Reactions of 2-Azidopyridine and 1-Pyridinio Ylides with Transition-metal Complexes

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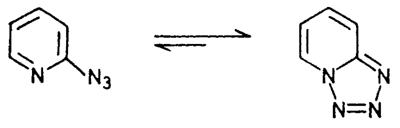
The reactions of 2-azidopyridine (L^1) and 1-pyridinio ylides $C_5H_5\overset{+}{N}-\overset{-}{N}R$ [R = $O_2SC_6H_4Me$-*p* (L^2) or OCC_6H_4Me-*p* (L^3)] with metal(II) halogeno-complexes give derivatives of formula [$MnL^1_2Cl_2$], [$FeL^1_3Cl_2$], [CoL^1Cl_2], [CuL^1Cl_2], [$ZnL^1_2Cl_2$], [$(NiL^1Cl_2)_n$], [$NiL^1_2Br_2$], [$(NiL^2Cl_2)_n$], [$NiL^2_2Br_2$], [$PdL^1_2Cl_2$], [$PdL^2_2Cl_2$], [$PdL^3_2Cl_2$], [$Ru(PPh_3)_2L^1_2X_2$], and [$Ru(SbPh_3)_2L^1_2Cl_2$] (X = Cl or Br). The complexes [$M(CO)_5L^1$] (M = W or Cr) have been obtained from [$M(CO)_5(thf)$] (thf = tetrahydrofuran) and tetrazolopyridine. In these complexes L^1 is present in its tetrazole form. From [$Pt(SMe_2)_2Cl_2$] and L^1, [$Pt(SMe_2)L^1Cl_2$] has been isolated, while L^3 gives a derivative in which the aryl group is metallated in the position *ortho* to the carbonyl group and the ylide is bidentate. The complex [$Ru(PPh_3)_2L^1_2Cl_2$] reacts with carbon monoxide to give [$Ru(PPh_3)_2(CO)L^1Cl_2$]. 2-Azido-5-nitropyridine (RN_3) reacts in its azide form with the hydride [$Pt(PEt_3)_2H(Cl)$] to give the amido-complex [$Pt(PEt_3)_2(NHR)Cl$] and with [$Pt(PPh_3)_2(C_2H_4)$] to give a complex of composition [$Pt(PPh_3)_2(N_3)(N_2R)$]. The spectroscopic properties of the new complexes are reported and their structures discussed.

WE have previously studied the reactions of organic azides RN_3 ($R = O_2SC_6H_4Me$-*p* or OCC_6H_4Me-*p*) with transition-metal complexes.[1-3] From these reactions a variety of products arising from the RN nitrene residue of the azide has been isolated.[3] We have thus undertaken a study of the reactivity with transition-metal complexes of 2-azidopyridine (a), which is known to exist mainly in its tetrazole form (b).[4] We were interested whether the metal co-ordination to the pyridine nitrogen atom could stabilize the azide form or whether nitrene complexes could be formed. Nitrene complexes have been assumed as intermediates in the copper-catalysed thermolysis of tetrazolopyridine and pyrimidines.[5] It was also of interest for us to investigate the possible role of 1-pyridinio ylides, $C_5H_5\overset{+}{N}-\overset{-}{N}R$ ($R = O_2SC_6H_4Me$-*p* or OCC_6H_4Me-*p*), as sources of the nitrene residue RN in reactions with transition-metal complexes. Derivatives containing such ylides as ligands have been only recently reported[6,7] while this work was in progress.



(a) (b)

RESULTS AND DISCUSSION

Reactions with 2-Azidopyridine.—The reactions of the complexes [$Ni(PPh_3)_2X_2$] (X = Cl or Br), [$Pd(NCPh)_2Cl_2$], [$Pt(SMe_2)_2Cl_2$], [$Ru(PPh_3)_3X_2$] (X = Cl or Br), and [$Ru(SbPh_3)_3Cl_2$] with 2-azidopyridine (L^1) gave a series of derivatives of the unchanged ligand in its tetrazole form (Table 1). Tetrazole complexes of transition-metal

$$n[\mathrm{Ni(PPh_3)_2Cl_2}] + n\mathrm{L^1} \longrightarrow [(\mathrm{NiL^1Cl_2})_n] + 2n\mathrm{PPh_3} \tag{1}$$

$$[\mathrm{Ni(PPh_3)_2Br_2}] + 2\mathrm{L^1} \longrightarrow [\mathrm{NiL^1_2Br_2}] + 2\mathrm{PPh_3} \tag{2}$$

$$[\mathrm{Pd(NCPh)_2Cl_2}] + 2\mathrm{L^1} \longrightarrow [\mathrm{PdL^1_2Cl_2}] + 2\mathrm{PhCN} \tag{3}$$

$$[\mathrm{Pt(SMe_2)_2Cl_2}] + \mathrm{L^1} \longrightarrow [\mathrm{Pt(SMe_2)L^1Cl_2}] + \mathrm{SMe_2} \tag{4}$$

$$[\mathrm{Ru(PPh_3)_3X_2}] + 2\mathrm{L^1} \longrightarrow [\mathrm{Ru(PPh_3)_2L^1_2X_2}] + \mathrm{PPh_3}\ (\mathrm{X = Cl\ or\ Br}) \tag{5}$$

$$[\mathrm{Ru(SbPh_3)_3Cl_2}] + 2\mathrm{L^1} \longrightarrow [\mathrm{Ru(SbPh_3)_2L^1_2Cl_2}] + \mathrm{SbPh_3} \tag{6}$$

halides have also been obtained by direct reaction of tetrazolopyridine with metal halides. By this method the complexes [$(NiL^1X_2)_n$] (X = Cl or Br), [$PdL^1_2Cl_2$], [$MnL^1_2Cl_2$], [$FeL^1_3Cl_2$], [CoL^1Cl_2], [CuL^1Cl_2], and [$ZnL^1_2X_2$] (X = Cl or Br) have been isolated. Cobalt(II) bromide affords adducts containing 1.5—4 mol of tetrazolo[1,5-*a*]pyridine per mol of Co^{II}. In these reactions opening of the tetrazole ring was never observed. Analogous complexes of transition-metal halides containing 1-substituted tetrazoles have been previously reported by Brubaker and his co-workers,[8] and those containing 6,7,8,9-tetrahydro-5*H*-tetrazoloazepine by Popov.[9]

The nickel complexes are insoluble polymeric materials. They have a polymeric octahedral structure with halide and/or tetrazole bridges as shown by the magnetic moment {$\mu_{\mathrm{eff.}}$ 3.20 and 3.31 B.M. for [$(NiL^1Cl_2)_n$] (4a) and [$NiL^1_2Br_2$] (5) respectively} † and by the electronic-reflectance spectra, in which bands at *ca.* 1 100—1 130,

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† Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

[1] W. Beck, M. Bauder, G. La Monica, S. Cenini, and R. Ugo, *J. Chem. Soc.* (*A*), 1971, 113.

[2] W. Beck, W. Rieber, S. Cenini, F. Porta, and G. La Monica, *J.C.S. Dalton*, 1974, 298.

[3] S. Cenini and G. La Monica, *Inorg. Chim. Acta Rev.*, 1976, **18**, 279 and refs. therein.

[4] 'The Chemistry of the Azido Group,' ed. S. Patai, Interscience, London, 1971; H. Reimlinger, *Chem. Ber.*, 1970, **103**, 1900 and refs. therein.

[5] K. v. Fraunberg and R. Huisgen, *Tetrahedron Letters*, 1969, 2599.

[6] S. A. Dias, A. W. Downs, and W. R. McWhinnie, *J.C.S. Dalton*, 1975, 162.

[7] L. Y. Chia, S. A. Dias, and W. R. McWhinnie, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1263.

[8] G. L. Gilbert and C. H. Brubaker, jun., *Inorg. Chem.*, 1963, **2**, 1216; N. A. Daugherty and C. H. Brubaker, *J. Inorg. Nuclear Chem.*, 1961, **22**, 193.

[9] A. J. Popov, *Co-ordination Chem. Rev.*, 1969, **4**, 463.

675, and 405—410 nm have been observed.[10] Thermogravimetric analyses have shown that (4a) and (5) intercalate water in variable amounts; this water is difficult to eliminate (according to the i.r. spectra). The palladium complex $[PdL^1_2Cl_2]$ (9), although too insoluble in the common solvents for a molecular-weight determination, probably has a *cis*-square-planar configuration, since two ν(Pd–Cl) bands at 370 and 320 cm^{-1} are clearly observed in the i.r. spectrum. Analogously, the $[PtL^1(SMe_2)Cl_2]$ complex (10) showed two ν(Pt–Cl) bands at 340 and 315 cm^{-1}; the presence of the SMe_2 ligand was confirmed by the i.r. (990 cm^{-1}) and ^1H n.m.r. spectra [τ 7.5, with satellites due to coupling with platinum, J(Pt–H) 45.5 Hz]. The single methyl signal in the ^1H n.m.r. spectrum of the co-ordinated SMe_2 is consistent with free rotation of the ligand around the platinum–sulphur bond, while the observed J(Pt–H) is in agreement with a ligand *trans* to chloride.[11]

TABLE 1

Analytical data (required values in parentheses) for derivatives of 2-azidopyridine (L^1)

	Complex	M.p. (θ_c/°C) (decomp.)	Colour	Analysis (%) C	H	N	Cl or Br	M[a]
(1)	$[MnL^1_2Cl_2]$	300	Colourless	32.9 (32.8)	2.5 (2.2)	30.0 (30.6)		*b* (366.1)
(2)	$[FeL^1_3Cl_2]$	190	Yellow	37.2 (37.0)	2.8 (2.5)	33.7 (34.5)		*b* (487.1)
(3)	$[CoL^1Cl_2]$		Blue	24.0 (24.1)	1.9 (1.6)	21.6 (22.4)		*b* (250.0)
(4a)	$[(NiL^1Cl_2)_n]$	300	Light green	24.2 (24.1)	1.7 (1.6)	21.7 (22.4)	28.5 (28.4)	*b* (249.7)[c]
(4b)	$[(NiL^1Br_2)_n]$		Light green	19.2 (17.7)	1.6 (1.2)	17.4 (16.5)		*b* (338.6)
(5)	$[NiL^1_2Br_2]$	180	Light green	26.5 (26.2)	1.7 (1.8)	23.9 (24.4)		*b* (458.8)
(6)	$[CuL^1Cl_2]$	210	Green	24.2 (23.6)	1.8 (1.6)	22.0 (22.0)		*b* (254.6)
(7)	$[ZnL^1_2Cl_2]$	198	Colourless	32.2 (31.9)	2.4 (2.1)	29.4 (29.8)		*b* (376.5)
(8)	$[ZnL^1_2Br_2]$	210	Colourless	25.8 (25.8)	1.8 (1.7)	23.5 (24.1)		*b* (465.4)
(9)	$[PdL^1_2Cl_2]$	280	Yellow	28.9 (28.8)	2.2 (1.9)	26.6 (26.8)		*b* (417.5)
(10)	$[PtL^1(SMe_2)Cl_2]$	143	Yellow	19.1 (18.8)	2.1 (2.3)	12.8 (12.5)		466[d] (448.2)
(11)	$[Ru(PPh_3)_2L^1_2Cl_2]$	160	Yellow-green	59.0 (59.0)	4.2 (4.1)	10.9 (12.0)	7.2 (7.6)	475[d] (936.8)
(12)	$[Ru(PPh_3)_2L^1_2Br_2]$	155	Yellow	55.9 (53.9)	3.9 (3.7)	10.0 (10.9)	15.0 (15.6)	510[d] (1 025.7)
(13)	$[Ru(SbPh_3)_2L^1_2Cl_2]$	>300	Yellow	50.3 (49.4)	3.4 (3.4)	9.4 (10.0)	6.2 (6.3)	*b* (1 118.4)
(14)	$[Ru(PPh_3)_2(CO)L^1Cl_2]$	207	Yellow-green	59.1 (59.7)	4.1 (4.1)	6.4 (6.6)		*b* (844.7)
(15)	$[Cr(CO)_5L^1]$	116	Yellow	38.7 (38.5)	1.6 (1.3)	17.8 (18.0)		 (312.2)
(16)	$[W(CO)_5L^1]$	127	Yellow	27.4 (27.1)	1.0 (0.9)	12.8 (12.6)		430[d] (444.0)
(17)	$[Pd\{C_5H_3N(NH_2\text{-}2)(NO_2\text{-}5)\}_2Cl_2]$	260	Grey	24.6 (26.4)	2.1 (2.2)	17.1 (18.5)		*b* (455.5)
(18)	$[Pt(PEt_3)_2\{NHC_5H_3N(NO_2\text{-}5)\}Cl]$		Yellow	32.8 (33.8)	5.5 (5.7)	7.4 (6.9)		 (605.0)
(19)	$[Pt(PPh_3)_2(N_3)\{N_2C_5H_3N(NO_2\text{-}5)\}]$		Deep violet	53.0 (53.9)	3.6 (3.6)	10.5 (10.7)		 (912.8)

[a] The soluble complexes were non-conductors in nitrobenzene. [b] Insoluble or slightly soluble. [c] $n = 1$. [d] In chloroform.

The soluble ruthenium complexes $[Ru(PPh_3)_2L^1_2X_2]$ [X = Cl (11) or Br (12)] exhibit a molecular weight of about half the calculated value in chloroform solution, suggesting complete dissociation of one ligand. The dissociated ligand is probably one tetrazolopyridine molecule. This is supported by the fact that on reaction of (11) with carbon monoxide complex (14) is formed [equation (7)]. This derivative shows in the i.r. spectrum a single ν(CO) band at 1 965 cm^{-1} (in CH_2Cl_2) a rather low value for a ruthenium(II) complex. The steric hindrance of the ligand is presumably responsible for

$$\underset{(11)}{[Ru(PPh_3)_2L^1_2Cl_2]} + CO \longrightarrow \underset{(14)}{[Ru(PPh_3)_2(CO)L^1Cl_2]} + L^1 \quad (7)$$

the dissociation of L^1. It has been reported that while pyridine reacts with $[Ru(PPh_3)_3Cl_2]$ to give $[Ru(PPh_3)_2(py)_2Cl_2]$, no reaction occurs with 2-methylpyridine probably because of steric inhibition.[12] In the electronic spectrum in $CHCl_3$ solution, complex (11) shows two absorptions at 337 and 653 nm which are not affected by the presence of free tetrazolopyridine. However,

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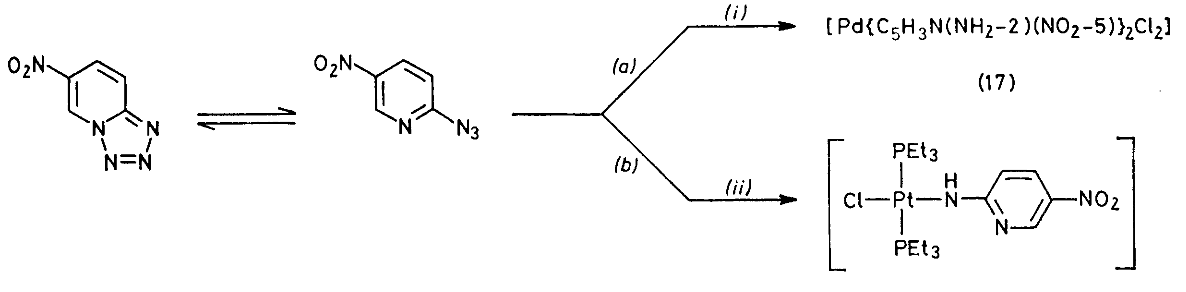
[10] S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, 1964, **3**, 671.

[11] H. Koezuka, G. Matsubayashi, and T. Tanaka, *Inorg. Chem.*, 1974, **13**, 443.

[12] J. D. Gilbert and G. Wilkinson, *J. Chem. Soc. (A)*, 1969, 1749.

yellow (11) when dissolved in chloroform gives a green solution. On adding diethyl ether to the solution a green material precipitates, the elemental analyses of which indicate a lower nitrogen content than the starting complex.



(17)

(18)

(*i*) $PdCl_2$–EtOH, $-N_2$; (*ii*) $[Pt(PEt_3)_2H(Cl)]$

In the far-i.r. spectra the ruthenium complexes show a single ν(Ru–Cl) band at *ca.* 305—310 cm^{-1}, indicative of a *trans* configuration. Complexes (1)—(14) [as for (15) and (16), see later] do not show i.r. absorptions markedly different from those of the free ligand L^1. In particular, the 2 000 cm^{-1} region is clear, suggesting that L^1 is co-ordinated to the metal in its tetrazole form (b). On the other hand, complexes (1)—(16) exhibit bands at *ca.* 1 630, 1 510, and 1 430 cm^{-1} due to conjugated double bonds, and bands at 1 010—1 150 cm^{-1} which are typical for the tetrazole ring. The ^{1}H n.m.r. spectra of some of these complexes have a number of bands in the aromatic region (*ca.* τ 1—1.5). In general, the signals due to the ligand are markedly shifted to lower field with respect to the free ligand (*ca.* τ 2.3—2.8). This seems to exclude a co-ordination

$$[M(CO)_5(thf)] \xrightarrow{L^1} [M(CO)_5L^1] \qquad (8)$$
$$(15)\ M = Cr,\ (16)\ M = W$$

to the metal *via* an olefinic double bond, and bonding *via* one nitrogen atom of the tetrazole ring is the most probable, as one would expect in this type of complex.

TABLE 2

Analytical data (required values in parentheses) for derivatives of 1-pyridinio ylides, $C_5H_5\overset{+}{N}-\overset{-}{N}R$ [R = $O_2SC_6H_4Me$-*p* (L^2) or OCC_6H_4Me-*p* (L^3)]

	Complex	M.p. (θ_c/°C)	Colour	Analysis (%) C	H	N	Cl	*M*
(20)	$[(NiL^2Cl_2)_n]\cdot nH_2O$	>240	Pink	36.55 (36.4)	3.45 (3.5)	6.75 (7.1)	17.2 (17.9)	*a* (395.9) [b]
(21)	$[NiL^2_2Br_2]$	>240	Turquoise	39.9 (40.3)	3.2 (3.4)	7.6 (7.8)		*a, c* (715.1)
(22)	$[PdL^2_2Cl_2]$	233 (decomp.)	Pink	42.9 (42.8)	3.3 (3.6)	8.2 (8.3)		*a* (673.9)
(23)	$[PdL^3_2Cl_2]\cdot 0.5CHCl_3$	164	Ochre-yellow	48.4 (48.1)	3.80 (3.7)	8.65 (8.5)	*d* (18.8)	*a* (661.5)
(24)	$[Pt(p\text{-}MeC_6H_3CO-\overset{-}{N}-\overset{+}{N}C_5H_5)(SMe_2)Cl]$	230 (decomp.)	Yellow	35.1 (35.8)	3.0 (3.4)	5.20 (5.6)	6.45 (7.0)	550 [e] (503.9)

[a] Insoluble or slightly soluble. [b] *n* = 1. [c] Non-conductor in nitrobenzene. [d] Cl, *ca.* 17%. [e] In chloroform.

Tetrazolo[1,5-*a*]pyridine (L^1) reacts with the tetrahydrofuran complexes $[M(CO)_5(thf)]$ (M = Cr or W) [13] to give $[M(CO)_5L^1]$. The corresponding molybdenum complex was too unstable to be isolated. The i.r. spectra of (15) and (16) show the expected three ν(CO) stretching bands ($2A_1 + E$) [(15), 2 072, 1 924, 1 868 (in KBr); (16), 2 073, 1 935, 1 868 (in KBr), 2 085, 1 931, and 1 896 cm^{-1} (in acetone)]. The wavenumbers for (16) in acetone are, as expected, similar to those of pentacarbonyl(5-phenyltetrazole)chromium.[14] It cannot be decided from the i.r. spectra which nitrogen atom of the tetrazole ring is co-ordinated to the metal. For pentacarbonyl complexes containing azoles the ^{14}N n.m.r. spectra allowed the determination of the co-ordination site of the ambivalent ligands.[15] However, the tetrazole complexes gave only very broad ^{14}N n.m.r. signals.

For 2-azido-5-nitropyridine the azide form is stabilized by the nitro-group [16] and the tetrazole–azide equilibrium can be followed by i.r. spectroscopy [$\nu_{asym}(N_3)$ at 2 142, $\nu_{sym}(N_3)$ at 1 300 cm^{-1} in $CHCl_3$]. There was no reaction of 2-azido-5-nitropyridine with cobalt(II) and nickel(II) chlorides in ethanol. Presumably, because of the electron-withdrawing nitro-group, the tetrazole is too weak a donor to be co-ordinated.

Three reactions of the azide form of 2-azido-5-nitropyridine have been observed. (*a*) With $PdCl_2$ in ethanol at 25 °C and with hydrogen abstraction from the solvent, 2-amino-5-nitropyridine is formed which

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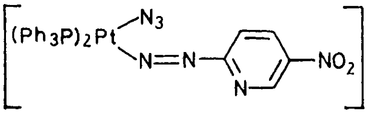
[13] W. Strohmeier and F. J. Müller, *Chem. Ber.*, 1968, **102**, 3608.

[14] J. Chr. Weis and W. Beck, *Chem. Ber.*, 1972, **105**, 3203.

[15] J. Chr. Weis and W. Beck, *J. Organometallic Chem.*, 1972, **44**, 325.

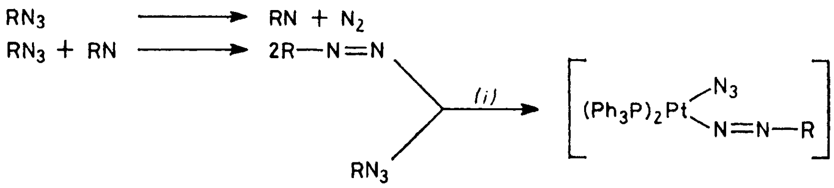
[16] J. H. Boyer and E. J. Miller, *J. Amer. Chem. Soc.*, 1959, **81**, 4671.

co-ordinates to the palladium [$\nu(NH_2)$ at 3 310 and 3 410 cm^{-1} in KBr]. The formation of amines from organic azides in the presence of metal complexes has been described previously.[4,5] (*b*) The reaction with *trans*-[$Pt(PEt_3)_2H(Cl)$] affords the amido-complex (18) [$\nu(NH)$ at 3 139 cm^{-1} in KBr]. This type of reaction has been previously observed for a number of organic azides RN_3 with electron-withdrawing groups R.[17] (*c*) The reactions of 2-azido-5-nitropyridine with [$Pt(PPh_3)_2(C_2H_4)$] gave a deep violet compound which shows i.r. bands (in KBr) at 2 062 [$\nu_{asym}(N_3)$] and 1 600 cm^{-1}. The latter absorption may be due to $\nu(N{=}N)$ of a platinum azo-complex, analogous to those obtained by oxidative addition of diazonium salts to platinum(0) complexes: [18a]



(19)

However, these vibrations are difficult to assign without ^{15}N labelling of the azo-group,[18b] and only the analytical data support the above formulation. The formation of a complex of this type could follow the Scheme (R = nitropyridyl):



(*i*) [$Pt(PPh_3)_2(C_2H_4)$], $-C_2H_4$ (−R)

Attempted reactions of 2-azidopyridine with [$Pt(PEt_3)_2H(Cl)$] and with complexes such as [$Pt(PPh_3)_3$] and [$Rh(PPh_3)_2(NO)(CO)$] were unsuccessful. Only with [$Ru(PPh_3)_2(CO)_3$] in boiling benzene was a reaction observed, giving a derivative of uncertain composition which was not further investigated.

Reactions with 1-*Pyridinio Ylides*.—The reactions of the complexes [$Ni(PPh_3)_2X_2$] (X = Cl or Br) and [$Pd(NCPh)_2Cl_2$] with the 1-pyridinio ylides $C_5H_5\overset{+}{N}\text{-}\overset{-}{N}R$ [R = $O_2SC_6H_4Me$-*p* (L^2) or OCC_6H_4Me-*p* (L^3)] gave

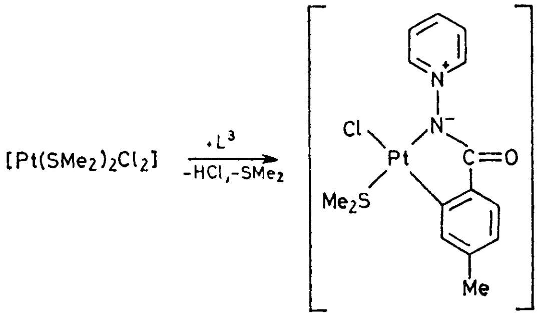
$$n[Ni(PPh_3)_2Cl_2] + nL^2 \xrightarrow{H_2O} [(NiL^2Cl_2)_n]\cdot nH_2O + 2nPPh_3 \quad (9)$$

$$[Ni(PPh_3)_2Br_2] + 2L^2 \longrightarrow [NiL^2{}_2Br_2] + 2PPh_3 \quad (10)$$

$$[Pd(NCPh)_2Cl_2] + 2L^2 \longrightarrow [PdL^2{}_2Cl_2] + 2PhCN \quad (11)$$

$$[Pd(NCPh)_2Cl_2] + 2L^3 \longrightarrow [PdL^3{}_2Cl_2] + 2PhCN \quad (12)$$

complexes (20)—(23) (Table 2). The complex [$(NiL^2Cl_2)_n]\cdot nH_2O$ (20) is an insoluble polymeric material, having an octahedral configuration, as shown by the electronic spectrum and by the magnetic moment ($\mu_{eff.}$ 3.30 B.M.). It contains water, which cannot be eliminated even by prolonged drying *in vacuo*. On the other hand, the complex [$NiL^2{}_2Br_2$] (21) has a tetrahedral configuration, since the electronic-reflectance spectrum gave bands at 1 050m, 650 (sh), and 600s nm, and its magnetic moment ($\mu_{eff.}$ 3.59 B.M.) is in agreement with this type of co-ordination.[10]



(13)

(24)

The complexes [$PdL^2{}_2Cl_2$] (22) and [$PdL^3{}_2Cl_2$] (23) appear to have a *trans*-square-planar structure, since a $\nu(Pd{-}Cl)$ band at *ca*. 340 cm^{-1} has been observed in the far-i.r. spectrum. However, the free ligands absorb in this region, and thus it is difficult to assign with certainty the absorptions observed. Complex (23) had already been isolated by other workers [6] from the reaction of $K_2[PdCl_4]$ with $Na[O_2CMe]$ and the ylide. A different type of product was obtained from the interaction of [$Pt(SMe_2)_2Cl_2$] and L^3, a reaction which requires a prolonged reflux of the reactants in ethanol [equation (13)]. This orthometallation reaction has been already observed in the interaction of this ylide with halide salts of Pd^{II}, Pt^{II}, Rh^{III}, and Ir^{III}.[6] The low $\nu(Pt{-}Cl)$ at 275 cm^{-1} for (24) suggests that chloride is *trans* to carbon in this complex. Also, a single signal due to SMe_2 was observed in the ^1H n.m.r. spectrum [τ 7.24 with satellites due to coupling with platinum, *J*(Pt–H) 27 Hz]. The formulation of this complex has been confirmed by the i.r. spectrum which shows bands at 880 and 820 cm^{-1}, in the region of the out-of-plane bending of the aromatic ring, consistent with a 1,2,4-trisubstituted benzene residue. Co-ordination of the ylide *via* nitrogen and not oxygen in complexes (20)—(24) is indicated by the shift of $\nu(CO)$ and $\nu(SO_2)$ to higher frequencies (Table 3) on complex formation.[6,7] A similar shift to higher

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[17] W. Beck and M. Bauder, *Chem. Ber.*, 1970, **103**, 583.

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frequencies has been observed on protonation of the benzamidate nitrogen atom in the free ligand.[6,19] On the other hand, attempted protonation reactions of complexes (21) and (22) with mineral acids were not successful, and reaction of (21) with HBr gave only $L^2{\cdot}HBr$.

TABLE 3

Infrared (in Nujol) and ^1H n.m.r. data for derivatives of 1-pyridinio ylides

Compound	$\nu(CO)$	$\nu_{asym}(SO_2)$	$\nu_{sym}(SO_2)$	$\nu(M{-}X)$	$\tau(Me)$
L^2		1 275	1 135		7.7 [a]
(20)		1 290	1 135	<300	7.68 [a]
(21)		1 330	1 160	335	7.63 [a]
(22)		1 325	1 150	335	7.64 [a]
L^3	1 540				7.65 [b]
(23)	1 690			350	7.63 [a]
(24)	1 645			275	7.61 [d]

[a] In deuteriated dimethyl sulphoxide. [b] In deuterioacetone. [c] $\tau(SMe_2)$ 7.24, with satellites due to coupling with platinum [J(Pt–H) 27 Hz]. [d] In $CDCl_3$.

Analogously to tetrazolo[1,5-*a*]pyridine, the sulphonyl ylide L^2 did not react with (triphenylphosphine)-platinum(0) complexes or with $[Ru(PPh_3)_2(CO)_3]$; no reaction was observed even in refluxing benzene.

EXPERIMENTAL

All the reactions were carried out under nitrogen, with stirring, but the work-up of the reaction mixtures was usually carried out in air. Infrared spectra were recorded with Perkin-Elmer 457 and 325 instruments, ^1H n.m.r. spectra with a Varian NV-14 instrument operating at 60 MHz and $SiMe_4$ as internal standard, and electronic spectra with a Beckman DK-2A spectrophotometer. The samples for reflectance spectra were diluted with magnesium oxide. Melting points were determined on a Leitz Heiztischmikroskop, and are not corrected. Elemental analyses were carried out by the Analytical Laboratories of Milan and Munich University. Molecular weights were obtained using a Mechrolab osmometer. The azidopyridines,[4] $[Ni(PPh_3)_2X_2]$ (X = Cl or Br), $[Pd(NCPh)_2Cl_2]$, $[Pt(SMe_2)_2Cl_2]$, $[Ru(PPh_3)_3X_2]$ (X = Cl or Br), $[Ru(SbPh_3)_3Cl_2]$, and the anhydrous metal halides were prepared as described in the literature. 1-Pyridinio ylides were prepared by a literature method [20] starting with 1-aminopyridinium iodide.[21] The solvents used were dried. The new nickel complexes isolated in this work were stored in a dry atmosphere.

Dichlorobis(tetrazolo[1,5-a]*pyridine)manganese*, $[MnL^1{}_2Cl_2]$ (1).—To a solution of $MnCl_2$ (60 mg, 0.48 mmol) in pure ethanol (25 cm^3) was added a solution of tetrazolopyridine (120 mg, 1 mmol) in ethanol (15 cm^3). After a few minutes the precipitate was filtered off, washed with ethanol, and dried *in vacuo*.

$[FeL^1{}_3Cl_2]$ (2).—To a solution of tetrazolopyridine (120 mg, 1 mmol) in ethanol (25 cm^3) was added a solution of $FeCl_2$ (65 mg, 0.51 mmol) in ethanol (25 cm^3). After stirring, the yellow crystals were collected, washed with diethyl ether, and dried *in vacuo*.

$[CoL^1Cl_2]$ (3).—This complex was isolated from $CoCl_2$ (65 mg, 0.5 mmol) and tetrazolopyridine (120 mg, 1 mmol) in ethanol (40 cm^3) as described above.

$[(NiL^1Cl_2)_n]$ (4a).—(*a*) To dry benzene (25 cm^3) were added tetrazolopyridine (226 mg, 1.88 mmol) and $[Ni(PPh_3)_2Cl_2]$ (400 mg, 0.61 mmol). After 1 h the light green precipitate was filtered off, washed with a little benzene, ethanol, and diethyl ether, and dried *in vacuo* for a long time (54% yield).

(*b*) Tetrazolopyridine (120 mg, 1 mmol) in ethanol (15 cm^3) was poured into a solution of $NiCl_2$ (65 mg, 0.5 mmol) in ethanol (15 cm^3). The light green precipitate was filtered off, washed with ethanol, and dried *in vacuo*.

$[(NiL^1Br_2)_n]$ (4b).—Nickel(II) bromide (220 mg, 1 mmol) in hot ethanol (50 cm^3) was added to tetrazolopyridine (360 mg, 3 mmol) in ethanol. After some minutes the light green substance precipitated. After stirring for 15 h the precipitate was collected, washed with ethanol, and dried *in vacuo*.

$[NiL^1{}_2Br_2]$ (5).—This complex was prepared as described for (4a) by using dry benzene (20 cm^3), $[Ni(PPh_3)_2Br_2]$ (300 mg, 0.4 mmol), and tetrazolopyridine (149 mg, 1.24 mmol) and by stopping the reaction after 0.5 h (95% yield).

$[CuL^1Cl_2]$ (6).—The precipitate from a solution of $CuCl_2$ (67 mg, 0.5 mmol) and tetrazolopyridine (120 mg, 1 mmol) in ethanol (40 cm^3) was isolated, washed with ethanol, and dried *in vacuo*.

$[ZnL^1{}_2Cl_2]$ (7).—Tetrazolopyridine (120 mg, 1 mmol) in dimethoxypropane (20 cm^3) was poured into a solution of $ZnCl_2$ (65 mg, 0.48 mmol) in 2,2-dimethoxypropane (30 cm^3). The precipitate was washed with diethyl ether and dried *in vacuo*.

$[ZnL^1{}_2Br_2]$ (8).—As described for (7), $ZnBr_2$ (90 mg, 0.4 mmol) and tetrazolopyridine (120 mg, 1 mmol) were allowed to react in glyme–methanol (1 : 1). After stirring for 10 min the precipitate was collected, washed with diethyl ether, and dried *in vacuo*.

$[PdL^1{}_2Cl_2]$ (9).—(*a*) To a yellow solution of $[Pd(NCPh)_2Cl_2]$ (300 mg, 0.78 mmol) in dry benzene (25 cm^3) was added tetrazolopyridine (288 mg, 2.40 mmol). After 1 h the yellow precipitate was filtered off, washed with a little benzene and diethyl ether, and dried *in vacuo* (86% yield).

(*b*) To a suspension of $PdCl_2$ (70 mg, 0.4 mmol) in ethanol (30 cm^3) was added a solution of tetrazolopyridine (120 mg, 1 mmol) in ethanol (15 cm^3). After stirring for 24 h the solid was filtered off, washed with ethanol, and dried *in vacuo*.

$[PtL^1(SMe_2)Cl_2]$ (10).—To dry benzene (15 cm^3) were added $[Pt(SMe_2)_2Cl_2]$ (150 mg, 0.38 mmol) and tetrazolopyridine (139 mg, 1.16 mmol). The yellow suspension was heated under reflux for 3 h. The resulting yellow solution was cooled and evaporated to a small volume. By adding

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diethyl ether a yellow precipitate was obtained. The product was filtered off, washed with diethyl ether, and dried *in vacuo*.

$[Ru(PPh_3)_2L^1{}_2Cl_2]$ (11).—To solid $[Ru(PPh_3)_3Cl_2]$ (300 mg, 0.31 mmol) and tetrazolopyridine (110 mg, 0.92 mmol) was added dry benzene (14 cm^3). After 15 min the yellow-green precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* (92% yield).

$[Ru(PPh_3)_2L^1{}_2Br_2]$ (12).—This complex was prepared as described for (11) by using $[Ru(PPh_3)_3Br_2]$ (300 mg, 0.29 mmol), tetrazolopyridine (110 mg, 0.92 mmol), and dry benzene (15 cm^3) but by stopping the reaction after 0.5 h and washing the product with benzene (85% yield).

$[Ru(SbPh_3)_2L^1{}_2Cl_2]$ (13).—A suspension of $[Ru(SbPh_3)_3Cl_2]$ (400 mg, 0.32 mmol) and tetrazolopyridine (125 mg, 1.04 mmol) in dry benzene (20 cm^3) was heated under reflux for 1 h. The resulting suspension was left to cool to room temperature and the yellow precipitate was filtered off, washed repeatedly with benzene, and dried *in vacuo* (60% yield).

$[Ru(PPh_3)_2(CO)L^1Cl_2]$ (14).—Carbon monoxide was bubbled through a suspension of (11) (160 mg) in benzene (18 cm^3) for 3—4 d. A solution was initially slowly formed, and then the yellow-green product slowly precipitated. It was filtered off and dried *in vacuo*.

$[Cr(CO)_5L^1]$ (15).—A solution of $[Cr(CO)_6]$ (220 mg, 1 mmol) in tetrahydrofuran (thf) (150 cm^3) was irradiated (mercury lamp TQ 150 Heraeus, Hanau). After 25 cm^3 of CO gas had been evolved a solution of tetrazolopyridine (180 mg, 1.5 mmol) in thf (40 cm^3) was added dropwise and the mixture was evaporated to 40 cm^3. The yellow precipitate was collected under N_2, washed with diethyl ether, dried *in vacuo*, and recrystallized from ethanol–light petroleum. The complex $[W(CO)_5L^1]$ (16) was obtained similarly.

Reaction of 2-*Azido*-5-*nitropyridine with* $PdCl_2$.—A solution of 2-azido-5-nitropyridine (165 mg, 1 mmol) in ethanol (20 cm^3) was added dropwise to a mixture of $PdCl_2$ (70 mg, 0.4 mmol) in ethanol (30 cm^3). After stirring for 36 h the grey precipitate was collected, washed with ethanol, and dried *in vacuo*. The complex $[Pd\{C_5H_3N(NH_2\text{-}2)(NO_2\text{-}5)\}_2Cl_2]$ (17) contained some palladium metal which could not be removed since the complex is insoluble in the common solvents.

Chloro(5-*nitro*-2-*pyridylamido*)*bis*(*triethylphosphine*)-*platinum*, $[Pt(PEt_3)_2\{NHC_5H_3N(NO_2\text{-}5)\}Cl]$ (18).—A solution of 2-azido-5-nitropyridine (74 mg, 0.45 mmol) in benzene was added dropwise to a solution of *trans*-$[Pt(PEt_3)_2H(Cl)]$ (210 mg, 0.45 mmol)[22] and slight gas evolution was observed. After stirring for 3 h the solution was evaporated to 5 cm^3 and cooled. The yellow crystals were collected and dried *in vacuo*.

Reaction of 2-*Azido*-5-*nitropyridine with* $[Pt(PPh_3)_2(C_2H_4)]$.—A solution of $[Pt(PPh_3)_2(C_2H_4)]$ (515 mg, 0.69 mmol) in thf (30 cm^3) was added dropwise to 2-azido-5-nitropyridine (240 mg, 1.45 mmol) in thf (30 cm^3). After stirring for 2 h the deep red solution was evaporated to 10 cm^3; by adding pentane (5 cm^3) a deep violet precipitate of complex (19) was obtained. The complex was recrystallized from thf–pentane. Recrystallization from CH_2Cl_2–pentane afforded a product which did not show a band at 1 600 cm^{-1}.

Poly{*dichloro*[N-(1-*pyridinio*)*toluene*-p-*sulphonamidate*]-*nickel*} *Hydrate*, $[(NiL^2Cl_2)_n]\cdot nH_2O$ (20).—To $[Ni(PPh_3)_2Cl_2]$ (200 mg, 0.31 mmol) dissolved in chloroform (10 cm^3) were added *N*-(1-pyridinio)toluene-*p*-sulphonamidate (150 mg, 0.60 mmol). The solution was heated under reflux for 2 h and then cooled to room temperature. The pink precipitate was filtered off, washed repeatedly with water, ethanol, and n-hexane, and dried *in vacuo* for a long time (95% yield).

$[NiL^2{}_2Br_2]$ (21).—This complex was prepared as described for (20) by using $[Ni(PPh_3)_2Br_2]$ (300 mg, 0.40 mmol), ylide (200 mg, 0.81 mmol), and chloroform (30 cm^3) but by stopping the reaction after 3 h (*ca.* 60% yield). The filtered product was not washed with any additional solvent.

$[PdL^2{}_2Cl_2]$ (22).—To a solution of $[Pd(NCPh)_2Cl_2]$ (300 mg, 0.78 mmol) in chloroform (10 cm^3) was added the ylide (390 mg, 1.57 mmol). After 4 h the pink precipitate was filtered off and dried *in vacuo* (93% yield).

Dichlorobis[N-(1-*pyridinio*)-p-*toluamidate*]*palladium*–*Chloroform* (2/1), $[PdL^3{}_2Cl_2]\cdot 0.5CHCl_3$ (23).—To a solution of $[Pd(NCPh)_2Cl_2]$ (250 mg, 0.51 mmol) in chloroform (10 cm^3) was added *N*-(1-pyridinio)-*p*-toluamidate (280 mg, 1.32 mmol). After 3 h the yellow precipitate was filtered off and dried *in vacuo* (*ca.* 70% yield).

Chloro(*dimethyl sulphide*)[N-(1-*pyridinio*)-p-*toluamidate*-NC^2]*platinum*, $[Pt(p\text{-}MeC_6H_3CO\text{–}\overset{-}{N}\text{–}\overset{+}{N}C_5H_5)(SMe_2)Cl]$ (24).—A suspension of $[Pt(SMe_2)_2Cl_2]$ (200 mg, 0.61 mmol) and *N*-(1-pyridinio)-*p*-toluamidate (218 mg, 1.03 mmol) in ethanol (20 cm^3) was heated under reflux for 8 h. The resulting solution was left to cool overnight. The yellow precipitate was filtered off and dried *in vacuo*.

Reaction of (21) *with* HBr.—To a suspension of (21) (100 mg, 0.14 mmol) in diethyl ether (20 cm^3) were added a few drops of an aqueous solution of HBr. After 0.5 h isopropyl alcohol was added and the white precipitate was filtered off. The product was shown to be $C_5H_5\overset{+}{N}\text{–}\overset{-}{N}\text{–}SO_2C_6H_4Me\text{-}p\cdot HBr$ by its i.r. spectrum, identical to that of an authentic sample, and elemental analyses (Found: C, 42.9; H, 3.95; N, 8.25. $C_{12}H_{13}BrN_2O_2S$ requires C, 43.8; H, 4.0; N, 8.5%).

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