Intramolecular Cyclisation of Cationic η^4-Diene Complexes of Molybdenum: A New Synthesis of Tetrahydrofurans, Tetrahydropyrans, and Cyclopentanes

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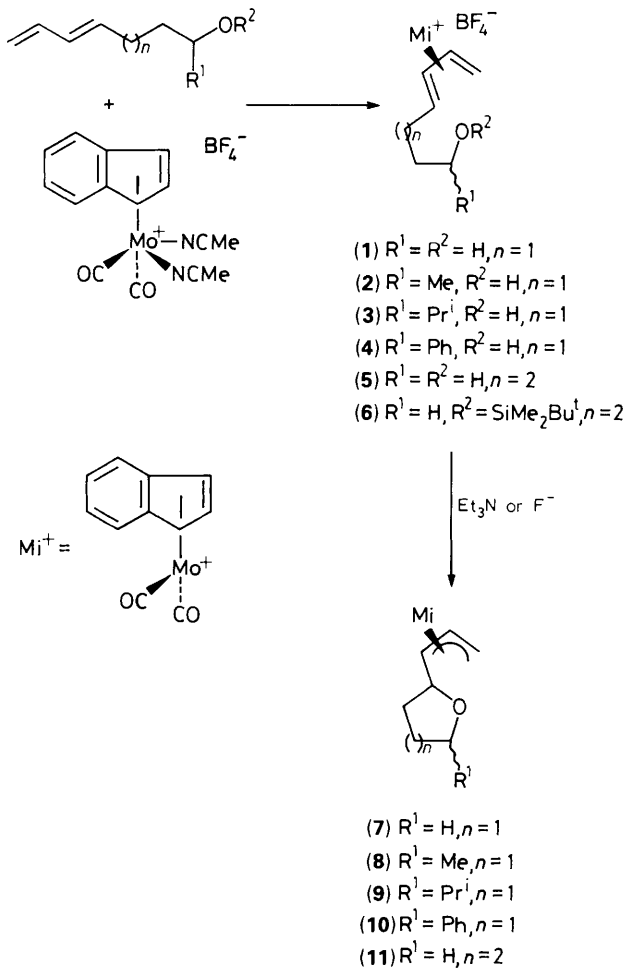
Bis(acetonitrile)dicarbonyl η^5-indenyl molybdenum tetrafluoroborate permits the direct complexation of functionalised dienes which undergo subsequent intramolecular reaction at the metal centre to provide a novel route for the synthesis of carbo- and hetero-cyclic compounds such as cyclopentanes, tetrahydrofurans, and tetrahydropyrans; the initially formed product is an η^3-allyl complex which can undergo further synthetic transformation upon reaction with nucleophiles.

Intermolecular nucleophilic attack on cationic η^4-diene complexes of molybdenum has been shown to be a useful method for the preparation of functionalised 1,3-dienes,[1,2] and stereodefined cycloalkanes.[3] Some of the problems inherent in using this chemistry, such as how to obtain ready and direct access to the cationic molybdenum complexes have been solved,[2] so leading to the possibility of achieving the potentially valuable intramolecular variant of this process. We now report that the use of bis(acetonitrile)dicarbonyl η^5-indenyl molybdenum tetrafluoroborate permits the direct complexation of functionalised dienes which undergo subsequent reaction at the metal centre to provide a novel route for the synthesis of carbo- and hetero-cyclic compounds. Additionally, we show that in this process the cyclic products are linked to a molybdenum allyl complex which is capable of further elaboration, so providing the basis for a potential multi bond forming synthetic sequence.

The functionalised dienes were prepared using simple modifications of known procedures[4,5] and gave upon addition of the η^5-indenyl cation $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$[1] the yellow dienyl cations (**1**)—(**6**) directly.† These were not isolated but treated with triethylamine [for (**1**)—(**5**)] or fluoride anion [for (**6**)] to form the tetrahydrofuranyl or pyranyl systems (**7**)—(**11**).‡ The yields of the reactions are good (53—77%) with the best results being obtained from the alcohols as opposed to the silyl ether. Additionally, high field n.m.r. showed that in every case we form the *exo*-η^3-allyl isomer.[1] The reactions of (**2**)—(**4**) were designed to measure any selectivity that may occur during ring closure. However in all cases an essentially 1:1 mixture of the *cis*:*trans* 2,5-disubstituted tetrahydrofurans was obtained, indicating that the cyclisation reaction does not possess any inherent diastereoselectivity.

We next studied the reaction of a cyclic diene (**12**) which, after complexation with the molybdenum cation, gave upon base treatment (Et_3N at 0 °C) the spiroether (**13**) in 42% yield along with 29% of the rearranged allyl complex (**14**) (obtained as a mixture of three double bond isomers), formed by competitive deprotonation of (**13**), as seen previously in compounds of this type.[2,3] The same ratio of products was obtained by fluoride treatment of the silyl ether (**15**) which probably arises owing to the basic nature of the fluoride reaction. The absence of this side reaction in the previous cases using monosubstituted dienes presumably reflects the fact that the slower closure onto the trisubstituted dienyl complex allows deprotonation to compete.

Having achieved the synthesis of oxygen heterocycles in this manner we turned our attention to the study of simple carbocyclisation reactions. The malonate and sulphone derivatives (**16**)—(**18**) were obtained from the dienyl alcohols used above *via* conventional chemistry. Upon complexation with $[Mo(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ and treatment of the subsequent cationic complexes (**19**)—(**21**) with 1,8-

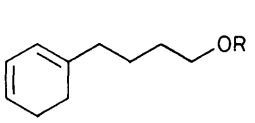


(**1**) $R^1 = R^2 = H, n = 1$
(**2**) $R^1 = Me, R^2 = H, n = 1$
(**3**) $R^1 = Pr^i, R^2 = H, n = 1$
(**4**) $R^1 = Ph, R^2 = H, n = 1$
(**5**) $R^1 = R^2 = H, n = 2$
(**6**) $R^1 = H, R^2 = SiMe_2Bu^t, n = 2$

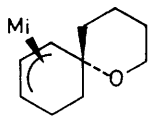
(**7**) $R^1 = H, n = 1$
(**8**) $R^1 = Me, n = 1$
(**9**) $R^1 = Pr^i, n = 1$
(**10**) $R^1 = Ph, n = 1$
(**11**) $R^1 = H, n = 2$

† All new compounds were characterised by high-field n.m.r. (270 and 400 MHz), mass spectrometry, and/or elemental analysis.

‡ *Selected spectroscopic data* for (**7**): $\nu_{CO}(CH_2Cl_2)$ 1949, 1864 cm^{-1}; ^1H n.m.r. ($CDCl_3$), δ −0.28 (t, 1H, dt, *J* 12.0, 8.0 Hz), 1.59 (dd, 1H, *J* 1.8, 12.0 Hz), 1.93—1.67 (m, 3H), 2.27—2.15 (m, 1H), 2.40 (dt, 1H, *J* 9.4, 6.7 Hz), 2.53 (dt, 1H, *J* 8.0, 1.7 Hz), 2.97 (br. t, 1H, 8.8 Hz), 3.4—3.5 (m, 1H), 3.73—3.8 (m, 1H), 5.56 (t, 1H, *J* 2.8 Hz), 5.94 (m, 1H), 6.01 (m, 1H), 7.01—7.06 (m, 4H); Compound (**22**): ν_{CO} (CH_2Cl_2) 1945, 1863, 1733 cm^{-1}; ^1H n.m.r. ($CDCl_3$), δ −0.56 (dt, 1H, *J* 12.2, 8.0 Hz), 1.38—1.42 (m, 1H), 1.65 (dd, 1H, *J* 0.9, 12.2 Hz), 1.71—1.82 (m, 3H), 1.98 (ddd, 1H, *J* 4.0, 8.0, 1.7 Hz), 2.27—2.39 (m, 2H), 2.52 (dt, 1H, *J* 8.0, 1.7 Hz), 2.81 (br.t, 1H, *J* 9.4 Hz), 3.59 (s, 3H), 3.64 (s, 3H), 5.57 (t, 1H, *J* 2.8 Hz), 5.85 (m, 1H), 6.01 (m, 1H), 6.96—7.08 (m, 4H).



(12) R = H
(15) R = $SiMe_2Bu^t$



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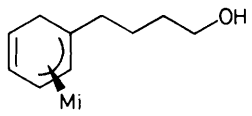

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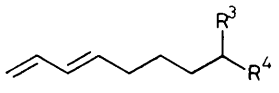
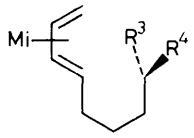
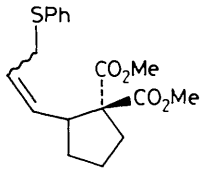


(16) $R^3 = R^4 = CO_2Me$
(17) $R^3 = CO_2Me$, $R^4 = SO_2Ph$
(18) $R^3 = R^4 = SO_2Ph$



(19) $R^3 = R^4 = CO_2Me$
(20) $R^3 = CO_2Me$, $R^4 = SO_2Ph$
(21) $R^3 = R^4 = SO_2Ph$



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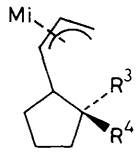

(22) $R^3 = R^4 = CO_2Me$
(23) $R^3 = CO_2Me$, $R^4 = SO_2Ph$
(24) $R^3 = R^4 = SO_2Ph$

diazabicyclo[5.4.0]undec-7-ene (DBU) at −78 °C we obtained the cyclopentane derivatives (**22**)—(**24**).§ The yields of this sequence increase in the order 33% to 61% to 89% as we move from (**19**) to (**21**), indicating, we believe, that the greater the ease of removal of the acidic proton in these derivatives, the faster the cyclisation process becomes. This allows the cyclisation to compete effectively with side reactions, such as deprotonation of the dienyl complex as observed above.

Finally we have demonstrated that the initially formed molybdenum allyl complex (**22**) readily undergoes a nitrosyl exchange reaction with $NOBF_4$[6] to regenerate a new, potentially electrophilic, cationic complex. Without isolation this new complex reacts with external nucleophiles, such as thiophenoxide, to give, after oxidative removal of the metal with cerium(IV) ammonium nitrate (CAN), the allyl sulphide (**25**) in 44% yield as a 1 : 1 mixture of *E* and *Z* isomers. The fact that the first formed products of the new cyclisation do not terminate the synthetic sequence is a significant feature of these new reactions.

In conclusion we have described an efficient new route to the synthetically valuable cyclopentanes and to tetrahydrofuranyl and -pyranyl systems, whilst demonstrating the feasibility of extending nucleophilic attack on cationic η^4-diene complexes to intramolecular cases. Furthermore, the new method gives cyclic compounds which are linked to a molybdenum allyl complex which is capable of further elaboration,[6,7] so enhancing the synthetic potential of the reaction.

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§ Cyclopentane (**23**) was obtained as a 3 : 2 mixture of, relative to the allyl group, *syn* : *anti* carbomethoxy diastereoisomers, as determined by high-field n.m.r.

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