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Bridge cleavage of transition metal dimers by chelating S,N ligands. X-ray crystal structure of [Pd{$SPPh_2N{=}C(NH_2)NH$-S,N}(η^3-C_3H_5)]

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Abstract

Deprotonation of the *N*-thiophosphoryl compounds $Me_2P(S)N{=}C(NH_2)_2$ (HL^1), $Ph_2P(S)N{=}C(Me)(NH_2)$ (HL^2) or $Ph_2P(S)N{=}C(NH_2)_2$ (HL^3) using potassium *t*-butoxide in thf, followed by treatment with $[Rh(\mu\text{-}Cl)(\eta^4\text{-cod})]_2$ (cod = 1,5-*cis*,*cis*-cyclooctadiene), $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ or $[RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)]_2$ affords $[Rh(L^n\text{-S,N})(\eta^4\text{-cod})]$ **1**–**3**, $[Pd(L^n\text{-S,N})(\eta^3\text{-}C_3H_5)]$ **4**–**6** and $[RhCl(L^n\text{-S,N})(\eta^5\text{-}C_5Me_5)]$ **7**–**9**, respectively. The $(L^n)^-$ anions form six-membered S,N chelate rings at the metal centre, in a manner analogous with β-diketonates and imidodiphosphinates. The complexes **1**–**9** have been characterised spectroscopically and by single crystal X-ray diffraction for $[Pd(L^3\text{-S,N})(\eta^3\text{-}C_3H_5)]$ **6**. The molecular structure of **6** confirms S,N chelation of the $(L^3)^-$ anion to give a palladacycle adopting a half boat conformation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Palladium; Rhodium; Thiophosphoryl guanidines; X-ray crystal structure

1. Introduction

Imidodiphosphinate anions $[R_2P(E)NP(E')R'_2]$ (R, R′ = alkyl, aryl or alkoxy; E, E′ = O, S or Se) have received substantial attention in recent years, finding usage in applications such as metal extraction agents, NMR shift reagents and in catalytic functions [1–8]. We are currently investigating the chemistry of structurally similar phosphorus(V) derivatised guanidines and amidines $R_2P(E)N{=}C(X)(NH_2)$ (R = alkyl or aryl; E = oxygen or sulphur; X = NH_2 or alkyl). These molecules, readily available from $[R_2P(E)(NCN)]^-$ [9–16], possess an ionisable nitrogen-bound proton and have the capacity for delocalisation of the resulting uninegative charge through the π-system of the $[R_2P(E)N{=}C(X)(NH)]^-$ anion; hence they could function as E,N-bidentate ligands in a manner analogous with imidodiphosphinates. We have previously prepared *cis*-$[Pt(L^n\text{-S,N})(PR_3)_2]Cl$ (PR_3=PMe_2Ph or 1/2dppe) from *cis*-$[PtCl_2(PR_3)_2]$ and the potassium salts of $Me_2P(S)N{=}C(NH_2)_2$ (HL^1), $Ph_2P(S)N{=}C(Me)(NH_2)$ (HL^2) or $Ph_2P(S)N{=}C(NH_2)_2$ (HL^3) (Fig. 1), in which $(L^n)^-$ forms six membered S,N chelate rings at platinum(II) [17]. This reactivity is comparable to that of $[(EPPh_2)_2N]^-$ (E = S or Se), which generates *cis*-$[Pt\{(EPPh_2)_2N\text{-E,E'}\}(PR_3)_2]Cl$ [18,19], although the combination of sulphur and nitrogen donor atoms supplied by $(L^n)^-$ is unmatched amongst imidodiphosphinates. Structural similarities are also evident between HL^n and 1-amidino-2-thioureas $RNHC(S)\text{-}N{=}C(NH_2)_2$ (R=H or alkyl), the anions of which form S,N chelates [20] and, in a recent example, act as scaffolds for heterometallic cage synthesis [21].

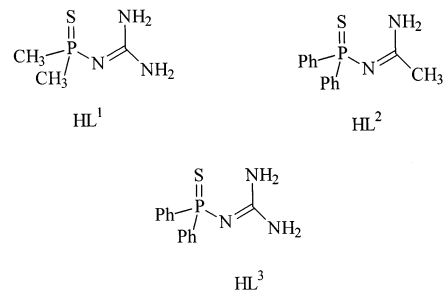

Fig. 1. Structures of HL^{1-3}.

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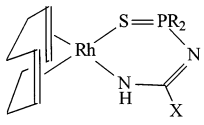

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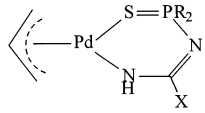
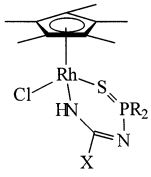
2 X = CH_3, R = Ph
3 X = NH_2, R = Ph



4 X = NH_2, R = Me
5 X = CH_3, R = Ph
6 X = NH_2, R = Ph



7 X = NH_2, R = Me
8 X = CH_3, R = Ph
9 X = NH_2, R = Ph

Fig. 2. Structures of complexes **1**–**9**.

We describe here the synthesis of [Rh(L^n-S,N)(η^4-cod)], [Pd(L^n-S,N)(η^3-C_3H_5)] and [RhCl(L^n-S,N)(η^5-C_5Me_5)] and the X-ray crystal structure of [Pd(L^3-S,N)-(η^3-C_3H_5)].

2. Results and discussion

We have previously shown that HL^n are deprotonated by potassium *t*-butoxide to give anions $(L^n)^-$ which react with *cis*-[$PtCl_2(PR_3)_2$] ($PR_3 = PMe_2Ph$ or 1/2dppe), giving *cis*-[Pt(L^n-S,N)$(PR_3)_2$]Cl [17]. By a similar method, $(L^n)^-$ reacts with $[Rh(\mu\text{-}Cl)(\eta^4\text{-cod})]_2$, $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ or $[RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)]_2$ to give [Rh(L^n-S,N)(η^4-cod)] **1**–**3**, [Pd(L^n-S,N)(η^3-C_3H_5)] **4**–**6** and [RhCl(L^n-S,N)(η^5-C_5Me_5)] **7**–**9** (Fig. 2), with by-production of KCl. Conversion is quantitative by $^{31}P\{^1H\}$ NMR, isolated yields are 40–70%. Compounds **1**–**9** are isostructural with those obtained when $[(EPPh_2)_2N]^-$, E = S or Se, cleave the chloro-bridged precursors although the mixed donor ligands $[Ph_2P(O)NP(E)Ph_2]^-$ exhibit a μ_2E-bridging geometry in $[Pd(\eta^3\text{-}C_3H_5)\{Ph_2P(O)NP(E)Ph_2\text{-E}\}]_2$ [19,22,23]. Complexes **1**–**9** are air and moisture stable with high solubility in chlorinated solvents, selected spectroscopic data are presented in Table 1. The FAB^+ mass spectra contain an intense peak from the molecular ion for **1**–**6** and $[M^+ - Cl]$ for **7**–**9**. The $^{31}P\{^1H\}$ NMR shows a shift to low frequency by approximately 10–20 ppm from the free ligand value upon deprotonation and coordination, comparable with coordination shifts generally noted in $[(EPPh_2)_2N]^-$ complexes [5,18,19,23]. For **1**–**3** ^2J(Rh–P) is 4 Hz, however this coupling is unresolved for **7**–**9**. In their IR spectra, **1**–**9** give bands of medium intensity between 3460–3120 cm^{-1} due to ν(NH, NH_2), essentially unchanged from HL^n (3437–3142 cm^{-1}) and strong absorptions at 1630–1480 cm^{-1} from ν(CN) and δ(NH) vibrations of $(L^n)^-$. The ν(PS) bands for the $(L^1)^-$ complexes **1**, **4** and **7** (561, 553 and 562 cm^{-1}, respectively) are 30–40 cm^{-1} below those for the $(L^{2,3})^-$ complexes **2**, **3**, **5**, **6**, **8** and **9** (583–600 cm^{-1}).

In the ^1H NMR, the amine protons of **1**–**9** give broad singlets between 3.6–6.1 ppm, cf. 6.1 for HL^1, 8.2 and 5.8 for HL^2, 5.7 for HL^3. Notably, δ(N*H*) in the $(L^2)^-$ complexes **2**, **5** and **8** (δ 4.74, 6.06 and 5.49, respectively) is approximately 1 ppm to high frequency of the values in the $(L^{1,3})^-$ complexes [δ(N*H*) approximately 3.6 for **1** and **3**, approximately 4.9 for **4** and **6**, 4.33 (**7**) and 4.79 (**9**)]. The NH_2 resonance of $(L^{1,3})^-$ appears to low frequency of N*H* for **1** and **3**, the order is reversed in **4** and **6**; a similar alternation occurs between **7** and **9**. In **2**, **5** and **8** the methyl protons of the amidinate moiety show a ^4J(*H*NCC*H*) coupling of 2 Hz, as seen in uncomplexed HL^2 (2 Hz).

The molecular structure of [Pd(L^3-S,N)(η^3-C_3H_5)] **6** (Fig. 3) confirms that $(L^3)^-$ is S,N-bidentate, forming a Pd–S–P–N–C–N palladacycle with an η^3-allyl group

Table 1
Selected spectroscopic data [$^{31}P\{^1H\}$ NMR, IR and FAB^+ MS] for HL^{1-3} and **1**–**9**

	$^{31}P\{^1H\}$ δ_P [a,b]	IR (cm^{-1}) ν(NH, NH_2)	ν(PS)	FAB^+ MS [c] M^+
HL^1 $Me_2P(S)N{=}C(NH_2)_2$	48.3	3377, 3142	558	151
HL^2 $Ph_2P(S)N{=}C(Me)(NH_2)$	42.2	3361, 3285, 3230	575	274
HL^3 $Ph_2P(S)N{=}C(NH_2)_2$	42.5	3437, 3350, 3299, 3201 586	275	
1 [Rh(L^1-S,N)(η^4-cod)]	38.9(4)	3389, 3287, 3178	553	362
2 [Rh(L^2-S,N)(η^4-cod)]	31.0(4)	3321	592	485
3 [Rh(L^3-S,N)(η^4-cod)]	35.3(4)	3415, 3287, 3173	600	486
4 [Pd (L^1-S,N)(η^3-C_3H_5)]	37.6	3460, 3340, 3122	561	298
5 [Pd (L^2-S,N)(η^3-C_3H_5)]	28.9	3346	589	420
6 [Pd (L^3-S,N)(η^3-C_3H_5)]	34.0	3399, 3304, 3169	591	422
7 [RhCl(L^1-S,N)(η^5-C_5Me_5)]	36.1	3309, 3166	562	388
8 [RhCl(L^2-S,N)(η^5-C_5Me_5)]	22.9	3245	583	511
9 [RhCl(L^3-S,N)(η^5-C_5Me_5)]	28.2	3474, 3297, 3172	585	512

[a] Spectra in $CDCl_3$ for $HL^{1,2}$ and **1**–**9**, CD_3OD for HL^3.
[b] ^2J(Rh–P) in parentheses for **1**–**3**, no coupling resolved in **7**–**9**.
[c] $[M^+ - Cl]$ for **7**–**9**.

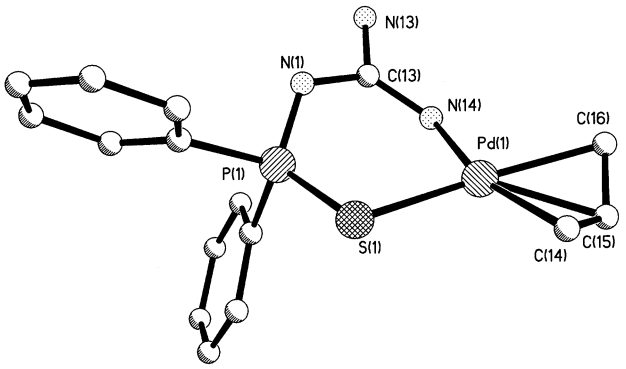


Fig. 3. X-ray crystal structure of $[Pd(L^3\text{-}S,N)(\eta^3\text{-}C_3H_5)]$ **6** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Pd(1)–N(14) 2.085(3), Pd(1)–S(1) 2.3536(10), Pd(1)–C(14) 2.137(4), Pd(1)–C(15) 2.097(4), Pd(1)–C(16) 2.151(4), S(1)–P(1) 2.0167(12), P(1)–N(1) 1.601(2), N(1)–C(13) 1.348(4), C(13)–N(14) 1.321(4), C(13)–N(13) 1.368(4); S(1)–Pd(1)–N(14) 99.00(8), Pd(1)–S(1)–P(1) 99.76(4), S(1)–P(1)–N(1) 119.88(10), P(1)–N(1)–C(13) 122.9(2), N(1)–C(13)–N(14) 125.4(3), C(13)–N(14)–Pd(1) 127.9(2), N(1)–C(13)–N(13) 113.8(3), N(13)–C(13)–N(14) 120.7(3).

completing the coordination sphere. The internal N–C and P–N distances [N(14)–C(13) 1.321(4), C(13)–N(1) 1.348(4), P(1)–N(1) 1.601(2) Å] of the Pd–S–P–N–C–N ring are, within experimental error, unchanged from *cis*-$[Pt(L^2\text{-}S,N)(PMe_2Ph)_2]Cl$, with P(1)–S(1) [2.0167(12) Å] marginally shorter than in the platinum complex [2.036(4) Å] [17]. The M–S–P, S–M–N and S–P–N angles of 6 [99.76(4), 99.00(8) and 119.88(10)°] are substantially enlarged compared with *cis*-$[Pt(L^2)(PMe_2Ph)_2]Cl$ [91.75(12), 90.8(3) and 115.3(3)°], whereas the M–N–C angle [127.9(2)°] is smaller than the platinum complex [134.5(7)°]. Within the chelate, the N(14)–Pd(1)–S(1)–P(1) chain has a mean deviation from planarity of 0.01 Å, N(1) and C(13) lie 0.82 and 0.59 Å, respectively below this plane. This contrasts with *cis*-$[Pt(L^2\text{-}S,N)(PMe_2Ph)_2]Cl$ in which only the sulphur atom is displaced (by 1.27 Å) from the platinacycle plane; the $(L^n)^-$ backbone appears to have the same conformational freedom available to $[(EPR_2)_2N]^-$.

In summary, cleavage of chloro-bridged bimetallic complexes is readily accomplished using anions derived from phosphorus(V) guanidines and amidines, with the formation of the six-membered chelate rings analogous to β-diketonates and imidodiphosphinate ligands.

3. Experimental

Complexations were performed under dinitrogen, work-ups were carried out in air. Thf was distilled from Na-benzophenone ketyl, Rh_2 and Pd_2 precursors were prepared by literature procedures [24–26], other solvents and reagents were as supplied. $^{31}P\{^1H\}$ and ^1H NMR (121.4 and 300.0 MHz, $CDCl_3$) and IR spectra (KBr discs) were on Varian Gemini 2000 and Perkin–Elmer System 2000 spectrometers, respectively, elemental analyses and FAB^+ mass spectra (3-NOBA matrix) were by the University of St Andrews Microanalytical Service and EPSRC National Mass Spectrometry Service Centre, Swansea. Selected spectroscopic data for HL^{1-3} and **1**–**9** are given in Table 1.

3.1. $[Rh(L^n\text{-}S,N)(\eta^4\text{-cod})]$ (L^1 = **1**, L^2 = **2**, L^3 = **3**)

To HL^n (0.24 mmol) and potassium *t*-butoxide (0.3 mmol) in thf (3 cm^3) was added $[Rh(\mu\text{-}Cl)(\eta^4\text{-cod})]_2$ (0.12 mmol) in one portion and the orange solution stirred for 2 h. The solvent was removed in vacuo, the product extracted into dichloromethane (5 cm^3) and filtered through celite. Addition of hexane (50 cm^3) gave **1**–**3** as yellow microcrystalline solids.

Compound **1**. *Anal*. Found: C, 36.4; H, 6.0; N, 11.9. Calc. for $C_{11}H_{21}N_3PSRh$: C, 36.6; H, 5.9; N, 11.6%. δ_H: 4.01 (m, 4H, C_8H_{12}), 3.81 (br s, 2H, NH_2), 3.62 (br s, 1H, NH), 2.41 (m, 4H, C_8H_{12}), 1.88 (m, 4H, C_8H_{12}), 1.83 (d, 6H, $^2J_{PH} = 13$ Hz, CH_3).

Compound **2**. *Anal*. Found: C, 55.6; H, 5.1; N, 5.5. Calc. for $C_{22}H_{27}N_2PSRh$: C, 54.4; H, 5.6; N, 5.8%. δ_H: 7.88 (m, 4H, C_6H_5), 7.35 (m, 6H, C_6H_5), 4.74 (br s, 1H, NH), 4.08 (m, 2H, C_8H_{12}), 3.65 (m, 2H, C_8H_{12}), 2.25 (m, 4H, C_8H_{12}), 2.13 (d, 3H, $^4J_{HH} = 2$ Hz, CH_3), 1.80 (m, 4H, C_8H_{12}).

Compound **3**. *Anal*. Found: C, 50.3; H, 4.9; N, 8.0. Calc. for $C_{21}H_{25}N_3PSRh$: C, 51.9; H, 5.2; N, 8.7%. δ_H: 7.93 (m, 4H, C_6H_5), 7.42 (m, 6H, C_6H_5), 4.16 (br s, 2H, NH_2), 4.11 (m, 2H, C_8H_{12}), 3.70 (m, 2H, C_8H_{12}), 3.63 (br s, 1H, NH), 2.29 (m, 4H, C_8H_{12}), 1.84 (m, 4H, C_8H_{12}).

3.2. $[Pd(L^n\text{-}S,N)(\eta^3\text{-}C_3H_5)]$ (L^1 = **4**, L^2 = **5**, L^3 = **6**)

To HL^n (0.50 mmol) and potassium *t*-butoxide (0.55 mmol) in thf (5 cm^3) was added $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ (0.25 mmol) in one portion and the yellow solution was stirred for 2 h. The solvent was removed in vacuo, the product extracted into dichloromethane (5 cm^3) and filtered through Celite. Addition of hexane (50 cm^3) gave the products as brown (**4**), orange (**5**) or yellow (**6**) solids.

Compound **4**. *Anal*. Found: C, 24.2; H, 3.9; N, 13.0. Calc. for $C_6H_{14}N_3PSPd$: C, 24.2; H, 4.7; N, 14.1%. δ_H: 5.24 (m, 1H, C_3H_5), 4.96 (br s, 1H, NH), 4.24 (br s, 2H, NH_2), 3.85 (d, 1H, $^3J_{HH} = 6$ Hz, C_3H_5), 3.56 (d, 1H, $^3J_{HH} = 6$ Hz, C_3H_5), 2.90 (d, 1H, $^3J_{HH} = 12$ Hz, C_3H_5), 2.53 (d, 1H, $^3J_{HH} = 12$ Hz, C_3H_5), 1.78 (d, 3H, $^2J_{PH} = 12$ Hz, CH_3), 1.72 (d, 3H, $^2J_{HH} = 12$ Hz, CH_3).

Compound **5**. *Anal*. Found: C, 47.5; H, 4.3; N, 6.2. Calc. for $C_{17}H_{19}N_2PSPd$: C, 48.5; H, 4.5; N, 6.7%. δ_H: 7.93 (m, 4H, C_6H_5), 7.30 (m, 6H, C_6H_5), 6.06 (br s, 1H, NH), 5.1 (m, 1H, C_3H_5), 3.75 (d, 1H, $^3J_{HH} = 7$ Hz, C_3H_5), 3.61 (d, 1H, $^3J_{HH} = 6$ Hz, C_3H_5), 2.76 (d, 1H,

$^3J_{HH} = 12$ Hz, C_3H_5), 2.54 (d, 1H, $^3J_{HH} = 12$ Hz, C_3H_5), 2.22 (d, 3H, $^4J_{HH} = 2$ Hz, CH_3).

Compound **6**. *Anal*. Found: C, 44.4; H, 4.1; N, 9.7. Calc. for $C_{16}H_{18}N_3PSPd$: C, 45.6; H, 4.3; N, 10.0%. δ_H: 7.90 (m, 4H, C_6H_5), 7.42 (m, 6H, C_6H_5), 5.14 (m, 1H, C_3H_5), 4.98 (br s, 1H, NH), 4.49 (br s, 2H, NH_2), 3.74 (br s, 1H, C_3H_5), 3.70 (br s, 1H, C_3H_5), 2.80 (d, 1H, $^3J_{HH} = 11$ Hz, C_3H_5), 2.56 (d, 1H, $^3J_{HH} = 11$ Hz, C_3H_5).

3.3. [RhCl(L^n-S,N)(η^5-C_5Me_5)] (L^1 = **7**, L^2 = **8**, L^3 = **9**)

To HL^n (0.3 mmol) and potassium *t*-butoxide (0.35 mmol) in thf (5 cm^3) was added [RhCl(μ-Cl)(η^5-C_5Me_5)]$_2$ (0.15 mmol) in one portion and the red mixture stirred for 24 h. The products **7** and **9** precipitate from thf as orange-brown solids; for **8** the solution was reduced to dryness in vacuo, the crude product extracted into dichloromethane (5 cm^3), filtered through Celite and precipitated with hexane (50 cm^3) to give **8** as a brown solid.

Compound **7**. *Anal*. Found: C, 36.9; H, 5.8; N, 9.9. Calc. for $C_{13}H_{24}N_3PSRhCl$: C, 36.8; H, 5.7; N, 9.9%. δ_H: 4.66 (br s, 2H, NH_2), 4.33 (br s, 1H, NH), 1.68 (d, 6H, $^2J_{PH} = 13$ Hz, PCH_3), 1.57 (s, 15H, C_5Me_5).

Compound **8**. *Anal*. Found: C, 53.7; H, 5.6; N, 4.9. Calc. for $C_{24}H_{29}N_2PSRhCl$: C, 52.7; H, 5.3; N, 5.1%. δ_H: 7.92 (m, 4H, C_6H_5), 7.37 (m, 6H, C_6H_5), 5.49 (br s, 1H, NH), 2.35 (d, 3H, $^4J_{HH} = 3$ Hz, CH_3), 1.43 (s, 15H, C_5Me_5).

Compound **9**. *Anal*. Found: C, 47.9; H, 5.0; N, 6.9. Calc. for $C_{23}H_{28}N_3PSRhCl$: C, 50.4; H, 5.1; N, 7.7%. δ_H: 7.87 (m, 4H, C_6H_5), 7.35 (m, 6H, C_6H_5), 4.79 (br s, 1H, NH), 4.59 (br s, 2H, NH_2), 1.48 (s, 15H, C_5Me_5).

4. X-ray crystallography

Crystallographic studies on crystals of **6** grown from dichloromethane–diethyl ether were performed at 293 K on a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods, non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms bound to carbon were idealised and fixed (C–H 0.95 Å), the NH protons associated with N(13) and N(14) were located by a ΔF map and allowed to refine anisotropically. Structural refinements were by full-matrix least-squares on F^2 using the program SHELXTL [27]. $C_{16}H_{18}N_3PPdS$, M = 421.76, monoclinic, space group $P2_1/c$, $a = 14.2943(3)$, $b = 10.7975(1)$, $c = 12.3736(2)$ Å, $\beta = 114.915(1)°$, V = 1732.04(5) Å^3, $Z = 4$, $D_{calc} = 1.617$ Mg m^{-3}, μ (Mo Kα) = 1.283 mm^{-1}, $F(000) = 848$, crystal size = 0.13 × 0.1 × 0.1 mm^3. Of the 7311 measured data, 2467 were unique (R_{int} 0.0239) to give $R_1[I > 2\sigma(I)] = 0.0255$ and $wR_2 = 0.0635$.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 151583 for compound **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] L. Barkoui, M. Charrouf, M.N. Rager, B. Denise, N. Platzer, H. Rudler, Bull. Soc. Chim. Fr. 134 (1997) 167.
[2] H. Rudler, B. Denise, J.R. Gregario, J. Vaissermann, Chem. Commun. (1997) 2299.
[3] E. Herrmann, O. Navratil, P. Sladek, Phosphorus, Sulphur Silicon Relat. Elem. 109-110 (1996) 201.
[4] G. Grossmann, E. Herrmann, O. Navratil, Collect. Czech. Chem. Commun. 55 (1990) 364.
[5] A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc., Dalton Trans., (1998) 1537.
[6] D.J. Birdsall, A.M.Z. Slawin, J.D. Woollins, Inorg. Chem. 38 (1999) 4152.
[7] J. Novosad, M. Necas, J. Marek, P. Veltsistas, C. Papadimitriou, I. Haiduc, M. Watanabe, J.D. Woollins, Inorg. Chim. Acta 290 (1999) 256.
[8] T.Q. Ly, J.D. Woollins, Coord. Chem. Rev. 176 (1998) 451.
[9] N. Inguimbert, L. Jäger, M. Taillefer, H.J. Cristau, J. Organomet. Chem. 529 (1997) 257.
[10] J. Münchenberg, O. Böge, A.K. Fischer, P.G. Jones, R. Schmutzler, Phosphorus, Sulphur Silicon Relat. Elem. 86 (1994) 103.
[11] A. Schmidpeter, J. Ebeling, Angew. Chem. 70 (1967) 534.
[12] M.A.R. Khayat, F.S. Al-Isa, J. Prakt. Chem. 331 (1988) 149.
[13] R. Appel, Chem. Ber. 105 (1972) 2476.
[14] G. Capozzi, P. Haake, J. Am. Chem. Soc. 94 (1972) 3249.
[15] L. Jäger, N. Inguimbert, M. Taillefer, H.J. Cristau, Synth. Commun. 25 (1995) 2857.
[16] N. Inguimbert, M. Biedermann, H. Stoeckli-Evans, H. Hartung, A. Kolbe, L. Jäger, M. Taillefer, H.J. Cristau, J. Mol. Struct. 519 (2000) 211.
[17] P. Bhattacharyya, A.M.Z. Slawin, J.D. Woollins, Polyhedron 19 (2000) 809.
[18] J.R. Phillips, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, Polyhedron 15 (1996) 3175.
[19] P. Bhattacharyya, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, J. Chem. Soc., Dalton Trans. (1995) 2489.
[20] C.R. Saha, N.K. Roy, J. Coord. Chem. 12 (1983) 163.
[21] R. Vilar, D.M.P. Mingos, A.J.P. White, D.J. Williams, J. Chem. Soc., Chem. Commun. (1999) 229.

[22] P. Bhattacharyya, A.M.Z. Slawin, M.B. Smith, J. Chem. Soc., Dalton Trans. (1998) 2467.
[23] J. Parr, A.M.Z. Slawin, M.B. Smith, J. Organomet. Chem. 588 (1999) 99.
[24] Y. Tatsuno, T. Yoshida, J. Otsuka, Inorg. Synth. 28 (1990) 343.
[25] G. Giordano, R.H. Crabtree, Inorg. Synth. 19 (1979) 218.
[26] C. White, A. Yates, P.M. Maitlis, Inorg. Synth. 29 (1992) 228.
[27] G.M. Sheldrick, SHELXTL, Version 5.03, program for crystal structure solution, University of Göttingen, Germany, 1994.