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# *Articles*

## The $\alpha$-Sulfinyl Ligand–Transition Metal Bond. 2. $\alpha$-Sulfinyl–Palladium(II) Complexes and Their Reactivity in Insertion Reactions

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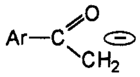
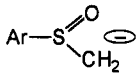
The deprotonation of $ArSOCH_3$ (Ar = $C_6H_5$, **1**; $p$-$MeC_6H_4$, **2**) with KH in THF, followed by reaction with *cis*-$[(PPh_3)_2PdCl_2]$, led to the Pd–C-bonded $\alpha$-sulfinyl complexes *trans*-$[(PPh_3)_2(Cl)PdCH_2SOAr]$ (Ar = $C_6H_5$, **3**; Ar = $p$-$MeC_6H_4$, **4**). As expected, the "$CH_2$" unit appears as an AB part of an $ABX_2$ system (the two heterotopic protons being coupled with both P atoms). The structure of **3** was confirmed by X-ray analysis. The reaction of **3** and **4** with $Bu^tNC$ afforded complexes $[(PPh_3)(Bu^tNC)(Cl)PdC(NBu^t)C(HNBu^t){=}CHSOAr]$ (Ar = $C_6H_5$, **5**; Ar = $p$-$MeC_6H_4$, **6**) *via* the replacement of $PPh_3$ by $Bu^tNC$ and insertion of two molecules of the isocyanide into the Pd–C bond. The organic fragment resulting from the insertion of $Bu^tNC$ was isolated in the $\beta$-enamino sulfoxide form and confirmed by an X-ray analysis on **5**. The ionization of the Pd–Cl bond in **3** and **4** in MeCN led to the corresponding solvated cationic forms *cis*-$[(PPh_3)_2(MeCN)PdCH_2SOAr]$ (Ar = $C_6H_5$, **10**; Ar = $p$-$MeC_6H_4$, **11**). The attempt to dehydrohalogenate **3** with the Wittig reagent $Ph_3P{=}CH_2$ led rather to the isolation of a zwitterionic complex where one of the $PPh_3$ groups had been replaced by $Ph_3PCH_2$, $[(Cl)(PPh_3)(CH_2PPh_3)(CH_2SOPh)Pd]$, **12**, containing two different $\alpha$-functionalized carbanions bonded to Pd(II). Crystallographic details: **3** is triclinic, space group $P\bar{1}$, $a = 12.517(2)$ Å, $b = 16.153(2)$ Å, $c = 12.420(2)$ Å, $\alpha = 104.16(2)°$, $\beta = 119.40(2)°$, $\gamma = 92.60(2)°$, $Z = 2$, and $R = 0.046$; **5** is monoclinic, space group $C2/c$, $a = 43.577(4)$ Å, $b = 9.214(1)$ Å, $c = 20.752(2)$ Å, $\alpha = \gamma = 90°$, $\beta = 101.20(1)°$, $Z = 8$, and $R = 0.037$; **10** is triclinic, space group $P\bar{1}$, $a = 15.111(1)$ Å, $b = 12.873(1)$ Å, $c = 12.332(1)$ Å, $\alpha = 99.89(1)°$, $\beta = 101.44(1)°$, $\gamma = 98.08(1)°$, $Z = 2$, and $R = 0.049$; **12** is triclinic, space group $P\bar{1}$, $a = 11.897(1)$ Å, $b = 14.891(2)$ Å, $c = 11.357(1)$ Å, $\alpha = 104.24(1)°$, $\beta = 98.49(1)°$, $\gamma = 96.87(1)°$, $Z = 2$, and $R = 0.025$.

### Introduction

Both the enolate (**A**)[1] and $\alpha$-sulfinyl anion (**B**)[2] have been developed largely as synthons in organic synthesis for making C–C bonds.



**A**



**B**

In a recent approach, early transition metals have been used to assist in the chemistry of the enolate **A**.[3] Those metals, which bind to the oxygen (**C**), maintain the well-known nucleophilic characteristic of enolates at the "$CH_2$" center and, in addition, play an important role in controlling the stereochemistry, *e.g.*, of the aldol condensation reaction. A more limited use of late or low oxidation state transition metals has been reported. In such cases, the

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(1) For general references to metal-assisted enolate chemistry, see: (a) Evans, D. A.; Nelson, J. V.; Taber, T. *Top. Stereochem.* **1982**, 1. (b) Evans, D. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3, Chapter 1, p 1. (c) Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3, Chapter 2, p 111. (d) Heathcock, C. H. In *Comprehensive Carbanion Chemistry, Studies in Organic Chemistry 5*; Buncel, E., Durst, T., Eds.; Elsevier: Lausanne, CH, 1984; p 177. (e) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1. (f) Heathcock, C. H. *Aldrichimica Acta* **1990**, *23*, 99. (g) Heathcock, C. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 2; Chapters 1.5 and 1.6. (h) Heathcock, C. H. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Helvetica Chimica Acta: Basle, CH, 1992; p 1.

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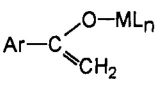
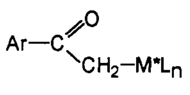
metals bind to the carbon of the enolate (**D**),[4] and the resulting chemistry is that expected for a M–C $\sigma$ bond.



**C**

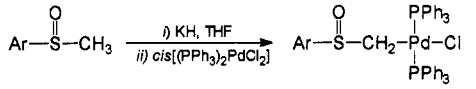


**D**

A similar use of transition metals has not, however, been introduced as a method of assisting in the chemistry of $\alpha$-sulfinyl anions.[2] Our preliminary investigation in this field revealed the unsuccessful use of high-valent early transition metals leading essentially to deoxygenation reactions.[5] Two classes of reactions leading to a metal–carbon-bonded $\alpha$-sulfinyl anion have been examined. The reaction of $\alpha$-sulfinyl anions with metal carbonyls is reported in a previous paper.[5] We report here the reaction with *cis*-[(PPh$_3$)$_2$PdCl$_2$][6] and the reactivity of the resulting C–M-bonded $\alpha$-sulfinyl anions. Some preliminary results have been communicated.[7]

## Results and Discussion

The synthesis of $\alpha$-sulfinyl–palladium(II) complexes has been carried out *via* the transmetalation reaction from the corresponding potassium derivative, eq 1, and complexes **3** and **4** have been isolated. Such a strategy is not applicable to the enolate chemistry, where the enolato anion reduces Pd(II) to Pd(0).[8]



(1)

Ar = C$_6$H$_5$, **1** Ar = C$_6$H$_5$, **3**

Ar = 4-MeC$_6$H$_4$, **2**, R(+) Ar = 4-MeC$_6$H$_4$, **4**

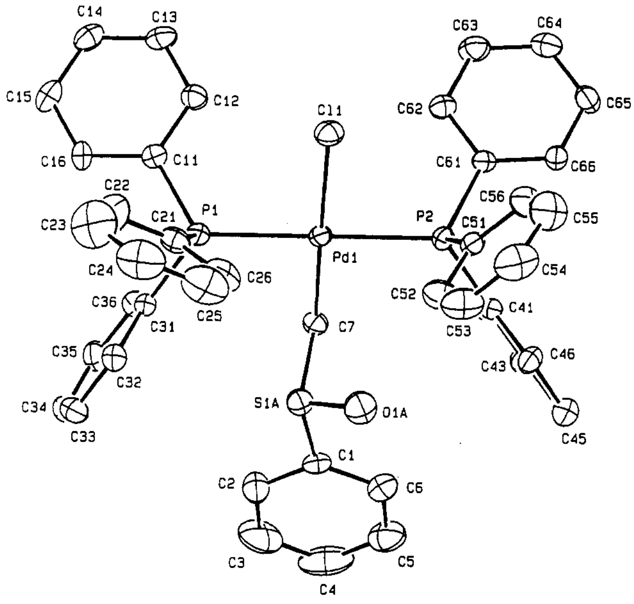


**Figure 1.** ORTEP view of complex **3** (30% probability ellipsoids). For clarity only the A position is given for the disordered $\alpha$-sulfinyl group.

The transmetalation reaction proceeds with the rearrangement of the bis(triphenylphosphine)palladium(II) from the *cis* to the *trans* form.[8,9] As expected, the CH$_2$ units appear as AB parts of ABX$_2$ systems in the $^1$H NMR spectra of **3** and **4** (two triplets as a result of coupling with one another and with the two phosphorus atoms). Complexes **3** and **4** have been obtained in high yield (90%) and isolated as white crystalline solids stable to air. A major difference between **3** and **4** is the much higher solubility of the latter species in THF and CH$_2$Cl$_2$. Although we started with enantiomerically pure **2**, under the reaction conditions of the experiment, the $\alpha$-sulfinyl anion undergoes partial racemization. The $\alpha_D$ of isolated **4** (116 ± 2°) decreases considerably after each recrystallization. In accord with this observation we can assume that the recrystallized solid is a mixture of the racemate and the pure enantiomer. By continuing recrystallization, the solid is enriched in the racemate, while the solution is enriched in the pure enantiomer. The crystal selected for an X-ray analysis happened to be a racemate. The structure of **3**, crystallizing with a THF molecule in the lattice, is shown in Figure 1, while selected bond distances and angles are listed in Table 6. A square planar coordination geometry at the Pd atom is formed by the *trans*-phosphine ligand, the chlorine atom, and the C-bound $\alpha$-sulfinyl anion. The displacements of atoms from the mean coordination plane show small but significant tetrahedral distortions: Pd1, −0.018(1) Å; P1, 0.079(2) Å; P2, 0.080(2) Å; Cl1, −0.011(2) Å; C7, −0.073(7) Å. The Pd–Cl [2.390(3) Å] bond length corresponds to the upper end of the range of values quoted in the literature [mean value 2.326(43) Å],[10] and it is consistent with a strong *trans* effect caused by the $\alpha$-sulfinyl carbanion. The Pd–C distance [2.053(9) Å] is in good agreement with the mean value [2.044(42) Å] quoted for Pd–CH$_2$R.[10] The $\alpha$-sulfinyl group shows a configurational disorder. Both enantiomers [*R*(A) and *S*(B)] sharing the carbon atom bound to palladium are

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**Table 1. Experimental Data from X-ray Diffraction Studies on Crystalline Compounds 3, 5, 10 and 12**

| | 3 | 5 | 10 | 12 |
|---|---|---|---|---|
| formula | $C_{43}H_{37}ClOP_2PdS{\cdot}C_4H_8O$ | $C_{40}H_{49}ClN_3OPPdS$ | $C_{45}H_{40}NOP_2PdS{\cdot}CF_3O_3S{\cdot}0.5C_2H_3N$ | $C_{44}H_{39}ClOP_2PdS$ |
| *a* (Å) | 12.517(2) | 43.577(4) | 15.111(1) | 11.897(1) |
| *b* (Å) | 16.153(2) | 9.214(1) | 12.873(1) | 14.891(2) |
| *c* (Å) | 12.420(2) | 20.752(2) | 12.332(1) | 11.357(1) |
| α (deg) | 104.16(2) | 90 | 99.89(1) | 104.24(1) |
| β (deg) | 119.40(2) | 101.20(1) | 101.44(1) | 98.49(1) |
| γ (deg) | 92.60(2) | 90 | 98.08(1) | 96.87(1) |
| $V$ (Å$^3$) | 2080.2(8) | 8173.6(14) | 2278.1(3) | 1903.1(4) |
| $Z$ | 2 | 8 | 2 | 2 |
| formula weight | 877.7 | 792.7 | 980.8 | 819.7 |
| space group | $P\bar{1}$ (No. 2) | $C2/c$ (No. 15) | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) |
| $t$ (°C) | 22 | 22 | 22 | 22 |
| λ (Å) | 0.710 69 | 0.710 69 | 0.710 69 | 0.710 69 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.401 | 1.288 | 1.430 | 1.430 |
| μ (cm$^{-1}$) | 6.65 | 6.32 | 6.12 | 7.19 |
| transmission coeff | 0.853–1.000 | 0.875–1.000 | 0.891–1.000 | 0.936–1.000 |
| $R^a$ | 0.046 | 0.037 | 0.049 | 0.025 |
| $R_w{}^b$ | 0.050 | 0.033 | 0.046 | |

[a] $R = \sum|\Delta F|/\sum|F_o|$. [b] $R_w = [\sum w^{1/2}|\Delta F|/\sum w^{1/2}|F_o|]$.

**Table 2. Fractional Atomic Coordinates (×10$^4$) for Complex 3[a]**

| atom | x/a | y/b | z/c | atom | x/a | y/b | z/c |
|---|---|---|---|---|---|---|---|
| Pd1 | 315.0(5) | 2982.3(3) | 1304.5(5) | C31 | −989(4) | 2866(3) | −2057(4) |
| Cl1 | −1141.7(17) | 2886.3(12) | 2007.2(18) | C32 | −1300(4) | 2102(3) | −3056(4) |
| P1 | −1324.1(16) | 2880.0(11) | −774.8(16) | C33 | −1047(4) | 2113(3) | −4028(4) |
| P2 | 1849.8(16) | 2952.6(11) | 3356.4(16) | C34 | −482(4) | 2888(3) | −4002(4) |
| S1A | 1579(3) | 2032(2) | −189(3) | C35 | −171(4) | 3652(3) | −3004(4) |
| S1B | 2047(5) | 2067(3) | 487(6) | C36 | −424(4) | 3641(3) | −2031(4) |
| O1A | 1912(8) | 1468(6) | 665(8) | C41 | 3488(3) | 2982(3) | 3789(4) |
| O1B | 886(16) | 1456(11) | −673(16) | C42 | 4146(3) | 3755(3) | 3916(4) |
| O2 | 2927(11) | 9452(8) | 6930(9) | C43 | 5390(3) | 3819(3) | 4240(4) |
| C1 | 2951(4) | 2348(3) | −176(5) | C44 | 5975(3) | 3110(3) | 4437(4) |
| C2 | 2712(4) | 2540(3) | −1300(5) | C45 | 5317(3) | 2336(3) | 4310(4) |
| C3 | 3703(4) | 2802(3) | −1440(5) | C46 | 4073(3) | 2273(3) | 3986(4) |
| C4 | 4933(4) | 2872(3) | −455(5) | C51 | 1400(5) | 1954(2) | 3593(5) |
| C5 | 5172(4) | 2679(3) | 669(5) | C52 | 1036(5) | 1183(2) | 2589(5) |
| C6 | 4181(4) | 2417(3) | 808(5) | C53 | 723(5) | 390(2) | 2726(5) |
| C7 | 1605(6) | 3097(4) | 758(6) | C54 | 774(5) | 370(2) | 3867(5) |
| C11 | −2196(4) | 3762(2) | −869(4) | C55 | 1139(5) | 1142(2) | 4871(5) |
| C12 | −2044(4) | 4326(2) | 266(4) | C56 | 1452(5) | 1934(2) | 4734(5) |
| C13 | −2700(4) | 5006(2) | 203(4) | C61 | 2086(4) | 3871(2) | 4700(3) |
| C14 | −3507(4) | 5122(2) | −994(4) | C62 | 1348(4) | 4502(2) | 4453(3) |
| C15 | −3658(4) | 4558(2) | −2129(4) | C63 | 1530(4) | 5205(2) | 5477(3) |
| C16 | −3003(4) | 3878(2) | −2066(4) | C64 | 2449(4) | 5277(2) | 6749(3) |
| C21 | −2441(5) | 1871(3) | −1435(5) | C65 | 3186(4) | 4646(2) | 6997(3) |
| C22 | −3690(5) | 1768(3) | −2397(5) | C66 | 3005(4) | 3943(2) | 5972(3) |
| C23 | −4492(5) | 963(3) | −2927(5) | C71 | 3024(18) | 8790(8) | 7512(12) |
| C24 | −4044(5) | 261(3) | −2496(5) | C72 | 3026(18) | 9153(9) | 8628(16) |
| C25 | −2795(5) | 364(3) | −1535(5) | C73 | 3050(18) | 10069(8) | 8834(17) |
| C26 | −1993(5) | 1170(3) | −1004(5) | C74 | 2914(19) | 10230(9) | 7722(17) |

[a] The site occupation factors for the disordered S1 and O1 atoms are 0.65 and 0.35 for A and B, respectively.

alternatively present with different occupancies (see Experimental Section and Table 2). The O1A and O1B oxygen atoms, not involved in coordination to Pd [Pd···O1A, 3.42(1) Å; Pd···O1B, 3.40(2) Å] are involved in C–H···O intramolecular and intermolecular contacts, respectively: C52···O1A, 3.19(2) Å; H52···O1A, 2.10 Å; C52–H52···O1A, 165°; C53···O1B′, 3.19(2) Å; H53···O1B′, 2.11 Å; C53–H53···O1B′, 164° [(′) = −x, −y, −z).[11a] The C1···C6 phenyl ring is nearly parallel to the coordination plane, the dihedral angle they form being 14.4(1)°. The S–C [mean values: S1–C7, 1.802(8) Å; S1–C1, 1.777(9) Å] and the S–O distances [mean value, 1.497(13) Å] are in good agreement with the mean values of 1.785(23) and 1.469(13) Å quoted for S–C and S–O bond lengths in $S(O)R_2$ sulfoxides bonded to Pd *via* sulfur.[10] Equally useful comparisons are with the Pd–O-bonded $S(O)R_2$ ligand [S–O, 1.520(21) Å; S–C, 1.788(20) Å][10] or the uncoordinated $S(O)R_2$ ligand [S–O, 1.497(13) Å; S–C, 1.806(25) Å].[11b] However, the low accuracy of the S–O distances due to the presence of the configurational disorder of the α-sulfinyl group prevents any bond discussion. The phenyl rings in the triphenylphosphine ligands adopt a conformation such that two pairs of hydrogen atoms (H12, H62, H26, H52, Pd···H range: 2.88–3.18 Å) cap above and below the coordination plane in a typical fashion for *trans*-$(PPh_3)$-Pd complexes.

Reports of complexes containing C-M-bonded α-sulfinyl and α-sulfonyl anions are rare, two examples being found in $[(\eta^5\text{-}R_5C_5)(CO)_3WCH_2S(O)Ph]$ [R = H, Me][12a] and $[(PPh_3)AuCH(Ph)SO_2Bu^t]$,[12b] though in the former case the sulfinyl anion is produced from the oxidation of the

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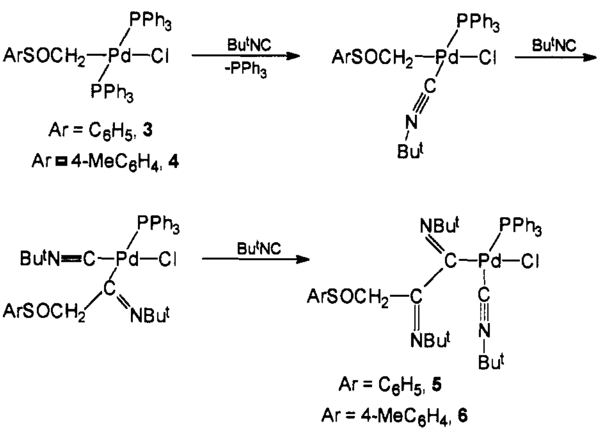
corresponding sulfido. The Pd–C bond in complexes **3** and **4** can be envisaged as suitable for insertion reactions. We found, however, a rather low reactivity for such a Pd–C bond except toward the rather reactive isocyanides. The following pathway is proposed for the observed double insertion of Bu$^t$NC into the Pd(II)–$\alpha$-sulfinyl ligand bond:



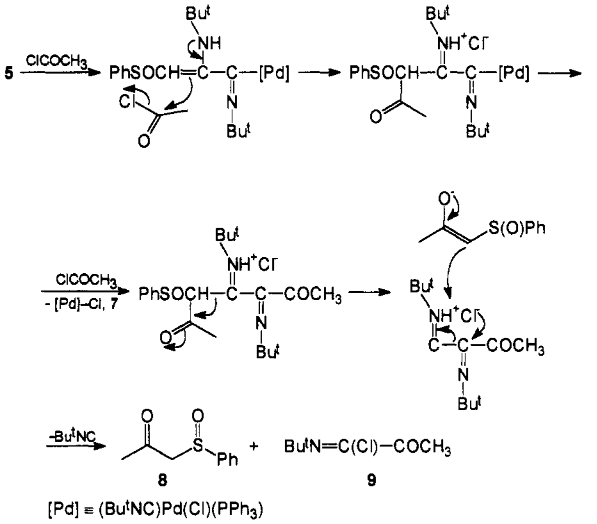
(2)

The structure of **5** is shown in Figure 2, and a selection of structural parameters is listed in Table 7. The square planar coordination of the metal is affected only by a significant out-of-plane distance of C13 [–0.212(5) Å]. The *trans* influence of the carbanion C13 causes the elongation of the Pd1–P1 distance [2.408(1) Å] in comparison with the conventional Pd–P bond lengths [2.320(38) Å].[10] The two Pd–C bond distances suggest a pure $\sigma$ bond[8d] for Pd–C13 [2.041(4) Å] and a bond with multiple character[13] for Pd–C18 [1.941(5) Å]. The proposed bonding scheme for the organic moiety formed from the insertion reaction is mainly supported by the following structural parameters: C7–C8, 1.343(7) Å; C13–N2, 1.264(6) Å; C8–N1, 1.349(6) Å; C8–C13, 1.509(8) Å. Some distortions in bond angles, particularly C8–N1–C9 [128.8(4)°] and C13–N2–C14 [127.0(5)°], should be related to intraligand steric hindrance, due to the presence of the bulky *tert*-butyl groups at the nitrogen atoms, rather than to electronic effects. This is suggested by the short intramolecular H102···H7 (1.92 Å) and H153···Pd (2.51 Å) contacts involving the hydrogen atoms from the C10 and C15 methyl carbons.

The torsion angles around the C8–C13 bond are N2–C13–C8–C7, 56.6(6)°, and N1–C8–C13–N2, –125.6(5)°. The N1, C8, C13, C7 group of atoms is planar within experimental error, with the sulfur atom deviating by 0.298(1) Å from the plane, which is nearly perpendicular to the mean coordination plane [dihedral angle 79.5(1)°]. The mutual orientations of the ligands are mainly determined by a strong intramolecular NH···Cl hydrogen bond [N1···Cl1, 3.262(4) Å; H1···Cl1, 2.28 Å; N1–H1···Cl1, 155°] and by two Pd···H contacts filling the axial positions. They involve the H52 atom from the triphenylphosphine and the H153 atom from the C15 methyl carbon (Pd····H52, 2.75 Å; Pd···H153, 2.50 Å; H52···Pd···H153, 155°).

Reaction 2 requires the replacement of PPh$_3$ by Bu$^t$NC leading to the appropriate *cis* arrangement of the migrating and the inserting group. Such a migratory insertion proceeds twice with the concomitant enolization of the imino group adjacent to the sulfinyl residue to give **5** and **6**. Regardless of the Bu$^t$NC/Pd ratio used, complexes **5** and **6** were formed, and it has not been possible to isolate any of the intermediates.

The spectroscopic results are in agreement with the suggested $\beta$-enamino sulfoxide form of **5** and **6**. In particular, the chemical shifts for the enolic proton at 5.11 (complex **5**) and 5.15 (complex **6**) are very close to those found in the range 5.10–5.20 ppm for different $\beta$-enamino sulfoxides.[14] The high [$\alpha_D$] value for **6** is rather meaningless because the starting compound **4** is a mixture of the racemic and the pure starting enantiomeric form. An attempt was carried out to remove the organic ligand derived from the double insertion of Bu$^t$NC into the Pd–C bond of **3**. The reaction was carried out by adding acetyl chloride to a THF solution of **5**. We propose the following pathways leading to **7**–**9**, which have been identified and characterized (see Experimental Section).

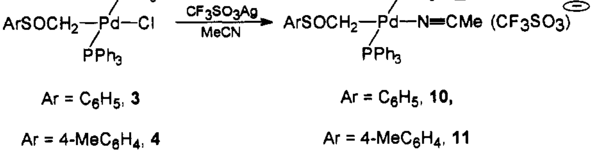


(3)

The demetalation of the organic fragment occurs with a partial degradation of the C–C skeleton. The alternative use of less reactive electrophilic reagents has not been pursued.

Complexes **3** and **4** were unreactive toward electron-rich olefins or carbon monoxide under the same mild conditions. The lack of reactivity seems inconsistent with the observed Pd(II)-assisted reactivity of $\alpha$-sulfinyl anions with olefins.[6] This reaction was, however, carried out in a different way (addition of lithium-$\alpha$-sulfinyl anion on Pd-complexed olefins) and does not proceed by insertion of the olefin on a preformed Pd-$\alpha$-sulfinyl complex.

The rather low reactivity of **3** and **4** toward the inserting molecules, like CO and olefins, may be attributed both to the low electrophilic properties of the metal and to its coordinative saturation. The ionization of the Pd–Cl fragment should free a coordination site. Such an approach is reported in eq 4.



(4)

A THF solution of CF$_3$SO$_3$Ag was added to an acetonitrile solution of **3** and **4**, with formation of AgCl. Compounds **10** and **11** have been obtained in good yield as crystalline solids. The $^1$H NMR spectra, both recorded in CD$_3$CN and CD$_2$Cl$_2$, are very similar to those of **3** and

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(13) Kitano, Y.; Hori, T. *Acta Crystallogr., Sect. B* **1981**, *B37*, 1919.

(14) Kawecki, R.; Kozerski, L. *Tetrahedron* **1986**, *42*, 1469.

Table 3. Fractional Atomic Coordinates (×$10^4$) for Complex 5

| atom | x/a | y/b | z/c | atom | x/a | y/b | z/c |
|---|---|---|---|---|---|---|---|
| Pd1 | 3875.5(1) | 1678.8(4) | 415.7(2) | C17 | 3008(2) | 535(8) | −1421(4) |
| Cl1 | 4204.7(3) | 1015.2(15) | −302.0(6) | C18 | 3573(1) | 2225(5) | 946(2) |
| S1 | 3099.7(3) | 4862.9(17) | −129.7(7) | C19 | 3206(1) | 2796(6) | 1754(3) |
| P1 | 4224.7(3) | 905.7(15) | 1401.4(6) | C20 | 2879(2) | 2771(9) | 1394(4) |
| O1 | 3078(1) | 5886(4) | 423(2) | C21 | 3277(2) | 4249(9) | 2009(4) |
| N1 | 3963(1) | 4368(4) | −479(2) | C22 | 3265(2) | 1731(9) | 2268(4) |
| N2 | 3339(1) | 2151(5) | −752(2) | C31 | 4018(1) | −297(5) | 1876(2) |
| N3 | 3407(1) | 2502(4) | 1289(2) | C32 | 3794(1) | −1200(6) | 1517(2) |
| C1 | 2830(1) | 5580(6) | −831(3) | C33 | 3621(1) | −2133(6) | 1828(3) |
| C2 | 2824(1) | 5046(7) | −1450(3) | C34 | 3674(2) | −2189(6) | 2501(3) |
| C3 | 2595(1) | 5579(7) | −1963(3) | C35 | 3895(1) | −1296(7) | 2860(2) |
| C4 | 2386(1) | 6613(8) | −1855(3) | C36 | 4068(1) | −359(6) | 2558(2) |
| C5 | 2397(1) | 7118(8) | −1237(4) | C41 | 4586(1) | −23(6) | 1352(2) |
| C6 | 2623(1) | 6590(7) | −717(3) | C42 | 4793(1) | 635(6) | 1022(2) |
| C7 | 3453(1) | 5220(6) | −371(2) | C43 | 5068(1) | −67(9) | 952(3) |
| C8 | 3664(1) | 4178(6) | −411(2) | C44 | 5132(2) | −1422(9) | 1200(4) |
| C9 | 4143(1) | 5713(7) | −448(3) | C45 | 4927(2) | −2060(8) | 1533(5) |
| C10 | 4025(1) | 6652(7) | −1053(3) | C46 | 4655(1) | −1381(8) | 1600(3) |
| C11 | 4477(1) | 5286(7) | −451(3) | C51 | 4356(1) | 2456(6) | 1931(2) |
| C12 | 4131(2) | 6574(7) | 163(3) | C52 | 4221(1) | 3781(6) | 1771(3) |
| C13 | 3576(1) | 2606(6) | −352(2) | C53 | 4309(2) | 4979(7) | 2164(4) |
| C14 | 3196(1) | 707(7) | −764(3) | C54 | 4536(2) | 4848(8) | 2710(4) |
| C15 | 3399(2) | −481(8) | −633(6) | C55 | 4679(1) | 3543(9) | 2877(3) |
| C16 | 2992(2) | 682(9) | −307(4) | C56 | 4593(1) | 2342(7) | 2490(3) |

Table 4. Fractional Atomic Coordinates (×$10^4$) for Complex 10[a]

| atom | x/a | y/b | z/c | atom | x/a | y/b | z/c |
|---|---|---|---|---|---|---|---|
| Pd1 | 1845.0(4) | 2237.6(4) | 7409.5(4) | C15 | 1251(5) | 33(6) | 2666(5) |
| S1A | 628(2) | 3777(3) | 8255(3) | C16 | 1179(5) | 939(6) | 3402(6) |
| S1B | 501(3) | 3821(4) | 7518(4) | C21 | 2380(3) | 3379(3) | 5321(4) |
| S2A | 5900(2) | 1552(3) | 3699(3) | C22 | 2803(3) | 3265(3) | 4410(4) |
| S2B | 5672(31) | 1303(37) | 2814(43) | C23 | 3447(3) | 4108(3) | 4302(4) |
| P1 | 1529.4(12) | 2328.7(14) | 5492.7(14) | C24 | 3667(3) | 5066(3) | 5105(4) |
| P2 | 2188.0(12) | 2101.3(15) | 9311.8(14) | C25 | 3243(3) | 5181(3) | 6015(4) |
| F1A | 4457(9) | 303(11) | 3926(13) | C26 | 2600(3) | 4337(3) | 6123(4) |
| F2A | 4413(15) | 710(18) | 2369(13) | C31 | 431(2) | 2622(3) | 4827(3) |
| F3A | 4638(20) | 2141(13) | 3971(23) | C32 | 366(2) | 3597(3) | 4497(3) |
| F1B | 4549(12) | 751(15) | 4366(13) | C33 | −487(2) | 3799(3) | 3993(3) |
| F2B | 4439(17) | 307(17) | 2613(16) | C34 | −1274(2) | 3025(3) | 3820(3) |
| F3B | 4209(10) | 1863(13) | 3391(13) | C35 | −1209(2) | 2050(3) | 4151(3) |
| O1A | 1004(6) | 4480(7) | 7597(7) | C36 | −356(2) | 1849(3) | 4654(3) |
| O1B | 1189(8) | 4439(10) | 8590(10) | C41 | 1348(3) | 2275(4) | 10166(3) |
| O2 | 6027(6) | 2213(6) | 2948(8) | C42 | 569(3) | 1477(4) | 9930(3) |
| O3 | 6254(5) | 551(5) | 3512(6) | C43 | −110(3) | 1590(4) | 10537(3) |
| O4A | 6060(6) | 2083(6) | 4902(6) | C44 | −12(3) | 2500(4) | 11380(3) |
| O4B | 4947(44) | 836(45) | 1953(48) | C45 | 767(3) | 3298(4) | 11615(3) |
| N1 | 3200(4) | 2149(5) | 7324(5) | C46 | 1447(3) | 3186(4) | 11008(3) |
| N2 | 5481(13) | 2287(15) | −688(16) | C51 | 3184(3) | 3090(4) | 10070(4) |
| C1 | −566(3) | 3772(4) | 7951(6) | C52 | 3227(3) | 4125(4) | 9862(4) |
| C2 | −1194(3) | 3688(4) | 6930(6) | C53 | 3950(3) | 4938(4) | 10483(4) |
| C3 | −2124(3) | 3650(4) | 6912(6) | C54 | 4630(3) | 4716(4) | 11311(4) |
| C4 | −2426(3) | 3697(4) | 7915(6) | C55 | 4587(3) | 3681(4) | 11518(4) |
| C5 | −1798(3) | 3782(4) | 8935(6) | C56 | 3864(3) | 2867(4) | 10898(4) |
| C6 | −868(3) | 3819(4) | 8953(6) | C61 | 2726(4) | −1268(3) | 9653(5) |
| C7 | 562(4) | 2425(5) | 7501(5) | C63 | 2638(4) | −965(3) | 8609(5) |
| C8 | 3892(6) | 2137(7) | 7159(8) | C62 | 2484(4) | 63(3) | 8514(5) |
| C9A | 4730(13) | 2209(15) | 6600(17) | C64 | 2418(4) | 787(3) | 9463(5) |
| C9B | 4887(16) | 2000(18) | 7190(20) | C65 | 2505(4) | 484(3) | 10506(5) |
| C11 | 1606(4) | 1124(5) | 4540(5) | C66 | 2659(4) | −544(3) | 10601(5) |
| C12 | 2121(4) | 392(5) | 4910(5) | C70 | 4569(19) | 1125(10) | 3445(11) |
| C13 | 2207(5) | −516(5) | 4169(6) | C71 | 5225(13) | 1534(14) | −403(16) |
| C14 | 1753(5) | −695(6) | 3047(6) | C72 | 4980(16) | 538(14) | −27(19) |

[a] The site occupation factors for the disordered atoms are 0.6 and 0.4 for S1A, O1A and S1B, O1B; 0.9 and 0.1 for S2A, O4A and S2B, O4B; 0.45 and 0.55 for F1A, F2A, F3A and F1B, F2B, F3B, respectively; 0.5 for C9A, C9B, N2, C71, C72.

4, with the enolic protons as AB systems coupled with the two P atoms (see previous discussion on 3). The *trans* geometry in solution is the same as that found in the solid state, as shown in the molecular structure of cation 10 reported in Figure 3. The structure consists of the packing of complex cations, $CF_3SO_3^-$ anions, and acetonitrile solvent molecules in the molar ratio 1/1/0.5. Selected bond distances and bond angles are given in Table 8. The structure of the cation is very close to that observed in the neutral complex 3. The coordination geometry is closer to planar than in complex 3, as shown by bond angles and displacements of atoms from the mean coordination plane: Pd1, −0.003(1) Å; P1, 0.022(2) Å; P2, 0.024(2) Å; N1, −0.070(7) Å; C7, −0.065(7) Å. Other parameters involving the $[(PPh_3)_2Pd\{CH_2S(O)Ph\}$ fragment of the two complexes compare well with those in complex 3. The sulfoxide group shows a configurational disorder. Both enantiomers [*R*(A) and *S*(B)] sharing the carbon atom

**Table 5. Fractional Atomic Coordinates (×10⁴) for Complex 12**

| atom | *x/a* | *y/b* | *z/c* | atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|---|---|---|---|
| Pd1 | 3350.0(3) | 7227.1(2) | 1590.1(3) | C26 | 4456(4) | 6246(3) | 4802(4) |
| S1 | 1028.2(9) | 6102.5(9) | 2141.4(11) | C31 | 5878(3) | 6536(2) | 2845(3) |
| P1 | 4862.1(8) | 7349.9(6) | 3200.0(8) | C32 | 6941(3) | 6647(3) | 3605(4) |
| P2 | 1355.8(8) | 8071.5(7) | −75.7(8) | C33 | 7688(3) | 6015(3) | 3335(4) |
| Cl1 | 4712.9(9) | 7347.8(7) | 239.6(9) | C34 | 7373(4) | 5253(3) | 2317(4) |
| O1 | 345(3) | 6149(3) | 3154(4) | C35 | 6325(4) | 5119(3) | 1582(4) |
| C1 | 1857(3) | 5177(3) | 2183(4) | C36 | 5569(4) | 5758(3) | 1823(3) |
| C2 | 2419(4) | 4836(3) | 1234(5) | C41 | 2326(3) | 9174(3) | 298(3) |
| C3 | 3022(5) | 4109(4) | 1257(6) | C42 | 3188(4) | 9414(3) | 1331(4) |
| C4 | 3047(6) | 3699(4) | 2208(8) | C43 | 3889(4) | 10285(3) | 1676(4) |
| C5 | 2468(8) | 4030(5) | 3146(7) | C44 | 3735(4) | 10912(3) | 967(5) |
| C6 | 1858(5) | 4766(4) | 3142(5) | C45 | 2854(5) | 10697(4) | −20(5) |
| C7 | 2142(3) | 7103(3) | 2675(3) | C46 | 2155(4) | 9823(3) | −365(4) |
| C8 | 2038(3) | 7104(3) | 52(3) | C51 | 578(3) | 7933(3) | −1624(3) |
| C11 | 5799(3) | 8500(2) | 3741(3) | C52 | 1027(4) | 7485(4) | −2626(4) |
| C12 | 6437(4) | 8844(3) | 4940(4) | C53 | 520(5) | 7475(5) | −3817(5) |
| C13 | 7185(4) | 9691(3) | 5283(4) | C54 | −440(6) | 7878(4) | −3992(5) |
| C14 | 7325(4) | 10203(3) | 4451(5) | C55 | −913(5) | 8287(4) | −3015(6) |
| C15 | 6706(4) | 9874(3) | 3264(4) | C56 | −416(4) | 8319(3) | −1815(4) |
| C16 | 5945(3) | 9034(3) | 2910(4) | C61 | 316(3) | 8222(3) | 928(3) |
| C21 | 4494(3) | 7129(2) | 4626(3) | C62 | −563(4) | 7478(3) | 790(4) |
| C22 | 4176(4) | 7833(3) | 5505(3) | C63 | −1336(4) | 7555(4) | 1595(5) |
| C23 | 3872(4) | 7651(3) | 6565(4) | C64 | −1240(4) | 8357(4) | 2526(5) |
| C24 | 3862(4) | 6774(3) | 6741(4) | C65 | −385(4) | 9106(4) | 2661(4) |
| C25 | 4132(4) | 6067(3) | 5853(5) | C66 | 392(3) | 9042(3) | 1860(4) |

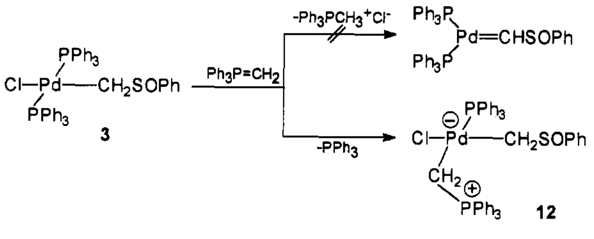
**Table 6. Selected Bond Distances (Å) and Angles (deg) for Complex 3**

| | | | |
|---|---|---|---|
| Pd1–Cl1 | 2.390(3) | P2–C51 | 1.821(5) |
| Pd1–P1 | 2.338(2) | P2–C61 | 1.827(4) |
| Pd1–P2 | 2.334(2) | S1A–O1A | 1.484(11) |
| Pd1–C7 | 2.052(9) | S1A–C1 | 1.760(7) |
| P1–C11 | 1.825(5) | S1A–C7 | 1.820(7) |
| P1–C21 | 1.816(5) | S1B–O1B | 1.510(14) |
| P1–C31 | 1.831(6) | S1B–C1 | 1.793(11) |
| P2–C41 | 1.842(4) | S1B–C7 | 1.783(9) |
| P2–Pd1–C7 | 91.8(2) | C1–S1B–C7 | 96.0(4) |
| P1–Pd1–C7 | 91.3(2) | O1B–S1B–C7 | 105.5(9) |
| P1–Pd1–P2 | 174.3(1) | O1B–S1B–C1 | 103.9(8) |
| Cl1–Pd1–C7 | 178.1(2) | S1B–C1–C6 | 103.4(4) |
| Cl1–Pd1–P2 | 86.9(1) | S1B–C1–C2 | 136.5(5) |
| Cl1–Pd1–P1 | 90.1(1) | S1A–C1–C6 | 127.1(4) |
| C1–S1A–C7 | 95.9(3) | S1A–C1–C2 | 112.9(4) |
| O1A–S1A–C7 | 106.8(4) | Pd1–C7–S1B | 107.8(4) |
| O1A–S1A–C1 | 105.5(5) | Pd1–C7–S1A | 109.4(4) |

bound to palladium are alternatively present with different occupancies (see Experimental Section and Table 4). The O1A and O1B oxygen atoms not engaged in coordination to Pd [Pd···O1A, 3.31(1) Å; Pd···O1B, 3.33(1) Å] are involved in C–H···O intramolecular contacts which should be considered hydrogen bonds:[11a] C26···O1A, 3.30(1) Å; H26···O1A, 2.19 Å; C26–H26···O1A, 153°; C52···O1B, 3.28(1) Å; H52···O1B, 2.33 Å; C52–H52···O1B, 150°. The C1···C6 phenyl ring is almost parallel to the coordination plane, the dihedral angle they form being 10.0(1)°. The S–C distances [mean values for S1–C7 and S1–C1, 1.808(8) and 1.780(7) Å, respectively] and the S–O distances [mean value 1.485(11) Å] are in good agreement with the values observed in complex **3**. The phenyl rings in the triphenylphosphine ligands adopt a conformation which results in two pairs of hydrogen atoms (Pd···H range: 2.68–3.11 Å for H12, H62, H26, H52) capping above and below the coordination plane, as found in complex **3**. The H atoms define approximately a plane perpendicular to the mean coordination plane (dihedral angle 74.6°). The acetonitrile ligand is coordinated in the normal linear fashion, with a Pd–N distance [2.089(6) Å] close to the value of 2.065(14) Å found, *e.g.*, in [(MeCN)PdCl$_2$($\mu$-dppm)PdCl$_2$(MeCN)].[15] Packing is determined by several contacts involving the CF$_3$SO$_3$$^-$ anion, the acetonitrile solvent molecule, and the cation, the shortest of which ranges from 3.2 to 3.5 Å.

The structure of **10** may contain the explanation for the lack of reactivity of **3** toward the inserting group. The coordination site freed from the ionization is *trans* to the potential migrating group and therefore does not allow a possible intramolecular process. The ease of reaction of **3** and **4** with isocyanides is due indirectly to the ability of Bu$^t$NC to replace one of the PPh$_3$ ligands, thus producing a *cis* position with respect to the migrating $\alpha$-sulfinyl anion.

The chemistry of **3** and **4**, involving mainly insertion reactions, is essentially controlled by the rather low polarity of the Pd–C $\sigma$ bond, and by unfavorable arrangement of the potentially available coordination site filled by Cl$^-$ *trans* to the $\alpha$-sulfinyl anion. Our attempt to generate a Pd–$\alpha$-sulfinyl carbene[5,8d] sought to take advantage of the easy ionization (see reaction 4) of the Pd–Cl bond, and the plausible elimination of HCl using the Wittig reagent as a base.



(5)

Reaction 5, however, led to the simple substitution of one of the PPh$_3$ groups by the much more basic ylide ligand. Such types of ylide complexes have been discovered recently,[16] and their use is quite interesting in acetylene and olefin polymerization.[17] We should emphasize the peculiar presence of two $\alpha$-functionalized carbanions

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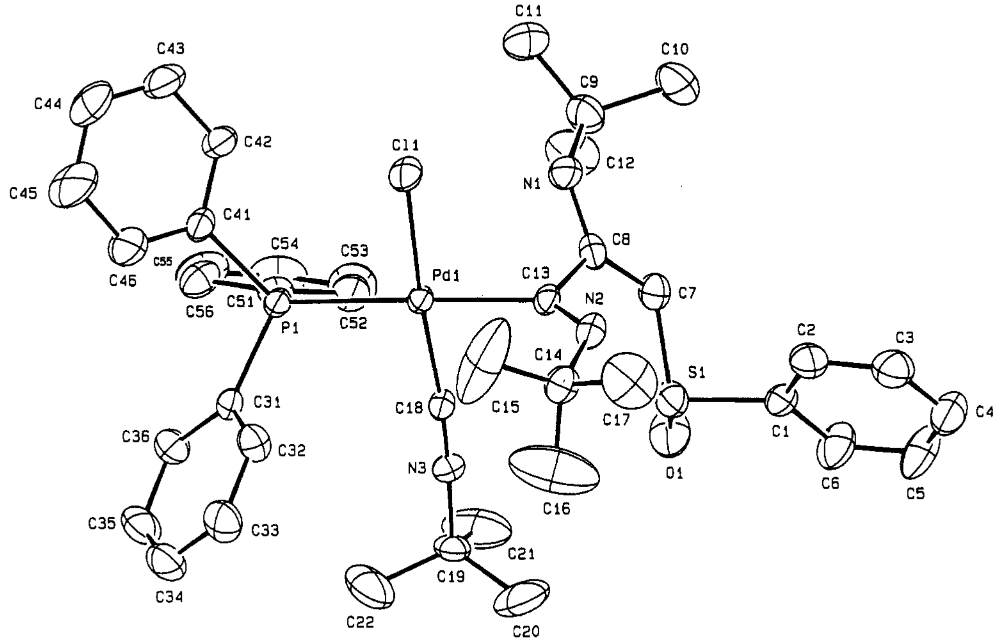

**Figure 2.** ORTEP view of complex **5** (30% probability ellipsoids).

**Table 7. Selected Bond Distances (Å) and Angles (deg) for Complex 5**

| | | | |
|---|---|---|---|
| Pd1–Cl1 | 2.341(2) | N3–C18 | 1.138(7) |
| Pd1–P1 | 2.408(1) | N3–C19 | 1.449(8) |
| Pd1–C13 | 2.040(4) | C7–C8 | 1.343(7) |
| Pd1–C18 | 1.940(5) | C8–C13 | 1.509(8) |
| S1–O1 | 1.502(4) | C9–C10 | 1.529(9) |
| S1–C1 | 1.809(5) | C9–C11 | 1.509(7) |
| S1–C7 | 1.740(5) | C9–C12 | 1.505(9) |
| P1–C31 | 1.831(5) | C14–C15 | 1.400(10) |
| P1–C41 | 1.812(5) | C14–C16 | 1.420(11) |
| P1–C51 | 1.825(5) | C14–C17 | 1.456(9) |
| N1–C8 | 1.349(6) | C19–C20 | 1.475(9) |
| N1–C9 | 1.461(7) | C19–C21 | 1.451(10) |
| N2–C13 | 1.264(6) | C19–C22 | 1.435(10) |
| N2–C14 | 1.467(8) | | |
| C13–Pd1–C18 | 86.1(2) | S1–C1–C6 | 117.6(5) |
| P1–Pd1–C18 | 89.0(1) | S1–C1–C2 | 120.9(4) |
| P1–Pd1–C13 | 171.9(1) | C2–C1–C6 | 121.3(5) |
| Cl1–Pd1–C18 | 175.1(1) | S1–C7–C8 | 122.5(4) |
| Cl1–Pd1–C13 | 89.5(1) | N1–C8–C7 | 126.9(5) |
| Cl1–Pd1–C1 | 95.7(0) | C7–C8–C13 | 119.5(4) |
| C1–S1–C7 | 99.9(2) | N1–C8–C13 | 113.5(4) |
| O1–S1–C7 | 106.9(2) | N2–C13–C8 | 116.9(4) |
| O1–S1–C1 | 104.9(2) | Pd1–C13–C8 | 109.3(3) |
| C8–N1–C9 | 128.8(4) | Pd1–C13–N2 | 133.7(4) |
| C13–N2–C14 | 127.0(5) | Pd1–C18–N3 | 175.7(4) |
| C18–N3–C19 | 176.6(5) | | |

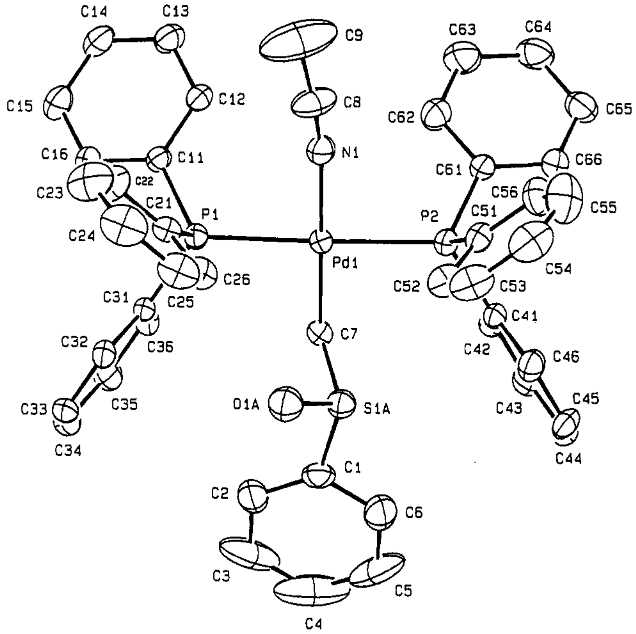

**Figure 3.** ORTEP view of complex **10** (30% probability ellipsoids). For clarity only the A position is given for the disordered α-sulfinyl group.

around Pd(II) in complex **12**, though the chemistry of such species has not yet been explored. The assignments for the rather complex $^1$H NMR spectrum of **12** have been made (see Experimental Section) by careful comparison with those of complexes **3** and **10**. A perspective view showing the atomic numbering scheme of **12** is reported in Figure 4. Selected bond distances and angles are given in Table 9. The four coordinated atoms are planar within experimental error, with palladium protruding by only 0.013(1) Å from the plane. Bond distances and angles within the coordination sphere are in good agreement with those observed in complex **3**. The lengthening of the Pd–C8 distance with respect to the Pd–C7 distance could be a consequence of intraligand steric effects. The sulfoxide group does not show any disorder. Bond distances and angles are in good agreement with those observed in complexes **3**, **5**, and **10**. The C1⋯C6 phenyl ring is tilted by 55.5(1)° with respect to the coordination plane, with the H2 hydrogen atom lying at a distance of 2.99 Å from palladium in a direction forming a dihedral angle of 19.3° with the normal to the coordination plane. The H42 hydrogen atom, belonging to one of the $PPh_3$ ligands, forms a bipyramidal geometry around palladium with a Pd⋯H42 distance of 2.45 Å. The Pd⋯H42 line forms a dihedral angle of 7.7° with the normal to the coordination plane. Such short distances can be viewed as three-center four-electron interactions,[18] though we cannot prove this by any NMR support, or they too may arise simply from rigid or sterically constrained ligands as pointed out by Lippard and co-workers.[19]

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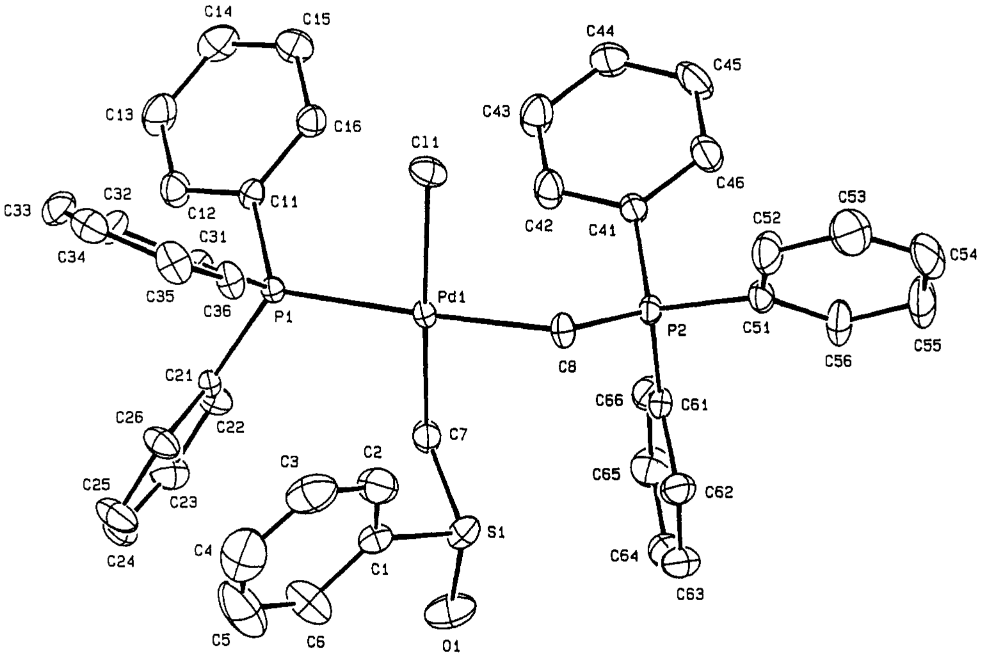

**Figure 4.** ORTEP view of complex 12 (30% probability ellipsoids).

**Table 8. Selected Bond Distances (Å) and Angles (deg) for Complex 10**

| | | | |
|---|---|---|---|
| Pd1–P1 | 2.344(2) | P1–C11 | 1.810(6) |
| Pd1–P2 | 2.342(2) | P1–C21 | 1.801(5) |
| Pd1–N1 | 2.089(6) | P1–C31 | 1.820(4) |
| Pd1–C7 | 2.010(6) | P2–C41 | 1.817(5) |
| S1A–O1A | 1.446(10) | P2–C51 | 1.804(4) |
| S1A–C1 | 1.767(6) | P2–C64 | 1.807(5) |
| S1A–C7 | 1.806(7) | N1–C8 | 1.106(12) |
| S1B–O1B | 1.524(11) | C8–C9A | 1.556(24) |
| S1B–C1 | 1.793(8) | C8–C9B | 1.532(27) |
| C1B–C7 | 1.809(8) | | |
| N1–Pd1–C7 | 176.3(3) | O1B–S1B–C1 | 102.2(6) |
| P2–Pd1–C7 | 90.6(2) | Pd1–N1–C8 | 171.7(7) |
| P2–Pd1–N1 | 90.1(2) | S1B–C1–C6 | 137.8(5) |
| P1–Pd1–C7 | 90.8(2) | S1B–C1–C2 | 102.1(4) |
| P1–Pd1–N1 | 88.5(2) | S1A–C1–C6 | 108.6(4) |
| P1–Pd1–P2 | 178.1(1) | S1A–C1–C2 | 131.3(4) |
| C1–S1A–C7 | 96.4(3) | Pd1–C7–S1B | 107.3(3) |
| O1A–S1A–C7 | 106.3(4) | Pd1–C7–S1A | 107.4(3) |
| O1A–S1A–C1 | 105.6(5) | N1–C8–C9B | 165.9(13) |
| C1–S1B–C7 | 95.4(3) | N1–C8–C9A | 163.2(11) |
| O1B–S1B–C7 | 105.1(6) | | |

**Table 9. Selected Bond Distances (Å) and Angles (deg) for Complex 12**

| | | | |
|---|---|---|---|
| Pd1–P1 | 2.323(1) | P1–C11 | 1.837(3) |
| Pd1–Cl1 | 2.411(1) | P1–C21 | 1.833(4) |
| Pd1–C7 | 2.047(4) | P1–C31 | 1.829(4) |
| Pd1–C8 | 2.119(3) | P2–C8 | 1.762(5) |
| S1–O1 | 1.496(5) | P2–C41 | 1.807(4) |
| S1–C1 | 1.794(5) | P2–C51 | 1.813(3) |
| S1–C7 | 1.786(4) | P2–C61 | 1.799(4) |
| C7–Pd1–C8 | 90.7(1) | O1–S1–C7 | 105.8(2) |
| Cl1–Pd1–C8 | 87.1(1) | O1–S1–C1 | 106.4(2) |
| Cl1–Pd1–C7 | 177.7(1) | S1–C1–C6 | 118.8(3) |
| P1–Pd1–C8 | 176.7(1) | S1–C1–C2 | 121.0(4) |
| P1–Pd1–C7 | 92.5(1) | C2–C1–C6 | 120.1(4) |
| P1–Pd1–Cl1 | 89.7(1) | Pd1–C7–S1 | 117.4(2) |
| C1–S1–C7 | 100.5(2) | Pd1–C8–P2 | 120.2(2) |

Some comments concerning the intramolecular contacts of the structurally determined α-sulfinyl complexes **3**, **5**, **10**, and **12** are worthy of mention at this point. Complexes **5** and **12**, where the sulfoxide group is not affected by disorder, show a strong intramolecular contact involving the oxygen atom and the adjacent α carbon of the phenyl group: C6···O1, 2.851(6) Å (**5**), 2.892(8) Å (**12**); H6···O1, 2.34 Å (**5**), 2.29 Å (**12**); C6-H6···O1, 106° (**5**), 113° (**12**). These contacts, which give rise to a five-membered ring, could be interpreted as strong hydrogen bonds.[11a]

In complexes **3** and **10**, where the sulfoxide group shows a configurational disorder, similar contacts are present involving both the A and B positions of the oxygen atoms. Complex **3**: C6···O1A, 3.070(13) Å; H6···O1A, 2.82 Å; C2···O1B, 3.31(2) Å; H2···O1B, 3.07 Å. Complex **10**: C2···O1A, 3.229(10) Å; H2···O1A, 3.04 Å; C6···O1B, 3.237(14) Å; H6···O1B, 3.04 Å. Nevertheless, the values of the H···O distances (2.82–3.07 Å) seem too long to be regarded as interactions. However, it is worthy of note that many of the peripheral carbon atoms which participate in the CH···Pd and CH···O contacts exhibit extremely large anisotropic displacements, indicating some degree of static and dynamic disorder. Thus, positions found for H atoms attached to these atoms are likely to be very inaccurate, a good example being C15 of complex **5**.

## Experimental Section

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. *cis*-[$(PPh_3)_2PdCl_2$][20] and $Ph_3P{=}CH_2$[21] were synthesized as reported in the literature. The sulfoxides used are commercially available. Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer, and $^1H$ NMR spectra were measured on a 2000-AC Bruker instrument.

**Preparation of 3.** Melted **1** (2.52 g, 18 mmol) was added with a syringe to a THF (100 mL) suspension of potassium hydride (0.76 g, 18.9 mmol) and the mixture stirred overnight. Then

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*cis*-[$(PPh_3)_2PdCl_2$] (11.37 g, 16.2 mmol) was added at room temperature and the suspension vigorously stirred for 1 day. A white microcrystalline solid formed after a few hours. It was filtered in the air, washed with THF (3 × 50 mL), and extracted under nitrogen with $CH_2Cl_2$ (50 mL) to eliminate KCl. A white crystalline solid formed (90%). Crystals suitable for X-ray analysis were obtained by recrystallization in THF. IR (Nujol): $\nu$(S=O) 1094 (w) $cm^{-1}$. Anal. Calcd for $C_{43}H_{37}ClOP_2PdS$: C, 64.11; H, 4.63. Found: C, 64.10; H, 4.68. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 2.18 (td, 1 H, A part of an $ABX_2$, $CH_2Pd$, $J_{Ab}$ = 9 Hz, $2J_{AX} \approx 6$ Hz), 2.56 (q, 2 H, B part of an $ABX_2$, $CH_2Pd$, $J_{AB}$ = 9 Hz, $2J_{BX}$ = 9 Hz) (the quartet is very likely from the overlap of two triplets due to the fact that the $J_{HH}$ and $J_{HP}$ are almost identical), 6.70 (m, Ph, 2 H), 7.15 (m, Ph, 3 H), 7.48 (m, Ph, 18 H), 7.78 (m, Ph, 12 H). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 49.1 ($CH_2Pd$), 124.1–136.3 (Ph). $^{31}P$ NMR ($CD_2Cl_2$): $\delta$ 29.2 (s).

**Preparation of 4.** Melted (*R*)-(+)-**2** (0.59 g, 3.83 mmol) was added with a syringe to a THF (50 mL) suspension of potassium hydride (0.156 g, 3.89 mmol) and the mixture stirred overnight. Then *cis*-[$(PPh_3)_2PdCl_2$] (2.70 g, 3.85 mmol) was added at room temperature and the suspension vigorously stirred for 1 day. A white microcrystalline solid formed after a few hours. It was filtered in the air, washed with THF (20 mL), and extracted under nitrogen with $CH_2Cl_2$ (50 mL) to eliminate KCl. A white crystalline solid formed, which was filtered and dried. Another crop of product was collected by evaporating solution to dryness and redissolving the residue in toluene (30 mL) and pentane (30 mL) (90%). Anal. Calcd for $C_{44}H_{39}ClOP_2PdS$: C, 64.48; H, 4.80. Found: C, 63.81; H, 4.93. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 2.18 (td, 1 H, A part of an $ABX_2$, $CH_2Pd$, $J_{AB}$ = 8.5 Hz, $J_{AP} \approx 6$ Hz), 2.55 (q, 1 H, B part of an $ABX_2$, $CH_2Pd$, $J_{AB}$ = 8.5 Hz, $J_{BP} \approx 9$ Hz), 6.65 (d, Ph, 2 H), 6.97 (d, Ph, 2 H), 7.48 (m, PPh, 20 H), 7.79 (m, PPh, 10 H). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 21.7 (s, MePh), 49.0 (s, $CH_2Pd$), 124.2–147.2 (m, Ph). $^{31}P$ NMR ($CD_2Cl_2$): $\delta$ 29.0 (s). $[\alpha]_D = +116 \pm 2°$ ($c$ = 0.665) in THF.

**Preparation of 5.** A THF (20 mL) solution of $Bu^tNC$ (0.90 g, 10.8 mmol) was added dropwise to a THF (40 mL) suspension of **3**, affording in a few minutes a clear solution. The solvent was evaporated and the yellow oil redissolved in ether (50 mL). White crystals suitable for X-ray analysis slowly grew, which were filtered and dried (81%). IR (Nujol): $\nu$(NH) 3309 (w), $\nu$(N≡C) 2206 (w), $\nu$(C=N) 1632 (w) $cm^{-1}$. Anal. Calcd for $C_{40}H_{49}ClN_3OPPdS$: C, 60.60; H, 6.23; N, 5.30. Found: C, 60.39; H, 6.39; N, 5.07. $^1H$ NMR ($C_6D_6$): $\delta$ 1.05 (s, $Bu^t$, 9 H), 1.17 (s, $Bu^t$, 9 H), 1.88 (s, $Bu^t$, 9 H), 5.11 (s, =CHSO, 1 H), 6.90–7.10 (m, Ph, 12 H), 7.7 (m, Ph, 6 H), 8.55 (m, Ph, 2 H). $^{31}P$ NMR ($C_6D_6$): $\delta$ 12.3 (s).

**Preparation of 6.** A THF (20 mL) solution of $Bu^tNC$ (0.23 g, 2.77 mmol) was added dropwise to a THF (20 mL) suspension of **4**, affording in a few minutes a clear solution. The solvent was evaporated and the yellow oil redissolved in ether (50 mL). A white crystalline solid slowly formed, which was filtered and dried (39%). Anal. Calcd for $C_{41}H_{51}ClN_3OPPdS$: C, 61.04; H, 6.37, N, 5.21; P, 3.84. Found: C, 61.56; H, 6.25, N, 5.40; P, 3.87. $^1H$ NMR ($C_6D_6$): $\delta$ 1.06 (s, $Bu^t$, 9 H), 1.19 (s, $Bu^t$, 9 H), 1.90 (s, $Bu^t$, 9 H), 2.06 (s, MePh, 3 H), 5.15 (s, =CHSO, 1 H), 6.9–7.1 (m, Ph, 12 H), 7.7 (m, Ph, 6 H), 8.55 (m, Ph, 2 H). $^{31}P$ NMR ($C_6D_6$): $\delta$ 12.2 (s). $[\alpha]_D = -131.1 \pm 2.0°$ ($c$ = 1.030) in THF.

**Reaction of 5 with MeCOCl.** To a suspension of **3** (3.05 g, 3.78 mmol) were added first $Bu^tNC$ (0.94 g, 11.35 mmol) and then, when all the solids had dissolved, $CH_3COCl$ (0.60 g, 7.64 mmol) dropwise with a syringe. After a few minutes, **7** formed as a light yellow precipitate and was filtered off (82%). The filtrate was evaporated to dryness, yielding a yellow oil, which was analyzed by IR, $^1H$ NMR, and GC–MS.

**7**: IR (Nujol), $\nu$(N≡C) 2235 (s) $cm^{-1}$. Anal. Calcd for $C_{23}H_{24}Cl_2NPPd$: C, 52.85; H, 4.63; N, 2.68. Found: C, 52.60; H, 4.95; N, 2.89. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 1.14 (s, $Bu^t$, 9 H), 7.4–7.8 (m, Ph, 15 H). $^{31}P$ NMR ($C_6D_6$): $\delta$ 28.1 (s).

**8**: IR (Nujol), $\nu$(C=O) 1751 (s) and $\nu$(S=O) 1021 (s) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 2.16 (s, Me, 3 H), 5.46 (s, $COCH_2SO$, 2 H), 7.35 (m, Ph, 5 H). MS: $M^+$ = 182.

**9**: MS, $M^+$ = 161.

**Preparation of 10.** A $CH_3CN$ (20 mL) solution of $CF_3SO_3Ag$ (0.90 g, 3.5 mmol) was added dropwise to a $CH_2Cl_2$ (80 mL) solution of **3**. A white precipitate suddenly formed, which was filtered off. The solvents were evaporated to 10 mL, and ether (50 mL) was added. At 0 °C a yellow microcrystalline solid formed (75%). Crystals suitable for X-ray analysis were obtained by recrystallization in a 1/3 $CH_2Cl_2$/ether mixture. IR (Nujol): $\nu$(CN) 2309 (w) and 2287 (w) $cm^{-1}$. Anal. Calcd for $C_{46}H_{40}F_3NO_4P_2PdS_2$: C, 57.54; H, 4.20; N, 1.46. Found: C, 57.26; H, 4.35; N, 1.87. $^1H$ NMR ($CD_3CN$): $\delta$ 2.02 (s, $CH_3CN$, 3 H), 2.43 (bm, $SOCH_2Pd$, 1 H), 2.88 (bm, $SOCH_2Pd$, 1 H), 6.63 (m, PhSO, 2 H), 7.3 (m, PhSO, 3 H), 7.6–7.9 (m, PPh, 30 H). $^{31}P$ NMR ($CD_3CN$): $\delta$ 31.3 (s). $^1H$ NMR ($CD_2Cl_2$): $\delta$ 1.97 (s, Me, 3 H), 2.36 (td, 1 H, A part of an $ABX_2$, $CH_2Pd$, $J_{AB}$ = 9 Hz, $2J_{AX} \approx 6$ Hz), 2.91 (td, 1 H, B part of an $ABX_2$, $CH_2Pd$, $J_{AB}$ = 9 Hz, $2J_{BX} \approx 11$ Hz), 6.5–7.9 (m, Ph, 35 H). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 2.4 (s, Me), 48.7 (s, $CH_2Pd$), 123.6 (s, $CF_3SO_3^-$), 123.8 (s, CNPd), 127.7–145.0 (m, Ph). $^{31}P$ NMR ($CD_2Cl_2$): $\delta$ 24.7 and 37.9 (2s).

**Preparation of 11.** A $CH_3CN$ (10 mL) solution of $CF_3SO_3Ag$ (0.22 g, 0.8 mmol) was added dropwise to a $CH_2Cl_2$ (40 mL) solution of **4**. A white precipitate was formed and filtered off. The solvents were evaporated to 10 mL, and ether (50 mL) was added. At 0 °C yellow crystals formed (77%). IR (Nujol): $\nu$(CN) 2311 (w) and 2281 (w) $cm^{-1}$. Anal. Calcd for $C_{47}H_{42}F_3NO_4P_2PdS_2$: C, 57.94; H, 4.34; N, 1.44. Found: C, 57.32; H, 4.35; N, 1.34. $^1H$ NMR ($CD_3CN$): $\delta$ 2.02 (s, $CH_3CN$, 3 H), 2.28 (s, MePh, 3 H), 2.40 (bm, $SOCH_2Pd$, 1 H), 2.88 (bm, $SOCH_2Pd$, 1 H), 6.52 (d, PhSO, 2 H), 7.08 (d, PhSO, 2 H), 7.6–7.9 (m, PPh, 30 H). $^{31}P$ NMR ($CD_3CN$): $\delta$ 31.2 (s). $[\alpha]_D = +272.0 \pm 1°$ ($c$ = 1.342) in THF.

**Preparation of 12.** To a THF (50 mL) suspension of **3** (0.72 g, 0.9 mmol) was added $Ph_3P{=}CH_2$ (0.25 g, 0.9 mmol) dropwise until complete dissolution of the starting product. The light yellow solution was evaporated to dryness, the residue redissolved in $CH_2Cl_2$ (10 mL), and ether (60 mL) added. A white crystalline solid formed (82%). Crystals suitable for X-ray analysis were grown in a 1/4 $CH_2Cl_2$/ether mixture. Anal. Calcd for $C_{44}H_{39}ClOP_2PdS$: C, 64.47; H, 4.80. Found: C, 64.80; H, 5.00. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 1.65 (td, 1 H, A part of an $ABX_2$, $CH_2$, $J_{AB}$ = 9 Hz, $2J_{AX} \approx 12$ Hz), 1.83 (bm, $CH_2$, 2 H), 2.39 (td, 1 H, B part of an $ABX_2$, $CH_2$, $J_{AB}$ = 9 Hz, $2J_{BX} \approx 12$ Hz), 7.30–7.85 (m, Ph, 35 H). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 1.90 (d, $CH_2Pd$), 4.10 (d, $CH_2Pd$), 43.2 (d, $PdCH_2SO$), 125.3–136.2 (12 s, Ph), 150.7 (s, Ph). $^{31}P$ NMR ($CD_2Cl_2$): $\delta$ 26.3 (s) and 33.2 (s).

**X-ray Crystallography.** The crystals of **3**, **5**, **10**, and **12** were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[22] Crystal data and details associated with structure refinement are given in Table 1. Data were collected at room temperature (295 K) on a single-crystal diffractometer (Rigaku AFC6S for **3**, Philips PW1100 for **5** and **12**, and Siemens AED for **10**). For intensities and background individual reflections profiles were analyzed.[23] The structure amplitudes were obtained after the usual Lorentz and polarization corrections, and the absolute scale was established by the Wilson method.[24] The crystal quality was tested by $\psi$ scans showing that crystal absorption effects could be neglected for complexes **5**, **10**, and **12** and not for complex **3**. Only the data of complex **3** were then corrected for absorption using a semiempirical method.[25] The function minimized during the least-squares refinement was $\sum w|\Delta F|^2$. A weighting scheme $\{w = k/[\sigma^2(F_o) + g|F_o|^2]\}$ based on counting statistics was applied.[26] Unit weights were used for **12** since this gave the best agreement factors and analysis of variance. Anomalous scattering corrections

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(26) Sheldrick, G. *SHELX-76 System of Crystallographic Computer Programs*; University of Cambridge: Cambridge, England, 1976.

were included in all structure factor calculations.[27b] Scattering factors for neutral atoms were taken from ref 27a for non-hydrogen atoms and from ref 28 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary. All calculations were carried out on an IBM AT personal computer equipped with an INMOS T800 Transputer using SHELX-76.[26] Solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map.

**Complex 3.** Refinement was first done isotropically, then anisotropically by full-matrix least squares for all non-H atoms except for those affected by disorder. All the hydrogen atoms but those related to the THF molecule, which were ignored, were located from a difference Fourier map and introduced in the final refinement as fixed contributors (isotropic $U$'s fixed at 0.10 Å$^2$). During the refinement the phenyl rings were constrained to be regular hexagons (C–C = 1.395 Å). The $SOCH_2$ group was found to be affected by a configurational disorder, implying the presence of the two enantiomeric forms sharing the C7 carbon atom. The disorder was solved by considering the sulfur and oxygen atoms to be statistically distributed over two positions (A and B) related by a pseudo mirror plane running through the phenyl ring. They were isotropically refined with the site occupation factors given in Table 2. The final difference map showed no unusual features, with no significant peaks above the general background.

**Complexes 5 and 12.** Refinement was first done isotropically, then anisotropically by full-matrix least squares for all non-H atoms. All the hydrogen atoms were located from a difference Fourier map and introduced in the final refinement as fixed contributors (isotropic $U$'s fixed at 0.08 Å$^2$). The final difference map showed no unusual features, with no significant peaks above the general background.

**Complex 10.** Refinement was first done isotropically, then anisotropically by full-matrix least squares for all non-H atoms except for the $CF_3SO_3^-$ anion and the sulfoxide group, which were found to be affected by disorder. The anion exhibits 2-fold disorder of the sulfur, oxygen, and fluorine sites with occupancy factors given in Table 4. The sulfoxide group was found to exhibit configurational disorder similar to that observed in complex 3. Two of the disordered atoms were allowed to vary anisotropically [S2A, O4A having site occupancy factors of 0.9(1)], the remainder being isotropically refined, as well as the three atoms of an acetonitrile solvent molecule which was found disordered around a center of symmetry. At the last stage of refinement the C9 methyl carbon reached a rather high $U_{33}$ thermal parameter showing an inconsistent contact with the N2 atom of acetonitrile solvent. It was then considered statistically disordered over two positions (A and B), one of them (A) consistent with the disordered acetonitrile solvent [C9···N2, 3.29(3) Å]. Except for those associated with the disordered acetonitrile solvent and C9 methyl carbon, all hydrogen atoms were located from difference Fourier maps and introduced in the final refinement as fixed contributors ($U_{iso}$ = 0.10 Å$^2$). During the refinement the phenyl rings were constrained to be regular hexagons (C–C = 1.395 Å). Constraints were also applied to the C–F bond distance of the $CF_3SO_3^-$ anion [1.30(1) Å] and to the N–C and C–C bonds of the acetonitrile solvent [1.13(1) and 1.46(1) Å, respectively]. The final difference map showed no unusual features, with no significant peaks above the general background.

Final atomic coordinates are listed in Tables 2–5 for non-H atoms and in Tables SII–SV for hydrogens. Thermal parameters are given in Tables SVI–SIX and bond distances and angles in Tables SX–SXIII.[29]

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**Supplementary Material Available:** Experimental details associated with data collection and structure refinement (Table SI), hydrogen atom coordinates (Tables SII–SV), thermal parameters (Tables SVI–SIX), and bond distances and angles (Tables SX–SXIII) for complexes 3, 5, 10, and 12 (17 pages). Ordering information is given on any current masthead page.

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(29) See paragraph at the end of this paper regarding supplementary material.