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Preliminary communication

CYCLIC CARBENE FORMATION THROUGH ALKYL MIGRATION TO MOLYBDENUM COORDINATED ISONITRILE, SYNTHESIS AND X-RAY STRUCTURE OF *cis*-$\text{MoI}\{\overline{\text{C(NMe)[CH}_2]_2\text{C}}\text{H}_2\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$. AN EXAMPLE OF A STERICALLY BLOCKED *cis-trans* ISOMERISATION FOR THE $[\text{Mo(X)(L)(CO)}_2(\eta\text{-C}_5\text{H}_5)]$ SYSTEM

HARRY ADAMS, NEIL A. BAILEY*, VALERIE A. OSBORN, and MARK J. WINTER*
Department of Chemistry, The University, Sheffield S3 7HF (Great Britain)

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Summary

Treatment of $\text{Mo(CNMe)(CO)}_2(\eta\text{-C}_5\text{H}_5)^-$ with $\text{I[CH}_2]_3\text{I}$ in tetrahydrofuran affords the carbene complex *cis*-$\text{MoI}\{\overline{\text{C(NMe)[CH}_2]_2\text{C}}\text{H}_2\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$, which has been characterised by X-ray crystallography. This complex does not isomerise to the corresponding *trans* isomer, as might have been expected by analogy with related 2-oxacyclopentylidene systems.

Migratory insertion of alkyl to coordinated carbonyl is a fundamental process in organotransition metal chemistry [1]. Analogous processes for ligated isonitrile are less common owing to a scarcity of suitable substrate molecules, but clearly the process is more facile than for the corresponding carbonyl insertion [2]. We report below the synthesis of a cyclic carbene complex making use of the ease of the isonitrile insertion process.

Treatment of a solution containing $\text{Mo(CNMe)(CO)}_2(\eta\text{-C}_5\text{H}_5)^-$ (1) with $\text{I[CH}_2]_3\text{I}$ leads to rapid darkening of the mixture, whose eventual IR spectrum contains two main bands (ν(CO) (THF): 1945s and 1857s cm) corresponding to the only isolated product *cis*-$\text{MoI}\{\overline{\text{C(NMe)[CH}_2]_2\text{C}}\text{H}_2\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ (2) (62%)*.

The suggested mechanism of formation of this complex is presented in Scheme 1, and is based upon the observation of η^2-iminoacyls in related reactions [3] and the postulated cyclisation mechanisms for syntheses of the

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*(2): m.p. 129—131°C; ν(CO) (CH_2Cl_2) 1952s and 1860s cm^{-1}; ^1H NMR δ(CDCl_3) 5.52 (s, 5 H), 3.88 (m, 1 H), 3.65 (m, 1 H), 3.53 (m, 1 H), 3.43 (m, 1 H), 3.32 (t, 3 H, J 1.4 Hz) and 2.00 (m, 2 H) ppm; ^{13}C NMR δ($\text{C}_6\text{D}_5\text{CD}_3$) 254.3 (s, CO), 253.2 (s, C), 247.2 (s, CO), 95.4 (d, C_5H_5), 60.3 (t, CH_2), 53.6 (t, CH_2), 43.0 (g, Me), and 21.0 (t, CH_2) ppm.

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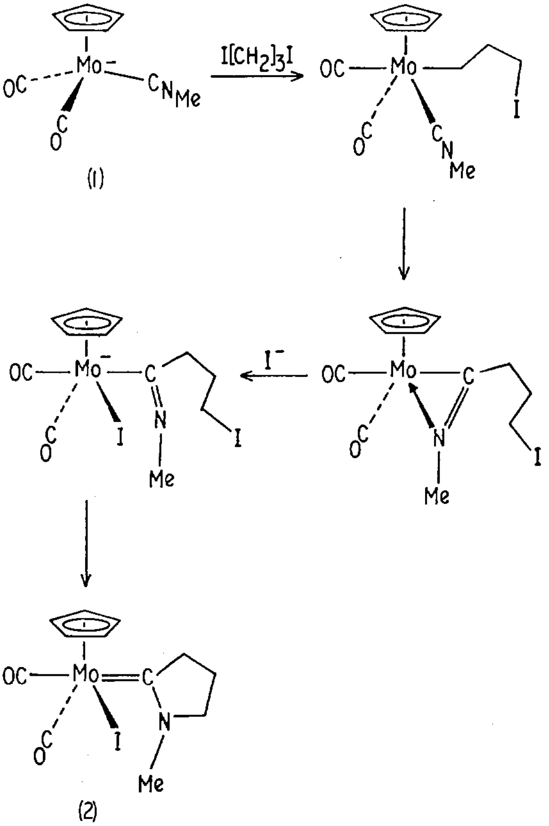
carbene ring $=\overline{CO[CH_2]_2C}H_2$ [4—7]. The preferential migration of $[CH_2]_3I$ to isonitrile rather than carbonyl is critical in this sequence. Molecules of formula $MX(CO)_2L(\eta\text{-}C_5H_5)$ (M = Mo, W; X = halide or pseudohalide; L = carbene) tend to exist in a thermodynamically preferred *trans* configuration [4,5,7]. However the band intensities in the carbonyl IR spectrum, the evident lack of symmetry within the ^{1}H NMR spectrum and two carbonyl signals in the ^{13}C NMR spectrum all indicated a *cis* configuration for 2. This was confirmed by the crystal structure.

SCHEME 1



Crystal data: $C_{12}H_{14}IMoNO_2$, M = 427.05, crystallises from dichloromethane/hexane as red needles, crystal dimensions 0.50 × 0.09 × 0.09 mm. Triclinic, a 7.824(3), b 13.363(6), c 14.559(6) Å, α 78.62(4), β 77.37(3), γ 80.99(4)°, U 1445.8(11) Å^3, D_c 1.962 g cm^{-3}, Z = 4, space group $P\bar{1}$ (C_i, No. 2, confirmed by the analysis), Mo-K_α radiation (λ 0.71069 Å), μ(Mo-K_α) 29.90 cm^{-1}, $F(000)$ = 816.

Three dimensional X-ray diffraction data for 2 were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3m diffractometer by the ω scan method. The 2378 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz, polarisation and absorption effects. The structure was solved by standard

Patterson and Fourier techniques and refined by block-diagonal least squares methods. Hydrogen atoms were placed in calculated positions (C—H 0.97 Å) but no refinement of positional parameters was permitted. Refinement converged at $R = 0.0385$ with allowance for thermal anisotropy of all non-hydrogen atoms and for the anomalous scattering of iodine and molybdenum.

The crystal structure comprises two independent but structurally rather similar molecules per equivalent position, one molecule only is illustrated (Fig. 1). The methyl substituent on the carbene hetero-atom requires the ring to bind to molybdenum in the reverse orientation to that found in related 2-oxacyclopentylidene complexes [4,7]; this avoids steric interference between the methyl and cyclopentadienyl hydrogens*.

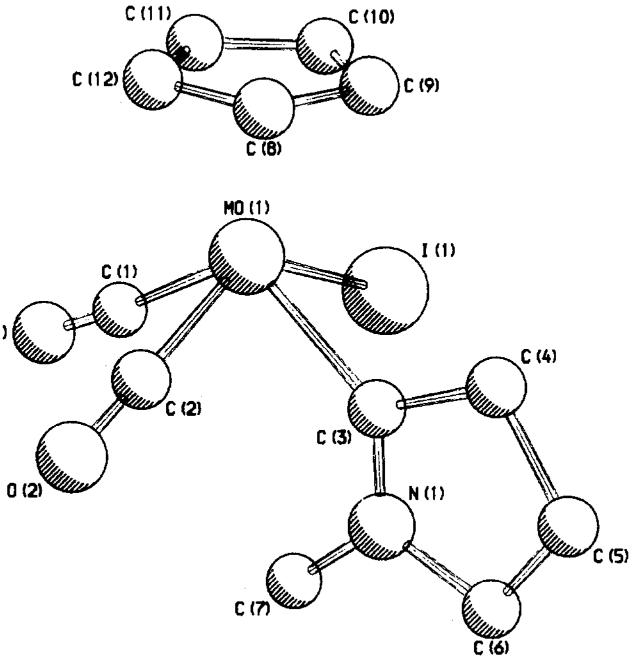


Fig. 1. The molecular structure of one independent molecule of $\mathrm{MoI\{\overline{C(NMe)[CH_2]_2CH_2}\}(CO)_2}$-$(\eta\text{-}\mathrm{C_5H_5})$ (2). Mean bond lengths for the two molecules: Mo(1)—I(1) 2.831, Mo(1)—C(3) 2.144, and N(1)—C(3) 1.284 Å. Mean bond angles for the two molecules: Mo(1)—C(3)—N(1) 132.3, Mo(1)—C(3)—C(4) 121.7, C(3)—N(1)—C(7) 126.7, C(6)—N(1)—C(7) 115.7, and I(1)—Mo(1)-C(3) 77°.

The effect of the reverse carbene orientation is that the methyl group partially blocks the metal site below the basal plane. The *cis-trans* isomerisation of $\mathrm{Mo(X)(CO)_2(PR_3)(\eta\text{-}C_5H_5)}$ systems has been investigated, and an intermediate postulated in which one of X or $\mathrm{PR_3}$ moves down so as to form an axial ligand along with the $\mathrm{C_5H_5}$ ring in a trigonal bipyramidal system [8]. An analogous process is not feasible for 2; our suggestion is that were iodine

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

to move in such a fashion it would interact unfavourably with the methyl group. Similarly, movement of the carbene ring would cause interaction of the methyl group with the other ligands, hence **2** remains in the *cis* configuration. Even prolonged heating in THF or toluene at reflux results only in the re-isolation of **2**, together with some decomposition.

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