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Preliminary communication

Ligand shift in mixed-cluster complexes: synthesis of alkyne-bridged Co_2Mo_2 clusters with two triply-bridging sulphur atoms: Crystal structure of $[Co_2Mo_2(\eta^5\text{-Cp})_2(\mu_3\text{-S})_2(\mu_4\text{-CF}_3C_2Me)(CO)_4]$

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Abstract

Reaction of the complexes $[(CO)_3Co(\mu\text{-RC}_2R')Co(CO)_3]$ (R = R′ = CF_3; R = Ph, CF_3 and R′ = H) with the Mo=Mo dinuclear derivative $[Mo_2Cp_2(\mu\text{-SMe})_2(CO)_2]$ leads to cleavage of both C–S and C–H bonds with the formation of *closo*-octahedral $Mo_2Co_2C_2$ clusters stabilised by a μ_4-η^2-bound alkyne. An X-ray diffraction study has shown that the two Mo_2Co faces of the octahedron are capped by triply-bridging sulphur atoms.

We very recently proposed a one-step preparation from two dissimilar dinuclear complexes of tetranuclear mixed -metal clusters containing a μ-η^2-alkyne [1]. While examining new synthetic routes to electron-rich metal clusters we have now discovered that the M=M multiple metal–metal bond can serve as a convenient synthon in the construction of tetranuclear clusters containing the M_2 unit. As an illustration of the method we report here the formation of *closo*-$Mo_2Co_2C_2$ clusters by condensation of the μ-alkyne-bridged dinuclear cobalt derivatives $[(CO)_3Co(\mu\text{-RC}_2R')Co(CO)_3]$, **1** [R = R′ = CF_3 (**1a**); R = CF_3, R′ = H (**1b**); R = Ph, R′ = H (**1c**)] with the Mo=Mo thiolato-complex $[Cp_2Mo_2(SMe)_2(CO)_2]$, **2**. Although the preparation of bimetallic clusters by reactions involving M–M single bonds is well-established [2], surprisingly few examples are known of corresponding reactions in which an M=M double bond is involved [3].

Complex **1** reacts with **2** under reflux in octane to give the new clusters **3** [yield: 27% (**3a**) and 17% (**3b**)] and **4** [yield: 34% (**4a**) and 9% (**4b**)] after 2 h (Scheme 1). The related complexes **3** and **4** have been characterised by their infrared, NMR and mass spectra [*] which are consistent with the formulation $[Co_2Mo_2Cp_2S_2(RC_2R')(CO)_4]$ [R = R' = CF_3 (**3a**); R = Ph, R' = H (**3b**)] and $[Co_2Mo_2Cp_2S_2(RC_2Me)(CO)_4]$ [R = CF_3 (**4a**) or Ph (**4b**)], respectively. The ^1H and ^{13}C NMR spectra of **3b**, **4a** and **4b** show two inequivalent cyclopentadienyl groups indicating that the Mo atoms are also inequivalent in these complexes whereas **3a** contains equivalent cyclopentadienyl groups. All the complexes display similar patterns in the carbonyl regions of their infrared spectra, suggesting that they have similar structures. An X-ray diffraction study of a single crystal of **4a** established its molecular structure (see Fig. 1). Crystals of **4a**, $C_{18}H_{13}Co_2F_3Mo_2S_2O_4$, $M = 724.16$, are monoclinic, space group $P2_1/c$, with $a = 8.277(1)$, $b = 10.175(1)$, $c = 25.535(2)$ Å, $\beta = 92.36(1)°$, $U = 2148.8(3)$ Å^3, $Z = 4$, $D_c = 2.238$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 28.7$ cm^{-1}, and $F(000) = 1400$. $R = 0.033$ and $R_w = 0.042$ after refinement on F to convergence of 280 parameters from 3564 independent reflections with $I \geq 3\sigma(I)$ and $\theta(\text{Mo-}K_\alpha) \leq 27°$. Crystallographic measurements were made with Mo radiation, $\lambda = 0.71069$ Å, on an Enraf–Nonius CAD4F diffractometer. Empirical absorption corrections were applied and allowance was made for all H-atoms [**].

The structure of **4a** can be described in terms of a Mo_2Co_2 butterfly with a μ_4-η^2-alkyne ligand σ-bonded to the hinge Mo atoms and π-bonded to the wingtip Co atoms. Alternatively, the $Mo_2Co_2C_2$ unit can be viewed as a *closo*-octahedron and this description is consistent with the presence of 7 polyhedral skeletal electron pairs. **4a** thus belongs to the well-known family of M_4-butterfly cluster compounds, typified by $[Co_4(CO)_{10}(C_2R_2)]$, in which the cluster valence electron count is 60 (alkyne being regarded as a 4-electron donor) [4]. However, **4a** shows two novel features: it contains transition metals from different periodic groups and also has μ_3-sulphido groups capping the two Mo_2Co triangles. The cluster C–C bond is fairly long [df. C(1)–C(3) = 1.455(7) Å with the mean value [5] of 1.353 Å for the bridging C≡C distance in species like **1**]. Other distances in **4a** appear unexceptional [5].

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[*] Spectroscopic data for 3 and 4 (satisfactory C, H, Co, Mo and S analyses have been obtained for these complexes).

3a $[Co_2Mo_2Cp_2S_2(CF_3C_2CF_3)(CO)_4]$: ^1H NMR ($CDCl_3$) δ 5.80 (s, C_5H_5); $\{^1H\}$-^{13}C NMR ($CDCl_3$) δ 202 (s br., CO), 147.17 (m, C–CF_3), 128 (q, J(CF) 278, CF_3), 99.12 (s, C_5H_5); ^{19}F NMR ($CDCl_3$) δ −41.9(s); IR (hexane) ν(CO) cm^{-1} 2042m, 2024s, 1994vs; m/z (EI) 778 (M^+).

3b $[Co_2Mo_2Cp_2S_2(PhC_2H)(CO)_4]$: ^1H NMR ($CDCl_3$) δ 8.30 (s, 1H, =CH), 7.2 (m, 5H, Ph), 5.90 (s, 5H, C_5H_5), 5.86 (s, 5H, C_5H_5); $\{^1H\}$-^{13}C NMR ($CDCl_3$) δ 204 (s br., CO, 164.06 (s, *C*Ph), 135.36 (s, CH), 154.97, 128.52, 127.03, 126.43 (s, C_6H_5), 98.70 (s, C_5H_5), 97.96 (s, C_5H_5); IR (hexane) ν(CO) cm^{-1} 2014m, 1996s, 1959s; m/z (EI) 690 ($M^+ - CO$).

4a $[Co_2Mo_2Cp_2S_2(CF_3C_2Me)(CO)_4]$: ^1H NMR ($CDCl_3$) δ 5.93 (s, 5H, C_5H_5), 5.90 (s, 5H, C_5H_5), 2.84 (s, 3H, Me); $\{^1H\}$-^{13}C NMR ($CDCl_3$) δ 202.6 (s br., CO), 165.68 (s, *x*-Me), 142.0 (m, *C*-CF_3), 129.0 (q, J(CF) 279, CF_3), 99.82 (s, C_5H_5), 99.08 (s, C_5H_5), 39.0 (s, CH_3); IR (hexane) ν(CO) cm^{-1} 2016m, 2008s, 1973vs; m/z (EI) 724 (M^+).

4b $[Co_2Mo_2Cp_2S_2(PhC_2Me)(CO)_4]$: ^1H NMR ($CDCl_3$) δ 7.46–7.16 (m, 5H, Ph), 6.00 (s, 5H, C_5H_5), 5.77 (s, 5H, C_5H_5), 2.68 (s, 3H, Me); ^{13}C NMR ($CDCl_3$) δ 166.5 (s, *C*-Ph), 161.6 (s, *C*-Me), 150.6, 131.1, 126.8, 126.0 (s, C_6H_5), 99.48 (s, C_5H_5), 99.34 (s, C_5H_5), 39.51 (s, CH_3); IR (CH_2Cl_2) ν(CO) cm^{-1} 2008m, 1988vs, 1048vs; m/z (EI) 732 (M^+).

[**] Atomic coordinates for this work can be obtained from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EW, UK. Any request should include the full literature citation for this communication.

The formation of **3** and **4** may be rationalised as follows (see Scheme 2): (i) condensation of **1** and **2** after pyrolytic decarbonylation to give the unsaturated species **A** which may be viewed, at least conceptually, as an adduct formed by insertion of a $Co_2(CO)_4(\mu\text{-}RC_2R')$ fragment across the Mo=Mo bond of **2**; (ii) conversion of **A** to either **B** or **C** according to the elimination of either two methyl groups (**B**) or a methane molecule (**C**) and concomitant migration of a methyl group to an alkyne carbon atom; (iii) formation of the saturated species **3** or **4** by coordination to Co of the two sulphur ligands which thereby expand their connectivities from μ_2 to μ_3. The formation of **C** obviously occurs via cleavages of C–H and C–S bonds in **A** and subsequent transfer of one cleaved methyl group to alkyne carbon as a replacement for the expelled hydrogen atom.

Activation of C–H and C–S bonds in polynuclear complexes is an established process [6], but the formation of **4** is the first example of such a transformation occurring on a *closo*-tetrametallic M_4C_2 cluster. The reactions of mixed transition

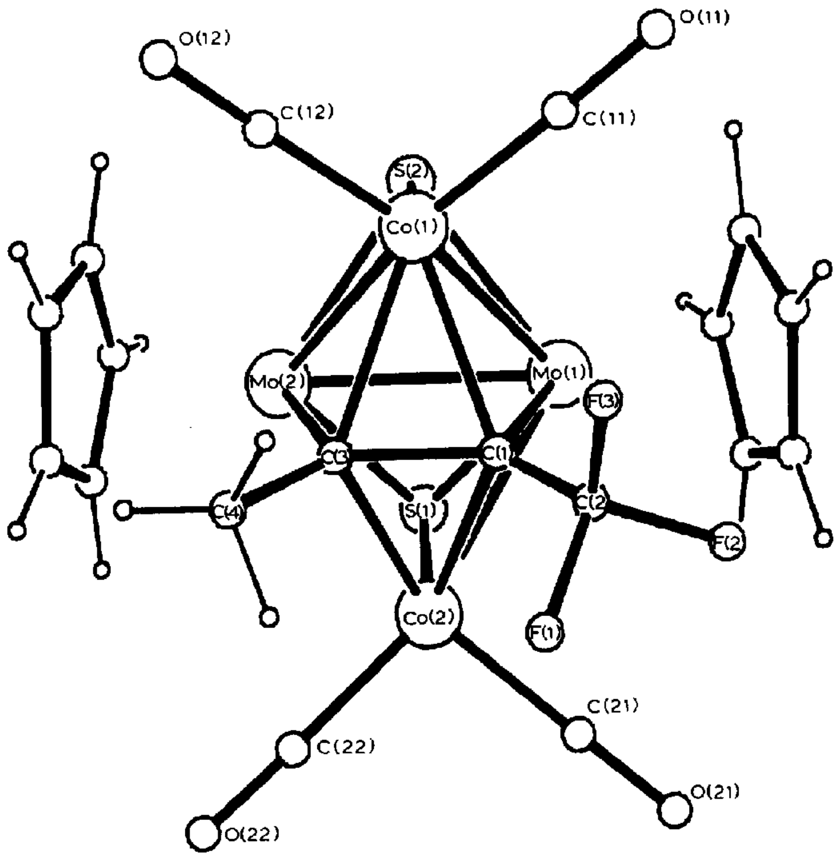
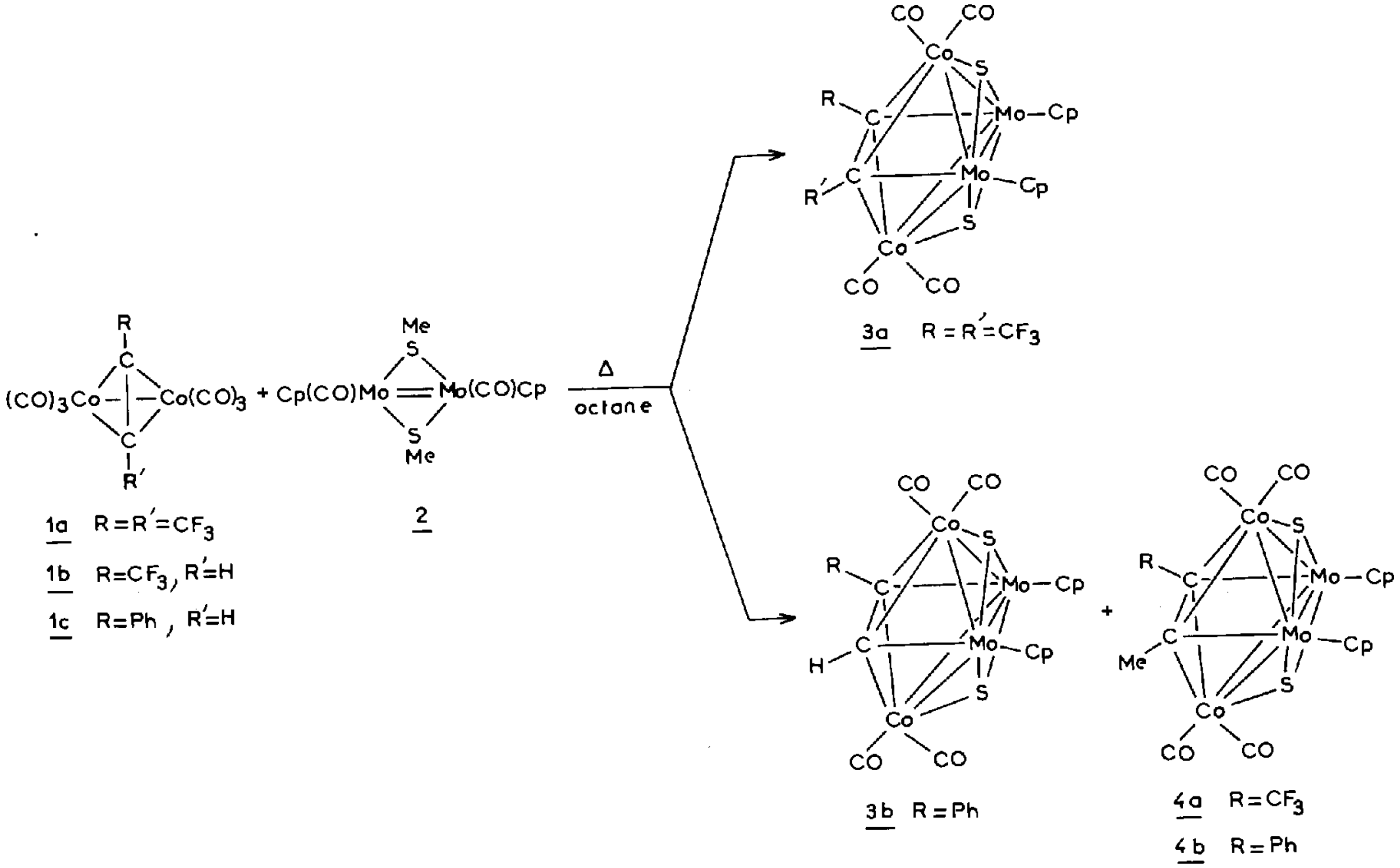
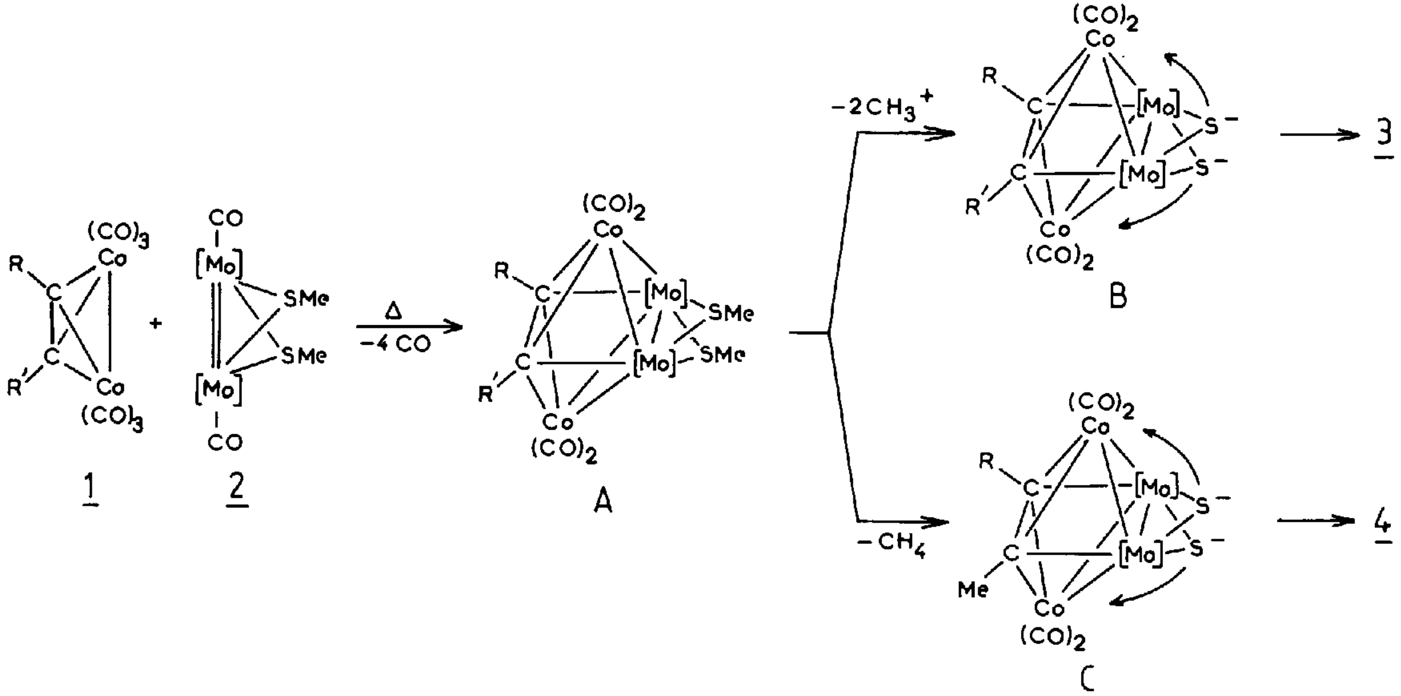


Fig. 1. Structure of $[Co_2Mo_2(\eta^5\text{-}Cp)_2(\mu_3\text{-}S)_2(\mu_4\text{-}CF_3C_2CMe)(CO)_4]$ (**4a**). Distances (Å) and angles (°) include: Mo(1)–Mo(2) 2.717(1), Mo–Co 2.598(1)–2.622(1) [mean 2.612(6)], Mo–S 2.319(2)–2.332(2) [mean 2.326(3)], Co–S 2.215(2) and 2.216(2), Mo(1)–C(1) 2.167(5), Mo(2)–C(3) 2.135(5), Co(1)–C(1) 2.091(5), Co(1)–C(3) 2.116(5), Co(2)–C(1) 2.086(5), Co(2)–C(3) 2.125(5), Mo(1)–Mo(2)–C(3) 73.8(2), Mo(2)–Mo(1)–C(1) 72.1(2), Mo(1)–C(1)–C(3) 107.5(3), Mo(2)–C(3)–C(1) 106.6(4), Mo(1)–Co(1)–Mo(2) 62.6(1) and Mo(1)–Co(2)–Mo(2) 62.8(1).


(CO)$_3$Co
Co(CO)$_3$
R
R'
C
+ Cp(CO)Mo
Mo(CO)Cp
S
Me
Δ
octane
1a R=R'=CF$_3$
1b R=CF$_3$, R'=H
1c R=Ph, R'=H
2
CO
Co
Mo—Cp
Mo
Cp
H
Me
3a R=R'=CF$_3$
3b R=Ph
+
4a R=CF$_3$
4b R=Ph

Scheme 1.



Scheme 2. Possible mechanism for the formation of 3 and 4 ([Mo] = CpMo).

metal clusters containing alkynes and organosulphur ligands described here may serve as models for transformations occurring on metal surfaces during heterogeneous catalysis where C–C bond formation, C–C or C–H bond cleavage and poisoning by organosulphur species are important processes [7].

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