Cationic Acetylene, Acetylide, and Carbene Complexes of Platinum(II)

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Summary Methoxycarbene, acetylene, and acetylide cationic platinum(II) complexes have been isolated from reactions of *trans*-PtClMeQ_2, where Q = PMe_2Ph or $AsMe_3$, with $R^1C \equiv CR^2$ and silver hexafluorophosphate in the presence of methanol.

BOTH cationic olefin complexes[1] and neutral carbene complexes[2] of platinum(II) have been described recently. We now find that reaction of *trans*-PtClMeQ_2, where Q = PMe_2Ph or $AsMe_3$, with $R^1C \equiv CR^2$ and silver hexafluorophosphate in the presence of methanol leads to the formation of cationic methoxycarbene complexes *trans*-$[PtMe(MeOCCH_2R^1)Q_2]^+PF_6^-$ (I) where $R^2 = H$ and R^1 = alkyl or aryl group, but to acetylene complexes *trans*-$[PtMe(R^1C \equiv CR^2)Q_2]^+PF_6^-$ (II) where $R^1 = R^2 = Ph$.

The cationic methoxycarbene complexes do not show $\nu_{st}(C{\equiv}C)$ in the region 1600—2200 cm^{-1} in either the i.r. or Raman spectra, and all n.m.r. spectra show an absorption δ $-4{\cdot}90$ to $-4{\cdot}70$ p.p.m., equivalent to three protons, with only weak platinum coupling, J(Pt–H) *ca.* 7Hz. A similar absorption is found in the region δ $-2{\cdot}9$ to $-2{\cdot}5$ p.p.m. with J(Pt–H) *ca.* 7 Hz. We assign the former to the methoxy-protons and the latter to the α-carbon protons of $MeO\ddot{C}CH_2R^1$. Characterization of the carbene in the i.r. spectrum is difficult, although a strong absorption at *ca.* 1300 cm^{-1} may well be due to ν_{st} (C–O). Thus our spectroscopic evidence closely resembles that originally reported[3] by Fischer for $(CO)_5W(MeOCMe)$.

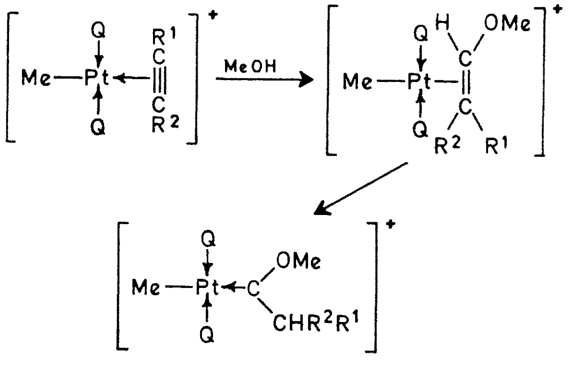
Further elucidation of the platinum–carbene bond comes from the n.m.r. spectral data of the platinum methyl group where $\delta(CH_3)$ is in the region $-0{\cdot}30$ to $+0{\cdot}10$ p.p.m. and J(Pt–H) falls in the range 48—51 Hz. An absorption at *ca* 514 cm^{-1} in the i.r. and Raman spectra is associated with the Pt–Me group, although it is unlikely to be due to a pure Pt–C stretch. The spectroscopic data are consistent with the carbene group exerting a high *trans*-influence.[4,5]

The n.m.r. spectra of (I) where Q = PMe_2Ph and R^1 = H or Bu^n are consistent with free rotation of the carbene about the platinum–carbene carbon bond, but where R^1 = Ph, the spectrum indicates that rotation is hindered.

The n.m.r. spectrum of (II) where $R^1 = R^2$ = Ph shows platinum–methyl resonances $\delta(CH_3)$ at *ca.* $-1{\cdot}0$ p.p.m. with J(Pt–H) *ca.* 80 Hz. Therefore in marked contrast to the carbene complexes the acetylene group appears to exert a *trans*-influence similar to those found[6] for compounds of the form $[PtMeLQ_2]^+$ where L = neutral donor ligand and Q = PMe_2Ph.

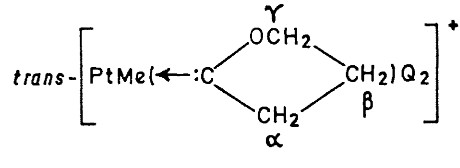
A plausible route for the formation of these complexes would involve the initial formation of an acetylenic complex, followed by reaction with methanol to give a vinyl ether which then by proton transfer would give the carbene, as shown in the Scheme.

The reaction of *trans*-PtClMe$(AsMe_3)_2$ with PhC $\equiv$ CH and silver hexafluorophosphate led to the isolation of the cationic acetylide complex, $[Pt{-}C{\equiv}CPh(AsMe_3)_2]^+$ PF_6^- which showed an intense absorption at 2100 cm^{-1} in the i.r. spectrum, characteristic of $\nu_{st}(C{\equiv}C)$ in metal acetylides. This suggests that carbene formation by reaction with the methanol present as solvent, and acetylide formation by elimination of methane, are competing reactions involving the unstable cation $[PtMe(R^1C{\equiv}CH)Q_2]^+$ which is initially formed.



SCHEME

An interesting reaction involving but-1-yn-4-ol, $CH{\equiv}CCH_2CH_2OH$, led to the isolation of a carbene complex which appears to have been formed by an intramolecular reaction with the hydroxyl group to give (III), where



(III)

Q = PMe_2Ph or $AsMe_3$, with $\delta(H^\alpha)$ $-2{\cdot}3$ p.p.m., $J(H^\alpha H^\beta)$ 8 Hz, J(Pt–H) 7 Hz, $\delta(H^\gamma)$ $-4{\cdot}8$ p.p.m., $J(H^\beta H^\gamma)$ 8Hz, J(Pt–H) 7 Hz, and $\delta(H^\beta)$ hidden beneath the Q methyl groups. The spectrum where Q = PMe_2Ph showed the equivalence of the phosphine methyl groups and, therefore confirmed free rotation about the platinum–carbene bond at room temperature.

All compounds are white or off-white, crystalline solids, stable in air and only slowly decomposed by chlorinated solvents such as chloroform and methylene dichloride.

Satisfactory analytical data for the above compounds have been obtained.

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