Journal of Organometallic Chemistry, 112 (1976) 209—225

CHEMISTRY OF METAL HYDRIDES

XVII. ISOCYANIDE INSERTION INTO THE Pt—H BOND, AND THE FORMIMIDOYL LIGAND

D.F. CHRISTIAN, H.C. CLARK and R.F. STEPANIAK
Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7 (Canada)
(Received October 31st, 1975)

Summary

The complexes *trans*-[PtH(CNR)L_2]Cl (R = *p*-tolyl; L = PEt_3, PMe_2Ph) undergo insertion of isocyanide into the platinum—hydride bond in non-polar solvents to give the platinum formimidoyl complexes *trans*-PtCl(CHNR)L_2, apparently via five coordinate intermediates of the type HPtCl(CNR)L_2. Other complexes prepared include *trans*-PtX(CHNR)$(PEt_3)_2$ (X = I or CN), *trans*-[Pt{C(OMe)NR}-(CHNR)$(PEt_3)_2$] and *trans*-[Pt{$C(NHR)_2$}(CHNR)$(PMe_2Ph)_2$]Cl.

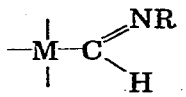
The infrared (ν(C—H) 2800 cm^{-1} and ν(C=N) ca. 1550 cm^{-1}) and ^{1}H NMR (τ(PtCH) —0.4 to —1.1 ppm) parameters characterize the formimidoyl ligand. The ^{1}H NMR spectra also show the presence of equilibria between *syn* and *anti* isomers, the mechanism of interconversion being thought to involve rotation through a polarized transition state. Contact shift studies on the complexes *trans*-PtCl(CHNR)L_2 indicate that the basicity of the imidoyl nitrogen varies between complexes and between *syn* and *anti* isomers of the same complex, but in general protonation—deprotonation results show it to be comparable to that of a weak amine.

Introduction

Just as the chemistry of the isocyanide ligand has recently attracted much interest, being a natural extension to the chemistry of the electronically similar carbonyl ligand, so also has the imidoyl ligand, the nitrogen analogue of the acyl group come under investigation. Three general methods of preparation of complexes containing the imidoyl group have been devised: (1) the insertion of isocyanides into metal—carbon bonds [1]; (2) nucleophilic attack on the isocyanide ligand by reagents like pentafluorophenyllithium [2,3], phenyllithium [4] and

the alkoxide ion [5]; and (3) oxidative addition of imidoyl chlorides [6,7].

The work reported here [8] concerns the investigation of platinum(II) complexes containing the formimidoyl ligand, CHNR, the nitrogen analogue of the formyl group, prepared by the insertion of isocyanide into a platinum—hydride bond.

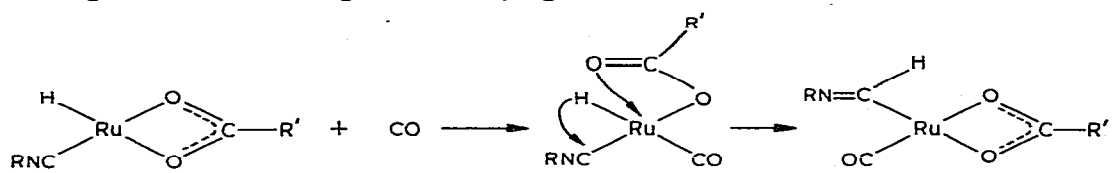


Other small unsaturated molecules found to interact with transition metal hydrides include CO_2 [9], NO [10], N_2 [11], CS_2 [12], SO_2 [13] and $(CF_3)_2CN$ [14] while such interactions with alkenes and alkynes have been extensively studied and the subject of many reviews.

An unusual reaction [15] between the dioxygen complex $Ru(O_2)(CO)(CNR)(PPh_3)_2$ and alcohols leading to the formimidoyl complex $Ru(CHNR)(R'CO_2)(CO)(PPh_3)_2$ (R = *p*-tolyl; R′ = methyl, ethyl or phenyl) initiated an earlier investigation which culminated in the isolation [16] of a series of formimidoyl complexes from the ruthenium hydride $RuH(R'CO_2)(CNR)(PPh_3)_2$. The present work serves not only to demonstrate the generality of this insertion reaction for other transition metal hydrides but also to provide further information about the formimidoyl ligand itself.

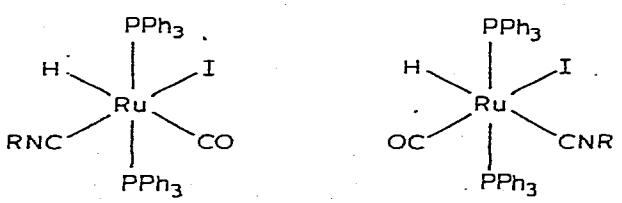
A. The synthesis of hydride precursors *

Two conditions favouring insertion into a transition metal—hydride bond became apparent from the earlier work with ruthenium. Of the many neutral and cationic ruthenium hydrido—isocyanide complexes prepared, complexes containing chelating ligands (viz. carboxylate and dialkyldithiocarbamate) were among the few to undergo insertion, e.g.:



(axial triphenylphosphine groups omitted for clarity)

In addition, of the two isomeric complexes $RuHI(CO)(CNR)(PPh_3)_2$, A and B, only A was converted to the formimidoyl complex on reaction with sodium



(A) (B)

* All new complexes reported in this paper have *trans*-phosphine groups. R = *p*-tolyl.

acetate. This implies, as expected, that a *cis*-hydride—isocyanide geometry is necessary before insertion takes place, but also, since several other complexes isolated with this geometry were stable, that the chelating effect of a potentially bidentate group must be an added inducement. Although initially in this study it was thought necessary to synthesize complexes of the type *cis*-$[PtH(CNR)L_2]^+$ for isocyanide insertion to take place, success was achieved with the well-known complex *trans*-$PtHCl(PEt_3)_2$ which is converted to an intermediate of appropriate geometry during the reaction.

The complexes $[PtH(CNR)L_2]Cl$ ($L = PEt_3$, PMe_2Ph; R = *p*-tolyl) proved to be suitable precursors for isocyanide insertion and could be obtained in quantitative yields as colourless precipitates from the slow dropwise addition of *p*-tolylisocyanide to a rapidly stirred ethereal solution (suspension for PMe_2Ph complex) of the starting hydrides, *trans*-$PtHClL_2$. Rapid addition, or use of an excess of isocyanide, led to the formation of an unidentified red byproduct which was difficult to separate from the product. The insertion product could be obtained directly from the reaction of *trans*-$PtHClL_2$ and isocyanide but the isolation of the cationic intermediates afforded a clean experimental route that avoided the formation of this byproduct. Both complexes $[PtH(CNR)L_2]Cl$ were hygroscopic and oiled after being exposed to air for several minutes. Due to its extreme sensitivity the dimethylphenylphosphine complex was characterized by comparison of physical properties and subsequent reaction rather than by elemental analyses.

Other hydride complexes examined include the complex $[PtH(CNR)(PEt_3)_2]$-

TABLE 1

IR AND ^{1}H NMR DATA FOR PLATINUM(II) HYDRIDE COMPLEXES [a]

Complex	Infrared frequencies [b] ν(C≡N) (cm^{-1})	^{1}H NMR signals [c]
$[PtH(CNR)(PEt_3)_2]Cl$	2190 vs	τ(PtH) 16.39 ppm J(PtH) 888 Hz ^2J(PPtH) 14.8 Hz τ(Me(*p*-tolyl)) 7.51 ppm
$[PtH(CNR)(PMe_2Ph)_2]Cl$	2195 vs [d]	
$[PtH(CNR)(PEt_3)_2]ClO_4$	2195 vs [d]	τ(PtH) 16.30 ppm J(PtH) 944 Hz ^2J(PPtH) 14 Hz
$[PtH(CNMe)(PEt_3)_2]ClO_4$	2270 vs	τ(PtH) 17.10 ppm J(PtH) 946 Hz ^2J(PPtH) 14 Hz τ(Me(CNMe)) 6.40 ppm ^4J(PtCNCH) 12.0 Hz
$[PtH(CNMe)(PEt_3)_2]SO_3F$	2238 vs	τ(PtH) 17.18 ppm J(PtH) 906 Hz ^2J(PPtH) 14 Hz τ(Me(CNMe) 6.40 ppm ^4J(PtCNCH) 12.0 Hz

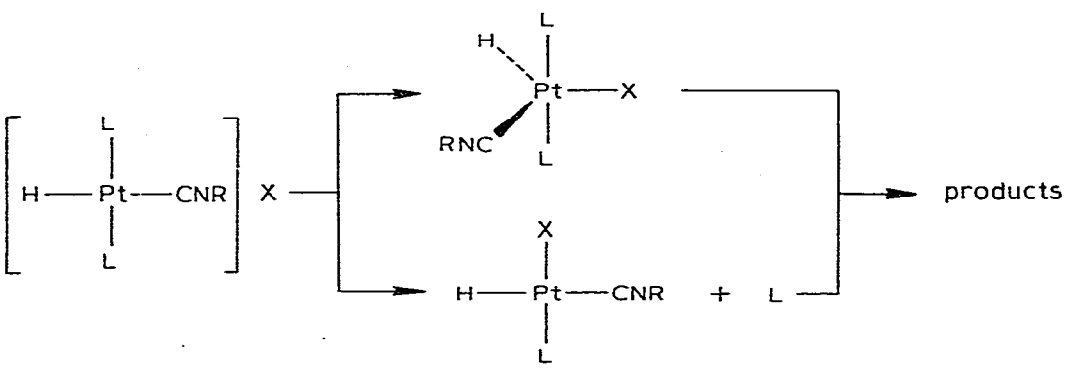
[a] All compounds were colourless and had *trans*-phosphine groups. R = *p*-tolyl. [b] IR spectra measured as Nujol mulls unless otherwise stated. [c] NMR spectra recorded in $CDCl_3$. [d] In dichloromethane.

ClO_4, prepared by the method [17] of Church and Mays, and the complexes $[PtH(CNMe)(PEt_3)_2]X$, ($X = SO_3F$, ClO_4) prepared by alkylation of *trans*-$PtHCN(PEt_3)_2$. All three compounds were colourless and obtained in nearly quantitative yields. The physical data for the hydride complexes are given in Table 1.

B. The insertion reaction

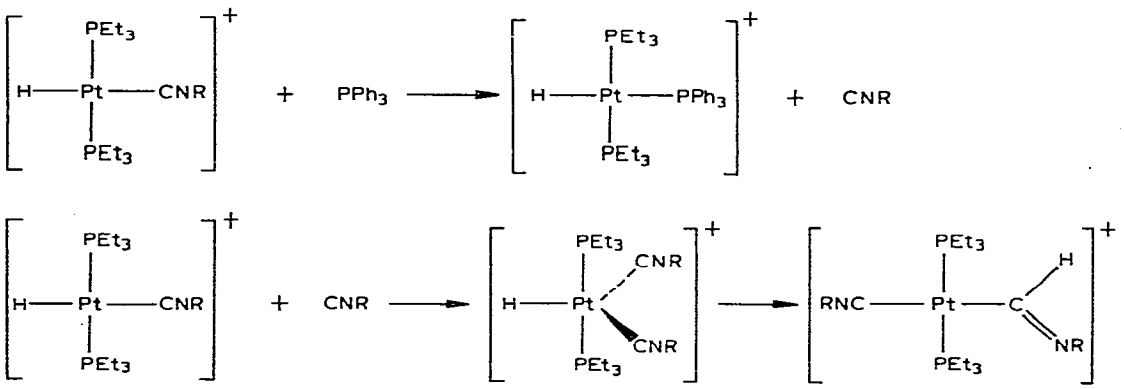
The insertion of isocyanide into the platinum—hydride bond of the complexes $[PtH(CNR)L_2]Cl$ ($L = PEt_3$, PMe_2Ph) takes place readily in non-polar solvents to give the formimidoyl complexes, $PtCl(CHNR)L_2$. NMR studies on samples of $[PtH(CNR)(PEt_3)_2]Cl$ show that the rate of insertion increases with an increase in temperature or with a decrease in polarity of the solvent. No reaction was observed in methanol at 35° C over 3 days, while quantitative insertion, at 35° C, took place in dichloromethane overnight and in a mixture of dichloromethane/n-pentane after 2 hours. On heating the cationic complex as a suspension in benzene, dissolution occurred at 60° C and the insertion reaction was found to have taken place immediately. On the other hand, the complex $[PtH(CN\text{-}p\text{-}tol)(PEt_3)_2]ClO_4$ and the complexes $[PtH(CNMe)(PEt_3)_2]X$ ($X = SO_3F$, ClO_4) were unaffected on dissolution in non-polar solvents even on extended heating for several hours. For example, in one experiment, the complex $[PtH(CNMe)(PEt_3)_2]SO_3F$ was recovered unchanged after heating to 95° C for three hours in dichloromethane/toluene (1 : 5).

Since non-polar solvents and a good coordinating anion are necessary for insertion to occur, a neutral intermediate is implicated. Of the two possibilities, $HPtCl(CNR)L_2$ and $HPtCl(CNR)L$, the five-coordinate complex is favoured since this can assume a suitable *cis*-hydride-isocyanide geometry immediately, without further rearrangement, while the four-coordinate intermediate, arising through phosphine dissociation requires further isomerization. On intuitive grounds, phosphine substitution by chloride at room temperature seems unlikely.



NMR studies on the insertion of $[PtH(CNR)(PEt_3)_2]Cl$ indicate that phosphine scrambling is occurring during the reaction but this does not shed light on the problem since the exchange can be rationalized by either mechanism. However, Treichel and Hess have proposed the same five-coordinate mechanism for the methylisocyanide insertion [16] into the platinum—carbon bond of the ionic complexes $[PtR(CNMe)(PEt_3)_2]X$ (R = Me, X = I; R = Ph, X = Cl, Br, or I). Fi-

nally, another five-coordinate intermediate was inferred in a related reaction in this study. The complexes $[PtH(CNR)(PEt_3)_2]ClO_4$ (R = Me, *p*-tolyl) were heated in solution at 50° C in the presence of excess triphenylphosphine to ascertain whether isocyanide insertion could be promoted by coordination of a good Lewis base instead of a coordinating anion. Since the intermediate would be cationic the relatively polar solvent, acetonitrile, was employed. The insertion reaction did take place, in one instance, but the unexpected product $[Pt(CHNR)(CNR)(PEt_3)_2]ClO_4$ (R = *p*-tolyl) was obtained as well as an equivalent amount of $[PtH(PPh_3)(PEt_3)_2]ClO_4$. This suggests initial isocyanide substitution by triphenylphosphine followed by coordination of the liberated isocyanide to another molecule of starting material with insertion.



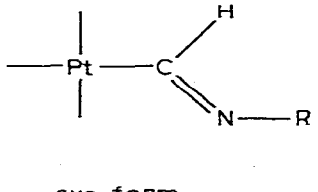
Whereas the reaction went to completion for the *p*-tolylisocyanide complex overnight, no reaction was observed for the methylisocyanide complex after one week. This could be due to greater difficulty of substitution since the better σ-donor would be more strongly bound in the cationic complex. Failure to isolate the expected product $[Pt(CHNR)(PPh_3)(PEt_3)_2]ClO_4$ could be attributed to the disinclination of triphenylphosphine to form a five-coordinate (18 electron) complex for electronic and possibly steric reasons.

Several other formimidoyl complexes were prepared. The strongly coordinating cyanide ligand was not displaced on addition of isocyanide to *trans*-$PtHCN(PEt_3)_2$ and the reaction gave $PtCN(CHNR)(PEt_3)_2$ directly, presumably via the analogous five-coordinate complex $HPtCN(CNR)(PEt_3)_2$. Removal of the chloride group from $PtCl(CHNR)(PEt_3)_2$ with silver perchlorate, in acetonitrile, followed by addition of lithium iodide gave the pale yellow iodo derivative $PtI(CHNR)(PEt_3)_2$, while reaction with isocyanide gave the cationic product $[Pt(CNR)(CHNR)(PEt_3)_2]ClO_4$. Unlike the analogous reaction [13] between $Ru(CHNR)(R'CO_2)(CO)(PPh_3)_2$ and iodide ions, no return of the hydrogen atom from ligand to metal was observed in the reaction between $PtCl(CHNR)(PEt_3)_2$ and silver perchlorate, in acetone, even on heating the solution under reflux. Two further interesting formimidoyl complexes, $Pt\{C(OMe)NR\}(CHNR)(PEt_3)_2$ and $[Pt\{C(NHR)_2\}(CHNR)(PMe_2Ph)_2]Cl$, were prepared from carbene complexes.

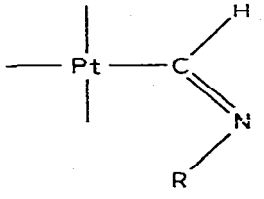
C. Properties

In common with many other imidoyl complexes reported [2,15,18,19,20], the formimidoyl compounds have a strong band in the 1500—1600 cm^{-1} region of the IR spectrum due to the C=N stretching mode. In addition, the solid state spectrum shows a characteristic medium sharp band near 2800 cm^{-1} arising from the CH stretching vibration. For the complex $PtCl(CHN\text{-}p\text{-}tol)(PEt_3)_2$ this occurs at 2810 cm^{-1} while it appears as a broader band at 2730 cm^{-1} in an acetonitrile solution spectrum.

The acidic character of the hydrogen atom in the formimidoyl group is further evidenced in the ^1H NMR spectrum by its resonance at low field (see Fig. 1). Parallel behaviour is reported [21] by Collman and Winter for the hydrogen atom of the electronically similar formyl ligand of $[Fe(HCO)(CO)_5]^-$ (ν(CH) 2690, 2540 cm^{-1}, τ(H of formyl) —4.95 ppm). For both the platinum complexes and the ruthenium complexes reported previously, coupling is observed between the formimidoyl hydrogen and the two mutually *trans*-phosphorus nuclei to give a 1 : 2 : 1 triplet but, in addition, some of the platinum complexes exhibit two sets of signals arising from different orientations of the *p*-tolyl group about the carbon—nitrogen double bond.



syn-form



anti-form

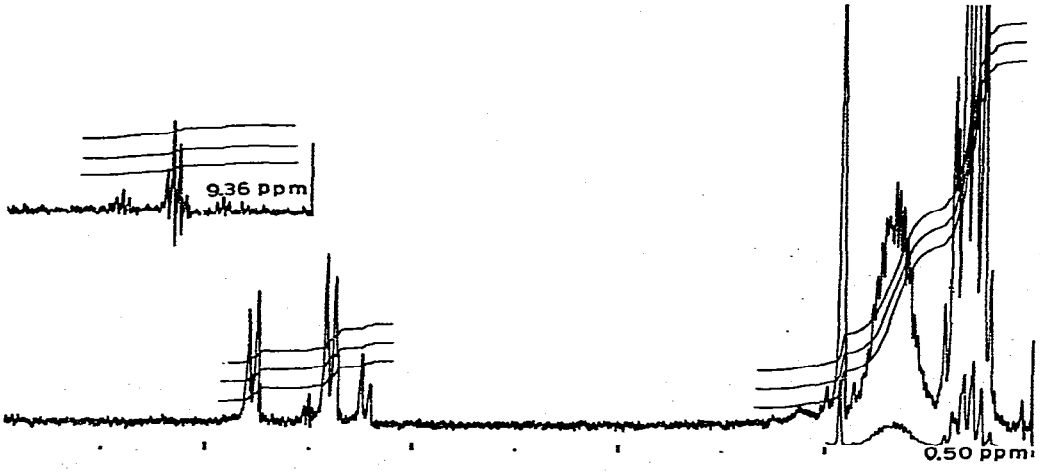


Fig. 1. ^1H NMR spectrum of *trans*-$PtCl(CHN\text{-}p\text{-}tol)(PEt_3)_2$ in $CDCl_3$. 1000 sweep width. 1 bold division = 2 ppm.

This isomerism has also been observed in the complexes $Mo(C(CH_2Ph)NC_6H_{11})(\pi\text{-Cp})(CO)_3$ [20] and $Fe(C(C_6F_5)NMe)(\pi\text{-Cp})(CO)(CNMe)$ [2], but whereas the isomers of the latter are separable by chromatography and undergo thermal isomerization, no change in isomer ratio was observed for $PtCl(CHNR)(PEt_3)_2$ after exposure to UV light in solution for 24 hours, or on extended heating (110° C in toluene for one week).

However, the ratio of intensity of the two sets of CHNR signals for $PtCl(CHNR)(PEt_3)_2$ and their relative positions varied in different solvents. This suggested an equilibrium that was delicately balanced being sensitive to small changes in solvation energies (see Table 2 and Fig. 2 and 3).

In a confirmatory test two identical stock samples were separately dissolved in chloroform-*d* and acetone-d_6 and their NMR spectra recorded. The samples were isolated, the solvents interchanged and the spectra recorded again. As expected, the intensity ratio of the signals observed was now characteristic of the new solvent. A variable temperature NMR study was performed in dimethylsulphoxide-d_6 using dimethylformamide as an internal standard. Coalescence of the two sets of signals occurred near 80° C giving an averaged signal. Above this temperature, the new signal sharpened further, while the original spectrum reappeared on cooling to room temperature. No change was observed at lower temperatures.

The two major pathways postulated [22] for *syn/anti* isomerization of organic imines are: (1) rotation about the C=N double bond made possible by polarization, (2) planar inversion of nitrogen (lateral shift mechanism).

In support of the torsion model the influence of substituents X on the imino carbon is seen as a dramatic decrease of the inversion barrier in the order: quinoneimine > ketimine > *C*-arylimine > iminoesters > guanidine. This shows that

TABLE 2

NMR PARAMETERS FOR *trans*-$PtCl(CHN\text{-}p\text{-}tol)(PEt_3)_2$ IN DIFFERENT SOLVENTS

Solvent	Isomer ratio (J small : J large)	τ(PtCH)	^2J(PtCH) (Hz)	^3J(PPtCH) (Hz)
C_6D_6	1.1 : 1	—0.88	91	5.5
		—0.78	115	6.5
C_7D_8	3 : 4	—0.77	92	5.8
		—0.73	116	6.3
$CDCl_3$	2 : 1	—0.67	93	5.5
		—0.62	117	5.8
CD_2Cl_2	3 : 2	—0.69	87	5.3
		—0.60	110.5	6.0
CD_3CN	1.1 : 1	—0.57	94	5.3
		—0.62	115	6.0
$(CD_3)_2CO$	1 : 1	—0.63	90	5.3
		—0.72	111	6.0
$(CD_3)_2SO$	1.4 : 1	—1.16	95.5	5.5
		—1.22	116	6.0
CH_3OH	2 : 1	—0.78	84	4.8
		—1.05	96	4.5

Fig. 2. ^{1}H NMR spectrum of *trans*-PtCl(CHN-*p*-tol)$(PEt_3)_2$ in CD_3CN. Downfield and aromatic region. 500 sweep width. 1 bold division = 1 ppm.

the better the electron-donating groups on carbon, the greater is the chance of isomerization. A recent report proposed such a dipolar mechanism for the isomerization about the C=C bond of transition metal vinylic complexes [21] since the rate of isomerization for the complexes RhIMe(CO)(vinyl)L_2 (L = phosphine) was found to increase with increasing donor ability of the phosphine ligands.

The results obtained here with the platinum complexes may also be interpreted on this basis. Two sets of downfield signals were evident for the complexes PtX(CHNR)$(PEt_3)_2$ (X = Cl, I or CN), PtCl(CHNR)$(PMe_2Ph)_2$ and [Pt(CNR)(CHNR)$(PEt_3)_2$]ClO_4 while for [Pt{C$(NHR)_2$}(CHNR)$(PMe_2Ph)_2$]Cl and Pt{C(OMe)NR}(CHNR)$(PEt_3)_2$ only one set was visible. The carbene ligand is known to be a good σ-donor. The fact that the formimidoyl ligand has a strong *trans* influence (the Ru—O distances for the bidentate acetate group of Ru(CHN-

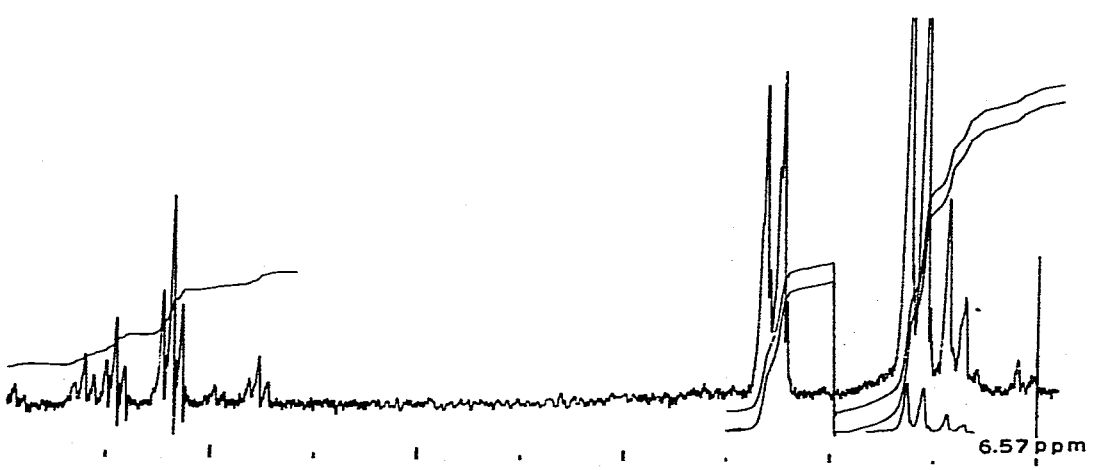
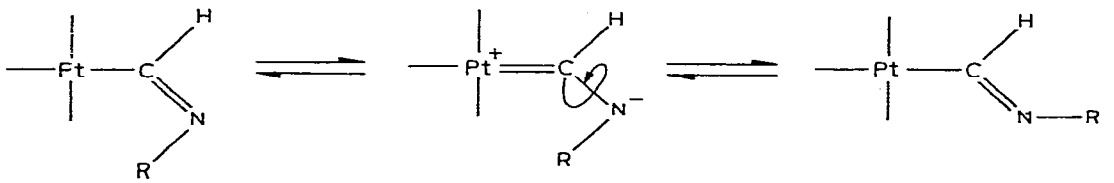


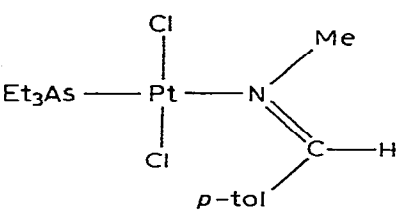
Fig. 3. ^{1}H NMR spectrum of *trans*-PtCl(CHN-*p*-tol)$(PEt_3)_2$ in MeOH. Downfield and aromatic region. 500 sweep width.

p-tol)($MeCO_2$)(CO)(PPh_3)$_2$ *trans* to CO and *trans* to formimidoyl are 2.173(8) and 2.279(8) Å respectively [24]) suggests that the methoxyimidoyl would also have a high *trans* influence and this is consistent with it acting as a good σ-donor. Consequently, more electron density on platinum is available for π-back donation to the carbon atom of the formimidoyl group in these cases increasing the chance of a polarized transition state and lowering the barrier to rotation. The significantly smaller platinum—imidoyl coupling constants, ^2J(PtCH), for the methoxyimidoyl and carbene complexes, a measure of the *s* character of the platinum—carbon bond, provides further support for this mechanism. (cf. Table 3). Thus, in these cases, the rate of interconversion may be too fast to be observed on the NMR time scale and an average signal is seen. The alternative pos-



sibility that only the thermodynamically stable isomers are present cannot be ruled out since cooling the methoxyimidoyl complex to —80° C in toluene-d_8 merely served to broaden the downfield signal.

Vrieze et al. have observed [25] that the *ortho* protons of the non-coordinated end of the imine ligand in PtCl (MeN=CH-*p*-tol)($AsEt_3$) show a large downfield shift (ca. 1.2 ppm) with respect to the free ligand. This effect was attributed to the close proximity of the platinum atom and an *ortho* proton due to a *trans* geometry of the coordinated ligand and this rationale is supported by preliminary structural results.



Similarly, one set of *ortho* aromatic protons in the complex PtCl(CHN-*p*-tol)-(PEt_3)$_2$ was displaced downfield (ca. 1 ppm) with respect to the free ligand. The *syn* and *anti* isomers could thus be assigned by analogy with the above results since the 2 : 1 ratio of isomers in chloroform-*d* made it easy to match the deshielded aromatic signal with the corresponding CHNR signal further downfield. The isomer with the smaller coupling constants was found to be the *anti* form.

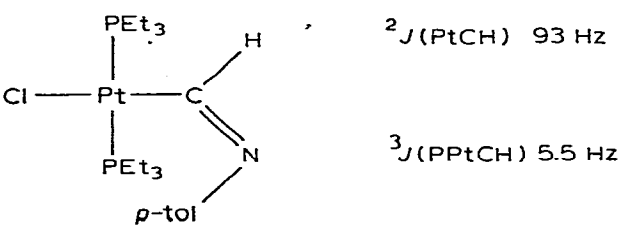


TABLE 3

IR AND ^{1}H NMR DATA FOR PLATINUM(II) FORMIMIDOYL COMPLEXES [a]

Complex	Infrared frequencies [b] (cm^{-1})	^{1}H NMR signals [c]
$PtCl(CHNR)(PEt_3)_2$	ν(CH) 2810m ν(C=N) 1560s (br) 1582s (sh)	τ(PtCH) —0.67, —0.62 ppm (2 : 1) [d] ^2J(PtCH) 93, 117 Hz ^3J(PPtCH) 5.5, 5.8 Hz τ(Me(*p*-tol)) 7.66 ppm
$PtCl(CHNR)(PMe_2Ph)_2$	ν(CH) — ν(C=N) 1550s [e]	τ(PtCH) —0.46, —0.57 ppm (1 : 1) ^2J(PtCH) 74, 78 Hz ^3J(PPtCH) 5.0, 5.5 Hz τ(Me(*p*-tol)) 7.77 ppm
$PtI(CHNR)(PEt_3)_2$	ν(CH) 2818m ν(C=N) 1565s (br) 1580vs (sh)	τ(PtCH) [f] —0.75, —0.54 ppm (3 : 1) ^2J(PtCH) 104, 135 Hz ^3J(PPtCH) 5.0, 6.5 Hz τ(Me(*p*-tol)) 7.66 ppm τ(PtCH) [g] —1.09, —0.75 ppm (3 : 2) ^2J(PtCH) 104.5, 133 Hz ^3J(PPtCH) 6.0, 6.5 Hz τ(Me(*p*-tol)) 7.80, 7.84
$PtCN(CHNR)(PEt_3)_2$	ν(CH) 2794m ν(C=N) 1558vs (br) 1580s (sh) ν(C≡N) 2119vs	τ(PtCH) —1.00, —0.77 ppm (1 : 1) ^2J(PtCH) 41, 58 Hz ^3J(PPtCH) 4.5, 5.0 Hz τ(Me(*p*-tol)) 7.63 ppm
$[Pt(CNR)(CHNR)(PEt_3)_2]ClO_4$	ν(CH) 2740m (br) ν(C=N) 1558s ν(C≡N) 2185vs	τ(PtCH) —0.75, —0.64 ppm (1 : 2) ^2J(PtCH) 56, 70 Hz ^3J(PPtCH) 6.0, 6.0 Hz τ(Me(*p*-tol)) 7.57, 7.64 ppm
$Pt(C(OMe)NR)(CHNR)(PEt_3)_2$	ν(CH) 2693s ν(C=N) 1545vs	τ(PtCH) —0.91, —1.12 ppm [h] ^2J(PtCH) 36.5, 39.3 Hz ^3J(PPtCH) 7.0, 7.8 Hz τ(Me(*p*-tol)) 7.74, 7.77, 7.75, 7.81 ppm τ(Me(OMe)) 6.35, 6.17 ppm
$[Pt\{C(NHR)_2\}(CHNR)(PMe_2Ph)_2]Cl$	ν(CH) 2728s (br) ν(C=N), ν(C=N) } 1540s (br)	τ(PtCH) —0.2 ppm ^2J(PtCH) 32 Hz ^3J(PPtCH) 6.5 Hz τ(NH) —2.17 ppm ^3J(PtCNH) 46 Hz τ(Me(*p*-tol)) 7.70, 7.77 ppm

[a] All compounds were colourless or pale yellow and had *trans*-phosphine groups; R = *p*-tolyl. [b] IR spectra measured as Nujol mulls unless stated otherwise. [c] NMR spectra recorded in $CDCl_3$ unless otherwise stated. [d] (x : y) Ratio of intensities of signals. [e] In dichloromethane. [f] NMR spectrum recorded in $CDCl_3/CD_2Cl_2$ (3 : 1). [g] NMR spectrum recorded in C_6D_6. [h] NMR spectrum recorded in $C_6D_5 \cdot CD_3$.

The fact that the nitrogen atom in imidoyl complexes is highly susceptible to electrophilic attack has been noted by several workers [6,26,27,28]. Protonation and methylation at nitrogen affords a simple route to carbene complexes and this will be dealt with more fully in a subsequent paper. Metathesis studies on $PtCl(CHNR)(PEt_3)_2$ with sodium cyanide and sodium perchlorate led to the cationic protonated carbene products $[PtCN(CHNHR)(PEt_3)_2]Cl$ and $[PtCl(CHNHR)(PEt_3)_2]ClO_4$ further demonstrating this susceptibility. Deprotonation of such carbene complexes was successful with triethylamine but not with *p*-toluidine indicating that the basicity of the formimidoyl nitrogen lay in

TABLE 4

PHYSICAL AND ANALYTICAL DATA FOR NEW PLATINUM COMPLEXES [a]

Complex	Analysis found (calcd.) (%)			Melting point [b] (°C)
	C	H	N	
$[PtH(CNR)(PEt_3)_2]Cl$ [c]	40.93 (41.06)	6.64 (6.55)	2.49 (2.39)	80
$[PtH(CNMe)(PEt_3)_2]SO_3F$	29.54 (29.37)	5.85 (5.99)	2.46 (2.45)	79—80
$[PtH(CNMe)(PEt_3)_2]ClO_4$	28.66 (29.35)	5.33 (5.98)	2.15 (2.45)	138—139
$PtCl(CHNR)(PEt_3)_2$ [d]	41.53 (41.06)	6.61 (6.55)	2.20 (2.39)	109
$PtCl(CHNR)(PMe_2Ph)_2$	46.29 (46.12)	4.81 (4.84)		133—135
$PtCN(CHNR)(PEt_3)_2$	43.64 (43.82)	6.64 (6.65)	4.93 (4.87)	96—97
$PtI(CHNR)(PEt_3)_2$ [e]	35.12 (35.51)	5.84 (5.66)	1.95 (2.07)	123—125
$Pt\{C(OMe)NR\}(CHNR)(PEt_3)_2$	50.32 (49.92)	6.89 (6.93)	3.98 (4.02)	105
$[Pt\{C(NHR)_2\}(CHNR)(PMe_2Ph)_2]Cl \cdot CH_2Cl_2$	51.68 (51.43)	5.11 (5.18)	4.46 (4.50)	170—172
$[Pt\{C(NHR)_2\}(CHNR)(PMe_2Ph)_2]PF_6$	48.27 (48.85)	4.73 (4.84)		196—197

[a] All complexes were colourless or pale yellow and has *trans*-phosphine groups; R = *p*-tolyl. [b] Melting points are uncorrected. [c] Found: Cl, 6.04. Calcd.: 6.06%. [d] Found: Cl, 6.50. Calcd.: 6.06%. [e] Found: I, 18.14. Calcd.: 18.76%.

this range. In fact, to reduce the likelihood of protonation, the complex $[Pt\{C(NHR)_2\}(CHNR)(PMe_2Ph)_2]Cl$ was crystallized for structural studies from pyridine.

Organic imines are known to be hydrolyzed easily by water to give the corresponding aldehyde and an amine.

$$R_2C{=}NR' + H_2O \rightarrow R_2CO + R'NH_2$$

In the hope of isolating the formyl complex $PtCl(CHO)(PEt_3)_2$, $PtCl(CHNR)(PEt_3)_2$ was heated under reflux in acetonitrile/water (50 ml; 2 : 1) for half an hour. The solution went from colourless to light orange and although some liberation of base was noted from pH measurements, unreacted starting material only was isolated.

When a lanthanide induced shift study was performed on $PtCl(CHNR)(PEt_3)_2$ using $Eu(fod)_3$ ($fod = CF_3(CF_2)_2COCH{=}C(O)^-C(CH_3)_3$) both the CHNR and the corresponding aromatic *ortho* proton signals of the *anti* isomer were broadened and considerably displaced downfield (see Fig. 4). The aromatic region, which had consisted of two overlapping AB quartets, now appeared as one AB and one AX quartet. Surprisingly, no interaction with the *syn* isomer was observed indicating a substantial difference in the basicities of the nitrogen atoms. However,

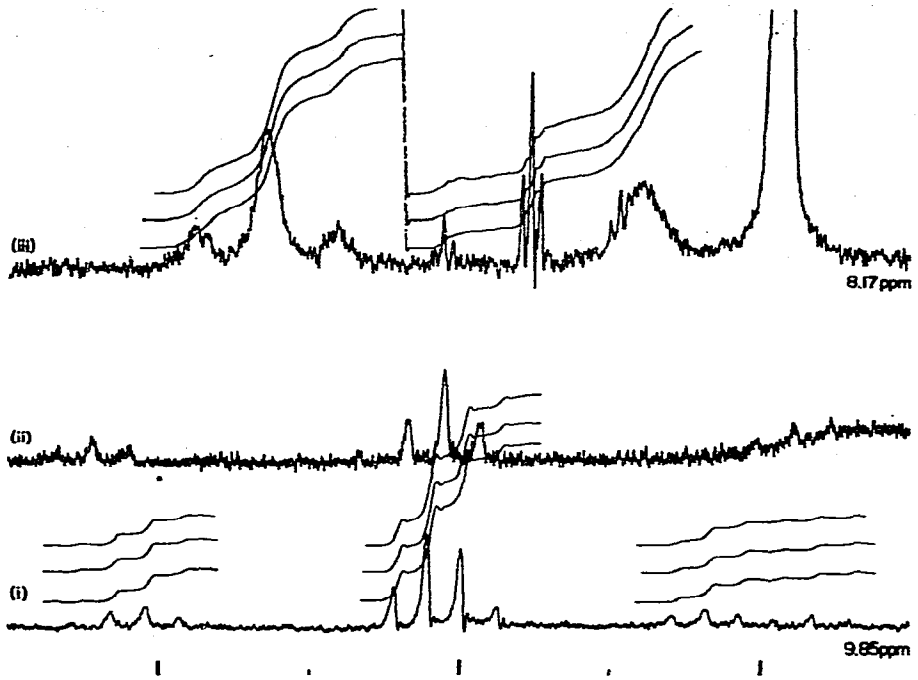


Fig. 4. Contact shift study on *trans*-PtCl(CHN-*p*-tol)$(PEt_3)_2$ in $CDCl_3$. (i) Original downfield spectrum. 250 sweep width. 1 bold division = 0.5 ppm. (ii) Downfield spectrum after addition of shift reagent, $Eu(fod)_3$. One isomer unaffected. 250 sweep width. (iii) Downfield spectrum after addition of shift reagent. 1000 sweep width. 1 bold division = 2 ppm. The strong signal at the right is from the *ortho* protons of the *anti* isomer. The broad signal next to it is from water.

both nitrogen atoms of the imidoyl isomers of $PtCl(CHNR)(PMe_2Ph)_2$ interacted with the europium complex although again the difference was quite marked. A clear record of changes occurring in the aromatic region was impossible due to masking by the aromatic protons of the phosphine ligands.

Conclusions

The successful preparation of a series of platinum formimidoyl complexes in addition to those obtained previously with ruthenium suggests that isocyanide insertion into transition metal—hydride bonds is a general reaction. Such is the case for isocyanide insertion into metal—alkyl and —aryl bonds which has now been reported for several different transition metals. However, for the insertion to occur, the starting complex should possess a *cis*-hydride-isocyanide geometry initially, or assume it during the reaction, and there must be a driving force to attain a more stable electronic configuration resulting from coordination by another ligand. Thus, in the ruthenium system, it was the chelating effect of a potentially bidentate ligand that provided the driving force for the reaction and in the platinum system the association of a coordinating anion in non-polar solvents. The fact that the insertion of isocyanide into the platinum—hydride bonds of these complexes appears to proceed via a five-coordinate mechanism may be compared with the results of studies on insertions with olefins and acetylenes.

In these latter studies, it has been found that the nature of the ligand *trans* to hydride determines whether four or five coordinate intermediates are involved in the insertion process. Five coordinate intermediates occur when the *trans* ligand is not readily displaced (e.g., $SnCl_3$), while for ligands such as Cl or NO_3, which are easily displaced by olefins or acetylenes, four coordinate intermediates occur [29]. While this suggests that $SnCl_2$ might catalyze isocyanide insertion just as it does for ethylene insertion [30] we found that $SnCl_2$ addition to a methanol solution of *p*-tolylisocyanide and *trans*-$PtHClL_2$ produced instantaneously a red coloration with neither hydrido nor formimidoyl resonances apparent in the ^1H NMR spectrum.

Syn/anti isomerism of the *p*-tolyl group about the C=N double bond was observed and the ease of interconversion found to be dependent on the platinum and its ligand environment. The presence of good σ-donor groups resulted in more π-back donation from the metal to the carbon of the *trans*-formimidoyl ligand and increased the rate of interconversion via a polarized transition state. The reduced *s* character of the platinum—carbon (formimidoyl) bond in these cases was evidenced by a substantially smaller platinum—hydrogen (formimidoyl) coupling constant.

The high susceptibility of the nitrogen atom of imidoyl ligands to electrophilic attack was further evidenced in this work. Lanthanide induced shift studies indicate that the basicity of the nitrogen does vary between complexes and between *syn/anti* isomers of the same complex but, in general, protonation—deprotonation results show it to be comparable to that of a weak amine. Although this property caused some difficulties in the preparation of formimidoyl compounds, in that protonation was occasionally encountered in work-ups, it nevertheless made possible the synthetic route to interesting secondary carbene complexes discussed in the subsequent paper.

Experimental

Infrared spectra in the range 4000—400 cm^{-1} were recorded on a Perkin—Elmer 621 Grating Spectrophotometer. Absorptions are quoted relative to the polystyrene band at 1601.4 cm^{-1}. The ^1H NMR spectra were recorded on a Varian HA 100 spectrometer. Analyses were obtained from Chemalytics, Inc., Tempe, Arizona. All reactions were performed with "spectro-analyzed" solvents without further purification. *p*-Tolylisocyanide was prepared by dehydration of the corresponding *N*-monosubstituted formamide.

(1) trans-Hydrido(p-tolylisocyanide)bis(triethylphosphine)platinum(II) chloride, trans-[HPt(CN-p-tol)(PEt_3)$_2$]Cl

To a vigorously stirred solution of *trans*-$HPtCl(PEt_3)_2$ (1.0 g) in anhydrous diethyl ether (30 ml) was added slowly dropwise a solution of *p*-tolylisocyanide (1 equiv.) in diethyl ether (10 ml). The clear solution became cloudy and the product was obtained as a colourless precipitate. The mother liquor was decanted and cooled to —15°C to give a small second crop of product, and the precipitate washed with diethyl ether and n-pentane and dried in vacuo. The yield was 1.1 g (88%). The product was hygroscopic but could be stored under nitrogen without decomposition.

(2) trans-Hydrido(p-tolylisocyanide)bis(dimethylphenylphosphine)platinum(II) chloride, trans-[HPt(CN-p-tol)(PMe_2Ph)$_2$]Cl

The colourless title complex was prepared from a suspension of *trans*-HPtCl(PMe_2Ph)$_2$ in anhydrous diethyl ether at —80° C by a method similar to (1). Since the product was very hygroscopic it was used immediately after preparation. The approximate yield was 90%.

(3) trans-Hydrido(p-tolylisocyanide)bis(triethylphosphine)platinum(II) perchlorate, trans-[HPt(CN-p-tol)(PEt_3)$_2$]ClO_4

The product was obtained as a colourless precipitate, in 90% yield, from an acetone solution of *trans*-HPtCl(PEt_3)$_2$ and *p*-tolylisocyanide using the method [17] of Church and Mays, and identified by comparison of physical properties (ν(C≡N) 2195 vs; τ(PtH) 16.30; J(PtH) 944 Hz; ^2J(PPtH) 14 Hz) with other analogues.

(4) trans-Hydrido(methylisocyanide)bis(triethylphosphine)platinum(II) fluorosulphate, trans-[HPt(CNMe)(PEt_3)$_2$]SO_3F

To a vigorously stirred solution of *trans*-HPtCN(PEt_3)$_2$ (0.2 g) in anhydrous diethyl ether (30 ml) was added a solution of methylfluorosulphate (0.05 g, 1 equiv.) in diethyl ether (10 ml). Colourless crystals were obtained which were filtered and washed with diethyl ether. Recrystallization was from dichloromethane/diethyl ether (0.18 g, 75%).

(5) trans-Hydrido(methylisocyanide)bis(triethylphosphine)platinum(II) perchlorate, trans-[HPt(CNMe)(PEt_3)$_2$]ClO_4

To a solution of *trans*-[HPt(CNMe)(PEt_3)$_2$]SO_3F (0.2 g) in acetone (20 ml) was added $NaClO_4$ (1 equiv.). The insoluble sodium fluorosulphate was removed by filtration, the solution evaporated to a small volume, and the colourless product precipitated by the addition of diethyl ether. Recrystallization was from dichloromethane/diethyl ether (0.18 g, 90%).

(6) trans-Chloro{N-(p-tolyl)formimidoyl}bis(triethylphosphine)platinum(II), trans-PtCl(CHN-p-tol)(PEt_3)$_2$

A saturated solution of *trans*-[HPt(CN-*p*-tol)(PEt_3)$_2$]Cl (2 g) in dichloromethane/n-pentane (1 : 3, 40 ml) was stirred slowly for 30 hours. The colour of the solution changed from light yellow to orange after about 2 hours. The end of the reaction was marked by the restoration of the yellow colour. The solution was evaporated under reduced pressure to a viscous oil, n-pentane (50 ml) was added and the product cooled to —15° C. Pale yellow crystals were obtained over one day (1.8 g, 90%). Recrystallization from acetonitrile gave colourless crystals.

(7) trans-Chloro{N-(p-tolyl)formimidoyl}bis(dimethylphenylphosphine)platinum(II), trans-PtCl(CHN-p-tol)(PMe_2Ph)$_2$

The title complex was obtained as a yellow-brown flocculant precipitate, in quantitative yields, by a method similar to (6). A few pale yellow crystals of analytical purity were obtained by recrystallization from dichloromethane/diethyl ether at —15° C. A better method of purification involved protonation of the

complex with concentrated hydrochloric acid (1 equiv.) in acetone, isolation of the carbene product and then deprotonation again with triethylamine. This removed the red byproduct that was formed in the preparation of the hydride starting material.

(8) trans-Cyano{N-(p-tolyl)formimidoyl}bis(triethylphosphine)platinum(II), trans-PtCN(CHN-p-tol)(PEt_3)$_2$

To a vigorously stirred solution of *trans*-HPtCN(PEt_3)$_2$ (0.2 g) in benzene (20 ml) was added slowly dropwise a solution of *p*-tolylisocyanide (1 equiv.) in benzene (10 ml) and the solution heated at 40°C overnight. The solution was evaporated to dryness and the product extracted into hot n-pentane. Pale yellow crystals of the title complex were obtained on cooling the pentane to —15°C for several hours (0.14 g, 70%).

(9) trans-Iodo{N-(p-tolyl)formimidoyl}bis(triethylphosphine)platinum(II), trans-PtI(CHN-p-tol)(PEt_3)$_2$

To *trans*-PtCl(CHN-*p*-tol)(PEt_3)$_2$ (0.3 g) in acetonitrile (15 ml) was added silver perchlorate (1 equiv.). The precipitate was removed by filtration and sodium iodide (1 equiv.) added. The solution was evaporated to dryness and the product extracted into dichloromethane. Pale yellow crystals were obtained on the addition of diethylether and cooling to —15°C (0.26 g, 75%). Recrystallization was from dichloromethane/diethyl ether.

(10) trans{N-(p-tolyl)formimidoyl}(p-tolylisocyanide)bis(triethylphosphine)-platinum(II) perchlorate, trans-[Pt(CN-p-tol)(CHN-p-tol)(PEt_3)$_2$](ClO_4)

Method 1. To *trans*-PtCl(CHN-*p*-tol)(PEt_3)$_2$ (0.3 g) and sodium perchlorate (1 equiv.) in acetone (50 ml) was added a solution of *p*-tolylisocyanide (1 equiv.) in acetone (10 ml) slowly dropwise. The solution was evaporated to an oil, and the product extracted into dichloromethane and worked up to a powdery solid with n-pentane. Analytically pure crystals were not obtained and the compound was characterized by spectroscopic methods and subsequent reactions which also indicated the reaction had taken place quantitatively (ν(C≡N) 2185 cm^{-1}, vs; ν(C=N) 1558 cm^{-1}, s).

The following formimidoyl complexes were prepared from carbene complexes, the preparation of these latter compounds being described in the subsequent paper.

(11) trans-(N-(p-tolyl)formimidoyl)(p-tolylisocyanide)bis(triethylphosphine)-platinum(II) perchlorate, trans-[Pt(CN-p-tol)(CHN-p-tol)(PEt_3)$_2$]ClO_4

Method 2. To *trans*-[Pt(CN-*p*-tol)(CHNH-*p*-tol)(PEt_3)$_2$](ClO_4)$_2$ in dichloromethane was added triethylamine (4 equiv. i.e., excess). The triethylammonium perchlorate byproduct was extracted into water, the dichloromethane dried over magnesium sulphate, filtered and evaporated to an oil. The product was worked up to a powdery solid with n-pentane, as previously.

(12) trans-{N-(p-tolyl)formimidoyl}{N-(p-tolyl)methoxyimidoyl}bis(triethylphosphine)platinum(II), trans-Pt(CHN-p-tol)(C(OMe)N-p-tol)(PEt_3)$_2$

To a suspension of *trans*-[Pt(CN-*p*-tol)(CHNH-*p*-tol)(PEt_3)$_2$](ClO_4)$_2$ (0.2 g) in

methanol (20 ml) was added a dilute solution of sodium methoxide (0.1 g NaOH in 15 ml methanol) until all the solid had dissolved. The solution was evaporated to an oil and washed with water. The product was extracted into dichloromethane, the solution dried over magnesium sulphate, filtered and evaporated to an oil. The colourless product was precipitated from n-pentane at −15°C. Recrystallization was from n-pentane at −15°C (0.12 g, 75%).

(13) trans-{N-(p-tolyl)formimidoyl}{di(p-tolylamino)carbene}bis(dimethylphenylphosphine)platinum(II) chloride, trans-[Pt(C(NH-p-tol)$_2$)(CHN-p-tol)-(PMe$_2$Ph)$_2$]Cl

To *trans*-[PtCl(CHNH-*p*-tol)(PMe$_2$Ph)$_2$]Cl (0.3 g) in dichloromethane (50 ml) was added dropwise over 30 minutes a solution of *p*-tolylisocyanide (1 equiv.) in dichloromethane (20 ml). Stirring was continued until the smell of isocyanide dissipated and then *p*-toluidine was added (4 equiv.) and the reaction continued overnight. The solution was evaporated to dryness and the excess *p*-toluidine removed by washing with diethyl ether. The product was redissolved in the minimum amount of dichloromethane, triethylamine (2 equiv.) added and the title complex obtained as a colourless precipitate on the addition of n-pentane. Recrystallization from dichloromethane/diethyl ether returned the complex as a dichloromethane solvate (0.3 g, 80%). Elemental analyses were also obtained on the hexafluorophosphate salt obtained by anion exchange using silver hexafluorophosphate. Successful recrystallization could also be effected from pyridine/diethyl ether.

Acknowledgements

The continued financial support of the National Research Council of Canada is gratefully acknowledged.

References

1 Y. Yamamoto and H. Yamazaki, Coord. Chem. Rev., 8 (1972) 225.
2 P.M. Treichel and J.P. Stenson, Inorg. Chem., 8 (1969) 2563.
3 P.M. Treichel, J.J. Benedict, R.W. Hess and J.P. Stenson, J. Chem. Soc. D, (1970) 1627.
4 Y. Yamamoto, H. Yamazaki and N. Hagihara, J. Organometal. Chem., 18 (1969) 189.
5 P.M. Treichel, W.J. Knebel and R.W. Hess, J. Amer. Chem. Soc., 93 (1971) 5424.
6 M.F. Lappert and A.J. Oliver, J. Chem. Soc., Chem. Commun., (1972) 274.
7 M.F. Lappert and A.J. Oliver, J. Chem. Soc., Dalton Trans., (1974) 65.
8 Preliminary communication: D.F. Christian and H.C. Clark, J. Organometal. Chem., 85 (1975) C9.
9 L.S. Pu, A. Yamamoto and S. Ikeda, J. Amer. Chem. Soc., 90 (1968) 3896.
10 K.R. Grundy, C.A. Reed and W.R. Roper, J. Chem. Soc., Chem. Commun., (1970) 1501.
11 J. Chatt, G.A. Heath and R.L. Richards, J. Chem. Soc., Chem. Commun., (1972) 1010.
12 D. Commereuc, I. Douek and G. Wilkinson, J. Chem. Soc. (A), (1970) 771.
13 J.J. Levison and S.D. Robinson, J. Chem. Soc., Dalton Trans., (1972) 2012.
14 B. Cetinkaya, M.F. Lappert and J. McMeeking, J. Chem. Soc., Chem. Commun., (1971) 215.
15 D.F. Christian, G.R. Clark, W.R. Roper, J.M. Waters and K.R. Whittle, J. Chem. Soc., Chem. Commun., (1972) 458.
16 D.F. Christian and W.R. Roper, J. Organometal. Chem., 80 (1974) C35.
17 M.J. Church and M.J. Mays, J. Chem. Soc. (A), (1968) 3074.
18 P.M. Treichel and R.W. Hess, J. Amer. Chem. Soc., 92 (1970) 4731.
19 Y. Yamamoto and H. Yamazaki, Bull. Chem. Soc. Jap., 44 (1971) 1873.
20 Y. Yamamoto and H. Yamazaki, J. Organometal. Chem., 24 (1970) 717.
21 J.P. Collman and S.R. Winter, J. Amer. Chem. Soc., 95 (1973) 4089.

22 H-O. Kalinowski and H. Kessler in N.L. Allinger and E.L. Eliel (Eds.), Topics in Stereochemistry, Vol. 7, Interscience, London, 1973, p. 332.
23 D.W. Hart and J. Schwartz, J. Organometal. Chem., 87 (1975) C11.
24 D.F. Christian, G.R. Clark, W.R. Roper, J.M. Waters and K.R. Whittle, unpublished results.
25 J.F. Van Baar, K. Vrieze and D.J. Stufkens, J. Organometal. Chem., 81 (1974) 247.
26 P.M. Treichel, J.J. Benedict, R.W. Hess and J.P. Stenson, J. Chem. Soc., Chem. Commun., (1970) 1627.
27 B. Crociani, M. Nicolini and T. Boschi, J. Organometal. Chem., 33 (1971) C81.
28 P.J. Fraser, W.R. Roper and F.G.A. Stone, J. Organometal. Chem., 50 (1973) C54.
29 H.C. Clark, C.R. Jablonski and C.S. Wong, Inorg. Chem., 14 (1975) 1332.
30 H.C. Clark, C.R. Jablonski, J. Halpern, A. Mantovani and T.A. Weil, Inorg. Chem., 13 (1974) 1541.