Conformational Changes about the Molybdenum–Nitrogen Bond in $[\mathrm{Mo}\text{-}(\pi\text{-}C_5H_5)(CO)_2N{:}C\mathrm{Bu}^t_2]$: Infrared and ^{1}H Nuclear Magnetic Resonance Studies

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Summary Reversible i.r. and ^{1}H n.m.r. spectral changes in the temperature range 28 to −45° are reported for the complex $[\mathrm{Mo}\text{-}(\pi\text{-}C_5H_5)(CO)_2N{:}C\mathrm{Bu}^t_2]$, and interpreted in terms of conformational changes about the multiple metal–nitrogen bond.

THE new complex, $[\mathrm{Mo}\text{-}(\pi\text{-}C_5H_5)(CO)_2N{:}C\mathrm{Bu}^t_2]$, was obtained from $\mathrm{LiN{=}CBu}^t_2$ [1] and $\mathrm{Mo}\text{-}(\pi\text{-}C_5H_5)(CO)_3Cl$ (1:1 molar ratio) in ether solution at 0°, as royal-blue crystals. Cryoscopic measurements in benzene, and the mass spectrum, confirmed the mononuclear formulation. Reversible changes in the i.r. and ^{1}H n.m.r. spectra with change in temperature are recorded in the Table and Figure.

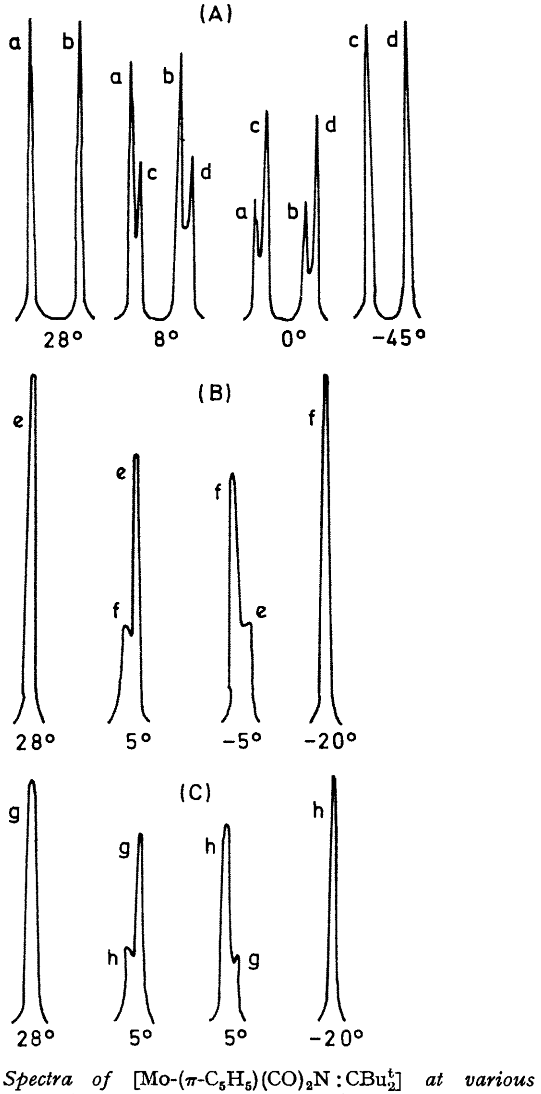
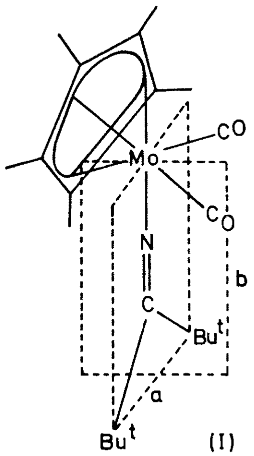


FIGURE. *Spectra of* $[\mathrm{Mo}\text{-}(\pi\text{-}C_5H_5)(CO)_2N{:}C\mathrm{Bu}^t_2]$ *at various temperatures.* (A) *I.r. spectrum in hexane*; (B) ^{1}H *n.m.r. spectrum arising from* Bu^t *groups* (τ, e 8·82, f 8·83) *in* $C_6D_{11}CD_3$; (C) ^{1}H *n.m.r. spectrum arising from the* π-C_5H_5 *group.* (τ, g 4·35, h 4·32) *in* $C_6D_{11}CD_3$.

I.r. spectral data for $[\mathrm{Mo}\text{-}(\pi\text{-}C_5H_5)(CO)_2N{:}C\mathrm{Bu}^t_2]$

Form	Temp. (°)	ν_{CO} (cm^{-1})		ν_{CN} (cm^{-1})
KBr disc	0 and 27	1946s	1848s	1621m-w
Hexane soln.	27	1967s	1883s	1616m-w
	−45	1938s	1847s	
Nujol mull and soln.	0 and 27	1968s	1884s	1618m-w
		1949m	1851m	

No changes were detected in the electronic spectrum on cooling solutions to −11°.



(I)

The suggested structure of the complex is (I). Steric properties of the Bu^t groups require the Mo–N–C unit to be approximately linear, which is confirmed by the single ^{1}H n.m.r. signal observed at −60° and preliminary *X*-ray structural data.[2] We believe the ketimido-group acts as a three electron donor on the basis of (i) the effective atomic number rule, and the presence of only two carbonyl groups; (ii) the relatively low carbonyl stretching frequencies; (iii) the failure of the complex to add a further neutral donor molecule.

The accumulated spectral data are consistent with only small changes in structure, and are in accordance with conformational changes about the Mo–N bond. The solid state and low temperature forms are thought on the basis of their i.r. data to be the same conformer, the most sterically favourable staggered form (Ia). Staggered conformers have been detected also for many complexes,[3,4] including carbene complexes,[5–7] *e.g.* $[\mathrm{W(CO)_5C(OR^2)R^1}]$. The cylindrical symmetry of the *d*-orbitals involved in the $d\pi$–$p\pi$ bonding will allow rotation about the Mo=N bond and the high temperature form may be either the staggered conformer (Ib) or the form with free rotation.

The ketimido- and carbene groups can be considered to be related in the same way as the carbonyl and nitrosyl groups, if carbon of the carbene donates two electrons,[5] and nitrogen three electrons to the metal. Each group then has a vacant *p*-orbital on the donating atom, capable of π-bonding to the metal orbital having π-cylindrical symmetry,[8] and rotation about the metal–nitrogen bond is theoretically possible in the same way as suggested for the carbene group.[8]

We thank the S.R.C. for a research Studentship (to C. M.)

(*Received, March* 16*th*, 1970; *Com.* 366.)

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