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Bidentate Group VB Chelates, Part VII.[1] Some Palladium(II) Complexes with Diphosphine, Phosphine–Arsine, and Diarsine Ligands, Including Some Thiocyanate Derivatives

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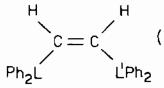
Eighteen complexes of palladium(II) salts and the bidentate chelating ligands cis-1,2-bis(diphenylphosphino)ethylene (vpp), cis-1,2-bis(diphenylarsino)ethylene (vaa), cis-1-diphenylarsino-2-diphenylphosphinoethylene (vasp), and 9,10-bis(diphenylphosphino)phenanthrene (dpph) have been prepared and studied by infrared and electronic spectroscopic techniques. The thiocyanate complexes are formulated $Pd(vpp)(SCN)_2$, $Pd(vaa)(SCN)_2$, $Pd(vasp)(SCN)_2$, and Pd(dpph)(NCS)(SCN), and the possible factors promoting the different types of coordination are discussed.

Introduction

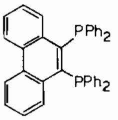
Palladium(II) salts form very stable complexes with tertiary phosphines and arsines.[2] Among the bidentate group VB chelates coordinated to palladium(II) are: 1,2-bis(diphenylphosphino)ethane (dpe) and 1,2-bis(diphenylarsino)ethane,[3,4] *cis-* and *trans*-1,2-bis-(dimethylarsino)ethylene,[5] *o*-phenylenebis(dimethylarsine),[6] 1,8-bis(dimethylarsino)naphthalene,[7] (*o*-diphenylphosphinophenyl)diphenylarsine (ap),[8,9] and *o*-phenylenebis(diphenylarsine).[10] Particular interest has centred upon the mode of coordination of the ambidentate thiocyanate ligand in palladium(II) complexes following the synthesis and interconversion of $Pd(AsPh_3)_2(SCN)_2$ and $Pd(AsPh_3)_2(NCS)_2$ by Burmeister and Basolo.[11] More recently Meek *et al.*[9,12] have prepared palladium(II) thiocyanate complexes of a range of bidentate chelates with two different donor atoms and with differing chelate chain lengths, and have examined the effect of these upon the mode of thiocyanate coordination. There appears to be growing interest in the coordination chemistry of bidentate ligands containing unusual carbon chain lengths.[13,14]

We have been interested in ambidentate thiocyanate coordination for some time[1,10,15] and have pointed out that the emphasis placed by workers in electronic explanations such as antisymbiosis[16,17] or stereochemical explanations[12] to justify M–NCS *vs.* M–SCN coordination is only partially correct, as both factors undoubtedly are important.

Here we wish to report the reactions of palladium(II) salts with the ligands *cis*-1,2-bis(diphenylphosphino)ethylene (vpp; I, E = E′ = P), *cis*-1,2-bis(diphenylarsino)ethylene (vaa; I, E = E′ = As), *cis*-1-diphenylarsino-2-diphenylphosphinoethylene (vasp; I, E = P, E′ = As), and 9,10-bis(diphenylphosphino)phenanthrene (dpph, II). A preliminary report of the formation of $Pd(vpp)(SCN)_2$ has already been published.[1]



(I)



(II)

Experimental

The ligands were prepared by established methods.[18–20]

The Complexes

$[PdLX_2]$ (L = vpp, vaa, vasp, dpph; X = Cl, Br, I).

An ethanolic solution (20 ml) of Na_2PdCl_4 (0.54 g, 2.00 mmol) was added to the ligand (2.0 mmol) in acetone (30 ml). A yellow solution was formed which was then stirred for half an hour. The solution was then taken to dryness on a rotatory evaporator to leave a pale yellow residue which was then recrystallised from CH_2Cl_2/EtOH. The bromide and iodide derivatives were synthesised by reacting a five-fold excess of NaBr or NaI with the $PDLCl_2$ reaction mixture, followed by filtration and recrystallisation from CH_2Cl_2/EtOH. Yields 90%.

$[Pd(vpp)_2]X_2$ (X = Br, NCS).

A filtered solution of $[PdX_4]^{2-}$ (2.0 mmol) in n-butanol was added to vpp (1.4 g, 4.0 mmol) in acetone. A

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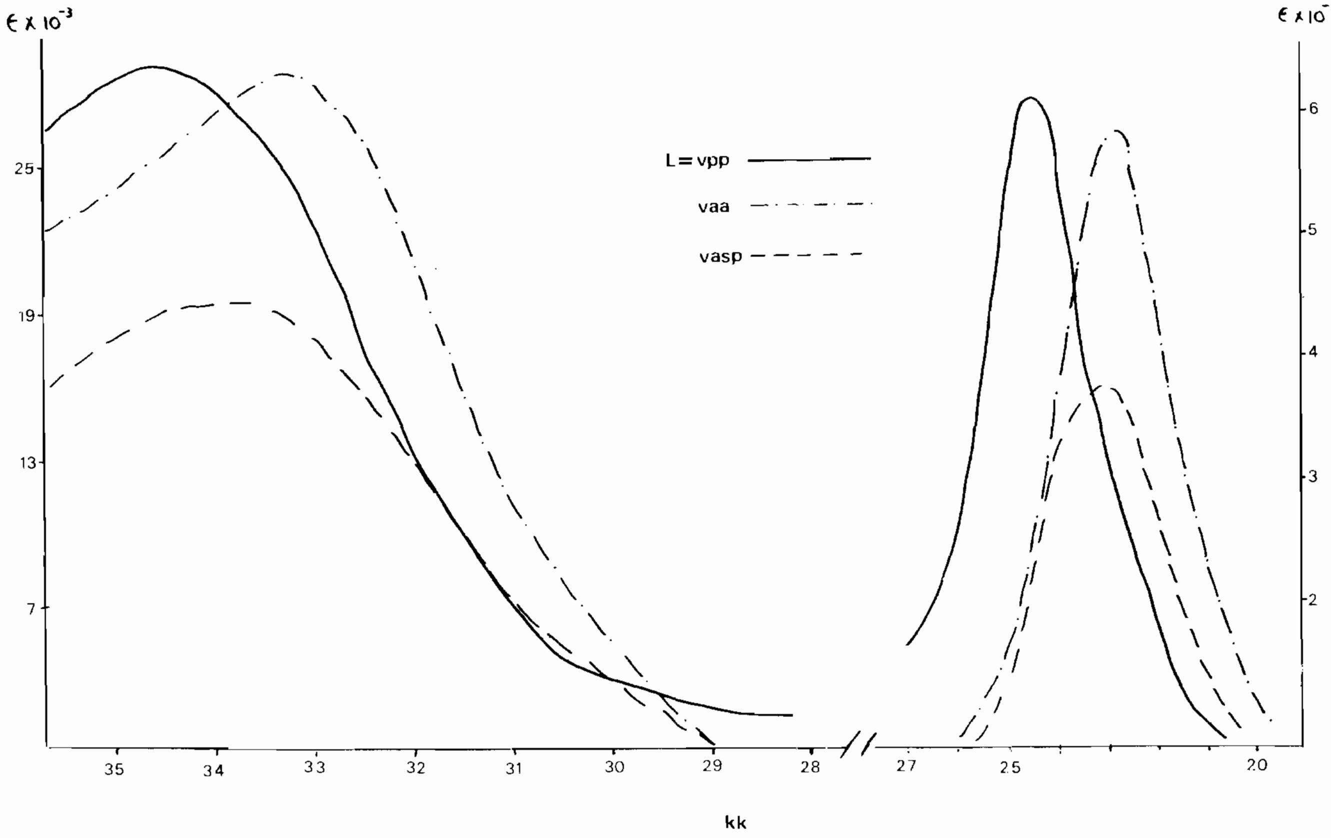

Figure 1. Electronic spectra of $[PdLI_2]$ complexes in dichloroethane.

TABLE I. Analytical Data and Some Physical Properties of the Palladium(II) Complexes.

Compound	Colour	Dec. Pt. (°C)	Λ_M[a]	% Carbon		% Hydrogen	
				Calc.	Fd.	Calc.	Fd.
$[Pd(vpp)Cl_2]$	White	280	0	54.4	54.1	3.8	4.0
$[Pd(vpp)Br_2]$	Yellow	300	0	47.1	47.2	3.3	3.4
$[Pd(vpp)I_2]$	Orange-yellow	300	0	41.2	41.8	2.9	3.3
$[Pd(vpp)(SCN)_2]$[b]	Pink	260	0	54.2	54.7	3.5	3.3
$[Pd(vpp)_2]Br_2$	Pale Yellow	265	161	58.9	59.9	4.1	4.2
$[Pd(vpp)_2](CNS)_2$	Pale Yellow	270	176	63.5	63.8	4.3	4.3
$[Pd(vaa)Cl_2]$	Yellow	220	0	47.3	48.2	3.3	3.7
$[Pd(vaa)Br_2]$	Yellow	260	0	42.4	42.8	2.9	3.1
$[Pd(vaa)I_2]$	Red	280	0	37.1	36.8	2.5	2.4
$[Pd(vaa)(SCN)_2]$[c]	Yellow	240	4	47.5	47.3	3.1	3.1
$[Pd(vasp)Cl_2]$	Pale Yellow	270	0	50.5	49.6	3.5	3.6
$[Pd(vasp)Br_2]$	Yellow	275	0	44.1	43.9	3.1	3.0
$[Pd(vasp)I_2]$	Orange	278	0	39.0	38.6	2.7	2.6
$[Pd(vasp)(SCN)_2]$[d]	Yellow	230	0	47.1	46.9	3.3	3.3
$[Pd(dpph)Cl_2]\cdot H_2O$	Orange	220	4.5	61.4	61.2	4.1	4.2
$[Pd(dpph)Br_2]$	Yellow	273	3	56.1	55.8	3.4	3.2
$[Pd(dpph)I_2]\cdot H_2O$	Orange-brown	150	7	49.0	48.8	3.2	3.0
$[Pd(dpph)(NCS)_2\cdot H_2O$[e]	Yellow	135	10.5	61.1	60.7	3.1	4.4

[a] For ~ $10^{-3}M$ solution in nitromethane at 22 °C ($cm^2\ ohm^{-1}\ mol^{-1}$). Nitrogen analyses: [b] calc. 4.5%, fd. 4.4%; [c] calc. 3.9%, fd. 4.1%; [d] calc. 4.2%, fd. 4.1%; [e] calc. 3.6%, fd. 3.9%.

pale yellow solution formed and a precipitate formed shortly afterwards. The reaction mixture was magnetically stirred for an additional one hour and the precipitate was collected on a filter, washed with ethanol, ether, and then recrystallised from $CH_2Cl_2/EtOH$. Yields 70–80%. For X = NCS, an alternative method is to warm an n-butanol solution of $[Pd(vpp)(NCS)_2]$ to 60° C, which yields the desired bis-vpp complex.

$[PdL(CNS)_2]$[*] *(L = vpp, vaa, vasp, dpph).*

An n-butanol solution (20 ml) $[Pd(SCN)_4]^{2-}$ (2.0 mmol) was added dropwise to a solution of the appropriate ligand (2.0 mmol) in n-butanol (20 ml). The red colour of the $[Pd(SCN)_4]^{2-}$ was soon discharged and the desired complex precipitated. The solid was collected, washed with ethanol and ether, and recrystallised from $CH_2Cl_2/EtOH$.

Physical Measurements

Melting points, conductivity measurements, and infrared and electronic spectra were obtained as previously described.[21] The Ramsay method[22] was used to calculate $\nu(C{\equiv}N)$ integrated absorptions.

Results and Discussion

The complexes isolated are listed in Table I. All of the complexes are of type $[PdLX_2]$ or $[PdL_2]X_2$. The $[PdLX_2]$ (X = Cl, Br, I; L = vpp, vaa, vasp) are all non-electrolytes in 10^{-3} *M* nitromethane but the $[Pd(dpph)X_2]$ show some evidence of slight dissociation in this solvent. The electronic spectra are listed in Table II, and the spectra in both the solid state and in dichloromethane are consistent with a planar structure. Figure 1 illustrates the $[PdLI_2]$ spectra, resolution of the low energy "*d–d*" (which indicate a ligand field strength vpp > vasp > vaa, as expected) and the charge-transfer bands in the 33,000–35,000 cm^{-1} region (assigned to metal–group VB donor charge transfer) is good.

TABLE II. Electronic Spectral Data of Palladium(II) Complexes.

Compound	E_{max} Solution[a] cm^{-1} (E_{max})	E_{max} Solid[b]
$[Pd(vpp)Cl_2]$	29,600(10,050)	27,200
$[Pd(vpp)Br_2]$	28,000(7,100)	26,700
	31,000(sh)	
	37,000(34,900)	
$[Pd(vpp)I_2]$	24,400(6,300)	22,500(sh)
	29,500(sh)	24,700
	34,500(29,100)	
$[Pd(vpp)(SCN)_2]$	20,500(9,100)	20,000
		27,200
$[Pd(vpp)_2]Br_2$	31,500(16,700)	(c)
	37,500(sh)	
$[Pd(vaa)Cl_2]$	27,500(3,500)	25,500
	37,000(15,400)	
$[Pd(vaa)Br_2]$	25,800(3,800)	25,300
	35,500(21,800)	
$[Pd(vaa)I_2]$	22,700(5,700)	20,000(sh)
	33,000(28,500)	23,300
		25,600(sh)
$[Pd(vaa)(SCN)_2]$	24,500(3,300)	23,300(sh)
	32,000(38,500)	25,500
$[Pd(vasp)Cl_2]$	28,200(4,800)	25,500
	37,800(22,600)	
$[Pd(vasp)Br_2]$	26,200(4,300)	25,400
	29,500(sh)	
	35,900(24,300)	
$[Pd(vasp)I_2]$	23,100(3,800)	23,800
	33,500(19,600)	
$[Pd(vasp)(SCN)_2]$	25,500(sh)	26,200
	32,500(12,600)	28,300
$[Pd(dpph)Cl_2]$	28,010(4,190)	27,800
$[Pd(dpph)Br_2]$	27,300(9,600)	21,000(sh)
	31,300(sh)	26,600
$[Pd(dpph)I_2]$	23,500(6,890)	24,600
	32,600(sh)	
$[Pd(dpph)(NCS)_2(SCN)]$	32,400(8,800)	27,500(sh)
	38,400(36,160)	

[a] Measured in dichloromethane. [b] Solid reflectance. [c] No resolved bands in visible region.

It is interesting to note that the vinyl ligands used in this study did not give rise to Magnus-type complexes with palladium(II) salts, unlike their analogous 1,2-dimethylene[3] or *o*-phenylene[8, 10] counterparts. Attempts to prepare pentacoordinate $[Pd(vpp)_2X]X$ were unsuccessful although the planar $[Pd(vpp)_2]X_2$ (X = Br, NCS) were obtained. The electronic spectra of the 2:1 complexes in both the solid state and solution (Table II) are consistent with a planar PdP_4^{2+} chromophore and the conductivity values in 10^{-3} *M* nitromethane (Λ_M = 161 (Br), 176 (NCS) ohm^{-1} cm^2 M^{-1}) support this formulation in solution. Moreover, the infrared spectrum of $[Pd(vpp)_2](NCS)_2$ in Nujol mull exhibits $\nu(CN)$ at 2050 cm^{-1} which is indicative of ionic thiocyanate groups.[23] The ability of vpp to promote association of the halide ions in $[PdL_2]X_2$ in solution appears to be about the same as that of dpe[3] but less than that of *o*-phenylenebis(diphenylphosphine).[24]

Considerable interest surrounds the mode of thiocyanate coordination to palladium(II), especially as it varies with other ligands present. The infrared spectra of $[PdL(CNS)_2]$ (L = vpp, vaa, vasp) in the solid state (Table III) exhibit sharp $\nu(CN)$ absorptions characteristic of S-bonded thiocyanate groups, and although the position of the $\nu(CN)$ vibration as a means of determining the mode of thiocyanate coordination has been criticised the identification of more reliable ab-

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[*] In this study CNS is used to describe coordinated thiocyanate when the mode of attachment to the metal ion is not specified.

TABLE III. Infrared Spectral Data in the ν(CN) Region of the Palladium(II) Thiocyanate Complexes.

Compound	Nujol Mull	Dichloro-methane	A × 10^{-4} cm^{-2} M^{-1} [a]
[Pd(vpp)(SCN)$_2$]	2105s	2110	1.9
[Pd(vaa)(SCN)$_2$]	2110s	2115 2080vw	2.1
[Pd(vasp)(SCN)$_2$]	2110s	2115 2080vw	2.3
[Pd(dpph)(SCS)(SCN)]	2120sh 2085br	2115 2080	

[a] Integrated intensity.

sorptions such as ν(CS) or δ(NCS) is difficult due to the presence of strong ligand absorptions in the same area of the spectrum.

The [Pd(vpp)(SCN)$_2$] complex retains this structure on dissolution in dichloromethane, but in this solvent both the vaa and vasp analogues exhibit additional very weak ν(CN) at ~2080 cm^{-1}, showing that a small degree of isomerisation to the N-bonded isomer occurs. This behaviour is not unexpected as dichloromethane belongs to the "group B solvents" listed by Burmeister *et al.* which promote N-bonding.[25] However, on evaporation of these solutions and recrystallisation from a number of solvents only the S-bonded species were obtained. Moreover, no isomerisation was observed on heating the solids and thus we conclude that the [PdL(SCN)$_2$] (L = vpp, vaa, vasp) are the thermodynamically stable forms. The electronic solution spectra of the PdLX$_2$ complexes (Table II) which can be interpreted to exhibit a spectrochemical series Cl > Br > CNS > I are also consistent with S-bonded thiocyanate groups, since Meek *et al.*[9] showed that [PdL(NCS)$_2$] complexes should exhibit a NCS > Cl > Br > I and [PdL(NCS)(SCN)] should exhibit a Cl ≥ CNS > Br > I series.

In contrast, the mull infrared spectrum of [Pd(dpph)(NCS)(SCN)] exhibits one broad ν(CN) absorption at 2085 cm^{-1} assignable to the Pd–NCS grouping and a sharp absorption at 2120 cm^{-1} assignable to the Pd–SCN grouping. There is also a ν(CS) absorption at 845 cm^{-1} assignable to the Pd–NCS linkage.[26] The complex is poorly soluble in dichloromethane in which it exhibits ν(CN) bands at 2115, 2080 cm^{-1}, but due to the low solubility integrated intensity measurements are probably unreliable. The low-energy electronic reflectance spectral absorptions (Table II) shift to lower energy in the order Cl > CNS > Br > I, consistent with the N,S formulation, but in solution the thiocyanate complex shows no distinct maxima < 32,400 cm^{-1}, whilst the [Pd(dpph)Cl$_2$] exhibits E_{max} = 28,010 cm^{-1}. The reason for this apparent reversal of the spectrochemical series is unclear, the most likely possibility is that a lower energy absorption in the thiocyanate complex is obscured by the tail of the 32,400 cm^{-1} band, since the possibility of N,S → N,N isomerism appears to be ruled out by the lack of change in the infrared spectrum.

These results are particularly interesting when compared with the 1,2-dimethylene and *o*-phenylene backbone ligands.[9, 10, 24] Thus, whilst dpe forms [Pd(dpe)(NCS)(SCN)][27] and *o*-C$_6$H$_4$(PPh$_2$)$_2$ (pp) forms [Pd(pp)(NCS)(SCN)],[24] vpp forms only [Pd(vpp)(SCN)$_2$]. X-ray crystallographic studies[12,27] on the dpe complex were interpreted as showing that S,S coordination was not possible in this complex on steric grounds; more specifically, that interaction between two non-linear Pd–SCN linkages and the phenyl groups on the phosphorus are prohibitive. The less sterically demanding N,S coordination is possible, however. In the vpp complex the shorter >C=C< backbone (~1.33 Å, *cf.* –CH$_2$CH$_2$– in dpe = 1.58 Å) will pull the phenyl groups back from the metal and decrease the interaction with the CNS ligands, hence S,S coordination becomes sterically possible. The same arguments can be applied to the vaa and vasp cases, and in addition the larger arsenic atoms will also decrease the steric interactions.[9] Equally, on steric grounds alone, if S,S coordination is possible then the less sterically demanding N,S and N,N linkages are also possible – hence, the actual occurrence of S,S bonding would appear to be the result of an electronic preference since no steric constraints apply for any of the three possible linkage arrangements. The Turco and Pecile[26] approach predicts that N-bonding should be increasingly favoured as the π-acceptor ability of the other ligands increases, which is inconsistent with the data reported here since the ligands with the vinyl backbone are believed to be better π-acceptors than the alkane analogues.[28, 29] Thus, we emphasise again that the mode of thiocyanate coordination in complexes of this type is frequently determined by a mix of subtle factors, and attempts to explain the known facts in terms of only steric or only electronic factors are unlikely to be successful.

The [Pd(dpph)(NCS)(SCN)] complex can be compared with the analogous [Pd(pp)(NCS)(SCN)].[24] The electronic spectra of corresponding complexes are very similar, which would appear to show that the presence of two extra fused benzene rings in the dpph ligand makes little difference to the donor properties of the phosphorus.

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