Journal of Organometallic Chemistry, 112 (1976) 227—241

CHEMISTRY OF METAL HYDRIDES

XVIII *. THE FORMATION OF SECONDARY CARBENE COMPLEXES FROM IMIDOYL DERIVATIVES

D.F. CHRISTIAN, H.C. CLARK and R.F. STEPANIAK
Department of Chemistry, University of Western Ontario, London, Ontario (Canada)

(Received October 31st, 1975)

Summary

Protonation of *trans*-$PtCl(CHNR)(PEt_3)_2$ occurs reversibly to give the cation *trans*-$[PtCl(CHNHR)(PEt_3)_2]^+$ while methylation gives *trans*-$[PtCl(CHNMeR)(PEt_3)_2]^+$. The further secondary carbene complexes *trans*-$[PtL(CHNMeR)(PEt_3)_2]^{2+}$ (L = PPh_3, CNR) and *trans*-$[Pt(CNR)(CHNHR)(PEt_3)_2]^{2+}$ were prepared from these and the complex *trans*-$[Pt(CNR)(CHNHR)(PMe_2Ph)_2]^{2+}$ by a similar route. The latter compound reacts with *p*-toluidine to give *trans*-$[Pt\{C(NHR)_2\}(CHNHR)(PMe_2Ph)_2]^{2+}$ which may be deprotonated by the stronger base triethylamine to the formimidoyl-carbene complex *trans*-$[Pt\{C(NHR)_2\}(CHNR)(PMe_2Ph)_2]^+$. *trans*-$[Pt(CNR)(CHNHR)(PEt_3)_2]^{2+}$ does not react with *p*-toluidine but gives the bis-imidoyl complex *trans*-$Pt\{C(OMe)NR\}(CHNR)(PEt_3)_2$ on reaction with methoxide ion.

The platinum secondary carbene complexes are characterized by a broad low-field C(carbene)—H signal in their ^1H NMR spectra and a strong absorption due to ν(C(carbene)—N) in the 1500—1600 cm^{-1} region of their infrared spectra. The infrared spectra of the *p*-tolylaminocarbene complexes indicate some hydrogen bonding interaction with the counteranion. The ^1H NMR spectra of the carbene complexes provide evidence for restricted rotation about the C—N bond, the ratio of the isomers varying with solvent. NH signals at very low field coupled to the C(carbene)—H signals were visible for *trans*-$[PtCl(CHNHR)(PMe_2Ph)_2]Cl$ and *trans*-$[Pt(CNR)(CHNHR)L_2]X_2$ (L = PEt_3, X = ClO_4; L = PMe_2Ph, X = PF_6) when recorded in chloroform-*d*. For *trans*-$[Pt(CNR)(CHNHR)(PEt_3)_2](ClO_4)_2$ in acetonitrile-d_3, however, the NH signal and the coupling were lost due to rapid NH exchange. Addition of acid, or cooling, always resulted in the appearance of the NH signals and the CH⎯NH coupling. The magnitude of this coupling (≈10 or ≈18 Hz) identified the signals for each isomer.

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* For part XVII see ref. 10.

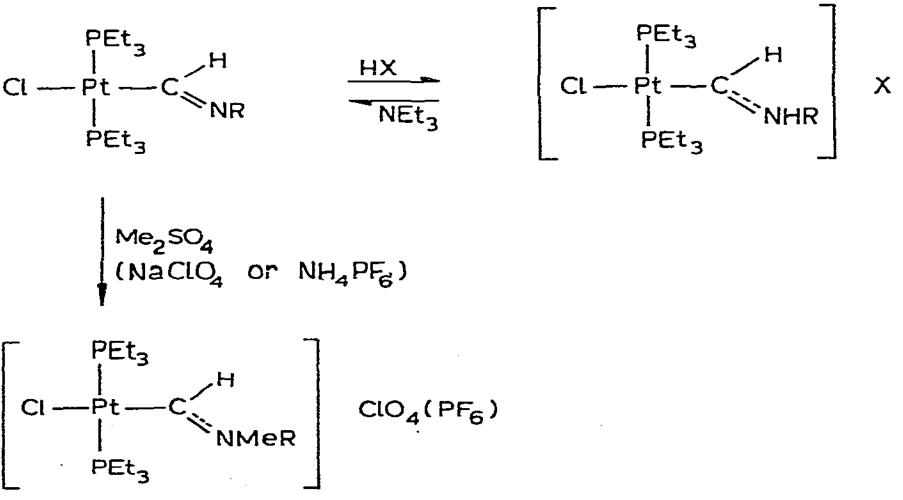
Introduction

Numerous transition metal carbene complexes have been synthesized in recent years but reports of carbene complexes with a hydrogen bound to the carbene carbon, called secondary, are still relatively uncommon. A series of rhodium(III) secondary carbene complexes [1] has been characterized by Lappert and coworkers (as well as some compounds [2] of iron, chromium, iridium and platinum) and several divalent ruthenium complexes [3] reported by Roper. The only other well-documented examples are some unusual boron heterocyclic chelate complexes [4] of molybdenum(II), manganese(II) and iron(III). Just as for the ruthenium system, the synthetic route to the platinum secondary carbene complexes reported here relies on the susceptibility to electrophilic attack of the coordinated imidoyl group, (M—C=NR). Methylation at nitrogen leads to stable carbene complexes which can be subsequently converted to doubly-charged carbene products, while protonation, being reversible, affords a system of additional versatility.

There is a striking correlation of chemical and physical properties between the rhodium and ruthenium systems, e.g. the structural data for the complexes RhCl$_3$(CHNMe$_2$)(PEt$_3$)$_2$ [1] and RuI$_2$(CHNMe-*p*-tol)(CO)(CN-*p*-tol)(PPh$_3$) [5] are in close accord, demonstrating a large *trans*-influence for the secondary carbene ligand, a high bond order for the carbon(carbene)—nitrogen bond and a marked deviation in the M—C—N bond angle from the idealized value of 120° for trigonal carbon. The generality of these observations finds additional support in the results obtained with the new platinum secondary carbene complexes.

A. Syntheses *

The complex PtCl(CHNR)(PEt$_3$)$_2$ reacts readily with hydrochloric, or perchloric acid and with dimethylsulphate (in the presence of sodium perchlorate or ammonium hexafluorophosphate) to give cationic secondary carbene products.



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

Protonation could be reversed with triethylamine which provided a means of isolating formimidoyl compounds particularly susceptible to protonation in their preparation or work-up. In particular, the formimidoyl complex, $PtCl(CHNR)(PMe_2Ph)_2$, could be separated from the red byproduct that persisted in its preparation by protonation to give the nicely crystalline colourless carbene complex $[PtCl(CHNHR)(PMe_2Ph)_2]^+$. A lengthy reaction sequence to the interesting tertiary carbene formimidoyl complex $[Pt\{C(NHR)_2\}(CHNR)(PMe_2Ph)_2]Cl$ incorporated such a protonation—deprotonation cycle. The presence of carbene complexes as intermediates ensured a clean experimental route and the strong *trans*-influence of the secondary carbene group both allowed facile displacement of chloride by isocyanide and subsequently activated the latter group to nucleophilic attack by the amine.

$$PtCl(CHNR)(PMe_2Ph)_2 \xrightarrow{HCl} [PtCl(CHNHR)(PMe_2Ph)_2]Cl \xrightarrow{CNR}$$

$$[Pt(CNR)(CHNHR)(PMe_2Ph)_2]Cl_2 \xrightarrow{RNH_2} [Pt\{C(NHR_2\}(CHNHR)(PMe_2Ph)_2]Cl_2$$

$$\xrightarrow{NEt_3} [Pt\{C(NHR)_2\}(CHNR)(PMe_2Ph)_2]Cl$$

Displacement of the chloride group in $[PtCl(CHNMeR)(PEt_3)_2]ClO_4$ by silver perchlorate followed by reaction with isocyanide or triphenylphosphine led to the formation of doubly-charged carbene complexes $[PtL(CHNMeR)(PEt_3)_2](ClO_4)_2$ ($L = CNR, PPh_3$). The protonated carbene complexes $[Pt(CNR)(CHNHR)(PEt_3)_2](ClO_4)_2$ and $[Pt(CNR)(CHNHR)(PMe_2Ph)_2](PF_6)_2$ were prepared by a similar method. Although the dimethylphenylphosphine complex underwent *p*-toluidine addition to the coordinated isocyanide no reaction was observed with the triethylphosphine complex. However, reaction of the latter with methoxide ion gave $Pt\{C(OMe)NR\}(CHNR)(PEt_3)_2$ as described in the previous paper.

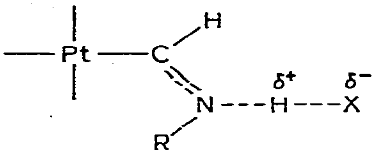
Such amine addition reactions appear to be taking place competitively with isocyanide insertion in the reactions of the well-known complexes *trans*-$PtHClL_2$ ($L = PEt_3, PMe_2Ph$) with isocyanide and *p*-toluidine in benzene. Whereas the complex $[PtH(CNR)(PEt_3)_2]Cl$ undergoes instantaneous isocyanide insertion on dissolution with heating in benzene, the presence of *p*-toluidine in the reaction of *trans*-$PtHCl(PEt_3)_2$ with isocyanide gives a 35% yield of the carbene compound $[PtH\{C(NHR)_2\}(PEt_3)_2]Cl$ as well as the expected product. The only other cationic hydrido-carbene complexes reported [6] *trans*-$[PtH(CNMeCH_2CH_2NMe)(PEt_3)_2]X$ ($X = Cl$, $\nu(PtH)$ 2025 cm^{-1}, $\tau(PtH)$ 17.2 ppm; $X = BF_4$, $\nu(PtH)$ 2040 cm^{-1}, $\tau(PtH)$ 16.9 ppm) have similar spectral parameters for the hydride ligand. It is interesting to note that although the complex $[PtH\{C(NHR)_2\}(PEt_3)_2]Cl$ was air stable the complex $[PtH(CNMeCH_2CH_2NMe)(PEt_3)_2]Cl$ is reported to be very hygroscopic just like the isocyanide complexes $[PtH(CNR)L_2]Cl$ ($L = PEt_3, PMe_2Ph$) employed in this study.

$$PtHCl(PEt_3)_2 + CNR + p\text{-}MeC_6H_4NH_2 \xrightarrow{C_6H_6} \left[\begin{array}{l} \rightarrow PtCl(CHNR)(PEt_3)_2 \\ \qquad (65\%) \\ \rightarrow [PtH\{C(NHR)_2\}(PEt_3)_2]Cl \\ \qquad (35\%) \end{array} \right.$$

The reaction of *trans*-$PtHCl(PMe_2Ph)_2$ with isocyanide and *p*-toluidine in benzene also gave the insertion product in major yield but, in addition, a small amount of the formimidoyl carbene complex $Pt\{C(NHR)_2\}(CHNR)(PMe_2Ph)_2$ was isolated.

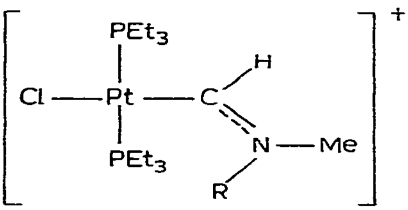
B. Properties

The platinum secondary carbene complexes are characterized by a broad C(carbene)—H signal in the low field of their ^1H NMR spectra (τ —1.9 to —0.6 ppm) and by a strong absorption (1535 to 1575 cm^{-1}) in their IR spectra due to the C(carbene)—N stretching mode (see Table 1). This is totally analogous to the ruthenium (ν(C═N) 1500 to 1560 cm^{-1}; τ —1.2 to 0.15 ppm) and rhodium (ν(C═N) 1580 to 1630 cm^{-1}; τ —1.5 to 1 ppm) systems and supports the previous conclusions that these secondary carbene ligands are characterized by a high C—N bond order. The solid state IR spectra of the platinum *p*-tolylaminocarbene complexes was of additional interest. Both the complexes $[PtCl(CHNHR)L_2]Cl$ (L = PEt_3, PMe_2Ph) exhibited very broad and low N—H stretching frequencies around 2600 cm^{-1} while the complexes $[PtCl(CHNHR)(PEt_3)_2]ClO_4$ and $[Pt(CNR)(CHNHR)(PEt_3)_2](ClO_4)_2$ had four absorptions between 3100 and 3250 cm^{-1}. In addition, the Cl—O stretching frequency of the perchlorate ions was split (τ_2 splitting 60 cm^{-1} for singly-charged and 45 cm^{-1} for doubly-charged cationic complex) for these *p*-tolylaminocarbene complexes but not in the corresponding *p*-tolylmethylaminocarbene complexes. Similar behaviour had been observed for some perchlorate complexes of ruthenium. Following D_2O exchange, ν(ND) for $[PtCl(CHNDR)(PEt_3)_2]Cl$ occurred at 2010 s (br) ($\nu(NH)/\nu(ND) = 1.28$) and for $[PtCl(CHNDR)(PEt_3)_2]ClO_4$, ν(ND) occurred at 2335 cm^{-1}. As expected, the two NH bending frequencies which had appeared near 1620 cm^{-1} were now absent but perchlorate association in the latter complex was still evident. There must be substantial hydrogen bonding in the solid state to account for these observations, particularly in the chlorides. The evidence of perchlorate association strongly suggests that this H-bonding is taking place with the anion. It was significant that the *p*-tolylaminocarbene complex with the most weakly coordinating anion, $[Pt(CNR)(CHNHR)(PMe_2Ph)_2](PF_6)_2$, did not show evidence of this interaction since its infrared spectrum had a single strong NH stretching absorption at higher frequency (viz., 3290 cm^{-1}).

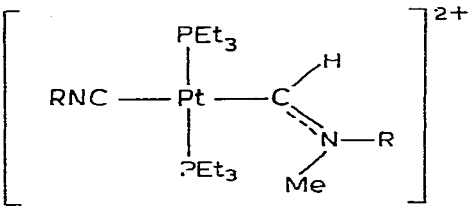


The C(carbene)—H signal in the ^1H NMR spectra of $[PtCl(CHNMeR)(PEt_3)_2]ClO_4$ and $[Pt(CNR)(CHNMeR)(PEt_3)_2](ClO_4)_2$, recorded in chloroform-*d*, appears as a broad triplet of triplets due to coupling of the hydrogen with the spins of the two mutually *trans*-phosphorus and platinum nuclei. Both coupling constants, ^2J(PtCH) and ^3J(PPtCH), for these and other platinum complexes studied, were proportionally smaller than in the parent formimidoyl complexes perhaps reflecting the increased π-character of the metal—carbon(carbene) bond [7].

For the complex $[Pt(CNR)(CHNMeR)(PEt_3)_2](ClO_4)_2$ the NMe signal is a broad singlet at τ 5.62 ppm while for $[PtCl(CHNMeR)PEt_3)_2](ClO_4)_2$ two NMe signals were located at τ 5.72 ppm (intensity 1) and τ 5.81 ppm (intensity 4). The appearance of the aromatic region confirmed the presence of more than one isomer in the latter case demonstrating restricted rotation about the C(carbene)—N bond. For reasons to be discussed subsequently the isomer of $[PtCl(CHNMeR)(PEt_3)_2](ClO_4)_2$ in 80% abundance is designated the one with the methyl group *cis* to the hydrogen whereas the complex $[Pt(CNR)(CHNMeR)(PEt_3)_2](ClO_4)_2$ is almost completely the *trans* isomer.



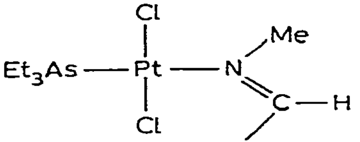
cis



trans

Two NMe signals, presumably of the same magnitude, were reported for the dimethylaminocarbenerhodium complexes and in a variable temperature study on one of them, in α-bromonaphthalene, no coalescence was observed up to 150°C. The complex $[Pt(PPh_3)(CHNMeR)(PEt_3)_2](ClO_4)_2$ had two NMe signals of similar intensity and two CH signals. The observations that the CH signals of the two isomers are not averaged on the ^1H NMR time scale in this case, and that the isomer ratio was substantially different for the three *p*-tolylmethylamino complexes studied, led to a more detailed investigation on the many *p*-tolylaminocarbene complexes prepared.

The ^1H NMR spectrum of $[PtCl(CHNHR)(PEt_3)_2]Cl$, recorded in chlorofrom-*d* at 32°C, also exhibited a broad triplet of triplets for the C(carbene)—H signal. The aromatic region which consisted of an *AB* and an *AX* quartet of equal intensity indicated that both *cis* and *trans* (hydrogen to hydrogen) isomers were present in equal amounts. The signal for the *ortho* protons of the complex $PtCl_2(MeN{=}CH\text{-}p\text{-}tol)(AsEt_3)$ [8] is considerably displaced downfield (ca. 1.2 ppm) with respect to the free ligand and this has been attributed to the interaction of the *ortho* protons of the *p*-tolyl group with the platinum as a result of the complex having the structure shown.



Such behaviour was also observed by us in the platinum formimidoyl complexes described in the preceding paper of this series [10] and made possible the assignment of *syn* and *anti* isomers in those systems. The effect is even more pronounced for the secondary carbene complexes where, for example, the centre of the *ortho* signal for the *cis* isomer of $[PtCl(CHNHR)(PEt_3)_2]Cl$ is as low

(continued on p. 234)

TABLE 1

IR AND ^{1}H NMR DATA FOR *p*-TOLYLAMINOCARBENE COMPLEXES [a]

Complex [b]	Infrared frequencies [c] (cm^{-1})	^{1}H NMR signals			
		CDCl$_3$	Other		
				cis	*trans*
			MeOH		
[PtCl(CHNHR)(PEt$_3$)$_2$]Cl	$\nu(\mathrm{C{\cdots}N})$ 1572s	τ(PtCH) −1.45 ppm	τ(PtCH)	−1.60	−1.89 ppm (1 : 1) [d]
	ν(NH) 2575vs (br)	^2J(PtCH) 42 Hz			
	δ(NH) 1615s	^3J(PPtCH) 2 Hz	^2J(PtCH)	38 Hz	50 Hz
		τ(Me(*p*-tolyl)) 7.64 ppm	^3J(PPtCH)	2.5 Hz	2.5 Hz
		+HCl	*+HCl*		
		τ(PtCH) −1.58 ppm	τ(PtCH)	−1.59	−1.89 ppm (3 : 2)
		τ(NH) −5.9 ppm	τ(NH)	−4.04	−3.84(br) ppm
		J(H—H) 10 Hz (4 : 1 *cis*)	J(H—H)	10 Hz	19 Hz
			HCONMe$_2$		
[PtCl(CHNHR)(PEt$_3$)$_2$]ClO$_4$	$\nu(\mathrm{C{\cdots}N})$ 1568s	τ(PtCH) −1.70 ppm	τ(PtCH)	−1.84	−2.10 ppm (1 : 2)
	ν(NH) 3250, 3205	^2J(PtCH) 42 Hz	^2J(PtCH)	36 Hz	49 Hz
	3150, 3105s (br)	^3J(PPtCH) 2 Hz	^3J(PPtCH)	2.5 Hz	2.5 Hz
	δ(NH) 1622s	τ(Me(*p*-tolyl)) 7.62 ppm			
	ν(ClO) 1115, 1054vs	*+HClO$_4$*	*+HClO$_4$*		
		τ(PtCH) −1.7 ppm	τ(PtCH)	−1.84	−2.11 (1 : 2)
		τ(NH) −2.77 ppm	τ(NH)	−4.58	−4.04
		J(H—H) 18 Hz (*trans*)	J(H—H)	11 Hz	17 Hz

					CD_3CN		
$[Pt(CNR)(CHNHR)(PEt_3)_2](ClO_4)_2$	ν(C≡N) 2215vs	τ(PtCH) −1.78 ppm			τ(PtCH)	−1.18	−1.53 (1 : 6)
	ν(C=N) 1570s	^2J(PPtCH) 33 Hz					
	ν(NH) 3250, 3200	τ(NH) −3.00 ppm			^2J(PtCH)	28.5 Hz	34 Hz
	3150, 3095m (br)	^3J(PtCNH) 54 Hz			^3J(PPtCH)	3 Hz	3 Hz
	δ(NH) 1623s	J(H—H) 18.5 Hz (*trans*)					
	ν(ClO) 1080vs (br)	τ(Me(*p*-tolyl)) 7.58, 7.66 ppm			$+HClO_4$		
					τ(PtCH)	−1.16	−1.51 (1 : 5)
					τ(NH)	−2.54	−2.77
					J(H—H)	12.5 Hz	18.5 Hz
$[Pt(CNR)(CHNHR)(PMe_2Ph)_2](PF_6)_2$	ν(C≡N) 2225vs	τ(PtCH) −0.91 ppm					
	ν(C=N) 1570s	^2J(PtCH) 33.5 Hz					
	ν(NH) 3290s	J(H—H) 16 Hz					
	δ(NH) 1620s	τ(Me(*p*-tolyl)) 7.73 (br) ppm					
	ν(PF) 835vs (br)						
			cis	*trans*			
$[PtCl(CHNHR)(PMe_2Ph)_2]Cl$	ν(C=N) 1575s	τ(PtCH)	−1.30	−0.66 (4 : 7)			
	ν(NH) 2745vs (br)	^2J(PtCH)	37.5 Hz	49.5 Hz			
	δ(NH) 1633s	J(H—H)	10 Hz	17.5 Hz			

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[a] These data replace those presented in the preliminary communication in which a compound was omitted by mistake and the ^3J(PPtCH) values were incorrect. [b] R = *p*-tolyl. Phosphine groups are *trans* in all cases. [c] IR spectra recorded as Nujol mulls. [d] Ratios of isomers are approximate often being estimated by inspection.

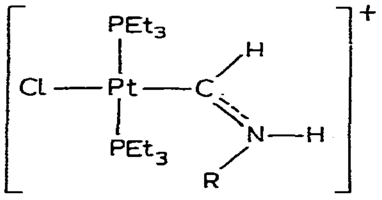
TABLE 2

IR AND ^{1}H NMR DATA FOR *p*-TOLYLMETHYLAMINO AND (Di-*p*-TOLYLAMINO)CARBENE COMPLEXES [a]

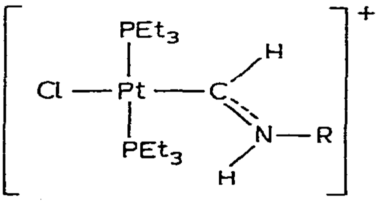
Complex [b]	Infrared frequencies [c]	^{1}H NMR signals [d]
$[PtCl(CHNMeR)(PEt_3)_2]ClO_4$	ν(C=N) 1545s ν(ClO) 1095vs	τ(PtCH) −1.59 ppm ^2J(PtCH) 36 Hz ^3J(PPtCH) 2.5 Hz J(CHNCH) 0.88 Hz τ(NMe) 5.81, 5.72 ppm τ(Me(*p*-tolyl) 7.58
$[PtCl(CHNMeR)(PEt_3)_2]PF_6$	ν(C=N) 1538s ν(PF) 840vs	τ(PtCH) −1.72 ^2J(PtCH) 37 Hz ^3J(PPtCH) 2 Hz τ(NMe) 5.87 ppm τ(Me(*p*-tolyl)) 7.59 ppm
$[Pt(CNR)(CHNMeR)(PEt_3)_2](ClO_4)_2$	ν(C≡N) 2205vs ν(C=N) 1560m (br)	τ(PtCH) −1.36 ppm ^2J(PtCH) 25 Hz ^3J(PPtCH) 2.3 Hz τ(NMe) 5.62 ppm τ(Me(*p*-tolyl)) 7.58, 7.50 ppm
$[Pt(PPh_3)(CHNMeR)(PEt_3)_2](ClO_4)_2$	ν(C=N) 1538s	τ(PtCH) −1.4, −1.6 ppm ^2J(PtCH) 42 Hz τ(NMe) 5.88, 5.93 ppm τ(Me(*p*-tolyl)) 7.63, 7.66 ppm
$[PtH\{C(NHR)_2\}(PEt_3)_2]Cl$	ν(PtH) 2045s ν(C=N) 1550s	τ(NH) −2.0 ppm ^3J(PtCNH) 55 Hz τ(Me(*p*-tolyl)) 7.70 ppm
$[Pt(CHNR)\{C(NHR)_2\}(PMe_2Ph)_2]Cl$	ν(CH) 2730m ν(C=N) 1540s (br) ν(NH) 3265s (v.br) δ(NH) 1610, 1590s	τ(PtCH) −0.21 ppm ^2J(PtCH) 32 Hz ^3J(PPtCH) 6.5 Hz τ(NH) −2.17 ppm ^3J(PtCNH) 46 Hz τ(Me(*p*-tolyl)) 7.70, 7.77 ppm
$[Pt(CHNR)(C(NHR)_2)(PMe_2Ph)_2]PF_6$	ν(C=N) 1540s ν(NH) 3370, 3300s (br) δ(NH) 1600s (br) ν(PF) 835vs	

[a] These data replace those represented in the preliminary communication in which a compound was omitted by mistake and the ^3J(PPtCH) values were incorrect. [b] R = *p*-tolyl. Phosphine groups are *trans* in all cases. [c] IR spectra recorded as Nujol mulls. [d] NMR spectra recorded in $CDCl_3$.

as τ 1.40 ppm while the *ortho* signal for the *trans* isomer is located at τ 2.44 ppm.



cis



trans

(R = *p* − tolyl)

Thus the complex $[PtCl(CHNMeR)(PEt_3)_2]ClO_4$ is predominantly *cis* since the major *ortho* signal is at τ 1.78 ppm and its separation from the *meta* signal 0.72 ppm, while the complex $[Pt(CNR)(CHNMeR)(PEt_3)_2](ClO_4)_2$ is mainly *trans*, the

TABLE 3

PHYSICAL AND ANALYTICAL DATA FOR NEW PLATINUM COMPLEXES [a]

Complex	Analysis found (calcd.) (%)			Melting point [b] (°C)
	C	H	N	
$[PtCl(CHNHR)(PEt_3)_2]Cl$ [c]	38.77 (38.65)	6.54 (6.33)	2.15 (2.25)	227—230
$[PtCl(CHNHR)(PEt_3)_2]ClO_4$	35.05 (35.04)	5.84 (5.73)	1.85 (2.04)	235—237
$[PtCl(CHNHR)(PMe_2Ph)_2]PF_6$	37.34 (37.39)	3.98 (4.05)	2.02 (1.82)	198—199
$[Pt(CNR)(CHNHR)(PEt_3)_2](ClO_4)_2$	38.53 (38.81)	5.23 (5.35)	3.20 (3.23)	225—227
$[Pt(CNR)(CHNHR)(PMe_2Ph)_2](PF_6)_2$	38.52 (38.50)	3.87 (3.84)	2.82 (2.81)	171—172
$[PtCl(CHNMeR)(PEt_3)_2]ClO_4$	36.10 (36.06)	5.82 (5.91)	1.80 (2.00)	198
$[PtCl(CHNMeR)(PEt_3)_2]PF_6$	33.71 (33.86)	5.39 (5.55)	1.89 (1.88)	155—156
$[Pt(CNR)(CHNMeR)(PEt_3)_2](ClO_4)_2$	39.64 (39.55)	5.72 (5.49)	3.71 (3.18)	226—227
$[Pt(PPh_3)(CHNMeR)(PEt_3)_2](ClO_4)_2 \cdot 1/2CH_2Cl_2$	43.99 (44.13)	5.67 (5.41)	1.26 (1.32)	185—186
$[PtH\{C(NHR)_2\}(PEt_3)_2]Cl$	47.03 (46.92)	6.93 (6.85)	3.66 (4.05)	
$[Pt(CHNR)\{C(NHR)_2\}(PMe_2Ph)_2]Cl \cdot CH_2Cl_2$	51.68 (51.43)	5.11 (5.18)	4.46 (4.50)	170—172
$[Pt(CHNR)\{C(NHR)_2\}(PMe_2Ph)_2]PF_6$	48.27 (48.85)	4.73 (4.84)		196—197

[a] All compounds were colourless and had *trans*-phosphine groups. R = *p*-tolyl. [b] Melting points are uncorrected. [c] Found: Cl, 11.59. Calcd. 11.41%.

ortho signal occurring at τ 2.23 ppm and the *ortho—meta* signal separation being less than 0.3 ppm. These assignments, though based on analogy with the imine complex $PtCl_2(MeN{=}CH\text{-}p\text{-tol})(AsEt_3)$, are strongly supported by the size of the CH=NH coupling constants (J(H—H)) in the *p*-tolylaminocarbene complexes when this coupling occurs. The C(carbene)—H signal was no longer averaged on going from chloroform-*d* to a more polar solvent. Thus the broad C(carbene)—H signal of $[PtCl(CHNHR)(PEt_3)_2]Cl$ at τ −1.45 ppm in chloroform-*d* (^2J(PtCH) 42 Hz) appears as two (triplet of triplet) signals at τ −1.89 ppm (^2J(PtCH) 50 Hz) and τ −1.60 ppm (J(PtCH) 38 Hz) in methanol, the ratio of isomers remaining nearly 1 : 1. The aromatic region indicated that the isomer with the smaller platinum—hydrogen coupling constant had *cis* geometry and the other *trans* geometry, and this was found to be general for all the secondary carbene complexes studied. This trend parallels that for the formimidoyl complexes where the *anti* isomer (lone pair *cis* to hydrogen) always had the smaller platinum—hydrogen coupling constant. The other *p*-tolylaminocarbene complexes $[PtCl(CHNHR)(PEt_3)_2]ClO_4$ (τ(PtCH) −1.70 $CDCl_3$; −2.15, −1.88 $HCONMe_2$) and $[Pt(CNR)(CHNHR)(PEt_3)_2](ClO_4)_2$ (τ(PtCH) −1.78 $CDCl_3$; −1.53, −1.18 CD_3CN) were similarly affected by change in solvent. The reason for this may lie in the smaller difference in chemical shift of the two CH signals in chloroform-*d* as opposed to more polar solvents which would favour coalescence at a lower temperature, or the presence of hydrogen bonding in more polar solvents slowing the rate of interconversion. The former argument finds support in the NMR data for the parent formimidoyl complex where the separation of the two CH signals is 0.05 ppm in chloroform-*d* but as high as 0.27 ppm in methanol. For several *p*-tolylaminocarbene complexes examined, no coalescence of the two sets of CH signals occurred on heating to 90°C which is in agreement with the findings from the high temperature study on the rhodium system, but nevertheless, surprising, in the light of the fact that coalescence of the CH signals in the formimidoyl complex, $\mathrm{PtCl(CHNR)(PEt_3)_2}$, which has a higher bond order (see [10]), occurs at this temperature. Again, the explanation must be that the difference in separation of CH signals between isomers of the carbene complexes (ca. 0.3 ppm) and formimidoyl system (0.06 ppm in dimethylsulphoxide-d_6 used) is sufficiently great to more than compensate for the lower rotation barrier due to reduction in bond order. The hydrogen bonding argument is further weakened by the fact that this would not be expected to have equal influence in both the *p*-tolylamino- and *p*-tolylmethylamino-carbene systems, as was observed. Although restricted rotation was also encountered for the rhodium secondary carbene complexes no mention was made of two sets of C(carbene)—H signals due to *cis/trans* isomerization. Presumably, the spectra were recorded in chloroform-*d* and the C(carbene)—H signals were averaged in all cases.

On heating $\mathrm{[PtCl(CHNHR)(PEt_3)_2]Cl}$ to 50°C in chloroform-*d* the C(carbene)—H signal sharpened while on cooling to —20°C it broadened and a broad NH signal became visible at τ —5.72 ppm (see Fig. 1). At —50°C, the NH signal had sharpened and CH/NH coupling was apparent, confirmed by decoupling experi-

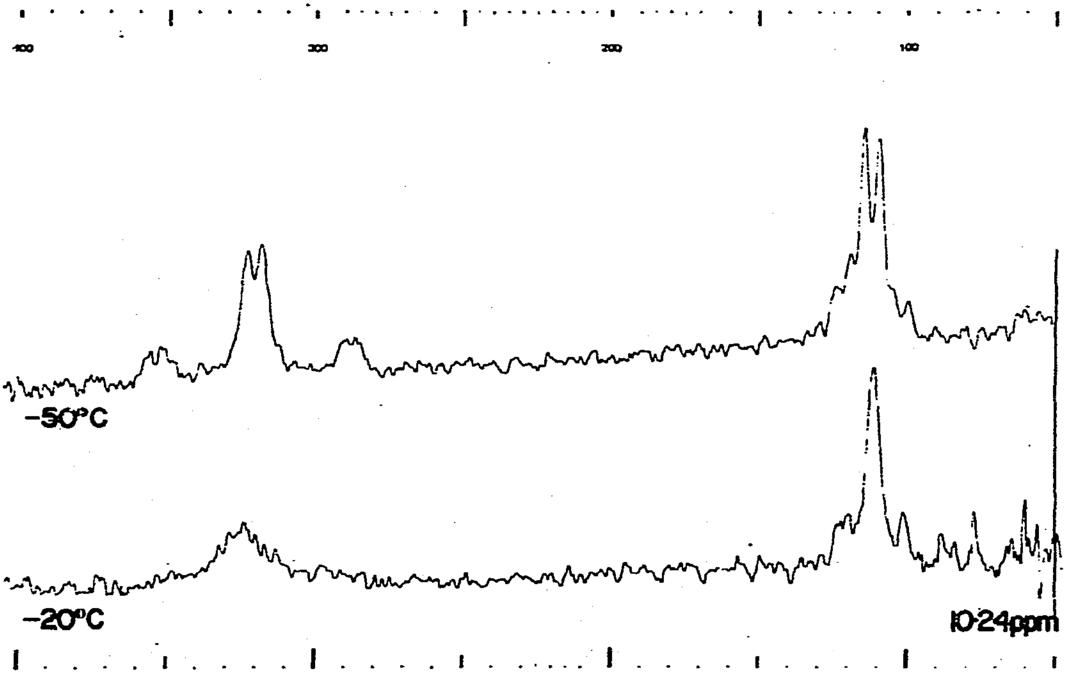
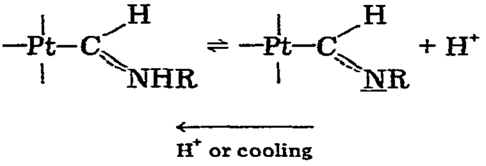


Fig. 1. Downfield region of the ^{1}H NMR spectrum of *trans*-$\mathrm{[PtCl(CHNH\text{-}}p\mathrm{\text{-}tol)(PEt_3)_2]Cl}$ at —20°C and —50°C. 1000 Hz sweep width. 1 bold division = 2 ppm.

ments and D_2O exchange. The aromatic region indicated that the ratio of isomers had changed from 1 : 1 to 4 : 1 in favour of the *cis* form. The CH=NH coupling constant (J(H—H) 10 Hz) supported the *cis* geometry, being of similar magnitude to *cis* coupling in a vinylic system. This contrasted with a similar low temperature study in methanol which, although less clearcut, showed no significant change in isomer ratio. The majority of the ruthenium secondary carbene complexes [3] exhibited both C(carbene)—H and NH signals coupling to one another in their ^{1}H NMR spectra recorded in chloroform-*d* and the larger CH=NH coupling constants (J(H—H) 17 to 21 Hz) in these cases suggested a *trans* geometry about the C=N bond. (*trans* vinylic coupling is about 18 Hz). However, a few of them had a broad C(carbene)—H and no NH visible just like the original spectrum for the platinum complex. The absence of an NH signal and lack of coupling in certain cases must be due to fast exchange of the hydrogen on nitrogen with the solution. This interpretation is supported by the fact that the addition of acid to various *p*-tolylaminocarbene complexes that showed a broad C(carbene)—H and no NH in a particular solvent ($[PtCl(CHNHR)(PEt_3)_2]X$ (X = Cl, ClO_4) in $CDCl_3$, $[PtCl(CHNHR)(PEt_3)_2]ClO_4$ in *N,N'*-dimethylformamide and $[Pt(CNR)(CHNHR)(PEt_3)_2](ClO_4)_2$ in CD_3CN) always resulted in the appearance of the NH signal and CH/NH coupling. However, the NH signal was substantially broadened again when the solution was heated to 80° C.



The position of the equilibrium above is dependent on the polarity of the solvent and is characteristic of the particular complex, e.g., in chloroform-*d*, the spectrum of the complex $[Pt(CNR)(CHNHR)(PEt_3)_2](ClO_4)_2$ had both C(carbene)—H and NH signals and coupling was occurring (J(H—H) 18.5 Hz implies *trans*) but in acetonitrile-d_4, a more polar solvent, although the ratio of isomers in the complex remained about the same (approx. 10 : 1, *trans* : *cis*) coupling was lost and no NH was visible. As expected, NH exchange is promoted by a more polar solvent.

No obvious reactions were apparent for the shift in the *cis*/*trans* isomer equilibrium throughout these studies and therefore the results will be presented without further comment. As for the formimidoyl complexes, the ratio of isomers changed from solvent to solvent. By comparison of NMR spectra, in the same solvent, it was found that the ratio of the *cis* isomer increased on going from the formimidoyl to the carbene system. Addition of acid to the complex $[PtCl(CHNHR)(PEt_3)_2]Cl$ in chloroform-*d* and methanol increased the amount of the *cis* isomer (4X and 1.5X resp.) but increased the amount of the *trans* isomer for $[PtCl(CHNHR)(PEt_3)_2]ClO_4$ in chloroform-*d*, while having little effect on the latter in *N,N'*-dimethylformamide. The effect of cooling on the isomer ratio of $[PtCl(CHNHR)(PEt_3)_2]Cl$ in chloroform-*d* has already been discussed.

Unlike the formimidoyl complex, $PtCl(CHNR)(PEt_3)_2$, which was very soluble and difficult to crystallize, a marked difference in solubility made possible the separation of isomers in the *p*-tolylaminocarbene derivative [PtCl(CHNHR)-$(PEt_3)_2$](ClO_4). As for the other carbene complexes, a nicely crystalline product was obtained on the addition of diethyl ether to the acetone reaction medium employed but, on this occasion, the yield was particularly low (50 to 65%). The ^{1}H NMR spectrum of this precipitate, showed it to be mainly the *trans* isomer while the spectrum of the reaction residue was characteristic of the *cis* form. It seems likely that other isomeric mixtures of the secondary carbene complexes may be separable by careful fractional crystallization or chromatography.

Conclusion

The susceptibility to electrophilic attack of the nitrogen in the coordinated imidoyl group has again afforded a straightforward route to complexes containing the secondary carbene ligand. These secondary carbeneplatinum complexes, like those of rhodium and ruthenium, are characterized by a high C—N bond order. Thus the C—N stretching frequency underwent only a small decrease on protonation or methylation of the parent formimidoyl complexes at nitrogen. In addition, restricted rotation about the C(carbene)—N bond was observed and the C(carbene)—H signal appeared at very low field in the ^{1}H NMR spectrum. The strong *trans* influence of the carbene ligand was again evidenced by facile substitution reactions in this study.

The relative abundance of the carbene isomers, apparently characteristic of the particular complex, could be estimated from the aromatic and downfield regions of the ^{1}H NMR spectrum. The C(carbene)—H signal and its associated coupling constants were often averaged in chloroform-*d* but, in more polar solvents, both sets of signals were apparent and the relative magnitude of the platinum—hydrogen coupling constants was the same as for the formimidoyl complexes, viz., $J(\mathrm{PtCH})_{trans} > J(\mathrm{PtCH})_{cis}$. The smaller size of J(PtCH), itself, relative to the formimidoyl complexes possibly reflects the increased π-character of the platinum—carbon bond.

The properties of the *p*-tolylaminocarbene complexes were especially interesting since the solid state infrared spectra suggested that hydrogen bonding was taking place with the counteranion while the appearance of NH signals in their ^{1}H NMR spectra was dependent on the polarity of the solvent, the temperature and the pH.

Experimental

Infrared spectra in the range 4000 to 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 ^{1}H 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 [9].

(1) trans-Chloro(p-tolylaminocarbene)bis(triethylphosphine)platinum(II) chloride, trans-$[PtCl(CHNH\text{-}p\text{-}tol)(PEt_3)_2]Cl$

To *trans*-$PtCl(CHN\text{-}p\text{-}tol)(PEt_3)_2$ (0.4 g) in acetone (15 ml) was added conc. HCl (2 equiv.). The colourless product was obtained on reducing the solution to a small volume and addition of diethyl ether. Recrystallization was from dichloromethane diethyl ether (0.42 g, 95%).

(2) trans-Chloro(p-tolylaminocarbene)bis(triethylphosphine)platinum(II) perchlorate, trans-$[PtCl(CHNH\text{-}p\text{-}tol)(PEt_3)_2]ClO_4$

To *trans*-$PtCl(CHN\text{-}p\text{-}tol)(PEt_3)_2$ (0.4 g) in acetone (20 ml) was added perchloric acid (2 equiv.). The solution was evaporated to an oil and the colourless product obtained on the addition of diethyl ether. Recrystallization was from dichloromethane/diethyl ether (0.30 g, 65%).

(3) trans-Chloro(p-tolylaminocarbene)bis(dimethylphenylphosphine)platinum(II) chloride, trans-$[PtCl(CHNH\text{-}p\text{-}tol)(PMe_2Ph)_2]Cl$

The colourless product was prepared by a method similar to (1) in 90% yield. Elemental analyses were obtained for the hexafluorophosphate salt prepared by anion exchange using silver hexafluorophosphate.

(4) trans-(p-Tolylaminocarbene)(p-tolylisocyanide)bis(triethylphosphine)platinum(II) diperchlorate, trans-$[Pt(CN\text{-}p\text{-}tol)(CHNH\text{-}p\text{-}tol)(PEt_3)_2](ClO_4)_2$

To *trans*-$PtCl(CHN\text{-}p\text{-}tol)(PEt_3)_2$ (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). The solution was centrifuged and perchloric acid (2 equiv.). was added to the filtrate. Colourless crystals of the product precipitated immediately (0.3 g, 70%).

(5) trans-(p-Tolylaminocarbene)(p-tolylisocyanide)bis(dimethylphenylphosphine)platinum(II) bishexafluorophosphate, trans-$[Pt(CN\text{-}p\text{-}tol)(CHNH\text{-}p\text{-}tol)(PMe_2Ph)_2](PF_6)_2$

To *trans*-$[PtCl(CHNH\text{-}p\text{-}tol)(PMe_2Ph)_2]Cl$ (0.3 g) in dichloromethane (50 ml) was added dropwise over 30 min a solution of *p*-tolylisocyanide (1 equiv.) in dichloromethane (20 ml). Stirring was continued until the smell of isocyanide had dissipated (15 min) after which silver hexafluorophosphate (2 equiv.) in acetone (10 ml) was added. After filtration, the product was obtained as a colourless precipitate on the addition of diethyl ether to a small volume of the filtrate (0.37, 85%).

(6) trans-Chloro(p-tolylmethylaminocarbene)bis(triethylphosphine)platinum(II) perchlorate, trans-$[PtCl(CHNMe\text{-}p\text{-}tol)(PEt_3)_2]ClO_4$

A solution of *trans*-$[PtCl(CHN\text{-}p\text{-}tol)(PEt_3]_2$ (0.50 g) and dimethylsulphate (1 equiv.) in acetone (20 ml) was heated under reflux for 5 min. Sodium perchlorate (1 equiv.) was then added, the solution evaporated to an oil and the product extracted into dichloromethane. The colourless product was obtained on addition of diethyl ether and n-pentane (0.50 g, 85%).

(7) trans-Chloro(p-tolylmethylaminocarbene)bis(triethylphosphine)platinum(II) hexafluorophosphate, trans-$[PtCl(CHNMe\text{-}p\text{-}tol)(PEt_3)_2]PF_6$

The title complex was prepared by the same method as for (6) but in the presence of ammonium hexafluorophosphate (80%).

(8) trans-(p-Tolylisocyanide)(p-tolylmethylaminocarbene)bis(triethylphosphine) platinum(II) diperchlorate, trans-$[Pt(CN\text{-}p\text{-}tol)(CHNMe\text{-}p\text{-}tol)(PEt_3)_2](ClO_4)_2$

A solution of *trans*-$[PtCl(CHNMe\text{-}p\text{-}tol)(PEt_3)_2]ClO_4$ (0.25 g) and silver perchlorate (1 equiv.) in acetone (25 ml) was heated at 40° C for 10 min. To this solution was then added a solution of *p*-tolylisocyanide (1 equiv.) in acetone (15 ml) and stirring continued for a further 10 min. The solution was evaporated to dryness and the product extracted into dichloromethane. The title complex was obtained as a colourless precipitate on the addition of diethyl ether (0.25 g, 80%).

(9) trans-(p-Tolylmethylaminocarbene)(triphenylphosphine)bis(triethylphosphine) platinum(II) diperchlorate, trans-$[Pt(PPh_3)(CHNMe\text{-}p\text{-}tol)(PEt_3)_2](ClO_4)_2$

A solution of *trans*-$[PtCl(CHNMe\text{-}p\text{-}tol)(PEt_3)_2]ClO_4$ (0.15 g) and silver perchlorate (1 equiv.) in acetone (25 ml) was heated under reflux for 5 min. The solution was evaporated to dryness and the product extracted into dichloromethane. To this solution was added triphenylphosphine (1 equiv.) and the solution heated under reflux for 15 min. The solution was again evaporated to dryness and the product digested in hot n-pentane. The title complex was recrystallized from dichloromethane, ethanol and n-pentane (0.16 g, 75%).

(10) trans-Hydrido{di(p-tolylamino)carbene}bis(triethylphosphine)platinum(II) chloride, trans-$[PtH\{C(NH\text{-}p\text{-}tol)_2\}(PEt_3)_2]Cl$

A solution of *trans*-$PtHCl(PEt_3)_2$ (0.3 g), *p*-tolylisocyanide (1 equiv.) and *p*-toluidine (2 equiv.) in benzene (10 ml) was stirred overnight. The colourless product was obtained on the addition of diethyl ether. Recrystallization was from dichloromethane/diethyl ether (0.15 g, 35%).

(11) trans-{N-(p-Tolyl)formimidoyl}{di(p-tolylamino)carbene}bis(dimethylphenylphosphine)platinum(II) chloride, trans-$[Pt\{C(NH\text{-}p\text{-}tol)_2\}(CHN\text{-}p\text{-}tol)(PMe_2Ph)_2]Cl$

To *trans*-$[PtCl(CHNH\text{-}p\text{-}tol)(PMe_2Ph)_2]Cl$ (0.3 g) in dichloromethane (50 ml) was added dropwise over 30 min 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. Successfull recrystallization could also be effected from pyridine/diethyl ether.

Acknowledgments

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

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