

## Oxidative Addition Reactions of an Iridium Nitrosyl Compound

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THE diverse substitution and oxidative addition reactions of  $d^{10}$  zerovalent derivatives of platinum, palladium, and nickel<sup>1</sup> have prompted our investigation of the electronically similar  $d^{10}$  compound  $\text{Ir}(\text{NO})(\text{PPh}_3)_3$ .<sup>2</sup> We report both an improved preparation of (I) and its oxidative addition with acids, halogens, and alkyl halides.

the geometry is depicted as a tetragonal pyramid with *trans*-phosphines and a bent nitrosyl group at the apex as has been reported<sup>5</sup> for the isoelectronic  $d^8$  complex  $[\text{IrCl}(\text{CO})(\text{NO})\text{L}_2]^+$ ,  $\nu\text{N}-\text{O}$  1680  $\text{cm}^{-1}$ . Good spectroscopic evidence supporting this geometry is found in the far-i.r. spectrum of (IV), which shows only one iridium-chlorine

### Some properties of iridium nitrosyl compounds

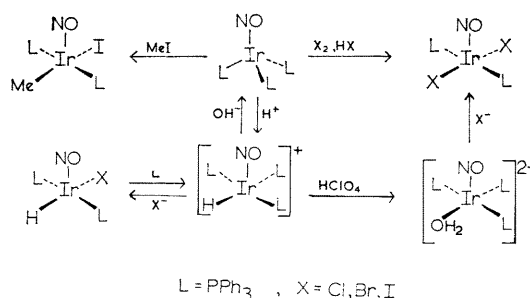
Compound(a)	Colour	I.r. data(b) ( $\text{cm}^{-1}$ )
(I) $\text{Ir}(\text{NO})\text{L}_3$	orange	$\nu\text{N}-\text{O}$ 1600
(II) $\text{Ir}(\text{CH}_3)\text{I}(\text{NO})\text{L}_2$	brown	$\nu\text{N}-\text{O}$ 1525, $\delta\text{CH}_3$ 1220
(III) $\text{IrI}_2(\text{NO})\text{L}_2$	red-brown	$\nu\text{N}-\text{O}$ 1560
(IV) $\text{IrCl}_2(\text{NO})\text{L}_2$	light brown	$\nu\text{N}-\text{O}$ 1560, $\nu\text{Ir}-\text{Cl}$ 325
(V) $[\text{Ir}(\text{H}_2\text{O})(\text{NO})\text{L}_2][\text{ClO}_4]_2$ (c)	orange	$\nu\text{N}-\text{O}$ 1855, $\nu\text{O}-\text{H}$ 3525
(VI) $[\text{IrH}(\text{NO})\text{L}_3][\text{ClO}_4]$ (d)	yellow-green	$\nu\text{N}-\text{O}$ 1715, $\nu\text{Ir}-\text{H}$ 2050, $\delta\text{Ir}-\text{H}$ 820
(VII) $\text{IrHCl}(\text{NO})\text{L}_2$	red-brown	$\nu\text{N}-\text{O}$ 1550, $\nu\text{Ir}-\text{Cl}$ 290, $\nu\text{Ir}-\text{H}$ 2070
(VIII) $\text{Ir}(\text{CH}_3)\text{Cl}(\text{NO})\text{L}_2$	brown	$\nu\text{N}-\text{O}$ 1525, $\nu\text{Ir}-\text{Cl}$ 285, $\delta\text{CH}_3$ 1220

(a) All compounds reported give good elemental analyses; (b) Recorded as KBr discs, petroleum jelly mulls below 400  $\text{cm}^{-1}$ ; (c)  $\Lambda_M = 37.5 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ , nitrobenzene, 25° (10<sup>-3</sup>M); (d)  $\Lambda_M = 25.3 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ , nitrobenzene, 25° (10<sup>-3</sup>M).

Reaction of *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide with  $\text{IrH}(\text{CO})\text{L}_3$  (L =  $\text{PPh}_3$ ) gives  $\text{Ir}(\text{NO})(\text{CO})\text{L}$  which upon being heated under reflux in an excess of  $\text{PPh}_3$  is converted into (I) (93%). Compound (I) with methyl iodide at 85° gives  $\text{Ir}(\text{CH}_3)\text{I}(\text{NO})\text{L}_2$  (II), remarkable for its low nitrosyl-stretching frequency (Table), and with  $\text{I}_2$  to form  $\text{IrI}_2(\text{NO})\text{L}_2$  (III), and with HCl to form  $\text{IrCl}_2(\text{NO})\text{L}_2$  (IV). With an excess of perchloric acid, (I) is converted into the orange diperchlorate  $[\text{Ir}(\text{H}_2\text{O})(\text{NO})\text{L}_2][\text{ClO}_4]_2$  (V). Intermediate in its formation is the yellow-green hydride complex  $[\text{IrH}(\text{NO})\text{L}_3][\text{ClO}_4]$  (VI). This protonation is reversible; treatment with KOH yields (I). Such reactions are analogous to those of zerovalent platinum compounds with acids.<sup>3</sup> With LiCl in ethanol, (VI) forms the neutral hydride  $\text{IrHCl}(\text{NO})\text{L}_2$  (VII), a probable intermediate in the formation of (IV) from HCl.

It has been suggested<sup>4</sup> that the low nitrosyl-stretching frequencies of (III) and (IV) (Table) might indicate bridging nitrosyl groups. However, (II) and (III) are found to be monomeric in benzene (osmometer) and

stretching frequency. With LiCl, (II) is converted into  $\text{Ir}(\text{Me})\text{Cl}(\text{NO})\text{L}_2$  (VIII). This lability of the halide group suggests that operation of some kinds of *trans* effect, as does steady decrease in Ir-Cl for compounds, (IV), (VII), and (VIII).



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