Organometallics **1990**, *9*, 1395-1399 1395

edge-face-edge-face orientations with the bulkier anisoyl rings preferring the "facial" orientation. Bosnich et al.,[12] on the basis of their investigations of the effect of varying ring size on ring conformational preferences, have stressed the chirality inherent in the quasi-equatorial and -axial dispositions of the arene rings. Recently, Brown and Evans[13] have extended the analysis of arene torsion angles originally reported by Oliver and Riley[14] to a broad range of crystallographically characterized complexes containing chiral diphosphines.

The structure of [Rh(DIPAMP)(MPAA)](BF_4) demonstrates arene ring conformations similar to those of [Rh(DIPAMP)(1,5-cyclooctadiene](BF_4).[11c] Using the conventions of Brown and Evans, the normalized arene ring torsion angle values (θ and ϕ for each ring) of 1 are $\theta = 45^\circ$, $\phi = 105^\circ$; $\theta = 52^\circ$, $\phi = 133^\circ$; $\theta = 12^\circ$, $\phi = 107^\circ$; $\theta = 61^\circ$, $\phi = 129^\circ$ for rings 1-4, respectively. (Values for [Rh(DIPAMP)(1,5-cyclooctadiene](BF$_4$) are $\theta = 3^\circ$, $\phi = 104^\circ$; $\theta = 75^\circ$, $\phi = 137^\circ$; $\theta = 23^\circ$, $\phi = 98^\circ$; $\theta = 66^\circ$, $\phi = 140^\circ$). Idealized edge-face arene ring arrays as defined by Brown and Evans correspond to $\theta = 0^\circ$ (edge) and $\theta = 70^\circ$ (face); axial groups have $\phi \simeq 100^\circ$ and equatorial groups have $\phi \simeq 130^\circ$. It should be noted that the closest interaction between an axial arene ring and a ligand in the cis-coordination site of the square plane does not occur at $\theta = 0^\circ$ but, rather, occurs in the range $\theta \simeq 30$-40°. Arene rings 3 and 4, which are cis to the C=C of the enamide, display a nearly ideal edge-face orientation, whereas the rings 1 and 2 conform less well to this idealized structure.

The oxygen atoms of *o*-anisoylphosphines can coordinate to metals, forming chelate rings. Indeed, such coordination has been invoked to explain the enhanced nucleophilicity of *o*-anisoylphosphine, relative to *p*-anisoylphosphine, analogues of Vaska's complex toward CH_3I[15] and has been observed by Brown and Maddox[16] for alkylhydridoiridium complexes containing the DIPAMP ligand. For [Rh(DIPAMP)(MPAA)](BF_4) the Rh-O distances for the anisoyl oxygens (Rh-O1111 = 2.903 Å, Rh-O211 = 3.607 Å) are sufficiently longer than normal Rh-O bonding distances (Rh-O = 2.1 Å) that normal bonding interactions are excluded, although weak interactions may be important. Additionally, agostic interactions involving ortho hydrogens of the diphosphine axial arene rings have been proposed;[13] addition of hydrogen atoms to the *o*-arene carbon atoms at normal bond lengths yields Rh-H(ortho) distances of 2.9 and 3.3 Å. The axial arene rings display smaller Rh-P-C(arene) bond angles (112 and 111°) than the equatorial arene rings (115 and 122°), which is not inconsistent with the possibility of an agostic interaction.

Acknowledgment. We are grateful to the National Science Foundation (J.H.) and to the National Institutes of Health (C.R.L.) for grants in support of this research, to Johnson Matthey Inc. for a generous loan of rhodium trichloride, and to Dr. J. W. Scott of Hoffman-LaRoche Inc. for a generous gift of MPAA.

Supplementary Material Available: Listings of H atom coordinates and anisotropic thermal parameters (Tables IV and V) (2 pages); a listing of structure factors (8 pages). Ordering information is given on any current masthead page.

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Stabilization of the First Selenogermylene as the Monomeric Pentacarbonyltungsten(0) Complex

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Received August 4, 1989

Bis[(2,4,6-tri-*tert*-butylphenyl)seleno]germylene, formed in situ by reaction of lithium 2,4,6-tri-*tert*-butylphenyl selenide with the germanium dichloride dioxane complex, was trapped as the monomeric pentacarbonyl[bis((2,4,6-tri-*tert*-butylphenyl)seleno)germylene]tungsten(0) complex. Reaction of bis(2,4,6-tri-*tert*-butylphenyl) diselenide with the germanium dichloride dioxane complex provides dichlorobis((2,4,6-tri-*tert*-butylphenyl)seleno)germane. This tetravalent germanium compound and bis(2,4,6-tri-*tert*-butylphenyl) diselenide were identified as byproducts when preparation and isolation of the monomeric selenogermylene was attempted. The structure of the selenogermylene tungsten(0) complex was determined from single-crystal X-ray diffraction data. The complex crystallizes (with one toluene per molecule) in the monoclinic space group $P2_1/c$ with $a = 1077.4$ (2), $b = 1667.2$ (2), $c = 2880.9$ (2) pm, $\beta = 98.33^\circ$, and $Z = 4$. The molecule contains trigonal planar germanium with bonds to tungsten and to two nonequivalent selenium atoms (Ge-Se, 231.4 (2) and 234.6 (2) pm; Ge-W, 252.8 (1) pm). Well-resolved ^1H, ^{13}C, and ^{77}Se NMR signals for the two (2,4,6-tri-*tert*-butylphenyl)seleno groups of the selenogermylene complex indicate hindered rotation around the Ge-Se bonds at room temperature in solution.

Introduction

Carbene-analogous germylenes are known with C, N, O, P, and S atoms bonded to divalent germanium, but a monomeric germylene with a post-transition element like As or Se adjacent to germanium has not yet been characterized.[1] Low molecular weight compounds with covalent bonds between unsaturated germanium and soft and easily polarizable selenium atoms would be of interest as

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[1] For the synthesis of t-$Bu_2AsGeCl$ and t-$Bu_2AsSnCl$ see: du Mont, W.-W.; Rudolph, G. *Z. Naturforsch.* **1981**, *36B*, 1215. Cowley, A. H.; Giolando, D. M.; Jones, R. A.; Nunn, C. M.; Power, J. M.; du Mont, W.-W. *Polyhedron* **1988**, *7*, 1317.

0276-7333/90/2309-1395$02.50/0

models for the kind of interaction in semiconducting materials such as GeSe or GeTe.

Compounds of tetravalent germanium with bonds to selenium are fairly well characterized, including a number of structure determinations, but selenolates of divalent germanium are still unknown.[2] Selenophenolates of divalent tin and lead have been described, but they appear to be insoluble coordination polymers.[3]

Monomeric arylthiolates of Ge^{II}, Sn^{II}, and Pb^{II} have been isolated by using the bulky (2,4,6-tri-*tert*-butylphenyl)thio substituent.[4] This led us to attempt the synthesis of bis((2,4,6-tri-*tert*-butylphenyl)seleno)germylene.

Experimental Section

Experiments were carried out under an argon atmosphere; solvents were purified and dried according to standard procedure. Mass spectra were obtained with an Finnigan MAT 312 instrument. ^{1}H, ^{13}C, and ^{77}Se NMR spectra were obtained by using C_6D_6 solutions with a Bruker WP 80 spectrometer (80 MHz for ^{1}H, 20.1 MHz for ^{13}C, and 15.3 MHz for ^{77}Se); shifts given are relative to Me_4Si (^{1}H, ^{13}C) and $Me_2{}^{77}Se$, respectively.

Synthesis of $GeCl_2$–Dioxane. The procedure given by Kolesnikov et al.[5] was modified in the following way: A quartz tube (90 cm long, 5 cm wide) was filled with layers of glass wool and 50 g (0.69 mol) of germanium powder to obtain an even distribution (important!) of finely divided germanium. Hydrogen chloride gas was passed through the tube in a moderate stream and the quartz tube was heated to 400 (±20) °C in an electric oven. The outlet of the tube was connected to a reflux condenser cooled with water followed by a vessel kept at dry ice temperature with help of powdered solid carbon dioxide. The rate of consumption of the HCl gas was monitored with the aid of paraffin-filled bubblers before the heated tube and after the dry ice cooled trap. After about 7 days no more HCl gas was consumed, and the condensed crude product was allowed to warm. Drops of water, separated as a lighter phase on the crude $HGeCl_3/GeCl_4$ mixture, were removed with help of a separating funnel. Subsequently, the $HGeCl_3/GeCl_4$ was transferred to a two-necked flask cooled with ice, and 70 g 1,4-dioxane was added with stirring. The solid $GeCl_2$–dioxane complex is formed instantaneously with evolution of gaseous HCl. Excess dioxane, traces of water, and $GeCl_4$ were removed under vacuum, and a white residue of 75 g (47%) $GeCl_2$–dioxane was isolated.

Dichlorobis((2,4,6-tri-*tert*-butylphenyl)seleno)germanium(IV) (4). Diselenide 3[6,7] (5.0 g, 7.7 mmol) and 1.78 g (7.7 mmol) of the $GeCl_2$–dioxane complex in 100 mL of toluene were stirred for 6 h at 80 °C. The color of the solution turned from orange to bright yellow. After evaporation of the solvent, the residue was recrystallized from pentane to give 4.95 g (81%) **4** as yellow plates, mp 206–208 °C. Anal. Found for $C_{36}H_{58}Cl_2GeSe_2$ (792.3): C, 54.41; H, 7.29; Cl, 9.10. Calcd: C, 54.57; H, 7.38; Cl, 8.94. MS (EI, 70 eV) 792 (5.8%, M^+), 650 (2.8, $M^+ - GeCl_2$ [$\equiv Ar_2Se_2{}^+$]), 413 (9.5, M^+ – SeAr – C_4H_8), 324 (18.3, $[ArSe - 1]^+$), 245 (5.5, $tBu_3C_6H_2{}^+ \equiv Ar^+$), 229 (86.5, $Ar^+ - CH_4$), 213 (23.9, $Ar^+ - 2\ CH_4$), 187 (7.5, $Ar^+ - C_4H_{10}$), 131 (11.8, $Ar^+ - C_4H_{10}, - C_4H_8$), 91 (10, $C_7H_7{}^+$), 57 (100, $C_4H_9{}^+$); ^{1}H NMR: δ 1.26 (s, 18 H), 1.70 (s, 36 H), 7.52 (s, 4 H); ^{13}C NMR: δ 31.42 (*p*-$(CH_3)_3C$), 33.43 (*o*-$(CH_3)_3C$), 35.2 (*p*-CC_3), 39.03 (*o*-CC_3), 123.3 (C_{meta}), 152.1 (C_{para}), 156.4 (C_{ortho}); ^{77}Se NMR: δ 361.3 (Me_2Se standard, sweep frequency 57.24 MHz).

Table I. Selected Bond Lengths (Å) and Angles (deg) for 5

Ge–W	2.528 (1)	C1–W–Ge	177.2 (5)
C1–W	1.946 (16)	C2–W–Ge	88.3 (4)
C2–W	2.046 (16)	C3–W–Ge	87.1 (5)
C3–W	2.010 (18)	C4–W–Ge	91.6 (4)
C4–W	2.022 (15)	C5–W–Ge	93.6 (4)
C5–W	2.026 (16)		
Se1–Ge	2.346 (2)	Se1–Ge–W	119.9 (1)
Se2–Ge	2.314 (2)	Se2–Ge–W	138.5 (1)
		Se2–Ge–Se1	101.4 (1)
C11–Se1	1.939 (12)	C11–Se1–Ge	101.5 (3)
C29–Se2	1.966 (12)	C29–Se2–Ge	104.1 (4)

Pentacarbonylbis[((2,4,6-tri-*tert*-butylphenyl)seleno)germylene]tungsten(0) (5). (2,4,6-Tri-*tert*-butylphenyl)selenolithium[6] (1) was prepared in situ by dropwise addition of 10 mL of a 1 M solution of $LiBEt_3H$ in THF to 3.25 g (5.0 mmol) of diselenide **3** partly dissolved in 5 mL of THF. Subsequently, 20 mL of THF was added, and the solution was cooled to –70 °C. At this temperature 1.16 g (5 mmol) of the solid $GeCl_2$–dioxane complex was added. The red solution was kept at –50 °C for 1.5 h, and then a THF solution containing about 5 mmol of photochemically generated $W(CO)_5THF$ (from 1.76 g (5 mmol) of $W(CO)_6$)[8] was added dropwise. The mixture was allowed to warm to room temperature overnight, and the solvent was removed under vacuum. Recrystallization of the residue from toluene at –18 °C gave a product that contained still about 30% of diselenide **3**. Repeated crystallization of the crude product from pentane/toluene (3:1) yielded 2.3 g (44%) of pure **5**, mp 185 °C. Anal. Found for $C_{41}H_{58}Cl_2GeO_5Se_2W$ (1045.2): C, 47.02; H, 5.62; W, 17.94. Calcd: C, 47.11; H, 5.60; W, 17.59. MS (EI, 70 eV), 1046 (2.3%, M^+ with correct isotopic pattern), 906 (<1%, M^+ – 140 [probably 5CO]), 850 (<1%, M^+ – 5CO – C_4H_8), 721 (4, M^+ – ArSe), 693 (1, M^+ – ArSe – CO), 665 (23.5, M^+ – ArSe – 56), 609 (10.5, M^+ – ArSe – 2 CO – C_4H_8), 581 (3, M^+ – ArSe – 3 CO – C_4H_8), 553 (8, M^+ – ArSe – 4 CO – C_4H_8), 525 (4.5, M^+ – ArSe – 5CO), 397 (17.8, M^+ – ArSe – $W(CO)_5$), 341 (12, $tBu_2C_6H_3SeGe^+$), 229 (8, $tBu_3C_6H_2{}^+ - CH_4$), 57 (100, $C_4H_9{}^+$). MS (at 22 eV) 1046 (18%, M^+), base peak at *m/e* 229. Chemical ionization with isobutane: highest fragment at *m/e* 721 (76%, M^+ – ArSe), base peak at *m/e* 245 (Ar^+); ^{1}H NMR: δ 1.28, 1.49, 1.58, 1.63, 1.67 (*tert*-butyl groups), 7.57, 7.59 (H at meta-carbon atoms); ^{13}C NMR [at 90 MHz] main isomer A: δ 31.29, 31.56 (*p*-$(CH_3)_3C$), 32.91, 33.14 (*o*-$(CH_3)_3C$), 35.07, 35.14 (*p*-CC_3), 38.91, 39.23, (*o*-CC_3), 122.64, 124.16 (C_{meta}), 123.03, 130.54 (C_{ipso}), 150.64, 151.08 (C_{para}), 153.45, 154.71 (C_{ortho}), 194.83 (*cis*-$C{=}O$, $^{1}J(^{183}W,^{13}C)$ = 123.23 Hz), 200.45 (*trans*-$C{=}O$); minor isomer B: δ 31.52 (*p*-$(CH_3)_3$), 32.19 (*o*-$(CH_3)_3C$), 35.05 (*p*-CC_3), 38.54 (*o*-CC_3), 122.98 (C_{meta}), 121.15 (C_{ipso}), 148.84 (C_{para}), 152.59 (C_{ortho}); ^{77}Se NMR: δ 627.9 and 709.4 ppm (main isomer A); IR (KBr) ν(CO) 2071 ($A_1{}^{cis}$), 1986 (sh), 1951 (E) cm^{-1}.

X-ray Crystal Structure Determination of 5. Suitable single crystals of **5** (·toluene) were grown from a pentane/toluene solution as yellow plates. A crystal with the dimensions 0.15 × 0.3 × 0.3 mm was sealed into a thin-walled glass capillary and mounted on a Siemens/STOE AED2 automated four-circle diffractometer. Graphite-monochromated Mo K_α radiation was used. Accurate lattice parameters were determined by measuring the centers of 36 reflections including Friedel pairs.

The crystal system was found to be monoclinic with space group $P2_1/c$ and cell dimensions a = 10.774 (2), b = 16.672 (2), c = 28.809 (2) Å, β = 98.33 (2)°, V = 5120.08 Å^3, Z = 4, M = 1137.4, D_{calcd} = 1.475 g/cm^3, μ = 42.96 cm^{-1}, at T = 295 K.

Intensity data were recorded by using the $\omega/2\theta$ scan technique with $2° \leq \theta \leq 24°$. A total of 7978 unique reflections was measured, of which 5196 were observed ($I > 2\sigma(I)$).

The structure was solved by direct methods with use of the structure solution program SHELX-86.[9] Other computer programs were SHELX-76[9] and ORTEP.[10] In the refinement the quantity

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Table II. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Coefficients ($Å^2 \times 10^3$) for 5[a,b]

atom	x	y	z	U_{eq}
W(1)	560 (1)	991 (1)	866 (1)	46 (1)
Ge(1)	1351 (1)	484 (1)	1683 (1)	43 (1)
Se(1)	567 (1)	1034 (1)	2331 (1)	52 (1)
Se(2)	2857 (1)	−390 (1)	2045 (1)	47 (1)
O(1)	−434 (12)	1719 (8)	−120 (4)	107 (7)
O(2)	−1498 (11)	1997 (7)	1294 (5)	102 (7)
O(3)	2494 (12)	2412 (8)	1054 (5)	113 (8)
O(4)	2516 (11)	−34 (8)	403 (4)	92 (6)
O(5)	−1398 (10)	−427 (7)	630 (4)	81 (6)
C(1)	−28 (13)	1434 (10)	249 (5)	68 (8)
C(2)	−763 (15)	1641 (8)	1146 (5)	55 (7)
C(3)	1798 (17)	1893 (10)	998 (6)	78 (9)
C(4)	1837 (14)	324 (9)	588 (5)	54 (7)
C(5)	−688 (14)	83 (9)	725 (5)	58 (7)
C(6)	1291 (11)	−208 (7)	3029 (4)	41 (6)
C(7)	2236 (14)	−667 (9)	3276 (5)	60 (7)
C(8)	3498 (12)	−407 (8)	3371 (4)	50 (6)
C(9)	3714 (12)	375 (9)	3254 (5)	54 (6)
C(10)	2836 (11)	879 (7)	3013 (4)	37 (5)
C(11)	1640 (12)	532 (8)	2849 (4)	43 (6)
C(12)	−69 (11)	−541 (9)	2985 (5)	59 (7)
C(13)	−954 (12)	134 (8)	3119 (6)	71 (7)
C(14)	−167 (14)	−1226 (9)	3327 (7)	99 (10)
C(15)	−573 (13)	−871 (10)	2497 (6)	80 (8)
C(16)	3151 (12)	1770 (8)	2959 (5)	55 (7)
C(17)	3367 (17)	2029 (10)	2468 (6)	97 (10)
C(18)	2131 (15)	2297 (8)	3135 (6)	74 (8)
C(19)	4362 (15)	1982 (9)	3295 (6)	85 (9)
C(20)	4547 (14)	−984 (12)	3581 (7)	92 (9)
C(21A)	5596 (34)	−981 (23)	3286 (13)	88 (11)
C(22A)	4133 (33)	−1846 (22)	3669 (13)	83 (10)
C(23A)	4960 (34)	−661 (21)	4118 (13)	88 (11)
C(21B)	5871 (32)	−620 (20)	3558 (12)	76 (10)
C(22B)	4558 (42)	−1798 (28)	3214 (16)	126 (15)
C(23B)	4238 (38)	−1423 (26)	3967 (15)	104 (13)
C(24)	4615 (12)	−586 (7)	1363 (5)	47 (6)
C(25)	4976 (12)	−917 (9)	966 (4)	53 (6)
C(26)	4358 (13)	−1532 (9)	717 (5)	54 (6)
C(27)	3343 (13)	−1884 (8)	907 (5)	55 (6)
C(28)	2933 (11)	−1598 (7)	1306 (4)	40 (5)
C(29)	3531 (11)	−908 (8)	1521 (4)	44 (5)
C(30)	5476 (12)	88 (8)	1615 (5)	59 (7)
C(31)	5837 (14)	−39 (11)	2149 (5)	77 (8)
C(32)	4824 (15)	902 (9)	1506 (6)	81 (8)
C(33)	6735 (13)	150 (10)	1416 (6)	81 (8)
C(34)	1872 (12)	−2087 (8)	1498 (5)	58 (7)
C(35)	601 (13)	−1634 (9)	1397 (5)	65 (7)
C(36)	1684 (14)	−2896 (8)	1230 (6)	74 (8)
C(37)	2218 (13)	−2283 (9)	2017 (5)	73 (8)
C(38)	4735 (13)	−1880 (10)	258 (5)	69 (8)
C(39A)	4490 (47)	−2761 (28)	188 (16)	118 (16)
C(40A)	6162 (40)	−1807 (26)	240 (15)	111 (14)
C(41A)	3889 (43)	−1485 (28)	−159 (15)	111 (15)
C(39B)	5221 (39)	−2748 (23)	332 (13)	85 (12)
C(40B)	5689 (41)	−1311 (25)	54 (15)	108 (14)
C(41B)	3482 (35)	−1955 (23)	−137 (13)	86 (11)
C(42)	1564 (15)	4183 (13)	10256 (4)	150
C(43)	1476 (15)	3481 (13)	9989 (4)	150
C(44)	1572 (15)	3515 (13)	9512 (4)	150
C(45)	1756 (15)	4250 (13)	9301 (4)	150
C(46)	1845 (15)	4952 (13)	9568 (4)	150
C(47)	1748 (15)	4915 (13)	10045 (4)	150
C(48)	1773 (25)	5721 (14)	10223 (9)	150

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] The atoms C21–C23 and C39–C41 are disordered. Two positions (A and B) for each atom were refined with occupancy factors of 0.5.

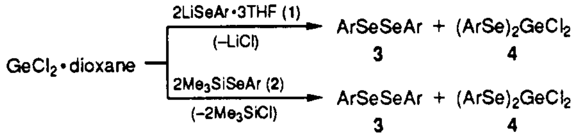
$\sum w(|F_o| - |F_c|)^2$ was minimized, w being defined as $w = k/(\sigma^2(F_o) + gF_o^2)$ with $g = 0.0002$.

All non-hydrogen atoms except the disordered C atoms and those of the toluene molecule (for which fixed U values were taken; see Table II) were refined anisotropically. The toluene molecule was refined with idealized geometry. The H atoms were given calculated positions, again except those of the disordered C atoms and the toluene molecule, which were not included in the refinement.

The final R and R_w values were 0.066 and 0.059, respectively. The final coordinates are listed in Table II.

Results and Discussion

Reactions of the germanium dichloride dioxane complex with (2,4,6-tri-*tert*-butylphenyl)selenolithium[6] or with [(2,4,6-tri-*tert*-butylphenyl)seleno]trimethylsilane[6] proceed with formation of lithium chloride or chlorotrimethylsilane to give mixtures of compounds, from which only bis(2,4,6-tri-*tert*-butylphenyl) diselenide (**3**)[6,7] and dichlorobis((2,4,6-tri-*tert*-butylphenyl)seleno)germane (**4**) were isolated in a pure state (eq 1–5). After removal of **3** and **4** by chromatography, small amounts of a material of an analytical composition close to that of the desired bis(arylseleno)germylene were isolated, but a monomeric bis(arylseleno)germylene could not be detected (MS, NMR) in this product. A separate experiment showed that **4** can be formed in high yield from diselenide **3** (product of the oxidation of **1** or **2**) and the germanium dichloride dioxane complex by oxidative addition of the Se–Se bond to divalent germanium. Attempts to reduce **4** (Mg/THF or naphthalene/lithium) did not lead to the desired monomeric selenogermylene.[11]



(1)

$$\mathrm{GeCl_2{-}dioxane} + \underset{\mathbf{3}}{\mathrm{ArSeSeAr}} \rightarrow \underset{\mathbf{4}}{\mathrm{(ArSe)_2GeCl_2}} \quad (2)$$

$$\underset{\mathbf{3}}{\mathrm{ArSeSeAr}} \xrightarrow{\mathrm{LiBEt_3H,\ THF}} \underset{\mathbf{1}}{\mathrm{2ArSeLi}} \quad (3)$$

$$\underset{\mathbf{1}}{\mathrm{2ArSeLi}} + \mathrm{GeCl_2{\cdot}dioxane} \xrightarrow{-50\ ^\circ\mathrm{C}} \underset{\text{[not isolated]}}{\mathrm{Ge(SeAr)_2}} + \mathrm{2LiCl} \quad (4)$$

$$\mathrm{Ge(SeAr)_2} + \mathrm{W(CO)_5THF} \xrightarrow[-\mathrm{THF}]{} \underset{\mathbf{5}}{\mathrm{(CO)_5W{=}Ge(SeAr)_2}} \quad (5)$$

Finally, we attempted to stabilize the intermediate selenogermylene by coordination of the 4s lone pair of germanium with a transition-metal acceptor. In situ generated (2,4,6-tri-*tert*-butylphenyl)selenolithium reacted with the germanium dichloride dioxane complex at −70 °C, and addition of pentacarbonyl(tetrahydrofuran)tungsten(0) to the reaction mixture at −50 °C gave the bis(arylseleno)germylene complex **5**. The latter was separated from the byproducts (about 30% of diselenide **3**) by crystallizations from toluene/pentane. Yellow crystalline **5** is moderately soluble in hydrocarbons and fairly soluble in ether and tetrahydrofuran. The peak of highest mass number in the EI mass spectrum of **5** is the molecular ion (m/z = 1046, correct isotopic pattern) of the monomeric selenogermylene complex $[(CO)_5W{=}Ge(SeAr)_2]^+$.

The main fragmentation pathway (EI, 70 or 22 eV) involves the loss of an arylseleno substituent (Ge–Se bond cleavage) to give the even-electron cation $[(CO)_5W{=}GeSeAr]^+$ (m/z 721). The isotopic pattern of this fragment is distinctly different from that calculated for the species $Ge(SeAr)_2$ (m/z 722). $[(CO)_5W{=}GeSeAr]^+$ subsequently

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[11] Lange, L., Ph.D. Thesis, Universität Oldenburg, 1987.

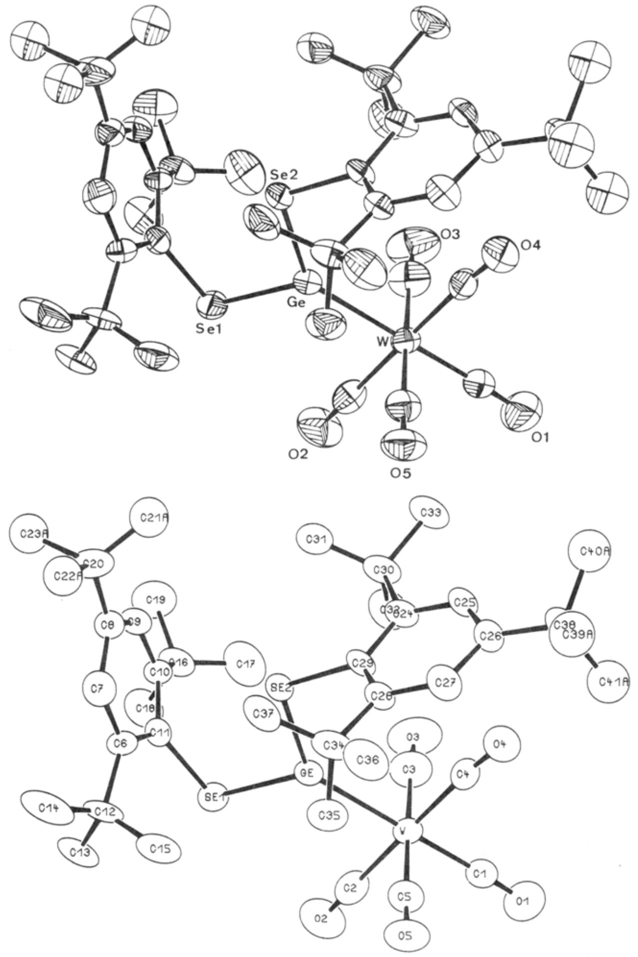


Figure 1. Molecular structure of the complex **5**. Hydrogen atoms have been omitted for clarity: top, ORTEP view; bottom, numbering scheme.

loses the carbonyl groups and 1 equiv of isobutene. Loss of carbon monoxide from the molecular ion of **5** occurs only to a minor extent (at 70 eV, M^+ 2.3%, M^+ − 5CO 0.1%, M^+ − ArSe 4%; at 22 eV, M^+ 18%, M^+ − 5CO not detected, M^+ − ArSe 17.5%). Under the conditions of chemical ionization with isobutane, the molecular ion of **5** could not be detected, but the cation $[(CO)_5W = GeSeAr]^+$ appeared in high intensity (76%, base peak was *m/z* 245, $[t\text{-}Bu_3C_6H_2]^+$). Loss of selenium atoms (like loss of sulfur from Jutzi's bis(mesitylthio)germylenechromium and -tungsten complexes[12] from the molecular ion of **5** was not observed.

The infrared absorptions of **5** in the region of carbonyl stretching vibrations (2071, 1986, and 1951 cm^{-1}) are very much related to those of other complexes with carbene-analogous ligands[12-15] that show donor/acceptor ratios comparable to those of triphenylphosphine or triphenyl phosphite.

The molecular structure of **5** (Figure 1) is similar to that of the pentacarbonyl [bis(mesitylthio)germylene]chromium(0) complex.[11] Germanium is in a tricoordinate planar environment. The SeGeSe plane is nearly in plane with the C2–W–C4 plane (see Figure 2). The germanium–tungsten bond is typically shorter than Ge–W single bonds,

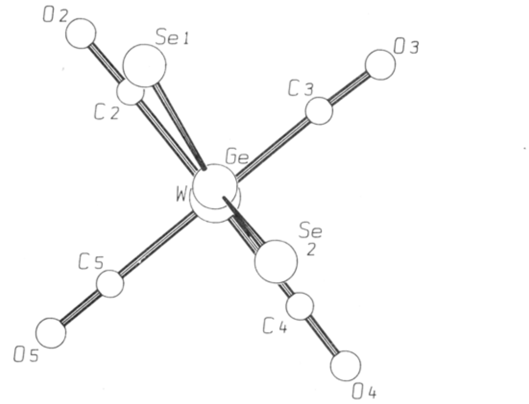
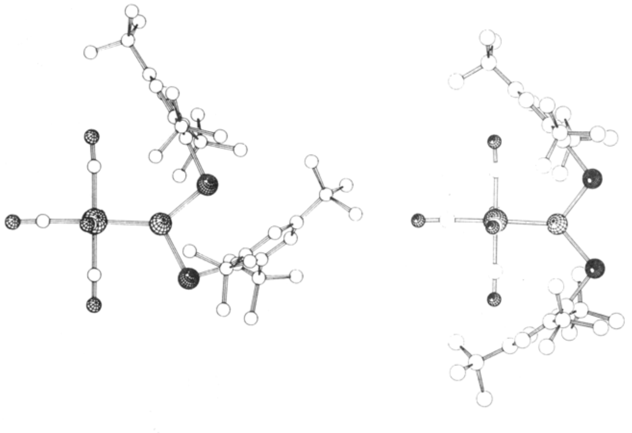


Figure 2. Orientation of the $(CO)_5W$ moiety relative to the plane including Ge, Se1, and Se2.



5 (Z,E): Isomer A 5 (Z,Z): Isomer B

Figure 3. Conformational isomers of **5A** and **5B**.

and the Ge^{II}–Se bond distances are comparable to those of single bonds between selenium and tetravalent germanium, i.e., there is no evidence for any significant "internal stabilization" via Ge(4p)–Se(4p) overlap leading to an enhanced bond order.

Relative to the Ge=W bond, the two Se–C(aryl) bonds are in the *E* and *Z* orientation; i.e., the coordinated germylene adopts a conformation different from that of the related noncoordinated stannylene $[(t\text{-}C_4H_9)_3C_6H_2S]_2Sn$.[4] Repulsion between the *Z*-orientated aryl and carbonyl groups of the $W(CO)_5$ moiety leads to opening of the angle WGeSe2 (∠138.5°) at the expense of ∠WGe–Se1 (∠119.9°), very similar to what was observed in Jutzi's $[(CO)_5CrGe(SMes)_2]$ (∠CrGeS: 137.5 and 119.9°).[12] Different from the latter complex, **5** shows no rapid equilibrium of the two different arylchalcogeno groups in solution (by NMR). The ^1H, ^{13}C, and ^{77}Se NMR spectra of **5A** give two well-resolved sets of resonances for the two types of arylseleno groups, i.e., rotation around the Ge–Se bonds is hindered at room temperature. Besides these two sets of main NMR signals, a third set of ^1H and ^{13}C NMR signals of the (tri-*tert*-butylphenyl)seleno group appears with minor intensity (about 15% relative to the main conformer); this should be attributed to the *Z,Z* isomer **5B**, which is also present in solution (see Figure 3).

No such frozen conformations were detected in the NMR spectra of the (mesitylthio)germylene complex $[(CO)_5Cr{=}Ge(SMes)_2]$,[12] the related stannylene complex $[(CO)_5Cr{=}Sn(SAr)_2]$,[4] or the bulky supermesitylselenogermane $Cl_2Ge(SeAr)_2$ (**4**).

The rather high barrier of rotation around the Ge–Se bonds in **5** will be due to steric effects and not to significant

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contributions from π-overlap.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and Professor H. Schumann and M. Dettlaff, Technical University Berlin, for recording ^{77}Se NMR spectra.

Registry No. 1, 126083-46-3; 3, 20875-32-5; 4, 126109-80-6; 5, 126083-45-2; $GeCl_2$–dioxane, 28595-67-7; $W(CO)_5\cdot THF$, 36477-75-5.

Supplementary Material Available: Tables of U_{ij} values and bond lengths and angles (14 pages); a listing of F_o/F_c values (31 pages). Ordering information is given on any current masthead page.

Electrochemical Investigation of the Substitution Reactions of the Solvent-Coordinated Acyl Complexes η-Cp(AC)(CO)FeCOMe$^{0,+}$ Involving Thioethers. Applications of the Quantitative Analysis of Ligand Effects

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Received August 1, 1989

The displacement of acetone from η-Cp(AC)(CO)FeCOMe$^{0,+}$ by thioethers (SMe_2, SEt_2, S(Ph)Me, S(Ph)Et, SBu_2, SPh_2, S(i-Pr)$_2$, S(t-Bu)$_2$) at −41 °C has been studied by square-wave voltammetry (SWV) coupled with computer simulation. The kinetic data were analyzed and interpreted via the quantitative analysis of ligand effects (QALE). A set of stereoelectronic parameters (χ^s and θ^s) for the thioethers was constructed by transference of the appropriate properties of the phosphorus(III) compounds to the sulfur compounds. It appears that substitution in the iron(III) state occurs via an associative ligand-dependent reaction whose rate depends on both electronic and steric factors. In the iron(II) state the substitution reaction occurs via a preequilibrium dissociative process. The iron(II) reaction is insensitive to the electronic properties of the thioethers but is sensitive to their steric bulk. These results are interpreted in terms of addition of the thioether to the coordinatively unsaturated complex η-Cp(CO)FeCOMe. On the basis of ligand effect data and analysis of the $E°$ values of the η-Cp(SR_2)(CO)FeCOMe$^{0,+}$ it is shown that the thioether complexes exhibit steric effects, in contrast to the analogous phosphorus(III) complexes, which show no steric effects.

Introduction

A growing body of evidence indicates that the stoichiometric rearrangement of alkyl metal carbonyls to acyl complexes is assisted by nucleophilic solvents or solutes.[1] The subsequent displacement of the solvent from the resulting weakly solvent-coordinated acyl complex by other potential ligands (metal hydrides, alkenes, alkynes) leads to the downstream chemistry that eventually affords organic products. The solvent-coordinated acyl complexes are clearly key players in this flow of chemistry; however, they are rarely observed and hence difficult to study.

Recently, we demonstrated that the solvent-coordinated complexes η-Cp(L)(solv)FeCOR$^{0,+}$ are formed in situ by low-temperature oxidation of η-Cp(L)(CO)FeR in coordinating solvents such as acetone (AC),[2] acetonitrile (AN),[3] and methanol.[3] These acyl complexes are generally short lived but are amenable to study by electrochemical methods. In electrochemical experiments we have even seen what appears to be the perchlorate complex, η-Cp(ClO_4)(CO)FeCOMe, formed from the supporting electrolyte $LiClO_4$ at −89 °C.[2] In either oxidation state, the complexes are labile although the iron(III) complexes are longer lived than their iron(II) counterparts. This is particularly obvious when X = ClO_4^-, where the iron(II) complex cannot be observed electrochemically even at −89 °C. The greater stability of the iron(III) complexes is probably associated with the hard acid iron(III) complex exhibiting a greater affinity for the hard base solvent.

Through studies with iron(III) acyl complexes (solv = MeOH and AN) we showed that these complexes undergo second-order ligand-dependent substitution reactions of the coordinated solvent.[2] The MeOH and AN complexes showed less reactivity toward substitution in the iron(II) state at −41 °C. When the solvent ligand is acetone, the complexes are more labile, offering the opportunity to study the chemistry of both oxidation states.[3] Our initial studies with the acetone complex demonstrated that the solvent ligand was readily displaced by thioanisole at −75 °C through a second-order reaction in the iron(III) state. This is probably an entering ligand-dependent reaction, although a preequilibrium dissociative reaction could not be excluded. In the iron(II) state, the substitution clearly follows a two-step rate law indicative of a classical dissociative process. This reactivity toward thioethers offers the opportunity to use ligand effects to gain insight into the stereoelectronic factors that influence the reactivity

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