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PLATINUM METAL COMPLEXES OF SECONDARY PHOSPHINES: SYNTHESIS AND NMR SPECTROSCOPIC STUDIES OF $[M(PCy_2H)_3Cl]^+$, M = Pt, Pd

ROBIN J. FORDER, IAN S. MITCHELL, GILLIAN REID* and RACHEL H. SIMPSON

Department of Chemistry, University of Southampton, Highfield, Southampton SO9 5NH, U.K.

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Abstract—Reaction of MCl_2 (M = Pd, Pt) with PCy_2H in EtOH under dinitrogen yielded the unusual tris-secondary phosphine complexes $[MCl(PCy_2H)_3]X$ ($X^- = Cl^-$, BF_4^-, PF_6^-) in high yield as stable products. Retention of the secondary phosphine protons in these complexes has been confirmed by ^1H, ^{31}P and ^{195}Pt NMR spectroscopic studies. These results confirm that the P—H bond in coordinated PCy_2H is stronger than in coordinated PPh_2H. Similar reaction of $NiCl_2 \cdot 6H_2O$ with PCy_2H yields the bis-secondary phosphine complex $[NiCl_2(PCy_2H)_2]$ as reported previously (R. A. Palmer, H. F. Giles and D. R. Whitcomb, *J. Chem. Soc.*, *Dalton Trans.* 1978, 1671; R. A. Palmer and D. R. Whitcombe, *J. Mag. Res.* 1980, **39**, 371). Variable temperature ^{31}P NMR spectroscopy confirms that the *cis* isomer exists exclusively in CH_2Cl_2 solution, while the *trans* isomer is the dominant form in benzene solution. Addition of excess PCy_2H leads to species with higher phosphine : metal ratios at low temperature as seen by ^{31}P NMR spectroscopy and FAB mass spectrometry.

In contrast to the vast literature associated with transition metal complexes of tertiary phosphines, there have been relatively few reports on the coordination of primary and secondary phosphines to metal centres.[1–5] This is partially a result of the sensitivity of these ligands to rapid oxidation and the notion that upon coordination the P—H bond becomes extremely weak and susceptible to cleavage. This is especially true for monodentate R_2PH ligands in the presence of halide ligands (X^-), where HX elimination can occur. It is not such a serious problem for disecondary phosphines, presumably due to the additional stability induced by the chelate effect of these bidentate ligands.

We are interested in the coordination chemistry of secondary phosphines since the resultant complexes should provide useful precursors with which to perform controlled deprotonation of the P—H functions under mild conditions, and functionalize the resultant phosphide species. This approach may provide a general route to ligands which are not readily synthesized *via* conventional methods. This strategy has been used by Stelzer and co-workers for example, to prepare tetraphosphine macrocycles.[3] In order for this method to be successful, it is essential that we can prepare coordination complexes with these secondary phosphines in high yield without spontaneous deprotonation, as this would be likely to afford complicated mixtures of phosphido-bridged species. Interestingly, Pregosin *et al.* have recently identified agostic Pd···H—P interactions in the binuclear secondary phosphine complex $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PHBu^t_2)(PHBu^t_2)_2]^+$. These may represent transition states in the deprotonation of coordinated P—H functions.[4] Leoni has also recently reported the complex $Pd(PBu^t_2H)_3$, the first Pd^0 species incorporating only secondary phosphines.[5]

Previous work has shown that Pd^{II} and Pt^{II} salts react with diphenylphosphine (PPh_2H) in a range of solvents to give the binuclear complexes $[M_2Cl_2(PPh_2H)_2(\mu\text{-}PPh_2)_2]$. These species have been

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*Author to whom correspondence should be addressed.

characterized in the solid state by single crystal X-ray analyses which confirm the presence of bridging phosphide ligands (PPh_2^-), and in solution by NMR spectroscopy.[2] As part of our preliminary work we report here the high yield syntheses of dicyclohexylphosphine complexes with Pd^{II} and Pt^{II} ions together with multinuclear NMR spectroscopic studies. We have also investigated the interconversion of *cis* and *trans* isomers of the complex $[NiCl_2(PCy_2H)_2]$. The synthesis of this complex has been reported previously, and a single crystal X-ray structure shows that it exists as the *cis* isomer in the solid-state (see reference in abstract).

RESULTS AND DISCUSSION

Reaction of MCl_2, M = Pd, Pt, with up to 4.5 molar equivalents (excess) of PCy_2H in degassed EtOH solution affords a clear solution. Addition of an excess of $NaBF_4$ gives a white precipitate which can be isolated by filtration and recrystallized from MeCN/diethyl ether. The IR spectra of these products show, in addition to peaks due to cyclohexyl groups and BF_4^- counterion, a weak absorption at 2340 cm^{-1} due to the P—H functions, ν(P—H). Fast-atom bombardment (FAB) mass spectrometry (3-NOBA matrix) reveals molecular ion peaks with the correct isotopic distributions corresponding to $[MCl(PCy_2H)_3]^+$ ($M^+ = 735$ and 825 for M = ^{106}Pd and ^{195}Pt, respectively). Very distinctive fragmentation patterns are also apparent, consistent with loss of Cl^-, C_6H_{11} and phosphorus (P) from the complexes. The intensity and clarity of the FAB mass spectra were rather surprising to us as we had anticipated the P—H protons to be very acidic, hence deprotonation and polymerization of the cations in the FAB matrix seemed likely. These data, together with microanalyses, confirm the formulation of the complexes as the tris-phosphine complexes $[MCl(PCy_2H)_3]BF_4$.

The ^1H NMR spectra of $[MCl(PCy_2H)_3]^+$, M = Pd, Pt, are very similar, each showing multiplets in the range 2.6 to 1.3 ppm due to the cyclohexyl protons. Additional resonances due to the P—H functions are also evident. These occur as a large doublet with further couplings which are not fully resolved. In each case the large doublet coupling corresponds to $^1J_{PH}$, with the other couplings being much smaller ($^3J_{PH}$). $\{^1H\}^{31}P$ NMR spectroscopy on each of these complexes confirms the presence of two P environments in a 1 : 2 ratio (M = Pd: δ 27.9 (P *trans* Cl), 20.4 (P *trans* P); M = Pt: δ 15.6 (P *trans* P, $^1J_{PtP} = 2215$ Hz), 10.4 (P *trans* Cl, $^1J_{PtP} = 3162$ Hz). The proton coupled ^{31}P NMR spectra show that these split into a doublet (P *trans* to Cl^-) and a second-order pseudo sextet (P *trans* to P), respectively. Again the large couplings are characteristic of P—H groups, i.e. H bound directly to P. ^{195}Pt satellites are also seen for M = Pt (Fig. 1) as expected. No other ^{31}P resonances are observed in the range +400 to −300 ppm. The $\{^1H\}$ ^{195}Pt NMR spectrum of $[PtCl(PCy_2H)_3]^+$ exhibits a doublet of triplets at −4791 ppm as expected for a central Pt^{II} ion coupling to a single PCy_2H ligand *trans* to Cl^- and to two other equivalent PCy_2H ligands (Fig. 2). All of these reson-

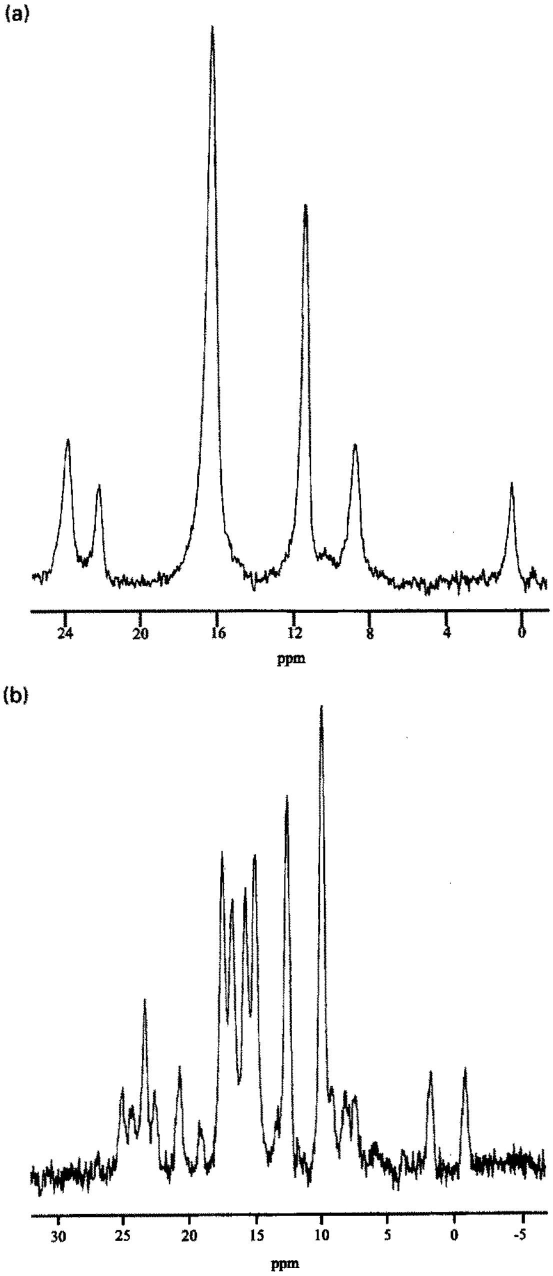

Fig. 1. $\{^1H\}^{31}P$ (a) and ^{31}P (b) NMR spectra of $[PtCl(PCy_2H)_3]^+$ (MeCN, 300 K).

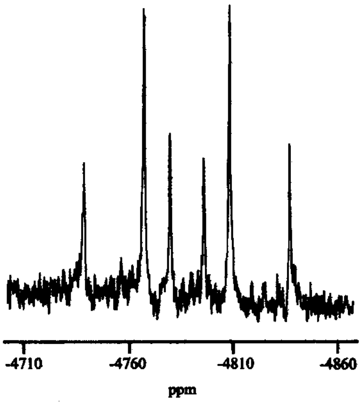

Fig. 2. $\{^1H\}^{195}Pt$ NMR spectrum of $[PtCl(PCy_2H)_3]^+$ (MeCN, 300 K).

ances broaden significantly when the decoupler is turned off, providing supporting evidence for the P—H functions remaining intact.

These results confirm that PCy_2H forms stable complexes with Pd^{II} and Pt^{II} centres with no deprotonation occurring in solution. Efforts to prepare the cations $[MCl(PPh_2H)_3]^+$, M = Pd, Pt, using similar conditions to those employed for synthesis of $[MCl(PCy_2H)_3]^+$ described above and by adding aqueous HBF_4, yielded the deprotonated binuclear complexes $[M_2Cl_2(\mu\text{-}PPh_2)_2(PPh_2H)_2]$ described previously in the literature.[2] This was confirmed by FAB mass spectrometry (Found $M^+ = 991$ and 1169; Calc. for $[M_2(PPh_2H)_2(PPh_2)_2Cl]^+$ $M^+ = 989$ and 1167; for M = ^{106}Pd and ^{195}Pt, respectively; peaks corresponding to the expected fragmentation via loss of Cl^- and PPh_2H groups from the parent dimers are also strongly evident) and ^{31}P NMR spectroscopy and suggests that the P—H bonds in coordinated R_2PH where R = phenyl are considerably weaker than when R = cyclohexyl.

Attempts to prepare other Pd^{II} and Pt^{II} complexes of PCy_2H by varying the metal : phosphine ratio from 1 : 2 to 1 : 6 does not alter the products, with only the 1 : 3 metal : ligand ratio being seen in each case in EtOH. This is surprising given the tendency for Pd^{II} and Pt^{II} halides to give the 1 : 2 M : phosphine complexes, $[MX_2(PR_3)_2]$, for most other phosphines.[6]

The large cone angle for PCy_2H (θ 142°) presumably disfavours the *tetrakis*-phosphine complexes and hence is probably responsible for 1 : 3 ratio being preferred. The 1 : 3 metal : ligand ratio found in our work contrasts with the 1 : 2 metal : ligand ratio observed in the related complex, *cis*-$[NiCl_2(PCy_2H)_2]$ (see reference in abstract). This may reflect both the larger ionic radii of Pd^{II} and Pt^{II} over Ni^{II} which enable three bulky phosphines to coordinate readily to the $4d^8$ and $5d^8$ metal centres but not to the $3d^8$ Ni^{II} centre and the harder nature of Ni^{II} which will tend to prefer the harder Cl^- ligands.

Previous NMR spectroscopic studies on $[NiX_2(PCy_2H)_2]$, X = Cl, Br, I, showed that these are $[AMY_2]_2$ spin systems, with equilibrium mixtures of *cis* and *trans* isomers present in solution (see reference in abstract). For comparison with the Pd^{II} and Pt^{II} dicyclohexylphosphine complexes, we also prepared $[NiCl_2(PCy_2H)_2]$. IR UV–vis, ^1H and ^{31}P NMR spectroscopy confirm the formulation of the complex, ν(P—H) = 2360 cm^{-1}, ν(Ni—Cl) = 330, 310 cm^{-1}, consistent with the literature data. The UV–vis spectrum measured in CH_2Cl_2 solution shows bands at $\lambda_{max} = 263$ nm (ε_{mol} = 11,700 dm^3 mol^{-1} cm^{-1}), 290 sh (2200) and 373 (1950), assigned to charge-transfer transitions on the basis of their large extinction coefficients. A further band of lower intensity at 464 nm (870 dm^3 mol^{-1} cm^{-1}) is assigned to a *d*–*d* transition.

In our hands VT $\{^1H\}^{31}P$ NMR spectroscopic studies on this species in $CH_2Cl_2/CDCl_3$ solution show at 300 K, a single, broad resonance at +36.2 ppm assigned to the *cis* isomer. This signal sharpens significantly, without shifting, upon cooling to 185 K. No other resonances are observed. In contrast, using $C_6H_6/(CD_3)_2CO$ as solvent results in loss of the resonance at +36.2 ppm, with a new signal appearing at +25.8 ppm. Again, at 300 K this is a broad signal which sharpens upon cooling to 275 K. This is attributed to the existence of the *trans* isomer exclusively in non-polar benzene, confirming that while the *cis* isomer is preferred in the solid-state, *cis*–*trans* isomerism occurs readily in solution. The literature data suggests that the other halide complexes, $[NiX_2(PCy_2H)_2]$, X = Br, I, exist as mixtures of *cis* and *trans* forms in CH_2Cl_2 solution (see reference in abstract). The ^1H coupled ^{31}P NMR spectra of the individual isomeric forms of $[NiCl_2(PCy_2H)_2]$ have also been recorded and exhibit similar second order spin patterns to those described by Whitcombe *et al.* (see reference in abstract).

Importantly, the FAB mass spectrum of $[NiCl_2(PCy_2H)_2]$ (3-NOBA matrix) exhibits a molecular ion peak at $M^+ = 687$, consistent with $[NiCl(PCy_2H)_3-2H]^+$. Other peaks at $M^+ = 489$, 454, 369, 289 and 253 are consistent with those expected for fragmentation of the complex $[NiCl_2(PCy_2H)_2]$. The *tris*-phosphine complex $[NiCl(PCy_2H)_3]Cl$ has not been observed previously, although complexes assigned as $Ni(PPh_2H)_3X_2$ and $Ni(PEt_2H)_3X_2$, X = Cl, Br, I, have been reported.[7] Our data suggest that although $[NiCl_2(PCy_2H)_2]$ is the species isolated in the solid state, the *tris*-phosphine complex also exists in solution. The ^{31}P NMR spectroscopic data described above also indicate rapid exchange at room temperature, although upon cooling, [NiCl$_2$(PCy$_2$H)$_2$] can be frozen out. In an attempt to establish whether [NiCl$_2$(PCy$_2$H)$_3$] genuinely exists in solution, we carried out a VT ^{31}P NMR spectroscopic study on [NiCl$_2$(PCy$_2$H)$_2$] in the presence of excess PCy$_2$H ligand. At 300 K in CH$_2$Cl$_2$/CDCl$_3$ solution the {^{1}H}^{31}P NMR spectrum shows a sharp resonance at -29.7 ppm due to free PCy$_2$H and a broad resonance at $+35.8$ ppm, as seen for *cis*-[NiCl$_2$(PCy$_2$H)$_2$]. Upon cooling this resonance gradually diminishes in intensity with concomitant growth of a new signal at $+28.5$. At 235 K these two signals are present in a 1 : 1 ratio. Further cooling to 185 K results in complete loss of the original signal ($+35.8$ ppm), and gives a second order spectrum with multiplets at $+30.4$, $+27.9$, $+12.8$ and $+11.2$ ppm together with a more intense signal at $+28.5$ ppm. Upon ^{1}H coupling, all of the resonances split further, indicating retention of the secondary phosphine protons. This behaviour contrasts with that seen in the absence of excess phosphine and may indicate the existence of species with higher PCy$_2$H : Ni ratios in solution e.g. *tris*- and/or *tetrakis*-phosphine complexes. This behaviour is completely reversible with the original broad resonance being regenerated upon warming. Noticeably also, in contrast to the orange–red coloured solution observed at all temperatures for [NiCl$_2$(PCy$_2$H)$_2$], cooling this species in the presence of excess PCy$_2$H yields a bright yellow coloured solution at 185 K. This colour change is also reversible, the original orange–red colour being regenerated rapidly upon warming.

EXPERIMENTAL

Infrared spectra were measured as KBr or CsI discs using a Perkin–Elmer 983 spectrometer over the range 200–4000 cm^{-1}. Mass spectra were run by electron impact or fast-atom bombardment (FAB) using 3-NOBA (3-nitrobenzyl alcohol) as matrix on a VG Analytical 70–250 SE spectrometer. Solution electronic spectra were recorded in quartz cells (1 cm path length) using a Perkin–Elmer UV–vis/NIR Lambda 19 spectrometer. ^{1}H NMR spectra were recorded using a Jeol FX90 or Bruker AM300 spectrometer operating at 90 MHz and 300 MHz, respectively. ^{31}P and ^{195}Pt NMR spectra were recorded using a Bruker AM360 spectrometer (operating at 145.8 MHz and 77.4 MHz, respectively) using 10 mm tubes with either 5 mm D$_2$O insert or the addition of 10–15% deuterated solvent as a lock. ^{31}P NMR spectra are referenced to 85% H$_3$PO$_4$ ($\delta = 0$), while ^{195}Pt NMR spectra are referenced against a solution of Na$_2$PtCl$_6$ in H$_2$O ($\delta = 0$). PCy$_2$H was purchased from Strem, [NiCl$_2$(PCy$_2$H)$_2$] and PPh$_2$H[8] (see reference in abstract) were prepared as described in the literature.

Synthesis of [Pd(PCy$_2$H)$_3$Cl]BF$_4$

To a suspension of PdCl$_2$ (39 mg, 0.220 mmol) in degassed EtOH (10 cm^3) at room temperature was added 4.5 molar equivalents of PCy$_2$H (0.2 cm^3, 0.988 mmol) *via* syringe. Stirring for 3 h under dinitrogen afforded a clear, very pale yellow solution. Addition of excess NaBF$_4$ and stirring for a further 1 h yielded a white precipitate which was collected by filtration and recrystallized from MeCN/CHCl$_3$/diethyl ether to give an air-stable white solid (yield 69%). Found: C, 48.9; H, 7.9. Calc. for [C$_{36}$H$_{69}$ClP$_3$Pd]BF$_4$·CHCl$_3$: C, 47.1; H, 7.5%; FAB mass spectrum (3-NOBA matrix): Found M$^+$ = 735, 537, 502, 417, 337, 303 and 221; Calc. for [PdCl(PCy$_2$H)$_3$]$^+$ M$^+$, 735; [PdCl(PCy$_2$H)$_2$]$^+$ M$^+$, 537; [Pd(PCy$_2$H)$_2$]$^+$ M$^+$, 502; [Pd(PCy$_2$H)(PCy)]$^+$ M$^+$, 418; [PdCl(PCy$_2$H)]$^+$ M$^+$, 339; [Pd(PCy$_2$H)]$^+$ M$^+$, 304; [Pd(PCyH)]$^+$ M$^+$, 220 (based on ^{106}Pd and ^{35}Cl). ^{1}H NMR spectrum (300 MHz, (CD$_3$)$_2$CO, 298 K): δ 2.6 – 1.3 (C$_6$*H*$_{11}$), 4.76 (P*H* *trans* Cl, *d* of *t*, $^1J_{\rm PH} = 365$ Hz), 4.36 (PH *trans* P, *d* of *d*, $^1J_{\rm PH} = 355$ Hz). {^{1}H}^{31}P NMR spectrum (145.8 MHz, MeCN, 300 K): δ 27.9 (P *trans* Cl, 1P), 20.4 ppm (P *trans* P, 2P). IR spectrum (KBr disc): 2930s, 2850s, 2340w, 2290w, 1450m, 1380w, 1350w, 1300w, 1260w, 1200w, 1080vs,b, 920w, 860w, 840w, 810w, 740w, 530w, 470w, 440w, 390w cm^{-1}.

Synthesis of [Pt(PCy$_2$H)$_3$Cl]BF$_4$

Method as for above, using PtCl$_2$ (66 mg, 0.247 mmol) and PCy$_2$H (0.22 cm^3, 1.09 mmol). The product was isolated as a white solid (yield: 67%). Found: C, 46.5; H, 7.1. Calc. for [C$_{36}$H$_{69}$ClP$_3$Pt]BF$_4$: C, 47.4; H, 7.6%; FAB mass spectrum (3-NOBA matrix): Found M$^+$ = 825, 790, 625, 589, 424, 389; Calc. for [PtCl(PCy$_2$H)$_3$]$^+$ M$^+$, 824; [Pt(PCy$_2$H)$_3$]$^+$ M$^+$, 789; [PtCl(PCy$_2$H)$_2$]$^+$ M$^+$, 626; [Pt(PCy$_2$H)$_2$]$^+$ M$^+$, 591; [PtCl(PCy$_2$H)]$^+$ M$^+$, 428; [Pt(PCy$_2$H)]$^+$ M$^+$, 393 (based upon ^{195}Pt and ^{35}Cl). ^{1}H NMR spectrum (300 MHz, CDCl$_3$, 298 K): δ 4.4 (PH *trans* Cl, *d* of *t*, $^1J_{\rm PH} = 391$ Hz), 4.2 (P*H* *trans* P, *d* of *d*, $^1J_{\rm PH} = 357$ Hz). {^{1}H}^{31}P NMR spectrum (145.8 MHz, MeCN, 300 K): δ 15.6 (P *trans* P, 2P, $^1J_{\rm PtP} = 2215$ Hz), 10.4 (P *trans* Cl, 1P, $^1J_{\rm PtP} = 3162$ Hz). {^{1}H}^{195}Pt NMR spectrum (77.4 MHz, MeCN, 300 K): δ -4791 (*d* of t, $^1J_{PtP} = 3162$ and 2215 Hz). IR spectrum (KBr disc): 2920s, 2850m, 2340w, 1450s, 1350w, 1300w, 1260m, 1200w, 1180m, 1080vs,b, 920m, 900m, 860m, 840m, 820m, 800m, 740w, 520m, 460m, 380m, 310m cm^{-1}.

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REFERENCES

1. For examples see: A. Bright, B. E. Mann, C. Masters, R. M. Slade and R. E. Srainbank, *J. Chem. Soc. A* 1971, 1826; D. J. Brauer, P. C. Knuppel and O. Stelzer, *Chem. Ber.* 1987, **120**, 81; C. W. Weston, G. W. Bailey, J. H. Nelson and H. B. Jonassen, *J. Inorg. Nucl. Chem.* 1972, **34**, 1752; J. R. Sanders, *J. Chem. Soc. A* 1971, 2991; F. A. Cotton, B. A. Frenz and D. L. Hunter, *Inorg. Chim. Acta* 1976, **16**, 203; M. Baacke, O. Stelzer and V. Wray, *Chem. Ber.* 1980, **113**, 1356; J. Vincente, M. T. Chicote and P. G. Jones, *Inorg. Chem.* 1993, **32**, 4960 and references therein.
2. R. G. Hayter, *J. Am. Chem. Soc.* 1962, **84**, 3046; W. Levason, C. A. McAuliffe and B. Riley, *Inorg. Nucl. Chem. Lett.* 1973, **9**, 1201; J. B. Brandon and K. R. Dixon, *Can. J. Chem.* 1981, **59**, 1188; A. J. Carty, F. Hartstock and N. J. Taylor, *Inorg. Chem.* 1982, **21**, 1349; T. Gebauer, G. Frenzen and K. Dehnicke, *Z. Naturforsch.* 1992, **47b**, 1505.
3. R. Bartsch, S. Hietkamp, S. Morton, H. Peters and O. Stelzer, *Inorg. Chem.* 1983, **22**, 3624; D. J. Brauer, F. Gol, S. Hietkamp, H. Peters, H. Sommer, O. Stelzer and W. S. Sheldrick, *Chem. Ber.* 1986, **119**, 349; D. J. Brauer, F. Dorrenbach, T. Lebbe and O. Stelzer, *Chem. Ber.* 1992, **125**, 1785.
4. P. Leoni, M. Pasquali, M. Sommovigo, F. Laschi, P. Zanello, A. Albatini, F. Lianza, P. S. Pregosin and H. Rueegger, *Organometallics* 1993, **12**, 1702.
5. P. Leoni, *Organometallics* 1993, **12**, 2432.
6. For examples see *Transition Metal Complexes of Phosphorus, Arsenic and Antimony* (Edited by C. A. McAuliffe), Ch. 14. Macmillan, London (1973); P. L. Goggin, R. J. Goodfellow, J. R. Knight, M. G. Norton and B. F. Taylor, *J. Chem. Soc., Dalton Trans.* 1973, 2220 and references therein.
7. K. Isslieb and G. Wilde, *Z. Anorg. Allg. Chem.* 1961, **312**, 287; J. A. Bertrand and D. L. Plymale, *Inorg. Chem.* 1966, **5**, 879; R. G. Hayter, *Inorg. Chem.* 1963, **2**, 932; P. Rigo and M. Bressan, *Inorg. Chem.* 1972, **6**, 1314.
8. V. D. Bianco and S. Doronzo, *Inorg. Synth.* 1976, **16**, 161.