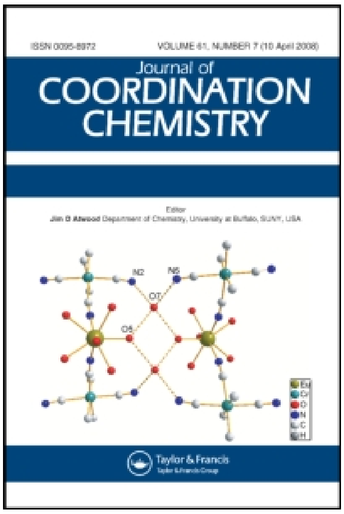

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses and crystal structures of Dimolybdenum complexes containing P_2 and functionalized Cyclopentadienyl ligands

Yao-Cheng Shi[a]
[a] School of Chemistry, Yangzhou University, Yangzhou 225002, P.R. China

To cite this Article Shi, Yao-Cheng(2004) 'Syntheses and crystal structures of Dimolybdenum complexes containing P_2 and functionalized Cyclopentadienyl ligands', Journal of Coordination Chemistry, 57: 5, 393 — 400

To link to this Article: DOI: 10.1080/00958970410001689076

URL: http://dx.doi.org/10.1080/00958970410001689076

J. Coord. Chem., Vol. 57, No. 5, 20 March 2004, pp. 393–400

Taylor & Francis
Taylor & Francis Group

SYNTHESES AND CRYSTAL STRUCTURES OF DIMOLYBDENUM COMPLEXES CONTAINING P_2 AND FUNCTIONALIZED CYCLOPENTADIENYL LIGANDS

YAO-CHENG SHI*

School of Chemistry, Yangzhou University, Yangzhou 225002, P.R. China

(Received 16 June 2003; Revised 10 October 2003; In final form 2 March 2004)

The dimolybdenum complex $[(\eta^5\text{-RC}_5H_4)_2Mo_2(CO)_6]$ (**1**, $R = CH_3CO$; **II**, $R = CH_3O_2C$) reacts with an equimolar amount of white phosphorus P_4 to yield the corresponding dimolybdenum complex containing the P_2 ligand $[(\eta^5\text{-RC}_5H_4)_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ (**1**, $R = CH_3CO$; **2**, $R = CH_3O_2C$) in moderate yield. The two new compounds have been characterized by elemental analyses, ^{1}H NMR, ^{13}C NMR, ^{31} P NMR and IR spectroscopies and their crystal structures have been determined by X-ray diffraction methods.

Keywords: Metal–metal bond; Dimolybdenum complex; P_2 Ligand; Crystal structure

INTRODUCTION

The isolobal principle and its applications in organometallic chemistry provide links between the various chemical disciplines of inorganic, organic and theoretical chemistry. Complexes with substituent-free acyclic and cyclic phosphorus and homologous ligands are a new and interesting research area [1–5]. In the last two decades this interdisciplinary area has undergone rapid growth, with increasing numbers of examples that support the original hopes of building bridges between inorganic and organic chemistry [6,7]. Recently group 6 metal dimers $[(\eta^5\text{-RC}_5H_4)_2M_2(CO)_4]$ and $[(\eta^5\text{-RC}_5H_4)_2M_2(CO)_6]$ ($M = Mo$, W; $\eta^5\text{-RC}_5H_4 =$ parent and substituted cyclopentadienyls) have received attention as synthons to react with inorganic, organic and organometallic substrates, generating a great variety of novel group 6 complexes [8–12]. Since no example of a singly bonded dimolybdenum complex containing functionalized cyclopentadienyl groups reacting with white phosphorus exists, herein I report the syntheses and crystal structures of new dimolybdenum complexes containing P_2 and functionalized cyclopentadienyl ligands $[(\eta^5\text{-RC}_5H_4)_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ (**1**, $R = CH_3CO$; **2**, $R = CH_3O_2C$).

---

*E-mail: yzssyc@yzcn.net

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001689076

EXPERIMENTAL

General Procedure

All reactions were carried out under a purified dinitrogen atmosphere. Toluene was distilled from Na/benzophenone under dinitrogen and deoxygenated by bubbling with dinitrogen for 15 min before use. Silica gel for preparative TLC was 300–400 mesh. $Mo(CO)_6$ was purchased from Acros. Dimolybdenum complexes $[(\eta^5\text{-}RC_5H_4)_2Mo_2(CO)_6]$ ($R = CH_3CO$, CH_3O_2C) were prepared from $Mo(CO)_6$ according to the literature method [13]. Progress of the reactions was monitored by TLC. NMR spectra were determined by a Bruker Avance 300 spectrometer using TMS (for ^{1}H NMR and ^{13}C NMR) and 85% H_3PO_4 (for ^{31}P NMR) as external standards in $CDCl_3$. IR spectra were recorded on a Perkin-Elmer 402 as KBr disks in the range of 4000–400 cm^{-1}. Analyses for C and H were performed on an Elementa Vario EL III instrument. Melting points were measured on a Yanagimoto apparatus and are uncorrected.

Synthesis of Complex 1 $[(\eta^5\text{-}CH_3COC_5H_4)_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)]$

A red solution of $[(\eta^5\text{-}CH_3COC_5H_4)_2Mo_2(CO)_6]$ (287 mg, 0.5 mmol) and P_4 (62 mg, 0.5 mmol) in 40 ml of toluene was refluxed under nitrogen for 2 h. The resulting brown mixture was evaporated to dryness under vacuum and the residue was subjected to preparative TLC. An orange band was eluted with CH_2Cl_2 to give an orange-red solid. The orange-red solid was further recrystallized from CH_2Cl_2/petroleum ether (60–90°C) to afford complex **1** $[(\eta^5\text{-}CH_3COC_5H_4)_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ (131 mg, 45%) as bright-red crystals suitable for an X-ray diffraction analysis. The same reaction of $[(\eta^5\text{-}CH_3COC_5H_4)_2Mo_2(CO)_6]$ (287 mg, 0.5 mmol) and P_4 (124 mg, 1 mmol) for 2 h after removal of the solvent by vacuum evaporation and excess P_4 by reduced sublimation furnishes complex **1** (79 mg, 27%). M.P. 160–161°C. Anal. Calc. for $C_{18}H_{14}Mo_2O_6P_2$ (%): C, 37.27; H, 2.43. Found: C, 37.41; H, 2.24. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.63–5.65, 5.33–5.35 (t, 4H, t, 4H, $2C_5H_4$); 2.36 (s, 6H, $2CH_3$). $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 223.49 (CO); 193.04 (carbonyl of acetyl); 90.83, 87.26 (C_5H_4R); 26.56 (CH_3). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ –35.15. IR: 1991, 1976, 1916 (vs, CO), 1682 (vs, CH_3CO).

Synthesis of Complex 2 $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)]$

A red solution of $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2Mo_2(CO)_6]$ (606 mg, 1 mmol) and P_4 (124 mg, 1 mmol) in 40 ml of toluene was refluxed under nitrogen for 2 h. The solvent was evaporated *in vacuo*, the resulting residue was chromatographed on silica gel plates using CH_2Cl_2 as eluent.The orange band was collected and further recrystallized from CH_2Cl_2 to furnish complex **2** $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ (261 mg, 43%) as an orange-red solid, D.P. 137°C. Bright-red single crystals for an X-ray study were obtained by slow evaporation of the solution from CH_2Cl_2 and petroleum ether of complex **2** at *ca.* 5°C. The same reaction of $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2Mo_2(CO)_6]$ (606 mg, 1 mmol) and P_4 (248 mg, 2 mmol) for 2 h after removal of the solvent by vacuum evaporation and excess P_4 by reduced sublimation affords complex **2** (134 mg, 22%). Anal. Calc. for $C_{18}H_{14}Mo_2O_8P_2$ (%): C, 35.32; H, 2.31. Found: C, 35.03; H, 2.24. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.67–5.68, 5.30–5.32 (t, 4H, t, 4H, $2C_5H_4$); 3.81 (s, 6H, $2CH_3$). $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$): δ 223.30 (CO); 192.5 (carbonyl of ester); 89.87, 87.69 (C_5H_4R); 51.91 (CH_3). $^{31}P\{^{1}H\}$ NMR (300 MHz, $CDCl_3$): δ –30.19. IR: 1997, 1979, 1915 (vs, CO); 1716 (vs, CH_3OCO).

Crystal Structure Determination

Measurements of diffraction intensity of single crystals of complexes **1** and **2** were carried out on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 293 K. The data were collected by using the ω–2θ scan mode. The structures were solved by direct methods and refined by full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in their calculated positions, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. All computations were carried out using SHELXS-97 and SHELXL-97 programs [14,15]. ORTEP drawings were made with ORTEP-3 for Windows [16]. Details of data collection and structure refinement are summarized in Table I. Selected bond distances and angles for the above complexes are present in Tables II and III.

TABLE I Crystallographic data for complexes **1** and **2**

	Complex 1	*Complex 2*
Formula	$C_{18}H_{14}Mo_2O_6P_2$	$C_{18}H_{14}Mo_2O_8P_2$
Formula weight	580.12	612.11
Crystal size	0.4×0.4×0.3	0.4×0.3×0.3
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
Unit cell dimensions		
a (Å)	14.470(3)	25.670(5)
b (Å)	7.3300(15)	7.8000(16)
c (Å)	19.400(4)	23.910(5)
α (°)	90	90
β (°)	102.23(3)	112.00(3)
γ (°)	90	90
V (Å^3)	2015.7(7)	4438.8(15)
Z	8	8
$D_{(calc)}$(g cm^{-1})	1.916	1.832
$F(000)$	1136	2400
T(K)	293(2)	293(2)
μ(Mo-K_α)(cm^{-1})	14.38	13.15
Scan mode	ω–2θ	ω–2θ
Limiting indices	$0 \le h \le 17$, $0 \le k \le 8$, $-23 \le l \le 22$	$-28 \le h \le 30$, $-9 \le k \le 0$, $-28 \le l \le 0$
Absorption correction	PSI-scan	PSI-scan
θ Range (°)	2.15; 24.98	1.71; 24.98
No. of unique reflections	1843	4009
No. of observed reflections	1768	3902
No. of parameters refined	128	271
Final R_1, wR_2 indices [$I > 2.0\sigma(I)$]	0.0249, 0.0866	0.0368, 0.0829
R_1, wR_2 indices (all data)	0.0301, 0.0943	0.0736, 0.0948
GoF	0.829	1.06
Largest diff. peak and hole (e Å^{-3})	0.308 and −0.818	0.713 and −0.475

TABLE II Selected bond distances (Å) and angles (deg) for the complex **1**†

Mo–Mo(A)	3.0161(8)	Mo–C(3)	1.983(4)
P–P(A)	2.074(2)	Mo–C(4)	1.977(4)
Mo–P(A)	2.5616(10)	C(2)–C(6)	1.479(5)
Mo–P	2.4608(10)	C(3)–O(3)	1.140(4)
Mo(A)–P	2.5616(10)	C(4)–O(2)	1.138(5)
P–Mo–P(A)	48.73(5)	P(A)–P–Mo	68.17(4)
P–Mo–Mo(A)	54.64(3)	Mo–P–Mo(A)	73.78(3)
P(A)–Mo–Mo(A)	51.58(2)	O(2)–C(4)–Mo	175.8(4)
P(A)–P–Mo(A)	63.10(4)	O(3)–C(3)–Mo	175.5(3)

†Symmetry transformations used to generate equivalent atoms (A = _2): $-x+1$, y, $-z+3/2$.

TABLE III Selected bond distances (Å) and angles (deg) for the complex **2**

Mo(1)–Mo(2)	3.0157(9)	Mo(1)–C(5)	1.982(6)
P(1)–P(2)	2.084(2)	Mo(1)–C(6)	2.001(6)
Mo(1)–P(1)	2.5480(16)	Mo(2)–C(3)	1.985(6)
Mo(1)–P(2)	2.4631(17)	Mo(2)–C(4)	1.997(7)
Mo(2)–P(1)	2.4703(18)	C(2)–C(21)	1.483(8)
Mo(2)–P(2)	2.5580(18)	C(7)–C(15)	1.504(8)
O(3)–C(4)	1.142(7)	O(5)–C(5)	1.146(7)
O(4)–C(3)	1.146(7)	O(6)–C(6)	1.132(7)
P(2)–Mo(1)–P(1)	49.11(6)	P(1)–P(2)–Mo(2)	63.34(6)
P(1)–Mo(2)–P(2)	48.93(6)	Mo(1)–P(2)–Mo(2)	73.80(5)
P(1)–Mo(1)–Mo(2)	51.89(4)	Mo(2)–P(1)–Mo(1)	73.86(4)
P(2)–Mo(1)–Mo(2)	54.54(4)	O(5)–C(5)–Mo(1)	175.2(5)
P(1)–Mo(2)–Mo(1)	54.25(4)	O(6)–C(6)–Mo(1)	175.9(6)
P(2)–Mo(2)–Mo(1)	51.66(4)	O(3)–C(4)–Mo(2)	177.1(7)
P(2)–P(1)–Mo(2)	67.73(6)	O(4)–C(3)–Mo(2)	175.3(6)
P(2)–P(1)–Mo(1)	63.32(6)	Mo(1)–P(2)–Mo(2)	73.80(5)
P(1)–P(2)–Mo(1)	67.57(6)	Mo(2)–P(1)–Mo(1)	73.86(4)

RESULTS AND DISCUSSION

Syntheses of Dimolybdenum Complexes 1 and 2 $[(\eta^5\text{-RC}_5\text{H}_4)_2\text{Mo}_2(\text{CO})_4(\mu,\eta^2\text{-P}_2)]$

Reaction of the dimolybdenum complex $[(\eta^5\text{-RC}_5\text{H}_4)_2\text{Mo}_2(\text{CO})_6]$ (**I**, R = CH_3CO; **II**, R = CH_3O_2C) and an equimolar amount of white phosphorus P_4 in refluxing toluene for 2 h, after removal of the solvent and preparative TLC, gave the corresponding dimolybdenum complex containing a P_2 ligand $[(\eta^5\text{-RC}_5\text{H}_4)_2\text{Mo}_2(\text{CO})_4(\mu,\eta^2\text{-P}_2)]$ (**1**, R = CH_3CO; **2**, R = CH_3O_2C) as red crystalline solids in moderate yield (43–45%). Although the same reaction of the singly bonded dimolybdenum complex and an excess of white phosphorus for 2 h after removal of the solvent by vacuum evaporation and excess P_4 by reduced sublimation affords the same product, the yield of each desired complex (22–27%) goes down. Reduced yields may result from insoluble residue. Also, combustion of white phosphorus which is incompletely removed can reduce the yields. However, through a similar reaction for 8 h, the dimolybdenum complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6]$ affords $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\mu,\eta^2\text{-P}_2)]$ in a yield of *ca.* 20%, in addition to the complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\eta^3\text{-P}_3)]$ [3]. Formation of these complexes can be explained according to the isolobal principle [1,6,7]. Since $(\text{RC}_5\text{H}_4)\text{Mo (CO)}_2$ is isolobal to CH and P, $(\text{RC}_5\text{H}_4)\text{Mo}(\text{CO})_2$ fragments, which are from triply bonded complexes [(η^5-$RC_5H_4)_2M_2(CO)_4$] derived from singly bonded complexes [(η^5-$RC_5H_4)_2M_2(CO)_6$] after heated decarbonylation, may displace one or two P atoms of the tetrahedral P_4 molecule to yield tetrahedral complexes [(η^5-RC_5H_4)$Mo(CO)_2$(η^3-P_3)] and [(η^5-$RC_5H_4)_2Mo_2(CO)_4$(μ,η^2-P_2)] (R = H, CH_3CO, CH_3O_2C, etc.) [17,18]. Because no complexes [(η^5-RC_5H_4)$Mo(CO)_2$(η^3-P_3)] (R = CH_3CO, CH_3O_2C) are produced, it seems that the electron-withdrawing groups favor and stabilize complexes with a P_2 ligand [(η^5-$RC_5H_4)_2Mo_2(CO)_4$(μ,η^2-P_2)] (R = CH_3CO, CH_3O_2C), which have been structurally characterized by X-ray diffraction methods as described below. The new dimolybdenum complexes are soluble in polar organic solvents such as CH_2Cl_2 and THF, and air-stable in the solid state and slightly air-sensitive in solution. Additionally, the functionalities on the cyclopentadienyl ligands in complexes **1** and **2** will be useful in the preparation of a series of derivatives by conventional functional transformation reactions [19].

Spectroscopic Characterization of Dimolybdenum Complexes 1 and 2 [(η^5-$RC_5H_4)_2Mo_2(CO)_4$(μ,η^2-P_2)]

IR spectra of the new compounds show three broad overlapping absorptions resulting from terminal carbonyls from 1915 to 1997 cm^{-1}. Compared with the parent complex [(η^5-$C_5H_5)_2Mo_2(CO)_4$(μ,η^2-P_2)] (1965 and 1913 cm^{-1}), these absorptions display blue shifts. As expected, functional groups show a respective absorption at 1682 for complex **1** and 1716 cm^{-1} for complex **2** [10–13]. The ^{1}H NMR spectrum of complex **1** shows two triplets at δ 5.64 and 5.34 ppm for protons of 2/5 and 3/4 positions of the substituted cyclopentadienyl rings, the formal coupling constants of which are 2.47 and 2.45 Hz, and one singlet at δ 2.36 ppm for methyl groups of the acetyl substituents [9,20]. Similarly, the ^{1}H NMR spectrum of complex **2** displays corresponding signals at δ 5.67 and 5.31 ppm for the substituted cyclopentadienyl rings (two triplets, the formal coupling constants of which are 2.45 and 2.36 Hz) and 3.81 ppm for the methyl groups of the methoxycarbonyl substituents (one singlet), while the cyclopentadienyl rings of the parent complex appear at δ 4.54 ppm as a singlet [9,20]. The ^{13}C NMR spectrum of complex **1** shows a set of signals assignable to terminal carbonyl, carbonyl of the acetyl, substituted cyclopentadienyl group and CH_3 of the acetyl substituent respectively at δ 223.5; 193.0; 90.8, 87.3; 26.6 ppm, whereas the parent complex shows the corresponding absorptions at δ 226.2 (CO) and 86.5 (Cp) ppm. As expected, the ^{13}C NMR spectrum of complex **2** exhibits corresponding signals at δ 223.3; 164.5 (carbonyl of ester group); 89.9, 87.7; 51.9(CH_3 of ester group) ppm [20]. Although the complex [(η^5-C_5H_5)$Mo(CO)_2$(μ-P_3)] with the naked phosphorus ligand shows weak P–C couplings (1.2 and 1.3 Hz for interactions of CO–P and Cp–P), no P–C couplings in the ^{13}C NMR spectra of complexes **1** and **2** are observed, which is similar to those of complexes [(η^5-$Cp)_2M_2(CO)_4$(μ,η^2-P_2)] (M = Mo, W) [1,3]. The lack of coupling is very difficult to explain [19–23]. In order to further characterize both new complexes, their ^{31}P NMR spectra were recorded. Each shows a singlet, at δ −35.15 for complex **1** and −30.19 ppm for complex **2**, whereas the above-mentioned parent complex shows the corresponding absorbtion at δ −42.9 ppm. Because of the electron-withdrawing groups, all NMR signals, except ^{13}C NMR of substituted cyclopentadienyl groups and terminal carbonyls, exhibit downfield shifts compared with the parent complex mentioned above.

Crystal Structures of Dimolybdenum Complexes 1 and 2 $[(\eta^5\text{-}RC_5H_4)_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)]$

As there was no previous example of a cyclopentadienyl-functionalized dimolybdenum complex with a P_2 ligand, crystal structures of the new compounds were determined. Their ORTEP views and packing diagrams are shown in Figs. 1–4. Both complexes belong to the space group of *C*2/*c*. Each is symmetric with a C_2 axis passing through the midpoints of the Mo–Mo and P–P bonds. As seen from Figs. 2 and 4, the packing of complex **1** is distinct from that of complex **2**; in contrast to complex **2**, complex **1** lies across a symmetry position and therefore there is only one half of the dimer in the asymmetric unit. In addition, complex **1** shows the shortest intermolecular distance (3.051 Å) of O(2) and O(3) atoms close to the sum of van der Waals radii of the O atoms (3.04 Å), which indicates that there is a weak nonbonded interaction in the solid state [26]. As indicated in Figs. 1 and 3, in each case, the Mo_2P_2 core forms a tetrahedral cluster with a side-on coordinated P_2 ligand and $(RC_5H_4)Mo(CO)_2$ fragment

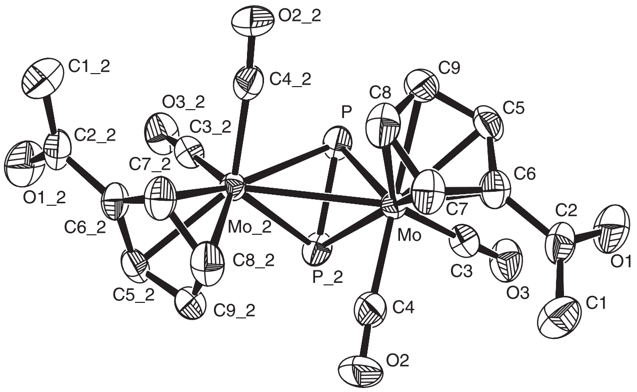

FIGURE 1 An ORTEP view of complex **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

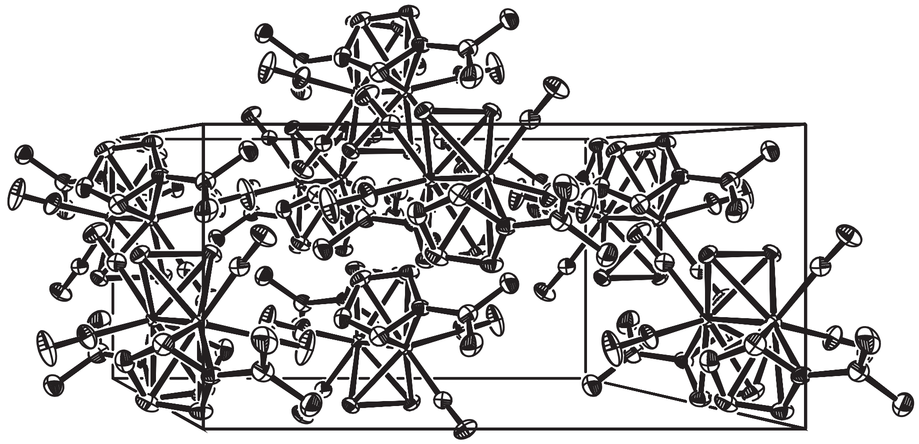

FIGURE 2 A packing diagram of complex **1**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

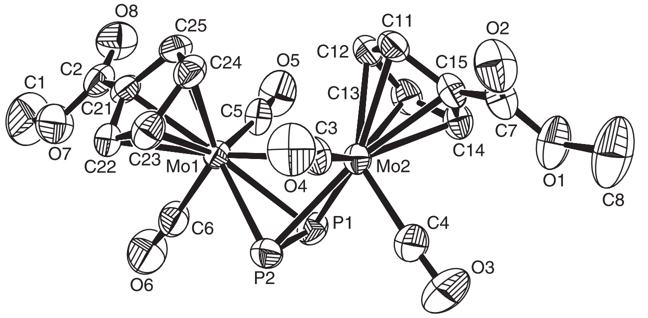

FIGURE 3 An ORTEP view of complex **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

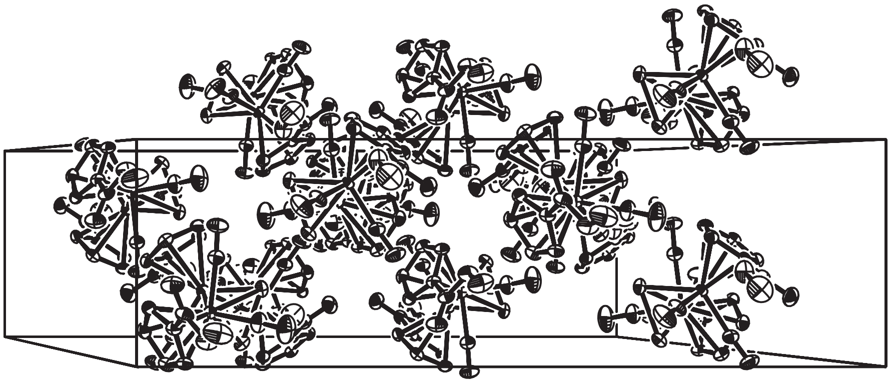

FIGURE 4 A packing diagram of complex **2**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

which is in agreement with the isolobal principle as described above. The Mo–Mo distances (3.0161(8) and 3.0157(9) Å) are consistent with the presence of a single metal–metal bond as shown by comparison of the Mo–Mo distances (3.022(1) and 3.1950(0) Å) in the complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ and $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-dppm})]$ [3,21]. The P–P distances of 2.074(2) and 2.084(2) Å are 0.18 and 0.19 Å longer than in uncoordinated P_2 (1.894 Å), respectively, but these values are very close to that of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ (2.079(2) Å) [3]. The Mo–P distances are 2.4608(10) (Mo–P) and 2.5616(10)(Mo–PA) Å for complex **1** and 2.4631(17) (Mo(1)–P(2)), 2.4703(18) (Mo(2)–P(1)), 2.5480(16) (Mo(1)–P(1)) and 2.5580(18) (Mo(2)–P(2)) Å for complex **2**, indicating one Mo atom with two P atoms forms two different Mo–P bonds. Values for Mo–C–O angles (175–177°) are very close to 180°, suggesting that the carbonyls in both complexes are terminal, which is in accordance with the spectroscopic data described above. Other angles and distances in the bridging region are very similar to those reported for related dimolybdenum complexes mentioned above. For complex **1**, each acetyl and corresponding substituted cyclopentadienyl ring form a dihedral angle of 4.6°, whereas for complex **2** two methoxycarbonyls and corresponding substituted cyclopentadienyl rings form two different dihedral angles of 1.3 and 7.1°, namely that for the planes C(1)O(7)C(2)O(8) and C(21)–C(25) and the planes C(8) O(1)C(7)O(2) and C(11)–C(15) (see Fig. 3). Because the planes of the functional groups (two acetyls and one methoxycarbonyl) are nearly coplanar with those of the corresponding substituted cyclopentadienyl rings and the bond distances of C(2)–C(6) (1.479(5) Å) in complex **1** and C(2)–C(21) (1.483(8) Å) in complex **2** become much shorter than a normal C–C single bond, these functional groups may be conjugated with the corresponding substituted cyclopentadienyl rings.

Supplementary Data

Full crystallographic data (CCDC 203956 for complex **1** and CCDC 203957 for complex **2**) have been deposited at the Cambridge Crystallographic Database Centre and are available on request from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk).

Acknowledgment

Shi Yao-Cheng thanks Mr. Wang Huaqing for crystallographic data collections. This work was supported by Yangzhou University (D0009107).

References

[1] O.J. Scherer, *Angew. Chem. Int. Ed. Engl.* **29**, 1044 (1990).
[2] G. Becker, W.A. Herrmann, W. Kalcher, G.W. Kriechbaum, C. Pahl, C.T. Wagner and M.L. Ziegler, *Angew. Chem. Int. Ed. Engl.* **22**, 501 (1983).
[3] O. J. Scherer, H. Sitzmann and G. Wolmershäuser, *J. Organomet. Chem.* **268**, C9 (1984).
[4] C.E. Laplaza, W.M. Davis and C.C. Cummins, *Angew. Chem. Int. Ed. Engl.* **34**, 2042 (1995).
[5] N.C. Zanetti, R.R. Schrock and W.M. Davis, *Angew. Chem. Int. Ed. Engl.* **34**, 2044 (1995).
[6] R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **21**, 711 (1982).
[7] L.C. Song, Y.B. Dong, Q.M. Hu, X.Y. Huang and J. Sun, *Organometallics* **16**, 4540 (1997).
[8] (a) P. Jaitner, *J. Organomet. Chem.* **233**, 333 (1982); (b) P. Li and M.D. Curtis, *Inorg. Chem.* **29**, 1242 (1990); (c) L.C. Song and Y.C. Shi, *J. Organomet. Chem.* **626**, 192 (2001).
[9] L.C. Song and Y.C. Shi, *Organometallics* **19**, 56 (2000).
[10] L.C. Song and Y.C. Shi, *J. Organomet. Chem.* **613**, 42 (2000).
[11] L.C. Song and Y.C. Shi, *Polyhedron* **18**, 2163 (1999).
[12] L.C. Song and Y.C. Shi, *Polyhedron* **18**, 19 (1998).
[13] L.C. Song and J.Y. Sun, *Chem. J. Chin. Univ.* **13**, 1227 (1999).
[14] G.M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures (University of Göttingen, Germany, 1997).
[15] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures (University of Göttingen, Germany, 1997).
[16] L.J. Farrugia, ORTEP-3 for Windows, Version 1.076 (University of Glasgow, UK, 2003).
[17] M.D. Curtis, *Polyhedron* **6**, 759 (1987).
[18] L.C. Song and J.Q. Wang, *Youjihuaxue* **14**, 225 (1994).
[19] L.C. Song, J.Q. Wang, Q.M. Hu, W.Q. Gao and B.S. Han, *Polyhedron* **16**, 481 (1997).
[20] F. Du, H. Huang, X.A. Mao, Y.C. Shi and L.C. Song, *Chin. J. Magn. Res.* **15**, 151 (1998).
[21] V. Riera, M.A. Ruiz, F. Villafañe, Y. Jeannin and C. Bois, *J. Organomet. Chem.* **345**, C4 (1988).
[22] S. Woodward and M.D. Curtis, *J. Organomet. Chem.* **439**, 319 (1992).
[23] K. Henrick, M. Mcpartlin, A.D. Horton and M.J. Mays, *J. Chem. Soc. Dalton Trans.* 1083 (1988).
[24] V. Riera, M.A. Ruiz, F. Villafañe, C. Bois and Y. Jeannin, *J. Organomet. Chem.* **382**, 407 (1990).
[25] V. Riera, M.A. Ruiz, F. Villafañe, C. Bois and Y. Jeannin, *Organometallics* **12**, 124 (1993).
[26] B.E. Douglas, D.H. McDaniel and J.J. Alexander, Concepts and Models of Inorganic Chemistry (John Wiley and Sons, New York, 1983), 2nd Edn., p. 190.