Intramolecular [4+2] Diels−Alder Cycloaddition of a 2*H*-Phosphole to Coordinated Unsaturated Phosphines, Phospholes, and an Arsine

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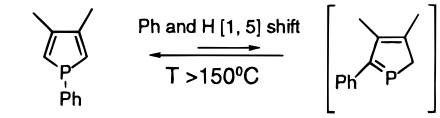
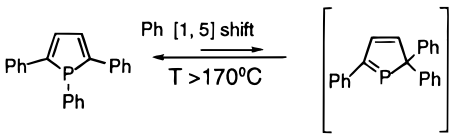
Abstract: Stereoselective [4+2] Diels−Alder cycloadditions occur between unsaturated tertiary phosphine, phosphole, and arsine molybedenum carbonyl complexes, *e.g.*, $(Ph_2E\text{-}trans\text{-}CH_2CH{=}CHCH_3)Mo(CO)_5$ [E = P, As] and 3,4-dimethyl-1-phenylphosphole (DMPP). The coordinated DMPP undergoes a [1,5] phenyl migration at about 145 °C prior to or concomitant with the [4+2] intramolecular cycloaddition reaction with the alkene moiety of the dienophile to produce a new class of conformationally rigid bidentate ligands containing the 1-phosphanorbornene bicyclic ring system. The characteristic ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopic features of these compounds are described. Crystal structures of most of the new compounds are reported.

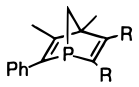
Introduction

The highly efficient and diastereoselective [4+2] Diels−Alder cycloaddition reactions of 1*H*-phospholes with various dienophiles is a classical approach that we have employed to prepare rigid unsymmetrical diphosphines and triphosphines.[1] In addition, asymmetric synthetic modifications of some of these reactions have recently been reported.[2] Mathey and co-workers in the course of their extensive studies relating to the properties and reactivities of phospholes have well established the existence of an equilibrium between 1*H*-phospholes and 2*H*-phospholes at elevated temperature.[3]

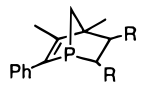




The 2*H*-phospholes appear to be very reactive dienes that undergo facile Diels−Alder cycloaddition reactions with alkynes and alkenes to produce bicyclic systems with phosphorus at the bridgehead, commonly known as the 1-phosphanorbornadiene and 1-phosphanorbornene systems, respectively.[4]



1-phosphanorbornadiene



1-phosphanorbornene

Rhodium complexes of a 2,2′-bis[1-phosphanorbornadienyl] (BIPNOR) ligand have recently been shown[5] to be excellent catalysts for asymmetric hydrogenation of C=C and C=O double bonds. The propensity of the 2*H*-phospholes to undergo [4+2] cycloaddition reactions offers an excellent new synthetic route for α,β-functionalization of 1-phosphanorbornenes and 1-phosphanorbornadienes.

In our laboratory the discovery that 2*H*-phospholes undergo intramolecular [4+2] Diels−Alder cycloadditions *within the coordination sphere of a transition metal* to form 1-phosphanorbornene derivatives, which is unprecedented in the literature, reveals a new aspect relating to the mechanistic pathway involving the reactions of the 2*H*-phospholes. The general question of whether [4+2] Diels−Alder cycloadditions are concerted or stepwise processes is of considerable current interest.[6] In this context, we herein report the reactions of 2,4-dimethyl-1-phenylphosphole (DMPP) at elevated temperatures with *trans*-crotylphosphino and -arsino complexes, $R_2E\text{-}trans\text{-}(CH_2CH{=}CHCH_3)Mo(CO)_5$ [E = As, P], and analogous allyl tertiary phosphine complexes to produce rigid unsymmetrical chiral diphosphines and arsinophosphines having the generic 1-phosphanorbornene bicyclic ring system in their molecular structures.

Results

In order to explore the scope of these reactions we developed a high-yield general synthesis of the crotyl tertiary phosphine complexes (**A** and **B**).[7] The synthesis of an analogous tertiary

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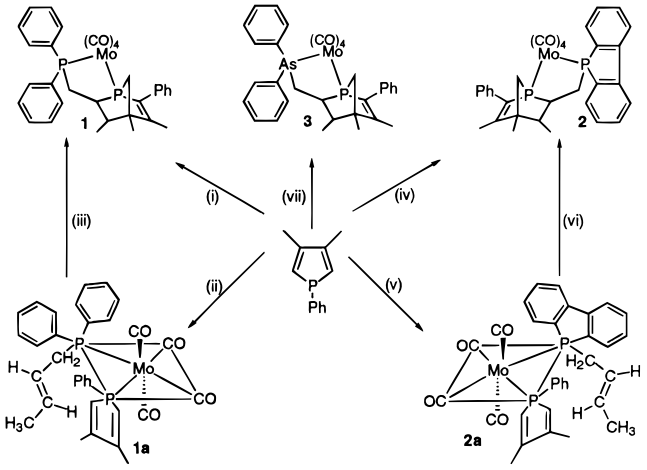
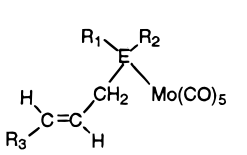
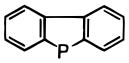
Scheme 1[a]



[a] (i) refluxed in diglyme with complex **A** at ∼150 °C for 5 h; (ii) refluxed in toluene at 110 °C with complex **A** for 8 h; (iii) refluxed in diglyme at ∼150 °C for 4 h; (iv) refluxed in diglyme with complex **B** at ∼150 °C for 4.5 h; (v) refluxed in toluene with complex **B** at 110 °C for 8 h; (vi) refluxed in diglyme at ∼150 °C for 4.5 h; (vii) refluxed in diglyme with complex **C** at ∼150 °C for 5 h.

arsine complex (**C**) is also described here (see Experimental Section). In this case the trans-crotyl complex was contaminated with trace quantities of the *cis* isomer. The reactions of such



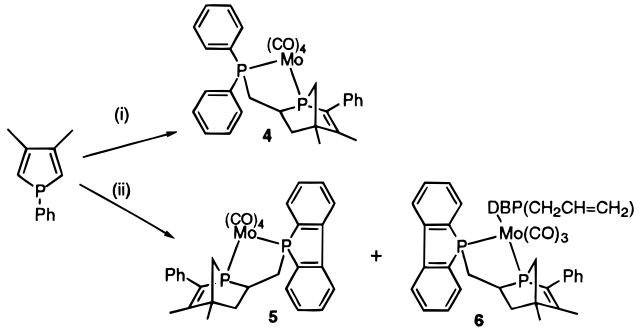
A : E = P, R_1 = R_2 = Ph, R_3 = CH_3;
B : ER_1R_2 = DBP ≡  , R_3 = CH_3;
C : E = As, R_1 = R_2 = Ph, R_3 = CH_3;
D : E = P, R_1 = R_2 = Ph, R_3 = H;
E : ER_1R_2 = DBP, R_3 = H;

trans-crotyl complexes (**A**, **B**, and **C**) with DMPP were conducted in refluxing diglyme. In all cases the changes in the compostion of the reaction mixtures were monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The first step involves the stereospecific formation of the *cis* mixed-ligand complex (*e.g.*, **1a**, **2a**) followed by its conversion into the [4+2] Diels−Alder cycloadduct of the 2*H*-phosphole of DMPP (Scheme 1). The latter is evidenced by the gradual decay of the resonances for the *cis* mixed-ligand complex followed by the growth of those for the products in the $^{31}P\{^1H\}$ NMR spectra. The *cis* mixed-ligand complexes **1a** and **2a** were also synthesized separately by reaction of DMPP with **A** and **B** respectively, in refluxing toluene. Complexes **1a** and **2a** could then be efficiently converted to the 2*H*-phosphole Diels−Alder products (**1** and **2**) in diglyme at ∼150 °C. The reactions in refluxing diglyme proceed to completion in a period of 4−5 h to give a single diastereomer as the major product in high yield. To further generalize these reactions, the allyl tertiary phoshine complexes (**D** and **E**) were reacted with DMPP under the same reaction conditions (Scheme 2). In both cases, the 2*H*-phosphole [4+2] adducts were formed in high yield. For the reaction of the dibenzophosphole- (DBP-) allyl complex **E**, a very minor amount of a triphosphine complex (**6**) was also isolated and was characterized only by $^{31}P\{^1H\}$ NMR spectroscopy and X-ray structure analysis (*vide infra*). The key step is the addition of the phosphole to a refluxing solution of the dienophile in diglyme at 145−150 °C.

Discussion

Phosphorus NMR Spectroscopy. The Diels−Alder products of the 2*H*-phospholes display two resonances in their $^{31}P\{^1H\}$ NMR spectra (Table 1), one for each unique phosphorus. In each case the resonance corresponding to the bridgehead phosphorus is downfield (64−75 ppm), typical for the phosphorus in a 1-phosphanorbornene ring.[4,8] The other resonance occurs in the region (52−55 ppm) typical of a phosphine coordinated to Mo in a five-membered chelate ring.[9] Formation of the [4+2] Diels−Alder adduct from the *cis* mixed-ligand complex is signaled by two significant changes in the $^{31}P\{^1H\}$ NMR spectra. The two resonances for the Diels−Alder adduct both appear downfield of those for the *cis* mixed-ligand complex with $\Delta\delta$ ^{31}P being about 27 and 40 ppm, respectively. The magnitude of ^2J(PP) decreases significantly from about 22 Hz in the *cis* mixed-ligand complexes to about 6 Hz for the Diels−Alder adducts. This is because the two contributions to J(PP) (through the ligand backbone and through the metal) are similar in magnitude and opposite in sign.[10] In these reactions the entering DMPP ligand occupies the site vacated by the departing carbon monoxide, which is *cis* to the other phosphine or arsine ligand already present within the metal coordination sphere. Earlier studies[11] 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 produce chiral bidentate ligands. In all cases when the reactions were monitored 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 2*H*-phosphole adduct. To verify this statement, in two cases the *cis* mixed-ligand intermediates were isolated and/or prepared separately, characterized, and then converted into the

Scheme 2[a]



[a] (i) refluxed in diglyme with complex **D** at ∼150 °C for 5 h; (ii) refluxed in diglyme with complex **E** at ∼150 °C for 4.5 h.

Table 1. 121.6 MHz $^{31}P\{^1H\}$ NMR Data for the Complexes

complex	δ ^{31}P (ppm)	^2J(PP) (Hz)
1a	30.93, 28.55	24.1
1	64.14, 54.58	4.0
2a	28.89, 26.12	21.7
2	66.74, 52.44	7.2
3a	29.60	
3	70.91	
4a	30.85, 27.25	24.6
4	72.74, 55.13	4.2
5a	29.96, 25.34	20.8
5	75.13, 52.19	7.8
6	85.31, 70.70, 26.12	178.9, 45.3, 20.5

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cycloaddition products (Scheme 1). During the conversion processes of **1a** and **2a** to products **1** and **2**, respectively, no resonances due to free phosphole were observed in the $^{31}P\{^1H\}$ NMR spectra. This indicates that there is no appreciable ligand dissociation during the reaction period. It therefore appears that after the formation of the *cis* mixed-ligand complex, at an elevated temperature, the coordinated 1*H*-phosphole rearranges to the 2*H*-phosphole within the metal coordination sphere prior to the [4+2] cycloaddition to produce the highly reactive hot diene. The fact that [1,5] sigmatropic shifts occur for a P-coordinated phosphole has been demonstrated for hydrogen.[12] The reactive coordinated 2*H*-phosphole spontaneously adds to the crotyl unit acting as the dienophile to give the Diels−Alder [4+2] cycloaddition product. So far we have not been able to detect or isolate this short-lived, highly reactive 2*H*-phosphole *cis* mixed-ligand intermediate. The reactions of other dienophiles, such as the allyl tertiary phosphine complexes (**D** and **E**), with DMPP at high temperature led to the formation of the same types of products (Scheme 2). $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixtures for each of these reactions at first showed resonances indicating the formation of the *cis* mixed-ligand complexes **4a** and **5a**, followed by their gradual decay and appearance of the resonances for the [4+2] cyclo adducts **4** and **5** (Table 1). For the reaction of **E** with DMPP, another product **6** was isolated in a trace amount that resulted from the further reaction of **5** with some unreacted DBP-allyl complex present in the reaction mixture, following the substitution of the CO group *trans* to the 1-phosphaphosphorus in **5** by the DBP-allyl unit. The $^{31}P\{^1H\}$ NMR spectrum of **6** showed resonances for three inequivalent phosphorus nuclei at δ 80.31 (dd), 70.70 (dd), and 26.12 ppm (dd) coupled to each other, with the most downfield resonance being for the nonchelated phosphorus of the DBP allyl arm and the higher coupling constant value being for the two mutually *trans* phosphorus nuclei. This manifests the greater *trans* effect of the 1-phosphaphosphorus ligand, which labilizes the *trans* CO bond.

Proton and Carbon NMR Spectroscopy. Proton and carbon chemical shift assignments (see Experimental Section) were accomplished with the aid of a variety of decoupling experiments, attached proton test (APT) spectra, along with correlated (COSY) and heteronuclear correlation (HETCOR) two-dimensional spectra. ^1H nuclear Overhauser effect (NOE) spectra confirmed that these molecules are very rigid and posses the same structures in both the solution and solid states. The ^1H resonance for H_6 is distinct in the spectra of all compounds. Its chemical shift is very sensitive to the substituent on E, moving upfield by more than 1 ppm when Ph_2P is replaced by DBP, due to the diamagnetic sheilding of the DBP ring. The much larger magnitude ^3J(PH) of about 38 Hz than ^2J(PH) of about 11 Hz for H_6 was confirmed by selective phosphorus decoupling experiments. Furthermore, this large coupling constant is also observed for compound **3**, which possesses only the bridgehead phosphorus.

Assignment of the $^{13}C\{^1H\}$ NMR spectra was also aided by the previous assignments for the P-oxo-substituted 1-phosphanorbornene system.[4] The $^{13}C\{^1H\}$ NMR spectra for all complexes display distinct sets of resonances for all the carbonyl carbons respectively *trans* to phosphorus and mutually *trans* to each other. The chemical shifts for the latter carbonyls are usually the more upfield. For the mixed-ligand complexes (**1a** and **2a**) the mutually *trans* carbonyl carbons have the same magnitude for ^2J(PC) to the two *cis* phosphorus atoms, and their resonances therefore appear as apparent triplets. The resonances

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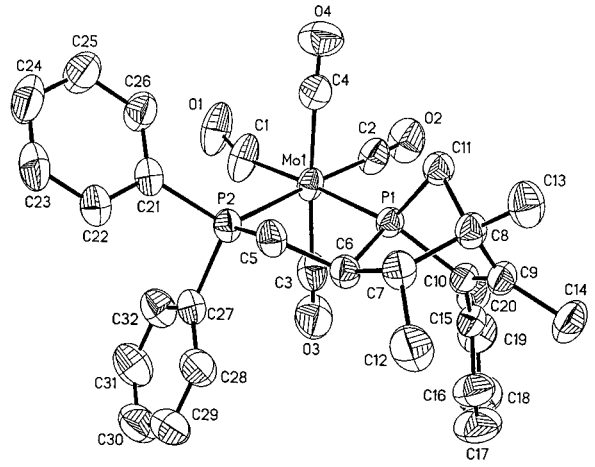


Figure 1. Structural drawing of **1** showing the atom numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

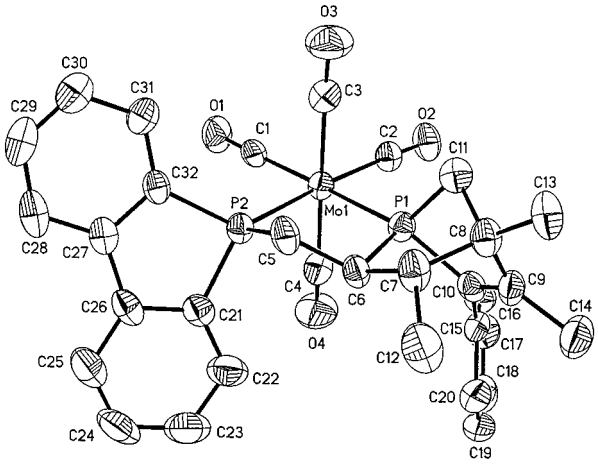


Figure 2. Structural drawing of **2** showing the atom numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

for the carbonyls *trans* to phosphorus appear as doublets of doublets with the larger ^2J(PC) value being to the *trans* phosphorus. The spectra for complexes **1**, **2**, **4**, and **5** show distinct resonances for each carbonyl carbon. For complex **3** all the carbonyl resonances appear as doublets with the larger ^2J(PC) value for the carbonyl *trans* to the phosphorus atom. The two phenyl groups derived from the dienophile phosphine and arsine arm for complexes **1**, **4**, and **3**, respectively, are diastereotopic and give rise to distinct sets of resonances for each carbon type in the phenyl rings. Similarly, the phenyl group emanating from the 2*H*-phosphole, which is now bound to an sp^2-hybridized carbon atom in the 1-phosphanorbornene ring of the product, gives rise to six distinct carbon resonances due to restricted phenyl group rotation. Likewise for complexes **2** and **5** each carbon atom of the DBP ring gives rise to a distinct resonance manifesting the complete lack of symmetry for these compounds.

Crystal Structure Analysis. X-ray crystal structures of these novel ligand complexes **1**−**6** were obtained to gain conclusive support for their structures. These structures are shown in Figures 1−6, respectively. Selected bond distances and angles for **1**−**6** are listed in Table 2. All these complexes exist as discrete molecules with no abnormal intermolecular contacts. Each asymmetric unit of **1** contains two crystallographically inequivalent molecules, which are enantiomers. None of these complexes contains any element of symmetry, and they are therefore chiral. The five-membered chelate rings are rigid for

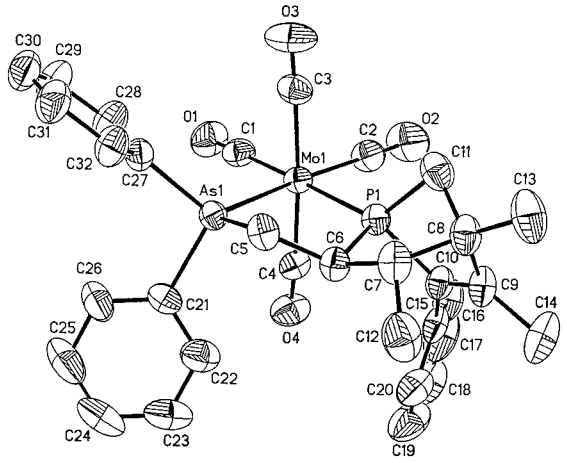


Figure 3. Structural drawing of **3** showing the atom numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

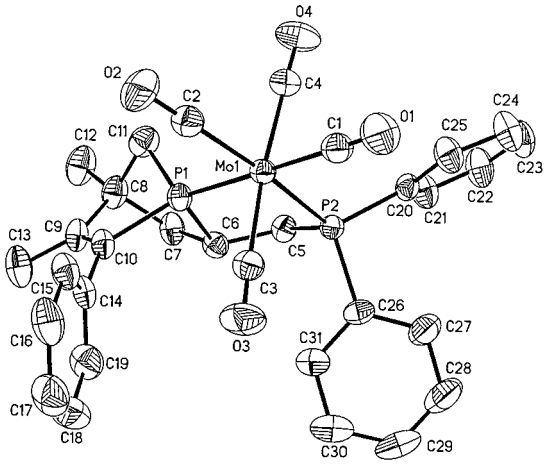


Figure 4. Structural drawing of **4** showing the atom numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

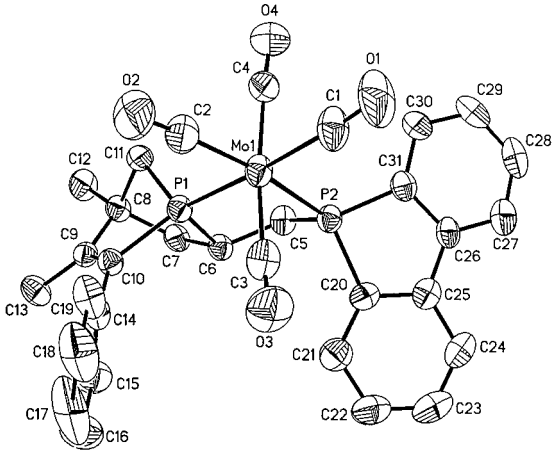


Figure 5. Structural drawing of **5** showing the atom numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

all the structures and are fused to the 1-phosphanorbornene ring at P1 and C6 for **1**−**5** and at P1 and C5 for **6**. The strain in the norbornene ring can be best examined by considering the angles made by the bridgehead carbon, the bridgehead phosphorus P1, and at the bridging carbon C11 for complexes **1**−**5** and C10 for **6**. These values are 97.3(2)°, 97.7(4)°, 97.0(3)°, 97.6(2)°, 97.0(3)°, and 98.1(4)° for complexes **1**−**6**, respectively. For the more commonly known [4+2] Diels−Alder adducts of the

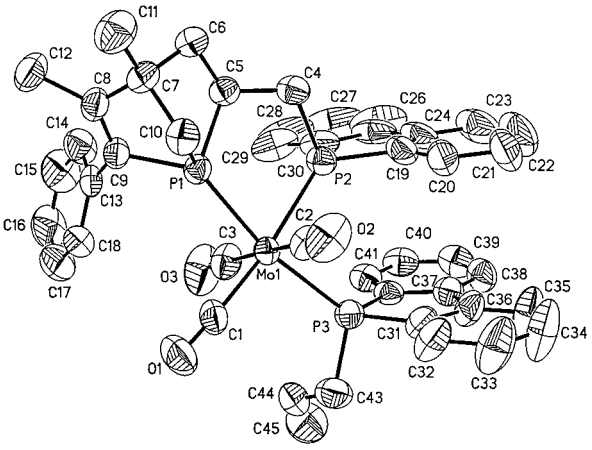


Figure 6. Structural drawing of **6** showing the atom numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

1*H*-phosphole of DMPP that results in the formation of the 7-phosphanorbornene ring with the phosphorus at the bridging position, the values of these angles are smaller, ranging from 79° to 81°.[1b] Hence the ring strain in the 1-phosphanorbornene systems is much reduced compared to the 7-phosphanorbornene ring systems. This highly reduced angle strain in the 2*H*-phosphole Diels−Alder adducts is in part responsible for the extreme upfield shift for the 1-phosphaphosphorus resonance in the $^{31}P\{^{1}H\}$ NMR spectra when compared to similar products of the 1*H*-phosphole of DMPP. For each of these complexes the coordination geometry at the metal center is a distorted octahedron. The equatorial plane is formed by the two phosphorus atoms and the two carbonyl groups *trans* to them for **1**−**5**, and by three phosphorus atoms for **6**, two of which are mutually *trans* and another phosphorus *trans* to a carbonyl. For all the diphosphine complexes the P1−Mo1−P2 angles are small due to the chelate effect and range between 78.49(4)° and 79.21(3)°. In the triphosphine complex **6** for the same reason the angle P1−Mo1−P2 [79.13(5)°] is smaller than the angle P3−Mo1−P2 [90.49(5)°], as P3 is not involved in a chelate ring. That the P1−Mo1−P3 angle is 169.04(5)° in **6** also suggests that P2 and P3 are in a *trans* orientation. The Mo−P bond lengths for **1**−**6** are in very good agreement with those reported for similar types of 7-phosphanorbornene−Mo(0) complexes.[1b] The Mo1−P1 bonds are shorter than the Mo1−P2 bonds in complexes **1**−**6**, signifying the better donor ability of the 1-phosphanorbornene ligand. The Mo−CO bond lengths are in the normal range. The C═C double bond of the norbornene ring in **1**−**5** is localized between C9 and C10 as expected and ranges between 1.337 ± 0.006 and 1.344 ± 0.005 Å. Similarly for **6** the bond distances of 1.341 ± 0.007 and 1.306 ± 0.001 Å between C8 and C9 and C44 and C45 respectively, suggest the presence of double bonds, the latter being for the allyl unit.

Finally, the structures of complexes **1**, **2** and **3** reveal a very important aspect about the mechanism involved for the [4+2] cycloaddition reactions of the 2*H*-phosphole of DMPP toward a dienophile. Conclusively, the cycloaddition reactions for all the crotyl complexes leads to the formation of only one major product with the -CH_2 unit of the crotyl moiety substituted in the *exo* position α to the bridgehead phosphorus. The dihedral angles for C12−C7−C6-C5 are 107.4°, 104.8°, and 99.3° for **1**, **2**, and **3** respectively, and such deviations may be attributed to the strain in the five-membered chelate ring due to ligand variation. For these complexes their molecular structures show that C5 and C12 are in the *exo*, *endo* configuration or rather *trans*-oriented on the 1-phosphanorbornene ring moiety. This

Table 2. Bond Distances and Bond Angles for Complexes **1**−**6**

	complex						
	1	**2**	**3**	**4**	**5**	**6**	
				Bond Distances (Å)			
Mo1−C1	1.984 (4)	1.994 (7)	2.000 (5)	2.005 (4)	1.996 (6)	Mo1−C1	1.968 (7)
Mo1−C2	2.006 (4)	1.987 (7)	1.969 (4)	1.981 (3)	1.995 (6)	Mo1−C2	2.012 (6)
Mo1−C3	2.051 (5)	2.012 (7)	2.040 (4)	2.036 (4)	2.054 (6)	Mo1−C3	2.009 (7)
Mo1−C4	2.029 (5)	2.061 (7)	2.040 (4)	2.048 (4)	1.992 (6)	Mo1−P1	2.402 (2)
Mo1−P1	2.4768 (9)	2.466 (2)	2.4607 (11)	2.4532 (9)	2.4795 (12)	Mo1−P2	2.482 (2)
Mo1−P2/As1	2.5168 (9)	2.496 (2)	2.6027 (6)	2.5348 (8)	2.4984 (13)	Mo1−P3	2.450 (2)
C9−C10	1.344 (5)	1.338 (8)	1.338 (5)	1.343 (5)	1.337 (6)	C8−C9	1.341 (7)
O1−C1	1.16 (2)	1.152 (7)	1.148 (5)	1.146 (4)	1.143 (6)	C44−C45	1.306 (10)
O2−C2	1.133 (5)	1.145 (7)	1.150 (5)	1.150 (4)	1.128 (6)	O1−C1	1.148 (6)
O3−C3	1.127 (6)	1.149 (7)	1.126 (5)	1.139 (4)	1.129 (6)	O2−C2	1.140 (6)
O4−C4	1.137 (5)	1.128 (7)	1.130 (5)	1.130 (4)	1.154 (7)	O3−C3	1.137 (7)
				Bond Angles (deg)			
C2−Mo1−C1	89.9 (2)	93.0 (2)	90.6 (2)	90.07 (13)	92.1 (2)	C1−Mo1−C2	88.9 (3)
C2−Mo1−C3	89.2 (2)	89.1 (3)	91.8 (2)	92.16 (13)	90.0 (2)	C1−Mo1−C3	87.0 (3)
C1−Mo1−C3	90.9 (2)	89.9 (2)	90.0 (2)	86.00 (13)	89.5 (2)	C3−Mo1−C2	175.7 (3)
C2−Mo1−C4	88.3 (2)	89.0 (3)	91.4 (2)	90.84 (13)	91.5 (2)	C1−Mo1−P1	93.2 (2)
C1−Mo1−C4	92.1 (2)	88.9 (2)	87.6 (2)	90.05 (13)	84.2 (2)	C3−Mo1−P1	93.4 (2)
C3−Mo1−C4	176.1 (2)	177.7 (3)	176.0 (2)	175.04 (13)	173.6 (2)	C2−Mo1−P1	85.7 (2)
P1−Mo1−P2/As1	79.21 (3)	79.13 (5)	79.00 (3)	78.69 (3)	78.49 (4)	C1−Mo1−P3	97.1 (2)
C8−C11−P1	97.3 (2)	97.7 (4)	97.0 (3)	97.6 (2)	97.0 (3)	C3−Mo1−P3	90.7 (2)
C12−C7−C6	112.6 (3)	112.7 (6)	111.9 (4)			C2−Mo1−P3	90.9 (2)
						P1−Mo1−P3	169.04 (5)
						C1−Mo1−P2	172.4 (2)
						C3−Mo1−P2	93.3 (2)
						C2−Mo1−P2	90.7 (2)
						P1−Mo1−P2	79.13 (5)
						P3−Mo1−P2	90.49 (5)
						C7−C10−P1	98.1 (4)

clearly indicates that the stereochemistry of the crotyl units in these molecules has been preserved during the [4+2] cycloaddition reaction with the rearranged 2*H*-phosphole unit of DMPP. For a stepwise process such complete retention of orientation of the -CH_3 and the -CH_2 unit of the crotyl moiety would not be likely, and the other diastereomers (*exo*, *exo*/*endo*, *endo*) would have been detected in the product mixture. We may therefore conclude that for all the above discussed complexes **1**−**6**, the metal-promoted [4+2] Diels−Alder cycloaddition of 2*H*-phospholes to the dienophile is most likely a concerted process. The concertedness of the [4+2] cycloadditions of 2*H*-phospholes with acetylene as the dienophile has been established on the basis of theoretical calculations.[13] Moreover, since only one diastereomer was obtained as the major isolated product in all cases, these reactions are highly stereoselective.

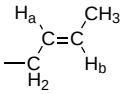
Experimental Section

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. $(RPh_2P)Mo(CO)_5$[7] and (RDBP)-$Mo(CO)_5$,[7] where R = -$CH_2CH{=}CH_2$ or -(*trans*)$CH_2CH{=}CHCH_3$, and 3,4-dimethyl-1-phenylphosphole (DMPP)[14] were prepared by literature methods. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl, 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 Galibraith 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 a Varian Unity Plus-500 spectrometer. Proton and carbon chemical shifts are relative to internal Me_4Si, and phosphorus chemical shifts are relative to external PPh_3 ($\delta^{31}P = -6.0$ ppm); all shifts to low field (high frequency) are positive.

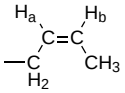
Synthesis of Ph_2As-*trans*-$(CH_2CH{=}CHCH_3)Mo(CO)_5$. To a solution of 5.0 g (16.33 mmol) of $AsPh_3$ in 15 mL of freshly distilled tetrahydrofuran was added 1.0 g (144.1 mmol) of lithium (cut into small flat pieces) under a nitrogen atmosphere with stirring. After 15−20 min, when the solution became deep red, 240 mL of freshly distilled THF was added and the reaction mixture was stirred at ambient temperature for 4 h. During this period, the color of the reaction mixture intensified to a deep orange-brown. The excess lithium was removed under a N_2 purge and disposed of by cautiously reacting it with approximately 300 mL of 95% ethanol. Then 0.73 g (5.44 mmol) of anhydrous $AlCl_3$ was added to the reaction mixture.[15] (**Caution**: the reaction of the $AlCl_3$ with phenyllithium is vigorous; white fumes may result.) The reaction mixture was stirred for 15 min and then 4.32 g (16.36 mmol) of $Mo(CO)_6$ was added under a N_2 purge. Effervescence was detected and the solution turned bright red-orange. The reaction mixture was stirred at ambient temperature for 1−2 h until the effervescence ceased, followed by the addition of 1.5 molar equiv of *trans*-crotyl chloride. The reaction mixture immediately paled in color. The mixture was allowed to stir at ambient temperature for about 30 min, followed by the addition of 100 mL of 1 M HCl and 100 mL of hexane. The contents of the reaction flask were then transferred to a 1 L separatory funnel and the aqueous layer was removed and discarded. To the organic phase was added 50 mL of ether, and the solution was washed with two 100 mL portions of 1 M HCl followed by two 100 mL portions of H_2O. The organic phase was dried with anhydrous magnesium sulfate and filtered by suction through 80 mL of silica gel covered with 2 cm of Celite in a 200 mL fritted glass funnel. The silica gel was washed with 200 mL of ether and the combined solvents were removed from the filtrate by rotary evaporation using a water bath that was initially at ambient temperature and gradually heated to 95−100 °C; the flask containing the product was left on the rotary evaporator until the unreacted $Mo(CO)_6$ had sublimed. The flask was allowed to cool and was removed from the rotary evaporator. The crude product was a viscous oil that solified to a gray-white solid when left at −20 °C for 6−8 h. The crude product was purified by column chromatography on silica gel with hexane as

(13) Bachrach, S. M. *J. Org. Chem.* **1994**, *59*, 5027.
(14) Brèque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983.
(15) Holand, S.; Mathey, F.; Fischer, J. *Polyhedron* **1986**, *5*, 1413.

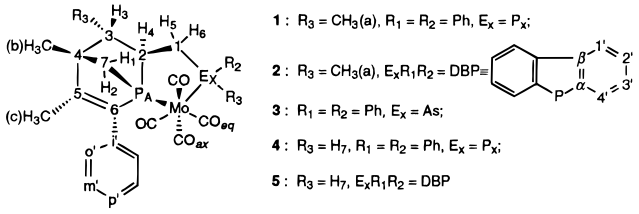
eluant. Several attempts were made to separate the *cis* and *trans* isomers by column chromatography or fractional crystallization without any success. Product was obtained (6.92 g, 13.30 mmol, 81.4%) that was shown by ^{1}H NMR spectroscopy to be a 3.33:1 mixture of the *trans* and *cis* isomers.



C (*trans*): Gray-white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.3−7.5 (m, 10 H, Ph), 5.45 [dqt, $^3J(H_bH_a)$ = 15.50 Hz, $^3J(H_bCH_3)$ = 6.5 Hz, $^4J(H_bCH_2)$ = 1.00 Hz, 1 H, H_b], 5.25 [apparent dt, $^3J(H_aH_b)$ = 15.50 Hz, $^3J(H_aCH_2)$ = 7.75 Hz, $^4J(H_aCH_3)$ = 1.50 Hz, 1 H, H_a], 3.06 [ddq, $^3J(CH_2H_a)$ = 7.75 Hz, $^4J(CH_2H_b)$ = $^5J(CH_2CH_3)$ = 1.00 Hz, 2 H, CH_2), 1.60 [ddt, $^3J(CH_3H_b)$ = 6.5 Hz, $^4J(CH_3H_a)$ = 1.5 Hz, $^5J(CH_3CH_2)$ = 1.0 Hz, 3 H, CH_3]. ^{13}C{^{1}H} NMR ($CDCl_3$, 125.71 MHz) δ 210.58 (s, CO_{trans}), 205.56 (s, 4CO_{cis}), 136.92 (s, C_i), 131.87 (s, C_o), 131.45 (s, C═*C*CH_3), 129.76 (s, C_p), 128.9 (s, C_m), 122.43 (s, C═*C*CH_2), 34.83 (s, CH_2), 17.97 (s, CH_3).



C (cis): Gray-white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.3−7.5 (m, 10 H, Ph), 5.58 [dqt, $^3J(H_bH_a)$ = 11.0 Hz, $^3J(H_bCH_3)$ = 7.0 Hz, $^4J(H_bCH_2)$ = 1.5 Hz, 1 H, H_b], 5.42 [dtq, $^3J(H_aH_b)$ = 11.0 Hz, $^3J(H_aCH_2)$ = 8.0 Hz, $^4J(H_aCH_3)$ = 1.5 Hz, 1 H, H_a], 3.12 [apparent dt, $^3J(CH_2H_a)$ = 8.0 Hz, $^4J(CH_2H_b)$ = $^5J(CH_2CH_3)$ = 1.00 Hz, 2 H, CH_2], 1.28 [ddt, $^3J(CH_3H_b)$ = 7.0 Hz, $^4J(CH_3H_a)$ = 1.5 Hz, $^5J(CH_3CH_2)$ = 1.0 Hz, 3 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.71 MHz) δ 210.54 (s, CO_{trans}), 205.52 (s, 4CO_{cis}), 136.83 (s, C_i), 133.07 (s, CH_3C═C), 131.92 (s, C_o), 129.78 (s, C_p), 128.9 (s, C_m), 121.48 (s, C═*C*CH_2), 29.63 (s, CH_2), 12.65 (s, CH_3).



Syntheses and Characterization of [4+2] Cycloadducts: (A) [2-Phenyl-3,4,5-trimethyl-6-methylene(diphenylphosphino)-1-phosphabicyclo[2.2.1]hept-2-ene]tetracarbonylmolybdenum(0) (Complex 1). (Method a) To a solution of 2.50 g (5.25 mmol) of **A** in 200 mL of freshly distilled diglyme maintained at 135 °C, was added 0.99 g (5.25 mmol) of DMPP under a nitrogen atmosphere with stirring. The temperature of the resulting reaction mixture was then maintained between 145 and 150 °C for a period of 4−5 h. This was followed by the removal of the solvent by vacuum distillation by heating the reaction vessel on a water bath. The reddish-brown oily residue was column-chromatographed on silica gel with benzene−hexane (10:90). The first few fractions eluted the oxides of the ligands and some unreacted starting materials. The concentration of the benzene in the eluant was gradually increased. The *cis* mixed-ligand tetracarbonyl complex **1a** (0.83 g, 1.57 mmol, 29.9%) was eluted next, followed by the 2*H*-phosphole Diels−Alder adduct **1** (1.5 g, 2.36 mmol, 45.0%). The latter was further purified by recrystallization from hot hexane.

(Method b) Complex **1a** (0.895 g, 1.41 mmol) was dissolved in 100 mL of freshly distilled diglyme and refluxed at 150 °C for 4 h under a nitrogen atmosphere. The solvent was then removed by vacuum distillation while the reaction vessel was warmed in a water bath. The residue left behind was dark brown in color and was flash-chromatographed through a bed of silica covered with Celite, using 50% benzene in hexane as the eluant. Removal of the solvent by rotary evaporation afforded an orange oil that was further purified by column chromatography on silica gel, with 20% benzene in hexane solution as the eluant. The recovered yellow oil was crystallized from hot hexane to obtain 0.66 g (0.103 mmol, 73.5%) of pale yellow crystals of **1**. Mp > 166−168 °C (decomp). IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2022 (w), 1922 (sh), 1908 (s, b), 1886 (sh). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.66 MHz) δ 64.14 [d, ^2J(PP) = 4.0 Hz, P_A], 54.58 [d, ^2J(PP) = 4.0 Hz, P_x). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.64−7.06 (m, 15 H, Ph), 3.33 [dddd, ^3J(PH) = 38.5 Hz, ^2J(PH) = 11.0 Hz, $^2J(H_5H_6)$ = 11.0 Hz, $^3J(H_4H_6)$ = 3.5 Hz, 1 H, H_6], 2.03 [d, $^2J(H_1H_2)$ = 11.50 Hz, 1 H, H_2], 1.87 [d, ^4J(PH) = 1.5 Hz, 3 H, $CH_{3(c)}$], 1.78 [qd, $^3J(CH_{3(a)}H_3)$ = 7.0 Hz, ^3J(PH) = 5.0 Hz, 1 H, H3], 1.63 [dd, $^2J(H_2H_1)$ = 11.5 Hz, ^2J(PH) = 4.0 Hz, 1 H, H_1], 1.43 (s, 3 H, $CH_{3(b)}$), 1.42−1.34 (m, 2 H, H_4 and H_5), 1.14 [d, $^3J(H_3CH_{3(a)})$ = 7.0 Hz, 3 H, $CH_{3(a)}$]. ^{13}C{^{1}H} NMR ($CDCl_3$, 125.70 MHz) δ 217.05 [dd, ^2J(PC) = 25.5 Hz, ^2J(PC) = 8.0 Hz, CO_{eq}], 216.85 [dd, ^2J(PC) = 27.4 Hz, ^2J(PC) = 9.1 Hz, CO_{eq}], 209.79 [dd, ^2J(PC) = 10.0 Hz, ^2J(PC) = 8.1 Hz, CO_{ax}], 207.13 [dd, ^2J(PC) = 10.1 Hz, ^2J(PC) = 8.8 Hz, CO_{ax}], 152.84 [d, ^2J(PC) = 3.5 Hz, $C_{i'}$], 139.49 [dd, ^1J(PC) = 22.9 Hz, ^3J(PC) = 3.1 Hz, C_6], 136.98 [d, ^1J(PC) = 29.7 Hz, C_i], 136.76 [dd, ^1J(PC) = 33.2 Hz, ^3J(PC) = 3.7 Hz, C_i], [135.55 [d, ^2J(PC) = 15.5 Hz, C_5], 132.39 [d, ^2J(PC) = 12.8 Hz, C_o], 130.59 [d, ^2J(PC) = 12.3 Hz, C_o], 129.92 [d, ^4J(PC) = 2.0 Hz, C_p], 129.55 (s, $C_{m'}$), 129.25 (s, $C_{m'}$), 129.38 [d, ^4J(PC) = 1.6 Hz, C_p], 128.51 [d, ^3J(PC) = 9.6 Hz, C_m], 128.49 [d, ^3J(PC) = 8.9 Hz, C_m], 128.30 (s, $C_{o'}$), 128.24 (s, $C_{o'}$), 128.23 (s, $C_{o'}$), 127.09 [d, ^5J(PC) = 1.8 Hz, $C_{p'}$], 61.09 [d, ^2J(PC) = 1.1 Hz, C_4], 50.72 [d, ^1J(PC) = 25.4 Hz, C_7], 48.75 [apparent t, ^1J(PC) = ^2J(PC) = 17.2 Hz, C_2], 47.84 [dd, ^2J(PC) = 14.7 Hz, ^3J(PC) = 2.3 Hz, C_3], 35.53 [dd, ^1J(PC) = 22.3 Hz, ^2J(PC) = 14.6 Hz, C_1], 19.90 [d, ^3J(PC) = 7.9 Hz, $CH_{3(c)}$], 17.61 [d, ^3J(PC) = 3.5 Hz, $CH_{3(b)}$], 16.13 [dd, ^3J(PC) = 5.9 Hz, ^4J(PC) = 1.1 Hz, $CH_{3(a)}$]. Anal. Calcd for $C_{32}H_{30}MoO_4P_2$:, C, 60.41; H, 4.72. Found: C, 60.47; H, 4.82.

[2-Phenyl-3,4,5-trimethyl-6-methylene(dibenzophosphole)-1-phosphabicyclo[2.2.1]hept-2-ene]tetracarbonylmolybdenum(0) (Complex 2). (Method a) A solution of 5.39 g (11.37 mmol) of **B** in 200 mL of freshly distilled diglyme maintained at 135 °C was reacted with 2.14 g (11.37 mmol) of DMPP under the same reaction conditions as mentioned for complex **1**, method a. The reddish-brown oily residue that was left after removal of the solvent was column-chromatographed on silica gel with benzene−hexane (10:90). The concentration of benzene in the eluant was gradually increased. The first few fractions eluted the oxides of the ligands and some unreacted pentacarbonyl complex followed by the elution of the 2*H*-phosphole Diels−Alder product **2**. Crystallization from hot hexane gave 5.75 g (9.06 mmol, 79.7%) of pale yellow crystals of pure **2**.

(Method b) (1.00 g, 1.58 mmol) Complex **2a** was reacted in the same way as described in method b for complex **1**. Purification of the crude product and crystallization following the same strategy gave 0.58 g (0.92 mmol, 57.8%) of pure pale yellow crystals of **2**. Mp > 210−212 °C (decomp). IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2023 (w), 1931 (sh), 1907 (s). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.66 MHz) δ 66.74 [d, ^3J(PP) = 7.2 Hz, P_A], 52.44 [d, ^3J(PP) = 7.2 Hz, P_X]. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.9−7.1 (m, 13 H, DBP, Ph), 2.24 [dddd, ^3J(PH) = 38.5 Hz, ^2J(PH) = 11.5 Hz, $^2J(H_5H_6)$ = 11.5 Hz, $^3J(H_4H_6)$ = 4.3 Hz, 1 H, H_6], 2.13 [d, $^2J(H_1H_2)$ = 11.6 Hz, 1 H, H_2], 1.94 [d, ^4J(PH) = 1.5 Hz, 3 H, $CH_{3(c)}$], 1.75 [dd, $^2J(H_2H_1)$ = 11.6 Hz, ^2J(PH) = 3.8 Hz, 1 H, H_1], 1.68 (qd, $^3J(CH_{3(a)}H_3)$ = 6.6 Hz, ^3J(PH) = 5.0 Hz, 1 H, H_3], 1.46 (s, 3 H, $CH_{3(b)}$), 1.40−1.35 (m, 2 H, H_4 and H_5), 1.02 [d, $^3J(H_3CH_{3(a)})$ = 6.6 Hz, 3 H, $CH_{3(a)}$]. ^{13}C{^{1}H} NMR ($CDCl_3$, 125.71 MHz) δ 216.63 [dd, ^2J(PC) = 24.9 Hz, ^2J(PC) = 8.8 Hz, CO_{eq}], 215.16 [dd, ^2J(PC) = 27.2 Hz, ^2J(PC) = 8.0 Hz, CO_{eq}], 209.72 [dd, ^2J(PC) = 10.4 Hz, ^2J(PC) = 8.2 Hz, CO_{ax}], 207.62 [apparent t, ^2J(PC) = ^2J(PC) = 9.3 Hz, CO_{ax}], 152.64 [d, ^2J(PC) = 3.8 Hz, $C_{i'}$], 142.18 [d, ^2J(PC) = 6.4 Hz, C_β], 141.84 [d, ^2J(PC) = 6.3 Hz, C_β], 140.16 [d, ^1J(PC) = 33.6 Hz, C_α], 139.78 [dd, ^1J(PC) = 25.6 Hz, ^3J(PC) = 3.3 Hz, C_6], 139.52 [dd, ^1J(PC) = 39.5 Hz, ^3J(PC) = 4.3 Hz, C_α], 135.58 [d, ^2J(PC) = 15.0 Hz, C_5], 130.53 [d, ^4J(PC) = 1.6 Hz, $C_{2'}$], 130.31 [d, ^4J(PC) = 1.1 Hz, $C_{2'}$], 129.77 [d, ^2J(PC) = 15.5 Hz, $C_{4'}$], 129.75 (s, $C_{m'}$), 129.71 (s, $C_{m'}$), 129.68 [d, ^2J(PC) = 16.0 Hz, $C_{4'}$], 128.63 [d, ^3J(PC) = 10.1 Hz, $C_{3'}$], 128.54 (s, $C_{o'}$), 127.83 [d, ^3J(PC) = 9.7 Hz, $C_{3'}$], 127.41 [d, ^5J(PC) = 1.5 Hz, $C_{p'}$], 121.59 [d, ^3J(PC) = 4.3 Hz, $C_{1'}$], 121.13 [d, ^3J(PC) = 4.8 Hz, $C_{1'}$], 61.33 [d, ^2J(PC) = 1.0 Hz, C_4], 50.80 [d, ^1J(PC) = 26.2 Hz, C_7], 48.44 [apparent t, ^1J(PC) = ^2J(PC) = 17.7 Hz, C_2], 47.39 [dd, ^2J(PC) = 15.5 Hz, ^3J(PC) = 1.6 Hz, C_3], 38.33 [dd, ^1J(PC) = 19.7 Hz, ^2J(PC) = 14.5 Hz, C_1], 19.91 [d, ^3J(PC) = 7.5 Hz, $CH_{3(c)}$], 17.49 [d, ^3J(PC)

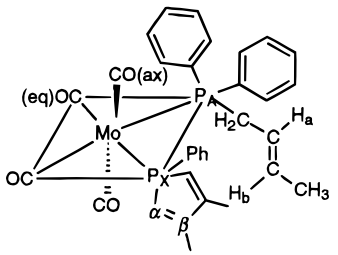
= 3.8 Hz, $CH_{3(b)}$], 16.20 [d, ^3J(PC) = 5.9 Hz, $CH_{3(a)}$]. Anal. Calcd for $C_{32}H_{28}MoO_4P_2$: C, 60.60; H, 4.41. Found: C, 60.46; H, 4.27.

[2-Phenyl-3,4,5-trimethyl-6-methylene(diphenylarsino)-1-phosphabicyclo[2.2.1]hept-2-ene]tetracarbonylmolybdenum(0) (Complex 3). Compound **C** (2.43 g, 4.67 mmol) was reacted with 0.88 g (4.67 mmol) of DMPP following the same reaction conditions and procedure as mentioned earlier in method a. The crude product was purified by column chromatography on silica gel with a 10:90 benzene−hexane mixture. Oxides of the ligands and unreacted pentacarbonyl complexes were eluted first. On increasing the concentration of benzene in the eluant gradually to 20−25%, complex **3** was eluted and was obtained as a pale yellow oil on removal of the solvents. Crystallization from hot hexane gave 1.96 g (2.88 mmol, 61.7%) of pale yellow crystals of **3**. Mp >184−185 °C (decomp). IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2024 (w), 1924 (sh), 1911 (s, b), 1886 (sh). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.66 MHz) δ 70.91. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.6−7.1 (m, 15 H, Ph), 3.28 [ddd, ^3J(PH) = 38.0 Hz, $^2J(H_5H_6)$ = 12.0 Hz, $^3J(H_4H_6)$ = 6.0 Hz, 1 H, H_6], 2.03 [dd, $^2J(H_1H_2)$ = 12.0 Hz, ^2J(PH) = 1.0 Hz, 1 H, H_2], 1.85 [d, ^4J(PH) = 1.0 Hz, 3 H, $CH_{3(c)}$), 1.74 [qd, $^3J(CH_{3(a)}H_3)$ = 6.8 Hz, ^4J(PH) = 5.0 Hz, 1 H, H_3], 1.61 [dd, $^2J(H_1H_2)$ = 12.0 Hz, ^2J(PH) = 3.8 Hz, 1 H, H_1], 1.43 (s, 3 H, $CH_{3(b)}$), 1.36−1.20 (m, 2 H, H_4 and H_5), 1.12 [d, $^3J(H_3CH_{3(a)})$ = 6.8 Hz, 3 H, $CH_{3(a)}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.70 MHz) δ 217.64 [d, ^2J(PC) = 8.8 Hz, CO_{eq}], 216.63 [d, ^2J(PC) = 27.5 Hz, CO_{eq}], 209.05 [d, ^2J(PC) = 10.1 Hz, CO_{ax}], 207.46 [d, ^2J(PC) = 10.1 Hz, CO_{ax}], 153.08 [d, ^2J(PC) = 3.6 Hz, $C_{i'}$], 139.78 [d, ^1J(PC) = 23.1 Hz, C_6], 137.61 [d, ^3J(PC) = 4.9 Hz, C_i], 137.24 (s, C_i), 135.75 [d, ^2J(PC) = 15.5 Hz, C_5], 132.06 (s, C_o), 130.98 (s, C_o), 129.72 (s, C_p), 129.60 (s, $C_{m'}$), 129.57 (s, $C_{m'}$), 129.47 (s, C_p), 128.90 (s, C_m), 128.82 (s, C_m), 128.30 (s, $2C_{o'}$), 127.16 [d, ^5J(PC) = 1.8 Hz, $C_{p'}$], 61.13 [d, ^2J(PC) = 0.8 Hz, C_4], 50.72 [d, ^1J(PC) = 25.4 Hz, C_7], 48.27 (s, C_3), 47.50 [d, ^1J(PC) = 16.1 Hz, C_2], 33.27 [d, ^2J(PC) = 15.0 Hz, C_1], 19.91 [d, ^3J(PC) = 7.8 Hz, $CH_{3(c)}$], 17.57 [d, ^3J(PC) = 3.8 Hz, $CH_{3(b)}$], 16.17 [d, ^3J(PC) = 6.0 Hz, $CH_{3(a)}$]. Anal. Calcd for $C_{32}H_{30}AsMoO_4P$: C, 56.51; H, 4.41. Found: C, 56.38; H, 4.53.

[2-Phenyl-3,4-dimethyl-6-methylene(diphenylphosphino)-1-phosphabicyclo[2.2.1]hept-2-ene]tetracarbonylmolybdenum(0) (Complex 4). Compound **D** (2.19 g, 4.74 mmol) was reacted with 0.89 g (4.74 mmol) of DMPP under the same reaction conditions as mentioned in method a earlier. By employing the same purification and crystallization techniques, 1.30 g (2.09 mmol, 44.10%) of pale yellow crystals of **4** was obtained. Mp > 164−166 °C (decomp). IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2022 (w), 1924 (sh), 1909 (s, b), 1886 (sh). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.66 MHz) δ 72.74 [d, ^2J(PP) = 4.2 Hz, P_A], 55.13 [d, ^2J(PP) = 4.2 Hz, P_x]. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.64−7.10 (m, 15H, Ph), 3.27 [dddd, ^3J(PH) = 39.0 Hz, $^2J(H_5H_6)$ = 14.0 Hz, ^2J(PH) = 11.0 Hz, $^3J(H_4H_6)$ = 4.5 Hz, 1 H, H_6], 1.92 (m, 2 H, H_3 and H_4), 1.91 [d, $^2J(H_1H_2)$ = 11.5 Hz, 1 H, H_2], 1.81 [d, ^4J(PH) = 2.0 Hz, 3 H, $CH_{3(c)}$], 1.51 [dd, $^2J(H_2H_1)$ = 11.5 Hz, ^2J(PH) = 3.5 Hz, 1 H, H_1], 1.49 (m, 1 H, H_7), 1.47 (s, 3 H, $CH_{3(b)}$), 1.39 (m, 1 H, H5). $^{13}C\{1H\}$ NMR ($CDCl_3$, 125.70 MHz) δ 216.92 [dd, ^2J(PC) = 25.6 Hz, ^2J(PC) = 8.8 Hz, CO_{eq}], 216.84 [dd, ^2J(PC) = 27.3 Hz, ^2J(PC) = 8.9 Hz, CO_{eq}], 209.76 [dd, ^2J(PC) = 10.1 Hz, ^2J(PC) = 8.0 Hz, CO_{ax}], 207.73 [dd, ^2J(PC) = 9.9 Hz, ^2J(PC) = 8.9 Hz, CO_{ax}], 154.04 [d, ^2J(PC) = 3.6 Hz, $C_{i'}$], 138.60 [dd, ^1J(PC) = 22.2 Hz, ^3J(PC) = 3.4 Hz, C_6], 137.04 [d, ^1J(PC) = 29.7 Hz, C_i], 136.75 [dd, ^1J(PC) = 33.3 Hz, ^3J(PC) = 3.6 Hz, C_i], 135.52 [d, ^2J(PC) = 15.3 Hz, C_5], 132.37 [d, ^2J(PC) = 12.9 Hz, C_o], 130.66 [d, ^2J(PC) = 12.3 Hz, C_o, 129.92 [d, ^4J(PC) = 2.0 Hz, C_p], 129.39 [d, ^4J(PC) = 1.8 Hz, C_p], 129.29 (s, $C_{m'}$), 129.26 (s, $C_{m'}$), 128.48 [d, ^3J(PC) = 9.6 Hz, C_m], 128.46 [d, ^3J(PC) = 9.1 Hz, C_m], 128.21 (s, $C_{o'}$), 128.20 (s, $C_{o'}$), 127.06 [d, ^5J(PC) = 1.9 Hz, $C_{p'}$], 58.60 [d, ^2J(PC) = 1.4 Hz, C_4], 48.45 [d, ^1J(PC) = 24.6 Hz, C_7], 41.80 [dd, ^1J(PC) = 18.3 Hz, ^2J(PC) = 4.2 Hz, C_2], 39.60 [dd, ^2J(PC) = 15.2 Hz, ^3J(PC) = 2.6 Hz, C_3], 36.45 [dd, ^1J(PC) = 22.9 Hz, ^2J(PC) = 14.3 Hz, C_1], 21.20 [d, ^3J(PC) = 7.5 Hz, $CH_{3(c)}$], 12.93 [d, ^3J(PC) = 6.0 Hz, $CH_{3(b)}$]. Anal. Calcd for $C_{31}H_{28}MoO_4P_2$: C, 59.84; H, 4.50. Found: C, 59.71; H, 4.63.

[2-Phenyl-3,4-dimethyl-6-methylene(dibenzophosphole)-1-phosphabicyclo[2.2.1]hept-2-ene]tetracarbonylmolybdenum(0) (Complex 5). Compound **E** (2.64 g, 4.92 mmol) was reacted with an equimolar amount of DMPP under the same reaction conditions as mentioned above. The crude product mixture was purified in the same manner using the same solvent system. The first few fractions eluted oxides of the ligand and a trace quantity of unreacted starting material **E**. With increasing benzene concentration in the eluant, **5** was eluted next, followed by a trace amount of the triphosphine complex **6**. The latter was crystallized from hot hexane to give only a few platelike yellow crystals. Complex **5** was recrystallized from hot hexane to give 1.00 g (1.61 mmol, 33%) of pale yellow crystals of the pure product. Mp >220 °C (decomp). IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2022 (w), 1930 (sh), 1906 (s, b), 1894 (sh). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.66 MHz) δ 75.13 [d, ^2J(PP) = 7.8 Hz, P_A], 52.19 [d, ^2J(PP) = 7.8 Hz, P_x]. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.9−7.18 (m, 13 H, DBP and Ph), 2.16 [dddd, ^3J(PH) = 39.5 Hz, $^2J(H_5H_6)$ = 14.0 Hz, ^2J(PH) = 12.0 Hz, $^3J(H_4H_6)$ = 5.8 Hz, 1 H, H_6], 2.02 [d, $^2J(H_1H_2)$ = 12.0 Hz, 1 H, H_2], 1.88 [d, ^4J(PH) = 1.5 Hz, 3 H, $CH_{3(c)}$], 1.86−1.80 (m, 2 H, H_3 and H_4), 1.63 [dd, $^2J(H_2H_1)$ = 12.0 Hz, ^2J(PH) = 3.5 Hz, 1 H, H_1], 1.49 (s, 3 H, $CH_{3(b)}$), 1.42−1.34 (m, 2 H, H_5 and H_7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.71 MHz) δ 216.49 [dd, ^2J(PC) = 24.9 Hz, ^2J(PC) = 8.80 Hz, CO_{eq}], 215.13 [dd, ^2J(PC) = 27.3 Hz, ^2J(PC) = 8.2 Hz, CO_{eq}], 209.70 [dd, ^2J(PC) = 10.3 Hz, ^2J(PC) = 8.0 Hz, CO_{ax}], 207.69 [apparent t, ^2J(PC) = ^2J(PC) = 9.5 Hz, CO_{ax}], 153.81 [d, ^2J(PC) = 3.6 Hz, $C_{i'}$], 142.21 [d, ^2J(PC) = 6.4 Hz, C_β], 141.84 [d, ^2J(PC) = 6.4 Hz, C_β], 140.25 [d, ^1J(PC) = 33.9 Hz, C_α], 139.51 [dd, ^1J(PC) = 39.6 Hz, ^3J(PC) = 4.4 Hz, C_α], 138.82 [dd, ^1J(PC) = 21.9 Hz, ^3J(PC) = 3.1 Hz, C_6], 135.52 [d, ^2J(PC) = 15.3 Hz, C_5], 130.54 [d, ^4J(PC) = 1.8 Hz, $C_{2'}$], 130.33 [d, ^4J(PC) = 1.15 Hz, $C_{2'}$], 129.72 [d, ^2J(PC) = 15.7 Hz, $C_{4'}$], 129.70 [d, ^2J(PC) = 16.2 Hz, $C_{4'}$], 129.53 (s, $C_{m'}$), 129.49 (s, $C_{m'}$), 128.64 [d, ^3J(PC) = 10.3 Hz, $C_{3'}$], 128.51 (s, $C_{o'}$), 128.50 (s, $C_{o'}$), 127.77 [d, ^3J(PC) = 9.6 Hz, $C_{3'}$], 127.39 [d, ^5J(PC) = 1.8 Hz, $C_{p'}$], 121.60 [d, ^3J(PC) = 4.4 Hz, $C_{1'}$], 121.34 [d, ^3J(PC) = 4.8 Hz, $C_{1'}$], 58.87 [d, ^2J(PC) = 1.3 Hz, C_4], 48.58 [d, ^1J(PC) = 25.0 Hz, C_7], 41.58 [dd, ^1J(PC) = 19.3 Hz, ^2J(PC) = 16.8 Hz, C_2], 39.28 [dd, ^1J(PC) = 20.0 Hz, ^2J(PC) = 14.0 Hz, C_1], 39.15 [dd, ^2J(PC) = 16.2 Hz, ^3J(PC) = 2.2 Hz, C_3], 21.22 [d, ^3J(PC) = 7.5 Hz, $CH_{3(c)}$], 13.03 [d, ^3J(PC) = 6.2 Hz, $CH_{3(b)}$]. Anal. Calcd for $C_{31}H_{26}MoO_4P_2$: C, 60.03; H, 4.19. Found: C, 59.87; H, 4.03.

Syntheses and Characterization of Complexes 1a and 2a: *cis*-(*trans*-crotyldiphenylphosphine)(1-phenyl-3,4-dimethylphosphole)-tetracarbonylmolybdenum(0) (Complex 1a). To a solution of 5.20 g (10.92 mmol) of **A** in 200 mL of freshly distilled toluene was added 2.1 g (10.92 mmol) of DMPP under a nitrogen atmosphere with stirring. The resulting reaction mixture was refluxed at 110 °C for 8 h. It was cooled to ambient temperature and the solvent was removed by vacuum distillation. The resulting oily brown-yellow residue was column-chromatographed on silica gel with benzene−hexane (5:95). The oxide of DMPP was eluted first followed by some of the unreacted pentacarbonyl complex. The *cis*-mixed-ligand tetracarbonyl complex was eluted next and obtained as a yellow oil after removal of the solvent. It was further purified by recrystallization from a mixture of 1:1 methylene chloride and methanol to give 4.00 g (6.30 mmol, 57.7%) of pale yellow crystals of **1a**.



Mp >145−147 °C (decomp). IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2020 (w), 1912 (s, b), 1876 (sh). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.66 MHz) δ 30.93 [d, ^2J(PP) = 24.1 Hz, P_A], 28.55 [d, ^2J(PP) = 24.1 Hz, P_x]. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.42−7.28 (m, 15 H, Ph), 6.10 [d, ^2J(PH) = 35.5 Hz, 2 H, H_α], 5.16 (m, 2 H, H_a and H_b), 2.98 (m, 2 H, CH_2), 1.97 (s, 6 H, CH_3 of DMPP), 1.49 (m, 3 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.70 MHz) δ 215.02 [dd, ^2J(PC) = 17.0 Hz, ^2J(PC) = 8.7 Hz, CO_{eq}], 214.82 [dd, ^2J(PC) = 21.9 Hz, ^2J(PC) = 8.7 Hz, CO_{eq}], 209.24 [apparent t, ^2J(PC) = 9.1 Hz, $2CO_{ax}$], 148.53 [d, ^2J(PC) = 7.9 Hz, C_β], 137.14 [dd, ^1J(PC) = 28.7 Hz, ^3J(PC) = 1.1 Hz, C_i], 133.12 [dd, ^1J(PC) = 32.4 Hz, ^3J(PC) = 1.1 Hz, C_i], 132.43 [d, ^2J(PC) = 6.2 Hz, C_o], 131.29

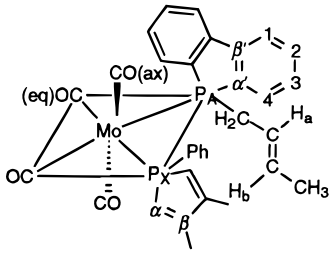
Table 3. Crystallographic Data for Complexes **1**−**6**

	complex					
	1	**2**	**3**	**4**	**5**	**6**
chemical formula	$C_{64}H_{60}Mo_2O_8P_4$	$C_{32}H_{28}MoO_4P_2$	$C_{32}H_{30}AsMoO_4P$	$C_{31}H_{28}MoO_4P_2$	$C_{31}H_{26}MoO_4P_2$	$C_{45}H_{39}MoO_3P_3$
formula weight	1272.88	634.42	680.39	622.41	620.40	816.61
crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a (Å)	10.0576 (14)	17.341 (3)	10.132 (2)	9.757 (2)	9.2723 (9)	11.8832 (13)
b (Å)	14.316 (2)	9.347 (2)	10.946 (2)	10.9580 (10)	23.242 (2)	16.924 (2)
c (Å)	22.726 (3)	18.195 (4)	13.985 (2)	13.7321 (12)	13.2746 (12)	20.059 (2)
α (deg)	79.692 (12)	90	91.289 (10)	92.740 (6)	90	90
β (deg)	85.132 (10)	91.866 (9)	93.890 (10)	91.883 (9)	92.848 (7)	94.108 (9)
γ (deg)	71.609 (11)	90	91.586 (13)	92.047 (10)	90	90
V (Å^3)	3053.4 (8)	2947.6 (10)	1546.4 (5)	1464.7 (3)	2857.3 (4)	4023.8 (8)
Z	2	4	2	2	4	4
ρ_{calcd} (g cm^{-3})	1.384	1.430	1.461	1.411	1.442	1.348
μ (mm^{-1})	0.568	0.588	1.571	0.590	0.605	0.484
min and max trans	0.9558, 0.8561		0.9309, 0.6189	0.7993, 0.7349	0.8758, 0.8444	0.7697, 0.7297
data/restrnt/params	13909/0/721	3849/0/352	5392/0/361	3826/0/343	5016/0/352	5247/0/469
GOF(F^2)[a]	1.052	1.016	1.037	1.028	1.052	1.030
$R_1(F)$[b]	0.0496	0.0478	0.0367	0.0281	0.0493	0.0488
$wR_2(F^2)$[c]	0.1422	0.0916	0.0883	0.0749	0.1065	0.0961

[a] GOF $= S = [\sum[w(F_o^2 - F_c^2)^2]/(n-p)]^{0.5}$. [b] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]^2]^{0.5}$.

[d, ^2J(PC) = 11.7 Hz, C_o], 130.69 [d, ^1J(PC) = 35.1 Hz, C_α], 130.62 [d, ^3J(PC) = 10.8 Hz, C═*C*CH$_3$], 129.25 (s, C_p), 129.24 (s, C_p), 128.34 [d, ^3J(PC) = 9.3 Hz, C_m], 128.03 [d, ^3J(PC) = 8.5 Hz, C_m], 122.47 [d, ^2J(PC) = 3.0 Hz, C═*C*CH$_2$), 37.41 [dd, ^1J(PC) = 19.4 Hz, ^3J(PC) = 2.0 Hz, CH_2], 17.97 [d, ^4J(PC) = 0.9 Hz, CH_3 of crotyl], 17.19 [dd, ^3J(PC) = 9.9 Hz, ^5J(PC) = 1.4 Hz, CH_3 of DMPP].

***cis*-(*trans*-Crotyldibenzophosphole)(1-phenyl-3,4-dimethylphosphole)tetracarbonylmolybdenum(0) (Complex 2a).** To a solution of 2.60 g (5.65 mmol) of **B** in 150 mL of freshly distilled toluene was added 1.06 g (5.65 mmol) of DMPP under a nitrogen atmosphere; the mixture was reacted under the same reaction conditions as described above. Purification of the crude product by the above method gave 2.8 g (4.41 mmol, 78.1%) of **2a** as a pale yellow viscous oil.



IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2020 (w), 1920 (sh), 1908 (s, b), 1882 (sh). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.66 MHz) δ 29.89 [d, ^2J(PP) = 21.7 Hz, P_A], 26.12 [d, ^2J(PP) = 21.7 Hz, P_x]. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.8−6.9 (m, 13 H, DBP and Ph), 5.74 [d, ^2J(PH) = 36.5 Hz, 2 H, $H_{\alpha'}$], 5.07 (m, 2 H, H_a and H_b), 2.67 (m, 2 H, CH_2), 1.68 (s, 6 H, CH_3 of DMPP), 1.43 (m, 3 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.70 MHz) δ 214.84 [dd, ^2J(PC) = 20.6 Hz, ^2J(PC) = 8.9 Hz, CO_{eq}], 213.53 [dd, ^2J(PC) = 24.8 Hz, ^2J(PC) = 8.4 Hz, CO_{eq}], 209.23 [apparent t, ^2J(PC) = ^2J(PC) = 9.4 Hz, $2CO_{ax}$], 148.38 [d, ^2J(PC) = 8.0 Hz, C_β], 142.37 [d, ^2J(PC) = 5.2 Hz, $C_{\beta'}$], 140.32 [d, ^1J(PC) = 34.2 Hz, $C_{\alpha'}$], 132.88 [dd, ^1J(PC) = 33.9 Hz, ^3J(PC) = 2.1 Hz, C_i], 130.70 [d, ^2J(PC) = 11.6 Hz, C_o], 130.30 [d, ^2J(PC) = 15.2 Hz, C_4], 130.01 [d, ^3J(PC) = 10.2 Hz, C═*C*CH$_3$], 129.73 [d, ^4J(PC) = 1.3 Hz, C_2], 129.39 [dd, ^1J(PC) = 33.7 Hz, ^2J(PC) = 2.5 Hz, C_α], 128.85 [d, ^4J(PC) = 2.0 Hz, C_p], 128.06 [d, ^3J(PC) = 9.4 Hz, C_m], 127.78 [d, ^3J(PC) = 9.7 Hz, C_3], 122.25 [d, ^2J(PC) = 6.9 Hz, C═*C*CH$_2$), 120.96 [d, ^3J(PC) = 4.2 Hz, C_1], 39.37 [dd, ^1J(PC) = 17.0 Hz, ^3J(PC) = 4.2 Hz, CH_2], 17.70 [d, ^4J(PC) = 2.6 Hz, CH_3 of crotyl], 17.07 [d, ^3J(PC) = 10.1 Hz, CH_3 of DMPP].

X-ray Data Collection and Processing. Pale yellow crystals of **1**−**6** were grown by slow cooling of saturated solutions of the complexes from hot hexane. Suitable crystals were mounted on glass fibers and placed on a Siemens P4 diffractometer. Crystal data and details of data collection for complexes **1**−**6** are given in Table 3. Intensity data were taken in the ω-mode at 298K with Mo-K$_\alpha$ graphite monochromated radiation (λ = 0.710 73 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), except for **2**, where no absorption correction was applied. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[16] 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.

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Supporting Information Available: X-ray characterization data for complexes **1**−**6**, including tables of experimental details, atomic coordinates, thermal parameters, bond distances and bond angles, anisotropic displacement parameters, and hydrogen coordinates (42 pages). See any current masthead page for ordering and Internet access instructions.

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(16) *International Tables For X-ray Crystallography*, D. Reidel Publishing Co., Boston, MA, 1992; Vol. C.