*Journal of Organometallic Chemistry*, 47 (1973) C17–C20

## Preliminary communication

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# Some reactions of iridium(III) cations with unsaturated ligands: formation of carbene and imino–ether complexes

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(Received October 9th, 1972)

## SUMMARY

Several reactions of iridium(III) cations with terminal acetylenes and pentafluorobenzonitrile in methanol have yielded methoxy carbene and imino–ether complexes. It is suggested that π-donation either from the carbene hetero-atoms or from the metal is not an important factor in the stabilization of carbene complexes.

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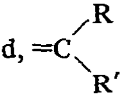
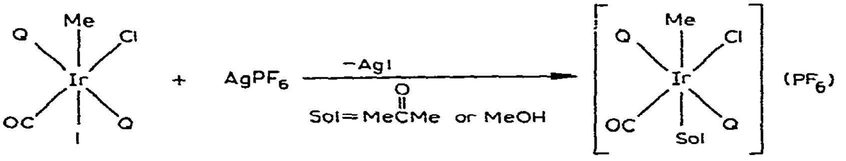
As a result of the many recent studies[1] of transition metal organometallic complexes containing the "carbene" ligand,  $=C\begin{smallmatrix}R\\R'\end{smallmatrix}$, the actual importance of $Md_\pi \rightarrow Lp_\pi$ bonding to stabilize these complexes has been questioned. The fact that several stable carbene complexes of metals in high oxidation states have now been prepared[2–7] suggests that such π-bonding is not entirely necessary. In this communication we describe the preparation of several carbene complexes of iridium(III) and other related compounds.

The iodide in I, Q = $PMe_2Ph$ or $PMePh_2$ is labile due to the high *trans* influence of methyl group[8] and may readily be removed by the silver salt of a non-coordinating anion in methanol or acetone to give a stable solvent cation II,

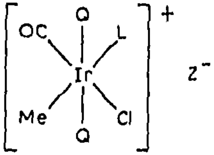


(I) (II)

The addition of a molar equivalent of the acetylene 1-butyn-4-ol rapidly leads to the formation of carbene complex III via an intramolecular rearrangement[9].

TABLE 1

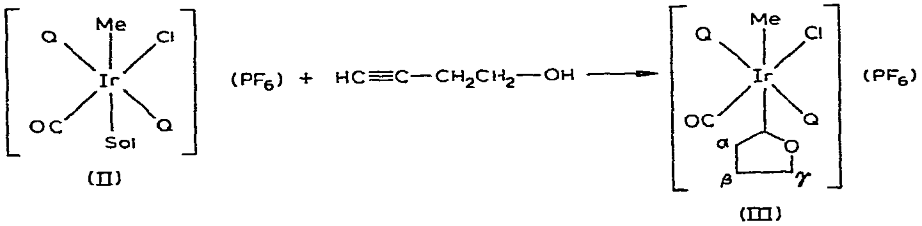
NMR DATA[a] FOR CATIONIC IRIDIUM(III) COMPLEXES



| *Q* | $Z^-$ | *L* | *Phosphine methyls* |  | *Iridium methyl* |  | *Other* |
|---|---|---|---|---|---|---|---|
|  |  |  | *δ(P–Me)* | *J(P–H)*[b] | *δ(Ir–Me)* | *J(P–H)* |  |
| $PMePh_2$ | $PF_6$ | $=\overline{CCH_2CH_2CH_2O}$ | 2.32 | 9.0 | 0.67 | 7.0 | $\delta(OCH_2)$4.85t, $\delta(C{-}CH_2)$ 1.85t<br>$\delta(OCCH_2)$0.96p |
| $PMe_2Ph$ | $PF_6$ | $=\overline{CCH_2CH_2CH_2O}$ | 2.12<br>2.00 | 7.8<br>9.3 | 0.52 | 7.5 | $\delta(OCH_2)$4.70t<br>$\delta(OCCH_2)$0.96p |
| $PMe_2Ph$ | $PF_6$ | =C(OMe)Me | 2.09<br>1.97 | 9.2<br>8.0 | 0.53 | 7.2 | $\delta(OCH_3)$3.91<br>$\delta(CH_3)$1.41 |
| $PMe_2Ph$ | $BPh_4$ | $NH{=}C(OMe)C_6F_5$ | 1.96<br>1.90 | 8.2<br>8.2 | 0.83 | 7.1 | $\delta(OCH_3)$3.49 |

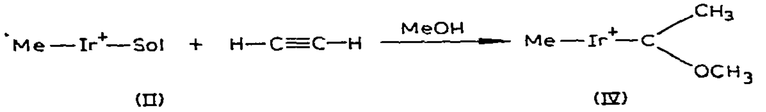
[a] Spectra were recorded using $CH_2Cl_2$ at internal lock and reference signal. Chemical shifts are given in ppm downfield from TMS and coupling constants are given in hertz. t = triplet, d = doublet, p = pentet.

[b] $^2J + {}^4J$(PH) is quoted (see ref. 10).

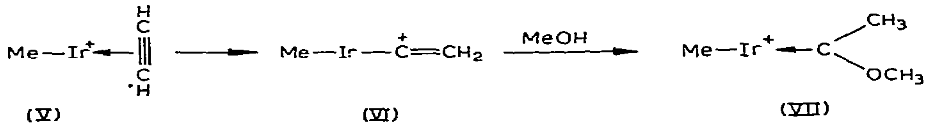


The ${}^1H$ NMR spectra (see Table 1) of the carbene cations support the structure shown. The iridium methyl group appears as a triplet due to coupling with the two phosphines, the phosphine methyl resonances (where Q = $PMe_2Ph$) appear as overlapping triplets indicating "virtually" coupled *trans*-phosphines[10] and the absence of a plane of symmetry through the P–Ir–P axis. The α and γ hydrogens of the carbene appear as triplets and the β hydrogens appear as a pentet.

A similar reaction occurs with II, Q = $PMePh_2$ and H–C≡C–H in methanol to give the methylmethoxycarbene IV.

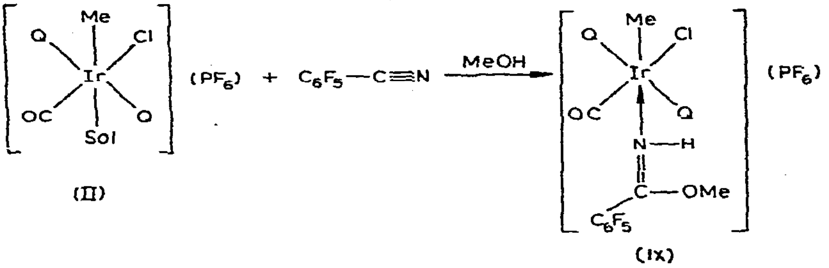


The mechanism of this reaction has been extensively investigated for platinum complexes[2] and presumably is also applicable in the present case. Initial coordination of the acetylene to the iridium cation (V), $H^-$ migration, with the formation of an "iridium stabilized carbonium ion" (VI), and nucleophilic attack by methanol gives the carbene (VII).



The only other carbene complexes of transition metals in high oxidation states have utilized chelating carbenes[2,4–6] or carbenes with good heteroatom substituents such as amines[3,6,7] which are capable of donating electron density into the vacant carbene carbon $2p_z$ orbital to enhance their stabilities. For most low-valent methylmethoxycarbene complexes[1] the carbene carbon–oxygen stretching frequencies are in range ~ 1250 $cm^{-1}$. If π-bonding was important, an increase in ν(C–O) (higher than C–O bond order) would be expected on oxidation to compensate for the loss of $Md_\pi \rightarrow C_2p_z$ bonding. However, the values of ν(C–O) observed for the $Ir^{III}$ complexes (1250–1260 $cm^{-1}$) are typical of other methylmethoxycarbenes. Hence, these results suggest that π-bonding into the carbene carbon $C_2p_z$ orbital (whether from the metal or heteroatom) is not responsible for the stability of transition metal-carbene complexes.

Perfluoroaryl nitriles react with methyl platinum cations[4,5,11] in methanol to give imino–ether complexes. These reactions also proceed via a π-bonded intermediate[11], in which the C≡N group is activated towards nucleophilic attack. This is a smooth reaction for $Ir^{III}$ to give the imino–ether complex IX in good yield.



These reactions emphasize the similarity of the methyliridium(III) and methylplatinum(II) cations, as well as the generality of the carbonium ion mechanism for carbene formation from terminal acetylenes. It should be noted that the reaction involves initial $\pi$-coordination of the acetylene to the cation; provided the relative energy levels of the acetylene and metal are suitable, carbene formation results. However if the energy separation of the metal "*spd*" hybrid orbitals and acetylene $p\pi$ orbitals is too great, only weak association takes place and polymerization occurs more rapidly than the rearrangement required for carbene formation, as noted for several $Pt^{IV}$ cations[5]. We have attempted several reactions with terminal acetylenes, silver hexafluorophosphate and *trans*-$Ir(CO)Cl[PMePh_2]_2$ and have been unable to isolate carbene complexes. Other workers[12,13] have isolated quite stable cationic acetylenic complexes of $Ir^{I}$ for which the low values of $\nu(C{\equiv}C)$ ($\sim$ 1800 $cm^{-1}$) suggest that there is sufficient $Md\pi \rightarrow L\pi^*$ bonding to stabilize the $\pi$-bonded acetylene, preventing the achievement of carbonium ion reactivity, and hence preventing intramolecular rearrangement and carbene formation.

## ACKNOWLEDGMENTS

We are grateful for the award of a Scholarship (to L.E.M.) and for financial support of this work from the National Research Council of Canada.

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