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 η^4-1,3-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_3CBF_4 to give the expected cyclohexa-1,3-diene cations. However, reaction (−78 °C) of, for example, (**9**) with $HBF_4{\cdot}Et_2O$ 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 $HBF_4{\cdot}Et_2O$ 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_3CBF_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.

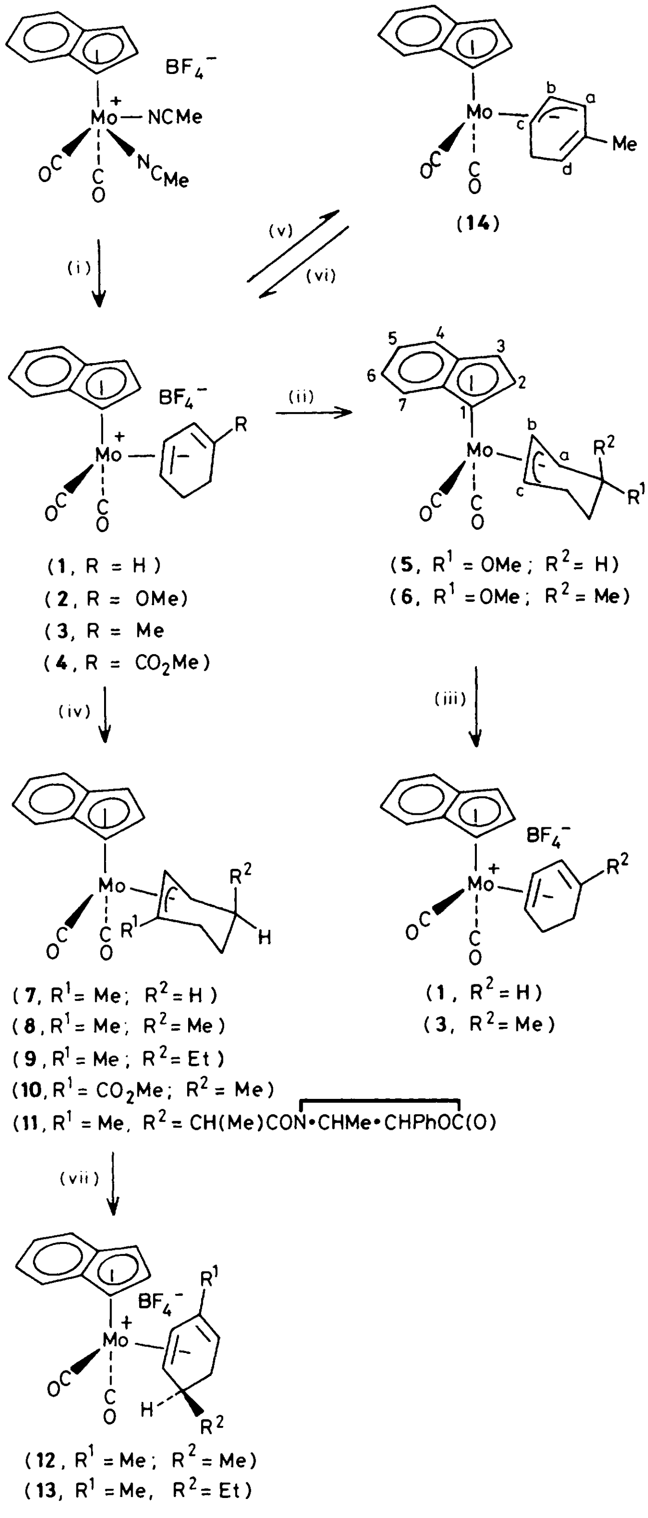
In principle these reactions can be extended to acyclic 1,3-dienes; however, a new problem arises in that *cis–trans*

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

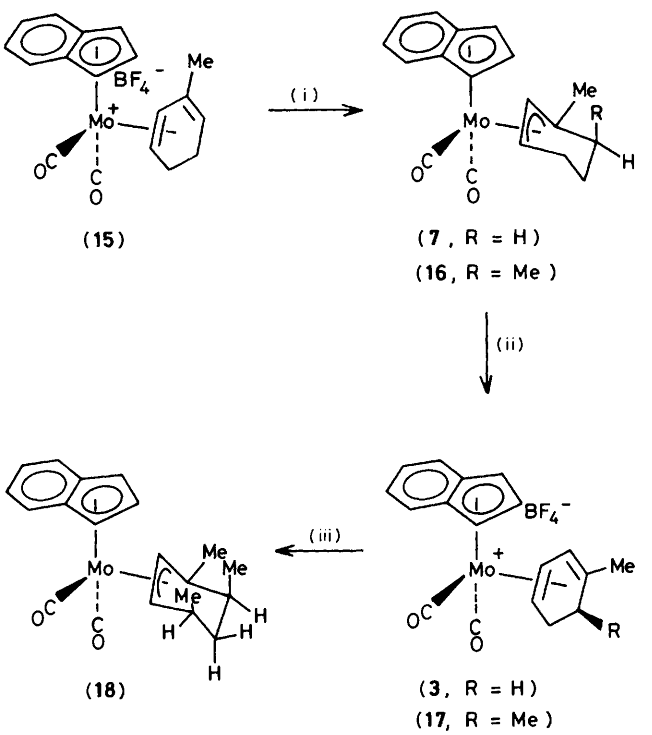
[‡] The complex $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ is readily prepared by protonation ($HBF_4{\cdot}Et_2O$, −78 °C, CH_2Cl_2) of $[MoMe(CO)_3(\eta\text{-}C_9H_7)]$ followed by reaction with MeCN.

[§] Selected spectroscopic data for (**6**): n.m.r. ^1H (C_6D_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_2Cl_2) 1 930s, 1 850s cm^{-1}; n.m.r. ^1H (C_6D_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).

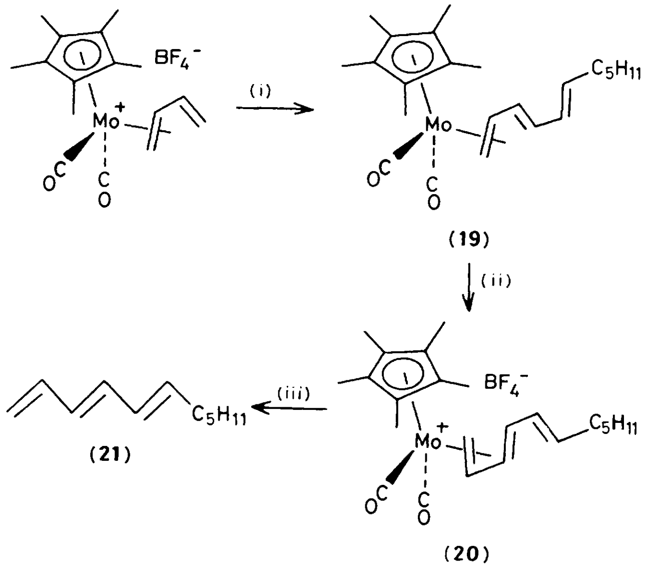
isomerism occurs with substituents in the 1-positions of the 1,3-diene. This has been previously[1] observed with the analogous η-cyclopentadienyl systems, and has been rationalised in terms of an envelope-flip process occurring with a metallacyclopent-3-ene. This problem can be avoided by using a pentamethylcyclopentadienyl ligand. For example, the buta-1,3-diene cation [Mo(η^4-1,3-C_4H_6)(η^5-C_5Me_5)][BF_4], which was prepared by reaction (room temp., CH_2Cl_2) of a mixture of buta-1,3-diene and [$Mo_2(CO)_6$(η-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), ^{1}H 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[BHBu$^s_3$], MeMgI; (iii) Ph_3CBF_4; (iv) K[BHBu$^s_3$], EtMgBr, $LiCuMe_2$, LiCH(Me)CON·CH-Me·CHPhOC(O); (v) LiNPr$^i_2$; (vi) HBF_4·Et_2O: (vii) HBF_4·Et_2O, DDQ.



Scheme 2. *Reagents:* (i) K[BHBu$^s_3$], $LiCuMe_2$; (ii) Ph_3CBF_4; (iii) $LiCuMe_2$.



Scheme 3. *Reagents:* (i) Li[Cu{(*E*)-CH=CHC_5H_{11}}$_2$]; (ii) Ph_3CBF_4; (iii) Me_3NO,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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