Synthesis and Molecular Structure of a Palladium Complex Containing a λ^5-Phosphinine-Based SPS Pincer Ligand

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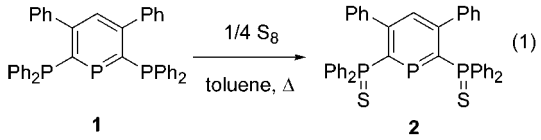
*Summary: 2,6-Bis(diphenylphosphino)-3,5-diphenylphosphinine (**1**) reacts with elemental sulfur to yield the corresponding 2,6-bis(diphenylphosphine sulfide)-3,5-diphenylphosphinine (**2**). Reaction of ligand **2** with [Pd(COD)Cl$_2$] affords the square planar complex **4** resulting from the displacement of one chloride ligand. An X-ray crystal study reveals that complex **4** features a λ^4-1-P-chlorophosphinine ligand which is bound to the palladium atom through the phosphorus atom. Reaction of **4** with methanol gives the corresponding P−OMe complex resulting from the nucleophilic substitution of the P−Cl bond. DFT calculations suggest that the formation of **4** results from the internal attack of the chloride counteranion onto the highly electrophilic P atom of the transient λ^3-phosphinine complex [Pd(**2**)Cl]$^+$ (**3**).*

Introduction

Pincer ligands play an increasing role in coordination chemistry and catalysis,[1] where their utility has been recently emphasized in some processes of importance such as the activation of alkanes.[2] Beside their intrinsic structural rigidity, which provides a significant thermodynamic stability to their complexes, one of their advantages relies on the possibility to finely tune the reactivity of the metal center by adjusting the nature and thus the electronic properties of the different pincer ligands. This allows for the continuous interest that has been devoted to the synthesis of various mixed systems incorporating different heteroatoms such as O, S, N, and P.[1] As part of a continuing program aimed at developing the use of sp^2-hybridized phosphorus ligands in coordination chemistry and catalysis we recently focused our attention on a mixed species featuring a central phosphinine unit and two pendant PPh$_2$═S ligands. Herein, we report on the surprising reactivity of this ligand toward the [PdCl$_2$] metal fragment.

Results and Discussion

Some years ago, we developed two synthetic approaches toward 2,6-bis(diphenyl)phosphino phosphinines.[3] These easily available phosphinines can be used as convenient precursors for the synthesis of mixed S−P−S pincer ligands through sulfurization of the two pendant diphenylphosphino groups. Thus, reaction of 2,6-bis(diphenylphosphino)-3,5-diphenylphosphinine (**1**) with 2 equiv of elemental sulfur in toluene under reflux cleanly affords the corresponding bis(diphenylphosphine sulfide) phosphinine **2** in good yields (eq 1). The preference for the sulfurization of the two phosphino groups over that of the phosphorus atom lone pair of phosphinine is obvious if we consider the respective basicity of the two groups. Indeed, the weaker basicity of sp^2-hybridized phosphorus ligands relative to classical tertiary phosphines is now well established.[4a] Thus, in most cases, high temperatures and long heating periods are usually required to achieve sulfurization of the phosphorus atom lone pair of phosphinines.[5] The formulation of **2** was easily established on the basis of its NMR data and elemental analysis.



(1)

To test the capability of **2** to act as a pincer ligand, we attempted to react it with [Pd(COD)Cl$_2$]. The reaction proceeds cleanly in dichloromethane at room temperature to yield the moisture-sensitive complex **4**, which exhibits an AB$_2$ spin system in ^{31}P NMR spectroscopy (eq 2). Though this pattern suggests that coordination through the three binding sites occurred, the upfield shift of the A part of the spectrum, δ (CD$_2$Cl$_2$) = 94.9 (AB$_2$, t, P$_A$), cannot be assigned to a phosphinine ring. Indeed, chemical shifts of free phosphinines and their corresponding complexes usually fall in the range from 160 to 250 ppm.[4b] Interesting insights on the structure of **4** are given by the ^{1}H and ^{13}C NMR data, which reveal the presence of a strongly shielded

(1) Albrecht A.; Van Koten G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750−3781.

(2) See for example: Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086−4087.

(3) See for example: (a) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1993**, *115*, 10665−10670. (b) Waschbüsch, K.; Le Floch, P.; Mathey, F. *Organometallics* **1996**, *15*, 1597−1603. (c) Avarvari, N.; Le Floch, P.; Ricard, L.; Mathey, F. *Organometallics* **1997**, *16*, 4089−4098.

(4) (a) Mézailles, N.; Mathey, F.; Le Floch, P. *Progress in Inorganic Chemistry;* Karlin, K. D., Ed.; John Wiley and Sons: New York, 2001; Vol. 49, pp 455−550. (b) Le Floch, P. In *Phosphorus−Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Mathey, F., Ed.; Pergamon: New York, 2001; pp 485−533.

(5) See for example: (a) Alcaraz, J.-M.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1984**, 508−509. (b) Holah, D. G.; Hugues, A. N. *J. Chem. Soc., Chem. Commun.* **1988**, 493−495. (c) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1991**, *113*, 667−669.

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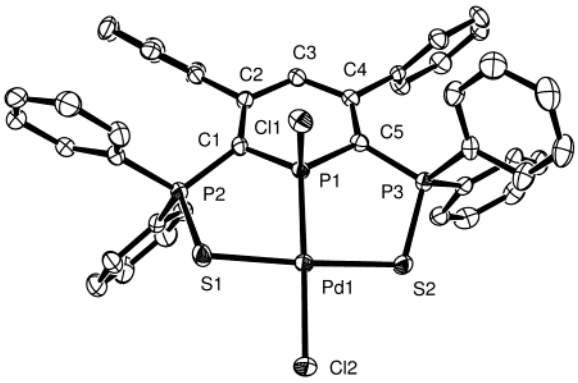
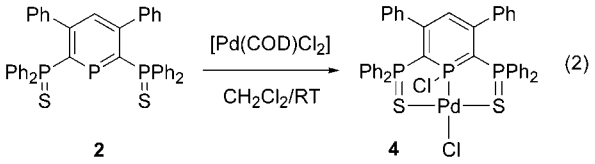


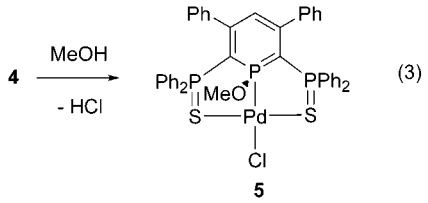
Figure 1. ORTEP view of one molecule of complex **4**. Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the assignment of NMR spectra. Relevant distances (Å) and bond angles (deg): P1−C1, 1.743(3); C1−C2, 1.409(3); C2−C3, 1.402(3); C3−C4, 1.405(3); C4−C5, 1.398(3); C5−P1, 1.754(2); C1−P2, 1.779(2); C5−P3, 1.777(3); P2−S1, 2.036(1); P3−S2, 2.036(1); P1−Cl1, 2.139(1); P1−Pd1, 2.1748(8); S1−Pd1, 2.317(1); S2−Pd1, 2.3277(8); Pd1−Cl2, 2.3720(8). P1−C1−C2, 119.5(2); C1−C2−C3, 122.6(2); C2−C3−C4, 126.2(2); C3−C4−C5, 122.4(2); C4−C5−P1, 119.9(2); C5−P1−C1, 105.7(1); P1−C1−P2, 110.3(1); P1−C5−P3, 11.7(1); P1−Pd1−S1, 85.33(3); P1−Pd1−S2, 90.13(3); S1−Pd1−Cl2, 92.97(3); S2−Pd1−Cl2, 91.73(3); P1−Pd1−Cl2, 177.34(2); S1−Pd1−S2, 173.36(2).

H4 proton (δ (CD_2Cl_2) = 5.84) and C2 (δ (CD_2Cl_2) = 94.3) and C4 (δ = 119.9) carbon atoms. Usually, such a shielding is encountered in λ^5-phosphinines.[4b]



The formulation of **4** was definitively established through an X-ray crystal structure study. An ORTEP view of one molecule of **4** is presented in Figure 1, and relevant bond distances and angles are listed below this. As suggested by NMR data, the aromaticity of the phosphinine ring has been destroyed and a chloride atom is now bound to the phosphorus atom. Thus complex **4** can be regarded as the coordination of a λ^4-1-*P*-chlorophosphinine anionic ligand onto a $[PdCl]^+$ fragment. Though a λ^4-phosphinine iron cyclopentadienyl complex has already been synthesized and spectroscopically identified,[6] **4** is the first structurally characterized complex.[7] As expected, the phosphorus atom is nearly tetrahedral and the chlorine atom points out of the mean plane defined by the ring. Curiously, the loss of aromaticity does not significantly modify the internal bond distances and angles within the ring, which roughly compare with that of a complexed λ^3-phosphinine. Nevertheless, the planarity of the ring is not totally preserved, and the phosphorus atom deviates from the plane defined by the carbocyclic system by 8.3°. Apart from this, the overall geometry around palladium is square planar, as expected for a d^8 center, and the four ligands are nearly located in the same plane. On the other hand, no significant distortion can be noted on examining Pd−S bond distances, which are very close to those recorded in phosphine sulfide palladium complexes.[8]

Complex **4** may be used as precursor in the synthesis of λ^4-1-R-*P* functional derivatives of complex **4** through the nucleophilic substitution of the chloride atom. Thus, when methanol is added onto a solution of freshly prepared **4**, an immediate reaction takes place leading to the formation of complex **5** and the concomitant release of HCl (eq 3). Complex **5**, which was recovered as a very stable yellow solid, was characterized by means of NMR spectroscopy and elemental analysis. In ^{31}P NMR spectroscopy, the substitution of the chlorine atom is only evidenced by a very small downfield shift of $\Delta\delta$ = 2.4 ppm, but the presence of a methoxy group in the ^1H NMR spectrum, at 3.84 ppm with a $^3J(H-P_A)$ = 14.4 Hz coupling constant, confirms the formulation proposed. Apart from this, NMR data of **5**, which are very similar to those of precursor **4**, do not deserve further comments.



Now it is worth discussing the formation of complex **4**. Phosphinines are relatively soft donors but display a very strong π-accepting power.[4a] As we recently showed, they logically behave as very efficient ligands for the stabilization of reduced transition metal centers.[9] On the other hand, their stability is very sensitive to the π-donating capability of the metal fragment to which they are coordinated. Though some complexes have been successfully characterized, coordination to Pd and Pt(II) fragments usually provokes a dearomatization of the ring which makes the P=C double bond very sensitive toward nucleophilic attack. Some 1,2-dihydrophosphinine complexes resulting from the attack of water or alcohols onto the P=C bond have been characterized.[10] Another important factor that must not be neglected is the substitution scheme of the ring. Indeed, studies on $P-W(CO)_5$ complexes have shown that the presence of strong acceptor groups, at the α-position at phosphorus,

(6) Dave, T.; Berger, S.; Bilger, E.; Kaletsch, H.; Pebler, J.; Knecht, J.; Dimroth, K. *Organometallics* **1985**, *4*, 1565−1572.

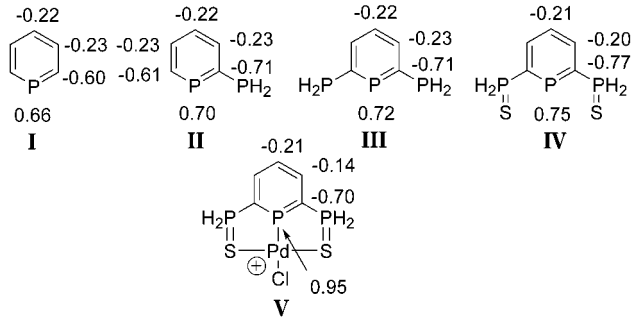
(7) Some complexes in which the phosphinine ring behaves as a bridging bidentate ligand between two metallic fragments were also characterized; see for example: (a) Schmid, B.; Venanzi, L.; Gerfin, T.; Gramlich, V.; Mathey, F. *Inorg. Chem.* **1992**, *31*, 5117−5122. (b) Reetz, M.; Bohres, E.; Goddard, R.; Holthausen, M. C.; Thiel, W. *Chem. Eur. J.* **1999**, *7*, 2101−2108.

(8) See for example: (a) Phillips J. R.; Poat J. C.; Slawin A. M. Z.; Williams D. J.; Wood P. T.; Woolins J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 2369−2375. (b) Forniés J.; Navarro R.; Sicilia V.; Thomas M. *Inorg. Chim. Acta* **1990**, *168*, 201−207.

(9) See for example: (a) Choua, S.; Sidorenkova, H.; Berclaz, T.; Geoffroy, M.; Rosa, P.; Mézailles, N.; Ricard, L.; Mathey, F.; Le Floch, P. *J. Am. Chem. Soc.* **2000**, *122*, 12227−12234. (b) Rosa, P.; Mézailles, N.; Ricard, L.; Mathey, Le Floch, P.; Jean, Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 1251−1253. (c) Rosa, P. Mézailles, N. Ricard, L.; Mathey, F. Le Floch, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 1823−1826

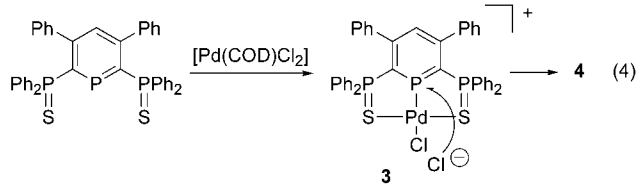
(10) (a) Schmid, B.; Venanzi, L.; Albinati, A.; Mathey, F. *Inorg. Chem.* **1991**, *30*, 4693−4699. (b) Carmichael, D.; Le Floch, P.; Mathey, F. *Phosphorus, Sulfur, Silicon* **1993**, *77*, 255.

Scheme 1



also activate the reactivity of the P=C system.[11] To estimate the importance of these two effects, a series of DFT calculations were carried out. As can be shown in Scheme 1, the introduction of phosphino groups at the C2 and C6 positions significantly enhances the positive charge (NBO charges) at phosphorus, which ranges from +0.66 in the parent compound **I** to +0.72 in the 2,6-bis(diphosphino)phosphinine **III**. Furthermore, this effect is slightly reinforced when the phosphino groups are replaced by the sulfide derivatives such as in **IV** (+0.75). As expected, coordination to the $[Pd-Cl]^+$ fragment is another important destabilizing factor which also enhances the polarization of the ring. Thus, in the theoretical structure [Pd(**IV**)Cl]$^+$ **V**, the NBO charge at phosphorus is very high (+0.95).

On the basis of these data, a tentative mechanism, which is depicted in eq 4, can be proposed to explain the formation of complex **4**. In a first step, coordination of ligand **2** leads to the formation of the transient cationic complex **3**, which undergoes a nucleophilic attack of the chloride counteranion at phosphorus to finally yield complex **4**. It must be noted that additional experiments aimed at converting complex **4** into the phosphinine complex **3** by abstraction of the chloride substituents were also attempted using $AgBF_4$ or $TlPF_6$ as chloride abstractor. Whatever the experimental conditions used (solvent, amount and nature of the salt), these experiments exclusively led to complicated mixtures of compounds that could not be identified.



In conclusion, we have established that the presence of π-accepting groups at the α-positions at phosphorus as well as coordination to a Pd(II) fragment strongly dearomatize the phosphinine nucleus, which becomes highly sensitive toward nucleophilic attacks. This method provides an easy entry to λ^4-1-R-*P* functional phosphinine complexes.

Experimental Section

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glovebox techniques and dry deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na/benzophenone, and dry CH_2Cl_2 and $CDCl_3$ from P_2O_5. Dry CD_2Cl_2 was distilled and stored, like $CDCl_3$, on 4 Å Linde molecular sieves. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P. Solvent peaks are used as internal reference relative to Me_4Si for ^{1}H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference, and coupling constants are expressed in hertz. The following abbreviations are used: b; broad, singlet; d, doublet; t, triplet; m, multiplet; p, pentuplet; sext, sextuplet; sept, septuplet; v, virtual. Mass spectra were obtained at 70 eV with a HP 5989B spectrometer coupled to a HP 5980 chromatograph by the direct inlet method. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. Phosphinine **1** was prepared according to a published procedure.[3c]

2,6-Bis(diphenylphosphine sulfide)-3,5-diphenylphosphinine (2). A solution of 2,6-bis(diphenylphosphino)-3,5-diphenylphosphinine (**1**) (4.00 g, 6.5 mmol) and elemental sulfur (0.415 g, 13 mmol) were heated in toluene for 12 h at 120 °C. The reaction mixture was cooled to room temperature and filtered, and the white solid collected on the frit was washed with toluene. After drying, sulfide **2** was recovered as a pale yellow powder. Yield: 4.23 g (96%). ^{31}P NMR ($CDCl_3$): δ 43.4 (AB_2, d, $^2J(P_A-P_B) = 115$, P_BPh_2), 253.1 (AB_2, t, P_A). ^{1}H NMR ($CDCl_3$): δ 6.94 (t, $^4J(H-P_B) = 3$, 1H, H4), 6.96−7.76 (m, 30H, CH of C_6H_5). ^{13}C NMR ($CDCl_3$): δ 127.1−131.6 (m, CH of C_6H_5), 132.5 (ABX, dd, $^1J(C-P_B) = 48.9$, $^3J(C-P_A) = 5.4$, C_{ipso} of PPh_2), 133.0−133.3 (m, CH of C_6H_5), 140.2 (t, $^3J(C-P_B) = 4$, C4), 140.6 (m, C3), 154.3 (d, $^3J(C-P_A) = 9$, C_{ipso} of C_6H_5), 159.7 (ABB′X, ddd, $^1J(C-P_A) = 85.3$, $^1J(C-P_B) = 66.2$, $^3J(C-P_{B'}) = 12.4$, C2). MS (CH_2Cl_2): *m*/*z* 683 $(M)^+$, 464 $(M - PPh_2S)^+$. Anal. Calcd for $C_{41}H_{31}P_3S_2$: C, 72.34; H, 4.59. Found: C, 72.08; H, 4.48.

Synthesis of Complex 4. In the glovebox, a mixture of [Pd(COD)Cl_2] (125 mg, 0.44 mmol) and 2,6-bis(diphenylphosphine sulfide)-3,5-diphenylphosphinine (**2**) (300 mg, 0.44 mmol) was stirred for 5 min in CH_2Cl_2 (5 mL). After the evaporation of the solvent, the yellow solid obtained was washed several times with hexanes (3 × 5 mL). After drying, complex **4** was recovered as a yellow powder. Yield: 370 mg (98%). ^{31}P NMR (CD_2Cl_2): δ 52.6 (AB_2, d, $^2J(P_A-P_B) = 115.3$, P_BPh_2) 94.9 (AB_2, t, P_A). ^{1}H NMR (CD_2Cl_2): δ 5.84 (AB_2X, dt, $^4J(H-P_B) = 4.8$, $^4J(H-P_A) = 3.3$, 1H, H4), 6.60−7.63 (m, 30H, CH of C_6H_5). ^{13}C NMR (CD_2Cl_2): δ 94.3 (ABB′X, ddd, $^1J(C-P_A) = 91.2$, $^1J(C-P_B) = 55.2$, $^3J(C-P_{B'}) = 7.6$, C2), 119.9 (AB_2X, dt, $^4J_{CA} = 18.2$, $^4J(C-P_B) = 9.1$, C4), 127.8−129.0 (m, CH of C_6H_5), 129.7 (ABX, dd, $^1J(C-P_B) = 86.1$, $^3J(C-P_A) = 10.2$, C_{ipso} of PPh_2), 130.5 (ABX, dd, $^1J(C-P_B) = 86.7$, $^3J(C-P_A) = 4.7$, C_{ipso} of PPh_2), 132.3−132.9 (m, CH of C_6H_5), 139.3 (ABB′X, dt, $^2J(C-P_A) = 8.0$, $^2J(C-P_B) = {}^4J(C-P_{B'}) = 3.0$, C3), 157.8 (d, $^3J(C-P_A) = 6.3$, C_{ipso} of C_6H_5). Complex **4** turns out to be too moisture sensitive to give satisfactory elemental data.

Synthesis of Complex 5. A solution of [Pd(COD)Cl_2] (125 mg, 0.44 mmol) and 2,6-bis(diphenylphosphine sulfide)-3,5-diphenylphosphinine **2** (300 mg, 0.44 mmol) was stirred for 5 min in CH_2Cl_2 (10 mL), and methanol (200 μL, 0.49 mmol) was added. After stirring for 10 min, the solvent was removed under vacuum, and the yellow powder obtained was washed several times with hexanes (3 × 5 mL). After drying, complex **5** was recovered as a yellow powder. Yield: 365 g (97%). ^{31}P NMR (CH_2Cl_2): δ 51.1 (AB_2, t, $^2J(P_A-P_B) = 102.3$, P_BPh_2), 97.3 (AB_2, t, P_A); ^{1}H NMR (CD_2Cl_2): δ 3.84 (d, $^3J(H-P_A) = 14.4$, CH_3O), 5.59 (AB_2X, dt, $^4J(H-P_B) = 8.9$, $^4J(H-P_A) = 4.7$, 1H, H4), 6.70−7.71 (m, 30H, CH of C_6H_5). ^{13}C NMR (CD_2Cl_2): δ 30.0 (s, CH_3), 93.5 (ABB′X, ddd, $^1J(C-P_A) = 91.3$, $^1J(C-P_B) = 67.2$, $^3J(C-P_{B'}) = 7.4$, C2), 115.6 (m, C4), 127.6−128.8 (m, CH of C_6H_5), 130.6 (ABX, dd, $^1J(C-P_B) = 84.8$, $^3J(C-P_A) = 7.5$, C_{ipso} of PPh_2), 131.6 (ABX, dd, $^1J(C-P_B) = 78.5$, $^3J(C-P_A) = 4.5$, C_{ipso} of PPh_2), 132.1−132.6 (m, CH of C_6H_5), 140.1 (ABB′X,

(11) Carmichael, D. Le Floch, P.; Mathey, F. *Organometallics* **1991**, *10*, 2432−2436.

dt, $^2J(C-P_A) = 8.2$, $^2J(C-P_B) = {}^4J(C-P_{B'}) = 3.2$, C3), 156.8 (d, $^3J(C-P_A) = 2.3$, C_{ipso} of C_6H_5). Anal. Calcd for $C_{42}H_{34}ClOP_3PdS_2$: C, 59.09; H, 4.01. Found: C, 58.85; H, 4.10.

Theoretical Methods. Geometry optimizations were carried out by means of a pure gradient-corrected exchange functional and the Lee−Yang−Parr nonlocal correlation functional BLYP as implemented in the Gaussian 98 program.[12,13] A 6-31G(d) basis set was used for H, C, P, and S atoms. The Hay−Wadt small core relativistic effective core-potential with a valence shell of double-ζ quality (441/2111/41) was used on Pd,[14] and the Stuttgart pseudopotential with a (31/31/1) basis set was used for Cl in calculations of complex **V**.[15] This type of basis set derives from the basis set II successfully used by Frenking and co-workers in many studies.[16] Vibrational frequencies of the stationary points were calculated at B3LYP with numerical second derivatives of the energy with respect to the coordinates. The structures calculated were located at minima on the potential-energy surface. The bonding situation of the optimized structures was analyzed using the natural bond orbital (NBO) method developed by Weinhold.[17]

X-ray Structural Determination. Single crystals of compound **4** suitable for X-ray crystallography were obtained by diffusing hexane into a dichloromethane solution of the compound. Data were collected on a Nonius Kappa CCD diffractometer using an Mo Kα ($\lambda = 0.71069$ Å) X-ray source and a graphite monochromator. Experimental details are described in Table 1. The crystal structures were solved using SIR 97[18] and SHELXL-97.[19] ORTEP drawings were made using ORTEP III for Windows.[20]

Table 1. Crystal Data and Structural Refinement Details for the Structure of Compound 4

emp formula	$C_{41}H_{31}Cl_2P_3PdS_2.CH_2Cl_2$
fw	942.91
temp, K	150.0(10)
wavelength, Å	0.71069
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	14.316(5)
b, Å	22.241(5)
c, Å	14.356(5)
β, deg	117.510(5)
V, Å^3	4054(2)
Z	4
D_{calcd}, g/cm^3	1.545
μ cm^{-1}	0.974
h,k,l ranges	−18, 18; −18, 26; −18, 18
cryst size, mm^3	0.20 × 0.20 × 0.20
cryst color and habit	orange cube
$2\theta_{max}$, deg	27.48
no. of reflns measd	16 947
no. of ind reflns	9282
no. of reflns used	7399
R1[a] [$I>2\sigma(I)$]	0.0369
wR2[b] [$I>2\sigma(I)$]	0.1025
GOF on F^2	1.056
largest diff peak, e Å^{-3}	1.290 (0.090)/−0.960 (0.090)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = (\sum w||F_o| - |Fc||^2/\sum w|F_o|^2)^{1/2}$.

Acknowledgment. The authors thank the CNRS and the Ecole Polytechnique for supporting this work.

Supporting Information Available: Listings of crystal data, atomic coordinates, including H atoms and equivalent isotropic displacement parameters, bond lengths, and bond angles. Listings of bond distances, bond angles, and NBO charges for calculated structures **I**−**V**. This material is available free of charge via the Internet at http://pubs.acs.org.

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