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CLEAVAGE OF THE CARBON–SILICON BONDS IN TRIMETHYLSILYLACETYLENES BY *trans*-$[(PR_3)_2PtX(R'OH)]PF_6$ CATIONS AND FORMATION OF CATIONIC ALKOXYCARBENE COMPLEXES OF PLATINUM(II)

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Summary

Cationic alkoxycarbene complexes of platinum(II) have been isolated in the reactions of *trans*-$[(PR_3)_2PtX(R'OH)]PF_6$ ($X = H$ or Me; $R' =$ Me or Et) with $Me_3SiC{\equiv}CR''$ ($R'' = H$, Me or $SiMe_3$). In these reactions cleavage of the carbon–silicon bond by the nucleophilic attack of alcohol has been observed. These carbene complexes have been characterized by elemental analyses and by IR, ^1H and ^{13}C NMR spectral data. ^{13}C NMR chemical shift data for carbene carbon atoms suggest that the carbene carbon may be very positively charged.

Introduction

Some years ago, a number of neutral and cationic acetylene complexes of platinum(II) were prepared in our laboratories [1–5]. Cationic platinum(II) acetylenic complexes of the type I [6–8] were obtained by the reaction shown in eq. 1 (where

$$trans\text{-}[L_2PtMeCl] + RC{\equiv}CR' + AgPF_6 \xrightarrow{\text{solvent}} \underset{(I)}{trans\text{-}[L_2PtMe(RC{\equiv}CR')]PF_6} + AgCl \qquad (1)$$

$L = PPhMe_2$ or $AsMe_3$; R and $R' =$ alkyl or aryl group; solvent = acetone or methanol).

However, the products obtained from reaction 1 were dependent on the nature of the acetylene, the ligands L, the solvent and the reaction conditions. Thus, monoal-

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kylacetylenes, $RC{\equiv}CH$, in methanol or ethanol gave [9,10] cationic alkoxycarbene complexes, II, according to eq. 2:

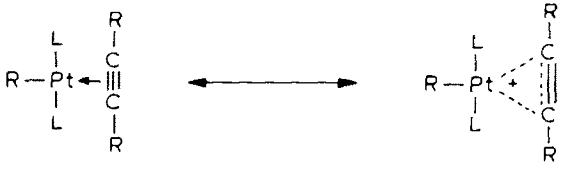
$$\textit{trans}\text{-}[L_2PtMeCl] + RC{\equiv}CH + AgPF_6 \xrightarrow{R'OH} \textit{trans}\text{-}\underset{(II)}{\left[L_2PtMe\left(C\begin{matrix}OR'\\ CH_2R\end{matrix}\right)\right]}PF_6 + AgCl \qquad (2)$$

Similarly, phenylacetylene gave the benzylalkoxycarbene complex when $L = PPhMe_2$, but with $L = AsMe_3$ only acetylide (III) formation occurred [6] (eq. 3):

$$\textit{trans}\text{-}\left[(AsMe_3)_2PtMeCl\right] + PhC{\equiv}CH + AgPF_6 \xrightarrow{MeOH}$$

$$\underset{(III)}{\left[(AsMe_3)_2Pt(C{\equiv}CPh)\right]}PF_6 + CH_4 + AgCl \qquad (3)$$

Acyl [8], vinyl ether [7] and cyclobutadiene [8,10] complexes can also be obtained via reaction 1 depending on R and R′ and the nature of the solvent. It has been suggested that, in all these reactions, the important intermediate is the platinum induced carbonium ion (IV) formed by delocalization of the cationic positive charge over the acetylene moiety.



(4)

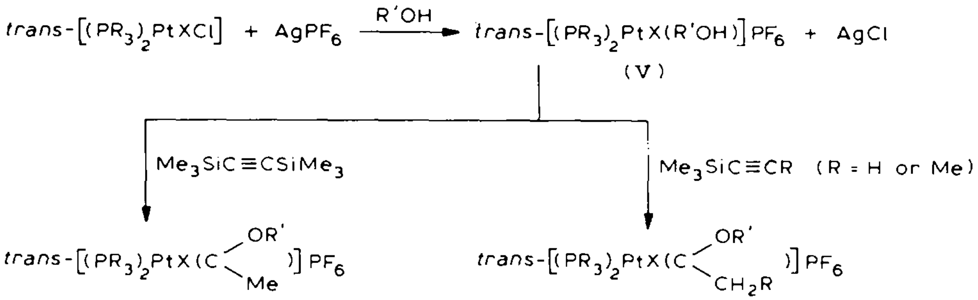
(IV)

Recently, bis(trimethylsilyl)acetylene has been observed to give unusual products in reactions with platinum(0) compounds [11,12]. A dinuclear platinum(0) complex results in which the alkyne bridges transversely between two platinum nuclei. Trimethylsilylacetylene complexes of transition metals other than platinum are also known [13–15]. However, in some cases cleavage of the alkenyl-carbon–silicon bond has also been observed [16,17].

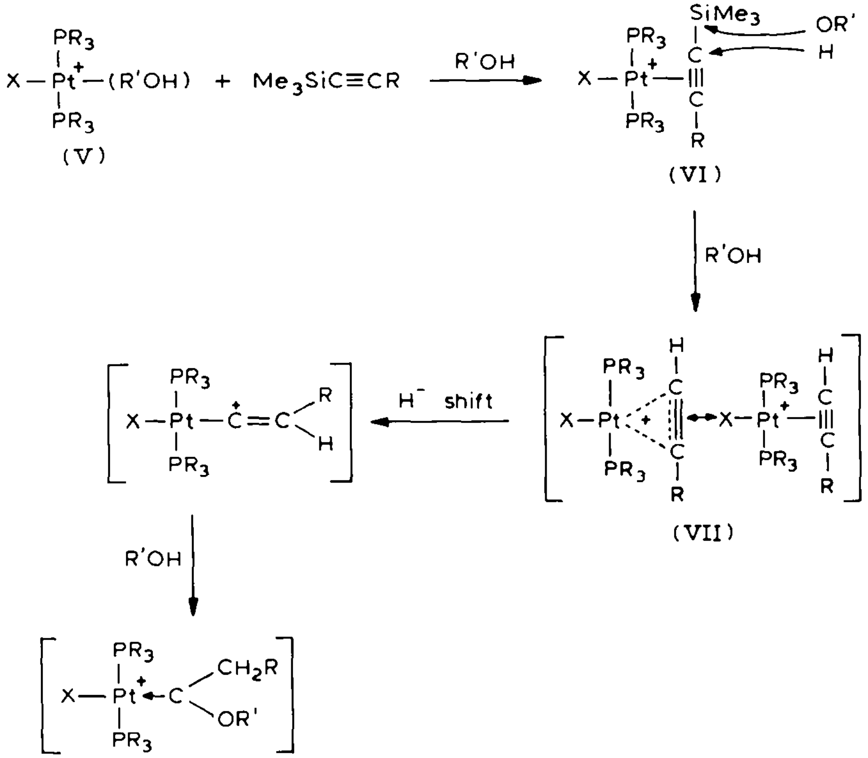
We have now examined the reactions of trimethylsilylacetylenes with platinum(II) cations, *trans*-$[(PR_3)_2PtX(R'OH)]PF_6$, expecting to form further cationic trimethylsilylacetylenic platinum(II) complexes, but instead observing an unusual C–Si bond cleavage process.

Results and discussion

The cation, *trans*-$[(PR_3)_2PtX(R'OH)]PF_6$, V, ($X = H$ or Me; R = alkyl or aryl groups; R' = Me or Et), which exists in alcoholic solution, can be prepared by the reaction of *trans*-$[(PR_3)_2PtXCl]$ ($X = H$ or Me) with silver hexafluorophosphate in alcohol. The cationic species *trans*-$[(PR_3)_2PtX(R'OH)]^+$ reacts with trimethylsilylacetylenes in R′OH at room temperature to give white or pale yellow crystalline alkoxycarbene complexes of platinum(II), which do not contain the trimethylsilyl group.



Formation of simple alkoxycarbene complexes with no silicon, in these reactions is only possible via the intermediate, VII. This can only be formed by a process in which trimethylsilylacetylenes react with platinum(II) cations to give trimethylsilylacetylene complexes, VI, which then undergo nucleophilic attack by alcohol to give the intermediate, VII. Further nucleophilic attack by alcohol ultimately gives the alkoxycarbene complexes, by a mechanism proposed earlier [8].



The silicon-containing product is presumably Me_3SiOR, although in view of the small scale on which the experiments are conducted, it, not surprisingly, has not been detected directly.

This proposed reaction mechanism is further supported by the isolation of *trans*-$[(PEt_3)_2PtMe(C(OCH_3)CD_3))]PF_6$ from the reaction of *trans*-$[(PEt_3)_2PtMe(CH_3OD)]PF_6$ with $Me_3SiC{\equiv}CSiMe_3$ in CH_3OD.

Attempts to detect the intermediates VI or VII by observing the ^{13}C NMR spectra of the reaction of *trans*-$[(PEt_3)_2PtMe(MeOD)]PF_6$ with $Me_3SiC{\equiv}CSiMe_3$ in

CH_3OD from −60°C to room temperature were thwarted by low solubilities, and above 10°C, white crystalline *trans*-$[(PEt_3)_2PtMe(C(OCH_3)CD_3)]PF_6$ deposited on the wall of the NMR tube. The reaction of $[(PEt_3)_2PtMe(THF)][PF_6]$ with $Me_3SiC{\equiv}CH$ in THF led only to extensive decomposition and thus prevented detection of VI in the ^{13}C NMR spectrum.

Interestingly, when the reaction of *trans*-$[(PEt_3)_2PtMe(MeOH)]PF_6$ with the carbon analogue of bis(trimethylsilyl)acetylene, $Me_3CC{\equiv}CCMe_3$, was carried out under similar conditions, neither alkoxycarbene nor cationic acetylene complexes of type VI could be isolated. It is somewhat surprising that the two analogous acetylenes behave so differently since the bond energy difference between C–C and Si–C is small (C–C 82.6 kcal/mol; Si–C 78.0 kcal/mol). Presumably, the greater polarity of the Si–C bond and also its binetic reactivity, renders it is more susceptible to cleavage through nucleophilic attack by alcohol. This is further supported by the fact that the platinum(II) cation, *trans*-$[(PEt_3)_2PtMe(MeOH)]PF_6$ reacts with $Me_3SnC{\equiv}CSnMe_3$ in MeOH giving rise to the formation of carbene complex, *trans*-$[(PEt_3)_2PtMe(C(OMe)Me)]PF_6$. Moreover, nucleophilic cleavage of Si–C in silylacetylenes in known to be promoted [16] by platinum(II), presumably by the above type of mechanism.

Recently, a similar Si–C bond cleavage has been observed in the reaction of $Me_3SiC{\equiv}CH$ with H_2PtCl_6 in isopropanol. The alkoxycarbene complex of platinum(II), $[Cl_2Pt(C(OPr^i)Me)_2]$, has been isolated, whereas the carbon analogue, $Me_3CC{\equiv}CH$ under similar conditions also gives the alkoxy carbene complex, $[Cl_2Pt(C(CH_2Bu^t)OPr^i)]_2$, in which the C–$Bu^t$ bond remains intact [18].

In the infrared spectra, the resulting alkoxycarbene complexes show no absorption assignable to $\nu(C{\equiv}C)$ in the region 1600–2100 cm^{-1}. A strong absorption in the region 1305–1315 cm^{-1} has been attributed to C–O stretching of the alkoxy group [9,19]. A weak absorption in the region 505–515 cm^{-1} can be attributed to ν(Pt–C) for the platinum-methyl group.

^1H NMR data for these complexes are given in Table 1. Reactions carried out in methanol gave products showing an absorption in the ^1H NMR spectrum in the region 4.43–4.85 ppm. This appears as a singlet with satellites due to ^{195}Pt coupling, J(Pt–H) 6.0 to 7.0 Hz and is assigned to the protons of the alkoxy group. Reactions carried out in ethanol led to a complex absorption for the methyl protons; and a quartet for methylene protons showing coupling with ^{195}Pt (J(Pt–H) 7.0 Hz). The absorption due to the carbene protons, $:CH_2R$, appears in the region δ 1.68 to 2.83 ppm. In the methyl complexes, the platinum-methyl group gives a triplet due to coupling with two equivalent ^{31}P nuclei, with platinum satellites of one fourth intensity. A similar pattern has also been observed in the spectrum of the hydride complex, due to the hydridic proton. The values of J(Pt–C–H) = 45–48 Hz for the platinum-methyl group and J(Pt–H) 560 Hz for the platinum-hydrido proton reflect the very high *trans* influence [9,20,21] exerted by the alkoxycarbene ligand.

^{13}C NMR chemical shift data for the carbene carbons (Table 2) of these complexes indicate that these atoms are very positively charged, although such a conclusion assumes that only diamagnetic contributions to chemical shifts are important. The observed chemical shift of ~ 320 ppm lies well within the range of shifts exhibited by purely organic carbo-cations as well as by other metal carbene complexes [22–25].

Our attempts to liberate carbene from *trans*-$[(PEt_3)_2PtMe(C(OCH_3)CH_3)]PF_6$

TABLE 1

^{1}H NMR DATA FOR CATIONIC PLATINUM(II) CARBENE COMPLEXES IN $CDCl_3$

Complex	Pt-Me or Pt-H			α-Alkoxy protons		Carbene protons	
	$\delta(CH_3)$ or δ(H) (ppm)	J(Pt-H) (Hz)	J(P-H) (Hz)	$\delta(O\text{-}CH_2R)$ (ppm)	J(Pt-H) (Hz)	δ(C-R) (ppm)	J(Pt-H) (Hz)
trans-$[(PEt_3)_2PtMe(C\langle^{OMe}_{Me})]PF_6$	0.11	47.0	8.0	4.8	7.0	2.53	7.5
trans-$[(PEt_3)_2PtMe(C\langle^{OMe}_{CD_3})]PF_6$	0.16	46.5	8.0	4.81	7.0	-	-
trans-$[(PEt_3)_2PtMe(C\langle^{Et}_{OMe})]PF_6$	0.14	47.0	8.0	4.85	6.5	2.83 [b]	[a]
trans-$[(PEt_3)_2PtMe(C\langle^{OEt}_{Me})]PF_6$	0.11	47.0	8.0	5.12 [b]	7.0	2.54	7.5
trans-$[(PMe_2Ph)_2PtMe(C\langle^{OMe}_{Me})]PF_6$	0.2	48.0	9.0	4.7	6.0	2.23	6.5
trans-$[(PMePh_2)_2PtMe(C\langle^{OMe}_{Me})]PF_6$	0.22	47.0	8.5	4.46	6.0	1.78	[a]
trans-$[(PMePh_2)_2PtMe(C\langle^{OEt}_{Me})]PF_6$	0.22	47.0	8.5	5.47 [b]	7.0	1.87	[a]
trans-$[(PPh_3)_2PtMe(C\langle^{OMe}_{Me})]PF_6$	−0.09	45.0	8.4	4.43	6.0	1.68	8.0
trans-$[(PEt_3)_2PtH(C\langle^{OMe}_{Me})]PF_6$	−7.11	560.0	19.0	4.72	6.0	2.56	[a]

[a] Not clear. [b] For CH_2 of the ethyl group.

TABLE 2

^{13}C NMR DATA FOR CATIONIC PLATINUM(II) CARBENE COMPLEXES IN $CDCl_3$

Complex	Pt-CH_3		Alkoxy carbene carbon		Alkyl carbene carbon		Carbene carbon	
	$\delta(CH_3)$ (ppm)	J(Pt-C) (Hz)	δ (ppm)	J(Pt-C) (Hz)	δ (ppm)	J(Pt-C) (Hz)	δ (ppm)	J(Pt-C) (Hz)
trans-$[(PEt_3)_2PtMe(C\langle^{OMe}_{Me})]PF_6$	−12.4	365.3	69.7	69.8	43.1	87.3	320.8	779.4
trans-$[(PEt_3)_2PtMe(C\langle^{OMe}_{CD_3})]PF_6$	−12.4	374.8	69.8	70.2	42.5	[a]	321.2	782.6
trans-$[(PMe_2Ph)PtMe(C\langle^{OMe}_{Me})]PF_6$	−9.5	373.4	70.3	64.4	42.8	77.6	320.9	767.9
trans-$[(PMePh_2)PtMe(C\langle^{OMe}_{Me})]PF_6$	−8.6	354.8	70.4	55.9	41.9	72.9	320.1	-
trans-$[(PEt_3)_2PtH(C\langle^{OMe}_{Me})]PF_6$	-	-	70.2	75.4	42.8	97.4	328.4	833.5

[a] Could not be observed due to broadening of signal.

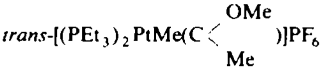
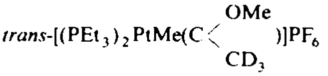
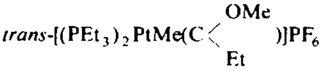
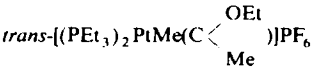
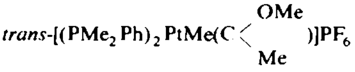
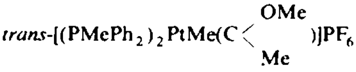
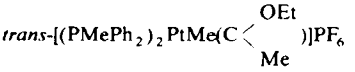
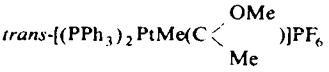
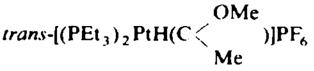
(VIII), by treatment with acetonitrile or PPh_3 at room temperature, or under reflux, were unsuccessful. However, the reaction of PPh_3 partially replaces triethylphosphine from the complex. The reaction of ethyl vinyl ether with VIII, either in the presence or absence of PPh_3, does not yield any substituted cyclopropane. Similarly, acetoxime is inert towards VIII. Iodine slowly reacts with VIII in methanol to give yellow $[(PEt_3)_2PtI(C(OMe)Me)]PF_6$.

Experimental

The following chemicals were obtained commercially and were used without further purification: trimethylsilylacetylenes ($Me_3SiC{\equiv}CR'$, $R' = H$, Me or $SiMe_3$) from Aldrich Chemical Co., $AgPF_6$ from Strem Chemical Inc. and K_2PtCl_4 from

TABLE 3

PHYSICAL AND ANALYTICAL DATA FOR CATIONIC ALKOXY CARBENE COMPLEXES OF PLATINUM(II) FORMED BY THE REACTIONS OF *trans*-$[(PR_3)_2PtX(R'OH)]PF_6$ WITH TRIMETHYLSILYLACETYLENES

Complex	Colour	M.p. [a] (°C)	Analysis (Found (Calcd.) (%))	
			C	H
 *trans*-$[(\mathrm{PEt_3})_2\mathrm{PtMe}(\mathrm{C}{<}^{\mathrm{OMe}}_{\mathrm{Me}})]\mathrm{PF_6}$	white	188-189	29.72 (29.63)	6.10 (6.06)
 *trans*-$[(\mathrm{PEt_3})_2\mathrm{PtMe}(\mathrm{C}{<}^{\mathrm{OMe}}_{\mathrm{CD_3}})]\mathrm{PF_6}$	cream	170-176	29.50 (29.45)	6.47 (6.49)
 *trans*-$[(\mathrm{PEt_3})_2\mathrm{PtMe}(\mathrm{C}{<}^{\mathrm{OMe}}_{\mathrm{Et}})]\mathrm{PF_6}$	white	176-180	30.81 (30.77)	6.16 (6.23)
 *trans*-$[(\mathrm{PEt_3})_2\mathrm{PtMe}(\mathrm{C}{<}^{\mathrm{OEt}}_{\mathrm{Me}})]\mathrm{PF_6}$	white	184-185	30.71 (30.77)	6.20 (6.23)
 *trans*-$[(\mathrm{PMe_2Ph})_2\mathrm{PtMe}(\mathrm{C}{<}^{\mathrm{OMe}}_{\mathrm{Me}})]\mathrm{PF_6}$	cream	108-110	34.89 (34.83)	4.48 (4.49)
 *trans*-$[(\mathrm{PMePh_2})_2\mathrm{PtMe}(\mathrm{C}{<}^{\mathrm{OMe}}_{\mathrm{Me}})]\mathrm{PF_6}$	cream	98-99	44.36 (44.29)	4.30 (4.34)
 *trans*-$[(\mathrm{PMePh_2})_2\mathrm{PtMe}(\mathrm{C}{<}^{\mathrm{OEt}}_{\mathrm{Me}})]\mathrm{PF_6}$	white	140-145	45.02 (44.99)	4.55 (4.51)
 *trans*-$[(\mathrm{PPh_3})_2\mathrm{PtMe}(\mathrm{C}{<}^{\mathrm{OMe}}_{\mathrm{Me}})]\mathrm{PF_6}$	white	190-195	51.35 (51.23)	4.25 (4.19)
 *trans*-$[(\mathrm{PEt_3})_2\mathrm{PtH}(\mathrm{C}{<}^{\mathrm{OMe}}_{\mathrm{Me}})]\mathrm{PF_6}$	white	154-155	27.95 (28.36)	6.16 (5.87)

[a] Melts with decomposition or decomposes.

Johnson Matthey and Mallory. *trans*-$(PR_3)_2PtMeCl$ were prepared by the reactions of dimethylplatinum(II) complexes with dry HCl in diethyl ether [26,27]. *trans*-$(PEt_3)_2PtHCl$ was prepared by the method of Chatt and Shaw [28].

Infrared spectra were recorded on a Perkin–Elmer 180 spectrometer and obtained from Nujol mulls between cesium iodide plates. Proton NMR spectra were recorded in $CDCl_3$ on a Varian EM-360 spectrometer; chemical shifts were relative to external tetramethylsilane. ^{13}C NMR spectra were recorded on a Bruker WH-400 instrument at 100.6 MHz in $CDCl_3$ and chemical shifts were reported downfield from external tetramethylsilane. Microanalyses were performed by Guelph Chemical Laboratories. Melting points were determined in a capillary tube and are uncorrected.

All reactions were carried out in spectrograde solvents under nitrogen atmosphere. All reactions of trimethylsilylacetylenes with *trans*-$[(PR_3)_2PtX(R'OH)]PF_6$ were carried out in the same way, a typical procedure is given below.

Reaction of trans-$[(PEt_3)_2PtMe(MeOH)]PF_6$ with $Me_3SiC{\equiv}CH$ in MeOH

The cation, *trans*-$[(PEt_3)_2PtMe(MeOH)]PF_6$, was prepared by the reaction of *trans*-$[(PEt_3)_2PtMeCl]$ (730 mg) with $AgPF_6$ (384 mg) in methanol (~ 20 ml), with vigorous stirring for 20 minutes under a nitrogen atmosphere. Silver chloride was filtered off. To the filtrate, excess $Me_3SiC{\equiv}CH$ (~ 1 ml) was added. The solution, which turned yellow after a few minutes, was kept for 4 h at room temperature and then the solvent was pumped off leaving a yellowish residue. The residue was dissolved in 1/1 (V/V) mixture of methanol and methylene chloride (~ 10 ml) and was passed through a short florisil column (6 cm thick and 0.6 cm wide) eluting with a 1/1 (V/V) mixture of methanol and methylene chloride. The solvent was slowly evaporated down to ~ 5 ml in a nitrogen stream giving white crystals. The supernatant liquid was decanted and the crystals were washed with small amount of methanol and dried under vacuum (yield = 610 mg). A small amount of additional product was recovered from the supernatant and washings by further concentration to ~ 3 ml. The compound was analysed $[(PEt_3)_2PtMe(C(OMe)Me)]PF_6$.

Pertinent data on these carbene complexes are given in Table 3.

Acknowledgements

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