Preparation, Properties, and Reactions of Metal-Containing Heterocycles, XCI[◇]

Insertion of Activated Alkynes and Sulfur into the P–P Bond of Diphosphamolybdacyclopropanes☆

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The insertion of the alkynes ZC≡CZ (**2a–i**) [Z = CO_2R: R = Me (**a**), Et (**b**), *n*Pr (**c**), *i*Pr (**d**), *n*Bu (**e**), *t*Bu (**f**), *neo*-Pent (**g**), *cyc-Hex* (**h**); Z = CF_3 (**i**)] into the P^1-P^2 bond of the diphosphamolybdacyclopropane $(\eta^5\text{-}C_5H_5)(OC)_2\overline{Mo-P^1Ph_2-P^2}Mes$ (**1**) (Mes = 2,4,6-trimethylphenyl) results in the formation of the diphosphamolybdacyclopentenes $(\eta^5\text{-}C_5H_5)(OC)_2\text{-}\overline{Mo-P^1Ph_2-CZ=CZ-P^2}Mes$ (**3a–i**). According to an X-ray structural analysis, **3a** crystallizes in the space group $P2_1/c$ with the mesityl function at P^2 and the cyclopentadienyl fragment at the metal atom on the opposite side of the planar five-membered ring. The same orientation is found in solution by NMR experiments (NOE; 2D ^1H, ^{13}C HETCOR). Kinetic investigations confirm that the rate constants decrease in the sequence R = Me > Et > *n*Pr > *iso*Prop > Cy > *n*Bu > *neo*-Pent > *t*Bu. The second-order reaction and the strongly negative activation entropy which was determined in the case of the reaction **1** + **2e** → **3e** are consistent with a nucleophilic attack of P^2 at one of the triply bonded carbon atoms of the alkyne. The reaction of **3a**, **h** with sulfur affords the diastereomeric compounds $(\eta^5\text{-}C_5H_5)(OC)_2\overline{Mo-P^1Ph_2-CZ=CZ-P^2}(S)Mes$ (**4a**, **h**). An X-ray structural analysis of the heterocycle **4h**, which crystallizes in the space group $P\bar{1}$, shows the presence of the enantiomeric pair SR/RS. The reaction of **1** with alkynes is hindered if this heterocycle is oxidized by sulfur to give $(\eta^5\text{-}C_5H_5)(OC)_2\text{-}\overline{Mo-P^1Ph_2-P^2}(S)Mes$ (**5**). Further reaction of **5** with sulfur leads to the ring-expanded heterocyclic intermediate $(\eta^5\text{-}C_5H_5)(OC)_2\overline{Mo-P^1Ph_2-S-P^2(S)Mes-S}$ (**6**) which crystallizes in the space group $P\bar{1}$. The five-membered ring in **6** has an envelope conformation. Upon thermally induced cleavage of the P^2S_2Mes fragment from **6** the three-membered ring $(\eta^5\text{-}C_5H_5)(OC)_2\overline{Mo-P^1Ph_2-S}$ (**7**) is formed as the final product.

The transition metal-catalyzed or -mediated cyclooligomerization of alkynes with heteroalkynes offers a well developed method for the preparation of four- and six-membered organic heterocycles[2,3]. Recently, it could be demonstrated that the P=S group in thiaphosphametallacyclopropanes behaves like a heteroalkyne because of similar covalent radii and comparable electronegativities of the phosphorus and sulfur atom[4]. It is therefore suitable for a metal-mediated cyclo-cotrimerization with alkynes. Starting from the three-membered heterocycles $\overline{[M]-PR_2=S}$, we obtained regiospecifically substituted thiophenes[5], phosphole complexes[6], and furans[7], respectively, which are obtained by oxidative or hydrolytic degradation of the resulting metallabicycloheptadienes. The latter were formed via the intermediately occurring thiaphosphametallacyclopentadienes which could be isolated[8].

Between sulfur and the PR fragment exists an isolobal relation. Meanwhile we are able to make accessible heterocycles of the type $\overline{[M]-PR_2^1-PR^2}$[9,10]. Since the $[R_2PS]^-$ and $[R_2^1PPR^2]^-$ systems exhibit similar structural features, we were interested in the question whether the phosphorus analog also displays alkyne-like properties. In principle, an alkyne may be inserted into the $Mo-PR_2^1$, $Mo-PR^2$ or into the $R_2^1P-PR^2$ bond of the above-mentioned three-membered heterocycle. In a communication[11] lately we reported on the insertion of dimethyl acetylenedicarboxylate into the P–P bond of the molybdacycle $\overline{[Mo]-PPh_2-P}Ar$ {[Mo] = $(\eta^5\text{-}C_5H_5)Mo(CO)_2$; Ar = 2,4,6-$(t\text{Bu})_3C_6H_2$}. In this article we describe the behavior of disphosphamolybdacyclopropanes toward electron-poor alkynes containing carboxylate residues with different steric demand. To get an insight into the course of this reaction we carried out kinetic investigations and examined also the reaction between diphosphamolybdacyclopropanes and sulfur.

Results and Discussion

1) Preparation and Characterization of the Diphosphamolybdacyclopentenes 3a–i and Sulfuration of 3a,h

The hitherto unknown yellow and thermally stable starting compound **1** (Scheme 1) was obtained according to its congeners by the reaction sequence $H[Mo]P^1Ph_2H \xrightarrow{n\text{BuLi}} Li_2\{[Mo]P^1Ph_2\} \xrightarrow{MesPCl_2} \mathbf{1}$[9,10] {[Mo] = $(\eta^5\text{-}C_5H_5)Mo(CO)_2$}. In the $^{31}P\{^1H\}$-NMR spectrum of **1** one observes the expected two doublets with a coupling constant of $^1J_{PP}$ = 537 Hz which indicates a direct P^1-P^2 bond. The monomeric composition of **1** was confirmed by a field-desorption mass spectrum.

[◇] Part XC: Ref.[1].

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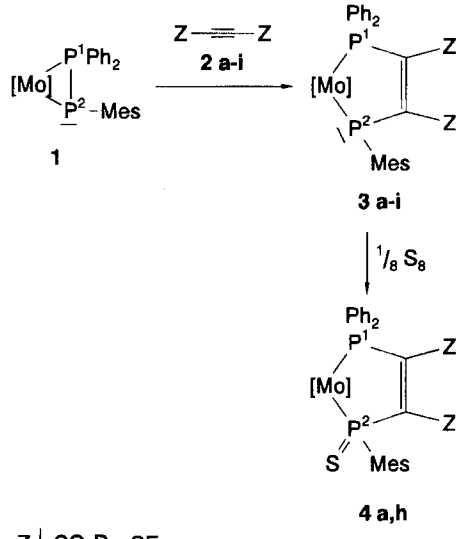
The addition of the dialkyl acetylenedicarboxylates **2a–h** and of hexafluoro-2-butyne (**2i**) to the three-membered heterocycle **1** in THF at ambient temperature was accompanied by a color change from yellow to deep red and resulted in the formation of the novel diphosphamolybdacyclopentenes **3a–i** (Scheme 1). The rather stable heterocycles **3a–i** were purified by column chromatography and dissolve readily in polar organic solvents.

Scheme 1



Z	CO_2R	CF_3
	a-h	i

R	Me	Et	Pr	*i*Pr	Bu	*t*Bu	*neo*-Pent	*cyc*-Hex
	a	b	c	d	e	f	g	h

[Mo] = $(\eta^5\text{-}C_5H_5)Mo(CO)_2$ Mes = 2,4,6-$Me_3C_6H_2$

In the field-desorption mass spectra the molecular peak is in favor of the expected composition of the five-membered heterocycles. Two absorptions in the 5 μm region of the IR spectra of **3a–i** are indicative of two *cis*-positioned terminal carbonyl groups. Compared to **1** both ^{31}P doublets are shifted to lower field in the $^{31}P\{^1H\}$-NMR spectra of **3a–i** and the P^1-P^2 coupling constants are decreased to an average value of 17 Hz. This finding is in agreement with an insertion of the alkyne into the P–P bond of the heterocycle **1**. In addition to the mutual splitting of the two phosphorus resonances further interaction of P^1 and P^2 with one and two CF_3 groups causes a quartet of doublets and a quartet of quartets of doublets in the $^{31}P\{^1H\}$-NMR spectrum of **3i**, respectively. The long-range interaction of ($^4J_{PF}$) P^2 with CF_3 could also be established in the ^{19}F-NMR spectrum. The ^{31}P, ^{13}C, and ^1H chemical shifts and the IR data are independent of the steric demand of the organic substituents attached to the olefinic carbon atoms.

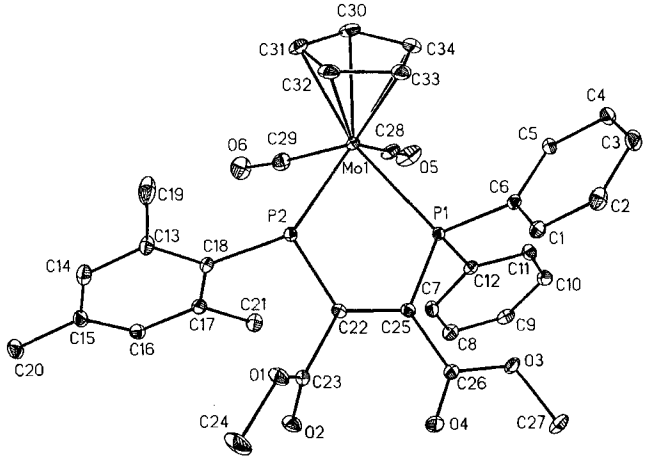
In the $^{13}C\{^1H\}$-NMR spectra of the heterocycles **3a–h** two doublets of doublets are observed between δ = 183–185 and 107–112 whereas only multiplets are found for **3i** caused by additional C–F couplings. Based on the order of magnitude of the $^1J_{PC}$ and $^2J_{PC}$ coupling constants and on DEPT135 experiments these signals are attributed to both ring carbon atoms. Selective ^{31}P decoupling investigations enable the assignment of the high-field resonance to the ring carbon atom which is adjacent to the PMes group. In the alkane region the two *ortho* and the *para* methyl carbon atoms of the mesityl group give rise to three resonances indicating a hindered rotation about the P–C bond. Remarkably, the one at lower field is split into a doublet. Unfortunately, solutions of the compounds **3a–h** begin to decompose above 50 °C. Therefore, it was not possible to carry out variable-temperature $^{13}C\{^1H\}$-NMR measurements to calculate the energy barrier of the hindered rotation about the P–C(Mes) axis.

The fact that the two *ortho*-positioned methyl groups of the mesityl fragment show a different coupling behavior with P^2 can be explained by their position with respect to the lone pair of P^2[12]. The C13–C18 bond and the lone pair of P2 of compound **3a** (Figure 1) are oriented *syn* leading to a significant coupling ($^3J_{PC}$ = 22.9 Hz) between C19 and P2. On the other hand, a singlet is observed for C21 due to the *anti* position of the C17–C18 bond and the lone pair of P^2. The signal of the CH_3 group in the ^1H-NMR spectrum which has been assigned by the aid of a 2D $^1H,^{13}C$ HETCOR experiment to the protons attached at C19 produces a weak positive NOE effect on the cyclopentadienyl protons. No NOE effect on the protons at C21 is observed. This is in agreement with a closer proximity of the $C(19)H_3$ group to the cyclopentadienyl fragment than the $C(21)H_3$ group. This orientation of C19 leads to the conclusion that the mesityl group and the cyclopentadienyl fragment are located on opposite sides of the planar five-membered heterocycle as shown also by an X-ray study of **3a**. The other possible diastereomer (analogous to those depicted in Scheme 3) with the two groups on the same side of the five-membered ring was not observed on the basis of NMR spectroscopic investigations in solution.

The structure of the heterocycle **3a** was confirmed by an X-ray structural analysis (Figure 1). The five-membered ring containing the atoms Mo1, P1, P2, C22, and C25 adopts a planar geometry. The influence of the lone pair of P2 leads to notable differences at the two phosphorus atoms. Bond distances of Mo1–P2 and P2–C22 are shorter than those of Mo1–P1 and P1–C25. The angle P2–C22–C25 is 121.5(2)°, while the angle P1–C25–C22 is reduced to 115.5(2)°. The dihedral angle between the mesityl plane and the plane of the five-membered ring is 70.3°.

The sequence of the reactions of the three-membered heterocycle **1** with the alkynes **2a–i** may be rationalized by a nucleophilic attack of the phosphorus atom P^2 at one of the triply bonded carbon atoms of the alkyne as the first step (Scheme 2)[13]. This is paralleled by the known reaction of tertiary phosphanes with the easily polarizable dialkyl acetylenedicarboxylates[14]. This Lewis basic behavior of P^2 has already been demonstrated by the addition of organometallic Lewis acids of the type $M(CO)_5$–THF (M = Cr, Mo, W)[9]. The polar intermediate **A** is immediately stabilized by an insertion of the alkyne into the P^1-P^2 bond of **1** with

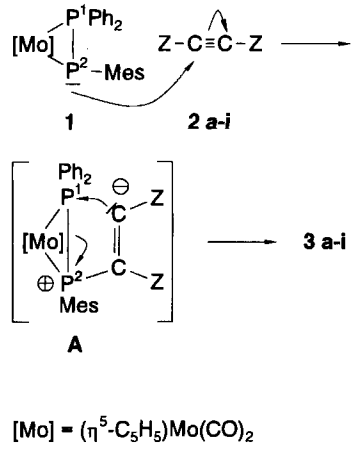
Figure 1. ORTEP plot of the molecular structure of compound **3a**[a]



[a] Selected bond lengths [pm] and angles [°]: Mo1–P1 250.5(1), Mo1–P2 248.8(1), P1–C25 181.0(3), P2–C22 176.4(2), C22–C25 136.9(4); P1–Mo1–P2 76.7(1), Mo1–P1–C25 112.8(1), Mo1–P2–C22 111.7(1), P1–C25–C22 115.5(2), P2–C22–C25 121.5(2).

the formation of the five-membered heterocycles **3a–i**. If the lone pair of P^2 is blocked by addition of sulfur to the three-membered heterocycle **1** with the formation of $[\overline{Mo}]-P^1Ph_2-P^2(S)Mes$ (**5**) (Scheme 4) no reaction is observed with activated alkynes. This behavior is a nice evidence that the first reaction step of the ring expansion **1** → **3a–i** is indeed a nucleophilic attack of P^2 at one of the carbon atoms of the alkyne. From kinetic investigations it was deduced that this is the rate-determining step. This process is described by a second-order reaction and by the strongly negative activation entropy $\Delta S^{\neq}$ (Table 1), which was obtained by temperature-dependent kinetic measurements in the case of the formation of **3e**. As expected the value of the activation entropy is in the range of a bimolecular reaction with a polarized alkyne in the activated complex[15]. The rate constants are strongly dependent on the steric demand of the ester moieties and they decrease in the sequence R = Me > Et > *n*Pr > *i*Pr > Cy > *n*Bu > *neo*-Pent > *t*Bu (Table 2).

Scheme 2



[Mo] = $(\eta^5\text{-}C_5H_5)Mo(CO)_2$

Table 1. Activation parameters for the formation of **3e**[a]

$\Delta H^{\neq}$ / kJ mol^{-1}	$\Delta S^{\neq}$ / J mol^{-1} K^{-1}	$\Delta G^{\neq}$ / kJ mol^{-1}
43.16(2.49)	-119.65(9.83)	73.45(4.98)

[a] Calculated according to ref.[16] at T = 253 K.

Table 2. Rate constants for the reactions of **1** with the alkynes **2a–h**

T / K	[**1**], [Comp.], (M[a])	k_{obs} / M^{-1}s^{-1}	R[b]
243	[**2a**], 42.00 x 10^{-3}	6.87(28) x 10^{-3}	0.996
243	[**2b**], 44.47 x 10^{-3}	4.09(3) x 10^{-3}	0.999
243	[**2c**], 42.83 x 10^{-3}	2.29(8) x 10^{-3}	0.996
243	[**2d**], 44.47 x 10^{-3}	2.09(3) x 10^{-3}	0.998
243	[**2e**], 41.93 x 10^{-3}	1.65(2) x 10^{-3}	0.997
248	[**2e**], 42.73 x 10^{-3}	2.29(5) x 10^{-3}	0.992
253	[**2e**], 42.47 x 10^{-3}	3.38(8) x 10^{-3}	0.996
258	[**2e**], 42.00 x 10^{-3}	6.00(13) x 10^{-3}	0.998
263	[**2e**], 45.30 x 10^{-3}	8.53(52) x 10^{-3}	0.991
243	[**2f**], 42.71 x 10^{-3}	0.74(3) x 10^{-3}	0.991
243	[**2g**], 43.43 x 10^{-3}	0.89(1) x 10^{-3}	0.998
243	[**2h**], 42.97 x 10^{-3}	1.72(7) x 10^{-3}	0.999

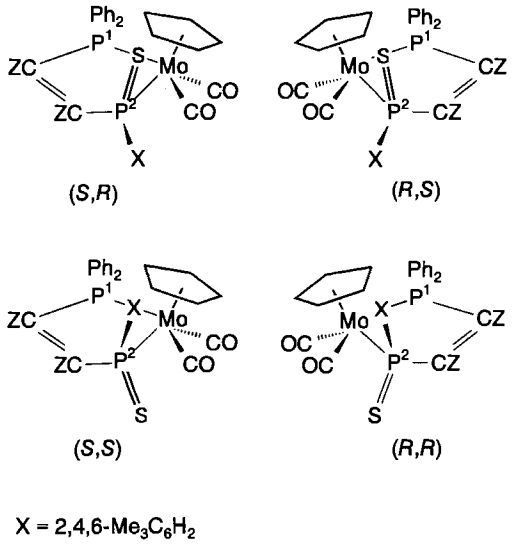
[a] Initial concentration. – [b] Correlation coefficient.

The lone pair of P^2 in the diphosphamolybdacyclopentenes **3a–i** displays Lewis basic properties. With the examples of **3a**, **h** we could demonstrate that cyclooctasulfur reacts readily to give the S adducts **4a**, **h** with a fourfold coordinated P^2 atom in the ring (Scheme 1). The heterocycles **4a**, **h** purified by column chromatography are relatively stable toward atmospheric oxygen and are less soluble in organic solvents than the starting compounds **3a**, **h**. The composition of **4a**, **h** was corroborated by their FAB mass spectra which show the corresponding molecular peaks.

In the IR spectra of **4a**, **h** (CCl_4) two absorptions in the 5-μm region are observed which can be assigned to the symmetric and antisymmetric C≡O stretching vibrations. In comparison with the starting compounds **3a**, **h** they are shifted to higher wavenumbers. Two distinct discernible shoulders at both absorptions indicate the existence of diastereomers which are attributed to the optically active centers at the molybdenum and phosphorus atom (P^2) (Scheme 3). The presence of diastereomers is confirmed by two sets of signals in the $^{31}P\{^1H\}$, ^1H, and to some extent also in the $^{13}C\{^1H\}$-NMR spectra. Upon integration of the ^1H-resonance lines an approximate ratio of 2:1 and 5:1 was obtained for **4a** and **4h**, respectively.

Compared to the starting compounds **3a**, **h** the doublets of P^1 and P^2 in the $^{31}P\{^1H\}$-NMR spectra of **4a**, **h** are shifted to lower field and are found in a rather narrow range between δ = 91 and δ = 97. With selectively ^{31}P decoupled $^{13}C\{^1H\}$-NMR measurements in the case of **4h** it was possible to ascribe the doublet at δ = 97 to P^2. Each ring carbon atom gives rise to a doublet of doublets in the $^{13}C\{^1H\}$-NMR spectra of **4a**, **h**. Because of the coordination of a sulfur atom at the lone pair of P^2 these ^{13}C resonances appear at similar chemical shifts. Selective ^{31}P decoupling

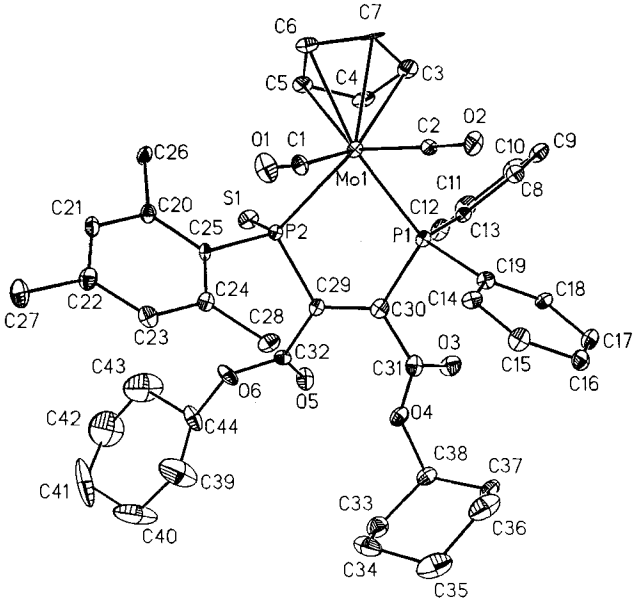
Scheme 3



experiments enable the assignment of the signal groups in the $^{13}C\{^1H\}$-NMR spectra to both ring carbon atoms.

An X-ray structural analysis of **4h** proved that this compound consists of a pair of enantiomers *SR*/*RS* (Scheme 3) and shows the effect of a sulfur atom being coordinated to the phosphorus atom (P2) (Figure 2). Only the surroundings of the heavy atoms will be discussed because the structure determination is of poor quality. There is a remarkable difference between the bond lengths of Mo1–P1 and Mo1–P2 of 12 pm. Similar to structure **3a** the five-membered ring is planar. The P–S bond length lies between that of a single and a double bond[17].

Figure 2. ORTEP plot of the molecular structure of compound **4h**[a]

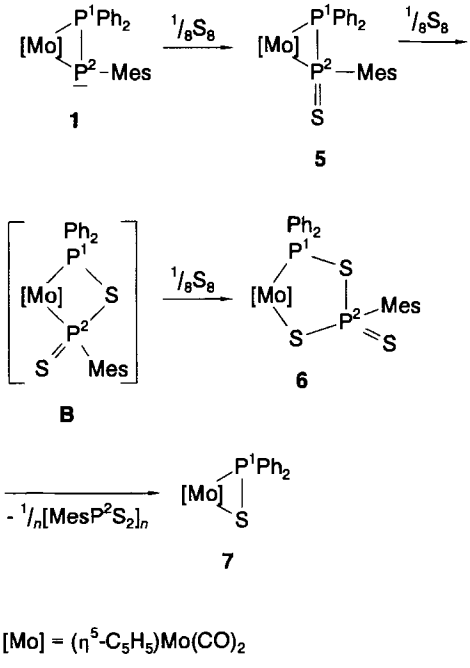


[a] Selected bond lengths [pm] and angles [°]: Mo1–P1 246.7(3), Mo1–P2 258.6(3), P2–S1 202.2(3); P1–Mo1–P2 76.8(1).

2) Behavior of 1 Toward Sulfur

Recently, it was reported that [W]–P^1(*o*Tol)$_2$–P^2Me {[W] = $(\eta^5\text{-}C_5H_5)W(CO)_2$} reacts with elemental sulfur in toluene with oxidation of P^2 and insertion of sulfur into the P^1–P^2 bond to give the four-membered heterocycle [W]–P^1(*o*Tol)$_2$–S–P^2(S)Me[18] as the only product. However, if the comparable molybdenum compound **1** was allowed to react with an excess of cyclooctasulfur, the final product was the three-membered ring [Mo]–P^1Ph_2–S (**7**). Interestingly, this reaction proceeds via the intermediates [Mo]–P^1Ph_2–P^2(S)Mes (**5**) and [Mo]–P^1Ph_2–S–P^2(S)Mes–S (**6**) which could be isolated. Supposedly another intermediate is the molybdenum analog **B** of the tungsten heterocycle which could not be detected within the reaction sequence (Scheme 4). Each of these intermediates **5** and **6** and the final product **7** could be synthesized separately from the corresponding starting compounds **1**, **5**, and **6**, and a stoichiometric amount of sulfur. The overall reaction of **1** with sulfur was controlled by $^{31}P\{^1H\}$-NMR spectroscopy. The heterocycles **5** and **7** were purified by column chromatography whereas **6** could only be reprecipitated from methylcyclohexane. The composition of the rather stable heterocycles **7** (orange), **6** (rust-colored), and **5** (yellow), the solubility of which decreases in nonpolar solvents,

Scheme 4

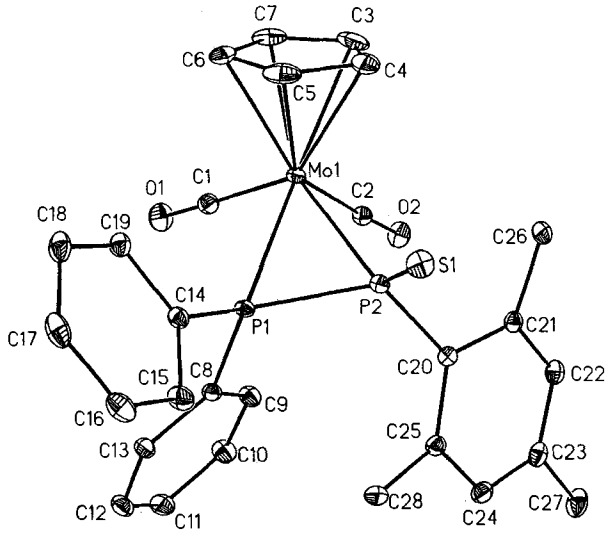


was confirmed by FAB and FD mass spectra, respectively.

No reaction was observed between the first intermediate **5** and activated alkynes. In the IR spectrum of **5** two C≡O absorptions are observed which are shifted to higher wave numbers compared to **1**. The $^{31}P\{^1H\}$-NMR spectrum is characterized by a typical AB pattern. The considerable high-field shift of the P^1 signal is attributed to a significant decrease of the endocyclic bond angle [Mo]–P^1–P^2 (Figure 3). The preservation of the P^1–P^2 bond is corroborated by the coupling constant of $^1J_{PP}$ = 473 Hz.

An X-ray structural analysis of compound **5** was performed (Figure 3). The oxidation of P2 with sulfur led to an extended P–P bond length compared to the analogous compound $[\overline{Mo}]-\overline{PPh_2-PPh}$ {[Mo] = $(\eta^5\text{-}C_5H_5)Mo(CO)_2$}[9]. Another consequence of this oxidation is the shortening of the Mo1–P2 bond and a larger endocyclic angle at Mo1. The P2–S1 bond length lies between that of a single and a double bond[17].

Figure 3. ORTEP plot of the molecular structure of compound **5**[a]



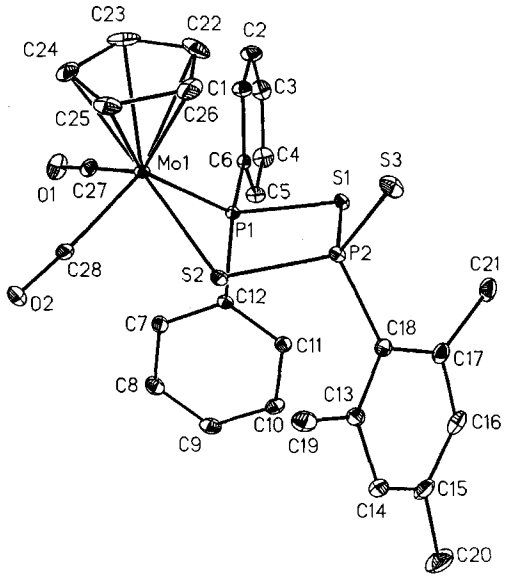
[a] Selected bond lengths [pm] and angles [°]: Mo1–P1 243.0(1), Mo1–P2 249.6(1), P1–P2 216.2(1), P2–S1 198.2(1); P1–Mo1–P2 52.1(1), Mo1–P1–P2 65.6(1), Mo1–P2–P1 62.4(1).

Upon oxidation of the phosphorus atom P^2 with sulfur and insertion of sulfur into the P^1-P^2 and $Mo-P^2$ bonds of **1** the five-membered intermediate **6** was obtained. Two bands in the 5-μm region of the IR spectrum of **6** are assigned to two terminal carbonyl groups. Compared to the monosulfur heterocycle **5** both ^{31}P doublets in the $^{31}P\{^1H\}$-NMR spectrum of **6** are shifted to lower field.

The molecular structure of compound **6** is illustrated in Figure 4. The five-membered ring adopts an envelope conformation with P1, S1, P2, and S2 essentially located in the plane, whilst Mo1 is out of the plane. The dihedral angle between this plane and the plane Mo1–P1–S2 is 127.4°. The ring distances of the heterocycle correspond to a single bond length[17,19], while the P2–S3 distance is in the range of a double bond.

The final product of the stepwise reaction of the three-membered heterocycle **1** with sulfur is again a three-membered heterocycle (**7**) which is formed by a thermally induced separation of $[MesP^2S_2]_n$ from **6** (Scheme 4). This fragment undergoes a dimerization or oligomerization. A particular signal in the $^{31}P\{^1H\}$-NMR spectrum of the reaction sequence at $\delta = 11$ points to the dimeric form[17]. Remarkably, the solid-state IR spectrum of **6** reveals six C≡O absorptions, whereas in solution the expected two carbonyl bands occur. A corresponding effect is observed in the ^{31}P-CP MAS and $^{31}P\{^1H\}$-NMR spectra which show two signals and one signal, respectively. This phenomenon

Figure 4. ORTEP plot of the molecular structure of compound **6**[a]



[a] Selected bond lengths [pm] and angles [°]: Mo1–P1 245.2(1), Mo1–S2 250.6(1), P1–S1 211.0(1), P2–S1 214.0(1), P2–S2 207.7(1), P2–S3 195.2(1); P1–Mo1–S2 73.1(1), Mo1–P1–S1 110.9(1), Mo1–S2–P2 111.6(1), P1–S1–P2 99.9(4), S1–P2–S2 102.4(1).

is explained by the existence of two independent molecules in the unit cell which results from an X-ray structural analysis[20].

The mechanism of the formation of the three-membered heterocycle **7** may be rationalized by two main reaction steps. The already mentioned basicity of the phosphorus atom P^2 (vide supra) is responsible for the oxidation with sulfur (**5**). In a following procedure the terminal sulfur atom is inserted either into the P^1-P^2 or into the $Mo-P^2$ bond. In this way the lone pair of P^2 is again available for an oxidation with sulfur. In an alternating sequence of these reaction steps the heterocycle **6** is obtained via **B**.

Conclusion

Depending on the steric demand of the phosphorus-bound substituents R^1, activated alkynes are generally inserted either into the M–P or into the M–S bond of three-membered heterocycles of the type $L_nM-PR^1_2=S$ (M = Mn, Co, Ni)[5,7,8]. An additional insertion into the $R^1_2P=S$ bond has not been established so far. If sulfur is replaced by an isolobal R^2P function the resulting three-membered rings $L_n\overline{M-PR^1_2-PR^2}$ in principle offer three possibilities for an alkyne insertion[21]. The course of the reaction, however, is determined by the increased basicity of P^2 compared to the sulfur atom which is expressed by a nucleophilic attack of this phosphorus atom at one of the triply bonded carbon atoms of the alkyne. The steric encumbrance of the $\eta^5\text{-}C_5H_5Mo$ moiety, however, prevents a participation of the metal center in the course of this reaction, thus, the formation of bicyclic compounds is preferred in the case of the less sterically demanding $Mn(CO)_4$ system[21]. The nucleophilic attack is followed by an insertion of the corre-

sponding alkyne into the P^1-P^2 bond of the three-membered heterocycle **1** with the formation of the five-membered heterocycles **3a–i**. Kinetic investigations confirmed a strong dependence of the reaction rate on the steric demand of the ester substituents and corroborated the course of the reaction with a second-order rate law and a strong negative activation entropy which was determined in the case of the reaction **1** + **2e** → **3e**. The reaction of **1** with sulfur afforded a further evidence for this mechanism. In a primary reaction step the three-membered heterocycle **5** is formed. Because the lone pair of P^2 is no longer available in that case, the nucleophilic attack at a carbon atom of an alkyne is impossible. In a further reaction sequence the three-membered ring **5** is expanded by a stepwise insertion of sulfur into the P^1-P^2 and P^2-Mo bond. Since the steric encumbrance of sulfur is much smaller thant hat of an alkyne the latter insertion is enabled. The novel five-membered heterocycle **6** could be isolated as an intermediate. Upon thermal cleavage of the PS_2Mes fragment which undergoes a di- or oligomerization the heterocycle **7** was obtained as the thermodynamically most stable final product.

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Experimental

All manipulations were carried out under argon by using standard Schlenk techniques under argon. Solvents were dried over appropriate reagents and stored under argon. The starting compounds H[Mo]PPh_2H[9], $MesPCl_2$[22] and the alkynes **2b–h**[23,24] were prepared as previously described.

MS (FD): Finnigan MAT 711A modified by AMD (8 kV, 60°C). – MS (FAB): Finnigan MAT TSQ 70 (10 kV, 50°C). – IR: Bruker IFS 48. – ^1H NMR: Bruker AMX 400, AC 250, and DRX 250 at 400.14 and 250.13 MHz. – $^{13}C\{^1H\}$ NMR: Bruker AMX 400 and Bruker AC 250 at 100.61 and 62.90 MHz. The assignments of the aromatic carbon and hydrogen atoms and those of the higher aliphatic substituents are reported in ref.[20] – $^{13}C\{^1H\}$ NMR (selective phosphorus decoupling experiments): Bruker AMX 400 at 100.61 MHz. – 2D $^1H^{13}C$ HETCOR: Bruker AMX 600 at 600.13 (^1H) and 150.90 MHz (^{13}C). – NOE: Bruker ARX 250 at 250.13 MHz. – $^{31}P\{^1H\}$ NMR: Bruker WP 80 at 32.90 MHz, external standard 1% H_3PO_4 in [D_6]acetone, Bruker DRX 250 at 101.25 MHz, and Bruker AMX 400 at 161.98 MHz. – ^{19}F NMR: Bruker DRX 250 at 235.35 MHz. – Except for $^{31}P\{^1H\}$ NMR with Bruker WP 80 the chemical shifts were measured relative to partially deuterated solvent peaks which are reported relative to tetramethylsilane. – ^{31}P-CP MAS NMR: Bruker ASX 300 at 121.49 MHz, multinuclear spectrometer with a wide-bore magnet (7.05 T) in double-bearing rotors of ZrO_2, external standard $NH_4H_2PO_4$. The spectrum was measured with cross-polarization (CP) and high-power proton decoupling. Magic-angle spinning was performed at 10 kHz. The spectrum was recorded by using a spectral width of 62.5 kHz. – Microanalyses: Carlo Erba, model 1106 and AAS Perkin-Elmer, model 4000.

Kinetic Studies of the Reactions of **1** *with* **2a–h**: These reactions were followed by $^{31}P\{^1H\}$-NMR spectroscopy (Bruker AC 80). Chemical shifts were measured with respect to the external reference of 1% H_3PO_4 in [D_6]acetone. The changes of the concentrations of **1** (determined from the areas of the resonances) were followed for at least 2 half-lives and were measured as a function of the time. The analyses of the kinetic data reveal a linear relation between $1/c$ and the time (t), hence the decrease of **1** is second order. The first measurement of each sequence started immediately after addition of **2a–h** to the frozen solution of **1** in $CDCl_3$. Every 32 min a repeated spectrum of the same sample was recorded. The time of each measurement required 17 min. The temperature was measured by means of an external thermocouple (PT 100). The NMR probe temperature was calibrated by using the method of van Geet[25] and is considered accurate to ±1 K.

1. *3,3-Dicarbonyl-3-(η⁵-cyclopentadienyl)-1,1-diphenyl-2-(2,4,6-trimethylphenyl)-1λ⁴,2-diphospha-3-molybdacyclopropane* (**1**): A solution of $H(\eta^5\text{-}C_5H_5)Mo(CO)_2(HPPh_2)$ (11.1 g, 27.5 mmol) in 400 ml of diethyl ether was allowed to react for 16 h at 20°C with 55 mmol of *n*BuLi (1.6 M solution in *n*-hexane) to give $Li_2[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_2)]$. Within 2 h a solution of $MesPCl_2$ (6.1 g, 27.5 mmol) in 50 ml of diethyl ether was added at −78°C. After stirring for 2 h, while the reaction mixture was slowly warmed to 20°C, the obtained suspension was concentrated in vacuo to ca. 20 ml. The yellow precipitate was filtered (D1) and purified in portions by column chromatography (15 × 2.5 cm, basic alumina, diethyl ether). Concentration of the first fraction to ca. 5 ml led to the precipitation of a yellow solid, which was filtered (D4), washed with *n*-hexane (5 × 5 ml), and dried in vacuo. Yield 10.48 g (69.0%), m.p. 152°C (dec.). – MS (FD), *m/z*: 554 [M^+, rel. to ^{98}Mo]. – IR (KBr): $\tilde{\nu}$ = 1927, 1854 cm^{-1} (C≡O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 2.10 (s, 3H, 4-CH_3), 2.25 (s, 6H, 2,6-CH_3), 5.12 (d, $^3J_{P^2H}$ = 1.7 Hz, 5H, C_5H_5). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 20.87 (s, 4-CH_3), 23.79 (s, 6-CH_3), 23.95 (s, 2-CH_3), 91.84 (s, C_5H_5), 202.88 (d, $^2J_{PC}$ = 31.5 Hz, C≡O), 211.42 (s, C≡O). – $^{31}P\{^1H\}$ NMR (32.90 MHz, THF): δ = −203.20 (d, $^1J_{PP}$ = 536 Hz, P^2), 28.59 (d, $^1J_{PP}$ = 536 Hz, P^1). – $C_{28}H_{26}MoO_2P_2$ (552.4): calcd. C 60.88, H 4.74, Mo 17.37; found C 61.16, H 4.79, Mo 17.07.

2. *General Procedure for the Synthesis of the Heterocycles* **3a–h**: To a solution of **1** in 100 ml of THF the corresponding alkyne **2a–h** was added and the solution was stirred at 20°C. During this procedure a color change from yellow to deep red took place. After removal of the solvent in vacuo, the compounds **3a–h** were purified by column chromatography (25 × 2.5 cm, basic alumina, diethyl ether acetone, 3:1 (**2a, b**), diethyl ether (**2c–h**)). The red second fraction was concentrated to ca. 5 ml in vacuo, and then 10 ml of *n*-hexane was added. The obtained precipitate was filtered off (D4), washed with three portions of *n*-hexane (10 ml) and dried in vacuo.

2.1. *Dimethyl 2,2-Dicarbonyl-2-(η⁵-cyclopentadienyl)-1,1-diphenyl-3-(2,4,6-trimethylphenyl)-1λ⁴,3-diphospha-2-molybda-4-cyclopentene-4,5-dicarboxylate* (**3a**): A solution of **1** (1.32 g, 2.39 mmol) was allowed to react during 1 h with **2a** (0.34 g, 2.39 mmol) to give 1.05 g (63.1%) of **3a**, m.p. 171°C (dec.). – MS (FD), *m/z*: 696 [M^+, rel. to ^{98}Mo]. – IR (KBr): $\tilde{\nu}$ = 1955, 1892 cm^{-1} (C≡O), 1727, 1678 (C=O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 2.17 (s, 3H, 4-CH_3), 2.31 (s, 3H, 6-CH_3), 2.49 (s, 3H, 2-CH_3), 3.31 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 4.82 (d, $^3J_{P^2H}$ = 1.7 Hz, 5H, C_5H_5). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 21.13 (s, 4-CH_3), 23.38 (s, 6-CH_3), 24.02 (d, $^3J_{PC}$ = 23.8 Hz, 2-CH_3), 50.91 (s, OCH_3), 52.14 (s, OCH_3), 94.29 (s, C_5H_5), 107.51 (dd, $^1J_{PC}$ = 47.5, $^2J_{PC}$ = 45.9 Hz, $P^2-C=$), 163.33 (dd, $^2J_{PC}$ = 5.9, $^3J_{PC}$ = 6.2 Hz, $=C(P^1)-C=O$), 168.69 (dd, $^2J_{PC}$ = 30.1, $^3J_{PC}$ = 8.6 Hz,

=C(P^2)−*C*=O), 184.58 (dd, $^1J_{PC}$ = 50.6, $^2J_{PC}$ = 22.9 Hz, P^1−C=), 207.03 (dd, $^2J_{P^1C}$ = 26.2, $^2J_{P^2C}$ = 11.0 Hz, C≡O), 214.64 (d, $^2J_{P^1C}$ = 16.2 Hz, C≡O). − ^{31}P{^{1}H} NMR (32.90 MHz, THF): δ = 12.00 (d, $^2J_{PP}$ = 12.0 Hz, P^2), 87.01 (d, $^2J_{PP}$ = 12.0 Hz, P^1). − $C_{34}H_{32}MoO_6P_2$ (694.5): calcd. C 58.80, H 4.64, Mo 13.81; found C 59.26, H 4.53, Mo 14.21.

2.2. *Diethyl 2,2-Dicarbonyl-2-(η^5-cyclopentadienyl)-1,1-diphenyl-3-(2,4,6-trimethylphenyl)-1λ^4,3-diphospha-2-molybda-4-cyclopentene-4,5-dicarboxylate* (**3b**): A solution of **1** (830 mg, 1.50 mmol) was allowed to react during 2 h with **2b** (256 mg, 1.50 mmol) to give 564 mg (51.9%) of **3b**, m.p. 175°C (dec.). − MS (FD), *m/z*: 724 [M$^+$, rel. to ^{98}Mo]. − IR (KBr): ṽ = 1953, 1888 cm^{-1} (C≡O), 1704, 1673 (C=O). − ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 2.25 (s, 3H, 4-CH_3), 2.39 (s, 3H, 6-CH_3), 2.57 (s, 3H, 2-CH_3), 4.91 (d, $^3J_{P^2H}$ = 1.7 Hz, 5H, C_5H_5). − ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$): δ = 21.14 (s, 4-CH_3), 23.56 (s, 6-CH_3), 24.06 (d, $^3J_{PC}$ = 23.8 Hz, 2-CH_3), 94.35 (s, C_5H_5), 107.73 (dd, $^1J_{PC}$ = 48.6, $^2J_{PC}$ = 44.8 Hz, P^2−C=), 162.98 [dd, $^2J_{PC}$ = 5.7, $^3J_{PC}$ = 5.7 Hz, =C(P^1)−*C*=O], 168.11 [dd, $^2J_{PC}$ = 30.5, $^3J_{PC}$ = 8.6 Hz, =C(P^2)−*C*=O], 184.77 (dd, $^1J_{PC}$ = 50.5, $^2J_{PC}$ = 23.8 Hz, P^1−C=), 206.76 (dd, $^2J_{P^1C}$ = 25.8, $^2J_{P^2C}$ = 10.5 Hz, C≡O), 214.56 (d, $^2J_{P^1C}$ = 16.2 Hz, C≡O). − ^{31}P{^{1}H} NMR (32.90 MHz, THF): δ = 12.29 (d, $^2J_{PP}$ = 16.2 Hz, P^2), 86.99 (d, $^2J_{PP}$ = 16.2 Hz, P^1). − $C_{36}H_{36}MoO_6P_2$ (722.6): calcd. C 59.84, H 5.02, Mo 13.28; found C 60.05, H 4.75, Mo 13.70.

2.3. *Dipropyl 2,2-Dicarbonyl-2-(η^5-cyclopentadienyl)-1,1-diphenyl-3-(2,4,6-trimethylphenyl)-1λ^4,3-diphospha-2-molybda-4-cyclopentene-4,5-dicarboxylate* (**3c**): A solution of **1** (913 mg, 1.65 mmol) was allowed to react during 4 h with **2c** (983 mg, 4.96 mmol) to give 723 mg (58.3%) of **3c**, m.p. 151°C (dec.). − MS (FD), *m/z*: 753 [M$^+$, rel. to ^{98}Mo]. − IR (KBr): ṽ = 1955, 1891 cm^{-1} (C≡O), 1710, 1678 (C=O). − ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 2.17 (s, 3H, 4-CH_3), 2.32 (s, 3H, 6-CH_3), 2.49 (s, 3H, 2-CH_3), 4.82 (d, $^3J_{P^2H}$ = 1.6 Hz, 5H, C_5H_5). − ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$): δ = 21.05 (s, 4-CH_3), 23.52 (s, 6-CH_3), 23.98 (d, $^3J_{PC}$ = 25.0 Hz, 2-CH_3), 94.27 (d, $^2J_{PC}$ = 2.78 Hz, C_5H_5), 108.18 (dd, $^1J_{PC}$ = 48.6, $^2J_{PC}$ = 44.4 Hz, P^2−C=), 163.08 (dd, $^2J_{PC}$ = 5.6 $^3J_{PC}$ = 5.6 Hz, =C(P^1)−*C*=O), 168.20 (dd, $^2J_{PC}$ = 29.8, $^3J_{PC}$ = 9.0 Hz, =C(P^2)−*C*=O), 184.65 (dd, $^1J_{PC}$ = 49.9, $^2J_{PC}$ = 25.0 Hz, P^1−C=), 234.48 (d, $^2J_{P^1C}$ = 15.3 Hz, C≡O), 242.12 (dd, $^2J_{P^1C}$ = 26.4, $^2J_{P^2C}$ = 11.1 Hz, C≡O). − ^{31}P{^{1}H} NMR (32.90 MHz, THF): δ = 12.08 (d, $^2J_{PP}$ = 16.5 Hz, P^2), 86.64 (d, $^2J_{PP}$ = 16.5 Hz, P^1). − $C_{38}H_{40}MoO_6P_2$ (750.6): calcd. C 60.57, H 5.33, Mo 12.88; found C 60.54, H 5.03, Mo 13.21.

2.4. *Diisopropyl 2,2-Dicarbonyl-2-(η^5-cyclopentadienyl)-1,1-diphenyl-3-(2,4,6-trimethylphenyl)-1λ^4,3-diphospha-2-molybda-4-cyclopentene-4,5-dicarboxylate* (**3d**): A solution of **1** (840 mg, 1.52 mmol) was allowed to react during 4 h with **2d** (904 mg, 4.56 mmol) to give 612 mg (53.6%) of **3d**, m.p. 161°C (dec.). − MS (FD), *m/z*: 753 [M$^+$, rel. to ^{98}Mo]. − IR (KBr): ṽ = 1949, 1878 cm^{-1} (C≡O), 1713, 1688 (C=O). − ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 2.18 (s, 3H, 4-CH_3), 2.31 (s, 3H, 6-CH_3), 2.50 (s, 3H, 2-CH_3), 4.84 (d, $^3J_{P^2H}$ = 1.8 Hz, 5H, C_5H_5). − ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$): δ = 21.17 (s, 4-CH_3), 23.55 (s, 6-CH_3), 23.98 (d, $^3J_{PC}$ = 24.8 Hz, 2-CH_3), 95.25 (d, $^2J_{PC}$ = 2.8, C_5H_5), 108.69 (dd, $^1J_{PC}$ = 47.7, $^2J_{PC}$ = 43.9 Hz, P^2−C=), 162.51 [dd, $^2J_{PC}$ = 5.7, $^3J_{PC}$ = 5.7 Hz, =C(P^1)−*C*=O], 167.42 [dd, $^2J_{PC}$ = 30.5, $^3J_{PC}$ = 9.5 Hz, =C(P^1)−*C*=O], 184.76 (dd, $^1J_{PC}$ = 49.6, $^2J_{PC}$ = 25.8 Hz, P^1−C=), 206.73 (dd, $^2J_{P^2C}$ = 25.8, $^2J_{P^2C}$ = 10.5 Hz, C≡O), 214.42 (d, $^2J_{P^1C}$ = 17.2 Hz, C≡O). − ^{31}P{^{1}H} NMR (32.90 MHz, THF): δ = 11.57 (d, $^2J_{PP}$ = 16.1 Hz, P^2), 86.14 (d, $^2J_{PP}$ = 16.1 Hz, P^1). − $C_{38}H_{40}MoO_6P_2$ (750.6): calcd. C 60.57, H 5.33, Mo 12.88; found C 60.55, H 5.21, Mo 12.55.

2.5. *Dibutyl 2,2-Dicarbonyl-2-(η^5-cyclopentadienyl)-1,1-diphenyl-3-(2,4,6-trimethylphenyl)-1λ^4,3-diphospha-2-molybda-4-cyclopentene-4,5-dicarboxylate* (**3e**): A solution of **1** (745 mg, 1.35 mmol) was allowed to react during 2 h with **2e** (915 mg, 4.06 mmol) to give 522 mg (49.7%) of **3e**, m.p. 143°C (dec.). − MS (FD), *m/z*: 780 [M$^+$, rel. to ^{98}Mo]. − IR (KBr): ṽ = 1953, 1889 cm^{-1} (C≡O), 1716, 1676 (C=O). − ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 2.16 (s, 3H, 4-CH_3), 2.32 (s, 3H, 6-CH_3), 2.49 (s, 3H, 2-CH_3), 4.83 (d, $^3J_{P^2C}$ = 1.5 Hz, 5H, C_5H_5). − ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$): δ = 21.09 (s, 4-CH_3), 23.58 (s, 6-CH_3), 24.01 (d, $^3J_{PC}$ = 23.6 Hz, 2-CH_3), 94.34 (s, C_5H_5), 108.33 (dd, $^1J_{PC}$ = 48.6, $^2J_{PC}$ = 44.4 Hz, P^2−C=), 163.17 [dd, $^2J_{PC}$ = 5.6, $^3J_{PC}$ = 5.6 Hz, =C(P^1)−*C*=O], 168.25 [dd, $^2J_{PC}$ = 29.8, $^3J_{PC}$ = 9.0 Hz, =C(P^2)−*C*=O], 184.66 (dd, $^1J_{PC}$ = 50.6, $^2J_{PC}$ = 24.2 Hz, P^1−C=), 234.54 (d, $^2J_{P^1C}$ = 16.7 Hz, C≡O), 242.18 (dd, $^2J_{P^1C}$ = 25.7, $^2J_{P^2C}$ = 10.4 Hz, C≡O). − ^{31}P{^{1}H} NMR (32.90 MHz, THF): δ = 12.02 (d, $^2J_{PP}$ = 16.3 Hz, P^2), 86.49 (d, $^2J_{PP}$ = 16.3 Hz, P^1). − $C_{40}H_{44}MoO_6P_2$ (778.7): calcd. C 61.70, H 5.70, Mo 12.32; found C 61.73, H 5.73, Mo 12.31.

2.6. *Di-tert-butyl 2,2-Dicarbonyl-2-(η^5-cyclopentadienyl)-1,1-diphenyl-3-(2,4,6-trimethylphenyl)-1λ^4,3-diphospha-2-molybda-4-cyclopentene-4,5-dicarboxylate* (**3f**): A solution of **1** (1.49 g, 2.7 mmol) was allowed to react during 6 h with **2f** (1.83 g, 8.10 mmol) to give 1.42 g (67.3%) of **3f**, m.p. 186°C (dec.). − MS (FD), *m/z*: 780 [M$^+$, rel. to ^{98}Mo]. − IR (KBr): ṽ = 1949, 1884 cm^{-1} (C≡O), 1716, 1685 (C=O). − ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 2.18 (s, 3H, 4-CH_3), 2.27 (s, 3H, 6-CH_3), 2.48 (s, 3H, 2-CH_3), 4.81 (d, $^3J_{P^2H}$ = 1.6 Hz, 5H, C_5H_5). − ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$): δ = 21.06 (s, 4-CH_3), 23.57 (d, $^3J_{PC}$ = 2.5 Hz, 6-CH_3), 23.98 (d, $^3J_{PC}$ = 24.4 Hz, 2-CH_3), 94.24 (d, $^2J_{PC}$ = 2.5 Hz, C_5H_5), 112.44 (dd, $^1J_{PC}$ = 46.4, $^2J_{PC}$ = 41.5 Hz, P^2−C=), 162.85 [dd, $^2J_{PC}$ = 4.9, $^3J_{PC}$ = 4.9 Hz, =C(P^1)−*C*=O], 166.48 [dd, $^2J_{PC}$ = 20.8, $^3J_{PC}$ = 11.0 Hz, =C(P^2)−*C*=O], 183.74 (dd, $^1J_{PC}$ = 48.8, $^2J_{PC}$ = 30.5 Hz, P^1−C=), 234.86 (d, $^2J_{P^1C}$ = 17.1 Hz, C≡O), 242.78 (dd, $^2J_{P^1C}$ = 25.6, $^2J_{P^2C}$ = 9.7 Hz, C≡O). − ^{31}P{^{1}H} NMR (32.90 MHz, THF): δ = 9.15 (d, $^2J_{PP}$ = 14.2 Hz, P^2), 85.03 (d, $^2J_{PP}$ = 14.2 Hz, P^1). − $C_{40}H_{44}MoO_6P_2$ (778.7): calcd. C 61.70, H 5.70, Mo 12.32; found C 61.54, H 5.57, Mo 12.72.

2.7. *Dineopentyl 2,2-Dicarbonyl-2-(η^5-cyclopentadienyl)-1,1-diphenyl-3-(2,4,6-trimethylphenyl)-1λ^4,3-diphospha-2-molybda-4-cyclopentene-4,5-dicarboxylate* (**3g**): A solution of **1** (1.15 g, 2.08 mmol) was allowed to react during 6 h with **2g** (1.59 g, 6.25 mmol) to give 786 mg (46.8%) of **3g**, m.p. 120°C (dec.). − MS (FD), *m/z*: 809 [M$^+$, rel. to ^{98}Mo]. − IR (KBr): 1953, 1881 cm^{-1} (C≡O), 1712, 1695 (C=O). − ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 2.14 (s, 3H, 4-CH_3), 2.30 (s, 3H, 6-CH_3), 2.48 (s, 3H, 2-CH_3), 4.80 (d, $^3J_{P^2H}$ = 1.4 Hz, 5H, C_5H_5). − ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$): δ = 22.98 (s, 4-CH_3), 23.61 (s, 6-CH_3), 23.86 (d, $^3J_{PC}$ = 23.6 Hz, 2-CH_3), 94.18 (s, C_5H_5), 110.07 (dd, $^1J_{PC}$ = 48.6, $^2J_{PC}$ = 44.4 Hz, P^2−C=), 163.43 [dd, $^2J_{PC}$ = 5.6, $^3J_{PC}$ = 5.6 Hz, =C(P^1)−*C*=O], 168.32 [dd, $^2J_{PC}$ = 30.5, $^3J_{PC}$ = 9.7 Hz, =C(P^2)−*C*=O], 184.01 (dd, $^1J_{PC}$ = 49.9, $^2J_{PC}$ = 27.7 Hz, P^1−C=), 234.36 (d, $^2J_{P^1C}$ = 16.6 Hz, C≡O), 242.02 (dd, $^2J_{P^1C}$ = 26.4, $^2J_{P^2C}$ = 9.7 Hz, C≡O). − ^{31}P{^{1}H} NMR (32.90 MHz, THF): δ = 13.37 (d, $^2J_{PP}$ = 16.3 Hz, P^2), 84.98 (d, $^2J_{PP}$ = 16.3 Hz, P^1). − $C_{42}H_{48}MoO_6P_2$ (806.8): calcd. C 62.53, H 6.00, Mo 11.89; found C 62.85, H 6.00, Mo 12.17.

2.8. *Dicyclohexyl 2,2-Dicarbonyl-2-(η^5-cyclopentadienyl)-1,1-diphenyl-3-(2,4,6-trimethylphenyl)-1λ^4,3-diphospha-2-molybda-4-cyclopentene-4,5-dicarboxylate* (**3h**): A solution of **1** (1.39 g, 2.52 mmol) was allowed to react during 6 h with **2h** (2.10 g, 7.55 mmol) to give 953 mg (45.6%) of **3h**, m.p. 190°C (dec.). − MS (FD),

m/z: 832 [M^+, rel. to ^{98}Mo]. – IR (KBr): $\tilde{\nu}$ = 1948, 1880 cm^{-1} (C≡O), 1708, 1678 (C=O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 2.16 (s, 3H, 4-CH_3), 2.32 (s, 3H, 6-CH_3), 2.49 (s, 3H, 2-CH_3), 4.82 (d, $^3J_{P^2H}$ = 1.5 Hz, 5H, C_5H_5). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 21.02 (s, 4-CH_3), 23.58 (s, 6-CH_3), 24.61 (d, $^3J_{PC}$ = 25.0 Hz, 2-CH_3), 94.24 (d, $^2J_{PC}$ = 2.8 Hz, C_5H_5), 108.93 (dd, $^1J_{PC}$ = 47.9, $^2J_{PC}$ = 43.7 Hz, P^2–C=), 162.55 [dd, $^2J_{PC}$ = 6.3, $^3J_{PC}$ = 6.3 Hz, =C(P^1)–*C*=O], 167.36 [dd, $^2J_{PC}$ = 29.8, $^3J_{PC}$ = 9.1 Hz, =C(P^2)–*C*=O], 184.88 (dd, $^1J_{PC}$ = 49.9, $^2J_{PC}$ = 26.4 Hz, P^1–C=), 234.62 (d, $^2J_{P^1C}$ = 15.3 Hz, C≡O), 242.36 (dd, $^2J_{P^1C}$ = 25.7, $^2J_{P^2C}$ = 10.4 Hz, C≡O). – $^{31}P\{^1H\}$ NMR (32.90 MHz, THF): δ = 11.49 (d, $^2J_{PP}$ = 15.4 Hz, P^2), 85.74 (d, $^2J_{PP}$ = 15.4 Hz, P^1). – $C_{44}H_{48}MoO_6P_2$ (830.8): calcd. C 63.61, H 5.82, Mo 11.55; found C 63.67, H 5.79, Mo 11.33.

2.9. *2,2-Dicarbonyl-2-(η^5-cyclopentadienyl)-1,1-diphenyl-4,5-bis-(trifluoromethyl)-3-(2,4,6-trimethylphenyl)-1λ^4,3-diphospha-2-molybda-4-cyclopentene* (**3i**): 2.4 g (14.81 mmol) of **2i** was condensed into a solution of 740 mg (1.34 mmol) of **1** in 80 ml of THF at −78 °C. After rendering the Schlenk line gas-proof the reaction mixture was allowed to warm to 20 °C and stirred for 1 d. The purification was carried out analogously as described for **3c**–**h**. Yield 593 mg (61.9%), m.p. 153 °C (dec.). – MS (FD), *m/z*: 716 [M^+, rel. to ^{98}Mo]. – IR (KBr): $\tilde{\nu}$ = 1952, 1880 cm^{-1} (C≡O), 1241, 1226, 1172, 1163, 1146 (CF_3). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 2.21 (s, 3H, 4-CH_3), 2.27 (s, 3H, 6-CH_3), 2.47 (s, 3H, 2-CH_3), 4.76 (d, $^3J_{P^2H}$ = 1.7 Hz, 5H, C_5H_5). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 21.03 (s, 4-CH_3), 23.42 (d, $^3J_{PC}$ = 3.6 Hz, 6-CH_3), 23.65 (d, $^3J_{PC}$ = 14.4 Hz, 2-CH_3), 94.52 (s, C_5H_5), 113.36–115.67 (m, P^2–C=), 122.60 (ddq, $^1J_{FC}$ = 280.1, $^2J_{PC}$ = 32.3, $^3J_{PC}$ = 12.5 Hz, CF_3), 122.81 (dq, $^1J_{FC}$ = 276.5, $^2J_{PC}$ = 5.4 Hz, CF_3), 169.77–172.76 (m, P^1–C=), 232.55 (d, $^2J_{P^2C}$ = 16.2 Hz, C≡O), 240.75 (dd, $^2J_{P^1C}$ = 26.9, $^2J_{P^2C}$ = 8.9 Hz, C≡O). – $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$): δ = 6.11 (dqq, $^3J_{PP}$ = 15.4, $^3J_{PF}$ = 22.0, $^4J_{PF}$ = 12.4 Hz, P^2), 95.73 (dq, $^3J_{PP}$ = 15.4, $^3J_{PF}$ = 4.1 Hz, P^1). – ^{19}F NMR (235.35 MHz, $CDCl_3$): −47.87 [dq, $^3J_{PF}$ = 21.6, $^5J_{FF}$ = 15.5 Hz, CF_3 (P^2)], −54.38 [ddq, $^3J_{PF}$ = 11.9, $^4J_{PF}$ = 4.3, $^5J_{FF}$ = 15.4 Hz, CF_3 (P^1)]. – $C_{32}H_{26}F_6MoO_2P_2$ (714.5): calcd. C 53.80, H 3.69, F 15.95, Mo 13.43; found C 53.67, H 3.81, F 16.53, Mo 13.84.

3. *General Procedure for the Synthesis of the Heterocycles* **4a**, **h**: To a solution of **3a**, **h** in 100 ml of THF a threefold excess of elementary sulfur was added. While stirring for 14 h at 20 °C the color changed from red to yellow. After removal of the solvent in vacuo **4a**, **h** were purified by column chromatography (15 × 2.5 cm, basic alumina, diethyl ether acetone, 3:1). The yellow, second fraction was concentrated to ca. 20 ml in vacuo, and then 10 ml of *n*-hexane was added. The obtained precipitate was filtered off (D4), washed with three 10-ml portions of *n*-hexane and dried in vacuo.

3.1. *Dimethyl 2,2-Dicarbonyl-2-(η^5-cyclopentadienyl)-3,3-diphenyl-1-thioxo-1-(2,4,6-trimethylphenyl)-1λ^5,3λ^4-diphospha-2-molybda-4-cyclopentene-4,5-dicarboxylate* (**4a**): A solution of **3a** (530 mg, 0.76 mmol) was allowed to react with sulfur (122 mg, 3.80 mmol) to give 421 mg (60.4%) of **4a**, m.p. 159 °C (dec.). – MS (FAB), *m/z*: 729 [M^+, rel. to ^{98}Mo]. – IR (KBr): $\tilde{\nu}$ = 1975, 1914 cm^{-1} (C≡O), 1731 (C=O). – ^1H NMR (250.13 MHz, $CDCl_3$) diastereomer A (diastereomer B): δ = 2.04 (2.19) (s, 3H, 4-CH_3), 2.19 (2.38) (s, 3H, 6-CH_3), 2.91 (3.02) (s, 3H, 2-CH_3), 3.28 (3.41) (s, 3H, OCH_3), 3.62 (3.57) (s, 3H, OCH_3), 4.88 (4.41) (s, 5H, C_5H_5). – $^{13}C\{^1H\}$ NMR (62.90 MHz, CD_2Cl_2) diastereomer A (diastereomer B): δ = 20.95 (20.97) (s, 4-CH_3), 24.23 (24.76) [d, $^3J_{PC}$ = 6.1 (6.7) Hz, 2-CH_3], 24.91 (25.02) [d, $^3J_{PC}$ = 7.4 (5.4) Hz, 6-CH_3], 52.76 (52.88) (s, OCH_3), 52.95 (52.95) (s, OCH_3), 98.99 (95.48) (s, C_5H_5), 163.51 (dd, $^1J_{PC}$ = 42.0, $^2J_{PC}$ = 28.6 Hz, P^1–C=), 164.87 (dd, $^1J_{PC}$ = 43.1, $^2J_{PC}$ = 25.9 Hz, P^2–C=), 165.63 (165.71) [dd, $^2J_{PC}$ = 28.5 (29.0), $^3J_{PC}$ = 4.3 (4.0) Hz, =C(P^1)–*C*=O], 166.35 (166.75) [dd, $^2J_{PC}$ = 26.3 (24.9), $^3J_{PC}$ = 3.6 (3.7) Hz, =C(P^2)–*C*=O], 234.68 (234.16) [d, $^2J_{P^2C}$ = 29.6 (30.0) Hz, C≡O], 240.85 (240.01) [d, $^2J_{P^1C}$ = 22.7 (29.0) Hz, C≡O]. – $^{31}P\{^1H\}$ NMR (32.90 MHz, THF) diastereomer A (diastereomer B): δ = 90.57 (90.42) [d, $^2J_{PP}$ = 50.8 (43.1) Hz, P^1], 96.35 (95.75) [d, $^2J_{PP}$ = 50.8 (43.1) Hz, P^2]. – $C_{34}H_{32}MoO_6P_2S$ (726.6): calcd. C 56.20, H 4.43, Mo 13.20, S 4.41; found C 56.66, H 4.52, Mo 13.57, S 4.45.

3.2. *Dicyclohexyl 2,2-Dicarbonyl-2-(η^5-cyclopentadienyl)-3,3-diphenyl-1-thioxo-1-(2,4,6-trimethylphenyl)-1λ^5,3λ^4-diphospha-2-molybda-4-cyclopentene-4,5-dicarboxylate* (**4h**): A solution of **3h** (673 mg, 0.81 mmol) was allowed to react with sulfur (126 mg, 4.05 mmol) to give 565 mg (80.7%) of **4h**, m.p. 181 °C (dec.). – MS (FAB), *m/z*: 866 [M^+, rel. to ^{98}Mo]. – IR (KBr): $\tilde{\nu}$ = 1966, 1904 cm^{-1} (C≡O), 1725, 1704 (C=O). – ^1H NMR (250.13 MHz, $CDCl_3$) diastereomer A (diastereomer B): δ = 2.06 (2.02) (s, 3H, 4-CH_3), 2.18 (2.40) (s, 3H, 6-CH_3), 2.92 (3.02) (s, 3H, 2-CH_3), 4.86 (4.38) (s, 5H, C_5H_5). – $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$) diastereomer A (diastereomer B): δ = 20.65 (20.58) (s, 4-CH_3), 24.14 (24.59) [d, $^3J_{PC}$ = 6.7 (6.7) Hz, 2-CH_3], 24.69 (24.98) [d, $^3J_{PC}$ = 5.7 (4.8) Hz, 6-CH_3], 98.52 (94.78) (s, C_5H_5), 163.85 (163.61) [dd, $^2J_{PC}$ = 28.6 (29.1), $^3J_{PC}$ = 3.8 (4.3) Hz, =C(P^1)–*C*=O], 164.42 (dd, $^1J_{PC}$ = 40.5, $^2J_{PC}$ = 27.2 Hz, P^1–C=), 164.98 (165.71) [dd, $^2J_{PC}$ = 26.4 (24.8), $^3J_{PC}$ = 4.2 (2.9) Hz, =C(P^2)–*C*=O], 165.54 (dd, $^1J_{PC}$ = 42.4, $^2J_{PC}$ = 24.3 Hz, P^2–C=), 234.11 (233.30) [d, $^2J_{P^2C}$ = 29.6 (29.6) Hz, C≡O], 240.77 (239.52) [d, $^2J_{P^1C}$ = 22.7 (33.4) Hz, C≡O]. – $^{31}P\{^1H\}$ NMR (161.98 MHz, THF) diastereomer A (diastereomer B): δ = 91.92 (91.49) [d, $^2J_{PP}$ = 41.4 (50.1) Hz, P^1], 96.62 (97.65) [d, $^2J_{PP}$ = 41.4 (50.1) Hz, P^2]. – $C_{44}H_{48}MoO_6P_2S$ (864.2): calcd. C 61.25, H 5.61, Mo 11.12, S 3.72; found C 61.64, H 5.83, Mo 11.31, S 3.76.

4. *3,3-Dicarbonyl-3-(η^5-cyclopentadienyl)-2,2-diphenyl-1-(2,4,6-trimethylphenyl)-1λ^5,2λ^4-diphospha-3-molybdacyclopropan-1-thione* (**5**): 81 mg (2.52 mmol) of elementary sulfur was added to a solution of **1** (1.39 g, 2.52 mmol) in 100 ml of THF. After stirring of the mixture for 14 h the solvent was removed in vacuo and to the residue 50 ml of methylcyclohexane was added. A yellow solid precipitated which was filtered off (D4) and purified by column chromatography (20 × 2.5 cm, basic alumina, 1. diethyl ether, 2. acetone). The second fraction (acetone) containing compound **5** was concentrated to ca. 10 ml in vacuo. The addition of *n*-hexane (20 ml) led to the precipitation of a yellow solid, which was filtered (D4), washed with *n*-hexane (3 × 5 ml) and dried in vacuo. Yield 833 mg (56.5%), m.p. 155 °C (dec.). – MS (FD), *m/z*: 587 [M^+, rel. to ^{98}Mo]. – IR (KBr): $\tilde{\nu}$ = 1966, 1887 cm^{-1} (C≡O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 2.10 (s, 3H, 4-CH_3), 2.30 (s, 3H, 6-CH_3), 2.83 (s, 3H, 2-CH_3), 5.37 (s, 5H, C_5H_5). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 21.09 (s, 4-CH_3), 22.17 (d, $^3J_{PC}$ = 3.4 Hz, 6-CH_3), 22.31 (d, $^3J_{PC}$ = 7.7 Hz, 2-CH_3), 94.14 (s, C_5H_5), 231.61 (dd, $^2J_{PC}$ = 11.9, $^2J_{PC}$ = 6.8 Hz, C≡O), 235.16 (dd, $^2J_{PC}$ = 25.5, $^2J_{PC}$ = 13.7 Hz, C≡O). – $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ = −50.16 (d, $^1J_{PP}$ = 473.0 Hz), −51.92 (d, $^1J_{PP}$ = 473.0 Hz). – $C_{28}H_{26}MoO_2P_2S$ (586.0): calcd. C 57.54, H 4.48, Mo 16.41, S 5.49; found C 57.53, H 4.62, Mo 16.55, S 5.43.

5. *4,4-Dicarbonyl-4-(η^5-cyclopentadienyl)-5,5-diphenyl-2-(2,4,6-trimethylphenyl)-1,3-dithia-2λ^5,5λ^4-diphospha-3-molybdacyclopentane-2-thione* (**6**): To a solution of **5** (1.02 g, 1.74 mmol) in 100 ml of THF 56 mg (1.74 mmol) of elementary sulfur was added. After stirring of the mixture for 10 h at 20 °C the solvent was removed in vacuo. The residue was treated with 25 ml of methylcyclo-

hexane and the unsoluble remainder was separated by filtration (D4). The filtrate was concentrated to 5 ml in vacuo, then 10 ml of *n*-hexane was added. The precipitate was filtered (D4), washed with diethyl ether (3 × 2 ml) and dried in vacuo. Yield 312 mg (27.6%), m.p. 146°C (dec.). – MS (FD), *m/z*: 650 [M^+, rel. to ^{98}Mo]. – IR (KBr): $\tilde{\nu}$ = 1959, 1885 cm^{-1} (C≡O). – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 2.14 (s, 3H, 4-CH_3), 2.81 (s, 6H, 2,6-CH_3), 5.60 (s, 5H, C_5H_5). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 20.69 (s, 4-CH_3), 26.22 (s, 6-CH_3), 26.26 (s, 2-CH_3), 95.36 (s, C_5H_5), 236.46 (d, $^2J_{PC}$ = 30.5 Hz, C≡O), 246.51 (d, $^2J_{PC}$ = 19.9 Hz, C≡O). – $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ = 108.01 (d, $^2J_{PP}$ = 40.5 Hz, P^1), 110.15 (d, $^2J_{PP}$ = 40.5 Hz, P^2). – $C_{28}H_{26}MoO_2P_2S_3$ (548.6): calcd. C 51.85, H 4.04, Mo 14.79, S 14.83; found C 51.94, H 3.99, Mo 14.98, S 14.01.

6. *3,3-Dicarbonyl-3-(η^5-cyclopentadienyl)-2,2-diphenyl-1-thia-2λ^4-phospha-3-molybdacyclopropan* (**7**): A stirred solution of **6** (532 mg, 0.82 mmol) in 75 ml of THF was refluxed for 10 h. After removal of the solvent in vacuo **7** was purified by column chromatography (20 × 2.5 cm, basic alumina, diethyl ether). The first fraction was concentrated to ca. 5 ml in vacuo. The addition of 20 ml of *n*-hexane led to the precipitation of an orange solid, which was filtered (D4), washed with *n*-hexane (3 × 2 ml) and dried in vacuo. Yield 267 mg (74.7%), m.p. 135°C (dec.). – MS (FD), *m/z*: 436 [M^+, rel. to ^{98}Mo]. – IR (*n*-hexane): $\tilde{\nu}$ = 1965, 1861 cm^{-1} (C≡O). – IR (KBr): $\tilde{\nu}$ = 1954, 1942, 1936, 1875, 1863, 1853 cm^{-1} (C≡O). – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 5.17 (s, 5H, C_5H_5). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 93.09 (s, C_5H_5), 237.44 (d, $^2J_{PC}$ = 15.8 Hz, C≡O), 247.03 (d, $^2J_{PC}$ = 32.9 Hz, C≡O). – $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ = 47.69 (s). – ^{31}P-CP MAS: δ = 50.09 (s), 53.53 (s). – $C_{19}H_{15}MoO_2PS$ (434.3): calcd. C 52.54, H 3.48, Mo 22.09, S 7.38; found C 52.49, H 3.52, Mo 21.97, S 7.67.

Crystal Structure Determinations: Single crystals were obtained by slow diffusion of *n*-hexane into concentrated CH_2Cl_2 solutions of **3a**, **4h**, **5**, and **6**, respectively. All crystals were mounted on a glass fiber and transferred to a P4 Siemens diffractometer by taking rotation photographs and performing a photo search to find a suitable reduced cell (graphite-monochromated Mo-K_α radiation). The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. The final cell parameters and specific data collection parameters for **3a**, **4h**, **5**, and **6**, respectively, are compiled in Table 3. All structures were solved by Patterson methods[26] and refined by the least-squares method (based on F^2) with anisotropic thermal parameters for all non-hydrogen atoms. The standard deviations of the lattice constants of compound **4h** are high. The use of a split model to solve the disorder of the cyclohexyl groups was unsuccessful. Investigation of bond lengths and angles shows that only the surroundings of the heavy atoms are reliable. Hydrogen atoms were included in calculated positions (riding model). An absorption correction ψ-scan was applied to all structures. Maximum and minimum peaks in the final difference synthesis were 0.45 and −0.32 (**3a**), 2.71 and −2.65 (**4h**), 0.44 and −0.38 (**5**) and 0.71 and −0.55 (**6**). Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58930, the names of the authors, and the journal citation.

Table 3. Crystal data and refinement details for compounds **3a**, **4h**, **5**, and **6**

	3a	**4h**	**5**	**6**
formula	$C_{34}H_{32}MoO_6P_2$	$C_{44}H_{48}MoO_6P_2S$	$C_{28}H_{26}MoO_2P_2S$	$C_{28}H_{26}MoO_2P_2S_3$
M_r	694.48	862.76	584.43	648.50
crystal system	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [pm]	1861.6(3)	1072.0(8)	1557.7(3)	859.4(2)
b [pm]	900.2(1)	1175.0(7)	1158.6(2)	1312.0(4)
c [pm]	1912.8(3)	1712.0(11)	1428.8(3)	1359.9(3)
α [°]	90	101.89(1)	90	98.00(2)
β [°]	97.84(1)	92.55(1)	95.25(1)	101.82(2)
γ [°]	90	98.34(1)	90	108.12
V [pm³]	3175.5(8) · 10^6	2082(2) · 10^6	2567.8(9) · 10^6	1392.1(6) · 10^6
$\rho_{calcd.}$ [g cm^{-3}]	1.453	1.376	1.512	1.547
Z	4	2	4	2
F(000) [e]	1424	896	1192	660
T [°C]	−100	−100	−100	−100
μ (Mo-K_α) [mm^{-1}]	0.558	0.488	0.741	0.836
scan mode	ω	ω	ω	Wyckoff
h range	−22 → +22	−12 → +12	−20 → +20	−10 → +7
k range	−10 → +10	−13 → +13	−15 → +15	−15 → +15
l range	−22 → +22	−20 → +20	−18 → +16	−16 → +16
2θ limits [°]	4-50	4-50	4-50	4-50
measured refl.	16222	14645	22543	9195
observed refl.	5600	7323	5899	4901
observed refl. ($F_o \geq 4\sigma F_o$)	4041	4648	4672	4352
refined parameters	389	488	308	326
w	$[\exp(5.0(\sin\theta/\lambda)^2)] / [\sigma(F_o^2) + [g \cdot (\max(0.333 F_o^2, 0)) + 0.6667 F_c^2]^2]$			
g	0.0353	0.0988	0.0420	0.0494
S	1.244	2.191	1.540	1.656
R1[a]	0.028	0.084	0.027	0.026
wR2[b]	0.061	0.212	0.062	0.066

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. – [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

☆ Dedicated to Professor *Herbert Schumann* on the occasion of his 60th birthday.

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