Preliminary communication

Synthesis of heterocyclic molybdenum carbene complexes using haloalkyl-substituted epoxides

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Abstract

The reaction of $I(CH_2)_2\overline{CHCH_2O}$ and an excess of LiI with $[Mo(CNMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ gives crystallographically characterized *cis*-$[MoI(CO)_2\{=\overline{C(CH_2)_2CH(CH_2OH)}\dot{N}Me\}(\eta\text{-}C_5H_5)]$. This reacts with C_5H_5NO to give a high yield of the γ-lactam $MeN\{C(=O)CH_2CH_2CH(CH_2OH)\}$. The corresponding reaction of $I(CH_2)_3\overline{CHCH_2O}$ with excess LiI and $[Mo(CNMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ gives *cis*-$[\{Mo(CO)_2\{\eta^2\text{-}\overline{C(CH_2)_3CH(CH_2I)O}\}NHMe\}]$ (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*-$[MI(CO)_2\{=\overline{C(CH_2)_3NMe}\}(\eta\text{-}C_5H_5)]$ (M = Mo or W) from the reactions between the anions $[M(CO)_2(CNMe)(\eta\text{-}C_5H_5)]^-$ (1) and $I(CH_2)_3I$. 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 metallacarbene 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 $I(CH_2)_2\overline{CHCH_2O}$ and an excess of LiI to a solution of $[Mo(CNMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ in THF at $-78°C$, followed by warming to ambient temperature, gave a maroon, alkaline, solution whose IR spectrum [ν_{CO}(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
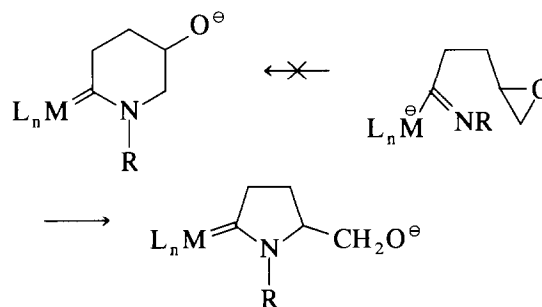
Scheme 1.

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 [δ_C(CDCl$_3$, − 50°C): 259.2, 252.0, 246.4] associated with two carbonyls and a carbene, in positions very similar to those found for cis-[MoI(CO)$_2$-{=C(CH$_2$)$_3$NMe}(η-C$_5$H$_5$)] [δ_C(C$_6$D$_5$CD$_3$, − 60°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 I(CH$_2$)$_2$CHCH$_2$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-[MoI(CO)$_2${=C(CH$_2$)$_3$NMe}(η-C$_5$H$_5$)] [1].

Reaction of complex **2** with C$_5$H$_5$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.
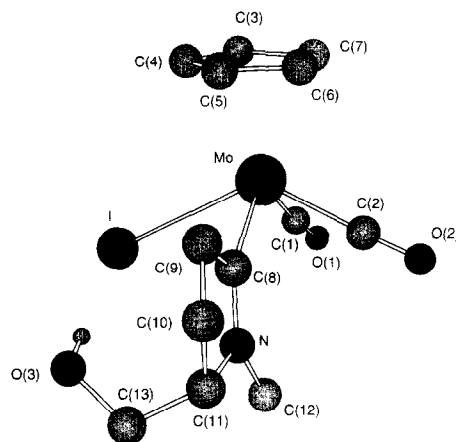

Fig. 1. Molecular structure of [MoI{=C(CH$_2$)$_2$CH(CH$_2$OH)NMe}-(CO)$_2$(η-C$_5$H$_5$)] (**2**). Selected bond lengths and angles: Mo(1)–I(1) 2.828(1), Mo(1)–C(2), 1.974(8), Mo(1)–C(1), 1.974(8), Mo(1)–C(8), 2.167(7), N(1)–C(8) 1.293(10), N(1)–C(11) 1.495(11), N(1)–C(12) 1.444(12), C(8)–C(9) 1.495(11), 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)°.

Rather surprisingly, the use of I(CH$_2$)$_3$CHCH$_2$O did not lead to isolation of an analogous azacarbene. Although the IR spectrum of the mixture formed from I(CH$_2$)$_2$CHCH$_2$O, [Mo(CNMe)(CO)$_2$(η-C$_5$H$_5$)]$^-$, and
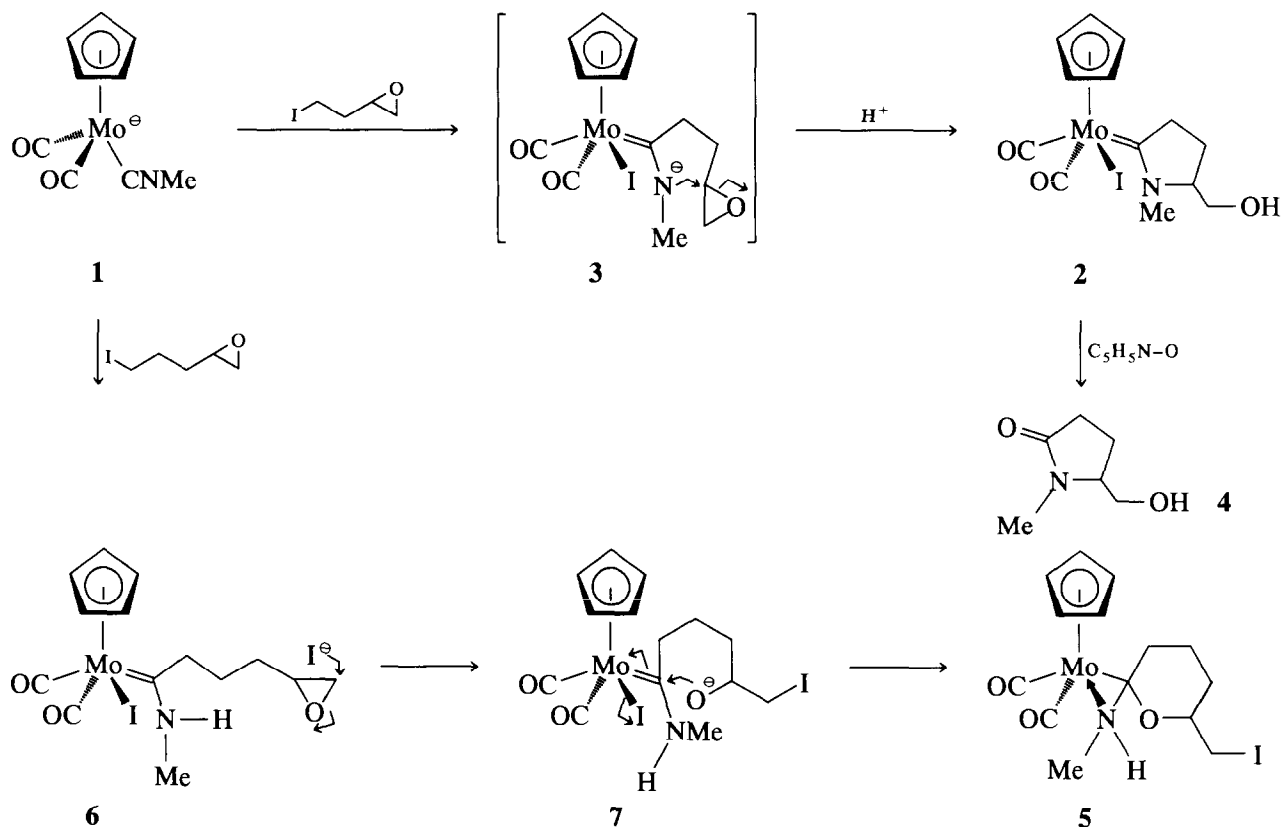
Scheme 2.
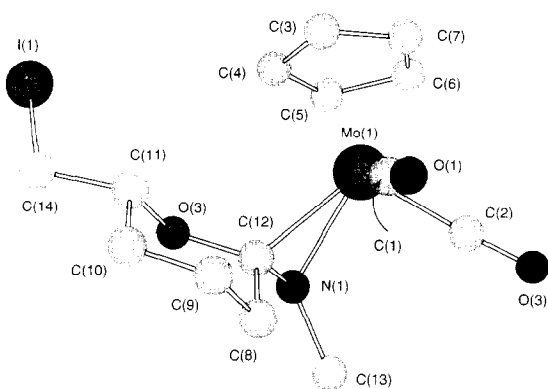
Fig. 2. Molecular structure of [(Mo(CO)₂{η²-C̄(CH₂)₃CH-(CH₂I)O}NHMe)(η-C₅H₅)] (5). Selected bond lengths and angles: Mo(1)–N(1)
2.168(10), Mo(1)–C(1) 1.927(12), Mo(1)–C(2) 1.927(13), Mo(1)–C(12) 2.219(13), I(1)–C(14) 2.121(14), N(1)–C(12) 1.409(13), N(1)–Mo(1)–C(2) 89.9(6), C(1)–Mo(1)–C(2) 78.8(5), C(1)–Mo(1)–C(12) 82.5(5), N(1)–Mo(1)–C(12) 37.4(3), N(1)–Mo(1)–C(1) 109.9(5), C(2)–Mo(1)–C(12) 109.5(6), Mo(1)–N(1)–C(12) 73.3(7), Mo(1)–C(12)–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 [ν_CO(THF): 1913s and 1819s cm⁻¹] assigned as the carbonyl ligands of compound 5. The ¹³C 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 η²-bonded to the MeHNC̄{(CH₂)₃CH(CH₂I)O} 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 CH₂I 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 right must be appreciably slower than intermolecular attack of iodide ion on the less substituted epoxide carbon atom.

Acknowledgements

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[12] Crystal data for [MoI{=C(CH₂)₂CH(CH₂OH)NMe}(CO)₂(η-C₅H₅)]: monoclinic, a = 11.612(6), b = 9.412(3), c = 14.213(6) Å, β = 92.53(4)°, U = 1551.9(12) Å³: D_c = 1.956 g cm⁻³, Z = 4. Space group P2₁/c (C₂ₕ⁵, No. 14); Nicolet R3 4-circle diffractometer, 2299 independent reflections, final R = 0.0512. Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

[13] Crystal data for [(Mo(CO)₂{η²-C̄(CH₂)₃CH(CH₂I)ONHMe}(η-C₅H₅)]: triclinic, a = 8.471(9), b = 12.069(5), c = 16.803(7) Å, α = 80.29(3), β = 75.68(6), γ = 79.49(7)°, U = 1622.8(20) Å³, Z = 4, D_c = 1.924 g cm⁻³, space group P1̄(C_i¹, 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.