The Formation and Reactivity of Dimolybdenum Acetylide Anions; Synthesis, Structure, and Thermal Rearrangement of Dimolybdenum η^1,η^2-(4e)-Vinylidene Complexes

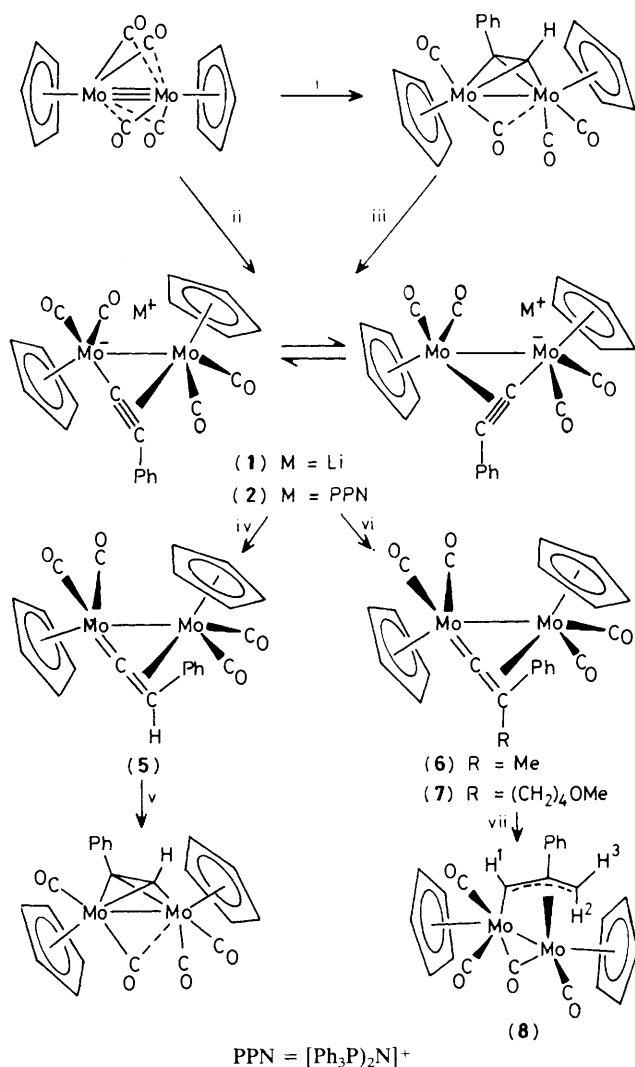Richard J. Mercer, Michael Green, and A. Guy Orpen

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Addition of PhC≡CLi to $[Mo_2(CO)_4(\eta^5\text{-}C_mH_n)_2]$ ($n = m = 5$; $n = 7$, $m = 9$) or Bu^{t}Li to $[Mo_2(\mu\text{-}HC_2Ph)(CO)_4(\eta^5\text{-}C_mH_n)_2]$ affords $Li[Mo_2(\mu\text{-}C_2Ph)(CO)_4(\eta^5\text{-}C_mH_n)_2]$ characterised as $[(Ph_3P)_2N]^+$ salts, protonation of the cyclopentadienyl salt affords $[Mo_2(\mu\text{-}\eta^1,\eta^2\text{-}C=CHPh)(CO)_4(\eta\text{-}C_5H_5)_2]$ which readily rearranges to $[Mo_2(\mu\text{-}HC_2Ph)(CO)_4(\eta\text{-}C_5H_5)_2]$, whereas methylation (CF_3SO_3Me) in CH_2Cl_2 or tetrahydrofuran affords respectively $[Mo_2\{\mu\text{-}\eta^1,\eta^2\text{-}C=C(Ph)R\}(CO)_4(\eta\text{-}C_5H_5)_2]$ [R = Me or $(CH_2)_4OMe$] the latter being characterised by X-ray crystallography; thermolysis of $[Mo_2\{\mu\text{-}\eta^1,\eta^2\text{-}C=C(Ph)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ gives $[Mo_2\{\mu\text{-}\eta^1,\eta^3\text{-}CH.C(Ph)CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$.

Molecules containing carbon bridged di- and poly-nuclear transition metal systems have recently[1] been the focus of attention because it is believed this could provide insight into the reaction path(s) involved in the Fischer–Tropsch reaction. Clearly, limitations are imposed on such studies by the synthetic methods available to access these molecules. We report a new approach which allows the introduction of

substituted C_2 and C_3 fragments, derived from acetylide moieties, into dimolybdenum complexes.

The unsaturated dinuclear complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$, which contains a formal molybdenum to molybdenum triple bond, is known[2,3] to react with a variety of donor ligands. Addition ($-78\,^{\circ}$C) of PhC≡CLi to a solution of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in tetrahydrofuran (thf) resulted in a rapid reaction

Figure 1. Molecular structure of (7) showing atomic labelling scheme. All hydrogen atoms have been omitted for clarity. Important geometric parameters include: bond lengths (Å): Mo(1)–Mo(2) 3.120(1), Mo(1)–C(1) 1.909(5), Mo(2)–C(1) 2.179(5), Mo(2)–C(2) 2.443(6), C(1)–C(2) 1.380(7); inter-bond angles (°): Mo(1)–C(1)–Mo(2) 99.3(2), Mo(2)–C(1)–C(2) 168.5(4), Mo(2)–C(1)–C(2) 83.5(3).

PPN = [Ph₃P]₂N]⁺

Scheme 1. i, +PhC₂H; ii, +PhC₂Li, −78 °C, thf; iii, BuᵗLi, −78 °C, thf; iv, +MeOH; v, room temp., C₆D₆; vi, CF₃SO₃Me in CH₂Cl₂ (6), thf (7); vii, 50 °C in toluene.

and the formation of a 1 : 1 adduct (1) (Scheme 1), which was characterised† as a crystalline, thermally stable PPN salt (2), [(Ph₃P)₂N][Mo₂(μ-C₂Ph)(CO)₄(η-C₅H₅)₂]. A similar reaction

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† Selected spectroscopic data for compound (2): ν_{CO} 1893m, 1847s, 1819m, 1787m cm⁻¹ (CH₂Cl₂); n.m.r. ¹H (CD₂Cl₂, −60 °C), δ 7.8—7.1 (m, 35 H, Ph), 5.17 (s, 5 H, C₅H₅), 5.15 (s, 5 H, C₅H₅); ¹³C-{¹H} (CD₂Cl₂, −60 °C), 248.4 (CO), 247.2 (CO), 244.4 (CO), 242.8 (CO), 182.6 (MoCCPh), 100.3 (MoCCPh), 91.8 (C₅H₅), 90.5 (C₅H₅). Compound (3): ν_{CO} 1891s, 1853s cm⁻¹ (CH₂Cl₂). Compound (4): ν_{CO} 1923w, 1891m, 1851s, 1799s cm⁻¹ (CH₂Cl₂). Compound (5): ν_{CO} 1963w, 1923w, 1899s, 1867m cm⁻¹ (hexane); n.m.r. ¹H (C₆D₅CD₃, −60 °C), δ 7.0 (m, 5 H, Ph), 5.08 (s, 1 H, CHPh), 4.93 (s, 5 H, C₅H₅), 4.62 (s, 5 H, C₅H₅); ¹³C-{¹H} (C₆D₅CD₃, −60 °C), δ 333.2 (MoCCHPh), 243.8 (CO), 235.8 (CO), 233.5 (CO), 226.3 (CO), 95.7 (C₅H₅), 92.0 (C₅H₅), 66.08 [CH, ¹J(CH) 162.1 Hz]. Compound (6): ν_{CO} 1971m, 1923s, 1903s, 1871w cm⁻¹ (hexane); n.m.r. ¹H (CD₂Cl₂), δ 7.2 (m, 5 H, Ph), 5.59 (s, 5 H, C₅H₅), 4.96 (s, 5 H, C₅H₅), 2.01 (s, 3 H, Me); ¹³C-{¹H} (CD₂Cl₂), δ 340.72 [MoCC(Me)Ph], 78.89 [MoCC(Me)Ph], 97.1 (C₅H₅), 93.1 (C₅H₅), 27.0 (Me). Compound (7): ν_{CO} 1968m, 1923s, 1898s, 1868w cm⁻¹ (hexane); n.m.r. ¹³C-{¹H} (C₆D₆) δ 338.7 [MoCC(Ph)R], 83.8 [MoCC(Ph)R]. Compound (8): ν_{CO} 1955s, 1915s, 1849s, 1771m cm⁻¹ (CH₂Cl₂); n.m.r. ¹H (CD₂Cl₂), δ 10.53 [d, H¹, ⁴J(HH) 3.06 Hz], 7.5 (m, 5 H, Ph), 5.35 (s, 5 H, C₅H₅), 4.81 (s, 5 H, C₅H₅), 3.78 [dd, H², ⁴J(HH) 3.06, ²J(HH) 1.32 Hz], 0.84 [d, H³, ²J(HH) 1.32 Hz].
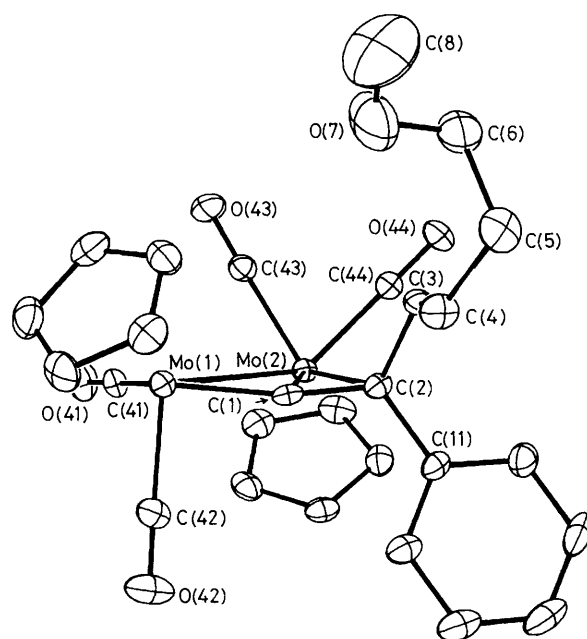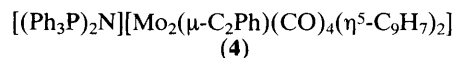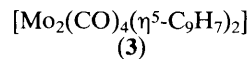
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between PhC≡CLi and (3) [Mo₂(CO)₄(η⁵-C₉H₇)₂],†⁴ which is readily synthesised by oxidation of Li[Mo(CO)₃(η⁵-C₉H₇)] with Ph₃CCl (thf) and subsequent thermolysis (toluene, 111 °C) of [Mo₂(CO)₆(η⁵-C₉H₇)₂], afforded the η⁵-indenyl analogue (4) [(Ph₃P)₂N][Mo₂(μ-C₂Ph)(CO)₄(η⁵-C₉H₇)₂]. It is particularly interesting that the same anions are also formed by deprotonation (BuᵗLi, thf, −78 °C) of the transversely bonded phenylethyne complexes, e.g. [Mo₂(μ-HC₂Ph)(CO)₄-(η-C₅H₅)₂] (see Scheme 1). The anions (2) and (4) show dynamic behaviour in solution. For example, the ¹H and ¹³C-{¹H} n.m.r. spectra of (2) showed resonances corresponding to four terminal CO's and two cyclopentadienyl ligands at −60 °C (CD₂Cl₂), coalescing ($\Delta G_{Tc}^{\ddagger}$ 50 kJ mol⁻¹) to two CO's and one C₅H₅ resonance at higher temperatures. In the ¹³C spectrum measured at −60 °C there are also resonances at δ 182.6 and 100.3, which are assigned to C_α and C_β respectively of a MoC₂Ph fragment, suggesting the illustrated μ-acetylide structure, rather than a deprotonated transverse bonded alkyne with a tetrahedral Mo₂C₂ core. Presumably a tetrahedral lithio species⁵ is formed initially in the deprotonation reaction, but this then rearranges to a lower energy μ-acetylide anion, with a structure resembling the isoelectronic species [Mo₂(μ-CNPh)(CO)₄(η-C₅H₅)₂]⁶ and [Mo₂(μ-CN)(CO)₄(η-C₅H₅)₂]⁻.⁷

[Mo₂(CO)₄(η⁵-C₉H₇)₂]
(3)

[(Ph₃P)₂N][Mo₂(μ-C₂Ph)(CO)₄(η⁵-C₉H₇)₂]
(4)

Clearly it was important to examine the reactivity of these anions towards electrophilic reagents. Addition

η^1,η^1 (2e)

η^1,η^2 (4e)

(A)   (B)

R = H, Me, MeO(CH$_2$)$_4$
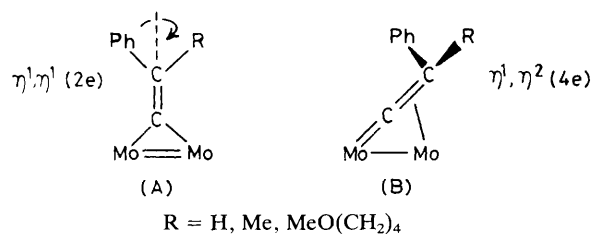
(25 °C) of methanol to (1), the lithium salt of the η-cyclopentadienyl substituted anion, results in β-protonation[8] and the formation (80%) of the kinetically controlled product, the dark purple crystalline complex (5), [Mo$_2$(μ-η^1,η^2-C=CHPh)(CO)$_4$(η-C$_5$H$_5$)$_2$]. This rearranged quantitatively in solution at room temperature (12 h, C$_6$D$_6$) or in the solid state (2 weeks) to give the alkyne complex [Mo$_2$(μ-HC$_2$Ph)(CO)$_4$(η-C$_5$H$_5$)$_2$]. A similar rearrangement has been reported[9] for the parent μ-η^1,η^2-vinylidene ligand in [Mo$_2$(μ-η^1,η^2-C=CH$_2$)(CO)$_4$(η-C$_5$Me$_5$)$_2$] prepared by u.v. irradiation of [Mo$_2$(CO)$_4$(η-C$_5$Me$_5$)$_2$] in the presence of ethyne.

Methyl trifluoromethanesulphonate (CF$_3$SO$_3$Me) also reacts with a solution of (1) in CH$_2$Cl$_2$ (−78 °C addition, warming to 25 °C) resulting in β-methylation‡ and formation (85%) of the dark blue crystalline complex (6) [Mo$_2${μ-η^1,η^2-C=C(Ph)Me}(CO)$_4$(η-C$_5$H$_5$)$_2$] which showed similar spectroscopic features (i.r., ^{1}H and ^{13}C n.m.r.)† to (5). In contrast with (5), the blue complex (6) is stable at room temperature. When the reaction with CF$_3$SO$_3$Me was carried out in thf as solvent simple methylation did not occur, instead a new blue complex (7) was formed. The i.r. and n.m.r. spectra† of (7) suggested that it contained a substituted μ-η^1,η^2-vinylidene {c.f. those present in (5), (6), and [Mo$_2$(μ-η^1,η^2-C=CH$_2$)(CO)$_4$(η-C$_5$Me$_5$)$_2$]}; in addition incorporation of ring-opened thf was indicated.

A single crystal X-ray analysis§ of (7) revealed the molecular geometry depicted in Figure 1 which allows, for the first time, detailed structural characterization of the 'side-on' co-ordination mode of a vinylidene ligand. In (7) this ligand asymmetrically bridges the Mo–Mo single bond [Mo(1)–Mo(2) 3.120(1) Å] and carries phenyl and (CH$_2$)$_4$OMe substituents, the latter derived from thf. The vinylidene ligand therefore acts a four-electron donor to the dimolybdenum centre, and may be seen as binding to Mo(1) via a Mo=C double bond [Mo(1)–C(1) 1.909(5) Å] and to Mo(2) via interaction of the C=C double bond [Mo(2)–C(1) 2.179(5), Mo(2)–C(2) 2.443(6) Å]. The asymmetry of the interaction with Mo(2), and the non-planarity of the Mo$_2$(μ-CC) system [the C=C bond is bent out of the Mo$_2$(μ-C) plane by 11.3°] are due at least in part to the bulky substituents at C(2). It would

appear that instead of adopting the familiar[10] symmetrical (2e) bridging mode (A), the inherent unsaturation (Mo=Mo) is relieved by rotation of the vinylidene about an axis through C–C, thus achieving the asymmetric bonding mode (B) where the C.C(Ph)R fragment now functions as a 4e ligand. An interesting parallel can be drawn between this dinuclear system and with mononuclear η^1(1e),η^2(3e)-vinyl,[11] and η^3(3e),η^4(5e)-butadienyl[12,13] species, where a metal to carbon multiple bond is also generated in order to relieve unsaturation at the metal.

With the establishment of a simple and potentially versatile synthetic route to 2,2-disubstituted μ-η^1,η^2-(4e)-vinylidene complexes it was possible to begin to explore their chemistry. As an initial study the thermolysis of (6) was examined. In a sealed vessel in toluene at 50 °C the blue complex smoothly transformed (55%) into a red crystalline species, which was identified by comparison[14] of i.r. and n.m.r. parameters as the μ-allylidene complex (8) (Scheme 1). This rearrangement provides a new route to these interesting molecules, and involves an apparent 1,3-hydrogen shift.

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‡ It is interesting that only one diastereoisomer is formed implying selective attack by the electrophile on one side of the acetylide ligand.

§ Crystal Data for (7): C$_{27}$H$_{26}$Mo$_2$O$_5$, M = 622.4, monoclinic, space group P2$_1$/n (No. 14), a = 11.828(3), b = 12.664(4), c = 17.422(4) Å, β = 105.20(2)°, U = 2518(1) Å^3, Z = 4, D$_c$ = 1.642 g cm^{-3}, F(000) = 1247.55 electrons, graphite-monochromated X-radiation, λ̄ = 0.710 69 Å, μ(Mo-K$_\alpha$) = 9.93 cm^{-1}. Intensity data were collected on a Nicolet P3m diffractometer, at ambient temperature, for a unique quadrant of reciprocal space in the range 4 < 2θ < 50°. Structure solution was by Patterson and difference Fourier methods. Least squares refinement gave final residuals R (R$_w$) 0.032 (0.038) for 2 834 unique, absorption corrected, observed [I > 1.5σ(I)] intensity data.

The atomic co-ordinates for this work are available on requests from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.