# PREPARATION AND REACTIVITY OF *CIS*-BIS(CYCLOPENTADIENYLDIPHENYLPHOSPHINE) (TETRACARBONYL)MOLYBDENUM AND *CIS*-[1,3-BIS(DIPHENYLPHOSPHINO)DICYCLOPENTADIENE] (TETRACARBONYL)MOLYBDENUM. X-RAY CRYSTAL STRUCTURE OF 2[(C<sub>5</sub>H<sub>5</sub>)Mo]<sub>2</sub>(µ-PPh<sub>2</sub>)<sub>2</sub>(CO)(O) · C<sub>6</sub>H<sub>14</sub>

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#### (Received 7 March 1990; accepted 7 June 1990)

Abstract—The interaction of  $C_7H_8Mo(CO)_4$  with 2 equivalents of  $Ph_2P(C_5H_5)$  in hexane at  $-2^\circ C$  gives two isomers of *cis*-[Ph\_2P(C\_5H\_5)]\_2Mo(CO)\_4 (II and III) in high yield. In toluene, the coordinated  $Ph_2P(C_5H_5)$  ligands of II and III undergo intramolecular Diels– Alder dimerization at room temperature producing *cis*-[1,3-bis(diphenylphosphino) dicyclopentadiene](tetracarbonyl)molybdenum (IV) in quantitative yield. Compound IV can also be prepared in high yield by the interaction of *cis*-Mo(CO)<sub>4</sub>(Ph\_2PCl)<sub>2</sub> with 2 equivalents of  $(C_5H_5)Tl$  in refluxing toluene. Pyrolysis of IV gives a hexane solvate  $2[(C_5H_5)Mo]_2(\mu$ -PPh\_2)\_2(CO)(O)  $\cdot C_6H_{14}$  (VI) in low yield, the structure of which was determined by X-ray crystallography.

We recently reported<sup>1</sup> the synthesis of *cis*-[1,3bis(diphenylphosphino)dicyclopentadiene](tetracarbonyl)molybdenum (IV), via the interaction of *cis*-Mo(CO)<sub>4</sub>(Ph<sub>2</sub>PCl)<sub>2</sub> with 2 equivalents of (C<sub>5</sub>H<sub>5</sub>)Tl and postulated that IV was produced via intramolecular Diels–Alder dimerization of the Ph<sub>2</sub>P (C<sub>5</sub>H<sub>5</sub>) ligands of the proposed intermediate *cis*-[Ph<sub>2</sub>P(C<sub>5</sub>H<sub>5</sub>)]<sub>2</sub>Mo(CO)<sub>4</sub> (II). Metal-promoted intramolecular Diels–Alder cycloaddition between coordinated phospholes and coordinated vinylphosphines has also been described recently.<sup>2</sup> Here we report the isolation of **II** and demonstrate that **IV** is indeed formed via intramolecular Diels-Alder dimerization of the coordinated cyclopentadienyldiphenylphosphine of **II**.

#### **RESULTS AND DISCUSSION**

Interaction of  $C_7H_8Mo(CO)_4$  with  $Ph_2P(C_5H_5)$ 

(i) At room temperature. When  $C_7H_8Mo(CO)_4$ was treated with 2 equivalents of  $Ph_2P(C_3H_5)$  in hexane, light yellow crystals of stoichiometry  $(C_{34}H_{30}P_2)Mo(CO)_4$  (IV) were obtained in high

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yield (85%). The IR spectrum (KBr) of IV exhibits three absorptions at 2017s, 1916s and 1880 vs(br)  $cm^{-1}$ . The absorption pattern is indicative of a *cis*configuration for the four terminal carbonyl groups. The mass spectrum shows the highest peak at m/z 596, corresponding to the  $(M-4CO)^+$  fragment ( $C_{34}H_{30}P_2Mo$ ). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum exhibits two doublets of relative intensity 1:1 centred at  $\delta$  23.4 (J = 24.4 Hz) and 37.2 ppm (J = 24.4 Hz), respectively. The <sup>1</sup>H NMR spectrum is very complicated. In addition to the phenyl resonances, it exhibits three multiplets of relative intensity 1:1:1 centred at  $\delta$  6.67, 6.19 and 5.19 ppm, respectively, in the olefinic proton region and four multiplets of relative intensity 2:1:3:1 centred at  $\delta$ 2.94, 2.74, 2.02 and 0.74 ppm, respectively, in the aliphatic proton region. The spectroscopic data suggest that the phosphine ligand is 1,3-bis(diphenylphosphino)dicyclopentadiene (I) formed via intramolecular Diels-Alder dimerization of (diphenylphosphino)cyclopentadiene as shown in Eq. (1):



The X-ray diffraction study of IV has established a *cis*-configuration for the four terminal carbonyl groups and confirmed that the two  $Ph_2P(C_5H_5)$ ligands indeed did undergo dimerization to produce the 1,3-bis(diphenylphosphino)dicyclopentadiene ligands.<sup>1</sup>

(ii)  $At - 2^{\circ}C$ . When  $C_7H_8Mo(CO)_4$  was treated with 2 equivalents of  $Ph_2P(C_5H_5)$  at  $-2^{\circ}C$  in hexane, compounds II and III were obtained. The major product, II, recrystallized from hexane, has a stoichiometry  $[Ph_2P(C_5H_5)]_2Mo(CO)_4$ . The IR spectrum in KBr exhibits three absorption at 2014s, 1899 vs(br), 1877 vs(br) cm<sup>-1</sup>, indicative of a *cis*configuration for the four terminal carbonyls. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum exhibits a singlet at  $\delta$  23.2 ppm indicating that the two phosphorus ligands are equivalent. Other than the broad complex multiplets centred at  $\delta$  7.18 ppm for the phenyl resonances, the <sup>1</sup>H NMR spectrum shows a broad complex multiplet and a broad singlet of relative intensity 3: 2 centred at  $\delta$  6.50 and 2.81 ppm for the olefinic protons and the aliphatic protons of the  $C_5H_5$  ring, respectively. Based on the above spectroscopic data, two structures are possible for II. These are IIa and IIb as shown below.



If II adopts structure IIb, one would then expect that the aliphatic protons of the carbon  $\beta$  to the phosphorus would couple with the phosphorus to give a doublet. The fact that the aliphatic protons resonance shows a singlet suggests that the protons are attached to the carbon  $\gamma$  to the phosphorus atom. In terms of steric hindrance the C<sub>3</sub>H<sub>5</sub> ring of IIa probably has less steric interaction with the other substituents on the phosphorus than that of IIb. Thus, based on the splitting pattern and steric argument, structure IIa is assigned to II. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR studies show that II in C<sub>6</sub>D<sub>6</sub> at ambient temperature isomerizes to IV quantitatively.

The minor product, III, is always contaminated with II. However, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR studies show that a mixture of II and III in  $C_6D_6$  at ambient temperature isomerizes to IV quantitatively, and no other products are observed. This suggests that the stoichiometry of III is the same as II and is  $[Ph_2P(C_5H_5)]_2Mo(CO)_4$ . The IR spectrum of III in KBr exhibits three absorptions at 2014s, 1988 vs(br), 1877 vs(br) cm<sup>-1</sup>, indicative of a *cis*-configuration for the four terminal carbonyls. The  ${}^{31}P{}^{1}H$  NMR spectrum exhibits two doublets of relative intensity 1 : 1 centred at  $\delta$  21.1 ( $J_{P-P} = 24.4$ Hz) and  $\delta$  30.8 ( $J_{P-P}$  = 24.4 Hz) ppm, suggesting the presence of two non-equivalent phosphorus ligands. Other than the phenyl and olefinic resonances, <sup>1</sup>H NMR shows a doublet  $(J_{P-H} = 15.0)$ Hz) and a singlet of relatively intensity 1 : 2 at  $\delta$  4.07 and 2.89 ppm, respectively. The chemical shift and coupling constant of the doublet at  $\delta$  4.07 ppm is similar to that of the unique proton of the (Me<sub>4</sub>C<sub>5</sub>H) ring ( $\delta$  4.23 ppm;  $J_{P-H} = 15.3$  Hz) of the complex  $[(Me_4C_5H)PPh_2]Mo(CO)_5$  (V) whose structure has been established by an X-ray diffraction study<sup>3</sup> and is shown below.



The chemical shift of the singlet at  $\delta$  2.89 ppm is similar to the aliphatic protons of **II**. Based on the above spectroscopic data, the following structure is assigned to **III**.



Based on the assigned structures, assignment of <sup>31</sup>P NMR data can be made and is shown in Table 1.

#### Interaction of cis-Mo(CO)<sub>4</sub>(Ph<sub>2</sub>PCl)<sub>2</sub> with (C<sub>5</sub>H<sub>5</sub>)Tl

When cis-Mo(CO)<sub>4</sub>(Ph<sub>2</sub>PCl)<sub>2</sub> was treated with 2 equivalents of (C<sub>5</sub>H<sub>5</sub>)Tl in toluene at room tem-

perature, no reaction was observed after 48 h. However, if the reaction was carried out overnight in refluxed toluene, compound IV was obtained in high yield (80%). The formation of IV probably involves the mechanism shown in Scheme 1. *Cis*- $Mo(CO)_4(Ph_2PCl)_2$  reacts with  $(C_5H_5)Tl$  to produce intermediate II which then undergoes a series of rearrangements and finally intramolecular Diels-Alder cycloaddition to produce the final product IV. The mechanism is further supported by the fact that II and III isomerize to IV quantitatively at room temperature.

### Thermolysis of IV

Pyrolysis of IV in the solid state produces a red crystalline compound VI of stoichiometry  $C_{35}H_{30}$  $O_2P_2MO_2$  in low yield. The IR spectrum (KBr) of VI exhibits a strong absorption at 1807 cm<sup>-1</sup> in the terminal carbonyl region. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum exhibits a singlet at  $\delta$  167.2 ppm.

#### Table 1. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR data

Compound	${}^{1}\mathbf{H}^{a}$	Assignment	<sup>31</sup> P <sup>b</sup>	Assignment
П	7.18m(20) 6.50m(6) 2.81br,s(4)	$Ph_2P(C_5H_5)$ Olefinic protons of $C_5H_5$ Aliphatic protons of $C_5H_5$	23.2s	$Ph_2P(C_5H_5)$
III	7.26m(20) 6.48m(7) 4.07d(1) 2.89s(2)	$Ph_2P(C_5H_5)$ Olefinic protons of $C_5H_5$ $H_b; J_{P-H} = 15.0 \text{ Hz}$ $H_a$	21.2d(1) 30.8d(1)	$Ph_2P_a(C_5H_5); J_{P\_P} = 24.2 Hz$ $Ph_2P_b(C_5H_5); J_{P\_P} = 24.2 Hz$
IV	7.33m(20) 6.67m(1) 6.19m(1) 5.19m(1)	$ \begin{cases} Ph_2P \\ Olefinic protons of \\ the dicyclopentadiene \\ ligand \end{cases} $	23.4d(1) 37.2d(1)	$P_{\rm a}; J_{\rm P-P} = 24.4 \text{ Hz}$ $P_{\rm b}; J_{\rm P-P} = 24.4 \text{ Hz}$
	2.94m(2) 2.74m(1) 2.02m(3) 0.74m(1)	Aliphatic protons of the dicyclopentadiene ligand		
V	7.80m(4) 7.55m(6) 4.23d(1) 1.74br,s(6) 1.42s(6)	$\begin{cases} Ph_2 P(C_5 Me_4 H) \\ P(C_5 Me_4 H); J_{P-H} = 15.3 \text{ Hz} \\ \end{cases} P(C_5 Me_4 H) \end{cases}$	37.0s	$Ph_2P(C_5Me_4H)$
VI	8.14m(4) 7.46m(4) 7.19m(12) 4.97s(5) 4.78m(5)	$ \begin{cases} \mu - \mathbf{P}Ph_2 \\ \mathbf{C}_{\mathbf{s}}\mathbf{H}_{\mathbf{s}} \\ \mathbf{C}_{\mathbf{s}}\mathbf{H}_{\mathbf{s}} \end{cases} \end{cases} $	167.2s	μ- <b>P</b> Ph <sub>2</sub>

<sup>*a*</sup>In CDCl<sub>3</sub> at 30°C, referenced to Me<sub>4</sub>Si ( $\delta$  0.00).

<sup>b</sup>In CDCl<sub>3</sub> at 30°C, referenced to external 85% H<sub>3</sub>PO<sub>4</sub> ( $\delta$  0.0), negative for upfield shift.

Abbreviations: s, singlet; d, doublet; m, multiplet; br, broad.



Scheme 1.

The low-field chemical shift suggests the presence of phosphido-bridged ligands.<sup>4</sup> The <sup>1</sup>H NMR spectrum exhibits a set of three multiplets of total relative intensity 20, centred at  $\delta$  8.14, 7.46 and 7.19 ppm for the phenyl protons, a singlet of intensity 5 at  $\delta$  4.97 ppm, and a multiplet of relative intensity 5 at  $\delta$  4.78 ppm for the C<sub>5</sub>H<sub>5</sub> rings.

The structure of VI was determined by an X-ray diffraction study of its hexane solvate,  $2 \text{ VI} \cdot \text{C}_6 \text{H}_{14}$ . The crystal data and other parameters for the X-ray structural analysis are listed in Table 2. The hexane molecules centred about a crystallographic inversion centre, exhibits two-fold disorder.

A perspective drawing of VI is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 3. The structure is consistent with its spectroscopic data and VI can be formulated as  $[(C_5H_5)Mo]_2(\mu$ -PPh<sub>2</sub>)\_2(CO)(O). The dimer can be considered as a Mo<sup>(II)</sup>—Mo<sup>(IV)</sup> mixed-valent compound. Mo(1) to which the oxo group is attached is formally in a +4 oxidation state and Mo(2) where the carbonyl is attached is formally in a +2 oxidation state. For the two molybdenum atoms to obey the 18-electron rule, a double bond should exist between them.

This is reflected by the shorter Mo—Mo distance of 2.941(1) Å in comparison with those in the analogous complexes  $M_2(CO)_8(\mu-PEt_2)_2$  (M = Mo, 3.06 Å and M = W, 3.05 Å).<sup>5</sup> The coordination polyhedron around each molybdenum atom can be described as a distorted tetrahedron if the metalmetal bond is neglected, with the cyclopentadienyl group occupying one coordination site, and two bridging phosphorus atoms and the oxo atom [for Mo(1)] or the carbonyl group [for Mo(2)] occupying the other three sites (Fig. 1). The oxo and carbonyl ligands are trans to each other as reflected by the torsion angle O(1)—Mo(1)—Mo(2)—C(2) of 178.6°. The planar  $Mo_2P_2$  core (within  $\pm 0.036$  Å) is similar to that found in  $M_2(CO)_8(\mu-PEt_2)_2$  $(M = Mo, W)^5$  and  $W_2(CO)_8(\mu - PPh_2)_2$ ,<sup>6</sup> but different from the butterfly Fe<sub>2</sub>P<sub>2</sub> core in  $Fe_2(CO)_6(\mu$ -PPh<sub>2</sub>)<sub>2</sub>.<sup>7</sup> The Mo=O bond distance of 1.687(6) Å falls in the range reported for the other

Table 2. Data collection and processing parameters

Molecular formula	$2[(C_5H_5)Mo]_2(\mu$ -PPh <sub>2</sub> ) <sub>2</sub> (CO)(O) · C <sub>6</sub> H <sub>14</sub>
Molecular weight	1559.14
Colour and habit	Dark red plate
Unit cell parameters	$a = 9.554(a) \text{ Å}$ $\alpha = 76.58(1)^{\circ}$
	$b = 13.418(2) \text{ Å}  \beta = 71.63(1)^{\circ}$
	$c = 14.363(2) \text{ Å}  \gamma = 88.00(1)^{\circ}$
	$V = 1698.3(5) \text{ Å}^3$ $Z = 1$ $F(000) = 790$
Density (calcd)	$1.524 \text{ g cm}^{-3}$
Space group	<i>P</i> I (No. 2)
Radiation	Graphite-monochromatized Mo $K_{\alpha}$ , $\lambda = 0.71073$ Å
Standard reflections	(112), (204)
Intensity variation	$\pm 8\%$
$R_{\rm int}$ (from merging of equivalent reflections)	0.053
Absorption coefficient	$8.45 \text{ cm}^{-1}$
Crystal size	$0.10 \times 0.32 \times 0.35 \text{ mm}^3$
Mean $\mu r$	0.108
Transmission factors	0.773-0.884
Scan type and rate	$\omega$ ; 3.01–15.63° min <sup>-1</sup>
Scan range	$0.60^{\circ}$ below $K\alpha_1$ to $0.70^{\circ}$ above $K\alpha_2$
Background counting	Stationary counts for one-fifth of scan time at each end of scan range
Collection range	$h, \pm k, \pm 1; 2\theta_{\max} = 50^{\circ}$
Unique data measured	5947
Observed data with $ F_o  \ge 6\sigma( F_o )$ , n	3839
Number of variables, p	391
$R_F = \Sigma \ F_{\rm o} -  F_{\rm c}\ /\Sigma  F_{\rm o} $	0.053
Weighting scheme	$w = [\sigma^2(F_o) + 0.0015 F_o ^2]\underline{1}$
$R_G = [\Sigma w ( F_o  -  F_c )^2 / \Sigma w  F_o ^2]^{1/2}$	0.082
$S = [\Sigma w( F_o  -  F_c )^2 / (n-p)]^{1/2}$	1.606
Residual extrema in final difference map	+1.78 to $-0.93$ eÅ <sup>-3</sup>



Fig. 1. A perspective drawing of VI with thermal ellipsoids at 30% probability.

Mo(1)—Mo(2) 2.9	941(1)	C(2)—O(2) 1.15(1	l)
Mo(1)—P(1) 2.4	59(2)	Mo(2)-P(1) 2.324	(2)
Mo(1)—P(2) 2.4	63(2)	Mo(2)—P(2) 2.324	(2)
Mo(1)-O(1) 1.6	87(6)	Mo(2)C(2) 1.95(1	i)
Mo(1) - Cp(1) 2.0	85(8) <sup>a</sup>	Mo(2)—Cp(2) 2.008	(8) <sup>a</sup>
Mo(2)—Mo(1)—P(1)	50.0(1)	Mo(1)—Mo(2)—P(1)	54.2(1)
Mo(2)—Mo(1)—P(2)	50.0(1)	Mo(1) - Mo(2) - P(2)	54.3(1)
P(1) - Mo(1) - P(2)	99.9(1)	P(1) - Mo(2) - P(2)	108.3(1)
Mo(2) - Mo(1) - O(1)	111.9(2)	Mo(1) - Mo(2) - C(2)	89.0(2)
P(1) - Mo(1) - O(1)	102.0(2)	P(1) - Mo(2) - C(2)	90.4(2)
P(2) - Mo(1) - O(1)	102.7(2)	P(2) - Mo(2) - C(2)	91.8(3)
Mo(2) - Mo(1) - Cp(1)	124.4(2)	Mo(1) - Mo(2) - Cp(2)	148.5(2)
P(1) - Mo(1) - Cp(1)	113.2(3)	P(1) - Mo(2) - Cp(2)	118.8(3)
P(2) - Mo(1) - Cp(1)	112.2(3)	P(2) - Mo(2) - Cp(2)	119.0(3)
O(1) - Mo(1) - Cp(1)	123.7(4)	C(2) - Mo(2) - Cp(2)	122.4(4)
Mo(1) - P(1) - Mo(2)	75.8(1)	Mo(1) - P(2) - Mo(2)	75.8(1)
Mo(1) - P(1) - C(13)	116.6(3)	Mo(1) - P(2) - C(25)	117.1(2)
Mo(2) - P(1) - C(13)	118.5(2)	Mo(2)P(2)C(25)	118.3(3)
Mo(1) - P(1) - C(19)	116.2(2)	Mo(1) - P(2) - C(31)	117.0(2)
Mo(2) - P(1) - C(19)	128.0(3)	Mo(2) - P(2) - C(31)	128.2(3)
C(13) - P(1) - C(19)	101.2(4)	C(25) - P(2) - C(31)	100.4(4)
$M_{0}(2) - C(2) - O(2)$	176.1(7)		

Table 3. Selected bond lengths (Å) and bond angles (°) in the  $Mo_2P_2$  core of the  $[(C_5H_5)Mo]_2(\mu$ -PPh<sub>2</sub>)<sub>2</sub>(CO)(O) molecule

<sup>*a*</sup>Cp(1) is the centre of the ring composed of carbon atoms C(3)—C(7), and Cp(2) is the centre of the C(8)—C(12) ring.

molybdenum oxo complexes.<sup>8,9</sup> In accordance with the different oxidation states of the metal atoms, the Mo(1)—P [av. 2.461(2) Å] and Mo(1)—Cp(1) [2.085(8) Å] bonds are significantly longer than Mo(2)—P [av. 2.324(2) Å] and Mo(2)—Cp(2) [2.008(8) Å], respectively. The bond lengths and angles involving the carbon atoms are all normal and there are no unusual intermolecular contacts in the crystal packing.

#### EXPERIMENTAL

Microanalyses were performed by Butterworth (U.K.). IR spectra were recorded on a Perkin– Elmer 983 spectrometer; data given in cm<sup>-1</sup> in KBr pellets. NMR spectra were recorded on a JEOL FX90Q spectrometer. Chemical shifts of <sup>1</sup> H NMR spectra were referenced to internal deuterated solvents and then recalculated to TMS = 0.0 ppm. <sup>31</sup>P NMR spectra were referenced to external 85% H<sub>3</sub>PO<sub>4</sub>.

All operations were carried out under nitrogen or *in vacuo*. All chemicals used were of reagent grade. Solvents were dried by standard procedures, distilled and deaerated prior to use. Melting points were taken in sealed capillaries and are uncorrected.

Ph<sub>2</sub>P(C<sub>5</sub>H<sub>5</sub>),<sup>10</sup> (C<sub>5</sub>H<sub>5</sub>)Tl,<sup>10</sup> C<sub>7</sub>H<sub>8</sub>Mo(CO)<sub>4</sub><sup>11</sup> and

cis-Mo(CO)<sub>4</sub>(Ph<sub>2</sub>PCl)<sub>2</sub><sup>12</sup> were prepared according to literature methods.

### Preparation of cis-[Ph<sub>2</sub>P(C<sub>5</sub>H<sub>5</sub>)]<sub>2</sub>Mo(CO)<sub>4</sub>

A solution of  $C_7H_8Mo(CO)_4$  (0.5 g, 1.7 mmol) in hexane (50 cm<sup>3</sup>) was added dropwise to a freshly prepared solution of Ph<sub>2</sub>P(C<sub>5</sub>H<sub>5</sub>) (0.9 g, 3.6 mmol) in hexane (50 cm<sup>3</sup>) at  $-2^{\circ}$ C. After stirring at  $-2^{\circ}$ C for 2 h, the solution was filtered. The filtrate was concentrated to *ca* 60 cm<sup>3</sup> and cooled to  $-20^{\circ}$ C to give white crystalline products which were a mixture of II and III.

The white crystalline products were then extracted with cold hexane  $(2 \times 20 \text{ cm}^3)$  at 0°C. The hexane solution was then concentrated to *ca* 20 cm<sup>3</sup> at 0°C and cooled to  $-20^{\circ}$ C to give pure **H** as a white crystalline solid, which was filtered and dried *in vacuo*. Yield: 0.9 g, 75%; m.p. 202–204°C (decomposed). Found (required): C, 64.5 (64.4); H, 4.0 (4.2); P, 9.0 (8.8)%. IR (KBr), v(CO): 2014s, 1899 vs(br), 1877 vs(br) cm<sup>-1</sup>.

Further recrystallization of the filtrate only produced a mixture of **II** and **III**.

#### Preparation of IV

(i) A solution of  $C_7H_8Mo(CO)_4$  (0.5 g, 1.7 mmol) in hexane (50 cm<sup>3</sup>) was added dropwise to a freshly prepared solution of Ph<sub>2</sub>P(C<sub>5</sub>H<sub>5</sub>) (0.9 g, 3.6 mmol) in hexane at ambient temperature. After stirring for 3 h at ambient temperature, white precipitates were obtained. The precipitates were filtered and recrystallized from a 1:1 toluene-hexane mixture (20 cm<sup>3</sup>) to give light yellow crystals which were dried *in vacuo*. Yield: 1.1 g, 88%; m.p. 198-200°C (decomposed). Found (required): C, 64.4 (64.4); H, 4.1 (4.2); P, 8.9 (8.8)%. IR (KBr),  $\nu$ (CO): 2017s, 1916s, 1880 vs(br) cm<sup>-1</sup>.

(ii) A solution of cis-Mo(CO)<sub>4</sub>(Ph<sub>2</sub>PCl)<sub>2</sub> (0.9 g, 1.5 mmol) in toluene (50 cm<sup>3</sup>) was added dropwise to a suspension of (C<sub>3</sub>H<sub>3</sub>)Tl (0.9 g, 3.3 mmol) in toluene (50 cm<sup>3</sup>) at ambient temperature. The solution was stirred at ambient temperature for 48 h, but no reaction was observed. The solution was then refluxed overnight and allowed to cool to room temperature and filtered. The filtrate was then concentrated under reduced pressure to ca 20 cm<sup>3</sup>. n-Hexane was then added until the solution turned cloudy. Upon standing at room temperature overnight, light yellow crystals of **IV** were obtained. Yield: 0.9 g, 85%.

#### Pyrolysis of IV

Compound IV (0.9 g, 1.2 mmol) was heated at 200°C in vacuo. The complex gradually turned black with evolution of gas as the temperature was raised. After heating for 4 h at 200°C, gas evolution ceased. The black residue was cooled down to room temperature, dissolved in a minimum amount of CHCl<sub>3</sub>, and chromatographed on silica gel using toluene as eluent. A brown band was collected and the solvent was evaporated in vacuo. The residue was redissolved in a minimum amount of CHCl<sub>3</sub> and chromatographed again on silica gel using a hexane-toluene mixture as eluent. Three bands were obtained. Band A was obtained by eluting with hexane-toluene (2:3), and bands B and C were obtained with hexane-toluene (1:2). Solvents were removed in vacuo. Bands A and B yielded only a small amount of solid material and were discarded. Band C gave considerably better yield and recrystallization of the residue, with toluene-hexane, gave dark red prisms which were dried in vacuo. Yield:  $0.2 \text{ g}, 22\%; \text{m.p.} > 280^{\circ}\text{C}$ . Found (required): C, 57.4 (57.1); H, 4.2 (4.1); P, 8.1 (8.4)%. IR (KBr),  $v(CO): 1807s cm^{-1}.$ 

#### <sup>31</sup>P{<sup>1</sup>H} NMR studies

(i) Isomerization of II. II (20 mg) was dissolved in 0.5 cm<sup>3</sup> of CDCl<sub>3</sub> at 10°C. The isomerization process was monitored by  ${}^{31}P{}^{1}H{}$  NMR spectroscopy at 4-h intervals for 12 h. Within the period.

Table 4. Atomic coordinates ( $\times 10^{5}$  for Mo;  $\times 10^{4}$  for other atoms) and equivalent isotropic temperature factors<sup>*a*</sup> (Å<sup>2</sup> × 10<sup>4</sup> for Mo and P; × 10<sup>3</sup> for other atoms)

Atom	x	у	Z	$U_{ m eq}$
Mo(1)	14224(8)	17883(5)	82515(5)	479(3)
Mo(2)	37807(8)	18294(5)	63410(5)	475(3)
P(1)	2432(2)	380(2)	7440(2)	473(6)
P(2)	3050(2)	3225(2)	7058(2)	478(6)
O(1)	2076(6)	1559(5)	9240(4)	65(1)
C(2)	2306(9)	2067(6)	5644(6)	66(1)
O(2)	1501(8)	2204(5)	5185(5)	94(1)
C(3)	- 1056(8)	1145(7)	8809(7)	73(1)
C(4)	- 1020(8)	1961(7)	9268(7)	69(1)
C(5)	- 592(8)	2872(7)	8500(7)	72(1)
C(6)	- 511(8)	2586(7)	7550(6)	65(1)
C(7)	- 786(8)	1529(7)	7765(7)	68(1)
C(8)	6196(9)	1517(9)	6371(9)	128(1)
C(9)	5867(9)	873(8)	5941(7)	84(1)
C(10)	5586(9)	1324(7)	5031(7)	85(1)
C(11)	5788(10)	2404(9)	4898(9)	142(1)
C(12)	6213(9)	2423(9)	5849(9)	130(1)
C(13)	3394(8)	- 598(6)	8112(6)	59(1)
C(14)	3550(9)	-1572(6)	7914(7)	76(1)
C(15)	4408(9)	-2283(7)	8289(8)	97(1)
C(16)	5092(10)	- 1993(8)	8969(8)	121(1)
C(17)	4936(10)	- 1075(8)	9167(8)	102(1)
C(18)	4108(9)	-351(7)	8727(7)	81(1)
C(19)	1104(8)	-413(6)	7234(6)	56(1)
C(20)	37(8)	- 1025(6)	8027(7)	66(1)
C(21)	- 1014(9)	-1585(7)	7867(8)	85(1)
C(22)	- 1036(9)	-1577(7)	6909(8)	92(1)
C(23)	45(10)	-998(7)	6120(7)	85(1)
C(24)	1116(8)	- 396(6)	6266(6)	61(1)
C(25)	4354(8)	3797(6)	7509(6)	53(1)
C(26)	4980(8)	4776(6)	6991(7)	67(1)
C(27)	6100(9)	5169(7)	7281(7)	78(1)
C(28)	6572(9)	4636(7)	7974(7)	78(1)
C(29)	5940(9)	3656(8)	8489(7)	84(1)
C(30)	4858(8)	3250(7)	8274(6)	67(1)
C(31)	2149(8)	4383(6)	6580(5)	49(1)
C(32)	2077(9)	4591(6)	5619(6)	64(1)
C(33)	1375(9)	5452(6)	5263(7)	72(1)
C(34)	746(9)	6087(7)	5899(8)	82(1)
C(35)	792(9)	5881(7)	6835(7)	75(1)
C(36)	1504(9)	5024(6)	7172(7)	68(1)
C(37)	3856(8)	4661(11)	-345(13)	171(1)
C(38)	2367(8)	4058(9)	193(12)	150(1)
C(39)	1092(6)	4746(5)	47(12)	134(1)
C(40)	-311	4058	361	54(1)
C(41)	-1713(8)	4644(8)	727(8)	158(1)
C(42)	-2277(12)	5144(11)	-158(10)	154(1)

<sup>*a*</sup> $U_{eq}$  defined as one third of the trace of the orthogonalized U tensor. Atoms C(37)—C(42) belong to the disordered hexane molecule and have site occupancy factors of  $\frac{1}{2}$ . II isomerized to IV quantitatively. Throughout the course of the reaction, no other resonance signals, other than those of II and IV, were observed.

(ii) Isomerization of a mixture of II and III. II and III (20 mg) were dissolved in 0.5 cm<sup>3</sup> of CDCl<sub>3</sub> at 10°C. The isomerization process was monitored by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy every 4 h for 12 h. Within the period, both II and III isomerized to IV quantitatively. Throughout the course of the reaction, no other resonances, other than those of II, III and IV were observed.

#### X-ray diffraction studies

Crystals of VI suitable for X-ray diffraction study were grown from toluene–n-hexane as a solvate of stoichiometry 2 VI  $\cdot$  C<sub>6</sub>H<sub>14</sub>.

Raw intensities collected at 21°C on a Nicolet R3m/V diffractometer were processed with the profile fitting procedure of Diamond<sup>13</sup> and corrected for absorption using  $\psi$ -scan data<sup>14</sup> (details in Table 4). Two molybdenum atoms was located by direct phase determination and the coordinates of the other non-hydrogen atoms were derived from successive difference Fourier syntheses. The carbon atoms of the disordered solvent (n-hexane) were found on a subsequent difference Fourier map and interatomic distance constraints of 1.540(2) and 2.52(1) Å were applied to adjacent carbons and alternate carbons. The non-hydrogen atoms were refined anisotropically and the carbon atoms of the solvent molecule isotropically. Hydrogen atoms of the phenyl and cyclopentadienyl groups were generated geometrically (C-H bond fixed at 0.96 Å) and allowed to ride on their respective parent carbon atoms. These hydrogen atoms were assigned appropriate isotropic thermal parameters and included in the structure factor calculation. The hydrogen atoms of the disordered hexane molecule were ignored. Computations were performed using the SHELTXL-PLUS program package<sup>15</sup> on a DEC MicroVAX-II computer. Analytic expressions of atomic scattering factors were employed,

and anomalous dispersion corrections were incorporated.<sup>16</sup> The maxima in the last difference map all lie in the neighbourhood of the solvent molecule.

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