Palladium Phosphinothiolato Complexes. Syntheses and Crystal Structures of Mononuclear $[PdCl(SC_2H_4PPh_2)PPh_3]$ and Binuclear $[Pd_2Cl_2(\mu\text{-}SC_3H_6PPh_2)_2]$ and Their Performance in Catalytic Carbonylation

Nuria Brugat,[†] Alfonso Polo,*[,†] Ángel Álvarez-Larena,[‡] J. Francesc Piniella,[‡] and Julio Real*[,§]

Departament de Química, Universitat de Girona, Campus de Montilivi, 17071 Girona, Spain, Servei de Difracció de Raigs-X and Unitat de Cristal·lografia i Mineralogia, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain, and Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

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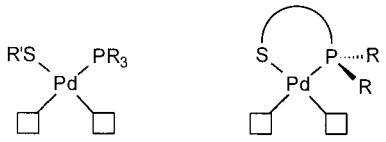
The phosphinothiolato complexes $[PdCl(dppet)PPh_3]$ (**3**), $[Pd(dppet)_2]$ (**4**), and $[Pd_2Cl_2(dpppt\text{-}P,\mu\text{-}S)_2]$ (**6**) (Hdppet = $HSC_2H_4PPh_2$; Hdpppt = $HSC_3H_6PPh_2$) have been synthesized in good yield by various base-free ligand exchange reactions on Pd(II), but $[Pd(dpppt)_2]$ (**5**) could only be obtained as a pure product employing an oxidative route from Pd(0). Both complexes **3** (^{31}P NMR, δ_P 66.8 (dppet), 24.1 (PPh_3); $^2J_{PP}$ = 459 Hz) and **5** (^{13}C NMR) are *trans*-P,P. Crystals of **3**·CH_2Cl_2 are orthorhombic ($P2_12_12_1$), with a = 9.247(3) Å, b = 17.956(9) Å, c = 19.869(9) Å. In **3** the Pd−S distance of 2.270(2) Å is short compared to the very different Pd−P distances of 2.280(2) (Pd−PPh_2R) and 2.343(2) Å (Pd−PPh_3). Crystals of **6**·CH_2Cl_2 are monoclinic ($P2_1/n$) with a = 12.701(3) Å, b = 12.040(4) Å, c = 22.495(2) Å, and β = 97.36(1)°. The structure of **6** consists of two Pd(dpppt)Cl moieties meeting at an angle of 105.81(3)°, linked by asymmetric thiolato bridges in a *syn-endo* configuration. The difference in the chelate angles of dppet (85.98(9)°) and dpppt (96.60(3)° and 97.42(3)°) seems to be crucial for palladium to form an unusual mononuclear complex (**3**) or a binuclear complex (**6**). Bischelate complexes **4** and **5** are inactive, but **3** and **6** catalyze the hydroesterification of styrene with CO (30 bar) and MeOH at moderate temperatures (60 and 80 °C) with no additives. The velocities are slow, but with **6** and with **3** at the lower temperature no decomposition to Pd metal is observed. Only esters are produced and regioselectivities of ca. 84% toward 2-phenylpropanoic acid methyl ester are achieved.

Introduction

The interest to introduce ligand atoms of a very different nature in the coordination sphere of a metal important in catalysis prompted our interest in the field of phosphinothiolato complexes. These chelate ligands place phosphorus and sulfur in a cis configuration, and this should imprint electronic asymmetry on the metal center to be transmitted to any trans groups. An important difference in bulk between coordinating atoms is also characteristic of this type of ligands. Asymmetry in size and electronic influence should be important to the stability of the key intermediates that control the stereochemistry of the products of interesting reactions that are thought to depend on two adjacent coordination sites, such as catalytic palladium mediated carbonylations. Furthermore, recent reports point to the particular nature of catalytic carbonylation systems that incorporate thiolato ligands. Aminothiolato complexes of palladium with triphenylphosphine catalyze the conversion of styrene to 2-phenylpropionic acid in high yield and excellent regioselectivity.[1,2] While these systems could only be acting with an *open* P,S-coordination, phosphinothiolato complexes could act with a *closed* P,S-coordination.



In the present study, our objective has been to develop high yield, convenient synthetic routes to hitherto unknown stable compounds containing palladium(II), the simple phosphinothiolato ligands from 2-(diphenylphosphino)ethanethiol ($HSCH_2CH_2PPh_2$, **1**, Hdppet) and 3-(diphenylphosphino)propanethiol ($HS(CH_2)_3PPh_2$, **2**, Hdpppt), and also triphenylphosphine in an effort to contain the tendency of thiolato ligands to form bridged species. Thus opening the possibility of the evaluation of structurally characterized complexes of palladium that incorporate thiolato sulfur and diarylphosphine phosphorus, tied in a cis geometry, as precursors for the palladium based catalytic carbonylation of olefins. Our specific interests at this point are centered in complexes of the type $[PdCl(S\text{-}E)(PPh_3)]$ with E = P, that is, with the chelating dppet and dpppt ligands. We have reported recently on the synthesis and structure of mononuclear complexes of this class with E = N: the aminothiolato-*S*,*N* complexes $[PdCl(S\text{-}N)(PPh_3)]$, where S-N are the ligands derived from cisteamine, cysteine ethyl ester, and penicillamine methyl ester.[1] To our knowledge, phosphinothiolato complexes of palladium have never been tested in any carbonylation

* Author to whom correspondence should be addressed. E-mail: real@cc.uab.es.

[†] Departament de Química, Universitat de Girona.

[‡] Servei de Difracció de Raigs-X and Unitat de Cristal·lografia i Mineralogia, Universitat Autònoma de Barcelona.

[§] Departament de Química, Universitat Autònoma de Barcelona.

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reaction, and catalysis reports on open P,S-coordinated thiolato phosphine palladium systems are rare.[3] Phosphinothiolato complexes of rhodium have been used as precursors in the catalytic carbonylation of methanol to acetic acid, in conditions that transform the thiolato group into a thioether.[4−6]

Compared to other functionalized phosphines and considering that group 10 metal complexes of these ligands were among the first to be prepared,[7−11] the chemistry of the simple phosphinothiolato complexes of the heavier elements of this group remains a slow growth area. In this line, a search of the CSD crystallographic records[12] revealed that most structures of group 10 phosphinothiolato ligand complexes contain nickel,[13−24] some have been reported with palladium,[25−29] and only the heterobinuclear polymeric $[AgPt(\mu\text{-}SC_2H_4PEt_2)_2]NO_3$ catena complex is known with platinum.[30] No crystal structures of compounds of palladium incorporating dppet or dpppt were found. In phosphinothiolato complexes, the phosphorus side is bulkier, so that, trans complexes are expected for the square planar coordination of d^8 ions. Complexes of palladium and platinum with the ligand *o*-(diphenylphosphino)benzenethiolato, such as *trans*-$[Pd(SC_6H_4PPh_2)_2]$ and $[Pd_2I_2(SC_6H_4PPh_2\text{-}P,\mu\text{-}S)_2]$, have been obtained by Roundhill et al. from the corresponding thioether complexes.[25−27] Diphenyl(phenyl-2-thiol)phosphine (*o*-$HSC_6H_4PPh_2$), synthesized by Zubieta et al.[36−40] as a free ligand, is a triarylphosphine while Hdppet and Hdpppt are alkyldiarylphosphines, and in this sense it is a rather different ligand that will not be dealt with in this work. In a series of studies on the resolution of ligands with chirality at phosphorus involving metal complexation, a series of group 10 metal complexes with 2-(methylphenylphosphino)ethanethiol have been reported, including the palladium bischelate $Pd(SC_2H_4PMePh)_2$.[41−44] Palladium complexes with a ferrocenyl phosphinothiolato ligand[28] and with a phosphacyclic thiolato ligand[29] have been recently described (vide infra).

The crystal structures of *trans*-$[Ni(S\text{-}P)_2]$ (with S-P = dppet,[17] 2-(dimethylphosphino)ethanethiolato,[18] and diphenyl(phenyl-2-thiolato)phosphine[15,16]) are known, as is that of *cis*-$[Ni(\mu\text{-}dppet)_2Mo(CO)_4]$,[17] showing the possibility of cis coordination of the large $-PPh_2$ groups on nickel. Also with Ni(II), other stable species of different nuclearity and metal:ligand ratio are known. In the reaction of *trans*-$[Ni(dppet)_2]$ with nickel perchlorate,[45] ligands and metal ions reorganize into the thiolato bridged binuclear cation $[Ni_2(dppet)_3]^+$, and do not form a trinuclear cation akin to the aminothiolato $[Ni_3(SCH_2CH_2NH_2)_4]^{2+}$, reported by Wei and Dahl in 1970.[46] Curiously, the anion bis(ethane-1,2-dithiolato)palladate $[Pd(edt)_2]^{2-}$ [47] follows the pattern of neutral $[Ni(dppet)_2]$, evolving into anionic $[Pd_2(edt)_3]^{2-}$, while dpppt with nickel(II) follows the pattern of cisteamine in the aforementioned trinuclear complex, to give the $[Ni_3(dpppt)_4]^{2+}$ cation,[23] forming neither 2:3 monocationic binuclear nor 1:1 neutral binuclear compounds such as $[Ni_2X_2(dppet\text{-}P,\mu\text{-}S)_2]$ (X = Cl, Br).[13,14]

Palladium complexes with dppet and dpppt are not expected to exhibit the behavior of those of nickel, but the precedence of structural diversity in the group make it difficult to predict the precise nature of dppet and dpppt palladium species of 1:1 stoichiometry.

Experimental Section

General Considerations. Reactions were performed under nitrogen using standard techniques, but the isolated products are air stable. Solvents were dried, distilled under nitrogen, kept over molecular sieves, and deaerated prior to use. Tetrakis(triphenylphosphine)palladium(0),[48−50] $[PdCl_2(PPh_3)_2]$,[51,52] and $[PdCl_2(PhCN)_2]$ [53,54] were prepared by estab-

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lished procedures. The syntheses of Hdppet[7,10] and Hdpppt[8,55] have been described. NMR spectra were obtained in a Bruker DPX-200 operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C and 80.01 MHz for ^{31}P; at room temperature (298 K) and using $CDCl_3$ solvent, except where noted. NMR data are given in the δ scale and are referred to TMS for ^{1}H and ^{13}C and to external H_3PO_4 (85%) for ^{31}P. IR spectra were recorded in KBr or mineral oil and data are in wavenumber units (cm^{-1}). Catalysis experiments were performed in a stainless steel, custom-built pressure reactor (ca. 75 mL) of a standard vase and cover design, fitted with glass and fluorocarbon linings to avoid contact of the reacting solutions with the SS-316 steel reactor body. GC analysis was performed with Shimatzu GC-17A (TRB-2 capillary column, 0.25 mm diameter × 30 m) and twin HP G1800A (HP-5 capillary columns, 0.25 mm diameter × 30 m) chromatographs, with FID and with MS detectors.

Preparation of [Pd(dppet)$_2$] (4), Bis[(2-diphenylphosphino)-ethanethiolato-*P,S*)palladium(II). Method A. The palladium(0) complex $Pd(PPh_3)_4$ (290 mg, 0.25 mmol) is dissolved in dichloromethane (ca. 10 mL) to give a clear yellow solution. Upon slow addition of Hdppet (2-diphenylphosphinoethanethiol, 154 mg, 0.5 mmol, neat) to the stirred solution, its color turns darker to yellow-orange. The formation of solid product **4** is observed a few minutes later. The evolution of hydrogen cannot be clearly observed owing to the stirring, but if the stirring is stopped, some frothing is apparent. The mixture is allowed to react for 30 min, the solvent is evaporated in vacuo down to 5 mL, and hexane (3−5 mL) is slowly added to complete the crystallization. The pale orange product is separated by filtration and washed with MeOH and Et_2O. Yield: 113 mg (75%) of pale orange microcrystalline **4**.

Method B. The palladium(II) complex $[PdCl_2(PhCN)_2]$ (80 mg, 0.21 mmol) is dissolved in 8 mL of dichloromethane, and Hdppet (103 mg, 0.42 mmol, neat) is added with stirring. After some time, a yellow precipitate starts to form. The mixture is allowed to react at room temperature for 30 min. A small amount of hexane (1 mL) is added, and the solid product is collected by filtration, washed with MeOH and Et_2O, and vacuum-dried. Yield: 108 mg (85%), yellow powder.

Method C. The palladium (II) complex **3** (50 mg, 0.077 mmol) is dissolved in dichloromethane (5 mL) to give an orange solution, and Hdppet (20 mg, 0.077 mmol) is added with stirring. The color of the solution turns lighter, and a yellow precipitate is formed within minutes. The product is isolated by filtration, washed with MeOH and Et_2O, and vacuum-dried. Yield: 35 mg (75%), yellow powder. Complex **4** is stable in air, only sparingly soluble in dichloromethane and chloroform, and insoluble in methanol, ether, and hexane. Data for **4**: elem. anal. for $C_{28}H_{28}P_2PdS_2$, found (calcd), C, 56.0 (56.3); H, 4.8 (4.7); S, 11.2 (10.7). ^{1}H NMR: δ 2.65 (m, 2H); 2.78 (m, 2H); 7−8 (m, 10H). ^{31}P{^{1}H} NMR: δ 63.6 (s, PPh_2R). IR (KBr): 3044, 2938, 2910, 2835, 1433, 1103, 751, 695. These data are consistent with that reported by Fujita et al.[18] The low solubility of **4** precluded the observation of a good-quality ^{13}C NMR from which the C−P coupling constants could be extracted.

Preparation of [Pd(dpppt)$_2$] (5), Bis[(3-diphenylphosphino)-propanethiolato-*P,S*)palladium(II). The palladium(0) complex $Pd(PPh_3)_4$ (555 mg, 0.48 mmol) is dissolved in dichloromethane (20 mL) to give a clear yellow solution, and Hdpppt (2-diphenylphosphinopropanethiol 260 mg, 1.0 mmol, neat) is added to the stirred solution, which turns to a darker yellow-orange in color. The reaction is allowed to take place for 30 min. During this period the color lightens again and the formation of a yellow solid is observed. The solution is concentrated to ca. 10 mL in vacuo and a few drops of Et_2O are added. The yellow solid product formed is filtered, washed with hexane (3 times with 4 mL), and dried in vacuo. Yield: 210 mg (70%) of a yellow microcrystalline solid. Complex **5** is stable in air, soluble in dichloromethane and chloroform, and insoluble in hexane. Data for **5**: elem. anal. for $C_{30}H_{32}P_2PdS_2$, found (calcd), C, 57.8 (57.7); H, 5.2 (5.2); S, 10.0 (10.3). NMR data for **5**: ^{1}H NMR: δ 2.38 (2H, br m, CH_2P); 2.16 (2H, br m, C−CH_2−C); 2.52 (2H, br m, CH_2S); 7.0−8.0 (10 H, PPh_2R). ^{13}C{^{1}H} NMR: δ 24.4 (t, *C*H_2P, J_{PC} = 14.7 Hz); 26.9 (t, C-*C*H_2-C, J_{PC} = 6.2 Hz); 28.0 (s, *C*H_2S); 131.4 (t, C_{ipso}, PPh_2R, J_{PC} = 23.6 Hz); 133.6 (t, C_o, PPh_2R, J_{PC} = 6 Hz); 128.1 (t, C_m, PPh_2R, J_{PC} = 5 Hz); 130.1 (s, C_p, PPh_2R). ^{31}P{^{1}H} NMR: δ 10.94 (s, PPh_2R). IR (KBr): 3039, 2893, 2837, 1434, 1097, 748, 694.

Preparation of [PdCl(dppet)(PPh$_3$)] (3), Chloro[(2-diphenylphosphino)ethanethiolato-*P,S*]triphenylphosphinepalladium(II). Method A. The complex $[PdCl_2(PPh_3)_2]$ (200 mg, 0.285 mmol) is dissolved in dichloromethane (15 mL), and Hdppet (74 mg, 0.3 mmol) is slowly added with stirring. The color of the solution turns from yellow to orange during the addition. It is allowed to react for 1 h, and then the volume of the solution is reduced to about 3 mL. Hexane (5 mL) is added, and the resulting solution is allowed to rest at −24 °C for 12 h. The orange crystalline product is collected by filtration, washed with hexane, and dried under vacuum. Yield: 140 mg (76%) of orange crystals.

Method B. The complex $[PdCl_2(PPh_3)_2]$ (165 mg, 0.23 mmol) is mixed with complex **4** (140 mg, 0.23 mmol) in toluene (20 mL). The solution is stirred at reflux temperature (ca. 110 °C) for 24 h. On cooling, complex **3** crystallizes as an orange solid. The product is collected by filtration, washed with hexane and Et_2O, and vacuum-dried. Yield: 122 mg (65%). Complex **3** is soluble in dichloromethane and chloroform, sparingly soluble in toluene, and insoluble in hexane and ether. Data for **3**: elem. anal. for $C_{32}H_{29}ClP_2PdS$, found (calcd), C, 59.0 (59.2); H, 4.6 (4.5); S, 4.5 (4.9). NMR data for **3**: ^{1}H NMR (and ^{1}H{^{31}P}; CD_2Cl_2): δ 2.42 (2H, dt, CH_2P, J_{PH} = 37.4 Hz, J_{HH} = 6.6 Hz); 2.78 (2H, dt, CH_2S, J_{PH} = 8.5 Hz, J_{HH} = 6.6 Hz); 7.0−8.0 (25 H, PPh_2R, PPh_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 26.6 (t, *C*H_2P, J_{PC} = 8.4 Hz); 39.8 (d, *C*H_2S, J_{PC} = 34.0 Hz); 125.0−135.0 (PPh_2R, PPh_3). ^{31}P{^{1}H} NMR: δ 24.1 (d, PPh_3 *trans*-P,P isomer, J_{PP} = 458.7 Hz); 66.8 (d, PPh_2R *trans*-P,P isomer, J_{PP} = 458.7 Hz); ^{31}P{^{1}H} NMR data for the *cis*-P,P isomer of **3** (taken from aged solutions of **3**, in which the *cis*-P,P is a minor component formed in solution by isomerization): δ 23.2 (d, PPh_3 cis isomer, J_{PP} = 18.8 Hz); 74.8 (d, PPh_2R cis isomer, J_{PP} = 18.8 Hz). The ratio [*trans*-P,P]/[*cis*-P,P] ≈ 95/5 in aged solutions of **3** was obtained from the integrals of the respective signals in a ^{31}P-gated {^{1}H} NMR spectrum recorded with a long relaxation delay.

Preparation of [Pd$_2$Cl$_2$(dpppt)$_2$] (6), Dichlorobis{μ-[(3-diphenylphosphino)propanethiolato]-*P,*μ-*S*}dipalladium(II). Method A. The complex $[PdCl_2(PPh_3)_2]$ (200 mg, 0.29 mmol) is disolved in dichloromethane (15 mL) and Hdpppt (75 mg, 0.29 mmol) is slowly added with stirring, resulting in a yellow solution that turns to orange in color upon the addition of the phosphinothiol. It is allowed to react for 30 min, and the solvent is removed by vacuum, leaving a final volume of about 3 mL. Hexane (5 mL) is added, and the solution is allowed to crystallize at −24 °C for 12 h. The crystalline orange product is collected by filtration, washed with hexane, and dried. Yield: 110 mg (92%) of orange crystalline **6**.

Method B. The complex $[PdCl_2(PPh_3)_2]$ (200 mg, 0.28 mmol) is mixed and allowed to react with complex **5** (180 mg, 0.28 mmol), dissolved in toluene (20 mL). The solution is stirred at reflux temperature (ca. 110 °C) for 24 h. Cooling causes the crystallization of complex **6**. The solid product is collected by filtration, washed with hexane and Et_2O, and vacuum-dried. Yield: 225 mg (85%). Complex **6** is soluble in dichloromethane and insoluble in hexane and ether. Data for **6**: elem. anal. for $C_{30}H_{32}Cl_2P_2Pd_2S_2$, found (calcd), C, 44.5 (44.9); H, 3.9 (4.0); S, 7.6 (8.0). ^{1}H NMR (CD_2Cl_2): δ 2.17 (1H, br m, CH_2P); 2.25 (3H, br m, CH_2-CH_2P); 2.53 (1H, br m, CH_2S); 2.98 (1H, br m, CH_2S), 7.0−8.0 (10 H, PPh_2R). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 24.3 (d, *C*H_2P, J_{PC} = 29.5 Hz); 26.4 (s, C-*C*H_2-C); 27.92 (s, *C*H_2S); 125.0−135.0 (PPh_2R). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 11.02 (s, PPh_2R). IR (KBr): 3050, 2913, 2850, 1434, 1102, 691.

Catalysis Experiments. Complexes **3**, **4**, **5**, and **6** were tested as catalyst precursors in the catalytic hydroesterification of styrene using the following common procedure. In a sidearm flask 1,2-dichloroethane (15 mL), methanol (15 mL), styrene (0.416 g, 4.0 mmol), and the

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Table 1. Crystallographic Data for **3**·CH_2Cl_2 and **6**·CH_2Cl_2

	3·CH_2Cl_2	**6**·CH_2Cl_2
empirical formula	$C_{33}H_{31}Cl_3P_2PdS$	$C_{31}H_{34}Cl_4P_2Pd_2S_2$
fw	734.33	887.24
T, °C	20(2)	20(2)
λ, Å	0.71069	0.71069
space group	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)
a, Å	9.247(3)	12.701(3)
b, Å	17.956(9)	12.040(4)
c, Å	19.869(9)	22.495(2)
β, deg		97.36(1)
V, Å^3	3299(3)	3412(2)
Z	4	4
ρ_{calc}, g cm^{-3}	1.478	1.727
μ, cm^{-1}	9.88	16.06
$R(F_o)$ [$I > 2\sigma(I)$][a]	0.0435	0.0274
$R_w(F_o^2)$ (all data)[b]	0.1023	0.0743

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

Table 2. Selected Distances [Å] and Angles [deg] for **3**·CH_2Cl_2 and **6**·CH_2Cl_2

	3·CH_2Cl_2		
Pd−S	2.270(2)	S−C(1)	1.829(9)
Pd−Cl	2.364(2)	C(1)−C(2)	1.522(11)
Pd−P(1)	2.288(2)	C(2)−P(1)	1.822(8)
Pd−P(2)	2.343(2)		
S−Pd−P(1)	85.98(9)	C(1)−C(2)−P(1)	106.4(5)
S−Pd−P(2)	89.34(9)	C(2)−P(1)−Pd	107.0(3)
S−Pd−Cl	178.32(9)	C(21)−P(1)−C(2)	106.9(3)
P(1)−Pd−P(2)	174.51(8)	C(21)−P(1)−C(11)	107.1(3)
P(1)−Pd−Cl	93.77(9)	C(2)−P(1)−C(11)	105.9(4)
P(2)−Pd−Cl	90.82(9)	C(21)−P(1)−Pd	119.3(2)
C(1)−S−Pd	106.2(3)	C(11)−P(1)−Pd	109.8(2)
C(2)−C(1)−S	111.8(6)		
	6·CH_2Cl_2		
Pd(1)···Pd(2)	2.9726(7)	S(1)−C(11)	1.810(4)
Pd(1)−S(1)	2.296(1)	C(11)−C(12)	1.478(6)
Pd(1)−S(2)	2.381(1)	C(12)−C(13)	1.542(5)
Pd(1)−Cl(1)	2.336(1)	C(13)−P(1)	1.816(4)
Pd(1)−P(1)	2.258(1)	S(2)−C(41)	1.817(4)
Pd(2)−S(2)	2.286(1)	C(41)−C(42)	1.499(6)
Pd(2)−S(1)	2.382(1)	C(42)−C(43)	1.533(5)
Pd(2)−Cl(2)	2.326(1)	C(43)−P(2)	1.816(4)
Pd(2)−P(2)	2.246(1)		
S(1)−Pd(1)−P(1)	96.60(3)	Pd(2)−S(2)−Pd(1)	79.09(3)
P(1)−Pd(1)−Cl(1)	92.41(4)	C(11)−S(1)−Pd(1)	118.8(1)
S(1)−Pd(1)−Cl(1)	170.19(3)	C(11)−S(1)−Pd(2)	113.3(2)
P(1)−Pd(1)−S(2)	171.20(3)	C(12)−C(11)−S(1)	117.5(3)
S(1)−Pd(1)−S(2)	75.70(3)	C(11)−C(12)−C(13)	114.1(3)
Cl(1)−Pd(1)−S(2)	95.59(4)	C(12)−C(13)−P(1)	111.9(3)
S(2)−Pd(2)−P(2)	97.42(3)	C(13)−P(1)−Pd(1)	112.8(1)
P(2)−Pd(2)−Cl(2)	89.75(4)	C(41)−S(2)−Pd(2)	117.5(1)
S(2)−Pd(2)−Cl(2)	172.80(4)	C(41)−S(2)−Pd(1)	112.6(1)
P(2)−Pd(2)−S(1)	171.50(3)	C(42)−C(41)−S(2)	117.9(3)
S(2)−Pd(2)−S(1)	75.87(3)	C(41)−C(42)−C(43)	114.1(4)
Cl(2)−Pd(2)−S(1)	96.93(4)	C(42)−C(43)−P(2)	111.7(3)
Pd(1)−S(1)−Pd(2)	78.88(3)	C(43)−P(2)−Pd(2)	114.4(1)

apropriate palladium phosphinothioato complex (0.04 mmol) were mixed under nitrogen. The solution was charged in a previously evacuated pressure reactor (described above). Temperature and pressure were adjusted to the values in Table 4, and the solution was magnetically stirred for a period of time. The reactor was then cooled to room temperature and the reaction mixture was analyzed (GC−MS and ^{1}H NMR). Only in the case of **3** at 80 °C palladium metal formation was observed.

X-ray Studies. Single crystals of **3** and **6** suitable for X-ray diffraction study were grown by slow diffusion of hexane into dichloromethane solutions of the complexes. This method resulted in the formation of solvent containing **3**·CH_2Cl_2 and **6**·CH_2Cl_2. Single-crystal data were collected on an Enraf-Nonius CAD4 diffractometer at room temperature, using graphite monochromatized Mo Kα radiation and the $\omega/2\theta$ scan mode. Cell parameters were determined by least-squares refinement on diffractometer parameters for 25 automatically centered reflections. Lp and empirical absorption corrections[56] were applied. The structures were solved by direct methods using SHELXS-86 program[57] and refined on F^2 for all reflections using the SHELXL-97 program.[58] The non-hydrogen atoms of the complexes were refined with anisotropic displacement parameters. Hydrogen atoms were placed at their calculated positions with isotropic temperature factors equal to 1.2 times the U_{eq} values of the corresponding carbons. Benzenic rings were refined as rigid bodies. In both structures the somewhat disordered CH_2Cl_2 crystallization solvent molecules could be well modeled using three sets of refined neighboring coordinates, with the appropriate site occupancy and isotropic temperature factors. The weighting scheme for **3**·CH_2Cl_2 was $w = 1/[\sigma^2(F_o^2) + (0.0616P)^2]$, and that for **6**·$CH_2Cl_2$ was $w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 5.0267P]$; in both cases $P = [\max(F_o^2,0) + 2F_c^2]/3$. Crystallographic data and structure refinement parameters are presented in Table 1, and selected distances and angles in Table 2.

Results and Discussion

The simplest palladium(II) species that incorporate the phosphinothiolato ligands dppet and dpppt are the homoleptic bischelates [Pd(dppet)$_2$] (**4**) and [Pd(dpppt)$_2$] (**5**). Complex **5** has not been reported, but complex **4** has been prepared in low yield (27%) from the reaction of Li_2PdCl_4 and Hdppet in the presence of NaOMe as a base;[18] and also complex [Pd(SC$_6$H$_4$-PPh$_2$)$_2$] has been obtained using NEt$_3$.[38] Although the addition of a base has been found strictly necessary for the synthesis of platinum thiolates[59] and even chelating dithiolates,[60,61] it may not be the best procedure in the case of the chelating phosphinothiolates, and in general it has objective drawbacks: the salt formed can complicate the isolation of the product; and also the presence of base throughout the synthesis favors the oxidation of both the phosphorus and the sulfur parts of the ligands. These potential problems, together with the low yield of **4** with this method, prompted us to explore alternative reactions for the good yield syntheses of both **4** and **5**.

The direct, base-free reaction of [PdCl$_2$(PhCN)$_2$] with 2 equiv of Hdppet in dichloromethane cleanly afforded bischelate **4**, which was isolated in 85% yield (Scheme 1). The HCl formed caused no problems, and the leaving PhCN ligand was simply washed away with hexane. But this method failed to give bischelate **5** cleanly and in the same good yield. Apparently, there is some halide retention on palladium and the final product is not pure. So that, the study of this reaction was discontinued for the Hdpppt ligand.

In a related line of work, we have recently reported that the S−H bonds of cysteine derivatives oxidatively add to Pt(0) to afford stable hydrido cysteinato complexes of platinum(II): [PtH(SCH$_2$CH(CO$_2$Et)NH$_2$-*N*,*S*)PPh$_3$].[62] In the case of palladium, we have shown that the chloro aminothiolato complexes [PdCl(S-N)(PPh$_3$)] (S-N = S(CH$_2$)$_2$NH$_2$, SCH$_2$CH(CO$_2$Et)NH$_2$, SCMe$_2$CH(CO$_2$Me)NH$_2$) are obtained by the reaction of Pd(PPh$_3$)$_4$ with the hydrochlorides of these aminothiolato ligands,

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Table 3. Data for Selected Structurally Characterized Palladium Complexes with Phosphine Phosphorus and Thiolato Sulfur Donors Relevant to *trans* Influence Effects[a]

entry no.	complex	*d*(M−S) [Å]	*d*(M−P) [Å]	chelate angle [deg]	ref
1	*cis*-P,S-[PdCl(dppet)(PPh_3)] (**3**)	2.270(2)-*t*-Cl	2.288(2)-*t*-P 2.343(2)-*t*-P	85.98(9)	this work
2	*cis*-P,S-[PdCl(cysEt-*N*,*S*)(PPh_3)]	2.253(2)-*t*-Cl	2.254(2)-*t*-N	85.7(1)	1
3	[Pd_2Cl_2(μ-dpppt)$_2$] (**6**)	2.296(1), 2.286(1)-*t*-Cl 2.381(1), 2.382(1)-*t*-P	2.258(1), 2.246(1)-*t*-S	96.60(3), 97.42(3)	this work
4	*trans*-[Pd(*o*-$Ph_2PC_6H_4S)_2$]	2.308(2)-*t*-S	2.291(1)-*t*-P	86.6(1)	25
5	[Pd_2(*o*-$Ph_2PC_6H_4S$-μ-*S*,*P*)$_2I_2$]	2.284(4), 2.308(4)-*t*-I 3.399(4), 2.372(4)-*t*-P	2.224(4), 2.237(4)-*t*-S	87.9(1), 88.3(1)	27
	second molecule	2.294(4), 2.312(4)-*t*-I 2.414(4), 2.407(4)-*t*-P	2.232(4), 2.240(4)-*t*-S	86.8(1), 87.4(1)	
6	[Pd_2Cl_2(μ-SPFc)$_2$][b]	2.269(2), 2.280(2)-*t*-Cl 2.345(2), 2.369(2)-*t*-P	2.267(2), 2.280(2)-*t*-S	96.35(7), 94.27(7)	28
7	[Pd_2(μ-SPFc)$_2$(CN*t*Bu)$_2$]$^{2+}$ [b]	2.296(4), 2.300(4)-*t*-P 2.373(4), 2.360(4)-*t*-C	2.299(4), 2.285(4)-*t*-S	94.7(1), 93.9(1)	28
8	[Pd_2(μ-$SC_8H_{11}PPh$)$_2$($AsPh_3$)$_2$]$^{2+}$ [c]	2.344(4)-*t*-As 2.374(4), 2.359(4)-*t*-P	2.266(4)-*t*-S	83.1(2), 83.5(2)	29
9	[Pd(S-As)$_2$][d]	2.325(3)-*t*-As	2.373(1)[d]-*t*-S	86.58(7)[d]	74
10	[Pd_2(SC_2H_4S-μ-*S*,*S*′)$_2$(PPh_3)$_2$]				67
	terminal Pd−S	2.292(4), 2.300(6)-*t*-S	2.281(5), 2.281(5)-*t*-S	88.6(2), 88.7(2)	
	Pd−μ-S	2.362(4), 2.372(5)-*t*-S			
	Pd−μ-S	2.327(5), 2.342(6)-*t*-P			
11	[Pd(SC_3H_6S)(dppp)]	2.316(2), 2.335(1)-*t*-P	2.292(1), 2.305(1)-*t*-S	94.0(1)(S) 91.9(1)(P)	75
12	[Pd(SC_4H_8S)(dppp)]	2.322(1), 2.354(1)-*t*-P	2.269(1), 2.276(1)-*t*-S	95.62(4)(S) 94.56(3)(P)	61
13	[Pd(SC_5H_9NMe)$_2$(dppe)]	2.348(1), 2.367(1)-*t*-P	2.284(1), 2.254(1)-*t*-S	−	76
14	[Pd(SCH_2Ph)$_2$(dppe)]	2.360(2)-*t*-P	2.277(2)-*t*-S	85.6(1)(P)	77
15	[Pd(SMe)(S_2CNMe_2-*S*,*S*′)(PEt_3)]	2.299(2)-*t*-S	2.264(1)-*t*-S	−	78
16	[Pd(SCH_2CH_2S)$_2$]$^{2-}$	2.312(3), 2.323(3)-*t*-S	−	89.0(2), 91.2(2)	47

[a] Chemically equivalent distances or angles in the same line, as reported in the corresponding reference. Distance values are followed by the symbol of the atom in trans. Chelate angle values are followed by the symbol of the donor atoms when necessary. [b] SPFc has been used for ligand (*R*)-1-(*S*)-(diphenylphosphino)ferrocenylethylthiolato-*P*,*S*; these are Pd_2Fe_2 tetranuclear complexes. [c] Ligand (1α,4α,5α,7*S*)-2,3-dimethyl-7-phenyl-5-thiolato-7-phosphabicyclo[2.2.1]hept-2-ene-*S*,^{5}*P*^{7}. [d] Arsenic instead of phosphorus in the ligand {$SC_2H_4AsMe(C_6H_4$-2-$CH_2OMe)$}, a *trans*-S,S complex.

Table 4. Phosphinothiolato Complexes of Palladium as Catalyst Precursors in the Hydroesterification of Styrene with CO and MeOH To Give 2-Phenylpropionic Acid Methyl Ester (2-PP-Me) and 3-Phenylpropionic Acid Methyl Ester[a]

entry no.	precursor complex	temp (°C)	time (h)	conversion (% esters)[b]	TOF (1/h)[c]	selectivity in 2-PP-Me (%)
1	[Pd(dppet)$_2$] (**4**)	80	24	0.3	−	−
2	[Pd(dpppt)$_2$] (**5**)	80	24	0.0	−	−
3	[Pd_2Cl_2(μ-dpppt)$_2$] (**6**)	80	24	7	0.3	84
4	[PdCl(dppet)(PPh_3)] (**3**)	60	72	29	0.4	84
5	**3**[d]	80	24	24	1.0	73
6	**3**[d]	80	48	47	1.0	67
7	**3**[d]	80	72	63	0.9	67

[a] Conditions: 4 mmol styrene in 15 mL of MeOH plus 15 mL of 1,2-dichloromethane; [styrene]/[Pd complex] = 100; P_{CO} = 30 bar. No cocatalysts or oxygen present. [b] Total conversion from styrene to esters (%); number values also correspond to turnover number (TON) taken as moles of esters produced over moles of complex precursor. [c] Equal to TON over time in hours, an average value. [d] Only in the case of **3** at 80 °C was Pd black observed at the end of the reaction.

presumably by the formation of a Pd−H intermediate and its subsequent reaction with the hydrochloric acid liberated upon *S*,*N*-ligand complexation.[1] Using this synthetic approach, and although the S−H bond is of course less acidic than the Cl−H bond, we have found that the reaction of $Pd(PPh_3)_4$ with two equivalents of the appropriate phosphinothiol, Hdppet or Hdpppt, gave the corresponding bischelates [Pd(dppet)$_2$] (**4**) and [Pd(dpppt)$_2$] (**5**) in good yields (Scheme 1), avoiding altogether the presence of halides or bases.

In this oxidative ligand substitution reaction, the acidic hydrogen of the ligand is removed by reduction. There is oxidation of the metal from Pd(0) to Pd(II) and displacement of all four triphenylphosphine ligands by two phosphinothiolates. We are proposing that a hydrido phosphinothiolato complex, the product of a chelate-assisted oxidative addition of the S−H bond to palladium(0), is formed as an intermediate species **A** (Scheme 2). A second molecule of phosphinothiol acting as an acid, reacts with this palladium hydride intermediate **A** to form hydrogen, and to finally displace all triphenylphosphine ligands from the metal. Oxidative synthetic routes are not very common but have been used with advantage for the synthesis of silyl[63] and stannyl[64] phosphino complexes, the first −SH hydrido complexes of platinum,[65] and an exemplary series of thiolato and dithiolato complexes including [PtH(SCH_2CH_2SMe)PPh_3] and dinuclear [Pd_2(μ-SC_2H_4S-*S*,*S*′)$_2$(PPh_3)$_2$], prepared by Rauchfuss and Roundhill in 1975.[66] The same palladium dithiolate was later obtained using a more conventional method, with the purpose of determining its crystal structure.[67]

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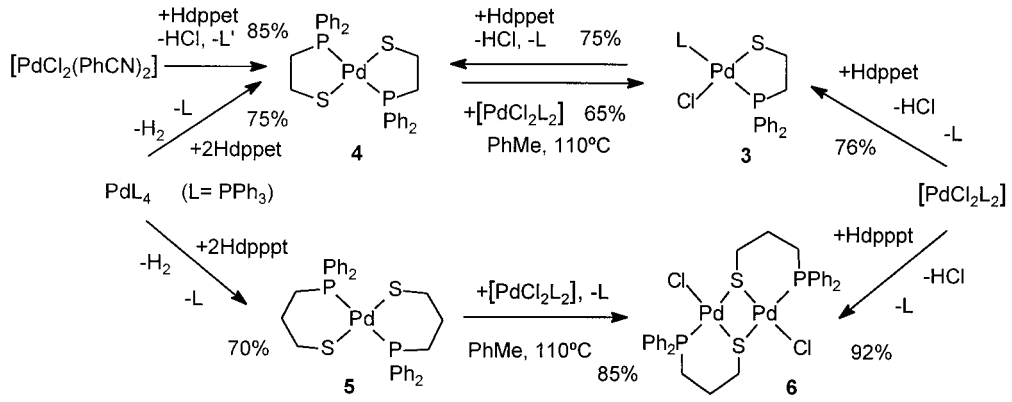
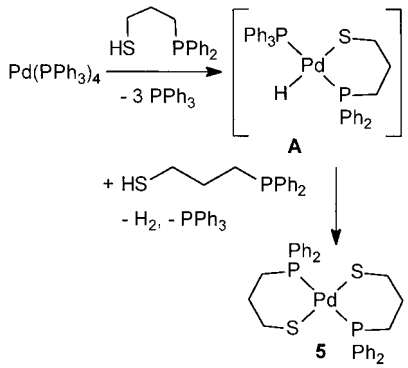
Scheme 1. Useful Synthetic Transformations of Palladium Complexes with the Ligands Hdppet and Hdpppt



Scheme 2. Proposed Chelate Assisted Oxidative Addition of a Phosphinothiol to Pd(0), Illustrated Here for Hdpppt



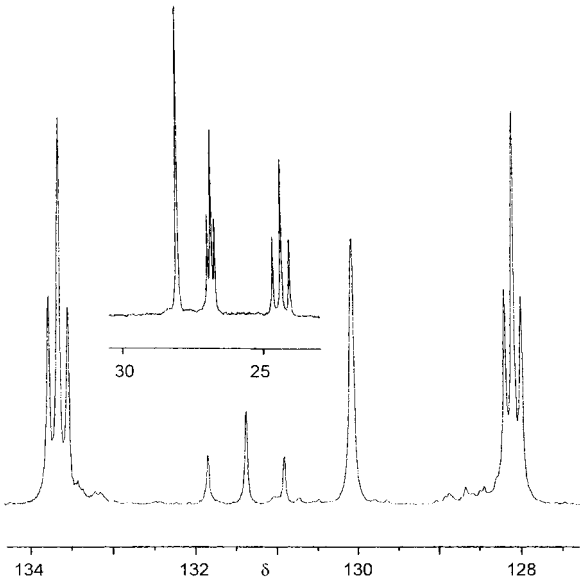
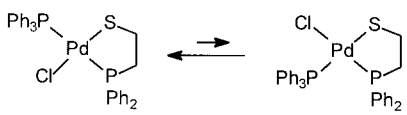


Figure 1. $^{13}C\{^1H\}$ NMR of **5**, the trans geometry of **5** is evidenced by the observation of virtual coupling to ^{31}P in the signals of all but two of the carbons of dpppt.

The *trans*-P,P configuration of the new bischelate **5** can be deduced from the presence of virtual C−P coupling, as observed in the $^{13}C\{^1H\}$ NMR spectrum of this soluble complex shown in Figure 1. The signals for the carbons of the chelate rings in **5**, corresponding to the α- and *β*-phosphorus positions as well as the *ipso*, *ortho*, and *meta* carbons of the phenyl rings, are all triplets owing to the coupling of these carbons to the two *virtually* equivalent trans phosphorus. This second-order effect is not observed when the phosphorus are placed cis to each other. As it has been pointed out before,[18] complex **4** is not soluble enough to obtain quality $^{13}C\{^1H\}$ NMR spectra from which C−P coupling constants can be measured.

To test the lability of dppet and dpppt complexes of palladium, and the stability of mixed versus homoleptic complexes, the bischelates **4** and **5** were allowed to react with $[PdCl_2(PPh_3)_2]$. As expected, palladium phosphinothiolates are not as labile as the nickel complexes mentioned above, and no reaction was observed at room temperature. However, in refluxing toluene over 24 h chelate ligand exchange takes place, but the products were different in each case. The reaction of **4** with $[PdCl_2(PPh_3)_2]$ gave the mixed ligand, mononuclear complex [PdCl(dppet)(PPh_3)] (**3**) (Scheme 1). The phosphorus NMR spectrum of **3** exhibits sharp signals at δ 66.8, corresponding to the $-PPh_2$ group of the chelate phosphinothiolate ligand, and at δ 24.1, corresponding to the PPh_3 ligand. The coupling constant $^2J_{PP} = 459$ Hz is typical of a *trans*-P,P arrangement that places the bulky $-PPh_2$ and PPh_3 groups away from each other. Aged solutions of **3** develop new, low intensity signals in the phosphorus NMR spectrum at the displaced positions of δ 74.8 (PPh_2R) and 23.2 (PPh_3) with a coupling constant $^2J_{PP} = 18.8$ Hz, indicative of a *cis*-P,P configuration which places the bulky groups close to each other. The cis-**3** complex is an isomerization product present only in solution, its concentration has never been observed to grow over ca. 5% of total **3**, and it has not been isolated in the solid state as an independent product. Crystallization of these *cis*-**3** containing solutions yields only the original *trans*-**3**. Presumably, a lower solubility and a greater concentration cause the crystallization *trans*-**3** exclusively.



In the course of the study of the trans/cis isomerization process and in repeated crystallizations, complex **3** proved to be stable. No loss of PPh_3 takes place, and no dimeric or polymeric palladium complexes were ever detected, even in the presence of air, using phosphorus NMR as a routine control tool.

The six-member ring containing bischelate complex **5** reacted with $[PdCl_2(PPh_3)_2]$ in the same conditions as **4**, to give the binuclear complex $[Pd_2Cl_2(dpppt\text{-}P,\mu\text{-}S)_2]$ (**6**), as the presence of PPh_3 cannot prevent the formation of sulfur bridges in this case (Scheme 1). The phosphorus NMR of **6** shows a single

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sharp resonance at δ 11.0, corresponding to the equivalent PPh_2R groups placed trans to the bridging sulfur. In both six-member ring containing chelate complexes **5** and **6**, the ^{31}P chemical shifts are practically identical, despite the different coordination of the metal; and are displaced toward higher frequencies by 28 ppm compared to free Hdpppt (δ_P −16.8). This kind of chemical shifts have been reported also for the cationic nickel trinuclear $[Ni_3(dpppt)_4]^{2+}$ and the heterobinuclear $[Cp_2Ti(\mu\text{-dpppt})Pd]$ (δ_P 12.3 and 13.2 respectively).[23] These seem small values compared to the displacement of the phosphorus chemical shift in the five-member ring containing complexes **3** and **4**, in which $\Delta\delta_P = 85$ and 82 ppm, respectively (free Hdppet δ_P −18), but these displacements are consistent with the dependency of phosphorus chemical shifts with ring size and the bond angles around phosphorus, an effect documented in diphosphine complexes.[68−70]

In the opposite synthetic direction (Scheme 1), complexes **3** and **6** are conveniently prepared using the direct base-free synthesis from $[PdCl_2(PPh_3)_2]$ and the corresponding phosphinothiol in a 1:1 ratio. No other products were observed. Again, the five-member ring forming Hdppet yields the mononuclear complex **3** that incorporates one PPh_3, but Hdpppt excludes all PPh_3 to give **6**, structurally following the pattern of the *five*-member ring dppet complexes of nickel.[13,14] Considering that 1:1 complexes are obtained even in reactions that take place at 110 °C and over 24 h, it can be safely assumed that **3** and **6** are the thermodynamic products for these ligand compositions.

The crystal structures of **3** and **6**, that included CH_2Cl_2 in the slow crystallization process, were determined by X-ray diffraction (Table 1). Selected distances and angles are listed in Table 2. The structure of **3** (Figure 2)[79,80] reveals a mononuclear, square planar *trans*-P,P palladium complex with a short Pd−S distance of 2.270(2) Å, owing to the terminal coordination of sulfur and the low trans influence of the chloro ligand. The two Pd−P distances are longer than the Pd−S distance and substantially different: 2.280(2) Å for the Pd−PPh_2R distance in the chelate and 2.343(2) Å for the Pd−PPh_3 distance. This difference may be interpreted in terms of the increased trans influence and the stronger bond of the alkyldiphenylphosphine group in the chelate compared to triphenylphosphine.

Binuclear complex **6** can be viewed as two Pd(dpppt)Cl fragments that have dimerized at an angle to give rise to the folded parallelogram shaped Pd_2S_2 center (Figure 3). The chelate angle S−Pd−P in the Pd(dpppt) six-member ring of **6** is larger (97°) than the corresponding chelate angle of 86° in the five-member ring of Pd(dppet) in **3** (Figure 2). The bridging sulfurs are in a *syn-endo* configuration, most probably influenced by the conformation of the chelate ligands. In the solid state, the coordination planes of each palladium in **6** are folded very far from coplanarity at a dihedral angle of 105.81(3)°. This value is very close to that of the five-member ring chelate dimers $[Ni_2X_2(\mu\text{-dppet})_2]$ (X = Cl, Br).[13,14] The molecule has noncrystallographic C_2 symmetry (Figure 3). There are two shorter Pd−S distances of 2.286(1) and 2.296(1) Å integrated in the

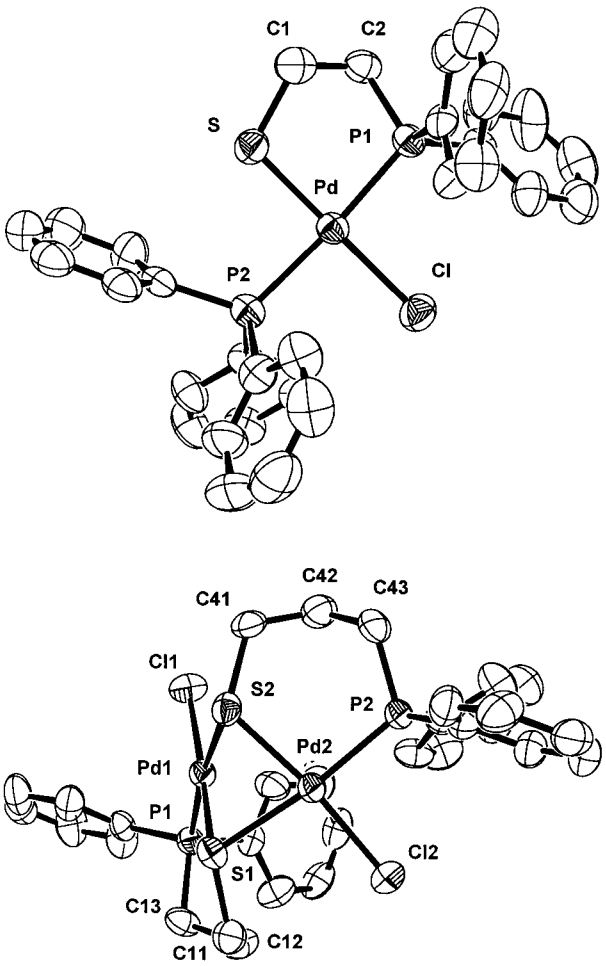

Figure 2. The projections of **3** (above) and **6** (below) on the S−Pd−P1 and S2−Pd2−P2 planes respectively, emphasize the structural similarities of the Pd(S-P)Cl fragments, the S−Pd distance in **3** is short, as is the S2−Pd2 distance in **6**, and the P2−Pd distance in **3** is long, as is the S1−Pd2 distance in **6** (ORTEP plots at 50% probability).

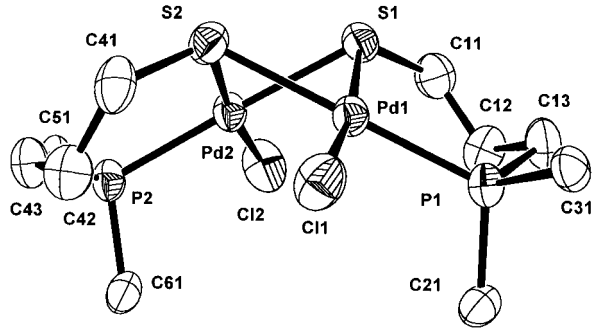

Figure 3. The noncrystallographic C_2 symmetry of **6** can be visualized in this projection, the aryl carbons have been omitted for the sake of clarity, with the exception of the C_{ipso}: C21, C31, C51, and C61.

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chelate ring that are trans to chloro ligands and two longer Pd−S distances of 2.381(1) and 2.382(1) Å that are trans to phosphorus.

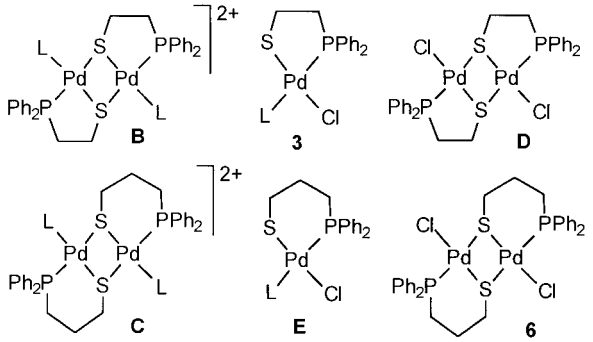
The bond distances in **3** and **6** are consistent with what would be expected from a conventional trans influence series, such as P(alkyldiphenylphosphine) > P(triphenylphosphine) > S(terminal) > S(bridge) > Cl. The Pd−Cl distances, trans to sulfur in both **3** and **6**, suggest that the terminal thiolato sulfur in **3** exerts a greater trans influence than a bridging sulfur in **6**. The effects of trans influence would also explain why the Pd−PPh_3 distance in **3** is long compared to the corresponding distance in [PdCl(cysEt)(PPh_3)] (Table 3, entry no. 2). In Table 3 the Pd−S and Pd−P distances of a series of palladium complexes with thiolato and phosphorus ligands are listed, tagged with the corresponding atom in trans. In these examples, the Pd−S distances tend to be longer than in complex **3** when they are trans to P (entries 11−15). Conversely, the Pd−P distances tend to be short when they are trans to S. But it is apparent from Table 3 that there are other important factors that influence Pd−S and Pd−P distances, such as the presence of a π-acceptor ligands (entry 7), or a negative charge that gives rise to electronic repulsion (entry 16).

In solution, the ^{1}H NMR of **6** in the methylene region (δ 1.5−3) consists of a complex and temperature dependent system of broad resonances not directly assignable to individual CH_2 groups down to −90 °C, while the ^{31}P{^{1}H} signal remains as a reasonably sharp singlet down to the same low temperature. In the case of **5**, broad but distinct resonances could be distinguished in the ^{1}H NMR for each methylene group at room temperature, while the ^{13}C NMR (Figure 1) and ^{31}P NMR resonances of **5** are narrow. The broadness of the ^{1}H NMR of **5** is interpreted in terms of the conformational movements of the six-member ring. In the case of **6**, considering that a soft potential energy function has been predicted for the folding process of these bridged dimers,[28,71−73] the more complex appearance of the ^{1}H NMR spectrum can be interpreted as the compounded effect of ring conformational movements and folding-unfolding motions of the palladium coordination planes over the S···S axis. However, the nature of these processes never pointed to the presence of structural variations such as those seen with nickel.

We regard the difference between ligands dppet and dpppt, in terms of mononuclear or binuclear complex formation, as a matter of the preference of a Pd(P-S)Cl fragment for a fourth neutral donor. In the case of dppet, PPh_3 binds to palladium and mononuclear **3** is preferentially formed, but in the case of dpppt, the triphenylphosphine is displaced in favor of the thiolato bridge to form binuclear **6** (Scheme 3).

The alternative structural preferences of two ligands that mainly differ in chelate ring size and chelate bite angle should be traced to these differences. The six-member ring forming dpppt requires more space around the metal, which should cause increased repulsion with PPh_3. Conversely, ligand dppet with a smaller bite angle leaves more room for PPh_3. It seems reasonable to think that the bonding energy involved in bridge formation is similar to the bonding energy of PPh_3 to palladium in the present situation, and that if a more basic and smaller phosphine were used, a mononuclear complex [PdCl(dpppt)-(PR_3)] should be as stable as **3**. However, when studying a new six-member ring forming ferrocenylphosphinothiolato ligand, in the complex [Pd_2Cl_2(μ-SPFc)$_2$] (Table 3, entry no. 6; this compound has the structural type of **6** in Scheme 3), Albinati et al. found that *tert*-butylisonitrile displaces not the bridge, but the chloride ligands to give a dicationic sulfur bridged dimer

Scheme 3. Structural Possibilities of 1:1 Phosphinothiolato Complexes[a]



[a] Only **3** and **6** are observed with dppet and dpppt, but B and C correspond to entries 8 and 7 in Table 3.

(Table 3, entry no. 7 and Scheme 3, structure type C).[28] Also, Leung et al., exploring a palladium complex that was difficult to structurally characterize which was also of stoichiometry [Pd_2-Cl_2(S-P)$_2$] with a five-member chelate ring forming phosphacyclic thiolato ligand (which could have structure D, although the authors also suggest as possible a chloride bridged structure not included in Scheme 3), found that triphenylarsine displaces chloride and a sulfur bridged dimer is formed (Table 3, entry no. 8 and structure type B).[29] We have seen that PPh_3 does not displace chloride to form [Pd_2(μ-dpppt)$_2$(PPh_3)$_2$]Cl_2 in the case of **6**, and that in the case of **3** the preferred structure is mononuclear, which is remarkable since thiolato ligands are prone to displace supposedly weaker ligands to form bridges (Scheme 3).

Hydroesterification[81] using CO gas and a suitable alcohol can be catalyzed by Pt/Sn/phosphine systems[82] but most studies have been carried out using various Pd/phosphine-based catalysts[83−90] for reasons of activity and cost. The use of additives, including other metals,[91] or alternate carbonyl sources has been reported,[93−95] but mostly simple, nonfunctionalized phosphines have been explored. High catalyst activity and stability is always important, but so are chemo- and regioselectivity. Catalytic carbonylation of aryl olefins could become an excellent route to the pharmacologically important aryl propionic acids (NSAIDs) if stable catalysts selective toward the branched products are developed and less expensive sources for the olefinic substrates are found.

In Table 4 we offer the first data on the evaluation of phosphinothiolato complexes of palladium as precursors in the

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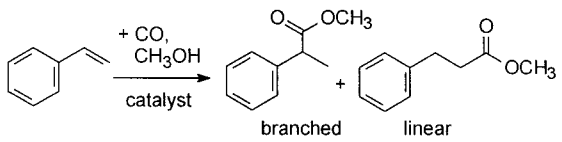
Scheme 4. Catalytic Hydroesterification of Styrene with CO and Methanol



reaction of catalytic hydroesterification of styrene with CO and MeOH (Scheme 4). The structurally characterized complexes **3**, **4**, **5**, and **6** were tested. The addition of cocatalysts that can affect the composition or the structure of these precursors has been avoided, thus foregoing any potential advantages of the more complex systems. The bischelate complexes **4** and **5** are inactive at 80 °C under 30 bar of CO (Table 4, entry nos. 1 and 2). This shows that complexes **4** and **5** are stable in these conditions, ligands dppet and dpppt remain coordinated and do not make coordination sites available to the catalytic process; no palladium black is formed either. Binuclear **6** shows some activity at the moderate temperature of 80 °C and its selectivity is toward the branched ester (entry 3). Mononuclear **3** seems more active than **6**: at the lower temperature of 60 °C a turnover frequency (TOF) number of the same order is calculated for **3**. Increasing the temperature and the time of reaction increases total conversion and average velocity, but the selectivity degrades and there is also decomposition of the soluble complex into palladium black. These preliminary results show that it is possible to get carbonylation activity without palladium black formation at low phosphorus/palladium ratios, using phosphinothiolato ligands under certain conditions.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures of **3**·CH_2Cl_2 and **6**·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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