

Preliminary communication

Synthesis of heterocyclic molybdenum carbene complexes using haloalkyl-substituted epoxides

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Abstract

The reaction of $\text{I}(\text{CH}_2)_2\text{CHCH}_2\text{O}$ and an excess of LiI with $[\text{Mo}(\text{CNMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ gives crystallographically characterized *cis*- $[\text{Mo}(\text{CO})_2\{\text{C}(\text{CH}_2)_2\text{CH}(\text{CH}_2\text{OH})\text{NMe}(\eta\text{-C}_5\text{H}_5)\}]$. This reacts with $\text{C}_5\text{H}_5\text{NO}$ to give a high yield of the γ -lactam $\text{MeN}[\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{OH})]$. The corresponding reaction of $\text{I}(\text{CH}_2)_3\text{CHCH}_2\text{O}$ with excess LiI and $[\text{Mo}(\text{CNMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ gives *cis*- $[\text{Mo}(\text{CO})_2\{\eta^2\text{-}\overline{\text{C}}(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{IO})\text{NMe}\}]$ (also crystallographically characterized) rather than a carbene complex.

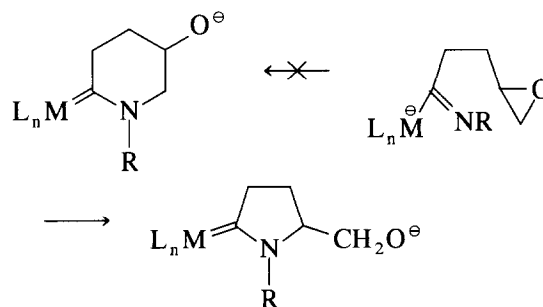
Keywords: Molybdenum; Carbene; Epoxides; Group 6; Isocyanide; Heterocycle

We discussed earlier [1] the use that can be made of the ease by which alkyl groups migrate to isocyanide [2–6] in making cyclic carbene complexes *cis*- $[\text{M}(\text{CO})_2\{\text{C}(\text{CH}_2)_3\text{NMe}(\eta\text{-C}_5\text{H}_5)\}]$ (M = Mo or W) from the reactions between the anions $[\text{M}(\text{CO})_2(\text{CNMe})(\eta\text{-C}_5\text{H}_5)]^-$ (1) and $\text{I}(\text{CH}_2)_3\text{I}$. We demonstrate here the utilization of epoxides for the synthesis of cyclic molybdenum aminocarbene complexes in a strategy which also involves alkyl to isocyanide migration. Completion of this strategy by decomplexation of the resulting carbene (in this case to give high yields of a γ -lactam) affords an efficient route to useful organic heterocycles. A closely related analogue of this γ -lactam is known to act upon the mammalian nervous system, [7] and related γ -lactams are used as nootropic drugs [8] or to combat arteriosclerosis [9].

We reasoned that a general approach to precursors of γ -hydroxymethyl γ -lactams could be provided by an intramolecular ring closure involving a nucleophilic attack of an imino nitrogen within a metallacarbenoid moiety on an epoxide group (Scheme 1). Although epoxides are usually attacked by anionic nucleophiles at the less substituted terminus, [10] the formation of a five-membered ring, as in **2** (Scheme 2), was expected because

5-*exo-tet* cyclizations are favoured over 6-*endo-tet* processes [11]. The isolation and characterization of the aminocarbene **2** reported here represents the first realization of the approach depicted in Scheme 1.

Addition of $\text{I}(\text{CH}_2)_2\text{CHCH}_2\text{O}$ and an excess of LiI to a solution of $[\text{Mo}(\text{CNMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ in THF at -78°C , followed by warming to ambient temperature, gave a maroon, alkaline, solution whose IR spectrum [$\nu_{\text{CO}}(\text{THF})$; 1948s and 1860s cm^{-1}] indicated the formation of a *cis*-dicarbonyl complex. The solution was neutralized by addition of dilute aqueous hydrochloric acid. Chromatography on alumina at ambient temperature afforded a red fraction from which dark red-purple crystals of the carbene complex **2** were obtained in 38% yield. This modest yield is the result of the sensitivity of the complex to decomposition, rather



Scheme 1.

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than competing by-product formation. Infrared monitoring revealed the presence only of the carbene complex **2** in the reaction mixture. The carbene carbon is manifest in the ^{13}C NMR spectrum, which shows three signals [$\delta_{\text{C}}(\text{CDCl}_3, -50^\circ\text{C})$: 259.2, 252.0, 246.4] associated with two carbonyls and a carbene, in positions very similar to those found for *cis*- $[\text{MoI}(\text{CO})_2(=\text{C}(\text{CH}_2)_3\text{NMe})(\eta\text{-C}_5\text{H}_5)]$ [$\delta_{\text{C}}(\text{C}_6\text{D}_5\text{CD}_3, -60^\circ\text{C})$: 254.3, 253.2, 253.2, 247.2] [1].

The anionic complex **3** is suggested as intermediate in this reaction. It is formed through nucleophilic replacement of iodide in $\text{I}(\text{CH}_2)_2\text{CHCH}_2\text{O}$ followed by migration of the resulting alkyl group to carbonyl. The occurrence of a subsequent 5-*exo-tet* cyclization is inferred from the constitution of the aminocarbene **2**. An X-ray crystal structure analysis for **2** [12] (Fig. 1) confirmed that it is the five-membered ring which is formed. The carbene ligand possesses an envelope conformation for the five-membered ring [r.m.s. deviation of plane C(11), N(1), C(8), C(9) 0.018 Å, deviation of C(10) 0.356 Å]. This conformation is similar to that found in *cis*- $[\text{MoI}(\text{CO})_2(=\text{C}(\text{CH}_2)_3\text{NMe})(\eta\text{-C}_5\text{H}_5)]$ [1].

Reaction of complex **2** with $\text{C}_5\text{H}_5\text{N-O}$ (three equivalents, toluene at reflux, 24 h) cleaved the carbene from the metal to give the γ -lactam **4** in 92% yield, with 96% purity (by GLC), after workup. The fate of the molybdenum was not determined, but recycling of the molybdenum is being investigated.

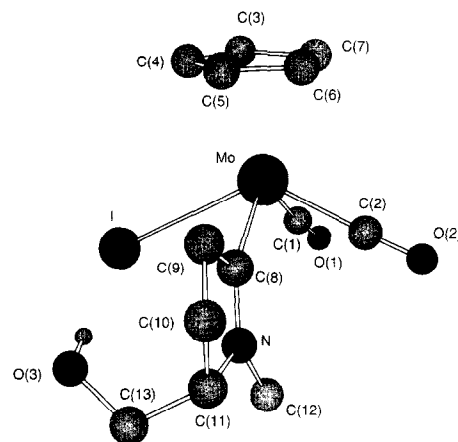
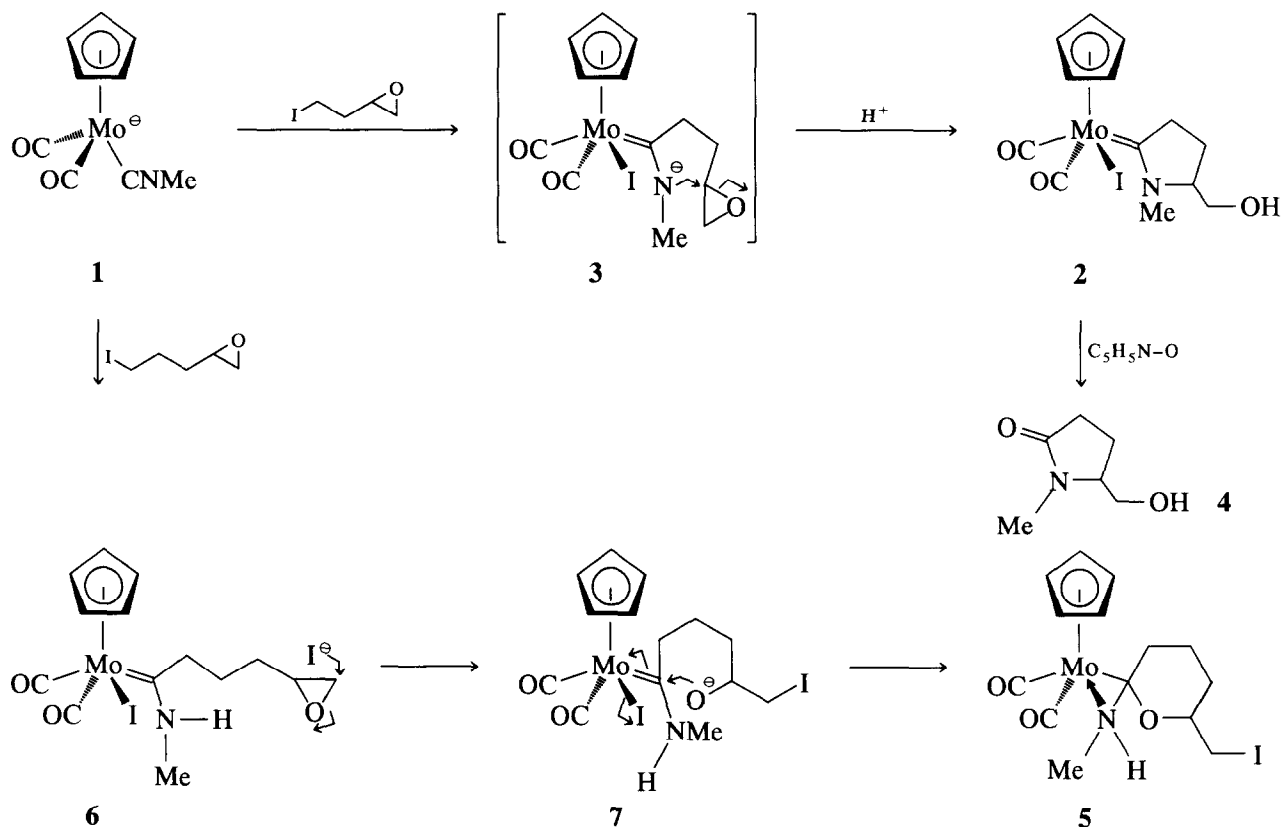


Fig. 1. Molecular structure of $[\text{Mo}\{\text{=C}(\text{CH}_2)_2\text{CH}(\text{CH}_2\text{OH})\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (**2**). Selected bond lengths and angles: Mo(1)–I(1) 2.828(1), Mo(1)–C(2), 1.974(8), Mo(1)–C(1), 1.974(8), Mo(1)–C(8), 2.167(7), N(1)–C(8) 1.293(10), N(1)–C(11) 1.495(11), N(1)–C(12) 1.444(12), C(8)–C(9) 1.495(11), I(1)–O(3) 3.703, I(1)–H(O(3)) 2.70 Å; I(1)–Mo(1)–C(1) 79.2(3), I(1)–Mo(1)–C(2) 128.6(3), C(1)–Mo(1)–C(2), 75.3(4), I(1)–Mo(1)–C(8) 77.2(2), C(1)–Mo(1)–C(8) 116.8(3), C(2)–Mo(1)–C(8) 75.8(3), Mo(1)–C(1)–O(1) 175.4(9), Mo(1)–C(2)–O(2) 177.8(9), N(1)–C(8)–C(9), 108.8(6) $^\circ$.

Rather surprisingly, the use of $\text{I}(\text{CH}_2)_3\text{CHCH}_2\text{O}$ did not lead to isolation of an analogous azacarbene. Although the IR spectrum of the mixture formed from $\text{I}(\text{CH}_2)_2\text{CHCH}_2\text{O}$, $[\text{Mo}(\text{CNMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$, and



Scheme 2.

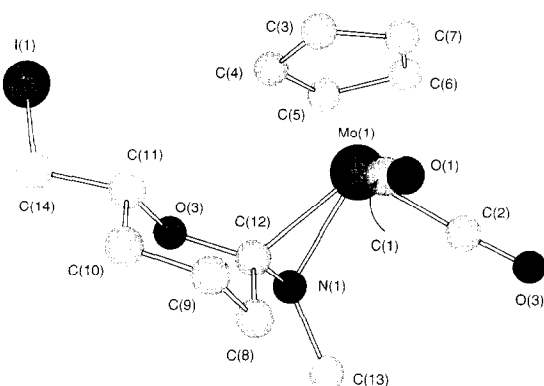


Fig. 2. Molecular structure of $[(\text{Mo}(\text{CO})_2\{\eta^2\text{-C}(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{IO})\text{NHMe}\})(\eta\text{-C}_5\text{H}_5)]$ (**5**). Selected bond lengths and angles: $\text{Mo(1)}\text{--}\text{N(1)}$

2.168(10), $\text{Mo(1)}\text{--}\text{C(1)}$ 1.927(12), $\text{Mo(1)}\text{--}\text{C(2)}$ 1.927(13), $\text{Mo(1)}\text{--}\text{C(12)}$ 2.219(13), $\text{I(1)}\text{--}\text{C(14)}$ 2.121(14), $\text{N(1)}\text{--}\text{C(12)}$ 1.409(13), $\text{N(1)}\text{--}\text{Mo(1)}\text{--}\text{C(2)}$ 89.9(6), $\text{C(1)}\text{--}\text{Mo(1)}\text{--}\text{C(2)}$ 78.8(5), $\text{C(1)}\text{--}\text{Mo(1)}\text{--}\text{C(12)}$ 82.5(5), $\text{N(1)}\text{--}\text{Mo(1)}\text{--}\text{C(12)}$ 37.4(3), $\text{N(1)}\text{--}\text{Mo(1)}\text{--}\text{C(1)}$ 109.9(5), $\text{C(2)}\text{--}\text{Mo(1)}\text{--}\text{C(12)}$ 109.5(6), $\text{Mo(1)}\text{--}\text{N(1)}\text{--}\text{C(12)}$ 73.3(7), $\text{Mo(1)}\text{--}\text{C(12)}\text{--}\text{N(1)}$ 69.3(7)°.

an excess of LiI was similar to that containing **2**, no product could be isolated. It appears that a carbene complex was formed, but decomposed upon work-up. A prolonged reaction time led to replacement of these two carbonyl bands by two new bands [$\nu_{\text{CO}}(\text{THF})$: 1913s and 1819s cm^{-1}] assigned as the carbonyl ligands of compound **5**. The ^{13}C NMR spectrum showed no carbenoid signals. Owing to the complexity of the NMR spectra of **5** and its unusual constitution, it was characterized by X-ray crystallography (Fig. 2) [13]. In both of the essentially identical crystallographically independent molecules, the molybdenum is η^2 -bonded to the $\text{MeHNC}[(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{IO})]$ ligand through the exocyclic CN bond. The saturated six-membered ring adopts a chair conformation [r.m.s. deviations through atoms C(8), C(10), C(11), C(12) 0.005, 0.011 Å, displacements of O(3) + 0.621, + 0.604 Å, and of C(9) − 0.651, − 0.665 Å]. Both the NHMe and CH_2I groups are equatorial. The bonding of oxygen, nitrogen, and molybdenum to a single carbon atom as in **5**, is to our knowledge, unique.

A plausible mechanism for formation of **5** is presented in Scheme 2. It involves an epoxide ring opening in complex **6** to give the intermediate **7**, and subsequent ring closure through intramolecular nucleophilic attack of the alkoxide upon the carbene. A requirement for this

process to take place exclusively is that the rate of attack of the aminocarbene nitrogen on the epoxide ring (as for complex **3**) to give a six-membered ring must be appreciably slower than intermolecular attack of iodide ion on the less substituted epoxide carbon atom.

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References and notes

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- [13] Crystal data for $[(\text{Mo}(\text{CO})_2\{\eta^2\text{-C}(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{IO})\text{NHMe}\})(\eta\text{-C}_5\text{H}_5)]$: triclinic, $a = 8.471(9)$, $b = 12.069(5)$, $c = 16.803(7)$ Å, $\alpha = 80.29(3)$, $\beta = 75.68(6)$, $\gamma = 79.49(7)^\circ$, $U = 1622.8(20)$ Å³, $Z = 4$, $D_c = 1.924$ g cm^{−3}, space group $\text{P}1(\text{C}_1^1)$, No. 2), Nicolet R3 4-circle diffractometer, 3732 independent reflections, final $R = 0.0707$. Tables of atomic coordinates, bond lengths and angles and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.