

Preliminary communication

Cationic cyclic carbene or carbon-bonded ylide complexes of iridium(III) and platinum(II)

P.J. FRASER, W.R. ROPER* and F.G.A. STONE

Department of Inorganic Chemistry, The University, Bristol BS8 1TS (Great Britain)

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SUMMARY

2-Chloro-4-methylthiazole, 2-chlorobenzoxazole and 2-chlorobenzthiazole oxidatively add to both $[\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2]$ and $[\text{Pt}(\text{PhCH}=\text{CHPh})(\text{PEt}_3)_2]$; protonation of the products at nitrogen produces cationic carbene complexes.

Molecules like thiazole, benzthiazole and benzimidazole normally coordinate to metal ions through a nitrogen atom, but for imidazole and benzimidazole attachment through carbon to ruthenium has recently been demonstrated¹, and benzthiazole "carbene" complexes have been derived from reactions involving the electron-rich olefin 1,1'-dimethyl-2,2'-bibenzothiazolinyliidene^{2,3}. We report herein a simple route to carbon-bonded metal complexes of these ligands through oxidative-addition of the 2-halo-derivatives to sufficiently reactive d^8 or d^{10} complexes followed by protonation at nitrogen. The ability of transition metal complexes containing the $\text{M}-\text{C}=\text{NR}$ group to be readily protonated has been used previously as a route to cationic carbene⁴ or carbon bonded ylide⁵ complexes.

The complex $[\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2]$ ⁶ reacts slowly (12h, 60° in benzene) with 2-chloro-4-methylthiazole, 2-chlorobenzoxazole and 2-chlorobenzthiazole to form neutral iridium(III) complexes $[\text{IrCl}_2(\text{CO})\{\overline{\text{C}}=\text{NCH}=\text{C}(\text{Me})\overline{\text{S}}\}(\text{PMe}_2\text{Ph})_2]$, $[\text{IrCl}_2(\text{CO})\{\overline{\text{C}}=\text{NC}_6\text{H}_4\overline{\text{O}}\}(\text{PMe}_2\text{Ph})_2]$ and $[\text{IrCl}_2(\text{CO})\{\overline{\text{C}}=\text{NC}_6\text{H}_4\overline{\text{S}}\}(\text{PMe}_2\text{Ph})_2]$, respectively. Treatment with perchloric or tetrafluoroboric acids protonates the nitrogen atoms in these complexes (see Table 1) e.g.:

* On study leave from the University of Auckland, New Zealand.

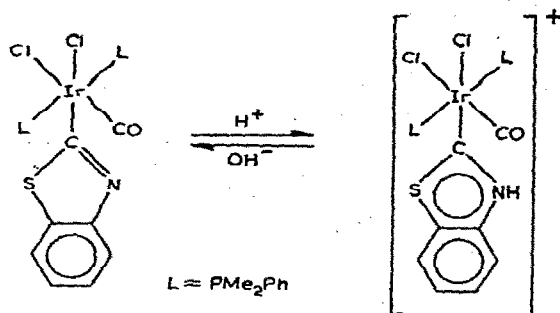


TABLE I

INFRARED DATA FOR REPRESENTATIVE IRIDIUM(III) AND PLATINUM(II) COMPLEXES

Compound ^{a,b}	$\nu(\text{CO}) (\text{cm}^{-1})$	$\nu(\text{NH}) (\text{cm}^{-1})$
$\text{IrCl}_2(\text{CO})(\text{C}=\text{NC}_2\text{H}_4\text{O})(\text{PMe}_2\text{Ph})_2$	2071	—
$\text{IrCl}_2(\text{CO})(\text{C}=\text{NC}_2\text{H}_4\text{S})(\text{PMe}_2\text{Ph})_2$	2069	—
$[\text{IrCl}_2(\text{CO})(\text{CNHC}_2\text{H}_4\text{O})(\text{PMe}_2\text{Ph})_2]^+$	2085	3280, 3240
$[\text{IrCl}_2(\text{CO})(\text{CNHC}_2\text{H}_4\text{S})(\text{PMe}_2\text{Ph})_2]^+$	2071	3200
$[\text{IrCl}_2(\text{CO})\{\text{CNHCHC}(\text{Me})\text{S}\}(\text{PMe}_2\text{Ph})_2]^+$	2078	3240, 3200
$[\text{PtCl}\{\text{CNHCHC}(\text{Me})\text{S}\}(\text{PEt}_3)_2]^+$	—	3205, 3173, 3108

^a All complexes are colourless. ^b Measured as Nujol mulls.

These protonations are reversible and base converts the cations to the neutral iridium(III) complexes. Similarly a reversible hydrohalogenation has been established for the Pt^{II} complex $\text{Pt}(\text{CPh}=\text{NMe})(\text{PPh}_3)_2$ ⁵.

The ligands in these cyclic Ir^{III} carbene complexes, like dimethylimidazolidene in $\text{Fe}(\text{CO})_4\{\text{CN}(\text{Me})\text{C}_2\text{H}_2\text{N}(\text{Me})\}$ ⁷ and the substituted pyran-2-ylidene complexes of chromium and molybdenum⁸, may be regarded as aromatic systems⁹. The cations are very inert to further substitution. Thus prolonged reaction of $[\text{IrCl}_2(\text{CO})\{\text{CNHCHC}(\text{Me})\text{S}\}(\text{PMe}_2\text{Ph})_2]\text{BF}_4$ with excess of iodide ion results only in anion exchange and recovery of the salt $[\text{IrCl}_2(\text{CO})\{\text{CNHCHC}(\text{Me})\text{S}\}(\text{PMe}_2\text{Ph})_2]\text{I}$.

The corresponding alkylated carbene complexes are obtained through direct oxidative-addition of the alkylated ligand, e.g. $[\text{ClCN}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{S}]\text{BF}_4$ yields $[\text{IrCl}_2(\text{CO})\{\text{CN}(\text{Me})\text{CHC}(\text{Me})\text{S}\}(\text{PMe}_2\text{Ph})_2]\text{BF}_4$. Direct alkylation of the neutral iridium(III) compounds by trialkyl-oxonium salts has not been successful, probably for steric reasons.

Among d^{10} complexes, $[\text{Pt}(\text{PhCH}=\text{CHPh})(\text{PEt}_3)_2]$ ¹⁰ reacts rapidly with 2-chloro-4-methylthiazole and protonation affords the cationic carbene complex $[\text{PtCl}\{\text{CNHCHC}(\text{Me})\text{S}\}(\text{PEt}_3)_2]\text{BF}_4$.

All the new compounds have been characterised by IR and NMR spectroscopy, and by elemental analyses.

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