and 19.9° for the fragments Si-O(6)-C(8)-C(9)-N, Si-O(5)-C(6)-C(7)-N, and Si-O(4)-C(4)-C(5)-N, respectively. The ring C-C bond distances vary between 1.382 (11) and 1.435 (9) Å, and the alternating longer C-C bonds (by 0.26 Å) are those that project on the Cr-CO bond. By examination of the density difference plots, Hall[10] suggested that the C-C bonds in a polyene eclipsed below by a carbonyl or similar ligand would be long while those trans to these ligands would be short. However, the alternation of the bond lengths in 1 is less prominent than that in α-phenylsilatrane.[4] When we consider complex 1 as a derivative of chromium tricarbonyl, 1 possesses a piano-stool structure in which the $Cr(CO)_3$ group lies directly below the arene ring, with the chromium approximately equidistant from each ring carbon except the C(11) atom. The arene ring may be regarded as essentially planar, although a slight folding is observed. The distance from the chromium to the center of the ring is 1.7329 (11) Å, which is close to the value for $(C_6H_6)Cr(CO)_3$ (1.726 Å).[13] The Cr-CO distances vary from 1.824 (8) to 1.836 (9) Å. Published Cr-CO distances range from 1.76 to 1.85 Å.[12] The Cr-CO distances in 1 fall in this range.

Therefore, we observed that the coordination of $Cr(CO)_3$ to the phenyl group of the phenylsilatrane causes no significant changes in the structure of the silatrane framework and, in particular, in the trigonal-bipyramidal geometry of the silicon atom.

Substitution Reactions of 1. For (arene)$Cr(CO)_3$ the substitution reaction by 2e donors proceeds very easily to give (arene)$Cr(CO)_2L$. The photochemical reaction proceeds more easily than the thermal reaction. Recently, Me_3NO has been used frequently to remove the carbonyls.[13] We tried to remove one or two carbonyls from 1 by reacting it with Me_3NO or by UV irradiation. We used several kinds of monodentate ligands, e.g., PPh_3, $P(CH_2CH_2CN)_3$, $AsPPh_3$, CS_2, PhC_2Ph, pyridine, vinylsilatrane, and a bidentate ligand, $Ph_2PCH_2CH_2PPh_2$ (dppe). When we used Me_3NO to remove one of the carbonyls from 1, the reaction did not go to completion and the IR spectra were not clear. Hence, we tried the photochemical reactions. When we monitored the reaction by IR spectroscopy (ν(CO)), the reaction proceeded to about 60-70% conversion. Thus, we had to separate the product from the reaction mixture. The separation of the reactants and product was straightforward because of their different R_f values in a mixed solvent. Usually the product and the reactants were stable in the solid state. However, when the reaction mixture was loaded on the column, it slowly decomposed to green solids. Generally the monodentate ligands reacted with 1, yielding (arene)$Cr(CO)_2L$ (L = PPh_3, $AsPh_3$, and $P(CH_2CH_2CN)_3$). The analogues complexes of CS_2, PhC_2Ph, pyridine, and vinylsilatrane could not be prepared in this way. The bidentate ligand, dppe, reacted with 1, yielding two kinds of products. When the IR ν(CO) band of the product was compared to the IR ν(CO) band of (arene)$Cr(CO)_2L$, the minor product was a (arene)$Cr(CO)_2$(L-L) type compound and the major product was the dimeric $\{[C_6H_5Si(OCH_2CH_2)_3N]Cr(CO)_2\}_2(\mu\text{-dppe})$. By column chromatography the dimeric compound was obtained in high purity. The dimeric structure was established by ^{31}P NMR and ^1H NMR studies and by comparison with the known compound $[(C_6H_6)Cr(CO)_2]_2(\mu\text{-dppe})$.[14] Phosphorus NMR spectral

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data for the dimeric structure show a doublet (proton decoupled, J_{PP} = 39.7 Hz)[15] at δ 89.08 ppm relative to external H_3PO_4. While the ^{31}P NMR spectrum of the dimeric compound was taken, it slowly decomposed and some precipitate was seen in the NMR tube. A new peak appeared at δ −12.40 ppm and grew with time. The new peak might be due to the liberation of free dppe. The ^1H NMR spectrum shows one singlet for the $-CH_2-$ units, centered at δ 2.63 ppm.

Complex 1 undergoes substitution reactions, as expected. The substituted products are stable in the solid state but unstable in solution. Complex 1 would be a versatile starting material for a wide range of complexes.

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Supplementary Material Available: Tables of anisotropic thermal parameters and of cell dimensions and symmetry operations (2 pages); a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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First Example of an Organogallium Compound Containing a Gallium–Tellurium Bond: Synthesis, Properties, and Molecular Structure of $[(Me_3CCH_2)_2GaTePh]_2$

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Summary: The first example of an organogallium compound with a Ga–Te bond, $[(Me_3CCH_2)_2GaTePh]_2$, which is stable at room temperature, has been synthesized and characterized by elemental analyses, IR, ^1H NMR, and ^{125}Te NMR spectroscopies, and an X-ray structural study. The dimeric molecule crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions of a = 18.864 (7) Å, b = 10.041 (5) Å, c = 19.869 (9) Å, β = 101.80 (3)°, V = 3684 (5) $Å^3$, Z = 4, D_{calcd} = 1.505 g cm^{-3}, R = 0.030, and R_w = 0.035. The four-membered Ga_2Te_2 ring has a butterfly arrangement with the phenyl groups in the anti position relative to the ring. The Ga–Te bond distances are in the range 2.7435 (8)–2.7623 (8) Å.

Organometallic compounds of gallium with bonds to group 15 elements such as $R_3Ga{\cdot}ER'_3$[2] (E = N, P, As) and $(R_2GaER'_2)_2$[3] (E = P, As) have been receiving increasing attention due to their potential usefulness as precursors for the preparation of films of group 13–15 materials.[4] In contrast, similar types of compounds with bonds to the heavier group 16 elements have been the subject of only limited research. The early work of Coates[5] revealed that $GaMe_3$ reacted with EMe_2 (E = Se, Te) to form 1:1 adducts that were extensively dissociated in the vapor phase. Thus, the simple adduct $Me_3Ga{\cdot}TeMe_2$ is the only example of a reported compound containing a Ga–Te bond prior to the present work. When selenols[6] were used, elimination reactions occurred at room temperature and dimeric derivatives of the type $(Me_2GaER)_2$ (E = Se; R = Me, Ph) were formed. These dimers were stable to dissociation in the gas phase at moderate temperatures, but the gallium–chalcogen bond was cleaved by NMe_3 to give monomeric species of the type $Me_2GaER{\cdot}NMe_3$.[6] The only other examples of derivatives containing Ga–Se bonds are $[Et_2GaSe(SiEt_3)]_2$[8][7] $[i\text{-}Pr(Br)GaSeEt]_3$,[8] and $(EtGaSe)_n$.[7]

Table I. Interatomic Distances (Å) for $[(Me_3CCH_2)_2GaTePh]_2$

(A) Gallium–Tellurium Distances			
Ga(1)–Te(1)	2.7623 (8)	Ga(2)–Te(2)	2.7525 (8)
Ga(1)–Te(2)	2.7435 (8)	Ga(2)–Te(1)	2.7623 (8)
(B) Gallium–Carbon Distances			
Ga(1)–C(7)	1.975 (7)	Ga(2)–C(23)	1.988 (7)
Ga(1)–C(12)	1.962 (8)	Ga(2)–C(28)	1.979 (8)
(C) Tellurium–Carbon Distances			
Te(1)–C(1)	2.125 (6)	Te(2)–C(17)	2.125 (6)

The first example of an organometallic gallium–tellurium compound, $(Me_3CCH_2)_2GaTePh$, which is not a simple adduct, has been prepared by the reaction of $Ga(CH_2CMe_3)_2Cl$ with LiTePh in Et_2O:

$$Ga(CH_2CMe_3)_2Cl + LiTePh \xrightarrow{Et_2O} (Me_3CCH_2)_2GaTePh + LiCl$$

The new compound has been fully characterized by partial elemental analyses (C and H), physical properties, infrared spectroscopy, ^1H and ^{125}Te NMR spectroscopies, and an X-ray structural study. The tellurium reagent[9] LiTePh

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