Synthesis, Characterisation and Reactivity towards Pd^{II} and Pt^{II} of *ortho*-, *meta*- and *para*-Xylyl-Based Phosphorus-Containing Macrocycles

Lluis Escriche,*[a] José Antonio Muñoz,[a] Raikko Kivekäs,[b] Reijo Sillampää,[c] and Jaume Casabó[a]

Keywords: Macrocycles / Palladium, Platinum / S ligands / Phosphanes

The new *meta*- and *para*-xylyl-based phosphadithiamacrocycles 6-phenyl-6-phospha-3,9-dithiabicyclo[9,3,1]pentadeca-1(15),12,14-triene (L2) and 6-phenyl-6-phospha-3,9-dithiabicyclo[9,2,2]pentadeca-1(13),12,14-triene (L3) have been synthesised and characterised. The reactivity of these ligands and the previously described *ortho*-xylyl macrocycle 6-phenyl-6-phospha-3,9-dithiabicyclo[9,4,0]pentadeca-1(11),12,14-triene (L1) with $[PdCl_2(cod)]$ and $K_2[PtCl_4]$ has been studied. $[MCl_2(L)]$ complexes have been obtained and characterised by NMR spectroscopy. X-ray structural analyses have been carried out in the case of $[PdCl_2L2]\cdot CH_3CN$ (**2·CH$_3$CN**) and $[PdCl_2L3]$ (**3**). In both compounds the Pd^{II} ion adopts a slightly distorted square-planar coordination defined by one *S*-thioether, the P-phosphane atoms of the ligand and two chlorine atoms, which are oriented in a mutual *cis* position, whereas the second *S*-thioether atom of the ligand remains uncoordinated. According to the spectroscopic data, the same coordination mode is found for the Pt^{II} complexes.

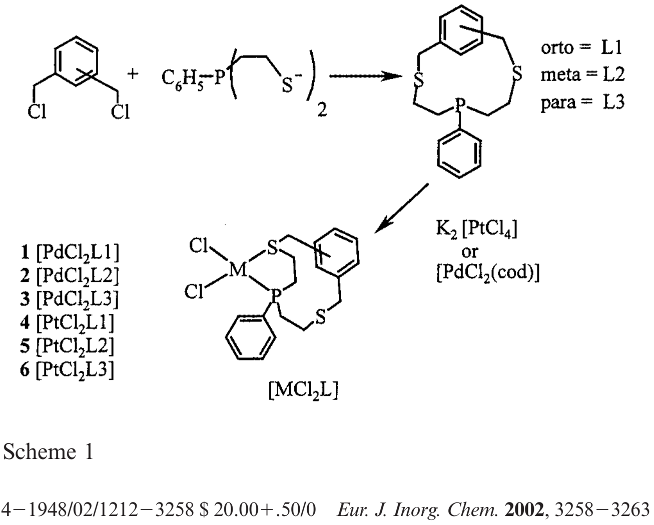
Introduction

The synthesis and chemical properties of phosphamacrocycles are less developed and studied than those of their oxygen or nitrogen equivalents.[1] This is partially due to the air-sensitivity of the reagents used in their preparations and problems in isolating the final products, especially in the case of homoleptic polyphosphamacrocycles,[2] which are usually obtained by template methods.[3] Phosphathiamacrocycles are more accessible as free ligands and several examples can be found in the literature.[4–6] Generally, the interest in asymmetric phosphorus-sulfur donor ligands, which has recently been reviewed,[7] is focused mainly towards their ability to act as hemilabile ligands and their potential use in catalytic processes.[8] Other interesting possibilities are found when these P–S donor systems are integrated in macrocyclic systems, such as the documented ability of their phosphoryl[9,10] and thiophosphoryl[11] derivatives to interact selectively with ionic species, thus acting as chemical sensors for anions.

As part of our work in this field, we report here the synthesis of the new xylyl-based phosphadithiamacrocycles 6-phenyl-6-phospha-3,9-dithiabicyclo[9,3,1]pentadeca-1(15),12,14-triene (L2) and 6-phenyl-6-phospha-3,9-dithiabicyclo[9,2,2]pentadeca-1(13),12,14-triene (L3), and the reactions of these compounds and the previously described 6-phenyl-6-phospha-3,9-dithiabicyclo[9,4,0]pentadeca-1(11),12,14-triene (L1),[12] with $[PdCl_2(cod)]$ and $K_2[PtCl_4]$.

Results and Discussion

The ligands L2 an L3 were obtained by reaction of 3-phenyl-3-phosphapenta-1,5-dithiolate (generated in situ)



Scheme 1

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[a] Departament de Química, Universitat Autònoma de Barcelona
08193 Bellaterra, Barcelona, Spain
Fax: (internat.) + 34-93/581-2497
E-mail: lluis.escriche@uab.es
[b] Department of Chemistry, University of Helsinki, Finland,
P. O. Box 55, 00014 Helsinki, Finland
[c] Department of Chemistry, University of Jyväskylä,
40351 Jyväskylä, Finland

and the appropriate α,α′-dichloro-xylene (Scheme 1) in similar conditions to those described for the synthesis of L1.[12] The yields of L2 and L3 (17% and 15%, respectively) were lower than that reported for L1 (23%), which reflects the steric hindrance imposed by the *meta* and *para* substitution of the xylyl unit to obtain the [1+1] macrocyclic compound.

The $^{31}P\{^1H\}$ NMR spectra of L2 and L3 show singlet at $\delta = -23.7$ and -27.2 ppm, respectively, corresponding to the intraannular phosphorus atom. These values are similar to that previously reported for the ligand L1 ($\delta = -21.4$ ppm)[12] and other similar phosphorus-containing macrocycles.[13,24] As can be seen, there is a small, but systematic, high-field shift of the P-resonances through the *ortho*, *meta* and *para* sequence, which probably reflects the increasing interaction between the aromatic π-system of the xylene ring and the phosphorus nucleus as a consequence of the different structural requirements in this series of macrocycles.

The ^1H NMR spectra of both macrocycles exhibit a complex pattern due to the high inversion energy barrier of the phosphane group,[14] which makes the geminal methylene protons non-equivalent. In both cases the aromatic protons of the phenyl rings appear as a complex multiplet between $\delta = 7$ and 7.5 ppm, whereas the $-S-CH_2-Ar$ methylene protons appear as a doublet of doublets (AB system) centred at $\delta = 3.74$ and 3.80 ppm for L2 and L3, respectively. The two remaining methylene groups give four groups of complex signals between $\delta = 1.0$ and 2.4 ppm. This reflects a coupling between all four protons and the phosphorus atom defining an ABMNX system similar to that found in the L1 ligand[12] and in other related phosphorous-containing macrocyclic molecules,[15,24] which makes the assignment of these signals difficult

The $^{13}C\{^1H\}$ NMR spectra of L2 and L3 are similar and only show one signal for each different carbon atom in the molecule, split in some cases by P−C coupling. The $-S-C-Ar$ carbon atoms appear as a sharp singlet at $\delta =$ 35.0 and 36.6 ppm for L2 and L3, respectively, whereas the $-S-C-C-P$ carbon atoms appear as a doublet of doublets centred at $\delta = 26.0$ ($J_{P,C} = 20.3$ Hz) and 26.9 ppm ($J_{P,C} =$ 22.2 Hz) for L2, and $\delta = 25.5$ ($J_{P,C} = 18.7$ Hz) and 28.6 ppm ($J_{P,C} = 16.4$ Hz) for L3. According to literature data for the P−C(13) coupling constants[16] and the observed chemical shift of similar phosphane-containing ligands,[12,17,24] we assigned the first and second doublets to the carbon atoms located in the α- and β-positions, respectively, with respect to the phosphorus atom.

The Pd^{II} complexes $[PdCl_2L1]$ (**1**), $[PdCl_2L2]\cdot CH_3CN$ (**2·CH$_3$CN**) and $[PdCl_2L3]$ (**3**) were obtained by reaction of equimolar amounts of $[PdCl_2(cod)]$ dissolved in methanol (**1**) or acetonitrile (**2**, **3**) and a dichloromethane solution of the corresponding ligand (Scheme 1).

The compound **1** containing the *o*-xylyl based macrocycle L1 was obtained as an amorphous yellow material highly insoluble in all tested solvents and no additional measurements could be done. However, compounds **2** and **3** are sufficiently soluble in acetonitrile to allow their slow crystallisation from the reaction mixture if large quantities of solvent are used in the synthesis. These complexes are also sufficiently soluble in DMSO to record their NMR spectra.

The $^{31}P\{^1H\}$ NMR spectra of **2** and **3** only show one signal each at $\delta = 73.7$ and 69.3 ppm, respectively, which suggests the presence of a unique species in solution. The positions of these resonances are similar to those found in other *cis*-$[PdCl_2L]$ complexes where L is a macrocyclic[18] or open-chain ligand[19] containing a phosphane-thioether donor-set of atoms coordinated to the Pd atom forming a five-membered chelate ring. It is well-known that chelating phosphanes in a five-membered ring are deshielded (by about 25−35 ppm) in the ^{31}P NMR spectrum, whereas in a six-membered ring they are shielded (by about 5−15 ppm), relative to related nonchelating ligands.[5,20]

The ^1H NMR spectra of both compounds are significantly more complex than those of the corresponding ligands, especially between $\delta = 0.3$ and 3.5 ppm where the number of broad signals seems to indicate that all eight $-S-CH_2-CH_2-P-$ protons become nonequivalent. The region between $\delta = 3.7$ and 5.0 ppm, where the $-S-CH_2-Ph-$ methylene proton resonances appear, is more informative regarding the coordinating behaviour of these macrocycles. Complex **2** shows two pairs of doublets in this area, indicating the presence of four nonequivalent protons (Figure 1b). The first high-field pair of doublets has an average position ($\delta = 3.87$ ppm) similar to that found in the free ligand ($\delta =$ 3.74 ppm), and the same coupling constant ($J_{H,H} =$ 13.8 Hz), although the chemical shift difference between the centre of gravity of both doublets increases from 0.08 ppm in L2 to 0.18 ppm in **2** (Figure 1a). The second pair of doublets ($J_{H,H} = 13.8$ Hz) is centred at $\delta = 4.51$ ppm with a $\Delta\delta$ value of 0.59 ppm. This situation is similar for **3**, although a more complex spectrum is obtained. This is a result of the small difference in the chemical shift of three of the four doublets, which appear between $\delta = 3.84$ and 4.02 ppm. To clarify this situation we performed a simulation of the above-mentioned spectra. Figure 1d and 1c show the experimental spectrum and the spectrum fitted with the gNMR simulation software,[21] respectively, for **3** in this region. The coincidence between them permits the calculation of the values of δ and the coupling constants for both pairs of doublets, which are centred at $\delta = 4.22$ ppm ($\Delta\delta =$ 0.59 ppm, $J_{H,H} = 12.4$ Hz) and $\delta = 3.97$ ppm ($\Delta\delta =$ 0.06 ppm, $J_{H,H} = 11.7$ Hz). As observed for **2**, the position and the appearance of the first high-field pair of doublets of **3** is similar to that found in free L3 ($\delta = 3.81$ ppm, $\Delta\delta =$ 0.07 ppm). These data indicate a loss of symmetry in ligands L2 and L3 when they coordinate to the Pd^{II} ion, making the two $-S-CH_2-Ph$ methylene groups nonequivalent. The fact that one of these CH_2 groups appears centred at a similar chemical shift to the free ligand in both complexes, whereas the other, more deshielded, shows a significant increase in the $\Delta\delta$ value between the two geminal protons suggests that only one of the *S*-thioether atoms is involved in coordination to the Pd^{II} atom. The structural information provided by the NMR spectra of **2** and **3** indicates that the behaviour of L2 and L3 as ligands with the Pd^{II} cation implies the simultaneous coordination of one *S*-thioether and the P-phosphane atoms, forming a five-membered chelate ring and leaving the remaining *S*-thioether atom uncoordinated.

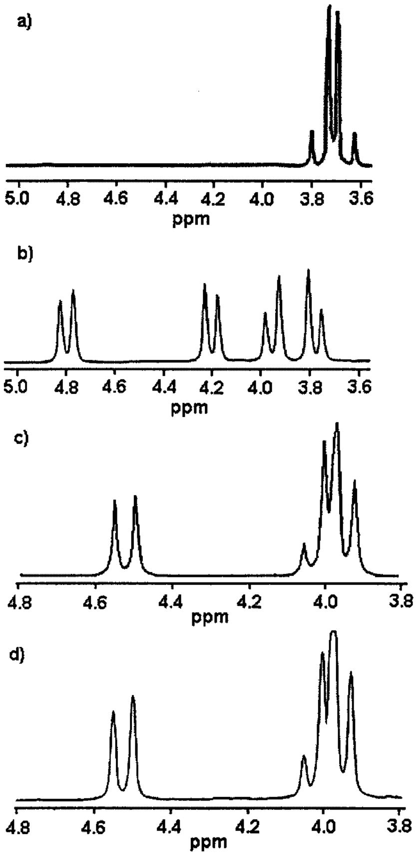

Figure 1. ^1H NMR spectra showing the -S$-$CH$_2$-Ar proton signals corresponding to: (a) the free ligand L2, (b) complex **2·CH$_3$CN**, (c) the simulation obtained with the gNMR software for **3** and (d) the complex **3**

The Pt^{II} complexes [PtCl$_2$L1] (**4**), [PtCl$_2$L2] (**5**) and [PtCl$_2$L3] (**6**) were obtained in a similar manner to that described for the Pd^{II} complexes using nitromethane solutions of K$_2$[PtCl$_4$] as starting material. These complexes are significantly less soluble than their Pd^{II} equivalents. The $^{31}P\{^1H\}$ NMR spectra of **5** and **6** show a singlet, with satellites corresponding to the ^{195}Pt-^{31}P coupling, at δ = 46.4 ppm ($J_{Pt,P}$ = 3583 Hz) and δ = 41.2 ppm ($J_{Pt,P}$ = 3674 Hz), respectively. These values are similar to those found in related [*cis*-PtCl$_2$(P$-$S)] complexes where the P$-$S ligand forms a five-membered chelate ring.[18-20,22] The ^1H NMR spectra of both compounds show the same pattern as those recorded for **2** and **3**. Taking these data into account, it can be concluded that the platinum complexes **5** and **6** are isostructural with the Pd complexes **2** and **3**.

The X-ray diffraction analysis of **2·CH$_3$CN** and **3** confirms these structural deductions. The ORTEP diagrams for **2** and **3** are shown in Figure 2 and 3, respectively. Crystallographic data for both structures are listed in Table 1, and selected bond lengths and angles are summarised in Table 2. The coordination geometry around the Pd atom in both complexes is a slightly distorted square-plane defined by one *S*-thioether, the P-phosphane atoms of the ligand and two chlorine atoms, which are oriented in a mutual *cis* position. The distortion from ideal geometry around the Pd metal ions is evidenced by the P$-$Pd$-$S1 angles [87.44(5)° and 87.79(6)° for **2·CH$_3$CN** and **3** respectively]; this distortion can be attributed to the bite angle of the chelating ligand. In both complexes, the two Pd$-$Cl distances [2.3851(12) Å and 2.3118(14) Å for **2**, 2.3874(18) Å and 2.3094(18) Å for **3**] differ significantly. The Pd$-$Cl distance *trans* to the phosphorus atom is larger, reflecting the stronger *trans* effect of the phosphorus ligand atom relative to sulfur. The values of these Pd$-$Cl distances and the Pd$-$P and Pd$-$S distances lie in the same range as those found in related *cis*-[PdCl$_2$L] compounds, where L is a *P,S*-chelating ligand.[18,19,23] An interesting feature of the L3 ligand skeleton in **3** is the marked distortion observed around the *para*-substituted xylene ring as seen by the significant displacement of the methylene carbon atoms C1 and C8 out of the plane defined by the aromatic ring [0.32(1) Å and 0.40 (1) Å, respectively]. This fact reflects the steric constraint imposed on this ligand by the *P,S*-chelate ring

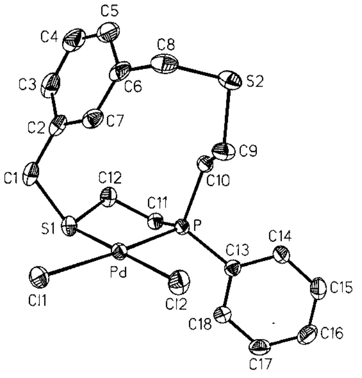

Figure 2. Perspective view of the complex unit of **2·CH$_3$CN** showing 30% displacement ellipsoids; hydrogen atoms are omitted for clarity

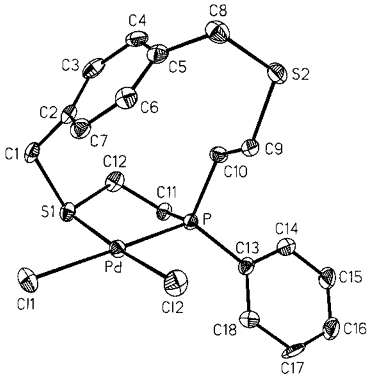

Figure 3. Perspective view of **3** showing 30% displacement ellipsoids; hydrogen atoms are omitted for clarity

formation, which forces the xylene unit to interact with the aliphatic chain.

Table 1. Crystallographic data for **2** and **3**

	2·CH_3CN	**3**
Chemical formula	$C_{20}H_{24}Cl_2$ NPPdS_2	$C_{18}H_{21}Cl_2PPdS_2$
M	550.79	509.74
Crystal colour	Yellow	Yellow
Crystal dimensions/mm	0.26 × 0.22 × 0.18	0.20 × 0.14 × 0.06
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$C2/c$ (no.15)
a (Å)	8.256(2)	20.100(4)
b (Å)	27.222(4)	13.289(2)
c (Å)	10.884(2)	15.582(2)
β (°)	112.005(14)	108.953(11)
U (Å^3)	2267.9(8)	3936.4(11)
Z	4	8
T (°C)	23	21
λ (Å)	0.71069	0.71069
D_c (g·cm^{-3})	1.613	1.720
μ (cm^{-1})	13.15	15.06
*R*1[a]	0.0363	0.0427
wR [b]	0.0706	0.0766

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

Table 2. Selected bond lengths (Å) and angles for compounds **2** and **3**

	2·CH_3CN	**3**
Pd−P	2.2182(12)	2.2248(18)
Pd−S(1)	2.2654(13)	2.2959(17)
Pd−Cl(1)	2.3851(12)	2.3874(18)
Pd−Cl(2)	2.3118(14)	2.3094(18)
S(1)−C(1)	1.836(5)	1.845(6)
S(1)−C(12)	1.827(4)	1.835(7)
S(2)−C(8)	1.819(5)	1.829(7)
S(2)−C(9)	1.810(4)	1.816(6)
P−C(10)	1.826(4)	1.827(6)
P−C(11)	1.828(4)	1.838(6)
P−C(13)	1.804(4)	1.814(6)
C(1)−C(2)	1.492(7)	1.522(9)
C(8)−C(Ar)*[a]	1.506(7)	1.494(9)
P−Pd−S(1)	87.44(5)	87.79(6)
P−Pd−Cl(2)	90.64(5)	91.75(7)
S(1)−Pd−Cl(2)	177.29(5)	175.19(8)
P−Pd−Cl(1)	174.85(5)	174.82(7)
S(1)−Pd−Cl(1)	87.43(5)	87.37(6)
Cl(2)−Pd−Cl(1)	94.50(5)	93.22(7)
C(12)−S(1)−C(1)	102.8(2)	102.1(3)
C(12)−S(1)−Pd	106.94(15)	105.7(2)
C(1)−S(1)−Pd	106.12(16)	104.9(2)
C(9)−S(2)−C(8)	101.0(2)	105.1(3)
C(13)−P−C(10)	109.4(2)	107.0(3)
C(13)−P−C(11)	107.4(2)	104.9(3)
C(10)−P−C(11)	104.6(2)	103.7(3)
C(13)−P−Pd	116.35(15)	120.5(2)
C(10)−P−Pd	112.43(14)	113.9(2)
C(11)−P−Pd	105.81(14)	105.1(2)
C(10)−C(9)−S(2)	113.2(3)	113.5(5)
C(9)−C(10)−P	115.5(3)	115.9(5)
C(12)−C(11)−P	110.1(3)	109.6(4)
C1(11)−C1(12)−S(1)	108.6(3)	109.5(4)

[a] C(Ar) = C(6) for **2·CH_3CN** and C(5) for **3**.

Conclusion

X-ray diffraction analysis of compounds **2·CH_3CN** and **3** shows an exocyclic coordination to Pd^{II} by these phosphorus- and sulfur-containing *meta*- and *para*-xylyl-based macrocyclic ligands. This coordination involves only one sulfur atom of the ligand and the P-phosphane unit. The coordination sphere is completed by two chlorine atoms. A comparative experimental and theoretical study of the ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra of compounds **2**, **3**, **5** and **6**, especially in the region in which the proton methylene resonances of the -S−CH_2-Ph unit appear, allowed us to assign the same coordination mode to the corresponding Pt^{II} compounds. The insolubility of **1** and **4** prevents further structural characterisation, but the similarity observed between the related ligands L2 and L3 in their coordinating behaviour permits us to extend it to the *o*-xylyl-based ligand L1.

Experimental Section

General Remarks: All syntheses were carried out using standard Schlenk techniques under a dry dinitrogen atmosphere. The solvents were dried by conventional methods and distilled under dinitrogen before use. Dilithium 3-phenyl-3-phosphapenta-1,5-dithiolate[24] and 6-phenyl-6-phospha-3,9-dithiabicyclo[9,4,0]pentadeca-1(11),12,14-triene (L1)[12] were prepared according literature procedures. Elemental analyses were performed using a Carlo Erba EA-1108 instrument in the Chemical Analysis Service of the Universitat Autònoma de Barcelona. All NMR spectra were run by the NMR Service of the Universitat Autònoma de Barcelona. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded using a Bruker 400 MHz AM instrument and the ^{31}P{^{1}H} NMR spectra were recorded using a Bruker 250 MHz AC instrument with chemical shifts given in ppm relative to 85% H_3PO_4. COSY and HETCOR ^{1}H-^{13}C experiments were made in order to assign the ^{1}H and ^{13}C spectra by using general standard parameters. Mass spectra were recorded using a HP298S GC/MS system.

6-Phenyl-6-phospha-3,9-dithiabicyclo[9,3,1]pentadeca-1(15),12,14-triene (L2): A solution of dilithium 3-phenyl-3-phosphapenta-1,5-dithiolate in THF (100 mL, 0.18 M) and a solution of α,α′-dichloro-*m*-xylene (3.13 g, 18 mmol) in THF (100 mL) were added simultaneously to THF (500 mL) over a period of five hours at room temperature under a dinitrogen atmosphere. The resulting mixture was then stirred for a further 48 h. The THF was removed under vacuum and the resulting oily yellow residue was treated with diethyl ether (150 mL). The LiCl precipitate was filtered off and the filtrate was evaporated to a final volume of 5 mL and chromatographed over neutral Al_2O_3. The fraction eluting with toluene/CH_2Cl_2 (1:1) was collected and evaporated to obtain L2 as a colourless oil. Yield 1.02 g, 17%. $C_{18}H_{21}PS_2$ (332.5): calcd. C 65.04, H 6.37, S 19.26; found C 64.9, H 6.2, S 19.1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66−1.84 (m, 4 H, -S−CH_2−CH_2-), 2.08−2.42 (m, 4 H, -S−CH_2−CH_2−P-), 3.71 (d, $J_{H,H}$ = 13.1 Hz, 2 H, -S−CH_2-Ph), 3.77 (d, $J_{H,H}$ = 13.1 Hz, 2 H, -S−CH_2-Ph), 7.07−7.45 (m, 9 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 26.0 (d, $J_{P,C}$ = 20.3 Hz, S−CH_2-*C*H_2−P-), 26.9 (d, $J_{P,C}$ = 22.2 Hz, −S-*C*H_2−CH_2−P-), 35.1 (-S-*C*H_2-Ph), 127.8 (-CH_2-*Ph*−CH_2-), 128.2 (s, P-Ph), 128.3 (d, $J_{P,C}$ = 7.4 Hz, P-Ph), 130.3 (-CH_2-*Ph*−CH_2-), 130.5 (-CH_2-*Ph*−CH_2-), 131.4 (d, $J_{P,C}$ = 16.6 Hz, P-Ph), 136.7 (d,

$J_{P,C}$ = 12.9 Hz, P-Ph), 137.3 (-CH$_2$-*Ph*−CH$_2$-) ppm. ^{31}P{^{1}H} NMR (101 MHz, CDCl$_3$): δ = −23.7 ppm. MS: (EI): *m*/*z* = 332 [M$^+$].

6-Phenyl-6-phospha-3,9-dithiabicyclo[9,2,2]pentadeca-1(13),12,14-triene (L3): The compound was prepared by the same procedure as for L2 using α,α′-dichloro-*p*-xylene (3.13 g, 18 mmol). Yield 0.89 g, 15%. $C_{18}H_{21}PS_2$ (332.5): calcd. C 65.04, H 6.37, S 19.26; found C 65.1, H 6.3, S 19.0. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.98−1.42 (m, 4 H, -S−C*H*$_2$−CH$_2$-), 2.32 (m, 4 H, -S−CH$_2$−C*H*$_2$−P-), 3.77 (d, $J_{H,H}$ = 13.1 Hz, 2 H, -S−C*H*$_2$-Ph), 3.84 (d, $J_{H,H}$ = 13.1 Hz, 2 H, -S−C*H*$_2$-Ph), 7.12−7.45 (m, 9 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 25.5 (d, $J_{P,C}$ = 18.7 Hz, S−CH$_2$-*C*H$_2$−P-), 28.7 (d, $J_{P,C}$ = 16.4 Hz, -S-*C*H$_2$−CH$_2$−P-), 36.6 (-S-*C*H$_2$-Ph), 128.2 (d, $J_{P,C}$ = 4.7 Hz, P-Ph), 128.4 (s, P-Ph), 130.4 (-CH$_2$-*Ph*−CH$_2$-), 131.8 (d, $J_{P,C}$ = 18.7 Hz, P-Ph), 136.6 (-CH$_2$-*Ph*−CH$_2$-), 136.9 (d, $J_{P,C}$ = 16.4 Hz, P-Ph) ppm. ^{31}P{^{1}H} NMR (101 MHz, CDCl$_3$): δ = −27.2. MS (EI): *m*/*z* = 332 [M$^+$].

[PdCl$_2$L1] (1): A solution of L1 (50 mg, 0.15 mmol) in dichloromethane (5 mL) was slowly added to a solution of [PdCl$_2$(cod)] (43 mg, 0.15 mmol) in methanol (10 mL). The yellow complex obtained was filtered off, washed with diethyl ether and vacuum dried. Yield 0.057 g, 74%. $C_{18}H_{21}Cl_2PPdS_2$ (509.8): calcd. C 42.53, H 4.17, S 12.59; found C 42.3, H 4.1, S 12.3.

[PdCl$_2$L2]·CH$_3$CN (2·CH$_3$CN): A solution of L2 (230 mg, 0.69 mmol) in dichloromethane (3 mL) was slowly added to a solution of [PdCl$_2$(cod)] (198 mg, 0.69 mmol) in acetonitrile (200 mL). The resulting mixture was refluxed for 48 h and cooled down slowly to room temperature. A yellow crystalline material suitable for X-ray diffraction analysis was filtered off, washed with diethyl ether and vacuum dried. Yield 0.266 g, 70%. $C_{20}H_{24}Cl_2NPPdS_2$ (562.9): calcd. C 43.72, H 4.41, N 2.55, S 11.65; found C 43.6, H 4.3, N 2.5, S 11.5. ^{1}H NMR [400 MHz, (CD$_3$)$_2$SO]: δ = 0.95−3.44 (m, 8 H, -S−C*H*$_2$−C*H*$_2$−P), 3.78 (d, $J_{H,H}$ = 13.8 Hz, 1 H, −S−C*H*$_2$-Ph), 3.96 (d, $J_{H,H}$ = 13.8 Hz, 1 H, −S−C*H*$_2$-Ph), 4.21 (d, $J_{H,H}$ = 13.1 Hz, 1 H, -S−C*H*$_2$-Ph), 4.80 (d, $J_{H,H}$ = 13.1 Hz, 1 H, −S−C*H*$_2$-Ph), 7.26−8.43 (m, 9 H, Ar) ppm. ^{13}C{^{1}H} NMR [100 MHz, (CD$_3$)$_2$SO]: δ = 24.6 (d, $J_{P,C}$ = 24.0 Hz, S-*C*H$_2$−CH$_2$-), 27.9 (s, -CH$_2$-*C*H$_2$−P-), 28.1 (s, -CH$_2$-*C*H$_2$−P-), 33.7 (d, $J_{P,C}$ = 33.3 Hz, S-*C*H$_2$−CH$_2$-), 38.6 (s, -S-*C*H$_2$-Ph), 40.7 (s, -S-*C*H$_2$-Ph), 127.1, 128.5, 128.6, 129.3, 129.9, 131.1, 131.9 132.3, 132.4, 133.26, 142.1 (Ar) ppm. ^{31}P{^{1}H} NMR [101 MHz, (CD$_3$)$_2$SO]: δ = 73.7 ppm.

[PdCl$_2$L3] (3): This compound was prepared by the same procedure as for **2** using L3 as ligand. Yield 0.270 g, 70%. $C_{18}H_{21}Cl_2PPdS_2$ (509.8): calcd. C 42.53, H 4.17, S 12.59; found C 42.2, H 4.0, S 12.4. ^{1}H NMR [400 MHz, (CD$_3$)$_2$SO]: δ = 0.33−3.25 (m, 8 H, -S−C*H*$_2$−C*H*$_2$−P), 3.84 (d, $J_{H,H}$ = 11.7 Hz, 1 H, -S−C*H*$_2$−Ph), 3.95 (d, $J_{H,H}$ = 12.4 Hz, 1 H, -S−C*H*$_2$−Ph), 4.02 (d, $J_{H,H}$ = 11.7 Hz, 1 H, -S−C*H*$_2$−Ph), 4.51 (d, $J_{H,H}$ = 12.4 Hz, 1 H, -S−C*H*$_2$-Ph), 7.32−8.75 (m, 9 H, Ar) ppm. ^{13}C{^{1}H} NMR [100 MHz, (CD$_3$)$_2$SO]: δ = 23.9 (s, -CH$_2$-*C*H$_2$−P), 26.5 (d, $J_{P,C}$ = 16.6 Hz, -S-*C*H$_2$−CH$_2$-), 28.9 (s, -CH$_2$-*C*H$_2$−P-), 34.8 (s, -S-*C*H$_2$-Ph), 36.1 (d, $J_{P,C}$ = 33.3 Hz, -S-*C*H$_2$−CH$_2$-), 42.1 (s, -S-*C*H$_2$-Ph), 127.3, 128.23, 128.55, 128.6, 130.9, 131.4, 131.8, 131.9, 132.29, 132.5, 132.8, 135.8, 137.8 (Ar) ppm. ^{31}P{^{1}H} NMR [101 MHz, (CD$_3$)$_2$SO]: δ = 69.3 ppm.

[PtCl$_2$L1] (4): A solution of L1 (100 mg, 0.30 mmol) in dichloromethane (2 mL) was slowly added to a solution of K$_2$[PtCl$_4$] (125 mg, 0.30 mmol) in nitromethane (100 mL) and the resulting mixture was refluxed for 3 h. A white precipitate of **4** mixed with KCl appeared which was filtered off, washed with water (50 mL) and diethyl ether (50 mL) and vacuum dried. Yield 0.173 g, 96%. $C_{18}H_{21}Cl_2PPdS_2$ (509.8): calcd. C 36.18, H 3.55, S 10.71; found C 35.9, H 3.5, S 10.6.

[PtCl$_2$L2] (5): A solution of L2 (190 mg, 0.57 mmol) in dichloromethane (2 mL) was slowly added to a solution of K$_2$[PtCl$_4$] (237 mg, 0.57 mmol) in nitromethane (100 mL) and the resulting mixture was refluxed for 48 h. The solvent was then removed under vacuum and the residue treated with dichloromethane (100 mL). The KCl precipitate was filtered off and the remaining solution was then evaporated to a final volume of 50 mL. A microcrystalline solid appeared, which was filtered off and recrystallised from acetonitrile. Yield 0.240 g, 70%. $C_{18}H_{21}Cl_2PPdS_2$ (509.8): calcd. C 36.18, H 3.55, S 10.71; found C 36.0, H 3.5, S 10.7. ^{1}H NMR [400 MHz, (CD$_3$)$_2$SO]: δ = 0.71−3.53 (m, 8 H, -S−C*H*$_2$−C*H*$_2$−P), 3.74 (d, $J_{H,H}$ = 13.4 Hz, 1 H, -S−C*H*$_2$-Ph), 3.90 (d, $J_{H,H}$ = 13.4 Hz, 1 H, -S−C*H*$_2$-Ph), 4.35 (d, $J_{H,H}$ = 13.4 Hz, 1 H, -S−C*H*$_2$-Ph), 4.75 (d, $J_{H,H}$ = 13.4 Hz, 1 H, -S−C*H*$_2$-Ph), 7.22−8.43 (m, 9 H, Ar) ppm. ^{13}C{^{1}H} NMR [100 MHz, (CD$_3$)$_2$SO]: δ = 23.2 (d, $J_{P,C}$ = 23.1 Hz, -S-*C*H$_2$−CH$_2$-), 26.5 (s, -CH$_2$-*C*H$_2$−P), 28.1 (s, -CH$_2$-*C*H$_2$−P-), 31.5 (d, $J_{P,C}$ = 38.8 Hz, S-*C*H$_2$−CH$_2$-), 37.5 (s, -S-*C*H$_2$-Ph), 38.8 (s, -S-*C*H$_2$-Ph), 125.3, 127.34, 127.52, 128.1, 128.5, 128.6, 130.3, 130.7, 130.8, 131.2, 131.37, 131.43, 140.7 (Ar) ppm. ^{31}P{^{1}H} NMR [101 MHz, (CD$_3$)$_2$SO]: δ = 46.4 (t, $J_{Pt,C}$ = 3583 Hz).

[PtCl$_2$L3] (6): This compound was prepared by the same procedure as for **5** using L3 as ligand. Yield 0.233 g, 68%. $C_{18}H_{21}Cl_2PPdS_2$ (509.8): calcd. C 36.18, H 3.55, S 10.71; found C 36.0, H 3.2, S 10.6. ^{1}H NMR [400 MHz, (CD$_3$)$_2$SO]: δ = 0.43−3.07 (m, 8 H, -S−C*H*$_2$−C*H*$_2$−P), 3.85−4.71 (m, 4 H, -S−C*H*$_2$-Ph), 7.28−8.48 (m, 9 H, Ar) ppm. ^{31}P{^{1}H} NMR [101 MHz, (CD$_3$)$_2$SO]: δ = 41.2 ppm (t, $J_{Pt,C}$ = 3674 Hz) ppm.

X-ray Crystallographic Study: Single-crystal data collections for compounds **2·CH$_3$CN** and **3** were performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite-monochromatised Mo-K_α radiation. The unit cell parameters for both compounds were determined by least-squares refinement of 25 carefully centred reflections. Both sets of data obtained were corrected for Lorentz and polarisation effects, and for dispersion. Corrections for empirical absorption (ψ scan) were also applied. A total of 4267 and 3566 reflections giving 3980 and 3462 unique reflections (R_{int}= 0.0199 and 0.0257) were collected by ω/2θ scan mode ($2\theta_{\max}$ = 50°) for **2·CH$_3$CN** and **3**, respectively.

Both structures were solved by direct methods by using the SHELXS-86 program[25] and least-squares refinements were performed using the SHELX-97 program system.[26] For both complexes non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the calculations at the fixed distances from their host atoms and treated as riding atoms using the SHELX-97 default parameters.

CCDC-193056 (**2·CH$_3$CN)** and -193057 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We acknowledge with thanks the financial assistance of Comisión Interministerial de Ciencia y Tecnología (C.I.C.Y.T.) of the Spanish Government provided by the project BQU2000−0233.

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Received May 3, 2002
[I02220]