5648 *Organometallics* **2004,** *23,* 5648−5651

Biphenylene-4,4′-diselenolate as a Molecular Bridge: Preparation and Characterization of [PdCl(P*n*Bu$_3$)$_2$Se-C$_6$H$_4$-C$_6$H$_4$-Se-PdCl(P*n*Bu$_3$)$_2$]

Andrew I. Wallbank, Martin J. Brown, Christian Nitschke, and
John F. Corrigan*

Department of Chemistry, The University of Western Ontario,
London, Ontario N6A 5B7, Canada

Received April 16, 2004

Summary: Biphenylene-4,4′-dilithiodiselenolate or biphenylene-4,4′-bis(trimethylsilylselenium) can be used to prepare the complex [PdCl(PnBu$_3$)$_2$SeC$_6$H$_4$C$_6$H$_4$SePdCl(PnBu$_3$)$_2$]. The dimer contains two trans-MCl(Se−)(PBu$_3$)$_2$ metal centers separated by a planar biphenylene moiety.

Introduction

The successful design and synthesis of new selenium reagents for the preparation of metal-selenolate (M-SeR) complexes has resulted in a rapid increase in development of this class of molecule.[1] The expansion of the chemistry of late transitional metal-selenolate complexes can be attributed in part to the interesting structural types obtained, due to the bridging ability of the heavier chalcogen element, and to the photophysical properties of these complexes, with strong luminescence behavior often observed.[2] 1,4-Phenylene-[3,4] and biphenylene-4,4′-diselenolate[4] and related reagents represent ideal candidates for the development of rigid dimeric, oligomeric, or even polymeric metal-selenolate structures with controlled architectures, yet their utility has not been described. This contrasts with the chemistry of the lighter congeners *para*-(poly)phenylene-thiolates, for which transition metal-based molecular[5] and surface chemistry[6] is actively being developed. A recent report has detailed the utility of biphenylene-4,4′-dithiolates as bridging ligands in Au(I) complexes.[7] Herein we report the details of the use of biphenylene-4,4′-diselenolates to link metal centers with the facile formation and properties of biphenylene-4,4′-diselenolate complexes of Pd(II), [PdCl(P*n*Bu$_3$)$_2$SeC$_6$H$_4$C$_6$H$_4$SePdCl(P*n*Bu$_3$)$_2$] (**2**) from 4,4′-LiSeC$_6$H$_4$C$_6$H$_4$SeLi (**1**), and the synthesis of the new silylated selenium reagents 4,4′-(Me$_3$Si)SeC$_6$H$_4$C$_6$H$_4$Se(SiMe$_3$) (**3**) and 1,4-Me$_3$SiSeC$_6$H$_4$-SeSiMe$_3$ (**4**).

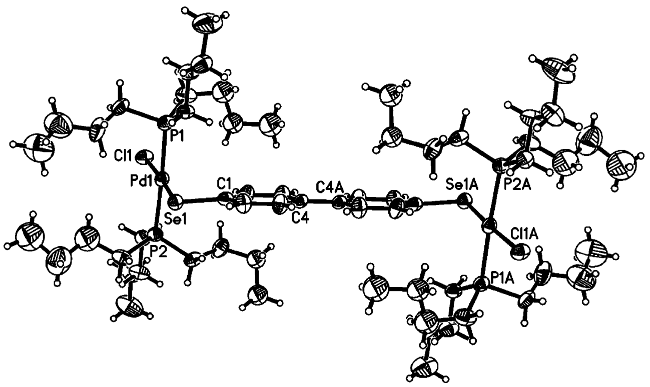

Figure 1. Molecular structure of [PdCl(P*n*Bu$_3$)$_2$SeC$_6$H$_4$C$_6$H$_4$SePdCl(P*n*Bu$_3$)$_2$] (**2**) illustrating the planar arrangement of the biphenylene unit. Thermal ellipsoids are drawn at the 25% probability level. The molecule resides about a crystallograhic inversion center relating the two halves of the molecule. Selected bond lengths (Å) and angles (deg): Pd1−P1 = 2.321(3), Pd1−P2 = 2.332(3); Pd1−Cl1 = 2.359(2); Pd1−Se1 = 2.4254(11), Se1−C1 = 1.901(9), C4−C4A = 1.46(2); P1−Pd1−P2 = 176.6(1), P1−Pd1−Cl1 = 87.91(8), P2−Pd1−Cl1= 92.22(8), P1−Pd1−Se1 = 91.41(7), P2−Pd1−Se1 = 88.15(7), Cl1−Pd1−Se1 = 174.80(9), C1−Se1−Pd1 = 104.6(3).

Results and Discussion

4,4′-LiSeC$_6$H$_4$C$_6$H$_4$SeLi (**1**) can be prepared via the insertion of 2 equiv of Se into the C−Li bonds of 4,4′-dilithiobiphenyl in tetrahydrofuran.[4] When suspensions of **1** in tetrahydrofuran are reacted with 2 equiv of *trans*-PdCl$_2$(P*n*Bu$_3$)$_2$ at room temperature, a gradual darkening of the reaction solutions from nearly colorless to red is observed. Removal of the solvent in vacuo and extraction of the red residue into pentane gives [PdCl(P*n*Bu$_3$)$_2$SeC$_6$H$_4$C$_6$H$_4$SePdCl(P*n*Bu$_3$)$_2$] (**2**) in good yields. The ^{1}H NMR spectrum of **2** in CDCl$_3$ displays, in addition to the aliphatic resonances of the PBu$_3$ ligands, a pair of doublets from the biphenylene at 7.65 ($J = 8.2$ Hz) and 7.14 ($J = 8.2$ Hz) ppm, and these are shifted downfield from those of the starting material **1**, which appear at 7.42 and 6.94 ppm in CD$_3$CN. Single crystals of **2** suitable for diffraction analysis can be obtained by cooling pentane solutions at −4 °C, and the molecular structure is illustrated in Figure 1. The structure

---

[1] (a) Englich, U.; Ruhlandt-Senge, K. *Coord. Chem. Rev.* **2000**, *210*, 135. (b) Arnold, J. *Prog. Inorg. Chem.* **1995**, *43*, 353. (c) Janssen, M. D.; Grove, D. M.; van Koten, G. *Prog. Inorg. Chem.* **1997**, *46*, 97.

[2] DeGroot, M. W.; Corrigan, J. F. In *Comprehensive Coordination Chemistry II: From Biology to Nanotechnology*; Fujita, M., Powell, A., Creutz, C., Eds.; Pergamon: Oxford, 2004; Vol. 7, p 57.

[3] de Boer, B.; Meng, H.; Perepichka, D. F.; Zheng, J.; Frank, M. M.; Chabal, Y. J.; Bao, Z. *Langmuir* **2003**, *19*, 4272.

[4] Engman, L.; Hellberg, J. S. E. *J. Organomet. Chem.* **1985**, *296*, 357.

[5] (a) Zhou, C.; Holm, R. H. *Inorg. Chem.* **1997**, *36*, 4066. (b) Ueyama, N.; Sugawara, T.; Nakamura, A.; Yamaguchi, K.; Fueno, T. *Chem. Lett.* **1988**, 223.

[6] Derosa, P. A.; Seminario, J. M. *J. Phys. Chem. B* **2001**, *105*, 471, and references therein.

[7] Ehlich, H.; Schier, A.; Schmidbaur, H. *Inorg. Chem.* **2002**, *41*, 3721.

10.1021/om049721n CCC: $27.50
Publication on Web 10/12/2004

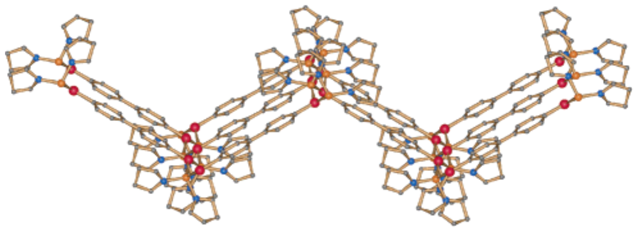

Figure 2. Projection of the "zigzag", sheetlike packing observed in 4,4′-$(C_4H_8O)_2LiSeC_6H_4C_6H_4SeLi(OC_4H_8)_2$ (**1**·$(thf)_4$) (Se: red; C: gray; O: blue; Li: orange).

consists of two distorted square planar *trans*-Pd(Cl)(Se)-$(PBu_3)_2$ centers linked by the biphenylene unit. The two phenylene rings in **2** are strictly coplanar, with a C4−C4A bond length of 1.46(2) Å between the two rings, which is comparable to the corresponding carbon−carbon bond length in **1** (1.49(1) Å, vide infra). The Pd−Se bond lengths in **2** of 2.425(1) Å are typical for palladium-selenolate complexes, *trans* to a chloride ligand.[8] Complex **2** represents the first structurally characterized transition metal complex containing the biphenylene-4,4′-diselenolate unit. The two P_2PdCl centers are slightly rotated out of the plane containing the biphenylene fragment, each unit being rotated 16.5° in opposite directions from this plane, with the terminal metal centers adopting an *anti* configuration with respect to each other. This arrangement appears to minimize the repulsions between the PBu_3 ligands and the aromatic spacer. The selenium atoms are themselves displaced from the plane of the biphenylene fragment, with C4···C1−Se1/C4A···C1A−Se1A angles equal to 174.1°. The overall arrangement in **2** is related to that observed in the gold-thiolate complex [4,4′-$(Cy_3P)AuSC_6H_4C_6H_4SAu(PCy_3)$] as reported by Schmidbaur and co-workers.[7]

The coplanarity of the two aromatic rings in **2** is consistent with the solid state structure of the starting reagent **1**,[4] which can be isolated as single crystals as 4,4′-$(C_4H_8O)_2LiSeC_6H_4C_6H_4SeLi(OC_4H_8)_2$ by layering dilute THF solutions with hexane. The molecular structure (Figure 2) of **1**·$(thf)_4$ illustrates that the phenyl rings are (crystallographically) coplanar, with Se(1)−C(1) = 1.905(6) Å. Each selenium center is symmetrically bonded to two tetrahedral lithium ions (Se−Li = 2.616(9) and 2.624(9) Å) to yield a "zigzag" polymeric sheet network.

Although often difficult to prepare, the solubility of $RSeSiMe_3$ reagents in common organic solvents can offer an advantage over using the related alkali metal-selenolates for M−Se bond formation. Silylation of **1** with Me_3SiCl affords 4,4′-$(Me_3Si)SeC_6H_4C_6H_4Se(SiMe_3)$ (**3**), which, in addition to the expected functionalization of the Se centers, possesses a non-coplanar arrangement of the two aromatic rings, with a dihedral angle of 29° between them (Figure 3). The reaction of the bis-selenolate salt 1,4-$Li_2[Se_2C_6H_4]$[3,4] leads similarly to the formation of the substituted phenylene 1,4-$Me_3SiSeC_6H_4SeSiMe_3$ (**4**) in good yield. Single-crystal X-ray analyses (Figures 3, 4) confirm Se−Si bond formation for both **3** and **4**, and these substituted phenylene complexes represent rare examples of Me_3SiSe-*spacer*-$SeSiMe_3$ reagents.[9,10] The silylated sulfur complexes 1,4-$Me_3SiSC_6H_4SSiMe_3$ and 4,4′-$Me_3SiSC_6H_4C_6H_4SSiMe_3$ have been used for the preparation of sulfur-based polymers.[11]

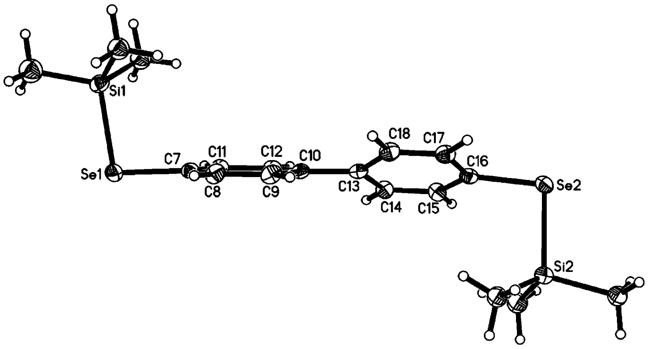

Figure 3. Molecular structure of 4,4′-$Me_3SiSeC_6H_4C_6H_4SeSiMe_3$, **3**. Thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths (Å) and angles (deg): Se1−C7 = 1.932(3), Se1−Si1 = 2.2976(9), Se2−C16 = 1.921(3), Se2−Si2 = 2.3041(9), C10−C13 = 1.483(4); C7−Se1−Si1 = 97.54(8), C16−Se2−Si2 = 95.67(8).

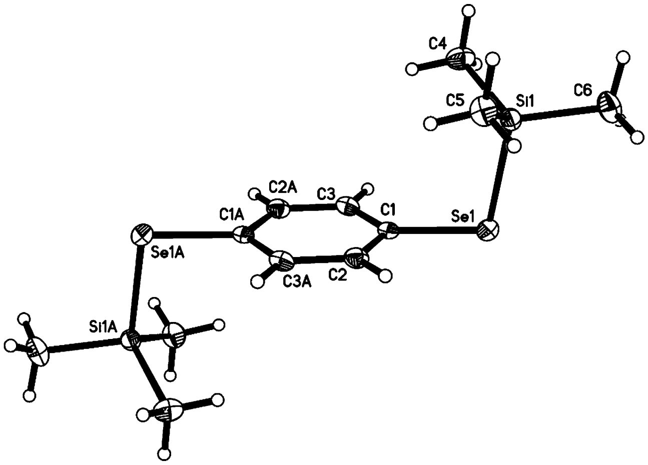

Figure 4. Molecular structure of 1,4-$Me_3SiSeC_6H_4SeSiMe_3$ (**4**), which resides about a crystallographic inversion center. Thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths (Å) and angles (deg): Se1−C1 = 1.931(3), Se1−Si1 = 2.297(1), Se2−C16 = 1.921(3); C1−Se1−Si1 = 97.05(9).

Although the Se−Si linkage in $RSeSiMe_3$ is prone to hydrolysis[12] and these complexes require rigorous inert atmosphere handling conditions, the homogeneous reaction solutions obtainable with this class of reagent have proven to be invaluable for the low-temperature synthesis of nanometer sized metal-selenium clusters when reacted with metal salts, M−X.[2,13] Similarly, solutions of *trans*-$PdCl_2(PnBu_3)_2$ react smoothly with **3** at room temperature to yield **2** quantitatively, as determined by NMR spectroscopy, via the formation of 2 equiv of $ClSiMe_3$. We are currently developing the general reaction chemistry of **3** and **4** for the preparation of dimeric and oligomeric metal-selenolate complexes.

---

(8) Oilunkaniemi, R.; Laitinen, R. S.; Ahlgren, M. *J. Organomet. Chem.* **2001**, *623*, 168.

(9) Wallbank, A. I.; Corrigan, J. F. *Chem. Commun.* **2001**, 377.

(10) Wallbank, A. I., Corrigan, J. F. *Can. J. Chem.* **2002**, *80*, 1592.

(11) Hara, A.; Oishi, Y.; Kakikoto, M.; Imai, Y. *J. Polym. Sci. A* **1991**, *29*, 1933.

(12) Detty, M. R.; Seidler, M. D. *J. Org. Chem.* **1981**, *46*, 1283.

(13) Dehnen, S.; Eichhöfer, A.; Fenske, D. *Eur. J. Inorg. Chem.* **2002**, *2*, 279.

Table 1. Crystallographic Data for 1−4

	1	**2**	**3**	**4**
chemical formula	$C_{28}H_{40}Li_2O_4Se_2$	$C_{60}H_{116}Cl_2P_4Pd_2Se_2$	$C_{18}H_{26}Se_2Si_2$	$C_{12}H_{22}Se_2Si_2$
fw	612.40	1403.0	456.5	380.40
temp (K)	200	200	200	200
diffractometer	Kappa CCD	STOE IPDS	Kappa CCD	Kappa CCD
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
space group	*Pbca*	*P*2(1)/*c*	$P\bar{1}$	$P\bar{1}$
a (Å)	9.1234(8)	12.057(1)	8.6351(2)	6.1838(2)
b (Å)	15.8433(9)	23.410(2)	10.2727(3)	7.0703(3)
c (Å)	20.255(2)	12.794(1)	13.1572(4)	10.3448(4)
α (deg)			81.049(1)	70.874(2)
β (deg)		91.91(1)	74.277(1)	88.268(2)
γ (deg)			74.535(2)	85.682(2)
V (Å^3)	2927.8(4)	3609.2(5)	1078.40(5)	426.10(3)
Z	4	2	2	1
μ (mm^{-1})	2.555	1.701	3.535	4.457
$2\theta_{max}$ (deg)	49.0	50.0	55.1	54.9
no. of reflns collected	3757	12 276	14 238	4668
no. of indep reflns (R_{int})	2128 (0.063)	6129 (0.11)	4941 (0.043)	1936 (0.054)
R indices $[(I)>2\sigma(I)]^a$	0.0547	0.0615	0.0384	0.0396
wR_2	0.1140	0.108	0.0787	0.0929
GoF	0.964	0.859	1.024	1.063

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = \sum[w(F_o^2 - F_c^2)^2/\sum[wF_o^2]^2]^{1/2}$.

Experimental Section

All synthetic and handling procedures were carried out under an atmosphere of high-purity dried nitrogen using standard double manifold Schlenk line techniques and gloveboxes. Solvents were dried and collected using an MBraun MB-SP Series solvent purification system. Chloroform-*d* was dried and distilled over P_2O_5, and C_6D_6 was distilled over a sodium−potassium alloy. NMR spectra [^{1}H (399.763 MHz), ^{13}C{^{1}H} (100.522 MHz), ^{77}Se{^{1}H} (76.217 MHz)] were recorded on a Varian Inova 400 NMR spectrometer. ^{1}H and ^{13}C NMR chemical shifts were referenced internally to $SiMe_4$ using the residual proton and carbon signal of the deuterated solvent. ^{77}Se{^{1}H} spectra were referenced to the external standards Me_2Se and using $PhSeSiMe_3$ as a secondary reference. Ultraviolet−visible spectroscopy was performed on a Varian Cary 100 spectrometer.

Synthesis of 1[4] and 3. *t*-BuLi (1.7 M, 15.1 mL, 25.7 mmol) was added dropwise to a solution of 4,4-dibromobiphenyl (2 g, 6.41 mmol) in THF (30 mL) at −78 °C. The resultant yellow-orange suspension was stirred, slowly returning to room temperature, to yield a white suspension. Selenium powder (1.0 g, 12.7 mmol) was added portionwise over 1 h at room temperature, and the resultant pale yellow suspension was stirred for 3 h, after which time the solvent was removed in vacuo from the crude THF suspension of **1**, which was used as is for subsequent reactions. Silylation: the flask with **1** was covered with aluminum foil and diethyl ether (50 mL) and chlorotrimethylsilane (1.65 mL, 13.0 mmol) were added. The suspension was heated to reflux for 3 h. Pentane (100 mL) was then added to cooled solutions of **3**, and the suspension was filtered. The filtrate was dried in vacuo to yield **3** as an off-white solid (75% yield, based on Se). Crystals suitable for X-ray crystallography and elemental analysis were obtained by cooling solutions to −20 °C. Data for **3**: NMR *δ* (C_6D_6): ^{1}H, 7.62 (d, $^3J = 8.3$ Hz, 4H), 7.16 (d, $^3J = 8.3$ Hz, 4H), 0.29 (s, 18 H); ^{13}C{^{1}H}, 138.4 (*C*-C), 127.0 (*C*-H), 121.7 (*C*-Se), 1.49 (Si-*C*H$_3$); ^{77}Se{^{1}H}, +76.0 ppm. Anal. Calcd for $C_{18}H_{26}Se_2Si_2$: C, 47.36; H, 5.74. Found: C, 47.36; H, 6.04.

Synthesis of 2. To a suspension of **1** (0.032 g, 0.0516 mmol) in tetrahydrofuran (15 mL) was added *trans*-$PdCl_2(PnBu_3)_2$ (0.050 g, 0.0859 mmol). The resulting suspension in a red mother liquor was allowed to stir overnight. Removal of the solvent under reduced pressure left a red-colored solid **2**. Extraction into pentane and cooling at −4 °C yielded X-ray quality **2**. Yield: 0.051 g (88%). Data for **2**: NMR *δ* ($CDCl_3$): ^{1}H, 7.65 (d, $^3J = 8.2$ Hz, 4H), 7.14 (d, $^3J = 8.2$ Hz, 4H), 1.86 (m, 24H), 1.44 (m, 24H), 1.34 (m, 24H), 0.87 (t, $^3J = 7.0$ Hz, 36H); ^{31}P{^{1}H}, 6.9 (s); ^{77}Se{^{1}H}, 107.8 (s) ppm. UV−vis: λ_{max} 500 nm (ϵ 1240 M^{-1} cm^{-1}). Anal. Calcd for $C_{60}H_{116}Cl_2P_4Pd_2Se_2$: C, 51.36; H, 8.33. Found: C, 51.45; H, 8.09.

Synthesis of 4 from $Li_2Se_2C_6H_4$.[4] *t*-BuLi (1.7 M, 20 mL, 34 mmol) was added dropwise to a solution of *para*-dibromobenzene (2.0 g, 8.5 mmol) in THF at −78 °C. The resultant yellow-orange suspension was stirred, slowly returning to room temperature until the color of the suspension changed from yellow-orange to finally white. Se powder (1.34 g, 17.0 mmol) was added portionwise over 1 h at room temperature and the yellow suspension stirred for 3 h. The solvent was then removed in vacuo and the flask covered with aluminum foil. Diethyl ether (50 mL) followed by $ClSiMe_3$ (2.15 mL, 17 mmol) were added, and the mixture was refluxed for 3 h. The solvent was removed in vacuo and replaced with 75 mL of pentane. The suspension was filtered and the solvent removed to yield a pasty off-white solid in 60% yield. Single crystals suitable for X-ray analysis were obtained by slow cooling pentane solutions. Data for **4**: NMR *δ* (C_6D_6): ^{1}H, 7.37 (s, 4H), 0.20 (s, 18H); ^{13}C{^{1}H}, (C_6D_6) 137.5 (*C*H), 124.8 (*C*Se), 1.38 (Si-*C*H$_3$); ^{77}Se{^{1}H}, 78 ppm. Anal. Calcd for $C_{12}H_{22}Se_2Si_2$: C, 37.89; H, 5.83. Found: C, 37.95; H, 5.77.

X-ray Crystallography. Crystals were mounted immersed in mineral oil and placed in a cold stream of N_2 during data collection. A single crystal suitable for X-ray analysis was mounted on a glass fiber. X-ray structural analyses were carried out on an Enraf-Nonius KappaCCD single-crystal X-ray diffractometer running COLLECT (Nonius, 1998) software using Mo Kα radiation with a graphite filter (complexes **1**, **3**, and **4**) or on a STOE IPDS diffractometer equipped with an imaging plate area detector and a rotating anode generator (complex **2**). Crystal data, data collection parameters, and analysis statistics for **1**−**4** are listed in Table 1. Data were corrected for Lorentz and polarization effects. The SHELXTL (G. M. Sheldrick, Madison, WI, v. 5.1) program package was used to solve and refine the structures. The weighting scheme employed was of the form $w = 1/[\sigma^2(F_{obs}^2) + (\alpha P)^2 + \beta P]$ (α, *β* = refined variables, $P = {}^1/_3\max(F_{obs}^2, \theta) + (2/3)F_c^2$).

Acknowledgment. We gratefully acknowledge the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Academic Development

Fund (UWO) for funding support. A.I.W. thanks the Government of Ontario for scholarship support.

Supporting Information Available: Tables giving crystallographic data including a full listing of bond lengths and angles for **1**−**4** are available free of charge via the Internet at http://pubs.acs.org.

OM049721N