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Synthesis and multinuclear NMR studies of 3-aminopropyl(aryl)chalcogenides, $NH_2CH_2CH_2CH_2EAr$ (E=Se, Te), and their complexes with Pt(II) and Pd(II)

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Abstract

The asymmetric ligands, 3-aminopropyl(aryl)tellurides (**1a**, **1b**) [Ar = Ph (**a**); C_6H_4–OMe (**b**)] and 3-aminopropyl(phenyl)selenide (**2**) and their complexes with platinum(II) and palladium(II), viz. [$PtCl_2$(**1a**, **1b**)] (**3**, **4**), [$PtCl_2$(**2**)] (**5**), [$PdCl_2$(**1a**, **1b**)] (**6**, **7**), [$PdCl_2$(**2**)] (**8**), [(Me)ClPd(**1b**)] (**9**) and [(Me)ClPd($\mathbf{1b}$)$_2$](**10**) have been made and characterized. Complexes **3–8**, have square planar geometry around the metal (Pd or Pt) with the (Te,N)- or (Se,N)-ligand coordinated in a bidentate mode and the two chlorines *cis* to each other. Complex **9** also has a square planar geometry, with Me *trans* to nitrogen and Cl *trans* to tellurium. In complex **10** where Pd appears to be in a square planar geometry the two tellurium atoms are judged to be *trans* to each other.

Keywords: Alkyl; Amine; Aryl; Group 16; Group 10; Chalcogenide

1. Introduction

There is a growing interest in the chemistry of hybrid organotellurium ligands that contain nitrogen or oxygen as a hard donor atom in addition to tellurium, a soft donor atom [1]. Some (Te,N) donors have been prepared to develop the idea that such ligands may interact with heavy metals strongly through tellurium and weakly through nitrogen, thereby generating species with unusual reactivities [2,9], for example they can be expected to find application in the design of novel heterobimetallic complexes. Recently we demonstrated the ability of telluroamine complexes to form some interesting heterobimetallic complexes [10]. In continuation of our studies on (Te,N) donors, and bearing in mind the importance of organopalladium and platinum-amine complexes in carbonylation reactions [11,12], we have now synthesized 3-aminopropyl(aryl)tellurides (**1a**, **1b**) and selenide (**2**) (Fig. 1) and their complexes with palladium (II) and platinum (II).

2. Experimental details

All solvents were dried and distilled before use. Manipulations were carried out under dry oxygen-free nitrogen or argon.

Published methods were used to prepare $(4\text{-}MeOC_6H_4)_2Te_2$, Ph_2Te_2 [13] and Ph_2Se_2 [14]. Although the complex [(Me)(Cl)Pd(COD)] has been used [11,12] to the best of our knowledge its synthesis has not been reported. We prepared it by addition of tetramethyltin to an ice-cold solution of [(COD)$PdCl_2$] in dichloromethane, followed by stirring for 24 h. Evaporation of the solution in vacuum yielded a light-green coloured solid, which was washed with diethyl ether and recrystallized from a mixture of dichloromethane and ether [^1H NMR, $CDCl_3$: δ 1.19 (Me–Pd); ^{13}C NMR, $CDCl_3$: δ 12.4 (Me–Pd); IR, ν (Pd–Cl): 313 cm^{-1}]. The compounds $3\text{-}Cl(CH_2)_3NH_2.HCl$ (Fluka), K_2PtCl_4, [$Pd(PhCN)_2Cl_2$], $SnMe_4$ and [(COD)$PdCl_2$] (Aldrich) were used as received. IR spectra over the range 4000–700 cm^{-1} were recorded on a Nicolet 5DX FT spectrophotometer with KBr/CsI pellets and far-IR spectra in polyethylene on a Perkin-Elmer 1700X FT

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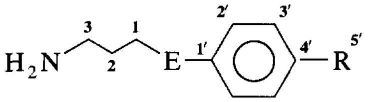


1a E = Te, R = H
1b E = Te, R = OMe
2 E = Se, R = H

Fig. 1.

instrument. All the NMR spectra were recorded for solutions in d_6 DMSO or $CDCl_3$. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on JEOL FX-100 FT instrument at 99.5 MHz and 25 MHz, respectively, with TMS as internal standard. The $^{125}Te\{^1H\}$, $^{77}Se\{^1H\}$, $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were recorded at 126, 76, 162 and 86 MHz on a Bruker AMX 400 FT spectrometer with $(Me)_2Te$, Ph_2Se_2, 85% H_3PO_4 and H_2PtCl_6, respectively, as external references. Conductance measurements were carried out with ca.1 mmol solutions in DMSO using a Metrohm 660 conductometer, and molecular weights were determined in chloroform with a Knauer vapour pressure osmometer. The mass spectrum (70 eV) was obtained on a JMS D300 (JEOL) GCMS spectrometer. Elemental analyses were performed with a Perkin-Elmer 240C analyser.

2.1. *Synthesis of 3-aminopropyl(aryl)tellurides (1a, 1b) and 3-aminopropyl(phenyl)selenide (2)*

An alkaline ethanolic solution of $NaBH_4$ was added dropwise to a solution of the diaryl-ditelluride or diphenyl-diselenide (1 mmol) in ethanol (40 cm^3) until it became colourless. A solution of 3-chloropropylamine hydrochloride (2 mmol) in ethanol (10 cm^3) was added dropwise with stirring and the mixture was refluxed for 3–4 h. The resultant liquid was extracted with chloroform, washed with water, and dried over anhydrous sodium sulphate. The chloroform extract was concentrated and the product was precipitated by addition of hexane. It was filtered off, recrystallised from chloroform, and dried in vacuo.

2.2. *Synthesis of [$PtCl_2$.1(a,b)] (3, 4) and [$PtCl_2$.2] (5)*

A solution of **1** or **2** (1 mmol) in a mixture of ethanol (15 cm^3) and acetone (5 cm^3) was added dropwise with stirring at room temperature to a solution of tetrachloroplatinate (0.42 g, 1 mmol) in water (10 cm^3). The mixture was stirred for 2 h and the resulting pale-yellow precipitate was then filtered off, washed with water and ethanol, and dried in vacuo.

2.3. *Synthesis of [$PdCl_2$.1(a,b)] (6, 7) and [$PdCl_2$.2] (8)*

A solution of compound **1** or **2** (1 mmol) in chloroform (10 cm^3) was added dropwise with stirring to a solution of bis-(benzonitrile)palladium(II) chloride (0.38 g, 1 mmol) in chloroform (15 cm^3). A yellow precipitate separated after about 15 min but the mixture was stirred for another 2 h and the solid then filtered off, washed with chloroform, and dried in vacuo.

Table 1
Elemental analysis and physical properties

Compound	Colour	Yield (%)	M.P.	C found (calc.) %	H	N	Mol. Wt. found (calc.)
1a	White	65	100	39.1	3.7	6.2	254
				(41.1)	(4.9)	(5.3)	(262.6)
1b	White	60	76	38.4	4.2	5.6	270
				(41.0)	(5.1)	(4.8)	(292.6)
2	White	55	80	49.1	5.1	6.0	200
				(50.4)	(6.0)	(6.5)	(214.0)
3	Light yellow	80	150(d)	20.7	2.0	2.3	–
				(20.4)	(2.4)	(2.6)	
4	Light yellow	80	180(d)	18.5	2.1	3.5	–
				(19.3)	(2.6)	(2.5)	
5	Mustard	80	180(d)	20.9	2.0	3.0	–
				(22.4)	(2.7)	(2.9)	
6	Dark yellow	75	145(d)	25.5	2.8	3.8	–
				(24.5)	(2.9)	(3.8)	
7	Dark yellow	75	120(d)	23.4	2.7	2.9	–
				(23.0)	(3.1)	(2.9)	
8	Dark yellow	75	160(d)	28.4	3.0	4.0	–
				(27.6)	(3.4)	(3.5)	
9	Greenish yellow	75	68	30.0	4.0	2.2	435
				(29.3)	(4.0)	(3.1)	(449.5)
10	Yellow	80	48	32.9	4.3	3.1	728
				(33.9)	(4.4)	(3.8)	(742.1)

Table 2
^{1}H NMR data (δ, ppm)

Compound	CH_3	NH_2	CH_2		H(R)	H(Ar)
			H(2)	H(1),H(3)		
1a	–	1.60–2.08(m) (NH_2 + CH_2(2))	merges with NH_2	2.70–3.00(m)	–	7.20–7.80(m)
1b	–	1.45(s)	1.81–1.96(m)	2.70–2.90(m)	3.80(s)	6.75(d, ^1J = 9 Hz) (m to Te) 7.60 (d, ^1J = 9 Hz) (o to Te)
2	–	1.41(s)	1.70–2.00(m)	2.70–3.00(m)	–	7.25–7.66(m)
3	–	2.07(s)	masked by DMSO		–	7.45–8.53(m)
4	–	2.00(s)	masked by DMSO		3.81(s)	7.04(d,m to Te) 8.04(d,o to Te)
5	–	1.98(s)	masked by DMSO		–	7.30–9.50(m)
6	–	2.24(s)	masked by DMSO		–	7.47–8.14(m)
7	–	2.20–2.30(m) (NH_2 + CH_2(2))	Other CH_2 peaks masked by DMSO		3.81(s)	7.00(d,m to Te) 8.00(d,o to Te)
8	–	2.10–2.30(m) (NH_2 + CH_2(2))		2.80–3.10(m)	–	7.50(d,m to Se) 8.30(d,o to Se)
9	0.40(s)	1.97–2.33 (NH_2 + CH_2(2))		2.60–3.15(m)	3.84(s)	6.90(d,m to Te) 8.00(d,o to Te)
10	0.32(s)	1.25, 1.76	2.12(m)	2.60–3.10(m)	3.82(s)	6.86(d,m to Te) 7.90(d,o to Te)

*2.4. Synthesis of [(Me)ClPd(**1b**)] (**9**)*

A solution of **1b** (0.29 g, 1 mmol) in dichloromethane (20 cm^3) was added dropwise with stirring to a solution of [(COD)Pd(Me)Cl] (0.29 g, 1 mmol) in dichloromethane (20 cm^3) cooled in an ice bath. The disappearance of [(COD)Pd(Me)Cl] was monitored by TLC. The resultant pale-yellow solution was concentrated in vacuo, and the complex precipitated by addition of hexane and recrystallized from dichloromethane/hexane.

*2.5. Synthesis of [(Me)ClPd(**1b**)$_2$] (**10**)*

A solution of **1b**, (0.58 g, 2 mmol) in dichloromethane (30 cm^3) was added in one portion to a solution of [(COD)Pd(Me)Cl] (0.29 g, 1 mmol) in dichloromethane (20 cm^3). The subsequent procedure was as described for the isolation **9**.

3. Results and discussion

The colour, m.p, analytical and molecular weight data (where possible) of the isolated ligands and their complexes with palladium(II) and platinum(II) are shown in Table 1.

The asymmetric potential ligands 3-aminopropyl (aryl)tellurides (**1a**, **1b**) and 3-aminopropyl(phenyl)selenide(**2**) have been made by the reactions with 3-chloropropylamine of sodium arylchalcogenolates, NaEAr (E=Se/Te), generated in situ by $NaBH_4$ reduction of the corresponding diaryldichalcogenides, Ar_2E_2, in al-

Table 3
Multinuclear NMR data: $^{13}C\{^1H\}$, $^{125}Te\{^1H\}$, $^{77}Se\{^1H\}$, (δ, ppm)

Compound	^{13}C									^{125}Te/^{77}Se
	CH_2			Aromatic						
	C1	C2	C3	C1′	C2′	C3′	C4′	C5′	Me	
1a	5.0	32.0	42.0	111.6	138.6	128.1	126.5	–	–	472.5
1b	5.0	32.0	41.0	100.4	139.8	114.5	159.3	57.0	–	459.7
2	25.0	30.0	40.5	125.7	132.0	128.7	127.3	–	–	306.0 [a]
3	13.2	26.7	43.8	118.6	137.8	129.2	127.8	–	–	617.8 ($^1J_{Pt-Te}$ = 1351 Hz)
7	14.2	26.9	42.7	107.4	138.2	115.2	160.4	55.2	–	–
9	11.6	28.2	42.5	128.3	140.0	115.6	161.0	55.0	−9.4	571.5
10	12.4	30.2	42.8	122.8	140.0	115.4	161.0	55.2	−8.8	576.0

[a] Converted with respect to Me_2Se.

Table 4
Infrared data (cm^{-1})

Compound	ν(N–H)	δ(N–H)	ν(C–N)	ν(Te/Se–C)	ν(M–X)
1a	3260	1572	1196	489	–
1b	3280	1546	1196	488	–
2	3256	1564	1208	495	–
3	3230	1583	1183	475	324,300
4	3222	1583	1173	475	328,294
5	3200	1581	1177	469	330,311
6	3233	1585	1174	481	311,290
7	3240	1584	1180	478	319,287
8	3235	1575	1158	479	330,304
9	3224	1576	1177	473	326
10	3290– 3210(b)	1545, 1560	1195, 1185	476	330

kaline ethanol. They are fairly soluble in organic solvents such as chloroform as dichloromethane, and behave as non-electrolytes in solution, are monomeric as indicated by molecular weight measurements on their ca.0.1 mmol solutions in chloroform. The ^{1}H NMR spectra (Table 2) of **1(a,b)** and **2** are as expected except for the overlap of Te–CH$_2$ and N–CH$_2$ protons, resulting in a multiplet ca. δ 2.7–3.0. The other CH$_2$ protons give a multiplet in the range δ 1.7–2.0, except in the case of **1a**, where they overlap with the NH$_2$ protons.

The ^{13}C NMR spectra (Table 3) of the compounds provide an insight into the nature of carbons attached to Te and N. The signal from the C$_1$ carbon in **1a**, **1b** being ca. 20 ppm further upfield than that for **2** owing to the higher electronegativity of Se than of Te. The C$'_1$ carbon signal also shows a similar effect. The compounds have been further characterized by ^{125}Te{^{1}H}/^{77}Se{^{1}H} NMR (Table 3) and IR (Table 4) spectroscopy. The mass spectrum of **1b** shows a peak (along with the parent ion peak at $m/e = 295$) at $m/e = 237$ corresponding to TeC$_6$H$_4$OMe, suggesting that the Te–C(alkyl) bond is cleaved in preference to the Te–C(aryl) bond.

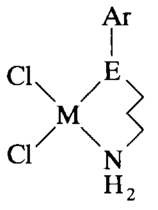
Reactions of **1** and **2** with potassium tetrachloroplatinate and bis-(benzonitrile)palladium(II) chloride result in the formation of [MCl$_2$.**1(a,b)**] and [MCl$_2$.**2**] (M = Pt (**3**–**5**) or Pd (**6**–**8**)). The resulting complexes are insoluble in solvents such as chloroform, dichloromethane, and ethanol, sparingly soluble in acetonitrile, but very soluble in DMSO. The molar conductances of **3**–**8** in DMSO indicate that they are non-electrolytes.

The IR spectra of complexes **3**–**8** (Table 4) show two bands, at ca. 330 cm^{-1} and 300 cm^{-1}, assignable to ν(M–Cl) vibrations, that are characteristic of terminal chlorines in a *cis* conformation in a square planar arrangement of the ligands around the metal atom [15]. The red shift of γ(N–H) by 30–35 cm^{-1} and γ(C–N) by 20–25 cm^{-1} and a blue shift of δ(N–H) by 15–20 cm^{-1} indicate that there is coordination to M via N [8]. The peaks in which there is contribution from the ν(E–C$_{\text{alkyl}}$) vibration also undergo a red shift (ca. 15 cm^{-1}), indicating that there is coordination to M via Se or Te.

The ^{1}H NMR spectra of these complexes (Table 2) in d$_6$-DMSO show that the signals from the NH$_2$ protons are deshielded by ca. 0.6 ppm and the aromatic protons by 0.3–0.5 ppm relative to those from the free ligands, again indicating that there is coordination of both nitrogen and tellurium or selenium to the metal atom. The signals of CH$_2$ protons overlap with those from the DMSO. In complexes **7** and **8** the –CH$_2$(2) peaks overlap with those NH$_2$ and show a multiplet centered at δ 2.20. In complex **8**, the Se–CH$_2$ and N–CH$_2$ peaks overlap over the range δ 2.8–3.1. The ^{13}C{^{1}H} NMR spectra (Table 3) of **3** and **7** clearly establish the coordination of the ligand through both Te and N to the metal atom with the signals from Te–C$_{\text{alkyl}}$, Te–C$_{\text{aryl}}$ and N–C undergoing downfield shifts of 8–9, 7, and 2 ppm, respectively. The ^{125}Te{^{1}H} NMR (Table 4) spectrum of 3 exhibits a single resonance lying 158 ppm downfield from that for **1a**, confirming the coordination of Te to Pt. The ^1J(Pt–Te) value is 1351 Hz. The ^{195}Pt{^{1}H} NMR spectrum shows a single resonance at δ −3866.

Thus, the IR and NMR data show that the aminopropyl-tellurides/selenide behave as heterobifunctional ligands coordinated through both Te or Se and N to Pd(II) or Pt(II). The geometry of the metal atom in the complexes is square planar, with the two Cl atoms in *cis* positions. The proposed structure of these complexes is shown in Fig. 2.

To throw light on the nature of complexes **3**–**8** the reaction of triphenylphosphine with **4** in approximately equimolar ratio in dichloromethane was examined. It gave a pale-yellow product of the approximate composition [PtCl]$_2$(**1b**)(PPh$_3$)] which gave an ^{1}H NMR spectrum in which the signal from the NH$_2$ protons (δ 1.5) is close to that from **1b**, suggesting that the amino group is uncoordinated in the product. The ^{125}Te{^{1}H} NMR spectrum of the complex displays a signal, showing platinum satellites, at δ 693, with a value of J(Pt–Te) = 1210 Hz, which points unambiguously to a *cis* configuration of the complex [16]. In keeping with this, the ^{31}P{^{1}H} signal is at δ 3.1 [^1J(Pt–P) = 3296 Hz]) and the ^{195}Pt{^{1}H} signal at δ −3511. In addition, the phosphorus and platinum NMR spectra each show a further signal of low intensity at δ 14.0 [^1J(Pt–P) =



E = Se, Te
M = Pd, Pt

Fig. 2.

3669 Hz] and δ −3544, respectively, which agree with the values for *cis*-[$PtCl_2(PPh_3)_2$] [17]. The upfield signal of the ^{31}P signal and the corresponding decrease in the value of ^{1}J(Pt–P), for [$PtCl_2$(**1b**)(PPh_3)] relative to *cis*-[$PtCl_2(PPh_3)_2$] suggests a weakening of the Pt–P bond; this is attributed to the formation of a strong Pt–Te sigma bond (as indicated by the large downfield shift {233 ppm} of the ^{125}Te signal relative to **1b** and the high value of Pt–Te coupling constant). Another factor in the weakening of the Pt–P bond, (in addition to the electronic effect) is the steric effect resulting from the presence of bulky groups on phosphorus and tellurium atoms that are *cis* to each other. The outcome of the above reaction of **4**, along with the IR data, suggests that the complex is monomeric.

In view of the significant *trans* influence usually exerted by aryltelluro group, attempts were made to substitute the Cl atoms *trans* to Te in [$PdCl_2$(**1b**)] by Me or Ph using $SnMe_4$ or PhHgCl in dioxane. No reactions took place at room temperature, and refluxing resulted in decomposition. However, the complexes [(Me)ClPd(**1b**)] (**9**) and [(Me)ClPd$(\mathbf{1b})_2$] (**10**) were obtained by mixing **1b** with [(Me)ClPd(COD)] in 1 : 1 and 2 : 1 molar ratios, respectively. These complexes are less stable than their dichloro-counterparts. Complex **10** dissolves in common organic solvents, except hexane and ether, to give stable solutions, but complex **9** is soluble only in chlorinated solvents such as dichloromethane or chloroform, and the decomposition occurs, when the solutions are kept at room temperature. Properties of the complexes are shown in Table 1.

The IR spectra (Table 4) of complexes **9** and **10** show ν(Pd–Cl) at ca. 330 cm^{-1}, characteristic of terminal Cl [15]. In the spectrum of **9** ν(N–H), ν(C–N) and ν(Te–C) bonds display red shifts, but in the case of complex **10** only ν(Te–C) shows such an effect clearly. The ν(N–H), δ(N–H) and ν(C–N) bands from the latter in some cases are broadened, and in other cases new bands arising from uncoordinated N appear along side the others, showing a slight shift. This suggests that there is some variation in the ligational behaviour of the donor in these two complexes.

Complex **10** has a conductance in methanol corresponding to 1 : 1 dissociation, but it behaves as a non-electrolyte in nitromethane and 1,2 dichloroethane. This indicates that in methanol, solvolysis of the complex takes place. To prove this the far IR spectrum was recorded for a drop of methanolic solution on a polyethylene pellet, and this showed the absence of ν(Pd–Cl).

Comparison of the ^{1}H NMR spectrum of **9** with that for **1b** shows a downfield shift of NH_2 (by 0.6 ppm), aryl (by 0.25 ppm) and CH_2 protons (by ca. 0.15 ppm) suggesting the coordination of both Te and N to the metal atom. There is also an upfield shift for the protons of the methyl attached to Pd protons (by 0.80 ppm) relative to that for [(Me)ClPd(COD)]; the position of the signal agrees well with that (δ 0.45) reported for the methyl protons *trans* to N in [(PC_3NMe_2)Pd(Me)Cl] [14]. The $^{13}C\{^{1}H\}$ NMR spectrum shows downfield shifts, relative to **1b**, of Te–C_{alkyl} (7 ppm), Te–C_{aryl} (28 ppm) and N–C (2 ppm), and upfield shift of the Pd–C_{methyl} (22 ppm), in keeping with the ^{1}H NMR data. The $^{125}Te\{^{1}H\}$ NMR spectrum exhibits a single peak ca. 112 ppm downfield relative to the ligand. On the basis of the above observations, the structure of **9** is suggested to that in Fig. 3.

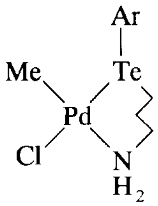


Fig. 3.

This arrangement around the square planar palladium should be more favourable than that in which the groups with high *trans* influences i.e. Te and Me, are opposite each other, particularly when, as in the present case there are no unfavourable steric effects.

The ^{1}H NMR spectrum of **10** reveals downfield shifts for the aryl (by 0.2 ppm) and CH_2 (by 0.1 ppm) protons. It further shows two peaks for amino protons, one somewhat shielded (δ 1.25) and the other deshielded (δ 1.76) with respect to the signals from **1b**. The methyl attached to Pd signal is shielded even relative to **9** (by 0.08 ppm). The ^{13}C NMR spectrum in general has features similar to those for **9**. The appearance of a single $^{125}Te\{^{1}H\}$ NMR signal 117 ppm downfield relative to ligand confirms not only that there is coordination of the ligand through Te but also that the two equivalent Te atoms are *trans* to each other. In view of this and the tendency of Pd(II) to favour planar four coordination, it seems rather difficult to account for the ^{1}H NMR of the signals from the amino groups; one possible reason may be exchange between the two NH_2 groups and the Cl atom in the complex.

On the basis of the multinuclear NMR, far IR, conductance and molecular weight data for complex **10**, a square planar arrangement of the ligands around Pd atom with the methyl group *trans* to Cl (Fig. 4) is proposed. This is supported by the UV-visible spectrum [409 (ϵ = 445), 310 (4485), 254 (sh, 33086) and 250

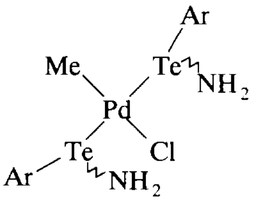


Fig. 4.

(35905) nm] which shows a d–d transition (409 nm) at lower energy than that for **9** [336 ($\epsilon = 1370$), 312 (4567), 254 (sh, 32333) and 251 (42285) nm], probably of the larger number of soft donors around palladium [18].

Attempts to grow good quality single crystals of any of these compounds were unsuccessful.

Acknowledgements

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References

[1] E.G. Hope and W. Levason, *Coord. Chem. Rev., 112* (1993) 109, and references therein.

[2] M.A.K. Ahmed, W.R. McWhinnie and T.A. Hamor, *J. Organomet. Chem., 281* (1985) 205.

[3] A.K. Singh, V. Srivastva and B.L. Khandelwal, *Polyhedron, 9* (1990) 495.

[4] A.K. Singh and V. Srivastva, *J. Coord. Chem., 21* (1990) 39.

[5] A.K. Singh V. Srivastva and B.L. Khandelwal, *Polyhedron, 9* (1990) 851.

[6] B.L. Khandelwal, A.K. Singh, V. Srivastva, D.C. Povey and G.W. Smith, *Polyhedron, 9* (1990) 2045.

[7] A.K. Singh and V. Srivastva, *Phosphorus, Sulfur and Silicon, 47* (1990) 471.

[8] A.K. Singh and V. Srivastva, *J. Coord. Chem., 21* (1990) 269.

[9] A. Khalid, B.L. Khandelwal, A.K. Singh, T.P. Singh and B. Padmanabhan, *J. Coord. Chem., 31* (1994) 19.

[10] B.L. Khandelwal and K. Uppal, *Polyhedron, 11* (1992) 1755.

[11] R.E. Rulka, L.M. Han, C.J. Elsevier, K. Vrieze, P.W.N. Van Leeuwen, C.F. Roobeek, M.C. Zoutberg, Y.F. Wang and C.H. Stam, *Inorg. Chim. Acta, 169* (1990) 5.

[12] G.P.C.M. Dekker, A. Buijis, C.J. Elsevier, P.W.N.M. Van Leeuwen, W.J.J. Smeets, A.L. Spek, Y.F. Wang and C.H. Stam, *Organometallics, 11* (1992) 1937.

[13] K.J. Irgolic and R.A. Zingaro in E. Becker and M. Tsutsui (eds.), *Organometallic Reactions*, John Wiley and Sons, New York, 2, 1971, p. 275.

[14] K.B. Sharpless and M.W. Young, *J. Org. Chem., 40* (1975) 947.

[15] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., John Wiley, New York, 1986, pp. 324 and 203.

[16] Tim Kemmitt and W. Levason, *Inorg. Chem., 29* (1990)) 731.

[17] R.G. Goel, *Inorg. Nucl. Chem. Lett., 15* (1979) 437.

[18] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1984.