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Synthesis of Palladium Sulfonium Ylides and the Structures of *trans*-$[PdCl(CH_2SR_2)(PBu^t_2H)_2]X$ (X = CF_3SO_3, SR_2 = Tetrahydrothiophene; X = PF_6, R = Et)

Piero Leoni,*[†,‡] Fabio Marchetti,[†] and Marco Paoletti[†]

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy, and Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy

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By reacting *trans*-$[PdCl(CH_2Cl)(PBu^t_2H)_2]$ with tetrahydrothiophene (THT) or diethyl sulfide in the presence of $AgCF_3SO_3$ or $TlPF_6$, the cationic palladium sulfur ylides *trans*-$[PdCl(CH_2SR_2)(PBu^t_2H)_2]X$ ((**2**)CF_3SO_3 SR_2 = THT, X = CF_3SO_3; (**2**)PF_6 SR_2 = THT, X = PF_6; (**3**)PF_6 SR_2 = SEt_2, X = PF_6) were isolated and characterized. The crystal and molecular structures of (**2**)CF_3SO_3 and (**3**)PF_6 were solved by X-ray analyses. The related complex *cis*-$[PdCl\{CH_2S(H)CH_3\}(PBu^t_2H)_2]CF_3SO_3$ was prepared by an independent route, *i.e.*, by the oxidative addition of the C−Cl bond of $Cl-CH_2SCH_3$ to $Pd(PBu^t_2H)_3$ to form *trans*-$[PdCl(CH_2SCH_3)(PBu^t_2H)_2]$, which was then protonated with triflic acid.

Introduction

Metal carbenes are organometallic intermediates of prominent interest for their applications in catalytic or stoichiometric reactions.[1] Although plenty of data are available on metal−carbene derivatives of transition metals, palladium−carbenes or their precursors are relatively unexplored. A certain number of heteroatom-stabilized (Fisher) palladium−carbenes have been characterized,[2] while only a few polynuclear μ-alkylidene derivatives are known.[3] *Mononuclear* alkylidene derivatives are rare in all late-transition-metal chemistry[4] and are presently unknown in palladium chemistry, although they have been proposed as intermediates in homogeneous[1b,5] and heterogeneous[6] catalysis. Sulfonium derivatives of general formula $[L_nMCH_2-SR_2]^+$,[7−9] currently viewed as metal-coordinated ylides, have been successfully employed as masked carbenes in methylene transfer reactions.[1a,7a−c] In at least one case, the existence of equilibrium 1 (eq 1) was demonstrated.[8]

$$[L_nM{=}CH_2]^+ + R_2S \rightleftarrows [L_nM-CH_2-SR_2]^+ \qquad (1)$$

To our knowledge, only two examples of palladium derivatives belonging to this class have been mentioned previously but not thoroughly characterized: recently, $(Me_2S)Pd(CH_2SMe_2)Cl_2$ has been tentatively identified in a complex mixture, but separation from other derivatives has not been attempted;[9a] moreover the dinuclear $Pd_2(\mu\text{-}I)_2(I)_2(CH_2SMe_2)$ was reported earlier, but scarce details were given.[9b] Furthermore, a few palladium sulfonium ylides stabilized by electron-withdrawing substituents on C_α have been described.[9b,10] Other structurally related compounds contain the $Pd-CH_2-S$ moiety in the fragments $Pd(CH_2)_2S(O)R$,[7a,11] $PdCH_2S(O)_2R$,[12] $PdCH_2S(O)R$,[13] $Pd(\eta^2\text{-}CH_2SCH_3)$,[7a,14] and Pd-

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[†] Università di Pisa.

[‡] Scuola Normale Superiore.

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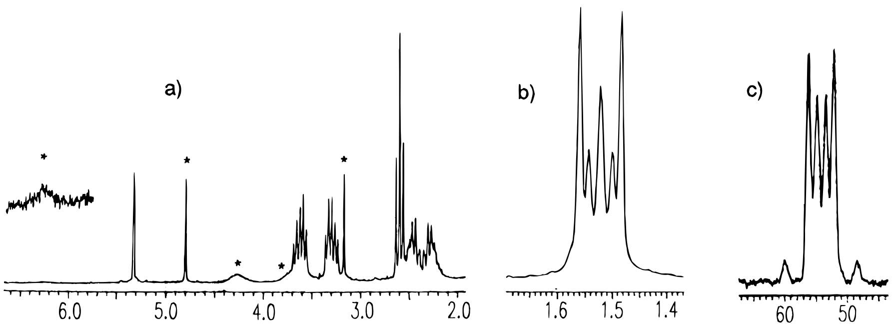
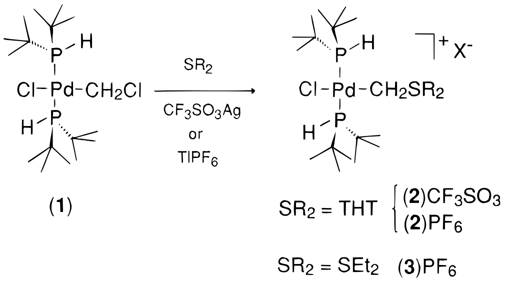


Figure 1. NMR spectra (CD_2Cl_2, 298 K) of (**2**)CF_3SO_3, showing portions A ((c) ^{31}P spectrum), M ((a) marked peaks, ^1H spectrum), and X ((b) ^1H spectrum) of the $[AMX_{18}]_2$ spin system.

$CH_2S(O)R_2$,[7a] but with the exception of sulfoxonium methylides,[15] their reactivity is presumed to be completely different; most of them are in fact *neutral* complexes and lack a good leaving group on the methylene carbon.

Results and Discussion

Preparation of *trans*-[PdCl(CH_2SR_2)(PBu^t_2H)$_2$]X Derivatives. The neutral palladium chloromethyl complex *trans*-[PdCl(CH_2Cl)(PBu^t_2H)$_2$] (**1**)[16] was supposed to be a suitable starting point for the preparation of various substituted methylene derivatives of palladium. As shown in eq 2, in the presence of silver triflate, complex **1** reacts smoothly with tetrahydrothiophene, giving *trans*-[PdCl($CH_2S\{CH_2CH_2\}_2$)(PBu^t_2H)$_2$]CF_3SO_3, (**2**)CF_3SO_3, which was characterized by elemental, spectroscopic, and X-ray analyses. Its IR spectrum shows significant absorptions at 2339 (vw) (ν_{PH}) and 1268 (vs), 1148 (s), 1032 (s), and 638 (s) cm^{-1} (uncoordinated $CF_3SO_3^-$).[17]



(2)

(**1**)

SR_2 = THT { (**2**)CF_3SO_3 ; (**2**)PF_6 }

SR_2 = SEt_2 (**3**)PF_6

The ^1H NMR spectrum (CD_2Cl_2, 298 K) consists of a triplet at δ 2.60 ($^3J_{PH} = 7.4$ Hz) for the methylene hydrogens (Figure 1a), coupled with two equivalent phosphine ligands; typical absorptions[16,18] due to the M and X part of the $[AMX_{18}]_2$ spin system (A = *P*, M = P−*H*, X = C*H*$_3$) were centered at 3.99 and 1.52 ppm, respectively. Both pairs of CH_2 protons of the tetrahydrothiophene ring are diastereotopic, and accordingly, two pairs of multiplets were observed, centered at 3.62 and 3.33 ppm (S−C*H*$_2$) and at 2.47 and 2.27 ppm (S−CH_2C*H*$_2$). The $^{31}P\{^1H\}$ NMR spectrum consists of a sharp singlet at 54.1 ppm, while the corresponding proton-coupled spectrum (Figure 1c) splits into the characteristic six-line signal, due to the A part of the $[AMX_{18}]_2$ spin system.[16,18]

All parts of the $[AMX_{18}]_2$ spin system give signals diagnostic of a *trans* arrangement of the chemically equivalent but magnetically inequivalent PBu^t_2H ligands.[16,18] $^1J_{P_AH_M}$ (324.5 Hz), $^2J_{P_AP_A'}$ (418.3 Hz), $^3J_{P_AH_M'}$ (3.3 Hz), $^3J_{P_AH_X}$ (14.8 Hz), and $^5J_{P_AH_X'}$ (0.3 Hz) were extracted directly from ^1H and ^{31}P NMR spectra according to the literature[16,18] and are consistent with the values of analogous *trans*-[MXY(PR_2H)$_2$] complexes.[16,18] Four singlets were observed in the $^{13}C\{^1H\}$ NMR spectrum at 48.0, 31.4, 28.4, and 19.4 ppm, which split in the corresponding proton-coupled spectrum, respectively, into a triplet ($^1J_{CH} = 147$ Hz), a quartet ($^1J_{CH} = 128$ Hz), a triplet ($^1J_{CH} = 135$ Hz), and a triplet ($^1J_{CH} = 144$ Hz) and were assigned to the $PdCH_2$, CH_3 (Bu^t), S(CH$_2$CH$_2$)$_2$, and S(CH$_2$$CH_2$)$_2$ carbons; the quaternary *tert*-butyl carbons gave a weak virtual triplet[19] ($J_{app} = 9.1$ Hz) at 35.7 ppm in the decoupled spectrum.

Complex (**2**)CF_3SO_3 was obtained in only 32% yield, probably because of parallel oxidation reactions induced by the reduction of Ag^+ to Ag^0. In fact, by removing the chloromethyl chloride with $TlPF_6$, we obtained (**2**)PF_6 in 81% yield (see Experimental Section). IR and NMR spectra of (**2**)PF_6 were identical to the corresponding spectra of (**2**)CF_3SO_3, excluding the signals of the PF_6^- anion: 841 s cm^{-1} (ν_{PF}), $\delta_P = -146.5$ ppm, septet, $^1J_{PF} = 708$ Hz.

When complex **1** was reacted with SEt_2 in the presence of $TlPF_6$, *trans*-[PdCl(CH_2SEt_2)(PBu^t_2H)$_2$]PF_6, (**3**)PF_6, was isolated in 81% yield. ^1H, ^{31}P, and ^{13}C NMR spectra (see Experimental Section) were similar to those discussed above for (**2**)PF_6 and will not be discussed

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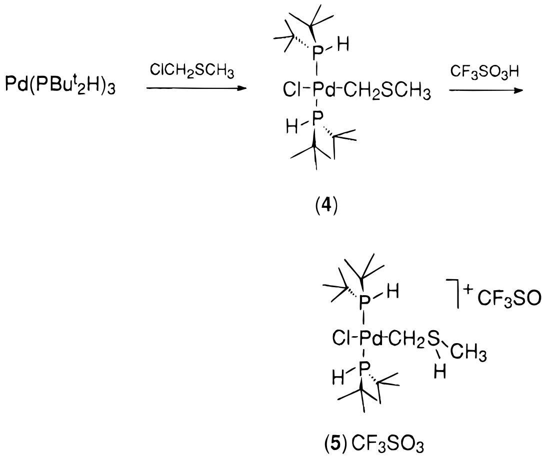
further. In the absence of Ag^+ or Tl^+ salts, complex **1** is totally unreactive, also with a large excess of the dialkylsulfides. Single crystals of (**2**)CF_3SO_3 and (**3**)PF_6 were obtained, and the crystallographic study confirmed the structures shown in eq 2 (see below).

The reactions of eq 2 demonstrate that an equimolar amount of a Tl^+ or Ag^+ salt extracts the chloride ion selectively from the chloromethyl ligand of complex **1**, leaving untouched the Pd−Cl bond. This seems to be a general trend in the reactivity of neutral nucleophiles with halo−halomethyl metal complexes. Many of these react, for example, with tertiary phosphines and give the fragments $[X-M-CH_2-PR_3]^+X^-$;[20] moreover, the palladium complex $(Me_2S)_2PdCl(CH_2Cl)$ slowly decomposes in the air to a complex mixture also containing $(Me_2S)Pd(CH_2SMe_2)Cl_2$.[9a] However, the reverse reactivity has been observed at least once, *i.e.*, in the reaction of *mer,cis*-$[(Me_3P)_3RhCl_2(CH_2Cl)]$ with an excess of PMe_3, which displaces Cl^- from Rh rather than $RhCH_2Cl$, yielding *trans*-$[(Me_3P)_4RhCl(CH_2Cl)]Cl$.[20f]

Preparation of *cis*-$[PdCl\{CH_2S(H)CH_3\}(PBu^t_2H)_2]CF_3SO_3$. Another ylide species, containing the $[PdCH_2S(H)CH_3]^+$ moiety, was prepared by an independent synthetic route (eq 3), which could be appropriate to achieve unsymmetrically substituted sulfur ylides of palladium. We reacted first $Pd(PBu^t_2H)_3$ with methyl chloromethyl sulfide[21] and obtained the nearly quantitative formation of the product of an oxidative addition of the C−Cl bond to the palladium(0) center: *trans*-$[PdCl(CH_2SCH_3)(PBu^t_2H)_2]$ (**4**).



(**4**)

(**5**) CF_3SO_3

(3)

Complex **4**, isolated as a pale yellow solid, exhibits the PH stretching absorption at 2340 cm^{-1} in the IR spectrum. The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at 62.8 ppm. In the corresponding proton-coupled spectrum, this signal splits into the six-line signal typical of complexes containing the *trans*-$[M(PBu^t_2H)_2]$ moiety, already discussed for complexes (**2**)X. The ^1H NMR spectrum of **4** exhibits resonances at 1.47 (X part of the $[AMX_{18}]_2$ spin system, 36H, Bu^t), 2.08 (s, 3H, SCH_3), 2.41 (t, $^3J_{PH} = 9$ Hz, 2H, CH_2), and 3.73 ppm (M part of the $[AMX_{18}]_2$ spin system, 2H, P*H*). According to the literature,[16,18] $^1J_{P_AH_M}$ (324.9 Hz), $^2J_{P_AP_{A'}}$ (402.8 Hz), $^3J_{P_AH_{M'}}$ (−1.6 Hz), $^3J_{P_AH_X}$ (12.4 Hz), and $^5J_{P_AH_{H'}}$ (−0.5 Hz) were extracted directly from the ^1H and ^{31}P NMR spectra and were found at the expected values.[16,18] In the $^{13}C\{^1H\}$ NMR spectrum, the methyl and methylene carbon atoms of the CH_2SCH_3 group give resonances at 23.4 (s) and 20.6 (s) ppm, which split, respectively, into the expected quartet ($^1J_{CH} = 146$ Hz) and triplet ($^1J_{CH} = 137$ Hz) in the corresponding proton-coupled spectrum.

The sulfur atom of complex **4** is susceptible to electrophilic attack and was protonated by the action of triflic acid in Et_2O. A yellow solution of **4** is rapidly discolored during the addition of CF_3SO_3H, and in a few minutes, a colorless solid precipitates out and can be identified as *cis*-$[PdCl\{CH_2S(H)CH_3\}(PBu^t_2H)_2]CF_3SO_3$, (**5**)$CF_3SO_3$ (eq 3). The $^{31}P\{^1H\}$ NMR spectrum consists of two singlets at 63.9 and 52.4 ppm, which split in two broad doublets in the corresponding proton-coupled spectrum by the large $^1J_{PH}$ values (330 and 317 Hz, respectively). Two separate resonances were observed in the ^1H NMR spectrum for the diastereotopic protons of the CH_2 group: a triplet ($J_{app} = 6.2$) at 3.47 and a doublet of doublets ($J = 6.2$ and 4.5 Hz) at 3.13 ppm. Other resonances were observed at 1.34 (m, 36 H, Bu^t), 2.21 (d, $^3J_{HH} = 4.4$ Hz, 3 H, SCH_3), 4.61 (dd, $^1J_{PH} = 330$ Hz, $^3J_{PH} = 15.4$ Hz, 1H, P*H*), 4.19 ppm (dd, $^1J_{PH} = 317$ Hz, $^3J_{PH} = 8.0$ Hz, 1H, P*H*), and 10.2 (broad s, 1H, SH); irradiation of the last signal induced the loss of the doublet splitting of the resonance at 2.21 ppm.

The *cis* geometry exhibited by the cation $(\mathbf{5})^+$ contrasts with the one observed in the complexes of general formula $[Pd(X)(Y)(PBu^t_2H)_2]$ prepared up to now;[16] all of them have in fact been shown to prefer the *trans* geometry, which keeps the bulky phosphine ligands distant. This exception could be due to a hydrogen bonding interaction between the triflate anion and the S−H bond, which is suggested by the low-field position (10.2 ppm) of the SH proton in the ^1H NMR spectrum. Such an interaction could be less favorable when the cation $(\mathbf{5})^+$ adopts the *trans* geometry, the approach of the triflate anion to the SH bond being hindered by the encumbrance of the *tert*-butyl substituents.

Crystal Structures. The crystal structure of complex (**2**)CF_3SO_3 consists of $(\mathbf{2})^+$ cations (Figure 2) and $CF_3SO_3^-$ anions. Some degree of disorder, present in both the ions, makes their positioning slightly inaccurate, but the quality of the result is good enough to discuss the general features of the coordination.

The shortest cation−cation distance (calculated as Pd···Pd distance) is 8.89 Å and each cation is surrounded by three anions at distances (calculated as Pd···centroid C(6)−S(2)) between 6.46 and 7.22 Å. Each anion is surrounded by three cations and has the closest neighboring anion at 6.12 Å.[22]

The geometry around palladium in the cation deviates only slightly from square planar the main deviation from planarity being that of P(2) (0.080 Å from the mean

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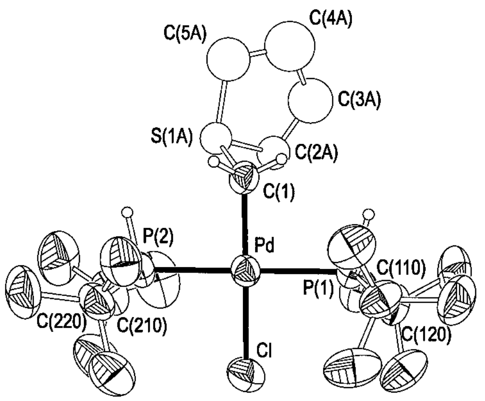

Figure 2. Perspective view of the molecular structure of the cation $(\mathbf{2})^+$. Thermal ellipsoids are at 50% probability. Only the more populated limit conformer of the disordered tetrahydrothiophenyl group has been represented for clarity.

Table 1. Bond Lengths (Å) and Angles (deg) around the Pd Atom in Molecular Structures of $(\mathbf{2})CF_3SO_3$ and $(\mathbf{3})PF_6$

$(\mathbf{2})CF_3SO_3$		$(\mathbf{3})PF_6$	
Pd−C(1)	2.065(9)	Pd−C(1)	2.064(9)
Pd−P(1)	2.327(3)	Pd−P(1)	2.327(3)
Pd−P(2)	2.325(3)	Pd−P(2)	2.331(3)
Pd−Cl	2.374(3)	Pd−Cl	2.358(3)
S(A)−C(1)	1.836(8)	S−C(1)	1.776(10)
S(B)−C(1)	1.748(7)		
C(1)−Pd−P(1)	89.8(2)	C(1)−Pd−P(1)	89.6(3)
C(1)−Pd−P(2)	88.7(3)	C(1)−Pd−P(2)	88.8(3)
P(1)−Pd−P(2)	173.74(10)	P(1)−Pd−P(2)	174.64(10)
C(1)−Pd−Cl	178.9(2)	C(1)−Pd−Cl	179.4(3)
P(1)−Pd−Cl	91.01(11)	P(1)−Pd−Cl	89.86(10)
P(2)−Pd−Cl	90.57(11)	P(2)−Pd−Cl	91.61(10)
Pd−C(1)−S(A)	113.9(5)	Pd−C(1)−S	111.3(5)
Pd−C(1)−S(B)	104.7(5)		

plane). The hydrogen atoms reported in Figure 2 have been localized on the difference Fourier map and not refined. The P−H hydrogen atoms lie close to the coordination plane, with the phosphine ligands in a conformation which alleviates the steric repulsion between the *tert*-butyl substituents and the tetrahydrothiophenyl ring; the phosphine ligands are near to being related by a mirror plane (Figure 2). Although close to the lower limit, the Pd−C(1) bond distance (2.065(9) Å, Table 1) is within the range (2.039(4)−2.156(5) Å) of Pd−C(sp^3) distances found in methyl derivatives of palladium with phosphine ligands.[23] Pd−C distances in Fisher-type carbene complexes have generally been observed in the range 1.94−2.04 Å,[2i−s] with the exception of a very short distance (1.63(5) Å, in a polymeric Pd−Pt complex)[2t] and some longer distances (2.049−2.137 Å, in crowded derivatives).[2u−z] Therefore, a carbene-like character of the complex should be excluded, as also suggested by the S−C(1) distance. This was found at 1.836(8) and 1.748(7) Å in the two different conformers, the first within the range of 1.78−1.84 Å reported for S−alkyl bond distances in organic sulfonium salts[8] and the second slightly shorter. The Pd−C(1)−S angles found in the two conformers are one slightly above (113.9(5)°) and one slightly below (104.7(5)°) the normal tetrahedral angle.

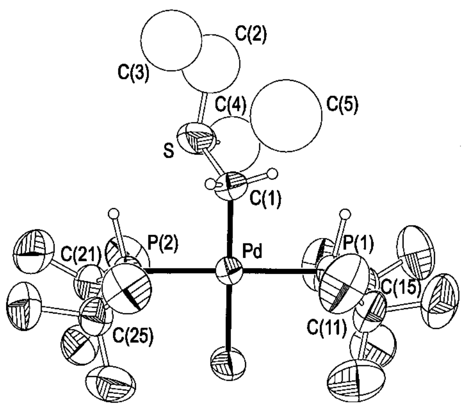

Figure 3. Perspective view of the molecular structure of the cation $(\mathbf{3})^+$. Thermal ellipsoids are at 50% probability. The disordered ethyl groups have been refined with isotropic thermal parameters.

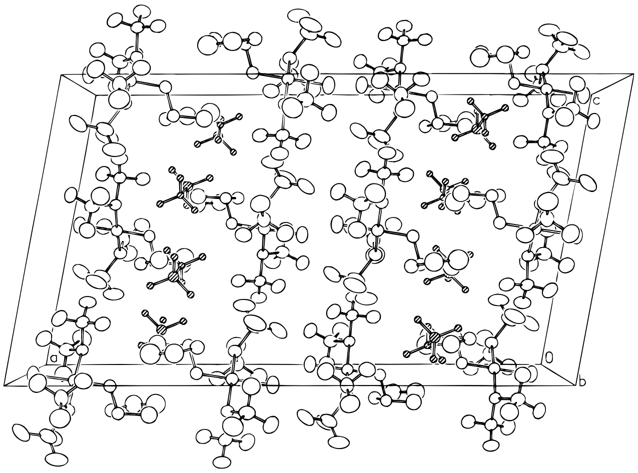

Figure 4. Perspective view of the crystal packing of $(\mathbf{2})CF_3SO_3$ projected along the *b* axis. For clarity, the anion atoms have been represented as shaded circles and only the more populated conformer of the disordered tetrahydrothiophenyl groups has been drawn.

Similar distances and angles were found in the structure of the cation $(\mathbf{3})^+$ (Figure 3); the Pd−C(1)−S angle, at 111.3(5)°, is slightly opened, as often found in metal sulfur[7c−f,8,15c] and phosphorus[20c,d,h,24] ylide complexes, and is assigned to steric repulsion factors.[7f,20d]

The crystal packing of $(\mathbf{2})CF_3SO_3$ is sketched in Figure 4. The cations and anions are ordered in layers perpendicular to the *a* direction. The packing requirements impose the cations to make double layers that alternate to simple anion layers. The tetrahydrothiophenyl groups leaning out of the main plane of the cations point to the anion layers. This could be due to

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(23) (a) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; Scapacci, G. *J. Chem. Soc., Dalton Trans.* **1989**, 211. (b) Reger, D. L.; Garza, D. G.; Lebioda, L. *Organometallics* **1991**, *10*, 902. (c) de Graaf, W.; Harder, S.; Boersma, J.; van Koten, G.; Kanters, J. A. *J. Organomet. Chem.* **1988**, *358*, 545. (d) Seligson, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 2520. (e) Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096. (f) Seligson, A. L.; Cowan, R. L.; Trogler, W. C. *Inorg. Chem.* **1991**, *30*, 3371. (g) Seligson, A. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 738. (h) Dekker, G. P. C. M.; Buijs, A.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Smeets, W. J. J.; Spek, A. L.; Wang, Y. F.; Stam, C. H. *Organometallics* **1992**, *11*, 1937. (i) Wisner, J. M.; Bartczak, T. J.; Ibers, J. A. *Organometallics* **1986**, *5*, 2044. (l) Srivastava, R. S.; Singh, G.; Nakano, M.; Osakada, K.; Ozawa, F.; Yamamoto, A. *J. Organomet. Chem.* **1993**, *451*, 221.

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the high positive charge on sulfur or to the dimensions of the five- membered rings, which fit well into the holes in the anion layer.

It is interesting to note that some degree of disorder is present in both the tetrahydrothiophenyl groups and the anions that occupy the same layer, suggesting that this concerted disorder is induced by the reciprocal ionic interaction. No disorder is present in the layers where covalent (van der Waals) interactions prevail.

Although (**3**)PF_6 crystallizes in a different space group, its crystal packing is very similar to the one described for (**2**)CF_3SO_3. The crystal is in fact built of double layers of cations perpendicular to the *a* axis, with the diethyl sulfide groups leaning out of the layers to plunge into the single layers of PF_6^- anions. Different from the crystal of (**2**)CF_3SO_3 where the layers repeat every six layers, in (**3**)PF_6, the repetition is every three layers, as reflected by the length of its *a* axis, approximately half of the corresponding length in (**2**)CF_3SO_3.

Experimental Section

General Data. All preparations were performed under dry nitrogen by using standard Schlenk techniques. Solvents were refluxed on a proper drying agent and distilled prior to use. IR spectra were recorded on a Perkin-Elmer 1725X spectrophotometer and NMR spectra on a Varian Gemini 200BB instrument, resonances are referenced to Me_4Si (^{1}H and ^{13}C) and to 85% H_3PO_4 (^{31}P). $Pd(PBu^t_2H)_3$ and *trans*-$[PdCl(CH_2Cl)(PBu^t_2H)_2]$ were prepared as previously described.[16]

Preparation of *trans*-$[PdCl(CH_2S\{CH_2CH_2\}_2)(PBu^t_2H)_2]CF_3SO_3$, (2)$CF_3SO_3$. Silver triflate (60 mg, 0.234 mmol) and a 10-fold excess of tetrahydrothiophene were added to a solution of complex **1** (108 mg, 0.223 mmol) in benzene (5 mL). The silver chloride, which precipitated out, was filtered off after 24 h. Slow evaporation of the filtrate gave large, air-stable, pale yellow crystals of complex (**2**)CF_3SO_3 (49 mg, 32% yield).

Anal. Calcd for $C_{22}H_{48}ClF_3O_3P_2PdS_2$: C, 38.5; H, 7.06. Found: C, 38.2; H, 7.00. IR (Nujol, KBr): 2339 (ν_{PH}), 1268, 1148, 1032, and 638 cm^{-1} (uncoordinated triflate).[17] $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 298 K): δ 54.1 (s, PBu^t_2H). ^{31}P NMR (CD_2Cl_2, 298 K): δ 54.1 (m, A part of the $[AMX_{18}]_2$ spin system, $^{1}J_{P_AH_M} = 324.5$ Hz, $^{2}J_{P_AP_A} = 418.3$ Hz, $^{3}J_{P_AH_{M'}} = 3.3$ Hz).[16,18] ^{1}H NMR (CD_2Cl_2, 298 K): δ 3.99 (m, M part of the $[AMX_{18}]_2$ spin system, $^{1}J_{P_AH_M} = 324.5$ Hz, $^{2}J_{P_AP_A} = 418.3$ Hz, $^{3}J_{P_AH_{M'}} = 3.3$ Hz,[16,18] 2H, $\mathrm{P}H$), 3.62 (m, 2H, $\mathrm{S(C}H\mathrm{HCH_2)_2}$), 3.33 (m, 2H, $\mathrm{S(CH}H\mathrm{CH_2)_2}$), 2.60 (t, $^{1}J_{PH} = 7.4$ Hz, 2H, $\mathrm{PdC}H_2\mathrm{S}$), 2.47 (m, 2H, $\mathrm{S(CH_2C}H\mathrm{H)_2}$), 2.27 (m, 2H, $\mathrm{S(CH_2CH}H\mathrm{)_2}$), 1.52 (m, X part of the $[AMX_{18}]_2$ spin system, $^{3}J_{P_AH_X} = 14.8$ Hz,^{5} $J_{P_AH_{X'}} = 0.3$ Hz,[16,18] 36H, $\mathrm{C(C}H_3\mathrm{)_3}$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 48.0 (s, $\mathrm{Pd}CH_2$), 35.7 (t, $J_{app} = 9.1$ Hz, $C\mathrm{(CH_3)_3}$), 31.4 (s, $\mathrm{C(}CH_3\mathrm{)_3}$), 28.4 (s, $\mathrm{S(}CH_2\mathrm{CH_2)_2}$), 19.4 (s, $\mathrm{S(CH_2}CH_2\mathrm{)_2}$). ^{13}C NMR ($CDCl_3$): δ 48.0 (t, $^{1}J_{CH} = 147$ Hz), 35.7 (br s), 31.4 (quart, $^{1}J_{CH} = 128$ Hz), 28.4 (t, $^{1}J_{CH} = 135$ Hz), 19.4 (t, $^{1}J_{CH} = 144$ Hz).

Preparation of *trans*-$[PdCl(CH_2S\{CH_2CH_2\}_2)(PBu^t_2H)_2]PF_6$, (2)$PF_6$. $TlPF_6$ (97 mg, 0.281 mmol) and tetrahydrothiophene (25 mg, 0.271 mmol) were added to a pale yellow solution of complex **1** (127 mg, 0.254 mmol) in CH_2Cl_2 (20 mL). The solution was stirred for 24 h at 35 °C, and a white solid, TlCl, precipitated out. Most of the solvent was evaporated, and acetone (30 mL) was added to the resulting slurry; TlCl was filtered off, the filtrate was evaporated to a small volume, and *n*-hexane was added. Complex (**2**)PF_6 precipitated out as a pale yellow microcrystalline solid, this was filtered and vacuum dried (140 mg, 81%).

Anal. Calcd for $C_{21}H_{48}ClF_6P_3PdS$: C, 37.0; H, 7.10. Found: C, 36.7; H, 7.05. IR (Nujol, KBr): 2342 (ν_{PH}), 841(ν_{PF}) cm^{-1}. NMR spectra were identical to those of complex (**2**)CF_3SO_3, except a septet at −146.5 ppm ($^{1}J_{PF} = 708$ Hz, PF_6^-) in the ^{31}P NMR spectra.

Preparation of *trans*-$[PdCl(CH_2SEt_2)(PBu^t_2H)_2]PF_6$, (3)$PF_6$. $TlPF_6$ and SEt_2 (50 mg, 0.555 mmol) were added to a pale yellow solution of complex **1** (245 mg, 0.506 mmol). The mixture was stirred for 48 h at room temperature. The resulting suspension was evaporated to a small volume, and acetone (30 mL) was added. A white solid (TlCl) was filtered off, and the orange solution was concentrated to *ca* 3 mL; after addition of *n*-hexane (20 mL), complex (**3**)PF_6 precipitated out and was filtered and vacuum dried (280 mg, 81%). Single crystals for crystal structure determination were obtained by recrystallization from acetone/Et_2O mixtures.

Anal. Calcd for $C_{21}H_{50}ClF_6P_3PdS$: C, 36.9; H, 7.37. Found: C, 36.3; H, 7.40. IR (Nujol, KBr): 2338 (ν_{PH}), 839 (ν_{PF}) cm^{-1}. $^{31}P\{^{1}H\}$ NMR (298 K, acetone-d_6): δ 61.2 (s, PBu^t_2H), −139 (sept, $^{1}J_{PF} = 708$ Hz, PF_6^-). ^{31}P NMR (298 K, acetone-d_6): δ 61.2 (m, A part of the $[AMX_{18}]_2$ spin system, $^{1}J_{P_AH_M} = 326.2$ Hz, $^{2}J_{P_AP_A} = 406.5$ Hz, $^{3}J_{P_AH_{M'}} = 2.8$ Hz,[16,18] −139 (sept, $^{1}J_{PF} = 708$ Hz). ^{1}H NMR (298 K, acetone-d_6): δ 4.17 (M part of the $[AMX_{18}]_2$ spin system system, $^{1}J_{P_AH_M} = 326.2$ Hz, $^{2}J_{P_AP_A} = 406.5$ Hz, $^{3}J_{P_AH_{M'}} = 2.8$ Hz,[16,18] 2H, $\mathrm{P}H$), 3.47 (m, 4H, $\mathrm{SC}H_2\mathrm{CH_3}$), 2.72 (t, $^{3}J_{PH} = 7.5$ Hz, 2H, $\mathrm{PdC}H_2$), 1.56 (X part of the $[AMX_{18}]_2$ spin system, $^{3}J_{P_AH_X} = 14.7$ Hz, $^{5}J_{P_AH_{X'}} = 0.5$ Hz,[16,18] 36H, $\mathrm{C(C}H_3\mathrm{)_3}$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 38.9 (s, $\mathrm{Pd}CH_2$), 36.0 (t, $J_{app} = 9.4$ Hz, $C\mathrm{(CH_3)_3}$), 31.7 (s, $\mathrm{C(}CH_3\mathrm{)_3}$), 14.8 (s, $\mathrm{S}CH_2\mathrm{CH_3}$), 10.0 (s, $\mathrm{SCH_2}CH_3$). ^{13}C NMR ($CDCl_3$): δ 38.9 (t, $^{1}J_{CH} = 146$ Hz), 31.7 (quart, $^{1}J_{CH} = 128$ Hz), 14.8 (t, $^{1}J_{CH} = 131$ Hz), 10.0 (quart, $^{1}J_{CH} = 147$ Hz).

Preparation of *trans*-$[PdCl(CH_2SCH_3)(PBu^t_2H)_2]$ (4). A toluene (10 mL) solution of $ClCH_2SCH_3$ (173 mg, 1.79 mmol) was dropped into a suspension of $Pd(PBu^t_2H)_3$ (939 mg, 1.723 mmol) in toluene (30 mL). The resulting orange solution was stirred for 20 min at room temperature, and the solvent was evaporated. The residue was dissolved in *n*-hexane (25 mL) and left overnight at −30 °C. Complex **4** precipitated out as a white solid and was filterd and vacuum dried (599 mg); a second crop (234 mg) was recovered from the filtrate as a pale orange solid and judged sufficiently pure for further uses by its NMR spectra (total yield 92.8%).

Anal. Calcd for $C_{18}H_{43}ClP_2PdS$: C, 43.6; H, 8.75. Found: C, 43.4; H, 8.60. IR (Nujol, KBr): 2340 (ν_{PH}) cm^{-1}. $^{31}P\{^{1}H\}$ NMR (298 K, C_6D_6): δ 62.8 (s, PBu^t_2H). ^{31}P NMR (298 K, C_6D_6): δ 62.8 (m, A part of the $[AMX_{18}]_2$ spin system system, $^{1}J_{P_AH_M} = 324.9$ Hz, $^{2}J_{P_AP_A} = 402.8$ Hz, $^{3}J_{P_AH_{M'}} = -1.6$ Hz).[16,18] ^{1}H NMR (298 K, C_6D_6): δ 3.73 (M part of the $[AMX_{18}]_2$ spin system system, $^{1}J_{P_AH_M} = 324.9$ Hz, $^{2}J_{P_AP_A} = 402.8$ Hz, $^{3}J_{P_AH_{M'}} = -1.6$ Hz,[16,18] 2H, $\mathrm{P}H$), 2.41 (t, $^{3}J_{PH} = 9$ Hz, 2H, $\mathrm{PdC}H_2$), 2.08 (s, $\mathrm{SC}H_3$), 1.47 (X part of the $[AMX_{18}]_2$ spin system, $^{3}J_{P_AH_X} = 12.4$ Hz, $^{5}J_{P_AH_{X'}} = -0.51$ Hz,[16,18] 36H, $\mathrm{C(C}H_3\mathrm{)_3}$). $^{13}C\{^{1}H\}$ NMR (298 K, C_6D_6): δ 34.8 (t, $J_{app} = 8.5$ Hz, $C\mathrm{(CH_3)_3}$), 31.5 (s, $\mathrm{C(}CH_3\mathrm{)_3}$), 23.4 (s, $\mathrm{S}CH_3$), 20.6 (s, $\mathrm{Pd}CH_2\mathrm{S}$). ^{13}C NMR (298 K, C_6D_6): δ 34.8 (br s), 31.5 (quart, $^{1}J_{CH} = 127$ Hz), 23.4 (quart, $^{1}J_{CH} = 146$ Hz), 20.6 (t, $^{1}J_{CH} = 137$ Hz).

Preparation of *cis*-$[PdCl\{CH_2S(H)CH_3\}(PBu^t_2H)_2]CF_3SO_3$, (5)$CF_3SO_3$. Triflic acid (15 μL, 0.169 mmol) was added to a pale yellow solution of complex **4** (79 mg, 0.16 mmol) in Et_2O (5 mL). An oil formed immediately and solidified after vigorous stirring. The pale orange solid was filtered and vacuum dried (38 mg, 42%).

Anal. Calcd for $C_{19}H_{44}ClF_3O_3P_2PdS$: C, 35.4; H, 6.87. Found: C, 35.2; H, 6.82. $^{31}P\{^{1}H\}$ NMR (298 K, $CDCl_3$) δ 63.9 (s, PBu^t_2H), 52.4 (s, PBu^t_2H). ^{31}P NMR (298 K, $CDCl_3$): δ 63.9 (br d, $^{1}J_{PH} = 330$ Hz), 52.4 (br d, $^{1}J_{PH} = 317$ Hz). ^{1}H NMR (298 K, $CDCl_3$): δ 10.2 (br s, 1H, $\mathrm{S}H$), 4.61 (dd, $^{1}J_{PH} = 330$ Hz, $^{3}J_{PH} = 15.4$ Hz, 1H, $\mathrm{P}H$), 4.19 (dd, $^{1}J_{PH} = 317$ Hz, $^{3}J_{PH} = 8.0$ Hz, 1H, $\mathrm{P}H$), 3.47 (t, $J_{app} = 6.2$ Hz, 1H, $\mathrm{PdC}H\mathrm{HS}$), 3.13 (dd, $J = 6.2$ and 4.5 Hz, 1H, $\mathrm{PdCH}H\mathrm{S}$), 2.21 (d, $J = 4.4$ Hz, 3H, $\mathrm{SC}H_3$), 1.34 (m, 36H, $\mathrm{C(C}H_3\mathrm{)_3}$).

X-ray Structure Determinations. The crystals of *trans*-$[PdCl(CH_2S\{CH_2CH_2\}_2)(PBu^t_2H)_2]CF_3SO_3$, (**2**)$CF_3SO_3$, are yellow monoclinic prisms. A fragment of one of them was glued at the end of a glass fiber and was studied on a Weissenberg

Table 2. Crystal Data and Structure Refinement Details

	(**2**)CF_3SO_3	(**3**)PF_6
empirical formula	$C_{22}H_{48}ClF_3O_3P_2PdS_2$	$C_{21}H_{50}ClF_6P_3PdS$
fw	685.51	683.43
temperature	293(2) K	293(2) K
wavelength	0.710 69 Å	0.710 69 Å
cryst syst	monoclinic	monoclinic
space group	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
unit cell dimensions	$a = 31.80(2)$ Å $b = 11.779(4)$ Å $c = 17.801(5)$ Å $\beta = 100.46(4)$ deg	$a = 16.6770(10)$ Å $b = 13.7930(10)$ Å $c = 14.3980(10)$ Å $\beta = 96.744(8)$ deg
volume	6558(5) Å^3	3289.0(4) Å^3
Z	8	4
density (calcd)	1.389 Mg/m^3	1.380 Mg/m^3
absorption coeff	0.910 mm^{-1}	0.898 mm^{-1}
$F(000)$	2848	1416
cryst size	0.27 × 0.36 × 0.45 mm	0.11 × 0.21 × 0.25 mm
θ range for data collection	2.60−22.52°	1.92−22.50°
index ranges	$0 \leq h \leq 34$, $0 \leq k \leq 12$, $-18 \leq l \leq 18$	$-1 \leq h \leq 17$, $-1 \leq k \leq 14$, $-15 \leq l \leq 15$
reflns collected	2886	5303
no. of independent reflns	2827 ($R_{int} = 0.0313$)	4294 ($R_{int} = 0.0334$)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	2827/2/285	4292/7/297
goodness-of-fit [a] on F^2	1.260	1.020
final R indices[a] $[I > 2\sigma(I)]$	R1 = 0.0601, wR2 = 0.1428	R1 = 0.0598, wR2 = 0.1332
R indices (all data)	R1 = 0.0601, wR2 = 0.1428	R1 = 0.1110, wR2 = 0.1646
A, B (w)[a]	0.0563, 48.51	0.0671, 8.44
largest diff peak and hole	1.170 and −0.468 e·Å^{-3}	0.733 and −0.612 e·Å^{-3}

[a] Goodness of fit $= [w(F_o^2 - F_c^2)^2/(N - P)]^{1/2}$; R1 $= \sum||F_o| - |F_c||/\sum|F_o|$; wR2 $= [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$, where $Q = [\max(F_o^2,0) + 2F_c^2]/3$.

camera. It showed a diffraction pattern with monoclinic symmetry and systematic absences, suggesting a lattice centering C and a glide c. The crystal was then mounted on an Ital-Structures automatic diffractometer, equipped with a graphite-monochromatized Mo Kα radiation. Cell parameters were calculated on the accurately centered setting angles of 25 strong reflections with $10° \leq \theta \leq 13°$. Details about the crystal parameters and intensity data collection are shown in Table 2.

Three standard reflections every 97 measurements indicated no decay in the crystal. The collected intensities were corrected for Lorentz and polarization effects, but not for absorption owing to the relatively small dimensions of the crystal. The structure was solved in the $C2/c$ space group by the automatic Patterson method contained in the SHELX86[25] program, and the molecule was completed by means of the next Fourier map. Disorder in the positions of tetrahydrothiophenyl group and in oxygen and fluorine atoms of the anion was suggested by exceedingly large thermal factors. The disorder in tetrahydrothiophenyl group was explained as a statistical distribution of two different conformations; accordingly, two different $S(CH_2)_4$ groups, restricted by some geometrical constraints, were introduced in the same position imposing the sums of the occupancies equal to 1 (molecule A, 60.2%; molecule B, 39.8%).

The final refinement cycles were made with anisotropic thermal factors for heavy atoms and isotropic thermal parameters for the disordered tetrahydrothiophenyl groups and for the hydrogen atoms. The final reliability factors are shown in Table 2.

A colorless prism of *trans*-$[PdCl(CH_2SEt_2)(PBu^t_2H)_2]PF_6$ (**3**)-PF_6 was glued at the end of a glass fiber and was examined on a Siemens P4 single crystal diffractometer, showing a monoclinic primitive cell. Table 2 summarizes the relevant crystal data and intensity data collection details. Cell parameters were calculated from the setting angles of 25 accurately centered strong reflections having $12° \leq \theta \leq 13°$.

A redundant set of data was collected to verify, on merging, the collection reliability. Three standard reflections every 97 measurements allowed us to exclude crystal decay. Collected data were corrected for Lorentz and polarization effects, but not for absorption, owing to the small dimensions of the crystal. The equivalent reflections in the set were then merged resulting in an internal R value ($R_{int} = \sum|F_o^2 - F_c^2(\text{mean})|/\sum(F_o^2)$) of 0.033.

The space group was unequivocally established as $P2_1/c$ by systematic extinctions, and the structure was solved by the direct methods contained in the TREF[26] procedure. The molecular ions have been completed in the successive Fourier maps, but exceedingly high thermal factors have been refined for fluorine atoms and ethyl groups. As for (**2**)CF_3SO_3, this is certainly the result of crystalline disorder.

The last refinement cycles have been done with anisotropic thermal parameters for all heavy atoms, except for disordered ethyl carbons, which were refined with constrained geometry and isotropic thermal factors. The final reliability parameters are shown in Table 2.

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Supporting Information Available: ORTEP diagrams of the molecular structures with the full numbering schemes and tables of atomic coordinates of heavy atoms, bond distances and angles, anisotropic thermal parameters, and coordinates of hydrogen atoms for *trans*-$[PdCl(P(t\text{-}Bu)_2H)_2(CH_2SC_4H_8)]CF_3SO_3$ and *trans*-$[PdCl(P(t\text{-}Bu)_2H)_2(CH_2SEt_2)]PF_6$ (15 pages). Ordering information is given on any current masthead page.

OM970030J

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