Bull Soc Chim Fr (1997) 134, 859-867

Regioselective intramolecular [4 + 2] Diels–Alder cycloaddition reactions of allenylphosphinepentacarbonylmolybdenum complexes with 3,4-dimethyl-1-phenylphosphole

Kalyani Maitra, John H Nelson*

Department of Chemistry–216, University of Nevada at Reno, Reno, NV 89557-0020, USA

(Received 5 August 1997; accepted 14 October 1997)

Summary — Intramolecular [4 + 2] Diels–Alder cycloaddition reactions of *cis*-(allenylphosphine)(3,4-dimethyl-1-phenylphosphole)tetracarbonylmolybdenum complexes occur regioselectively at the allenyl $C_\alpha=C_\beta$ double bond to form 2-phosphino-3-*exo*-methylene-7-phosphanorbornenetetracarbonylmolybdenum complexes. Analogous *cis*-(propargylphosphine)-(3,4-dimethyl-1-phenylphosphole)tetracarbonylmolybdenum complexes do not undergo intramolecular cycloadditions. The new complexes were characterized by elemental analyses, physical properties, ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectroscopy, infrared spectroscopy and X-ray crystallography.

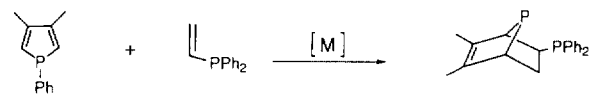
phosphole / [4 + 2] Diels–Alder cycloaddition / crystal structure / molybdenum carbonyl complex

Résumé — Réactions régiosélectives intramoléculaires de cycloaddition [4 + 2] de Diels–Alder de complexes allénylphosphinepentacarbonylmolybdénium avec les 3,4-diméthyl-1-phénylphospholes. Les réactions de cycloaddition intramoléculaires de Diels–Alder de complexes de *cis*-(allénylphosphine)(3,4-diméthyl-1-phénylphosphole)tétracarbonylmolybdénium se font de manière régiosélective sur la double liaison allényl $C_\alpha=C_\beta$ pour former les complexes 2-phosphino-3-*exo*-méthylène-7-phosphanorbornènetétracarbonylmolybdénium. Les analogues *cis*-(propargylphosphine)(3,4-diméthyl-1-phénylphosphole)tétracarbonylmolybdénium ne conduisent pas à des cycloadditions intramoléculaires. Les nouveaux complexes sont caractérisés par leur analyse élémentaire, spectroscopies ^1H, ^{13}C, ^{31}P, IR et cristallographie aux rayons X.

phosphole / Diels–Alder cycloaddition [4 + 2] / complexe molybdène-carbonyle

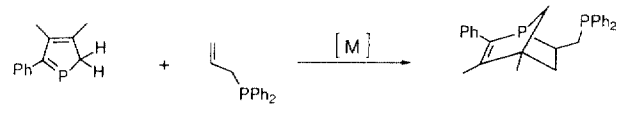
Introduction

Transition metal mediated [4 + 2] Diels–Alder cycloaddition reactions of 1*H*-phospholes is a classical synthetic method that we have employed to prepare a variety of complexes containing rigid unsymmetrical chelating chiral diphosphines [1]. The 1*H*-phosphole, 3,4-dimethyl-1-phenylphosphole (DMPP) reacts readily with vinylphosphines within the coordination spheres of several different metals to form complexes of 2-phosphino-7-phosphanorbornenes (5-phosphino-7-phosphabicyclo[2.2.1.]hept-2-enes). Asymmetric modifications of these reactions have been reported recently [2].



1*H*-phosphole — 2-phosphino-7-phosphanorbornenes

Similar reactions with complexes of allylphosphines, which are poorer dienophiles than vinylphosphines, are more limited [3]. We have recently found [4] that allylphosphine complexes of molybdenum react with DMPP at about 145 °C, after rearrangement to the more reactive 2*H*-phosphole [5] to form complexes of 2-(phosphinomethyl)-1-phosphanorbornenes:



2*H*-phosphole — 2-phosphinomethyl-1-phosphanorbornene

The nature of the cycloaddition product for the molybdenum promoted reactions appears to be a strong function of the dienophilicity of the dienophile. The studies described herein were conducted in order to further probe this issue and also to determine the regiochemistry of additions to coordinated allenylphosphines, ie, whether the cycloaddition would occur to the $C_\alpha=C_\beta$ or $C_\beta=C_\gamma$ double bond of the allenyl phosphine or both.

* Correspondence and reprints

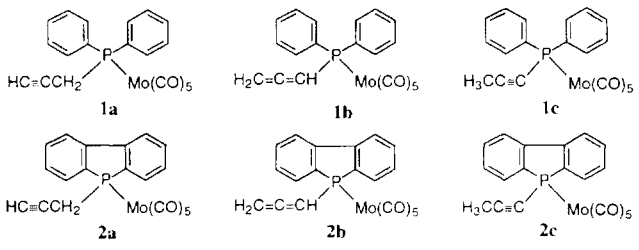
Table I. Ratios of different species determined by $^{31}P\{^1H\}$ NMR spectroscopy of the crude product mixtures in diglyme.

Reactants	*Temp (°C)*	*Time (h)*	*Detectable species in the crude reaction mixtures (fractional amount)*					
1b + DMPP	115	1.5	**5** (0.38)	**3b** (0.15)	**DMPP** (0.29)	**7** (0.18)		
	115	4.5	(0.71)	(0)	(0.18)	(0.11)		
1a/1b/1c + DMPP[a] (8:3:1)	115	4.5	**9** (0.15)	**3a** (0.22)	**DMPP** (0.15)	**1c** (0.06)	**1a** (0.22)	
2a/2b/2c + DMPP[a] (6:9:2)	115	4.5	**6** (0.17)	**10** (0.15)	**7** (0.03)	**4a** (0.15)	**2a** (0.30)	**2b** (0.20)

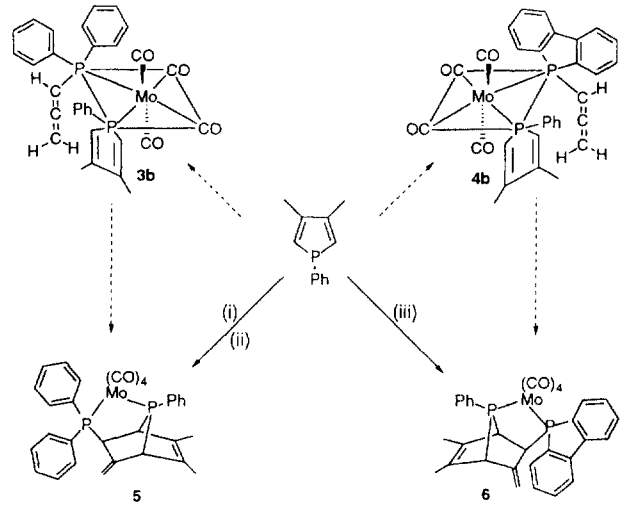
[a] Resonances for some of the other products isolated after purification were not readily identified or apparent in the spectra of the crude reaction mixtures.

Results and discussion

Earlier we reported the syntheses of complexes **1b**, **1c** and **2b**, **2c** by base-promoted isomerizations of the tertiary propargylphosphine and phosphole complexes **1a** and **2a** respectively [6]. Complex **1b** was prepared by this method and separated from its isomers **1a** and **1c** by column chromatography on silica gel. The reaction of **1b** with DMPP in diglyme at 115 °C gave complex **5** as the major product in high yield.



As evidenced from the $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixture (table I), the first step involves the stereospecific formation of the thermodynamically favored *cis* mixed-ligand complex **3b** (scheme 1) followed by its conversion into the [4 + 2] Diels–Alder cycloadduct of the 1*H*-phosphole of DMPP. This is consistient with the appearance of two doublets at δ 28.40 and 30.38 ppm (^2J(PP) = 25.3 Hz) for **3b** followed by their decay and the gradual growth of the resonances for the product **5**. We have not isolated this intermediate *cis* mixed-ligand complex but its formation is evident from the spectral analysis. In order to compare the reactivity of all the isomers towards cycloaddition, a mixture of the isomers **1a/1b/1c** in the ratio 8:3:1 was allowed to react with DMPP under the same reaction conditions. The $^{31}P\{^1H\}$ NMR spectra of the crude product mixture showed resonances for unreacted **1a**, **1c**, an unidentified compound **9** (δ 72.48, 48.13 ppm, ^2J(PP) = 37.7 Hz), and the *cis* mixed-ligand complex (**3a**: δ 30.76 (d), 30.58 (d) ppm; ^2J(PP) = 24.1 Hz) which was formed from the reaction of the isomer **1a** with DMPP. Complex **3a** was separated during the purification process and completely characterized (vide infra). We were not able to detect the *cis* mixed-ligand complex **3c** of the isomer **1c**. The crude product mixture was purified by column chromatography. We isolated some other products that were formed in

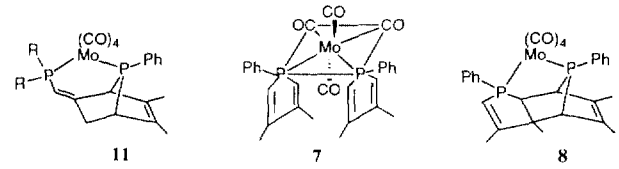


(i) refluxed in diglyme with complex **1b** at ~115 °C for 5 h
(ii) refluxed in diglyme with a mix of **1a**:**1b**:**1c** at ~115 °C for 4 h
(iii) refluxed in diglyme with a mix of **2a**:**2b**:**2c** at ~115 °C for 5 h

Scheme 1

lesser amounts that were not apparent in the crude mixture with one such prime example being complex **5** which was isolated during the purification process. Other detected complexes are *cis*-$(DMPP)_2Mo(CO)_4$ (**7**, δ = 31.27 ppm) [7] and the Diels–Alder adduct of **7** on itself to produce complex **8** [7]. Notably, complex **9** detected in the crude product mixture was not recovered during this purification process. Most likely it decomposes on the column during the purification process. Of note, although **1a** was eluted in early column fractions still more of it was recovered in the last few column fractions. Repeating the same reaction under more forcing conditions, at a higher temperature ~ 150 °C, gave almost the same results as discussed above except that now the $^{31}P\{^1H\}$ NMR spectrum of the crude product mixture was more complicated, **3a** was absent and the unknown complex **9** was formed to a greater extent. The high temperature seems to initiate decomposition in these reaction systems producing various byproducts which makes product purification and characterization a difficult tedious process. Several attempts to crystallize **9** using different solvent systems to separate it from other impurities were unsuccessful.

For the reaction of a mixture of the isomers of the analogous DBP complexes (**2a/2b/2c**, 6:9:2) with DMPP conducted in diglyme at ~ 115 °C, the changes in the compostion of the crude reaction mixture were also monitored by $^{31}P\{^1H\}$ NMR spectroscopy (table I). The $^{31}P\{^1H\}$ NMR spectra showed the appearance of resonances for the *cis* mixed-ligand complex **4b** (δ 30.20, 25.65; $^2J(PP)$ = 20.3 Hz), followed by its decay and growth of the resonances for complex **6**. Resonances of the other *cis* mixed-ligand complexes derived from **2a** and **2c** were also observed (table II). The crude product mixture also showed resonances at δ 31.27 ppm for **7** and at δ 72.57, 48.28 ppm ($J(PP)$ = 37.4 Hz) for **10** an analog of **9**. We also could not recover **10** which underwent decomposition on the silica gel column during the purification process. On the basis of the very similar values of the chemical shifts and the coupling constant it could be that **9** and **10** are the same complex that is formed from some reaction of DMPP. Unreacted **2a** was obtained both at the earlier and later stages of the purification process. During the purification process, the presence of other complexes were noted, which were not apparent in the crude reaction mixture. A few fractions eluted compounds **7** and **8** and the *cis* mixed-ligand complex **4b**. More forcing conditions, a higher temperature (~ 150 °C) and longer reaction period, caused more decomposition, but the formation of **10** in a much higher ratio was also evident. Perfect quantization of the composition of the crude reaction mixtures in all cases was not possible. Table II lists the $^{31}P\{^1H\}$ NMR data for all the compounds previously discussed and those detected in the different fractions during the process of purification by column chromatography. Analysis of the $^{31}P\{^1H\}$ NMR data lead us to conclude that the allenyl isomers of the tertiary phosphine and phosphole complexes viz, **1b** and **2b** are the more reactive dienophiles and are activated towards the formation of the [4 + 2] Diels–Alder cycloaddition products. It is important to note that β,γ-addition of DMPP to these allenyl complexes **1b** and **2b** would lead to the formation of the 7-phosphanorbornene ring with the *exo*-methylene double bond in conjunction with the six-membered chelate ring (as in **11**), which is geometrically unfavorable. In contrast, α,β-addition leads to the formation of the 7-phosphanorbornene ring with the isolated *exo*-methylene double bond not involved in the five membered chelate ring and as already seen it is the latter addition that occurs.



11 7 8

The other isomers **1a**, **1c** and **2a**, **2c** have the potential of forming *cis* mixed-ligand complexes but in each case the ensuing cycloaddition step would produce a highly strained norbornadiene ring system in conjunction with the chelate ring, which would be an energetically unfavorable configuration for the molecule. Competing formation of **7** and **8** in all the reaction systems indicates that ligand displacement of **1a**, **1c**, **2a** and **2c** by DMPP occurs to various extents. This is also supported by the fact that at higher temperatures with longer reaction times we did not recover any of the *cis* mixed-ligand complexes **3a**, **3c** or **4a**, **4c**, although their formation was evident from the $^{31}P\{^1H\}$ NMR spectra in the early stages of the reactions.

Mathey [8] et al have extensively studied the temperature dependent sigmatropic rearrangement of 1*H*-phospholes of DMPP to the 2*H*-phospholes and their reactivity with alkenes and alkynes. From our recent studies we have found that at elevated temperatures, rearrangement of a coordinated 1-phenyl-1*H*-phosphole to a coordinated 2-phenyl-2*H*-phosphole concomitant with its Diels–Alder cycloaddition to a dienophile within the metal coordination sphere, leads to the formation of cycloaddition products which have the 1-phosphanorbornene ring system in their molecular structures as in reaction 2 [4]. The coordinated 2*H*-phosphole is a more reactive diene than the coordinated 1*H*-phosphole [9]. When the other ligand in the mixed-ligand complexes is a poor dienophile, such as an allylphosphine, then the 1*H*-phosphole does not participate in an intramolecular [4 + 2] Diels–Alder cycloaddition to form a 7-phosphanorbornene. Instead, the coordinated 1*H*-phosphole rearranges to the coordinated 2*H*-phosphole which then undergoes an intramolecular [4 + 2] Diels–Alder cycloaddition to form a 1-phosphanorbornene [4]. When the other ligand in the mixed-ligand complexes is a good dienophile such as a vinylphosphine then the 7-phosphanorbornene is formed even at temperatures at which the 1*H*-phosphole to 2*H*-phosphole rearrangement can occur. This statement is supported by the observation that the reaction of DMPP with $Ph_2P(CH{=}CH_2)Mo(CO)_5$ at either 110 or 150 °C, gave the same 7-phosphanorbornene cycloadduct [1b] in high yield. These results lead us to conclude that the type of product formed, a 7-phosphanorbornene or a 1-phosphanorbornene, is a strong function of the dienophilicity of the dienophile.

Table II. 121.6 MHz $^{31}P\{^1H\}$ NMR data for the complexes.

Complex	$\delta^{31}P$ *(ppm)*	$^2J(PP)$ *(Hz)*
1a	31.00	–
1b	26.90	–
1c	11.10	–
2a	25.70	–
2b	22.00	–
2c	16.60	–
3a	30.76, 30.58	24.1
3b	30.38, 28.40	25.3
4a	30.10, 26.44	19.5
4b	30.20, 25.65	20.3
4c	29.09, 20.71	18.4
5	148.53, 47.52	18.2
6	151.61, 39.96	20.1
7	31.27	–
8	159.80, 52.60	10.0
9	72.48, 48.13	37.7
10	72.57, 48.28	37.4
11	71.63, 54.15	3.5

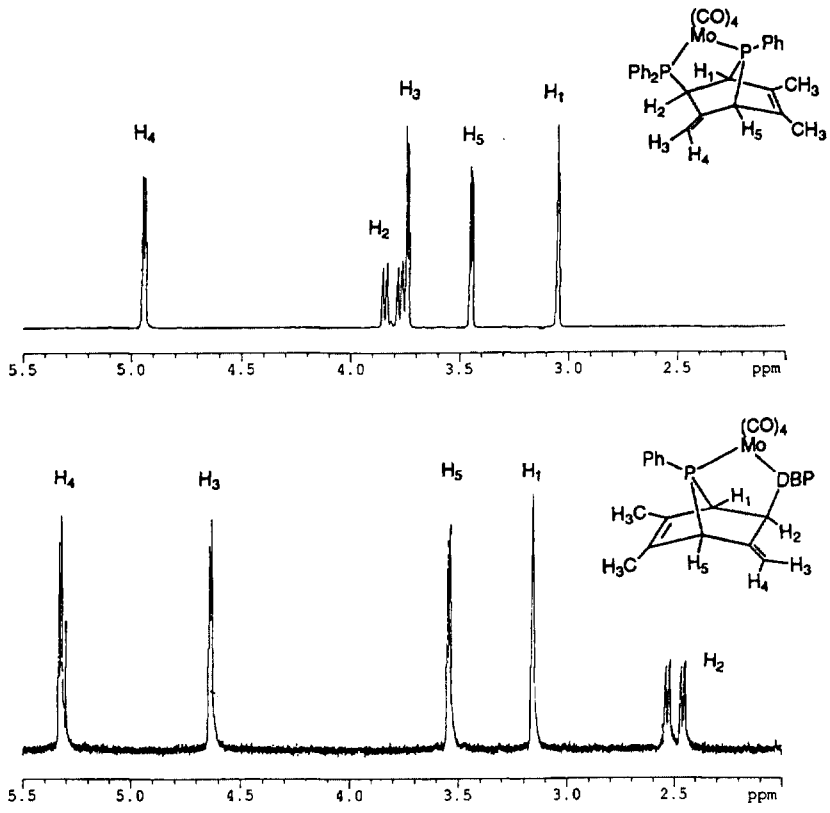


Fig 1. Expansions of the 499.86 MHz ^{1}H NMR spectra of **5** (upper) and **6** (lower) showing the 7-phosphanorbornene ring hydrogen resonances.

$^{31}P\{^1H\}$ NMR spectroscopy and the mechanisms of the reactions

In all cases when monitoring the reactions by $^{31}P\{^1H\}$ NMR spectroscopy, the stereospecific formation of the *cis* mixed-ligand complex was evident prior to the formation of the Diels–Alder 1*H*-phosphole adduct. In these reactions the entering DMPP ligand occupies the site vacated by the departing carbon monoxide which is *cis* to the other phosphine ligand already present within the metal coordination sphere. Earlier studies [10] have established the fact that this mutually *cis* coordination geometry of the ligands is a necessary condition for transition metal promoted intramolecular [4 + 2] Diels–Alder cycloaddition reactions, which produces rigid chiral bidentate ligands. Formation of the [4 + 2] Diels–Alder cycloadducts from the *cis* mixed-ligand complexes is signaled in the $^{31}P\{^1H\}$ NMR spectra by the appearance of two new resonances for the Diels–Alder adducts that are shifted considerably downfield compared to those for the *cis* mixed-ligand complexes (see table II). The $^{31}P\{^1H\}$ NMR spectrum for complex **3a** shows a second-order AB splitting pattern for the two inequivalent *cis* phosphorus nuclei present in the molecule. The spectra of the Diels–Alder cycloadducts **5** and **6** each exhibit a pair of doublets for the two inequivalent phosphorus nuclei coupled to each other by a magnitude of 18.2 and 20.1 Hz respectively, as is generally observed for complexes of this type [1b]. The low field resonance (table II) occurs in a region that is characteristic of phosphorus in the 7-phosphanorbornene ring [1, 7]. The other resonance occurs in the region typical of a phosphine coordinated to molybdenum in a five-membered chelate ring [11].

^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy

Assignments of the ^{1}H and ^{13}C chemical shifts were made by comparison with the data reported for similar molybdenum complexes [1b, 6] and were confirmed by a variety of decoupling experiments, APT, COSY and HETCOR two-dimensional spectroscopy. The large values of ^3J(PH) for H_2 are in keeping with expectations from previous studies [1b]. The chemical shifts and their differences for the vinylic hydrogens H_3 and H_4 are a strong function of the substituents on P_1 (fig 1). Both resonances for **5** lie upfield of those for their counterparts for **6** and their differences in chemical shift, $\Delta\delta$ ^{1}H (1.20 ppm (**5**), 0.86 ppm (**6**)) result from diamagnetic shielding effects of the phenyl rings. In both cases the H_4 resonance is downfield of the H_3 resonance as a result of this shielding effect. The diamagnetic anisotropy of the DBP ring causes the chemical shift for H_2 in **6** to be 1.2 ppm upfield of the chemical shift of H_2 in **5**. The ^{13}C chemical shifts of the 7-phosphanorbornene ring carbons, except for C_5 and C_6, were assigned from $^{13}C/^1H$ HETCOR two-dimensional spectra (fig 2).

The phenyl carbon resonances (C_o and C_m) for **3a** are broader than all the other carbon resonances in the spectrum of this molecule suggesting that this molecule is sterically congested with restricted rotation about the P-phenyl carbon bonds. All complexes display distinct sets of carbonyl ^{13}C resonances for the carbonyl groups respectively *cis* to both phosphorus atoms and *trans* to

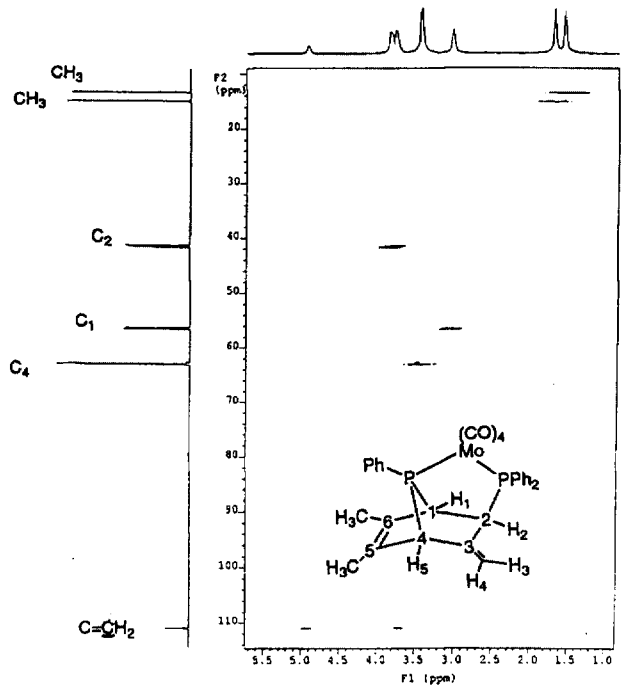


Fig 2. Expansions of the 125.71 MHz $^{13}C/^{1}H$ HETCOR spectrum of **5** showing the $^{13}C/^{1}H$ chemical shift correlation for the protonated carbons of the 7-phosphanorbornene ring. Splittings in the F2 dimension result from J(PC) couplings.

one phosphorus atom. The chemical shifts for the *trans* carbonyls are downfield of those for the *cis* carbonyls and the *trans* carbonyls have larger magnitude ^{2}J(PC) as expected. The NMR data are fully consistent with the molecular structures (see experimental).

Crystal structure analysis

X-ray crystal structures of complexes **5**, **6** and **3a** were obtained to gain conclusive support for their structures. These structures are shown in fig 3, 4 and 5 respectively. Selected bond distances and angles are listed in table III. All three complexes exist as discrete molecules with no abnormal intermolecular contacts. The asymmetric unit of **5** contains two crystallographically independent molecules and disordered solvent molecules (50% methanol and 50% water, the latter being disordered over two sites). None of these complexes contain any element of symmetry and they are therefore chiral. For **5** and **6** the five membered chelate rings are rigid and are fused to the 7-phosphanorbornene ring at P2 and C6 (note that the atom numbering schemes for the crystal structures and NMR spectroscopy are different). The strain in the norbornene ring can be best examined by considering the angles made by the bridgehead carbons and the 7-phospha phosphorus P2 atom. Here the values are 79.8(2)° for both molecules and are in close agreement with those observed for similar Mo(0) complexes [1b]. This angle strain in the 1*H*-phosphole Diels–Alder adducts is in part responsible for the extreme downfield shift for the 7-phospha phosphorus resonance in the $^{31}P\{^{1}H\}$ NMR spectra. For each of these complexes the coordination geometry at the metal center is a distorted octahedron and the angles at the Mo atom range from 77.22(4)° to 97.9(2)°, 76.72(5)° to 96.0(2)° and 85.3(2)° to 98.2(2)° for **5**, **6** and **3a** respectively. The equatorial plane in all cases is formed by the two phosphorus atoms and the two carbonyl groups *trans* to them. The C3–Mo1–C4 bond angle values of 173.2(2)°, 172.2(2)° and 172.4(2)° in complexes **5**, **6** and **3a** respectively, signify the mutual

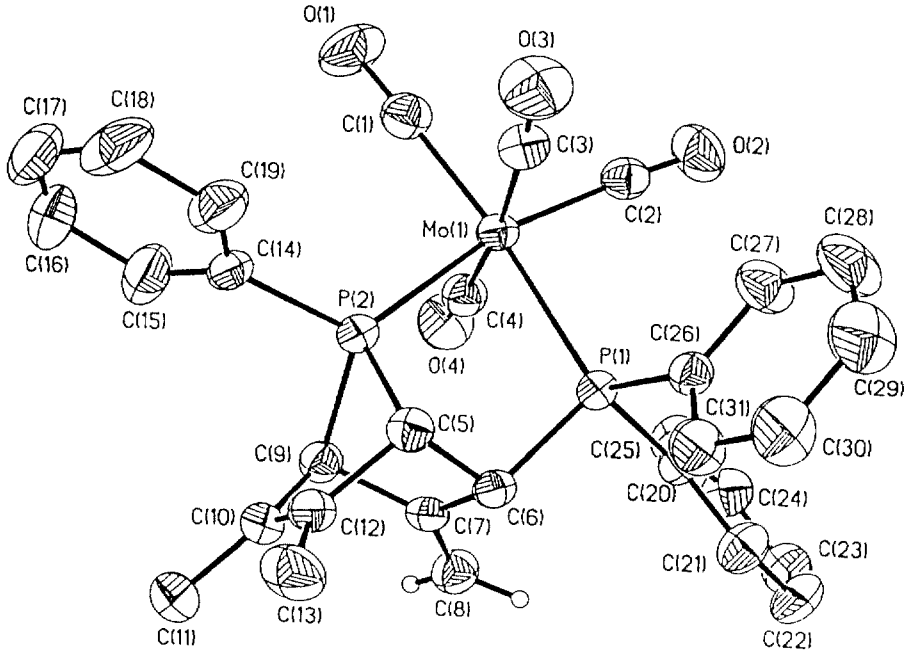


Fig 3. Structural drawing of **5** showing the atom numbering scheme (40% probability ellipsoids). Hydrogen atoms on C(8) have an arbitrary radius of 0.1 Å.

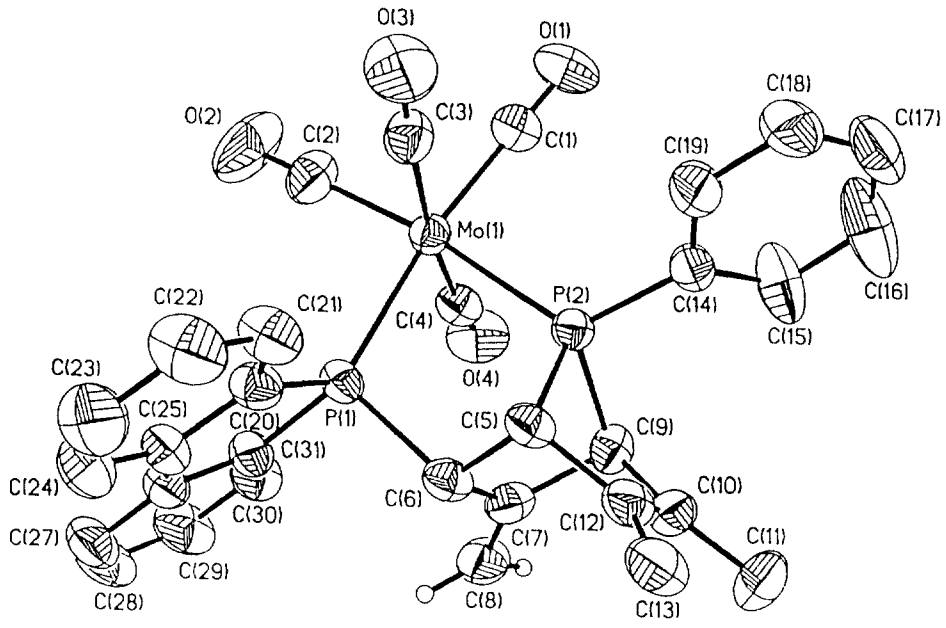


Fig 4. Structural drawing of **6** showing the atom numbering scheme (40% probability ellipsoids). Hydrogen atoms on C(8) have an arbitrary radius of 0.1 Å.

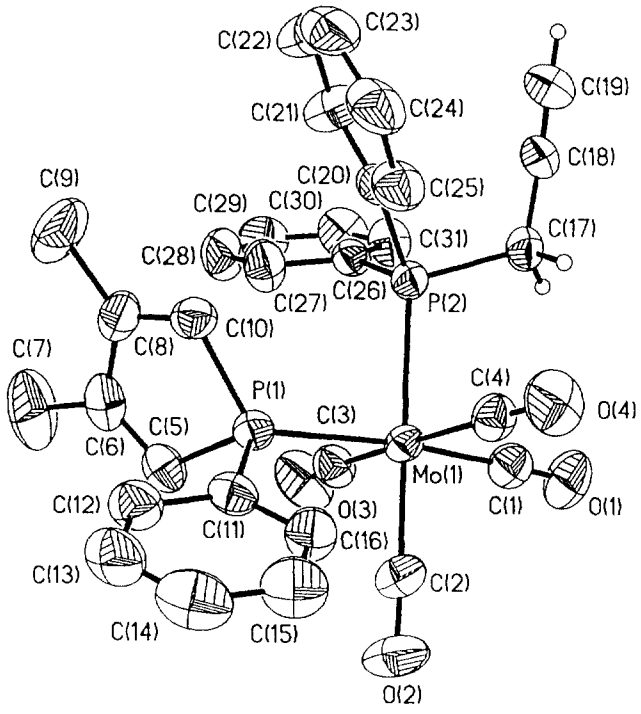


Fig 5. Structural drawing of **3a** showing the atom numbering scheme (40% probability ellipsoids). Hydrogen atoms on C(7) and C(19) have an arbitrary radius of 0.1 Å.

trans orientation of the two axial CO groups. The P1–Mo1–C1 and P2–Mo1–C2 bond angles are 170.68(14)° and 167.85(12)°, 170.5(2)° and 172.0(2)°, 173.5(2)° and 179.7(2)° for **5**, **6** and **3a** respectively, signifying the relative *trans* orientation of the equatorial carbonyls with respect to the two phosphorus atoms. Moreover, for **3a** the P1–Mo1–P2 bond angle value of 95.02(4)° suggests the mutual *cis* orientation of the two phosphine ligands in the molecule. For the chelate diphosphine complexes the P1–Mo1–P2 bite angles are small due to the chelate effect and are 77.22(4)° and 76.72(5)° for **5** and **6** respectively. All the Mo–P bond lengths are in very good agreement with those reported for similar 7-phosphanorbornene-Mo(0) complexes [1b]. The Mo1–P2 bonds are shorter than the Mo1–P1 bonds in complexes **5** and **6** signifying the better donor ability of the 7-phosphanorbornene phosphorus. In contrast, for the *cis* mixed-ligand complex **3a** the Mo1–P1 (2.540(2) Å) bond is slightly longer than the Mo1–P2 (2.5238(13) Å) bond suggesting that diphenylpropargylphosphine is a slightly better donor than DMPP. For all these complexes the Mo–CO bond lengths lie in the normal range. For **3a** the bond distances of 1.463(8) Å for C17–C18, and 1.156(8) Å for C18–C19 confirm the presence of double and triple bonds respectively. Moreover, the C17–C18–C19 bond angle (179.5(6)°) is indicative of sp hybridization at C18 and C19. The bond distances of 1.304(5) Å and 1.316(7) Å in **5** and **6** respectively confirm the presence of the *exo* methylene double bond to the norbornene ring in each case. Similarly, the distances of 1.320(6) Å and 1.319(8) Å in the 7-phosphanorbornene ring between C10 and C12 for **5** and **6** respectively, also suggest the presence of double bonds. For both structures the *exo*-methylene unit is *endo* to the norbornene ring. All the other metrical parameters are unexceptional.

Experimental section

Reagents and physical measurements

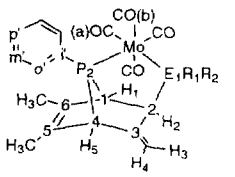
Commercially available, reagent-grade chemicals were used unless otherwise indicated. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk line techniques. Complex **1b**, its isomers **1a**, **1c**, and the mixture of isomers **2a**, **2b**, **2c** [6] and 3,4-dimethyl-1-phenylphosphole (DMPP) [12] were prepared by literature

Table III. Bond distances (Å) and bond angles (°) for complexes **5**, **6** and **3a**.

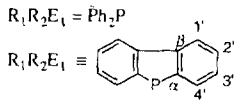
Complexes	**5**	**6**		**3a**
Bond distances (Å)				
Mo1–C1	1.987(5)	1.984(60	Mo1–C1	1.984(6)
Mo1–C2	2.008(5)	1.994(6)	Mo1–C2	1.979(6)
Mo1–C3	2.030(5)	2.035(6)	Mo1–C3	2.058(7)
Mo1–C4	2.024(5)	2.022(6)	Mo1–C4	2.018(6)
Mo1–P1	2.5056(14)	2.4961(14)	Mo1–P1	2.540(2)
Mo1–P2	2.4542(13)	2.4668(14)	Mo1–P2	2.5238(13)
O1–C1	1.146(5)	1.148(6)	O1–C1	1.143(6)
O2–C2	1.136(5)	1.142(7)	O2–C2	1.164(7)
O3–C3	1.140(5)	1.142(7)	O3–C3	1.133(7)
O4–C4	1.142(5)	1.144(6)	O4–C4	1.144(6)
C7–C8	1.304(5)	1.316(7)	P2–C17	1.857(5)
C10–C12	1.320(6)	1.319	C17–C18	1.463(8)
			C18–C19	1.156(8)
Bond angles (°)				
C1–Mo1–C2	97.9(2)	93.5(3)	C1–Mo1–C2	89.7(2)
C1–Mo1–C4	88.1(2)	88.0(2)	C1–Mo1–C4	86.1(2)
C2–Mo1–C4	90.8(2)	88.2(2)	C2–Mo1–C4	91.4(2)
C1–Mo1–C3	85.1(2)	84.2(2)	C1–Mo1–C3	86.5(2)
C2–Mo1–C3	90.2(2)	91.6(2)	C2–Mo1–C3	90.5(2)
C4–Mo1–C3	173.2(2)	172.2(2)	C4–Mo1–C3	172.4(2)
C1–Mo1–P2	94.23(14)	93.9(2)	C1–Mo1–P2	90.0(2)
C2–Mo1–P2	167.85(12)	172.0(2)	C2–Mo1–P2	179.7(2)
C4–Mo1–P2	90.31(13)	89.0(2)	C4–Mo1–P2	88.5(2)
C3–Mo1–P2	90.14(13)	92.2(2)	C3–Mo1–P2	89.6(2)
C1–Mo1–P1	170.68(14)	170.5(2)	C1–Mo1–P1	173.5(2)
C2–Mo1–P1	90.63(12)	96.0(2)	C2–Mo1–P1	85.3(2)
C4–Mo1–P1	95.54(13)	93.2(2)	C4–Mo1–P1	98.2(2)
C3–Mo1–P1	91.14(12)	94.6(2)	C3–Mo1–P1	89.3(2)
P1–Mo1–P2	77.22(4)	76.72(5)	P1–Mo1–P2	95.02(4)
C5–P2–C9	79.8(2)	79.8(2)	C17–C18–C19	179.5(6)

methods. Tetrahydrofuran was distilled under nitrogen from sodium benzophenoneketyl, and diglyme was distilled under nitrogen over sodium. Silica gel for column chromatography (grade 12, 28–200 mesh) was obtained from Aldrich. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Solution infrared spectra were obtained on a Perkin-Elmer Paragon 1000 PC FT spectrometer in sealed CaF_2 cells. $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^1H NMR spectra were recorded at 121.66 (202.35), 75 (125.71) and 300 (499.86) MHz respectively on either a General Electric GN-300 or Varian Unity Plus-500 spectrometer. Proton and carbon chemical shifts are relative to internal Me_4Si, phosphorus chemical shifts are relative to external PPh_3 ($\delta^{31}P = -6.0$ ppm); all shifts to low field (high frequency) are positive.

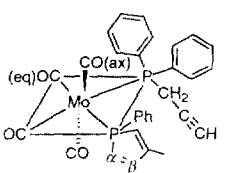
Syntheses and characterization of **5**, **6** *and* **3a**



5: $R_1R_2E_1$ = Ph_2P



6: $R_1R_2E_1$ ≡



3a

• *[2-(Diphenylphosphino)-3-methylene-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]tetracarbonylmolybdenum(0)* **5**

Method a: To a solution of 1.36 g (2.96 mmol) of **1b** in 200 mL of freshly distilled diglyme maintained at 115 °C, 0.56 g (2.96 mmol) of DMPP was added under a nitrogen atmosphere with stirring. The resulting reaction mixture was maintained at this temperature for a period of 4–5 h and followed by the removal of the solvent by vacuum distillation while heating the reaction vessel on a water bath. The reddish yellow oily residue was flash chromatographed through a 3 cm thick celite bed with benzene/hexane (30:70). The solvent was removed under vacuum and the yellow brown oily crude product was purified by column chromatography on silica gel using benzene/hexane solution (10:90). The first few fractions eluted the oxides of the ligands, some unreacted DMPP and trace amounts of **3a**, **7**, **1c**, and **8** as observed by $^{31}P\{^1H\}$ NMR spectroscopy. The concentration of the benzene in the eluant was gradually increased. The 1*H*-phosphole Diels–Alder product was eluted next as a yellow band on the column. The latter was further purified by recrystallization from hot hexane to give pure pale yellow crystals of **5** (1.40 g, 2.26 mmol, 76.4%).

Mp: >194 °C (dec).

IR (CH_2Cl_2): ν_{CO} (cm^{-1}) 2 020 (w), 1 922 (sh), 1 908 (s, b), 1 890 (sh).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.34 MHz) δ 148.53 (d, $^2J(PP)$ = 18.2 Hz, P_2), 47.52 (d, $^2J(PP)$ = 18.2 Hz, P_1).

^1H NMR ($CDCl_3$, 499.85 MHz) δ 7.85–7.35 (m, 15H, Ph), 4.94 (d, $^2J(H_4H_3)$ = 5.0 Hz, 1H, H_4), 3.81

(ddd, ^3J(PH) = 34.5 Hz, ^2J(PH) = 10.0 Hz, $^3J(H_1H_2)$ = 1.5 Hz, 1H, H_2), 3.74 (d, $^2J(H_3H_4)$ = 5.0 Hz, 1H, H_3), 3.45 (dd, ^2J(PH) = 5.0 Hz, $^4J(H_5H_1)$ = 2.0 Hz, 1H, H_5), 3.05 (dd, $^4J(H_1H_5)$ = 2.0 Hz, $^3J(H_1H_2)$ = 1.5 Hz, 1H, H_1), 1.72 (s, 3H, CH_3), 1.59 (d, ^4J(PH) = 1.0 Hz, 3H, CH_3).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.70 MHz) δ 217.78 (dd, ^2J(PC) = 24.2 Hz, ^2J(PC) = 9.9 Hz, $CO_{a,\ eq}$), 215.71 (dd, ^2J(PC) = 25.5 Hz, ^2J(PC) = 7.7 Hz, $CO_{a',\ eq}$), 210.41 (dd, ^2J(PC) = 10.6 Hz, ^2J(PC) = 8.4 Hz, $CO_{b,\ ax}$), 209.01 (apparent t, ^2J(PC) = ^2J(PC) = 8.9 Hz, $CO_{b',\ ax}$), 144.27 (d, ^2J(PC) = 15.08 Hz, C_5), 136.82 (d, ^2J(PC) = 27.3 Hz, C_6), 134.60 (dd, ^2J(PC) = 4.3 Hz, ^2J(PC) = 2.1 Hz, C_3), 134.26 (d, ^2J(PC) = 13.8 Hz, C_o), 133.68 (dd, ^1J(PC) = 24.3 Hz, ^3J(PC) = 4.9 Hz, C_i), 133.30 (dd, ^1J(PC) = 30.7 Hz, ^3J(PC) = 3.7 Hz, C_i), 131.21 (d, ^2J(PC) = 12.2 Hz, $C_{o'}$), 130.80 (d, ^2J(PC) = 10.7 Hz, C_o), 130.60 (dd, ^1J(PC) = 28.2 Hz, ^3J(PC) = 9.4 Hz, $C_{i'}$), 130.30 (d, ^4J(PC) = 2.1 Hz, C_p), 129.61 (d, ^4J(PC) = 1.6 Hz, C_p), 129.48 (s, $C_{p'}$), 128.77 (d, ^3J(PC) = 8.8 Hz, C_m), 128.40 (d, ^3J(PC) = 10.1 Hz, C_m), 128.29 (d, ^3J(PC) = 8.3 Hz, $C_{m'}$), 110.98 (apparent t, ^3J(PC) = ^3J(PC) = 7.7 Hz, $=CH_2$), 63.00 (d, ^1J(PC) = 19.6 Hz, C_4), 56.44 (dd, ^1J(PC) = 22.8 Hz, ^2J(PC) = 12.1 Hz, C_1), 41.51 (dd, ^1J(PC) = 29.7 Hz, ^2J(PC) = 18.5 Hz, C_2), 14.96 (s, CH_3), 13.39 (s, CH_3).

Anal Calc for $C_{31}H_{26}MoO_4P_2$; C, 60.03; H, 4.19. Found: C, 59.88; H, 4.32.

Method b: A solution of 1.51 g (3.28 mmol) of the mixture of the isomers of **1a**, **1b** and **1c** present in the ratio of 3:8:1 in 175 mL of freshly distilled diglyme was reacted with an equimolar amount of DMPP (0.61 g) under a nitrogen atmosphere at 115 °C for 4 h. The solvent was removed by vacuum distillation while heating the reaction vessel on a water bath. The reddish brown oily residue was column chromatographed on silica gel with 10% benzene in hexanes solution. The first few fractions eluted the oxides of the ligands and 0.35 g of the unreacted isomers **1a** and **1c**. The concentration of the benzene in the eluent was gradually increased. The next few fractions eluted a mixture of **3a** and **1a** (about 0.02 g). This was followed by the elution of 0.30 g of an oily mixture comprised of complexes **3a**, **7** and **8** and a trace quantity of the unknown complex **9** (see above). The later fractions eluted 0.39 g of an yellow oil. $^{31}P\{^1H\}$ NMR spectra showed the presence of **5** as the major complex contaminated with some **3a** and **1a** and some decomposition products. Addition of methanol to this oil gave a yellow powdery precipitate. Recrystallization of the latter from hot hexane gave 0.03 g of pure **5**. Complex **3a** (0.19 g, 0.31 mmol) was eluted next and was recrystallized from a 1:1 mixture of methylene chloride and methanol. The last few fractions eluted some more of **1a** and mostly decomposed materials.

- *cis-(Diphenylpropargylphosphine)(3,4-dimethyl-1-phenylphosphole)tetracarbonylmolybdenum(0)* **3a**

Mp: 126–128 °C.

IR (CH_2Cl_2): ν_{CO} (cm^{-1}) 2 024 (w), 1 922 (sh), 1 908 (s, b), 1 882 (sh).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.34 MHz) δ 30.76, 30.58 (^2J(PP) = 24.1 Hz).

^1H NMR ($CDCl_3$, 500 MHz) δ 7.60–7.25 (m, 15H, Ph), 6.15 (d, ^2J(PH) = 35.0 Hz, 2H, H_α), 3.09 (dd, ^2J(PH) = 2.5 Hz, ^4J(HH) = 2.0 Hz, 2H, CH_2), 1.98 (s, 6H, CH_3), 1.94 (apparent t, ^4J(PH) = ^4J(HH) = 2.0 Hz, C≡CH).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.70 MHz) δ 214.45 (dd, ^2J(PC) = 20.1 Hz, ^2J(PC) = 7.9 Hz, CO_{eq}), 214.36 (dd, ^2J(PC) = 26.4 Hz, ^2J(PC) = 7.5 Hz, CO_{eq}), 209.05 (t, ^2J(PC) = 9.0 Hz, CO_{ax}), 148.74 (d, ^2J(PC) = 7.8 Hz, C_β), 136.00 (dd, ^1J(PC) = 29.4 Hz, ^3J(PC) = 1.8 Hz, C_i {PPh_2}), 132.94 (dd, ^1J(PC) = 32.1 Hz, ^3J(PC) = 1.8 Hz, C_i {Ph-DMPP}), 132.08 (m, C_o {PPh_2}), 131.23 (m, C_o {Ph-DMPP}), 130.64 (dd, ^1J(PC) = 34.4 Hz, ^3J(PC) = 2.5 Hz, C_α), 129.71 (s, C_p {PPh_2}), 129.38 (s, C_p {Ph-DMPP}), 128.40 (m, C_m {Ph-DMPP}), 128.22 (m, C_m {PPh_2}), 78.03 (d, ^2J(PC) = 6.7 Hz, $CH_2C{\equiv}CH$), 72.82 (d, ^3J(PC) = 6.2 Hz, $C{\equiv}CH$), 24.65 (dd, ^1J(PC) = 16.0 Hz, ^3J(PC) = 3.4 Hz, PCH_2), 17.24 (d, ^3J(PC) = 9.8 Hz, CH_3).

Anal calc for $C_{31}H_{26}MoO_4P_2$; C, 60.01; H, 4.22. Found: C, 59.78; H, 4.34.

- *[2-(Dibenzophosphol-5-yl)-3-methylene-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]tetracarbonylmolybdenum(0)* **6**

To a solution of 2.00 g (4.35 mmol) of the mixture of isomers of **2a**, **2b** and **2c** present in the ratio 6:9:2 in 200 mL of freshly distilled diglyme maintained between a temperature of 110–115 °C was added 0.82 g (4.35 mmol) of DMPP under a nitrogen atmosphere with stirring. The resulting reaction mixture was then maintained at this temperature for a period of 4–5 h followed by removal of the solvent by vacuum distillation while heating the reaction vessel on a water bath. The reddish brown oily residue was column chromatographed on silica gel with 5% benzene in hexanes solution. The first few fractions eluted the oxides of the ligands and some of the unreacted isomers **2a** and **2c** (~ 0.4 g). The concentration of the benzene in the eluent was gradually increased. The next few fractions eluted a mixture of the complexes as an yellow oil (0.11 g) comprised of **4a**, **4c** (in trace amount), **7**, **10** (in very trace quantity), **8** and some unreacted **2a** as seen from the $^{31}P\{^1H\}$ NMR spectra. The later fractions eluted 0.58 g of an yellow oil which was comprised of a mixture of **6**, **4a** and **4c** in trace amounts accompanied with some decomposition products as noted by $^{31}P\{^1H\}$ NMR spectroscopy. Addition of methanol gave a pale yellow precipitate which was further crystallized from hot hexane to obtain 0.15 g of the 1*H*-phosphole Diels–Alder adduct **6** (0.24 mmol, 5.5%). The last few fractions eluted more of the unreacted isomer **2b**.

Mp: >195 °C (dec).

IR (CH_2Cl_2): ν_{CO} (cm^{-1}) 2 019 (w), 1 928 (sh), 1 905 (s, b), 1 894 (sh).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.66 MHz) δ 151.61 (d, ^2J(PP) = 20.1 Hz, P_2), 39.96 (d, ^2J(PP) = 20.1 Hz, P_1).

^1H NMR ($CDCl_3$, 500 MHz) δ 8.10–7.40 (m, 13H, Ph, DBP), 5.33 (d, $^2J(H_4H_3)$ = 5.5 Hz, 1H, H_4), 4.64 (d, $^2J(H_3H_4)$ = 5.5 Hz, 1H, H_3), 3.55 (dd, ^2J(PH) = 5.5 Hz, $^4J(H_5H_1)$ = 2.0 Hz, 1H, H_5), 3.16 (apparent t, $^3J(H_1H_2)$ = $^4J(H_1H_5)$ = 2.0 Hz, 1H, H_1), 2.50 (ddd, ^3J(PH) = 44.0 Hz, ^2J(PH) = 9.0 Hz, $^3J(H_1H_2)$ = 2.0 Hz, 1H, H_2), 1.55 (s, 3H, CH_3), 1.50 (s, 3H, CH_3).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.70 MHz) δ 215.76 (dd, ^2J(PC) = 24.4 Hz, ^2J(PC) = 9.2 Hz, $CO_{a,\ eq}$), 215.44 (dd, ^2J(PC) = 24.4 Hz, ^2J(PC) = 7.8 Hz, $CO_{a',\ eq}$), 210.35 (dd, ^2J(PC) = 8.6 Hz, ^2J(PC) = 4.3 Hz, $CO_{b,\ ax}$), 210.28 (dd, ^2J(PC) = 8.0 Hz, ^2J(PC) = 4.9 Hz, $CO_{b',\ ax}$), 145.54 (d, ^2J(PC) = 2.0 Hz, C_β), 145.43 (d, ^2J(PC) = 2.0 Hz, C_β), 142.83 (d, ^2J(PC) = 6.0 Hz, C_5), 142.22 (d, ^1J(PC) = 6.0 Hz, C_6), 139.25 (d, ^2J(PC) = 31.0 Hz, $C_{i'}$), 137.01 (dd, ^1J(PC) = 35.1 Hz, ^3J(PC) = 2.9 Hz, C_α), 134.77 (dd, ^2J(PC) = 5.0 Hz, ^2J(PC) = 2.2 Hz, C_3), 133.96 (dd, ^1J(PC) = 24.7 Hz, ^3J(PC) = 5.6 Hz, C_α), 132.81 (d, ^2J(PC) = 14.8 Hz,

Table IV. Crystallographic data for complexes **5**, **6** and **3a**.

Complexes	**5**	**6**	**3a**
Chemical formula	$C_{62.50}H_{52}Mo_2O_9P_4$	$C_{31}H_{24}MoO_4P_2$	$C_{31}H_{26}MoO_4P_2$
Formula weight	1262.80	618.38	620.40
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	11.026(4)	15.361(2)	8.7571(10)
b (Å)	16.400(6)	10.3020(10)	10.0240(12)
c (Å)	16.698(5)	19.273(2)	18.187(2)
α (°)	90.91(3)	90	93.166(8)
β (°)	91.35(3)	110.870(10)	96.481(10)
γ (°)	93.30(3)	90	109.860(9)
V (Å^3)	3012(2)	2849.8(5)	1484.4(3)
Z	2	4	2
ρ calc (g cm^{-3})	1.392	1.44	1.388
μ (mm^{-1})	0.576	0.607	0.582
R_1 $(F)^a$	0.0427	0.0477	0.0518
$_wR_2(F^2)^b$	0.1036	0.1020	0.1153

[a] $R_1(F) = \Sigma||F_0| - |F_c||/\Sigma|F_0|$; [b] $_wR_2(F^2) = [\Sigma[W(F_0^2 - F_c^2)^2]/\Sigma[W(F_0^2)]^2]^{0.5}$.

$C_{4'}$), 131.14 (d, ^4J(PC) = 1.8 Hz, $C_{2'}$), 130.90 (d, ^2J(PC) = 11.1 Hz, $C_{o'}$), 130.63 (d, ^4J(PC) = 1.5 Hz, $C_{2'}$), 130.52 (d, ^2J(PC) = 15.2 Hz, $C_{4'}$), 129.60 (d, ^4J(PC) = 1.0 Hz, $C_{p'}$), 128.45 (d, ^3J(PC) = 8.5 Hz, $C_{m'}$), 128.34 (d, ^3J(PC) = 9.2 Hz, $C_{3'}$), 127.70 (d, ^3J(PC) = 9.8 Hz, $C_{3'}$), 121.63 (d, ^3J(PC) = 4.3 Hz, $C_{1'}$), 121.28 (d, ^3J(PC) = 4.8 Hz, $C_{1'}$), 111.47 (d, ^2J(PC) = 3.0 Hz, $=C(H_3H_4)$), 62.64 (d, ^1J(PC) = 20.1 Hz, C_4), 56.82 (dd, ^1J(PC) = 22.5 Hz, ^2J(PC) = 14.0 Hz, C_1), 45.78 (dd, ^1J(PC) = 29.6 Hz, ^2J(PC) = 14.9 Hz, C_2), 14.87 (s, CH_3), 13.29 (s, CH_3).

Anal Calc for $C_{31}H_{24}MoO_4P_2$: C, 60.23; H, 3.88. Found: C, 60.41; H, 3.69.

X-ray data collection and processing

Pale yellow crystals of **5** and **6** were grown by slow cooling of saturated solutions of the complexes from hot hexane. Pale yellow crystals of **3a** were grown from dichloromethane/methanol (1:1). Suitable crystals were mounted on glass fibers and placed on a Siemens P4 diffractometer. Crystal data and details of data collection are given in table IV. Intensity data were taken in the ω-mode at 298 K with Mo-K_α graphite monochromated radiation (λ = 0.71073 Å). Three check reflections monitored every 100 reflections showed random (<2%) variation during the data collections. The data were corrected for Lorentz, polarization effects and absorption (using an empirical model derived from azimuthal data collections). Scattering factors and corrections for anomalous dispersion were taken from a standard source [13]. Calculations were performed with the Siemens SHELXTL PLUS version 5.03 software package on a personal computer. The structures were solved by direct methods. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were refined at calculated positions with a riding model in which the C–H vector was fixed at 0.96 Å.

Acknowledgment

We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Supplementary material

X-ray characterization data for complexes **5**, **6** and **3a** including tables of experimental details, atomic coordinates, thermal parameters, bond distances and bond angles, anisotropic displacement parameters, hydrogen coordinates, and calculated and observed structure factors have been deposited with the British Library, Document Supply Centre, Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK as Supplementary Publication N° SUP 90476 and is available on request from the Document Supply Centre.

References

1 a) Solujić Lj, Milosavljević EB, Nelson JH, Alcock NW, Fischer J, *Inorg Chem* (1989) 28, 3453
b) Affandi S, Nelson JH, Fischer J, *Inorg Chem* (1989) 28, 4536
c) Bhaduri D, Nelson JH, Day CL, Jacobson RA, Solujić Lj, Milosavljević EB, *Organometallics* (1992) 11, 4069

2 Aw B-H, Hor TSA, Selvaratnam S, Mok KF, White AJP, Williams DJ, Rees NH, McFarlene W, Leung P-H, *Inorg Chem* (1997) 36, 2138 and references therein

3 Nelson JH, In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*, Quin LD, Verkade JG (Eds), VCH, Deerfield Beach, Florida (1994) pp 203–214

4 Maitra K, Catalano VJ, Nelson JH, *J Am Chem Soc* (1997) 119, 12560

5 a) Mathey F, *Chem Rev* (1988) 88, 429 and references cited therein
b) Holand S, Jeanjean M, Mathey F, *Angew Chem Int Ed Engl* (1997) 36, 98

6 Maitra K, Wilson WL, Jemin MM, Yeung C, Rader WS, Redwine KD, Striplin DP, Catalano VJ, Nelson JH, *Syn React Inorg Met Org Chem* (1996) 26, 967

7 Santini CC, Fischer J, Mathey F, Mitschler A, *J Am Chem Soc* (1980) 102, 5809

8 a) Le Goff P, Mathey F, Ricard L, *J Org Chem* (1989) 54, 4754
b) Bevierre MO, Mercier F, Ricard L, Mathey F, *Bull Chim Soc Fr* (1992) 129, 1

9 Bachrach SM, *J Org Chem* (1994) 59, 5027

10 a) Holt MS, Nelson JH, Savignac P, Alcock NW, *J Am Chem Soc* (1985) 107, 6396
b) Rahn JA, Holt MS, Gray GA, Alcock NW, Nelson JH, *Inorg Chem* (1989) 28, 217

11 Garrou PE, *Chem Rev* (1981) 81, 229

12 Brèque A, Mathey F, Savignac P, *Synthesis* (1981) 983

13 *International Tables For X-Ray Crystallography*, Reidel, Boston (1992) Vol C