Journal of Organometallic Chemistry, 390 (1990) C32–C35
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20958PC

Preliminary communication

Charge relocation in cationic diene complexes: formation of an iminium-substituted allyl complex and its deprotonation to an enamine

Stephen A. Benyunes and Michael Green *

Department of Chemistry, King's College London, Strand, London WC2R 2LS (U.K.)

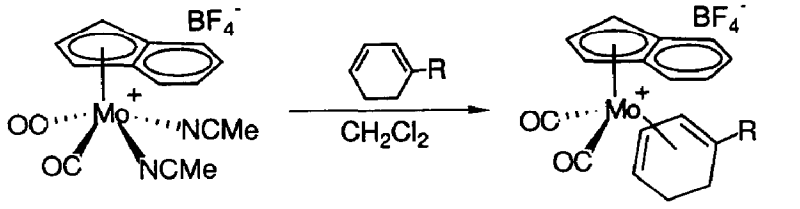
(Received April 2nd, 1990)

Abstract

The reaction of $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (**1**) with 1-dimethylamino-cyclohexa-1,3-diene affords the cationic η^3-allyl complex $[Mo(\eta^3\text{-}C_6H_7NMe_2)(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (**3**), in which the positive charge is located at an exocyclic iminium centre. Addition of $Li[N(SiMe_3)_2]$ to **3** results in deprotonation and the formation of an enamine species $[Mo(\eta^3\text{-}C_6H_6NMe_2)(CO)_2(\eta^5\text{-}C_9H_7)]$ (**8**), which undergoes stereofacial attack upon treatment with electrophiles.

During the past few years, it has become increasingly apparent that there is considerable scope for the use of organotransition metal complexes as stoichiometric reagents in organic synthesis [1]. The utilisation of neutral complexes bearing 1,3-dienes has been widely investigated, leading to the development of synthetic pathways based on the functionalisation and modification of the coordinated diene [2]. More recently, the establishment of efficient syntheses for the preparation of cationic 1,3-diene complexes has permitted elucidation of a wholly different pattern of reactivity for the coordinated diene [3]. This arises from a substantial increase in the level of π-donation to the cationic metal centre, which leaves the electron-deficient diene ligand susceptible to nucleophilic attack. We have previously demonstrated the synthetic potential of this approach via the addition of a range of nucleophilic reagents to diene complexes of formula $[Mo(\eta^4\text{-}C_6H_7R)(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (**2a–d**) [4]. The resulting η^3-allyl complexes were found to be generated regioselectively with complete stereospecific control, the identity of the product in each case corresponding to attack having occurred on the opposite face of the cyclohexadiene ring with respect to the molybdenum centre.

Our interest in these systems was heightened by the simplicity and versatility with which complexes **2** could be obtained from the labile bisacetonitrile cation $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (**1**) (Scheme 1), and hence our attention was



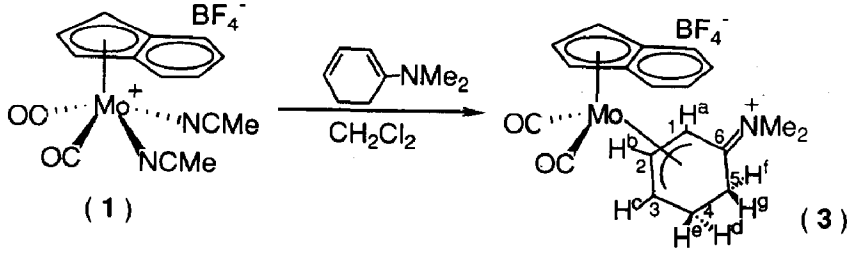
(1) (2)

(**2a**, R = H ; **2b**, R = Me ; **2c**, R = OMe ; **2d**, R = CO_2Me)

Scheme 1

directed towards the preparation of analogous species bearing differently substituted dienes.

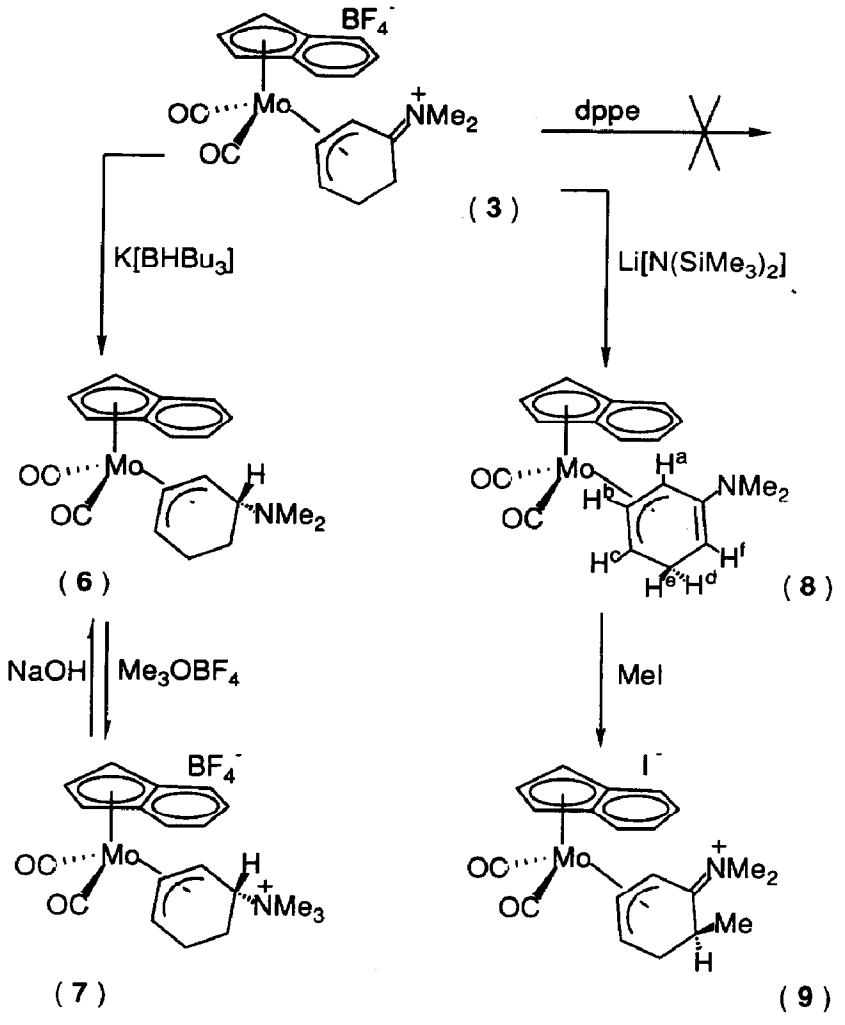
Treatment of **1** with 1-dimethylamino-cyclohexa-1,3-diene (CH_2Cl_2, 25 °C, 12 h) resulted in quantitative conversion to a new species (**3**), which was purified by column chromatography (Al_2O_3/MeCN) to give an orange crystalline solid. Complex **3** was shown to have an empirical formula of $[Mo(C_6H_7NMe_2)(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$, as expected. The IR data, however, were not consistent with the formation of a cationic η^4-diene complex, suggesting instead that the metal centre was comparatively electron rich. This observation was confirmed upon examination of the ^1H NMR spectrum of **3** [5*], which showed no particular resemblance to those of **2a–d**. In addition, a pair of singlets at δ 3.26 and 3.20, each integrating for three protons, revealed the presence of chemically inequivalent NMe groups. This indicated a restriction of rotation, such as might be expected for a C=N double bond, and hence the presence of a cationic iminium centre could be inferred. This implied a relocation of the positive charge from molybdenum to nitrogen, necessitating a change in coordination of the "diene" ligand from η^4 to η^3, which thus becomes formally allylic in nature. We were therefore able to identify **3** as an iminium substituted allyl complex, as shown in Scheme 2, additional evidence for this being the remarkable similarity in its spectroscopic properties with those for the analogous 4-oxo-allyl complex $[Mo(\eta^3\text{-}C_6H_7O)(CO)_2(\eta^5\text{-}C_9H_7)]$ (**5**) [6]. Unlike the η^4-diene complexes **2a–d**, the C_6 ligand in **3** was not displaced upon treatment with dppe, suggesting that an equilibrium involving an η^4-diene species **4** was most unlikely. This cast into doubt the intermediacy of **4** during the formation of **3** from



(1) (3)

Scheme 2

* Reference number with asterisk indicates a note in the list of references.



Scheme 3

the free diene, though the isolation of an η^4-diene complex from the reaction of $[Fe(CO)_5]$ with 1-*N*-morpholinocyclohexa-1,3-diene [7] indicates otherwise.

The reaction pattern exhibited by **3** parallels closely that of the diene complexes **2a–d** (Scheme 3). Thus, addition of $K[BHBu^s_3]$ (THF, −78° C) gave the 4-dimethylamino allyl species **6** with stereofacial delivery of "H^-" to the cyclohexenyl ligand. Methylation of **6** using $[Me_3O][BF_4]$ afforded the quaternary ammonium salt **7**, which upon treatment with hydroxide ion regenerated **6** following N–C bond cleavage. Reaction of **3** with $Li[N(SiMe_3)_2]$ resulted in a facile deprotonation, to give an orange crystalline species (**8**), which was isolated by extraction into hexane. Complex **8** was deduced from ^1H NMR spectroscopic data [8*] to contain an enamine functionality, as illustrated. This comprises part of an electron-rich η^3-cyclohexadienyl system, directly analogous with that in the anionic enolate complex obtained by deprotonation of the oxo-allyl species **5**. As expected, complex **8** undergoes electrophilic attack; thus addition of a proton results in the regeneration of **3**. Similarly, treatment with MeI yields the methylated derivative **9**, this reaction

again showing complete stereofacial selectivity. Though the scope of this type of reaction is at present limited to this one example, use of more powerful electrophilic reagents should permit further exploitation of this potentially very useful system.

References and notes

1 S.L. Blystone, Chem. Rev., 89 (1989) 1663, and references therein.

2 R. Gfee, Synthesis, (1989) 341.

3 M. Bottrill and M. Green, J. Chem. Soc., Dalton Trans., (1977) 2365; J.S. Baxter, M. Green and T.V. Lee, J. Chem. Soc., Chem. Commun., (1989) 1595; A.J. Pearson, Synlett. (1990) 10.

4 M. Green, S. Greenfield and M. Kersting, J. Chem. Soc., Chem. Commun., (1985) 18.

5 Spectroscopic data for **3**; IR (CH_2Cl_2): ν(CO) 1972, 1902 cm^{-1}; ^1H NMR (CD_2Cl_2): δ 7.46 (1H, d), 7.40 (1H, ddd), 7.25 (2H, m), 6.50 (1H, m), 6.06 (1H, m), 5.61 (1H, t) (indenyl resonances), 3.95 (1H, m, H^c), 3.37 (1h, d, H^a, $J_{ab} = 5.9$ Hz), 3.26 (3H, s, NMe_2), 3.20 (3H, s, NMe_2), 2.31 (1H, m, H^e), 2.10 (1H, dd, H^g, $J_{ge} = 9.3$, $J_{gf} = 19.4$ Hz), 2.04 (1H, ddt, H^d, $J_{dc-dg} = 2.4$, $J_{de} = 16.5$, $J_{df} = 10.1$ Hz), 1.74 (1H, ddd, H^f, $J_{fd} = 10.1$ $J_{fe} = 5.7$, $J_{fg} = 18.9$ Hz), 0.93 (1H, t, H^b, $J_{ba-bc} = 6.8$ Hz) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 234.8 (CO), 232.8 (CO), 174.1 (C^1), 128.5, 127.5, 124.8, 124.8, 114.2, 112.4 (indenyl carbon atoms), 89.7 (indenyl), 84.0 (C^3), 82.0, 81.7 (indenyls), 67.2, 56.3 (C^2, C^4), 42.7, 41.4 (NMe_2), 23.5, 21.3 (C^5, C^6) ppm.

6 M. Green, S. Greenfield, M.J. Grimshire, M. Kersting, A.G. Orpen and R.A. Rodrigues, J. Chem. Soc., Chem. Commun., (1987) 97.

7 A.J. Birch, L.F. Kelly and D.J. Thompson, J. Chem. Soc., Perkin Trans. I, (1981) 1006.

8 ^1H NMR data (CD_2Cl_2) for **8**, $\delta = 7.13$–7.01 (4H, m, indenyl protons), 6.07 (1H, br s, indenyl), 5.83 (1H, br s, indenyl) 5.55 (1H, t, indenyl), 3.80 (1H, m, H^f), 3.28 (1H, d, H^a, $J = 6.8$ Hz), 3.19 (1H, br, H^c), 2.53 (1H, m, $H^{d/e}$), 2.52 (6H, s, NMe_2), 2.32 (1H, ddd, $H^{d/e}$, $J = 21.5$, 4.2, 1.7 Hz), -0.37 (1H, t, H^b, $J = 7.0$ Hz) ppm.