

PPh(2-C₆H₄S)₂ as a Pincer Ligand in Nickel(II) and Palladium(II) Complexes — X-ray Structure of [Ni{PPh(C₆H₄S)₂}(PPh₂Me)], [Pd₂(μ-dppe){PPh(C₆H₄S)₂}₂] and [Ni{PPh(C₆H₄S)₂}]₂

Elena Cerrada,^[a] Larry R. Falvello,^[a] Michael B. Hursthouse,^[b] Mariano Laguna,^{*,[a]} Asunción Luquín,^[a] and Cristina Pozo-Gonzalo^[a]

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The phosphanylthiol PPh(2-C₆H₄SH)₂ reacts with the Ni^{II} and Pd^{II} complexes [MCl₂L₂] in the presence of NaOEt to give the mononuclear derivatives [M{PPh(C₆H₄S)₂}L] [M = Ni, L = PPh₃ (**1**), PPh₂Me (**2**); M = Pd, L = PPh₃ (**3**)]. The analogous reaction starting with complexes containing bidentate ligands [MX₂(L-L)] produces different results depending on the ligand used. The complexes [M{PPh(C₆H₄S)₂}(dppm)] [M = Ni (**4**), Pd (**5**)], with an unligated phosphorus atom in the diphosphane are obtained with bis(diphenylphosphanyl)methane (dppm), while the dinuclear complexes [M₂(μ-dppe){PPh(C₆H₄S)₂}] [M = Ni (**6**), Pd

(**7**)] are isolated in the case of 1,2-bis(diphenylphosphanyl)ethane (dppe). With 1,10-phenanthroline (phen), the complexes [M{PPh(C₆H₄S)₂}(phen)] [M = Ni (**8**), Pd (**9**)] are obtained, but when 2,2'-bipyridine is used the dinuclear compounds [M{PPh(C₆H₄S)₂}]₂ [M = Ni (**10**), Pd (**11**)] are isolated instead. Complexes **10** and **11**, which can be obtained starting from NiCl₂ or [PdCl₂(NCPh)₂] respectively, afford complexes **1–7** when treated with the respective phosphanes in the appropriate stoichiometries. The structures of **2**, **7** and **10** have been confirmed by X-ray analysis.

Introduction

Transition metal chemistry involving sulfur donor groups is of current interest because of its relevance in biology, because of its many industrial applications, and because of its importance in the area of novel complex synthesis.^[1] Thus, sulfur-ligated transition metal complexes form the inorganic parts of the biologically active centres of some metalloproteins and enzymes. Consequently, some of these have found applications in pharmacology,^[2–4] and industrial chemistry.^[5–7] As for synthetic chemistry as such, transition metal thiolate complexes have received special interest because of their ability to adopt different structures and nuclearities.^[8]

It is fairly common that these thiolate complexes contain phosphane moieties which, operating as ancillary ligands, are able to enhance the properties of interest. For this reason the chemistry of polydentate ligands with sulfur and phosphorus donor atoms in their frameworks has attracted increasing interest, augmented by the observation of unusual structures and reactivities in the resulting transition metal complexes.^[9] In this regard, the systems most studied

have been the prolignands PR₂(CH₂SH), PR₂(CH₂CH₂SH) and PR₂(C₆H₄SH).^[10–16]

Species with more than two donor atoms — PR(CH₂CH₂SH)₂, PR(C₆H₄SH)₂, P(CH₂CH₂SH)₃ and P(C₆H₄SH)₃ — have received much less attention,^[17–20] although they possess intrinsic interest in as much as they stably occupy three or more coordination sites, thus permitting more specific chemistry to be performed at the remaining sites. Such is the case for PPh(C₆H₄S)₂^{2–}, which possesses a three-donor set “PS₂” and can be described as a pincer ligand similar to van Koten’s^[21] [C₆H₃(CH₂NMe₂)₂][–] and [2,6-(Ph₂PCH₂)₂C₆H₃][–], Milstein’s^[22] [C₆H₃(CH₂PBu₂)₂][–] and [C₆H₄(CH₂PPr₂)₂] or to Sellmann’s [bis(2-mercaptophenyl)sulfide^{2–}].^[23]

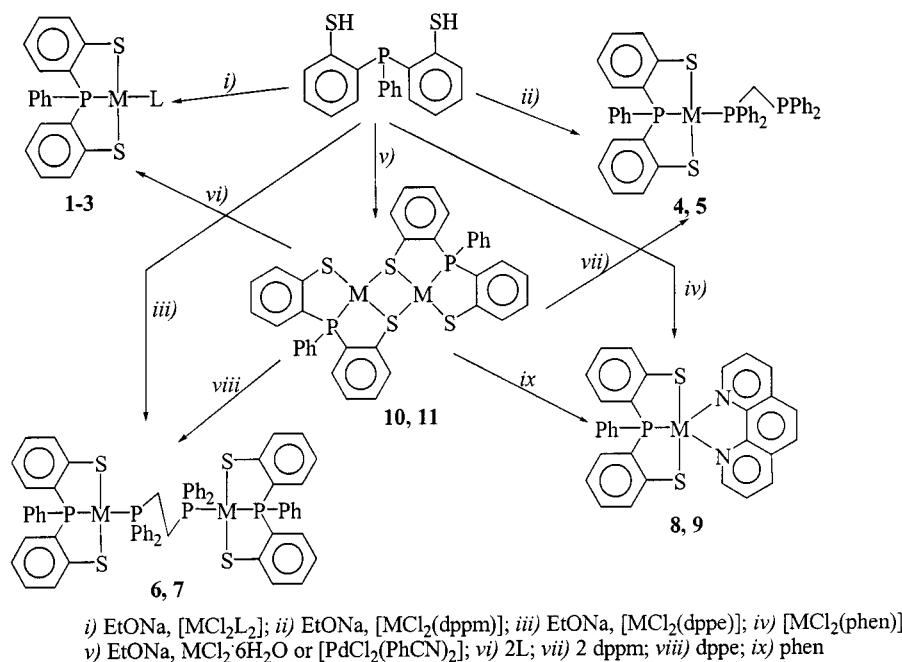
In this paper we describe some mono- and dinuclear complexes of Ni^{II} and Pd^{II}, with PPh(C₆H₄S)₂^{2–} acting as a pincer ligand in an *S,S',P* coordination mode, as confirmed by the X-ray structures of [Ni{PPh(C₆H₄S)₂}(PPh₂Me)], [Pd₂(μ-dppe){PPh(C₆H₄S)₂}₂] and [Ni{PPh(C₆H₄S)₂}]₂.

Results and Discussion

The reaction of a solution of PPh(C₆H₄SH)₂ and sodium ethoxide with the nickel(II) and palladium(II) species MCl₂L₂ (L = monodentate phosphane; step *i*, Scheme 1), yields the mononuclear derivatives [M{PPh(C₆H₄S)₂}(L)]

^[a] Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain
E-mail: mlaguna@posta.unizar.es

^[b] Department of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ, UK



Scheme 1. Synthesis of complexes 1–11

[M = Ni, L = PPh₃ (1), PPh₂Me (2); M = Pd, L = PPh₃ (3)]. This process can be described as the result of deprotonation of the starting phosphanylthiol ligand at room temperature, followed by coordination to the metal centre with the concomitant dissociation of one monodentate phosphane. To date the most common synthetic routes to complexes with these ligands have involved electrochemical procedures^[24] or reflux conditions in the presence of NEt₃ as a base. The preparation of 1–3 occurs under milder conditions than those reported for related complexes.

The IR spectra of complexes 1–3 do not show the ν(S–H) band, which appears at 2495 cm^{–1} in the free ligand. This fact, and the absence of the S–H signal in the ¹H NMR spectrum, indicates the presence of the anionic form of the ligand. The ¹H NMR spectra exhibit multiplets in the aromatic region and, for 2, a doublet at δ = 1.93 due to the methyl group of the PPh₂Me ligand. The ³¹P NMR spectra of the complexes show two doublets due to the two nonequivalent phosphorus atoms. The phosphanylthiolate resonance, which appears at δ = –19.4 in the free ligand, is shifted to about δ = 85 in complexes 1–3. This downfield shift could be considered as being due to the coordination of the phosphorus atom to the metal. The second doublet appears at higher field: δ = 26.0 (1), 9.4 (2) and 22.6 (3). The LSIMS⁺ mass spectra show the parent peak at *m/z* = 644 (1), 582 (2) and 692 (3), with appropriate isotope distributions, in agreement with the mononuclear description of the three products. Electrovoltammetry studies show a non-reversible one-electron oxidation at 0.412 V only in the case of [Ni{PPh(C₆H₄S)₂}(L)] (1).

When the same reaction as described in i) is carried out in the presence of a nickel or palladium complex with a bidentate phosphane [MCl₂(L–L)] (steps ii and iii, Scheme 1), the results obtained are different depending on

the diphosphane used. Thus, in the case of bis(diphenylphosphanyl)methane (dppm) the mononuclear complexes 4 and 5 are isolated, whereas the dinuclear species 6 and 7 are formed when 1,2-bis(diphenylphosphanyl)ethane (dppe) is used instead.

The complexes [M{PPh(C₆H₄S)₂}dppm] [M = Ni (4), Pd (5)] show IR spectra similar to those of compounds 1–3, with the S–H vibration absent and the phosphane bands present. The ¹H NMR spectra show multiplets in the aromatic region, and broad signals centred at δ = 3.17 (4) and 3.33 (5), even at low temperature, due to the –CH₂– group of dppm. The room temperature ³¹P NMR spectrum of 4 shows a triplet at δ = 85 assignable to the P atom of the phosphanylthiolate, although no signal was observed for the phosphorus atoms of dppm. A new broad signal appears in the negative region upon lowering the sample temperature that could be attributed to the dppm ligand. Decoalescence occurs at 283 K and a pattern corresponding to an AMX spin system becomes well-resolved at 223 K with the parameters δ_A = 85.9 (d, *J*_{AM} = 284 Hz), δ_M = 18.6 (dd, *J*_{MX} = 77.4 Hz) and δ_X = –27.1 (d). The high-field signal at δ = –27 is indicative of a free P-atom in the diphosphane. At 283 K Δ*G*[‡] has a value of 12.18 kcal/mol.^[25] Complex 5 exhibits a similar three-resonance pattern at room temperature. The LSIMS⁺ spectra show the parent peaks at *m/z* = 766 (4) and 813 (5) with the appropriate isotope distribution, again in agreement with the proposed formulation.

When the diphosphane 1,2-bis(diphenylphosphanyl)ethane (dppe) is used instead of dppm, the dinuclear derivatives [Pd₂(μ-dppe){PPh(C₆H₄S)₂}]₂ [M = Ni (6), Pd (7)] can be isolated as air stable solids (step iii, Scheme 1). The ¹H NMR spectra in CDCl₃ solution display the resonances characteristic of the phosphanyldithiolate ligand in the aro-

matic region, as well as those of the dppe. The ^{31}P NMR spectra reveal AA'XX' systems for both complexes: **6** ($\delta_{\text{A}} = 87.46$, $\delta_{\text{X}} = 22.47$, $J_{\text{AA}'} = 21.32$, $J_{\text{AX}} = 234.13$, $J_{\text{XX}'} = 21.60$ Hz), **7** ($\delta_{\text{A}} = 84.8$, $\delta_{\text{X}} = 20.85$, $J_{\text{AA}'} = 23.7$, $J_{\text{AX}} = 414.2$, $J_{\text{XX}'} = 25.1$ Hz). This is consistent with a dinuclear formulation. The mass spectrum (LSIMS⁺) does not show the molecular peak for **6** and shows only weak intensity for **7** ($m/z = 1258$, 5%).

The reaction of $[\text{MCl}_2(\text{N-N})]$ [N-N = 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen)] with $\text{PPh}(\text{C}_6\text{H}_4\text{SH})_2$ in the presence of sodium ethoxide, depends on the N-containing ligand. This ligand remains bound to the metal only in the case of 1,10-phenanthroline, yielding $[\text{M}\{\text{PPh}(\text{C}_6\text{H}_4\text{S})_2\}(\text{phen})]$ [M = Ni (**8**), Pd (**9**); process *iv*, Scheme 1]. Curiously, the nickel complex is soluble in conventional solvents, while the palladium-containing product is not soluble enough, so that no solution data could be measured for complex **9**. The ^{31}P NMR spectrum of **8** shows a singlet at $\delta = 75.4$, as a consequence of the coordination of the P atom to the metal centre, meaning that complex **8** is in all likelihood pentacoordinated. With bipy present as the auxiliary ligand, the reaction proceeds with the formation of the dinuclear species $[\text{M}\{\text{PPh}(\text{C}_6\text{H}_4\text{S})_2\}_2]$ [M = Ni (**10**) and Pd (**11**)].

The dinuclear derivatives **10** and **11** can also be obtained from the reaction between $\text{PPh}(\text{C}_6\text{H}_4\text{SH})_2$ in NaOEt, and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $[\text{PdCl}_2(\text{PhCN})_2]$, in which PhCN serves as a leaving group (step *v*, Scheme 1). The ^1H NMR spectra show only signals in the aromatic region, while the ^{31}P NMR spectra display the expected singlets at $\delta = 72.7$ and 76.9 , respectively, due to the equivalent phosphorus donors in each complex. The mass spectra show the molecular peaks at $m/z = 764$ (45%) (**10**) and 861 (12%) (**11**), in agreement with a dinuclear formulation.

Complexes **10** and **11** react readily with mono- and bidentate phosphanes in dichloromethane in the appropriate stoichiometries, to give mixtures of products in which complexes **1–9** are the major products, as shown by ^1H and ^{31}P NMR spectroscopic data. This fact is in agreement with the dinuclear formulation of **10** and **11**. $[\text{M}\{\text{PPh}(\text{C}_6\text{H}_4\text{S})_2\}(\text{bipy})]$ complexes are again inaccessible by this route, and when the corresponding reaction was attempted the starting materials were recovered unchanged.

Crystal Structures of $[\text{Ni}\{\text{PPh}(\text{C}_6\text{H}_4\text{S})_2\}(\text{PPh}_2\text{Me})]$ (**2**), $[\text{Pd}_2(\mu\text{-dppe})\{\text{PPh}(\text{C}_6\text{H}_4\text{S})_2\}_2]$ (**7**) and $[\text{Ni}\{\text{PPh}(\text{C}_6\text{H}_4\text{S})_2\}_2]$ (**10**)

Zubieta et al.^[20] have previously reported a complex similar to **1**, and described it as a dinuclear derivative. Because the data for complexes **1–5**, and particularly the mass spectra, point more to them being mononuclear, we undertook the X-ray analysis of one of these complexes, namely $[\text{Ni}\{\text{PPh}(\text{C}_6\text{H}_4\text{S})_2\}(\text{PPh}_2\text{Me})]$ (**2**), which yielded the most suitable crystals for X-ray studies. Figure 1 shows a view of the molecule, a mononuclear, distorted square planar *trans*-P,P and *trans*-S,S nickel complex with the Ni atom 0.031 Å out of the plane formed by S(1), P(1), S(2) and P(2) (planar within 0.208 Å). The main distortion from square-planar geometry arises from closure of the S(2)–Ni–S(1) angle [$166.22(4)^\circ$], and to a much lesser extent, of the angles S(1)–Ni–P(2) and S(2)–Ni–P(2) [$87.05(3)^\circ$ and $88.66(3)^\circ$, respectively] most likely imposed by the rigidity of the phosphaneyldithiolate ligand. The two Ni–P distances are quite different from each other. The Ni–P(1) distance of 2.2054(8) Å is similar to that found for Ni–PPh₃ bonds such as that found in $[\text{Ni}(\text{S}_3)\text{PPh}_3]$ [$\text{S}_3^{2-} = \text{bis}(2\text{-mercapto-phenyl})\text{sulfide}$, 2.197(1) Å].^[23] However, the Ni–P(2) bond

Table 1. Summary of crystallographic data for complexes $[\text{Ni}\{\text{PPh}(\text{C}_6\text{H}_4\text{S})_2\}(\text{PPh}_2\text{Me})]$ (**2**), $[\text{Pd}_2(\mu\text{-dppe})\{\text{PPh}(\text{C}_6\text{H}_4\text{S})_2\}_2]$ (**7**) and $[\text{Ni}\{\text{PPh}(\text{C}_6\text{H}_4\text{S})_2\}_2]$ (**10**)

	2	7	10
Empirical formula	$\text{C}_{31}\text{H}_{26}\text{NiP}_2\text{S}_2$	$\text{C}_{64}\text{H}_{52}\text{Cl}_4\text{P}_4\text{Pd}_2\text{S}_4$	$\text{C}_{18}\text{H}_{13}\text{NiPS}_2$
Molecular mass	583.29	1427.78	383.08
Temperature	295(2) K	293(2) K	301(2) K
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
<i>a</i> , Å	9.8082(6)	9.648(2)	16.645(7)
<i>b</i> , Å	28.9852(19)	10.858(2)	11.073(15)
<i>c</i> , Å	9.9463(6)	15.054(3)	18.24(3)
α , deg	90	97.99(3)	90
β , deg	104.5850(10)	98.78(3)	107.80(8)
γ , deg	90	100.31(3)	90
<i>V</i> , Å ³	2736.5(3)	1510.8(5)	3201(7)
<i>Z</i>	4	1	8
<i>D_c</i> (Mg/m ³)	1.416	1.569	1.590
μ , mm ^{−1}	0.998	1.057	1.564
Crystal size (mm)	0.28 × 0.25 × 0.18	0.2 × 0.2 × 0.12	0.18 × 0.17 × 0.01
θ range	1.41 to 25.00°	2.36 to 25.02°	2.18 to 22.99°
<i>R</i> 1, ^[a] <i>wR</i> 2 ^[b] [<i>I</i> > 2σ(<i>I</i>)]	0.0530, 0.1621	0.0344, 0.0941	0.1491, 0.2748
Residual ρ , e Å ^{−3}	0.252, −0.425	0.821, −0.720	1.215, −1.133

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

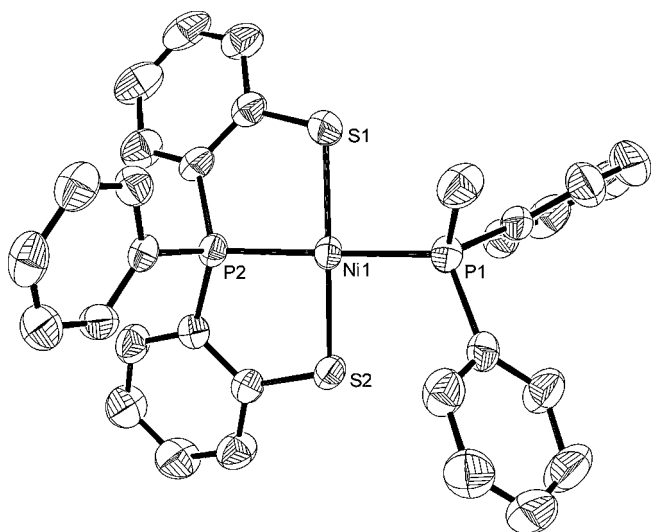


Figure 1. Compound **2** in the crystal; displacement parameter ellipsoids represent 50% probability surfaces; H atoms are omitted for clarity

length of 2.1186(8) Å is shorter than the former and shorter than other Ni-phosphanylthiolate complexes:^[26] [Ni(PS)₂] with PS = PPh₂(C₆H₄S) and PPh₂[C₆H₃(SiMe₃)S], 2.181(2) and 2.172(3) Å, respectively. The Ni–P(2) bond is similar to that found in the binuclear compound [Ni₂{P(C₆H₄S)₃}₂]^[27] [2.109(4) Å]. This short distance is again consistent with the constraints imposed by the PS₂ ligand. The Ni–S distances, which average 2.1693(8) Å, are in the range reported for terminal nickel-thiolate bonds^[23] and lie in the range found for [Ni(PS)₂]:^[25,26] PS = PPh₂(C₆H₄S), 2.180(2); PPh₂(C₆H₃(SiMe₃)S), 2.151(3) Å. Moreover, the Ni–S distances are similar to those found for other phosphanylthiolate derivatives.^[28–30] Complexes **1**, **3**, **4** and **5** presumably adopt similar mononuclear dispositions.

The crystal structure of **7**, which includes an interstitial molecule of CH₂Cl₂, was also determined by X-ray diffraction. The structure (Figure 2) displays two Pd-phosphanylthiolate units connected to each other by the dppe ligand. The geometry around each palladium centre, *trans*-P,P and -S,S, is close to square planar, as was the case in **2**, and

Table 2. Selected bond lengths [Å] and angles [°] for **2**

Ni(1)–P(2)	2.1186(8)	Ni(1)–S(1)	2.1756(9)
Ni(1)–S(2)	2.1630(8)	Ni(1)–P(1)	2.2054(8)
P(2)–Ni(1)–S(2)	88.66(3)	C(4)–P(1)–Ni(1)	113.55(11)
P(2)–Ni(1)–S(1)	87.05(3)	C(1)–P(1)–Ni(1)	112.37(12)
S(2)–Ni(1)–S(1)	166.22(4)	C(10)–P(1)–Ni(1)	115.74(10)
P(2)–Ni(1)–P(1)	170.41(3)	C(16)–S(1)–Ni(1)	104.97(11)
S(2)–Ni(1)–P(1)	94.18(3)	C(32)–P(2)–C(21)	115.43(14)
S(1)–Ni(1)–P(1)	92.19(3)	C(32)–P(2)–Ni(1)	109.63(10)
C(4)–P(1)–C(1)	105.50(16)	C(21)–P(2)–Ni(1)	108.97(10)
C(4)–P(1)–C(10)	105.42(13)	C(31)–S(2)–Ni(1)	105.83(10)
C(1)–P(1)–C(10)	103.21(15)		

Table 3. Selected bond lengths [Å] and angles [°] for **7**·CH₂Cl₂

Pd(1)–P(1)	2.2265(10)	Pd(1)–S(2)	2.3316(10)
Pd(1)–S(1)	2.3137(9)	Pd(1)–P(2)	2.3402(11)
P(1)–Pd(1)–S(1)	86.78(4)	C(13)–P(1)–C(7)	108.41(14)
P(1)–Pd(1)–S(2)	84.24(4)	C(6)–P(1)–Pd(1)	109.03(11)
S(1)–Pd(1)–S(2)	164.93(3)	C(13)–P(1)–Pd(1)	105.78(10)
P(1)–Pd(1)–P(2)	171.77(3)	C(7)–P(1)–Pd(1)	115.55(10)
S(1)–Pd(1)–P(2)	93.79(4)	C(20)–P(2)–Pd(1)	104.99(10)
S(2)–Pd(1)–P(2)	93.39(4)	C(1)–S(1)–Pd(1)	103.97(11)
C(6)–P(1)–C(13)	113.20(14)	C(18)–S(2)–Pd(1)	101.51(11)
C(6)–P(1)–C(7)	105.08(13)		

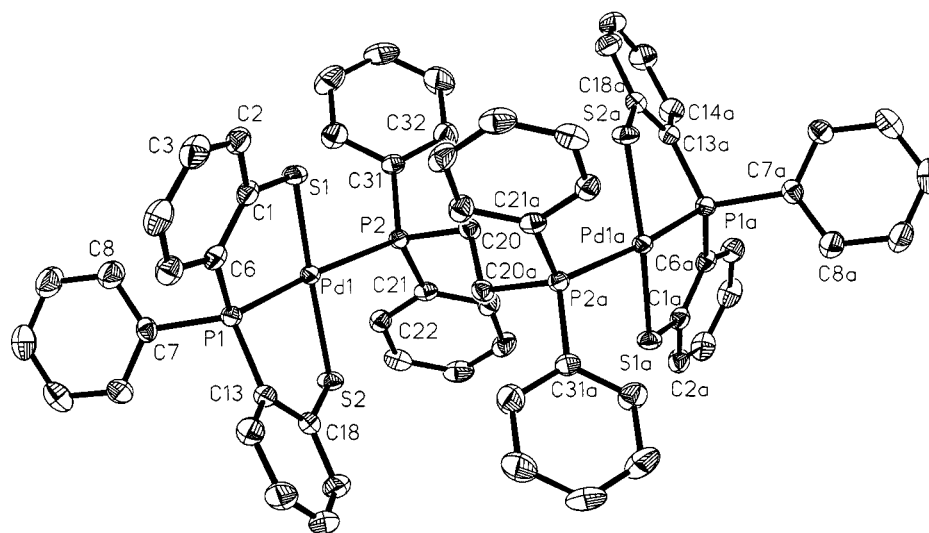


Figure 2. Compound **7** in the crystal; displacement parameter ellipsoids represent 50% probability surfaces; H atoms are omitted for clarity

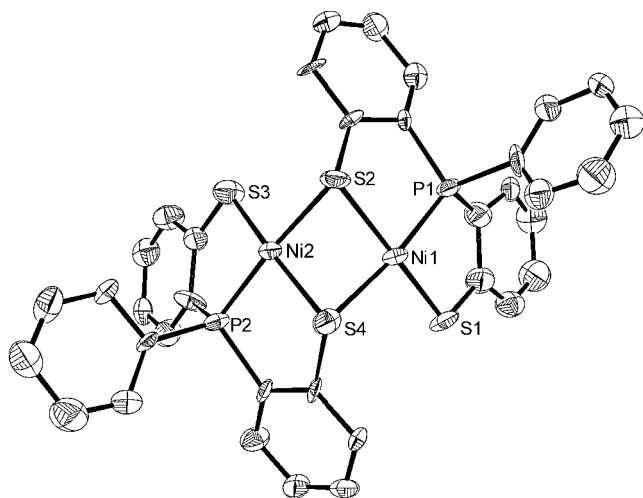


Figure 3. Compound **10** in the crystal; displacement parameter ellipsoids represent 50% probability surfaces; H atoms are omitted for clarity

Table 4. Selected bond lengths [Å] and angles [°] for **10**

Ni(1)–P(1)	2.078(10)	Ni(2)–P(2)	2.088(10)
Ni(1)–S(1)	2.147(11)	Ni(2)–S(3)	2.168(11)
Ni(1)–S(4)	2.215(11)	Ni(2)–S(4)	2.201(10)
Ni(1)–S(2)	2.229(10)	Ni(2)–S(2)	2.257(10)
Ni(1)–Ni(2)	2.714(6)		
P(1)–Ni(1)–S(1)	89.0(4)	S(3)–Ni(2)–Ni(1)	120.8(3)
P(1)–Ni(1)–S(4)	171.4(4)	S(4)–Ni(2)–Ni(1)	52.3(3)
S(1)–Ni(1)–S(4)	99.4(4)	S(2)–Ni(2)–Ni(1)	52.3(3)
P(1)–Ni(1)–S(2)	86.9(4)	C(1)–P(1)–Ni(1)	109.7(12)
S(1)–Ni(1)–S(2)	170.0(4)	C(7)–P(1)–Ni(1)	117.4(13)
S(4)–Ni(1)–S(2)	84.5(4)	C(13)–P(1)–Ni(1)	110.2(11)
P(1)–Ni(1)–Ni(2)	122.1(3)	C(2)–S(1)–Ni(1)	106.6(14)
S(1)–Ni(1)–Ni(2)	122.5(3)	C(14)–S(2)–Ni(1)	102.1(11)
S(4)–Ni(1)–Ni(2)	51.8(3)	C(14)–S(2)–Ni(2)	112.3(12)
S(2)–Ni(1)–Ni(2)	53.2(3)	Ni(1)–S(2)–Ni(2)	74.5(3)
P(2)–Ni(2)–S(3)	88.9(4)	C(19)–P(2)–Ni(2)	109.9(11)
P(2)–Ni(2)–S(4)	88.5(4)	C(25)–P(2)–Ni(2)	115.1(11)
S(3)–Ni(2)–S(4)	167.9(4)	C(31)–P(2)–Ni(2)	106.6(11)
P(2)–Ni(2)–S(2)	172.2(4)	C(20)–S(3)–Ni(2)	105.2(13)
S(3)–Ni(2)–S(2)	98.8(4)	C(32)–S(4)–Ni(2)	101.5(11)
S(4)–Ni(2)–S(2)	84.2(4)	C(32)–S(4)–Ni(1)	111.7(11)
P(2)–Ni(2)–Ni(1)	124.3(3)	Ni(2)–S(4)–Ni(1)	75.8(3)

the Pd atom lies out of the plane by 0.167 Å, with the main deviations due to contraction of the S(2)–Pd–S(1) [164.93(3)°], S(1)–Pd–P(1) [86.78(4)°], and S(2)–Pd–P(1) [84.24(4)°] angles. The two Pd–P distances are different from each other, as in **2**. The Pd–P(phosphanyldithiolate) bond [Pd(1)–P(1) = 2.2265(10) Å] is shorter than that in Pd–P(dppe) [Pd(1)–P(2) = 2.3402(10) Å]. This reinforces the notion that the shorter bond distance from Pd to the phosphanyldithiolate phosphorus atom results from constraints imposed by the ligand. Accordingly, several systems with palladium coordinated by less restrictive P,S ligands show larger Pd–P distances, such as in [Pd{PPh₂(CH₂CH₂S)}Cl(PPh₃)] [2.280(2) Å],^[31] *trans*-[Pd{PPh₂(C₆H₄S)}₂] [2.291(1) Å]^[32] or *cis*-[Pd{PPh₂(C₆H₄S)}₂] [2.2845(8) and 2.2802(8) Å].^[33] The Pd–P bonds involving the dppe ligand are slightly longer

[2.3402(11) Å] than in other derivatives with this diphosphane.^[34] The Pd–S bond lengths [average value 2.3227(10) Å] are similar to those found in the complexes mentioned above and in other bisdithiolene derivatives.^[35–37]

The structure determination of **10** was undertaken in order to establish the chemical connectivity, although it was clear from the outset that the data would not be of high quality. The analysis reveals (Figure 3) a dinuclear complex consisting of two Ni-phosphanyldithiolate units linked by a double sulfur bridge. Although the accuracy of the structure determination does not permit a systematic comparison of distances, the Ni–P and Ni–S(terminal) distances are similar to those found in complex **2**; the Ni–S(bridging) distances are greater than those for Ni–S(terminal) as is the case in other systems with terminal and bridging sulfur atoms, such as [Ni(S₃)₃] [S₃^{2–} = bis(2-mercaptophenyl)sulfide]^[23] and [Ni₂{P(C₆H₄S)₃}₂].^[27] It is worth noting that the Ni–Ni distance of 2.714(6) Å is rather short, which could be indicative of some degree of metal-metal interaction.^[27,38,39]

Experimental Section

General Procedures: All reactions were performed under argon using standard Schlenk techniques, although the products are air stable. [MCl₂L₂] (M = Ni, Pd; L = PPh₃, PPh₂Me),^[40,41] and [MCl₂(L-L)] (M = Ni, Pd; L-L = dppe,^[42,43] bipy, phen^[44]) were prepared by established procedures. All other reagents were used as supplied. The synthesis of PPh(2-C₆H₄SH)₂ was carried out using the standard literature procedure.^[45] IR spectra were recorded on a Perkin–Elmer 883 spectrophotometer, over the range 4000–200 cm^{–1}, using Nujol mulls between polyethylene sheets. ¹H and ³¹P NMR spectra were measured on a Varian UNITY 300 or Bruker 300 spectrometer in CDCl₃ or CD₂Cl₂ solution; chemical shifts are quoted relative to SiMe₄ (¹H) or H₃PO₄ (external, ³¹P). The C, H N and S analyses were performed with a Perkin–Elmer 2400 microanalyser. Mass spectra were recorded on a VG Autospec, by liquid secondary ion mass spectrometry (LSIMS+) using nitrobenzyl alcohol as matrix and a cesium gun.

Preparation of the Phosphanyldithiolate Complexes [Ni{PPh(C₆H₄S)₂}PPh₃] (1**), [Ni{PPh(C₆H₄S)₂}PPh₂Me] (**2**), and [Pd{PPh(C₆H₄S)₂}PPh₃] (**3**):** A solution of 0.1 M NaOEt (3 mL, 0.3 mmol) and [NiCl₂(PPh₃)₂] (0.098 g, 0.15 mmol), [NiCl₂(PPh₂Me)₂] (0.079 g, 0.15 mmol) or [PdCl₂(PPh₃)₂] (0.105 g, 0.15 mmol) was added, over a period of 10 minutes, to a suspension of PPh(C₆H₄SH)₂ (0.048 g, 0.15 mmol) in 10 mL of ethanol. After 5 h of stirring, green (**1**, **2**) or brown (**3**) solids precipitated; these were filtered off, washed with ethanol and dried in vacuo.

1: Yield: 73 mg (75%). C₃₆H₂₈NiP₂S₂ (645.4); calcd. C 66.99, H 4.37, S 9.93; found C 66.45, H 4.20, S 9.50. ¹H NMR (CDCl₃): δ = 6.69 (m, 2 H, Ph), 7.18 (m, 2 H, Ph), 7.62–7.26 (m, 24 H, Ph). ³¹P{¹H} NMR (CDCl₃): δ = 86.2 (d, J_{P-P} = 270 Hz), 26 (d). MS: *m/z* (%) = 644 (100) [M]⁺.

2: Yield: 62 mg (70%). C₃₁H₂₆NiP₂S₂ (583.3); calcd. C 63.83, H 4.49, S 10.99; found C 63.42, H 4.21, S 10.38. ¹H NMR (CDCl₃): δ = 1.93 (d, ²J_{P-H} = 8.3 Hz, 3 H, Me), 7.0 (m, 2 H), 7.64–7.22 (m, 21 H, Ph). ³¹P{¹H} NMR (CDCl₃): δ = 87.4 (d, J_{P-P} = 280 Hz), 9.4 (d). MS: *m/z* (%) = 582 (100) [M]⁺, 382 (60) [M – PPh₂Me]⁺.

3: Yield: 94 mg (90%). C₃₆H₂₈P₂PdS₂ (693.1); calcd. C 62.38, H 4.07, S 9.25; found C 61.95, H 4.21, S 8.69. ¹H NMR (CDCl₃): δ = 6.99 (m, 2 H, Ph), 7.21 (m, 2 H, Ph), 7.62–7.27 (m, 24 H, Ph).

³¹P{¹H} NMR (CDCl₃): δ = 85.2 (d, *J*_{P-P} = 406 Hz), 22.6 (d). MS: *m/z* (%) = 692 (100) [M]⁺, 430 (55) [M – PPh₃]⁺.

[Ni{PPh(C₆H₄S)₂}(dppm)] (4) and [Pd{PPh(C₆H₄S)₂}(dppm)] (5): A solution of 0.1 M NaOEt (3 mL, 0.3 mmol) and either [NiCl₂dppm] (0.077 g, 0.15 mmol) or [PdCl₂dppm] (0.084 g, 0.15 mmol) was added, over a period of 10 minutes, to a suspension of PPh(C₆H₄SH)₂ (0.048 g, 0.15 mmol) in 10 mL of ethanol. Green (**4**) or orange (**5**) solids precipitated immediately, and were filtered off, washed with ethanol and dried in vacuo.

4: Yield: 80 mg (70%). C₄₃H₃₅NiP₃S₂ (767.5): calcd. C 67.29, H 4.59, S 8.35; found C 66.96, H 4.35, S 7.85. ¹H NMR (CDCl₃): δ = 3.17 (br. s, 2 H, CH₂), 6.95 (m, 2 H), 7.45–7.14 (m, 29 H, Ph), 7.54 (m, 2 H, Ph). ³¹P{¹H} NMR (CD₂Cl₂): δ = (–50 °C): δ_A = 85.9 (d, *J*_{AM} = 284 Hz), δ_M = 18.6 (dd, *J*_{MX} = 77.4 Hz), δ_X = –27.1 (d). MS: *m/z* (%) = 766 (100) [M]⁺, 383 (70) [M – dppm]⁺.
5: Yield: 107 mg (88%). C₄₃H₃₅PdP₃S₂ (815.2): calcd. C 63.35, H 4.3, S 7.85; found C 62.94, H 3.92, S 7.71. ¹H NMR (CDCl₃): δ = 3.33 (br. s, 2 H, CH₂), 6.95 (m, 2 H, Ph), 7.71–7.15 (m, 31 H, Ph). ³¹P{¹H} NMR (CDCl₃): δ = 83.2 (d, *J*_{P-P} = 399 Hz), 11.3 (d), –26.1 (br. s.). MS: *m/z* (%) = 813 (100) [M]⁺, 430 (70) [M – dppm]⁺.

[Ni₂(μ-dppe){PPh(C₆H₄S)₂}]₂ (6) and [Pd₂(μ-dppe){PPh(C₆H₄S)₂}]₂ (7): The procedure followed was similar to that described for **4** and **5**, using [NiCl₂dppe] (0.078 g, 0.15 mmol) or [PdCl₂dppe] (0.085 g, 0.15 mmol). Green (**6**) or brown (**7**) solids precipitated from the reaction media, and were filtered off and washed with EtOH.

6: Yield: 123 mg (70%). C₆₂H₅₀Ni₂P₄S₄ (1164.6): calcd. C 63.94, H 4.32, S 11.01; found C 63.55, H 4.15, S 10.52. ¹H NMR (CDCl₃): δ = 2.74 (br. s, 4 H, CH₂–CH₂), 7.61–6.66 (m, 46 H, Ph). ³¹P{¹H} NMR (CDCl₃): AA'XX': δ_A = δ_{A'} = 87.46, δ_X = δ_{X'} = 22.47, *J*_{AA'} = 21.32 Hz, *J*_{AX} = 234.13 Hz, *J*_{AX'} = *J*_{A'X} = 0 Hz, *J*_{XX'} = 21.60 Hz. MS: *m/z* (%) = 780 (30) [M – Ni(PPh(C₆H₄S)₂)]⁺.

7: Yield: 123 mg (65%). C₆₂H₅₀Pd₂S₄ (1260.0): calcd. C 59.09, H 3.99, S 10.17; found C 58.82, H 3.81, S 9.85. ¹H NMR (CDCl₃): δ = 3.33 (br. s, 4 H, CH₂–CH₂), 7.0 (m, 4 H), 7.61–7.17 (m, 42 H, Ph). ³¹P{¹H} NMR (CDCl₃): AA'XX': δ_A = δ_{A'} = 84.8, δ_X = δ_{X'} = 20.85, *J*_{AA'} = 23.7 Hz, *J*_{AX} = 414.2 Hz, *J*_{AX'} = *J*_{A'X} = 0 Hz, *J*_{XX'} = 25.1 Hz. MS: *m/z* (%) = 1258 (5) [M]⁺, 780 (30) [M – Ni(PPh(C₆H₄S)₂)]⁺.

[Ni{PPh(C₆H₄S)₂}(phen)] (8) and [Pd{PPh(C₆H₄S)₂}(phen)] (9): A 0.1 M solution of NaOEt (3 mL, 0.3 mmol) was added over a period of 10 minutes to a suspension of PPh(C₆H₄SH)₂ (0.048 g, 0.15 mmol) in 10 mL of ethanol, and then [NiCl₂phen] (0.046 g, 0.15 mmol) or [PdCl₂phen] (0.054 g, 0.15 mmol) was added. After stirring overnight brown solids precipitated, which were filtered off, washed with ethanol and dried in vacuo.

8: Yield: 55 mg (65%). C₃₀H₂₁N₂NiPS₂ (563.3): calcd. C 64.06, H 3.76, N 4.98, S 11.40; found C 63.65, H 3.35, N 4.52, S 10.98. ¹H NMR (CDCl₃): δ = 7.58–6.79 (m, 14 H, Ph), 7.62 (m, 2 H, phen), 7.78 (s, 2 H, phen), 8.23 (m, 2 H, phen), 9.72 (m, 1 H, phen). ³¹P{¹H} NMR (CDCl₃): δ = 4.5(s). MS: *m/z* (%) = 562 (5) [M]⁺, 780 (30) [M – Ni(PPh(C₆H₄S)₂)]⁺.

9: Yield: 64 mg (70%). C₃₀H₂₁PPdN₂S₂ (611.0): calcd. C 58.97, H 3.46, N 4.58, S 10.49; found C 58.75, H 3.5, N 4.35, S 11.05.

[Ni{PPh(C₆H₄S)₂}]₂ (10) and [Pd{PPh(C₆H₄S)₂}]₂ (11): a) Following the same procedure as described for the previous complexes, using NiCl₂·6H₂O (0.036 g, 0.15 mmol) or [PdCl₂(PhCN)]₂ (0.057 g, 0.15 mmol), afforded green or brown solids which precipitated from their respective reaction media and were filtered off and washed with EtOH.

10: Yield: 40 mg (70%). C₃₆H₂₆Ni₂P₂S₄ (766.2): calcd. C 56.43, H 3.42, S 16.73; found C 56.10, H 3.21, S, 16.25. ¹H NMR (CD₂Cl₂):

δ = 6.99 (m, 4 H), 7.22 (m, 4 H), 7.49–7.19 (m, 10 H), 7.56 (m, 4 H), 7.76 (m, 4 H, Ph). ³¹P{¹H} NMR (CD₂Cl₂): δ = 72.7 (s). MS: *m/z* (%) = 764 (65) [M]⁺.

11: Yield: 56 mg (87%). C₃₆H₂₆Pd₂S₄ (861.6): calcd. C 50.18, H 3.04, S 14.88; found 50.45, H 3.14, S 15.26. ¹H NMR (CD₂Cl₂): δ = 7.61–7.17 (m). ³¹P{¹H} NMR (CD₂Cl₂): δ = 76.9 (s). MS: *m/z* (%) = 861 (15) [M]⁺.

b) A 0.1 M solution of NaOEt (3 mL, 0.3 mmol) was added, over a period of 10 minutes, to a suspension of PPh(C₆H₄SH)₂ (0.048 g, 0.15 mmol) in 10 mL of ethanol. Then, [NiCl₂·bipy] (0.042 g, 0.15 mmol) or [PdCl₂·bipy] (0.050 g, 0.15 mmol) was added. After stirring overnight green (**10**) or brown (**11**) solids precipitated, which were filtered off, washed with ethanol and dried in vacuo. Yields: **10**: 42 mg (73%); **11**: 55 mg (85%).

Reaction of [Ni{PPh(C₆H₄S)₂}]₂ (10) and [Pd{PPh(C₆H₄S)₂}]₂ (11) with Ligands: 0.1 mmol of L (L = PPh₃, PPh₂Me, dppe, or phen), or 0.05 mmol of dppe was added to a suspension of [Ni{PPh(C₆H₄S)₂}]₂ (**10**; 0.076 g, 0.05 mmol) or [Pd{PPh(C₆H₄S)₂}]₂ (**11**; 0.086 g, 0.05 mmol) in dichloromethane (30 mL) and stirred for 6 hours to give clear solutions. Partial evaporation of the solvents and addition of ethanol (20 mL) afford complexes **1–8**. Complex [Pd{PPh(C₆H₄S)₂}(phen)] (**9**) was obtained as a brown insoluble solid from dichloromethane.

X-ray Crystallography: Single crystals of [Ni{PPh(C₆H₄S)₂}(PPh₂Me)] (**2**) and of [Pd₂(μ-dppe){PPh(C₆H₄S)₂}]₂ CH₂Cl₂ (**7**) were grown by slow diffusion of hexane into dichloromethane solutions of the complexes. Data collection^[46] at low temperature was carried out on a Bruker SMART diffractometer for **2** and on a Nonius–KappaCCD diffractometer for **7**. Crystal parameters and experimental details are summarised in Table 1. The structures were solved by direct methods for **2**^[47] and for **7**,^[48] and refined on *F*_o² by full-matrix least-squares using the program SHELXL-97.^[49] Data were corrected for absorption using SADABS^[50] for **2** and SORTAV^[51] for **7**. All hydrogen atoms were included at idealised positions. Selected bond lengths and angles are given in Table 2 and 3. The details of the crystal structures have been deposited at the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-162696, CCDC-162697 and CCDC-162698 for complexes **2**, **7** and **10** respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge UK CB2 1EZ [E-mail: deposit@ccdc.cam.ac.uk, Fax: (internat.) +44-1223/336-033].

A very thin plate-like crystal of **10**, suffering from severe anisotropic mosaicity, was used for X-ray measurements. An initial, slow reflection search yielded 12 reflections, which were indexed to a primitive monoclinic cell.^[52] Preliminary data collection between 26 and 32° (2θ) was used in an attempt to obtain better reflections for cell determination and for ψ-scans, but the results were not satisfactory. The positions of 13 reflections with lower values of 2θ were used to calculate the unit cell parameters reported. Accurate centring of reflections in the higher 2θ range was rendered difficult because of the mosaic spread of the crystal. As for the ψ-scans, in addition to producing low signal-to-noise ratios, they also suffered from the effects of mosaicity; this compromises the validity of the absorption corrections so obtained, and so absorption corrections were not applied.

Intensity data were gathered in the 2θ range of 4.0–46.0°. Omega-scans were used, with the ω scan speed set for each reflection on the basis of a preliminary measurement made at a speed of 4°/min. The weakest data were gathered at the slowest speed; no reflection was skipped on the basis of a poor showing on the initial scan. The

maximum scan time for any reflection was limited to 270 sec, and most reflections were measured for that amount of time. The photon count for the preliminary scan was added to that of the final scan to give the datum. A single monitor reflection was measured after every 30 min of accumulated beam time, as a check on experimental stability. An orientation check was made after every 1000 intensity measurements. In all, 5630 intensity measurements were made, in a single quadrant of reciprocal space.

Following data reduction,^[53] the structure was solved by direct methods, which yielded the positions of all of the non-hydrogen atoms in the asymmetric unit. The hydrogen atoms, all of which are in phenyl groups, were placed at calculated positions and refined as riders, with isotropic displacement parameters set to 1.2-times the equivalent isotropic displacement parameters of their respective parent carbon atoms. All non-hydrogen atoms were refined anisotropically, but it was necessary to apply both rigid bond restraints and restraints to isotropic behavior to the anisotropic displacement parameters of the carbon atoms. The isotropic restraints had one-quarter the relative weight of the rigid bond restraints. The heavier atoms were refined freely.

In all, 397 parameters were adjusted to all 4437 unique data (used as F_o^2) and to 288 restraints in the full-matrix least-squares calculation, giving an observation-to-parameter ratio of 11.9:1. The final residuals are shown in Table 1.

The diffraction data were weak, with mean $I/\sigma(I) = 1.45$ in the data set before averaging of equivalents. Only 16% of the data had $I > 3\sigma(I)$. Consequently, the standard uncertainties in the derived bond distances and angles are high, and we emphasize that it would not be useful to try to derive conclusions beyond the connectivity from this structure determination.

As already mentioned, the results reported here are based on data without correction for absorption. We also performed a separate refinement of the structure with data that had been treated with an *a posteriori* calculated absorption correction.^[54] The residual R_1 was found to be lowered by only slightly more than 0.01, and it was still necessary to apply restraints to the anisotropic displacement parameters of the carbon atoms to avoid having the large majority of them emerge nonpositive definite. The results of this second refinement are available from the authors upon request. Selected bond lengths and angles are given in Table 4.

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