Isocyanide Complexes of Platinum(0)

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Treatment of $[Pt(C_2H_4)(PPh_3)_2]$ with t-butyl isocyanide yields the complex $[Pt(CNBu^t)_2(PPh_3)_2]$, and evidence for the existence of related species $[Pt(CNR)_2(PPh_3)_2]$ ($R = Pr^i$, C_6H_{11}, p-$MeOC_6H_4$, or p-ClC_6H_4) has been obtained from solution studies. Displacement of the arsine ligand from $[Pt(AsPh_3)_2(C_2F_4)]$ with RNC ($R = Pr^i$ or Bu^t) yields the complexes $[Pt(CNR)_2(C_2F_4)]$. Oxidative-addition reactions of $[Pt(CNBu^t)_2(PPh_3)_2]$ occur with I_2, MeI, CF_3I, and $[SnPh_3Cl]$, the products being best formulated as $[Pt(CNBu^t)_2(PPh_3)_2I]I$ or $[Pt(CNBu^t)(CR{=}NBu^t)(PPh_3)_2]I$ except for the adduct with $[SnPh_3Cl]$. Alternative routes to some of the products have been found, such as the interaction of $[PtMe(I)(PPh_3)_2]$ with Bu^tNC. An unusual reaction occurs on attempted alkylation of the cyanide $[Pt(CN)_2(PPh_3)_2]$ with MeI in that the phosphine ligands are displaced and $[Pt(CNMe)_2I_2]$ is obtained.

ISOCYANIDE complexes of the Ni,Pd,Pt triad illustrate particularly well some of the remarkable features associated with this ligand and have consequently received considerable attention in recent years.[1] The majority of complexes isolated contain the metal in the bivalent state although some interesting differences are observed. Thus for nickel very few derivatives of Ni^{II} are known, in contrast to the numerous complexes of Pd^{II} and Pt^{II}, and attempts to prepare them have led to ill defined products.[2] On the other hand, while several derivatives of zerovalent nickel, *e.g.* $[Ni(CNPh)_4]$ [3] and $[Ni(CNMe)_3(CO)]$,[4] have been reported, only a few ill defined Pd complexes are known. Malatesta [5] has described a series of complexes $[Pd(CNR)_2]$ ($R = Ph$, p-MeC_6H_4, or p-$MeOC_6H_4$) which were obtained by reduction of $[PdI_2(CNR)_2]$ using alcoholic potassium hydroxide. They are insoluble in organic solvents and appear to be polymeric. This view was substantiated by a study of similar Pd^0 complexes, $[Pd(CNC_6H_{11})_2]$ and $[Pd(CNPr^i)_2]$, prepared by the addition of the isocyanide to cyclohexenyl(cyclopentadienyl)palladium.[6] Other palladium derivatives such as $[Pd(CNR)(PR'_3)_3]$ ($R = p$-$MeOC_6H_4$; $R' = p$-MeC_6H_4, p-ClC_6H_4O, or PhO),[7] $[Pd(CNR)_2L]$ [$R = Bu^t$ or Ph; $L = C_2(CN)_4$,[8,9] fumaronitrile, maleic anhydride, dimethyl maleate, C_2Ph_2,[9] or $(CF_3)_2C{=}C(CN)_2$[10]] and $[Pd(CNPh)\{C_2(CN)_4\}(MPh_3)]$ (M = P or As) [8] have also been formed from $[Pd(CNR)_2]$. However, the only Pt^0 complexes known are $[Pt(CNC_6H_{11})(PF_3)]$, isolated in the course of a kinetic study,[11] the recently reported trimer $[Pt_3(CNBu^t)_6]$,[12] and those which we have described in a preliminary communication.[13] The purpose of this paper is to report more fully on these latter complexes and on some related studies.

An extensive chemistry of complexes which contain Pt^0 has been developed, and many mixed phosphine–ligand complexes are known.[14] These are generally of the composition $[Pt(PR_3)_2L]$, where L may be a variety of unsaturated ligands such as alkenes, alkynes, oxygen, and compounds containing $\gt C{=}O$ and $\gt C{=}S$ bonds. The carbonyl complexes $[Pt(CO)(PR_3)_2]$ and $[Pt(CO)_2(PR_3)_2]$ have also been prepared, as have the trinuclear and tetranuclear clusters $[Pt_3(CO)_3(PR_3)_n]$ and $[Pt_4(CO)_5(PR_3)_n]$ ($n = 3$ or 4).[15] Since isocyanide ligands are isoelectronic with carbon monoxide, and resemble both this ligand and tertiary phosphines in their π-acceptor ability, they should also be capable of stabilising Pt^0 in suitable complexes.

RESULTS AND DISCUSSION

Because of their ease of preparation, complexes containing Pt^0, *e.g.* $[Pt(PPh_3)_4]$,[16] $[Pt(PPh_3)_3]$,[17] and $[Pt(C_2H_4)(PPh_3)_2]$ [18] were chosen initially as starting materials in this study, especially since early results had indicated that such complexes are extensively dissociated in benzene solution affording the two-co-ordinate species $[Pt(PPh_3)_2]$.[19,20] Thus benzene solutions of these three complexes were treated with alkyl and aryl isocyanides and the i.r. spectra of the resulting solutions were examined in the 2 200—2 000 cm^{-1} region to seek evidence of co-ordination. It is established that the strong N≡C stretching frequency, which occurs at 2 200—2 100 cm^{-1} in the free isocyanide, shows a significant decrease when the group is co-ordinated to a transition metal in a low oxidation state.[21]

The addition of various isocyanides (Table 1) to

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[1] (*a*) 'Isocyanide Complexes of Metals,' eds. L. Malatesta and F. Bonati, Wiley–Interscience, London, 1969; (*b*) 'Isonitrile Chemistry,' ed. I. Ugi, Academic Press, London, 1971.

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

[3] H. Behrens and K. Meyer, *Z. Naturforsch.*, 1966, **B21**, 489.

[4] W. Hieber, *Z. Naturforsch.*, 1950, **B5**, 129.

[5] L. Malatesta, *J. Chem. Soc.*, 1955, 3924.

[6] E. O. Fischer and H. Werner, *Ber.*, 1962, **95**, 703.

[7] L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1957, 1186.

[8] T. Boschi, P. Uguagliati, and B. Crociani, *J. Organometallic Chem.*, 1971, **30**, 283.

[9] S. Otsuka, T. Yoshida, and Y. Tatsuno, *J. Amer. Chem. Soc.*, 1971, **93**, 6462.

[10] H. D. Empsall, M. Green, S. K. Shakshooki, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 3472.

[11] R. D. Johnston, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1971, **10**, 247.

[12] M. Green, J. A. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1975, 3.

[13] G. A. Larkin, R. Mason, and M. G. H. Wallbridge, *Chem. Comm.*, 1971, 1054.

[14] 'Zerovalent Compounds of Metals,' eds. L. Malatesta and S. Cenini, Academic Press, London, 1974.

[15] J. Chatt and P. Chini, *J. Chem. Soc. (A)*, 1970, 1538.

[16] R. Ugo, F. Cariati, and G. La Monica, *Inorg. Synth.*, 1968, **11**, 105.

[17] R. Ugo, F. Cariati, and G. La Monica, *Inorg. Synth.*, 1968, **11**, 107.

[18] C. D. Cook and G. S. Jauhal, *J. Amer. Chem. Soc.*, 1968, **90**, 1464.

[19] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.

[20] J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, 1968, **90**, 4491.

[21] See ref. 1(*b*), p. 218.

solutions of $[\mathrm{Pt(PPh_3)_n}]$ ($n = 3$ or 4), in a molar ratio $\mathrm{RNC}:[\mathrm{Pt(PPh_3)_n}] \geqslant 2:1$, resulted in only one absorption in the above region and a sharp decrease in the isocyanide ($\mathrm{N{\equiv}C}$) stretching frequency of the order of 50—100 $\mathrm{cm^{-1}}$, indicating that co-ordination of the isocyanide had occurred. The addition of a further quantity of isocyanide caused the appearance of a further $\mathrm{N{\equiv}C}$ absorption at the value corresponding to the free isocyanide, indicating the presence in solution of a species $[\mathrm{Pt(CNR)_2(PPh_3)_2}]$. An exception to this behaviour was observed with *p*-tolyl isocyanide when, after addition of 2 mol, no absorption in the 2 200—2 000 $\mathrm{cm^{-1}}$ region could be detected. While the fate of the isocyanide in this reaction is uncertain, the most likely possibility is that polymerisation of the isocyanide occurs although only a weak absorption was observed in the region characteristic of polyisocyanides (1 645—1 615 $\mathrm{cm^{-1}}$). The results for benzene solutions of $[\mathrm{Pt(PPh_3)_4}]$ and $[\mathrm{Pt(PPh_3)_3}]$ are summarised in Table 1. We were unable to isolate the species $[\mathrm{Pt(CNR)_2(PPh_3)_2}]$ from the benzene solutions of $[\mathrm{Pt(PPh_3)_n}]$, the difficulty being caused by the similar solution behaviour of the product, starting material, and triphenylphosphine in a range of solvents.

TABLE 1

Behaviour of various isocyanides in benzene solutions of $[\mathrm{Pt(PPh_3)_4}]$, $[\mathrm{Pt(PPh_3)_3}]$, and $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ [a]

Isocyanide \ Complex	$[\mathrm{Pt(PPh_3)_4}]$	$[\mathrm{Pt(PPh_3)_3}]$	$[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$
$\mathrm{Bu^tNC}$ (2 130)	c (2 030)	c (2 030)	c (2 030) [b]
$\mathrm{Pr^iNC}$ (2 140)	c (2 070)	c (2 070)	n.c.
$\mathrm{C_6H_{11}NC}$ (2 140)	c (2 070)	c (2 070)	n.c.
p-$\mathrm{MeOC_6H_4NC}$ (2 130)	c (2 020)	c (2 020)	n.c.
p-$\mathrm{ClC_6H_4NC}$ (2 130)	c (2 080)	c (2 080)	n.c.
p-$\mathrm{MeC_6H_4NC}$	p	p	

[a] The $\mathrm{N{\equiv}C}$ stretching band ($\mathrm{cm^{-1}}$) in the free (or co-ordinated) ligand is given in parentheses. c = Co-ordination, n.c. = no co-ordination, and p = polymerisation. [b] Recorded from a Nujol mull.

The behaviour of the ethylene complex, $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$, with various isocyanides is in sharp contrast to that of the phosphine complexes. In benzene solution, displacement of the ethylene, and subsequent co-ordination of the isocyanide, was observed only in the case of t-butyl isocyanide, and with all the other isocyanides examined no decrease in the $\mathrm{N{\equiv}C}$ stretching frequency was observed in the i.r. spectra. The reaction with $\mathrm{Bu^tNC}$ was best performed in pentane solution at low temperature [equation (1)]. Ethylene was evolved quantitatively

$$[\mathrm{Pt(C_2H_4)(PPh_3)_2}] + 2\mathrm{Bu^tNC} \xrightarrow[\text{n-pentane}]{-20\,^{\circ}\mathrm{C}} [\mathrm{Pt(CNBu^t)_2(PPh_3)_2}]\downarrow + \mathrm{C_2H_4}\uparrow \quad (1)$$

during the reaction, and the product precipitated from solution as a pale yellow solid which decomposes slowly in the air but is stable under dry nitrogen. The solid is moderately soluble in benzene and toluene and slightly soluble in n-pentane. The $\mathrm{N{\equiv}C}$ stretching frequency occurred at 2 030 $\mathrm{cm^{-1}}$, a value in agreement with the previous solution studies and indicating appreciable back donation of charge from the metal to the ligand. Benzene solutions of the complex slowly deposit pale yellow crystals of the carbonate, $[\mathrm{Pt(CO_3)(PPh_3)_2}]$, on standing in air, thus showing similar behaviour to $[\mathrm{Pt(PPh_3)_n}]$ ($n = 3$ or 4).[22,23] The methyl, isopropyl, cyclohexyl, and *p*-chlorophenyl derivatives failed to displace ethylene under similar conditions, even after extended reaction times (5—6 h) at 0 °C.

From recent studies on the nature of the species present in solutions of $[\mathrm{Pt(PR_3)_n}]$ ($n = 3$ or 4) and $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ it has been suggested that $[\mathrm{Pt(PR_3)_4}]$ species dissociate only to $[\mathrm{Pt(PR_3)_3}]$ and that $[\mathrm{Pt(PR_3)_3}]$ and $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ are both undissociated in benzene solution,[24,25] and it is only when R is a bulky group (*e.g.* $\mathrm{C_6H_{11}}$) that $[\mathrm{Pt(PR_3)_2}]$ is stabilised.[26] The present results may be rationalised in the light of this evidence in that one molecule of isocyanide adds to the co-ordinatively unsaturated species $[\mathrm{Pt(PPh_3)_3}]$ together with substitution of phosphine by isocyanide to yield $[\mathrm{Pt(CNR)_2(PPh_3)_2}]$. This situation is closely paralleled in the reaction of carbon monoxide with the $[\mathrm{Pt(PPh_3)_n}]$ complexes, where substitution cannot be effected beyond the $[\mathrm{Pt(CO)_2(PPh_3)_2}]$ stage.[27] In the case of $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ the results imply that for the different isocyanides used the relative nucleophilicity of the ligand is important in that only $\mathrm{Bu^tNC}$ will displace the ethylene. However, since the stability of complexes of the type $[\mathrm{PtL(PPh_3)_2}]$ evidently depends on the delicate interaction of σ- and π-bonding effects, any extension of the comparison to other ligands would be unwise.

When solid $[\mathrm{Pt(CNBu^t)_2(PPh_3)_2}]$ was treated with a modest (*ca.* 25 atm) * pressure of carbon monoxide, 1 mol of isocyanide was displaced and the carbonyl $[\mathrm{Pt(CNBu^t)(CO)(PPh_3)_2}]$ was obtained as a pale yellow solid [equation (2)]. In this complex the $\mathrm{N{\equiv}C}$ stretching

$$[\mathrm{Pt(CNBu^t)_2(PPh_3)_2}] \xrightarrow{\mathrm{CO}} [\mathrm{Pt(CNBu^t)(CO)(PPh_3)_2}] + \mathrm{Bu^tNC}\uparrow \quad (2)$$

mode occurred at 2 110 $\mathrm{cm^{-1}}$ (with the $\mathrm{C{\equiv}O}$ mode at 1 910 $\mathrm{cm^{-1}}$), and in comparison with the bis(isocyanide) (2 030 $\mathrm{cm^{-1}}$) this higher value suggests that the CO ligand competes more effectively than $\mathrm{Bu^tNC}$ for the overall charge on the metal atom. This conclusion is

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* 1 atm = 101 325 Pa.

[22] C. J. Nyman, C. E. Wymore, and G. Wilkinson, *Chem. Comm.*, 1967, 407.

[23] F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *Chem. Comm.*, 1967, 408.

[24] C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, 1972, **94**, 2669.

[25] H. C. Clark and K. Itoh, *Inorg. Chem.*, 1971, **10**, 1707.

[26] A. Immirzi and A. Musco, *J.C.S. Chem. Comm.*, 1974, 400.

[27] P. Chini and G. Longoni, *J. Chem. Soc.* (*A*), 1970, 1542.

consistent with previous studies on mixed isocyanide–carbonyl compounds, *e.g.* $[Ni(CNR)_n(CO)_{4-n}]$ (n = 1—3), containing metal atoms in the zerovalent state.[28,29] The ^1H n.m.r. spectra of both the carbonyl and bis(isocyanide) complexes $[Pt(CNBu^t)L(PPh_3)_2]$ (L = Bu^t-NC or CO) in deuteriated benzene solution were simple, showing a sharp singlet for the Bu^t group(s) and a multiplet for the Ph protons. The i.r., n.m.r., and microanalytical data for these complexes are in Table 2.

In view of the several reported examples of addition reactions to $[Pt(PPh_3)_n]$ (n = 2—4),[14] we attempted similar reactions with the complex $[Pt(CNBu^t)_2(PPh_3)_2]$. Typically, phosphine elimination occurred in the former case [equation (3), n = 0—2; RX = alkyl, acyl, aroyl,

$$[Pt(PPh_3)_{4-n}] + RX \longrightarrow [Pt(PPh_3)_2(R)X] + (2-n)PPh_3 \quad (3)$$

halogeno-olefin, acetylene, and metal halide]. It is evident from our studies that the presence of the isocyanide ligand modifies the course of the oxidative-addition reaction. The addition of 1 mol of reagents such as I_2, MeI, CF_3I, and $[SnPh_3Cl]$ to a benzene solution of $[Pt(CNBu^t)_2(PPh_3)_2]$ at ambient temperatures yielded yellow solid products of empirical formula $[Pt(CNBu^t)_2(PPh_3)_2]\cdot RX$, although some noteworthy differences were observed in the type of product obtained. With iodine the product is quite stable and can be recrystallised from boiling benzene or dichloromethane–diethyl ether mixtures, but the reaction products from the other reactions decompose slowly when left in solution and could not be recrystallised. However, with these complexes it was possible to obtain pure complexes from the crude reaction product by rapid extraction with dichloromethane [equation (4)].

$$[Pt(CNBu^t)_2(PPh_3)_2] + RX \xrightarrow[25\,^{\circ}C]{C_6H_6} [Pt(CNBu^t)_2(PPh_3)_2R]X \text{ or } [Pt(CNBu^t)_2(PPh_3)_2]\cdot RX \quad (4)$$

TABLE 2

Analytic, spectral, and conductivity data for the isocyanide complexes

	Analyses [a]/%				I.r. spectra (cm^{-1}) [b]		N.m.r. spectra			λ (in (MeNO$_2$)
Compound	C	H	N	Halogen	ν(NC)	Other absorptions	τ(Ph) [c]	δ(F) [d]	τ(Bu^t or Pr^i)[c]	S cm^2 mol^{-1}
$[Pt(CNBu^t)_2(PPh_3)_2]$	61.7 (62.4)	5.3 (5.4)	3.1 (3.2)		2 030		2.4—3.1(m) (30)		9.1(s) (18) [e]	
$[Pt(CNBu^t)(CO)(PPh_3)_2]$	60.3 (60.7)	4.3 (4.7)	2.0 (1.7)		2 110	ν(CO) 1 910	2.1—3.0(m) (30)		9.3(s) (9) [e]	
$[Pt(CNBu^t)_2I(PPh_3)_2]I$	48.1 (48.5)	4.3 (4.2)	2.7 (2.5)	21.4 (22.3)	2 225		2.0—2.6(m) (30)		9.25(s) (18) [f]	87.2
$[Pt(CNBu^t)_2(Me)I(PPh_3)_2]$	54.9 (54.8)	5.0 (5.0)	2.4 (2.7)	12.8(12.4)	2 200		2.2—2.7(m) (30)		8.7(s) (9), 9.3(s) (9) [f]	64.4 [g]
$[Pt(CNBu^t)_2(CF_3)I(PPh_3)_2]$	51.2 (52.2)	4.7 (4.5)	2.6 (2.6)	11.3 (11.7)	2 220	ν(CF) 1 040—1 010	2.3—2.8(m) (30)		8.7—9.4(m) (18) [f]	72.5
$[Pt(CNBu^t)_2(PPh_3)_2][SnPh_3Cl]$	60.4 (60.5)	4.9 (5.0)	1.2 [h] (2.2)	2.6 (2.8)	2 190		2.5—3.6(m) (45)		8.9—9.4(m) (18) [f]	21.1
$[Pt(CNBu^t)_2(C_2F_4)]$ [i]	31.7 (31.2)	4.1 (3.9)	6.2 (6.1)		2 207, 2 185	ν(CF) 1 100—1 030		122.8 [j]	8.47(s) [j]	
$[Pt(CNPr^i)_2(C_2F_4)]$ [k]	27.7 (27.7)	3.4 (3.2)	6.4 (6.5)		2 230, 2 212	ν(CF) 1 100—1 030		81.2 [l]	8.48, 8.37 (CH_3),[l] 5.82(CH)	
Bu^tNC					2 130 [m]				8.53(s) [n]	

[a] Calculated values are given in parentheses. [b] Recorded as Nujol mulls or KBr discs. [c] s = Singlet and m = multiplet; relative intensities are given in parentheses [d] Relative to trichlorofluoromethane increasing to high field. [e] In C_6D_6. [f] In $CDCl_3$. [g] The value in Me_2CO is 116 S cm^2 mol^{-1}. Typical values for 1:1 salts in $MeNO_2$ and Me_2CO are 80—100 and 120—150 S cm^2 mol^{-1} respectively. [h] Persistently low analysis. [i] M.p. 133—135 °C (decomp.). [j] In $CDCl_3$; J_{PtF} 316 Hz. [k] M.p. 146—148°C (decomp.). [l] In CH_2Cl_2; J_{PtF} 408 Hz. [m] Liquid film. [n] In $CHCl_3$.

The fact that oxidative addition had occurred in every case was clearly established from a sharp rise in the N≡C stretching frequency in the products to values in the range 2 225—2 190 cm^{-1}, which is higher than that of the free isocyanide and typical of isocyanides bonded to Pt^{II}. The products obtained from I_2, MeI, and CF_3I exhibit appreciable conductivity in nitromethane (Table 2), all showing values typical of, or closely approaching, a 1 : 1 electrolyte. However, the product from $[SnPh_3Cl]$ shows a much lower conductivity suggesting only partial dissociation or possibly that more rapid decomposition takes place. Products with similar empirical formulations to those reported above have been obtained from dihalogenoplatinum(II) complexes $[Pt(PR_3)_2X_2]$, by reaction with MeNC in benzene solution[30] or from $[Pt(CNMe)_2(PR_3)_2][BF_4]_2$ by reaction with $[Me_4N]I$ in dichloromethane.[31] The products were suggested to contain five-co-ordinate Pt^{II} cations, principally on the basis of conductivity data and an intense yellow colouration [*e.g.* equation (5), X = Br or I]. The variation in

$$[Pt(PPh_3)_2X_2] + 2MeNC \longrightarrow [Pt(CNMe)_2(PPh_3)_2X]X \quad (5)$$

the type of product from this type of reaction is illustrated by the fact that, with the dichloride in benzene solution, displacement of phosphine occurs and a four-co-ordinate species, $[Pt(CNMe)Cl_2(PPh_3)]$, results.[30]

The most suitable description of the 1 : 1 adducts in the present work is that they may be of two types, that is either $[Pt(CNBu^t)_2(PPh_3)_2X]X$ or $[Pt(CNBu^t)\{C(X)=NBu^t\}(PPh_3)_2]X$ containing five or four-co-ordinate cations respectively. The general limited solubility and instability in solution of the oxidative-addition products prevented reliable molecular-weight data being obtained and, although satisfactory conductivity data were recorded from nitromethane solution, for the adduct with methyl iodide reasonable molecular weight and conductivity measurements were obtained using acetone solution. The ^1H n.m.r. spectrum of a freshly prepared

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[28] F. A. Cotton and F. Zingales, *J. Amer. Chem. Soc.*, 1961, **83**, 351.

[29] M. Bigorgne and A. Bouquet, *J. Organometallic Chem.*, 1963, **1**, 101.

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

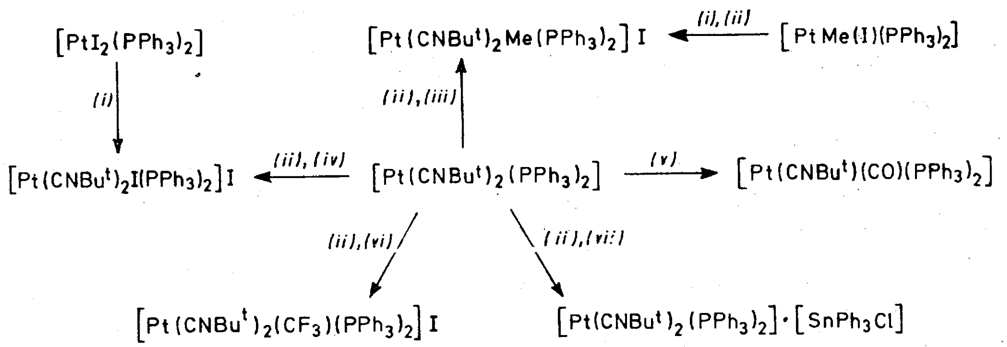
[31] P. M. Treichel and W. J. Knebel, *J. Co-ordination Chem.*, 1972, **2**, 67.

solution of $[Pt(CNBu^t)_2I_2(PPh_3)_2]$ in deuteriochloroform showed a complex multiplet at τ 2.0—2.6 attributable to the Ph protons and a singlet at τ 9.25 arising from the protons of the Bu^t group with an overall integration ratio of 30 : 18. This, together with the other data, indicates that this adduct is best formulated as containing the five-co-ordinate cation $[Pt(CNBu^t)_2I(PPh_3)_2]^+$. The spectra of the remaining adducts were less satisfactory in that, although the integrated intensities of the two sets of signals were as expected (30 : 18), the signal from the Bu^t protons appeared as a pair of poorly resolved singlets at τ 8.7 and 9.3 for $[Pt(CNBu^t)(Me)I(PPh_3)_2]$ (no clear singlet signal from the Me group could be detected), while for the CF_3I and $[SnPh_3Cl]$ adducts the Bu^t protons appeared as poorly resolved complex multiplets. We therefore assume that in these cases decomposition occurs in the solution, or that rearrangement of the cation occurs, yielding a four-co-ordinate species as formulated above. However, it is difficult to distinguish between the various possibilities at present. The four-co-ordinate cations should possess inequivalent Bu^t groups which should be reflected in the n.m.r. spectra, but the complexity of the resonances suggest further reactions are occurring, and we are unable to assign with certainty any absorption in the i.r. spectra arising from C=N vibrations although weak absorptions did occur in the 1 600—1 500 cm^{-1} region. Only for the iodine adduct can we propose with confidence the existence of a five-co-ordinate cation.

Results from other workers support the view that rearrangement reactions are likely in five-co-ordinate cations containing a Pt–C bond.[32,33] Thus insertion reactions of the type (6) (X = Br or I) have been reported suggesting that the four-co-ordinate cation is favoured in

$$\begin{tikzcd} {[PtPh(PPh_3)_2X] + MeNC} \arrow[r] & {[Pt(CPh{=}NMe)(PPh_3)_2X]} \arrow[d, "MeNC"] \\ & {[Pt(CNMe)(CPh{=}NMe)(PPh_3)_2]X \quad (6)} \end{tikzcd}$$

these systems. In these cases the Me group in (C=NMe) showed a doublet in the ^1H n.m.r. spectra (from Pt–H coupling) and a C=N absorption of medium intensity at 1 585 cm^{-1} in the i.r. spectra. Of the complexes reported here, it is $[Pt(CNBu^t)(Me)I(PPh_3)_2]$ which approaches this pattern most closely and appears therefore to contain the $[Pt(CNBu^t)(CMe{=}NBu^t)(PPh_3)_2]^+$ cation.



SCHEME (*i*), 2 Bu^tNC; (*ii*), C_6H_6 at 25 °C; (*iii*), MeI; (*iv*), I_2; (*v*), 25 atm CO; (*vi*), CF_3I; (*vii*), $[SnPh_3Cl]$.

We prepared two of the above 1 : 1 adducts by an alternative procedure using Pt^{II} precursors. The reaction of Bu^tNC with $[Pt(PPh_3)_2(X)Y]$ afforded products which had identical properties to the respective 1 : 1 adducts prepared as above, *e.g.* equation (7). The re-

$$[PtMe(I)(PPh_3)_2] + 2Bu^tNC \longrightarrow [PtMe(CNBu^t)_2(PPh_3)_2]I \quad (7)$$

actions of the isocyanide with $[Pt(PPh_3)_2(X)Y]$ (XY = CF_3I or $[SnPh_3Cl]$) were not studied since attempts to prepare the necessary precursors by oxidative addition of the halides to $[Pt(PPh_3)_3]$ were unsuccessful. In each case the dihalides $[Pt(PPh_3)_2X_2]$ (X = Cl or I) were obtained, the reaction with $[SnPh_3Cl]$ being contrary under our conditions to that reported earlier.[34] An independent attempt to prepare $[PtCl(PPh_3)_2(SnPh_3)]$ from $[Pt(PPh_3)_4]$ and $[SnPh_3Cl]$ also yielded the dichloride $[PtCl_2(PPh_3)_2]$ [35] although trimethyltin chloride has been reported to react with $[Pt(PMePh_2)_4]$ to yield *trans*-$[PtCl(PMePh_2)_2(SnMe_3)]$.[26] A summary of the main reactions is given in the Scheme.

As an alternative route to the MeI adduct we attempted to alkylate the cyanide complex $[Pt(CN)_2(PPh_3)_2]$ with methyl iodide. At the temperature required to effect the methylation (80—100 °C) an interesting side reaction occurred in that the phosphine was eliminated and the di-iodide $[Pt(CNMe)_2I_2]$ was obtained [equation (8)]. Similar alkylation reactions are well established for

$$[Pt(CN)_2(PPh_3)_2] + MeI(excess) \xrightarrow[\text{tube}]{\text{sealed}} [Pt(CNMe)_2I_2] + 2PPh_3 \quad (8)$$

several metal cyanides (Ag, Cu, *etc.*), but some unusual variations occur with platinum cyanide–isocyanide complexes since both alkylation and dealkylation reactions occur together with isocyanide insertion.[30,32,33]

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

[33] P. M. Treichel, K. P. Wagner, and R. W. Hess, *Inorg. Chem.*, 973, **12**, 1471.

[34] A. J. Layton, R. S. Nyholm, G. A. Preumatikas, and M. L. Tobe, *Chem. and Ind.*, 1967, 464.

[35] M. Fishwick and M. G. H. Wallbridge, unpublished work.

Thus it has been reported that $[Pt(CN)_2L_2]$ complexes ($L =$ a phosphine ligand) cannot be alkylated with MeI although no experimental conditions were given, but with the more effective alkylating agent $[R_3O][BF_4]$ ($R =$ Me or Et) reaction proceeds easily in refluxing dichloromethane to yield $[Pt(CNR)_2L_2][BF_4]_2$.[30] An attempt has been made to rationalise the influence of the different groups attached to the metal atom in these reactions, and an explanation for the difference observed here may lie in the reaction conditions used since while it has been suggested [30] that the volatility and loss of MeI may provide a driving force in the dealkylation reactions the reaction conditions in the present work involve sealed tubes. It is also noteworthy that at the reaction temperatures used no isomerisation of the isocyanide to the cyanide complex $[Pt(NCMe)_2I_2]$ occurred.

We also made a limited investigation of the action of isocyanides on the complex $[Pt(AsPh_3)_2(C_2F_4)]$, prompted by the earlier observation that the arsine ligands are labile and may be replaced by a variety of phosphines.[36] In contrast to these reactions, where extended reaction times were required, an instantaneous reaction occurred between the arsine complex and 2 mol of the isocyanide at ambient temperatures [equation (9), $R = Pr^i$ or Bu^t].

$$[Pt(AsPh_3)_2(C_2F_4)] + 2RNC \xrightarrow[\text{room. temp}]{Et_2O} [Pt(CNR)_2(C_2F_4)] + 2AsPh_3 \quad (9)$$

The products were obtained in good yields as air-stable white crystalline solids (Table 2) which decomposed slowly in chloroform solution over several days. A similar reaction using *p*-chlorophenyl isocyanide afforded a reaction product which appeared to contain co-ordinated isocyanide (i.r. spectrum) but which was so insoluble that it could not be obtained in a pure state. Both the alkyl isocyanide products showed strong C–F absorptions (1 100—1 031 cm^{-1}) in their i.r. spectrum (KBr disc) and a doublet in the N≡C region (2 240—2 180 cm^{-1}) (Table 2). This value is only 90—70 cm^{-1} higher than that in the free ligand, indicating that the isocyanide is accepting very little back donation from the metal. The two N≡C vibrations suggest a square-planar arrangement around the platinum with the isocyanides in *cis* positions, in spite of the difficulties associated with assignments from spectra of this type obtained from solid samples.[37] The ^1H and ^{19}F n.m.r. spectra (Table 2) were consistent with the above formulation. Thus the former showed resonances expected for the alkyl group of the isocyanide, while the latter showed one sharp line with satellites of relative intensities 0.25 from coupling with the ^{195}Pt ($I = \frac{1}{2}$, relative abundance 34%) nucleus. The ^{19}F n.m.r. spectra show a close similarity to those from $[Pt(bipy)(C_2F_4)]$ and $[Pt(AsPh_3)(C_2F_4)]$ (bipy = 2,2′-bipyridyl). The values of J_{PtF} observed for the isocyanide complexes were in the order predicted from the N≡C stretching frequencies in the i.r. spectra, and are consistent with previous results for the series $[Pt(C_2F_4)L_2]$($L = PPh_3$, $AsPh_3$, bipy, *etc.*).[36] It was observed for these complexes that high values of J_{PtF} indicated a significant contribution from an ionic formulation $[PtL_2][C_2F_4]$, and a similar conclusion appears to be valid for the isocyanide complexes.

EXPERIMENTAL

All solvents were dried (using lithium tetrahydroaluminate, calcium hydride, or molecular sieves) and distilled prior to use. ^1H N.m.r. spectra were recorded using Perkin-Elmer R12 (60 MHz) or Varian HA100 (100 MHz) spectrometers, i.r. spectra on a Perkin-Elmer 457 Infracord. Our own experience of the preparation of isocyanides by the dehydration of N-monosubstituted formamides (see ref. 1 for summary) has been that while the use of dehydrating agents such as phosphoryl chloride or toluene-*p*-sulphonyl chloride gave good yields of the alkyl isocyanides, only the $POCl_3$ method gave appreciable yields of the aryl isocyanides. *N*-Methylformamide was purchased from B.D.H. Ltd., and *N*-t-butyl-,[38] *N*-isopropyl-,[38] and *N*-cyclohexyl-formamide [39] were prepared by literature methods. The N-substituted aromatic formamides were prepared by the reported methods.[40] The complexes, $[Pt(PPh_3)_4]$ [16] $[Pt(PPh_3)_3]$,[17] $[Pt(C_2H_4)(PPh_3)_2]$,[18] $[Pt(Me)(I)(PPh_3)_2]$,[41] $[Pt(AsPh_3)_4]$,[36] $[Pt(AsPh_3)_2(C_2F_4)]$,[36] and $[Pt(CN)_2(PPh_3)_2]$ [42] were all prepared using published procedures.

Bis(t-butyl isocyanide)bis(triphenylphosphine)platinum-(0), $[Pt(CNBu^t)_2(PPh_3)_2]$.—To a stirred suspension of $[Pt(C_2H_4)(PPh_3)_2]$ (1.0 g, 1.34 mmol) in dry n-pentane (35 cm^3) at 233 K under dry nitrogen, t-butyl isocyanide (0.44 g, 5.36 mmol) was added as a solution in n-pentane (10 cm^3). The reaction mixture was allowed to warm slowly to 253 K when an intense yellow colour developed. After 10 min at 253 K the mixture was stirred for a further 30 min at 243 K. The mixture was then cooled further to 193 K, transferred to a nitrogen-filled glove-box, and filtered as quickly as possible. After washing with chilled n-pentane (10 cm^3) the product was obtained as a yellow solid (yield *ca.* 80%) which was dried *in vacuo*.

Reactions of $[Pt(CNBu^t)_2(PPh_3)_2]$.—(a) *With iodine*. Iodine (0.143 g, 0.565 mmol) was dissolved in dry benzene (10 cm^3) and added dropwise to a stirred solution of $[Pt(CNBu^t)_2(PPh_3)_2]$ (0.5 g, 0.565 mmol) in benzene (30 cm^3) under nitrogen at ambient temperature. The iodine colour was discharged, and the yellow solid which precipitated was filtered off, washed successively with benzene (30 cm^3) and hexane (30 cm^3), and dried *in vacuo*. Yields of the principal product were *ca.* 60%. The complex was too insoluble in acetone for reliable molecular-weight measurements to be made.

(b) *With methyl iodide*. Methyl iodide (0.08 g, 0.565 mmol) dissolved in benzene (10 cm^3) was added dropwise to a solution of $[Pt(CNBu^t)_2(PPh_3)_2]$ (0.5 g, 0.565 mmol) in benzene (30 cm^3) under nitrogen at room temperature. The colour of the solution faded and became clear yellow on standing. After removal of all the solvent *in vacuo*, the

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[36] R. D. W. Kemmitt and R. D. Moore, *J. Chem. Soc.* (*A*), 1971, 2472.

[37] R. A. Walton, *Spectrochim. Acta*, 1965, **21**, 1795.

[38] J. Casanova, N. D. Werner, and R. W. Schuster, *J. Org. Chem.*, 1966, **31**, 3473.

[39] I. Ugi, R. Myer, M. Lipinski, F. Bodesheim, and F. Rosendahl, *Org. Synth.*, 1961, **41**, 13.

[40] I. Ugi and R. Myer, *Org. Synth.*, 1961, **41**, 101.

[41] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705.

[42] J. C. Bailar and H. Itatani, *J. Amer. Chem. Soc.*, 1967, **89**, 1592.

resulting oily yellow solid was washed with hexane. The pure solid was then extracted from this crude product with dichloromethane (*ca.* 10 cm^3), the solvent quickly removed, and the resulting pale yellow solid finally stirred overnight under hexane. After filtration and washing with pentane, the solid (yield *ca.* 50%) was dried *in vacuo, M* (cryoscopy, in acetone) 607 (calc. for dissociated complex: 514).

(c) *With triphenyltin chloride.* The procedure adopted was identical to that given in (b), the same quantity of $[Pt(CNBu^t)_2(PPh_3)_2]$ being used and treated with $[SnPh_3Cl]$ (0.127 g, 0.565 mmol). The product was obtained as a pale yellow solid (yield *ca.* 60%). The complex was too insoluble in acetone for reliable molecular weight measurements.

(d) *With trifluoromethyl iodide.* A slow stream of CF_3I was passed into a benzene solution of $[Pt(CNBu^t)_2(PPh_3)_2]$ (0.5 g, 0.565 mmol) under nitrogen at room temperature until a clear pale yellow solution was obtained (after *ca.* 5 min). The benzene solution of the product was then worked up in the same way as the products from (b) and (c), the final yield being *ca.* 60%.

Reaction of Di-iodobis(triphenylphosphine)platinum(II) *with* Bu^tNC.—The isocyanide (0.1 g, 1.03 mmol) in benzene (5 cm^3) was added to a stirred suspension of $[PtI_2(PPh_3)_2]$ (0.5 g, 0.515 mmol) in benzene (30 cm^3), and after stirring the reaction mixture for 15 min the intense yellow colour of the original solution had faded slightly. The solution was concentrated and the resulting yellow solid filtered off, washed with benzene and pentane, and dried *in vacuo.* The product was identical with that obtained in (a), namely $[Pt(CNBu^t)I(PPh_3)_2]I$, and a near quantitative yield (0.51 g) was obtained (Found: C, 47.9; H, 4.2; I, 21.4; N, 2.1. Calc. for $C_{48}H_{48}I_2N_2P_2Pt$: C, 48.5; H, 4.2; I, 22.3; N, 2.5%).

Reaction of Iodo(methyl)bis(triphenylphosphine)platinum(II) *with* Bu^tNC.—Using similar reaction conditions to the above reaction with the di-iodide, Bu^tNC (0.089 g, 0.107 mmol) was added to $[Pt(Me)(I)(PPh_3)_2]$ and the product (*ca.* 65% yield) was identical to the addition product obtained from the earlier reaction of $[Pt(CNBu^t)_2(PPh_3)_2]$ with MeI (Found: C, 53.5; H, 5.1; I, 13.4; N, 2.5. Calc. for $C_{49}H_{51}IN_2P_2Pt$: C, 54.8; H, 5.0; I, 12.4; N, 2.7%).

Preparation of Carbonyl(t-butyl isocyanide)bis(triphenylphosphine)platinum(0) $[Pt(CO)(CNBu^t)(PPh_3)_2]$.—Solid $[Pt(CNBu^t)_2(PPh_3)_2]$ (0.5 g, 0.565 mmol) was treated with carbon monoxide at 25 atm for 48 h, and after this time a compacted yellow solid was obtained. The solid was stirred in hexane under nitrogen for 2 h when the product was obtained as a pale yellow powder; after removal of the solvent it was dried by pumping *in vacuo* (yield *ca.* 80%) (Found: C, 60.3; H, 4.3; N, 2.0. Calc. for $C_{42}H_{39}NOP_2Pt$: C, 60.7; H, 4.7; N, 1.7%).

Reaction of Tris(triphenylphosphine)platinum(0) *with Triphenyltin Chloride.*—The complex $[Pt(PPh_3)_3]$ (2.5 g, 2.55 mmol) and $[SnPh_3Cl]$ (0.98 g, 2.55 mmol) were shaken together in benzene for 1 h. The white precipitate which was obtained was filtered off, washed with both benzene and pentane, and then dried *in vacuo* (Found: C, 55.2; H, 4.4; Cl, 8.9. Calc. for $C_{36}H_{30}Cl_2P_2Pt$: C, 54.5; H, 3.8; Cl, 8.9%).

Reaction of Dicyanobis(triphenylphosphine)platinum(II) *with* MeI.—The complex $[Pt(CN)_2(PPh_3)_2]$ (1.0 g, 1.3 mmol) was heated in a sealed tube with excess of MeI at 373 K for 2 h. The resulting yellow precipitate was filtered off, washed with hexane, recrystallised from dichloromethane, and dried *in vacuo* to yield yellow crystals. The i.r. spectrum of the product showed a ν(NC) absorption at 2 230 cm^{-1}, but no absorptions from Ph hydrogen atoms (Found: C, 9.5; H, 1.2; I, 47.8; N, 5.1. Calc. for $C_4H_6I_2N_2Pt$: C, 9.0; H, 1.1; I, 48.0; N, 5.3%).

Reaction between Bu^tNC (*and* Pr^iNC) *and Tetrafluoroethylenebis(triphenylarsine)platinum*(0).—A stirred suspension of $[Pt(AsPh_3)_2(C_2F_4)]$ (0.9 g, 1 mmol) in diethyl ether at room temperature was treated with Bu^tNC (0.16 g, 2 mmol) dissolved in a small quantity of ether. A clear solution formed immediately, and after stirring for 1 h the solvent was removed *in vacuo.* The crude solid was dissolved in dichloromethane and reprecipitated with hexane. The colourless crystals [m.p. 134 °C (decomp.)] were washed with hexane and dried *in vacuo*, average yield 60%. The preparation of the Pr^iNC complex was achieved in a similar way, except the colourless crystals [m.p. 147 °C (decomp.)] were precipitated on addition of absolute alcohol and yields averaged 55%.

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