Isocyanide, Carbene, Diethyldithiocarbamate, and Cyclo-octa-1,5-diene Complexes of Platinum(II)

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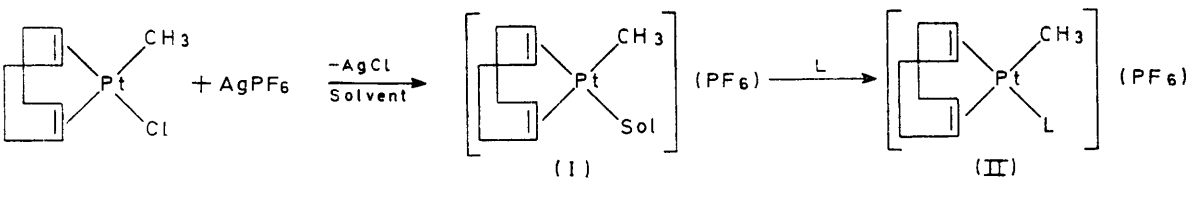
Several complexes of the type $[Pt(CH_3)(\pi\text{-}1,5\text{-}C_8H_{12})L](PF_6)$ (L = one of a variety of neutral ligands) have been prepared. The coupling constant $J(Pt{-}CH)$ to the vinyl protons *trans* to L is dependent upon the nature of L and this coupling constant is apparently insensitive to platinum–olefin π-back bonding. The cyclo-octa-1,5-diene ligand is easily displaced from these salts by sodium diethyldithiocarbamate to give the neutral compounds $Pt(CH_3)(S_2CNEt_2)L$. Ethyl and *p*-tolyl isocyanide react with $[Pt(CH_3)(\pi\text{-}1,5\text{-}C_8H_{12})(solvent)](PF_6)$ to give $[Pt(CH_3)(CNR)_3](PF_6)$. The reaction of $[Pt(CH_3)(CN{-}C_6H_4{-}CH_3)_3](PF_6)$ with sodium benzenethiolate gives *cis*-$Pt(CH_3)(SC_6H_6)(CNC_6H_4CH_3)_2$, and with dialkylamines gives *trans*-$[Pt(CH_3)(CNC_6H_4CH_3)\{:C(NR_2)\cdot(NHC_6H_4CH_3)\}_2](PF_6)$.

A VARIETY of oxidative addition and displacement reactions of compounds of the type $PtR_2(cod)$ (where cod = cyclo-octa-1,5-diene, R = alkyl or aryl group) has recently been described.[1,2] New trialkylplatinum(IV) compounds of the type $[PtR_2R'I]_4$ were prepared as well as the insoluble dialkylplatinum(IV) compounds $[PtR_2I_2]_n$. Several displacement reactions of cod from $Pt(CH_3)_2(cod)$ and $Pt(CH_3)Cl(cod)$ were described. The cyclo-octa-1,5-diene was fairly strongly bonded to platinum and could be displaced only by the more basic ligands such as phosphines, arsines, isocyanides, and bipyridyl. However, if the chloride was removed from $Pt(CH_3)Cl(cod)$ with $AgPF_6$ it was found [2] that the cod was quite labile and could be displaced by a variety of ligands. In this paper is described the preparation of a series of cationic cyclo-octa-1,5-diene complexes of platinum(II), some displacement reactions of cod, and the reactivity of the resulting complexes.

RESULTS AND DISCUSSION

Preparation of the Complexes $[Pt(CH_3)(cod)L](PF_6)$.—The chloride in $Pt(CH_3)Cl(cod)$ is very labile and is easily removed by the silver salt of a non-co-ordinating anion such as $AgPF_6$, in acetone or tetrahydrofuran to give the solvated complex (I) [equation (1)]. The addition of a molar equivalent of a Lewis base readily displaces the solvent molecule giving a series of complexes $[Pt(CH_3)(cod)L](PF_6)$ (II). The analytical, physical, and i.r. data for these complexes are collected in Table 1. The complexes where L = $4\text{-}NC_5H_4CH_3$, $AsPh_3$, PPh_3, $p\text{-}NCC_6H_4OCH_3$, and CNEt were prepared directly as shown in equation (1). The imino-ether complex [II; L = $NH{=}C(OCH_3)C_6F_5$], was prepared from the reaction of $Pt(CH_3)Cl(cod)$ and $AgPF_6$ with pentafluorobenzonitrile in methanol [equation (2)]. We have previously examined a number of similar



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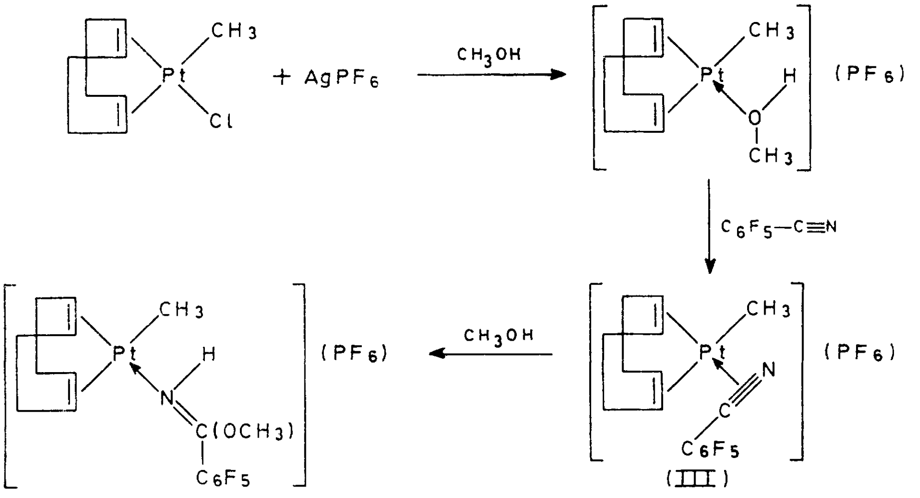
[1] H. C. Clark and L. E. Manzer, *J. Organometallic Chem.*, 1972, **38**, C41.

[2] H. C. Clark and L. E. Manzer, *J. Organometallic Chem.*, 1973 **59**, 411.

reactions resulting in the formation of Pt^{II},[3,4] Pt^{IV},[5] and Ir^{III} [6] imino-ether complexes. A mechanism was postulated[4] which involved initial π-co-ordination of pentafluorobenzonitrile (III), delocalization of charge from platinum onto the $-C{\equiv}N$ bond, and activation of the bond towards nucleophilic attack by the alcohol.



(2)

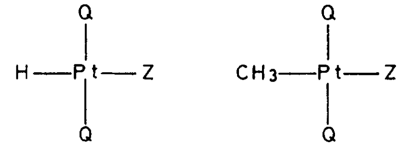
TABLE 1

Analytical and physical data for the new platinum(II) complexes

Compound	Carbon % Calc.	Carbon % Found	Hydrogen % Calc.	Hydrogen % Found	Nitrogen % Calc.	Nitrogen % Found	M.p. (t/°C) [a]	Infrared data (cm^{-1})
$[Pt(CH_3)(cod)(\gamma\text{-}NC_5H_4CH_3)](PF_6)$	32·38	32·5	3·98	3·85			120—122	
$[Pt(CH_3)(cod)(AsPh_3)](PF_6)$	42·14	42·8	3·93	3·9			203—205	
$[Pt(CH_3)(cod)(PPh_3)](PF_6)$	44·69	44·85	4·17	4·05			210—212	
$[Pt(CH_3)(cod)(p\text{-}NCC_6H_4OCH_3)](PF_6)$	34·23	34·0	3·72	3·55			150—152	
$[Pt(CH_3)(cod)(CNEt)](PF_6)$	27·81	27·65	3·89	3·65			141—142	$\nu(C{\equiv}N)$ 2257
$[Pt(CH_3)(cod)\{NH{=}C(OCH_3)C_6F_5\}](PF_6)$	29·66	29·35	2·78	2·8			153—155	$\nu(N{-}H)$ 3299; $\nu(C{=}N)$ 1661, 1640
$Pt(CH_3)(S_2CNEt_2),1/2(cod)$	29·00	28·8	4·61	4·6			130—160	
$Pt(CH_3)(S_2CNEt_2)(PPh_3)$	46·44	46·65	4·55	4·35			170—172	
$Pt(CH_3)(S_2CNEt_2)(AsPh_3)$	43·37	43·4	4·25	4·35			159—160	
$[Pt(CH_3)(CNEt)_3](PF_6)$	23·08	23·25	3·49	3·3	8·08	8·35	90—92	$\nu(C{\equiv}N)$ 2250
$[Pt(CH_3)(p\text{-}CNC_6H_4CH_3)_3](PF_6)$	42·50	42·7	3·42	3·4	5·95	6·1	182—185	$\nu(C{\equiv}N)$ 2211
$[Pt(CH_3)(CNC_6H_4CH_3)\{C(NHC_6H_4CH_3)(NMe_2)\}_2](PF_6)$	43·70	43·65	4·64	4·8	8·83	9·05	175—178	$\nu(C{\equiv}N)$ 2165; $\nu(C{\cdots}N)$ 1553; $\nu(N{-}H)$ 3362
$[Pt(CH_3)(CNC_6H_4CH_3)\{C(NHC_6H_4CH_3)(NEt_2)\}_2](PF_6)$	45·80	46·05	5·47	5·45	8·34	8·2	128—130	$\nu(C{\equiv}N)$ 2158; $\nu(C{\cdots}N)$ 1540; $\nu(N{-}H)$ 3363
$Pt(CH_3)(CNC_6H_4CH_3)_2(SPh)$	49·90	49·8	4·01	3·95	5·06	5·05	93—95	$\nu(C{\equiv}N)$ 2199, 2164

[a] M.p.s are uncorrected.

Nuclear Magnetic Resonance Studies.—A number of papers have appeared[7] in which are discussed factors which affect the coupling constant between ^{195}Pt (I = 1/2, 33·8% natural abundance) and other nuclei with a spin of one-half such as ^{13}C, ^{31}P, ^{19}F, ^{1}H, and ^{15}N. In most discussions it is assumed that these coupling constants are dominated by the Fermi contact term and that changes in these coupling constants for closely related series of complexes may be attributed to variations in the Pt(6s) character in the Pt–L bond, where L contains the nucleus with spin of one-half. For example, in the two series of complexes (IV) and (V) ^{1}J(PtH) in (IV) varies from 768 to 1466 Hz for Z = CN^- and ClO_4^-; ^{1}J(PtC) in (V) varies from 698 to 395 Hz for Z = Me_2NCHO and $:\overline{CCH_2CH_2CH_2O}$; and $^{2}J(PtCH_3)$ in series (V) varies from 49 to 88 Hz for Z = $p\text{-}F\text{-}C_6H_4^-$ and Me_2CO.[8] Since π-bonding from the filled platinum



(IV) (V)

(a) Z = anionic ligand, n = 0
(b) Z = neutral ligand, n = 1

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[3] H. C. Clark and L. E. Manzer, *Chem. Comm.*, 1971, 387.

[4] H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 1971, **10**, 2699.

[5] H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 1972, **11**, 2749.

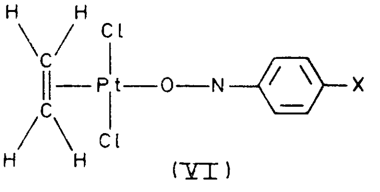
[6] H. C. Clark and L. E. Manzer, *J. Organometallic Chem.*, 1973, **47**, C17.

[7] See references in a recent review on the *trans*-Influence by T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335.

[8] The coupling constant data are extracted from Tables in ref. 7 and M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Amer. Chem. Soc.*, 1973, **95**, 8574.

d-orbitals to empty orbitals on the hydrido- and methyl groups is not possible, the variations in ^1J(PtH), ^2J(PtCH$_3$), and ^1J(PtC) presumably result from changes in the Pt(6*s*) character in the σ-bonding orbitals.

Several authors have examined ^{195}Pt coupling constants to ligands which are capable of π-back bonding. Kaplan and Orchin[9] found that in complexes (VI), electron-withdrawing substituents, X, increased the coupling between ^{195}Pt and the olefinic protons, although chemical shifts were consistent with the expected decrease in Pt ⟶ olefin π-bonding. Braterman[10] explained these results in terms of the *s*-character of the Pt σ-orbital in the platinum–olefin bond, varying with the nature of the *trans* group in an analogous way to that discussed for variations in ^1J(PtC), ^2J(PtCH),[7] *etc.* For the Pt^{II} olefin complexes (II) and (VI) the olefin C=C bond is perpendicular to the platinum square plane and consequently a mirror plane, in the platinum square-plane passing through the centre of the C=C bond, prevents *s*-character in the Pt hybrid orbitals used for π-back bonding from contributing to the coupling constant. Since there is no mirror plane perpendicular to the platinum square plane, containing the C=C bond, symmetry does not prevent mixing of olefinic C(2*s*) character into the olefin π-orbital which is used to form the olefin to metal σ-bond.[10] The *s*-character of this π-orbital will presumably depend on such factors as changes in Pt ⟶ olefin π-bonding caused by changes in the *trans*-ligand, but by Braterman's model such changes are outweighed by those in the Pt σ-orbital. This theory was also used by Fritz and Sellmann[11] in discussing *J*(PtC$_2$H$_4$) in the complexes *trans*-PtCl$_2$-(C$_2$H$_4$)L, where L was an amine ligand. Over the narrow range of coupling constants observed (59·5—63 Hz) the coupling constant increased with increased electron withdrawing power of the amine substituents.



(VI)

TABLE 2

^{1}H N.m.r. data[a] for the complexes [Pt(CH$_3$)(cod)L](PF$_6$)

		Platinum methyl		Olefin resonances			
No.	L	δ	^2J(PtH)	δ(CH)	*J*(PtH)	δ(CH$_2$)	Other resonances
1	*p*-NCC$_6$H$_4$OCH$_3$	1·17	68·2	5·24 5·94	83 36	*ca.* 2·74	δ(OCH$_3$) 4·10
2	NH=C(OCH$_3$)C$_6$F$_5$	0·71	72·0	5·02 5·54	75 32	*ca.* 2·50	δ(OCH$_3$) 4·24
3	4-NC$_5$H$_4$CH$_3$	0·79	71·0	5·10 5·22	72 35	*ca.* 2·52	δ(CH$_3$) 2·46
4	AsPh$_3$	0·96	67·3	5·84 4·84	66 35	*ca.* 2·56	
5	CNEt	1·04	70·4	5·60 5·72	63 35	*ca.* 2·60	δ(CH$_2$) 3·96 δ(CH$_3$) 1·51
6	PPh$_3$	0·86[b]	67·2	5·98[c] 4·71	57 36	*ca.* 2·60	

[a] Spectra were recorded in CDCl$_3$; chemical shifts are in p.p.m. (positive) downfield from tetramethylsilane; coupling constants are in Hz. [b] ^3J(PH) 4·4 Hz. [c] *J*(PH) 4·5 Hz.

We have examined the coupling constant, *J*(PtCH), to the vinyl hydrogens [in complexes (II)] as a function of the *trans* ligand L, in an attempt to assess the contribution from π-bonding to this coupling constant. The n.m.r. data for these complexes are listed in Table 2. The range of *J*(PtCH) to the vinyl hydrogens *trans* to L is 57—83 Hz. According to Braterman's model,[10] this coupling constant should be relatively insensitive to Pt *d*π ⟶ olefin π* back bonding, depending mainly on the nature of the Pt-olefin σ-bond. To test this hypothesis, we have plotted, in the Figure, the values of *J*(PtCH) (for the vinyl hydrogens *trans* to L) obtained from series (II) against ^2J(PtCH$_3$) obtained from series V(b). A linear correlation exists with the exception of the nitrile ligand, for which the value of *J*(PtCH) is slightly greater than expected. The degree of π-back donation from filled metal *d*-orbitals into empty anti-bonding olefin orbitals is generally related to the electron density on the metal. As the electron density on the metal increases, the *d*-orbitals expand resulting in a greater degree of π-back bonding. For the closely related series of complexes (II) the degree of π-back bonding should decrease as the ligand, L, is changed from PPh$_3$ to *p*-NC–C$_6$H$_4$–OCH$_3$. If π-back bonding was a major factor affecting the magnitude of *J*(PtCH), as the degree of π-back bonding decreased, a smaller value of *J*(PtCH) would result, causing the line in the Figure to curve downward to the right. In fact, the value of *J*(PtCH) is slightly greater than expected. Secondly, if π-bonding was an important factor the value of *J*(PtCH) for the olefinic hydrogens *trans* to the methyl group in (II) should also vary as the electron density on platinum was altered, by varying L. Neither of these two effects is observed so that we can support the proposal[10] that the coupling constant between ^{195}Pt and the vinyl hydrogens is probably not affected to any great extent by π-back bonding from platinum into empty π* orbitals on the olefin. A corollary to this statement may be that the ^{195}Pt–X spin–spin coupling is not dependent upon

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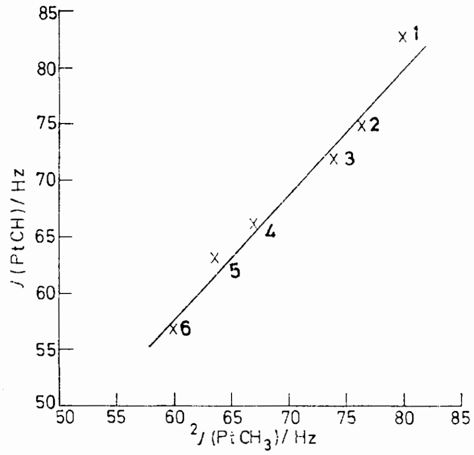
[9] P. D. Kaplan and M. Orchin, *Inorg. Chem.*, 1965, **4**, 1393.

[10] P. S. Braterman, *Inorg. Chem.*, 1966, **5**, 1085.

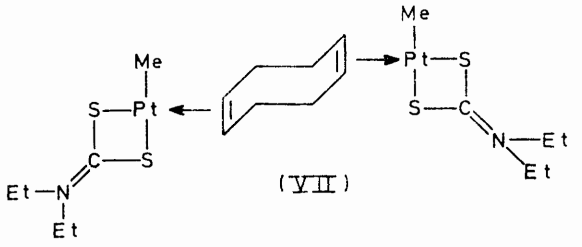
[11] H. P. Fritz and D. Sellmann, *Z. Naturforsch. B*, 1967, **22**, 610.

the charge on the platinum for a given co-ordination number and oxidation state.

*Displacement Reactions of Cyclo-octa-*1,5*-diene from the Platinum Complexes.—Diethyldithiocarbamate complexes.* The displacement reaction of cod from complexes of the type Pt(R)$_2$(cod) and Pt(R)Cl(cod) has recently been shown to be a good route to a variety of new organoplatinum complexes. The reactions proceed slowly, presumably due to the fact that the platinum atom is fairly electron rich and consequently the olefin is tightly bonded as a result of considerable Pt $\longrightarrow$ olefin π-bonding. By formation of the solvated cation, (I), the platinum $5d$ orbitals that are used for π-back bonding are contracted, resulting in less overlap with the olefin π^* orbitals and a weaker Pt–olefin bond. Therefore it is not surprising that the addition of an equimolar amount of Na$^+$S$_2$CN(C$_2$H$_5$)$_2$$^-$,3H$_2$O to a solution of [Pt(CH$_3$)(cod)-(sol)](PF$_6$) readily liberates cod. An insoluble yellow complex is formed, which on the basis of analytical data is believed to have a bridging olefin ligand as shown by (VII). Triphenylphosphine and triphenylarsine readily react with (VII) to give the soluble neutral complexes Pt(CH$_3$)LS$_2$CN(C$_2$H$_5$)$_2$, (VIII) (L = PPh$_3$, AsPh$_3$) plus unco-ordinated cyclo-octa-1,5-diene, which is consistent with structure (VII). The neutral complexes (VIII) may be synthesised more cleanly by adding a molar equivalent of sodium diethyldithiocarbamate trihydrate to a solution of [Pt(CH$_3$)L(cod)](PF$_6$). The complexes can then be extracted from the sodium hexafluorophosphate with dichloromethane.



A plot of J(PtCH) *vs.* J(PtCH$_3$) for the group *trans* to L in complexes [Pt(CH$_3$)L(cod)](PF$_6$) and *trans*-[Pt(CH$_3$)L(PMe$_2$Ph)](PF$_6$). The numbering scheme is given in Table 2



(VII)

Isocyanide and carbene complexes. During the last few years, there has been a considerable increase in the number of publications concerned with the synthesis and reactivity of transition metal isocyanide complexes.[12,13] A common reaction of co-ordinated isocyanide ligands is their susceptibility to nucleophilic attack by protic nucleophiles giving carbene complexes.[14,15] We were interested in utilizing [Pt(CH$_3$)(cod)(thf)](PF$_6$) to prepare another class of platinum(II) isocyanide complexes and to examine their reactivity.

Three equivalents of ethyl or p-tolyl isocyanide react very cleanly with (I) to give the methylplatinum(II) tris(isocyanide) complexes [Pt(CH$_3$)(CNR)$_3$](PF$_6$), (IX). These complexes are stable crystalline solids, moderately soluble in polar solvents and are analogous to the complex [PtBr(CNCH$_3$)$_3$](PF$_6$) prepared by Balch and Miller.[16]

[Pt(CH$_3$)(CNC$_6$H$_4$CH$_3$)$_3$](PF$_6$) reacts very rapidly with an excess of dimethyl- or diethyl-amine to give white crystalline complexes. Their i.r. spectra show bands due to ν(N–H), ν(C≡N), and ν(C$\overset{\cdots}{-}$N) *ca.* 3360, 2160, and 1550 cm^{-1} respectively, characteristic of a mixed isocyanide–carbene complex.[17,18] The platinum-methyl resonances in the ^{1}H n.m.r. spectra are considerably shielded (absorbing 0·10—0·30 p.p.m. *upfield* from tetramethylsilane) and the coupling constant ^2J(PtCH$_3$) 70·5 Hz is consistent with a methyl group *trans* to an isocyanide ligand.[19] If the methyl group were *trans* to a carbene the value of ^2J(PtCH$_3$) would be expected to be *ca.* 50 Hz.[20] Integration of the N-methyl resonances against the platinum methyl resonance indicated that two amine ligands had reacted to give a bis-carbene complex. The n.m.r. spectra also showed that the N-methyl and tolyl-methyl resonances were magnetically equivalent for each carbene ligand so the following structures have been assigned.

The geometry about the carbene carbon is most likely planar and perpendicular to the platinum square plane.[21] The C≡N stretching frequency of the co-ordinated isocyanide in the carbene complexes (X) is lowered by *ca.* 50 cm^{-1} relative to the tris(isocyanide) complex (IX), which is consistent with an increase in electron density on platinum [18] resulting from the fact that carbenes are

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[12] Y. Yamamoto and H. Yamazaki, *Co-ordination Chem. Rev.*, 1972, **8**, 225.

[13] P. M. Treichel, *Adv. Organometallic Chem.*, 1973, **11**, 21.

[14] F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487.

[15] D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545.

[16] J. S. Miller and A. L. Balch, *Inorg. Chem.*, 1972, **11**, 2069.

[17] H. C. Clark and L. E. Manzer, *J. Organometallic Chem.*, 1971, **30**, C89.

[18] H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 1972, **11**, 503.

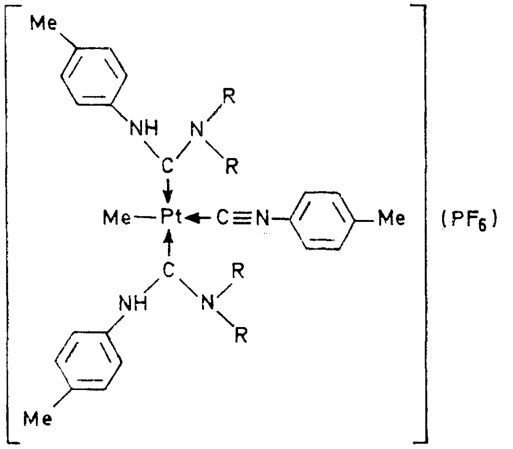
[19] P. M. Treichel, W. J. Knebel, and R. W. Hess, *J. Amer. Chem. Soc.*, 1971, **93**, 5424.

[20] J. Ugi, U. Fetzer, U. Eholzer, K. Knupler, and K. Offerman, *Angew. Chem. Internat. Edn.*, 1965, **4**, 472.

[21] W. M. Butler and J. H. Enemark, *Inorg. Chem.*, 1973, **12**, 540.

better σ-donors and weaker π-acceptors than isocyanides as ligands.[22]

No reaction occurs between $[Pt(CH_3)(CNC_6H_4CH_3)_3](PF_6)$ and sodium iodide or sodium azide;[19] however, with sodium benzenethiolate, one isocyanide ligand is displaced to give the bright yellow complex $Pt(CH_3)(CNC_6H_4CH_3)_2(SPh)$. The coupling constant, $^2J(PtCH_3)$ 64·6 Hz, is consistent with a methyl group *trans* to an isocyanide ligand and the presence of two distinct tolyl-CH_3 resonances in the n.m.r. spectrum indicate that the complex has a *cis*-configuration.



(X) (a) R = CH_3
(b) R = CH_2CH_3

EXPERIMENTAL

p-Tolyl isocyanide was prepared by the phosgene method [20] and ethyl isocyanide by the method of Casanova, Schuster, and Werner.[23] $Pt(CH_3)Cl(\pi\text{-}1,5\text{-}C_8H_{12})$ was synthesised as previously reported.[2] The other ligands were obtained commercially and were used without further purification. All reactions and recrystallisations were carried out using ' spectro '-analysed solvents, without purification.

I.r. spectra were recorded on a Perkin-Elmer 621 grating spectrometer as Nujol mulls or dichloromethane solutions using potassium bromide cells.

N.m.r. spectra were recorded on a Varian HA 100 spectrometer operating at 100 MHz using [^{2}H]chloroform solutions and tetramethylsilane as internal lock-reference signal.

Microanalyses were performed by Chemalytics Inc., Tempe, Arizona.

Since several of the complexes were prepared by similar methods only a few representative examples will be described in detail.

Preparation of $[Pt(CH_3)(cod)(\gamma\text{-}NC_5H_4CH_3)](PF_6)$.—To a solution of $Pt(CH_3)Cl(cod)$ (0·158 g, 0·446 mmol) in acetone (10 ml) was added a solution of $AgPF_6$ (0·113 g, 0·446 mmol) in acetone (2 ml). Silver chloride precipitated immediately and was removed by centrifugation to give a clear, colourless solution. γ-Picoline (0·045 ml, 0·446 mmol) was added to the solution and the acetone was removed by rotary evaporation to give a clear oil. The oil was dissolved in methanol and ether was slowly added to the solution until crystals separated. The flask was cooled at −14 °C for several hours, the crystals filtered off and dried under vacuum (yield, 85%).

Preparation of $[Pt(CH_3)(cod)(CNC_2H_5)](PF_6)$.—Ethyl isocyanide (0·046 ml, 0·615 mmol) was syringed into a solution of $Pt(CH_3)Cl(cod)$ (0·218 g, 0·615 mmol) in methanol (10 ml). $AgPF_6$ (0·156 g, 0·615 mmol) in methanol (2 ml) was added and the solution was magnetically stirred for 5 min. The silver chloride was centrifuged off and the methanol was removed to give white crystals. The crystals were dissolved in dichloromethane and ether was added. The flask was cooled at −14 °C for several hours then the crystals were filtered off, washed with ether, and air dried (yield, 82%).

Preparation of $[Pt(CH_3)(cod)\{NH{=}C(OCH_3)C_6F_5\}](PF_6)$.—To a solution of $Pt(CH_3)Cl(cod)$ (0·332 g, 0·940 mmol) in methanol (10 ml) was added a solution of $AgPF_6$ (0·237 g, 0·940 mmol) in methanol (5 ml). The solution was magnetically stirred for 10 min then the silver chloride was removed by centrifugation. Pentafluorobenzonitrile (0·181 g, 0·940 mmol) was syringed into the flask and the flask was then stoppered and magnetically stirred for four days. The methanol was removed by rotary evaporation to give a pale yellow oil. The oil was dissolved in dichloromethane and passed through a short Florisil column, eluting with dichloromethane. The volume of the solvent was reduced and ether was added dropwise to give white crystals. The flask was cooled for several hours and the crystals were filtered off and washed with ether, then air dried (yield, 78%).

Preparation of $Pt(CH_3)(S_2CNEt_2),1/2(cod)$.—$AgPF_6$ (0·160 g, 0·632 mmol) in methanol (2 ml) was added to a solution of $Pt(CH_3)Cl(cod)$ (0·224 g, 0·632 mmol) in methanol (10 ml). The precipitated silver chloride was removed by centrifugation and a solution of sodium diethyldithiocarbamate trihydrate (0·243 g, 0·632 mmol) in methanol (5 ml) was added. The solution turned to a bright yellow colour. The methanol was removed to give a yellow solid which was washed with water (50 ml), to remove the sodium hexafluorophosphate, then with ethanol (25 ml), and air dried (yield, quantitative).

Preparation of $Pt(CH_3)(S_2CNEt_2)(PPh_3)$.—To a suspension of $Pt(CH_3)(S_2CNEt_2),1/2(cod)$ (0·114 g, 0·277 mmol) in dichloromethane (5 ml) was added triphenylphosphine (0·073 g, 0·277 mmol). The solids immediately dissolved to give a pale yellow solution. The dichloromethane was removed by rotary evaporation and the resultant solid was recrystallised from methanol (yield, 86%). Alternatively the compound may be prepared from $[Pt(CH_3)(cod)(PPh_3)]PF_6$ and $Na^+(S_2CNEt_2)^-,3H_2O$ as illustrated for $AsPh_3$, below. N.m.r. in $CDCl_3$: δ (Pt–CH_3) 0·51, ^2J(Pt–CH_3) 77·0, ^3J(P–H) 4; δ (CH_2) 3·59, 3·67; δ (CH_3) 1·18, 1·27, ^3J(H–H′) 7·4.

Preparation of $Pt(CH_3)(S_2CNEt_2)(AsPh_3)$.—To a solution of $[Pt(CH_3)(cod)(AsPh_3)](PF_6)$ (0·115 g, 0·150 mmol) in methanol (10 ml) was added a solution of $Na(S_2CNEt_2),3H_2O$ (0·034 g, 0·150 mmol) in methanol (5 ml). The solution was magnetically stirred for 10 min and the

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methanol was removed by rotary evaporation. The compound was extracted with diethyl ether and filtered. Pentane was added and the solution was cooled at −14 °C for 24 h to give pale yellow crystals which were filtered off and air dried (yield, 74%). N.m.r. in $CDCl_3$: δ (Pt–CH_3) 0·54, ^2J(Pt–H) 77·8; δ (CH_2) 3·64, 3·67; δ (CH_3) 1·23, 1·31, ^3J(H–H′) 7·4.

Preparation of $[Pt(CH_3)(CNEt)_3](PF_6)$.—Ethyl isocyanide (0·033 ml, 0·462 mmol) was syringed into a magnetically stirred solution of $[Pt(CH_3)(cod)(CNEt)](PF_6)$ (0·120 g, 0·231 mmol) in dichloromethane (10 ml). The solution was stirred for 4 h and the volume of solvent was reduced to *ca.* 2 ml. Hexane was added dropwise until an oil separated. The flask was then cooled at −14 °C for several hours causing the oil to crystallise. The pale yellow crystals were filtered off and air dried (yield, 87%). N.m.r. in $CDCl_3$: δ (Pt–CH_3) 0·64, ^2J(Pt–CH_3) 64·8; mutually *trans*-isocyanides, δ (CH_3) 1·51, δ (CH_2) 3·88; isocyanide *trans* to platinum methyl, δ (CH_3) 1·48, δ (CH_2) 3·85.

Preparation of $[Pt(CH_3)(CNC_6H_4CH_3)_3](PF_6)$.—$AgPF_6$ (0·250 g, 0·988 mmol) in acetone (5 ml) was added to a solution of $Pt(CH_3)Cl(cod)$ (0·350 g, 0·988 mmol) in acetone (10 ml). The solution was magnetically stirred for 5 min and the silver chloride centrifuged off. Isocyanide (0·347 g, 2·96 mmol) was syringed into the solution and it was stirred for 1 h, after which time the odour of isocyanide was no longer detectable. The solvent was removed to give a pale yellow solid which was dissolved in the minimum amount of dichloromethane. Ether was slowly added to precipitate colourless crystals (yield, 0·600 g, 87%). N.m.r. in $CDCl_3$: δ (Pt–CH_3) 0·99, ^2J(Pt–CH) 63·2; isocyanide *trans* to platinum methyl, δ (CH_3) 2·35; mutually *trans*-isocyanides, δ (CH_3) 2·39.

Preparation of cis-$Pt(CH_3)(CNC_6H_4CH_3)_2(SPh)$.—A solution of $Na^+S(C_6H_5)^-$ (0·028 g, 0·212 mmol) in acetone (10 ml) was added to a magnetically stirred solution of $[Pt(CH_3)(CNC_6H_4CH_3)_3](PF_6)$ (0·150 g, 0·212 mmol) in tetrahydrofuran (5 ml). An immediate dark yellow colour resulted which slowly turned pale yellow. After 1 h, the solvent was removed and a strong odour of isocyanide was detected. Diethyl ether was added and the pale yellow solution was passed through a short Florisil column, eluting with diethyl ether, to remove the $Na^+PF_6^-$. The solvent volume was reduced and pentane was added to give a yellow oil which crystallised overnight at −14 °C. The crystals were then filtered off, washed with pentane, and air dried (yield, 67%). N.m.r. in $CDCl_3$: δ (Pt–CH_3) 0·74, ^2J(Pt–H) 64·6; δ (CH_3) 2·30, 2·37.

Preparation of $[Pt(CH_3)(CNC_6H_4CH_3)\{:C(NMe_2)(NHC_6H_4CH_3)\}_2](PF_6)$.—A suspension of $[Pt(CH_3)(CNC_6H_4CH_3)_3](PF_6)$ (0·220 g, 0·312 mmol) in tetrahydrofuran (5 ml) was stirred magnetically. Dimethylamine was bubbled through the solution for 1 min. The suspension dissolved almost immediately to give a clear, colourless solution. The solution was stirred for 5 min and a precipitate formed. The solvent was removed by rotary evaporation to give a white solid which was dissolved in dichloromethane. Ether was added dropwise to give colourless crystals. The solution was cooled for several hours, then the crystals were filtered off, washed with ether, and air dried (yield, 83%). N.m.r. in $CDCl_3$: δ (Pt–CH_3) −0·17, ^2J(Pt–H) 70·7; mutually *trans* carbene ligands, δ (N–H) 7·71, ^3J(Pt–H) 63·0; δ (N–CH_3) 2·86, 3·01, ^4J(Pt–H) 3·5, 2·9; δ (tolyl-CH_3) 2·32; isocyanide *trans* to platinum methyl, δ (tolyl-CH_3) 2·24.

Preparation of $[Pt(CH_3)(CNC_6H_4CH_3)\{:C(NEt_2)(NHC_6H_4CH_3)\}_2](PF_6)$.—Diethylamine (2 ml) was added to a suspension of $[Pt(CH_3)(CNC_6H_4CH_3)_3](PF_6)$ (0·210 g, 0·298 mmol) in tetrahydrofuran (5 ml). The solid immediately dissolved to give a clear colourless solution. The solution was stirred for 1 h and the solvent was removed by rotary evaporation. The oil was dissolved in dichloromethane and ether was added dropwise to give colourless crystals. The solution was cooled for several hours, the crystals were filtered off, washed with ether, and air dried (yield, 88%). N.m.r. in $CDCl_3$: δ (Pt–CH_3) −0·24, ^2J(Pt–H) 70·5; mutually *trans* carbene ligands, δ (N–H) 7·53, ^3J(Pt–H) 63·0; δ (N–CH_2) ≈3·31 (multiplet), δ (N–C–CH_3) 0·80, 1·17; δ (tolyl-CH_3) 2·33; isocyanide *trans* to platinum methyl, δ (tolyl-CH_3) 2·39.

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