

Molybdenum-stabilized Carbanions: a Novel Decyanation Reaction with Stereoelectronic Requirement suggesting Participation of the η^3 -Allyl-Mo(CO)₂(cp) (cp = η^5 -C₅H₅) Moiety in Stabilizing Neighbouring Carbanions

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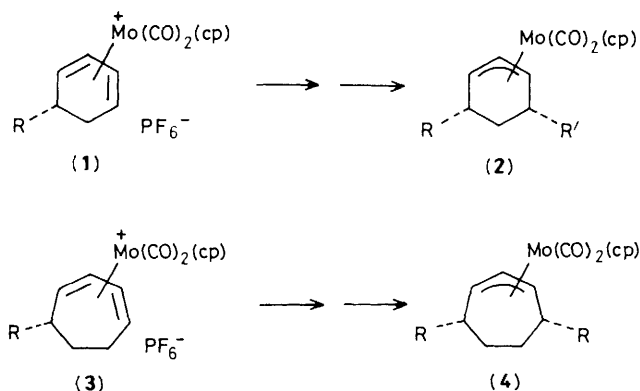
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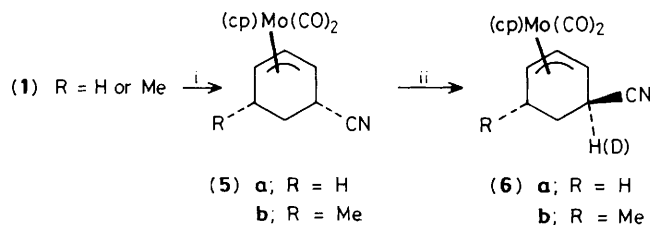
Carbanions stabilized by a nitrile group are readily generated in the presence of an η^3 -allyl-Mo(CO)₂(cp) (cp = η^5 -C₅H₅) group, by treatment of complexes (5) with lithium di-isopropylamide, and undergo regio- and stereo-specific reaction with suitable electrophiles; a novel decyanation reaction is observed when (5) is treated with butyl-lithium, resulting in the generation of carbanion species (15), which also undergoes regio- and stereo-controlled reaction with electrophiles.

We¹ and others² have recently reported on the addition of nucleophiles to cationic diene-Mo(CO)₂(cp) (cp = η^5 -C₅H₅) complexes such as (1) and (3), allowing stereocontrolled double functionalization to be carried out and leading ultimately to η^3 -allyl-Mo(CO)₂(cp) complexes such as (2) and (4), respectively. While these tactics have some potential for organic synthesis, there are inherent limitations on the types of substituents which can be introduced as nucleophiles. Consequently, we have explored alternative procedures for functionalizing the η^3 -allyl-Mo(CO)₂(cp) system based on the generation of carbanions α to a substituent such as CN, and this has led to the discovery of a novel decyanation reaction reported in the present communication.

The required nitriles (5) were easily prepared by reaction of the appropriate diene complex with sodium cyanide, using procedures reported earlier.¹ On treatment of (5) with strong base [lithium di-isopropylamide (LDA), tetrahydrofuran (THF), -78 °C] a deep red colour developed, indicative of

anion formation, and quenching the reaction mixture with H₂O or D₂O resulted in the formation of (6), showing

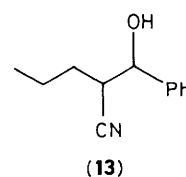
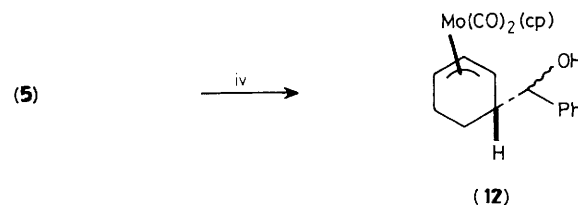
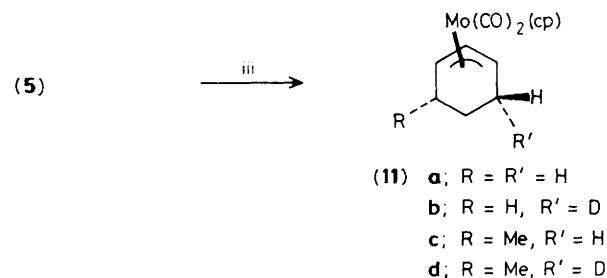
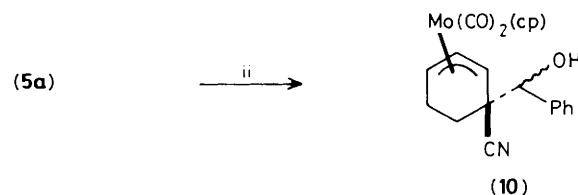
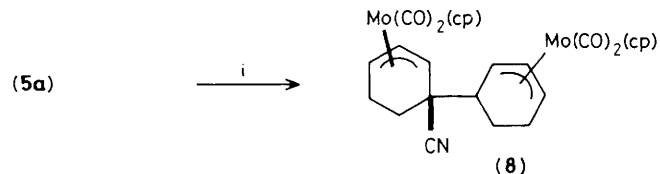
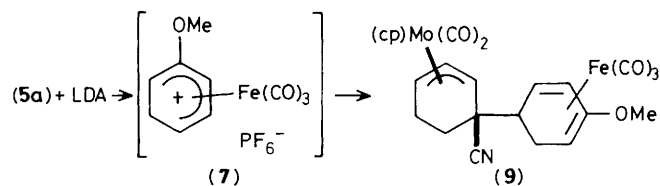




Reagents: i, NaCN; ii, (a) LDA, THF, -78°C ; (b) H_2O (D_2O).

complete inversion of CN stereochemistry[†] and regiospecific incorporation of deuterium from D_2O . Thus, it appears that the intermediate behaves as a normal carbanionic species, as opposed to a metal anion which might be expected to be protonated first on the metal and maintain the stereochemical integrity of the starting molecule.³

However, reaction of the carbanion with other electrophiles proved somewhat problematic: using conditions under which the anion intermediate is stable (below -20°C) no alkylation was observed on treatment with methyl iodide or allyl bromide. The more reactive electrophiles (1) (R = H) and (7) were better behaved, leading to complexes (8) (70–75% yield) and (9) (20–25% yield), respectively.[†] Similarly, reaction with benzaldehyde led to the formation of complex (10) (65–70% yield) as a mixture of diastereoisomers. In this way, a quaternary carbon centre can be constructed in a stereospecific manner on the organomolybdenum system.⁴ In order to avoid potential side reactions due to di-isopropylamine in the above system, which we felt would be most problematic during reaction with (7), we examined alternative techniques for effecting the deprotonation. To our surprise, treatment of (5) with Bu^nLi (1.2 equiv., THF, -78°C), followed by H_2O or D_2O quench, led to the formation of complexes (11), showing complete loss of CN and stereospecific and regiospecific deuterium incorporation.[‡] On the other hand, treatment of the epimeric



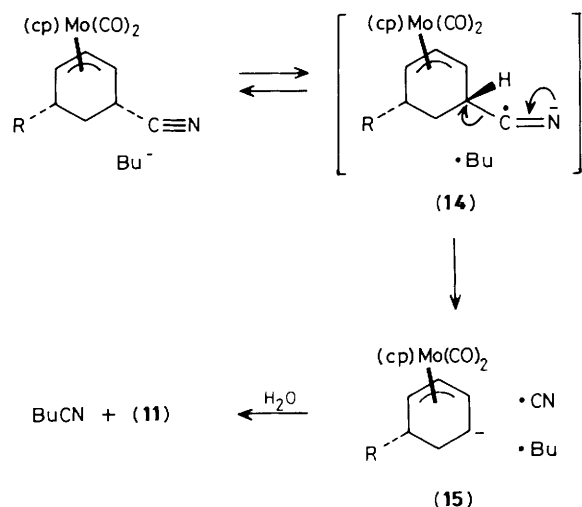
Reagents: i, (a) LDA, -78°C ; (b) (1), $-78 \rightarrow 0^\circ\text{C}$; ii, (a) LDA, -78°C ; (b) PhCHO, -78°C ; iii, (a) Bu^nLi , -78°C ; (b) H_2O (D_2O); iv, (a) BuLi , -78°C ; (b) PhCHO, -78°C .

nitrile (6a) with Bu^nLi resulted in simple deprotonation rather than decyanation, as indicated by deuterium incorporation on quenching with D_2O . Identical results of de-cyanation were obtained when Bu^iLi and Bu^sLi were used in place of Bu^nLi .

Carbon-carbon bond formation was readily effected by sequential treatment of (5) with Bu^iLi and benzaldehyde (THF, -78°C), when complex (12) was isolated as an equimolar mixture of diastereoisomers in 81% yield after chromatographic purification. Interestingly, when this reaction was conducted using Bu^nLi , appreciable amounts of compound (13) were observed in the product. This arises owing to competing deprotonation of valeronitrile, a product

[†] All new compounds were obtained as racemic mixtures and were characterized using n.m.r., i.r., and high resolution mass spectrometry or combustion analysis. ^1H n.m.r. spectroscopy may be used to assign stereochemistry by comparison with compounds reported in refs. 1 and 2. Typical data are as follows. (6a): m.p. $172\text{--}175^\circ\text{C}$; i.r. (CHCl_3): ν_{max} 2240w, 1955, and 1875 cm^{-1} ; ^1H n.m.r. (CDCl_3 , 200 MHz): δ 5.34 (5 H, s), 4.20 (1 H, t, J 7.3 Hz), 3.75 (1 H, m), 3.61 (1 H, br. d, J 7.3 Hz), 3.16 (1 H, ddd, J 9, 4, 1.5 Hz, CHCN), 1.93–1.76 (2 H, m), 1.45 (1 H, dt, J 14, 6 Hz), and 0.72 (1 H, m). The diaxial coupling (9 Hz) observed for the CHCN proton is a distinguishing feature of (6) compared to (5), which shows the CHCN resonance as a narrow multiplet at δ 2.8. (10) (one diastereoisomer) i.r. (CHCl_3): ν_{max} 3600, 3400, 2250, 1940, and 1855 cm^{-1} ; ^1H n.m.r., δ 7.5–7.3 (5 H), 5.34 (5 H, s), 4.6 (1 H, d, J 3.8 Hz, benzylic CH, collapses to singlet on D_2O addition), 4.36 (1 H, t, J 7 Hz), 4.09 (1 H, dt, J 7, 1.7 Hz), 3.88 (1 H, m), 2.33 (1 H, d, J 3.8 Hz, exch. D_2O , OH), 2.1 (1 H, m), 1.76 (1 H, m), 1.02 (1 H, dd, J 15, 6 Hz), and 0.75 (1 H, m). (12): i.r. (CHCl_3), ν_{max} 3610, 3460, 1940, and 1855 cm^{-1} ; ^1H n.m.r. (one diastereoisomer): δ 7.5–7.35 (5 H), 5.32 (5 H, s), 4.59 (1 H br. d, J 7.5 Hz, sharpens to d, J 7.5 Hz, on D_2O addition), 4.34 (1 H, t, J 7 Hz), 3.76 (2 H, m), 2.2–1.8 (3 H), 1.6 (1 H, m), 0.75 (1 H, dd, J 14, 6 Hz), and 0.45 (1 H, m).

[‡] Faller *et al.* (ref. 2) have completely assigned the ^1H n.m.r. spectra of complexes (11a) and (11c). Complex (11a) shows the *M-exo* protons at C(4) and C(6) as a dddd at δ 1.91 while the corresponding *M-endo* protons occur at higher field (dddd, δ 1.67). In our experiments, product (11b) showed reduction of the integrated intensity of the δ 1.91 resonance by 50%, while the δ 1.67 signal remained the same intensity as in (11a). Similar spectral differences were observed for (11d) compared to (11a).



of the decyanation reaction, followed by reaction of the resulting carbanion with benzaldehyde. Similar by-products are not possible when Bu^tLi is used, resulting in a much cleaner reaction.

On the basis of the above results, we favour an electron transfer mechanism (Scheme 1) as a plausible explanation of the decyanation process.[§] The reaction has a definite stereoelectronic requirement, since (6) fails to undergo decyanation, suggesting that the radical anion intermediate (14) will only collapse to give anion (15) when the C–Mo and C–CN bonds have an antiperiplanar alignment.[¶] On this basis, it appears that developing overlap between the orbital carrying the carbanion electron pair and a molybdenum-centred orbital is an important factor in

[§] An alternative mechanism involves nucleophilic addition of the alkyl-lithium to the CN group, followed by loss of the anion (15) as a leaving group. While this is acceptable for Bu^nLi , the same reaction using Bu^tLi is less likely. Electron transfer is possible using both lithium reagents.

[¶] A possible alternative explanation for the difference in reactivity between (5) and (6) is that the nitrile, being *cis* to the $\text{Mo}(\text{CO})_2(\text{cp})$, is sterically more hindered in (6). However, based on *X*-ray data (ref. 2) the η^3 -cyclohexenyl- $\text{Mo}(\text{CO})_2(\text{cp})$ complexes have a chair-like cyclohexane ring structure. The nitrile in (5) is thus quasi-axial, whereas that in (6) is quasi-equatorial, and on this basis the former may actually be more sterically encumbered.

stabilization of the transition state and/or the resulting carbanion. The exact nature of the Mo-based orbital is unknown, but the observed stereoelectronic effect is consistent with this having C–Mo antibonding orbital character. When the C–CN bond is not properly aligned, as in (6), the favoured reaction is deprotonation. The inferred stabilizing effect is insufficient to overcome the activation energy for C–H bond heterolysis, since (11a) does not undergo deprotonation after prolonged treatment with LDA. Radical combination of Bu^\cdot and CN^\cdot within a solvent cage is supported by the observation of (13) as a prominent by-product when Bu^nLi is employed. No such product was observed using Bu^tLi , owing to the inertness of Bu^tCN to the basic reaction conditions.

In summary, carbanions may be generated α to an η^3 -allyl- $\text{Mo}(\text{CO})_2(\text{cp})$ system in the absence of extra stabilizing groups by a novel decyanation process, suggesting participation of the $\text{Mo}(\text{CO})_2(\text{cp})$ group in stabilization of developing negative charge. These carbanions react with electrophiles in a regio- and stereo-controlled manner, leading to a new and potentially useful C–C bond-forming process. Future work will be aimed at examining the generality of this behaviour and elucidating the mechanistic details of the decyanation reaction.

We thank the U.S. Public Health Service, National Institutes of Health, and the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. High field n.m.r. equipment was purchased with the aid of grants from the National Science Foundation and National Institutes of Health.

Received, 23rd June 1986; Com. 860

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- 3 Protonation on the metal followed by migratory insertion is common for many organometallic anions. See, for example: M. Brookhart and A. Lukacs, *J. Am. Chem. Soc.*, 1984, **106**, 4161; G. F. Schmidt and M. Brookhart, *ibid.*, 1985, **107**, 1443.
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