DALTON
FULL PAPER

Formation, characterization, and structural studies of novel thiosemicarbazone palladium(II) complexes. Crystal structures of [{Pd[$C_6H_4C(Et)$=NN=C(S)NH_2]}$_4$], [Pd{$C_6H_4C(Et)$=NN=C(S)NH_2}($PMePh_2$)] and [{Pd[$C_6H_4C(Et)$=NN=C(S)NH_2]}$_2$-(μ-$Ph_2PCH_2PPh_2$)]

José M. Vila,*[a] M[a] Teresa Pereira,[a] Juan M. Ortigueira,[a] María Graña,[a] Darío Lata,[a] Antonio Suárez,[b] Jesús J. Fernández,[b] Alberto Fernández,[b] Margarita López-Torres[b] and Harry Adams[c]

[a] *Departamento de Química Inorgánica, Universidad de Santiago de Compostela, 15706 Santiago de Compostela, Spain*
[b] *Departamento de Química Fundamental e Industrial, Universidad de La Coruña, 15071 La Coruña, Spain*
[c] *Department of Chemistry, The University of Sheffield, Sheffield, UK S3 7HF*

Received 3rd August 1999, Accepted 11th October 1999

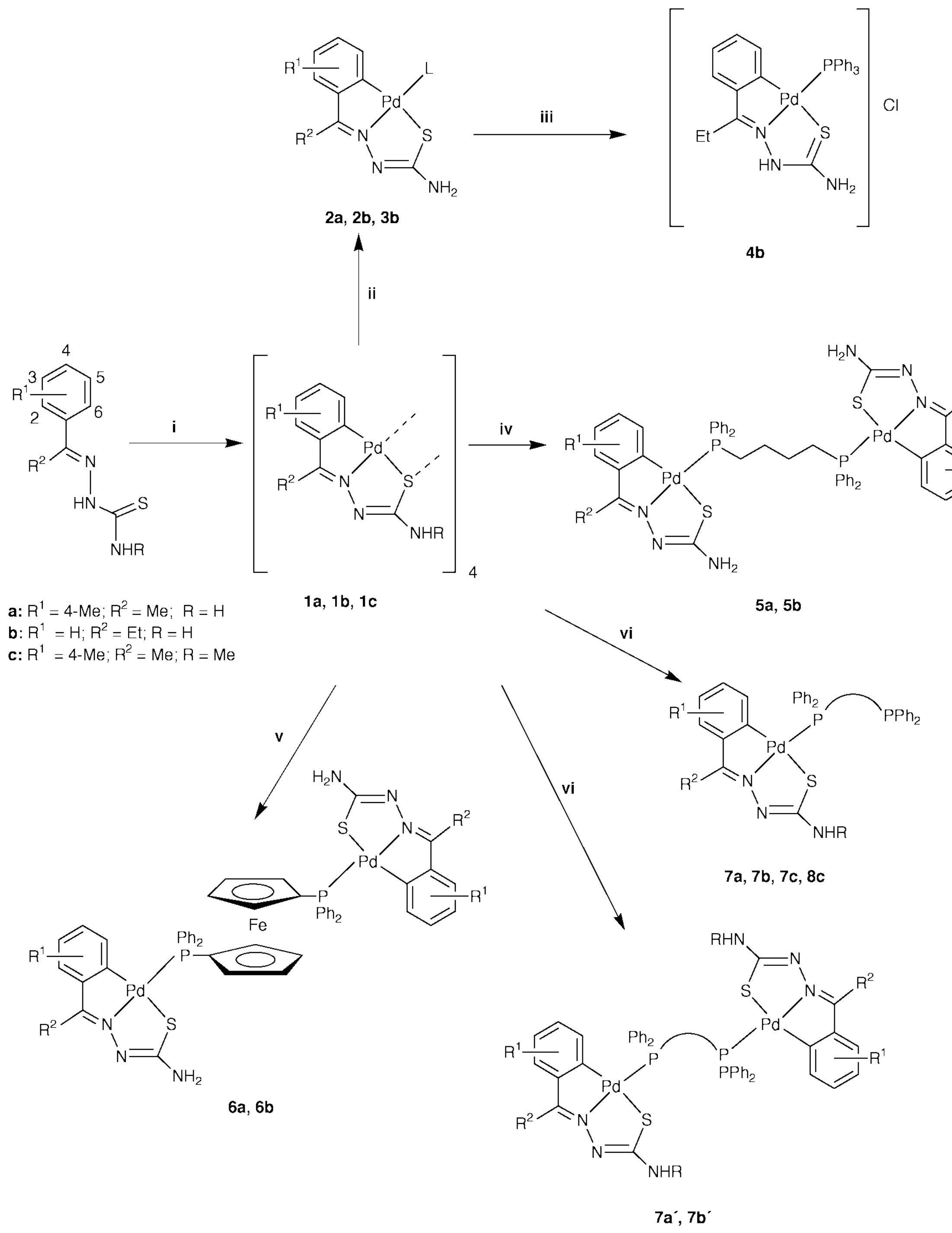
The reaction of thiosemicarbazones 4-$MeC_6H_4C(Me)$=NN(H)C(=S)NH_2 **a**, $C_6H_5C(Et)$=NN(H)C(=S)NH_2 **b** and 4-$MeC_6H_4C(Me)$=NN(H)C(=S)NHMe **c** with $K_2[PdCl_4]$ led to tetranuclear palladium(II) compounds, [{Pd[4-$MeC_6H_3C(Me)$=NN=C(S)NH_2]}$_4$], **1a**, [{Pd[$C_6H_4C(Et)$=NN=C(S)NH_2]}$_4$] **1b**, and [{Pd[4-$MeC_6H_3C(Me)$=NN=C(S)NHMe]}$_4$] **1c**; the ligands are tridentate through the [*C*, *N*, *S*] atoms and they are deprotonated at the NH group. The Pd–S$_{chelating}$ bond is sufficiently strong for the complexes to undergo reactions with nucleophiles without bond cleavage. The molecular structure of **1b** has been determined by single-crystal diffraction, confirming the formation of the tetranuclear moieties. Hydrogen bonding N · · · H and S · · · H links Pd_4 clusters into strands in the solid state. Reaction of **1a** and **1b** with phosphines gave mono- and di-nuclear species, **2a**, **2b**, **3b** and **5a**, **5b**, respectively. Treatment with 1,1′-bis(diphenylphosphino)ferrocene led to trimetallic compounds **6a** and **6b**. The molecular structure of **3b** has been determined by X-ray crystallography; dimer units are present through N · · · H hydrogen bonds. The reaction of **2b** with hydrochloric acid resulted in a 1 : 1 electrolyte, **4b**, with NH and C=S groups. Alternatively, treatment of **1a**, **1b** and **1c** with strong chelating phosphines produced mononuclear compounds with only cleavage of the Pd–S$_{bridging}$ bonds, **7a**, **7b**, **7c** and **8c** with the diphosphine monodentate; **7a** and **7b** were obtained with the dinuclear species **7a′** and **7b′**, respectively, as impurities, where the bidentate phosphine ligand bridges two metallated units. The crystal structure of one such compound, **7b′**, with a bridging bis(diphenylphosphino)methane ligand, is also described.

Introduction

Nitrogen donor ligands, such as Schiff bases and azines, are prone to undergo cyclometallation reaction with formation of a stable five-membered metalacycle containing a carbon–metal σ bond; many examples of this reaction are known[1–5] and it is important because of its potential use in, *e.g.*, regiospecific organic and organometallic synthesis[6] and in catalytic materials.[7] In previous work we have shown that tridentate [*C*,*N*,*N*] Schiff bases[8,9] and tridentate [*C*,*N*,*O*] semicarbazones[10] are easily metallated by palladium(0), palladium(II) or by platinum(II) to yield compounds with two five-membered fused rings at the metal center. When they were treated with nucleophiles, such as tertiary phosphines, breakage of the oxygen– or nitrogen–metal bond of the chelate ring results, prior to ring opening of the five-membered metalacycle upon continued reaction with the corresponding phosphine. We reasoned that use of a "softer" base, in the terms of Pearson's concept,[11] such as sulfur as a donor atom in the chelate ring would strengthen the bonding to the metal atom, for which purpose we chose terdentate [*C*,*N*,*S*] thiosemicarbazones. This is the case with monodentate as well as with long chain bidentate phosphines, where only the Pd–S$_{bridging}$ bond is cleaved; furthermore, even if strong chelating bidentate phosphines such as bis(diphenylphosphino)methane (dppm) or 1,1-bis(diphenylphosphino)ethene (vdpp) are used, the Pd–S$_{chelating}$ bond remains uncleaved giving complexes with co-ordinated dppm-*P* or vdpp-*P* sustaining our initial assumption, as we report in the present paper. Examples of cyclometallated *C*,*N*,*S* bonded ligands are scarce[12–14] and work with thiosemicarbazone ligands only results in coordination compounds. In the course of this work we have found that reaction of thiosemicarbazone ligands with $K_2[PdCl_4]$ gives new complexes of tetrameric nature with two fused chelate rings at palladium: cyclometallated thiosemicarbazone Pd_4 clusters as shown by the X-ray diffraction analysis; they are also interesting because they form polymers through hydrogen bonds. The self-assembly of molecules through hydrogen bonds is of current interest.[15–17] The crystal structures have been determined of **3b** and **7b′** and are the first examples of mononuclear and dinuclear cyclometallated palladium(II) thiosemicarbazone compounds, with monodentate and with a bridging bidentate phosphine, respectively. Both show hydrogen bonding between the molecular units to give dimers in the former case, and a one-dimensional helicoidal polymer in the latter. The potentially beneficial,

---

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4193/



Scheme 1 (i) $K_2[PdCl_4]$–EtOH–water; (ii) for **2a**, **2b**, L = PPh_3, acetone; **3b**, $PMePh_2$, acetone; (iii) HCl(aq); (iv) $Ph_2P(CH_2)_4PPh_2$, acetone; (v) 1,1′-bis(diphenylphosphino)ferrocene, acetone; (vi) for **7a**–**c**, **7a′**, **7b′**, $Ph_2PCH_2PPh_2$, acetone, water; **8c**, $Ph_2PC(=CH_2)PPh_2$, acetone, water.

biological activity of thiosemicarbazones and of their metal complexes has been discussed,[18] a feature we are presently studying in order to develop compounds of pharmaceutical importance.

Results and discussion

The thiosemicarbazones **a**, **b** and **c** were prepared by reaction of thiosemicarbazide or 4-methylthiosemicarbazide with 4-methylaceto-phenone or propio-phenone as appropriate (see Experimental section and Table 1). The NH_2 protons in **a**, **b** gave rise to two characteristic broad resonances in the ^1H NMR spectra which were attributed to the restricted rotation of the NH_2 group about the $C(=S)NH_2$ bond axis. The NH proton shows a broad signal *ca.* δ 8–9 (**a**, **b**) and broad resonances at δ 8.61 and 7.65 (**c**). From them the new cyclometallated complexes were obtained and these are shown in Scheme 1. Preparative details, characterising microanalytical, mass spectra, IR and $^{13}C-\{^1H\}$ data are in the Experimental section, $^{31}P-\{^1H\}$ and ^1H NMR data in Table 1. Treatment of a suspension of potassium tetrachloropalladate in ethanol–water with the corresponding thiosemicarbazone ligand gave clear solutions from which complexes $[\{Pd[4-MeC_6H_3C(Me){=}NN{=}C(S)NH_2]\}_4]$, **1a**, $[\{Pd[C_6H_4C(Et){=}NN{=}C(S)NH_2]\}_4]$ **1b**, and $[\{Pd[4-MeC_6H_3C(Me){=}NN{=}C(S)NHMe]\}_4]$ **1c** were isolated as yellow air-stable solids, with the ligand in the *E*,*Z* configuration. The products were characterised by elemental analysis (C, H and N) and the mass spectrum (FAB) showed a peak at *m*/*z* 1247 (**1a**, **1b**) and 1295 (**1c**) for the molecular ion whose isotopic composition suggests a tetranuclear complex of formula $C_{40}H_{44}N_{12}Pd_4S_4$ (**1a**, **1b**) and $C_{44}H_{52}N_{12}Pd_4S_4$ (**1c**) in each case. This seems to be the trend for these and other related tetranuclear compounds of tridentate

Table 1 The ^{31}P^a and ^{1}H^b NMR Data^c

		^{1}H	
Compound	^{31}P	Aromatic	Others
a		7.60 [d, 2 H, H^2, H^6, 8.2^d]	8.80 [br, 1 H, NH]
		7.21 [d, 2 H, H^3, H^5, 8.2^d]	6.9 [br, 1 H, NH$_2$]
			6.4 [br, 1 H, NH$_2$]
			2.38 [s, 3 H, Me]
			2.28 [s, 3 H, Me]
1a		7.28 [s, 1 H, H^5]	5.2 [br, 2 H, NH$_2$]
		6.67 [d, 1 H, H^3, 7.2^d]	2.32 [s, 3 H, Me]
		6.57 [d, 1 H, H^2, 7.2^d]	1.76 [s, 3 H, Me^e]
2a	36.8 [s]	6.95 [d, 1 H, H^2, 7.6^d]	4.9 [br, 2 H, NH$_2$]
		6.65 [d, 1 H, H^3, 7.6^d]	2.33 [s, 3 H, Me]
		6.05 [d, 1 H, H^5, 4.5^f]	1.71 [s, 3 H, Me^e]
5a^g	34.4 [s]	6.91 [d, 1 H, H^2, 7.7^d]	6.6 [br, 2 H, NH$_2$]
		5.97 [d, 1 H, H^5, 3.7^f]	1.60 [s, 3 H, Me^e]
6a^h	27.0 [s]	6.96 [d, 1 H, H^2, 7.3^f]	5.1 [br, 2 H, NH$_2$]
		6.67 [d, 1 H, H^3, 7.3^d]	2.34 [s, 3 H, Me]
		5.96 [d, 1 H, H^5, 4.4^d]	1.74 [s, 3 H, Me^e]
b		7.70–7.41m	8.9 [br, 1 H, NH]
			7.2 [br, 1 H, NH$_2$]
			6.6 [br, 1 H, NH$_2$]
			2.74 [q, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$, 7.7^d]
			1.21 [t, 3 H, $\mathrm{CH}_2\mathrm{C}\mathit{H}_3$, 7.7^d]
1b		7.48 [d, 1 H, H^5, 7.2^d]	5.1 [br, 2 H, NH$_2$]
		6.93 [t, 1 H, H^3, 7.2^d]	2.74 [dq, 1 H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$, 7.6^d, 12.6^i]
		6.84 [t, 1 H, H^4, 7.2^d]	1.76 [dq, 1 H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$, 7.6^d, 12.6^i]
		6.62 [d, 1 H, H^2, 7.2^d]	0.96 [t, 3 H, $\mathrm{CH}_2\mathrm{C}\mathit{H}_3$, 7.6^d]
2b	36.6 [s]	7.06 [dd, 1 H, H^2, 7.5^d, 0.9^j]	4.8 [br, 2 H, NH$_2$]
		6.85 [dt, 1 H, H^3, 7.5^d, 0.7^j]	2.85 [q, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$, 7.6^d]
		6.48 [dt, 1 H, H^4, 7.5^d, 0.9^j]	1.21 [t, 3 H, $\mathrm{CH}_2\mathrm{C}\mathit{H}_3$, 7.6^d]
		6.30 [m, 1 H, H^5, 7.5^d, 0.7^j, 4.5^f]	
3b	13.3 [s]	7.07 [d, 1 H, H^2, 7.5^d]	4.9 [br, 2 H, NH$_2$]
		6.89 [t, 1 H, H^3, 7.5^d]	2.77 [q, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$, 7.5^d]
		6.64 [t, 1 H, H^4, 7.5^d]	2.13 [d, 3 H, PCH$_3$, ^3J(PH) = 9.2]
		6.45 [dd, 1 H, H^5, 7.5^d, 4.5^f]	1.22 [t, 3 H, $\mathrm{CH}_2\mathrm{C}\mathit{H}_3$, 7.5^d]
4b	38.3 [s]	7.17 [d, 1 H, H^2, 7.5^d]	9.3 [br, 1 H, NH]
		6.96 [t, 1 H, H^3, 7.5^d]	6.0 [br, 2 H, NH$_2$]
		6.62]t, 1 H, H^4, 7.5^d]	3.06 [q, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$, 7.6^d]
		6.33 [dd, 1 H, H^5, 7.5^d, 5.2^f]	1.41 [t, 3 H, $\mathrm{CH}_2\mathrm{C}\mathit{H}_3$, 7.6^d]
5b^g	34.2 [s]	7.03 [d, 1 H, H^2, 7.4^d]	6.7 [br, 2 H, NH$_2$]
		6.79 [t, 1 H, H^3, 7.4^d]	2.73 [q, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$, 7.4^d]
		6.45 [t, 1 H, H^4, 7.4^d]	1.08 [t, 3 H, $\mathrm{CH}_2\mathrm{C}\mathit{H}_3$, 7.4^d]
		6.25 [dd, 1 H, H^5, 7.4^d, 4.0^f]	
6b^h	27.4 [s]	7.07 [dd, 1 H, H^2, 7.4^d, 1.4^j]	5.1 [br, 2 H, NH$_2$]
		6.88 [t, 1 H, H^3, 7.4^d]	2.82 [q, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$, 7.3^d]
		6.52 [t, 1 H, H^4, 7.4^d]	1.23 [t, 3 H, $\mathrm{CH}_2\mathrm{C}\mathit{H}_3$, 7.3^d]
		6.45 [dd, 1 H, H^5, 7.4^d, 4.4^f]	
c		7.58 [d, 2 H, H^2, H^6, 8.3^d]	8.6 [br, 1 H, NH]
		7.20 [d, 2 H, H^3, H^5, 8.3^d]	7.7 [br, 1 H, NHMe]
			3.27 [d, 3 H, NMe, 4.9^d]
			2.38 [s, 3 H, Me]
			2.25 [s, 3 H, Me^e]
1c		7.27 [d, 1 H, H^5, 1.0^j]	5.03 [m, 1 H, NH]
		6.70 [dd, 1 H, H^3, 7.9^d, 1.0^j]	2.98 [d, 3 H, NMe]
		6.65 [d, 1 H, H^2, 7.9^d]	2.29]s, 3 H, Me]
			1.65 [s, 3 H, Me^e]
7a^k	27.6 [d]	6.86 [d, 1 H, H^2, 7.8^d]	4.9 [br, 1 H, NH$_2$]
	−23.7 [d]	6.61 [dd, 1 H, H^3, 7.8^d, 2.9^j]	3.28 [d, 2 H, PCH$_2$P]
		6.01 [m, 1 H, H^5]	2.28 [s, 3 H, Me]
			1.77 [s, 3 H, Me^e]
7a′^{k}	25.4 [s]	6.81 [d, 1 H, H^2, 6.9^d]	5.0 [br, 1 H, NH$_2$]
		6.55 [dd, 1 H, H^3, 7.9^d, 2.9^j]	3.53 [t, 2 H, PCH$_2$P]
		5.87 [m, 1 H, H^5]	1.75 [s, 3 H, Me^e]
7b^k	27.2 [d]	6.97 [dd, 1 H, H^2, 7.3^d, 1.5^j]	4.9 [br, 1 H, NH$_2$]
	−24.0 [d]	6.80 [td, 1 H, H^3, 7.32^d, 1.0^j]	3.28 [d, 2 H, PCH$_2$P]
		6.49 [td, 1 H, H^4, 7.3^d, 1.4^j]	2.76 [q, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$, 7.8^d]
		6.26 [m, 1 H, H^5]	1.21 [t, 3 H, $\mathrm{CH}_2\mathrm{C}\mathit{H}_3$, 7.8^d]
7b′^{k}	25.4 [s]	6.93 [dd, 1 H, H^2, 6.4^d, 1.5^j]	5.0 [br, 1 H, NH$_2$]
		6.78 [t, 1 H, H^3, 8.3^d]	3.82 [t, 2 H, PCH$_2$P]
		6.17 [m, 1 H, H^5]	1.23 [t, 3 H, $\mathrm{CH}_2\mathrm{C}\mathit{H}_3$, 7.8^d]
7c^k	22.3 [d]	6.93 [d, 1 H, H^2, 7.9^d, 2.3^j]	4.8 [br, 1 H, NH]
	−30.2 [d]	6.66 [dd, 1 H, H^3, 7.9^d]	3.32 [d, 2 H, PCH$_2$P]
		6.06 [m, 1 H, H^5]	3.02 [d, 3 H, NMe, 5.0^d]
			2.37 [s, 3 H, Me]
			1.81 [s, 3 H, Me^e]

Table 1 (*Contd*)

Compound	^{31}P	^{1}H	
		Aromatic	Others
8c[k]	42.7 [d]	7.00 [d, 1 H, H^2, 7.6[d]]	5.89 [t, 2 H, PC(=C*H*$_2$)P, *N* = 30]
	−16.4 [d]	6.73 [dd, 1 H, H^3, 7.6[d], 1.3[j]]	4.8 [br, 1 H, NH]
		6.29 [m, 1 H, H^5]	2.99 [d, 3 H, NMe, 5.0[d]]
			2.40 [s, 3 H, Me]
			1.90 [s, 3 H, Me[e]]

[a] In $CDCl_3$ unless otherwise stated. Measured at 100.6 MHz (*ca.* 20 °C); chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H_3PO_4. [b] In $CDCl_3$ unless otherwise stated. Measured at 250 or 300 MHz; chemical shifts (δ) in ppm (±0.01) to high frequency of $SiMe_4$. [c] Coupling constants in Hz. s, Singlet; d, doublet, dd, doublet of doublets; t, triplet; dt, doublet of triplets; q, quadruplet; dq, doublet of quadruplets; m, multiplet; br, broad. [d] ^3J(HH). [e] C(4)-Me. [f] ^4J(PH). [g] In DMSO-d^6. [h] CH$^{\text{Ferrocene}}$ at δ 4.84 (**5a**), 4.84 (**5b**) [br, 2H], 4.33 (**5a**), 4.34 (**5b**) [m, 2 H]. [i] ^2J(HH). [j] ^4J(HH). [k] **7a**, ^2J(PP) = 71, ^2J(HP) = 9.3 Hz, PC*H*$_2$P; **7a′**, ^2J(HP) = 14.8 Hz, PC*H*$_2$P; **7b**, ^2J(PP) = 73, ^2J(HP) = 9.3 Hz PC*H*$_2$P; **7b′**, ^2J(HP) = 9.8 Hz, PC*H*$_2$P; **7c**, ^2J(PP) = 71, ^2J(HP) = 75 Hz, PC*H*$_2$P; **8c**, ^2J(PP) = 65.7 Hz, *N* = 30 Hz, PC(=C*H*$_2$)P.

[*C*,*N*,*S*] ligands which have been reported recently.[13,14] This has been confirmed by the crystal structure resolution of complex **1b** (see below). The absence of the signal for the NH group in the ^{1}H NMR spectra reveals deprotonation as observed in co-ordination compounds of these ligands.[18a] Only one NH_2 resonance was observed in the complexes showing an upfield shift of *ca.* 1.5 ppm (when the spectra were recorded in DMSO-d$_6$ the signal showed a downfield shift due to hydrogen bonding of the NH_2 protons with the solvent molecules). For complexes **1a**, **1c** metallation of the ligand is clear from the absence of the AA′BB′ system of the *para*-substituted phenyl ring; three (**1a**, **1c**) and four (**1b**) protons were assigned, respectively, for each metallated aromatic ring (see Table 1). The ^{13}C-{^{1}H} data reveal the upfield shift of the N*C*S nucleus relative to the "free" ligands, whilst the C=N, C1 and C6 resonances reveal low-field shifts for the complexes, confirming metallation of the phenyl ring.[19] In the ^{1}H NMR spectrum for **1b** the C*H*$_2$CH$_3$ resonance is a doublet of quartets.

The main bands in the IR spectra for the ligands and complexes are in the Experimental section. Those between 3500 and 3150 cm^{-1} are due to ν(N–H) of the NH_2 and NH groups, with that at 3200–3150 cm^{-1} assigned to NH; the latter disappears in the spectra of the complexes.[20] The position of the NH_2 bands in the spectra of the complexes shows this group is not co-ordinated. The ν(C=N) bands shift to lower wavenumbers upon complex formation,[21] a trend that is opposite to that observed for other thiosemicarbazone complexes where the shift is towards higher wavenumbers.[20] In the present complexes we suggest this should be attributed to the C=N moiety being part of a five-membered metalacycle, as has been found by us and others.[22] The bands involving the C=S group are often difficult to assign. Co-ordination by sulfur induces changes in the position and intensity of these bands, although the degree of ν(C=S) in each band and the proximity of phenyl ring bands in the IR spectra (especially in complexes with phosphine ligands) makes difficult a clear assignment of the vibration modes. Nevertheless, in our opinion the band at 850–820 cm^{-1} may be assigned to the ν(C=S) mode in the "free" ligands (Experimental section), even if the bands observed at *ca.* 1100–1000 cm^{-1} also contribute to the C=S stretching mode. This band disappears for the complexes, in accordance with loss of the double bond character upon deprotonation of the NH group; this is shown in the lengthening of the C–S bond in the structures of **1b** and **2c** (see below). As further proof, for compound **2b**, after protonation with aqueous HCl, a strong band appears at 841 cm^{-1}. No ν(Pd–Cl) band was found in the IR spectra of the complexes indicating absence of a chloride ligand in the co-ordination geometry of the palladium atom, contrary to the case of the related semicarbazone complexes;[10] furthermore, when **1a**, **1b** and **1c** were treated with silver perchlorate in an attempt to remove possible existing chloride ligands at palladium no precipitate of silver chloride was formed. These findings are in agreement with the mass spectroscopy prediction of a tetranuclear disposition (see above). This geometry was confirmed by the X-ray diffraction analysis, as is further described.

Reactivity of the complexes

The reaction of complexes **1a** and **1b** with nucleophiles such as amines, thallium(I) acetylacetonate, thallium(I) cyclopentadienide or tertiary phosphines is difficult when compared to the analogous palladium(II) semicarbazone compounds; we believe this is due to the presence of the stronger Pd–S bond as compared to the Pd–O bond in terms of Pearson's concept,[11] and to the tetranuclear nature of the Pd_4 cluster complexes. Only in the case of tertiary phosphines was the reaction successful as we report here. Thus, treatment of **1a** and **1b** with tertiary phosphines gave mono- or di-nuclear species, as appropriate, where only the bond at palladium to the S$_{\text{bridging}}$ atom was cleaved. The Pd–S$_{\text{chelating}}$ bond of the tridentate thiosemicarbazone ligands remains, even when a large excess of monophosphine or diphosphine was used; in the latter case stabilisation caused by the chelate effect of the bidentate phosphine did not promote Pd–S$_{\text{chelating}}$ bond cleavage. This behavior is in contrast with that shown by semicarbazone ligands, in related cyclometallated palladium(II) complexes, where the Pd–O bond was easily cleaved by the phosphine.[10] Some examples are given here with PPh_3, $PMePh_2$, $Ph_2P(CH_2)_4PPh_2$ (dppb) and 1,1′-bis(diphenylphosphino)ferrocene (dppf). Thus, when **1a** and **1b** were treated with the corresponding phosphine in 1 : 4 or in 1 : 2 molar ratio, as appropriate, the compounds [Pd{4-MeC$_6$H$_3$-C(Me)=NN=C(S)NH$_2$}(PPh$_3$)] **2a**, [Pd{C$_6$H$_4$C(Et)=NN=C(S)-NH$_2$}(L)] (L = PPh$_3$ **2b** or PMePh$_2$ **3b**), [Pd{4-MeC$_6$H$_3$-C(Me)=NN=C(S)NH$_2$}$_2$(L–L)] (L–L = dppb **5a** or dppf **6a**), [Pd{C$_6$H$_4$C(Et)=NN=C(S)NH$_2$}$_2$(L–L)] (L–L = dppb; **5b** or dppf **6b**) were obtained as pure air-stable solids, which were fully characterised (see Experimental section and Table 1). The ^{1}H NMR spectra showed the H5 resonance was shifted to lower frequency and coupled to the phosphorus nucleus (this coupling was not observable for complex **5a**). The C=S, C=N, C1 and C6 resonance signals in the ^{13}C-{^{1}H} spectra appeared shifted, as discussed above. The ^{31}P resonance was a singlet signal for **5a**, **5b**, **6a**, and **6b**, in accordance with centrosymmetric compounds;[23] the chemical shift values are consistent with a phosphorus *trans* to nitrogen geometry.[24,25]

Reaction of complex **2b** with concentrated hydrochloric acid gave **4b** as a 1 : 1 electrolyte, as shown by electric conductivity data, which was fully characterised (Experimental section and Table 1). The most noticeable feature of this compound is that protonation occurs at the NC(=S) nitrogen atom as is shown by a broad resonance at δ 9.3 in the ^{1}H NMR spectrum, and a band assignable to the ν(C=S) mode at 841 cm^{-1} (see above).

In view of the results discussed above we sought to develop the chemistry of the tetranuclear compounds with strong chelating phosphines such as the small bite dppm and/or vdpp, and we would like briefly to discuss some preliminary results of these investigations. Thus, in a typical reaction **1a** and **1b** were treated with dppm in 1 : 4 molar ratio which produced yellow air-stable solids. However, even these short bite bidentate phosphines were incapable of splitting the Pd–S$_{\text{chelating}}$ bond and the products obtained were the mononuclear compounds with the thiosemicarbazone as a tridentate [*C,N,S*] ligand and with the diphosphine ligand acting as monoco-ordinate. An interesting feature is the presence of two species in each of these solids: one, the mononuclear compound where only the Pd–S$_{\text{bridging}}$ bonds were cleaved and the phosphine was bonded through one phosphorus atom, [Pd{4-MeC$_6$H$_3$C(Me)=NN=C(S)NH$_2$}(dppm-*P*)] **7a** and [Pd{C$_6$H$_4$C(Et)=NN=C(S)NH$_2$}(dppm-*P*)] **7b**; and the other, the dinuclear complex [{Pd[4-MeC$_6$H$_3$C(Me)=NN=C(S)NH$_2$]}$_2$(μ-Ph$_2$PCH$_2$PPh$_2$)], **7a′** and [{Pd[C$_6$H$_4$C(Et)=NN=C(S)NH$_2$]}$_2$(μ-Ph$_2$PCH$_2$PPh$_2$)] **7b′**. The mononuclear species were in major proportion, *ca.* 90% (calculated from the integrals of the resonances in the ^{31}P and ^{1}H NMR spectra). Separate signals were identified for both species (see Table 1). The ^{1}H NMR spectra of **7a** and **7b** showed the H5 resonance as a multiplet owing to coupling to the corresponding phenyl ring protons and to the phosphorus nucleus, this signal was strongly shifted to lower frequency with respect to the parent tetranuclear compound. The remaining signals were unequivocally assigned, as well as those for compounds **7a′** and **7b′** (Table 1). The most significant change is in the PC*H*$_2$P resonance; the protons are part of an ABXY system giving rise to an apparent doublet at δ 3.28 for **7a** and **7b**. This signal is a triplet for **7a′** and **7b′** due to two equivalent protons coupled to two equivalent phosphorus nuclei. The ^{31}P NMR spectra of **7a** and **7b** showed two doublets assigned to the two inequivalent phosphorus nuclei; the resonance of the phosphorus nucleus bonded to the metal center appears at higher frequency. A singlet in each of the ^{31}P NMR spectra was assigned for **7a′** and **7b′**, respectively, revealing the existence of equivalent phosphorus nuclei. Attempts to obtain single crystals for X-ray diffraction studies were only successful in the case of **7b**; however, surprisingly the compound which crystallised preferentially was the dinuclear compound **7b′**, *i.e.* the one in smaller proportion, *ca.* 10%. Reaction of **1a** or **1b** with more than a fourfold amount of phosphine also produced some dinuclear compound. We are currently investigating the nature of this behavior. We synthesized analogous complexes derived from **1c** in the hope that changing one of the hydrogens in the NH$_2$ group to methyl would give only the mononuclear species, maybe due to less extended hydrogen bonding, which is present at least in the solid state in **1b** and **7b′** (see below). For this we treated **1c** with dppm or vdpp in 1 : 4 molar ratio which gave compounds [Pd{4-MeC$_6$H$_3$C(Me)=NN=C(S)NHMe}(dppm-*P*)] **7c** and [Pd{C$_6$H$_4$C(Et)=NN=C(S)NHMe}(vdpp-*P*)] **8c**, as air-stable yellow solids. Characteristic microanalytical and spectroscopic data are given in the Experimental section and in Table 1. The ^{31}P and ^{1}H NMR spectra unequivocally showed that there was only one species present in each solid, *i.e.* the mononuclear complex where only the Pd–S$_{\text{bridging}}$ bonds have been cleaved giving co-ordination of the phosphine to the metal atom only through one phosphorus atom. As would be expected for **7c** and **8c** both the ^{31}P and ^{1}H NMR spectra are very similar; the most distinguishable feature among them is in the methylene and vinylidene proton regions: the former shows an apparent doublet for the protons of the ABXY spin system, whilst in the latter an apparent triplet may be observed for the proton part of the approximately AA′XX′ system, with an *N* value of 30 Hz (see Table 1).

Crystal structures of complexes 1b·0.5CH$_3$OCH$_2$CH$_2$OCH$_3$, 3b·CH$_2$Cl$_2$ and 7b′·2CH$_3$COCH$_3$

The crystal structures of the complexes are shown in Fig. 1, 3 and 6, respectively. Selected bond lengths and angles are listed in Tables 2–4.

Table 2 Selected bond distances (Å) and angles (°) for compound **1b**

Pd(1)–C(1)	1.997(7)	Pd(1)–N(1)	2.004(6)
Pd(1)–S(4)	2.302(1)	Pd(1)–S(1)	2.377(1)
Pd(2)–C(11)	2.005(7)	Pd(2)–N(4)	1.997(6)
Pd(2)–S(3)	2.2983(18)	Pd(2)–S(2)	2.3795(19)
Pd(3)–C(21)	2.014(7)	Pd(3)–N(7)	2.007(6)
Pd(3)–S(1)	2.316(2)	Pd(3)–S(3)	2.3624(19)
Pd(4)–C(31)	2.015(8)	Pd(4)–N(10)	1.994(7)
Pd(4)–S(2)	2.319(2)	Pd(4)–S(4)	2.3611(19)
S(1)–C(10)	1.790(8)	N(1)–C(7)	1.313(10)
N(1)–N(2)	1.382(8)	N(2)–C(10)	1.306(10)
N(3)–C(10)	1.304(10)	C(1)–C(6)	1.427(10)
C(6)–C(7)	1.455(10)		
C(1)–Pd(1)–N(1)	81.6(3)	C(1)–Pd(1)–S(4)	94.9(2)
N(1)–Pd(1)–S(4)	176.5(1)	C(1)–Pd(1)–S(1)	163.5(2)
N(1)–Pd(1)–S(1)	82.9(1)	S(4)–Pd(1)–S(1)	100.55(7)
C(11)–Pd(2)–N(4)	81.4(3)	C(11)–Pd(2)–S(3)	94.9(2)
N(4)–Pd(2)–S(3)	176.31(18)	C(11)–Pd(2)–S(2)	163.1(2)
N(4)–Pd(2)–S(2)	82.94(18)	S(3)–Pd(2)–S(2)	100.74(7)
C(21)–Pd(3)–N(7)	81.1(3)	C(21)–Pd(3)–S(1)	96.1(2)
N(7)–Pd(3)–S(1)	175.95(17)	C(21)–Pd(3)–S(3)	163.0(2)
N(7)–Pd(3)–S(3)	83.17(17)	S(1)–Pd(3)–S(3)	99.94(7)
C(31)–Pd(4)–N(10)	81.0(3)	C(31)–Pd(4)–S(2)	96.7(3)
N(10)–Pd(4)–S(2)	176.35(18)	C(31)–Pd(4)–S(4)	162.6(3)
N(10)–Pd(4)–S(4)	82.66(18)	S(2)–Pd(4)–S(4)	99.82(7)
C(10)–S(1)–Pd(3)	105.9(3)	C(10)–S(1)–Pd(1)	92.7(3)
Pd(3)–S(1)–Pd(1)	111.95(8)	C(7)–N(1)–Pd(1)	117.5(5)
C(6)–C(1)–Pd(1)	110.9(5)	C(1)–C(6)–C(7)	117.0(7)
N(1)–C(7)–C(6)	112.9(7)		

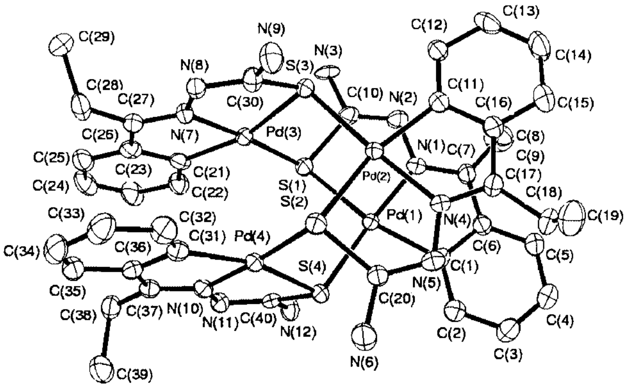


Fig. 1 Crystal structure of complex **1b** with the labelling scheme. Hydrogen atoms have been omitted for clarity.

In complex **1b**·0.5CH$_3$OCH$_2$CH$_2$OCH$_3$ the core of the molecule consists of an eight-membered ring of alternating Pd and S atoms. The remaining two sites of each square planar palladium co-ordination sphere are occupied by the aryl carbon atom and the nitrogen atom of the C=N unit. The resulting cluster has approximate C_2 symmetry; the C_2 axis is perpendicular and bisecting Pd(1)–Pd(2) and Pd(3)–Pd(4). Each of the four palladium atoms belongs to two fused five-membered chelate rings: the *C,N* metalacycle and the *N,S*-chelate moiety, as a result of bonding to a tridentate *C,N,S* ligand. The C(10)–S(1) bond distance, 1.790(8) Å, is consistent with increased single-bond character, and the C(10)–N(2) distance, 1.306(10) Å, with increased double-bond character in the deprotonated form. The Pd(1) ··· Pd(2) and Pd(3) ··· Pd(4) lengths of 3.375(9) and 3.434(9) Å, respectively, preclude any Pd–Pd interactions. In spite of the similarity of the four Pd–S$_{\text{chelating}}$ bond lengths, the Pd–S distances for Pd(1) and Pd(2) are longer than their Pd(3) and Pd(4) counterparts by *ca.* 0.02 Å [*cf.* Pd(1)–S(1) 2.377(1), Pd(3)–S(3) 2.362(1) Å]; the reverse is true for the four Pd–S$_{\text{bridging}}$ bond lengths [*cf.* Pd(1)–S(4) 2.302(1), Pd(4)–S(2) 2.319(2) Å]. In our opinion such differences are due to the intermolecular interactions. The Pd–S$_{\text{bridging}}$ bond lengths, *trans* to nitrogen, are shorter than the Pd–S$_{\text{chelating}}$ ones, *trans* to carbon, for each metal atom [*cf.* Pd(1)–S(4) 2.302(1), Pd(1)–

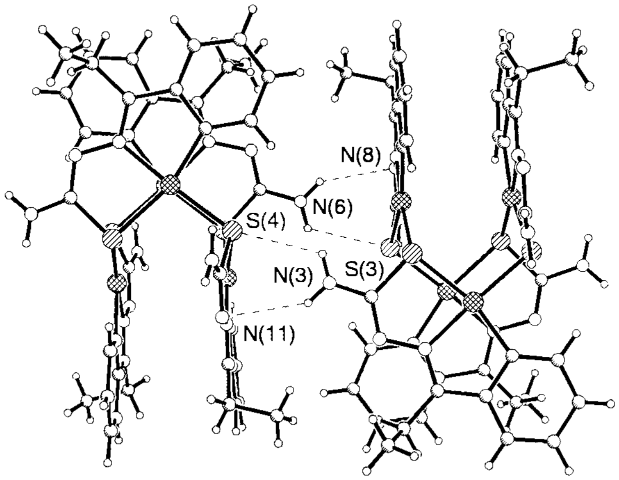


Fig. 2 A view of hydrogen bond interactions in complex **1b**.

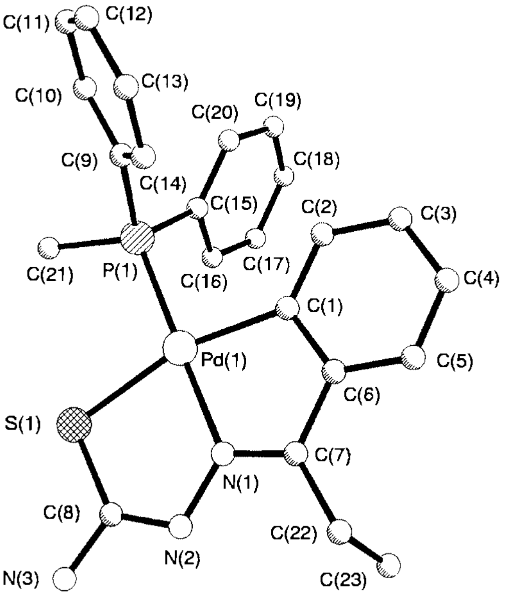


Fig. 3 Crystal structure of complex **3b**. Details as in Fig. 1.

Table 3 Selected bond distances (Å) and angles (°) for compound **3b**

Pd(1)–N(1)	2.029(4)	Pd(1)–C(1)	2.033(5)
Pd(1)–P(1)	2.2527(13)	Pd(1)–S(1)	2.3270(14)
S(1)–C(8)	1.750(5)	P(1)–C(9)	1.811(5)
P(1)–C(15)	1.820(6)	P(1)–C(21)	1.823(5)
N(1)–C(7)	1.304(6)	N(1)–N(2)	1.394(5)
N(2)–C(8)	1.319(6)	N(3)–C(8)	1.356(6)
C(1)–C(6)	1.424(7)	C(6)–C(7)	1.477(6)
Cl(1)–C(1S)	1.63(2)	Cl(2)–C(1S)	1.62(2)
N(1)–Pd(1)–C(1)	81.3(2)	N(1)–Pd(1)–P(1)	178.75(11)
C(1)–Pd(1)–P(1)	97.65(14)	N(1)–Pd(1)–S(1)	83.19(11)
C(1)–Pd(1)–S(1)	164.5(2)	P(1)–Pd(1)–S(1)	97.85(5)
C(8)–S(1)–Pd(1)	94.6(2)	C(7)–N(1)–N(2)	119.7(4)
C(7)–N(1)–Pd(1)	117.3(3)	N(2)–N(1)–Pd(1)	123.0(3)
C(8)–N(2)–N(1)	111.6(4)	C(2)–C(1)–Pd(1)	132.0(4)
C(6)–C(1)–Pd(1)	110.8(3)	C(1)–C(6)–C(7)	116.9(4)
N(1)–C(7)–C(6)	113.7(4)	N(2)–C(8)–S(1)	127.6(4)
Cl(2)–C(1S)–Cl(1)	95.4(11)		

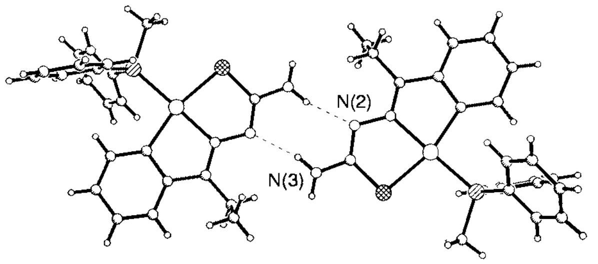


Fig. 4 Hydrogen bond interactions in complex **3b**.

S(1) 2.377(1) Å,]; this reflects the differing *trans* influence of the phenyl carbon and nitrogen atoms of the co-ordinated ligand. An intermolecular self-assembly between the tetramers is established through four hydrogen bonds by the imine group, the sulfur atoms and the amido hydrogen atoms [N(3)···N(11) 3.347(9), H(3A)···N(11), 2.61(8) Å, N(3)–H(3A)···N(11) 140.1°; N(3)···S(4) 3.408(7), H(3B)···S(4) 2.92(7) Å, N(3)–H(3B)···S(4) 115.5°; N(6)···S(3) 3.298(7) Å, H(6A)···S(3) 2.80(9) Å, N(6)–H(6A)···S(3) 116.6°; N(6)···N(8) 3.286(9), H(6B)···N(8) 2.54(9) Å, N(6)–H(6B)···N(8) 140.4°] (see Fig. 2).

The one-dimensional polymers in complex **1b** are assembled in parallel strands; within each strand two parallel sets of nearly co-planar palladium co-ordination planes along the strand are linked by perpendicular units.

The structure of complex **3b**·CH_2Cl_2 comprises a molecule with the palladium(II) atom bonded in a slightly distorted square planar co-ordination to four different donor atoms, a tridentate thiosemicarbazone through the aryl C(1) carbon, the imine N(1) nitrogen, and the thioamide S(1) sulfur atom, and to a phosphorus atom P(1) of the methyldiphenylphosphine.

The deviations from the mean plane are as follows: Pd, −0.0105, C(1), 0.0032, N(1), −0.0020, P(1), 0.0026, S(1), 0.0028 Å. The angles between adjacent atoms in the co-ordination sphere are close to the expected value of 90°, in the range 97.85(5) to 81.3(2)°, with the distortions being most noticeable in the thiosemicarbazone ligand. The angles N(1)–Pd–C(1) 81.3(2) and N(1)–Pd–S(1) 83.19(11) are less than 90° and C(1)–Pd–P(1) 97.65(14) and S(1)–Pd–P(1) 97.85(5)° are thus greater than 90°. All bond distances are within the expected range, with allowance for the strong *trans* influence of the phosphorus donor ligand, which is reflected in the Pd(1)–N(1) distance of 2.029(4) Å [*cf.* sum of the covalent radii for palladium and nitrogen, 2.01 Å[26]]. The Pd(1)–C(1) bond length [2.033(5) Å] is shorter than the expected value of 2.081 Å;[26] partial multiple-bond character has been invoked as a reasoning.[27,28] The S(1)–C(8) bond length, 1.750(5) Å, and the N(2)–C(8) length, 1.319(6) Å, are consistent with increased single and double bond character, respectively. The metalacycle Pd, C(1), C(6), C(7), and N(1) is planar with mean deviations from the plane in the range ±0.0057 Å.The molecular units are stacked in dimers held together by intermolecular hydrogen bonding between the amide hydrogen atoms and the hydrazinic nitrogen atom (see Fig. 4) with N(2)···N(3) 3.058(6) and H(3B)···N(2) 2.16(8) Å, with an N(2)–H(3B)···N(3) angle of 160(6)°. The molecular units are parallel and nearly coplanar, with the ethyl group and phenyl and methyl groups of the phosphine ligand twisted away from the molecular plane (see Fig. 4). The groups of parallel units are separated by *ca.* 65°, each group forming an angle of 30° with the *a* axis, and of 90° with the *b* axis (see Fig. 5).

The crystal structure of complex **7b′**·$2CH_3COCH_3$ shows the palladium atoms in square-planar environments with thiosemicarbazone acting as a tridentate ligand, and the phosphine ligand bonded *trans* to the iminic nitrogen atoms. All bond distances are in their typical ranges, with allowance for Pd–N bond lengthening due to the *trans* influence of the phosphine ligand.

The angles surrounding each palladium center show deviations from the ideal 90° similar to those described above for compounds **1b** and **3b**. The two metallated moieties are close to 90°, *e.g.* the palladium co-ordination planes Pd(1)C(1)N(1)S(1)P(1) and Pd(2)C(11)N(4)S(2)P(2) are at 97.2°. This we think is due to intermolecular interactions whereby the resulting dinuclear species are connected through

Table 4 Bond distances (Å) and angles (°) for compound **7b′**

P(1)–Pd(1)	2.253(2)	S(1)–Pd(1)	2.348(2)
N(1)–N(2)	1.380(9)	N(1)–Pd(1)	2.028(7)
C(1)–Pd(1)	2.046(7)	C(1)–C(6)	1.421(12)
C(6)–C(7)	1.458(12)	C(7)–N(1)	1.301(9)
C(8)–N(2)	1.304(9)	C(8)–N(3)	1.348(9)
C(8)–S(1)	1.766(9)	C(21)–P(2)	1.840(7)
C(21)–P(1)	1.850(7)		
N(1)–Pd(1)–C(1)	81.5(3)	N(1)–Pd(1)–P(1)	178.31(18)
C(1)–Pd(1)–P(1)	97.1(3)	N(1)–Pd(1)–S(1)	82.27(19)
C(1)–Pd(1)–S(1)	163.3(3)	P(1)–Pd(1)–S(1)	99.16(7)
C(6)–C(1)–Pd(1)	109.4(6)	C(1)–C(6)–C(7)	118.2(7)
N(1)–C(7)–C(6)	113.9(8)	N(2)–C(8)–S(1)	126.7(6)
N(3)–C(8)–S(1)	114.2(6)	C(7)–N(1)–Pd(1)	117.0(6)
N(2)–N(1)–Pd(1)	124.0(5)	C(8)–N(2)–N(1)	112.4(7)
C(8)–S(1)–Pd(1)	94.6(3)	C(18)–S(2)–Pd(2)	94.8(3)

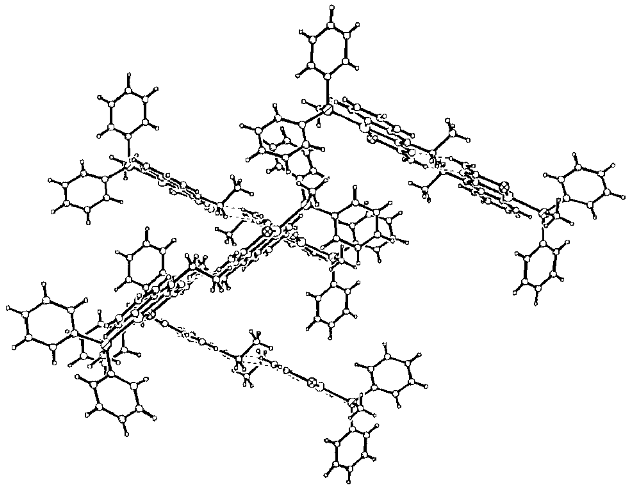


Fig. 5 Packing diagram of compound **3b** showing the angle between the parallel stacks of dimer units.

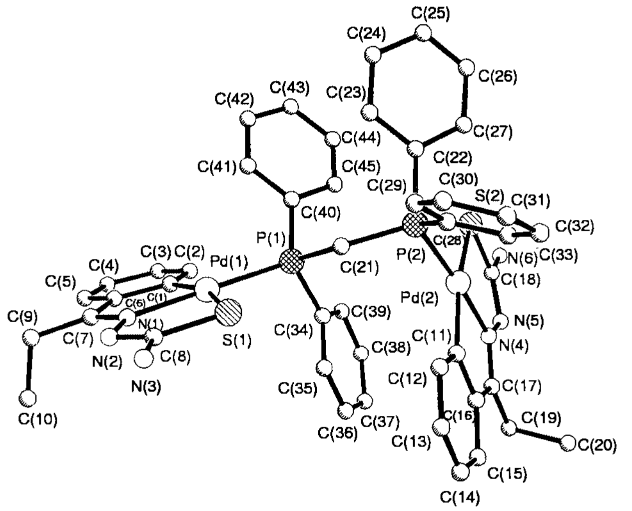


Fig. 6 Crystal structure of complex **7b′**. Details as in Fig. 1.

hydrogen bonds between the amide group and the sulfur and nitrogen atoms (N(3)–H(3B)···N(11) 3.389(8) Å, 147.6°; N(12)–H(12C)···S(1) 3.413(6) Å, 167.4°; see Fig. 7).

Thus four hydrogen bonds are established between each dinuclear molecule and two other molecules displaying a one-dimensional helicoidal polymer along the *c* axis (see Fig. 8). Additionally, two molecules of acetone are hydrogen bonded to each of the amide nitrogen atoms (N(3)–H(3C)···O(1S) 3.064(11) Å, 172.9°; N(6)–H(6A)···O(4S) 2.936(11) Å, 160.1°).

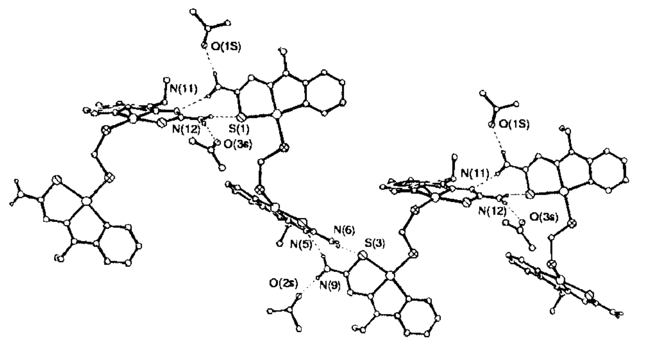


Fig. 7 A view of hydrogen bond interactions in complex **7b′**. The phenyl rings on the phosphine have been omitted for clarity.

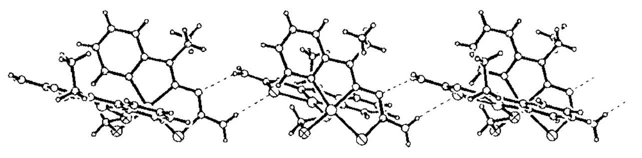


Fig. 8 Packing diagram of compound **7b′** along the *c* axis showing the strands of Pd_4 units. The phenyl rings on the phosphine have been omitted for clarity.

Experimental

Solvents were purified by standard methods.[29] Chemicals were reagent grade. Potassium tetrachloropalladate was purchased from Alfa Products, PPh_3, $PMePh_2$, dppm, dppb and dppf from Aldrich-Chemie; vdpp was prepared as described.[30] Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago using a Carlo Erba Elemental Analyzer, Model 1108. The NMR spectra were obtained as $CDCl_3$ or DMSO-d_6 solutions and referenced to $SiMe_4$ (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P-{^1H}) on Bruker WM250 and AMX-300 spectrometers. All chemical shifts were reported downfield from standards. The FAB mass spectra were recorded using a Fisons Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

Syntheses

Thiosemicarbazone 4-$MeC_6H_4C(Me)$=NN(H)C(=S)NH_2 (a). To a solution of thiosemicarbazide (0.68 g, 7.46 mmol) in ethanol (25 cm^3) 4-methylacetophenone (1 g, 7.45 mmol) and acetic acid (0.1 cm^3) were added and the mixture was heated under reflux for 4 h. After cooling to −10°C the solid formed was filtered off, washed with cold ethanol and dried *in vacuo*. IR: ν(N–H) 3412s, 3375s, 3234s, 3153s; $\delta(NH_2)$ 1617; ν(C=N) 1591s (br); ν(C=S) 849m cm^{-1}. ^{13}C-{^1H} NMR (75.48 MHz DMSO-d_6) 178.9 (C=S); 148.2 (C=N); 139.0 (C1); 134.9 (C4); 129.0 (C3, C5); 126.6 (C2, C6); 20.9, 13.9 (Me).

Thiosemicarbazones $C_6H_5C(Et)$=NN(H)C(=S)NH_2 (**b**) and 4-$MeC_6H_4C(Me)$=NN(H)C(=S)NHMe (**c**) were synthesized following a similar procedure. **b** IR ν(N–H) 3404s, 3300s, 3205s; $\delta(NH_2)$ 1614s; ν(C=N) 1601s; ν(C=S) 839m cm^{-1}; ^{13}C-{^1H} NMR (62.46 MHz $CDCl_3$) 179.2 (C=S); 153.3 (C=N); 136.2 (C1); 129.8, 128.7, 126.5 (C2, C3, C4, C5, C6); 20.4 (CH_2CH_3) and 10.7 (CH_2CH_3). **c**: IR ν(N–H) 3329s, 3260s; ν(C=N) 1616s; ν(C=S) 821m cm^{-1}.

[{Pd[4-$MeC_6H_3C(Me)$=NN=C(S)NH_2]}$_4$] 1a. To a stirred solution of potassium tetrachloropalladate (200 mg, 0.61 mmol) in water (6 cm^3) was added ethanol (40 cm^3). The fine yellow suspension of potassium tetrachloropalladate obtained was treated with 4-$MeC_6H_4C(Me)$=NN(H)C(=S)NH_2 (**a**) (140 mg, 0.67 mmol). The mixture was stirred for 48 h at room temperature. The yellow precipitate was filtered off, washed with ethanol and dried. Yield 55%. IR: ν(N–H) 3470m, 3364m;

Table 5 Crystal data for complexes **1b**·$0.5CH_3OCH_2CH_2OCH_3$, **3b**·CH_2Cl_2 and **7b′**·$2CH_3OCH_3$

	1b	**3b**	**7b′**
Molecular formula	$C_{42}H_{49}N_{12}OPd_4S_4$	$C_{24}H_{26}Cl_2N_3PPdS$	$C_{51}H_{56}N_6O_2P_2Pd_2S_2$
Molecular weight	1291.77	596.81	1123.88
T/K	143(2)	293(2)	293(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	12.0858(2)	15.366(3)	13.8547(2)
b/Å	30.0403(3)	9.174(2)	17.8565(2)
c/Å	17.6950(16)	18.525(3)	29.4984(2)
α/°			93.937(1)
β/°	108.7089(6)	104.20(2)	90.993(1)
γ/°			92.303(1)
V/Å^3	6084.90(16)	2531.6(8)	5207.02(10)
Z	4	4	4
μ/mm^{-1}	1.338	1.107	0.876
Reflections collected	25325	5653	27248
Independent reflections	10690 (R_{int} = 0.0496)	4448 (R_{int} = 0.0540)	17986 (R_{int} = 0.0449)
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0576, 0.1561	0.0500, 0.1393	0.0613, 0.1121
(all data)	0.0728, 0.1622	0.0587, 0.1468	0.1334, 0.1424

$\delta(NH_2)$ 1593s; ν(C=N) 1583s cm^{-1}. Found: C, 38.4; H, 3.7; N, 13.6; S, 10.3. Calc. for $C_{10}H_{11}N_3PdS$: C, 38.5; H, 3.6; N, 13.5; S, 10.3%.^{13}C-{^{1}H} NMR (62.46 MHz DMSO-d$_6$): δ 167.3, 166.8, 165.1 (C=S, C=N, C1); 147.5 (C6); 136.9 (C4); 133.6 (C5); 123.3, 124.2 (C2, C3); 22.2, 13.2 (Me).

The complex [{Pd[C_6H_4C(Et)=NN=C(S)NH_2]}$_4$] **1b** was obtained following a similar procedure, as a yellow solid. Yield 50%. IR: ν(N–H) 3437m, 3375s, 3350m; $\delta(NH_2)$ 1624m; ν(C=N) 1587s cm^{-1}. Found: C, 38.2; H, 3.5; N, 13.4; S, 10.2. Calc. for $C_{10}H_{11}N_3PdS$: C, 38.5; H, 3.6; N, 13.5; S 10.3%. ^{13}C-{^{1}H} NMR (62.46 MHz DMSO-d$_6$): δ 172.0 (C=S); 167.2, 166.5 (C=N, C1); 148.5 (C6); 132.6 (C5); 127.4, 125.2, 123.3 (C2, C3, C4); 20.1 (CH_2CH_3) and 11.4 (CH_2CH_3).

The complex [{Pd[4-MeC_6H_3C(Me)=NN=C(S)NHMe]}$_4$] **1c** was obtained similarly as a yellow solid. Yield 58%. IR: ν(N–H) 3420 (br) m, 3375s, 3350m; ν(C=N) 1577s cm^{-1}. Found: C, 38.2; H, 3.5; N, 13.4; S, 10.2. Calc. for $C_{11}H_{13}N_3PdS$: C, 38.5; H, 3.6; N, 13.5; S, 10.3%.

[Pd{4-MeC_6H_3C(Me)=NN=C(S)NH_2}(PPh_3)] 2a. Triphenylphosphine (42 mg, 0.16 mmol) was added to a suspension of complex **1a** (50 mg, 0.04 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h, the resulting yellow solid filtered off and dried. Yield 70%. IR: ν(N–H) 3420m, 3340m; $\delta(NH_2)$ 1601s; ν(C=N) 1580s cm^{-1}. Found: C, 58.4; H, 4.7; N, 7.2; S, 5.8. Calc. for $C_{28}H_{26}N_3PPdS$: C, 58.6; H, 4.6; N, 7.3; S, 5.6%. ^{13}C-{^{1}H} NMR (62.46 MHz DMSO-d$_6$): δ 174.1 (C=S); 166.2 (C=N); 158.5 (C1); 151.1 (C6); 137.2 (d, C5, J(PC) = 9.2); 125.9, 124.0 (C2, C3, C4); 20.2 (CH_2CH_3); 11.5 (CH_2CH_3); PPh C_i 131.8 (d, J(PC) 48.4); C_o 134.7 (d, J(PC) 13.1); C_m 128.4 (d, J(PC) 10.6 Hz) and C_p 130.8.

The complex [Pd{C_6H_4C(Et)=NN=C(S)NH_2}(PPh_3)] **2b** was synthesized following a similar procedure as a white solid. Yield 70%. IR: ν(N–H) 3462s, 3287m; $\delta(NH_2)$ 1622m; ν(C=N) 1589m cm^{-1}. Found: C, 58.5; H, 4.7; N, 7.1; S, 5.9. Calc. for $C_{28}H_{26}N_3PPdS$: C, 58.6; H, 4.6; N, 7.3; S, 5.6%. ^{13}C-{^{1}H} NMR (62.46 MHz DMSO-d$_6$) 175.2 (C=S); 165.6 (C=N), 163.7 (C1); 149.0 (C6); 136.9 (C5); 124.6, 123.8 (C2, C3, C4); 20.6 (CH_2CH_3) and 12.7 (CH_2CH_3); P-phenyl C_i 131.7 (d, J(PC) 46.7); C_o 133.8 (d, J(PC) 13.1); C_m 128.2 (d, J(PC) 10.6 Hz) and C_p 130.5.

The complex [Pd{C_6H_4C(Et)=NN=C(S)NH_2}(PMePh_2)] **3b** was synthesized analogously as a white solid. Yield 82%. IR: ν(N–H) 3458m, 3383m; $\delta(NH_2)$ 1616m; ν(C=N) 1572s cm^{-1}. Found: C, 54.0; H, 4.7; N, 8.3; S, 6.3. Calc. for $C_{23}H_{24}N_3PPdS$: C, 54.0; H, 4.7; N, 8.2; S, 6.3%.

[Pd{C_6H_4C(Et)=NN(H)C(S)NH_2}(PPh_3)]$^+$Cl$^-$ 4b. A suspension of complex **2b** (50 mg, 0.087 mmol) in ethanol (15 cm^3) was treated with two drops of concentrated hydrochloric acid (35%). The mixture was stirred for 4 h and the resulting pale yellow solid filtered off and dried. Yield 92%. Λ_M (acetonitrile, 4×10^{-4} mol L^{-1}): 95 Ω^{-1} cm^2 mol^{-1}. IR: ν(N–H) 3362m, 3213m; $\delta(NH_2)$ 1601s; ν(C=N) 1570s; ν(C=S) 841m cm^{-1}. Found: C, 54.9; H, 4.5; N, 6.9; S, 5.1. Calc. for $C_{28}H_{27}ClN_3PPdS$: C, 55.1; H, 4.5; N, 6.9; S, 5.2%.

Compounds **5a**, **6a** and **5b**, **6b** were obtained as yellow air-stable solids following a similar procedure to that for **2a** but using a complex : diphosphine 1 : 2 molar ratio.

[{Pd[4-MeC_6H_3C(Me)=NN=C(S)NH_2]}$_2$(μ-$Ph_2P(CH_2)_4PPh_2$)] **5a**. Yield 81%: IR ν(N–H) 3465m, 3350m; $\delta(NH_2)$ 1590s; ν(C=N) 1580s cm^{-1}. Found: C, 54.6; H, 4.8; N, 7.5; S, 5.9. Calc. for $C_{24}H_{25}N_3SPPd$: C, 54.9; H, 4.8; N, 8.0; S, 6.1%.

[{Pd[4-MeC_6H_3C(Me)=NN=C(S)NH_2]}$_2$(μ-$Ph_2PC_5H_4FeC_5H_4PPh_2$)] **6a**. Yield 85%. IR: ν(N–H) 3460m, 3350m; $\delta(NH_2)$ 1610m; ν(C=N) 1581s cm^{-1}. Found: C, 54.6; H, 4.7; N, 7.5; S, 5.0. Calc. for $C_{54}H_{50}FeN_6P_2Pd_2S_2$: C, 55.1; H, 4.3; N, 7.1; S, 5.4%.

[{Pd[C_6H_4C(Et)=NN=C(S)NH_2]}$_2$(μ-$Ph_2P(CH_2)_4PPh_2$)] **5b**. Yield 85%. IR: ν(N–H) 3489m, 3379s, 3304m (sh); $\delta(NH_2)$ 1591m cm^{-1}. Found: C, 54.2; H, 4.5; N, 8.1; S, 6.3. Calc. for $C_{24}H_{25}N_3PPdS$: C, 54.9; H, 4.8; N, 8.0; S, 6.1%.

[{Pd[C_6H_4C(Et)=NN=C(S)NH_2]}$_2$(μ-$Ph_2PC_5H_4FeC_5H_4PPh_2$)] **6b**. Yield 58%. IR: ν(N–H) 3470m, 3366m, 3315m; $\delta(NH_2)$ 1590s; ν(C=N) 1572s cm^{-1}. Found: C, 55.5; H, 4.5; N, 7.0; S, 5.0. Calc. for $C_{54}H_{50}FeN_6P_2Pd_2S_2$: C, 55.1; H, 4.3; N, 7.1; S, 5.4%.

[Pd{4-MeC_6H_3C(Me)=NN=C(S)NH_2}(dppm-*P*)] 7a. The diphosphine $Ph_2PCH_2PPh_2$ (60 mg, 16 mmol) was added to a suspension of complex **1c** (50 mg, 0.04 mmol) in acetone (15 cm^3). The mixture was stirred for 1 h and then water added (10 cm^3), and stirred for 4 h. The resulting yellow solid was filtered off and dried. Yield 95%. IR: ν(N–H) 3445m, 3057m; ν(C=N) 1579s cm^{-1}.

Compounds **7b**, **7c** and **8c** were obtained as yellow air-stable solids following a similar procedure to that for **7a**.

[Pd{C_6H_4C(Et)=NN=C(S)NH_2}(dppm-*P*)] **7b**. Yield 89%. IR: ν(N–H) 3448m, 3051m; ν(C=N) 1579s cm^{-1}.

[Pd{4-MeC_6H_3C(Me)=NN=C(S)NHMe}(dppm-*P*)] **7c**. Yield 85%. IR: ν(N–H) 3449m, 3052m; ν(C=N) 1581s cm^{-1}. Found: C, 60.7; H, 5.2; N, 5.9; S, 4.8. Calc. for $C_{36}H_{35}N_3P_2PdS$: C, 60.9; H, 5.0; N, 5.9; S, 4.5%.

[Pd{4-MeC_6H_3C(Me)=NN=C(S)NHMe}(vdpp-*P*)] **8c**. Yield 88%. IR: ν(N–H) 3446m, 3054m; ν(C=N) 1578s cm^{-1}. Found: C, 61.3; H, 4.9; N, 5.9; S, 4.3. Calc. for $C_{37}H_{35}N_3P_2PdS$: C, 61.5; H, 4.9; N, 5.8; S, 4.4%.

Crystal structures

Crystals of complexes **1b**, **3b** and **7b′** were mounted on a glass fiber and transferred to the diffractometer. For **1b** and **7b′** data collection was performed with a Siemens SMART charge coupled device (CCD) detector system single-crystal X-ray diffractometer using graphite monochromated Mo-Kα radiation. An absorption correction was carried out with the program SADABS ($T_{\mathrm{max}}/T_{\mathrm{min}} = 1.000/0.6121$, **1b**; 1.000/0.759, **7b′**). The structures were solved by direct methods and refined by blocked cascade least squares methods on F^2. Hydrogen atoms were included in calculated positions (except NH_2 hydrogens which were located from the Fourier-difference map) and refined in riding mode, with allowance for thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -2.137 and 1.893 e Å^{-3} near the palladium (**1b**); -0.490 and 0.738 e Å^{-3} (**7b′**). The structure solution and refinement was carried out using the program package SHELX 97.[32]

For compound **3b** three-dimensional, room temperature X-ray data were collected on a Siemens P4 diffractometer in the range $4 < 2\theta < 50°$ by the ω scan method. The 5653 reflections measured were corrected for Lorentz-polarisation effects (but not for absorption). The structure was solved by direct methods and refined by blocked cascade least squares methods on F^2. Hydrogen atoms were treated as above. Minimum and maximum final electron density -0.772 and 0.684 e Å^{-3}. Complex scattering factors were taken from the program package SHELXL 93[33] as implemented on the Viglen 486dx computer. Crystal data are given in Table 5.

CCDC reference number 186/1682.

See http://www.rsc.org/suppdata/dt/1999/4193/ for crystallographic files in .cif format.

Acknowledgements

We thank the Xunta de Galicia, Spain (Proyecto XUGA20913B96) for financial support.

References

1 I. Omae, *Organometallic-coordination Compounds*, Elsevier, Amsterdam, New York, 1986.

2 V. V. Dunina, O. A. Zalevskaya and V. M. Potapov, *Russ. Chem. Rev.*, 1984, **571**, 250.

3 G. R. Newkome, W. E. Puckett, W. K. Gupta and G. E. Kiefer, *Chem. Rev.*, 1986, **86**, 451.

4 A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403.

5 M. Pfeffer, *Recl. Trav. Chim. Pays-Bas*, 1990, **109**, 567.

6 M. Pfeffer, J. P. Sutter, M. A. Rottvel, A. de Cian and J. Fischer, *Tetrahedron*, 1992, **48**, 2440.

7 A. Bose and C. H. Saha, *J. Mol. Catal.*, 1989, **49**, 271.

8 J. M. Vila, M. Gayoso, M. T. Pereira, M. López Torres, J. J. Fernández, A. Fernández and J. M. Ortigueira, *J. Organomet. Chem.*, 1997, **532**, 171.

9 J. M. Vila, M. T. Pereira, J. M. Ortigueira, D. Lata, M. López Torres, J. J. Fernández, A. Fernández and H. Adams, *J. Organomet. Chem.*, 1998, **566**, 93.

10 J. M. Vila, M. T. Pereira, J. M. Ortigueira, M. López Torres, A. Castiñeiras, J. J. Fernández, A. Fernández and D. Lata, *J. Organomet. Chem.*, 1998, **556**, 21.

11 R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533.

12 P. Chattopadhyay, M. K. Nayak, S. P. Bhattacharyya and C. Sinha, *Polyhedron*, 1997, **16**, 1291.

13 T. Kawamoto and Y. Kushi, *Chem. Lett.*, 1992, 1057.

14 T. Kawamoto, I. Nagasawa, H. Kuma and Y. Kushi, *Inorg. Chem.*, 1996, **35**, 2427.

15 J. C. MacDonald and G. M. Whitsides, *Chem. Rev.*, 1994, **94**, 2383.

16 A. D. Burrows, C. W. Chan, M. M. Chowdhry, J. E. McGrady and D. M. P. Mingos, *Chem. Soc. Rev.*, 1995, **24**, 329.

17 A. D. Burrows, D. M. P. Mingos, A. J. P. White and D. J. Williams, *J. Chem. Soc.*, *Chem. Commun.*, 1996, 97.

18 (*a*) D. Kovala-Demertzi, A. Domopoulou, M. A. Demertzis, C. P. Raptopoulou and A. Terzis, *Polyhedron*, 1994, **13**, 1917; (*b*) D. Kovala-Demertzi, A. Domopoulou, M. A. Demertzis, J. Valdés-Martínez, S. Hernández-Ortega, G. Espinosa-Pérez, D. X. West, M. M. Salberg, G. A. Bain and P. D. Bloom, *Polyhedron*, 1996, **15**, 665.

19 J. M. Vila, M. Gayoso, M. T. Pereira, M. López-Torres, J. J. Fernández, A. Fernández and J. M. Ortigueira, *J. Organomet. Chem.*, 1996, **506**, 165.

20 T. S. Lobana, A. Sánchez, J. S. Casas, A. Castiñeiras, J. Sordo, M. S. García-Tasende and E. M. Vázquez-López, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 4289.

21 D. X. West, J. S. Ives, G. A. Bain, A. E. Liberta, J. Valdés-Martínez, K. H. Ebert and S. Hernández-Ortega, *Polyhedron*, 1997, **16**, 1995.

22 H. Onoue and I. Moritani, *J. Organomet. Chem.*, 1972, **43**, 431; H. Onoue, K. Minami and K. Nakawaga, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 3480.

23 J. M. Vila, M. Gayoso, A. Fernández, N. Bailey and H. Adams, *J. Organomet. Chem.*, 1993, **448**, 233.

24 P. S. Pregosin and R. W. Kuntz, in *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, eds. P. Diehl, E. Fluck and R. Kosfeld, Springer, Berlin, 1979.

25 J. Albert, M. Gómez, J. Granell and J. Sales, *Organometallics*, 1990, **9**, 1405; R. Bosque, J. Granell, J. Sales, M. Font-Bardía and X. Solans, *J. Organomet. Chem.*, 1994, **453**, 147; J. Albert, J. Granell, J. Sales, M. Font-Bardía and X. Solans, *Organometallics*, 1995, **14**, 1393.

26 L. Pauling. *The Nature of the Chemical Bond*, Cornell University Press, New York, 3rd edn., 1960.

27 J. M. Vila, M. Gayoso, M. T. Pereira, A. Romar, J. J. Fernández and M. Thornton-Pett, *J. Organomet. Chem.*, 1991, **401**, 385.

28 J. Selbin, K. Abboud, S. F. Watkins, M. A. Gutirérrez and F. R. Fronczek, *J. Organomet. Chem.*, 1983, **241**, 259; C. Navarro-Ranninger, I. López-Solera, A. Alvarez-Valdés, J. H. Rodríguez-Ramos, J. R. Masaguer and J. L. García-Ruano, *Organometallics*, 1993, **12**, 4104.

29 D. D. Perrin, W. L. F. Armarego and D. P. Perrin, *Purification of Laboratory Chemicals*, 2nd edn., Pergamon, Oxford, 1983.

30 I. Colquhoun and W. MacFarlane, *J. Chem. Soc.*, *Dalton Trans.*, 1982, 1915.

31 G. M. Sheldrick, SADABS. Program for empirical absorption correction of area detector data, University of Göttingen, 1996.

32 G. M. Sheldrick, SHELXL 97, University of Göttingen, 1997.

33 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

Paper 9/06276I