Characterization of rigid *endo*- and *exo*-η^3-allyl carbonyl diethyldithiophosphate molybdenum complexes: crystal structure of *endo*-Mo(η^3-allyl)(CO){η^2-S$_2$P(OEt)$_2$}(Dppe)

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Abstract

The stereochemical rigid complexes *endo*-Mo(η^3-allyl)(CO){η^2-S$_2$P(OEt)$_2$}(η^2-dppm) (**2a**) and *exo*-Mo(η^3-allyl)(CO){η^2-S$_2$P(OEt)$_2$}(η^2-dppm) (**2b**) are accessible by the reaction of complex Mo(η^3-allyl)(CO)$_2${η^2-S$_2$P(OEt)$_2$}(CH$_3$CN) (**1**) with dppm in refluxing acetonitrile. Treatment of **1** with dppe in the similar reactive conditions of **2** affords the sole complex *endo*-Mo(η^3-allyl)(CO){η^2-S$_2$P(OEt)$_2$}(η^2-dppe) (**3**). Complex **3** is characterized by X-ray diffraction analysis. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Stereochemical rigid complex; *endo*; *exo*; Orientation

Previously, the stereochemistry and fluxionality of complexes containing the [Mo(CO)$_2$(η^3-allyl)AX] [1–5] (A: pyrazolylborate, β-diketonate, diphos, X: neutral monodentate, halide, anionic monodentate) type have been well investigated. Furthermore, X-ray crystallographic studies [6–16] have revealed three different solid-state structures. The most important of these is that on each Mo atom discussed above, the coordinated η^3-allyl group adopts a conformation that places the open face of the allyl group toward the adjacent cis (CO)$_2$ grouping, indicating an electronic stabilization for this particular orientation. Until now, no conformational complex [Mo(CO)(η^3-allyl)(η^2-L$_2$)(η^2-dppm)] has been discussed in the literature. Herein we report a high yield synthesis of the stereochemical rigid *endo*- and *exo*-η^3-allyl monocarbonyl molybdenum complexes.

The trigonal twist behavior, free rotational energy calculation and crystal structure of [Mo(CH$_3$CN)(η^3-C$_3$H$_5$)(CO)$_2${η^2-S$_2$P(OEt)$_2$}] (**1**) has been reported [17]. Treatment of **1** with PPh$_3$ gave no reaction [18]. However, the reaction of **1** with dppm in refluxing acetonitrile yielded the air-stable and orange–yellow complexes
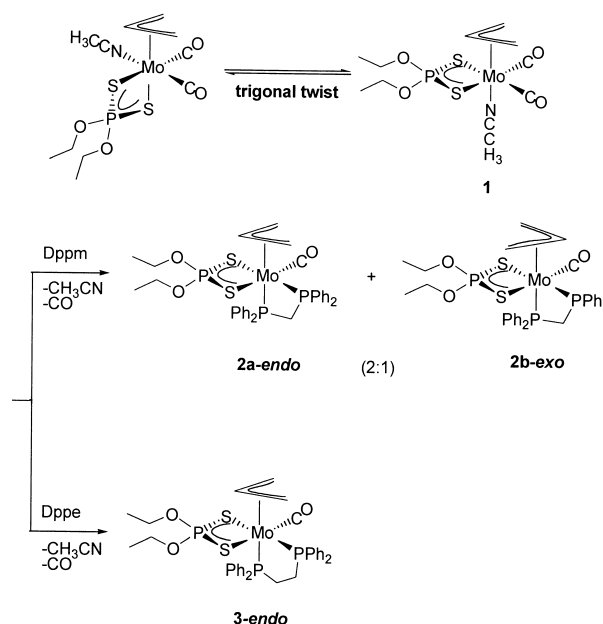
Scheme 1.

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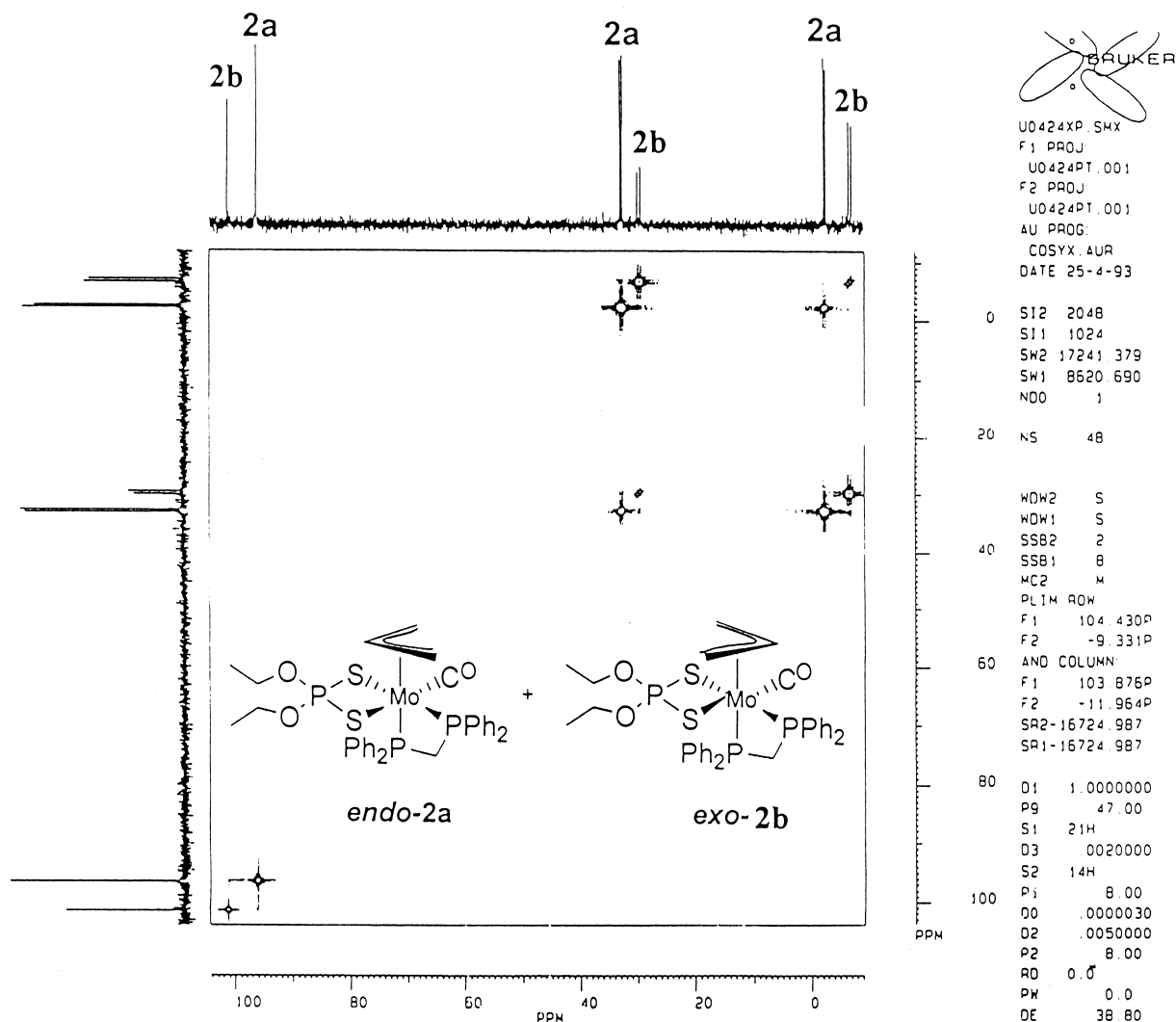 *E-mail address:* khyih@sunrise.hkc.edu.tw (K.-H. Yih).

Fig. 1. Homonuclear shift-correlated 2D NMR spectrum for ^{31}P nuclei with ^{1}H decoupling for the mixture **2a** and **2b** in acetone-d_6.

[Mo(η^3-C$_3$H$_5$)(CO){η^2-S$_2$P(OEt)$_2$}(η^2-dppm)] (**2a**, *endo*; **2b**, *exo*) (Scheme 1) with a 2:1 ratio from the integration of ^{31}P{^{1}H} NMR spectrum. The orientations of *endo* and *exo* are defined to the open face of the allyl group and carbonyl group facing in the same direction for *endo* and in opposite directions for *exo*. The mixture of the complexes **2a** and **2b** is isolated by recrystallization from hexane–CH$_2$Cl$_2$ in ca. 82% yield. The spectroscopic[1] and analytical data of the mixture of **2a** and **2b** are obtained. In the FAB mass spectra, base peaks with the typical Mo isotope distribution are in agreement with the [M$^+$–CO] molecular masses of **2a** and **2b**. The IR spectra of **2a** and **2b** show one terminal carbonyl-stretching band at 1799 cm^{-1}. In the ^{31}P{^{1}H} NMR spectrum of the mixture of **2a**

and **2b**, two sets of resonances are clearly distinguishable. The relative highfield resonances are assigned to the coordination of the dithiophosphato ligands. Four doublet resonances result from two inequivalent dppm ligands. Complexes **2a** and **2b** were also characterized by a homonuclear shift-correlated 2D ^{31}P{^{1}H} NMR spectrum (Fig. 1). The ^{31}P{^{1}H} NMR spectrum shows two sets of resonances at δ −2.6 and 33.4 ppm (with ^2J(PP) of 49.5 Hz) for **2a** and at δ −7.0 and 30.8 ppm (with ^2J(PP) of 67.8 Hz) for **2b**. The ^{31}P{^{1}H} NMR spectrum of the *exo*-Mo(η^3-C$_3$H$_5$)(CO)(η^2-S$_2$CNEt$_2$)(η^2-dppm) complex[2] was also consistent with this assignment.

To investigate the relation between orientations and phosphine ligand, we carried out the reaction of **1** with

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[1] Spectroscopy for the mixture of *endo*-**2b** and *exo*-**2b**: IR (KBr, v_{CO} /cm^{-1}) 1799(vs). ^{31}P{^{1}H} NMR: *endo*-**2a**: δ −2.6 (d, ^2J(PP) 49.5 Hz), 33.4 (d, ^2J(PP) 49.5 Hz), 97.5. *exo*-**2b**: δ −7.0 (d, ^2J(PP) 67.8 Hz), 30.8 (d, ^2J(PP) 67.8 Hz), 102.1. MS (FAB, NBA, m/z) 708 [M^+–CO]. *Anal.* Calcd. for C$_{33}$H$_{37}$O$_3$P$_3$S$_2$Mo: C, 53.95; H, 5.09%. Found: C, 54.12; H, 5.53%.

[2] The ^{31}P{^{1}H} NMR Spectrum of Mo(η^3-C$_3$H$_5$)(CO){η^2-S$_2$CNEt$_2$}(η^2-dppm): *exo*-form: δ −0.8 (d, ^2J(PP) 64.1 Hz), 26.2 (d, ^2J(PP) 64.1 Hz); *endo*-form: δ 2.5 (d, ^2J(PP) 51.0 Hz), 31.2 (d, ^2J(PP) 51.0 Hz).

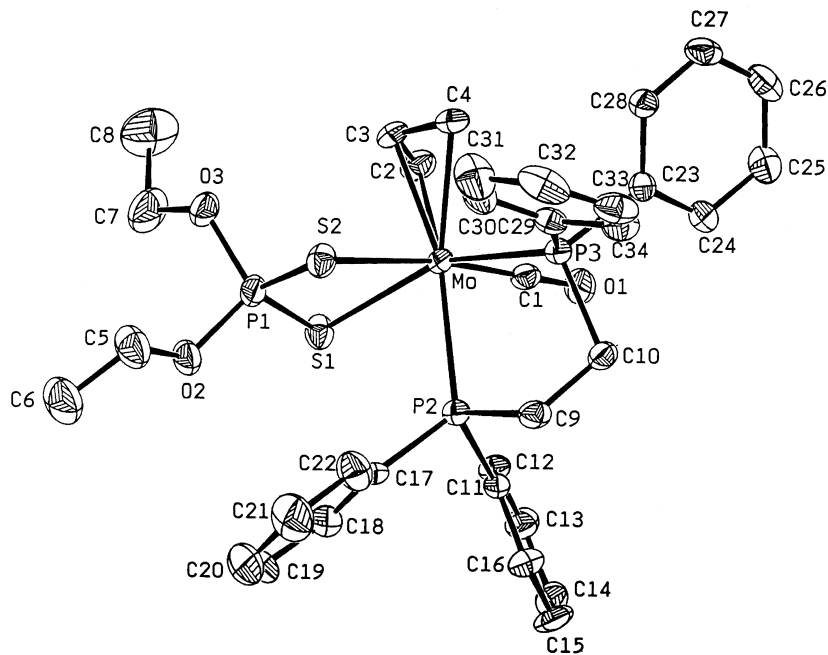Fig. 2. X-ray structure with atom numbering scheme for complex *endo*-[Mo(η^3-C$_3$H$_5$)(CO){η^2-S$_2$P(OEt)$_2$}(η^2-dppe)] (**3**). X-ray structure with atom numbering scheme for complex *endo*-[Mo(η^3-C$_3$H$_5$)(CO){η^2-S$_2$P(OEt)$_2$}(η^2-dppe)] (**3**). Selected bond distances (Å) and angles (°) are as follows: Mo–S(1), 2.6095(17); Mo–S(2), 2.6756(17); Mo–P(2), 2.5562(16); Mo–P(3), 2.4368(16); Mo–C(1), 1.895(6); Mo–C(2), 2.345(6); Mo–C(3), 2.242(6); Mo–C(4), 2.309(6); C(2)–C(3), 1.369(9); C(3)–C(4), 1.397(9); S(2)–Mo–S(1), 76.02(5); C(2)–C(3)–C(4), 116.9(6); C(1)–Mo–P(3), 80.04(18); P(2)–Mo–P(3), 79.16(5); C(1)–Mo–S(2), 172.42(17); S(1)–Mo–P(3), 157.10(6).

dppe. This reaction in refluxing acetonitrile resulted in the formation of the complex *endo*-[Mo(η^3-C$_3$H$_5$)(CO){η^2-S$_2$P(OEt)$_2$}(η^2-dppe)] (**3**) in 87% yield as the sole product. The air-stable yellow–orange compound, **3**, is soluble in dichloromethane and acetonitrile and is insoluble in diethyl ether and *n*-hexane. The FAB mass spectrum of **3**[3] shows a base peak in agreement with the [M$^+$–CO] ion fragment. The ^{31}P{^{1}H} NMR resonance of **3** appears at δ 45.9, 82.9 (with ^2J(PP) 26.6 Hz) and 96.4 ppm. In the ^{1}H NMR spectrum of **3**, the ethylene of the dppe ligand and allyl protons are observed at δ 2.22 and 3.10 ppm and at δ 0.40 (H*anti*), 2.58 (H*syn*) and 4.58 (H*c*) ppm, respectively. The corresponding ^{13}C{^{1}H} NMR signals are at δ 31.6, 48.6 ppm and at δ 74.6, 86.4 ppm, respectively. Compared to the ^{31}P{^{1}H} NMR spectra of **2a**, **2b** and **3**, it can be said that when the resonances appear relatively up-field there is a large coupling constant assigned to the *exo*-orientation, and when they appear relatively down-field

there is a small coupling constant assigned to the *endo*-orientation.

The *endo* conformation of **3** has been determined by X-ray diffraction study[4], indicating that the crystal conforms to the space group $P2_1/c$. ORTEP plot of **3** are shown in Fig. 2, where the structure confirms unequivalent allyl groups. One of the sulfur atoms of dithiophosphato is *trans* to the diphos: S(1)–Mo–P(3), 157.10(6)°, while the other is *trans* to carbonyl: S(2)–Mo–C(1), 172.42(17)°. The angle subtended at the molybdenum atom by the two phosphorus atoms of the diphos is 79.16(5)°, causing some distortion from an ideal octahedral arrangement. However, the two Mo–P bond lengths (2.5562(16) Å and 2.4368(16) Å) appear to be normal. The carbonyl ligand is essentially linear with Mo–C(1)–O(1) = 179.0(5)°. The allyl group has an intercarbon angle of 116.9(6)°, which is consistent with the values of 115.7(1)° for Mo(CO)$_2$(η^3-C$_3$H$_5$)(bpy)(NCS) [2a], 111.5(2)° for Mo(CO)$_2$(η^3-2-methylallyl)(phen)(NCS) [2b], 111.4(1)° for Mo(CO)$_2$(η^3-C$_3$H$_5$)(bpy)(py)(BF$_4$) [2d], and 117(2)° for Mo(CO)$_2$(η^3-C$_3$H$_5$)(Et$_2$Bpz$_2$) [1a]. The Mo–S and Mo–allyl bond distances in **3** are consistent with the values reported for

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[3] Spectroscopy for **3**: IR (KBr, ν_{CO}/cm^{-1}) 1801(vs). ^{31}P{^{1}H} NMR: δ 45.9 (d, ^2J(PP) 26.6 Hz), 82.9 (d, ^2J(PP) 26.6 Hz), 96.4 (*endo*). ^{1}H NMR: δ 0.40 (m, 2H, H*anti*), 0.79, 1.32 (t, J(HH) 7.2 Hz, 3H, OCH$_2$CH$_3$), 2.22 (m, 2H, PCH$_2$), 2.58 (d, J(HH) 10.8 Hz, H*syn*), 2.84 (m, 2H, OCH$_2$), 3.10 (m, 2H, PCH$_2$), 4.02 (m, 2H, OCH$_2$), 4.58 (m, 1H, H*c*). ^{13}C{^{1}H} NMR: δ 15.5, 15.9 (d, ^3J(PC) 8.4 Hz, OCH$_2$CH$_3$), 31.6, 48.6 (br, PCH$_2$), 74.6 (s, =CH$_2$), 60.6, 61.4 (d, ^2J(PC) 10.0 Hz, OCH$_2$), 86.4 (br, CH), 127–134 (m, Ph), 228.6 (s, CO). MS (FAB, NBA, *m/z*) 721.5 [*M$^+$*–CO]. *Anal.* Calcd. for C$_{34}$H$_{39}$O$_3$P$_3$S$_2$Mo: C, 54.54; H, 5.26%. Found: C, 54.76; H, 5.40%.

[4] Crystal data for **3**: C$_{34}$H$_{39}$O$_3$P$_3$S$_2$Mo, space group $P2_1/c$, a = 9.915(2) Å, b = 12.236(1) Å, c = 28.591(5) Å, β = 95.05(1)°, V = 3455.1(10) Å^3, Z = 4, D_{calcd} = 1.439 g cm^{-3}, μ = 0.6541 mm^{-1}, observed reflections 3157, $2\theta_{range}$ = 18.96–24.18°. Total number of parameters: 389. R = 0.037, R_w = 0.032; GOF = 1.81, Mo-Kα radiation; λ = 0.71073 Å; T = 293(2) K.

Mo^{II}–S and numerous molybdenum–allylic systems. Significantly, the mean C–C bond distance (1.383(9) Å) of the allyl group in *endo*-**3** is longer than that in *exo*-Mo(η^3-C$_3$H$_5$)(CO)(η^2-S$_2$CNEt$_2$)(η^2-dppm) (1.309(15) Å) [19].

In order to investigate the mechanism of complexes **2a** and **2b**, the variable-temperature ^{1}H and ^{31}P{^{1}H} NMR spectra were undertaken. In the range of 210–330 K, none of these spectra changed and the ratio was retained. Addition of free dppm or S$_2$P(OEt)$_2^-$ had no effect on the spectra of **2a** and **2b** and therefore a rearrangement involving dissociation of the diphos or dithiophosphate ligand seems unlikely. The reaction of **1** with dppm was monitored by ^{31}P{^{1}H} NMR at -20°C. During the reactive period, the ^{31}P{^{1}H} NMR spectra showed one set of resonances at δ 25.8 and -27.2 (with ^2J(PP) 61 Hz) and the resonances of **2a** and **2b**. This revealed the η^1-P-coordination of the dppm ligand of the intermediate. Since no other information could be obtained, we cannot at present define the formative mechanism further. To our knowledge, this is the first example of the *endo*- and *exo*-η^3-allyl monocarbonyl complexes in the literature. The other anionic bidentate ligands are currently being used to investigate the *endo*, *exo*-orientations.

Acknowledgements

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