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GENERATION AND REACTIONS OF CARBANIONS IN THE PRESENCE OF A NEIGHBORING η^3-ALLYL-Mo(CO)$_2$Cp MOIETY; A NOVEL REARRANGEMENT SUGGESTING PARTICIPATION OF Mo IN CARBANION STABILIZATION.

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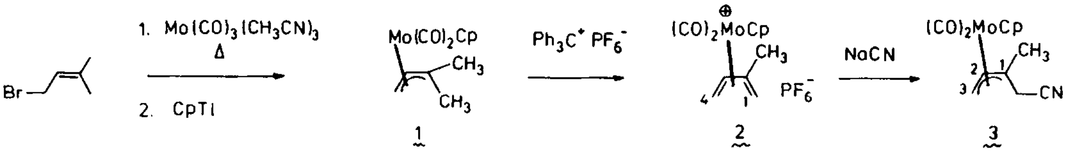
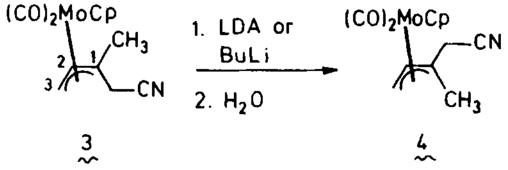
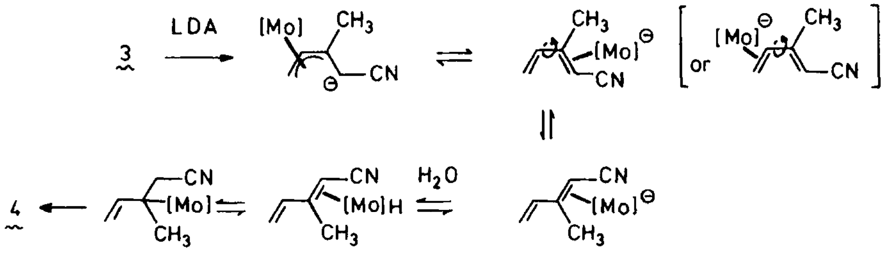
Abstract. The cyano-substituted η^3-allyl-Mo(CO)$_2$Cp complex 3 is readily deprotonated using a variety of bases (NaH, BuLi, LDA) and the so-formed carbanion undergoes a novel rearrangement leading to complexes such as 4, 5 and 7 after treatment with electrophiles.

During the course of investigations into the synthetic utility of cyclohexadiene- and cycloheptadiene - Mo(CO)$_2$Cp cations,[1] we became interested in the chemistry of related acyclic diene complexes,[2] which might be useful as building blocks for organic synthesis. The isoprene complex 2, which is readily prepared as shown below using standard techniques,[3] is a potentially useful candidate for, e.g., terpene synthesis and is known[4] to undergo highly regioselective reaction with borohydride to regenerate the π-allyl-Mo(CO)$_2$Cp complex 1. However, in our hands 2 was found to react with sterically more demanding carbon nucleophiles such as NaCH(CO$_2$Me)$_2$ and NaCH(SO$_2$Ph)CO$_2$Me to give mixtures of complexes from nucleophile addition to C(1) and C(4), which is clearly problematic in terms of synthetic application. On the other hand, addition of cyanide to 2 occurs with excellent regiocontrol (>10:1) to give 3 as the major product[5] (92% yield after purification). We considered that complex 3 would be an excellent candidate for exploring methods for regiocontrolled C-C bond formation by generation of a carbanion alpha to the nitrile followed by its reaction with carbon electrophiles. This Letter describes experiments which test the feasibility of this process, and which have led to the discovery of a novel rearrangement of the putative carbanion intermediate.



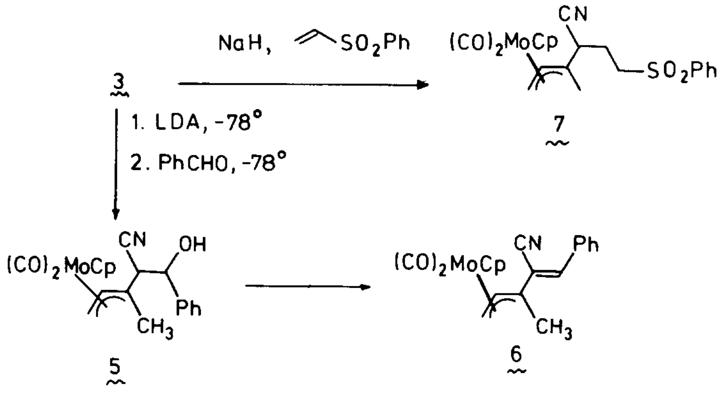
Treatment of 3 with base (LDA, THF, -78°C, 45 min) gave a deep red colored solution, and aqueous quench led to a new complex (98% yield) shown to be 4 by ^1H NMR analysis.[5,6] It is especially noteworthy that complex 3 is quite stable under normal conditions, clearly showing that the rearrangement to 4 occurs at the carbanion stage. When the anion was quenched with D_2O, deuterium label was incorporated regiospecifically alpha to the CN group, and gave a product for which an abnormally small (much less than 1H intensity) $C\underline{H}_2CN$ resonance (δ3.05, singlet) was observed in the NMR spectrum. Field desorption mass spectrometry indicated the presence of <u>ca</u> 60% d_2, 21% d_1 and 13% d_0 labelled complexes.[7] A plausible explanation for this rearrangement and unusual double deuterium incorporation is embodied in the mechanism shown in the Scheme, in which facile reversibility of the steps shown permits H/D exchange to occur.





SCHEME

The rearrangement of 3 to 4 is strongly indicative of participation of the $Mo(CO)_2Cp$ group in stabilizing the intermediate carbanion. Once formed, the anion is relatively unreactive: attempted methylation under standard conditions (CH_3I, THF, 0°C) gave no methyl-substituted compounds and only led to eventual decomposition of the complex. However, treatment of the anion with benzaldehyde (-78°C to 0°C) gave good yield (75-80%) of complex 5, obtained as a single diastereomer (NMR) which underwent extremely facile dehydration on silica gel to give 6. That complex 5 has the rearranged structure is evident from the high field singlet for the CH_3 group in the NMR spectrum (δ 1.04 compared to δ 1.85 for 3 and δ 0.95 for 4)[5]. Similarly, treatment of the anion from 3 (generated using NaH, THF, room temp.) with phenyl vinyl sulfone, gave the Michael adduct 7 as a mixture of diastereomers in 60% yield.[5]



In conclusion, regiocontrolled C-C bond formation can be accomplished using carbanion chemistry in which the η-allyl-Mo(CO)$_2$Cp group appears to play a stabilizing role. This, coupled with the observed rearrangement, provides access to systems which are not obtainable by carbon nucleophile addition to diene-molybdenum complexes such as 2.

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References and Notes

1) Pearson, A.J.; Khan, N.M.I. *J. Am. Chem. Soc.*, **1984**, 106, 1872; *Tetrahedron Lett.*, **1984**, 25, 3507; **1985**, 26, 1407. Pearson, A.J.; Khan, M.N.I.; Clardy, J.C.; Cun-Heng, H. *J. Am. Chem. Soc.* **1985**, 107, 2748. Pearson, A.J.; Khan, M.N.I., *J. Org. Chem.* **1986**, 51, 5276. Khan, M.N.I. Ph.D. Thesis, Case Western Reserve University, 1985.

2) Faller, J.W.; Rosan, A.M. *Ann. N. Y. Acad. Sci.*, **1977**, 295, 186; *J. Am. Chem. Soc.*, **1977**, 99, 4853, Green, M.; Greenfield, S.; Kersting, M.; *J. Chem. Soc. Chem. Commun.*, **1985**, 18.

3) Hayter, R.G. *J. Organomet. Chem.*, **1968**, 13, 1. Faller, J.W.; Murray, H.H.; White, D.L.; Chao, K.H. *Organometallics*, **1983**, 2, 400.

4) Merour, J.Y.; Charrier, C.; Beraim, J.; Roustan, J.L.; Commereuc, D. *J. Organomet. Chem.*, **1972**, 39, 321.

5) All new compounds reported were obtained as racemic mixtures and fully characterized by NMR, IR and mass spectrometry or combustion analysis. Selected data are as follows: 3: m.p. 95-96°C; IR (CCl_4) ν_{max} 2245, 1955, 1875 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200MHz) δ 5.24 5H, s), 4.12 (1 H, dd, J = 11, 7 Hz, 2-H), 2.69 (1 H, dd, J = 7, 4 Hz, 3-H, syn), 2.68 (1 H, d, J_{gem} = 17 Hz, one of CH_2CN), 1.85 (3 H, s), 1.13 (1 H, dd, J = 11, 4 Hz, 3-H, anti), 1.08 (1 H, d, J_{gem} = 17 Hz, one of CH_2CN). 4: oil; IR (CCl_4) ν_{max} 2245, 1950, 1875 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.29 (5H, s), 4.25 (1 H, dd, J = 10, 7 Hz, 2-H), 3.05 (2 H, CH_2CN), 2.60 (1 H, dd, J = 7,3 Hz, 3-H, syn), 1.21, (1 H, dd, J = 10, 3 Hz, 3-H anti), 0.95 (3 H, s). **5**: IR (CCl_4) ν_{max} 3700-3100, 2220, 1955, 1 875 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.3-7.8 (5 H, m, aromatic), 5.31 (5 H, s), 4.86 (1 H, dd, J = 10, 7 Hz), 3.68 (1H, benzylic), 2.72 (1 H, dd, J = 7,3 Hz), 1.8-2.0 (2 H, m, CHCN and OH), 1.53 (1 H, dd, J = 10,3 Hz), 1.04 (3 H, s). **6**: IR (CCl_4) ν_{max} 2225, 1955, 1880 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.75 (2 H), 7.42 (3 H), 7.39 (1 H, s, vinyl), 5.40 (5 H, s), 4.92 (1 H, dd, J = 10,7 Hz), 2.80 (1 H, dd, J = 7,3 Hz), 1.61 (1 H, dd, J = 10,3 Hz), 1.12 (3 H, s). **7**: one diastereomer was obtained pure and gave IR (CCl_4) ν_{max} 2225, 1955, 1880 cm^{-1}; NMR ($CDCl_3$, 200 MHz), δ 8.0 (2 H), 7.65 (3 H), 5.18 (5 H, s), 4.33 (1 H, dd, J = 10,7 Hz), 3.2-3.5 (3 H, m, CHCN, CH_2SO_2Ph), 2.82 (1 H, dd, J = 7,3 Hz), 2.6 (1 H, m), 2.4 (1 H, m), 1.22 (1 H, dd, J = 10,3 Hz), 0.56 (3 H, s).

6) A characteristic trend is observed for the CH_3 singlet in these types of complex, which reflects their stereochemistry. Typically, complexes such as **3** show a much lower field CH_3 absorption than complexes of type **4**. This is also observed in the NMR spectrum of 1. See Merour et al, reference 4 for previous assignments.

7) Accurate determination of the extent of deuterium incorporation is hampered by the presence of multiple isotopes of molybdenum. The values given are the best estimate available.

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