

Interplay of P–H and E–H (E = S, Se) Bonds in Palladium Derivatives: Synthesis and Disruption of New Mixed-Valence Palladium Triangular Clusters Mediated by Proton Mobility. Crystal and Molecular Structure of $[\text{Pd}_3(\mu\text{-PCy}_2)_2(\mu\text{-SPh})(\text{PCy}_2\text{H})_2(\text{SPh})]$

Milena Sommovigo,[†] Marco Pasquali,^{*,†} Fabio Marchetti,[†] Piero Leoni,^{*,†,‡} and Tiziana Beringhelli[§]

Dipartimento di Chimica e Chimica Industriale, Via Risorgimento, 35, I-56126 Pisa, Italy, Scuola Normale Superiore, Piazza dei Cavalieri, 7, I-56100 Pisa, Italy, and Dipartimento di Chimica Inorganica e Metallorganica, Via Venezian 21, I-20123 Milano, Italy

Received November 30, 1993[®]

An excess of PhEH (E = S, Se) reacts with $\text{Pd}_2(\text{PCy}_2\text{H})_2(\mu\text{-PCy}_2)(\mu\text{-}\eta^3\text{-C}_3\text{H}_5)$ causing, by protonation of the bridging ligands, the disruption of the dinuclear unit and the formation of the monomers *trans*- $[\text{Pd}(\text{EPh})_2(\text{PCy}_2\text{H})_2]$. The isolated monomers were reacted with the same π -allyl dimer providing a synthetic route to the clusters $[\text{Pd}_3(\mu\text{-PCy}_2)_2(\mu\text{-EPh})(\text{PCy}_2\text{H})_2(\text{EPh})]$; these mixed-valence triangular complexes exhibit high stability both in the solid state and in solution, but are reactive toward weak proton donors. Reaction with an excess of PhEH and PCy_2H rapidly and quantitatively gives the monomers *trans*- $[\text{Pd}(\text{EPh})_2(\text{PCy}_2\text{H})_2]$. All complexes were characterized by multinuclear NMR analyses. $[\text{Pd}_3(\mu\text{-PCy}_2)_2(\mu\text{-SPh})(\text{PCy}_2\text{H})_2(\text{SPh})]$ crystallizes in the *Pnma* space group (orthorhombic, *Z* = 4) with the following unit cell dimensions: *a* = 13.587(4), *b* = 25.231(8), *c* = 18.306(6) Å.

Introduction

The development of selective synthetic methodologies for the construction of molecular clusters by the assembly of smaller organometallic fragments is one of the important goals of cluster chemistry. This area has been extensively surveyed in recent reviews by Braunstein^{1a} and Puddephatt,^{1b} with special emphasis on the synthesis of small heteronuclear clusters. A number of clusters, containing three to five metal atoms of different late transition metals has been reported; some of them contain palladium and/or platinum with the phosphido group as an usual bridging ligand.¹ A few homonuclear Pd nanoclusters have been reported,^{1–7} including trinuclear Pd(O) clusters,² $\text{Pd}_3(\mu\text{-CO})_3(\text{PPh}_3)_3$ being the first example.^{2a,b} Dixon and co-workers³ later reported the first structurally characterized triangular Pd_3 clusters with palladium in an oxidation state other than zero, namely $[\text{Pd}_3(\mu\text{-Cl})(\mu\text{-PPh}_2)_2(\text{PR}_3)_3]\text{BF}_4$ (R = Et, Ph). Since then only three triangular cationic mixed-valence Pd_3 clusters have been

fully characterized, $[\text{Pd}_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$ ^{1b,4} and $[\text{Pd}_3(\mu\text{-dppm})_3(\mu_3\text{-CO})(\text{X})]^+$ (X = Cl,^{5a} CN^{5b}), by Puddephatt and co-workers and $[\text{Pd}_3(\mu\text{-dppm})_3(\mu_3\text{-PF}_3)(\mu_2\text{-Cl})]^+$, by Balch and co-workers.⁶ In 1987 Jones and co-workers reported the synthesis and the X-ray crystal structure of $\text{Pd}_3(\mu\text{-PBu}^t)_3(\text{CO})_2\text{Cl}$ which represents a unique example of full characterization of a neutral mixed-valence Pd_3 cluster;⁷ $\text{Pd}_3(\mu_2\text{-PPh}_2)(\mu_2\text{-S})(\text{PPh}_3)_3$ was characterized later, only by ³¹P{¹H} NMR spectroscopy.⁸

We now report a new methodology resulting in the selective assembly of mono and dinuclear Pd fragments to form neutral mixed-valence trinuclear palladium clusters in high yield. The neutral phosphido-bridged palladium derivatives reported herein proved to be highly reactive toward weak proton donors such as PhEH (E = S, Se), which transform the phosphido ligands into secondary phosphines; the polynuclear framework is destroyed accordingly, and stable mononuclear complexes are quantitatively formed.

Results and Discussion

trans- $[\text{Pd}(\text{SePh})_2(\text{PCy}_2\text{H})_2]$. We have recently reported the reaction of $\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)$ with secondary phosphines giving diphosphido, $[\text{Pd}(\mu\text{-PBu}^t)_2(\text{PBu}^t\text{H})_2]$, (1),⁹ or monophosphido-bridged, $[\text{Pd}_2(\mu\text{-PCy}_2)(\mu\text{-}\eta^3\text{-C}_3\text{H}_5)(\text{PCy}_2\text{H})_2]$ (2),¹⁰ dinuclear derivatives.

Complex 1 was transformed by reaction with strong acids into $[\text{Pd}_2(\mu\text{-PBu}^t)_2(\mu\text{-PBu}^t\text{H})(\text{PBu}^t\text{H})_2]\text{X}$ (X = CF₃SO₃, BF₄) (3), containing secondary phosphines as terminal or bridging (through a P–H–Pd agostic interaction) ligands.¹¹ The reactivity of the cationic complex 3 studied so far, indicates a good stability of the central $\text{Pd}_2(\mu\text{-PBu}^t)$ core, which survives both the substitution of the secondary phosphines^{11b,12} and ethylene insertion¹² into

[†] Dipartimento di Chimica e Chimica Industriale.

[‡] Scuola Normale Superiore.

[§] Dipartimento di Chimica Inorganica e Metallorganica.

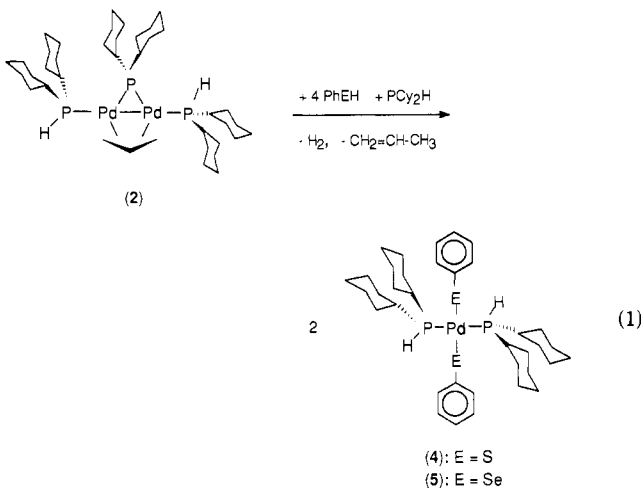
[®] Abstract published in *Advance ACS Abstracts*, April 15, 1994.

- (a) Braunstein, P. In *Perspective in Coordination Chemistry*; Williams, A. F., Floriani, C., Merbach, A. M., Eds.; Verlag Helvetica Chimica Acta: Basel, Switzerland, 1992; pp 67–107. (b) Puddephatt, R. J.; Milajlovic-Muir, L.J.; Muir, K. W. *Polyhedron* 1990, 9, 2767–2802.
- (a) Hidai, M.; Kokura, M.; Uchida, Y. *J. Organomet. Chem.* 1973, 52, 431–435. (b) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* 1977, 99, 2134–2140. (c) Otsuka, S.; Tatsuno, Y.; Miki, M.; Aoki, T.; Matsumoto, M.; Yoshioka, H.; Nakatsu, K. *J. Chem. Soc., Chem. Commun.* 1973, 445–446. (d) Francis, C. G.; Khan, S. I.; Morton, P. R. *Inorg. Chem.* 1984, 23, 3680–3681. (e) Lee, S. W.; Troglor, W. C. *Inorg. Chem.* 1990, 29, 1099–1102.
- (a) Bushnell, G. W.; Dixon, K. R.; Moroney, P. M.; Rattray, A. D.; Wan, C. *J. Chem. Soc., Chem. Commun.* 1977, 709–710. (b) Dixon, K. R.; Rattray, A. D. *Inorg. Chem.* 1978, 17, 1099–1103. (c) Berry, D. E.; Bushnell, G. W.; Dixon, K. R.; Moroney, P. M.; Wan, C. *Inorg. Chem.* 1985, 24, 2625–2634. (d) Cartwright, S. J.; Dixon, K. R.; Rattray, A. D. *Inorg. Chem.* 1980, 19, 1120–1124.
- (a) Milajlovic-Muir, L.J.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* 1983, 1336–1337. (b) Milajlovic-Muir, L.J.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* 1985, 536–537. (c) Jennings, M. C.; Puddephatt, R. J.; Milajlovic-Muir, L.J.; Muir, K. W.; Mwariri, B. N. *Organometallics* 1992, 11, 4164–4166.
- Balch, A. L.; Davis, B. J.; Olmstead, M. M. *J. Am. Chem. Soc.* 1990, 112, 8592–8593.
- Arif, A. M.; Heaton, D. M.; Jones, R. A.; Nunn, C. M. *Inorg. Chem.* 1987, 26, 4228–4231.

- Hadj-Bagheri, N.; Browning, J.; Dehghan, K.; Dixon, K. R.; Meanwell, N. J.; Veighi, R. *J. Organomet. Chem.* 1990, 396, C47–C52.
- Leoni, P.; Sommovigo, M.; Pasquali, M.; Sabatino, P.; Braga, D. *J. Organomet. Chem.* 1992, 423, 263–270.
- Pasquali, M.; Marchetti, F.; Leoni, P.; Beringhelli, T.; D'Alfonso, G. *Gazz. Chim. Ital.* 1993, 11, 659.
- (a) Albinati, A.; Lianza, F.; Pasquali, M.; Sommovigo, M.; Leoni, P.; Pregosin, P. S.; Rügger, H. *Inorg. Chem.* 1991, 30, 4690–4692. (b) Leoni, P.; Pasquali, M.; Sommovigo, M.; Laschi, F.; Zanello, P.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Rügger, H. *Organometallics* 1993, 12, 1702–1713.
- Leoni, P.; Pasquali, M.; Sommovigo, M.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Rügger, H. *Organometallics* 1993, 12, 4503.

the P-H bonds, allowing the isolation of new dinuclear mono-phosphido bridged compounds.

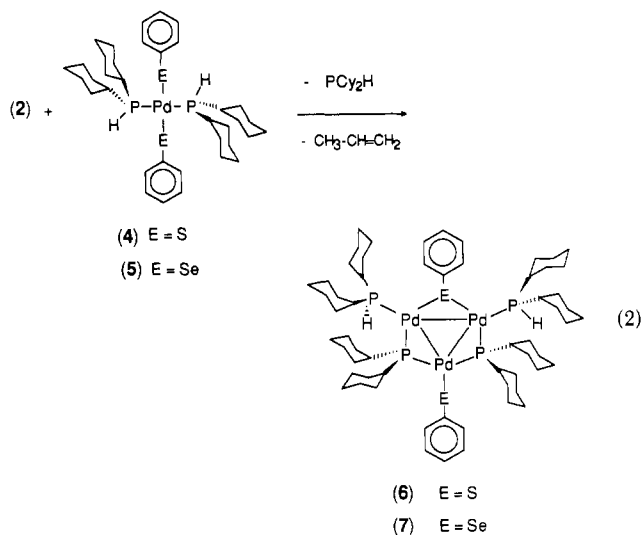
The *neutral* derivative **2** proved to be much less resistant, and the dinuclear structure was destroyed under mild conditions by reaction with PhSH giving the monomeric *trans*-[Pd(SPh)₂(PCy₂H)₂] (**4**), which was fully characterized by X-ray crystallography and multinuclear NMR analyses.¹⁰ In the earlier procedure **2** was reacted with an excess of PhSH, and **4** was isolated in 45–55% yield (and it often needed recrystallization). Since the P/Pd ratio is 1.5 in complex **2** and 2 in complex **4**, the reaction has been subsequently performed with PhSH and PCy₂H excess; much higher yields (quantitative by NMR, 85% isolated) of analytically pure **4** were obtained by this route (eq 1). The reaction takes place with 2 equiv out of the 4 equiv of PhSH formally acting as proton donors toward the allyl ligand (eliminated as propene) and the phosphido ligand (transformed into a secondary phosphine); the protons of the remaining 2 equiv of PhSH are lost as molecular hydrogen (propene and molecular hydrogen were identified as coproducts of the reaction by GC).



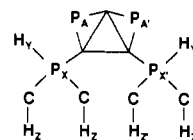
Following a similar experimental procedure, we have prepared the corresponding Se derivative *trans*-[Pd(SePh)₂(PCy₂H)₂] (**5**); IR and NMR (¹H, ¹H{³¹P}, ³¹P{¹H} and ³¹P) spectra of complex **5** were consistent with the suggested structure and quite similar to the corresponding spectra of complex **4**.¹⁰ The [AMX₂]₂ spin system (A = P, M = P-H, X = P-C-H) produced typical patterns in ¹H and proton-coupled ³¹P NMR spectra, whose analysis gave the following values of coupling constants (corresponding values for **4** in parentheses): ¹J_{PH} = 346 (345), ³J_{PH} = 6 (8), ²J_{PP} = 458 (474), ³J_{HH} = 6.5 (7) Hz.^{10,13} Reference is made to the previous communication, regarding complex **4**, for a detailed analysis of the NMR spectra.¹⁰

[Pd₃(μ-PCy₂)₂(μ-EPh)(PCy₂H)₂(EPh)]. By reaction of equimolar amounts of the dimer **2** and the monomer **4** in toluene a new polynuclear derivative was slowly formed in 72% yield (eq 2), which was characterized as [Pd₃(μ-PCy₂)₂(μ-SPh)(PCy₂H)₂(SPh)] (**6**) by elemental and spectroscopic analyses and by single-crystal X-ray diffraction; propene is evolved during the reaction, as verified by GC analysis. Complex **6** may form by transfer of a proton from a P-H bond to the allyl ligand, giving free propene and creating unsaturation at the Pd centres together with a new phosphido ligand; all these processes favor the formation of oligomers of higher nuclearity.

Spectroscopic analyses on complex **6** confirm that the solid-state structure (see below) is retained in solution. Typical absorptions for the aromatic rings were observed in the IR spectrum (Nujol) of complex **6** at 3093 vw and 3057 w cm⁻¹, ν_{=CH}, and at 1574 m cm⁻¹, ν_{C=C}, while ν_{PH} was observed at 2296 w cm⁻¹. The ¹H NMR spectrum of a benzene solution of complex



6 clearly shows the signals of the hydrogens directly bound to the phosphorus atoms of the PCy₂H ligands. The multiplet, centered at δ = 4.55 ppm exhibits a set of six broad resonances (Figure 1) from which the presence of two secondary phosphines which are magnetically nonequivalent can be inferred.¹⁰



From this spectrum (¹J_{H_YP_X} + ⁴J_{H_YP_{X'}}}) = 314 Hz and ³J_{P_XP_{X'}}} = 89 Hz can be estimated. The reduced interphosphine *J*_{PP'} coupling and the absence of the resolved coupling with the methinic protons of the cyclohexyl rings, with respect to the data for mononuclear compounds **4** and **5**, suggest a more complex structure. Indeed the gated decoupled ³¹P{¹H} NMR spectrum consists of two triplets (integrated intensity ratio 1:1) centered at δ = 254.9 and 4.19 ppm, respectively (Figure 2), which can be assigned to two μ-PCy₂ and two PCy₂H ligands, indicating a polynuclear structure. As shown by the solid state X-ray structure, this is an [AX]₂ spin system (A = μ-PCy₂ and X = PCy₂H) and the apparent *J* measured (*J*_{app} = 13 Hz) is indeed 1/2 (²J_{P_AP_X}} + ³J_{P_AP_{X'}}}).}}}

The reaction of complex **2** with complex **5** in a 1/1 molar ratio gives in 60% yield [Pd₃(μ₂-PCy₂)₂(μ₂-SePh)(PCy₂H)₂(SePh)] (**7**), the NMR properties of complex **7** are very similar to those observed for compound **6**, confirming that their solution structures are the same. Both the resonances of the hydrogens of the secondary phosphines in the ¹H spectrum and those of the two pseudotriplets in the ³¹P{¹H} spectrum are shifted to lower fields (δ = 4.69 ppm for ¹H; δ = 262.1 and 7.71 ppm for ³¹P), but the coupling pattern is the same [(¹J_{H_YP_X}} + ⁴J_{H_YP_{X'}}}) = 313 Hz, ³J_{P_XP_{X'}}} = 89 Hz from the ¹H spectrum and *J*_{app} = 14 Hz from the ³¹P{¹H} spectrum]. The experimental values of ³J_{PP'} between the terminal phosphines are comparable with those reported for related trinuclear palladium clusters (e.g. 93 Hz in [Pd₃(μ-Cl)(μ-PPh₂)₂(PEt₃)₃]^{+,3d}, 89.3 Hz in [Pd₃(μ-Cl)(μ-PPh₂)₂(PPh₃)₃]^{+,8}, 78 Hz in [Pd₃(μ-PPh₂)₃(PPh₂)(PPh₃)₂]^{+,3d}). The "deceptively simple" spectra require that the coupling constant between the two bridging phosphorus atoms (²J_{P_AP_X}}) should be very different from ³J_{P_XP_{X'}}}¹⁴ and computer simulations have been performed to get some estimates of the four coupling constants involved, even if a unique solution cannot be obtained.}

(13) Palmer, R. A.; Whitcomb, D. R. *J. Magn. Reson.* **1980**, *39*, 371–379.

(14) Abraham, R. J. In *Analysis of High Resolution NMR Spectra*; Elsevier: Amsterdam, **1971**.

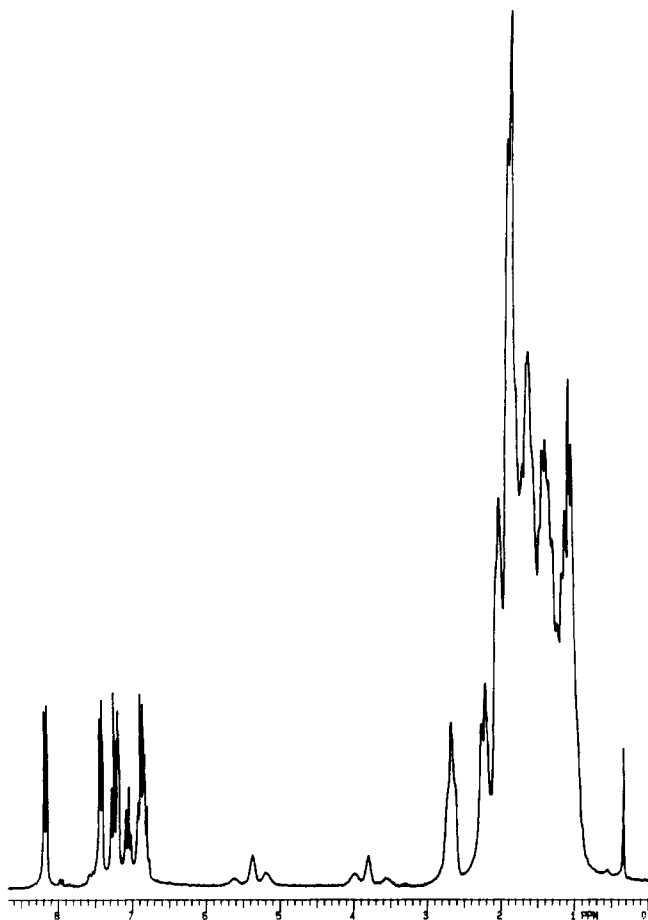


Figure 1. ^1H NMR spectrum of complex **6** (C_6D_6 , 200.13 MHz, 295 K) showing the multiplet at 4.55 ppm.

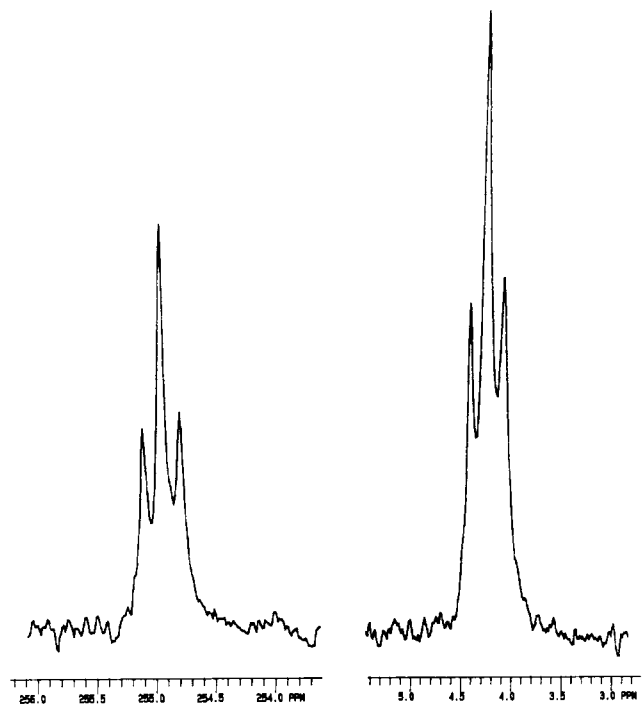


Figure 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **6** (C_6D_6 , 81.015 MHz, 295 K).

Following ref 3b, $^2J_{\text{P}_A\text{P}_X}$ was assumed to be negative with respect to $^3J_{\text{P}_A\text{P}_X}$. As shown in Figure 3, when $^3J_{\text{P}_A\text{P}_X} = 0$ Hz, $^2J_{\text{P}_A\text{P}_A'}$ should be >350 Hz in order to observe the experimental height ratio in each pseudotriplet (see Figure 2). When $^2J_{\text{P}_A\text{P}_X}$ and $^3J_{\text{P}_A\text{P}_X}$ are assumed to be of the same sign, the experimental results are

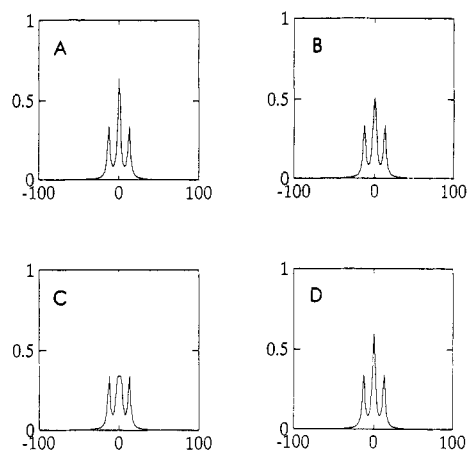


Figure 3. Computer simulations for a $[\text{AX}]_2$ spin system using the following parameters: (A) $J_{\text{P}_A\text{P}_X} = 89$ Hz, $J_{\text{P}_A\text{P}_X'} = 200$ Hz, $J_{\text{P}_A\text{P}_X} = -20$ Hz, $J_{\text{P}_A\text{P}_X'} = -6$ Hz; (B) the same as A, but with $J_{\text{P}_A\text{P}_X} = -26$ Hz, $J_{\text{P}_A\text{P}_X'} = 0$ Hz; (C) the same as A but with $J_{\text{P}_A\text{P}_X} = -32$ Hz, $J_{\text{P}_A\text{P}_X'} = +6$ Hz; (D) the same as C but with $J_{\text{P}_A\text{P}_X} = 600$ Hz. Conditions: resolution, 1 Hz/point; line width, 4 Hz.

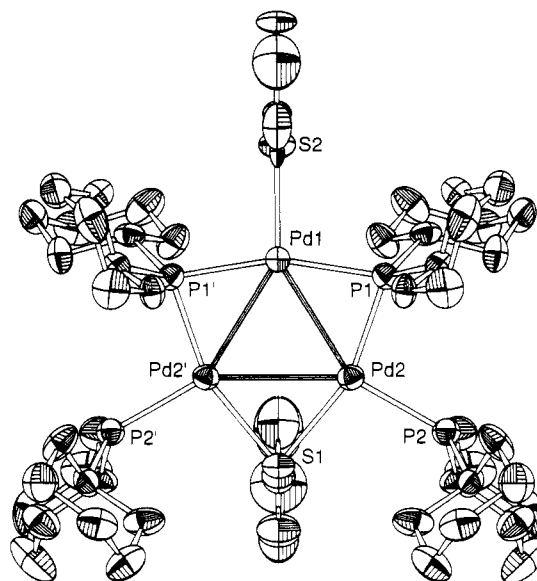
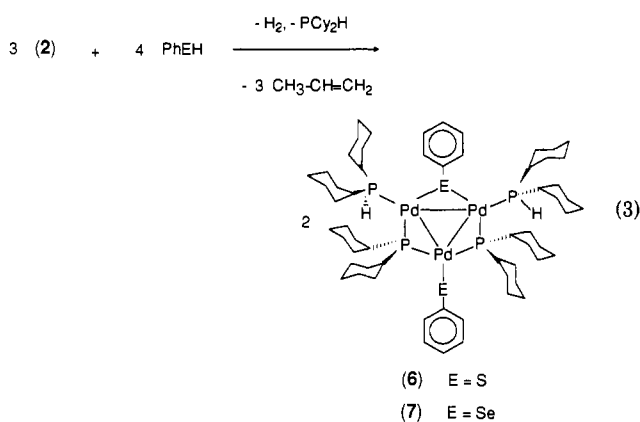


Figure 4. ORTEP view of the molecular structure of **6** and the atom numbering projected on the plane containing the palladium atoms. A single prime denotes the symmetry-related position = $x, 1/2 - y, z$. Thermal ellipsoids are represented at 30% probability.

reproduced with smaller values of $^2J_{\text{P}_A\text{P}_A'}$ (e.g. >150 Hz when $^3J_{\text{P}_A\text{P}_X} = -6$ Hz), while the assumption of different signs for $^2J_{\text{P}_A\text{P}_X}$ and $^3J_{\text{P}_A\text{P}_X}$ required for $^2J_{\text{P}_A\text{P}_A'}$ values higher than 600 Hz. The measured values reported in the literature for $^2J_{\mu\text{-P}\mu\text{-P}}$ in similar compounds are *ca.* 200 Hz (see for instance $[\text{Pt}_3(\mu\text{-S})(\mu\text{-PPh}_2)_2(\text{PPh}_3)_3]$, 176 Hz;⁸ $[\text{Pd}_3(\mu\text{-PPh}_2)_3(\text{PPh}_2)(\text{PPh}_3)_2]^+$, 197 Hz;^{3d} $[\text{Pd}_3(\mu\text{-PPh}_2)_3(\text{PEt}_3)_3]^+$, 200 Hz^{3d}) but greater values have been suggested in other cases (e.g. $[\text{Pd}_3(\mu\text{-Cl})(\mu\text{-PPh}_2)_2(\text{PEt}_3)_3]^+$, $[\text{Pd}_3(\mu\text{-Cl})(\mu\text{-PPh}_2)_2(\text{PPh}_3)_3]^+$, and $[\text{PtPd}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)_2(\text{PPh}_3)_3]^+$, 400 Hz in ref 3c). Indeed, as shown from the solid-state X-ray structure, the two phosphido ligands are almost *trans* to each other ($\text{P1-Pd1-P1}' = 160.2(2)^\circ$; see Figure 4) and a value greater than 200 Hz can safely be expected. Since an upper value for $^2J_{\text{P}_A\text{P}_A'}$ can be set from the $^2J_{\text{P}_A\text{P}_X}$ measured in the related mononuclear complexes **4** and **5**, we can set $470 (450) > ^2J_{\text{P}_A\text{P}_A'} > 150$ Hz, while $-6 (-8) < ^3J_{\text{P}_A\text{P}_X} < 0$ Hz and $-26 (-28) < ^2J_{\text{P}_A\text{P}_X} < -20$ Hz (the values in parentheses refer to compound **7**). The partial simulation of the proton spectra (in principle an $[\text{AXYZ}]_2$ spin system, where $\text{A} = \text{PCy}_2$, $\text{X} = \text{PCy}_2\text{H}$, $\text{Y} = \text{P-H}$, and $\text{Z} = \text{P-C-H}$) indicates that in both complexes $^3J_{\text{P}_A\text{H}_Y} < 7$ Hz.

The isolation of the monomers **4** or **5** is not strictly necessary

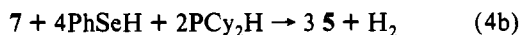
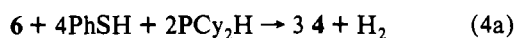
to obtain the trimers **6** and **7**, which can also be prepared in high yield by adding the proper amount of PhEH to complex **2**, according to eq 3 [the sum of eq 1 plus twice eq 2]; in this case, both H₂ and propene were found as coproducts of the reaction.



A detailed mechanistic study of these reactions was not attempted, but ³¹P NMR spectra show that significant amounts of new dimers¹⁰ and of the monomers **4** or **5** are transiently formed in the early steps of the reactions depicted in eq 3. A reasonable (though probably oversimplified) working hypothesis is that 1 equiv out of the 3 equiv of complex **2** reacts rapidly with all the PhEH available (as in eq 1) giving 2 equiv of the monomers **4** or **5** which then react (as in eq 2) with the remaining complex **2** to give the trimers **6** and **7**.

The tendency exhibited by complex **2** to lose the allyl ligand when reacted with weak acids (as in eqs 2 and 3), may be of value in the synthesis of new homo- and heteropolynuclear systems; particular attention should however be paid to the reaction conditions. In fact, in the presence of an excess of proton donor, the bridging phosphido ligands are also susceptible to electrophilic attack, and this can destroy the polynuclear framework, as we observed in the reactions of eq 1.

A further indication of the sensitivity of these systems to weak proton donors comes from the reaction of the trimers **6** and **7** with an excess of PhEH and PCy₂H giving the corresponding monomers **4** and **5** in nearly quantitative yields (eq 4), with evolution of molecular hydrogen (GC).



A further point of interest concerns the mechanism of proton transfers which mediate all the transformations summarized in Scheme 1; *i.e.* do the protons move through the phosphorus, sulfur (or selenium) and carbon atoms by means of oxidative-addition reductive-elimination, or do they transfer "externally", without formation of intermediate Pd-H bonds? While further studies are necessary to answer this question thoroughly, the formation of molecular hydrogen in some of the reactions is suggestive of the first type of mechanism.

Finally, the dramatic difference in the behavior of *neutral* and *cationic* palladium μ -phosphido derivatives should be emphasized; while neutral derivatives are sensitive to weak proton donors, as demonstrated in this work, cationic μ -phosphido complexes are exceptionally robust and [Pd₂(μ -PBU₂)(μ -PBU₂H)(PBU₂H)₂]X is inert to acids as strong as CF₃SO₃H.

X-ray Structure of Complex 6. A projection of the molecular structure of **6** is shown in Figure 4. Significant bond distances and angles are reported in Table 1. Four molecules of **6** are contained in the orthorhombic unit cell (Figure 5): each molecule presents a mirror plane passing through the Pd1 atom and the two thiophenyl rings, the overall molecular geometry ap-

Scheme 1

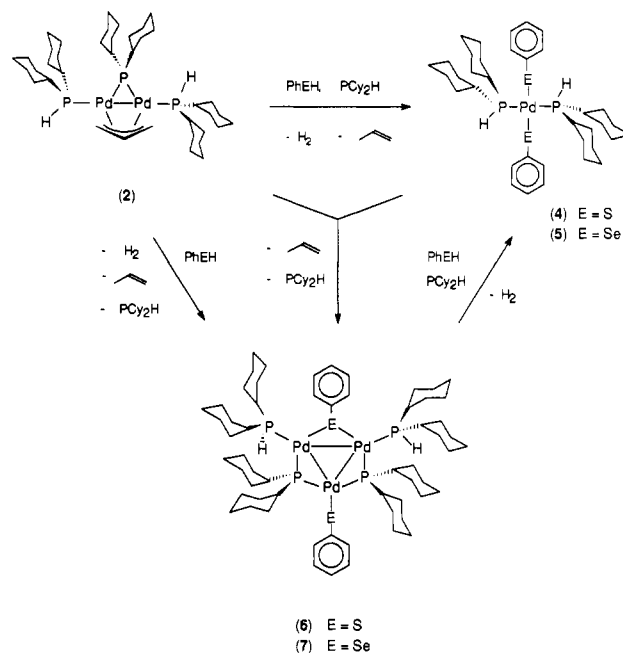


Table 1. Relevant Structural Parameters in Pd₃(SPh)₂(PCy₂)₂(PHCy₂)₂ with Distances in Å, Angles and deg and Esds Given in Parentheses

| | | | |
|--------------|-----------|--------------|-----------------------|
| Pd1-Pd2 | 2.898(2) | Pd2-Pd2' | 2.985(2) ^a |
| Pd1-P1 | 2.235(4) | Pd2-P1 | 2.224(4) |
| Pd1-S2 | 2.344(7) | Pd2-P2 | 2.267(5) |
| Pd2-S1 | 2.393(5) | | |
| P1-Pd1-S2 | 99.1(1) | Pd2-Pd1-P1 | 49.3(1) |
| Pd2-Pd1-Pd2' | 61.99(4) | Pd1-P1-Pd2 | 81.1(2) |
| Pd1-Pd2-P1 | 49.6(1) | Pd1-Pd2-Pd2' | 59.00(4) |
| P1-Pd2-P2 | 101.31(1) | P2-Pd2-S1 | 98.7(2) |
| Pd2'-Pd2-S1 | 51.41(9) | | |

^a where ' and '' have the same meaning than in Figure 1.

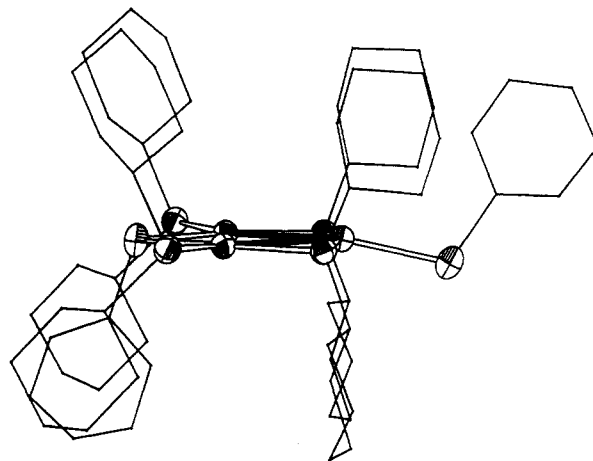


Figure 5. Molecular structure of **6** from a viewpoint near the metal coordination plane.

proximating to C₃ symmetry. The actual disposition of the phenyl groups on the mirror plane *m* is not strictly stated; the abnormally high thermal motion of some carbon atoms could, in fact, mask a statistical distribution of the thiophenyl group as a whole around the mirror plane using the sulfur atom as a pivot.

The three palladium atoms make an isosceles, *quasi*-equilateral triangle with each of the two identical edges spanned by a bridging phosphido and the third edge spanned by a bridging thiophenyl ligand. The Pd₃P₂S core, where P and S refer to the bridging

ligands, is roughly planar (maximum deviation 0.1 Å), while the S2 atom deviates 0.52 Å from this plane.

The Pd-Pd distances [2.898(2), 2.985(2) Å] are within the limits for weak single bonds,¹⁵ and much similar to those observed in Pd₃(μ-Bu₂P)₃(CO)₂Cl [**8**, 2.949(6), 3.000(5) Å]⁷ and [Pd₃(μ-Cl)(μ-PPH₂)₂(PR₃)₃]BF₄ [**9a**, R = Et, 2.93(2), 2.89(2) Å; **9b**, R = Ph, 2.933(2), 2.936(2), 2.906(2) Å]^{3c} which, with respect to the ligand set and the metal oxidation states, are closer to complex **6** than other Pd₃ clusters. The phosphido units adopt a fairly symmetrical bridging arrangement with the P1-Pd distances [2.224(4)-2.235(4) Å] slightly shorter than those observed in complex **8** [2.273(10)-2.305(2) Å]⁷ and in complexes **9a** [2.22(2)-2.28(2) Å] and **9b** [2.203(6)-2.282(6) Å].^{3c} The P2-Pd distance [2.267(5) Å] is significantly shorter than Pd-P distances observed in other PCy₂H palladium complexes [2.309(2) Å in complex **4**¹⁰ and 2.312(3)-2.380(5) Å in (CO)₄M(μ-PCy₂)Pd(PCy₂H)₂,¹⁶ with M = Mn, Mo]; this may be due to the reduction, in the present case, of the S1-Pd2-P1 angle (159.9°) with respect to 180°, the normal value for square planar coordination. The P-H hydrogen atoms lie on the Pd coordination plane, as usual.¹⁰

The Pd1-S2 distance of 2.344(7) Å for the terminal thiophenyl ligand is well in the range of those observed in Pd(SPh)₂(dppe)¹⁷ [2.3486(7) Å], in [Pd(μ-SC₆F₅)(SC₆F₅)PPH₃]₂ (**10**),¹⁸ [2.311(11), 2.328(14) Å], and in complex **4** [2.337(2) Å].¹⁰ The symmetrically bridged thiophenyl ligand presents a longer Pd-S distance [2.393(5) Å], this can be compared with only three known structures of sulfido-bridged palladium compounds: Pd₂(μ-η³-C₃H₅)(μ-SPh)(PMe₃)₂¹⁹ [2.379(2), 2.363(1) Å], Pd₆(μ₂-SPRⁿ)₁₂ [2.288(4), 2.454(4) Å],²⁰ and **10** [2.360(13)-2.381(13) Å].¹⁸ The phenyl rings of the thiophenyl ligands lie on a plane perpendicular to the Pd₃ plane, and bisecting the Pd2-Pd1-Pd2' angle, and are tilted in opposite directions, with respect to the Pd₃ plane; the bridging thiophenyl ligand fits a cavity created by the substituents of the phosphine ligands, with the phenyl ring threaded between two cyclohexyl rings, in a nearly 'eclipsed' way (Figure 5).

The total number of valence electrons in the cluster is 44, consistent with other mixed valence clusters with M₃(μ-PR₂)₂(μ-X) (X = PR₂, Cl) cores.^{3c,7}

Experimental Section

General Data. All preparations and manipulation were carried out under an atmosphere of purified nitrogen by using standard Schlenk techniques. Solvents were purified by refluxing on a proper drying agent and distilled prior to use. IR spectra were recorded as Nujol mulls (KBr) on a Perkin-Elmer 1725 FT-IR spectrophotometer. NMR spectra were recorded on a Varian 200BB or a Bruker AC200 spectrometer operating at 200.13 MHz for ¹H and 81.015 Hz for ³¹P. The ¹H{³¹P} spectrum of complex **5** was recorded using a 'reverse' 5-mm probe while a BSV3 unit with a second synthesizer was used to decouple ¹H from ³¹P. Chemical shifts are referred to Me₄Si (¹H) or to H₃PO₄ (³¹P, downfield signals taken as positive); owing to their sparing solubility, saturated solutions of compounds **6** and **7** in benzene-*d*₆ were employed. Computer simulations were performed on a personal computer using a noniterative version of the UEA NMR simulation program²¹ modified for the graphic output provided by MATLAB. Analyses by gas chromatography were carried out with a DANI 8400 chromatograph equipped with a column packed with 10% OV on Chromosorb W-AW(80-100 mesh) for propene and with a DANI 3200 chromatograph equipped with a D-SM 5A column for hydrogen. Retention times were compared to those of authentic

samples. CpPd(η³-C₃H₅) was prepared as described²² and sublimed prior to use; PCy₂H²³ was prepared according to the literature. PhSH (Aldrich) and PhSeH (Aldrich) were used as purchased.

Preparation of trans-[Pd(SPh)₂(PCy₂H)₂] (4**).** A solution of 0.1 mL of PCy₂H (0.49 mmol) and 0.2 mL of PhSH (1.95 mmol) in hexane (5 mL) was added dropwise to a solution of 335 mg of **2** (0.396 mmol) in hexane (15 mL). The solution turned from yellow to orange and a yellow solid started to precipitate; propene and molecular hydrogen were identified in solution and in the gas phase, respectively, by GC analyses. The reaction mixture was then concentrated at ca. 2 mL and acetone (10 mL) was added. After the reaction was cooled to -30 °C for 1 night, the solid was filtered off and vacuum dried (yield 486 mg, 0.674 mmol, 85%). Similar results were obtained in one-pot reaction, generating *in situ* complex **2** from CpPd(η³-C₃H₅) and the appropriate amount of PCy₂H.¹⁰ IR and NMR spectroscopic data were identical to those of samples prepared as previously described.¹⁰

Preparation of trans-[Pd(SePh)₂(PCy₂H)₂] (5**).** An identical procedure to the preceding one, described for **4**, was followed: 334 mg of **2** (0.393 mmol), 0.1 mL of PCy₂H (0.49 mmol), and 0.2 mL of PhSH (1.95 mmol) were used. A total of 541 mg (0.664 mmol, 84% yield) was recovered. Anal. Calcd for C₃₆H₅₆P₂PdSe₂: C, 53.0; H, 6.92. Found: C, 52.0; H, 7.08. IR (Nujol, KBr): 3060 m (ν_{C-H}), 2357 m (ν_{P-H}), 1573 s (ν_{C-C}), 1469 s (ν_{C-C}) cm⁻¹. ¹H NMR: δ 7.0-8.2 m (10 H, C₆H₅), 3.79 (2 H, P-H, M part of the [AMX₂]₂ spin system), 0.9-2.5 (broad m, 44 H, C₆H₁₁) ppm. ¹H{³¹P} NMR: the complex signal at 3.79 ppm of the P-H protons reduces to a triplet, due to the coupling with the methynic protons of the cyclohexyl rings (³J_{HH} = 6.5 Hz), in the phosphorus decoupled spectrum.¹⁰ ³¹P{¹H} NMR: δ 29.0 s ppm. ³¹P NMR: δ 29.0 ppm (A, part of the [AMX₂]₂ spin system); ¹J_{PH} = 346, ²J_{PH} = 6, ²J_{PP} = 458, ³J_{HH} = 6.5 Hz.^{10,13}

Preparation of [Pd₃(μ-PCy₂)₂(μ-SPh)(PCy₂H)₂(SPh)] (6**).** **Method a.** To a solution of **2** (392 mg, 0.451 mmol) in toluene (10 mL) was added PhSH (0.06 mL, 0.602 mmol). The solution was stirred at room temperature for 6 days; propene and molecular hydrogen were identified in solution and in the gas phase, respectively, by GC analyses. The solvent was then evaporated almost to dryness, and hexane (15 mL) was added. The orange solid obtained was filtered and vacuum dried. A total of 290 mg (0.224 mmol, 74% yield) was recovered.

Method b. A solution of **2** (324 mg, 0.382 mmol) in toluene (20 mL) and a solution of **4** (275 mg, 0.382 mmol) and PCy₂H (0.08 mL, 0.382 mmol) in toluene (20 mL) were dropped at the same speed in the reaction flask. After 6 days of stirring at room temperature, the product was recovered as described in method a (366 mg, 0.275 mmol, 72% yield); propene was identified in the reaction solution by GC. Anal. Calcd for C₆₀H₁₀₀P₄Pd₃S₂: C, 54.2; H, 7.59. Found: C, 54.0; H, 7.65. See Results and Discussion for ¹H and NMR spectra.

Preparation of [Pd₃(μ₂-PCy₂)₂(μ₂-SePh)(PCy₂H)₂(SePh)] (7**).** **Method a.** An identical procedure to method a of the preceding description for **6** was followed; 360 mg (0.425 mmol) of **2** in toluene (20 mL) and 0.06 mL (0.565 mmol) of PhSeH were used. A total of 90 mg (0.063 mmol, 22% yield) was recovered.

Method b. A procedure identical to method b of the preceding description for **6** was followed; 372 mg (0.44 mmol) of **2** in toluene (10 mL), 357 mg (0.44 mmol) of **5**, and 0.09 mL (0.44 mmol) of PCy₂H in toluene (10 mL) were used. A total of 377 mg (0.265 mmol, 60% yield) was recovered. Anal. Calcd for C₆₀H₁₀₀P₄Pd₃Se₂: C, 50.7; H, 7.09. Found: C, 50.2; H, 7.27. IR (Nujol, KBr): 3055 m (ν_{C-H}), 3038 m (ν_{C-H}), 2313 s (ν_{P-H}), 1571 s (ν_{C-C}), 1447 s (ν_{C-C}) cm⁻¹. See Results and Discussion for NMR data.

Reaction of 6 with PhSH and PCy₂H. PCy₂H (147 mg, 0.741 mmol) and PhSH (161 mg, 1.47 mmol) were added to a solution of complex **6** (267 mg, 0.201 mmol) in toluene (50 mL). The orange solution was stirred overnight at room temperature. Molecular hydrogen was identified in the atmosphere by GC analysis, the yellow solution was then concentrated, and acetone (30 mL) was added. After the mixture was cooled for 3 h at -30 °C, the yellow solid was filtered and vacuum dried. Recovered 254 mg (0.35 mmol) of complex **4** (60% yield, quantitative by NMR).

Reaction of 7 with PhSH and PCy₂H. A procedure similar to the preceding was followed by using complex **7** (367 mg, 0.258 mmol) in

(15) Maitlis, P. M.; Espinet, P.; Russel, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. Pergamon: Oxford, England, 1982, Vol. 6, pp 265-278.

(16) Braunstein, P.; de Jesús, E.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Organomet. Chem.* **1989**, *368*, C5-C10.

(17) Wei, G.; Liu, H. *Acta Crystallogr.* **1990**, *C46*, 2457-2458.

(18) Fenn, R. H.; Segrott, G. R. *J. Chem. Soc. A* **1970**, 3197-3201.

(19) Osakada, K.; Ozawa, Y.; Yamamoto, A. *J. Organomet. Chem.* **1990**, *399*, 341-348.

(20) Kunchur, N. R. *Acta Crystallogr.* **1968**, *B24*, 1623-1633.

(21) (a) Harris, R. K.; Woodman, C. M. *Mol. Phys.* **1966**, *10*, 437-449. (b) Woodman, C. M. Ph.D. Thesis, University of East Anglia, 1967.

(22) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220-223.

(23) (a) Issleib, K.; Brack, A. Z. *Angew. Allg. Chem.* **1954**, *277*, 258-270.

(b) Issleib, K.; Tzschach, A. *Chem. Ber.* **1959**, *92*, 704-711. (c) Ashby, E. C.; DePriest, R. N.; Su, W.-Y. *Organometallics* **1984**, *3*, 1718-1727.

Table 2. Experimental Data for the Crystallographic Analysis of $\text{Pd}_3(\text{SPh})_2(\text{PCy}_2)_2(\text{PHCy}_2)_2$

| | |
|--|--|
| chem formula | $\text{C}_{60}\text{H}_{100}\text{P}_4\text{Pd}_3\text{S}_2$ |
| fw | 1328.7 |
| space group | <i>Pnma</i> |
| <i>a</i> , Å | 13.587(4) |
| <i>b</i> , Å | 25.231(8) |
| <i>c</i> , Å | 18.306(6) |
| <i>V</i> , Å ³ | 6276(3) |
| <i>Z</i> | 4 |
| ρ_{calc} , g cm ⁻³ | 1.406 |
| reflcs for lattice params | |
| no. | 30 |
| θ range, deg | 10.0–12.0 |
| radiation | Mo $K\alpha_1$ |
| λ , Å | 0.709 30 |
| <i>F</i> (000) | 2760 |
| <i>T</i> , K | 294 |
| cryst size, mm | 0.13 × 0.33 × 0.47 |
| diffractometer | Ital Structures |
| μ , cm ⁻¹ | 10.3 |
| abs cor (min, max) | 0.83, 1.17 |
| scan speed, deg s ⁻¹ | 0.025 |
| scan width, deg | 1.0 |
| θ range, deg | 2.5–22.5 |
| <i>h</i> range | 0–14 |
| <i>k</i> range | 0–27 |
| <i>l</i> range | 0–19 |
| std reflcs | 1,1,2–0,0,14 |
| intens variation | $< \pm 3\sigma(I_{\text{sr}})^a$ |
| scan mode | $\theta/2\theta$ |
| condition for obsd reflcs | $I > 3\sigma(I)$ |
| no. of unique measd reflcs | 3569 |
| no. of reflcs used in the refinement | 2192 |
| anisotropic least-squares on <i>F</i> | full-matrix |
| max least-squares shift-to-error ratio | 0.53 |
| min, max ht in final Fourier map, ρ , e Å ⁻³ | –1.30, 0.98 |
| no. of refined parameters | 334 |
| <i>R</i> ^b | 0.064 |
| <i>R</i> ^c | 0.074 |
| <i>S</i> ^d | 7.80 |
| <i>k</i> , <i>g</i> | 8.08, 2.06×10^{-4} |

^a *I* = Intensity of the standard reflection. ^b *R* = $\sum \Delta F / \sum |F_o|$; *R* = $[\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$. ^c *S* = $[\sum w(\Delta F)^2 / (N - P)]^{1/2}$, where *P* = number of parameters and *N* = number of observations. ^d *w* = $k / [\sigma^2(F_o) + g F_o^2]$.

toluene (100 mL), PCy_2H (98 mg, 0.495 mmol), and PhSeH (177 mg, 1.13 mmol). Recovered 480 mg of complex 5 (76% yield, quantitative by NMR).

Crystal Structure Analysis. Orange prismatic crystals of complex 6, obtained from a *n*-hexane solution, were glued at the end of glass fibers and studied through Weissenberg diffraction patterns. The crystal producing the sharpest spots on the film was used for the following intensity data collection, which was performed through a single-crystal four-circle diffractometer by using the experimental conditions summarized in Table 2. The periodic rescan of the reflections 1,1,2 and 0,0,14, used as a standard, entitled us to exclude any measurable decay of the specimen. After correction of the collected data for Lorentz and polarization effects, the intensities of equivalent reflections were merged, obtaining a total of 3569 intensity data. The absorption correction was applied by using the method of Walker and Stuart.²⁴

The positions of the palladium, sulfur, phosphorus, and some carbon atoms were determined by the direct phasing method included in the TREF routine of SHELX 86 program,²⁵ and the atom search was completed by standard Fourier synthesis contained in SHELX 76 program.²⁶ The atomic positions were refined by full-matrix least-squares methods. The positional parameters of hydrogen atoms could in part be determined on the difference Fourier map, but they were all introduced

Table 3. Atomic Coordinates of Non-Hydrogen Atoms of $\text{Pd}_3(\text{SPh})_2(\text{PCy}_2)_2(\text{PHCy}_2)_2$

| atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>B</i> _{equiv} , Å ² |
|------|------------|------------|-------------|--|
| Pd1 | 0.2071(1) | 1/4 | –0.10115(9) | 3.71(5) |
| Pd2 | 0.10605(8) | 0.19084(5) | 0.01197(6) | 3.93(3) |
| P1 | 0.1957(3) | 0.1627(2) | –0.0820(2) | 4.0(1) |
| P2 | 0.0541(3) | 0.1130(2) | 0.0603(2) | 4.5(1) |
| S1 | 0.0308(4) | 1/4 | 0.0975(3) | 5.5(2) |
| S2 | 0.3319(5) | 1/4 | –0.1895(4) | 6.4(2) |
| C11 | 0.107(3) | 1/4 | 0.173(2) | 7.(1) |
| C12 | 0.206(4) | 1/4 | 0.165(2) | 10.(2) |
| C13 | 0.271(4) | 1/4 | 0.225(5) | 17.(3) |
| C14 | 0.234(7) | 1/4 | 0.288(4) | 15.(4) |
| C15 | 0.142(5) | 1/4 | 0.302(3) | 12.(2) |
| C16 | 0.083(3) | 1/4 | 0.243(2) | 11.(1) |
| C21 | 0.284(2) | 1/4 | –0.278(1) | 5.4(8) |
| C22 | 0.183(2) | 1/4 | –0.295(2) | 5.3(9) |
| C23 | 0.147(2) | 1/4 | –0.364(3) | 8.(1) |
| C24 | 0.210(6) | 1/4 | –0.418(3) | 17.(3) |
| C25 | 0.310(4) | 1/4 | –0.406(3) | 13.(2) |
| C26 | 0.341(3) | 1/4 | –0.337(2) | 9.(1) |
| C101 | 0.132(1) | 0.1185(6) | –0.1490(8) | 4.4(4) |
| C102 | 0.199(1) | 0.1036(7) | –0.2134(9) | 5.6(6) |
| C103 | 0.139(2) | 0.0692(7) | –0.2673(9) | 7.0(7) |
| C104 | 0.047(2) | 0.0981(8) | –0.292(1) | 8.2(8) |
| C105 | –0.016(1) | 0.1140(8) | –0.228(1) | 7.5(7) |
| C106 | 0.042(1) | 0.1473(6) | –0.1773(9) | 4.9(5) |
| C107 | 0.312(1) | 0.1294(6) | –0.0597(8) | 4.4(5) |
| C108 | 0.368(1) | 0.1646(7) | –0.0049(9) | 6.3(6) |
| C109 | 0.469(1) | 0.1420(9) | 0.017(1) | 7.4(7) |
| C110 | 0.457(1) | 0.086(1) | 0.041(1) | 7.4(8) |
| C111 | 0.407(1) | 0.0509(7) | –0.016(1) | 6.9(7) |
| C112 | 0.305(1) | 0.0726(6) | –0.0329(9) | 5.9(6) |
| C201 | 0.078(1) | 0.1044(7) | 0.1576(8) | 5.9(7) |
| C202 | 0.190(1) | 0.1031(8) | 0.169(1) | 7.2(7) |
| C203 | 0.214(2) | 0.093(1) | 0.250(1) | 10.(1) |
| C204 | 0.165(2) | 0.0454(9) | 0.280(1) | 10.(1) |
| C205 | 0.057(2) | 0.050(1) | 0.271(1) | 11.(1) |
| C206 | 0.033(1) | 0.0562(8) | 0.191(1) | 7.3(7) |
| C207 | –0.074(1) | 0.0933(7) | 0.042(1) | 5.3(6) |
| C208 | –0.143(1) | 0.1402(8) | 0.054(1) | 6.9(7) |
| C209 | –0.250(1) | 0.1253(9) | 0.038(1) | 8.7(9) |
| C210 | –0.263(1) | 0.1021(9) | –0.036(1) | 7.4(7) |
| C211 | –0.191(2) | 0.0558(8) | –0.048(1) | 7.8(8) |
| C212 | –0.087(1) | 0.0721(7) | –0.032(1) | 7.0(7) |

by imposing an ideal geometry. Their thermal parameters were let to vary in the refinement, but those rising more than 0.1 were fixed to 0.1. In the final cycles the non-hydrogen atoms were refined with anisotropic thermal parameters. The final reliability factor *R* was 0.064, refining 334 parameters on 2192 observed independent reflections.

Atomic scattering factors and anomalous scattering coefficients were taken from the literature;²⁷ ORTEP II²⁸ and PARST²⁹ programs were also used. The calculations were carried out on a computer IBM 3081 of the Centro Nazionale Universitario di Calcolo Elettronico, Pisa, Italy. A list of the final atomic coordinates with equivalent isotropic thermal factors (*B*_{eq}) is shown in Table 3.

Acknowledgment. Financial support from the “Ministero della Ricerca Scientifica e Tecnologica” (MURST) and the Consiglio Nazionale delle Ricerche (CNR, Rome) is gratefully acknowledged.

Supplementary Material Available: Lists of bond angles and distances, anisotropic thermal parameters of non-hydrogen atoms, and atomic coordinates and thermal factors for hydrogen atoms and a figure showing the atomic numbering scheme for complex 6 (4 pages). Ordering information is given on any current masthead page.

- (24) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166.
 (25) Sheldrick, G. M. SHELX 86, Program for Crystal Structure Solution. University of Göttingen, 1986.
 (26) Sheldrick, G. M. SHELX 76, Program for Crystal Structure Determination. University of Cambridge, 1976.

- (27) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynock Press: Birmingham, U.K., 1974; Vol. IV, Table 2.28.
 (28) Johnson, C. K. *ORTEP*; Report ORNL-3794, Oak Ridge National Laboratory: Oak Ridge, TN, 1965.
 (29) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95–98.