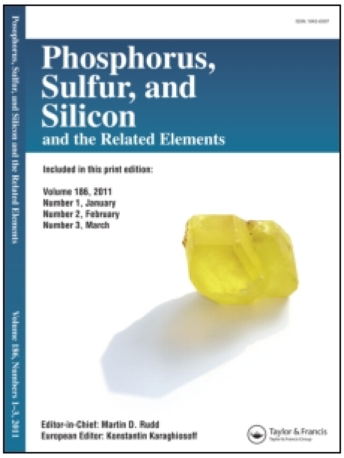


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Bridge Cleavage Reactions of Dinuclear Diselenolenes: Preparation of Palladium Complexes of Novel Chelating Selenolato/Selenide Ligands, $[PdX(Se\{R'\}C_nH_{2n-4}Se)(PR_3)](n = 6, 7, 8; R = Ph, Bu; X = Br, I; R' = Me, Et, etc.)$

Christopher P. Morley[a]; Christopher D. Jones[a]; Christopher A. Webster[a]; Massimo Di Vaira[b]
[a] Department of Chemistry, University of Wales Swansea, Singleton Park, Swansea, United Kingdom [b] Dipartimento di Chimica, Università degli Studi di Firenze, Sesto Fiorentino (FI), Italy

To cite this Article Morley, Christopher P. , Jones, Christopher D. , Webster, Christopher A. and Vaira, Massimo Di(2005) 'Bridge Cleavage Reactions of Dinuclear Diselenolenes: Preparation of Palladium Complexes of Novel Chelating Selenolato/Selenide Ligands, $[PdX(Se\{R'\}C_nH_{2n-4}Se)(PR_3)](n = 6, 7, 8; R = Ph, Bu; X = Br, I; R' = Me, Et, etc.)$', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 3, 801 — 813
To link to this Article: DOI: 10.1080/10426500590906292
URL: http://dx.doi.org/10.1080/10426500590906292

Phosphorus, Sulfur, and Silicon, 180:801–813, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500590906292

Taylor & Francis
Taylor & Francis Group

Bridge Cleavage Reactions of Dinuclear Diselenolenes: Preparation of Palladium Complexes of Novel Chelating Selenolato/Selenide Ligands, [PdX(Se{R′}C_nH_{2n-4}Se)(PR_3)](n = 6, 7, 8; R = Ph, Bu; X = Br, I; R′ = Me, Et, etc.)

Christopher P. Morley
Christopher D. Jones
Christopher A. Webster
Department of Chemistry, University of Wales Swansea, Singleton Park, Swansea, United Kingdom

Massimo Di Vaira
Dipartimento di Chimica, Università degli Studi di Firenze, Sesto Fiorentino (FI), Italy

The dinuclear palladium diselenolenes [$Pd_2(Se_2C_nH_{2n-4})_2(PR_3)_2$] react with haloalkanes, via *electrophilic attack at the bridging selenium atoms, to yield the neutral mononuclear square planar palladium(II) complexes [PdX(Se{R′}C_nH_{2n-4}Se)(PR_3)] (n = 6, 7, 8; R = Ph, Bu; X = Br, I; R′ = Me, Et, etc.), containing a novel chelating selenolato/selenide ligand, in which the alkylated selenium and halogen donor atoms occupy* cis-*positions. The products have been characterised by mass spectrometry and multinuclear NMR spectroscopy; the molecular structure of the compound with n = 8, R = Ph, R′ = Et has been determined by X-ray crystallography.*

Keywords Diselenolene; palladium; selenium; X-ray

INTRODUCTION

Although the electrochemical and photophysical properties of transition metal dithiolenes have been thoroughly explored over the last

---

Received January 28, 2004; accepted October 7, 2004.

We thank Joanna Leek for experimental assistance, Johnson Matthey plc for the loan of palladium and platinum salts, and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica for financial support to Massimo Di Vaira.

Address correspondence to Christopher P. Morley, University of Wales Swansea, Department of Chemistry, Swansea, Singleton Park, Swansea SA2 8PP, United Kingdom. E-mail: c.p.morley@swam.ac.uk

30 years, their chemistry is less well studied.[1] In the most extensive study to date, Kajitani et al. have shown in a series of papers that cyclopentadienylcobalt and -rhodium dithiolenes react with a variety of reagents, via addition either to the metal, or to the metal-chalcogen bond.[2] Metal bis(dithiolenes) additionally may yield products in which the added reagent bridges between two sulfur atoms on different ligands.[3]

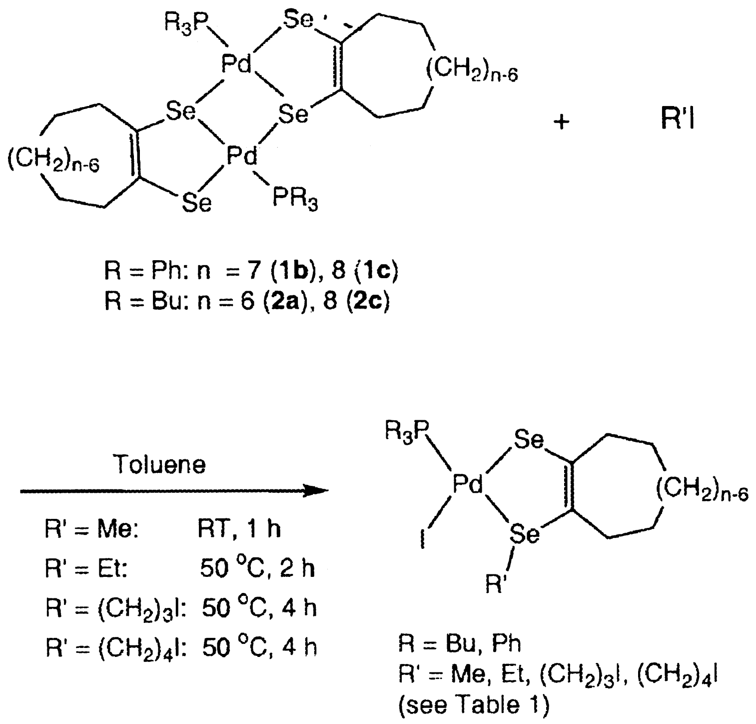
The selenium analogues of dithiolenes (*diselenolenes*) are comparatively rare, and even fewer chemical studies of their reactivity have been undertaken. Mizobe et al. showed that a cyclopentadienyliridium diselenolene reacted with the electron-deficient alkyne DMAD ($MeO_2CC{\equiv}CCO_2Me$) to yield the expected addition product, whose X-ray crystal structure was determined.[4] We have obtained spectroscopic evidence for similar behaviour by a bis(phosphine)platinum diselenolene.[5]

We recently have reported that palladium diselenolenes may be readily prepared from Pd(0) phosphine complexes, using cyloalkeno-1,2,3-selenadiazoles or bis(cycloalkeno)-1,4-diselenins as the selenium-containing precursors.[6–8] Bridging chalcogen atoms in dinuclear metal complexes are known to be highly nucleophilic.[9] Our investigations of the reactivity of dinuclear palladium diselenolenes therefore have begun with the study of their reactions with simple electrophiles such as alkyl halides, and the results are reported in this article.

RESULTS AND DISCUSSION

The representative dinuclear palladium diselenolenes **1b**, **c** and **2a**, **c** all react cleanly with an excess of iodomethane or -ethane in toluene solution, via alkylation of the bridging selenium atom and coordination of the iodide, to form the yellow-brown or orange mononuclear compounds $[PdI(Se\{R'\}C_nH_{2n-4}Se)(PR_3)]$, **3b**, **c**, **4b**, **c**, **5a**, **c** and **6c** (Scheme 1 and Table I) in virtually quantitative yield. The products are neutral complexes of palladium(II) containing a novel chelating selenolato/selenide ligand. The three-coordinate selenium atom and the iodide occupy cis-positions in the square planar coordination sphere, so that the geometry at palladium is comparable with that in the starting materials.

Apart from those resonances due to the additional alkyl group, the ^1H and ^{13}C NMR spectra of the products (Tables II–V) resemble those of the parent dinuclear diselenolenes, as the carbon atoms of the alicyclic ring, and the pairs of hydrogen atoms bound to them all remain



SCHEME 1 Preparation of mononuclear palladium complexes.

inequivalent. There are only small differences in chemical shifts, the most significant of which relates to the carbon atoms in the α-position and the C=C double bond. The carbon skeleton thus appears to be relatively insensitive to the changes in bonding at selenium (Se-C cf. Se-Pd) and palladium (Pd-I cf. Pd-Se).

TABLE I Compound Numbering Scheme for [PdI(Se{R′}C$_n$H$_{2n-4}$Se)(PR$_3$)]

R	R′	n = 6	n = 7	n = 8
Ph	CH_3	—	**3b**	**3c**
	CH_2CH_3	—	**4b**	**4c**
Bu	CH_3	**5a**	—	**5c**
	CH_2CH_3	—	—	**6c**
	$(CH_2)_3I$	—	—	**7c**
	$(CH_2)_4I$	—	—	**8c**

TABLE II ^{1}H NMR Spectroscopic Data[a] for 3b,c, 4b,c in $CDCl_3$ Solution

	3b	**3c**	**4b**	**4c**
m-C_6H_5	7.69 (m)	7.70 (m)	7.69 (m)	7.70 (m)
o, *p*-C_6H_5	7.48–7.37 (m)	7.49–7.39 (m)	7.48–7.38 (m)	7.48–7.39 (m)
α–CH_2	2.46 (m, 2H) 2.40 (m, 2H)	2.48 (m, 3H) 2.28 (m, 1H)	2.51 (m, 2H) 2.38 (m, 2H)	2.57 (m, 1H), 2.47 (m, 2H) 2.19 (m, 1H)
β-CH_2	1.50 (m)	1.47 (m)	1.52 (m)	1.49 (m)
γ-CH_2	1.76 (m)	1.60 (m)	1.79 (m)	1.60 (m)
CH_2 (R′)	—	—	3.45 (m), 3.21 (m)	3.45 (m), 3.24 (m)
CH_3 (R′)	2.71 (d)[b]	2.74 (d)[b]	1.58 (t)[c]	1.54 (t)[c]

[a] Chemical shift (δ) in ppm (multiplicity, relative intensity). Abbreviations: m = multiplet; d = doublet; t = triplet.

[b] $^4J(^1H\text{-}^{31}P) = 3.9$ Hz.

[c] $^3J(^1H\text{-}^1H) = 7.3$ Hz.

In **4b**, **c** and **6c** the two hydrogen atoms of the ethyl group are diastereotopic, as the alkylated selenium atom is an asymmetric center. They thus give rise to separate multiplets in the ^{1}H NMR spectrum.

TABLE III ^{1}H NMR Spectroscopic Data[a] for 5a, c, 6c, 7c in $CDCl_3$ Solution

	5a	**5c**	**6c**	**7c**
CH_2P	2.02 (m)	1.99 (m)	2.00 (m)	2.01 (m)
$CH_3CH_2CH_2$	1.49–1.37 (m)	1.51–1.39 (m)	1.52–1.36 (m)	1.52–1.36 (m)
CH_3	0.91 (t)[b]	0.91 (t)[b]	0.90 (t)[b]	0.91 (t)[b]
α-CH_2	2.56 (m, 2H) 2.31 (m, 2H)	2.60 (m, 2H) 2.48 (m, 2H)	2.60 (m, 2H) 2.48 (m, 1H), 2.20 (m, 1H)	2.59 (m, 2H) 2.41 (m, 1H), 2.22 (m, 1H)
β-CH_2	1.70–1.50 (m)	1.68 (m, 2H) 1.57 (m, 2H)	1.69 (m, 2H) 1.56 (m, 2H)	1.69 (m, 2H) 1.59 (m, 2H)
γ-CH_2	—	1.51–1.39 (m)	1.52–1.36 (m)	1.52–1.36 (m)
CH_2 (R′)	—	—	3.28 (m, 1H), 3.12 (m, 1H)	3.34–3.15 (m, 4H) 2.22 (m, 2H)
CH_3 (R′)	2.56 (d)[c]	2.56 (d)[c]	1.42 (t)[d]	—

[a] Chemical shift (δ) in ppm (multiplicity, relative intensity). Abbreviations: m = multiplet; d = doublet; t = triplet.

[b] $^3J(^1H\text{-}^1H) = 7.1$ Hz.

[c] $^4J(^1H\text{-}^{31}P) = 3.7$ Hz.

[d] $^3J(^1H\text{-}^1H) = 7.3$ Hz.

TABLE IV ^{13}C NMR Spectroscopic Data (δ, ppm) for 3b, c, 4b, c in $CDCl_3$ Solution

	3b	**3c**	**4b**	**4c**
$m\text{-}C_6H_5$	135.0[a]	135.0[a]	134.9[a]	134.9[a]
$p\text{-}C_6H_5$	130.8[b]	130.8[b]	130.7[b]	130.7[b]
$o\text{-}C_6H_5$	128.1[c]	128.0[c]	128.0[c]	128.0[c]
$ipso\text{-}C_6H_5$	130.7[d]	130.7[d]	130.7[d]	130.8[d]
$C{=}C$	149.6[e]	147.8[e]	151.9[e]	149.8[e]
	127.5[f]	126.7[f]	124.8[f]	124.1[f]
$\alpha\text{-}CH_2$	37.2	34.9	37.5	35.1
	37.0	34.5	37.3	34.6
$\beta\text{-}CH_2$	27.3	26.2	27.0	26.3
	26.3	25.9	26.5	25.9
$\gamma\text{-}CH_2$	32.7	30.2	32.8	30.2
	—	29.9	—	29.9
CH_2 (R′)	—	—	29.6	29.5
CH_3 (R′)	16.2[g]	16.5[g]	15.8	15.9

[a] $^3J(^{13}C\text{-}^{31}P) = 11.2$ Hz.
[b] $^4J(^{13}C\text{-}^{31}P) = 2.5$ Hz (**3b**, **3c**, **4b**), not resolved (**4c**).
[c] $^2J(^{13}C\text{-}^{31}P) = 10.8$ Hz.
[d] $^1J(^{13}C\text{-}^{31}P) = 49.8$ Hz.
[e] $^3J(^{13}C\text{-}^{31}P) = 10.7$ Hz (**3b**, **4b**), not resolved (**3c**, **4c**).
[f] $^3J(^{13}C\text{-}^{31}P) = 3.0$ Hz (**3b**), not resolved (**3c**, **4b**, **4c**).
[g] $^3J(^{13}C\text{-}^{31}P) = 2.6$ Hz (**3c**), not resolved (**3b**).

There is a small upfield shift of the ^{31}P resonance of the triphenylphosphine ligand between analogous starting material and product (e.g. 30.4 ppm (**1c**) vs. 24.4 ppm (**3c**)), and for the tributylphosphine complexes the shift is slightly downfield (e.g. 9.6 ppm (**2c**) vs. 12.7 ppm (**5c**)). In the ^{77}Se NMR spectra more dramatic changes are observed (Table VI). As in the starting materials, the three-coordinate selenium nucleus always resonates significantly upfield of the two-coordinate one. The precise chemical shift of the former is, however, strongly dependent on the nature of the alkyl group, whereas that of the latter is relatively invariant for a given tertiary phosphine.

Coupling of both resonances to ^{31}P is observed. The *trans*-coupling constant (for the three-coordinate ^{77}Se) is the same for both series of tertiary phosphine complexes and its value (180 Hz) is higher than that in either **1** or **2**. As expected, the cis-coupling constant (for the two-coordinate ^{77}Se) is much smaller: In the triphenylphosphine series $^2J(^{31}P\text{-}^{77}Se_{cis}) = 26$ Hz; the corresponding cis-coupling to tributylphosphine could not be resolved, implying $^2J(^{31}P\text{-}^{77}Se_{cis}) < 3$ Hz in this case.

TABLE V ^{13}C NMR Spectroscopic Data (δ, ppm) for 5a, c, 6c, 7c in CDCl$_3$ Solution

	5a	**5c**	**6c**	**7c**
$C\mathrm{H_2P}$	25.0[a]	25.0[a]	24.9[a]	25.0[a]
$C\mathrm{H_2CH_2P}$	24.0[b]	24.1[b]	24.1[b]	24.1[b]
$\mathrm{CH_3}C\mathrm{H_2CH_2}$	26.4	26.5	26.4	26.4
$C\mathrm{H_3}$	13.6	13.7	13.7	13.8
$C{=}C$	141.8[c]	146.4[c]	148.2[c]	148.5[c]
	123.7[d]	125.6[d]	123.2[d]	123.6[d]
α-$C\mathrm{H_2}$	34.0	35.7	35.7	35.7
	32.2	34.1	34.2	34.2
β-$C\mathrm{H_2}$	22.4	26.2	26.3	26.3
	21.9	25.9	25.8	25.9
γ-$C\mathrm{H_2}$	—	30.2	30.2	30.2
	—	30.0	30.0	30.1
$C\mathrm{H_2}$ (R′)	—	—	28.8	34.6
	—	—	—	29.8
	—	—	—	34.0
$C\mathrm{H_3}$ (R′)	14.8[e]	15.6[e]	15.5	—

[a] $^{1}J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 29$ Hz.
[b] $^{2}J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 14$ Hz.
[c] $^{3}J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 9$ Hz.
[d] $^{3}J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 2$ Hz (**5a**), not resolved (**5c**, **6c**, **7c**).
[e] $^{3}J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 2$ Hz (**5a**), not resolved (**5c**).

The molecular formula of the products have been established by mass spectrometry (Table VII). The spectra for the two series of complexes were obtained using different ionisation methods: Fast Atom Bombardment (FAB) worked best for the tributylphosphine complexes, and

TABLE VI ^{31}P and ^{77}Se NMR Spectroscopic Data for 3b, c, 4b, c, 5a, c, 6c, 7c in CDCl$_3$ Solution

	$\delta(^{31}\mathrm{P})$, ppm	$\delta(^{77}\mathrm{Se_{trans}})$, ppm	δ $(^{77}\mathrm{Se_{cis}})$, ppm
3b	25.3[a,b]	409[a]	666[b]
3c	24.4[a,b]	387[a]	662[b]
4b	24.8[a,b]	533[a]	666[b]
4c	23.7[a,b]	509[a]	664[b]
5a	13.2[a,c]	409[a]	542[c]
5c	12.7[a,c]	400[a]	562[c]
6c	11.9[a,c]	518[a]	563[c]
7c	12.1[a,c]	Not recorded	Not recorded

[a] $^{2}J(^{31}\mathrm{P}\text{-}^{77}\mathrm{Se_{trans}}) = 180$ Hz.
[b] $^{2}J(^{31}\mathrm{P}\text{-}^{77}\mathrm{Se_{cis}}) = 26$ Hz.
[c] $^{2}J(^{31}\mathrm{P}\text{-}^{77}\mathrm{Se_{cis}})$ not resolved.

TABLE VII Mass Spectrometric Data[a] for 3b, c, 4b, c, 5a, c, 6c, 7c

	Method[b]	$[M]^+$	$[M{-}I]^+$	Other ions
3b	FAB	No ions observed		
3c	ES[c]	778 (<1%)	651 (47%)	913 (M^+-I+PPh_3, 30%), 277 (PPh_3Me^+, 75%)
4b	FAB	No ions observed		
4c	ES[c]	792 (<1%)	665 (22%)	927 (M^+-I+PPh_3, 12%), 291 (PPh_3Et^+, 100%)
5a	FAB	690 (2%)	563 (16%)	203 (PBu_3H^+, 100%)
5c	FAB	718 (5%)	591 (26%)	203 (PBu_3H^+, 100%)
6c	FAB	732 (2%)	605 (14%)	203 (PBu_3H^+, 100%)
7c	EI	872 (2%)	745 (78%)	203 (PBu_3H^+, 100%)

[a] m/z (relative intensity).

[b] FAB = Fast Atom Bombardment; ES = Electrospray; EI = Electron Impact.

[c] The negative ion spectrum consisted of a peak at $m/z = 127$, corresponding to I^-.

Electron Impact (EI) also yielded useful data. Both techniques gave poor results with the triphenylphosphine complexes, but Electrospray (ES) proved effective for these compounds. A molecular ion was observed in each case, and there was a good match between the calculated and observed isotope distribution patterns. The ion corresponding to loss of iodide was always more abundant than the molecular ion itself, and in the spectra obtained using electrospray the iodide anion was observed when the instrument was operated in negative ion mode.

The crystal structure of **4c** (as its toluene solvate) has been determined by X-ray diffraction. In spite of the poor quality of the data, the connectivity unambiguously could be determined. There are two symmetry-independent molecules of the complex in the asymmetric unit that, however, substantially possess the same geometry. The metal atom is in an approximately square planar environment (Figure 1) formed by the iodine, the PPh_3 phosphorus atom, and the two selenium atoms of the bidentate ligand. Selected bond lengths and angles are listed in Table VIII.

There is close similarity between the present Pd-P and Pd-Se distances and those of the dinuclear **1c** parent.[8] The Se-Pd-Se angle, however, now is larger (by ca. 10°) than before. The palladium bond to the three-coordinate selenium is significantly longer (by ca. 0.04 Å) than α to the two-coordinate selenium in both molecules of **4c**. Surprisingly, this is not the case for the related rhodium(I) complexes $[Rh\{S(Et)C(CN)C(CN)S\}(CO)(PPh_3)]$[10] and $[Rh\{S(Me)C(CN)C(CN)S\}(C_8H_{12})]$,[11] where the rhodium in each case is closer to the alkylated sulfur atom. This might be due to partial

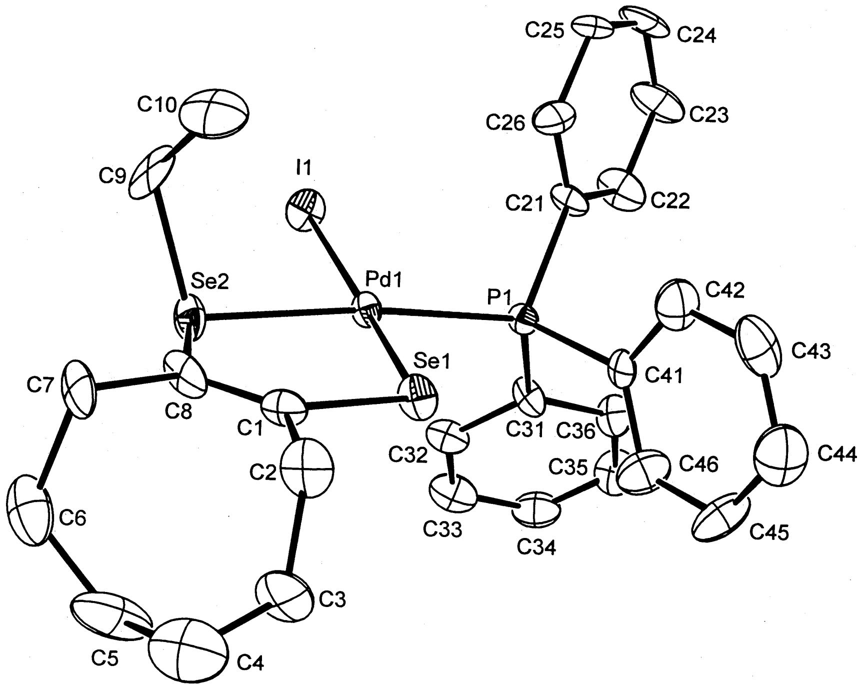


FIGURE 1 A view of one of the symmetry-independent, substantially identical molecules in the asymmetric unit of the structure of [PdI(Se{Et}C_8H_{12}Se)(PPh_3)], **4c**. Twenty percent probability ellipsoids are shown. Hydrogen atoms are omitted for clarity.

mismatch in the donor sets, besides the substitution of S for Se, or to the smaller *trans*-effect of iodide.

The reactivity of α,ω-diiodides also was examined. More than one product appeared to be formed when **2c** was treated with an excess of CH_2I_2, CH_2Br_2, or CH_2ICH_2I under comparable conditions, and these reactions were not examined further. The longer-chain derivatives $CH_2I(CH_2)_nCH_2I$ (n = 1, 2) behaved more simply, yielding the complexes [PdI(Se{R′}C_8H_{12}Se)(PBu_3)], R′ = $(CH_2)_3I$ (**7c**), $(CH_2)_4I$ (**8c**). Reaction was complete after heating to 50°C for 4 h in toluene solution. Spectroscopic data for **7c** are included in Tables II–VII. Compound **8c** is believed to have an analogous structure based on ^{31}P NMR spectroscopic ($\delta = 12.0$ ppm, $^2J(^{31}P\text{-}^{77}Se) = 180$ Hz) and EI mass spectrometric data ($m/z = 886$ (4%), $[M]^+$; 759 (48%), $[M\text{–}I]^+$; 203 (100%), $[PBu_3H]^+$).

Compound **7c** slowly reacted with further **2c** on heating to 90°C in toluene for 48 h. The product could not be isolated in a pure state,

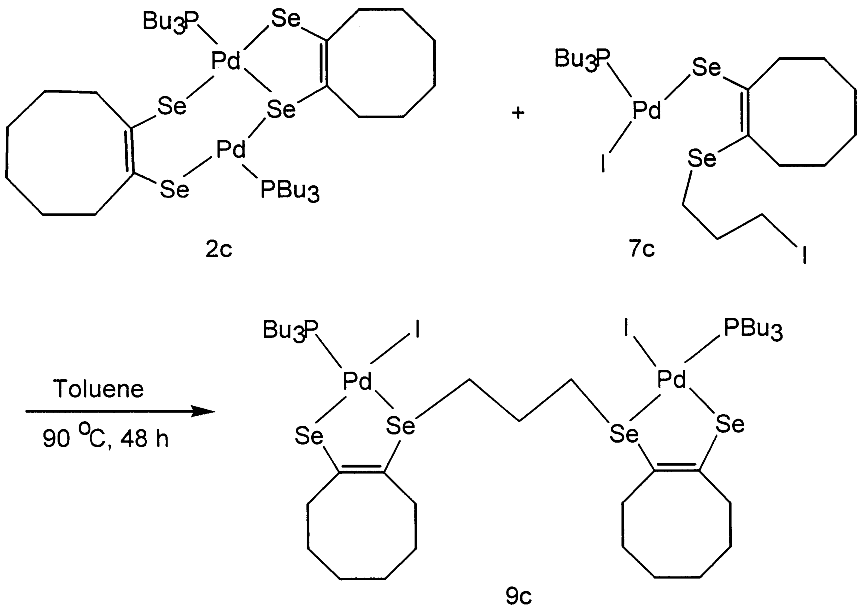
TABLE VIII Selected Bond Lengths (Å) and Angles (°) for 4c

Molecule 1		Molecule 2	
Pd(1)-P(1)	2.277(5)	Pd(2)-P(2)	2.279(5)
Pd(1)-I(1)	2.651(2)	Pd(2)-I(2)	2.654(2)
Pd(1)-Se(1)	2.372(3)	Pd(2)-Se(3)	2.382(3)
Pd(1)-Se(2)	2.410(3)	Pd(2)-Se(4)	2.425(3)
Se(1)-C(1)	1.921(22)	Se(3)-C(11)	1.850(21)
Se(2)-C(8)	1.938(25)	Se(4)-C(18)	1.966(21)
Se(2)-C(9)	1.948(28)	Se(4)-C(19)	1.968(28)
C(1)-C(8)	1.36(4)	C(11)-C(18)	1.29(3)
P(1)-Pd(1)-I(1)	92.77(13)	P(2)-Pd(2)-I(2)	92.18(13)
I(1)-Pd(1)-Se(2)	88.19(9)	I(2)-Pd(2)-Se(4)	88.64(8)
Se(2)-Pd(1)-Se(1)	88.28(10)	Se(4)-Pd(2)-Se(3)	87.84(9)
Se(1)-Pd(1)-P(1)	91.19(14)	Se(3)-Pd(2)-P(2)	91.34(14)
I(1)-Pd(1)-Se(1)	174.54(9)	I(2)-Pd(2)-Se(3)	176.47(9)
P(1)-Pd(1)-Se(2)	173.78(15)	P(2)-Pd(2)-Se(4)	174.75(14)
Pd(1)-Se(1)-C(1)	103.2(8)	Pd(2)-Se(3)-C(11)	103.7(7)
Se(1)-C(1)-C(8)	126.5(1.6)	Se(3)-C(11)-C(18)	127.7(1.4)
C(1)-C(8)-Se(2)	115.2(1.4)	C(11)-C(18)-Se(4)	117.2(1.3)
C(8)-Se(2)-Pd(1)	106.3(8)	C(18)-Se(4)-Pd(2)	103.3(7)
C(9)-Se(2)-Pd(1)	103.9(9)	C(19)-Se(4)-Pd(2)	105.0(1.0)
C(9)-Se(2)-C(8)	99.0(1.2)	C(19)-Se(4)-C(18)	99.5(1.3)

but on the basis of ^{31}P NMR spectroscopy ($\delta = 12.0$ ppm, $^2J(^{31}P\text{-}^{77}Se) = 180$ Hz), and FAB mass spectrometry ($m/z = 1443$ (5%), $[M]^+$; 1316 (100%), $[M{-}I]^+$), it is believed to be the dinuclear species **9c** (Scheme 2), in which two square planar palladium units are linked by a hydrocarbon bridge.

It is noteworthy that in no case, either using a dihalide or an excess of monohalide, was di-alkylation of a diselenolene observed. This implies that the nucleophilicity of the remaining two-coordinate selenium atom in the mono-alkylated product (**3b**, **c**, **4b**, **c**, **5a**, **c**, **6c**, **7c**, or **8c**) is much reduced. It would, however, be incorrect to assume that only dinuclear complexes having bridging chalcogen atoms can undergo this type of reaction. The mononuclear diselenolene $[Pd(Se_2C_8H_{12})(PBu_3)_2]$ also reacts with iodomethane or -ethane to yield **5c** and **6c** respectively, together with a second product believed to be $[Pd\{Se(R')C_8H_{12}Se\}(PBu_3)_2]I$ (R′ = Me or Et).[12]

As expected these reactions are slower for bulkier alkyl groups. Changing from iodide to bromide also results in a substantial decrease in reaction rate. For example, the reaction of bromoethane with **2c** proceeded only to ca. 50% completion after eight hours heating under reflux



SCHEME 2

in toluene. The product in this case was isolated by column chromatography (Al_2O_3/toluene) and, on the basis of partial characterisation by ^{31}P NMR spectroscopy ($\delta = 15.7$ ppm, $^2J(^{31}P\text{-}^{77}Se) = 175$ Hz) and EI mass spectrometry ($m/z = 684$ (18%), $[M]^+$; 605 (47%), $[M\text{-}Br]^+$; 203 (100%), $[PBu_3H]^+$), was identified as $[PdBr(Se\{Et\}C_8H_{12}Se)(PBu_3)]$. The ^{31}P resonance is downfield of that for **5c**, as would be expected on the basis of the greater electronegativity of bromine.

The mechanism of the reaction is believed to involve initial electrophilic attack on the bridging selenium atoms in **1** or **2**. In order to test an alternative hypothesis, **2c** was treated with an excess of $[NBu_4]I$: If nucleophilic attack at palladium were to be the key step, this should yield $[NBu_4][PdI(Se_2C_8H_{12})(PBu_3)]$. No change in the ^{31}P NMR spectrum of the mixture occurred, however, even after stirring at room temperature for 2 days, and heating to 50°C for 6 hours, effectively ruling out this possibility. We now are proceeding to examine the reactions of diselenolenes with other electrophilic reagents.

EXPERIMENTAL

All reactions were performed using standard Schlenk techniques and predried solvents under an atmosphere of dinitrogen. ^1H and ^{13}C NMR spectra: Bruker 400; tetramethylsilane as internal standard. ^{31}P and ^{77}Se NMR spectra: Bruker AC250; 85% phosphoric acid or dimethyl selenide as external standard. Mass spectra were recorded by the EPSRC Mass Spectrometry Centre, using FAB, ES, or EI. Values of *m/z* quoted are for isotopomers containing ^{79}Br, ^{80}Se, and ^{106}Pd; expected isotope distribution patterns were observed. $[Pd_2(Se_2C_nH_{2n-4})_2(PR_3)_2]$ (R = Ph: n = 7 (**1b**), 8 (**1c**); R = Bu: n = 6 (**2a**), 8 (**2c**)) were prepared as described in the literature.[6–8]

Preparation of [PdX(Se{R′}C$_n$H$_{2n-4}$Se)(PR$_3$)] (n = 6, 7 or 8; R = Ph or Bu; X = Br or I; R′ = Me, Et, etc.)

In a typical experiment, **1c** (24 mg, 0.02 mmol) or **2c** (25 mg, 0.02 mmol) was dissolved in toluene (20 mL), MeI (25 μL, 57 mg, 0.4 mmol) or EtI (32 μL, 62 mg, 0.4 mmol) added in excess, and the resultant solution stirred in the dark either at room temperature for one h (MeI), or at 50°C for 2 h (EtI). In all cases a color change from dark green (**1c**) or purple (**2c**) to brown-yellow was observed. The progress of the reactions was monitored by thin layer chromatography (Al_2O_3/toluene). On completion, the solvent was removed by evaporation under reduced pressure, and the solid recrystallised from hexane/dichloromethane (10:1).

X-Ray Crystallography

Crystals of **4c** did not provide good material for X-ray diffraction, giving relatively low-angle reflections. This limited the quality of the structural model, although it did not prevent complete structure solution and elucidation of the chemically important aspects. Crystal data and details on data collection and structure refinement are given in Table IX. Data were collected at room temperature with a Bruker CCD diffractometer, equipped with Göbel mirrors, and mounted on a rotating-anode generator, using Cu Kα radiation ($\lambda = 1.5418$ Å). Cell constants were obtained by least-squares refinement of the setting angles of 5217 reflections in the range $5 < 2\theta < 114$°C. A correction for absorption was applied with SADABS.[13] The structure was solved by direct methods with SIR-97[14] and was extended and refined on F^2 with SHELXL-97.[15] A possible ambiguity between the Cc and C2/c space groups was solved in favor of the former, since the two complex molecules in the Cc asymmetric unit only approximately mimic the presence of an inversion center (C2/c) and toluene solvate molecules do not satisfy that symmetry requirement. All phenyl rings of the phosphine ligand and

TABLE IX Crystallographic Data for 4c

Formula	$C_{70}H_{80}I_2P_2Pd_2Se_4$
M	1765.72
Crystal system	Monoclinic
Space group	Cc
a(Å)	35.690(5)
b(Å)	11.890(2)
c(Å)	16.788(3)
β(°)	101.51(1)
U(Å^3)	6981(2)
Z	4
D_c (g cm^{-3})	1.680
Crystal size (mm)	0.30 × 0.40 × 0.60
μ(mm^{-1})	14.20
Radiation	Cu Kα ($\lambda = 1.5418$ Å)
2θ range (°)	5–114
Reflections collected	8875
Unique reflections	5816
Unique observed reflections, with $I > 2\sigma(I)$	5198
Number of parameters	626
$R1$ (observed reflections)	0.069
$R1$ (all unique reflections)	0.075
$wR2$ (all unique reflections)	0.186
Goodness of fit	1.017
Largest features (max, min) in final ΔF map (e Å^{-3})	1.96, −1.43

those of the solvent molecules were refined as rigid groups with idealized geometry. The methyl group of one toluene molecule was distributed over two positions with essentially equal probability. Geometrical restraints were applied on that methyl's position and on three C—C bond lengths of a cyclooctene ring. Anisotropic temperature factors, with mild isotropic restraints, were assigned to all nonhydrogen atoms, except for the disordered toluene methyl carbon. Hydrogen atoms were in calculated positions, riding on the respective carrier atom, with $U_{\mathrm{H}} = 1.2U_{\mathrm{C}}^{\mathrm{eq}}$ ($U_{\mathrm{H}} = 1.5U_{C}^{\mathrm{eq}}$ for methyl hydrogens). The absolute structure[16] could not be assigned unambiguously, probably as a consequence of the pseudo-centricity of the structure and of the poor quality of the data. The highest peaks in the final difference synthesis were all in proximity of heavy atom positions and were devoid of chemical meaning. Computer programs used included PARST[17] for geometry calculations, and ORTEP[18,19] for graphics.

SUPPLEMENTARY DATA

Crystallographic data for **4c** have been deposited with the CCDC (12 Union Road, Cambridge, CB2 1EZ, UK) and are available on request quoting the deposition number CCDC xxxxxx.

REFERENCES

[1] U. T. Müller-Westerhoff and B. Vance, in *Comprehensive Coordination Chemistry*, G. Wilkinson (ed.), vol. 2, ch. 16.5, p. 595 (Pergamon, Oxford, 1988).

[2] M. Nomura, H. Hatano, T. Fujita, Y. Eguchi, R. Abe, M. Yokoyama, C. Takayama, T. Akiyama, A. Sugimori, and M. Kajitani, *J. Organomet. Chem.*, **689,** 997 (2004).

[3] R. M. Wing, G. C. Tustin, and W. H. Okamura, *J. Amer. Chem. Soc.*, **89,** 1935 (1970).

[4] S. Nagao, H. Seino, T. Okada, Y. Mizobe, and M. Hidai, *J. Chem. Soc.*, 3546 (2000).

[5] S. Ford, M. R. Lewtas, C. P. Morley, and M. Di Vaira, *Eur. J. Inorg. Chem.*, 933 (2000).

[6] S. Ford, C. P. Morley, and M. Di Vaira, *New J. Chem.*, **23,** 811 (1999).

[7] S. Ford, C. P. Morley, and M. Di Vaira, *Inorg. Chem.*, submitted for publication.

[8] S. Ford, P. K. Khanna, C. P. Morley, and M. Di Vaira, *J. Chem. Soc.*, 791 (1999).

[9] P. K. Khanna, C. P. Morley, M. B. Hursthouse, K. M. A. Malik, and O. W. Howarth, *Heteroatom Chem.*, **6,** 520 (1995).

[10] C.-H. Cheng and R. Eisenberg, *Inorg. Chem.*, **18,** 2438 (1979).

[11] D. G. Vanderveer and R. Eisenberg, *J. Am. Chem. Soc.*, **96,** 4994 (1974).

[12] J. L. Leek and C. P. Morley, unpublished observations.

[13] G. M. Sheldrick (ed.), SADABS, Program for Empirical Absorption Corrections, University of Göttingen (1986).

[14] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. Spagna, *J. Appl. Cryst.*, **32,** 115 (1999).

[15] G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, University of Göttingen (1993).

[16] H. D. Flack, *Acta Crystallogr., Sect. A*, **39,** 876 (1983).

[17] M. Nardelli, *J. Appl. Crystallogr.*, **28,** 659 (1995).

[18] C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory (1976).

[19] L. J. Farrugia, *J. Appl. Crystallogr.*, **30,** 565 (1997).