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Synthesis, structure and properties of molybdenum(0) bialkyne complexes

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Abstract

The reaction of $Mo(NN)(CO)_4$ (NN = bipyridine, phenathroline) with $CH_3OOCC{\equiv}CCOOCH_3$ (DMAC) gives $Mo(NN)(CO)_4(DMAC)_2$. An X-ray diffraction study of the product (NN = bipyridine) indicates that the two CO groups are cis to each other, while the two DMAC ligands are in trans arrangement, and are mutually perpendicular with each DMAC eclipsing and N–Mo–CO vector. In solution, the DMAC ligands appear to rotate about the Mo–DMAC bond as shown by the fluxional behavior in the NMR spectra of the products.

Introduction

Complexes of molybdenum and tungsten containing alkynes as ligands have attracted keen interest in recent years [1–4]. It has been shown that the coordinated alkynes in these complexes can formally donate two to four electrons to the metal center by way of the filled $\pi_{\parallel}$ and $\pi_{\perp}$ orbitals. In addition, the alkyne ligands are known to exhibit various orientational preferences [5]. While numerous monoalkyne complexes are known, few bialkyne complexes, nearly all in the d^4 configuration, have been reported [8]. Octahedral d^6 bialkyne complexes deserve special attention in view of the presence of four-electron repulsion between filled d_{π} of the complex and $\pi_{\perp}$ of the alkyne ligands. The influence of the repulsion on the stability of the complex and the conformations of the ligands has not been fully explored. However, an octahedral bialkyne tugnsten(0) compound was recently synthesized [9]. Up to now no such molybdenum(0) complex was known. In this paper we describe the synthesis and structure of molybdenum(0) compounds which contain two alkyne ligands.

Experimental

The title compounds, $Mo(NN)(CO)_2(DMAC)_2$ [NN = bipyridine (**1**), phenanthroline (**2**); DMAC = dimethylacetylenedicarboxylate], were obtained from the reaction of the relevant $Mo(NN)(CO)_4$ with DMAC (eq. 1) in THF.

$$Mo(NN)(CO)_4 + 2CH_3OOCC{\equiv}CCOOCH_3 \rightarrow$$
$$Mo(NN)(CO)_2(CH_3OOCC{\equiv}CCOOCH_3)_2 + 2CO \quad (1)$$

After five hours of heating at 60 ° C, the solution was condensed and passed through a silica gel column with CH_2Cl_2 as the eluent. Collection of the desired portion, evaporation of the solvent, followed by recrystallization from CH_2Cl_2–ether gave the expected product (**1** in 72%; **2** in 39% yield).

X-Ray diffraction study

The structure of the bialkyne complex **1** was determined by a single crystal X-ray diffraction study. Crystal data: orthorhombic, $P2_12_12_1$, $a = 8.267(2)$, $b = 14.899(3)$, $c = 21.300(7)$ Å, $Z = 4$, $\rho_{obs} = 1.45$ g/cm^3, $\rho_{calc} = 1.500$ g/cm^3. Intensity data were collected at room temperature on a Nicolet R3m/V diffractometer, equipped with graphite-monochromated Mo-K_α radiation, by use of a $\theta/2\theta$ scan method. The structure was solved by a direct method with SHELXTL PLUS[10]. Full-matrix least-squares refinement was based on F with anomalous-dispersion corrections for atoms with atomic numbers greater than 16. Neutral-atom scattering form factors were taken from International Tables for X-Ray Crystallography [11]. The weights were: $\omega = [\sigma^2(F) + gF^2]^{-1}$ with $g = 0.0010$. All hydrogen atoms included in the refinement were placed in idealized positions (C–H = 0.96 Å, H–C–H = 109.4°) and fixed U (0.08Å^2) after the non-hydrogen atoms were refined anisotropically. The final agreement factors are $R = 0.0305$ and $R_w = 0.0328$ for 2467 independent reflections.

Results

During the course of the reaction of $Mo(bipy)(CO)_4$ with DMAC, the infrared carbonyl absorptions at 2014 (m), 1911 (vs), 1882 (sh), 1830 (s) cm^{-1} are gradually replaced by two new absorptions at 2012 (s), 1952 (vs) cm^{-1}. The observation strongly indicates that the product is a cis dicarbonyl species. In addition, the IR exhibits a broad absorption at 1810 cm^{-1} and two medium intensity absorption at 1700 and 1680 cm^{-1} due to alkyne C≡C and ester substituents, respectively. The results of IR studies reveal that no mono-coordinated DMAC intermediate is formed in significant concentrations during the reaction.

Discussion

In Fig. 1 is depicted the structure of **1**. The coordination geometry of the complex is nearly octahedral. In accord with the IR results, the two CO groups are cis to each other, while the two DMAC ligands are in a trans arrangement. One of most intriguing aspects of the structure is the orientations of the alkyne ligands—they are mutually perpendicular (81.1°) and each DMAC eclipses a N–Mo–CO vector

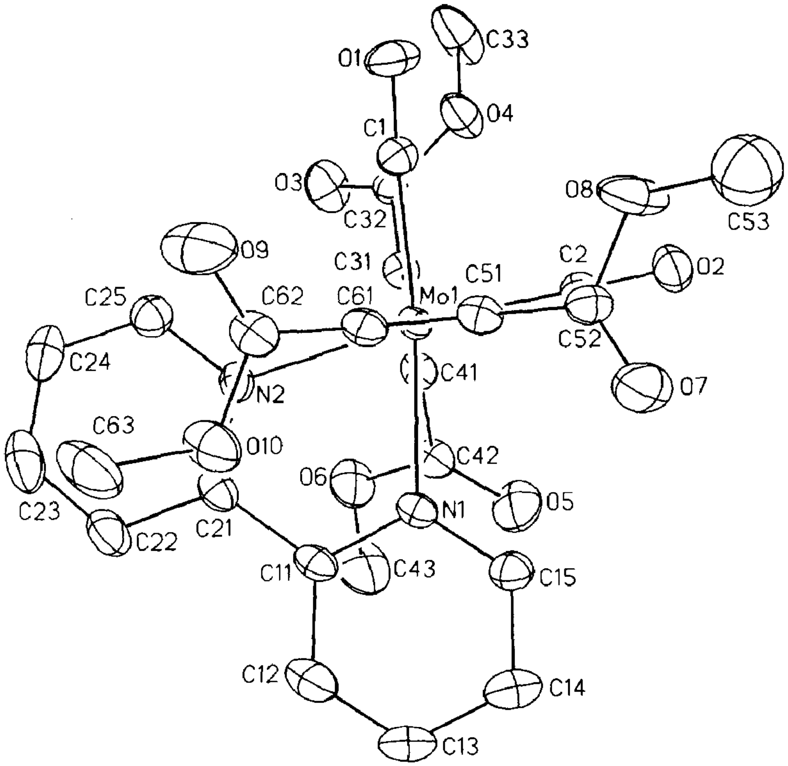
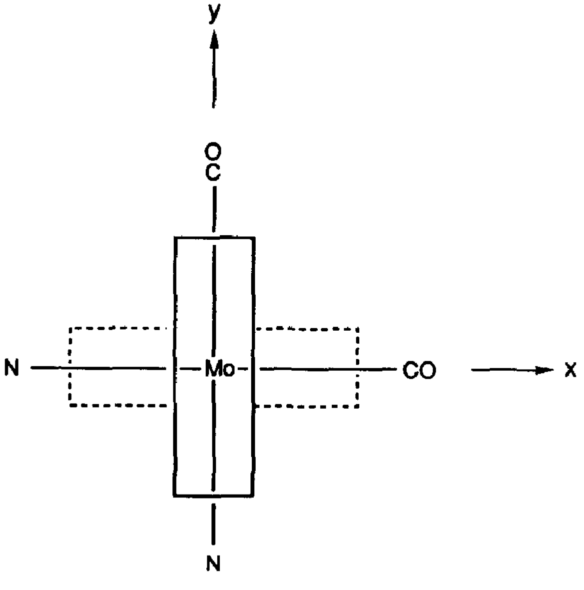


Fig. 1. A perspective drawing of Mo(bipy)(DMAC)$_2$(CO)$_2$, (1) Important bond parameters are: Mo1–C1, 2.005(5); Mo1–C2, 1.997(5); Mo1–N1, 2.243(4); Mo1–N2, 2.250(4); Mo1–C31, 2.171(5); Mo1–C41, 2.152(5); Mo1–C51, 2.177(5); Mo1–C61, 2.169(5); C31–C41, 1.282(7); C51–C61, 1.298(7) Å; angle C1–Mo1–C2, 84.8(2); N1–Mo1–N2, 72.9(10); N1–Mo1–C2, 101.6(2); N2–Mo1–C1, 103.1(2)°.



(3)

(1.7°). A clearer view of the conformation of DMAC ligands is shown by structure 3, in which each DMAC is represented by a rectangle. The geometry of 1 is thus similar to that of the previously reported $W(dppe)(CO)_2(DMAC)_2$. However, in contrast to our present results, the alkyne ligands in the d^4 octahedral bialkyne complexes reported are all cis and parallel to each other [6,7].

The mutually perpendicular arrangement enables the strongly acidic $\pi_{\parallel}^{\star}$ orbitals of DMAC ligands to overlap different, filled d_{π} orbitals. On the other hand, this trans structure also causes four-electron repulsion between the filled $\pi_{\perp}$ of the DMAC ligands and the d_{π} orbitals. This interaction raises the energy of the latter orbitals and facilitates back-donation from d_{π} to the $\pi_{\parallel}^{\star}$ of the DMAC ligands and to $\pi^{\star}$ of the CO groups. Thus, a strong π-acceptor acetylene is necessary to lower the energy of the d_{π} orbitals and stabilize the complex. Indeed we found that it was

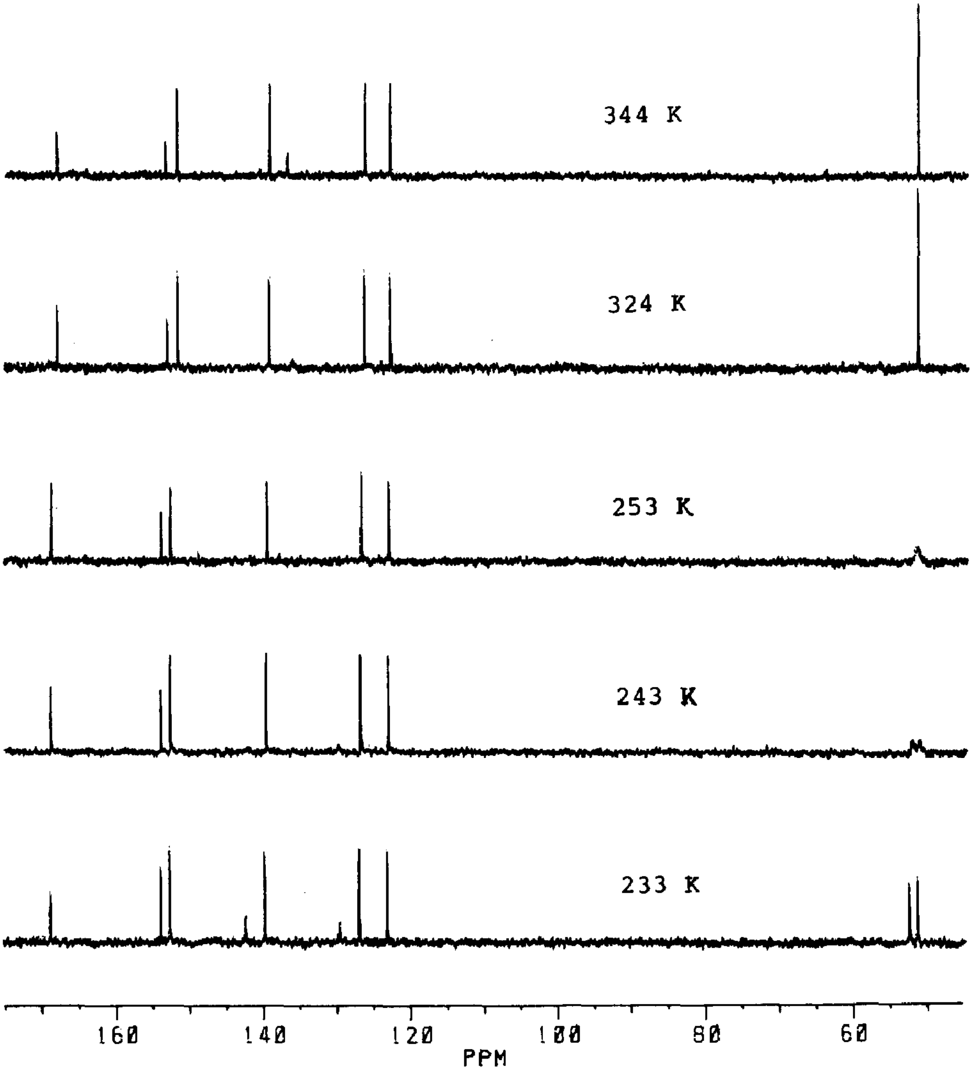


Fig. 2. The ^{13}C NMR spectra of $Mo(bipy)(DMAC)_2(CO)_2$ in CD_3COCD_3 at various temperatures.

impossible to synthesize the bialkyne Mo complex by treating a less π-acidic acetylene ligand with Mo(NN)(CO)$_4$.

The conformational preference of a π-acid ligand eclipsing a ligand–metal–ligand vector has been observed in a number of complexes [10–13]. A staggered conformation is energetically unfavorable owing to the four-electron repulsion between the filled d_{xy} and $\pi_{\parallel}$ orbitals. In the eclipsed geometry, the $\pi_{\parallel}$ orbital meets the $d_{x^2-y^2}$ σ bonding orbital which is less repulsive than d_{xy}. The δ bonding between $\pi_{\perp}^*$ and d_{xy} also favors the exclipsed geometry.

In solution, the DMAC ligands of complex (**1**) and (**2**) appear to rotate about the molybdenum–acetylene bond. The dynamic NMR spectra of complex (**1**) are shown in Fig. 2. Only a singlet at ambient temperature was observed for the protons of the four methoxy groups. This singlet coalesces at ca. 253 K but splits into two sharp signals at lower temperatures. No signal was observed for the two triple bond carbons at temperatures between 253 and 300 K. However, at 233 K two ^{13}C resonances at 142.3 and 129.2 ppm were detected. These two peaks merge in one signal at 136.8 ppm at temperatures above 344 K. From these NMR data, the barrier of alkyne rotation was calculated to be 11.6 kcal/mol, which is significantly lower than that for W(dppe)(CO)$_2$(DMAC)$_2$ [9].

Acknowledgements

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