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Synthesis, characterization and structure of dicarbonyl(η^5-indenyl)(η^3-pentadienyl)molybdenum and its phosphine derivatives

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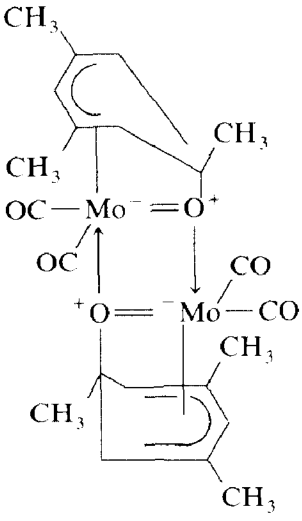
Abstract

The reaction between $Mo(CO)_2(\eta^3\text{-}C_5H_7)(CH_3CN)_2Cl$ and LiC_9H_7 or $NaC_{13}H_9$ gives $(\eta^5\text{-}C_9H_7)Mo(CO)_2(\eta^3\text{-}C_5H_7)$ (**1**) or $(\eta^5\text{-}C_{13}H_9)Mo(CO)_2(\eta^3\text{-}C_5H_7)$ (**2**) respectively. Photolysis of **1** with excess PMe_3 and PMe_2Ph in ether at −20 °C yields $(\eta^5\text{-}C_9H_7)Mo(CO)(PR_3)(\eta^3\text{-}C_5H_7)$ ($PR_3 = PMe_3$ (**3**), PMe_2Ph (**4**)). Complexes **3** and **4** exist as *exo* and *endo* isomers and have been fully characterized by elemental analyses, and from their IR, mass, and ^1H NMR spectra. The crystal structure of **1** has been determined by an X-ray diffraction study; crystallographic data: space group $P2_1/C$ a 7.955(10), b 12.531(3), c 13.987(5) Å, β 100.86(7)°, $Z = 4$, R 2.4%, R_w 2.3%.

Introduction

In recent years, there has been a resurgence of interest in the chemistry of transition-metal-pentadienyl complexes [1–3]. One notable feature of this class of compound is the variety of bonding modes by which the ligand is linked to the metal center, viz., η^1, η^3, and η^5 complexation. More recently, studies on η^5-pentadienyl complexes have revealed an interesting pattern of reactivity. The η^5 ligand is capable of undergoing a coupling reaction with metal atoms or small molecules to form metallobenzene [4], 1,3,7,9-decatetraene [5] and an interesting [5 + 1] acetylation adduct [6] as depicted below. In addition, the η^1-pentadienyl ligand undergoes

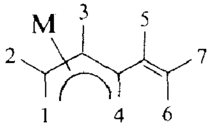


[4 + 2], [3 + 2] cycloaddition and insertion reactions with alkenes and alkynes [7]. It was recently reported that an *cis*-η^1-pentadienyliridium ligand undergoes intramolecular C–H bond activation to form a metallohexadiene complex [8]. Although numerous pentadienyl complexes have been prepared in combination with various ligands, no complex containing the indenyl group has been reported. Previous studies [9] have revealed that the indenyl group often promotes η^5–η^3 slippage and gives rise to a novel chemistry. Here we report the synthesis and characterization of indenyl-η^3-pentadienyl molybdenum complexes including their phosphine derivatives.

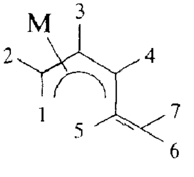
Results and discussion

Previously, we reported the synthesis of $CpMo(CO)_2(\eta^3$-pentadienyl) from the reaction between $CpMo(CO)_3Na$ and 1-chloro-2,4-pentadiene, followed by photolysis at −20 °C in ether [7c]. $(\eta^5\text{-}C_9H_7)Mo(CO)_2(\eta^3\text{-}C_5H_7)$ (**1**) was prepared by this synthetic method in very low yield (~ 1.5%) from the reaction between $(\eta^5\text{-}C_9H_7)Mo(CO)_3Na$ and 1-chloro-2,4-pentadiene. A very low yield of the fluorenyl complex $(\eta^5\text{-}C_{13}H_9)Mo(CO)_2(\eta^3\text{-}C_5H_7)$ (**2**) has also been obtained from the analogous reaction. An efficient synthesis of **1** and **2** was achieved by the reaction between $(\eta^3\text{-}C_5H_7)Mo(CO)_2(CH_3CN)_2Cl$ [7d] and LiC_9H_7 or $NaC_{13}H_9$; the yield was 30–45%. The two compounds were isolated as yellow crystals after purification by alumina column chromatography followed by recrystallization from ether. Elemental analyses and mass spectra are consistent with the given formulae.

Two isomers (in a 6 : 1 molar ratio) were detectable for 1, whereas only one isomer was detected for **2** as revealed by the ^{1}H NMR spectra. The observed coupling constants $J_{13} = J_{34} = 9.2$ Hz and $J_{23} = 6.8$ Hz indicate that the pentadienyl ligand of the two isomers of **1** have the *syn*-η^3 configuration. The *exo* isomer is the



syn-η^3



anti-η^3

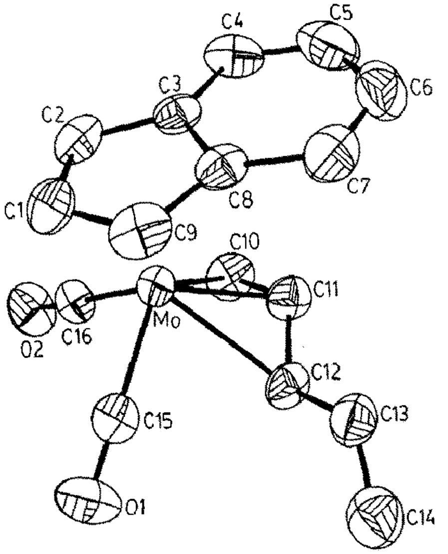


Fig. 1. ORTEP drawing of the molecular structure of (η^5-C_9H_7)Mo(CO)$_2$(η^3-C_5H_7) (1).

major because of the larger vicinal coupling constants. In the (η^5-C_5H_5)M(η^3-allyl)Ln system [10], the vicinal coupling constants and chemical shifts of the two *anti* protons H^1 and H^4 were used to assign the *exo* and *endo* isomers. In this case, like complex **1** having the η^5-indenyl ligand, the chemical shifts of the two *anti* protons were unreliable for structural assignment because of the extra shielding by the benzene ring. For the major isomer of **1**, the proton resonances of H^3 lie the most upfield (δ 0.57 ppm); this feature suggests that the allyl moiety lies under the benzene ring of the indenyl group. The *endo* isomer has the same allylic orientation in its molecular structure, as indicated by the chemical shifts of the two *anti* protons H^1 (0.42 ppm) and H^4 (0.65 ppm). These chemical shifts are about 2 ppm upfield from the *endo* isomer of CpMo(CO)$_2$(η^3-C_5H_7) [7c], which reflects the shielding effect of the benzene ring. Only one isomer was detected for the fluorenyl complex **2**, to which the *exo-syn-*η^3 conformation was assigned. The proton NMR resonances of the pentadienyl ligand of **2** have chemical shifts similar to those of the *endo* isomer of (C_5H_5)Mo(CO)$_2$(η^3-C_5H_7) [7c]. The two aromatic rings of the fluorenyl ligand show no shielding effects. This feature suggests that the allyl moiety lies between the two benzene groups of the fluorenyl ligand.

X-ray diffraction study of 1. An ORTEP drawing of the molecular structure is shown in Figure 1, and the bond distances and angles are given in Table 1. The coordination geometry about the molybdenum atom is approximately tetrahedral with the two carbonyls, the cyclopentadienyl, and the allyl groups occupying the four coordination sites. The allyl groups lie under the benzene ring of the indenyl ligand in accord with our expectations from the ^{1}H NMR data. The mouth of the allyl moiety faces away from the indenyl group and is aligned with the CO group. The pentadienyl ligand is bonded asymmetrically to the molybdenum atom, with Mo–C_{10} 2.320(5), Mo–C_{11} 2.212(4), and Mo–C_{12} 2.393(4) Å. Notably, a ring slippage pattern was observed in the metal–indenyl bonding. The carbon atoms C_1, C_2, C_9 lie closer to the molybdenum center at distances between 2.310 and 2.350(5)

Table 1

Atomic parameters x, y, z and B_{iso} e.s.d.'s refer to the last digit

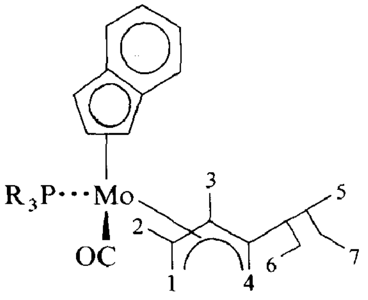
	x	y	z	B_{iso} [a]
Mo	0.31742(3)	0.106873(22)	0.175003(19)	2.371(13)
C1	0.1013(5)	0.2326(3)	0.1601(3)	3.76(18)
C2	0.2231(5)	0.2587(3)	0.2433(3)	3.43(18)
C3	0.2169(4)	0.1792(3)	0.3149(23)	2.91(14)
C4	0.3069(5)	0.1640(4)	0.4105(3)	4.30(21)
C5	0.2732(7)	0.0793(4)	0.4615(3)	5.28(24)
C6	0.1488(7)	0.0037(4)	0.4206(4)	5.4(3)
C7	0.0596(5)	0.0125(3)	0.3284(3)	4.15(21)
C8	0.0926(4)	0.1017(3)	0.27250(24)	2.95(15)
C9	0.0250(4)	0.1348(3)	0.1752(3)	3.65(17)
C10	0.4216(5)	0.5441(3)	0.2412(3)	3.92(18)
C11	0.5534(5)	0.4681(3)	0.2452(3)	3.44(16)
C12	0.6270(5)	0.4196(3)	0.3316(3)	3.35(16)
C13	0.7699(5)	0.3455(3)	0.3404(3)	3.94(19)
C14	0.8187(7)	0.2788(4)	0.4114(4)	4.87(23)
C15	0.2796(4)	0.0681(3)	0.0396(3)	3.35(17)
C16	0.4956(4)	0.1908(3)	0.13376(23)	3.25(16)
O1	0.2568(4)	0.04634(23)	−0.04263(18)	5.40(15)
O2	0.5996(3)	0.24152(21)	0.10849(18)	4.76(14)
H1	0.078(4)	0.272(3)	0.1076(22)	3.8(9)
H2	0.289(4)	0.324(3)	0.2530(23)	4.0(8)
H4	0.375(4)	0.209(3)	0.4367(24)	3.8(9)
H5	0.345(5)	0.071(3)	0.525(3)	6.2(11)
H6	0.139(5)	−0.057(3)	0.454(3)	5.7(11)
H7	−0.019(5)	−0.042(3)	0.2992(24)	4.4(9)
H9	−0.056(4)	0.098(3)	0.1270(23)	4.6(9)
H10A	0.384(4)	0.5820(25)	0.1826(22)	3.5(8)
H10B	0.352(5)	0.530(3)	0.285(3)	5.2(10)
H11	0.590(4)	0.457(3)	0.1831(23)	3.9(8)
H12	0.562(4)	0.4081(25)	0.3825(21)	3.4(8)
H13	0.826(5)	0.345(3)	0.287(3)	6.7(11)
H14A	0.743(5)	0.271(3)	0.470(3)	7.0(11)
H14B	0.886(5)	0.233(3)	0.414(3)	5.7(12)

[a] B_{iso} is the mean of the principal axis of the thermal ellipsoid.

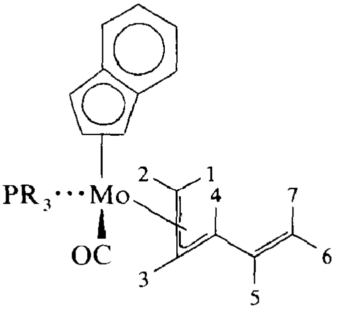
Å compared with the distances, Mo–C_3 2.414(3) and Mo–C_8 2.441(4). This allyl–ene, metal–ligand pattern is a common feature in metal–indenyl bonding [11].

The metal indenyl complex is known to undergo ready ligand substitution because of facile η^5–η^3 indenyl ring slippage [11]. Attempts to replace one carbonyl group of complex **1** with a phosphine ligand, however, were unsuccessful even when the solution was heated under reflux in toluene for 24 h. Photolysis of **1** in ether at −20 °C for 18 h in the presence of PR_3(PR_3 = PMe_2Ph, PMe_3) led to the formation of (η^5-C_9H_7)Mo(η^3-C_5H_7)(CO)(PR_3) (PR_3 = PMe_3 (**3**), PMe_2Ph (**4**)). Attempts to obtain analogous phosphine derivatives of the fluorenyl complex **2** were unsuccessful. The isolated fluorenyl phosphine complex could not be further characterized owing to its thermal instability. The air-sensitive, orange-red crystals of **3** and **4** were isolated in 25 ~ 30% yield after purification by column chromatography and recrystallization from ether. Elemental analyses and mass spectra are consistent with the given formulae.

The IR spectra of solid **3** and **4** show single ν(CO) bands at 1825 and 1832 cm^{-1} respectively. The pentadienyl ligand has W-shaped (*syn*-η^3) configuration as indicated by its ^{1}H NMR spectrum. Two isomers, in a 4 : 1 molar ratio in equilibrium, were observed for **3**. On the basis of the magnitude of the vicinal coupling constant J_{12} 2.0 Hz, the *exo-syn*-η^3 conformation was assigned to the major, and the *endo-syn*-η^3 structure to the minor. In the *exo* isomer the allyl mouth faces away from the indenyl group. Similarly, the proton resonance of the H^3 of the *exo*-isomer was observed at δ 0.58 ppm which indicates that the allyl moiety lies under the benzene ring of the indenyl group. Moreover, all the chemical shifts of the pentadienyl protons of the *exo* isomer are nearly identical to those of the *exo* isomer of **1**. The *endo* isomer must have a similar structure because the proton NMR resonances of the pentadienyl ligand closely resemble those of the *endo* isomer of **1**. Further structural elucidation is provided by the proton–phosphorus nuclear coupling constants. The proposed structures of **3** and **4** depicted above were elucidated from the coupling constants $J(PH^1)$ 14 and $J(PH^2)$ 4.7 Hz for the *exo* isomer and from $J(PH^2)$ 13.0 Hz for the *endo* isomer. In both structures, the vinyl group lies away from the bulky phosphine group to minimize the steric hindrance. This structural assignment stems from the stereochemistry of the closely related pseudo-tetrahedral complex $Co(CO)_2(PPh_3)$(*syn*-η^3-pentadienyl) as well as from a comparison of their proton NMR spectra [12].

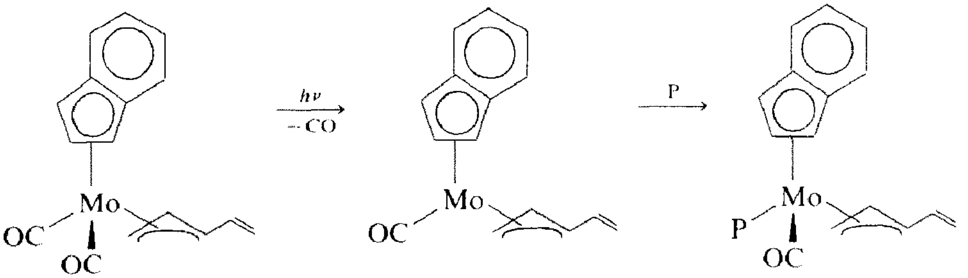


$PR_3 = PMe_3$ (**3**)
$PR_3 = PMe_2P$ (**4**)
exo-syn-η^3



$PR_3 = PMe_3$ (**3**)
$PR_3 = PMe_2Ph_3$ (**4**)
endo-syn-η^3

Exo-syn-η^3 and *endo-syn*-η^3 isomers have also been observed for **4**. The ^{1}H NMR spectra of these two isomers show similar chemical shifts and coupling constants to those of the two isomers of **3**. The relative amounts of these two isomers depend on the period of irradiation. In a typical run, after 16 h irradiation of **1** with PMe_2Ph, a 1 : 1 molar ratio was observed immediately after workup. An NMR sample containing this mixture was allowed to stand for 3 days; a final molar ratio of 7 (*endo*) : 1 (*exo*) in equilibrium was observed. In the initial formation of **4**, a major proportion of the *exo-syn*-η^3 isomer probably arises from the *exo* isomer of **1** which is present in 85% in solution. The *exo* isomer of **4** is unstable and slowly undergoes isomerization to the *endo* isomer. The isomerization follows a π–σ–π allylic rearrangement in light of the structures of the two isomers. η^5–η^3 Indenyl ring slippage is probably not involved in the photolytic ligand-substitution of **1**. The fact that the *exo* isomer of **1** gives the *exo* isomer of the phosphine complex **4**, indicates the involvement a



16-e intermediate as depicted. Photolytic substitution is also feasible in the cyclopentadienyl analogue $CpMo(CO)_2(\eta^3\text{-}C_5H_7)$, but thermal activation is not operative in this case, which implies that η^5–η^3 indenyl ring slippage is not involved in the ligand substitution.

Experimental

All reactions were carried out under dry nitrogen by Schlenk-tube techniques. The solvents, diethyl ether, tetrahydrofuran, and pentane, were dried with sodium benzophenone and distilled before use. NMR spectra were recorded on either a JEOL FX-100 or a Bruker AM-400 spectrometer. Microanalyses were performed by the microanalytic laboratory at the National Taiwan University, Taipei.

Preparation of $(\eta^5\text{-}C_9H_7)Mo(CO)_2(\eta^3\text{-}C_5H_7)$ *(1)*

Method A. Indene (0.32 ml, 2.62 mmol) was treated with 1.6 ml hexane solution of butyllithium (1.6 *M*, 2.60 mmol) at −78 °C. The resulting yellow solution was warmed to room temperature and added dropwise to 1.0 g of $(\eta^3\text{-}C_5H_7)Mo(CO)_2(CH_3CN)_2Cl$ [7d] at 0 °C. The mixture was stirred for 12 h, the solvent was removed, and the residues were chromatographed on a neutral alumina column. The yellow band that developed was collected, and evaporated to dryness to leave a yellow solid. Recrystallization from ether gave yellow crystals (0.39 g, 1.14 mmol). Analysis. Found: C, 57.84, H, 4.22. $C_{16}H_{14}MoO_2$ calcd.: C, 57.4; H, 4.22%. ^1H NMR (400 MHz, $CDCl_3$): *exo* isomer δ 0.57(1H, td, H^3), 1.12(1H, dd, H^1), 2.03(1H, dd, H^2), 2.28(1H, t, H^4), 4.56(1H, dd, H^7), 5.32(1H, dd, H^6), 5.68(1H, td, H^5), 5.75(1H, t), 5.93(1H, d), 6.13(1H, t), 7.21–7.39(4H, m), J_{12} 2.1, J_{13} 10.5, J_{23} 6.8, J_{34} 10.4, J_{43} 10.5, J_{57} 10.2, J_{56} 16.5, J_{67} 1.2 Hz; *endo* isomer, δ −0.42(1H, d, H^1), 0.65(1H, t, H^4), 3.41(1H, d, H^2), 3.69(1H, td, H^3), 4.90(1H, dd, H^7), 5.23(1H, td, H^3), 4.90(1H, dd, H^7), 5.23(1H, dd, H^6), 6.33(1H, td, H^5), 5.93(1H, d), 6.13(1H, t), 7.21–7.39(4H, m). Mass spectrum (12 eV, ^{98}Mo 23.78%): *m/e* 336(M^+), 308($M^+ - CO$), 280($M^+ - 2CO$). IR spectrum (CH_2Cl_2): $\nu(C{=}C)$ 1610(w) cm^{-1}; $\nu(CO)$ 1940(s), 1860(s) cm^{-1}.

Method B. 1-Chloro-2,4-pentadiene was added dropwise to a tetrahydrofuran solution (50 ml) of $(\eta^5\text{-}C_9H_7)Mo(CO)_3Na$ (2.08 g, 6.65 mmol) at 0 °C and stirred for 3h. The solution was evaporated to dryness and chromatographed on a neutral alumina column with ether as eluant. The yellow band that developed was collected and evaporated to dryness to give a yellow solid. Recrystallization from ether gave orange crystals (0.042, 0.12 mmol).

Preparation of (η^5-$C_{13}H_9$)Mo(CO)$_2$(η^3-C_5H_7) (2)

Method A. Sodium fluorenide (0.50 g, 2.62 mmol) was added dropwise to **2** (1 g, 2.62 mmol) in 30 ml of tetrahydrofuran solution and stirred at 0 °C for 16 h. The solution was evaporated to dryness and chromatographed on a neutral alumina column with ether as eluant. The yellow band that developed, was collected and evaporated to dryness. The residues were heated under vacuum (4.0×10^{-4} Torr) at 60 °C until all the solid fluorene had been completely removed. The residues were chromatographed on a neutral alumina column with ether as eluant; a yellow band was collected, concentrated and cooled to 0 °C to give yellow crystals (0.399 g, 1.04 mmol). Analysis. Found: C, 62.74; H, 4.34. $C_{20}H_{16}MoO_2$ calcd.: C, 62.51; H, 4.20%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.57(1H, dd, H^1), 0.85(1H, dd, H^2), 1.51(1H, t, H^4), 3.17(1H, td, H^3), 4.69(1H, dd, H^6), 5.05(1H, td, H^5), 7.05(2H, m), 7.20(2H, m), 7.57(1H, d), 7.61(1H, d), 7.62(1H, d), 7.65(1H, d), J_{12} 2.4, J_{13} 10.2, J_{23} 7.1, J_{34} 10.4, J_{45} 10.4, J_{56} 16.4, J_{57} 10.0, J_{67} 1.3 Hz. Mass spectrum (12 eV, ^{98}Mo 23.78%): m/e 386(M^+), 358($M^+ - CO$), 336($M^+ - 2CO$). IR spectrum (CH_2Cl_2): ν(C=C) 1614 cm^{-1}; ν(CO) 1943(s), 1864(s) cm^{-1}.

Method B. Complex **1** can also be prepared by the reaction of (η^5-$C_{13}H_9$)Mo(CO)$_3$Na with 1-chloro-2,4-pentadiene in tetrahydrofuran at 0 °C. The yield is 2–0.5%.

Preparation of (η^5-C_9H_7)Mo(CO)(PMe$_3$)(η^3-C_5H_7) (3)

An solution of **1** (0.30 g, 0.89 mmol) and PMe$_3$ (0.17 g, 2.40 mmol) in ether (20 ml) was irradiated by a 400 W mercury lamp for 16 h. After removal of the solvent, the residues were chromatographed on a neutral alumina column, with ether as eluant; the orange band that developed, was collected and evaporated to dryness. Recrystallization from ether gave an orange crystalline solid (0.084 g, 0.22 mmol). Analysis. Found: C, 56.80; H, 6.17. $C_{18}H_{23}MoOP$ calcd.: C, 56.53; H, 6.07%. ^{1}H NMR (400 MHz, $CDCl_3$): *exo* isomer δ −0.22(1H, ddd, H^1), 0.70(1H, td, H^3), 0.91(1H, ddd, H^2), 1.39(3H, d, CH_3–P), 2.03(1H, t, H^4), 4.68(1H, dd, H^7), 5.15(1H, dd, H^6), 5.84(1H, dt, H^5), J_{12} 2.0, J_{13} 9.3, J_{23} 7.5, J_{34} 10.2, J_{45} 10.2, J_{56} 16.8, J_{57} 10.1, J(1P) 14, J(2P) 4.7, J(P–CH_3) 8.0 Hz; *endo* isomer δ −1.28 (1H, dd, H^1), 1.27(d, 3H, P–CH_3) 1.95(dd, 1H, H^2), 3.39 ~ 3.45 (complex m, $H^3 + H^4$), 4.51(dd, 1H, H^6), 4.85(dd, 1H, H^7), 6.34(ddd, 1H, H^5), J_{12} 1.0, J_{13} 10.8, J_{23} 6.2, J_{34} 10.4, J_{45} 10.2, J_{56} 10.1, J_{57} 16.9, J_{67} 2.1, J_{2P} 13.0, J(P–CH_3) 8.3 Hz, Mass spectrum (12 eV, ^{98}Mo 23.75%): m/e 384(M^+), 356($M - CO$)$^+$, 308($M - P(CH_3)_3$)$^+$, 280($M - CO - P(CH_3)_3$)$^+$, $P(CH_3)_3{}^+$. IR spectrum (CH_2Cl_2) ν(CO) 1825(s) cm^{-1}.

Preparation of (η^5-C_9H_7)Mo(CO)(PMe$_2$Ph)(η^3-C_5H_7) (4)

Complex **4** was prepared similarly by irradiation of **1** (0.30 g, 0.89 mmol) and PMe$_2$Ph (0.21 g, 1.50 mmol) in ether at −20 °C. The usual work up gave orange crystals in 26% yield (0.11 g, 0.24 mmol). Analysis. Found: C, 62.40; H, 5.48. $C_{23}H_{25}MoOP$ calcd.: C, 62.17; H, 5.63%. ^{1}H NMR (400 MHz, $CDCl_3$): *endo* isomer δ −0.93 (1H, d, H^1), 1.22 (1H, dd, H^4), 1.50 (3H, d, PCH_3), 1.65(3H, d, PCH_3), 2.07(1H, dd, H^2), 3.33(1H, td, H^3), 4.61(1H, dd, H^6), 4.95(1H, dd, H^7), 6.44(1H, dt, H^5), J_{13} 11.0, J_{23} 6.1, J_{34} 10.2, J_{45} 10.1, J_{56} 10.2, J_{57} 16.9, J_{67} 2.0, J(2P) 12.3, J(HP) 8.0 Hz; *exo* isomer δ −0.04(1H, dd, H^1), 0.75(1H, td, H^3), 1.10(1H, d, H^2), 1.69(3H, d, PCH_3), 1.72(3H, d, PCH_3), 2.17(1H, t, H^4), 4.79(1H, dd, H^6), 5.26(1H, dd, H^7), 5.93(1H, dt, H^5), J_{13} 9.6, J_{23} 7.0, J_{34} 10.2, J_{12} 2.1, J_{45}

Table 2

Bond distances (Å) and angles (deg.)

Mo–C(1)	2.310(4)	C(3)–C(4)	1.413(5)
Mo–C(2)	2.315(4)	C(3)–C(8)	1.430(5)
Mo–C(3)	2.414(3)	C(4)–C(5)	1.333(7)
Mo–C(8)	2.441(4)	C(5)–C(6)	1.410(8)
Mo–C(9)	2.350(4)	C(6)–C(7)	1.354(7)
Mo–C(10)	2.320(5)	C(7)–C(8)	1.416(5)
Mo–C(11)	2.212(4)	C(8)–C(9)	1.427(5)
Mo–C(12)	2.393(4)	C(10)–C(11)	1.408(5)
Mo–C(15)	1.923(4)	C(11)–C(12)	1.381(5)
Mo–C(16)	1.936(4)	C(12)–C(13)	1.453(5)
C(1)–C(2)	1.405(6)	C(13)–C(14)	1.300(6)
C(1)–C(9)	1.401(6)	C(15)–O(1)	1.161(4)
C(2)–C(3)	1.414(5)	C(16)–O(2)	1.149(4)
C(1)–Mo–C(2)	35.36(14)	C(11)–Mo–C(15)	105.66(15)
C(1)–Mo–C(3)	57.62(14)	C(11)–Mo–C(16)	106.30(15)
C(1)–Mo–C(8)	57.29(14)	C(12)–Mo–C(15)	73.14(14)
C(1)–Mo–C(9)	34.96(15)	C(12)–Mo–C(16)	111.75(14)
C(1)–Mo–C(10)	148.85(15)	C(15)–Mo–C(16)	80.37(15)
C(1)–Mo–C(11)	148.03(15)	Mo–C(1)–C(2)	72.50(21)
C(1)–Mo–C(12)	143.56(14)	Mo–C(1)–C(9)	74.07(21)
C(1)–Mo–C(15)	96.14(15)	C(2)–C(1)–C(9)	109.3(3)
C(1)–Mo–C(16)	100.11(16)	Mo–C(2)–C(1)	72.14(21)
C(2)–Mo–C(3)	34.72(13)	Mo–C(2)–C(3)	76.49(19)
C(2)–Mo–C(8)	57.66(12)	C(1)–C(2)–C(3)	107.9(3)
C(2)–Mo–C(9)	58.74(14)	Mo–C(3)–C(2)	68.79(18)
C(2)–Mo–C(10)	113.49(14)	Mo–C(3)–C(4)	122.11(24)
C(2)–Mo–C(11)	126.43(14)	Mo–C(3)–C(8)	73.92(18)
C(2)–Mo–C(12)	153.94(13)	C(2)–C(3)–C(4)	13.2(3)
C(2)–Mo–C(15)	127.62(14)	C(2)–C(3)–C(8)	107.7(3)
C(2)–Mo–C(16)	89.27(15)	C(4)–C(3)–C(8)	119.0(3)
C(3)–Mo–C(8)	34.24(11)	C(3)–C(4)–C(5)	119.9(4)
C(3)–Mo–C(9)	57.80(13)	C(4)–C(5)–C(6)	120.9(4)
C(3)–Mo–C(10)	96.88(15)	C(5)–C(6)–C(7)	122.3(4)
C(3)–Mo–C(11)	94.64(13)	C(6)–C(7)–C(8)	118.1(4)
C(3)–Mo–C(12)	119.38(12)	Mo–C(8)–C(3)	71.85(18)
C(3)–Mo–C(15)	150.94(13)	Mo–C(8)–C(7)	124.04(23)
C(3)–Mo–C(16)	114.01(13)	Mo–C(8)–C(9)	69.20(19)
C(8)–Mo–C(9)	34.59(13)	C(3)–C(8)–C(7)	119.7(3)
C(8)–Mo–C(10)	112.80(15)	C(3)–C(8)–C(9)	107.5(3)
C(8)–Mo–C(11)	90.96(14)	C(7)–C(8)–C(9)	132.8(4)
C(8)–Mo–C(12)	98.92(12)	Mo–C(9)–C(1)	70.97(21)
C(8)–Mo–C(15)	123.13(14)	Mo–C(9)–C(8)	76.21(20)
C(8)–Mo–C(16)	146.38(13)	C(1)–C(9)–C(8)	107.5(3)
C(9)–Mo–C(10)	147.20(16)	Mo–C(10)–C(11)	67.77(23)
C(9)–Mo–C(11)	118.83(14)	Mo–C(11)–C(10)	76.12(25)
C(9)–Mo–C(12)	109.61(13)	Mo–C(11)–C(12)	79.89(24)
C(9)–Mo–C(15)	93.78(16)	C(10)–C(11)–C(12)	121.5(4)
C(9)–Mo–C(16)	134.25(15)	Mo–C(12)–C(11)	65.49(21)
C(10)–Mo–C(11)	36.11(14)	Mo–C(12)–C(13)	118.8(3)
C(10)–Mo–C(12)	62.15(13)	C(11)–C(12)–C(13)	123.4(3)
C(10)–Mo–C(15)	111.81(16)	C(12)–C(13)–C(14)	126.3(4)
C(10)–Mo–C(16)	72.54(16)	Mo–C(15)–O(1)	178.9(3)
C(11)–Mo–C(12)	34.61(13)	Mo–C(16)–O(2)	179.0(3)

10.1, J_{56} 10.3, J_{57} 16.9, J_{67} 1.6, J(1P) 12.0, J(2P) 3.0, J(P–CH_3) 8.0 Hz. Mass spectrum (12 eV, ^{98}Mo 23.76%): 446(M^+), 418(M – CO)$^+$, 308(M – PPh$(CH_3)_2$)$^+$, 280/M – CO – PMe$_2$Ph)$^+$, 138P($(CH_3)_2$Ph)$^+$. IR spectrum (CH_2Cl_2): ν(CO) 1832(s) cm^{-1}.

Crystal data for 1. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with lattice parameters: a 7.955(10), b 12.531(3), c 13.987(5) Å, β 100.86(7)°, mol. wt. 334.22, D(calcd) 1.624 g/cm^3, $Z = 4$. The structure was solved and refined to give final discrepancy factors of $R = 0.024$ and $R_w = 0.023$ for 1988 reflections with $[I > 3\sigma(I)]$.

Collection and reduction of X-ray data

A yellow crystal of dimensions 0.05 × 0.35 × 1.00 mm, coated with paraffin and sealed in a capillary tube, was used for data collection. Diffraction data were collected on a CAD4 diffractometer by use of graphite-monochromated Mo-K_α radiation. Unit cell dimensions were determined from a least-squares refinement of 25 carefully centered reflections ($20.92° < 2\theta < 27.80°$). Intensity data within $2\theta < 50°$ were collected at various scan speeds 16.48/16 to 16.48/2°/min by θ–2θ scan techniques, in a scan range calculated from the expression, $0.65 + 0.35 \tan\theta$. Stationary background measurements were taken before and after each scan for a period of time equal to a quarter of the scan time. Three standard reflections measured every 2 hours were found to fluctuate randomly within 2% over the entire period of data collection. After correction for background, the intensities were reduced to F and $\sigma(F)$ by counting statistics, and the weights were assigned as $w = 1/\sigma^2(F)$. Of the 2402 total reflections, 1998 with $I > 3\sigma(I)$, were considered observed. Intensity data were corrected for Lorentz polarization effects and elliptical absorption.

Solution and refinement of the structure

All calculations were by a VAX-785 computer, with an NRCC-SDP-VAX package. The Mo atom position was located from the Patterson map. Subsequent Fourier syntheses revealed the positions of all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were added at idealized positions and were included in the structure factor calculations. The final least-squares cycle converged to R_1 2.4% and R_w 2.3%. The positions and thermal parameters are given in Table 1. The bond distances and angles are listed in Table 2. The ORTEP drawing of the molecular structure is presented in Figure 1.

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