4494 *Inorg. Chem.* **1994,** *33,* 4494–4501

Synthesis and Characterization of Palladium(II) and Platinum(II) Complexes of Dibenzyl Disulfide and Dibenzyl Diselenide. X-ray Structure of *cis*-$[PtCl_2(PMe_2Ph)]_2(Se_2Bz_2)$

Walter Baratta[†] and Paul S. Pregosin*

Inorganic Chemistry, ETH-Zentrum, CH-8092 Zürich, Switzerland

Alessia Bacchi and Giancarlo Pelizzi

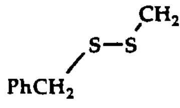
Instituto di Chimica Generale ed Inorganica, University of Parma, I-43100 Parma, Italy

Received January 4, 1994[®]

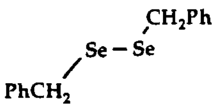
The coordination chemistry of the ligands dibenzyl disulfide, **1**, and dibenzyl diselenide, **2**, with Pd(II) and Pt(II) has been investigated. These ligands are shown to coordinate via one or both of the donor atoms. For **1**, the tendency for both chalcogens atoms to complex resulted in the unexpected trinuclear complexes $(MCl_2)_3(\mathbf{1})_4$, M = Pd and Pt, in which there are two different ligand types: one bridging two different metal centers using both S atoms and one acting as a terminal, single sulfur donor. One equivalent of **2** plus $[Pt(\mu{-}Cl)Cl(PMe_2Ph)]_2$ gave the dinuclear compound $[PtCl_2(PMe_2Ph)]_2\{\mathbf{2}\}$, **7**, whose solid-state structure has been determined by X-ray diffraction. Crystal data for **7**: $C_{30}H_{36}Cl_4P_2Pt_2Se_2{\cdot}0.75CH_2Cl_2$, $M = 1212.2$, space group $P2_1/a$, $a = 33.278(6)$ Å, $b = 14.056(4)$ Å, $c = 17.603(3)$ Å, $\beta = 104.71(2)°$, $V = 7964(3)$ Å^3, and $Z = 8$. Unusual ^{77}Se NMR behavior has been observed in that, for the $Pt{-}^{77}Se^1(CH_2Ph){-}^{77}Se^2CH_2Ph$ fragment, the coordination chemical shift for $^{77}Se^2$, not complexed, is much larger than that for $^{77}Se^1$, the coordinated ligand atom. The trans-influence for **1**, as determined by ^{31}P NMR, is found to be similar to that of other neutral sulfur donors. ^{195} Pt spectra were recorded for several compunds.

Introduction

There is an extensive literature concerned with the transition metal chemistry of thiolate and other negatively charged S-donor ligands.[1] The reaction chemistry of neutral sulfur and selenium ligands, and particularly disulfides and diselenides, is not so extensive.[2–4] Our interest in these ligands arises from the possibility of using them as models for the binding of elemental sulfur or selenium in that the S (or Se) donor is bound to another S (or Se). However, apart from this consideration, there is relatively little known[5–10] on the coordination capabilities of alkyl disulfides and diselenides. These compounds are potentially bridging ligands via both[9] of the chalcogen atoms or, naturally, these compounds can act as normal two-electron donors so that new results concerned with how these ligands bind should be of general interest. To date most reports on complexes of such disulfides and diselenides have been for phenyl or methyl derivatives.[9,10] We report here on the synthesis and characterization of a series of Pd(II) and Pt(II) compounds containing the dibenzyl analogs **1** and **2**.



1



2

Results and Discussion

Trinuclear Complexes. The reactions of **1** with a variety of simple Pd(II) and Pt(II) starting materials led to unexpected results, as shown in Scheme 1. For $PdCl_2$, use of a 1:2 ratio of metal to ligand, gave products whose proton NMR spectra suggested a mixture together with free **1**. A 1 equiv excess in CH_2Cl_2 led to isolable *trans*-$PdCl_2(\mathbf{1})_2$, **3**, which slowly disappears in toluene solution to afford a new complex with the empirical formula $(PdCl_2)_3(\mathbf{1})_4$, **4**. For the platinum chemistry only the trinuclear complex, **5**, could be obtained.

The characterization of **3** is straightforward in that there is the usual single IR stretch at 360 cm^{-1} indicative of the trans geometry,[11] together with a satisfactory microanalysis and ^{1}H and ^{13} C NMR spectra.

The structure of **4** and its Pt(II) analog, **5**, is more complicated, as suggested by their empirical formulas. For the Pd(II) complex there is a single, somewhat broad, Pd—Cl stretch at

---

[†] Current address: Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, I-56126 Pisa, Italy.

[®] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

(1) Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121.

(2) Canich, J. A. M.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R. *Inorg. Chem.* **1988**, *26*, 804.

(3) Aye, K. T.; Vittal, J. J.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1993**, 1835.

(4) Kuniyasu, H.; Ogawa, A.; Miyazaki, S.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796.

(5) Baratta, W.; Calderazzo, F. *Organometallics* **1993**, *12*, 1489. Atwood, J. T.; Bernal, I.; Calderazzo, F.; Canada, L. G.; Poli, R.; Rogers, R. D.; Veracini, C.A.; Vitali, D. *Inorg. Chem.* **1983** *22*, 1797.

(6) Abel, E. W.; Bhargava, S. K.; Orrell, K. G. *Progr. Inorg. Chem.* **1984**, *32*, 1 and references therein.

(7) Chivers, T.; Edwards, M.; Meetsma, A.; van de Grampel, J. C.; van der Lee, A. *Inorg. Chem.* **1992**, *31*, 2156.

(8) Fazlur-Rahman, A. K.; Verkade, J. G. *Inorg. Chem.* *1992*, *31*, 2064.

(9) (a) Abel, E. W.; Khan, A. R.; Kite, K.; Orrell, K. G.; Sik, V.; Cameron, T. S.; Cordes, R. *J. Chem. Soc., Chem. Commun.* **1979**, 713. (b) Abel, E. W.; Khan, A. R.; Kite, K.; Hursthouse, M. B.; Malik, K. M. A.; Mazid, M. A. *J. Organomet. Chem.* **1982**, *235*, 121. (c) Abel, E. W.; Moss, I. M.; Orrell, K. G.; Quershi, K. B.; Sik, V.; Stephenson, D. *J. Chem. Soc., Dalton Trans.* **1988**, 1489.

(10) Treichel, P. M.; Rosenheim, L. D. *Inorg. Chem.* **1984**, *23*, 4018. Roesky, H. W.; Gries, T.; Jones P. G.; Weber, K.; Sheldrick, G. M. *J. Chem. Soc.*,

(11) Adams, D. M. *Metal-Ligand and Related Vibrations*; E. Arnold: London, 1967.

0020-1669/94/1333-4494$04.50/0

Scheme 1

$$\underset{\mathbf{1}}{PdCl_2(CH_3CN)_2 + 3PhCH_2SSCH_2Ph} \xrightarrow[T = 263\ K,\ 1\ h]{CH_2Cl_2} \underset{\mathbf{3}}{trans\text{-}PdCl_2(1)_2} + 1 \qquad (a)$$

$$PdCl_2 + 3(1) \xrightarrow[RT,\ 2\ d]{CH_2Cl_2} \underset{\mathbf{4}}{trans\text{-}PdCl_2(1)_2} + 1 \qquad (b)$$

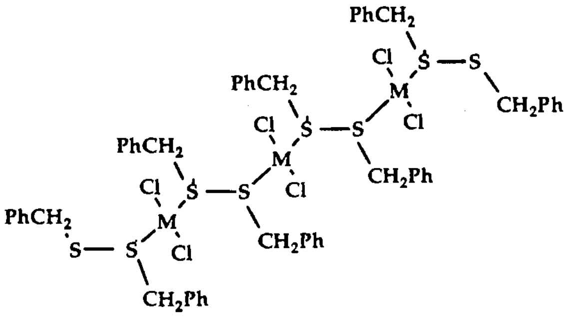
$$3trans\text{-}PdCl_2(1)_2 \xrightarrow[RT,\ 1\ d]{toluene} (PdCl_2)_3(1)_4 + 2(1) \qquad (c)$$

$$\left.\begin{array}{l} 3PtCl_2 + 4(1) \xrightarrow[RT,\ 1\ d]{CH_2Cl_2} \qquad (d) \\ 3K(PtCl_3(C_2H_4)) + 4(1) \xrightarrow[RT,\ 12\ h]{CH_2Cl_2} \qquad (e) \end{array}\right\} \underset{\mathbf{5}}{(PtCl_2)_3(1)_4}$$

$$3PtCl_2(styrene)_2 + 4(1) \xrightarrow[RT]{CDCl_3} \underset{\mathbf{5}}{(PtCl_2)_3(1)_4} \qquad (f)$$

(this reaction was observed *in situ*)

328 cm^{-1}, again suggestive of a trans geometry. The ^{1}H and ^{13}C NMR spectra are broad at room temperature but relatively sharp at 243 K. The low-temperature proton spectra show four AX (in one case AB) spin systems from eight different CH$_2$ protons, with chemical shifts in the range ca. 2.0–5.6 ppm. As **1** has its CH$_2$ protons at δ = 3.57, it is likely that we have (i) M–S–(**CH$_2$**Ph)–S–Bz and M–S(Bz)–S–**CH$_2$**Ph, i.e. complexed and uncomplexed S-donors and (ii) some anisotropic shielding due to one or more proximate Ph groups. The corresponding ^{13}C spectrum reveals four relatively sharp CH$_2$ signals (49.6, 48.8, 46.6, and 41.9 ppm with free ligand CH$_2$ at 42.9 ppm), three of which are shifted to lower field. One can make all of these NMR data compatible with *four* ligands, i.e. eight CH$_2$ groups, by postulating the following structure:



4, M = Pd; 5, M = Pt

We do not mean to imply that we are certain about either the geometric placement of the benzyl groups or other configurational isomers[6] due to the sulfur atoms and their uncoordinated lone pairs, rather that the suggested trimetallic complex has the necessary symmetry and satisfies the microanalytical data. For the Pd complex, further addition of **1** leads to formation of the trans-mononuclear complex, **3**. A 2-D NOESY and a ^{13}C,^{1}H-correlation assisted in the proton and carbon assignments, and a 2-D proton exchange measurement shows that there are several slow exchange processes occurring simultaneously at low temperature; however, their exact nature is not certain as small impurities (or dissociation products) are present and these are also involved in the dynamics. In solution at room temperature **4** slowly decomposes to afford, among others, benzyl chloride (identified by comparison with an original sample). Compound **4** decomposes somewhat faster than does **3** under the same conditions.

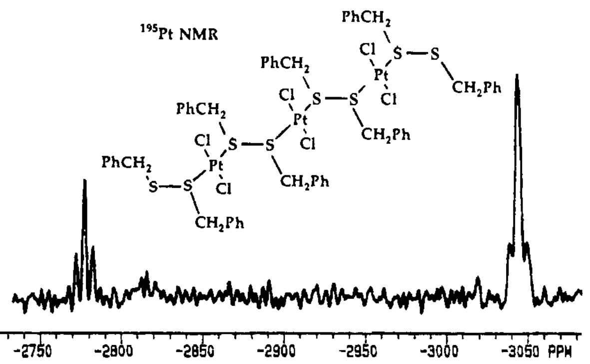


Figure 1. ^{195}Pt NMR spectrum of **5**, showing the two different platinum absorptions and the differing intensities of the ^{195}Pt satellites as a result of the different probabilities of finding a second adjacent ^{195}Pt.

The NMR and mass spectroscopy for the platinum complex, **5**, provide additional support for a trinuclear complex. The ^{195}Pt spectrum, shown in Figure 1, reveals two ^{195}Pt signals in the ratio of 2:1, both with satellites which can be attributed to platinum–platinum spin–spin coupling, ^3J(Pt,Pt) = 427 Hz. The absorption with relative integral = 1, δ = –2777, shows ^{195}Pt satellites with *twice* the intensity as those of the satellites for the signal with relative integral = 2, δ = –3043. This is reasonable since the center metal atom has two possibilities for its neighboring platinum to have ^{195}Pt. A higher oligomer would most likely show a more complicated ratio of intensities. The metal chemical shift is as expected[12] for this type of coordination sphere. The positive ion FAB mass spectrum for **5** shows strong signals around *m/e* = 1236 (=(PtCl$_2$)$_2$(**1**)$_3$ – Cl), a medium-to-weak set around *m/e* = 1502.8 (={PtCl$_2$}$_3$(**1**)$_3$ – Cl), and a weak set around *m/e* = 1747.1 (=(PtCl$_2$)$_3$(**1**)$_4$ – Cl). The ^{1}H and ^{13}C characteristics for **5** are very similar to those observed for **4** (eight different CH$_2$ protons and four different CH$_2$ carbons), and a summary of all of these NMR data is given in the Experimental Section. For **5**, there are two Pt–Cl stretches at 320 and 333 cm^{-1}.

Although our proposed structure is in excellent agreement with our analytical and chemical results, it is not clear as to why this complex is formed. Its existence does show that coordination of one S atom does not prevent coordination of the second, adjacent sulfur donor.

Bridge-Splitting Reactions. Given the unexpected results with mononuclear starting materials of Pd(II) and Pt(II), we reacted **1** and **2** with known[13,14] chloro-bridged dimeric complexes and these reactions are shown in Scheme 2. Several of the complexes have been isolated and others studied *in situ*. Bridge-splitting reactions using dinuclear complexes of Pt(II) are well-known[15-17] to afford trans-mononuclear complexes; however, this geometric isomer arises due to the relatively fast kinetics and does not always represent the thermodynamic product. Indeed, the cis isomer is often found[18] if solutions of

---

(12) Pregosin, P. S. *Annual Reports on NMR Spectroscopy*; Academic Press: London, 1986; Vol. 17, p 285.

(13) Baratta, W.; Pregosin, P. S. *Inorg. Chim. Acta* **1993**, *209*, 85.

(14) Chatt, J.; Duncanson, A.; Venanzi, L. M. *J. Chem. Soc.* **1955**, 4456 and 4461.

(15) Clark, H. C.; Ferguson, G.; Jain, V. K.; Parvez, M. *Inorg. Chem.* **1986**, *25*, 3808.

(16) Cross, R. J.; Davidson, M. F.; Rocomora, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1147.

(17) Kaufmann, W.; Venanzi, L. M.; Albinati, A. *Inorg. Chem.* **1980**, *27*, 1178.

(18) Brigg, J. R.; Crocker, C.; Shaw, B. L. *Inorg. Chim. Acta* **1980**, *40*, 245.

Scheme 2. Bridge Splitting Reactions

reactions leading to isolated products:

$$\mathrm{[Pt(\mu\text{-}Cl)Cl(PMe_2Ph)]_2 + 2PhCH_2SSCH_2Ph} \xrightarrow[\mathrm{RT,\ 2\ h}]{\text{toluene}} 2\mathit{cis}\text{-}\mathrm{[PtCl_2(PMe_2Ph)]_2(\mathbf{1})} \quad \text{(a)}$$

6

$$\mathrm{[Pt(\mu\text{-}Cl)Cl(PMe_2Ph)]_2 + 2PhCH_2SeSeCH_2Ph} \xrightarrow[\mathrm{RT,\ 2\ h}]{\text{toluene}} 2\mathit{cis}\text{-}\mathrm{[PtCl_2(PMe_2Ph)]_2(\mathbf{2})} \quad \text{(b)}$$

7

reactions studied in situ:

$$\mathrm{[Pt(\mu\text{-}Cl)Cl(PMe_2Ph)]_2} + 2\ \mathbf{2} \xrightarrow[T = 233\ \mathrm{K}]{\mathrm{CDCl_3}} 2\mathit{trans}\text{-}\mathrm{PtCl_2(PMe_2Ph)(\mathbf{2})} \quad \text{(c)}$$

8

$$\mathrm{[Pt(\mu\text{-}Cl)Cl(P\text{-}\mathit{n}\text{-}Bu_3)]_2} + 2\ \mathbf{2} \xrightarrow[T = 233\ \mathrm{K}]{\mathrm{CDCl_3}} 2\mathit{trans}\text{-}\mathrm{PtCl_2(P\text{-}\mathit{n}\text{-}Bu_3)(\mathbf{2})} \quad \text{(d)}$$

9

$$\mathrm{[Pt(\mu\text{-}Cl)Cl(P\text{-}\mathit{n}\text{-}Bu_3)]_2} + 2\ \mathbf{1} \xrightarrow[T = 233\ \mathrm{K}]{\mathrm{CDCl_3}} 2\mathit{trans}\text{-}\mathrm{PtCl_2(P\text{-}\mathit{n}\text{-}Bu_3)(\mathbf{1})} \quad \text{(e)}$$

10

the trans isomer are left at room temperature for protracted periods of time.

Equations a and b in Scheme 2 show that the dinuclear products, **6** and **7**, form when *sym-trans*-$[Pt(\mu Cl)Cl(PMe_2Ph)]_2$ is treated with equimolar amounts of **1** or **2**. For **7** suitable crystals for X-ray diffraction were obtained.

Solid-State Structure of 7. Compound **7** crystallizes with two symmetry independent $[PtCl_2(PMe_2Ph)]_2(PhCH_2SeSeCH_2Ph)$ molecules in the asymmetric unit, which also contains 1.5 CH_2Cl_2 solvent molecules, and we show one of these platinum complexes in Figure 2. The two independent molecules are not significantly different from one another and are related to each other by a pseudo mirror plane approximately perpendicular to *b*. Moreover, in each of the molecules there is a pseudo 2-fold axis about the Se—Se bond. The two Pt atoms in each molecule are held together by a bridging diselenide group. Coordination about each Pt also involves one P and two cis Cl atoms. It is noteworthy that the four Pt atoms are in slightly different bonding situations. In fact, while the four ligand atoms about Pt1 and Pt3 show, as expected, a nearly square planar arrangement, those about Pt2 and Pt4 are located at the apices of a slightly distorted flattened tetrahedron (maximum deviation 0.14 Å). Such behavior can be presumably explained in terms of packing distortions, as the Cl atoms engaged in the shortest intermolecular contacts are those bonded to Pt2 and Pt4.

Only three platinum compounds characterized by X-ray crystallography have been reported to contain bridging diselenide ligands, and these are Pt(IV) complexes and contain halogen bridges.[9ab,19]

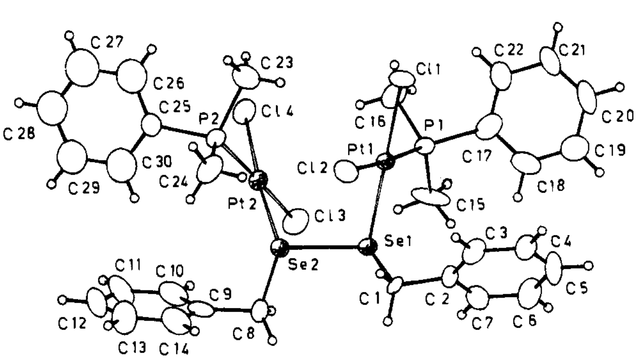


Figure 2. ORTEP diagram and numbering scheme for **7**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented by arbitrary small spheres.

The Pt—Se distances found in **7** (2.363(2)—2.370(3) Å) are significantly shorter than those observed in the above platinum(IV) compounds (2.556—2.598 Å), this being readily explained by the oxidation state and coordination number differences. However, our data agree well with those reported for the structurally characterized four-coordinate platinum(II) compounds with both Pt—Se and Pt—Cl bonds (Pt—Se = 2.302—2.417 Å).[20-23] The Pt—P distances in **7** range from 2.225(7) to 2.247(6) Å, with the mean value = 2.237 Å. The Pt—Cl bonds *trans* to P (2.346(7)—2.369(6) Å) are significantly longer than the remaining ones (2.288(6)—2.323(8) Å), indicating the expected difference in *trans-* influence between PMe_2Ph and Cl.

The Pt—Se—Se—Pt fragment in both molecules is not planar, with the torsional angle about the Se—Se bond being *ca.* 56.5°. The C—Se—Se—C torsion angle is ca. 90.1(1)°. The Se—Se bond distances of 2.396(3) and 2.404(3) Å are (a) longer than in the free ligand, 2.285 Å,[24a] (b) a little longer than that (2.375 Å) found in $[Re_2Br_3(CO)_6(PhCH_2SeSeCH_2Ph)]$,[24b] the only other crystallographically determined example of a molecule containing this ligand, (c) longer than those (2.359—2.362 Å) found in the above mentioned diselenide-containing Pt(IV) compounds, and (d) only slightly shorter than the 2.41 Å value reported for $[Re_2Br_2(CO)_6(PhSeSePh)]$.[25] The dihedral angles between the planes defined by each Se—Se—C moiety and the corresponding phenyl ring fall in the range 62.6—81.7°.

A list of selected bond lengths and bond angles is given in Table 1, experimental parameters are in Table 2, and atomic coordinates and isotropic displacement parameters are in Table 3.

NMR Studies. Complex **7** , in $CDCl_3$, affords a ^{31}P NMR spectrum with a single resonance plus two sets of satellites, $^1J(^{195}Pt,^{31}P) = 3339$ Hz and $^2J(^{77}Se,^{31}P) = 25$ Hz, with the latter consistent with the geometry found in the dinuclear structure. The ^{77}Se NMR spectrum shows a doublet, $\delta = 652$ (the free ligand has $\delta = 402$), with $^2J(^{77}Se,^{31}P) =$ ca. 25 Hz. The ^{195}Pt spectrum affords the expected superposition of isotopomers,

---

(19) Abel, E. W.; Mittal, P. K.; Orrell, K. G.; Šik, V.; Cameron, T. S. *J. Chem. Soc., Chem. Commun.* **1984**, 1312.

(20) Siedle, A. R.; Etter, M. C.; Jones, M. E.; Filipovich, G.; Mishmash, H. E.; Bahmet, W. *Inorg. Chem.* **1982**, *21*, 2624.

(21) Chadha, R. K.; Chehayber, J. M.; Drake, J. E. *Inorg. Chem.* **1986**, *25*, 611.

(22) Behrens, U.; Berges, P.; Bieganowski, R.; Hinrichs, W.; Schiffling, C.; Klar, G. *J. Chem. Res.* **1986**, *326*, 2801.

(23) Kelly, P. F.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Chem. Commun.* **1989**, 408.

(24) (a) McWhinnie, W. R. *The Chemistry of Organic Selenium and Tellurium Compounds*; Patei, S. Ed.; J. Wiley: New York, 1987; Vol. 2. (b) Abel, E. W.; Bhargava, S. K.; Bhatti, M. M.; Mazid, M. A.; Orrell, K. G.; Sik, V.; Hursthouse, M. B.; Malik, K. M. A. *J. Organomet. Chem.* **1983**, *250*, 373.

(25) Korp, J.; Bernal, I.; Atwood, J. L.; Calderazzo, F.; Vitali, D. *J. Chem. Soc., Dalton Trans.* **1979**, 1492.

Table 1. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses

Pt—Se1	2.368(2)	Pt3—Se3	2.363(2)
Pt1—Cl1	2.308(5)	Pt3—C15	2.288(6)
Pt1—Cl2	2.369(6)	Pt3—C16	2.366(6)
Pt1—P1	2.231(6)	Pt3—P3	2.247(6)
Pt2—Se2	2.366(3)	Pt4—Se4	2.370(3)
Pt2—Cl3	2.363(7)	Pt4—C17	2.346(7)
Pt2—Cl4	2.305(7)	Pt4—C18	2.323(8)
Pt2—P2	2.245(6)	Pt4—P4	2.225(7)
Se1—Se2	2.396(3)	Se3—Se4	2.404(3)
Se1—C1	2.018(21)	Se3—C31	1.986(24)
Se2—C8	1.987(21)	Se4—C38	1.941(20)
P1—C15	1.824(20)	P3—C45	1.838(23)
P1—C16	1.832(25)	P3—C46	1.826(21)
P1—C17	1.811(16)	P3—C47	1.793(15)
P2—C23	1.851(23)	P4—C53	1.819(26)
P2—C24	1.837(25)	P4—C54	1.850(28)
P2—C25	1.833(14)	P4—C55	1.759(17)
C1—C2	1.479(20)	C31—C32	1.469(23)
C8—C9	1.557(23)	C38—C39	1.521(22)
Cl2—Pt1—P1	174.9(2)	Cl6—Pt3—P3	175.5(2)
Cl1—Pt1—P1	87.0(2)	Cl5—Pt3—P3	87.3(2)
Cl1—Pt1—Cl2	88.0(2)	Cl5—Pt3—Cl6	88.6(2)
Se1—Pt1—P1	93.6(1)	Se3—Pt3—P3	92.9(2)
Se1—Pt1—Cl2	91.4(2)	Se3—Pt3—Cl6	91.3(2)
Se1—Pt1—Cl1	179.4(1)	Se3—Pt3—Cl5	176.9(2)
Cl4—Pt2—P2	87.4(2)	Cl8—Pt4—P4	87.3(3)
Cl3—Pt2—P2	173.7(2)	Cl7—Pt4—P4	173.6(3)
Cl3—Pt2—Cl4	88.0(2)	Cl7—Pt4—Cl8	88.7(3)
Se2—Pt2—P2	93.6(2)	Se4—Pt4—P4	93.6(2)
Se2—Pt2—Cl4	174.8(2)	Se4—Pt4—Cl8	175.3(2)
Se2—Pt2—Cl3	91.3(2)	Se4—Pt4—C17	90.8(2)
Pt1—Se1—C1	103.2(6)	Pt3—Se3—C31	103.5(6)
Pt1—Se1—Se2	98.8(1)	Pt3—Se3—Se4	102.0(1)
Se2—Se1—C1	100.0(5)	Se4—Se3—C31	98.7(6)
Pt2—Se2—Se1	95.1(1)	Pt4—Se4—Se3	97.9(1)
Se1—Se2—C8	100.0(6)	Se3—Se4—C38	96.3(7)
Pt2—Se2—C8	106.3(6)	Pt4—Se4—C38	106.6(6)
Pt1—P1—C17	111.5(6)	Pt3—P3—C47	113.6(6)
Pt1—P1—C16	111.8(7)	Pt3—P3—C46	117.9(7)
Pt1—P1—C15	118.4(7)	Pt3—P3—C45	110.5(8)
C16—P1—C17	107.4(9)	C46—P3—C47	104.4(9)
C15—P1—C17	103.1(10)	C45—P3—C47	104.8(9)
C15—P1—C16	103.8(11)	C45—P3—C46	104.4(9)
Pt2—P2—C25	111.2(6)	Pt4—P4—C55	112.1(7)
Pt2—P2—C24	117.2(8)	Pt4—P4—C54	116.6(8)
Pt2—P2—C23	111.0(8)	Pt4—P4—C53	112.2(9)
C24—P2—C25	104.7(9)	C54—P4—C55	106.7(11)
C23—P2—C25	107.4(10)	C53—P4—C55	107.6(13)
C23—P2—C24	104.7(11)	C53—P4—C54	100.6(14)
Se1—C1—C2	105.3(10)	Se3—C31—C32	105.6(14)
Se2—C8—C9	103.3(12)	Se4—C38—C39	106.8(12)

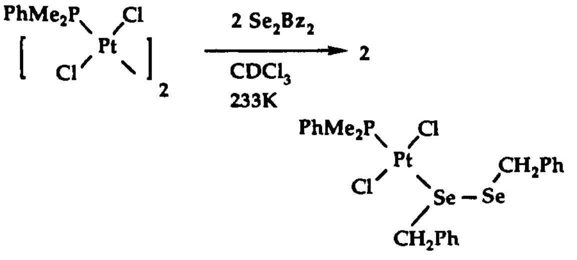
Table 2. Crystallographic Data for Compound **7**

chem formula $C_{30}H_{36}Cl_4P_2Pt_2Se_2{\cdot}0.75CH_2Cl_2$
fw = 1212.2
space group $P2_1/a$ (No. 15)
$a = 33.278(6)$ Å
$b = 14.056(4)$ Å
$c = 17.603(3)$ Å
$\beta = 104.71(2)°$
$V = 7964(3)$ Å^3
$Z = 8$
$\varrho_{\mathrm{calcd}} = 2.022$ g cm^{-3}
$T = 22$ °C
$\lambda = 0.710\,73$ Å
μ(Mo Kα) = 93.17 cm^{-1}
transm coeff = 1.0209−0.9127
$R_1(F_o) = 0.0490^a$
$R_{w2}(F_o^2) = 0.1736^a$

[a] $R_1 = \sum|F_o - F_c|/\sum(F_o)$, calculated on 5234 observed reflections ($I > 2\sigma(I)$). $R_{w2} = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ on 19 136 unique reflections with $w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$, $P = [\max(F_o^2,0) + 2F_c^2]/3$.

centered at −3867 ppm, containing the 3339 Hz doublet and additional weaker signals arising from ^{77}Se and the isotopomer with two ^{195}Pt spins. We estimate $^3J(^{195}\mathrm{Pt},^{195}\mathrm{Pt})$ to be ca. 164 Hz. The ^{1}H spectrum shows both nonequivalent phosphine methyl groups and nonequivalent geminal CH_2 protons, the latter at 4.67 and 3.83 ppm. Both methylene protons couple to the ^{195}Pt, although with markedly different $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ values of 18 and 53 Hz, respectively. The ^{1}H CH_2 chemical shift difference is presumably anisotropic in origin (one proton is likely to be shifted upfield by a proximate Ph ring) whereas the different $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ values most likely stem from a dihedral angle dependence. There are two IR stretches at 280 and 322 cm^{-1}, and there is a relatively strong signal (11% of maximum height) in the FAB mass spectrum at 1112.8 (=**7** − Cl).

Despite the solid-state structure for the Se derivative **7** and the isolation of an analogous S complex (see Scheme 2 and Experimental Section), it was likely that intermediates might form in solution during the development of **6** and **7**. To this end we have considered the reaction of the dinuclear complexes [$Pt(\mu{-}Cl)Cl(PMe_2Ph)]_2$ with 2 equiv of **2** (see eq 1). A $CDCl_3$ solution was prepared at 223 K, and the NMR spectra were measured at 233 K.



8

(1)

The ^{31}P NMR spectrum of the solution shows a new major component, to which we assign the structure **8**, plus compound **7** as a second minor component (the **8**/**7** ratio is ca. 5:1). The assignment of geometry for **8** was made using the observed relatively large $^2J(^{77}\mathrm{Se},^{31}\mathrm{P})_{\mathrm{trans}}$ value, 183 Hz; this coupling is known[26,27] to be in excess of 100 Hz. In a cis orientation, the two spins would result[27] in a much smaller value. The observation of two ^{77}Se resonances for the main component, $\delta = 464.8$ and 411.3, with the latter revealing the 183 Hz spin−spin coupling, is consistent with **8**; however, these ^{77}Se chemical shift values are by no means obvious and we shall return to them shortly. The corresponding proton spectrum for **8** shows four nonequivalent CH_2 signals, two of which appear close to the resonance position for the uncoordinated ligand. These data suggest that a trans geometry for the complex is possible. It is interesting that $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ at 3457 Hz suggests only a moderate-to-weak trans influence for **2**. This would be consistent with our observation that **7**, with a cis-geometry, is more stable than **8**. Based on $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$, dissociation of **2** from **8**, and subsequent isomerization, might not be difficult. NMR data for **7** and **8** are given in Table 4.

To further develop the geometric dependence of $^2J(^{77}\mathrm{Se},^{31}\mathrm{P})$ and simultaneously try to increase our understanding of the ^{77}Se chemical shifts in our complexes of **2**, we have measured a series

---

(26) Chivers, T.; Doxsee, D. D.; Hilts, R. W. *Inorg. Chem.* **1993**, *32*, 3244.
(27) Pan, W. H.; Fackler, J. F.; Chen, H. W. *Inorg. Chem.* **1981**, *20*, 856.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^4$) (One-Third of the Trace of the Diagonalized Matrix) for Non-Hydrogen Atoms, with Esd's in Parentheses

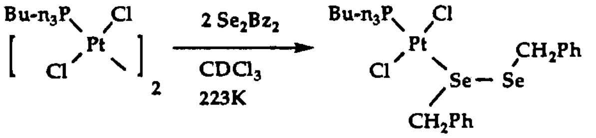
atom	*x/a*	*y/b*	*z/c*	U_{eq}	atom	*x/a*	*y/b*	*z/c*	U_{eq}
Pt1	2466.9(2)	970.5(5)	1111.5(5)	366(3)	Pt3	2510.1(3)	1266.3(5)	−3870.5(5)	398(3)
Pt2	1389.1(2)	1911.8(6)	483.2(5)	453(3)	Pt4	1354.3(3)	435.1(7)	−4442.5(6)	551(4)
Se1	2433.4(6)	2633.5(14)	889.3(13)	432(8)	Se3	2410.8(6)	−389.3(14)	−4062.8(12)	441(8)
Se2	1828.3(6)	2678.4(15)	−193.0(13)	455(8)	Se4	1776.1(7)	−453.1(16)	−5085.6(13)	512(8)
Cl1	2502(2)	−653(4)	1315(3)	620(24)	Cl5	2644(2)	2857(4)	−3682(4)	746(28)
Cl2	2409(2)	666(4)	−236(3)	584(23)	Cl6	2384(2)	1524(4)	−5239(3)	669(25)
Cl3	1557(2)	3042(4)	1510(4)	758(28)	Cl7	1568(2)	−516(6)	−3317(4)	933(33)
Cl4	1015(2)	1096(5)	1210(4)	728(27)	Cl8	990(2)	1379(6)	−3765(4)	975(35)
P1	2536(2)	1121(4)	2400(3)	421(21)	P3	2620(2)	1143(4)	−2561(3)	523(25)
P2	1159(2)	842(4)	−476(4)	513(23)	P4	1080(2)	1318(5)	−5496(4)	642(27)
C1	2878(5)	2861(14)	316(12)	501(81)	C31	2805(7)	−736(14)	−4695(12)	608(96)
C2	3273(4)	2610(11)	884(9)	563(75)	C32	3221(4)	−526(11)	−4194(9)	585(80)
C3	3518(5)	1859(10)	750(9)	689(86)	C33	3454(5)	198(10)	−4410(9)	718(90)
C4	3903(4)	1692(10)	1266(12)	966(109)	C34	3855(5)	378(11)	−3962(12)	957(112)
C5	4044(4)	2278(14)	1916(10)	1038(110)	C35	4023(4)	−166(14)	−3297(11)	1025(116)
C6	3799(5)	3029(12)	2049(8)	842(96)	C36	3789(5)	−890(13)	−3081(8)	936(104)
C7	3414(4)	3196(10)	1534(10)	688(87)	C37	3388(5)	−1070(10)	−3530(10)	694(87)
C8	1694(6)	4056(15)	−201(14)	636(96)	C38	1658(6)	−1785(14)	−4947(14)	614(92)
C9	1255(5)	4117(10)	−783(11)	757(83)	C39	1232(4)	−1989(10)	−5488(10)	742(77)
C10	903(7)	4188(12)	−500(10)	966(106)	C40	874(5)	−1950(12)	−5221(9)	1004(107)
C11	511(5)	4204(13)	−1020(15)	1176(116)	C41	488(4)	−2090(13)	−5742(12)	1192(121)
C12	472(5)	4150(13)	−1824(13)	1384(126)	C42	460(3)	−2269(11)	−6530(11)	975(90)
C13	825(8)	4079(14)	−2107(9)	1597(162)	C43	819(5)	−2308(12)	−6797(8)	1092(110)
C14	1216(6)	4063(13)	−1587(13)	1031(111)	C44	1205(4)	−2168(11)	−6276(10)	874(88)
C15	2550(9)	2316(14)	2810(13)	946(136)	C45	2240(6)	1864(14)	−2217(14)	657(99)
C16	2111(6)	539(17)	2709(13)	768(109)	C46	2584(5)	−37(14)	−2149(12)	535(84)
C17	3018(5)	599(13)	2962(9)	771(84)	C47	3116(4)	1583(13)	−2026(10)	655(82)
C18	3388(6)	1105(11)	3085(12)	1156(141)	C48	3441(6)	931(10)	−1889(12)	1114(129)
C19	3760(5)	682(15)	3480(13)	1368(154)	C49	3838(5)	1205(13)	−1476(13)	1436(186)
C20	3762(4)	−247(15)	3752(11)	1097(114)	C50	3910(5)	2131(15)	−1198(12)	1171(121)
C21	3392(6)	−753(10)	3629(11)	958(104)	C51	3585(6)	2783(11)	−1334(12)	1307(145)
C22	3020(4)	−330(13)	3234(10)	816(92)	C52	3188(5)	2509(12)	−1748(12)	1025(117)
C23	1312(7)	−380(15)	−128(16)	863(128)	C53	1165(10)	2583(18)	−5303(20)	1350(187)
C24	1340(7)	971(18)	−1374(13)	787(114)	C54	1305(8)	1173(19)	−6347(14)	936(130)
C25	590(4)	865(15)	−817(10)	609(63)	C55	542(5)	1137(18)	−5845(12)	808(80)
C26	352(7)	52(11)	−825(12)	1378(127)	C56	378(8)	256(15)	−6118(15)	2000(186)
C27	−78(7)	98(15)	−1100(14)	1691(155)	C57	−50(9)	132(16)	−6362(15)	2063(199)
C28	−269(4)	958(19)	−1367(13)	1381(126)	C58	−314(5)	890(23)	−6332(14)	1600(143)
C29	−30(7)	1771(14)	−1358(13)	1312(124)	C59	−150(7)	1771(18)	−6059(15)	1830(170)
C30	399(6)	1725(12)	−1084(12)	1364(127)	C60	278(8)	1895(13)	−5815(14)	1820(170)

Table 4. Selected NMR Data[a] for the Tertiary Phosphine Complexes of **1** and **2**

complex	^1H	^{31}P	$^1J(^{195}Pt,^{31}P)$	^{77}Se	$^2J(^{77}Se,^{31}P)$
6[b,c]	1.94, 2.07; CH_3 (32) (32), 4.07, 5.04; CH_2 (71) (29)	−14.5	3359		
7[d]	1.97, 2.16; CH_3 (32) (32), 3.83, 4.67; CH_2 (53) (18)	−16.9	3339	652	25
8[e]	233 K, 1.88; CH_3 3.45, 3.79, 3.89, 4.61; CH_2	−13.6	3457	411, 465	183
9[f]	233 K, 3.50, 3.72, 3.83, 4.60; CH_2	3.6	3361	405, 463	170
10		3.9	3352		
$[PtCl(\mathbf{2})(PEt_3)_2](BF_4)$[g]	3.76, 3.93, 4.16, 5.00; CH_2	6.1, 18.5	3316, 3125	376, 530, 116	12
$[PtCl(\mathbf{1})(PEt_3)_2](BF_4)$[h]	3.83, 3.86, 4.01, 5.01; CH_2	7.3, 18.3	3325, 3125		

[a] $CDCl_3$. Chemical shifts in ppm, coupling constants in Hz, J(Pt,H) values in parentheses. [b] $^2J(P,H) = 12$. [c] $^2J(H,H) = 11$. [d] $\delta(^{195}Pt) = -3867$, $\delta(^{13}C) = 12.5$, 14.3 (CH_3), 40.2 (CH_2). [e] $^2J(H,H) =$ ca. 10.7 for both pairs. [f] $^2J(H,H) = 11$. [g] $\delta(^{195}Pt) = -4671$, $^2J(P,P) = 17$ Hz. [h] $^2J(P,P) = 18.5$ Hz.

of low-temperature NMR spectra for the P-*n*-Bu_3 analog, **9**, produced by the usual bridge splitting reaction shown in eq 2.



9
(2)

The complex was generated at 223 K and measured at 233 K, since at room temperature **9** is not stable and reacts further to give a mixture of five products. The ^{31}P NMR spectrum of **9** at 233 K shows a single resonance at $\delta = 3.6$ flanked by both ^{195}Pt and ^{77}Se satellites, $^1J(^{195}Pt,^{31}P) = 3361$ Hz and $^2J(^{77}Se,^{31}P) = 170$ Hz. The magnitude of the latter coupling constant points to a trans geometry. The ^{195}Pt NMR spectrum shows the expected doublet at $\delta = -3816$. As with **8**, there are two ^{77}Se resonances, $\delta = 463.3$ and 405.3, with the latter revealing the 170 Hz spin–spin coupling . These ^{77}Se data suggest that the noncoordinated Se spin is markedly shifted downfield whereas the bound Se stom is only marginally moved from the position of the free ligand ($\delta = 402$ at ambient temperature and 392 at 233 K in $CDCl_3$). To confirm this unexpected result we have measured (a) the conventional ^1H spectrum, (b) a ^{195}Pt-filtered proton spectrum (only the CH_2 protons coupled to ^{195}Pt through three bonds[28] will appear: the first and the third from low field

---

(28) Relatively rapid relaxation of the metal at this magnetic field, due to the chemical shift anisotropy mechanism, affords broad, frequently poorly resolved ^{195}Pt satellites (see ref 12) so that this type of multiple quantum experiment can be useful.

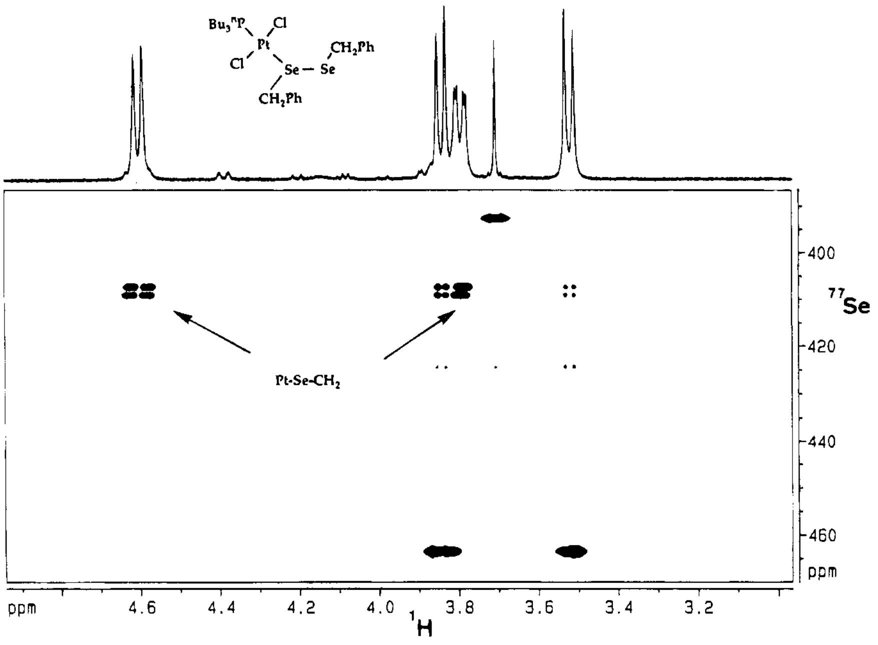


Figure 3. $^{77}Se,^{1}H$ 2-D correlation spectrum, for a solution containing **9**, revealing three Se signals. The two ^{77}Se signals for **9** each correlate to their respective nonequivalent protons of the adjacent CH_2 groups. The splitting in the ^{77}Se direction for the high-field resonance arises from $^{2}J(^{77}Se,^{31}P)$. The impurity with the proton signal at ca. 3.7 ppm is most likely uncoordinated **2** (the ligand ^{77}Se and ^{1}H chemical shifts are somewhat temperature dependent).

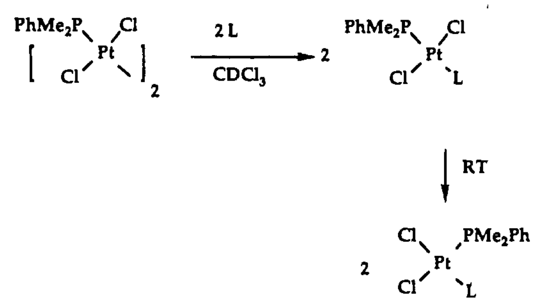
to high field in Figure 3), and (c) a ^{77}Se, ^{1}H correlation to connect the now assigned protons to their respective ^{77}Se resonances (also shown in Figure 3). The figure clearly reveals that the low-field ^{77}Se absorption at 463.3, without the large ^{31}P splitting, correlates to the second and fourth protons, i.e., $Pt-Se(CH_2Ph)-SeC\mathit{H}_2Ph$, and thus represents the uncoordinated Se atom.

In the cis-bis(phosphine) cationic complex $[PtCl\{\mathbf{2}\}(PEt_3)_2](BF_4)$, generated *in situ* from $[PtCl(PEt_3)_2]_2(BF_4)_2$ and 2 equiv of **2**, there is only one Se atom coordinated and a cis arrangement of phosphorus ligands. We find $\delta(^{77}Se) = 529.8$ and 376.1, with the high-field resonance, once again, showing the larger $^{2}J(^{77}Se,^{31}P) = 116$ Hz. From its ^{31}P spectrum, which reveals two nonequivalent PEt_3 ligands ($\delta(^{31}P) = 18.5$, $^{1}J(^{195}Pt,^{31}P) = 3125$ Hz, trans to Se and $\delta(^{31}P) = 6.1$, $^{1}J(^{195}Pt,^{31}P) = 3316$ Hz, cis to Se, $^{2}J(P,P) = 17.4$ Hz) we find the cis phosphorus−selenium coupling to be ca. 12 Hz.

It is commonly the case that coordinated ^{77}Se is found at lower field (higher frequency) relative to the free ligand[29-31] or noncomplexed ^{77}Se signals,[32] e.g. as in **7**. Perhaps the electronic effect of the trans tertiary phosphine results in only a relatively small $\Delta\delta$; however, we have no explanation for the observed chemical shift change of the noncomplexed ^{77}Se atom. Rather than seek an answer in chemical shift theory, we choose simply to note this unexpected result and caution against the blind use of ^{77}Se chemical shifts as a yardstick for complexation.

The sulfur analog of **9**, $[PtCl_2(\mathbf{1})(P\text{-}n\text{-}Bu_3)]$, **10**, at 228 K, shows a single ^{31}P resonance with satellites, $^{1}J(^{195}Pt,^{31}P) = 3352$ Hz, and we assume that it has the same structure. Again, on the basis of $^{1}J(^{195}Pt,^{31}P)$, at 3352 and 3361 Hz, for **9** and **10**, respectively, ligands **1** and **2** show only a moderate-to-weak trans influence. This is in contrast to the $^{1}J(^{195}Pt,^{31}P)$ values of ca. 2700 Hz found in many dithiolate, diphosphine complexes of platinum(II).[33]

Scheme 3



^{31}P NMR data for $PtCl_2(PMe_2Ph)(L)$ in $CDCl_3$, δ (ppm), ^{1}J (Hz)

		trans		cis	
	L	δ	$^{1}J(Pt,P)$	δ	$^{1}J(Pt,P)$
11	SBz_2	-13.9	3377	-15.6	3484
12	$SOBz_2$	-13.5	3223	-9.3	3575
	$SH(C_5H_{11})$*			-16.2	3529

* C_6D_6, RT, C_5H_{11} = n-pentyl, complex is presumed to be cis.

In the course of seeking model sulfur complexes for comparison with **6**, we carried out several bridge-splitting reactions using $[Pt(\mu\text{-}Cl)Cl(PMe_2Ph)]_2$ and a sulfur ligand as shown in Scheme 3. The solutions were studied using ^{31}P NMR at ambient temperature immediately after mixing and then several hours later. For dibenzyl sulfide and dibenzyl sulfoxide we observe relatively rapid formation of new complexes, **11** and **12**, to which we assign the trans-geometry, and then slow conversion to a more stable product, to which we assign the cis-geometry. ^{31}P data for these complexes are shown in Scheme 3, and we note again that the $^{1}J(^{195}Pt,^{31}P)$ values, at

---

(29) Colton, R.; Ebner, J.; Hoskins, B. F. *Inorg. Chem.* **1988**, *27*, 1993. Colton, R.; Ebner, J. *Inorg. Chem.* **1989**, *28*, 1559.

(30) Gulliver, D. J.; Hope, E. E.; Levason, W.; Murray, S. G.; Marshall, G. L. *J. Chem. Soc. Dalton Trans.* **1985**, 1265. Hope, E. G.; Levason, W.; Murray, S. G.; Marshall, G. L. *J. Chem. Soc., Dalton Trans.* **1985**, 2185.

(31) Abel, E. W.; Orrell, K.; Platt, A. W. G. *J. Chem. Soc., Dalton Trans.* **1983**, 2345.

(32) McConnachie, J. M.; Ansari, M. A.; Ibers, J. A. *Inorg. Chem.* **1993**, *32*, 3250.

(33) Fazlur-Rahmen, A. K.; Verkade, J. G. *Inorg. Chem.* **1992**, *31*, 5331.

3377 and 3223 Hz for the trans complexes with dibenzyl sulfide and dibenzyl sulfoxide, respectively, are very similar to the values cited above, suggesting that all three ligands may have similar trans influences. The $^1J(^{195}\text{Pt},^{31}\text{P})$ values for the cis-isomers are slightly larger.

We conclude that **1**, as a ligand, is comparable to other neutral model sulfur ligands and that both **1** and **2** can coordinate via one or both of the chalcogen atoms, with the latter mode favored in some cases. For **1**, the relative stability of complexes with both S-donors complexed has lead to unexpected trinuclear compounds.

Experimental Section

General Methods. NMR measurments were carried out using Bruker AC-250 and AMX-500 Bruker spectrometers. Chemical shifts, in ppm, are relative to TMS for ^{1}H and ^{13}C, whereas H_3PO_4, Me_2Se, and K_2PtCl_6 were used for ^{31}P, ^{77}Se, and ^{195} Pt, respectively. Infrared measurements were made using a Perkin-Elmer 883 spectrometer, and mass spectra and analytical measurements were performed by the analytical laboratory of the ETH, Zurich. The dinuclear starting materials were prepared according to the literature.[13,14] Se_2Bz_2 and the tertiary phosphines PMe_2Ph, $PBu^n{}_3$, and PEt_3 were obtained from Aldrich, whereas S_2Bz_2, SBz_2, and $SOBz_2$ were available from Fluka.

Unless otherwise specified, reactions were carried out under an inert atmosphere using previously dried solvents.

X-ray Determination. The crystal selected for X-ray analysis was a deep yellow parallelepiped of dimensions 0.11 × 0.31 × 0.53 mm. Intensity data were measured at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The crystal belongs to the monoclinic system with systematic absences characteristic of space group $P2_1/a$. Crystal data: $C_{30}H_{36}Cl_4P_2Pt_2Se_2{\cdot}0.75CH_2Cl_2$, $M = 1212.2$, $a = 33.278(6)$ Å, $b = 14.056(4)$ Å, $c = 17.603(3)$ Å, $\beta = 104.71(2)°$, $V = 7964(3)$ Å^3, $Z = 8$, $D_c = 2.022$ g cm^{-3}, $F(000) = 4556$, μ(Mo Kα) = 93.17 cm^{-1}.

The unit-cell parameters and their estimated standard deviations were obtained from a least-squares refinement of the setting angles of 25 reflections automatically centered. The intensities of 20,496 reflections ($\pm h,+k,+l$; $3 < \theta < 28°$) were measured using the $\omega-2\theta$ scan technique with a ω scan range of $(0.80 + 0.35 \tan \theta)°$ centered on the calculated peak position. The averaging of equivalent reflections and removal of space-group forbidden data gave 19,136 unique reflections (of which 85 were discarded having $F_o{}^2 < -3\sigma(F_o{}^2)$).

The data were monitored by measuring two standard reflections every 2.5 h of X-ray exposure time. Corrections for Lorentz and polarization effects as well as for absorption were applied.

The structure was solved by Patterson (SHELXS86[34]) and difference Fourier techniques and refined by full-matrix least-squares based on F^2. Anisotropic thermal parameters were assumed for all non-hydrogen atoms except for the solvent molecules and two phenyl rings (C25–C30 and C55–C60) which had significantly larger thermal parameters than the other ones. All the phenyl rings were treated as rigid bodies of D_{6h} symmetry. Hydrogen atoms were all placed in calculated positions and refined riding on their carrier atoms. The final R factors for 593 variables are $R_1 = 0.0495$ on 5234 observed reflections ($I \geq 2\sigma(I)$) and $R_{w2} = 0.1747$ for all data with $w = 1/[\sigma^2(F_o{}^2) + (0.02P)^2]$, where $P = [\max(F_o{}^2,0) + 2F_c{}^2]$.

The calculations were carried out on the Gould Powernode-6040 and Encore-91 computers of the "Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma)" using the progrmas SHELXL92,[35] ABSORB,[36] PARST,[37] and ORTEP.[38] The final atomic fractional coordinates are given in Table 3, while selected bond distances and angles are in Table 1.

Synthesis of *trans*-[PdCl$_2$(S$_2$Bz$_2$)$_2$]. Method 1. $PdCl_2$ (173 mg, 0.976 mmol) and S_2Bz_2 (773 mg, 3.14 mmol) were added to 35 mL of CH_2Cl_2. The resulting suspension was stirred for 2 d at room temperature and filtered, and the solvent was removed to obtain an orange oil. The oil was then treated with 20 mL of *n*-heptane and stirred for 1 h to afford the product as a yellow precipitate. The complex was filtered out and washed twice with 20 mL of *n*-heptane to give 470 mg (72%) of a yellow solid. Anal. Calcd for $C_{28}H_{28}Cl_2S_4Pd$: C, 50.19; H, 4.21. Found: C, 50.27; H, 4.26. IR (Nujol): 360 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.52 (s, 2H; CH_2), 4.12 (s, 2H; CH_2), 7.1–7.6 (m, 10H; aromatic protons). ^{13}C NMR ($CDCl_3$): δ 41.9 (s, C; CH_2), 48.4 (s, C; CH_2), 128–132 (m, 12 C; aromatic carbons).

Method 2. $PdCl_2(CH_3CN)_2$ (146 mg, 0.563 mmol) was added to 15 mL of CH_2Cl_2, the suspension cooled to 263 K, and S_2Bz_2 (423 mg, 1.72 mmol) added. The resulting orange solution was stirred for 30 min, the solvent was removed in vacuo at 263 K, and the oil was dried at room temperature for 1 h under high vacuum. The oil was treated with 20 mL of *n*-heptane and then stirred for 30 min. The yellow precipitate which results was filtered out and washed with another 20 mL of *n*-heptane to afford 293 mg (78%) of product as a yellow solid. Anal. Calcd for $C_{28}H_{28}Cl_2S_4Pd$: C, 50.19; H, 4.21; S, 19.14. Found: C, 49.98; H, 4.27; S, 18.90. IR (Nujol): 360 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.52 (s, 2H; CH_2), 4.12 (s, 2H; CH_2), 7.1–7.6 (m, 10H; aromatic protons). ^{13}C NMR ($CDCl_3$): δ 41.9 (s, C; CH_2), 48.4 (s, C; CH_2), 128–132 (m, 12 C; aromatic carbons).

Synthesis of (PdCl$_2$)$_3$(S$_2$Bz$_2$)$_4$. Method 1. $PdCl_2$ (299 mg, 1.69 mmol) and S_2Bz_2 (1.04 g, 4.23 mmol) were added to 50 mL of CH_2Cl_2. The resulting suspension was stirred for 2 d at room temperature and filtered. The solvent was removed, and the orange oil was dried for 3 h at high vacuum. The solidified mass was treated with 20 mL of toluene and the yellow suspension stirred for 2 h to afford an orange precipitate. This was filtered and washed twice with 20 mL of toluene and then with 20 mL of pentane, to afford 590 mg (69%) of an orange product. Anal. Calcd for $C_{56}H_{56}Cl_6S_8Pd_3$: C, 44.32; H, 3.72; S, 16.90. Found: C, 44.28; H,3.83; S, 16.64. IR (Nujol): 328 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 243 K), δ CH_2's (^2J(H,H) in Hz): σ^1 ligand (uncomplexed S) 2.44 (10), 3.08 (10); complexed S 4.83 (13), 5.26 (13); μ-ligand 2.02 (10), 4.93 (10) (= SCH_2 on Pd with σ^1) and 5.40 (13), 5.59 (13). ^{13}C NMR ($CDCl_3$) δ CH_2's: σ^1-ligand 41.9 (uncoordinated S), 49.6; μ-ligand 46.6 (= SCH_2 on Pd with σ^1), 48.8. These assignments were made using NOESY and C,H-correlation experiments.

Method 2. $PdCl_2(CH_3CN)_2$ (151 mg, 0.582 mmol) and S_2Bz_2 (296 g, 1.20 mmol) were added to 10 mL of CH_2Cl_2. The orange solution was stirred for 10 min at room temperature, the solvent removed in vacuo, and the solid dried for 4 h under vacuum. The solid was treated with 20 mL of toluene, and the suspension was stirred for 1 h and then filtered. The product was washed with another 20 mL of toluene and twice with 20 mL of heptane, before drying to give an orange product, yield 182 mg (62%). Anal. Calcd for $C_{56}H_{56}Cl_6S_8Pd_3$: C, 44.32; H, 3.72; S, 16.90. Found: C, 44.41; H, 3.82; S, 16.65. IR (nujol): 328 (m) cm^{-1}.

Synthesis of (PtCl$_2$)$_3$(S$_2$Bz$_2$)$_4$. $PtCl_2$ (235 mg, 0.883 mmol) and S_2Bz_2 (282 mg, 1.15 mmol) were added to 20 mL of CH_2Cl_2. The resulting suspension was stirred for 1 d at room temperature and filtered through Celite. The yellow solution was concentrated to about 7 mL and slowly treated with 20 mL of pentane to afford a yellow precipitate. The solid was washed with 20 mL of pentane and then recrystallized from a CH_2Cl_2–pentane mixture to afford 300 mg (58%) of a yellow product. Anal. Calcd for $C_{56}H_{56}Cl_6S_8Pt_3$: C, 37.71; H, 3.16; S, 14.38. Found: C, 37.88; H, 3.00; S, 14.01. IR (Nujol): 333 (m) and 320 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 243 K) δ CH_2's (^2J(H,H) in Hz): σ^1 ligand (uncomplexed S) 2.41 (10), 3.09 (10); complexed S 4.91 (13), 5.20 (13); μ-ligand 2.07 (11), 5.15 (11) and 5.40 (13), 5.64 (13). ^{13}C NMR ($CDCl_3$, 293 K) δ CH_2's: 41.5, 45.7, 47.3, 48.7. These assignments were made by analogy with the Pd analog and are not based on 2-D work. No ^{195}Pt satellites were observed; however, ^{195}Pt data are given in the text.

Synthesis of *cis*-[PtCl$_2$(PMe$_2$Ph)]$_2$(Se$_2$Bz$_2$). $[Pt(\mu\text{-}Cl)Cl(PMe_2Ph)]_2$ (425 mg, 0.526 mmol) and Se_2Bz_2 (191 mg, 0.561 mmol) were suspended in 10 mL of toluene, and the suspension was stirred for 3 h

---

(34) Sheldrick, G. M. SHELXS86, *A Program for Crystal Structure Determination*, University of Göttingen: Göttingen, Germany, 1986.

(35) Sheldrick, G. M. SHELXL92, *A Program for Structure Refinement*; University of Göttingen: Göttingen, Germany, 1992.

(36) Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 109.

(37) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

(38) Johnson, C. K. *Report ORNL-5138*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

in the dark to afford a yellow light precipitate. The solid was filtered out, washed with 5 mL of pentane, and dissolved in 12 mL of CH_2Cl_2. The yellow solution was filtered and then slowly treated with 30 mL of pentane to afford the product as a yellow solid, yield 480 mg (80%). Anal. Calcd for $C_{30}H_{36}P_2Cl_4Se_2Pt_2$: C, 31.38; H, 3.16. Found, C, 31.55; H, 2.91. IR (Nujol): 322 (m) and 280 (m) cm^{-1}. Mass spectrum (FAB^+) [*m/z* (assignment)]: 1150 (M^+), 1112.8 ($M^+ - Cl$), 986.8, 941.9, 858.8, 815.8, 708.9, 582.8, 537.9, 502.9, 460.

Synthesis of *cis*-$[PtCl_2(PMe_2Ph)]_2(S_2Bz_2)$. $[Pt(\mu\text{-}Cl)Cl(PMe_2Ph)]_2$ (81.5 mg, 0.101 mmol) and S_2Bz_2 (29.0 mg, 0.118 mmol) were dissolved in 8 mL of toluene to obtain a light-yellow solution. After 15 min at room temperature a colorless precipitate began to form. The reaction was complete after 3 h. The solid was filtered out and washed with 5 mL of toluene, after which time the solvent was removed in vacuo. The colorless solid was dissolved in 15 mL of CH_2Cl_2 at about 313 K, and the solution was filtered, concentrated to 10 mL, and then slowly treated with 10 mL of pentane to afford the product as a colorless solid, yield 79 mg (74%). Anal. Calcd for $C_{30}H_{36}P_2Cl_4S_2Pt_2$: C, 34.17; H, 3.44; S, 6.08. Found: C, 34.41; H, 3.23; S, 6.15. IR (Nujol): 330 (m) and 281 (m) cm^{-1}.

Reactions Observed Spectroscopically by NMR. Reaction between $(Pt(\mu\text{-}Cl)Cl(PMe_2Ph))_2$ and Se_2Bz_2. $(Pt(\mu\text{-}Cl)Cl(PMe_2Ph))_2$ (15.1 mg, 0.0187 mmol) and Se_2Bz_2 (12.8 mg, 0.0376 mmol) were dissolved in 0.5 mL of $CDCl_3$ at 223 K, and the NMR spectra were registered at the 233 K.

Reaction between $[Pt(\mu\text{-}Cl)Cl(P\textit{n}\text{-}Bu_3)]_2$ and Se_2Bz_2. $(Pt(\mu\text{-}Cl)\text{-}Cl(PBu^{n}_{3}))_2$ (13.7 mg, 0.0146 mmol) and Se_2Bz_2 (10.3 mg, 0.0303 mmol) were dissolved in 0.5 mL of $CDCl_3$ at 223 K, and the NMR spectra were registered at the 233 K.

Reaction between $[Pt(\mu\text{-}Cl)Cl(P\textit{n}\text{-}Bu_3)]_2$ and S_2Bz_2. $Pt(\mu\text{-}Cl)Cl\text{-}(PBu^{n}_{3}))_2$ (9.4 mg, 0.0100 mmol) and S_2Bz_2 (5.1 mg, 0.0207 mmol) were dissolved in 0.5 mL of $CDCl_3$ at 223 K, and the NMR spectra were registered at the 233 K.

Reaction between $(Pt(\mu\text{-}Cl)(PEt_3)_2)_2(BF_4)_2$ and Se_2Bz_2. $[Pt(\mu\text{-}Cl)\text{-}(PEt_3)_2)]_2(BF_4)_2$ (13.4 mg, 0.0121 mmol) and Se_2Bz_2 (8.3 mg, 0.0244 mmol) were dissolved in 0.5 mL of $CDCl_3$ at room temperature. The NMR spectra were registered at 233 K.

Reaction between $(Pt(\mu\text{-}Cl)Cl(PMe_2Ph))_2$ and SBz_2 and $SOBz_2$. The dimer and the ligand were dissolved in 0.5 mL of $CDCl_3$ and ^{31}P NMR spectra recorded at different intervals.

Acknowledgment. P.S.P. thanks the Swiss National Science Foundation as well as the ETH for support and the Johnson-Matthey Research Foundation, Reading, England, for the loan of precious metals. We also thank Prof. F. Calderazzo for valuable discussion and Dr. H. Rüegger for experimental assistance.

Supplementary Material Available: For structure **7**, tables of isotropic and anisotropic displacement parameters, atomic coordinates and isotropic displacement parameters for disordered solvent molecules and hydrogen atoms, and experimental data for the X-ray diffraction study (5 pages). Ordering information is given on any current masthead page.