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**Preliminary communication**

# MOLECULAR GEOMETRY OF THE *trans* (DIAGONAL) ISOMER OF DICARBONYL($\pi$-CYCLOPENTADIENYL)IODO(PHENYLISONITRILE)-MOLYBDENUM: OBSERVATIONS ON THE $\pi$-ACCEPTOR ABILITIES OF ISONITRILE LIGANDS

G.A. SIM, J.G. SIME, D.I. WOODHOUSE

*Chemistry Department, University of Glasgow, Glasgow G12 8QQ (Great Britain)*

and G.R. KNOX

*Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL (Great Britain)*

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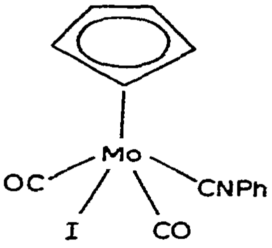
## Summary

The Mo—C(isonitrile) distance in the complex ($\pi$-$C_5H_5$)Mo(CO)$_2$I(CNPh) is 2.025(10) Å, only slightly longer than the Mo—C(carbonyl) distances of 1.973(10), 1.983(10) Å, and accordingly $d \rightarrow \pi^*$ back donation from the metal to the isonitrile ligand must be appreciable.

Whereas coordination of carbon monoxide to transition metals is accompanied by a marked decrease in $\nu$(CO), coordination of isonitriles to transition metals leads to only a slight decrease or indeed to an increase in $\nu$(NC) and this spectroscopic distinction has been interpreted as indicating that $d \rightarrow \pi^*$ back donation from the metal is unimportant for isonitrile ligands [1]. Nevertheles, the Pt—C distance in *cis*-PtCl$_2$(CNPh)$_2$, 1.896(16) Å, is shorter than an estimate of 2.02 Å for a (hypothetical) Pt—C(*sp*) single bond, which suggests that the Pt—CNPh bond has some double-bond character though $\nu$(NC) for the complex is ca. 100 cm$^{-1}$ higher than that for the free ligand [2]. In the complexes Mn(CO)$_3$(CNMe)$_2$Br [3] and Mn(CO)$_3$(CNPh)$_2$Br [4] the Mn—C(isonitrile) distances are ca. 0.15 Å longer than the Mn—C(carbonyl) distances, but still probably ca. 0.1 Å shorter than a (hypothetical) Mn—C single bond: here there is a small increase in $\nu$(NC) on formation of the MeNC complex [5] and an increase of ca. 65 cm$^{-1}$ on formation of the PhNC complex [6].

We have now obtained a direct comparison of metal—carbonyl and metal—isonitrile bond distances in the transition-metal complex *trans*-($\pi$-$C_5H_5$)Mo(CO)$_2$I(CNPh) (I) [7] and find that the Mo—C(isonitrile) distance, 2.025(10) Å, is only slightly longer than the Mo—C(carbonyl) distances, 1.973(10) and 1.983(10) Å.



(I)

Moreover, this Mo—C(isonitrile) distance is comparable with Mo—C(carbonyl) distances of 2.00 Å in $(\pi\text{-}C_5H_4CH_3)Mo(CO)_2I[P(OMe)_3]$ [8] and 2.02 Å in $(\pi\text{-}C_5H_5)Mo(CO)_2I[P(OMe)_3]$ [8] and is shorter than the Mo—C(carbonyl) distance of 2.06 Å in $Mo(CO)_6$ [9]: a (hypothetical) Mo—C(*sp*) single-bond distance of ca. 2.32 Å can be estimated from the Mo—C($sp^3$) distance of 2.38 Å in $(\pi\text{-}C_5H_5)Mo(CO)_3Et$ [10]. These results establish that the Mo—C(isonitrile) distance in the $d^4$ $Mo^{II}$ complex (I) must have appreciable double-bond character and that $d \rightarrow \pi^*$ back donation from the metal to the isonitrile ligand cannot be unimportant. The stretching frequency $\nu$(NC) of 2098 $cm^{-1}$ for this complex (and its *cis*-isomer) is 34 $cm^{-1}$ lower than that of the free ligand.

In view of these results we conclude that caution is necessary in interpreting the direction and magnitude of IR frequency shifts between free ligand and complex as absolute indicators of the absence or existence of $\pi$-bonding between isonitriles and metals. At present infrared methods should probably only justifiably be used to demonstrate trends in isonitrile—metal $\pi$-bonding in related series of complexes.

Crystals of the isonitrile complex (I) are orthorhombic, space group *Pbca*, with $a$ 12.035(4), $b$ 17.284(5), $c$ 14.510(5) Å, $D_m = 1.95$, $Z = 8$, $D_c = 1.97$. Intensity data were measured on an automatic four-circle diffractometer with Mo-$K_\alpha$ radiation and the crystal structure elucidated by Fourier and least-squares methods. The calculations converged at $R$ 4.0% over 1471 reflections for which $I > 3\sigma(I)$.

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