Pathways for Carbon–Chain Growth Reactions at a Dimolybdenum Centre

Michael Green,† Philip A. Kale, and Richard J. Mercer
Department of Inorganic Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.

Reaction of [$Mo_2(CO)_4(\eta^5\text{-}C_9H_7)_2$] with MeC_2Me forms, *via* competitive reaction paths, the dinuclear complexes [$Mo_2(\mu\text{-}MeC_2Me)(CO)_4(\eta^5\text{-}C_9H_7)_2$] and [$Mo_2\{\mu\text{-}(\sigma,\sigma\text{-}\eta^4\text{-}C_4Me_4)\}(CO)_4(\eta^5\text{-}C_9H_7)(\eta^3\text{-}C_9H_7)$]; the latter on heating decarbonylates to give [$Mo_2\{\mu\text{-}(\sigma,\sigma\text{-}\eta^4\text{-}C_4Me_4)\}(\mu\text{-}CO)(\eta^5\text{-}C_9H_7)_2$], which reacts with MeC_2Me to form the 'fly-over' complex [$Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}C_6Me_6)\}(\eta^5\text{-}C_9H_7)_2$].

Recently[1,2,3] there has been a renewed interest in alkyne coupling reactions at two metal centres, stimulated by the suggestion[1] that the nickel catalysed formation[4] of cyclooctatetraene from ethyne involves carbon coupling reactions at two adjacent nickel atoms. Support for this idea was provided by the report of apparently sequential coupling of alkynes at dichromium and dimolybdenum centres,[5,6] and the observation[7] that C_8H_8 was liberated on reaction of CO with the four alkyne 'fly-over' complex [$Cr_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2$]. We have previously noted the enhanced reactivity[8,9] of complexes containing η^5-indenyl rather than η^5-cyclopentadienyl ligands, and therefore, the development of a simple and reliable procedure for the preparation of the unsaturated dimolybdenum indenyl species [$Mo_2(CO)_4(\eta^5\text{-}C_9H_7)_2$] (**1**)[10] provided an opportunity to carefully examine alkyne coupling at an Mo_2 centre.[11]

Treatment of (**1**) with a molar equivalent of but-2-yne in toluene at room temperature led to formation of (**3**) (Scheme 1), the indenyl analogue of the well-known[12] family of complexes [$Mo_2(\mu\text{-alkyne})(CO)_4(\eta\text{-}C_5H_5)_2$] (M = Cr, Mo) containing a transversely bridging but-2-yne. Reaction of (**1**) with an excess of but-2-yne at 80 °C (sealed vessel, toluene solvent) also resulted in formation of (**3**). However, there was a second dark green crystalline product (**4**), formed in 20% yield, which was separated by column chromatography and was identified by analysis and mass spectroscopy as a 1:2 adduct of (**1**) and but-2-yne. Examination of the ^1H and $^{13}C\{^1H\}$ n.m.r. spectra‡ of (**4**) suggested the structure illustrated in Scheme 1. The complex is fluxional,[13] the indenyl ligands showing interchange of environment, while two sets of pairwise equivalent methyl groups (δ 2.54 and 1.77, ^1H n.m.r.) and quaternary carbons (δ 183.0 and 137.3, $^{13}C\{^1H\}$ n.m.r.) remain sharp throughout the temperature range −60 to 80 °C.

When a toluene solution of (**4**) is refluxed for 3 h, a smooth thermal decarbonylation reaction occurs, with formation of

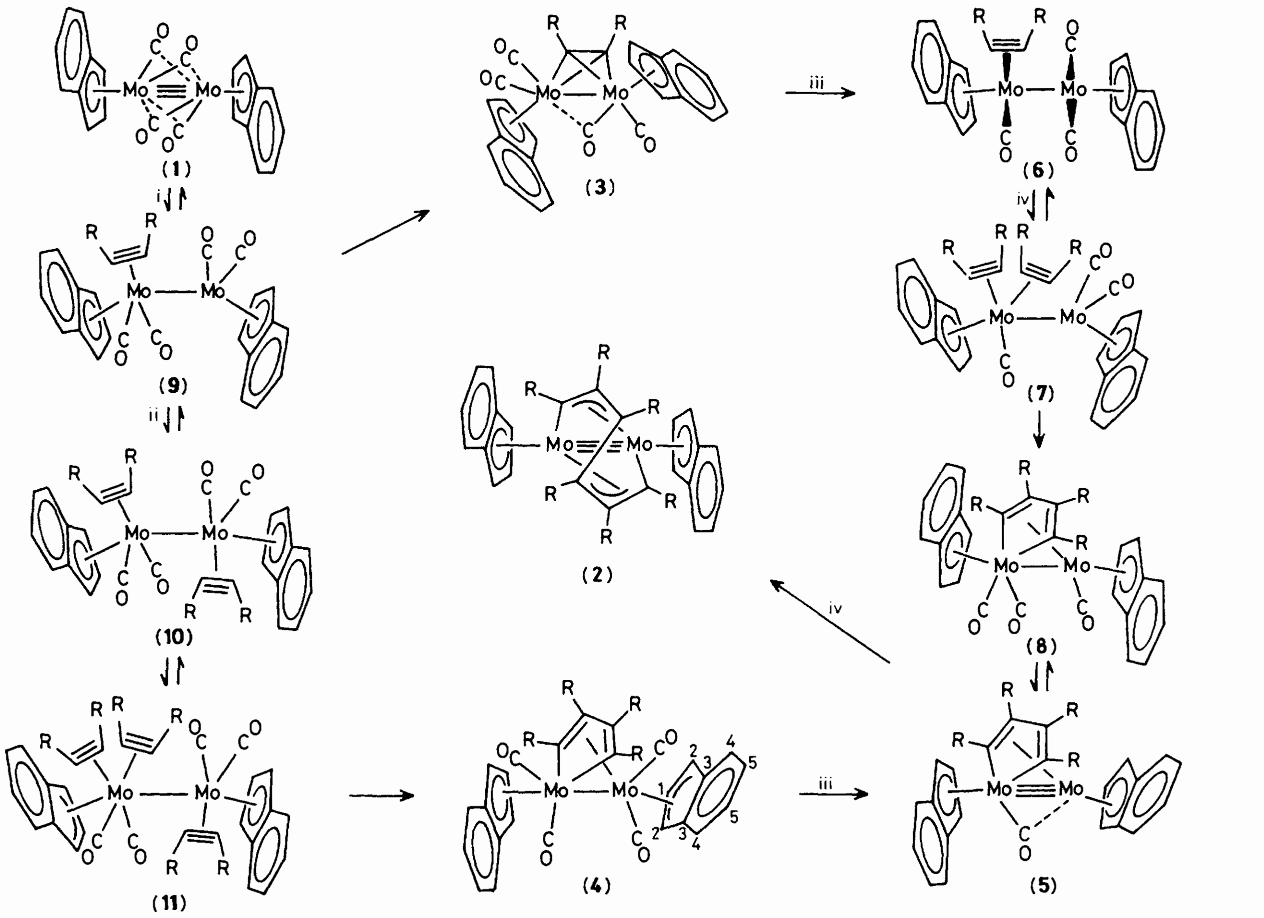
---

† *Present address:* Department of Chemistry, King's College London, Strand, London WC2R 2LS, U.K.

‡ *Selected spectroscopic data* for compound (**3**): ν(CO) (CH_2Cl_2) 1961m, 1903s, and 1823m cm^{-1}; n.m.r. ^1H (CD_2Cl_2), δ 7.43 (m, 4H, C_9H_7), 7.09 (m, 4H, C_9H_7), 5.43 (s, 6H, C_9H_7), and 1.99 (s, 6H, Me).

Compound (**4**): ν(CO) (CH_2Cl_2) 1979s, 1931s, 1907m, and 1864m cm^{-1}; n.m.r. ^1H (CD_2Cl_2, 253 K) δ 7.23, 6.94, 6.53, 6.42 (m, 2H, C_9H_7), 6.14 [t, 1H, 1-H, C_9H_7, *J*(HH) 3.8 Hz], 5.39 [d, 2H, 2-, 3-H, C_9H_7, *J*(HH) 3.4 Hz], 5.03 [t, 1H, 1-H, C_9H_7, *J*(HH) 3.4 Hz], 3.85 [d, 2H, 2-, 3-H, C_9H_7, *J*(HH) 3.8 Hz], 2.56 (s, 6H, 2Me), and 1.77 (s, 6H, 2Me); $^{13}C\{^1H\}$ (CD_2Cl_2, 213 K), δ 239.6 (CO), 238.4 (CO), 182.5 (α-C of ring), 147.9 (C of η^3-C_9H_7), 136.6 (β-C of ring), 126.2, 125.2, 122.0, 115.7 (C_9H_7), 110.3 (C of η^5-C_9H_7), 98.7, 82.9, 76.1, 62.8 (C_9H_7), 32.7, and 19.3 (Me).

Compound (**5**): ν(CO) (CH_2Cl_2) 1697 cm^{-1}; n.m.r. ^1H (CD_2Cl_2), δ 7.33, 7.17, 6.94, 6.80 (m, 2H, C_9H_7), 5.65 [d, 2H, C_9H_7, *J*(HH) 3.3 Hz], 5.41 [t, 1H, C_9H_7, *J*(HH) 3.3 Hz], 5.14 [t, 1H, C_9H_7, *J*(HH) 3.0 Hz], 4.95 [d, 2 H, C_9H_7, *J*(HH) 3.0 Hz], 2.10 (s, 6H, Me), and 1.53 (s, 6H, Me); $^{13}C\{^1H\}$ (CD_2Cl_2), δ 304.9 (CO), 197.3 (α-C of ring), 124.8, 124.2, 124.1, 123.8 (C_9H_7), 112.7, 111.1 (C_9H_7), 100.3, 95.3 (C_9H_7), 92.1 (β-C of ring), 90.5, 85.6 (C_9H_7), 29.9, and 16.0 (Me).



Scheme 1. *Reagents and conditions:* R = Me. i, MeC_2Me, room temperature in toluene; ii, MeC_2Me, 80 °C, toluene; iii, reflux, toluene; iv, MeC_2Me, reflux, toluene.

the green crystalline air-sensitive complex (**5**) (Scheme 1), which was identified by analysis, mass, i.r., and ^{1}H and $^{13}C\{^{1}H\}$ n.m.r. spectroscopy.‡ Thus, the i.r. spectrum of (**5**) shows a CO stretch at 1697 cm^{-1}, ^{13}C chemical shifts associated with the metallacyclopentadiene ring carbons at δ 197.3 and 92.1, and a carbonyl resonance at δ 304.9 (by $^{13}C\{^{1}H\}$ n.m.r.). This data corresponds closely to that of the cyclopentadienyl analogues of (**5**),[6,14,15] obtained by reacting alkynes with $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (M = Cr, Mo), and which, it has been suggested,[5,6] are formed from the transversely bridged complexes $[M_2(CO)_4(\mu\text{-alkyne})(\eta\text{-}C_5H_5)_2]$ by sequential coupling of co-ordinated alkynes. It was, therefore, expected that the immediate precursor to (**4**), and hence (**5**), would be the mono-alkyne complex (**3**). However, when (**3**) was treated with an excess of but-2-yne at 80 °C, the conditions under which (**4**) is formed, no reaction occurred. Hence (**4**) results not from (**3**), but from some competitive reaction pathway that is open to an intermediate which can form either (**3**) or (**4**). Complex (**5**) is also interesting in another context, in that species like (**5**) have been implicated[5,6,15] as precursors of three alkyne 'fly-over' complexes; however, previous attempts to establish this important point have been unsuccessful. With the more reactive η^5-indenyl system this step can be firmly established. When a solution of (**5**) in toluene in the presence of an excess of but-2-yne is heated under reflux, the three but-2-yne 'fly-over' complex (**2**), which has previously[11] been obtained by one electron reduction of $[Mo(NCMe)(\eta^2\text{-}MeC_2Me)_2(\eta^5\text{-}C_9H_7)][BF_4]$ and structurally characterised by *X*-ray crystallography, is formed in good yield. Also of considerable interest is the observation that (**1**), (**3**), and (**4**) will react with excess of but-2-yne under conditions of toluene reflux (111 °C) to give (**2**), all in greater than 50% yield.

The observation that (**3**) reacts with but-2-yne under forcing conditions to give (**2**) presents a mechanistic dilema since (**2**) results from (**5**), and it has already been shown that (**3**) is not the precursor to (**4**) and hence (**5**), at least at 80 °C in a sealed tube. To investigate this process further, a sample of (**3**) containing but-2-yne labelled at the methyl groups with deuterium[16] was prepared, and refluxed in toluene with unlabelled but-2-yne. If, as has been suggested[5,6] for the cyclopentadienyl substituted system, the 'fly-over' is assembled by a sequential reaction starting with the $M_2(\mu\text{-alkyne})$ complex, then the deuterium label would be completely retained with (**2**). In fact, starting with 66% deuteriation of (**3**) at the methyl groups (by n.m.r.), the deuterium content of (**2**) was negligible (by n.m.r.). Hence in forming (**2**) from (**3**), the initially co-ordinated but-2-yne is lost. This poses the problem as to how (**3**) is transformed into (**2**).

A previous study[17] by Muetterties and Slater of alkyne exchange reactions of the cyclopentadienyl analogues of (**3**) provides valuable insight. This showed that exchange takes place with modest rates at 110 °C and that the byproduct of such reactions was a dimetallacyclopentadiene analogue to (**5**). It was also shown that the rate determining step for alkyne exchange was CO dissociation, and labelling experiments demonstrated that the metal–metal bond remained intact. Thus a rationale for the formation in refluxing toluene of (**2**) from (**3**) is that $[Mo_2(\mu\text{-}MeC_2Me)(CO)_4(\eta^5\text{-}C_9H_7)_2]$ initially loses carbon monoxide to form the intermediate (**6**) (see Scheme 1). This reacts reversibly with a second molecule of MeC_2Me providing a pathway for loss of $CD_3C_2CD_3$ to form (**7**). Oxidative coupling of the two but-2-yne molecules co-ordinated to the one molybdenum centre affords (**8**), the cyclopentadienyl hex-3-yne analogue of which has been characterised by Muetterties and Slater.[15] Thermal decarbonylation of (**8**) then yields (**5**), which reacts further with but-2-yne as we have shown to form the 'fly-over' complex (**2**). Thus, (**3**) acts as a precursor to the 'fly-over' complex (**2**) *via* rupture of the transversely bonded alkyne bridge under the forcing conditions of toluene reflux. However, since (**3**) is not the precursor to (**4**), there must be an alternative pathway, specific to the indenyl system, which is accessible at lower temperatures, and does not involve (**3**). Hoffmann and co-workers analysis[18] of the bonding in molecules like (**1**) suggests that on reaction with an alkyne the intermediate (**9**) would be formed. Clearly, this could collapse after rotation about the Mo–Mo bond to give (**3**), or alternatively (**9**) could be captured by an excess of alkyne to form (**10**). Slippage (η^5 to η^3) of an indenyl ligand would then allow co-ordination of a second alkyne to one of the molybdenum centres, thereby setting things up for the formation of (**4**).

Thus, in summary this study shows that alkyne coupling reactions at two molybdenum centres are more subtle than originally thought. It will be interesting to discover conditions under which (**2**) can be transformed into a four-alkyne 'fly-over' and hence a cyclo-octatetraene.

We thank the S.E.R.C. for support and a for a studentship (R. J. M.).

Received, 18th August 1986; Com. 1179

References

1 G. Wilke, *Pure Appl. Chem.*, 1978, **50**, 677.
2 R. E. Colborn and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1981, **103**, 6259.
3 M. J. Winter in 'The Chemistry of the Metal-Carbon Bond,' vol. 3, p. 259, eds. F. R. Hartley and S. Patai, John Wiley, 1985.
4 W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Liebigs Ann. Chem.*, 1948, **560**, 1.
5 S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1978, 221.
6 S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 173.
7 W. Geilbel, G. Wilke, R. Gold, C. Krüger, and R. Mynott, *J. Organomet. Chem.*, 1978, **160**, 139.
8 J. W. Faller, R. H. Crabtree, and A. Habib, *Organometallics*, 1985, **4**, 929, and references therein.
9 D. E. Smith and A. J. Welch, *Organometallics*, 1986, **5**, 760, and references therein.
10 R. J. Mercer, M. Green, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1986, 567.
11 L. Brammer, M. Green, A. G. Orpen, K. E. Paddick, and D. R. Saunders, *J. Chem. Soc., Dalton Trans.*, 1986, 657.
12 W. I. Bailey, M. H. Chisholm, F. A. Cotton, and L. A. Rankel, *J. Am. Chem. Soc.*, 1978, **100**, 5764.
13 A. N. Nesmeyanov, N. A. Ustynyuk, L. G. Makovova, V. G. Andrianov, Yu. T. Struchkov, S. Andrae, Yu. A. Ustynyuk, and S. G. Malyugina, *J. Organomet. Chem.*, 1978, **159**, 189.
14 J. S. Bradley, *J. Organomet. Chem.*, 1978, **150**, C1.
15 S. Slater and E. L. Muetterties, *Inorg. Chem.*, 1981, **20**, 946.
16 P. L. Watson and R. G. Bergman, *J. Am. Chem. Soc.*, 1980, **102**, 2698.
17 S. Slater and E. L. Muetterties, *Inorg. Chem.*, 1980, **19**, 3337.
18 E. D. Jemmis, A. R. Pinhas, and R. Hoffmann, *J. Am. Chem. Soc.*, 1980, **102**, 2576.