3144 *Organometallics* 1992, *11*, 3144–3148

An Organoindium Compound Containing an Indium–Selenium Bond: Synthesis, Properties, and Molecular Structure of $[(Me_3CCH_2)_2InSePh]_2$

O. T. Beachley, Jr.,*[,1a] Jesse C. Lee, Jr.,[1a] Henry J. Gysling,[1b] Sun-Hua L. Chao,[1a] Melvyn Rowen Churchill,[1a] and Charles H. Lake[1a]

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, and Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

Received March 3, 1992

Summary: An organoindium compound with an In–Se bond, $[(Me_3CCH_2)_2InSePh]_2$, has been synthesized and characterized by elemental analyses, IR, ^1H NMR, and ^{13}C NMR spectroscopy, cryoscopic molecular weight studies, and an X-ray structural study. The dimeric molecule crystallizes in the centrosymmetric monoclinic spacegroup $P2_1/c$ (No. 14) with a = 18.973 (4) Å, b = 10.105 (1) Å, c = 19.998 (6) Å, β = 103.66 (2)°, V = 3725.4 (14) Å^3, and Z = 4. Diffraction data (Mo Kα, 2θ = 5–45°) were collected on a Siemens R3m/V automated four-circle diffractometer, and the structure was solved and refined to R = 3.44% and R_w = 3.73% for those 2557 unique data with $|F_o| > 6\sigma(|F_o|)$ (R = 8.35% for all 4891 data). The four-membered In_2Se_2 ring has a butterfly arrangement with the phenyl groups in the anti position relative to the ring. The In–C(neopentyl) distances range from 2.135 (11) to 2.168 (10) Å, while In–Se bond distances range from 2.748 (1) to 2.756 (1) Å. There is some rotational disorder of the methyl groups within (at least) one of the neopentyl ($-CH_2CMe_3$) groups.

Compounds of gallium and indium with bonds to the heavier group 16 elements selenium and tellurium have been the subject of limited research. The list of organoindium selenides includes only three compounds, $[Et_2InSe(SiEt_3)]_2$,[2] $[(i\text{-}Pr)_2InSeEt]$[3] and $[EtInSe]_n$.[2] The first two compounds in the above series were prepared by facile elimination reactions between the triorganoindium compound and the appropriate organo selenol, whereas the third compound was prepared from the first by a thermal decomposition reaction. None of the above compounds was characterized by an X-ray structural study.

Table I. Bond Lengths (Å)

In(1)–Se(3)	2.745 (2)	In(1)–Se(4)	2.735 (1)
In(1)–C(10)	2.163 (10)	In(1)–C(15)	2.169 (10)
In(2)–Se(3)	2.756 (1)	In(2)–Se(4)	2.738 (1)
In(2)–C(20)	2.159 (9)	In(2)–C(25)	2.135 (11)
Se(3)–C(31)	1.934 (9)	Se(4)–C(41)	1.917 (9)
C(10)–C(11)	1.516 (15)	C(11)–C(12)	1.513 (17)
C(11)–C(13)	1.499 (17)	C(11)–C(14)	1.53 (2)
C(15)–C(16)	1.508 (17)	C(16)–C(17)	1.48 (2)
C(16)–C(18)	1.45 (2)	C(16)–C(19)	1.476 (18)
C(20)–C(21)	1.499 (14)	C(21)–C(22)	1.465 (19)
C(21)–C(23)	1.471 (19)	C(21)–C(24)	1.47 (2)
C(25)–C(26)	1.494 (16)	C(26)–C(27)	1.43 (4)
C(26)–C(28)	1.50 (3)	C(26)–C(29)	1.54 (3)
C(26)–C(27′)	1.44 (5)	C(26)–C(28′)	1.48 (5)
C(26)–C(29′)	1.55 (3)	C(31)–C(32)	1.366 (15)
C(31)–C(36)	1.349 (16)	C(32)–C(33)	1.409 (14)
C(33)–C(34)	1.34 (2)	C(34)–C(35)	1.35 (2)
C(35)–C(36)	1.417 (17)	C(41)–C(42)	1.363 (15)
C(41)–C(46)	1.358 (15)	C(42)–C(43)	1.346 (18)
C(43)–C(44)	1.39 (2)	C(44)–C(45)	1.34 (3)
C(45)–C(46)	1.347 (18)		

Table II. Bond Angles (deg)

Se(3)–In(1)–Se(4)	89.7 (1)	Se(3)–In(1)–C(10)	111.6 (3)
Se(4)–In(1)–C(10)	108.0 (3)	Se(3)–In(1)–C(15)	105.8 (3)
Se(4)–In(1)–C(15)	101.5 (3)	C(10)–In(1)–C(15)	131.8 (4)
Se(3)–In(2)–Se(4)	89.5 (1)	Se(3)–In(2)–C(20)	103.2 (3)
Se(4)–In(2)–C(20)	107.7 (3)	Se(3)–In(2)–C(25)	107.8 (3)
Se(4)–In(2)–C(25)	104.0 (3)	C(20)–In(2)–C(25)	135.4 (4)
In(1)–Se(3)–In(2)	85.8 (1)	In(1)–Se(3)–C(31)	107.1 (3)
In(2)–Se(3)–C(31)	103.7 (2)	In(1)–Se(4)–In(2)	86.4 (1)
In(1)–Se(4)–C(41)	107.2 (3)	In(2)–Se(4)–C(41)	100.1 (3)
In(1)–C(10)–C(11)	121.1 (7)	C(10)–C(11)–C(12)	112.0 (9)
C(10)–C(11)–C(13)	109.8 (9)	C(12)–C(11)–C(13)	110.7 (11)
C(10)–C(11)–C(14)	107.0 (10)	C(12)–C(11)–C(14)	108.1 (10)
C(13)–C(11)–C(14)	109.1 (10)	In(1)–C(15)–C(16)	120.4 (7)
C(15)–C(16)–C(17)	109.3 (12)	C(15)–C(16)–C(18)	112.1 (12)
C(17)–C(16)–C(18)	106.2 (13)	C(15)–C(16)–C(19)	112.9 (10)
C(17)–C(16)–C(19)	102.6 (12)	C(18)–C(16)–C(19)	113.0 (13)
In(2)–C(20)–C(21)	121.0 (6)	C(20)–C(21)–C(22)	112.6 (10)
C(20)–C(21)–C(23)	112.5 (10)	C(22)–C(21)–C(23)	107.4 (13)
C(20)–C(21)–C(24)	108.9 (11)	C(22)–C(21)–C(24)	106.1 (13)
C(23)–C(21)–C(24)	109.1 (12)	In(2)–C(25)–C(26)	121.5 (7)
C(25)–C(26)–C(27)	107 (2)	C(25)–C(26)–C(28)	116 (2)
C(27)–C(26)–C(28)	109 (2)	C(25)–C(26)–C(29)	113.5 (11)
C(27)–C(26)–C(29)	107 (2)	C(28)–C(26)–C(29)	104 (2)
C(25)–C(26)–C(27′)	95 (3)	C(25)–C(26)–C(28′)	114 (2)
C(27′)–C(26)–C(28′)	112 (3)	C(25)–C(26)–C(29′)	114 (2)
C(27′)–C(26)–C(29′)	113 (3)	C(28′)–C(26)–C(29′)	108 (3)
Se(3)–C(31)–C(32)	120.6 (7)	Se(3)–C(31)–C(36)	117.9 (8)
C(32)–C(31)–C(36)	121.3 (9)	C(31)–C(32)–C(33)	118.7 (10)
C(32)–C(33)–C(34)	120.4 (12)	C(33)–C(34)–C(35)	120.8 (12)
C(34)–C(35)–C(36)	119.8 (12)	C(31)–C(36)–C(35)	119.1 (12)
Se(4)–C(41)–C(42)	124.2 (7)	Se(4)–C(41)–C(46)	118.7 (8)
C(42)–C(41)–C(46)	117.1 (9)	C(41)–C(42)–C(43)	123.1 (11)
C(42)–C(43)–C(44)	118.1 (14)	C(43)–C(44)–C(45)	119.0 (13)
C(44)–C(45)–C(46)	121.2 (14)	C(41)–C(46)–C(45)	121.4 (12)

An organometallic indium–selenium compound, $(Me_3CCH_2)_2InSePh$, which is not a simple adduct, has been prepared by a stoichiometric ligand redistribution reaction between $In(SePh)_3$ and $In(CH_2CMe_3)_3$ in pentane at room temperature:

$$In(SePh)_3 + 2In(CH_2CMe_3)_3 \xrightarrow[25\ ^\circ C]{C_6H_{12}} 3(Me_3CCH_2)_2InSePh$$

This reaction avoids the use of benzeneselenol, an unpleasant-smelling compound. The reagent $In(SePh)_3$ was readily prepared from indium metal and diphenyl diselenide in refluxing toluene.[4] The new compound $(Me_3CCH_2)_2InSePh$ has been fully characterized by partial elemental analyses (C and H), physical properties, infrared spectroscopy, ^1H NMR and ^{13}C NMR spectroscopy, cryoscopic molecular weight studies in benzene, and an X-ray structural study.

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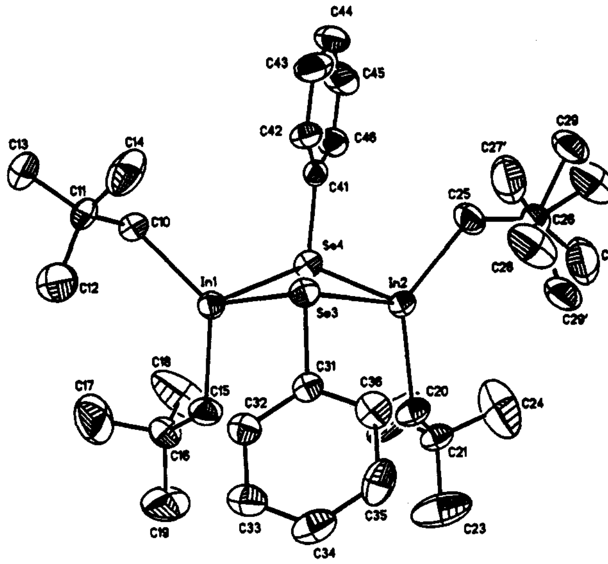

Figure 1. Labeling of atoms in $[(Me_3CCH_2)_2InSePh]_2$.

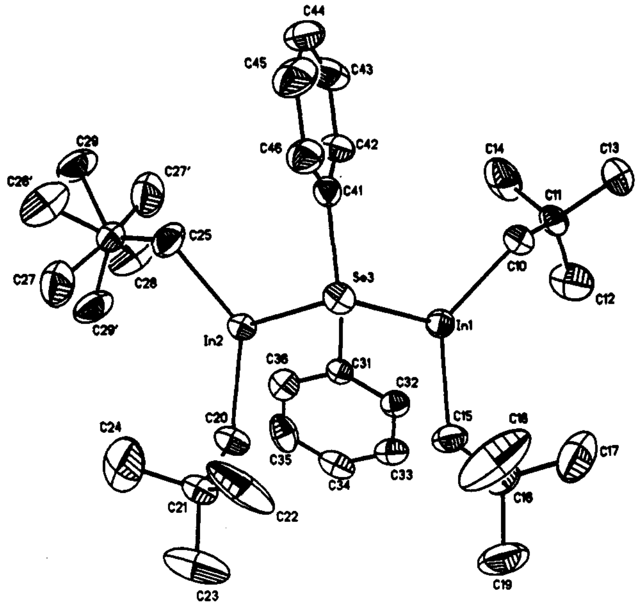

Figure 2. The $[(Me_3CCH_2)_2InSePh]_2$ molecule, viewed down the Se(3)···Se(4) axis.

The unit cell contains four dimeric molecules of $[(Me_3CCH_2)_2InSePh]_2$. The molecules possess no crystallographic symmetry and are mutually separated by normal van der Waals distances. There are no anomalously short intermolecular contacts. The labeling of the atoms in the molecule is shown in Figure 1. Selected interatomic distances and angles are collected in Tables I and II. Crystals of this indium–selenium compound are isomorphous with those of $[(Me_3CCH_2)_2GaTePh]_2$.[5] These two compounds have very similar unit cell parameters and structural features, including abnormally large thermal ellipsoids representing terminal carbon atom positions on the neopentyl ligands. Corrections were made for these large thermal ellipsoids in $[(Me_3CCH_2)_2InSePh]_2$ by using a disordered model. However, the gallium–phenyl telluride structure was previously treated as an ordered system.

The In_2Se_2 core has a butterfly configuration with the following distances: In(1)–Se(3) = 2.745 (2) Å, In(1)–Se(4) = 2.735 (1) Å, In(2)–Se(3) = 2.756 (1) Å, and In(2)–Se(4) = 2.738 (1) Å. The In(1)···In(2) distance is 3.746 Å and the Se(3)···Se(4) distance is 3.866 Å. Internal angles are Se(3)–In(1)–Se(4) = 89.7 (1)°, Se(3)–In(2)–Se(4) = 89.5 (1)°, In(1)–Se(3)–In(2) = 85.8 (1)° and In(1)–Se(4)–In(2) = 86.4 (1)°. The fold angle about the In(1)···In(2) axis, defined as the angle of intercept between the In(1)–Se(3)–In(2) plane and the In(1)–Se(4)–In(2) plane, is 149.2°. The fold angle about the Se(3)···Se(4) axis is 148.3°. One possible explanation for the fold in the four-membered ring is that it relieves steric interactions between the surrounding ligands, as seen from the view of the molecule down the Se(3)···Se(4) axis (Figure 2). Note that the phenyl ligand associated with Se(4) is located between two neopentyl ligands on the same side of the core. These two neopentyl ligands are bent away from the phenyl ring, due to the folding of the In_2Se_2 system. If the In_2Se_2 ring were forced into a planar conformation, two neopentyl ligands would be forced into locations with more severe interactions with the phenyl ring. Therefore, the fold of the molecular core seems to be caused by steric interactions between the surrounding ligands.

The formation of a nonplanar, rather than planar, In_2Se_2 molecular core appears to be related to steric factors which are almost always related to interactions between the bridging ligands and substituents on the indium(III) atom. Thus, if the bridging ligand is small, we expect a planar In_2X_2 ring. This is observed for $[(Me_3CCH_2)(Me_3SiCH_2)InCl]_2$,[6] despite the fact that there are inequivalent ligands at indium. Also, if the bridging ligand has a 2-fold symmetry element (either a C_2 axis or a mirror plane) which *could* be coincident with a potential equivalent axis in the M_2X_2 system, then we will probably observe a planar In_2X_2 ring. In this case, bending the In_2X_2 system will typically relieve interactions on the opened side of the ring and simultaneously increase interactions on the closed side of the ring. Thus, $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$,[7] $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$,[8] and $[(Me_3SiCH_2)_2InPPh_2]_2$[9] each have planar In_2P_2 or In_2As_2 rings.

The nonplanarity of $[(Me_3CCH_2)_2InSePh]_2$ has been explained above (note that the SePh ligand itself has no appropriate symmetry axis). Species with nonequivalent bridging ligands are more difficult to analyze. Thus, the InAsInCl ring in $(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2Cl$[8] is planar, whereas the InPInCl bridge in $(Me_3SiCH_2)_2InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl$[7] is bent. In this case it appears that the longer In–As vs In–P distances (In–As = 2.677 (1) Å; In–P = 2.601 (3)–2.605 (2) Å) reduce interactions about the InAsInCl ring, relative to the InPInCl ring, enabling it to remain planar. We should also note that extending these generalizations to Ga_2X_2 systems must also take into account the smaller radius of Ga(III) versus that of In(III).

Each selenium atom has one phenyl group bonded to it in the trans configuration. Some relevant distances are Se(3)–C(31) = 1.934 (9) Å and Se(4)–C(41) = 1.917 (9) Å, while the angles of interest are In(1)–Se(3)–C(31) = 107.1 (3)°, In(2)–Se(3)–C(31) = 103.7 (2)°, In(1)–Se(4)–C(41) = 107.2 (3)°, and In(2)–Se(4)–C(41) = 100.1 (3)°. The orientations of the phenyl selenide ligands can be seen in Figure 3. Each selenium atom has approximately sp^3

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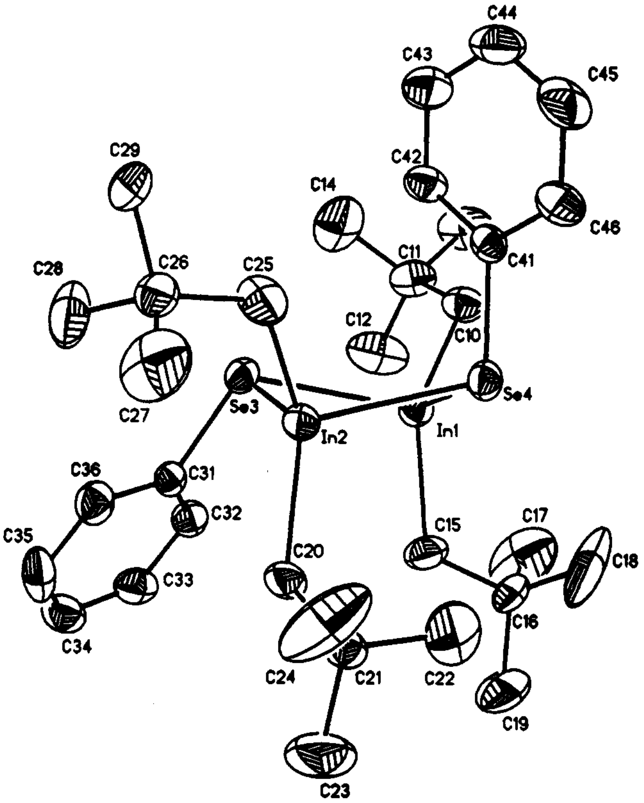

Figure 3. The $[(Me_3CCH_2]_2InSePh]_2$ molecule, showing the relative orientation of the μ-phenyl selenide ligands. (Only the major conformation of the methyl groups about C(26) is shown.)

hybridization, with the lone pairs of electrons occupying sites trans to one another across the ring. The planes defined by the two phenyl rings are mutually perpendicular.

Each indium atom is linked to two neopentyl ligands with In(1)–C(10) = 2.163 (10) Å, In(1)–C(15) = 2.169 (10) Å, In(2)–C(20) = 2.159 (9) Å, and In(2)–C(25) = 2.135 (11) Å. Interligand angles are C(10)–In(1)–C(15) = 131.8 (4)° and C(20)–In(2)–C(25) = 135.4 (4)°. These interligand angles are substantially smaller than in the chloro-bridged indium dimer $[(Me_3CCH_2)(Me_3SiCH_2)InCl]_2$, which has interligand angles of 148.1 (9)°.[6] This effect could be attributed to the difference in size of the bridging ligands. The phenyl selenide ligand is much more bulky than the chloride ion. Therefore, the larger the bridging ligand, the more steric repulsion between the bridging ligand and neopentyl ligands on the indium atoms.

The terminal methyl groups on the neopentyl ligands are associated with some rotational disorder. With an ordered model, there remained a large amount of residual electron density between adjacent carbon atoms of the terminal methyl groups, despite abnormally large "anisotropic thermal parameters" for these carbon atoms. This problem was particularly severe for that neopentyl ligand containing atoms C(25)–C(29). There were three large peaks on the electron density map corresponding to the three initially defined terminal carbon atoms, but there were also three smaller but significant peaks between these positions. This second set of peaks defined an alternate conformation of terminal methyl groups about C(26) of this neopentyl ligand. The three larger peaks were labeled as C(27), C(28), and C(29) while the three smaller peaks were labeled as C(27′), C(28′), and C(29′). These two sets of peaks were related to each other by an approximate 2-fold rotation about the C(25)–C(26) bond. Thus, there are six "partial atoms" arranged in a hexagon. Each atom of the minor component is approximately trans to an atom of the major component. Since the thermal ellipsoids should have approximately the same orientation, the six U_{ij}'s of the minor component were coupled to those of that major component trans to it. (Uncoupled refinement of these anisotropic thermal parameters proved not to be possible.) Bond lengths within the disordered neopentyl ligand are as follows: C(26)–C(27) = 1.43 (4) Å, C(26)–C(28) = 1.50 (3) Å, C(26)–C(29) = 1.54 (3) Å, C(26)–C(27′) = 1.44 (5) Å, C(26)–C(28′) = 1.48 (5) Å, and C(26)–C(29′) = 1.55 (3) Å. Angles at C(26) are C(27)–C(26)–C(28) = 109 (2)°, C(27)–C(26)–C(29) = 107 (2)°, C(28)–C(26)–C(29) = 104 (2)°, C(27′)–C(26)–C(28′) = 112 (3)°, C(27′)–C(26)–C(29′) = 113 (3)°, and C(28′)–C(26)–C(29′) = 108 (3)°. The use of this model led to statistically significant reductions in the discrepancy indices, with *R*(all data) being reduced from 8.85% to 8.35% and a corresponding reduction in the other indicators. Thermal parameters for carbon atoms of the major component in this neopentyl ligand were reduced by about 45%. The other three neopentyl ligands were associated with problems similar to those above, but alternate conformations of the terminal carbon atoms were not so obvious and these features were not further investigated. Disorder of the neopentyl ligands can be either static or dynamic, with both causing a smearing of the electron density. If the peaks are local minima in a dynamic rotation, we have the classical "hindered rotor" problem.

The cryoscopic molecular weight studies of $(Me_3CCH_2)_2InSePh$ in benzene solution and the NMR spectroscopic data are consistent with the presence of dimeric molecules in solution. Thus, the solid phase and a solution contain molecules of the same degree of association. The NMR spectral data are consistent either with the presence of the trans isomer in solution or with a rapidly equilibrating mixture of cis and trans isomers, as only one set of lines is observed for the methyl and methylene protons of the neopentyl groups and for the phenyl protons. Similar results were obtained for the ^{13}C NMR spectrum at room temperature. When a CD_2Cl_2 solution of $[(Me_3CCH_2)_2InSePh]_2$ was cooled to −80 °C, the lines broadened slightly. This change in the spectrum is probably indicative of an increase in the viscosity of the solvent rather than slowing of an exchange process.

Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or under a purified argon atmosphere. The starting compounds $In(CH_2CMe_3)_3$[10] and $In(SePh)_3$[4] were prepared and purified by literature methods. Solvents were dried by conventional procedures. Elemental analyses were performed by E + R Microanalytical Laboratory, Inc., Corona, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. The ^1H NMR spectra were recorded at 400 MHz by using a Varian VXR-400 S spectrometer or at 300 MHz by using a Varian Gemini-300 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to C_6H_6 at δ 7.15 ppm or CD_2Cl_2 at δ 5.32 ppm. The $^{13}C\{^1H\}$ NMR spectra were recorded at 75 MHz by using a Varian Gemini-300 spectrometer or at 101 MHz by using a Varian VXR-400 S instrument. The proton-decoupled ^{13}C spectra are reported relative to benzene at δ 128.0 ppm or CD_2Cl_2 at 53.8 ppm. All samples for NMR spectra were contained in sealed NMR tubes. Melting points were observed in sealed capillaries. Molecular weights were measured cryoscopically in benzene solution

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Table III. Experimental Data for the X-ray Diffraction Study on $[(Me_3CCH_2)_2InSePh]_2$

A. Crystal Data

molecular formula	$C_{32}H_{54}In_2Se_2$	volume	3725.4 (14) Å^3
		Z	4
cryst syst	monoclinic	fw	826.3
space group	$P2_1/c$	density (calc)	1.473 Mg/m^3
unit cell dimens	a = 18.973 (4) Å	abs coeff	2.995 mm^{-1}
	b = 10.105 (1) Å	F(000)	1648
	c = 19.998 (6) Å		
	β = 103.66 (2)°		

B. Data Collection

diffractometer used	Siemens R3m/V
radiation	Mo Kα (λ = 0.71073 Å)
temperature	298 K
monochromator	highly oriented graphite cryst
2θ range	5.0–45.0°
scan type	2θ–θ
scan speed	constant; 2.00°/min in ω
scan range (ω)	0.45° plus Kα separation
bkgd measmt	stationary cryst and stationary counter at beginning and end of scan, each for 25.0% of total scan time
std rflns	3 measd every 97 rflns
index ranges	$0 \le h \le 20$, $0 \le k \le 10$, $-21 \le l \le 20$
no. of reflns collected	5411
no. of indep rflns	4891 (R_{int} = 0.86%)
no. of obs rflns	2557 ($F > 6.0\sigma(F)$)
abs cor	semiempirical
min/max transmissn	0.4464/0.5698

C. Solution and Refinement

syst used	Siemens SHELXTL PLUS (VMS)
soln	direct methods
refinement method	full-matrix least squares
quantity minimized	$\sum w(F_o - F_c)^2$
H atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0016F^2$
no. of params refined	336
R indices (all data)	R = 8.35%, R_w = 6.43%
R indices (6.0σ)	R = 3.44%, R_w = 3.73%
goodness of fit	0.89
largest and mean Δ/σ	0.007, 0.003
data-to-param ratio	14.6:1
largest diff peak	0.66 e Å^{-3}
largest diff hole	−0.63 e Å^{-3}

using an instrument similar to that described by Shriver and Drezdzon.[11]

Synthesis of $(Me_3CCH_2)_2In(SePh)$. The reagents $In(CH_2CMe_3)_3$ (0.490 g, 1.49 mmol) and $In(SePh)_3$ (0.433 g, 0.743 mmol) were mixed in 20 mL of pentane and stirred at room temperature for 15 min. Removal of pentane provided a crude product, which was recrystallized in 20 mL of pentane at −30 °C. X-ray-quality crystals of $(Me_3CCH_2)_2In(SePh)$ (0.621 g, 1.50 mmol, 67.4% yield based upon $In(SePh)_3$) were obtained. Mp: 103.8–105.5 °C. Anal. Calcd for $C_{16}H_{27}InSe$: C, 46.51; H, 6.59. Found: C, 46.64; H, 6.65. ^{1}H NMR (C_6D_6): δ 1.12 (s, 18 H, $InCCCH_3$), 1.47 (s, 4 H, $InCH_2$), 6.94 (m, 3 H, *m*-H and *p*-H of Ph), 7.59 (m, 2 H, *o*-H of Ph). ^{1}H NMR (CD_2Cl_2): δ 0.99 (s, 18 H, $InCCCH_3$), 1.23 (s, 4 H, $InCH_2$), 7.22 (m, 3 H, *m*-H and *p*-H of Ph), 7.44 (m, 2 H, *o*-H of Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 33.1 ($InCH_2CMe$), 35.1 ($InCCCH_3$), 40.5 ($InCH_2$), 127.3 (*p*-C of Ph), 129.7 (*m*-C of Ph), 136.2 (*o*-C of Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 33.1 ($InCH_2CMe$), 34.9 ($InCCCH_3$), 40.4 ($InCH_2$), 127.2 (*p*-C of Ph), 129.7 (*m*-C of Ph), 136.1 (*o*-C of Ph). IR (Nujol mull): 1569 (m), 1431 (m), 1358 (m), 1293 (vw), 1232 (s, sh), 1112 (m), 1090 (m), 1065 (m), 1018 (m), 997 (m), 729 (vs), 701 (m), 684 (s), 661 (m), 588 (m), 460 (m), 447 (vw), 378 (vw) cm^{-1}. Cryoscopic molecular weight, formula weight 413.17 (observed molality, observed molecular weight, association): 0.0426, 800.1, 1.94; 0.0298, 797.8, 1.93; 0.0195, 852.3, 2.06.

Collection of X-ray Diffraction Data for $[(Me_3CCH_2)_2InSePh]_2$. The crystal selected for the diffraction study (dimensions 0.35 mm × 0.30 mm × 0.30 mm) was sealed into a thin-walled capillary under anaerobic conditions and was aligned on a Siemens R3m/V diffractometer. Details of the data collection appear in Table III.

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	U(eq)[a]
In(1)	2697 (1)	401 (1)	7394 (1)	68
In(2)	2117 (1)	2307 (1)	8779 (1)	64
Se(3)	2364 (1)	−344 (1)	8603 (1)	67
Se(4)	1915 (1)	2677 (1)	7390 (1)	71
C(10)	2139 (6)	−809 (11)	6541 (5)	88
C(11)	2203 (6)	−2304 (10)	6566 (6)	90
C(12)	2971 (7)	−2754 (12)	6875 (8)	148
C(13)	1934 (7)	−2866 (14)	5857 (7)	146
C(14)	1721 (9)	−2801 (12)	7027 (7)	153
C(15)	3800 (5)	1143 (12)	7680 (5)	94
C(16)	4158 (6)	1680 (13)	7139 (6)	93
C(17)	4238 (10)	599 (19)	6660 (10)	214
C(18)	3725 (9)	2693 (18)	6722 (11)	250
C(19)	4916 (8)	2093 (16)	7423 (8)	184
C(20)	3181 (5)	3052 (9)	9267 (5)	83
C(21)	3363 (6)	4489 (10)	9229 (6)	82
C(22)	3276 (12)	4951 (15)	8520 (8)	234
C(23)	4110 (9)	4794 (16)	9602 (9)	211
C(24)	2858 (11)	5273 (13)	9520 (12)	240
C(25)	1055 (5)	2502 (13)	8954 (6)	107
C(26)	923 (6)	2396 (11)	9659 (6)	79
C(27)	1156 (21)	3617 (34)	10001 (17)	190
C(28)	1290 (16)	1267 (33)	10092 (15)	156
C(29)	118 (11)	2238 (33)	9662 (12)	134
C(27′)	696 (33)	1034 (51)	9590 (28)	190
C(28′)	343 (26)	3285 (55)	9779 (23)	156
C(29′)	1607 (18)	2616 (58)	10250 (18)	134
C(31)	3271 (5)	−684 (8)	9261 (5)	60
C(32)	3835 (6)	−1268 (9)	9058 (5)	75
C(33)	4469 (6)	−1579 (10)	9561 (7)	92
C(34)	4510 (8)	−1319 (12)	10228 (8)	106
C(35)	3944 (9)	−766 (12)	10429 (6)	107
C(36)	3302 (7)	−445 (10)	9931 (6)	89
C(41)	910 (5)	2217 (10)	7090 (4)	66
C(42)	628 (6)	1024 (11)	7210 (5)	81
C(43)	−83 (8)	733 (16)	7007 (7)	121
C(44)	−552 (7)	1708 (20)	6665 (8)	128
C(45)	−276 (8)	2881 (17)	6538 (7)	128
C(46)	438 (6)	3140 (12)	6751 (6)	95

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The crystal belongs to the monoclinic system and crystallizes in the centrosymmetric space group $P2_1/c$ (space group No. 14), as indicated unequivocally by the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$.

Solution and Refinement of the Structure. All crystallographic calculations were carried out with the use of the Siemens SHELXTL PLUS[12] program set. The analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $i\Delta f$ components of anomalous dispersion.[13] The structure was solved by the use of direct methods. Abnormally large thermal parameters associated with the terminal carbon atoms of the neopentyl ligands were interpreted as due to some form of rotational disorder associated with the neopentyl ligands, as discussed above. Positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were not located directly but were input in calculated positions with d(C–H) = 0.96 Å[14] and with the appropriate staggered-tetrahedral geometry. The isotropic thermal parameter of each hydrogen was defined as equal to the U_{eq} value of that carbon atom to which it was bonded. Following refinement, the extreme features left on the difference-Fourier map were a peak of height 0.66 e Å^{-3} and a negative feature of −0.63 e Å^{-3}. Refinement of the model converged with R = 3.44%

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and R_w = 3.73% for 336 parameters refined against those 2557 reflections with $|F_o| > 6\sigma|F_o|$ and R = 8.35% for all data. Final atomic coordinates appear in Table IV.

Acknowledgment. This work was supported in part by the Office of Naval Research and by a generous grant from Eastman Kodak Co. Purchase of the Siemens R3m/V diffractometer was made possible by Grant 89-13733 from the Chemical Instrumentation Program of the National Science Foundation.

Supplementary Material Available: Tables of anisotropic thermal parameters and calculated positions for hydrogen atoms (3 pages). Ordering information is given on any current masthead page.

OM920114M

C–S Bond Cleavage at an Electrophilic Zirconium Center: Synthesis, Structure, and Thermal Decomposition of $[Cp_2Zr(S\text{-}t\text{-}C_4H_9)(THF)][BPh_4]$

Warren E. Piers,[*,†] Linda Koch,[†] Diane S. Ridge,[†] Leonard R. MacGillivray,[‡] and
Michael Zaworotko[‡]

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, Canada B3H 3C3

Received March 30, 1992

Summary: Protonolysis of $[Cp_2ZrCH_3(THF)][BPh_4]$ with *tert*-butyl mercaptan leads to the (thiolato)zirconocene cation $[Cp_2Zr(S\text{-}t\text{-}C_4H_9)(THF)][BPh_4]$ in 79% yield. In addition to the usual spectroscopic methods the complex was characterized by X-ray crystallography (monoclinic, $P2_1/c$, a = 10.111 (4) Å, b = 18.6066 (18) Å, c = 19.408 (7) Å, β = 94.31 (2)°, Z = 4, R = 0.036). Structural parameters and THF exchange rates point to a less electrophilic Zr center than in the parent alkyl species. Nevertheless, the center is electrophilic enough to induce C–S bond cleavage under thermal duress.

Introduction

Much attention has recently been directed toward d^0 group 4 metallocene alkyl cations of general formula $[Cp_2M(R)(B)][BAr_4]$, where Cp is a cyclopentadienyl donor, B is some stabilizing Lewis base, and the counterion is a noncoordinating tetraarylborate anion.[1] With the exception of alkoxides,[2] uninegative heteroatom-containing donors isoelectronic with hydrocarbyl ligands have not been used in place of R in $[Cp_2M(R)(B)][BAr_4]$. We are seeking convenient routes for incorporation of higher chalcogenato ligands (^-SR, ^-SeR, ^-TeR) into these cations to explore the reactivity of the resultant hard metal–soft element bonds. Herein we report our initial results on the synthesis and thermal decomposition of a *tert*-butyl mercaptan–zirconocene cation, 1a, which occurs by heterolytic cleavage of the alkanethiolato C–S bond, an important primary step in hydrosulfurization procedures.[3]

Experimental Section

General Considerations. All operations were performed under a purified argon atmosphere in a Braum MB-150 inert-atmosphere glovebox or on high-vacuum lines using standard techniques.[4] Solvents were purified as follows: toluene was distilled from sodium benzophenone ketyl and stored over "titanocene";[5] tetrahydrofuran (THF) was predried with activated (10^{-4} Torr, 200 °C, 3 h) 3-Å molecular sieves, distilled from and stored over sodium benzophenone ketyl; hexanes were distilled from lithium aluminum hydride (Aldrich) and stored over "titanocene"; dichloromethane was distilled from CaH_2; benzene-d_6 was dried sequentially over activated 3-Å sieves and "titanocene" and stored in the glovebox; other NMR solvents were dried analogously to the perprotio solvents. Unless otherwise mentioned, reagents were obtained from commercial suppliers and used as received. $Cp_2Zr(CH_3)_2$[6] was made by a published method and reacted with 2,6-di-*tert*-butylpyridinium tetraphenylborate (1:1 in THF) to obtain $[Cp_2Zr(CH_3)(THF)][BPh_4]$. Thiols (*stench!*) were dried, degassed, and stored over activated 3-Å molecular sieves and used only on the vacuum line or in a well-ventilated fume hood.

^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian Gemini 200 or Unity 400 instrument using Wilmad 528-PP NMR tubes. Variable-temperature NMR experiments were performed on samples sealed in 5-mm NMR tubes under ≈700 mm of argon purified by passing through activated 3-Å molecular seives and MnO on vermiculite. Microanalyses were performed by Onieda Research Services, Inc., One Halsey Rd., Whitesboro, NY 13492.

Synthesis of 2,6-Di-*tert*-butylpyridinium Tetraphenylborate. To a solution of 2,6-di-*tert*-butylpyridine (6.6 mL, 29.2 mmol) in 25 mL of methanol under nitrogen atmosphere was added 2.4 mL (29.2 mmol) of concentrated HCl. The solution was stirred for 15 min and diluted with 100 mL of deionized water. Solid $NaBPh_4$ (10.0 g, 29.2 mmol) was added in portions and the resulting slurry stirred for 2 h. The white product was isolated by filtration and washed twice with 50-mL portions of deionized water and dried in vacuo for 24 h. Yield: 13.4 g, 90%. ^1H NMR (200 MHz, CD_3CN, ppm): C–H_p, 8.34 (t, J = 8.4 Hz, 1 H); C–H_m, 7.82 (d, 2 H); $B(C_6H_5)_4$, 7.28 (m, 8 H, ortho), 6.99 (m, 8 H, meta), 6.83 (m, 4 H, para); $C(CH_3)_3$, 1.51 (s, 18 H); N–H, not observed.

Synthesis of $[Cp_2Zr(S\text{-}t\text{-}C_4H_9)(THF)][BPh_4]$ (1a). $[Cp_2Zr(CH_3)(THF)][BPh_4]$ (1.045 g, 1.69 mmol) was loaded into a 50-mL round-bottomed flask and attached to a swivel frit assembly equipped with a 90° needle valve adaptor. A 30-mL volume of dry dichloromethane was vacuum transferred into the vessel, and after dissolution of the methyl cation, the pale yellow solution was cooled to −78 °C. *tert*-Butyl mercaptan (0.19 mL, 1.69 mmol) was introduced via vacuum transfer from a graduated

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[†] University of Guelph.

[‡] Saint Mary's University.

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