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REACTION OF MOLYBDENUM–MOLYBDENUM TRIPLE BONDED COMPOUNDS WITH GROUP VIII PEROXO-TRANSITION METAL COMPLEXES

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Summary

The reaction of (t-butyl-NC)$_2$NiO$_2$ with $(C_5Me_5)_2Mo_2(CO)_4$ results in complete decarbonylation with retention of the metal–metal bond and formation of one oxo and one μ-oxo group per molybdenum. The structure has been established from spectral data and a single crystal X-ray study.

Introduction

There has been much work in recent years on the chemistry of complexes containing a metal–metal triple bond [1,2]. A group of such complexes which has been extensively studied includes the cyclopentadienylmolybdenum dicarbonyl dimer (**1**) and related complexes [3], which undergo facile reactions with a variety of reagents including nucleophiles [4], electrophiles [5], and unsaturated organic substrates [6,7]. Recently [8] **1** was shown to react with nitro compounds with complete decarbonylation and formation of oxo ligands on molybdenum, the dimeric nature being maintained through a metal–metal single bond and μ-oxo and μ-nitrene bridges.

During a study of peroxo ligand transfer from metal to metal [9,10] we became interested in multibonded metal complexes as the host component of such a transfer. We report here the reactions of $Mo_2(C_5H_5)_2(CO)_4$ [11] and related compounds with Group VIII metal-peroxo complexes.

Results and discussion

Reaction of the pentamethylcyclopentadienylmolybdenum dicarbonyl dimer (**2**) [12] with an equimolar amount of bis(t-butylisocyanide) peroxonickel (**3**) [13] in CH_2Cl_2 gives an orange colored crystalline solid (**4**) whose infrared spectrum exhibits two bands at 914 and 804 cm^{-1} characteristic of a terminal oxo and μ-oxo group, eq. 1. Respectively, the ^{1}H NMR spectrum shows a singlet at 1.93 ppm, fully

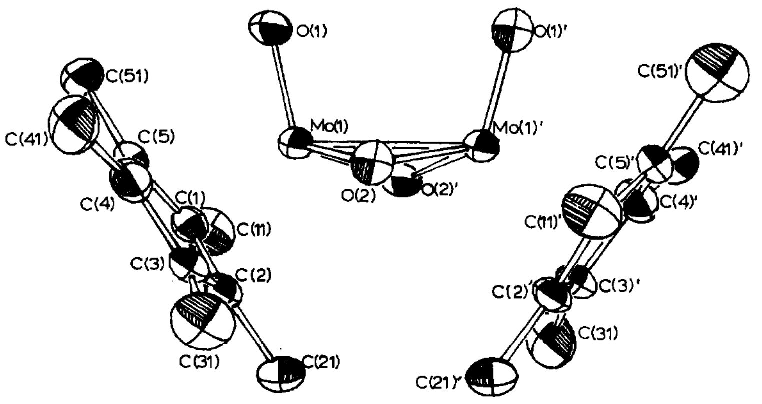
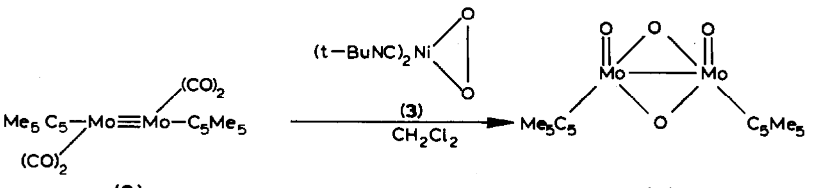


Fig. 1. ORTEP diagram of 4 with atoms labelling scheme. The molecule possesses a crystallographic 2-fold axis lying in the plane of the figure and perpendicular to the Mo–Mo bond.

in accord with **4**, whose structure was confirmed by a single crystal X-ray determination. An ORTEP view of the molecule is shown in Fig. 1, and the relevant bond distances and angles are listed in Table 1.



(2) (4) (1)

The molybdenum–molybdenum distance of 2.57 Å is consistent with a metal–metal single bond in a Mo^V dimer [14–16]. Similarly the molybdenum–oxygen distances are consistent with terminal and bridging oxo groups when compared with complexes having analogous structural features [16]. The formation of **4** [17] constitutes another unusual case of complete decarbonylation with retention of the metal–metal bond [8]. Dimeric molybdenum complexes simultaneously bearing a metal–metal single bond and two oxo groups per molybdenum are often encoun-

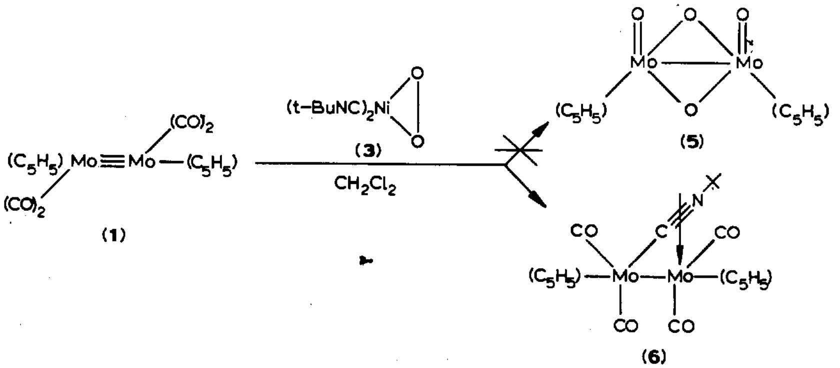
TABLE 1

SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Mo(1)–Mo(1)′	2.587(1)	Mo(1)–Mo(1)′–O(1)′ 103.8
Mo(1)–O(1)	1.692(3)	O(1)–Mo(1)–O(2) 110.6
Mo(1)–O(2)	1.946(3)	Dihedral angle between plane Mo(1) O(2) Mo(1)′ and plane Mo(1)O(2)′Mo(1)′
O(1)–O(1)′	3.406(5)	149°
O(2)–O(2)′	2.786(5)	Dihedral angle between plane Mo(1) O(2) O(2)′ and plane Mo(1)′ O(2) O(2)′
O(1)–O(2)	2.995(5)	146,5°
Mo–Cp center	2.097(4)	Dihedral angle between Cp planes 71°

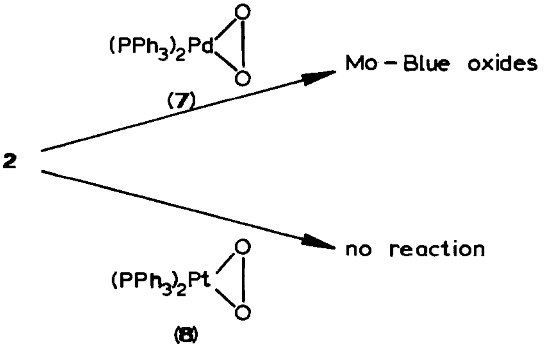
tered in compounds containing the $(Mo_2O_4)^{2+}$ unit [14,16,18–23]. Such a structure was also suggested on the basis of IR data for the closely related unmethylated compound obtained by oxygen treatment of $Mo_2(C_5H_5)_2(CO)_6$ [24]. Interestingly the *cis*-character of the oxo group in compound **4** might possibly be the result of the mode of "transfer" of oxygen atoms from nickel to molybdenum, since all such complexes bearing a cyclopentadienyl ligand yield compounds having a *trans*-configuration [24–26].

The presence of the pentamethylcyclopentadienyl ligand confers stability on the dimer and apparently prevents the oligomerization which is observed for similar compounds obtained from the reaction of triply bonded molybdenum alkoxides with oxygen [16]. It is noteworthy that the related compound containing the unmethylated cyclopentadienyl ligand **1** did not give the analogous molybdenum dimer **5** [24] but yielded instead complex **6** from the addition to **1** of an isocyanide ligand dissociated from nickel [6]. This side reaction was absent in eq. 1 since complex **2** does not react with isocyanides under mild conditions [6].



(2)

The reaction with other metal peroxo complexes was different in nature. Treatment of bis(triphenylphosphine)peroxopalladium (**7**) [27] with **2** gave no detectable amount of **4** but yielded green solutions containing molybdenum blue oxides from which no well defined species could be isolated [28]. Bis(triphenylphosphine)peroxoplatinum **8** [27], on the other hand, was inert towards **2** under the reaction conditions (eq. 3). Under the same conditions compound **8** reacted with **1** to give $CpMo(CO)_3Cl$ (**9**) [29] indicating the involvement of the chlorinated solvent. Complex **9** was also obtained under very mild conditions by treating **1** with t-BuOOH in CH_2Cl_2 [3].



(3)

Experimental

General

The molybdenum complexes $Mo_2(C_5H_5)_2(CO)_4$ (**1**) [11], $Mo_2(C_5Me_5)_2(CO)_4$ (**2**) [12] and peroxo complexes $(t\text{-}BuNC)_2NiO_2$ (**3**) [13], $(PPh_3)_2PdO_2$ (**7**) [27] and $(PPh_3)_2PtO_2$ (**8**) [27] were prepared by published procedures. All other reagents were obtained from commercial sources. All reactions were performed under dry and oxygen-free nitrogen atmospheres using vacuum line and Schlenk techniques. IR spectra were recorded on a Nicolet MX-5 FT spectrophotometer using KBr pellets. NMR spectra were recorded on a Varian EM 360 instrument using $CDCl_3$ as the solvent and TMS as internal standard.

A crystal of $(CH_3)_5C_5(MoO(\mu\text{-}O))_2$, $M_r = 526.34$, with approximate dimensions $0.3 \times 0.3 \times 0.5$ mm^3 was mounted on a CAD4 Enraf–Nonius diffractometer equipped with a graphite monochromator for Mo-K_α radiation, λ Mo-K_α 0.71073 Å. The crystal was tetragonal, space group $P\bar{4}2_1c$ (No. 114). Unit cell parameters were refined by least squares on $2 \sin \theta/\lambda$ values for 25 reflections ($15° \leqslant \theta \leqslant 20°$): a 11.681(5) Å; c 15.470(9) Å; V 2111(2) Å^3; Z 4; D_c 1.656 g cm^{-3}; $F(000)$ 1064; μ(Mo-K_α) 118 cm^{-2} (absorption was neglected).

Intensities were measured at 20°C using an ω–2θ scan of 0.91 to 10.06° min^{-1}, range $\Delta\omega = (0.9 + 0.35 \tan \theta)°$, θ_{max} 27°. Intensities of three standard reflections measured every 10000 s throughout data collection remained constant within 1%. A total of 1320 independent reflections was obtained from which 1027 with $I > 3\sigma(I)$ were used in structure determination.

All computations were performed on a PDP 11/44 (SDP-soft ware [3] and atomic scattering factors [3]). The structure was solved by heavy atom method and completed by difference Fourier analysis with hydrogen atoms not included. Full matrix least-squares refinement included anisotropic thermal parameters and minimized the function: $\Sigma w(|F_0| - |F_c|)^2$, w $1/6^2$ (F_0). Final refinements converged with R 0.029 ($R_w = 0.043$), S 1.52 and $(\Delta/6)_{max} = 0.03$. Tables of thermal parameters and structure factors may be obtained from the authors.

Typical experiment

A cold solution (−30°C) of $(t\text{-}BuNC)_2NiO_2$ (**3**) (0.257 g, 1.0 mmol) in CH_2Cl_2 (10 ml) was added to an equimolar amount of $Mo_2(C_5Me_5)_2(CO)_4$ (0.575 g) in CH_2Cl_2 (10 ml) at −30°C. The mixture was stirred for 12 h while the temperature was allowed to reach 20°C. The orange-red solution was concentrated and compound **4** was isolated by silica gel thin-layer chromatography using diethyl ether as eluent. Recrystallization from a 1/1 dichloromethane/n-hexane mixture gave orange crystals (15%).

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