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Synthesis and Characterization of Arsacycloalkanes and their Palladium and Platinum Complexes, and X-ray Structure of $[PdCl_2(PhAsCH_2CH_2CH_2CH_2CH_2)_2]$

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Reactions of $PhAsCl_2$ with $BrMg(CH_2)_nMgBr$ ($n = 4$ or 5) in THF gave phenylarsacycloalkanes as colourless oily liquids which could be distilled under vacuum. Treatment of $PhAs(CH_2)_n$ with $MCl_2(RCN)_2$ (M = Pd or Pt; R = Ph or Me) afforded mononuclear complexes, $[MCl_2\{PhAs(CH_2)_n\}_2]$. Reactions with $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ gave mixed-ligand complexes, $[PtCl_2(PEt_3)\{PhAs(CH_2)_n]$. The palladium complexes adopt a *trans* geometry whereas the platinum complexes exist in a *cis* configuration. The crystal and molecular structure of $[PdCl_2(PhAsCH_2CH_2CH_2CH_2CH_2)_2]$ was determined by X-ray diffraction methods. The molecule consists of a square-planar palladium atom with *trans* chlorides and *trans* arsa ligands. The six-membered 'AsC_5' ring adopts a chair conformation. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: arsacycloalkanes; palladium; platinum; X-ray

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INTRODUCTION

The utility of organoarsenic compounds in the deposition of III–V semiconductor materials by organometallic vapour-phase epitaxy (OMVPE) has stimulated considerable interest in organoarsenic chemistry.[1–5] In order to replace the conventional arsenic source AsH_3 (an extremely toxic gas, hazardous to handle), in OMVPE processes, a variety of organoarsenic compounds have been examined.[4,5] The search for better precursor molecules with desirable properties has been a driving force for continued current interest in organoarsenic chemistry.[5]

Metallocycloalkanes have been known to give volatile hydrocarbons with clean cleavage of the M–C bond.[6] This has prompted us to examine heterocyclic organoarsenic compounds. Although a few five- and six- membered arsacycloalkanes have been known since the beginning of the 20th century,[7–9] they have not been well characterized.[10,11] Furthermore, despite an extensive literature on transition-metal complexes with teriary arsines,[12] the coordination chemistry of heterocyclic arsenic compounds is still unexplored.[7–9,12,13] Only recently metal complexes with analogous heterocyclic phosphorus ligands such as 1-phenylphospholane[14] have been isolated and some of them have shown high activity in carbonylation reactions.[15] In view of the above, we have synthesized and characterized $PhAs(CH_2)_n$ ($n = 4$, 5) and their palladium and platinum complexes. Results of this work are reported here.

RESULTS AND DISCUSSION

The reactions of $PhAsCl_2$ with a di-Grignard reagent, $BrMg(CH_2)_nMgBr$ ($n = 4$ or 5) in THF readily gave phenylarsacycloalkanes, $PhAs(CH_2)_n$ {$n = 4$ (**2**) or 5 (**1**)} as colourless oily liquids which could be distilled under vacuum.[10,11] The mass spectra showed molecular ion peaks and a peak due to $PhAs^+$ in addition to hydrocarbon peaks. No peak assignable to an $As(CH_2)_n$ fragment was observed. The IR spectra displayed $\nu_{As\text{–}C}$ absorptions in the region 466–575 cm^{-1} associated with PhAs and $As(CH_2)_n$ fragments.[16] The ^1H NMR

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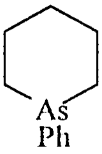
spectra exhibited multiplets in the region 0.89–1.99 and 7.24–7.46 ppm for acyclic and phenyl protons. The $^{13}C\{^1H\}$ NMR spectra showed the expected carbon resonances.



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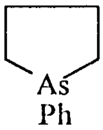

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Treatment of phenylarsacycloalkanes with $MCl_2(RCN)_2$ (M = Pd or Pt; R = Me or Ph) gave mononuclear complexes, $[MCl_2\{Ph\overline{As(CH_2)_n}\}_2]$. Similar reactions with $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ gave mixed-ligand complexes, $[PtCl_2(PEt_3)\{Ph\overline{As(CH_2)_n}\}]$. The palladium complexes adopt a *trans* configuration, as suggested by IR spectra which showed only one $\nu_{Pd–Cl}$ stretching mode (352 and 354 cm^{-1}).[17] This configuration is confirmed by X-ray structural analysis of $[PdCl_2(Ph\overline{AsCH_2CH_2CH_2CH_2CH_2})_2]$ (see below).

The platinum complexes have been assigned a *cis* configuration on the basis of $\nu_{Pt–Cl}$ stretches and ^1J(Pt–P). These complexes exhibited two $\nu_{Pt–Cl}$ absorptions,[17] as expected for a *cis* configuration. The ^1J(Pt–P) coupling constants for $[PtCl_2(PEt_3)\{Ph\overline{As(CH_2)_n}\}]$ are in accord with the values reported for $[PtCl_2(PR_3)(AsPh_3)]$ complexes.[18] It may be noted that on complexation the acyclic CH_2 proton resonances of $As(CH_2)_5$ tend to separate, and accordingly each CH_2 proton set gave a broad signal.

Thermogravimetric analysis (TGA) of $[PdCl_2(Ph\overline{AsCH_2CH_2CH_2CH_2CH_2})_2]$ was carried out under a static atmosphere in order to assess whether purification of arsacycloalkanes (for their use in OMVPE) can be achieved by thermolysis of their adducts. It is evident from the TGA curve (Fig. 1) that both the ligands are liberated at ~275 °C, leaving palladium chloride behind.

The molecular structure of $[PdCl_2(Ph\overline{AsCH_2CH_2CH_2CH_2CH_2})_2]$ (Fig. 2) shows that the palladium atom is in a square-planar environment (Table 1) with the arsacycloalkane ligands in a *trans* arrangement. The two Pd–Cl and Pd–As distances are the same and are in good agreement with the literature values.[19–23] The coordination around arsenic is typically a trigonal-pyramidal AsC_3 skeleton with C-As–C angles (100.3°–104.6°) which do not differ significantly from those reported for coordinated tertiary arsines.[24] The As–C bond lengths are in accord with the reported values.[24–26] The six-

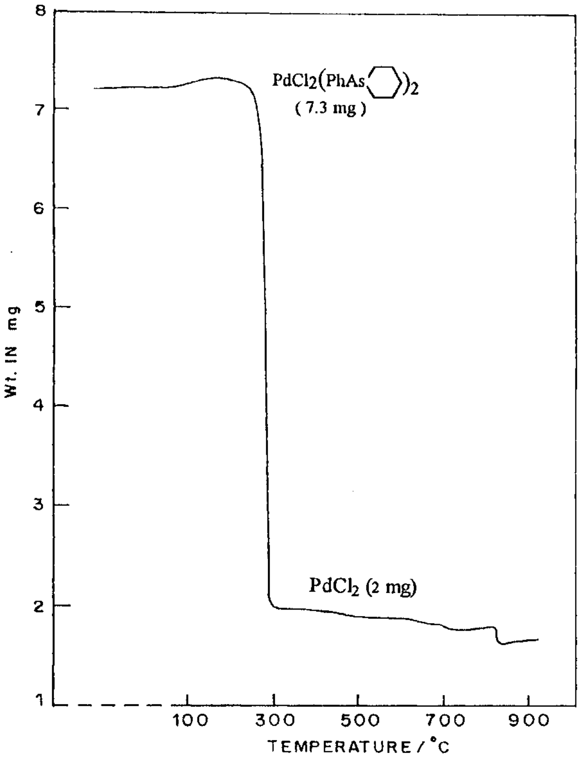

Figure 1 TGA curve for $[PdCl_2(Ph\overline{AsCH_2CH_2CH_2CH_2CH_2})_2]$ in static air; heating rate = 10 K min^{-1}.

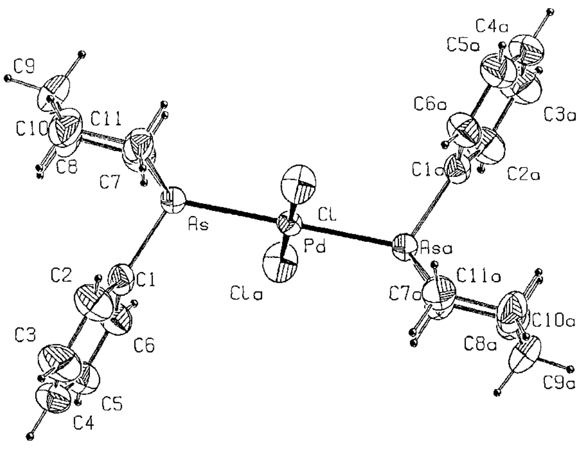

Figure 2 ORTEP diagram for $[PdCl_2(Ph\overline{AsCH_2CH_2CH_2CH_2CH_2})_2]$.

Table 1 Selected bond lengths (Å) and angles (°) for $[PdCl_2(PhAsCH_2CH_2CH_2CH_2CH_2)_2]$

Pd–Cl	2.2961 (13)	Pd–As#1	2.3999 (6)
As–C(7)	1.926 (5)	As–C(1)	1.929 (5)
As–C(11)	1.942 (5)		
Cl-Pd-Cl#1[a]	180.0	Cl-Pd-As#1	88.96 (4)
Cl#1-Pd-As#1	91.04 (4)	Cl-Pd-As	91.04 (4)
Cl#1-Pd-As	88.96 (4)	As#1-Pd-As	180.0
C(7)-As-C(1)	103.5 (2)	C(7)-As-C(11)	100.3 (3)
C(1)-As-C(11)	104.6 (2)	C(7)-As-Pd	117.1 (2)
C(1)-As-Pd	111.97 (14)	C(11)-As-Pd	117.5 (2)

[a] Symmetry transformations used to generate equivalent atoms: #1, −*x*, −*y*, −*z*.

membered metallocyclic ‘AsC_5’ ring is puckered and adopts a chair conformation. Selected interatomic parameters are given in Table 1.

EXPERIMENTAL

$PhAsCl_2$,[27] $MCl_2(RCN)_2$ (M = Pd or Pt; R = Ph or Me)[17] and $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$[17] were prepared according to published methods. All the reactions were carried out in dry solvents under a nitrogen atmosphere. Infrared spectra were recorded either as neat liquid or in a Nujol mull between CsI plates on a Bomem MB-102 spectrometer. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were obtained in $CDCl_3$ in 5-mm tubes on a Bruker DPX-300 NMR spectrometer. Chemical shifts were referenced to an internal chloroform peak (δ 7.26 ppm for ^1H and 77.0 ppm for ^{13}C) and external 85% H_3PO_4 for ^{31}P. Mass spectra were recorded on a Shimadzu GCMS QP 1000 A mass spectrometer using an EI source. Thermogravimetric analysis was carried out on a Shimadzu DT-30 thermal analyser with a heating rate of 10 K min^{-1}.

***Caution:* All arsenic compounds reported here should be treated as toxic and care must be taken while handling such derivatives.**

Preparation of $PhAsCH_2CH_2CH_2CH_2CH_2$ (1)

To a cold (∼10 °C) stirred tetrahydrofuran solution (30 ml) of phenyldichloroarsine (4.34 g, 19.5 mmol) was added dropwise through a canula an excess of 1,5-$BrMg(CH_2)_5MgBr$ [prepared from 1,5-$Br(CH_2)_5Br$ (14.2 g,61.8 mmol) and an excess of magnesium turnings (15 g,617 mmol) in tetrahydrofuran]. After all the Grignard reagent had been added, the reaction mixture was either stirred at room temperature for 3 h or refluxed for 2 h. After cooling, deoxygenated cold water was added slowly to the reaction mixture with stirring. The organic phase was extracted with ether (50 ml × 3), dried over $CaCl_2$ (2 h) and then filtered. The ether was evaporated *in vacuo* and the pale yellow oil was distilled under vacuum to give a colourless liquid (2.31 g, 53%) (b. p. 115–120 °C/1–2 mmHg, lit. 84 °C/0.5 mmHg[10,11]). Found: As, 33.5; Calcd for $C_{11}H_{15}As$: 33.7%. Mass spectra: *m*/*z*, 222 (molecular ion), 152 $[PhAs]^+$. IR as a neat liquid: 575, 554 [asym,sym,$\nu_{As–C}$, $As(CH_2)_5$], 487, 466 ($\nu_{As–C}$, AsPh), 378, 311, 282 cm^{-1}. ^1H NMR in $CDCl_3$: δ, 1.27–1.99 [m, $As(CH_2)_5$], 7.24–7.46 (m, AsPh). ^{13}C NMR in $CDCl_3$: δ, 22.4 (C-4), 24.1 (C-3,5), 28.7(C-2,6) [$As(CH_2)_5$]; 127.1 (C-4), 128.2 (C-3,5), 131.6 (C-2,6), 132.5 (C-1) [AsPh].

Preparation of $PhAsCH_2CH_2CH_2CH_2$ (2)

This was prepared in a similar way to 1. The product was distilled under vacuum as a colourless liquid (yield 66%) (b. p. 120 °C/6–7 mmHg, lit. 67 °C/0.2 mmHg[10,11]). Found: As, 35.5; calcd for $C_{10}H_{13}As$: 36.0%. Mass spectra: *m*/*z*, 208 (molecular ion), 152 $[PhAs]^+$. IR as a neat liquid: 567 [$\nu_{As–C}$, $As(CH_2)_4$], 469 ($\nu_{As–C}$, AsPh). ^1H NMR in $CDCl_3$: δ, 0.89–1.98 [m, $As(CH_2)_4$], 7.27–7.46 (m, AsPh): ^{13}C NMR in $CDCl_3$: δ; 27.3 (C-3,4), 30.3 (C-2,5), [$As(CH_2)_4$]; 127.1 (C-4), 128.1 (C-3,5), 131.4 (C-2,6), 132.5 (C-1) [AsPh].

Preparation of $[PdCl_2(PhAsCH_2CH_2CH_2CH_2CH_2)_2]$ (3)

To a benzene solution of $[PdCl_2(PhCN)_2]$ (380 mg, 0.99 mmol) was added a solution of $PhAsCH_2CH_2CH_2CH_2CH_2$ (450 mg, 2.02 mmol) with vigorous stirring, whereupon a yellow solution formed. The reactants were stirred at room temperature for 4 h. The solvent was stripped off *in vacuo* to give a yellow solid which was washed thoroughly with hexane and recrystallized from a dichloromethane–benzene–hexane mixture as yellow crystals (422 mg, 68%) (m. p. 162 °C). Found: C, 42.8%; H, 5.1; calcd for $C_{22}H_{30}Cl_2As_2$ Pd: C, 42.5; H, 4.9%. IR in Nujol: 594, 580 [$\nu_{As–C}$, $As(CH_2)_5$], 486, 461 ($\nu_{As–C}$, PhAs); 419, 397, 384, 375, 352 ($\nu_{Pd–Cl}$), 326. ^1H NMR in $CDCl_3$: δ, 1.52 (br), 1.74 (br) 1.90 (br), 2.19 (br), 2.58 (m) (each corresponds to one CH_2); 7.40 (br), 7.62 (br)

[AsPh]. ^{13}C NMR in $CDCl_3$: δ, 21.6 (C-4), 23.9 (C-3,5), 27.6 (C-2,6) [$As(CH_2)_5$]; 128.9 (C-3,5), 129.6 (C-4), 131.9 (C-2,6), 132.7 (C-1) [AsPh].

Preparation of $[PdCl_2(PhAsCH_2CH_2CH_2CH_2)_2]$ (4)

This was prepared in a similar manner to **3** and recrystallized from a benzene–hexane mixture (yield 36%) (m.p. 182 °C). Found: C, 40.0; H, 4.6; calcd for $C_{20}H_{26}Cl_2As_2Pd$: C, 40.5; H, 4.4%. IR in Nujol: 593 [ν_{As-C}, $As(CH_2)_4$], 483, 466 (ν_{As-C}, PhAs); 379, 354 (ν_{Pd-Cl}), 298, 288. ^{1}H NMR in $CDCl_3$: δ, 1.61–2.68 [m, $As(CH_2)_4$]; 7.29–7.71 (m, PhAs).

Preparation of $[PtCl_2(PhAsCH_2CH_2CH_2CH_2CH_2)_2]$ (5)

This was prepared analogously from $PtCl_2(MeCN)_2$ and $PhAsCH_2CH_2CH_2CH_2CH_2$ as an off-white crystalline solid which was recrystallized from CH_2Cl_2–EtOH–hexane in 52% yield. [m.p. 185 °C (dec.)]. Found: C, 36.5; H, 3.7; calcd for $C_{22}H_{30}Cl_2As_2Pt$: C, 37.2; H, 4.2%. IR in Nujol: 592, 578 [ν_{As-C}, $As(CH_2)_5$], 489, 466 (ν_{As-C}, PhAs); 309, 302, 292 (ν_{Pt-Cl}). ^{1}H NMR in $CDCl_3$: δ, 1.48–1.59 (m, $2CH_2$); 1.75 (m), 2.00 (m), 2.54 (m) (each corresponds to one CH_2); 7.35(m) [AsPh].

Preparation of $[PtCl_2(PhAsCH_2CH_2CH_2CH_2)_2]$ (6)

This was prepared analogously from $PtCl_2(MeCN)_2$ and $PhAsCH_2CH_2CH_2CH_2$ as an off-white crystalline solid which was recrystallized from CH_2Cl_2–EtOH–hexane in 37% yield. [m.p. 205 °C (dec.)]. Found: C, 34.5; H, 3.6; calcd for $C_{20}H_{26}Cl_2As_2Pt$: C, 35.2; H, 3.8%. IR in Nujol: 592 [ν_{As-C}, $As(CH_2)_4$], 483, 463 (ν_{As-C}, PhAs); 357, 307, 291 (ν_{Pt-Cl}). ^{1}H NMR in $CDCl_3$: δ, 1.63–2.58 [m, $As(CH_2)_4$], 7.23–7.42 (m) [AsPh].

Preparation of $[PtCl_2(PEt_3)(PhAsCH_2CH_2CH_2CH_2CH_2)]$ (7)

To a dichloromethane solution (20 ml) of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ (100 mg, 0.13 mmol) a solution of $PhAsCH_2CH_2CH_2CH_2CH_2$ (66 mg, 0.29 mmol) was added dropwise with vigorous stirring, whereupon a colourless solution was formed. The reactants were stirred at room temperature for 3 h. The solvent was stripped off *in vacuo*, leaving a white solid which was washed with hexane and recrystallized twice from a dichloromethane–hexane mixture as a white crystalline solid (yield 133 mg, 84%) (m.p. 150 °C). Found: C, 34.4; H, 5.5; calcd for $C_{17}H_{30}PAsCl_2Pt$: C, 33.7; H, 5.0%. IR in Nujol: 586, 486, 470, 439, 351, 311 (ν_{Pt-Cl}), 283. ^{1}H NMR in $CDCl_3$: δ, 0.98 (d, t, 7.5 Hz (t), 17.4 Hz (d), PCH_2Me); 1.18 (m, CH_2); 1.72 (m, $PCH_2 + CH_2$); 1.95 (m, CH_2CH_2); 2.35 (m, CH_2); 2.89 (m, CH_2); 7.34–7.67 (m, AsPh). ^{31}P{^{1}H} NMR in $CDCl_3$: δ, 6.8, ^1J(Pt–P) = 3416 Hz.

Preparation of $[PtCl_2(PEt_3)(PhAsCH_2CH_2CH_2CH_2)]$ (8)

The complex was prepared in an analogous manner and was recrystallized as a white crystalline solid from a dichloromethane–hexane mixture in quantitative yields (m.p. 164 °C). Found: C, 33.3; H, 5.3; calcd for $C_{16}H_{28}PAsCl_2Pt$: C, 32.5; H, 4.8%. IR in Nujol: 591, 483, 471, 438, 384, 306 (ν_{pt-Cl}), 290, 254, 241 cm^{-1}. ^{1}H NMR in $CDCl_3$: δ, 1.02

Table 2 Crystal data and structure refinement details for $[PdCl_2(PhAsCH_2CH_2CH_2CH_2CH_2)_2]$

Empirical formula	C_{22} H_{30} As_2 Cl_2 Pd
Molecular weight	621.60
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P*1
a	8.2273(10) Å
b	8.4612(9) Å
c	8.7430(12) Å
α	94.521(9)°
β	102.059(12)°
γ	95.419(7)°
Volume	589.49(14) Å^3
Z	1
Density (calculated)	1.751 g cm^{-3}
Absorption coefficient	3.805 mm^{-1}
F(000)	308
Crystal size	0.3 mm × 0.2 mm × 0.2 mm
θ range for data collection	2.39–24.97°
Index ranges	$0 \leq h \leq 9$, $-10 \leq k \leq 10$, $-10 \leq l \leq 10$
Reflections collected	2224
Independent reflections	2067 [*R*(int) = 0.0274]
Absorption correction	PSISCAN
Max. and min. transmission	0.995 and 0.647
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2066/0/125
Goodness-of-fit on F^2	1.105
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0332$, $wR_2 = 0.0762$
R indices (all data)	$R_1 = 0.0487$, $wR_2 = 0.0873$
Extinction coefficient	0.0020(13)
Largest difference, peak and hole	0.919 and −0.685 *e* Å^{-3}

Table 3 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (× 10^3) for $[PdCl_2(PhAsCH_2CH_2CH_2CH_2CH_2)_2]$. *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	*U* (eq)
Pd	0	0	0	28 (1)
As	2092 (1)	1803 (1)	1800 (1)	32 (1)
Cl	1850 (2)	−1862 (2)	−50 (2)	52 (1)
C(1)	1650 (6)	1987 (5)	3884 (5)	35 (1)
C(2)	2430 (8)	1148 (7)	5067 (7)	56 (2)
C(3)	1986 (9)	1255 (8)	6527 (7)	67 (2)
C(4)	794 (8)	2164 (8)	6793 (7)	60 (2)
C(5)	−18 (8)	2969 (8)	5637 (7)	60 (2)
C(6)	417 (7)	2878 (7)	4185 (6)	48 (1)
C(7)	2358 (8)	3983 (6)	1322 (6)	52 (1)
C(8)	3844 (8)	4976 (7)	2432 (7)	64 (2)
C(9)	5506 (8)	4258 (9)	2474 (8)	70 (2)
C(10)	5605 (7)	2686 (8)	3127 (8)	62 (2)
C(11)	4393 (6)	1323 (7)	2108 (7)	50 (1)

[d,(t),7.6 Hz t,17.5 Hz (d),PCH_2*Me*]; 1.73–2.08 (m, $PCH_2 + 2CH_2$); 2.33 (m, CH_2), 2.80 (m, CH_2); 7.44 (m), 7.74 (m) [AsPh]. $^{31}P\{^1H\}$ NMR in $CDCl_3$: δ, 8.7, ^1J(Pt–P) = 3375 Hz.

Crystallography

Yellow cube-shaped crystals of $[PdCl_2(PhAsCH_2CH_2CH_2CH_2CH_2)_2]$ (**3**) were selected for single-crystal X-ray data collection. All the measurements were performed at room temperature on an Enraf–Nonius CAD-4 diffractometer using graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) employing the ω–2θ scan technique. The unit cell parameters were determined from 25 reflections measured by random search routine and indexed by the method of short vectors followed by least-squares refinement. The intensity data were corrected for Lorentz, polarization and absorption effects. The structure was solved using the SHELXS-86[28] computer program and refined using the SHELXL-93[29] computer program.

Figure 2 shows the ORTEP[30] diagram of the molecule. The crystallographic data together with data collection details are given in Table 2. Atomic coordinates and equivalent isotropic displacement parameters are given in Table 3.

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REFERENCES

1. D. W. Bruce and D. O. Hare, *Inorganic Materials*, John Wiley, New York, 1992, p. 491.
2. M. L. Hitchman and K. F. Jensen, *Chemical Vapor Deposition: Principles and Applications*, Academic Press, London, 1993, p. 245.
3. J. O. Williams, *Angew Chem., Int. Ed. Engl.* **28**, 1110 (1989).
4. A. H. Cowley and R. A. Jones, *Angew Chem., Int. Ed. Eng.* **28**, 1208 (1989).
5. P. Zanella, G. Rossetto, N. Brianese, F. Ossola, M. Porchia and J. O. Williams, *Chem. Mater.* **3**, 225 (1991).
6. R. J. Puddephatt, *Coord. Chem. Rev.* **33**, 149 (1980).
7. E. V. Zappi, *Bull. Soc. Chim. Fr.* **19**, 151, 290 (1916).
8. G. Gruttner and E. Krause, *Berichte* **49**, 437 (1916).
9. F. G. Mann, *The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony and Bismuth*, Wiley–Interscience, New York, 1970.
10. K. Von Sommer, *Z. Anorg. Allg. Chem.* **377**, 278 (1970).
11. J. B. Lambert and H. Sun, *J. Org. Chem.* **42**, 1315 (1977).
12. C. A. McAuliffe and W. Levason, *Phosphine, Arsine and Stibine Complexes of the Transition Elements*, Elsevier Scientific, 1979.
13. G. O. Doak and L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony and Bismuth*, John Wiley, New York, 1970.
14. S. J. Coles, P. G. Edwards, M. B. Hursthouse, K. M. A. Malike, J. L. Thick and R. P. Tooze, *J. Chem. Soc., Dalton Trans.* 1821 (1997).
15. R. P. Tooze, British Patent Application WO95/15938, 1995.
16. E. J. Maslowsky Jr., *J. Organometal Chem.* **70**, 153 (1974).
17. F. R. Hartley, *The Chemistry of Platinum and Palladium*, Applied Science, London, 1973.
18. H. C. Clark, A. B. Goel, V. K. Jain, K. G. Tyers and C. S. Wong, *J. Organometal. Chem.* **321**, 123 (1987).
19. A. F. Wells, *Proc. R. Soc. London Ser. A* **167**, 169 (1938).
20. C. M. Harries, R. S. Nyholm and N. C. Stephenser, *Nature (London)* **177**, 1127 (1956).
21. S. F. Watkins, *J. Chem. Soc., Chem. Commun.* 50 (1968).
22. J. P. Beale and N. C. Stephenser, *Acta Crystallogr. sect. B* **26**, 1655 (1970).
23. V. K. Jain, R. P. Patel, K. V. Muralidharan and R. Bohra, *Polyhedron* **8**, 2151 (1989).
24. N. Bricklebank, S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.* 157 (1996).
25. S. Kamepalli, C. J. Carmalt, R. D. Culp, A. H. Cowley, R. J. Jones and N. C. Norman, *Inorg. Chem.* **35**, 6179 (1996).
26. R. C. Olivares, J. G. Alvarado, G. E. Perez, C. Silvestru and I. Haiduc, *J. Chem. Soc., Dalton. Trans.* 2191 (1994).
27. S. S. Garje and V. K. Jain, *Main Group Met. Chem.* **19**, 355 (1996).
28. G. M. Sheldrick, *SHELXS-86, Program for Crystal Structure Determination*, University of Göttingen, Germany, 1986.
29. G. M. Sheldrick, *SHELXL-93, Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1993.
30. C. K. Johnson, *ORTEP II, A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, ORNL-5138, 1976.