Functionalisation of 1,3-Dienes using Cationic Complexes of Molybdenum

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Reaction of $[Mo(NCMe)_2(CO)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ with substituted cyclohexa-1,3-dienes affords the cations $[Mo(1,3\text{-diene})(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$, which undergo regioselective reactions with nucleophiles and from which the diene can be readily displaced with carbon monoxide; with acyclic 1,3-dienes *cis–trans* isomerisation of the 1-substituent is avoided by using the corresponding pentamethylcyclopentadienyl system allowing the stereoselective synthesis of (*E,E*)-undeca-1,3,5-triene.

The development of synthetic pathways for the controlled functionalisation of 1,3-dienes is of potential importance in the synthesis of complex organic molecules. One possibility is to utilise the reactivity towards nucleophilic reagents of cationic 1,3-diene complexes of the type $[Mo(\eta^4\text{-}1,3\text{-diene})(CO)_2(\eta\text{-}C_5H_5)]^+$ (refs. 1—5). However, with these systems a major problem is the manipulation of the resultant $[Mo(\eta^3\text{-allyl})(CO)_2(\eta\text{-}C_5H_5)]$ complexes, and displacement of the organic fragment. In addition there is the difficulty that access to the required $\eta^4\text{-}1,3$-diene complexes has so far been gained *via* a four-step sequence starting with a mono-olefin, a limitation which makes it very difficult to introduce substituents onto the diene selectively, and then to address the problem of their directing effect† on nucleophilic attack. We report studies which provide answers to some of these problems.

Reaction (CH_2Cl_2, room temperature, 12 h) of the labile η^5-indenyl cation $[Mo(NCNe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (ref. 2‡) with cyclohexa-1,3-dienes affords in one step high yields of the yellow crystalline 1,3-diene cations (1)—(4) (Scheme 1). The 1-methoxycyclohexa-1,3-diene cation (2) reacts [tetrahydrofuran (thf), 0 °C] with K[BHBu$^s_3$] or MeMgI to afford the η^3-allylic complexes (5) and (6),§ resulting from selective *exo*-attack on the methoxy-substituted carbon. Surprisingly, treatment of (5) or (6) with trityl tetrafluoroborate does not lead to the expected[3] *exo*-hydride abstraction reaction, but to loss of the *endo*-methoxy group, and formation of the known cyclohexa-1,3-diene and 1-methylcyclohexa-1,3-diene cations respectively. Thus, this two-step high-yield sequence allows the replacment of an OMe group by an H or R substituent, and in principle provides easy access to a wide range of 1-substituted cyclohexa-1,3-dienes. In contrast, the 1-methylcyclohexa-1,3-diene and 1-methoxycarbonylcyclohexa-1,3-diene cations (3) and (4) react with K[BHBu$^s_3$], MeMgI, LiCuMe$_2$, and EtMgBr in thf to form the η^3-allyl complexes (7)—(10) where the nucleophile is delivered selectively in all cases to the *exo*-4-position, suggesting that these reactions cannot be

simply interpreted in terms of charge[7] or frontier orbital control,[8] but that steric factors are also important in a kinetically controlled reaction.

In contrast with the simple η^3-cyclohexenyl systems described by Faller,[3] and the examples outlined in Scheme 2, the η^3-allyls (8) and (9) do not react satisfactorily with Ph$_3$CBF$_4$ to give the expected cyclohexa-1,3-diene cations. However, reaction (-78 °C) of, for example, (9) with HBF$_4$·Et$_2$O and an activated benzoquinone, such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), in CH_2Cl_2 affords a good yield of (13). This latter observation is important synthetically in that it establishes a possible pathway to certain monoterpenes, and mechanistically suggests that the initial step in the formal hydride abstraction reaction involves a one-electron transfer process.

In examining the reaction of (3) with one of the Evans' enolate anions[9] it was found that in addition to the expected product (11), a low yield (11%) of a neutral yellow-orange complex (14) was formed. Examination of the n.m.r. data§ for (14) suggested that this product had arisen by competitive, but selective, deprotonation, and in agreement, reaction of (3) with the sterically hindered base LiNPr$^i_2$ afforded (14) regioselectively in good yield. Significantly (14) reacted with HBF$_4$·Et$_2$O to reform (3). Thus, the new deprotonation reaction followed by reaction with an electrophile offers an alternative strategy for the formation of substituted cyclohexa-1,3-dienes.

Whereas nucleophiles are directed to the unsubstituted end of the 1-methylcyclohexa-1,3-diene cation (3), the 2-methylcyclohexa-1,3-diene cation (15) (Scheme 2), which is formed more slowly than the 1-methyl analogue from $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$, reacts exclusively at the 1-position with both K[BHBu$^s_3$] and LiCuMe$_2$ to form the *exo*-substituted η^3-allyls (7) and (16). Both these complexes react regioselectively with trityl tetrafluoroborate to form cyclohexa-1,3-diene cations. With (7) the product is the 1-methylcyclohexa-1,3-diene cation (3) resulting from selective abstraction of an *exo*-hydride from a position remote from the methyl substituent. Therefore, this sequence of hydride attack followed by hydride abstraction transforms a 2-substituted cyclohexa-1,3-diene into a 1-substituted cyclohexa-1,3-diene with concomitant movement of the double bonds. In the case of (16), reaction with Ph$_3$CBF$_4$ affords only the 1,6-dimethylcyclohexa-1,3-diene cation (17), which can react further with LiCuMe$_2$ to form the trimethyl substituted η^3-allyl complex (18).

With regard to the previously mentioned problem of removing the organic fragment from the metal, the 1,3-diene (η^5-indenyl) cations react (50 °C, 50 atm) smoothly with carbon monoxide to form the free 1,3-diene and $[Mo(CO)_4(\eta^5\text{-}C_9H_7)][BF_4]$. The enhanced reactivity towards ligand substitution can be explained in terms of an η^5- to η^3-slippage[10] of the η^5-indenyl ligand.
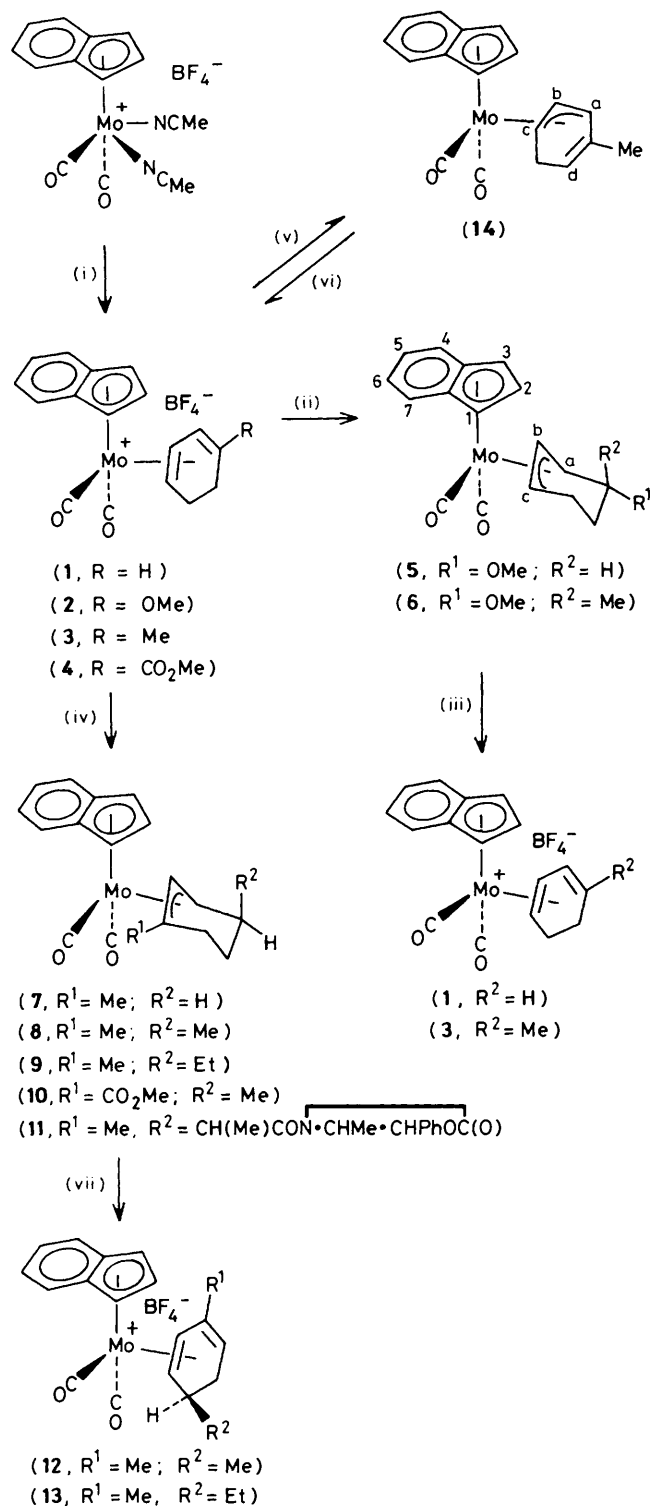
In principle these reactions can be extended to acyclic 1,3-dienes; however, a new problem arises in that *cis–trans*

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† A recent study[6] shows that the reaction of substituted (1,3-diene)Fe(CO)$_3$ complexes with nucleophiles is thermodynamically controlled.

‡ The complex $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ is readily prepared by protonation (HBF$_4$·Et$_2$O, -78 °C, CH_2Cl_2) of $[MoMe(CO)_3(\eta\text{-}C_9H_7)]$ followed by reaction with MeCN.
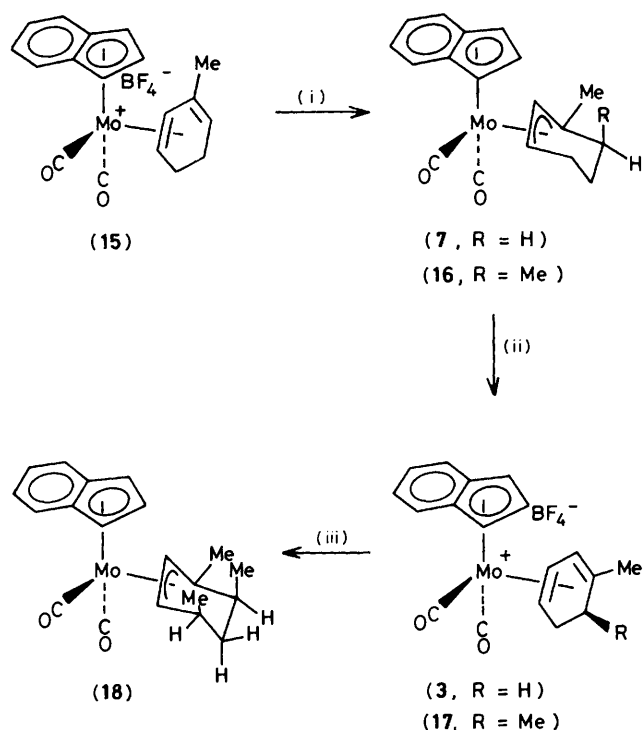
§ Selected spectroscopic data for (6): n.m.r. ^{1}H (C$_6$D$_6$), δ -0.78 (t, 1 H, H^b, J 7.4 Hz), 0.42—0.96 (m, 2 H, CH$_2$), 1.14 (d, 3 H, Me, J 0.8 Hz), 1.44—2.10 (m, 2 H, CH$_2$), 3.06 (m, 1 H, H^c), 3.17 (s, 3 H, OMe), 3.31 (d, 1 H, H^a, J 7.9 Hz), 5.10 (t, 1 H, H^2, J 3.1 Hz), 5.47 (m, 2 H, H^1, H^3), and 6.58 (m, 4 H, H^4—H^7). Compound (14): ν_{CO} (CH$_2$Cl$_2$) 1 930s, 1 850s cm^{-1}; n.m.r. ^{1}H (C$_6$D$_6$), δ -0.63 (t, 1 H, H^b, J 6.8 Hz), 1.80 (q, 3 H, Me, J 2.0 Hz), 2.48 (m, 2 H, CH$_2$), 3.24 (d, 1 H, H^a, J 6.4 Hz), 3.33 (m, 1 H, H^c), 4.22 (br.s, 1 H, H^d), 4.99 (t, 1 H, H^2, J 2.7 Hz), 5.34 (m, 1 H, H^3 or H^4), 5.48 (m, 1 H, H^4 or H^3), and 6.56 (m, 4 H, H^4—H^7).

isomerism occurs with substituents in the 1-positions of the 1,3-diene. This has been previously[1] observed with the analogous η-cyclopentadienyl systems, and has been rationalised in terms of an envelope-flip process occurring with a metallacyclopent-3-ene. This problem can be avoided by using
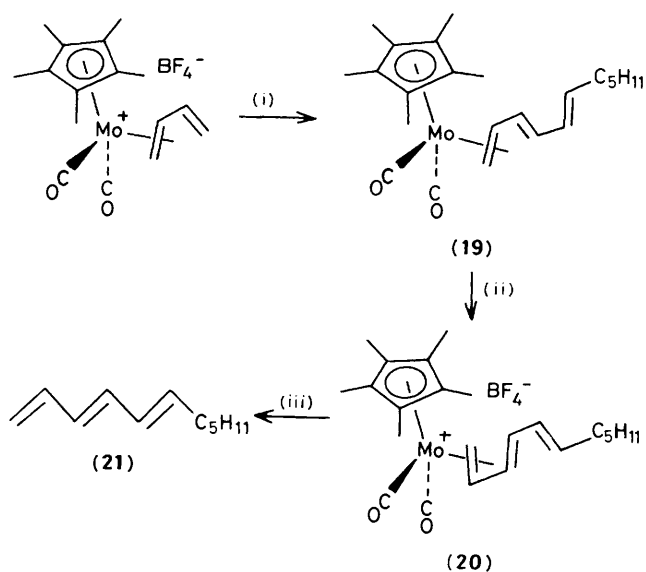
a pentamethylcyclopentadienyl ligand. For example, the buta-1,3-diene cation $[Mo(\eta^4\text{-}1,3\text{-}C_4H_6)(\eta^5\text{-}C_5Me_5)][BF_4]$, which was prepared by reaction (room temp., CH_2Cl_2) of a mixture of buta-1,3-diene and $[Mo_2(CO)_6(\eta\text{-}C_5Me_5)_2]$ with $AgBF_4$, reacts (-78 °C, thf) with lithium-di-[(E)-hept-1-enyl]copper to form the endo-η^3-allyl complex (19) (Scheme 3), ^1H n.m.r. spectroscopy confirming that the (E)-stereochemistry of the hept-1-enyl fragment is retained.

Scheme 1. *Reagents:* (i) + 1,3-diene; (ii) K[BHBuˢ₃], MeMgI; (iii) Ph₃CBF₄; (iv) K[BHBuˢ₃], EtMgBr, LiCuMe₂, LiCH(Me)CON·CH-Me·CHPhOC(O); (v) LiNPrⁱ₂; (vi) HBF₄·Et₂O; (vii) HBF₄·Et₂O, DDQ.

Scheme 2. *Reagents:* (i) K[BHBuˢ₃], LiCuMe₂; (ii) Ph₃CBF₄; (iii) LiCuMe₂.

Scheme 3. *Reagents:* (i) Li[Cu{(E)-CH=CHC₅H₁₁}₂]; (ii) Ph₃CBF₄; (iii) Me₃NO,MeCN.

Addition of trityl tetrafluoroborate (-78 °C, CH_2Cl_2) afforded the exo-$(E,E,)$-1,3,5,-triene cation (20). In the case of the corresponding η^5-indenyl system a mixture of the (E,E)- and (Z,E)-1,3,5-triene cations was obtained. However, with the η-C_5Me_5 system it is interesting mechanistically and synthetically significant that no isomerisation occurs. In contrast, with the η^5-C_9H_7 systems described earlier the 1,3,5-triene could not be displaced from (20) with carbon monoxide, but reaction (room temp., MeCN) with Me_3NO liberated in good yield (E,E)-undeca-1,3,5-triene (21)[11] a component of the Hawaiian seaweed *Dictyopteris plagiogramma* and *D. australis*,[12] which is valued in perfumery. This methodology should in principle be extendable to the synthesis of certain insect sex pheromones.

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