Contribution from the Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, United Kingdom.

Bidentate Group VB Ligands. IV. Cobalt, Nickel, and Palladium Complexes of *trans*-1,2-bisdiphenylphosphinoethylene

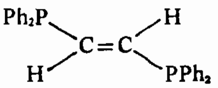
K.K. Chow, W. Levason, and C.A. McAuliffe*

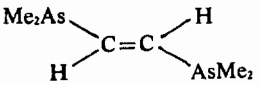
Received December 20, 1972

Metal complexes of the type $[M(ligand)X_2]$ (*M* = *Ni, X=Cl, Br, I, NCS, CN; M=Co, X=Br, I; M=Pd, X=Cl) and* $[Pd_2(ligand)(CNS)_4]$ *have been obtained by reaction of the metal salts with* trans-*1,2-bisdiphenylphosphinoethylene* (*tvpp*). *This ligand is incapable of chelating to metal ions and acts as a bridging ligand in these complexes. Electronic and infrared spectra, magnetic and conductivity measurements have been used to characterise the complexes. Pseudotetrahedral configurations have been assigned to the nickel(II) halide and cobalt(II) halide complexes, whereas the* $Ni(NCS)_2$ *and* $Ni(CN)_2$ *derivatives are diamagnetic and planar.*

Introduction

Although the synthesis and characterisation of a large number of transition metal complexes containing bidentate chelating diphosphine ligands has been achieved,(2) relatively few studies have been carried out with diphosphines which are incapable of chelation on steric grounds. Carty, *et. al.*,[3-6] prepared complexes of 1,2-bisdiphenylphosphinoacetylene, $Ph_2PC\equiv CPPh_2$, and some work with therelated $Ph_2PCH_2C\equiv CCH_2PPh_2$ has been reported.[7] The *trans*-diphosphine containing a vinyl backbone, *trans*-1,2-bisdiphenylphosphinoethylene, (I), tvpp, has been little studied, the only complexes reported being $[Rh(CO)\text{-}(tvpp)Cl]_n$[8] and some dithiolates of cobalt and iron.[9] Bennett and co-workers[10-13] have recently characterised cobalt, nickel palladium, and platinum complexes of *trans*-1,2-bisdimethylarsinoethylene, (trans-edas), (II).


(I)


(II)

Experimental Section

The tvpp ligand was prepared by a modification[14] of the method of Aguiar and Daigle.[15]

Ni(tvpp)X_2(*X=Cl, Br, I*). The preparation of these complexes is exemplified by that used for the chloro derivative: anhydrous nickel(II) chloride (0.16 g, 1.23 mmole) was dissolved in warm n-butanol (15 ml), and tvpp (0.5 g; 1.25 mmole) in dichloromethane (5 ml) was added with stirring. The mixture was refluxed for 30 min and then cooled. The brown powder which separated was filtered off and dried *in vacuo*. Yield 0.33 g (50%).

Ni(tvpp)(NCS)$_2$. Nickel(II) iodide monohydrate (0.5 g; 1.5 mmole) in ethanol (15 ml) was stirred with tvpp (0.7 g; 1.75 mmole), resulting in the formation of a black precipitate. Excess of powdered KNCS (1.0 g) was added with stirring and the black precipitate changed to red. Stirring was continued for 20 min, the precipitate filtered, and dried *in vacuo*. Yield 0.8 g (67%).

Ni(tvpp)(CN)$_2$. Nickel(II) cyanide tetrahydrate (0.23 g; 1.25 mmole) was dissolved in refluxing *n*-butanol (20 ml) and tvpp (0.5 g; 1.25 mmole) was added with stirring. A red-brown solid immediately formed and the mixture was refluxed for a further 30 min, filtered hot, and dried *in vacuo*. Yield 0.5 g (78%).

Co(tvpp)Br$_2$. Hydrated cobalt(II) bromide (0.5 g; ~2.1 mmole) in ethanol (20 ml) and tvpp (0.85 g; 2.2 mmole) in dichloromethane (10 ml) were stirred together. An immediate green precipitate formed, which was filtered, washed with ethanol (20 ml) and ether (20 ml), and dried *in vacuo*. Yield 0.4 g (32%). *Co(tvpp)I*$_2$ was prepared in an analogous manner.

Pd(tvpp)Cl$_2$. To sodium tetrachloropalladate(II) (0.3 g; 1.0 mmole) in ethanol (30 ml) was added tvpp (0.4 g; 1.0 mmole) in dichloromethane with stirring, and the mixture refluxed. The pale yellow precipitate was filtered while hot, washed with ethanol

---

(1) Part III, K.K. Chow and C.A. McAuliffe, *Inorg. Nucl. Chem. Letts.*, *8*, 1031(1972).
(2) W. Levason and C.A. McAuliffe, *Adv. Inorg. Chem. and Radiochem.*, *14*, 173 (1972).
(3) W.A. Anderson, A.J. Carty and A. Efraty, *Can. J. Chem.*, *47*, 3361 (1969).
(4) A.J. Carty and A. Efraty, *Can. J. Chem.*, *47*, 2573 (1969).
(5) A.J. Carty and A. Efraty, *Inorg. Chem.*, *8*, 543 (1969).
(6) A.J. Carty, T.W. Ng and A. Efraty, *Can. J. Chem.*, *47*, 1429 (1969) .
(7) R.B. King and A. Efraty, *Inorg. Chim. Acta*, *4*, 123 (1970).
(8) J.T. Mague and J.P. Mitchener, *Inorg. Chem.*, *8*, 119 (1969).
(9) G.R. Eaton and R.H. Holm, *Inorg. Chem.*, *10*, 805 (1971).
(10) M.A. Bennett, G.J. Erskine and J.D. Wild, *Inorg. Chim. Acta*, *2*, 379 (1968).
(11) G.J. Erskine, *Can. J. Chem.*, *47*, 2699 (1969).
(12) M.A. Bennett and J.D. Wild, *J. Chem. Soc. (A)*, 536 (1971).
(13) M.A. Bennet and J.D. Wild, *J. Chem. Soc. (A)*,545 (1971).
(14) K.K. Chow, Ph.D. Thesis, University of Manchester, 1972.
(15) A.M. Aguiar and D. Daigle, *J. Amer. Chem. Soc.*, *86*, 2299 (1964).

Table I. Analytical Data and Some Physical Properties of the Complexes.

Complex	Colour	M. Pt. °C	Analyses[a] % C	% H
Ni(tvpp)Cl_2	brown	175-180	58.8(59.4)	4.3(4.2)
Ni(tvpp)Br_2	dark brown	210	51.3(50.7)	3.3(3.6)
Ni(tvpp)I_2	dark brown	202-208	44.8(44.0)	3.1(3.1)
Ni(tvpp)$(NCS)_2$[b]	maroon	185-193	58.3(58.8)	3.8(3.8)
Ni(tvpp)$(CN)_2$[c]	red-brown	160-163	66.0(66.3)	4.6(4.3)
Co(tvpp)Br_2	bright green	190	49.8(50.7)	3.8(3.6)
Co(tvpp)I_2	red-purple	220	43.0(44.0)	3.3(3.0)
Pd(tvpp)Cl_2	yellow	260(d)[d]	53.5(54.4)	3.8(3.8)
Pd_2(tvpp)$(CNS)_4$[e]	yellow	~300(d)[d]	43.5(42.8)	2.9(2.6)

[a] % found (% calcd); [b] % nitrogen: 4.9(4.9); [c] % nitrogen 5.5(5.5); [d] decomposition; [e] % nitrogen: 6.9(6.7).

Table II. Magnetic Data and Some Infrared Absorption Maxima.

Complex	$\chi_{M(corr)} \times 10^6$ (cgs units)	μ_{eff} (B.M.)	I.R. Maxima (cm^{-1})
Ni(tvpp)Cl_2	3,841	3.03	335, 300 ν(Ni-Cl)
Ni(tvpp)Br_2	4,196	3.14	260, 230 ν(Ni-Br)
Ni(tvpp)I_2	4,236	3.16	205 ν(Ni-I)
Ni(tvpp)$(NCS)_2$	diamagnetic[a]		2090 ν(CN) 858 δ(CS)
Ni(tvpp)$(CN)_2$	diamagnetic[a]		2130, 2110 ν(CN)
Co(tvpp)Br_2	8,243	4.40	265, 230 ν(Co-Br)
Co(tvpp)I_2	8,460	4.49	
Pd(tvpp)Cl_2	diamagnetic		310, 283 ν(Pd-Cl)
Pd_2(tvpp)$(CNS)_4$	diamagnetic		2120 ν(CN), 765 ν(CS), 435 δ(NCS)

[a] With a small T.I.P. contribution.

(20 ml) and ether (20 ml), and dried *in vacuo*. Yield 0.35 g (60%). The $Pd_2L(NCS)_4$ was made by an analogous method.

Physical Measurements. Infrared spectra were measured in Nujol and hexachlorobutadiene mulls on a Perkin Elmer 621 spectrophotometer; electronic solution spectra in dichloromethane solution on a Unicam SP700 spectrophotometer, and solid reflectance spectra on a Beckmann DK2A spectrophotometer using MgO as dilutant. Conductivities were determined in 10^{-3} *M* solutions in N,N′–dimethylformamide on a Cambridge Instruments Ltd. conductivity bridge. Magnetic susceptibilities were determined by the Gouy method using $HgCo(NCS)_4$ as standard.

Results and Discussion

Nickel(II) Complexes. The reaction of tvpp with NiX_2 (X = Cl, Br, I, CN) in a 1:1 molar ratio in n-butanol/dichloromethane produces Ni(tvpp)X_2 complexes (Table I). The corresponding thiocyanate complex was obtained by treatment of the iodocomplex with excess KNCS in ethanol. The reaction of nickel(II) bromide with tvpp in a 1:2 ratio produced only Ni(tvpp)Br_2, in contrast to *trans*-edas which forms Ni(*trans*-edas)$_2Br_2$.[12]

The complexes are insoluble in nitromethane, alcohols, or acetone, but dissolved readily in N,N'-dimethylformamide. The resulting solutions (*ca.* 10^{-3} *M*) had low conductivities, $\leqslant$ 12 $ohms^{-1}$ cm^2 M^{-1}, too low for 1:1 electrolytes[16] and probably indicative of partial solvolytic displacement of coordinated anions.

The three halides have magnetic moments of ~ 3.0-3.2 B.M., which is within the range usually quoted for octahedral nickel(II) or for tetrahedral nickel(II) containing ligands well separated in the spectrochemical series[17] The latter condition reduces the degeneracy of the ground state, and hence the magnitude of the orbital contribution. A number of pseudotetrahedral nickel(II) complexes of monodentate tertiary phosphines have magnetic moments of about 2.9-3.4 M., *e.g.* $Ni(PPh_3)_2X_2$.[18,19] The far IR spectrum of Ni(tvpp)Cl_2 (Table II) exhibits two bands assignable as ν (Ni-Cl) modes at 335,300 cm^{-1}, reasonable values for a tetrahedral configuration.[20] These values are too high for bridging Ni-Cl frequencies, ruling out octahedral coordination of the nickel complexes of stoichiometry Ni(bidentate)X_2 must contain bridging X if octahedral. The Ni(tvpp)Br_2 derivative exhibits ν(Ni-Br) at 260,230 cm^{-1}, which approximate to the expected values, assuming ν(Ni-Br)/ν(Ni-Cl) ≃ 0.77, and indicate similar structures for these complexes. Only one ν(Ni-I) vibration could be assigned with any degree of certainty in the IR spectrum of Ni(tvpp)I_2. The electronic spectra of these complexes, both in the solid state and in dichloromethane solution are similar (Table III, Figures 1 and 2), arguing strongly in favour of similar structures in both physical states. The Ni(tvpp)Cl_2 derivative decomposes

---

(16) W.J. Geary, *Coord. Chem. Revs.*, *7*, 81 (1971).

(17) L. Sacconi, *Trans. Metal Chem.*, *4*, 199 (1968).

(18) G. Garton, D.E. Henn, H.M. Powell, and L.M. Venanzi, *J. Chem. Soc.*, 3625 (1963).

(19) P.J. Stone and Z. Dori, *Inorg. Chim. Acta*, *5*, 434 (1971).

(20) R.J.H. Clark in "Halogen Chemistry", *ed. V. Gutman, Academic* Press, New York, N.Y., 1967, Vol. 3, p. 85.

Table III. Electronic Spectra of the Complexes.[a]

		kK
$Ni(tvpp)Cl_2$	soln.[b]	~31.0 (s), 24.8, 19.4 (sh), 12.3[c]
	d.r.s.[d]	24.2, 18.8, ~15.2 (sh), 10.4, 8.4 (sh)
$Ni(tvpp)Br_2$	soln.	29.0 (sh), 25.8 (1,250), 23.5 (1,160), 18.5 (sh), 11.3 (370)
	d.r.s.	22.8, 18.2, 11.2, 8.4 (sh)
$Ni(tvpp)I_2$	soln.	28.5 (sh), 22.0 (2,920), 18.5 (sh), 15.0 (sh), 10.3 (467)
	d.r.s.	21.0, ~18.0, ~15.0 (sh), 10.5, 8.7 (sh)
$Ni(tvpp)(NCS)_2$	soln.	~38.5, 31.5, 24.2
	d.r.s.	21.1, 19.2 (sh)
$Ni(tvpp)(CN)_2$	soln.	~30.0 (sh), 25.4 (1,706), 20.0 (sh)
	d.r.s.	23.5, 20.0 (sh)
$Co(tvpp)Br_2$	soln.	26.8 (4,500), 25.3 (4,000), 16.0 (1,130), 15·1 (1,500), 13.5 (860), 10.7 (140), 7.7 (110)
	d.r.s.	25.2, ~22.0 (sh), 15.7, 14.7, 12.5, 10.5, 7.1
$Co(tvpp)I_2$	soln.	26.5 (4,530), 25.3 (4,030), 14.6 (2,440), 13.75 (3,098), 12.75 (sh), 12.5 (2.472), 10.6 (230), 7.75 (200)
$Pd(tvpp)Cl_2$	soln.	29.6 (1,045)
	d.r.s.	~26.5
$Pd_2(tvpp)(CNS)_4$	d.r.s.	25.0

[a] Extinction coefficients in parentheses; [b] dichloromethane; [c] dissolves, apparently with some decomposition; [d] diffuse reflectance spectra in samples diluted with MgO.

partially on dissolution in CH_2Cl_2, and thus extinction coefficients could not be obtained, but both the position of the band maxima and the magnitude of the extinction coefficients for $Ni(tvpp)X_2$ ($X = Br$, I) are characteristic of tetrahedral nickel(II). It is not possible to compare the spectra of the tvpp complexes with those of the isomeric *cis*-1,2-bisdiphenylphosphinoethylene, vpp, since the latter, which chelates to nickel(II), produces only planar $[Ni(vpp)X_2]$ and pentacoordinate $[Ni(vpp)_2X]^+$ complexes.[21] However, a comparison with the triphenylphosphine complexes,[22] which are tetrahedral, is interesting. In general the extinction coefficients of the tvpp complexes are approximately twice as large as those of the PPh_3 derivatives. This may well be attributable to increased distortion from strict t_d symmetry in the tvpp complexes because of steric restrictions due to bridging of the ligands. On the other hand the increased ε values may also be attributable to a mixing of d-d transitions with transitions of the type $\pi^* \leftarrow \pi$ of the benzene rings on tvpp.[23] The typical d-d transitions expected for pseudotetrahedral nickel(II) complexes[17,24,25] are exhibited; thus, the doublet at 15-19 kK is assigned to the $\Gamma_1(^3T_{1g}) \rightarrow {}^3P$ transition, the band at *ca* 10 kK to the $\Gamma_1(^3T_{1g}) \rightarrow {}^3\Gamma_5(^3F)$ transition, and the band or shoulder at *ca* 24 kK is most probably due to the$\Gamma_1(^3T_{1g}) \rightarrow {}^1\Gamma^3(^1G)$ transition. This last absorption, however, is very near to some intense charge-transfer bands, and it is probably because these charge-transfer bands have moved into the visible region that the colour of the tvpp complexes (brown) differ from the usual blue or green $Ni(PPh_3)_2X_2$ complexes. It is not clear, however, why the 'borrowing' of charge-transfer intensity is so prevalent in these tvpp complexes. Because the intense band at 31-28 kK moves to lower energy in theorder $Cl^- > Br^- > I^-$ it may be assigned as metal-halogen charge-transfer

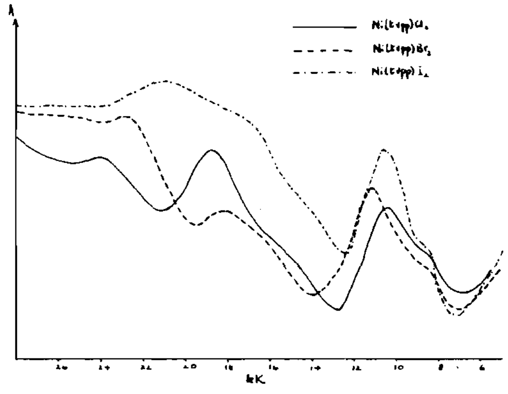


Figure 1. Electronic Spectra of the $Ni(tvpp)X_2$ (X = Cl, Br, I) Complexes in the Solid State.

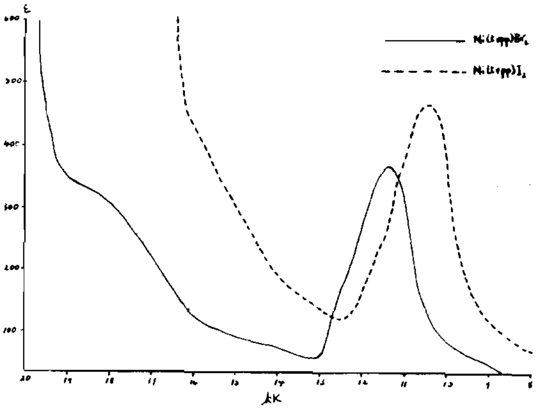


Figure 2. Electronic Spectra of $Ni(tvpp)Br_2$ and $Ni(tvpp)I_2$ in Dichloromethane.

---

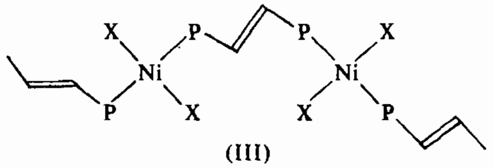
(21) C.A. McAuliffe and D.W. Meek, *Inorg. Chem.*, *8*, 904 (1969).
(22) F.A. Cotton, O.D. Faut, and D.M.L. Goodgame, *J. Amer. Chem. Soc.*, *83*, 344 (1961).
(23) O.St.C. Headley, R.S. Nyholm, C.A. McAuliffe, L. Sindellari, M.L. Tobe and L.M. Venanzi, *Inorg. Chim. Acta*, *4*, 93 (1970).
(24) F.A. Cotton and D.M.L. Goodgame, *J. Amer. Chem. Soc.*, *82*, 5771 (1960).
(25) A.D. Liehr and C.J. Ballhausen, *Ann.phys.*, *6*, 134 (1959).

and is thus not due to metal-phosphorus charge-transfer.

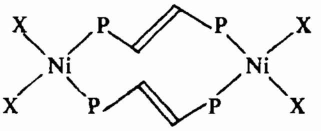
The isothiocyanato and cyano complexes of nickel (II) and tvpp are both effectively diamagnetic (Table II, indicative of planar coordination. The IR spectrum of Ni(tvpp)(NCS)$_2$ exhibits ν(CN) at 2090 cm^{-1}, and ν(CS) at 858 cm^{-1}, indicating that the CNS$^-$ groups are N-bonded to the nickel.[26] It was not possible to assign the ν(NCS) vibration with any certainty since tvpp absorbs strongly in the region where this vibration is expected. The insolubility of this complex is evidence of polymeric constitution, presumably *via* bridging tvpp ligands since there is no evidence of bridging –NCS– groups. There is also some evidence for slight structural changes (Table III) upon dissolution of Ni(tvpp)(NCS)$_2$ in CH$_2$Cl$_2$. There are two bands assignable to ν(CN) in the IR spectrum of Ni(tvpp)(CN)$_2$ (Table II), and this may be taken to indicate that the CN$^-$ groups are *cis* in this complex.[27]

The IR spectra of all these nickel(II) complexes show no absorption in the region where ν(C=C) is expected, confirming the *trans* configuration of the ligand.

It was not possible to obtain molecular weight measurements for any of these complexes, and so their overall structure must remain in some doubt. The tvpp must behave as a bridging ligand, but whether the structures consists of infinite chains, (III), or of dimeric units, (IV), is unknown. The insolubility of these complexes would seem to favour the former postulate.



(III)



(IV)

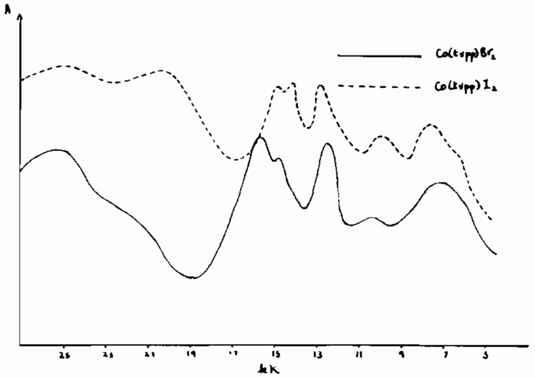


Figure 3. Electronic Spectra of the Co(tvpp)Br$_2$ and Co(tvpp)I$_2$ Complexes in the Solid State.

Cobalt(II) Complexes. Cobalt(II) complexes, Co(tvpp)X$_2$ (X = Br, I) were obtained by direct reaction in alcohol. A solution of CoCl$_2$·6H$_2$O in ethanol underwent a colour change from pink through dark blue to green upon reaction with the ligand, but no complex could be isolated.

The electronic spectra (Table III, Figure 3 and 4) are quite similar in most respects in dichloromethane and in the solid state. Moreover, they resemble those reported for the dihalobis(triphenylphosphine) cobalt(II) complexes and related tertiary phosphine complexes.[28] This may be taken to indicate the presence of pseudotetrahedral coordination of the cobalt atom with the accompanying fairly large splittings due to the combined effects of the C$_{2v}$ component and spin-orbit coupling[29] The centres of gravity of the observed bands fit the calculated Tanabe-Sugano diagrams for tetrahedral d^7 with B ≃ 710 cm^{-1} quite well.[28] The bands in the 12.5–16.0 kK region are assigned to $^4A_2 \rightarrow {}^4T_1$ (P) and those at *ca* 7kK to the $^4A_2 \rightarrow {}^4T_1$ (F) transitions in strict t$_d$ symmetry.[28,29]

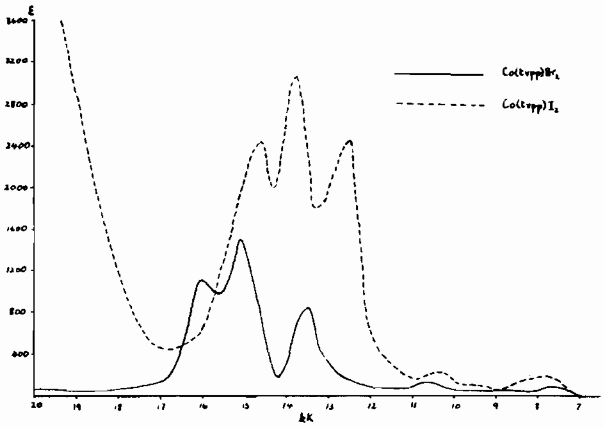


Figure 4. Electronic Spectra of the Co(tvpp)Br$_2$ and Co(tvpp)I$_2$ Complexes in Dichloromethane.

The magnetic moments of theCo(tvpp)X$_2$ complexes are in the range expected for tetrahedral cobalt(II) species, and the observed I$^-$ > Br$^-$ values (Table II) are also expected.

Palladium(II) Complexes. The product of reaction of tvpp with Na$_2$PdCl$_4$ is the yellow Pd(tvpp)Cl$_2$ The presence of two ν(Pd-Cl) frequencies in the far IR spectrum (Table II) suggests that the chlorines are in a *cis* configuration.[20] As with the complexes of the other metals it is not possible to arrive at a definite conclusion about the structure; the data is consistent with some degree of polymerisation, but in view of the known tendency of *trans*-edas[11] and DPPA[4] to form dimeric complexes with palladium(II) it may

---

(26) J.L. Burmeisteir, *Coord. Chem. Revs.*, *1*, 205 (1966), and references therein.

(27) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley Inc., 1970, p. 188, 2nd Edn.

(28) F.A. Cotton, D.M.L. Goodgame, and M. Goodgame, *J. Amer Chem. Soc.*, *83*, 4690 (1961).

(29) W.DeW. Horrocks, Jr., G.R. Van Hecke, and D. DeW. Hall, *Inorg. Chem.*, *6*, 694 (1967).

well be that $[Pd(tvpp)Cl_2]_n$ is also dimeric.

The analytical data of the complex isolated from the palladium thiocyanate reaction indicates a $Pd_2(tvpp)(CNS)_4$ stoichiometry. The IR spectrum exhibits only one ν(CN) band at 2120 cm^{-1}, the high energy of which indicates bridging Pd-SCN-Pd groups.[26] Other bands can tentatively be assigned at 765 cm^{-1}, ν(CS), and 435 cm^{-1}, ν(NCS). The extreme insolubility of this complex supports the proposal of bridging –NCS– groups. If bidentate tvpp is present in this complex then pentacoordinate palladium(II) is present.

Acknowledgements. We are grateful to the British Council for a Fees Award (K.K.C.), to the Science Research Council for a Research Studentship (W.L.), and to Dr. D.J. Machin for the use of the Beckmann DK2A spectrophotometer.