Metal Derivatives of Azoles. Part 4.[1] Platinum(II) and Palladium(II) Complexes

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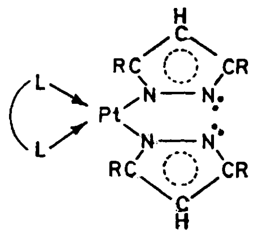
The reaction of $[MCl_2(L-L)]$ [M = Pd or Pt, L–L = 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diphenylarsino)ethane (dpae), 2,2′-bipyridine (bipy), or cyclo-octa-1,5-diene (cod)] with alkali and an azole [pyrazole (Hpz), 3,5-dimethylpyrazole (3,5Me$_2$-Hpz), indazole, or tetrazole] or with a potassium pyrazolate gives the [M(azolate-*N*)$_2$(L–L)] complexes, where the azolato-ligands are unidentate. While I_2 or HCl cleaves the metal–nitrogen bonds, the reaction with HBF_4 acid affords either mono- or bi-nuclear cations, $[M(azole)_2(L-L)]^{2+}$ or $[(L-L)M(\mu\text{-pyrazolato-}NN')_2M(L-L)]^{2+}$ respectively; the latter compounds contain esobidentate pyrazolato-ligands.

POLYHETEROMETALLIC compounds which are not cluster-like can be assembled using two different complexes, one of which must be a Lewis acid and generally easily available, and the other a Lewis base. Therefore, in a stepwise synthesis of such heterometallic systems a suitable complex is first required where potential donor centres are available, *i.e.* are not engaged in co-ordination.

Following up our interest in heteropolymetallic systems involving transition metals,[2] we describe here a series of new platinum(II) and palladium(II) complexes having the general formula [M(azolate)$_2$(L–L)] where the chelating ligand L–L may be $Ph_2ECH_2CH_2EPh_2$ [E = P (dppe) or As (dpae)], cyclo-octa-1,5-diene (cod), or 2,2′-bipyridine (bipy) and the azolate is formed from pyrazole (Hpz), 3,5-dimethylpyrazole (3,5Me$_2$-Hpz), indazole, or tetrazole. In all these complexes the azolato-groups are unidentate so that all the molecules described are, at least in principle, bidentate metal-containing ligands, and, as such, they can react either as bridging, or, more frequently, as chelating ligands, a kind of sophisticated analogue of 2,2′-bipyridine. While this aspect of the reactivity has been briefly reported,[3] and will be treated in a forthcoming paper, some other general reactions of the azolates will be described here.



Amongst the azolates, the pyrazolates reported here are rare examples of transition-metal derivatives where this group is uni- rather than bi-dentate. Unidentate behaviour is not unprecedented for pyrazolato-ligands, for it was found in those cases where nucleophilic attack by the [pz]$^-$ anion is hampered by the existence of a negative charge or electron pair on the co-ordination centre, *e.g.* $[BH_n(pz)_{4-n}]^-$ (n = 0—2),[4] $[GaH_2(pz)_2]^-$,[5] or $P(pz)_3$.[6] In addition, recent results[1] have shown that gold(I) derivatives of 3,5-dimethyl-4-nitropyrazole (3,5Me$_2$-4NO$_2$-Hpz) may contain either uni- or bidentate [3,5Me$_2$-4NO$_2$-pz]$^-$ anion, as in [Au(3,5Me$_2$-4NO$_2$-pz)(PPh$_3$)] or [{Au(3,5Me$_2$-4NO$_2$-pz)}$_n$] respectively.

RESULTS AND DISCUSSION

Preparation and Properties of the Azolates.—As starting material, square-planar dichloro-platinum(II) and -palladium(II) derivatives were always employed where one chelating rather than two unidentate ligands were present. With this choice the displacement of ligand is minimized, both the starting and the final product must be the *cis* isomer, and the two azolato-groups are in a position suitable for the use of the resulting molecule as a chelating metal-containing ligand.

The reaction of these dichlorometal(II) derivatives with an azole (Hqz) and potassium hydroxide in methanol gave several compounds of the type [M(azolate-*N*)$_2$-(L–L)], according to Scheme 1. However, when the chelating ligand was 2,2′-bipyridine only one of the two chlorine atoms could be replaced under the experimental conditions used, and in addition, the compound [PtCl-(3,5Me$_2$-pz)(bipy)] (14) was obtained in low yield. Therefore the potassium salt of pyrazole or of 3,5-dimethylpyrazole was employed, and platinum(II) or palladium(II) pyrazolates were obtained where the chelating ligand was either 2,2′-bipyridine or cyclo-octa-1,5-diene, according to Scheme 2. This reaction, nevertheless, did not afford the required product in case (1).

$$[MCl_2(L\text{–}L)] + 2\,Haz + 2\,K[OH] \longrightarrow [M(az)_2(L\text{–}L)] + 2\,KCl + 2\,H_2O$$

(1), (4), (6)—(8), (18), and (20)

SCHEME 1

$$[PdCl_2(bipy)] + 2\,K[pz] \longrightarrow 2\,KCl + bipy + \frac{1}{n}[\{Pd(\mu\text{-}pz)_2\}_n] \qquad (1)$$

The cyclo-octa-1,5-diene derivative [Pt(3,5Me$_2$-pz)$_2$(cod)] (17) was obtained in low yield according to Scheme 2, accompanied by another product not yet identified. It is known that a co-ordinated diene may undergo nucleophilic attack by a [pz]$^-$ ion according to reaction (2).[7]

The solid compounds are stable in air, and stable, or at least fairly stable, to heat. They were characterized

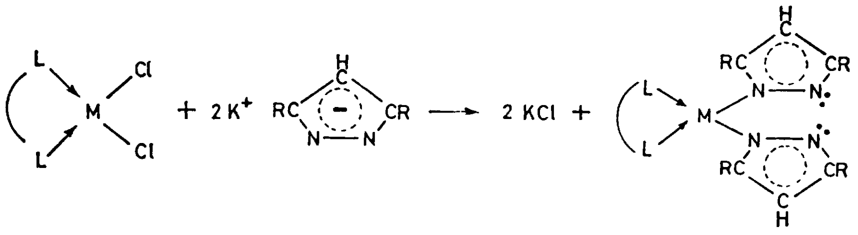
TABLE 1

Analytical and other data

Compound	M.p. (θ_c/°C)	Analysis (%) [a] C	H	N	Other data [a,b]
(1) $[Pt(pz)_2(dppe)]$	245—250 decomp. >230	51.95 (52.45)	3.95 (4.00)	7.20 (7.30)	*M* 863 (727)
(2) $[Pt_2(\mu\text{-}pz)_2(dppe)_2][BF_4]_2$	>250	46.15 (46.6)	3.60 (3.60)	3.55 (3.75)	
(3) $[Pt_2(\mu\text{-}pz)_2(dppe)_2][PtCl_4]$	210—215	41.45 (42.0)	3.25 (3.25)	3.30 (3.40)	$\Lambda = 174$ (0.27×10^{-3} mol dm^{-3} $MeNO_2$, 293 K)
(4) $[Pt(3,5Me_2\text{-}pz)_2(dppe)]$	255—260	55.8 (55.3)	4.90 (4.85)	7.00 (7.15)	*M* 815 (783) P, 7.95 (7.95)% Pt, 25.05 (24.9)%
(5) $[Pt(3,5Me_2\text{-}Hpz)_2(dppe)][BF_4]_2$ [c]	*ca.* 250	44.65 (45.05)	4.15 (4.15)	5.75 (5.85)	*M* 1 000 (959) F, 15.9 (15.85)% $\Lambda = 211$ (0.59×10^{-3} mol dm^{-3} $MeNO_2$, 291 K)
(6) $[Pt(C_7H_5N_2)_2(dppe)]$ [d]	248—258 decomp. >210	57.4 (58.0)	3.90 (4.10)	6.40 (6.75)	*M* 786 (827)
(7) $[Pt(CHN_4)_2(dppe)]$ [e]	226—227	45.45 (46.0)	3.30 (3.55)	14.85 (15.3)	*M* 854 (731)
(8) $[Pt(3,5Me_2\text{-}pz)_2(dpae)]$	decomp. 195	49.75 (49.5)	4.60 (4.40)	6.35 (6.40)	
(9) $[Pt(3,5Me_2\text{-}Hpz)_2(dpae)][BF_4]_2$	240—250	40.8 (41.3)	3.95 (3.80)	5.00 (5.35)	
(10) $[Pt(pz)_2(bipy)]$	decomp. 280	38.8 (39.6)	2.85 (2.40)	16.9 (17.3)	$\Lambda = 13.8$ (0.9×10^{-3} mol dm^{-3} MeOH, 293 K)
(11) $[Pt(pz)_2(bipy)]\cdot H_2O$	decomp. 280	38.25 (39.15)	2.65 (3.20)	16.5 (16.7)	
(12) $[Pt(Hpz)_2(bipy)][BF_4]_2$	222—226	29.15 (29.05)	2.45 (2.40)	12.8 (12.7)	$\Lambda = 225$ (0.4×10^{-3} mol dm^{-3} Me_2CO, 293 K)
(13) $[Pt_2(\mu\text{-}pz)_2(bipy)_2][PtCl_6]$	decomp. 250	24.15 (25.1)	1.70 (1.75)	9.50 (9.00)	
(14) $[PtCl(3,5Me_2\text{-}pz)(bipy)]$	>120	37.5 (37.4)	3.55 (3.10)	11.4 (11.6)	
(15) $[Pt(3,5Me_2\text{-}pz)_2(bipy)]$	decomp. 270	44.15 (44.3)	3.90 (4.05)	15.5 (15.5)	$\Lambda = 25$ (0.4×10^{-3} mol dm^{-3} MeOH, 293 K)
(16) $[Pt(3,5Me_2\text{-}Hpz)_2(bipy)][BF_4]_2$	242—246	33.75 (33.5)	3.55 (3.35)	11.7 (11.7)	$\Lambda = 179$ (0.37×10^{-3} mol dm^{-3} Me_2CO, 293 K)
(17) $[Pt(3,5Me_2\text{-}pz)_2(cod)]$	199—201	43.7 (43.8)	5.20 (5.25)	10.55 (11.5)	Pt, 38.7 (39.55)%
(18) $[Pd(pz)_2(dppe)]$	190 decomp. >175	59.7 (60.15)	4.80 (4.70)	8.45 (8.75)	
(19) $[Pd_2(\mu\text{-}pz)_2(dppe)_2][BF_4]_2$	decomp. 240	52.0 (52.8)	4.00 (4.10)	4.10 (4.25)	
(20) $[Pd(3,5Me_2\text{-}pz)_2(dppe)]\cdot 1.5H_2O$		59.8 (59.8)	5.35 (5.70)	7.45 (7.75)	Pd, 14.9 (14.75)% O, 3.80 (3.30)%
(21) $[Pd(3,5Me_2\text{-}Hpz)_2(dppe)][BF_4]_2$	235—245	49.6 (49.65)	4.40 (4.60)	6.30 (6.45)	$\Lambda = 181$ (0.45×10^{-3} mol dm^{-3} Me_2CO, 293 K)
(22) $[Pd(3,5Me_2\text{-}pz)_2(bipy)]$	240 decomp. 180	53.7 (53.05)	4.55 (4.85)	18.9 (18.55)	
(23) $[Pd(3,5Me_2\text{-}Hpz)_2(bipy)][BF_4]_2$	160—166	37.4 (38.2)	3.45 (3.80)	12.65 (13.4)	$\Lambda = 158$ (0.65×10^{-3} mol dm^{-3} Me_2CO, 293 K)
(24) $[\{Pd(pz)_2\}_n]$	>280	30.75 (29.95)	2.60 (2.50)	22.8 (13.3)	

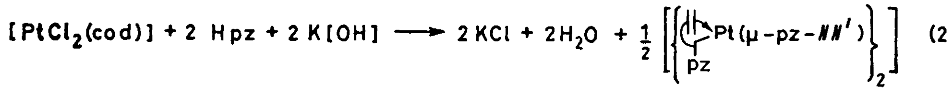
[a] Calculated values are given in parentheses. [b] Molecular-weight determinations by osmometry in chloroform; Λ is expressed in S cm^2 mol^{-1}. [c] Some preparations afforded a compound with clathrated CH_2Cl_2 (n.m.r. evidence) or H_2O. [d] $C_7H_6N_2$ is indazole. [e] CH_2N_4 is tetrazole.

through elemental analyses, molecular-weight determinations, and spectral evidence. The azolato-compounds are not very soluble in organic solvents, and their solutions are more stable in the case of platinum than of palladium compounds. Detection of n.m.r. signals is easier in the case of the dimethylpyrazolates, which are more soluble, than for the derivatives of the unsubstituted pyrazole. In the case of the platinum-containing derivatives, assignment of the ^1H n.m.r. spectra was assisted by the appearance of satellite bands due to

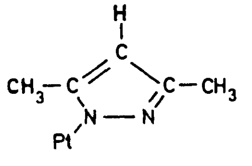


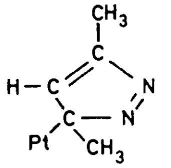
SCHEME 2

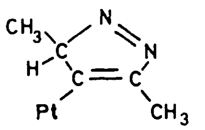
coupling between hydrogen and ^{195}Pt (spin $\frac{1}{2}$; natural abundance 33%). Since the Pt–H coupling can generally be observed only if the number of intervening bonds is not greater than four,[8] in the 3,5-dimethylpyrazolates [Pt(3,5Me$_2$-pz)$_2$(dppe)] (4) or [Pt(3,5Me$_2$-pz)$_2$(bipy)] (15) only the 5-Me and the 4-H (but not the 3-Me) signals should be affected. For these compounds the observed values for ^4J(Pt–Me^5), 4 or 6 Hz respectively, and for ^4J(Pt–H^4), 9 or 14 Hz respectively, agree with the proposed *N*-substitution, (A). The n.m.r. spectra of the same compounds (4) or (15) rule out other structures, such as (B)—(D), *i.e. C*-derivatives of an isopyrazole, a non-aromatic but known system.[9] Indeed, (B) requires two non-equivalent methyl groups, as observed, but one of the methyl signals and the 4-CH signal should show satellites with a coupling (^3J) one order of magnitude larger than those observed. Moreover, in structure (C) one of the two methyl groups should give a 1 : 1 doublet owing to coupling with the neighbouring hydrogen; in structure (D) both methyl groups should be coupled to ^{195}Pt, in contrast to the experimental results. Analogous Pt–H couplings were observed also for the corresponding pyrazolate (1) but the 5-CH signal lies in the same region as the aryl protons of dppe and so escapes detection.

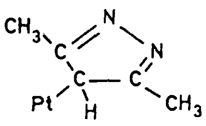

(2)

For the compounds (15) and [Pd(3,5Me$_2$-pz)$_2$(bipy)] (22) only two methyl signals (with the required coupling due to ^{195}Pt for the former) were observed in CD$_3$OD solution, thus proving that the two pyrazolato-groups are equivalent. With the related compound (4) such a conclusion was reached independently though the ^{31}P n.m.r. spectrum, which shows one signal at 32.97 p.p.m. downfield from 85% phosphoric acid. The coupling constant ^1J(Pt–P) is 3 300 Hz, a value comparable with the 3 322 Hz observed[10] for the coupling of phosphorus *trans* to the nitrogen ligand in [Pt(CH$_3$)(NHCOCH$_3$)-(dppe)]. The ^{1}H n.m.r. spectra of compounds (15) and (22) in CDCl$_3$ solvent showed more signals (three and four respectively) than are observed in the CD$_3$OD solvent. This fact points to restricted rotation around the metal–nitrogen bonds or intermolecular association, which cannot be checked by molecular-weight determination owing to insufficient solubility in chlorinated solvents.


(A)


(B)


(C)


(D)

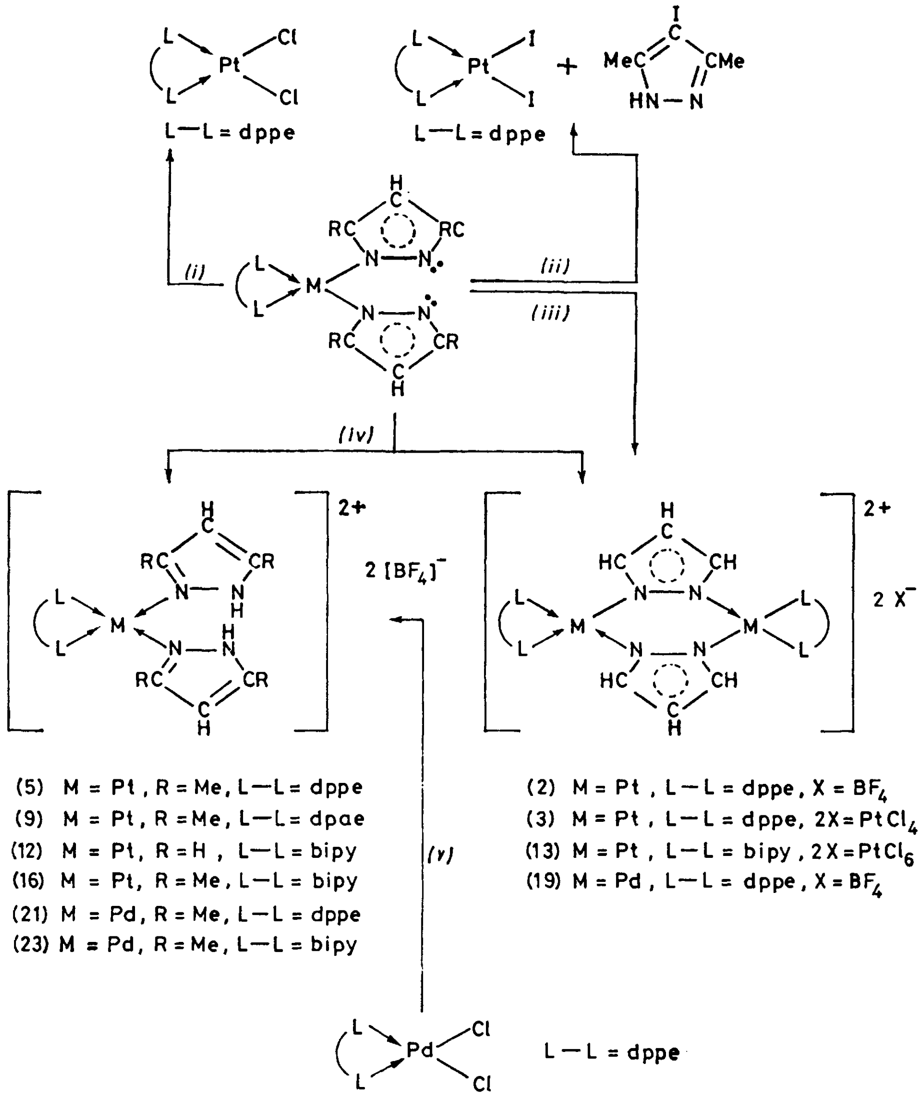
In the case of compound (15) two forms were detected not only in solution but also in the solid state. Indeed, the sample obtained from the orange chloroform solution is orange while the sample from the yellow methanol solution is yellow (at least until moistened by the solvent) and becomes orange only when completely dry. It should be remembered that two forms were isolated in the case of [PtCl$_2$(bipy)]:[11,12] in the red form the flat square-planar platinum(II) unit was found to be arranged in stacks along a Pt–Pt axis allowing an interaction between the metal atoms, which are only 340 pm apart. No such stacking, and, consequently, no interaction was found in the yellow form, where the Pt–Pt distance is 450 pm.

The n.m.r. spectrum of the tetrazolato-complex (7) showed the dppe signals and a singlet with no satellites. This and the absence of any ν(NH) or δ(NH) in the i.r. spectrum support an *N*-bonded structure and rule out a *C*-bonded tetrazolyl group. Platinum(II) and palladium(II) derivatives of 5-substituted tetrazoles, *cis*-[M(5Me-CN$_4$)$_2$L$_2$], were obtained[13a] by treatment of the heterocyclic molecule with the appropriate [ML$_4$] complex (L = PPh$_3$), and are *N*-bonded; other tetrazolates, such as *cis*-[M(CN$_4$R)$_2$(CNR)(PPh$_3$)] (M = Pd or Pt, R = phenyl or cyclohexyl) or *cis*-[Pt(CN$_4$CH$_3$)$_2$-(CNCH$_3$)$_2$], are *C*-bonded and were obtained[13b] from *cis*-[M(N$_3$)$_2$(PPh$_3$)] and an isocyanide.

Reactivity of the Azolates.—The reactions reported in the Experimental section are summarized in Scheme 3.

All the pyrazolates reacted with acids. The Pt–N bonds in compound (4) were cleaved by hydrochloric acid, while tetrafluoroboric acid protonated both pyrazolato-groups affording a mononuclear cation, [M(pyrazole)$_2$(L–L)]$^{2+}$, in agreement with the bifunctional base nature of the azolato-complexes, which can be reformed by deprotonation with potassium hydroxide. The same type of complexes can be obtained independently by reaction of [PdCl$_2$(dppe)] with silver fluoroborate, removal of silver chloride, and addition of 3,5-dimethylpyrazole. The protonation of [M(pz)$_2$(dppe)] [M = Pt (1) or (18)] with HBF$_4$ took a different course leading to a binuclear complex [M$_2$(μ-pz)$_2$(dppe)$_2$]$^{2+}$ [M = Pt (2) or (19)]. The tetrachloroplatinate(II) of the same cation (3; M = Pt) was obtained when the corresponding (1) was treated with [NBu$^n_4$]$_2$[PtCl$_4$]. A similar species, (13), having bipy in the place of dppe resulted by reaction of [Pt(pz)$_2$(bipy)] with Na$_2$[PtCl$_6$], in an attempt to obtain a binuclear compound having each co-ordination centre in a different oxidation state.

All the mononuclear salts and the binuclear salts (2) and (19) exhibited a very strong and broad band at *ca.* 1 050 cm^{-1} in the i.r. spectrum (Nujol mull), due to the tetrahedral [BF$_4$]$^-$ anion, in agreement with the ionic



SCHEME 3

(*i*) HCl; (*ii*) I_2; (*iii*) X^-; (*iv*) HBF_4; (*v*) $Ag[BF_4]$, $3,5Me_2$-Hpz

nature of these species and as shown also by their conductivity in solution.

The n.m.r. spectra support the formulae given. The 4-H of the heterocycle either showed satellites due to ^{195}Pt, as with compound (16), or was rather complex and broad, as with compounds (2), (5), and (12). Like the starting pyrazolates, the nearer methyl group was coupled with ^{195}Pt [compound (5)] although satellites were not evident in the case of (16) owing to the overlapping of signals. By analogy with the behaviour of the compounds $[M(3,5Me_2\text{-}pz)_2(bipy)]$ [M = Pt (15) or Pd (22)], the n.m.r. spectrum of $[Pd(3,5Me_2\text{-}Hpz)_2(bipy)][BF_4]_2$ (23) in CD_2Cl_2 showed more signals than required assuming free rotation around the metal–nitrogen bond.

EXPERIMENTAL

General techniques and details of spectroscopic methods have been described previously.[2b] Analytical and other data are shown in Table 1 and n.m.r. data in Table 2.

Scheme 1.—Compounds (1), (4), (6)—(8), (14), (18), (20), and (24) were obtained according to this reaction, which is described in detail for compound (1).

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*bis*(*pyrazolato*-N)-*platinum*(II), (1). A methanol solution (10 cm³) of pyrazole (0.31 g, 4.56 mmol) and potassium hydroxide (0.252 g, 4.50 mmol) in the same solvent (25 cm³) were added to a stirred methanol suspension (80 cm³) of $[PtCl_2(dppe)]$[14] (1.485 g, 2.23 mmol). The mixture was refluxed gently and after 1.5 h the resulting solution was evaporated to dryness. The residue was extracted with dichloromethane (40 cm³); diethyl ether (40 cm³) was added to the extract, affording the colourless compound (1) (1.28 g, 78%), soluble in methanol, ethanol, and chloroform, but insoluble in acetone, benzene, and acetonitrile.

In the case of complexes (20) (nitrogen atmosphere) and (24) the reaction was carried out at room temperature and the crude product was filtered off, washed with methanol and with water, and dried at 373 K.

TABLE 2

Hydrogen-1 n.m.r. data [a]

Compound	Solvent	
(1)	$CDCl_3$	8—7.5 (br m) (CH_2); 4.05 (t) (4-CH), ^3J 2, ^4J 7; 3.20 (d) (3-CH), ^3J 2, ^4J 8—10; 2.8—2.0 (m) (aryl + 5-CH)
(2)	$CDCl_3$	7.6—7.1 (m) (CH_2); 4.04 (br s) (4-CH); 3.44 (br s) (3- + 5-CH); 3.2—2.2 (m) (aryl)
(4)	$CDCl_3$	8.25 (s) (5-Me), ^4J 4; 8.12 (s) (3-Me); 7.9—7.5 (m) (CH_2); 4.54 (br s) (4-CH), ^4J 9; 2.7—2.1 (m) (aryl)
(5)	$CDCl_3$	8.19 (s) (Me), ^4J 5; 7.89 (s) (Me); 7.5—7.0 (m) (CH_2); 4.27 (br s) (CH); 2.40 (m) (aryl); −1.4 [b] (s) (NH)
(7)	$CDCl_3$	7.9—7.2 (m) (CH_2); 2.8—2.0 (m) (aryl); 1.77 (br s) (CH)
(12)	CD_3OD	3.28 (m) (4-CH [c]); 2.38—1.70 (m), 1.4 (m) (aromatic + 3- + 5-CH [c])
(15)	$CDCl_3$ [d]	8.28 (s), 8.23 (s), 7.64 (s) (Me), ^4J not determined; 4.27 (s) (CH [c]), ^4J 14; 2.96—0.87 (m) (bipy)
	CD_3OD	8.19 (s) (5-Me), ^4J 6; 7.82 (s) (3-Me); 4.37 (s) (4-CH [c]), ^4J 14; 2.71—2.34 (m), 2.10—1.60 (m) (bipy)
(16)	CD_3OD	7.65 (s), 7.60 (s) (Me); 3.75 (s) (4-CH [c]), ^4J 12; 2.63—2.03 (m), 1.77—1.27 (m) (bipy)
(17)	$CDCl_3$	7.89—7.38 (m) (Me + CH_2); 4.29 (s) (4-CH [c]); no other signal detected
(21) [e]	CD_3OD	8.17 (s), 7.94 (s) (Me); 7.86—6.6 (m) (CH_2); 4.35 (br s) (4-CH); 2.6—2.0 (m) (aryl); −1.05 (br s) (NH)
(22)	CD_3OD	8.01 (s), 7.78 (s) (Me); 4.34 (s) (4-CH [c]); 2.6—1.5 (m) (bipy)
	$CDCl_3$	8.25 (s), 8.15 (s), 7.75 (s), 7.69 (s) (Me); 4.4—4.2 (m) (CH [c]); 2.5—2.1 (m) (bipy)
(23)	CD_2Cl_2	7.78 (s), 7.50 (s), 7.30 (s) (*ca.* 1 : 2 : 1) (Me); 3.92 (br s), 3.82 (br s) (CH [c]); 3.0—1.5 (m) (bipy); −1.9 [b] (br s), −2.2 [c] (br s) (NH)

[a] Obtained on a Varian–Neva operating at 60 MHz and room temperature; τ units. ^3J means $^3J(HCCH)$ and ^4J means $^4J(^{195}PtCCH)$ both in Hz. [b] The signal disappears after shaking the solution with D_2O. [c] Belonging to the pyrazole ring. [d] Fourier-transform spectrum recorded on a Bruker instrument operating at 60 MHz. [e] Same spectrum at 298 and 328 K.

Scheme 2.—Compounds (10), (15), (17), (22), and (24) were obtained by this reaction from the appropriate [MCl_2-(L–L)] complex [15–17] and ligand.[18]

2,2′-Bipyridinebis(*3,5-dimethylpyrazolato*-N)*platinum*(II), (15). A suspension of [$PtCl_2$(bipy)] (3.26 g, 7.72 mmol) and of potassium 3,5-dimethylpyrazolate (15.5 mmol) in tetrahydrofuran (20 cm^3) was refluxed under nitrogen for 5 h. The precipitate obtained after filtering the cold solution was extracted repeatedly with chloroform (1 dm^3 in all). The extract was concentrated to a small volume. Addition of diethyl ether (80 cm^3) precipitated an orange-red solid which was crystallized from methanol–diethyl ether (80 + 50 cm^3) by concentration affording the yellow compound (15) (2.51 g, 60%). The compound is yellow when crystallized from methanol, when not completely dry, orange when crystallized from chloroform. Visible spectra: in MeOH, $\lambda_{max.}$ 384 nm (ε = 1 280 dm^3 mol^{-1} cm^{-1}); in $CHCl_3$, $\lambda_{max.}$ 410 nm (ε = 2 290 dm^3 mol^{-1} cm^{-1}).

For compound (17) the filtered reaction mixture was evaporated to dryness and the residue was crystallized from chloroform–hexane. For (22) and (24) stirring was carried out for 1 h without any heating, the precipitate (22) being washed with water and dried at 120 °C. The insoluble complex (24) was obtained also when [$PdCl_2(NCC_6H_5)_2$] and K[$C_3H_3N_2$] were allowed to react in acetone solution. Electronic spectra of (22): in MeOH, $\lambda_{max.}$ 306 (ε = 6 200 dm^3 mol^{-1} cm^{-1}); in $CHCl_3$, $\lambda_{max.}$ 316 and 306 nm (ε = 6 900 and 10 130 dm^3 mol^{-1} cm^{-1}).

Reactions with Acids.—(*a*) *Protonation with tetrafluoroboric acid.* Reaction with HBF_4 resulted in protonation of complexes (4), (8), (10), (15), and (22) to give (5), (9), (12), (16), and (23) respectively, as below.

[*1,2-Bis*(*diphenylphosphino*)*ethane*]*bis*(*3,5-dimethylpyrazole*-N)*platinum*(II) *tetrafluoroborate*, (5). To a suspension of compound (4) (351 mg, 0.448 mmol) in ethanol (30 cm^3) was added HBF_4 (0.896 mmol) in the same solvent (1 cm^3). After 5 min the solution was evaporated to dryness, the residue was extracted with dichloromethane (20 cm^3), and the product (5) (0.412 g, 96%) separated upon addition of diethyl ether and concentration to a small volume. Phosphorus-31 n.m.r. in $CDCl_3$: 27.04 (s) p.p.m. downfield from external 85% H_3PO_4, $^1J(^{195}Pt–P)$ 3 100 Hz.

(*b*) *Other reaction with* HBF_4. The binuclear complexes (2) and (19) were obtained from the reaction of compounds (1) and (18), with HBF_4, as below.

Bis[*1,2-bis*(*diphenylphosphino*)*ethane*]-*di*(*μ-pyrazolato*-NN′)-*diplatinum*(II)*tetrafluoroborate*, (2). Addition of HBF_4 (0.546 mmol) in methanol (1 cm^3) to a solution of compound (1) (0.152 g, 0.209 mmol) in the same solvent (30 cm^3) gave a precipitate, which was crystallized twice from dichloromethane (5 cm^3) and diethyl ether to afford complex (2) (63 mg, 40%).

(*c*) *With hydrochloric acid.* A methanol suspension of complex (4) (0.239 g) was treated with two drops of concentrated HCl. The white precipitate which formed was crystallized from dichloromethane–hexane and identified as [$PtCl_2$(dppe)] by analysis and the i.r. spectrum.

Deprotonation Reactions.—Compound (12) (0.196 g, 0.296 mmol) reacted with the stoicheiometric amount of potassium hydroxide in methanol (40 cm^3 in all) to give a yellow solution. This was evaporated to dryness, and the residue extracted with chloroform (200 cm^3). Upon addition of diethyl ether to the concentrated extract a yellow precipitate formed which was filtered off and washed with ether to afford complex (11). Similarly, compound (15) was obtained from (16) and was crystallized by concentration from methanol–diethyl ether (1 : 1).

Bis[*1,2-bis*(*diphenylphosphino*)*ethane*]-*di*(*μ-pyrazolato*-NN′)-*diplatinum*(II) *Tetrachloroplatinate*(II), (3).—A dichloromethane solution (10 cm^3) of tetrabutylammonium tetrachloroplatinate(II) (0.239 g, 0.29 mmol) was added to a stirred solution of complex (1) (0.21, 0.29 mmol) in the same solvent (20 cm^3). After 1 h compound (3) (56 mg, 23%) was filtered off and washed with ethanol and diethyl ether.

Bis(*2,2′-bipyridine*)-*di*(*μ-pyrazolato*-NN′)-*diplatinum*(II) *Hexachloroplatinate*(IV), (13).—A solution of complex (10) (0.185 g, 0.38 mmol) and $Na_2[PtCl_6]$ (0.175 g, 0.38 mmol) in methanol (50 cm^3) was refluxed for 2 h. After cooling, the required complex (0.213 g, 90%) was filtered off and washed with water, methanol, and diethyl ether. It is insoluble in chloroform, dichloromethane, benzene, acetonitrile, nitromethane, and dimethyl sulphoxide.

[*1,2-Bis*(*diphenylphosphino*)*ethane*]*bis*(*3,5-dimethylpyrazole*-N)*palladium*(II) *Tetrafluoroborate*, (21).—A methanol suspension of [$PdCl_2$(dppe)] (0.583 g, 1.01 mmol) and silver tetrafluoroborate (0.420 g, 2.16 mmol) was stirred for 20 min. The filtered solution was evaporated to dryness, and the residue was extracted with dichloromethane. 3,5-Dimethylpyrazole [18] (0.32 g, 3.37 mmol) was added, the solution was concentrated, and diethyl ether was added to give the crude product (0.808 g, 92%) which was crystallized from dichloromethane–diethyl ether; the crystals were dried at 393 K for 24 h.

Reaction of Complex (4) *with Iodine*.—Iodine (0.136 g, 0.538 mmol) in chloroform (18 cm^3) was added dropwise to a solution of compound (4) (0.204 g, 0.26 mmol) in the same solvent (20 cm^3). Upon addition of hexane (60 cm^3) a yellow precipitate was obtained which was crystallized twice from chloroform–hexane (50 + 50 cm^3) to afford [PtI_2(dppe)] (0.136 g, 62%), identified through its melting point (348—351 °C), i.r. spectrum, and elemental analyses [Found: C, 36.8; H, 2.95%; *M* (osmometry in $CHCl_3$) 805. Calc. for $C_{26}H_{24}I_2P_2Pt$: C, 36.8; H, 2.85%; *M* 847]. The mother liquor of the reaction was evaporated to dryness, the residue was extracted with hexane (2 × 50 cm^3), and the extract was again evaporated to dryness. The residue was sublimed at 65—70 °C at a water pump. Upon addition of an ether solution of picric acid to an ether solution of the sublimate, yellow crystals separated on concentration. These were identified as the picrate of 4-iodo-3,5-dimethylpyrazole by comparison of the m.p. (183 °C) and of the i.r. spectrum with those of an authentic sample obtained from the known pyrazole,[19] and through analyses (Found: C, 29.7; H, 2.45; N, 14.7. Calc. for $C_{11}H_{10}IN_5O_7$: C, 29.45; H, 2.20; N, 15.5%).

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