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N-Allylpyrazole as a Ligand. II. The Preparation and Reaction of Some Palladium(II) and Platinum(II) Complexes

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New complexes of *N*-allylpyrazole(L) with Pd(II) and Pt(II) have been prepared and characterized; they have the general formulae of MX_2L_2 and MX_2L (X=Cl or Br). IR and ^1H NMR studies indicate that the latter complexes are *cis*-planar-chelate and involve both the pyrazolyl nitrogen and the olefinic group in bonding to the metal, while the former are *syn-* and *anti-trans*-planar and contain only uni-dentate pyrazole donor ligands. The treatment of the chelate complex $PtCl_2L$(L=1-(2-methylallyl)-3,4,5-trimethylpyrazole) with donor ligands (L′) such as phosphines, $AsPh_3$, and py displaces the coordinated olefin,forming *cis*-$PtCl_2LL'$ with a retention of the *cis*-configuration.

Allylpyrazole (Fig. 1), which has both σ-donating nitrogen and π-accepting olefin, can be bound with metal ions in more than one way. We have already reported that the ligand forms bidentate complexes with copper(I) halide and silver nitrate; it also coordinates to metal halides of the first transition series by using only pyrazolyl nitrogen.[1] By analogy with other chelate olefin complexes,[2–9] the coordination chemistry of platinum(II) and palladium(II) has proved to be of interest because they form not only monodentate pyrazolyl-nitrogen complexes, but also stable olefin complexes, with the chelation of allylpyrazole through the nitrogen donor and the olefinic group.

We wish now to report the details of the preparation of palladium(II) and platinum(II) compounds and their properties, especially their spectroscopic characteristics and their substitution reactions.

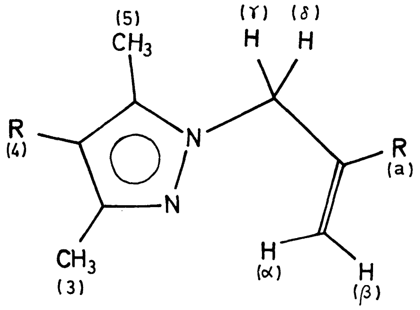


Fig. 1. *N*-Allylpyrazole, R_a, R_4=H or CH_3. Numbers and Greek letters represent the position of the hydrogen atoms.

Experimental

The molecular weight was determined by the Rast method. X-Ray powder diagrams were obtained by means of a Rigaku D-2F apparatus. The other physical measurements were made as has previously been described.[1] The IR and NMR data are collected in Tables 3 and 4 respectively.

Synthesis of Ligands. The four ligands were prepared by the method of Finar and Utting[10] in a *ca.* 40% yield. The names of the ligands are abbreviated thus, based on Fig. 1: admp(R_a=R_4=H); atmp (R_a=H, R_4=Me); amdmp(R_a=Me, R_4=H); amtmp(R_a=R_4=Me).

Preparation of trans-MX_2L_2 *(M=Pd or Pt; X=Cl or Br; L=substituted* N-*allylpyrazoles).* Dipotassium tetrachlorometallate (II) (0.01 M) was dissolved in water, and then an excess of allylpyrazole (0.10 M) was stirred in. Yellow crystals were obtained after stirring at 25 °C for a day and were recrystallized from cold chloroform. The complexes were also prepared by adding allylpyrazole to MCl_2L in cold chloroform. In general, throughout the reaction, the temperature must be maintained below 25 °C. If the temperature is allowed to rise above *ca.* 50 °C, a mixture of MCl_2L and MCl_2L_2 is obtained. The bromo-complex, MBr_2L_2 was prepared by the metathesis of the corresponding chloro-complex with lithium bromide. All the complexes are easily soluble in chloroform or dichloromethane. The analytical data and some properties of the complexes are shown in Table 1. The *trans* structure of $PtCl_2L_2$ was checked by Kurnakov's test.[11]

Preparation of PtX_2L. Dipotassium tetrachloroplatinate (II) (0.01 M) was dissolved in water (20 ml). Into this solution a mixture of allylpyrazole (0.01 M) and concd hydrochloric acid solution (*ca.* 5 ml) was vigorously stirred. Then, the reaction mixture was gently heated on a water bath for about half an hour. After they had been cooled to room temperature, the precipitated crystals were filtered, washed with water, and dried *in vacuo*. Crude products were recrystallized from chloroform(10)–ethanol(90) (yield: 95%). In boiling ethanol, these complexes partly decompose to yield platinum(0) metal. The purified crystals are stable to light and air. The analytical data and physical properties are summarized in Table 2. The complexes were also obtained by a displacement reaction from bis(benzonitrile)dichloroplatinum(II) (0.01 M) or bis(dimethyl sulfide)dichloroplatinum(II) (0.01 M) with allylpyrazole (0.01 M) in chloroform (yield: *ca.* 80%).

Preparation of $PdCl_2L$. The palladium complexes are prepared by procedures similar to those used for the diolefin complexes.[12] A solution of $PdCl_2$ (0.01 M) in concd hydrochloric acid (5 ml) is diluted with 50 ml ethanol. To this solution, the ligand (0.01 M) is added. Immediately, brown crystals are precipitated. After stirring for 20 min, they are filtered, and washed successively with water, ethanol, and diethyl ether (yield: *ca.* 80%). The analytical data and some properties are given in Table 2. The complexes, except for the case of L=amtmp, are not soluble enough in any solvent to give meaningful structural information in a solution.

Substitution Reaction of 1-(2-Methylallyl)-3,4,5-trimethylpyrazoledichloroplatinum(II) with Neutral Donor Ligands. The general scheme of the reaction is summarized in Fig. 2. The analytical data and some properties of new complexes are tabulated in Table 5. When tertiary alkylphosphines such as PBu^n_3, PPr^i_3 and PCy_3 were used, all the manipulations were carried out under a nitrogen atmosphere. Some typical reactions will be described:

With PPh_3: In 50 ml of benzene, the yellow complex, $PtCl_2L$ (2.1 g, 0.0051 M), was dispersed. When an equimolar

TABLE 1. ANALYTICAL DATA AND PROPERTIES OF *trans*-MX_2L_2 TYPE COMPLEXES

M	X	L[a]	Color	Mp (°C)[b]	% Found (Calcd) C	H	N	X
Pt	Cl	admp	yellow	Nm	35.6 (35.7)	4.3 (4.5)	10.6 (10.4)	13.8 (13.2)
Pt	Cl	atmp	yellow	Nm	39.0 (38.2)	4·8 (5.0)	9.5 (9.9)	12.8 (12.5)
Pt	Cl	amtmp	yellow	207	40.5 (40.4)	5.5 (5.4)	9.4 (9.4)	11.8 (11.9)
Pt	Br	amtmp	yellow	214	35.6 (35.2)	4.8 (4.7)	7.9 (8.2)	22.6 (23.4)
Pd	Cl	amtmp	orange	198	47.9 (47.5)	6.8 (6.4)	11.2 (11.1)	13.8 (14.0)

a) Name of ligands, abbreviated in Experimental. b) All melting points were uncorrected.

TABLE 2. ANALYTICAL DATA AND PROPERTIES OF MX_2L TYPE COMPLEXES

M	X	L	Mp (°C)[a]	Color	% Found (Calcd) C	H	N	X
Pt	Cl	admp	Nm	white	24.2 (23.9)	3.0 (3.0)	6.8 (7.0)	Nm
Pt	Cl	atmp	Nm	white	26.2 (26.0)	3.5 (3.4)	6.7 (6.7)	17.2 (17.0)
Pt	Cl	amdmp	248	light-yellow	26.2 (26.0)	3.1 (3.4)	6.7 (6.7)	16.7 (17.0)
Pt	Cl	amtmp[b]	238	light-yellow	28.2 (28.0)	3.5 (3.8)	6.5 (6.5)	16.2 (16.5)
Pt	Br	amtmp	215	yellow	23.3 (23.1)	3.1 (3.1)	5.1 (5.4)	Nm
Pd	Cl	amdmp	204	brown	33.3 (33.0)	4.2 (4.3)	8.5 (8.6)	21.4 (21.7)
Pd	Cl	amtmp	183	brown	35.2 (35.2)	4.5 (4.7)	7.9 (8.2)	21.0 (20.8)

a) All melting points were uncorrected. b) Molecular Weight: Found, 530; Calcd, 430.

quantity of triphenylphosphine (1.4 g, 0.0053 M) was added to the above mixture, the dispersed complex spontaneously dissolved in the solution. This light-yellow solution was then evacuated to dryness. The residue on crystallization from ethanol (20 ml)–hexane (60 ml) gave *cis*-$PtCl_2LPPh_3$ (yield: 3.2 g, 94% based on $PtCl_2L$). If two equivalents of PPh_3 (2.8 g) were used, snow-white crystals of *cis*-$PtCl_2(PPh_3)_2$ were precipitated from the benzene solution quantitatively.

With PCy_3: A benzene solution (100 ml) containing PCy_3 (7.0 g, 0.025 M) and $PtCl_2L$ (4.3 g, 0.010 M) was concentrated under reduced pressure at room temperature to about half its volume. White, puffy crystals of *cis*-$PtCl_2LPCy_3$ precipitated on the addition of hexane (100 ml). They could be recrystallized from ethanol (10)–hexane (90), even in the presence of excess PCy_3 (2.8 g, 0.01 M) (yield: 5.6 g, 79%).

With $P(OPh)_3$: The addition of $P(OPh)_3$ (3.1 g, 0.010 M) to $PtCl_2L$ (2.1 g, 0.0049 M) in benzene gave a homogeneous solution, from which white crystals of the empirical formula of $Pt_2Cl_4L(P(OPh)_3)_3$ were isolated (yield: 3.0 g, 85%). (Found: C, 39.1; H, 4.4; N, 2.6%, $C_{64}H_{61}N_2O_9P_3Cl_4Pt_2$ requires: C, 38.3; H, 4.5; N, 2.5% which corresponds to a 1: 1 mixture of *cis*-$PtCl_2LP(OPh)_3$ and *cis*-$PtCl_2(P(OPh)_3)_2$).

With Pyridine: A chloroform solution of pyridine (1.8 g, 0.023 M) and $PtCl_2L$ (4.3 g, 0.010 M) was evacuated to give an oily residue. On the addition of ethanol to it, crystals of *cis*-$PtCl_2Lpy$ were formed (yield: 2.5 g, 49%). The *cis* configuration of the product was confirmed by Kurnakov's reaction.[11]

With CO: A benzene solution in which the $PtCl_2L$ complex had been dispersed was bubbled with CO gas. After about 10 min, a homogeneous yellow solution was obtained. The IR spectrum of this solution showed an absorption of a C–O stretching vibration at 2060 cm^{-1}. However, on crystallization, the original comples, $PtCl_2L$, was recovered.

Results and Discussion

The complexing ability of allylpyrazole has been investigated with Ni(II), Pd(II), and Pt(II) ions. As for Pd(II) and Pt(II), two types of complexes, MX_2L and MX_2L_2, have been obtained. The blue nickel complex has been prepared in the presence of a large excess of the ligand, but, unfortunately, its extreme sensitivity to moisture has prevented any accurate analysis or characterization.

Bis-allylpyrazole Complexes, MX_2L_2. The KBr disk or Nujol mull IR spectra of the complexes closely resemble those of the free ligands. Particularly, the C=C vibration of the allyl group found at 1660 or 1640 cm^{-1} does not differ from that of the free ligands (Table 3). This indicates that the olefinic part is free and that only the pyrazolyl nitrogen coordinates to the metal.

The *trans* configuration of PtX_2L_2 has been confirmed by Kurnakov's test. Attempts to isolate *cis*-PtX_2L_2 have been unsuccessful; probably the bulky nature of the ligands hinders the formation of the *cis*-isomer. In the case of palladium complexes, although it has not been

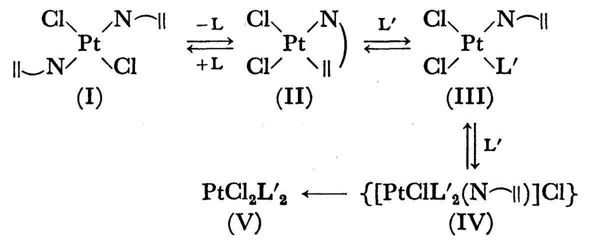


Fig. 2. Scheme.
N⌒|| =amtmp; III, L′=py, AsPh$_3$, PR$_3$ (R=Ph, Bu^n, Pr^i, Cy, OMe, OPh); IV ionic intermediate (not isolated); V, L′=AsPh$_3$; *trans*, PR$_3$; *cis* when R=Ph, OMe, OPh; *trans* when R=Bu^n, Pr^i.

definitely determined, the *trans* structure (Fig. 2-I) seems most likely in view of the following NMR results, similar to those for platinum complexes.

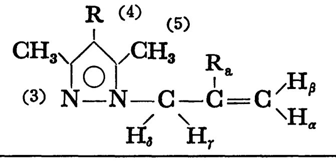
The NMR spectra of MX_2L_2 as a whole shift towards a lower magnetic field from the position of the free ligands, also indicating the apparent absence of the coordinated olefin; the coordinated olefin in metal complexes usually shows a remarkable shielding of olefinic protons.[9] Both 3-Me and allyl protons, except for H_β, have two sets of signals as is shown in Table 4. These signals can be assigned to two possible stereoisomers, *syn* and *anti*, which have been assumed in the NMR analysis of tetrazole complexes.[13] It is likely that the low symmetry of the ligand, together with its restricted rotation about M–N bonds, generates these rotational isomers.

Mono-allylpyrazole Complexes, MX_2L. The IR spectra of palladium complexes (Table 3) exhibit a sharp band at 1525 cm^{-1} for L=amdmp and at 1520 cm^{-1} for L=amtmp. No band was observed in the vicinity of 1660 cm^{-1}, the position of the C=C vibration for the free ligand. The above sharp band probably indicates the presence of a palladium-olefin bond (a lowering from the free ligand of $\Delta\nu$=135 or 140 cm^{-1}

Table 3. Vibration frequencies (in cm^{-1}) of the olefin part in MCl_2L_n

	Free ligand	$PdCl_2L_2$	$PdCl_2L$	*trans*-$PdCl_2L_2$	$PtCl_2L$
		L=admp			
$\nu_{CH_2=}$	3080w	—	—	3075m	3080m
$\nu_{C=C}+\ \delta_{C-H}$	1640m			1640m	1500ms
δ_{C-H}	995 s	—	—	980 s	1000 s
ν_{M-C_2}	920 s			930 s	—
					515ms
		L=atmp			
$\nu_{CH_2=}$	3080m	3080mw	—	3080mw	3075w
$\nu_{C=C}+\ \delta_{C-H}$	1640 s	1640m		1640m	1500ms
$\nu_{C=C}$	1320m	1320 s		1320vs	1290vs
		1005 s	—	1005 s	1005 s
δ_{C-H}	985vs				
ν_{M-C_2}		940 s		940vs	
					525ms
		L=amdmp			
$\nu_{CH_2=}$	3090mw	—	3075w	—	3075w
$\nu_{C=C}+\ \delta_{C-H}$	1660 s		1525 s		1500ms
$\nu_{C=C}$	1320m		1295 s		1290 s
			1075 s		1080ms
			1040 s		1045 s
			1005 s		
		—		—	995 s
δ_{C-H}	980w		980 s		
			965ms		970ms
			955sh		
			930ms		925ms
	900vs				
ν_{M-C_2}		—	480ms	—	505 s
		L=amtmp			
$\nu_{CH_2=}$	3070m	3090w	3075m	3080m	3080m
$\nu_{C=C}+\ \delta_{C-H}$	1660ms	1660m	1520 s	1660ms	1500ms
$\nu_{C=C}$	1320 s	1335 s	1320 s	1335 s	1300 s
			1255 s		1250 s
	1240 s	1240m	1240 s	1245 s	1230 s
			1040ms		1040 s
			975 s		990br s
δ_{C-H}	900vs	900vs	875ms	900vs	870ms
ν_{M-C_2}			840ms		840ms
			490ms		510 s

Table 4. NMR data$^{a)}$ in $CDCl_3$ (relative to TMS τ 10 ppm)



	3-Me	R_4		5-Me	R_a		H_α	H_β	H_γ	H_δ
		4-Me	4-H		a-Me	a-H				
L=admp										
Free ligand	7.94		4.35	7.91		4.20	5.12	4.98	5.54	
$PtCl_2L_2$	7.31 7.24		4.11	7.73		3.61 3.70	4.83 4.77	4.71	4.45 4.53	
L=atmp										
Free ligand	8.00	8.28		8.08		4.19	5.15	4.97	5.53	
$PtCl_2L_2$	7.44 7.36	8.26		7.98		3.72 3.83	4.95 4.90	4.85	4.57 4.64	
$PdCl_2L_2$	7.27 7.20	8.13		7.86		3.60 3.68	4.78 4.74	4.69	4.45 4.54	
L=amdmp										
Free ligand	7.80		4.25	7.86	8.34		5.52	5.20	5.53	
$PtCl_2L$	7.46 (4)		4.01 (14)	7.66 (—)	7.99 (40)		6·54 (65)	5.46 (60)	6.38 (50)	5.58 (14)
L=amtmp										
Free ligand	7.90	8.21		8.01	8.37		5.51	5.27	5.56	
$PtCl_2L_2$	7.32 7.26	8.10		7.80	8.13 8.18		5.42 5.36	5.00	4.52 4.58	
$PtBr_2L_2$	7.36 7.28	8.10		7.80	8.13 8.18		5.42 5.36	5.02	4.50 4.56	
$PdCl_2L_2$	7.26 7.16	8.12		7.88	8.06 8.16		6.32 5.25	4.95	4.52 4.60	
$PtCl_2L_2$	7.55 (5)	8.08 (—)		7.82 (—)	8.00 (40)		6.53 (66)	5.50 (62)	6.30 (51)	5.78 (14)
$PtBr_2L$	7.55 (5)	8.08 (—)		7.70 (—)	8.09 (44)		6.49 (64)	5.50 (63)	6.35 (54)	5.57 (15)
$PdCl_2L$	7.56	8.11		7.73	7.70		5.64	4.98	5.70	5.24

a) Coupling constants ($|J_{pt-H}|$, Hz) in parentheses.

respectively). The sharp bands of medium intensity at 480 cm^{-1} (amdmp) and 490 cm^{-1} (amtmp) may be assigned to $\nu(Pd\text{-}C_2)$. These bands are present in the region thought to indicate Pd-olefin stretching, as has been found for $PdCl_2$[tri(2-butenyl)arsine][3] (425 cm^{-1}) and $Pd_2Cl_4(C_2H_4)_2$ (427 cm^{-1}). The ^1H NMR spectrum of $PdCl_2L$ (L=amtmp) in $CDCl_3$ shows that the H_γ- and H_δ-protons differ in their chemical shifts ($|J_{H_\gamma-H_\delta}|=16$ Hz), while in the free ligand in $PdCl_2L_2$, the two protons are equivalent (Table 4). This inequality in the chemical shifts suggests that the olefinic group coordinates to palladium.

The platinum(II) complexes, PtX_2L, are generally more soluble than $PdCl_2L$ and can be well characterized by ^1H NMR (Table 4). All the protons of the allyl group in PtX_2L, except for a-Me, are shifted towards higher fields. Changes in the chemical shifts similar to that of the above spectra have been reported for pnicogen-olefin chelate complexes by several workers.[9,14,15] Since a rapid, bonded$\rightleftharpoons$non-bonded equilibrium of the Pt-olefin bond shows a rather small spin coupling ($|J_{Pt-H_\alpha}|=23$ Hz),[16] the large coupling constants ($|J_{Pt-H}|=60$ Hz) on the present complexes indicate that the allyl group is not liberated from platinum. The IR spectra of platinum complexes also show a characteristic band (*ca.* 1500 cm^{-1}) of the coordinated olefin ($\Delta\nu=140$—160 cm^{-1}). The band in the range of 500—530 cm^{-1} in the PtX_2L series may be assigned to $\nu(Pt\text{-}C_2)$.

The above IR and NMR results of MX_2L support Fig. 2-II as a possible structure. The molecular weight of $PtCl_2$(amtmp) confirms that the structure of the complex is not that of a chlorine-bridged dimer with monodentate amtmp. The measurement of powder X-ray diagrams has revealed isomorphism in both the palladium and platinum complexes; this also indirectly supports the idea that both Pd(II) and Pt(II) complexes have the same structure (Fig. 2-II).

The observation that the chemical shifts of the allyl protons of MCl_2L, where M=Pd or Pt and L=amtmp, move downfield when platinum is replaced by palladium is consistent with the lower olefin-metal interaction present in the palladium complex, such as in MX_2-(diolefin)[17] and olefinic tertiary phosphine complexes.[9]

Substitution Reaction of $PtCl_2L$ with Donor Molecules. The reaction scheme is outlined in Fig. 2. Only the 1-(2-methylallyl)-3,4,5-trimethylpyrazole complex, $PtCl_2L$, was investigated in detail.

In the reaction of an equivalent donor ligand with $PtCl_2L$ in benzene at room temperature, stable com-

TABLE 5. ANALYTICAL DATA AND PROPERTIES OF THE ISOLATED NEW COMPLEXES (L=amtmp)

	Color	Mp (°C)[a]	% Found (Calcd)		
			C	H	N
cis-$PtCl_2LPPh_3$[b]	white	208 (dec.)	49.2 (48.6)	4.0 (4.5)	4.1 (4.1)
cis-$PtCl_2LPBu^n_3$[b]	white	128	40.8 (41.8)	6.1 (6.9)	4.1 (4.4)
cis-$PtCl_2LPPr^i_3$[b]	white	177	39.0 (38.7)	6.2 (6.3)	5.0 (4.7)
cis-$PtCl_2LPCy_3$[b]	white	217 (dec.)	47.3 (47.3)	6.7 (7.0)	3.8 (3.9)
cis-$PtCl_2LPy$	light-yellow	135	35.4 (35.4)	3.9 (4.2)	8.1 (8.3)
cis-$PtCl_2LAsPh_3$	light-yellow	174	46.0 (45.7)	4.1 (4.2)	3.6 (3.8)

a) All melting points were uncorrected. b) *cis*-Configuration of the complexes is judged from their color.

plexes with the empirical formula of $PtCl_2LL'$ ($L'=PR_3$, $AsPh_3$ or py) have been isolated and characterized (Table 5). All the new complexes, which are easily soluble in benzene, have a sharp IR absorption at *ca.* 1660 cm^{-1}, indicating the existence of free olefin.

In our system, "mixed" complexes of the *cis*-configuration have been specifically obtained, maintaining the *cis*-configuration of the original chelate complex, whereas the bridge-splitting reaction of Chatt and Venanzi[18] has usually been used in the laboratory to prepare mixed complexes with a *trans*-configuration. This selectivity of the *cis*-configuration can be explained by the relatively higher lability of olefin and the *cis*-directing power of the pyrazolyl nitrogen to the incoming ligand.

With one more equivalent donor ($L'=PPh_3$, PBu^n_3, PPr^i_3 or $AsPh_3$), the mixed complex, $PtCl_2LL'$, reacted to give a complex of the $PtCl_2L'_2$ type, displacing an equivalent allylpyrazole. The configurations of the isolated complexes depended upon the entering ligand; that is, a configuration favorable to each ligand was observed: *cis* to PPh_3, *trans* to PBu^n_3, PPr^i_3 and $AsPh_3$. These results can be interpreted by means of the consecutive displacement mechanism[19—21] *via* an ionic intermediate, as is shown in Fig. 2.

The equilibrium for the formation of $PtCl_2LL'$ lies too far to the left to permit the isolation of the complexes when $L'=CO$ or $PhNH_2$, and, for steric reasons,[22,23] excess PCy_3 does not displace L from *cis*-$PtCl_2L(PCy_3)$.

When phosphite is used as a donor ligand, a mixture of *cis*-$PtCl_2LP(OR)_3$ and *cis*-$PtCl_2(P(OR)_3)_2$ is obtained. This is attributable to the analogous solubilities of the two compounds.

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