Journal of Organometallic Chemistry, 384 (1990) C12–C16
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20605PC

Preliminary communication

Formation of trinuclear metal clusters by reaction of dimolybdenum μ-acetylide anions with electrophilic metal species. Crystal structure of $[Mo_3(\mu_3\text{-}C_2Ph)(CO)_5(\eta\text{-}C_5H_5)_3]$

Abdul Wahab Al-Saadoon, Michael Green,
Department of Chemistry, King's College London, Strand, London WC2R 2LS, (Great Britain)

Richard J. Mercer and A. Guy Orpen
Department of Inorganic Chemistry, The University, Bristol BS8 1TS, (Great Britain)

(Received August 7th, 1989)

Abstract

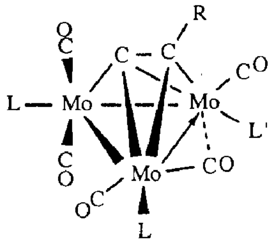
Treatment of $Li[Mo_2(\mu\text{-}C_2R)(CO)_4L_2]$ (R = alkyl or aryl) with $[Mo(NCMe)_2(CO)_2L$ or $L'][BF_4]$($L = \eta\text{-}C_5H_5$, $L' = \eta^5\text{-}C_9H_7$) $[Rh(NCMe)_2(nbd)][BF_4]$, or $[Ru(NCMe)_2(CO)L][BF_4]$ affords trinuclear metal clusters. Extension to the corresponding reactions of $Li[Mo_2\{\mu\text{-}C_2C(Me){=}CH_2\}(CO)_4L_2]$ allows the development of the chemistry of organic fragments bonded to an Mo_3 array.

There is considerable interest [1] in modelling organic transformations on metal surfaces, and to some extent progress is limited by restrictions in synthetic methodology. We have previously [2,3] shown that addition of $RC{\equiv}CLi$ to $[Mo_2(CO)_4L_2$ or $L'_2]$ ($L = \eta\text{-}C_5H_5$, $L' = \eta^5\text{-}C_9H_7$); R = alkyl or aryl) affords the μ-acetylide anions $Li[Mo_2(\mu\text{-}C_2R)(CO)_4L_2$ or $L'_2]$, which on protonation or alkylation give the side-on bonded vinylidene complexes $[Mo_2(\mu\text{-}\sigma,\eta^2\text{-}C{=}CRR')(CO)_4L_2$ or $L'_2]$. We have now established that trinuclear complexes carrying organic fragments can be synthesised through reactions of electrophilic metal species with these Mo_2-μ-acetylide anions.

Treatment (3 h at room temperature) of $[Mo(NCMe)_2(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ with $Li[Mo_2(\mu\text{-}C_2R)(CO)_4(\eta\text{-}C_5H_5)_2]$ (R = Ph) in dichloromethane solution gave 65% yield of the crystalline trimolybdenum complex I [8*], which was isolated by column chromatography. Complex II was prepared similarly from complexes with $L' = C_9H_7$ and $R = Bu^t$. This synthetic method was extended to mixed metal clusters. For example, reaction of $[Rh(NCMe)_2(nbd)][BF_4]$ with $Li[Mo_2(\mu\text{-}C_2Ph)(CO)_4L_2]$ afforded III, which on treatment (room temperature, CH_2Cl_2) with

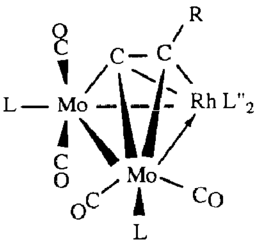
---

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



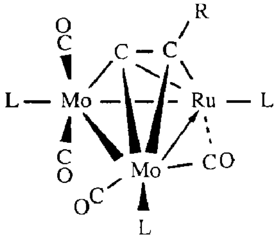
(I, $L=L'=\eta\text{-}C_5H_5$, R=Ph)

(II, $L=\eta\text{-}C_5H_5$, $L'=\eta^5\text{-}C_9H_7$, $R=Bu^t$)

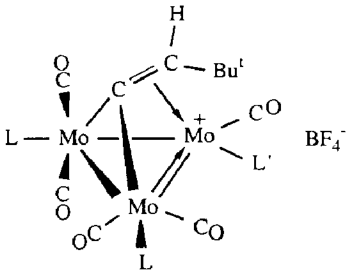


(III, $L=\eta\text{-}C_5H_5$, L''_2=nbd, R=Ph)

(IV, $L=\eta\text{-}C_5H_5$, L''=CO, R=Ph)



(V, $L=\eta\text{-}C_5H_5$, $R=Bu^t$)



(VIII, $L=\eta\text{-}C_5H_5$, $L'=\eta^5\text{-}C_9H_7$)

carbon monoxide gave IV. Similar reaction of $[Ru(NCMe)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ with $Li[Mo_2(\mu\text{-}C_2Bu^t)(CO)_4L_2]$ gave V.

The solid state structure of I was established by X-ray crystallography [9*] and is illustrated in Fig. 1. The molecule is a 48 electron cluster, with five carbonyl and three cyclopentadienyl ligands, together with the acetylide ligand. One of the carbonyls, CO(5) is semi-bridging (Mo(2)–C(5) 1.978(5) Å, Mo(1)–C(5) 2.419(6) Å). Electron counting at the three molybdenum centres reveals Mo(1) to be electron deficient (17 electrons), Mo(2) to be coordinatively saturated, and Mo(3) to have one electron too many (19 electrons). Hence, Mo(3) may be regarded as providing two electrons to Mo(1) via a donor bond. The α-carbon of the acetylide ligand symmetrically bridges the metal triangle, whereas the β-carbon (C(2)), which bridges between Mo(1) and Mo(3), adopts a more asymmetric bonding mode, lying 2.165(4) from Mo(1), and 2.343(5) Å from Mo(3). Thus, the acetylide ligand is tilted toward the formally electron deficient Mo(1). Owing to the symmetrical bridging mode adopted by C(1), the system can be regarded as a Mo_3C tetrahedron face-capped by CPh. In solution complex I shows dynamic behaviour at ambient temperature, and examination of the variable temperature ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra suggests that there is a synchronous rotation of the acetylide fragment, carbonyls, and metal–metal donor bond around the Mo_3 triangle, leading to equivalence of all three Mo atoms. This will be discussed in detail in a full paper.

In order to begin to explore the chemistry of these cluster complexes and in particular to examine the reactivity of the organic fragments bonded to the Mo_3 triangle, the analogous complex VI (Scheme 1) was synthesised by the reaction of $Li[Mo_2\{\mu\text{-}C_2C(Me)=CH_2\}(CO)_4L_2]$ with $[Mo(NCMe)_2(CO)_2L'][BF_4]$. Protona-

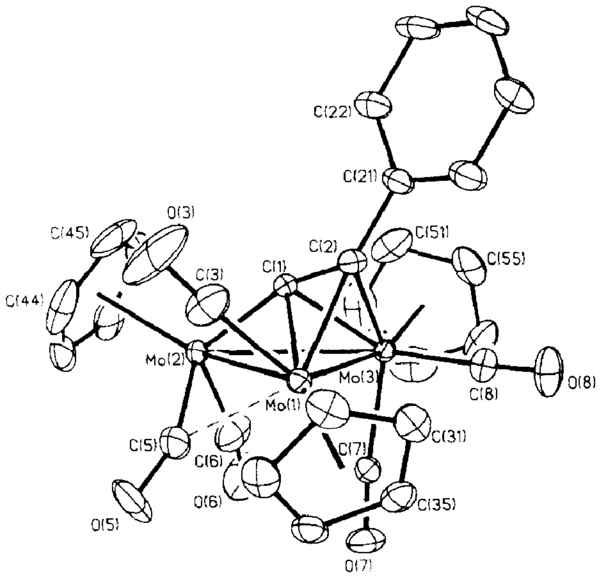
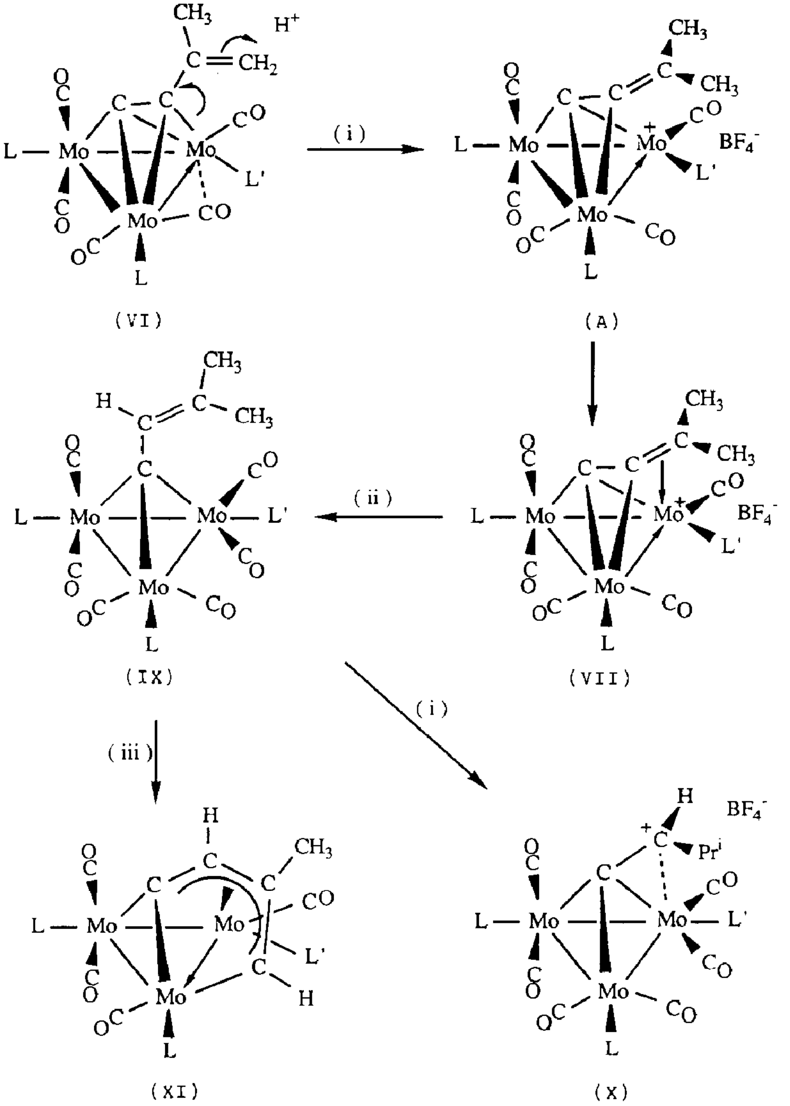


Fig. 1. Molecular geometry of I, important molecular geometry parameters include: bond lengths Mo(1)–Mo(2) 2.984(1), Mo(1)–Mo(3) 2.948(1), Mo(2)–Mo(3) 3.057(1), Mo(1)–C(1) 2.173(4), Mo(2)–C(1) 2.012(4), Mo(3)–C(1) 2.175(4), Mo(1)–C(2) 2.165(4), Mo(3)–C(2) 2.343(5), C(1)–C(2) 1.333(6) Å; Bond angle C(1)–C(2)–C(21) 138.5(4)°.

tion ($HBF_4 \cdot Et_2O$) of VI afforded the stable crystalline cation VII, in a reaction which probably involves the intermediate A (Scheme 1) formed via electrophilic attack on the exocyclic double bond with concomitant cleavage of a carbon–molybdenum bond. This is in contrast with the reaction path followed in the corresponding reaction of the Bu^t substituted cluster II. In this case protonation occurs at the β-carbon of the original acetylide fragment to form initially the cation $[Mo_3(\mu_3\text{-}CC^+HBu^t)(CO)_5L_2L']$, which achieves stability in the product VIII by forming carbon–carbon and molybdenum–molybdenum double bonds rather than through an agostic $Mo(\mu\text{-}H)C$ interaction [4]. Treatment of the cation VII with $K[BHBu^s_3]$ in thf led to the delivery of hydride into the β-carbon of the allenylidene fragment, and the formation of the vinyl substituted cluster IX, rather than the expected isopropyl substituted analogue of II. This is an unusual reaction, which involves both carbon–molybdenum bond cleavage and an electronic rearrangement.

Because of the isolobal [5] relationship $MoL_2(\eta\text{-}C_5H_5) \leftrightarrow Co(CO)_3$, and the known ability of the $Co_3(CO)_9C$ cluster to stabilise adjacent carbonium ions it was obviously also of interest to explore the reactivity of the unsaturated cluster IX toward electrophiles. When $HBF_4 \cdot Et_2O$ was added to a CH_2Cl_2 solution of IX the latter underwent rapid protonation to form the stable crystalline isopropyl substituted cation X. Examination of the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of X revealed temperature-dependent behaviour, with two methyl and two $\eta\text{-}C_5H_5$ signals present at low temperature with estimated barriers to site exchange of $\Delta G^{*}_{283}(Me)$ 57.5 (± 2.0) kJ mol^{-1} and $\delta G^{\neq}_{283}(Me)$ 57.5 (± 2.0) kJ mol^{-1} and $\Delta G^{\neq}_{283}(C_5H_5)$ 55.1 (± 2.0) kJ mol^{-1}. The diastereotopic behaviour of the isopropyl methyl groups can be accounted for if the $CHPr^i$ group is tilted as illustrated in Scheme 1, the observed coalescence corresponding to a process of enantiomerisation involving a correlated rotation of the $CHPr^i$ group around the Mo_3 triangle. It is especially



Scheme 1. $L = \eta^5\text{-}C_5H_5$, $L' = \eta^5\text{-}C_9H_7$; (i) $HBF_4 \cdot Et_2O$, CH_2Cl_2; (ii) $K[BHBu_3^s]$, CO, thf; (iii) toluene, 80 °C, −2CO, $-H_2$.

noteworthy that the theoretical ideas developed to account for the behaviour of the cation $[Co_3(CO)_9CCH_2]^+$ have general applicability [6].

Complex IX is also interesting in the context of modelling of hydrocarbon rearrangement reactions on metal surfaces. Thermolysis (80 °C) of IX in toluene in a sealed tube afforded (60% yield) the green crystalline Mo_3 complex XI, which was structurally identified by comparison of the spectral data with that of the X-ray crystallographically-identified complex $[Mo_3\{\mu_3\text{-}\eta^4\text{-}CCHC(Me)CH\}(CO)_4L_3]$ obtained by thermolysis of $[Mo_2(\mu\text{-}\sigma:\eta^3\text{-}CHCHCMe_2)(CO)_4L_2]$ [7]. Thus, the transformation IX → XI involves loss of carbon monoxide and an apparent dehydrogenation. This reaction probably involves initial loss of CO followed by the folding over of the organic fragment so as to interact with an unsaturated molybdenum centre. There is no precedent for such a dehydrogenation.

Acknowledgement. We thank the S.E.R.C. and the Iraq Government for support and studentships (to R.J.M. and A.W.A.-S respectively).

References and notes

1 E.L. Muetterties, T.N. Rhodin, E. Band, C.F. Brucker, and W.R. Pretzer, Chem. Rev., 79 (1979) 91; D. Nucciarone, S.A. Maclaughlin, N.J.Taylor, and A.J. Carty, Organometallics, 7 (1988) 106.

2 R.J. Mercer, M. Green, and A.G. Orpen, J. Chem. Soc., Chem. Commun., (1986) 567.

3 S.F.T. Froom, M. Green, R.J. Mercer, K.R. Nagle, A.G. Orpen, and S. Schwiegk, J. Chem. Soc. Chem. Commun., (1986) 1666.

4 G.C. Conole, S.F.T. Froom, M. Green, and M. McPartlin, J. Chem. Soc., Chem. Commun., (1989) 92.

5 T.A. Albright, J.K. Burdett, and M.H. Whangbo, Orbital Interactions in Chemistry, Wiley, New York, 1985, p. 402.

6 R.T. Edidin, J.R. Norton, and K. Mislow, Organometallics, 1 (1982) 561, and ref. therein.

7 W.E. Carroll, M. Green, A.G. Orpen, C.J. Schaverien, I.D. Williams, and A.J. Welch, J. Chem. Soc., Dalton Trans., (1986) 1021.

8 Selected spectroscopic data. Compound I: NMR ^{1}H ($C_6D_5CD_3$, 343 K); δ 7.54–6.95 (m, 5H, Ph), 4.96 (s, 15H, C_5H_5); ^{1}H (CD_2Cl_2, 213 K), δ 7.51–7.17 (m, 5H, Ph), 5.63 (s, 5H, C_5H_5), 5.26 (s, 5H, C_5H_5), 5.08 (s, 5H, C_5H_5); ^{13}C-{^{1}H} (CD_2 Cl_2, 213 K): δ 243.0, 240.8, 235.8, 233.9, 233.3 (CO), 178.5 (C^α), 146.7 (Ph), 131.2 (Ph), 128.6 (Ph), 126.6 (Ph), 116.9 (C^β), 96.4 (C_5H_5), 95.8 (C_5H_5) and 95.2 p.p.m. (C_5H_5); ν(CO) (CH_2Cl_2) 1967m, 1929s, 1911s, 1861m cm^{-1}. Compound (III): NMR ^{13}C-{^{1}H} (CD_2Cl_2, 298 K), δ 181.0 [d, C^α, ^1J(RhC) 9.2 Hz], 96.8 [d, C^β, ^1J(RhC) 9.2 Hz]; ν(CO) (CH_2Cl_2) 1935s, 1911s, 1863s cm^{-1}. Compound IV: NMR ^{1}H ($C_6D_5CD_3$, 298 K), δ 7.73–6.96 (m, 5H, C_6H_5), 5.10 (s, 5H, C_5H_5), 4.70 (s, 5H, C_5H_5); ^{1}H ($C_6D_5CD_3$, 363 K, Cp region), δ 5.02 (s, 10H, C_5H_5); ν(CO) (CH_2Cl_2) 2019s, 1965s, 1949m, 1923m, 1895m, cm^{-1}. Compound V: NMR ^{1}H (CD_2Cl_2, 298 K), δ 5.57 (s, 5H, C_5H_5), 5.03 (s, 5H, C_5H_5), 4.98 (s, 5H, C_5H_5), 1.26 (s, 9H, Bu^t); ν(CO) (CH_2Cl_2), 1950s, 1918s, 1867m, 1734s cm^{-1}. Compound VI: NMR ^{1}H (CD_2Cl_2, 293 K), δ 5.20 (m, 2H, $C{=}CH_2$), 4.72 (s, 5H, C_5H_5), 4.51 (s, 5H,C_5H_5), 2.27 [t, 3H, Me, ^4J(HMe) 1.0 Hz]; ν(CO) (CH_2Cl_2) 1941sh, 1933sh, 1910vs, 1710m,cm^{-1}. Compound VII: ^{1}H NMR (CD_2Cl_2, 213 K), δ 4.92 (s, 5H, C_5H_5), 4.87 (s, 5H, C_5H_5), 2.64 (s, 3H, Me), 1.91 (s, 3H, Me); ^{13}C-{^{1}H} (CD_2Cl_2, 213K): δ 236.4, 231.4, 227.4, 226.6, 225.4 (CO), 202.7 (C^α), 134.8 (C^β), 129.3–112.8 (C_9H_7), 110.2 (*C*Me_2), 98.0 (C_5H_5), 93.3 (C_5H_5), 83.1–66.4 (C_9H_7), 40.8 (Me), 28.1 (Me); ν(CO) (CH_2Cl_2): 1986w, 1963vs, 1933sh, 1850m cm^{-1}. Compound VIII: NMR ^{1}H (CD_2Cl_2, 298 K): δ 7.63–5.53 (C_9H_7), 5.33 (s, 5H, C_5H_5), 5.01 (s, 5H, C_5H_5), 2.85 (s, 1H, C^βH), 1.28 (s, 9H, Bu^t); ^{13}C-{^{1}H} (CD_2Cl_2, 298 K): δ 234.3, 229.4, 222.9, 218.5, 217.7 (*C*O), 191.4 (C^α), 130.0–101.9 (C_9H_7), 96.1 (C_5H_5), 94.7 (C_5H_5), 93.5–87.4 (C_9H_7), 73.9 (C^βH), 48.6 (*C*Me_3), 34.3 (C(*C*H_3)); ν(CO) (CH_2Cl_2) 2005m, 1961vs, 1981w, 1824mbr cm^{-1}. Compound IX: NMR ^{1}H (CD_2Cl_2, 203 K); δ 8.26 (s, 1H, C*H*=CMe_2), 7.6–4.9 (C_9H_7), 5.1 (s, 5H, C_5H_5), 4.45 (s, 5H, C_5H_5), 2.11 (s, 3H, Me), 2.0 (s, 3H, Me); ν(CO) (CH_2Cl_2), 1985s, 1940vs, 1876s, 1810m, cm^{-1}. Compound X: NMR ^{1}H (CD_2Cl_2, 293 K): δ 7.48–7.4 (C_9H_7), 5.99 (br.s,C*H*Pr^i), 5.64 (br, s, 10H, C_5H_5), 2.53 (br, s, 1H, $CHMe_2$), 1.36 (br, s, 6H, CH_3); ^{1}H (CD_2Cl_2, 213 K) 7.5–5.6 (C_9H_7), 5.81 (m, 1H, C*H*Pr^i), 5.5 (s, 5H, C_5H_5), 4.7 (s, 5H, C_5H_5), 1.5 (d, 3H, Me, J(HH) 5.5 Hz), 1.2 (d, 3H,Me, J(HH) 5.3 Hz); ^{13}C-{^{1}H} (CD_2Cl_2, 213 K), δ 190.2 (C^α), 116.2 (*C*HPr^i), 97.7 (C_5H_5), 89.9 (C_5H_5), 42.3 (*C*HMe_2), 28.2 (Me), 22.8 (Me); ν(CO) (CH_2Cl_2) 2030s, 1987vs, 1936s, 1865m cm^{-1}. Compound XI: NMR ^{13}C-{^{1}H} (CD_2Cl_2, 298 K), δ 288.3 (C^α), 242.3, 239.4, 239.1, 238.3 (CO), 137.5 (C^β), 124.2 (C_9H_7), 123.96 (C_9H_7), 123.87 (C_9H_7), 120.2 (C^γ), 113.3 (C_9H_7), 111.54 (C_9H_7), 110.5 (C^δ), 97.49 (C_5H_5), 95.38 (C_9H_7), 89.55 (C_5H_5), 80.4 (C_9H_7), 21.0 (Me); ν(CO) (CH_2Cl_2), 1933w, 1873vs, 1775m, cm^{-1}.

9 Crystal data for I: $C_{28}H_{20}O_5Mo_3$, $M = 724.3$, orthorhombic, space group *Pbca* (No. 61), a 20.800(3), b 15.553(3), c 15.534(3) Å, V 5205(2) Å^3, $Z = 8$, D_x 1.91 gcm^{-3} $\bar{\lambda}$ 0.71069 Å, μ 14.8 cm^{-1}, $F(000) = 2832$, T 295 K. Data were collected on a Nicolet P3m diffractometer for $4 < 2\theta < 50°$. The structure was solved by heavy atom methods and refined by least-squares to R 0.0303 for 3736 unique, observed $[(I > 1.5\sigma(I)]$ intensity data.