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Dimolybdenum Cyclopentadienyl Complexes with Bridging Chalcogenophosphinidene Ligands

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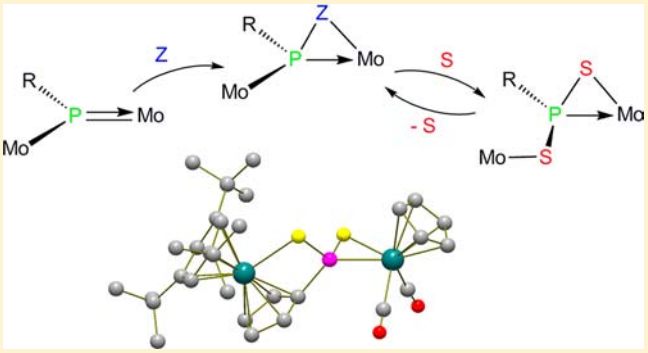
Supporting Information

ABSTRACT: The reactions of the phosphinidene-bridged complex $[Mo_2Cp_2(\mu\text{-}PH)(\eta^6\text{-}HMes^*)(CO)_2]$ (**1**), the arylphosphinidene complexes $[Mo_2Cp_2(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^6\text{-}PMes^*)(CO)_2]$ (**2**), $[Mo_2Cp_2(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^4\text{-}PMes^*)(CO)_3]$ (**3**), $[Mo_2Cp_2(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^4\text{-}PMes^*)(CO)_2(CN^tBu)]$ (**4**), and the cyclopentadienylidene-phosphinidene complex $[Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2]$ (**5**) toward different sources of chalcogen atoms were investigated (Mes* = 2,4,6-$C_6H_2{}^tBu_3$; Cp = η^5-C_5H_5). The bare elements were appropriate sources in all cases except for oxygen, in which case dimethyldioxirane gave the best results. Complex **1** reacted with the mentioned chalcogen sources at low temperature, to give the corresponding chalcogenophosphinidene derivatives $[Mo_2Cp_2\{\mu\text{-}\kappa^2{}_{P,Z}\text{:}\kappa^1{}_P\text{-}ZPH\}(\eta^6\text{-}HMes^*)(CO)_2]$ (Z = O, S, Se, Te; P−Se = 2.199(2) Å). The arylphosphinidene complex **2** was the least reactive substrate and gave only chalcogenophosphinidene derivatives $[Mo_2Cp_2(\mu\text{-}\kappa^2{}_{P,Z}\text{:}\kappa^1{}_P,\eta^6\text{-}ZPMes^*)(CO)_2]$ for Z = O and S (P−O = 1.565(2) Å), along with small amounts of the dithiophosphorane complex $[Mo_2Cp_2(\mu\text{-}\kappa^2{}_{P,S}\text{:}\kappa^1{}_{S'},\eta^6\text{-}S_2PMes^*)(CO)_2]$, in the reaction with sulfur. The η^4-complexes **3** and **4** reacted with sulfur and gray selenium to give the corresponding derivatives $[Mo_2Cp_2(\mu\text{-}\kappa^2{}_{P,Z}\text{:}\kappa^1{}_P,\eta^4\text{-}ZPMes^*)(CO)_2L]$ (L = CO, CN^tBu), obtained respectively as syn (Z = Se; P−Se = 2.190(1) Å for L = CO) or a mixture of syn and anti isomers (Z = S; P−S = 2.034(1)−2.043(1) Å), with these diastereoisomers differing in the relative positioning of the chalcogen atom and the terminal ligand at the metallocene fragment, relative to the Mo_2P plane. The cyclopentadienylidene compound **5** reacted with all chalcogens, and gave with good yields the chalcogenophosphinidene derivatives $[Mo_2Cp(\mu\text{-}\kappa^2{}_{P,Z}\text{:}\kappa^1{}_P,\eta^5\text{-}ZPC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2]$ (Z = S, Se, Te), these displaying in solution equilibrium mixtures of the corresponding cis and trans isomers differing in the relative positioning of the cyclopentadienylic rings with respect to the MoPZ plane in each case. The sulfur derivative reacted with excess sulfur to give the dithiophosphorane complex $[Mo_2Cp(\mu\text{-}\kappa^2{}_{P,S}\text{:}\kappa^1{}_{S'},\eta^5\text{-}S_2PC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2]$ (P−S = 2.023(4) and 2.027(4) Å). The structural and spectroscopic data for all chalcogenophosphinidene complexes suggested the presence of a significant π(P−Z) bonding interaction within the corresponding MoPZ rings, also supported by Density Functional Theory calculations on the thiophosphinidene complex *syn*-$[Mo_2Cp_2(\mu\text{-}\kappa^2{}_{P,S}\text{:}\kappa^1{}_P,\eta^4\text{-}SPMes^*)(CO)_3]$.



INTRODUCTION

The chemistry of molecules having low-coordinated phosphorus atoms is an attractive area of research with a rich potential in the functionalization of phosphorus and in the preparation of unusual organophosphorus derivatives, but most of these species are too reactive to be isolated in the free state and are only stable when coordinated to one or several metal centers.[1,2] Phosphinidene chalcogenides (R−P═Z; with Z = O, S, Se, Te) are one of such a class of substances, with the oxides being the most extensively investigated members of this family. In contrast to their lighter analogues (the organic nitroso compounds −RNO−), the phosphinidene chalcogenides are unstable under ordinary conditions but are thought to be generated in the thermal or photochemical decomposition of several precursors such as phospholene, phosphirane or phosphanorbornadiene chalcogenides, among others.[3] These transient species undergo processes, such as addition to dienes and diones or insertion into C−H, O−H, and S−S bonds, and are therefore interesting synthons for new organophosphorus derivatives.[3a,b,4]

Phosphinidene chalcogenides are isolobal-related to singlet carbenes, as first pointed out by Schoeller and Niecke,[5] and, as it is the case of carbenes, substantial stabilization of these unsaturated molecules can be achieved through coordination to metal centers, a strategy that might allow for a more detailed study of their chemical behavior. However, in spite of the rich variety of coordination modes available for these molecules, only a very limited number of complexes have been described in the literature so far,[6] and their chemical behavior has been

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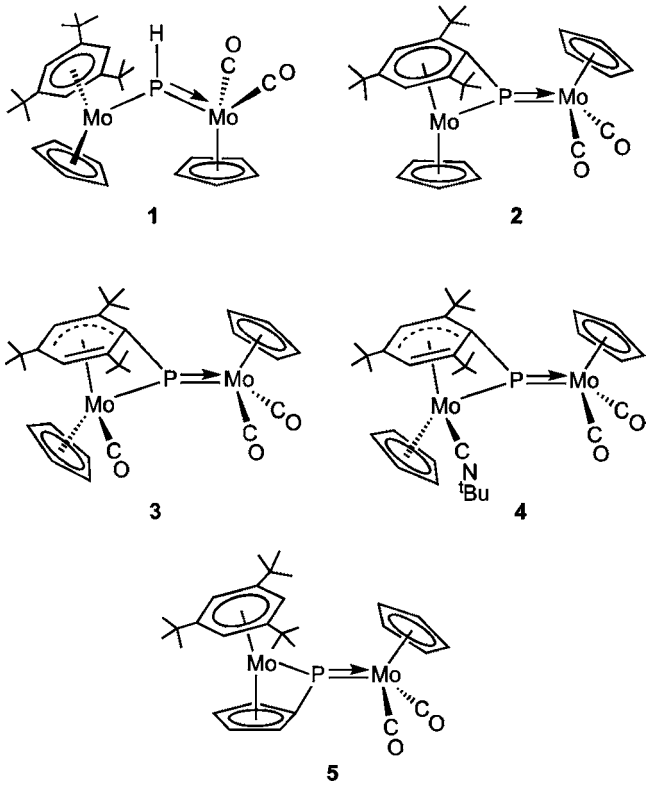
little explored, if we except the reactions of the thiophosphinidene complex $[Mn_2(CO)_9\{(\mu\text{-}\kappa^2_{P,S}:\kappa^1_P\text{-}SP(Me)\}]$ with alkynes.[7] Our own interest in the chemistry of chalcogenophosphinidene complexes was stimulated by the rich chemical behavior displayed by the anionic oxophosphinidene complex $[MoCp(P(O)Mes^*\}(CO)_2]^-$ (Mes* = 2,4,6-$C_6H_2{}^tBu_3$; Cp= η^5-C_5H_5),[8] a molecule exhibiting unique acid−base and redox properties with a multisite reactivity located at their O, P and Mo atoms, depending on the reagent used. The binding of different reagents to these sites allows the rational synthesis of derivatives having novel organophosphorus ligands or unusual coordination modes that cannot be prepared otherwise, these including *P,O*-bound phosphinite and phosphonite, thiooxophosphorane, phosphonothiolate and thiolophosphinide ligands.[8d,e] In a recent preliminary report we described the reaction of the binuclear phosphinidene complex $[Mo_2Cp_2(\mu\text{-}\kappa^1:\kappa^1,\eta^6\text{-}PMes^*)(CO)_2]$ with elemental sulfur to give the corresponding thiophosphinidene derivative $[Mo_2Cp_2(\mu\text{-}\kappa^2_{P,S}:\kappa^1_P,\eta^6\text{-}SPMes^*)(CO)_2]$.[9] This product displayed an unexpected behavior, with the P−S bond of the P(S)R ligand being easily cleaved upon reaction with different metal carbonyls, to give novel dinuclear and tetranuclear complexes displaying a μ_2-PR ligand attached to different metals, a circumstance rarely met in the chemistry of PR complexes.[10] As a result, the thiophosphinidene complex might effectively behave as a synthetic intermediate for new phosphinidene complexes operating under mild conditions, thus opening the way to future studies on molecules displaying multiple bonds between P and a variety of transition-metal atoms. To ascertain the role of the chalcogen atom on the chemical behavior of these unusual R−P═Z complexes we considered of interest to expand the set of available chalcogenophosphinidene-bridged substrates similar to the mentioned dimolybdenum complex, which is the purpose of the present paper. Moreover, from our previous work on the reactivity of related dimolybdenum phosphinidene-bridged complexes we might also anticipate a strong influence of the nature and geometry of the substituent at the P atom.[11,12] To tackle both variables (R and Z) we have investigated the addition of chalcogen atoms (Z = O to Te) to five different phosphinidene-bridged dimolybdenum complexes, ranging from the unsubstituted phosphinidene complex $[Mo_2Cp_2(\mu\text{-}PH)(\eta^6\text{-}HMes^*)(CO)_2]$ (**1**),[11] to the arylphosphinidene complexes $[Mo_2Cp_2(\mu\text{-}\kappa^1:\kappa^1,\eta^6\text{-}PMes^*)(CO)_2]$ (**2**), $[Mo_2Cp_2(\mu\text{-}\kappa^1:\kappa^1,\eta^4\text{-}PMes^*)(CO)_3]$ (**3**), $[Mo_2Cp_2(\mu\text{-}\kappa^1:\kappa^1,\eta^4\text{-}PMes^*)(CO)_2(CN^tBu)]$ (**4**),[12] and the cyclopentadienylidenephosphinidene complex $[Mo_2Cp(\mu\text{-}\kappa^1:\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2]$ (**5**) (Chart 1).[12] The steric and electronic environment around the P atoms in these isoelectronic phosphinidene complexes are significantly different from each other,[11,12] and might therefore lead to differently behaved chalcogenophosphinidene derivatives. At discussed below, this is indeed the case at a significant extent.

Chart 1

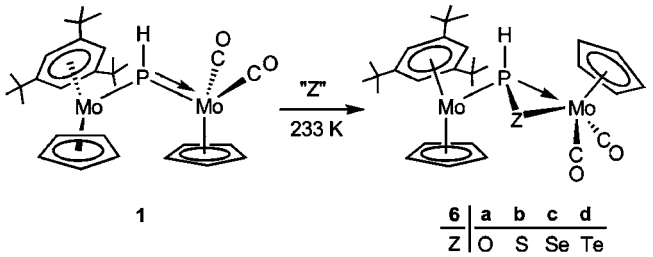


RESULTS AND DISCUSSION

Synthesis of Dimolybdenum Chalcogenophosphinidene Complexes. To this purpose, we have systematically examined the reactions of the phosphinidene complexes **1** to **5** toward different sources of chalcogen atoms. The bare elements were appropriate sources in all cases except for oxygen, in which case dimethyldioxirane, Me_2CO_2,[13] was a much more selective reagent. All these reactions formally involve a [2 + 1] addition of a chalcogen atom to the multiple Mo−P bond in the phosphinidene substrate, to yield a $\mu\text{-}\kappa^2_{P,Z}:\kappa^1_P$-bound chalcogenophosphinidene ligand, and are analogous to the reactions of elemental sulfur and selenium with the complexes $[MM'Cp_2(\mu\text{-}PMes)(CO)_5]$ previously studied by Malish et al. (M, M′ = Mo, W).[6i] However we note that, beyond the above formalisms, the mechanism whereby compounds **1** to **5** react with chalcogens is unknown, but most likely involve a nucleophilic attack of the P atom to the Z_n chains and cycles of the chalcogen sources.

Complex **1** is the most reactive species among the phosphinidene substrates studied, since it is able to react with all mentioned chalcogen sources at low temperature, to give the corresponding chalcogenophosphinidene derivatives $[Mo_2Cp_2(\mu\text{-}\kappa^2_{P,Z}:\kappa^1_P\text{-}ZPH)(\eta^6\text{-}HMes^*)(CO)_2]$ [Z= O (**6a**), S (**6b**), Se (**6c**), Te (**6d**)] (Scheme 1), the stability of which increase when going from O to Te.

Scheme 1



The arylphosphinidene complex **2** is the least reactive substrate investigated, this preventing the formation of some of the corresponding derivatives. Thus, although the reaction with dimethyldioxirane and elemental sulfur proceeded at room temperature to give the corresponding oxo- and thiophosphinidene derivatives $[Mo_2Cp_2(\mu\text{-}\kappa^2_{P,Z}:\kappa^1_P,\eta^6\text{-}ZPMes^*)(CO)_2]$

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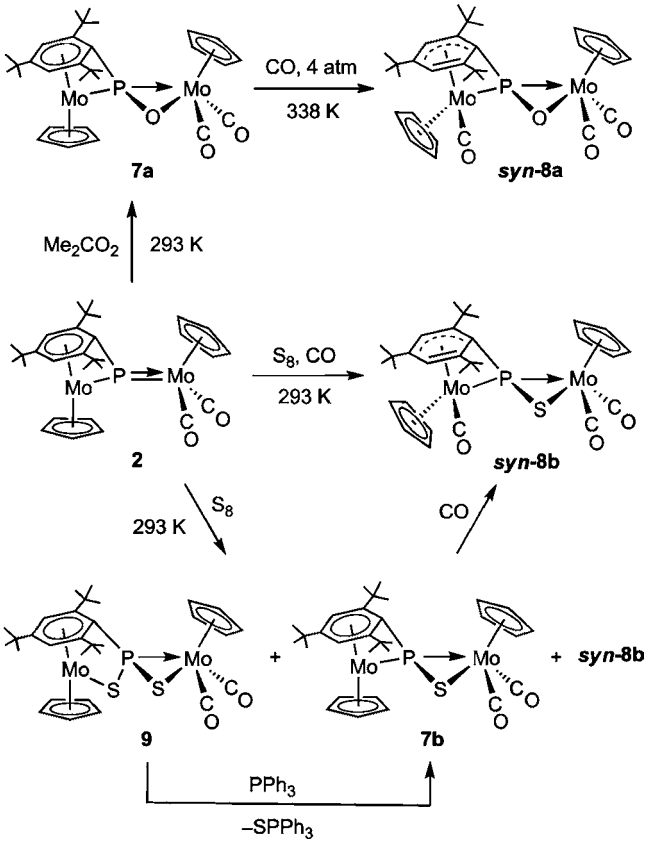
(**7a**–**b**) (Scheme 2), no reaction was observed in the case of elemental selenium or tellurium. Unfortunately, heating of the

Scheme 2

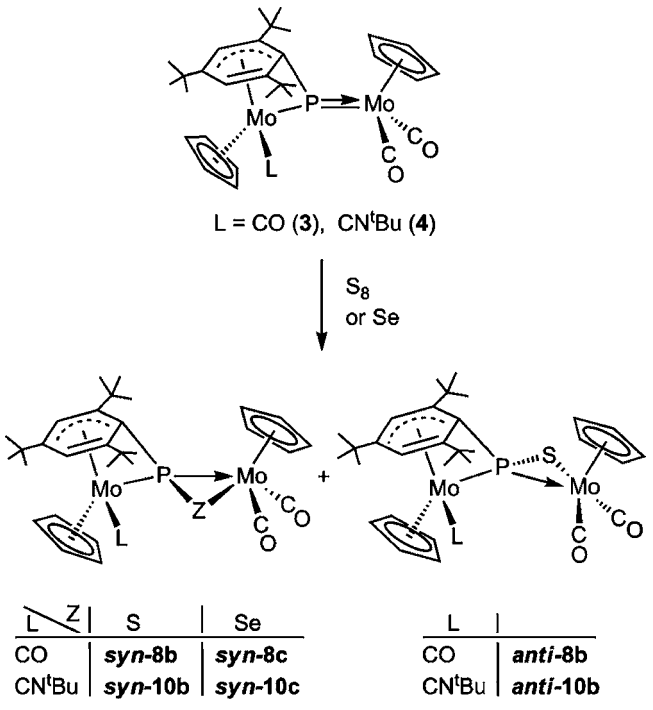


corresponding mixtures in the latter cases was of no use, since the arylphosphinidene complex **2** then rearranges into its cyclopentadienylidene-phosphinidene isomer **5**,[12] and thus the selenium and tellurium derivatives of **5** are obtained instead (see below). This relatively low reactivity of complex **2** must be attributed mostly to the steric shielding that the *ortho* ^{t}Bu groups of the PMes* ligand impose on the surroundings of the short Mo–P bond of the molecule, a circumstance noted previously.[11]

The reaction of **2** with sulfur also gives small and variable amounts of two additional species, a circumstance that passed unadvertised in our preliminary work.[9] These have been now identified as the tricarbonyl complex *syn*-[$Mo_2Cp_2(\mu$-$\kappa^2_{P,S}$:κ^1_P,η^4-SPMes*)$(CO)_3$] (***syn*-8b**) and the dithiophosphorane complex [$Mo_2Cp_2(\mu$-$\kappa^2_{P,S}$:$\kappa^1_{S'}$,η^6-S_2PMes*)$(CO)_2$] (**9**) (Scheme 2). The formation of ***syn*-8b** can be explained by assuming the liberation of trace amounts of CO during the reaction, perhaps because of partial decomposition of either **2** or **9**. Indeed a separate experiment revealed that **2** reacted with sulfur in the presence of CO (1 atm) to give ***syn*-8b** as the unique product, and that **7b** itself reacted rapidly with CO with the same result (Scheme 2). Actually, the latter reaction can be also applied to the oxophosphinidene complex **7a** to give analogously the tricarbonyl *syn*-[$Mo_2Cp_2(\mu$-$\kappa^2_{P,O}$:κ^1_P,η^4-OPMes*)$(CO)_3$] (***syn*-8a**), although a somewhat higher pressure (ca. 4 atm, Scheme 2) is here required for completion in a convenient reaction time. We should note that both **7a** and **7b** were carbonylated more easily than the phosphinidene precursor **2**,[12] an effect probably associated to the reduction in electron density operated at the metallocene center upon addition of the chalcogen atom to the phosphinidene ligand, although steric effects might be also important, since the reactivity of the thiophosphinidene complex is higher. As for compound **9**, a separate experiment revealed that this complex can be partially desulfurized upon reaction with a common sulfur trap as PPh_3,[14] to yield **7b** and $SPPh_3$, the latter product being identified through its characteristic ^{31}P NMR resonance.[15] However, the reverse reaction (that of **7b** with sulfur), took place very slowly at room temperature and only small amounts of **9** were formed. Instead, a progressive decomposition of the **7b** took place, to give small amounts of the tricarbonyl ***syn*-8b** along with insoluble materials.

Because of the η^4-coordination of the arylphosphinidene ligand in the tricarbonyl complex **3** and in the isocyanide complex **4**, the short Mo–P bond in these substrates is more accessible to external reagents. In agreement with this, these complexes are able to react with elemental sulfur and selenium at room temperature, although no reaction was observed with tellurium even in refluxing toluene solution. In contrast, these complexes were too reactive toward dimethyldioxirane, elemental oxygen, and other sources of oxygen atoms, and complex mixtures of products were obtained in all these cases that could not be properly characterized. Interestingly, the reaction of the tricarbonyl complex **3** with sulfur did not give just ***syn*-8b** but instead an equimolecular mixture of the latter complex with its anti isomer, these diastereoisomers differing in the relative positioning of the sulfur atom and the metallocene carbonyl relative to the Mo_2P plane (Scheme 3). Analogously, the reaction of the isocyanide complex **4** with sulfur gave an equimolecular mixture of the corresponding thiophosphinidene derivatives ***syn*-10b** and ***anti*-10b**. These diastereoisomers could be separated through conventional chromatographic workup and did not convert into each other even in refluxing toluene solutions. As opposed to this behavior, the reactions of **3** and **4**

Scheme 3



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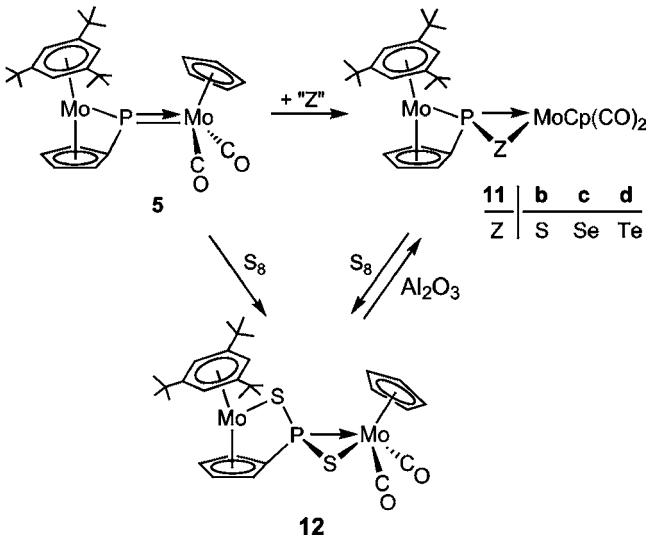
with gray selenium took place in a stereoselective way, to give exclusively the corresponding *syn* isomers ***syn*-8c** and ***syn*-10c** respectively (Scheme 3). However, because of the different structures of gray selenium and S_8, we cannot tell whether this difference has a kinetic or a thermodynamic origin (or both). That kinetic factors are important to these reactions is obvious at least for the sulfur derivatives, since only the syn isomer is obtained when reacting **2** first with S_8 and then with CO, whereas a mixture of syn and anti diastereoisomers is obtained when reacting **2** first with CO (to give **3**) and then with S_8, but the explanation for such a difference is not obvious.

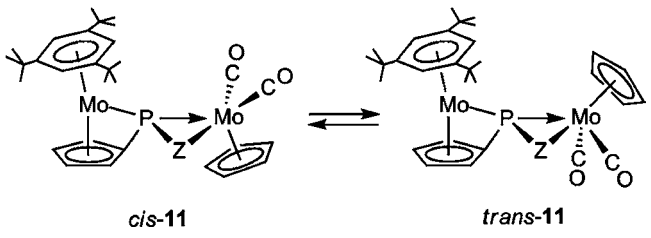
The cyclopentadienylidene-phosphinidene complex **5** is much more reactive than any of the arylphosphinidene complexes **2**, **3**, or **4**, and it is able to react with all chalcogens, as it was the case of the bare phosphinidene complex **1**. Compound **5** actually turned to be too reactive toward dimethyldioxirane, dioxygen and other sources of oxygen atoms, even at low temperature, and gave mixtures of uncharacterized products. In contrast, the reactions with the heavier chalcogens took place selectively under mild conditions [263 K (S), 293 K (Se), 313 K (Te)] to give the corresponding chalcogenophosphinidene derivatives $[Mo_2Cp(\mu\text{-}\kappa^2_{P,Z}{:}\kappa^1_P,\eta^5\text{-}ZPC_5H_4)(\eta^6\text{-HMes*})(CO)_2]$ (Z = S (**11b**), Se (**11c**), Te (**11d**), Scheme 4) in good yields. These products, however,

Scheme 4



were obtained in all cases as equilibrium mixtures of the corresponding cis and trans isomers differing in the relative positioning of the cyclopentadienylic rings with respect to the MoPZ plane in each case (Scheme 5). Besides this, we noticed that the reaction of **5** with sulfur did not stop at the thiophosphinidene step when excess sulfur was present. Under

Scheme 5



the latter conditions, a dithiophosphorane complex $[Mo_2Cp(\mu\text{-}\kappa^2_{P,S}{:}\kappa^1_S,\eta^5\text{-}S_2PC_5H_4)(\eta^6\text{-HMes*})(CO)_2]$ (**12**), analogous to complex **9**, was obtained instead. A separate experiment confirmed that **11b** reacted rapidly with excess sulfur in dichloromethane solution at room temperature to give **12** quantitatively (Scheme 4). As it was the case of the dithiophosphorane **9**, complex **12** could be partially desulfurized to yield the corresponding thiophosphinidene **11b**, but this now occurred very easily, just when attempting its chromatographic purification on alumina at room temperature.

The formation of the dithiophosphorane complexes **9** and **12** involves the insertion of a sulfur atom into the P−Mo(metallocene) bond of the corresponding thiophosphinidene precursor and it was totally unexpected, as it was its easy desulfurization to give the thiophosphinidene precursors **7b** and **11b**. Indeed, dithiophosphorane (or phosphinidene disulfide) complexes are extremely rare species and their chemistry is virtually unknown, a matter to be discussed later on.

Solid-State Structure of New Chalcogenophosphinidene Complexes. We have determined the crystal structures of the selenophosphinidene complex **6c**, the oxophosphinidene complex **7a**, the syn and anti isomers of the thiophosphinidene complex **8b**, the selenophosphinidene complex ***syn*-8c** and the *syn* isomer of the isocyanide thiophosphinidene complex **10b**. ORTEP plots of representative examples are collected in the Figures 1−3, while the more relevant bond lengths and angles are collected in the Table 1. All of these complexes can be viewed as derived from the corresponding precursors by following a formal [2 + 1] addition process of the chalcogen atom to the π(Mo−P) bond in the phosphinidene precursor. This implies that the added atom would be initially positioned perpendicularly to the Mo_2P plane of the precursor, which is in good agreement with the final position found for the chalcogen atom in all these complexes, with the angle between the Mo_2P and MoPZ planes (given by the complementary of the torsion angle Mo2−P−Mo1−Z) being close to 60° for most complexes (~70° for the oxophosphinidene complex **7a**). As a result, all these compounds display two molybdenum centers connected by a chalcogenophosphinidene ligand coordinated in a $\mu\text{-}\kappa^2_{P,Z}{:}\kappa^1_P$-ZPR fashion, therefore providing the metal atoms with four electrons. Besides, the Mes* ring keeps the coordination mode of the corresponding precursor, that is, η^6-bound in complex **7a**, and η^4-bound in the case of complexes **8** and **10**, so the chalcogenophosphinidene ligands in these cases effectively act as a 10- and 8-electron donors, respectively. As for the $MoCp(CO)_2$ fragment, we note that the presence of the chalcogen atom has modified its coordination environment (relative to the corresponding precursor), now being of the classical four-legged piano stool type, with a reduced C−Mo−C angle below 80° somehow reflecting the steric demands of the different groups in the molecule: the more acute angle corresponds to the more crowded isocyanide complex, and the reverse effect is observed for the Mo−P−Mo angles (Table 1). With the exception of **10b**, the $MoCp(CO)_2$ moiety in all these complexes is positioned so that the Cp ligands of the molecule are arranged trans with respect to the MoPZ ring. This conformation, more favored on steric grounds, is presumably retained in solution (vide infra). However, the $MoCp(CO)_2$ moiety of **10b** in the crystal is disordered over two positions implying trans and cis arrangements of the Cp rings of the molecule (50% occupancy for each position, Figure 3); surprisingly, this conformational change has little effect on

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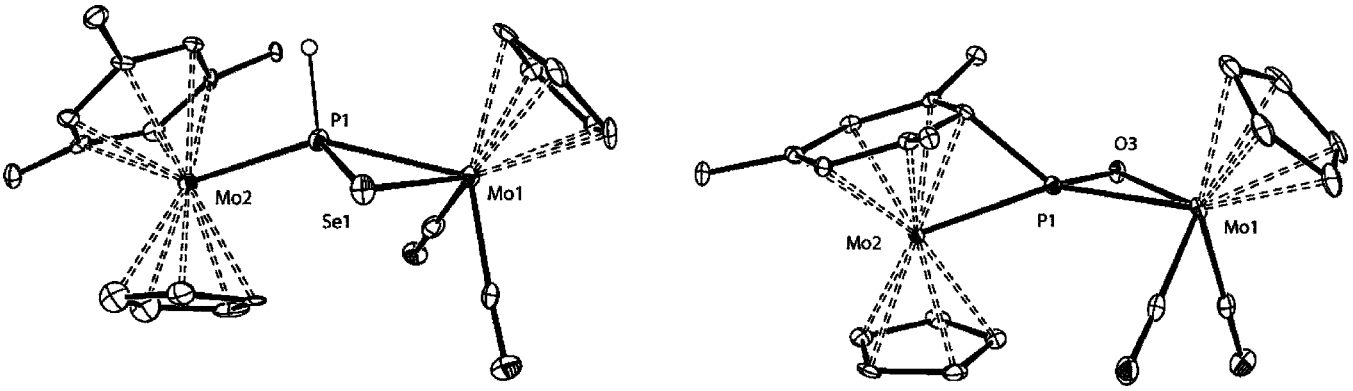

Figure 1. ORTEP diagrams (30% probability) of compound **6c** (left) and **7a** (right), with H atoms (except that bound to P in **6c**) and ^{t}Bu groups (except the C^{1} atoms) omitted for clarity.

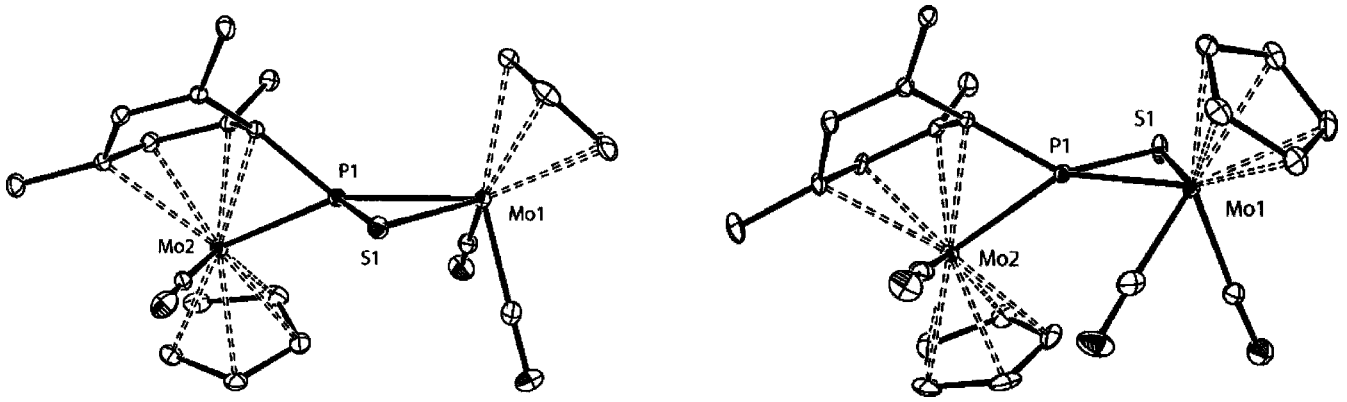

Figure 2. ORTEP diagrams (30% probability) of compound ***syn*-8b** (left) and ***anti*-8b** (right), with H atoms and ^{t}Bu groups (except the C^{1} atoms) omitted for clarity.

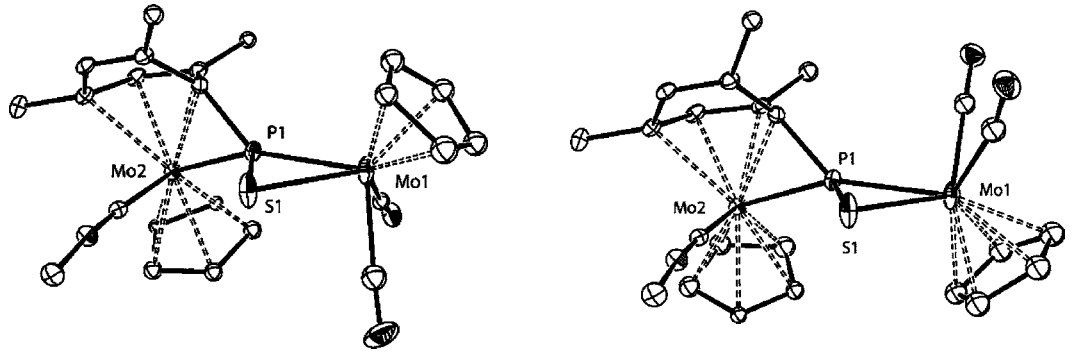

Figure 3. ORTEP diagrams (30% probability) of the two conformers (trans and cis, with 50% occupancy) found in the unit cell of compound ***syn*-10b**, with H atoms and ^{t}Bu groups (except the C^{1} atoms) omitted for clarity.

the rest of the molecule. We recall here that the cyclopentadienylidene-phosphinidene complexes **11** presumably display in solution both cis and trans isomers. We finally note that in all these complexes the coordination environment around the P atom is quite distorted with respect to the tetrahedral geometry, since the Mo1, Mo2, P, and C/H atoms remains close to the same plane that these atoms define in the precursors, as indicated by the sum of Mo1−P−Mo2, Mo1−P−C/H, and Mo2−P−C/H angles, above 350° in all cases. We might actually describe the coordination environment around phosphorus in these complexes as of a distorted trigonal-pyramidal type, with the chalcogen atom occupying the apical position. This geometrical environment has been found previously in several heterometallic complexes having μ_3-PR ligands.[11,16]

We have found previously that the attachment of a 16-electron metal fragment to the *short* multiple Mo−P bond in the phosphinidene complexes **1** and **5** results in a considerable lengthening of *both* Mo−P lengths, to give values approaching the reference figures for single Mo−P (above ∼2.55 Å) and single dative P → Mo bonds (∼2.45 Å) respectively.[11] Therefore we might have anticipated a similar effect upon addition of chalcogen atoms to compounds **1** to **5**, but this is only strictly observed in the phosphinidene derivative **6c** (Mo−P = 2.561(2) and 2.476(2) Å). Incidentally, the Mo−P lengths in the latter complex compare well with the values reported for

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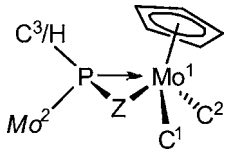
Table 1. Selected Bond Lengths and Angles for New Chalcogenophosphinidene Complexes

parameter[a]	**6c**[b] Z = Se	**7a** Z = O	***syn*-8b** Z = S	***syn*-8b**[c] Z = S	***anti*-8b**[b] Z = S	***syn*-8c** Z = Se	***syn*-10b**[d] Z = S
Mo1–P	2.476(2)	2.3738(9)	2.4337(8)	2.499	2.429(1)	2.4473(9)	2.440(1)
Mo1–Z	2.6557(8)	2.210(2)	2.5646(8)	2.630	2.549(1)	2.6765(5)	2.546(1)
Mo2–P	2.561(2)	2.3737(9)	2.4152(8)	2.460	2.389(1)	2.4151(9)	2.390(1)
Mo1–C1	1.943(7)	1.954(4)	1.959(3)	1.976	1.953(5)	1.960(4)	2.115(12)
Mo1–C2	1.965(7)	1.946(4)	1.951(3)	1.969	1.960(4)	1.939(4)	2.026(7)
P–C3/H	1.49(9)	1.819(3)	1.784(2)	1.815	1.798(4)	1.784(4)	1.776(3)
P–Z	2.199(2)	1.565(2)	2.0365(9)	2.059	2.043(1)	2.190(1)	2.034(1)
C1–Mo1–C2	79.0(3)	76.4(1)	77.7(1)	80.5	76.5(2)	77.6(2)	72.9(4)
Mo1–P–Mo2	137.9(1)	151.8(1)	148.1(1)	146.4	140.9(1)	147.2(1)	151.6(1)
Mo1–P–Z	68.9(1)	64.5(1)	69.4(1)	69.8	68.9(1)	70.3(1)	68.7(1)
Mo1–P–C3/H	110(4)	142.3(1)	140.5(1)	142.0	144.4(1)	141.3(1)	138.6(1)
Mo2–P–Z	125.1(1)	122.0(1)	124.3(1)	123.0	124.1(1)	123.2(1)	122.6(1)
Mo2–P–C3/H	104(3)	62.1(1)	64.0(1)	64.2	64.1(1)	64.3(1)	64.2(1)
P–Mo1–Z	50.6(1)	39.7(1)	48.0(1)	47.2	48.4(1)	50.4(1)	48.1(1)
P–Z–Mo1	60.5(1)	75.7(1)	62.6(1)	63.0	62.7(1)	59.4(1)	63.2(1)

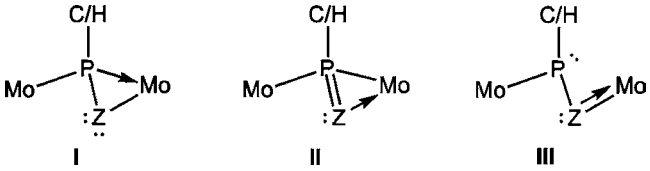
[a]Bond lengths and angles in Å or deg. respectively, according to the labeling shown in the figure below; Mo2 corresponds to the Mo atom of the metallocene fragment and C^3 to the ipso carbon of the aryl ring. [b]Data for one of the two independent molecules present in the unit cell. [c]Data for the DFT-optimized structure of the complex (see text). [d]Data for one of the two disordered molecules present in the unit cell (trans conformation).



the phenylthiophosphinidene complex $[Mo_2Cp_2(\mu\text{-}\kappa^2\text{:}\kappa^1\text{-SPPh})(CO)_5]$ (2.553(3) and 2.447(3) Å).[61] For our arylphosphinidene derivatives, however, we note that the short Mo1–P bond in their precursors (~2.25 Å)[12] is enlarged up to ~2.45 Å upon addition of the chalcogen, as expected, but the Mo2–P bonds (~2.36 Å in the precursors) are just marginally enlarged by less than 0.05 Å. As a result, the Mo2–P lengths in the chalcogenophosphinidene complexes are equal (**7a**) or slightly shorter than the Mo1–P lengths, which is unexpected.

The P–Z lengths in our chalcogenophosphinidene complexes are shorter than the reference single-bond values, and therefore suggest the presence of significant multiplicity in the corresponding bonds, this effect being less pronounced for the heavier chalcogens, as expected. Thus the P–O length of 1.565(2) Å in **7a** is only 0.05 Å longer than the values measured in related molecules formally displaying P=O double bonds, cf. 1.514(3) Å in the anion $[MoCp\{P(O)Mes^*\}(CO)_2]^-$,[8e] 1.49(2) Å in the phosphorus monoxide complex $[Mo\{NR(Ar)\}_3(PO)]$ [R = ^{t}Bu, Ar = 3,5-$Me_2C_6H_3$],[6f] 1.503(3) Å in the $\mu\text{-}\kappa^1_P\text{:}\kappa^1_P$-oxophosphinidene complex $[Fe_2Cp_2\{\mu\text{-P(O)Cy}\}(\mu\text{-CO})(CO)_2]$,[6c] or 1.489(6) Å in $P(O)Me_3$.[17] In any case, this length is substantially shorter than the reference P–O single bond length of ca. 1.65 Å. Besides this, the O–Mo1 length of 2.210(2) Å compares well with conventional O→Mo donor bonds (e.g., 2.20–2.26 Å in three isomers of the complex $[Mo_2Cp_2\{\mu\text{-}\eta^1,\kappa_O\text{:}\eta^2\text{-C}(CO_2Me)CH(CO_2Me)\}(\mu\text{-PCy}_2)(CO)_2]$.[18] This can be accounted for by assuming that, in addition to the conventional canonical form **I**, the oxophosphinidene bonding to the $MoCp(CO)_2$ center has a significant contribution from the canonical form **II**, with P=O and O → Mo bonds (Chart 2). In the thiophosphinidene complexes, however, the P–S distances of ~2.03 Å depart a bit more from the reference P=S lengths (in the range 1.85–1.95 Å for either free or coordinated $P(S)R_3$ ligands,[19] or for a terminal PS ligand),[20] and are similar or just slightly shorter than those in

Chart 2



related complexes displaying comparable side-bound RPS or R_2PS ligands.[6b,i–n] Thus, the contribution of form **II** to the bonding in the thiophosphinidene complexes is likely to be somewhat smaller than in the case of the oxophosphinidene analogues. As for the selenophosphinidene complexes **6c** and ***syn*-8c**, we note that the P–Se lengths of ~2.20 Å still are slightly shorter than the reference P–Se single bond lengths (cf. 2.24(1) Å in P_4Se_3),[21] although substantially longer than the value expected for a P=Se bond (cf. 2.117(2) Å in $[FeCp\{\kappa^1_P\text{-P(Se)}(OR)_2\}(CO)_2]$,[22] while the Mo–Se lengths of ~2.66 Å compare well with the value of 2.6897(4) Å measured in the related selenoacyl complex $[Mo(\eta^2\text{-SeCR})(CO)_2\{HB(pz)_3\}]$.[23] Interestingly, two canonical forms involving either single or double Se–C bonds were proposed in the latter complex to account for the bonding within the corresponding MoCSe ring.

DFT Calculations on the Thiophosphinidene Complex *syn*-8b. To gain further insight into the bonding in our chalcogenophosphinidene complexes we analyzed the thiophosphinidene complex ***syn*-8b** using Density Functional Theory (DFT) methods (see the Experimental Section for details).[24] First we note that the optimized geometrical parameters for this molecule are in good agreement with the experimental values (Table 1), although the computed figures for lengths involving the metal atoms are slightly higher (by less than 0.05 Å) than the corresponding experimental data, as usually found with the functionals currently used in the DFT computations of transition-metal compounds.[24a,25] We then

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examined the Kohn−Sham molecular orbitals (see the Supporting Information) in search for any π bonding interactions, particularly those involving the sulfur atom. As expected, the HOMO of the molecule has a large contribution from a lone electron pair at sulfur (Figure 4). Evidence for the

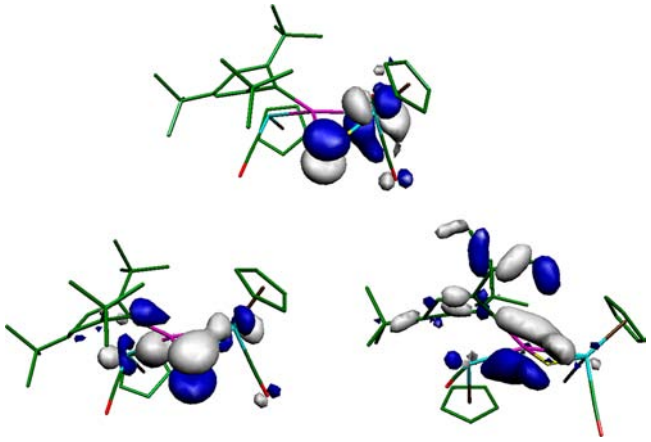

Figure 4. Selected molecular orbitals of compound ***syn*-8b**: HOMO (upper, −4.91 eV), HOMO−4 (left, −6.01 eV) and HOMO−13 (right, −8.23 eV).

presence of π(Z−Mo) bonding interactions in these complexes (represented by the canonical form **II** in Chart 2) is found in the HOMO−13, implying a multicentric interaction with not only π(P−S) but also σ(P−Mo2) and σ(P−C) bonding character (Figure 4). Yet the orbital analysis reveals a further and unsuspected interaction, since not far below the HOMO there is an orbital (HOMO−4) having σ(P−Mo2) and some π(S−Mo1) bonding character. We have found recently that oxygen atoms bridging Mo atoms can act as π donors to one of the metal centers,[26] but this interaction might not be anticipated in the absence of electronic insaturation at the corresponding metal center. Indeed, in our complexes, such a π(S−Mo1) interaction, partially canceled by the π^*(S−Mo1) character of the HOMO, would oversaturate the $MoCp(CO)_2$ center and should be accompanied by some loss of P−Mo binding. The canonical form **III** would illustrate this effect, perhaps in an exaggerated way. It seems that more chalcogenophosphinidene complexes should be investigated under such a perspective before any definitive conclusion can be extracted on the extent of the π interactions within this family of complexes.

Solution Structure of Dimolybdenum Chalcogenophosphinidene Complexes. Spectroscopic data in solution for compounds **6**−**11** (Table 2 and Experimental Section) are essentially consistent with the solid-sate structures discussed above. The binding of the chalcogen to the phosphinidene P atom of complexes **1**−**5** causes a dramatic shielding of some 400−500 ppm on the corresponding P nuclei. The arylchalcogenophosphinidene resonances are found in the range 65−140 ppm, and similar values are observed for the cyclopentadienylidene compounds of type **11**. These figures are not far from those measured for related μ-$\kappa^2_{P,Z}$:κ^1_P-ZPR complexes previously reported in the literature, such as $[Cr_2Cp_2(\mu\text{-}\kappa^2\text{:}\kappa^1\text{-SPAr})(CO)_5]$ (Ar = $C_6H_4OCH_3$, δ_P 74.7 ppm),[6d] $[Fe_2Cp_2(\mu\text{-}\kappa^2\text{:}\kappa^1\text{-SPPh})(CO)_3]$ (δ_P 86.8 ppm),[6h] $[Mo_2Cp_2(\mu\text{-}\kappa^2\text{:}\kappa^1\text{-SPAr})(CO)_5]$ (Ar = $C_6H_4OCH_3$, δ_P 5.0 ppm),[6l] and $[Mo_2Cp_2(\mu\text{-}\kappa^2\text{:}\kappa^1\text{-SePMes})(CO)_5]$ (δ_P −51.3 ppm).[6i]

Table 2. IR and ^{31}P NMR Data for New ZPR- and S_2PR-Bridged Complexes

compound	ligand	ν_{st}(CO)[a] (cm^{-1})	δ_P (ppm),[b] [J_{PZ} (Hz)]
6a	OPH	1913 (vs), 1818 (s)[c]	38.6
6b	SPH	1919 (vs), 1830 (s)[c]	−32.4
6c	SePH	1920 (vs), 1832 (s)[c]	−24.7 [391]
6d	TePH	1919 (vs), 1835 (s)[c]	−38.3 [740]
7a	OPMes*	1933 (vs), 1844 (s)	141.6
7b	SPMes*	1933 (vs), 1848 (s)	124.8
***syn*-8a**	OPMes*	1960 (s), 1931 (vs), 1844 (s)	98.9
***syn*-8b**	SPMes*	1959 (s), 1933 (vs), 1847 (s)	73.5
***anti*-8b**	SPMes*	1962 (vs), 1932 (m), 1854 (m)	103.2
***syn*-8c**	SePMes*	1963 (s), 1932 (vs), 1848 (s)	84.6 [440]
9	S_2PMes*	1933 (vs), 1846 (s)	64.1[d]
***syn*-10b**	SPMes*	2134 (m),[e] 1921 (vs), 1833 (s)	73.8
***anti*-10b**	SPMes*	2120 (m),[e] 1927 (vs), 1839 (s)	97.5
***syn*-10c**	SePMes*	2134 (m),[e] 1921 (vs), 1836 (s)	88.3 [430][d]
11b[f]	SPC_5H_4	1952 (vs), 1871 (m)[g]	94.8 (cis), 114.8 (trans)[h]
11c[f]	$SePC_5H_4$	1950 (vs), 1871 (m, sh), 1867 (m)[g]	109.8 (cis), 126.3 (trans)[i]
11d[f]	$TePC_6H_4$	1947 (vs), 1868 (m)[g]	106.5 (cis), 118.1 (trans)[j]
12	$S_2PC_5H_4$	1948 (vs), 1858 (s)	82.8

[a]C−O stretching frequencies recorded in dichloromethane solution, unless otherwise stated. [b]Recorded in C_6D_6 solution at 290 K and 121.50 MHz unless otherwise stated; δ relative to external 85% aqueous H_3PO_4. [c]Recorded in tetrahydrofuran solution. [d]Recorded in CD_2Cl_2 solution. [e]C−N stretch of the CN^{t}Bu ligand. [f]Mixture of cis and trans isomers (see text). [g]Recorded in petroleum ether solution. [h]Recorded in CD_2Cl_2 solution at 233 K. [i]Recorded in CD_2Cl_2 solution at 253 K. [j]Recorded in CD_2Cl_2 solution at 213 K.

The nature of the chalcogen has a significant influence on the ^{31}P chemical shifts of these complexes, but the observed trend O > Se > S > Te does not seem to follow from a single atomic property. Moreover, the conformation has an influence just as important, with the anti isomers giving resonances some 25−30 ppm more deshielded than the corresponding syn isomers, and the cis and trans isomers of compounds **11** differing analogously by 10−15 ppm. The resonances of the selenophosphinidene complexes **6c**, **8c** and **10c** display observable ^{31}P−^{77}Se couplings in the range 390−440 Hz that compare well with the value of 413 Hz measured for $[Mo_2Cp_2(\mu\text{-}\kappa^2\text{:}\kappa^1\text{-SePMes})(CO)_5]$.[6i] Analogously, the resonance of the tellurophosphinidene complex **6d** displays a ^{31}P−^{125}Te coupling of 740 Hz, not far from the value of 856 Hz reported by Huttner et al. for the diiron complex $[Fe_2(\mu\text{-TeMes})\{\mu\text{-PMe(TeMes)}\}(CO)_6]$.[27] All of them are fairly high values for one-bond P−Z couplings (Z = Se, Te),[28] which is consistent with the relatively short P−Z lengths measured in the solid state and with the presence of a significant π(P−Z) bonding interaction within the MoPZ ring of these compounds

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(canonical form **II**). We finally note that compounds **11** exist in solution as equilibrium mixtures of cis and trans isomers. In contrast, compound **10b**, which in the solid state displays a 50% mixture of analogous cis and trans isomers, displays just a single ^{31}P NMR resonance in solution, identified as originated from the trans isomer (see below).

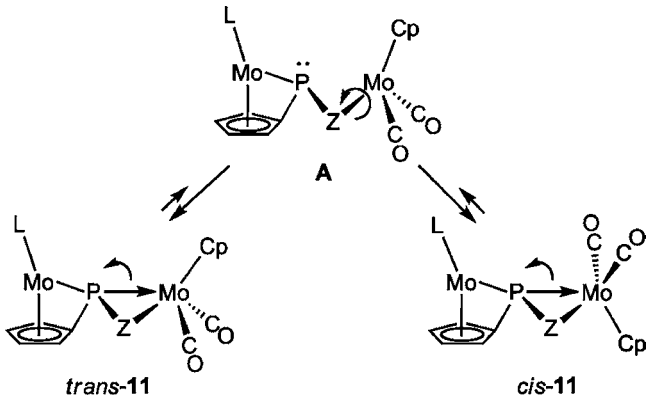
The ^{1}H and ^{13}C{^{1}H} NMR spectra of compounds **6**−**11** are consistent with the number and symmetry relationships of the groups present, then deserving no detailed comments (see the Experimental Section). We just note that for compounds **8** and **10** the retention of the η^4-coordination of the aryl ring of the chalcogenophosphinidene ligand is denoted by the appearance of six different aryl resonances in the corresponding ^{13}C NMR spectra, four of them strongly shielded (by ∼40−50 ppm for C^2, C^3 and C^4; ∼80−90 ppm for C^1) and two of them with chemical shifts (∼128 and 157 ppm) similar to those for substituted cyclohexenes, which are thus assigned to the two nonbonded aryl carbon atoms. These spectroscopic features are comparable to those observed for their phosphinidene precursors **3** and **4**.[12] The presence of the chalcogen atom is particularly reflected in the C^1 resonances, that become more shielded and more weakly coupled to phosphorus ($\delta_C \approx 60$ ppm, $J_{PC} \approx 40$ Hz). We finally note that the μ-ZPH complexes give rise to a relatively deshielded proton resonance (4.6−6.3 ppm), displaying a strong one-bond P−H coupling between 250 and 270 Hz. These couplings are somewhat higher than those measured in the heterometallic derivatives of **1** ($J_{HP} \approx$ 220 Hz),[11] which could be related with a somewhat higher degree of pyramidalization around the P atom in the chalcogenophosphinidene complexes, when compared to the mentioned heterometallic complexes.

As noted above, all complexes derived from arylphosphinidene substrates were found in the solid state to exist as trans isomers, and presumably this conformation is retained in solution. In the case of **10b** this was not granted because of the 50% cis/trans disorder found in the crystal. In solution, however, only one isomer is present, which we have identified as the trans isomer on the basis of a standard NOESY ^{1}H NMR experiment. Indeed the latter experiment revealed the absence of NOE enhancements between the protons of the Cp rings and the presence of strong NOEs from the *ortho*-^{t}Bu(Mes*) groups to the protons of the $MoCp(CO)_2$ fragment.

All compounds **6** to **11** display two C−O stretching bands, as anticipated for molecules having cisoid $M(CO)_2$ oscillators, except for the tricarbonyls **8**, which display an additional C−O stretch at ∼1960 cm^{-1} corresponding to the carbonyl ligand bound to the metallocene moiety, and for the isocyanide complexes **10**, which display an additional C−N stretch at ∼2130 cm^{-1}. The average stretching frequencies of the $Mo(CO)_2$ oscillators in these compounds are higher than in the corresponding precursors, as expected from the reduction in the electron density at the $MoCp(CO)_2$ fragment caused by the presence of a relatively electronegative chalcogen atom bound to the metal. However, the observed ordering of frequencies within each family of complexes (O < S ≤ Se ≤ Te) is unexpected, with the most electronegative element (O) giving the lowest C−O stretches. However, if we take into account the presence of weak π(Z→Mo) bonding interactions, as discussed in the preceding section (ie. the canonical form **III** in Chart 2), and since the lighter chalcogen (O) is expected to be the stronger π donor, then an ordering such as the one observed might be perhaps justified. We finally note that, while the average C−O stretches in the pairs **2**/**7**, **3**/**8**, **4**/**10**, and **5**/**11** differ by some 30−40 cm^{-1}, this difference in the PH compounds **1**/**6** is reduced to only 6−17 cm^{-1}. This might be related to the electronic structure of the phosphinidene compound **1**, with a π(Mo−P) interaction essentially located at the P−$MoCp(CO)_2$ bond, whereas in the phosphinidene complexes **2** to **5** this π bonding interaction is widely delocalized over the Mo−P−Mo skeleton of these molecules.[11]

The cis/trans equilibrium in compounds **11** is moderately fast on the NMR time scale so as to give somewhat broad ^{1}H NMR resonances at room temperature that become sharper upon cooling. The equilibrium constants are also solvent- and temperature-dependent. For instance, the ratio cis/trans for **11b** changes from 4/1 in C_6D_6 to ∼1/1 CD_2Cl_2, while in the latter solvent the ratio cis/trans changes to 2/3 at 233 K. A standard NOESY ^{1}H NMR experiment carried out on **11b** in the latter conditions confirmed the exchange process between these isomers, and also that the major isomer (the one with the more deshielded ^{31}P NMR resonance, Table 2) exhibits positive NOE enhancements of the Cp protons from the ^{t}Bu and CH protons of the aryl ring, thus identifying it as the trans isomer. In contrast, the minor isomer displayed none of these NOE enhancements but one between the Cp and one of the C_5H_4 resonances (δ 4.48 ppm), thus identifying it as the cis isomer. To account for the facile cis/trans interconversion in solution we propose a rearrangement involving the cleavage of the P → $MoCp(CO)_2$ bond to give an unsaturated intermediate **A** (Scheme 6) that could easily undergo rotation of the $MoCp(CO)_2$ moiety around the Z−Mo bond, as required to complete the isomerization.

Scheme 6[a]



[a] L = η^6-HMes*.

Structural Characterization of Dithiophosphorane Complexes. The structure of compound **12** in the solid state (Figure 5 and Table 3) can be visualized as derived from that of its thiophosphinidene precursor **11b** (trans isomer) after insertion of a sulfur atom into the P−Mo(metallocene) bond. This yields a dithiophosphorane ligand *P*,*S*-bound to one metal and *S*′-bound to another one, a novel coordination mode for this type of ligand (**A** in Chart 3). Actually only a few dithiophosphorane complexes have been reported in the literature, they being limited to the nickel complex [Ni($\kappa^2_{P,S}$-S_2PPh)(PEt_2Ph)$_2$] (type **B**),[29] the binuclear complexes [M_2(μ-$\kappa^2_{S,S'}$-κ^1_P-S_2PR)$L_2(CO)_n$] (type **C**; M = Cr, L = Cp or Cp*, R = C_6H_4OMe, n = 5;[6d] M = Mo, L = Cp, R = Ph, n = 5; M = Mn, L = CO, R = Ph, n = 7),[30] and the triiron complex [Fe_3(μ_3-$\kappa^2_{S,S'}$:$\kappa^2_{S,S'}$:κ^1_P-$S_2P(C_6H_4OMe)(CO)_7$][31] (type **D**, Chart 3). All

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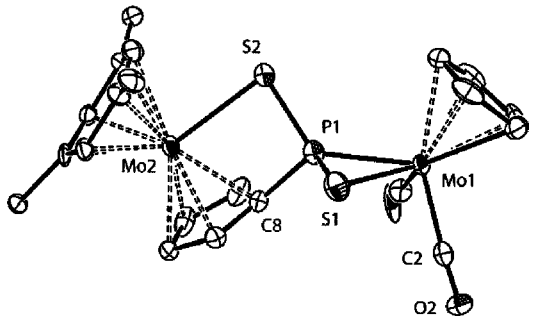
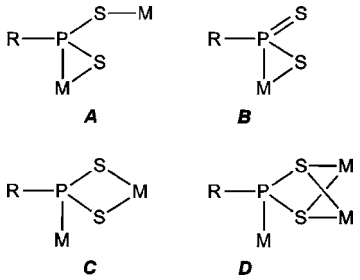


Figure 5. ORTEP diagram (30% probability) of compound **12**, with H atoms and ^{t}Bu groups (except their C^{1} atoms) omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 12

Mo1−P1	2.336(3)	C1−Mo1−C2	81.8(4)
Mo1−S1	2.536(3)	P1−Mo1−C1	78.3(3)
Mo1−C1	2.057(12)	P1−Mo1−C2	110.2(3)
Mo1−C2	1.979(10)	Mo1−S1−P1	48.9(1)
P1−S1	2.023(4)	Mo1−P1−S1	70.7(1)
P1−S2	2.027(4)	Mo1−P1−S2	129.0(1)
P1−C8	1.833(10)	Mo1−P1−C8	128.6(3)
Mo2−S2	2.616(3)	S2−P1−C8	93.6(3)
Mo2−C8	2.294(9)	S2−P1−S1	123.8(2)
Mo2−C9	2.307(10)	C8−P1−S1	112.0(4)

Chart 3



these complexes are usually formulated as containing the corresponding phosphonodithioite (RPS_2^{2-}) ligand.

The coordination environment around phosphorus in **12** is of the distorted trigonal pyramidal type persistently found in the chalcogenophosphinidene complexes **7**−**10**, with the C8, S2, Mo1, and P atoms almost in the same plane (sum of angles around P ≈ 351°) and the S1 atom occupying the apical position. The P−S1 and S1−Mo distances within the PSMo ring (2.023(4) Å and 2.536(3) Å respectively) are very similar to the corresponding values of ∼2.03 Å and 2.55 Å in our thiophosphinidene complexes (Table 1). Thus we conclude that some multiplicity must be still present at the P−S bond. Surprisingly, the exocyclic P−S2 length is also very short (2.027(4) Å). In fact all these P−S lengths are comparable to those measured for the coordinated S atoms in the mentioned nickel and chromium complexes (types **B** and **C**),[29,6d] and are only 0.05 Å longer than the P═S bond in the nickel complex. In contrast, the P−S lengths in the mentioned triiron complex of type **D**, where no multiplicity in the P−S bonds can be present, are substantially higher (ca. 2.14 Å). All of this suggests the retention of significant multiplicity at the P−S bonds of the dithiophosphorane ligands in most of their coordination modes. On the other hand we note a significant shortening of ∼0.1 Å for the Mo−P length in **12**, compared to the corresponding distances in our thiophosphinidene complexes (Table 1), a geometrical feature with no clear explanation. Finally, we note that the S2−Mo2 length of 2.616(3) Å is substantially longer than the values usually found in comparable molybdenum metallocene complexes (cf. 2.46−2.50 Å for $[MoCp_2(SR)_2]$ complexes)[32] or even in the sulfido-bridged complex $[Cp_2Mo(\mu_3\text{-}S)_2Fe_2(CO)_6]$ (Mo−S ca. 2.55 Å),[33] where no π-bonding interactions involving the S atoms are to be expected. It thus appears that the Mo−S linkage of the dithiophosphorane ligand to the metallocene moiety in **12** is very weak, and possibly the complex would not be stable in the absence of the strong P−C8 bond additionally linking these fragments.

The IR data for the dithiophosphorane complexes **9** and **12** are expectedly very similar to those of the corresponding thiophosphinidene complexes **7b** and **11b**, but their ^{31}P resonances are significantly more shielded (by 30 to 60 ppm), an effect that might be related to the formal increase in the oxidation state of the phosphorus atom at the dithiophosphorane ligand. The presence of one of the S atoms of the S_2PR ligand bound to the metallocene center might be related to the significant shielding or deshielding observed in some of the proton resonances of the C_6H_3 or C_5H_4 rings in these compounds (see the Experimental Section), but otherwise the spectroscopic features of these complexes are unremarkable. However we note that, in contrast to its precursor **11b**, complex **12** displays a single isomer in solution, identified as the trans isomer (the same present in the solid state) on the basis of a standard NOESY ^{1}H NMR experiment, as described for **11b**.

CONCLUDING REMARKS

The phosphinidene-bridged complexes **1** to **5** react readily with the elemental chalcogens to give with good yield chalcogenophosphinidene derivatives having $\mu\text{-}\kappa^2_{P,Z}\text{:}\kappa^1_{P}$-ZPR ligands resulting from the formal [2 + 1] addition of a chalcogen atom (Z) to the multiple Mo−P bond in the phosphinidene substrates. The reactions proceed more rapidly for the substrates having a less crowded phosphorus environment (**1** and **5**), whereas the more congested phosphinidene complexes fail to react with the heaviest chalcogen (**2** to **4**) or even with gray selenium (**2**). Elemental oxygen is too reactive in these reactions, and better results are obtained when using dimethyldioxirane as a milder source of oxygen atoms. On the other hand, elemental sulfur is unique in being able to transfer a second chalcogen atom to some of the phosphinidene substrates. This reaction proceeds by selective insertion of sulfur into the P−Mo(metallocene) bond to yield dithiophosphorane complexes with an unprecedented $\mu\text{-}\kappa^2_{P,S}\text{:}\kappa^1_{S}$-coordination mode. The structural and spectroscopic data of the new chalcogenophosphinidene complexes here reported suggest that the chalcogen atom in these molecules is involved in a significant π bonding interaction with phosphorus and perhaps even with the metal atom of the ZPMo ring, which is in agreement with the orbital interactions computed, using DFT methods, for one of the thiophosphinidene complexes. Significant π bonding interactions between sulfur and phosphorus seem to be present even in the dithiophosphorane complexes.

EXPERIMENTAL SECTION

General Comments. All manipulations and reactions were carried out using standard Schlenk techniques under an atmosphere of dry,

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oxygen-free nitrogen (99.995%). Solvents were purified according to standard literature procedures,[34] and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 333–338 K. Compounds $[Mo_2Cp_2(\mu\text{-}PH)(\eta^6\text{-}HMes^*)(CO)_2]$ (**1**),[10] $[Mo_2Cp_2(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^6\text{-}PMes^*)(CO)_2]$ (**2**), $[Mo_2Cp_2(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^4\text{-}PMes^*)(CO)_3]$ (**3**), $[Mo_2Cp_2(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^4\text{-}PMes^*)(CO)_2(CN^tBu)]$ (**4**), and $[Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2]$ (**5**),[11] were prepared according to literature procedures. Other reagents were obtained from the usual commercial suppliers and used without further purification. Filtrations were usually carried out through diatomaceous earth, or using a canula. Aluminum oxide for column chromatography (alumina, activity IV) was deactivated by addition of the appropriate amount of water to the commercial material (Aldrich, neutral, activity I). Chromatographic separations were carried out using jacketed columns (2 × 30 cm) refrigerated by tap water unless otherwise stated (~288 K), or with a closed 2-propanol circuit kept at the desired temperature with a cryostat. NMR spectra were recorded at 400.13 MHz (^{1}H), 121.50 MHz (^{31}P{^{1}H}), and 75.47 MHz (^{13}C{^{1}H}), on C_6D_6 solutions at room temperature unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal TMS (^{1}H, ^{13}C) or external 85% H_3PO_4 aqueous solution (^{31}P), with positive values for frequencies higher than that of the reference. Coupling constants (J) are given in Hertz.

Preparation of $[Mo_2Cp_2(\mu\text{-}\kappa^2_{P,O}\text{:}\kappa^1_P\text{-}OPH)(\eta^6\text{-}HMes^*)(CO)_2]$ (6a). An acetone solution of Me_2CO_2 (1 mL of a 0.08 M solution, 0.080 mmol)[13] was added to a tetrahydrofuran solution (4 mL) of compound **1** (0.026 g, 0.040 mmol) at 233 K, and the mixture was stirred while allowing it to reach room temperature for ca. 20 min. The solvent was then removed under vacuum, the residue was extracted with toluene/petroleum ether (2:1), and the extracts were filtered using a canula. Removal of the solvents from the filtrate gave an orange residue containing compound **6a** as the major species. However, all attempts to isolate this highly air-sensitive compound as a pure solid were unsuccessful and led instead to its progressive decomposition. ^{1}H NMR: δ 6.33 (d, J_{HP} = 252, 1H, PH), 5.21 (s, 5H, Cp), 4.70 (d, J_{HP} = 7, 3H, C_6H_3), 4.54 (d, J_{HP} = 6, 5H, Cp), 1.16 (s, 27H, ^{t}Bu).

Preparation of $[Mo_2Cp_2(\mu\text{-}\kappa^2_{P,S}\text{:}\kappa^1_P\text{-}SPH)(\eta^6\text{-}HMes^*)(CO)_2]$ (6b). A tetrahydrofuran solution of S_8 (2 mL of a 0.02 M solution, 0.040 mmol) was added to a tetrahydrofuran solution (4 mL) of compound **1** (0.026 g, 0.040 mmol) at 233 K, and the mixture was stirred while allowing it to reach room temperature for ca. 20 min to give an orange-brown solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/8) and the extracts were chromatographed on alumina. Elution with the same solvent mixture gave an orange fraction yielding, after removal of solvents, compound **6b** as a brown microcrystalline solid (0.026 g, 94%). Anal. Calcd for $C_{30}H_{41}Mo_2O_2PS$: C, 52.33; H, 6.00. Found: C, 52.23; H, 5.92. ^{1}H NMR: δ 5.06 (s, 5H, Cp), 4.59 (d, J_{HP} = 8, 3H, C_6H_3), 4.57 (d, J_{HP} = 269, 1H, PH), 4.34 (d, J_{HP} = 5, 5H, Cp), 1.15 (s, 27H, ^{t}Bu).

Preparation of $[Mo_2Cp_2(\mu\text{-}\kappa^2_{P,Se}\text{:}\kappa^1_P\text{-}SePH)(\eta^6\text{-}HMes^*)(CO)_2]$ (6c). Gray selenium (0.006 g, 0.076 mmol) was added to a tetrahydrofuran solution (4 mL) of compound **1** (0.026 g, 0.040 mmol) at 233 K, and the mixture was stirred while allowing it to reach room temperature for ~20 min to give an orange-brown solution. Workup as described for **6b** yielded compound **6c** as a light brown microcrystalline solid (0.028 g, 95%). The crystals used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a concentrated toluene solution of the complex at 253 K. Anal. Calcd for $C_{30}H_{41}Mo_2O_2PSe$: C, 49.00; H, 5.62. Found: C, 48.85; H, 5.49. ^{1}H NMR: δ 5.03 (s, 5H, Cp), 4.75 (d, J_{HP} = 263, 1H, PH), 4.62 (d, J_{HP} = 8, 3H, C_6H_3), 4.35 (d, J_{HP} = 5, 5H, Cp), 1.15 (s, 27H, ^{t}Bu).

Preparation of $[Mo_2Cp_2(\mu\text{-}\kappa^2_{P,Te}\text{:}\kappa^1_P\text{-}TePH)(\eta^6\text{-}HMes^*)(CO)_2]$ (6d). The procedure is completely analogous to that described for **6c**, but using solid tellurium instead (0.020 g, 0.156 mmol). This yielded compound **6d** as an ocher microcrystalline solid (0.030 g, 95%). Anal. Calcd for $C_{30}H_{41}Mo_2O_2PTe$: C, 45.95; H, 5.27. Found: C, 45.78; H, 5.11. ^{1}H NMR: δ 5.17 (d, J_{HP} = 256, 1H, PH), 4.98 (s, 5H, Cp), 4.68 (d, J_{HP} = 8, 3H, C_6H_3), 4.35 (d, J_{HP} = 5, 5H, Cp), 1.14 (s, 27H, ^{t}Bu).

Preparation of $[Mo_2Cp_2(\mu\text{-}\kappa^2_{P,O}\text{:}\kappa^1_P,\eta^6\text{-}OPMes^*)(CO)_2]$ (7a). An acetone solution of Me_2CO_2 (2 mL of a 0.08 M solution, 0.160 mmol)[13] was added to a dichloromethane solution (3 mL) of compound **2** (0.025 g, 0.038 mmol), and the mixture was stirred at room temperature for 30 min to give a red solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (3/1) and the extracts were chromatographed on alumina. Elution with the same solvent mixture gave a red fraction yielding, after removal of solvents, compound **7a** as a red microcrystalline solid (0.018 g, 70%). X-ray-quality crystals were grown from a concentrated petroleum ether solution of the complex at 253 K. Anal. Calcd for $C_{30}H_{39}Mo_2O_3P$: C, 53.74; H, 5.86. Found: C, 53.62; H, 5.81. ^{1}H NMR (300.13 MHz): δ 5.50 (s, 1H, C_6H_2), 5.35 (s, 5H, Cp), 5.34 (s, 1H, C_6H_2), 4.85 (d, J_{HP} = 3, 5H, Cp), 1.44, 1.40, 0.91 (3s, 3 × 9H, ^{t}Bu).

Reaction of Compound 2 with Sulfur. A dichloromethane solution of S_8 (1 mL of a 0.125 M solution, 0.125 mmol) was added to a dichloromethane solution (4 mL) of compound **2** (0.075 g, 0.115 mmol), and the mixture was stirred at room temperature for 2 h to give an orange solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/2) and the extracts were chromatographed on alumina. Elution with the same solvent mixture gave an orange fraction yielding, after removal of solvents, compound $[Mo_2Cp_2(\mu\text{-}\kappa^2_{P,S}\text{:}\kappa^1_P,\eta^6\text{-}SPMes^*)(CO)_2]$ (**7b**) as an orange microcrystalline solid (0.050 g, 64%). Elution with a 2/1 solvent mixture gave a second orange fraction and then a red fraction, these yielding respectively the complexes *syn*-$[Mo_2Cp_2(\mu\text{-}\kappa^2_{P,S}\text{:}\kappa^1_P,\eta^4\text{-}SPMes^*)(CO)_3]$ (*syn*-**8b**) and $[Mo_2Cp_2(\mu\text{-}\kappa^2_{P,S}\text{:}\kappa^1_{S'},\eta^6\text{-}S_2PMes^*)(CO)_2]$ (**9**) in variable amounts, typically around 5–8%.

Data for Compound ***7b***. Anal. Calcd for $C_{30}H_{39}Mo_2O_2PS$: C, 52.48; H, 5.73. Found: C, 52.30; H, 5.60. ^{1}H NMR (300.09 MHz, CD_2Cl_2): δ 5.68 (d, J_{HH} = 1, 1H, C_6H_2), 5.56 (dd, J_{HP} = 3, J_{HH} = 1, 1H, C_6H_2), 5.47 (s, 5H, Cp), 4.90 (d, J_{HP} = 3, 5H, Cp), 1.43, 1.36, 1.21 (3s, 3 × 9H, ^{t}Bu). ^{1}H NMR (400.54 MHz, C_6D_6): δ 5.49 (d, J_{HH} = 1, 1H, C_6H_2), 5.38 (dd, J_{HP} = 3, J_{HH} = 1, 1H, C_6H_2), 5.19 (s, 5H, Cp), 4.85 (d, J_{HP} = 3, 5H, Cp), 1.60, 1.41, 0.88 (3s, 3 × 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ 255.8 (d, J_{CP} = 27, CO), 243.0 (d, J_{CP} = 3, CO), 119.2 [s, $C(C_6H_2)$], 109.4 [d, J_{CP} = 9, $C(C_6H_2)$], 98.0 [d, J_{CP} = 4, $C(C_6H_2)$], 94.2, 88.8 (2s, Cp), 82.0 [d, J_{CP} = 5, $CH(C_6H_2)$], 78.5 [d, J_{CP} = 9, $CH(C_6H_2)$], 63.6 [d, J_{CP} = 96, $C^1(C_6H_2)$], 35.7 [s, $CH(^tBu)$], 35.5 [d, J_{CP} = 2, $C(^tBu)$], 34.5, 34.3 [2s, $C(^tBu)$], 34.0, 31.5 [2s, $CH(^tBu)$].

Data for Compound ***9***. ^{1}H NMR (300.09 MHz, CD_2Cl_2): δ 5.58 (d, J_{HP} = 2, 5H, Cp), 5.50 (s, 5H, Cp), 4.85 (s, br, 1H, C_6H_2), 3.18 (dd, J_{HP} = 8, J_{HH} = 1, 1H, C_6H_2), 1.18, 1.152, 1.148 (3s, 3 × 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (DEPT, 100.62 MHz, CD_2Cl_2, 213K): δ 107.2 [s, $CH(C_6H_2)$], 95.0, 92.7 (2s, Cp), 90.0 [s, $CH(C_6H_2)$], 32.1 [s, $2CH(^tBu)$], 32.0 [s, $CH(^tBu)$].

Preparation of *syn*-$[Mo_2Cp_2(\mu\text{-}\kappa^2_{P,O}\text{:}\kappa^1_P,\eta^4\text{-}OPMes^*)(CO)_3]$ (*syn*-8a). A toluene solution (2 mL) of compound **7a** (0.035 g, 0.052 mmol) was placed in a bulb equipped with a Young's valve. The bulb was cooled at 77 K, degassed under vacuum, and then refilled with CO. The valve was then closed, the solution was allowed to reach room temperature and then further stirred at 338 K for 2.5 h to give a yellowish solution. After removal of the solvent under vacuum, the residue was dissolved in a minimum dichloromethane and was chromatographed on alumina. Elution with petroleum ether gave a rose fraction containing a small amount of $[Mo_2Cp_2(CO)_6]$. Elution with dichloromethane/petroleum ether (3/1) gave a yellow-orange fraction yielding, after removal of solvents, compound *syn*-**8a** as a yellow microcrystalline solid (0.030 g, 82%). Anal. Calcd for $C_{31}H_{39}Mo_2O_4P$: C, 53.31; H, 5.63. Found: C, 53.08; H, 5.50.^{1}H NMR: δ 5.94 (s, 1H, C_6H_2), 5.49 (d, J_{HP} = 5, 1H, C_6H_2), 5.33 (s, 5H, Cp), 4.88 (d, J_{HP} = 2, 5H, Cp), 1.34, 1.08, 0.87 (3s, 3 × 9H, ^{t}Bu).

Preparation of *syn*-$[Mo_2Cp_2(\mu\text{-}\kappa^2_{P,S}\text{:}\kappa^1_P,\eta^4\text{-}SPMes^*)(CO)_3]$ (*syn*-8b). A dichloromethane solution of S_8 (1 mL of a 0.125 M solution, 0.125 mmol) was added to a dichloromethane solution (4 mL) of compound **2** (0.075 g, 0.115 mmol) in a bulb equipped with a Young's valve. The bulb was cooled at 77 K, degassed under vacuum,

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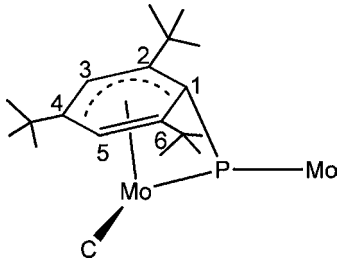
and then refilled with CO. The solution was allowed to reach room temperature, the valve was then closed, and the mixture was further stirred for 3 h to give an orange solution. After removal of the solvent under vacuum, the residue was extracted with petroleum ether (10 mL) and the extract filtered. Removal of the solvent from the filtrate yielded compound ***syn*-8b** as an orange microcrystalline solid (0.060 g, 73%). X-ray-quality crystals were grown from a concentrated petroleum ether solution of the complex at 253 K. Anal. Calcd for $C_{31}H_{39}Mo_2O_3PS$: C, 52.11; H, 5.50. Found: C, 51.85; H, 5.35. ^{1}H NMR (300.09 MHz): δ 6.04 (s, 1H, C_6H_2), 5.34 (d, J_{HP} = 5, 1H, C_6H_2), 5.16 (s, 5H, Cp), 4.83 (d, J_{HP} = 2, 5H, Cp), 1.31, 1.18, 0.85 (3s, 3 × 9H, ^{t}Bu). ^{1}H NMR (CD_2Cl_2): δ 6.02 (s, 1H, C_6H_2), 5.69 (d, J_{HP} = 5, 1H, C_6H_2), 5.45, 5.25 (2s, 5H, Cp), 1.44, 1.06, 1.01 (3s, 3 × 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.63 MHz, CD_2Cl_2): δ 256.7 (d, J_{CP} = 26, CO), 241.6 (s, CO), 234.8 (d, J_{CP} = 11, CO), 155.4 [s, $C^6(C_6H_2)$], 131.6 [s, $C^5(C_6H_2)$], 105.5 [d, J_{CP} = 12, $C^2(C_6H_2)$], 105.3 [s, $C^4(C_6H_2)$], 93.2, 90.7 (2s, Cp), 84.4 [d, J_{CP} = 6, $C^3(C_6H_2)$], 64.8 [d, J_{CP} = 40, $C^1(C_6H_2)$], 39.4, 35.5, 35.3 [3s, C(^{t}Bu)], 34.0, 32.4, 31.4 [3s, CH(^{t}Bu)]. Numbering of the ring carbons according with the diagram shown below:



Reaction of Compound 3 with Sulfur. A dichloromethane solution of S_8 (1 mL of a 0.063 M solution, 0.063 mmol) was added to a dichloromethane solution (3 mL) of compound **3** (0.040 g, 0.058 mmol), and the mixture was stirred at room temperature for 3.5 h to give a yellow-orange solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/5) and the extracts were chromatographed on alumina. Elution with the same solvent mixture gave a yellow fraction yielding, after removal of solvents, compound ***anti*-8b** as a yellow-orange solid (0.018 g, 43%). Elution with a 2/1 solvent mixture gave an orange fraction yielding analogously compound ***syn*-8b** as an orange solid (0.018 g, 43%). The crystals of ***anti*-8b**·0.5C_6H_{14} used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a concentrated dichloromethane-toluene solution of the complex at 253 K.

*Data for Compound **anti-8b**.* Anal. Calcd for $C_{31}H_{39}Mo_2O_3PS$: C, 52.11; H, 5.50. Found: C, 51.79; H, 5.25. ^{1}H NMR (CD_2Cl_2): δ 5.99 (d, J_{HP} = 1, 1H, C_6H_2), 5.85 (d, J_{HP} = 5, 1H, C_6H_2), 5.46 (s, 5H, Cp), 5.04 (d, J_{HP} = 2, 5H, Cp), 1.64, 1.03, 1.01 (3s, 3 × 9H, ^{t}Bu). ^{1}H NMR: δ 5.92 (d, J_{HP} = 5, 1H, C_6H_2), 5.69 (d, J_{HP} = 1, 1H, C_6H_2), 5.15 (s, 5H, Cp), 4.78 (d, J_{HP} = 2, 5H, Cp), 1.67, 1.07, 0.86 (3s, 3 × 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.63 MHz, CD_2Cl_2): δ 251.7 (d, J_{CP} = 30, CO), 241.2 (s, CO), 237.7 (d, J_{CP} = 14, CO), 156.1 [d, J_{CP} = 5, $C^6(C_6H_2)$], 128.5 [d, J_{CP} = 5, $C^5(C_6H_2)$], 110.5 [d, J_{CP} = 3, $C^2(C_6H_2)$], 106.2 [s, $C^4(C_6H_2)$], 93.9, 92.9 (2s, Cp), 89.9 [d, J_{CP} = 4, $C^3(C_6H_2)$], 59.8 [d, J_{CP} = 45, $C^1(C_6H_2)$], 37.9 [s, C(^{t}Bu)], 36.2 [s, CH(^{t}Bu)], 35.3, 35.0 [2s, C(^{t}Bu)], 31.2, 30.6 [2s, CH(^{t}Bu)].

Preparation of *syn*-[$Mo_2Cp_2(\mu$-$\kappa^2_{P,Se}$:κ^1_P,η^4-SePMes*)(CO)$_3$] (*syn*-8c). Gray selenium (0.012 g, 0.152 mmol) was added to a dichloromethane solution (5 mL) of compound **3** (0.040 g, 0.058 mmol) in a bulb equipped with a Young's valve. The valve was then closed and the mixture was stirred at 313 K for 10 h to give an orange solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/2) and the extracts were chromatographed on alumina. Elution with the same solvent mixture gave an orange fraction yielding, after removal of solvents, compound ***syn*-8c** as an orange microcrystalline solid (0.035 g, 79%). The crystals used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{31}H_{39}Mo_2O_3PSe$: C, 48.90; H, 5.16. Found: C, 48.65; H, 5.01. ^{1}H NMR (300.13 MHz): δ 6.03 (s, 1H, C_6H_2), 5.72 (d, J_{HP} = 5, 1H, C_6H_2), 5.42 (s, 5H, Cp), 5.25 (d, J_{HP} = 2, 5H, Cp), 1.44, 1.06, 1.04 (3s, 3 × 9H, ^{t}Bu). ^{1}H NMR (300.13 MHz, C_6D_6): δ 6.00 (s, 1H, C_6H_2), 5.36 (d, J_{HP} = 5, 1H, C_6H_2), 5.11 (s, 5H, Cp), 4.82 (d, J_{HP} = 2, 5H, Cp), 1.30, 1.16, 0.85 (3s, 3 × 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ 255.2 (d, J_{CP} = 25, CO), 240.7 (s, CO), 234.7 (d, J_{CP} = 10, CO), 155.3 [s, $C^6(C_6H_2)$], 131.9 [d, J_{CP} = 2, $C^5(C_6H_2)$], 106.6 [d, J_{CP} = 12, $C^2(C_6H_2)$], 105.3 [d, J_{CP} = 2, $C^4(C_6H_2)$], 92.7, 91.0 (2s, Cp), 84.3 [d, J_{CP} = 6, $C^3(C_6H_2)$], 68.0 [d, J_{CP} = 42, $C^1(C_6H_2)$], 39.3, 35.5, 35.4 [3s, C(^{t}Bu)], 34.0, 32.6, 31.3 [3s, CH(^{t}Bu)].

Preparation of *syn*-[$Mo_2Cp_2(\mu$-$\kappa^2_{P,S}$:κ^1_P,η^4-SPMes*)(CN^{t}Bu)(CO)$_2$] (*syn*-10b). A dichloromethane solution of S_8 (1 mL of a 0.125 M solution, 0.125 mmol) and neat CN^{t}Bu (13 μL, 0112 mmol) were added to a dichloromethane solution (3 mL) of compound **2** (0.070 g, 0.107 mmol), and the mixture was stirred at room temperature for 2 h to give an orange solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/4) and the extracts were chromatographed on alumina. Elution with dichloromethane/petroleum ether (1/2) gave an orange fraction yielding, after removal of solvents, compound ***syn*-10b** as an orange microcrystalline solid (0.068 g, 83%). X-ray-quality crystals were grown by the slow diffusion of a layer of petroleum ether into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{35}H_{48}Mo_2O_2NPS$: C, 54.62; H, 6.29; N, 1.82. Found: C, 54.97; H, 6.38; N, 1.85. ^{1}H NMR: δ 5.99 (s, 1H, C_6H_2), 5.37 (d, J_{PH} = 5, 1H, C_6H_2), 5.27 (s, 5H, Cp), 4.95 (d, J_{PH} = 1, 5H, Cp), 1.41, 1.24, 1.18, 0.95 (4s, 4 × 9H, ^{t}Bu). ^{1}H NMR (400.13 MHz, CD_2Cl_2): δ 5.96 (s, 1H, C_6H_2), 5.51 (d, J_{PH} = 5, 1H, C_6H_2), 5.40 (s, 5H, Cp), 5.00 (d, J_{PH} = 1, 5H, Cp), 1.54, 1.39, 1.03, 0.99 (4s, 4 × 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ 257.3 (d, J_{CP} = 27, CO), 244.1 (s, CO), 171.7 (d, J_{CP} = 12, MoCN), 151.5 [s, $C^6(C_6H_2)$], 133.2 [s, $C^5(C_6H_2)$], 99.4 [d, J_{CP} = 14, $C^2(C_6H_2)$], 95.6 [s, $C^4(C_6H_2)$], 92.9, 89.2 (2s, Cp), 84.5 [d, J_{CP} = 6, $C^3(C_6H_2)$], 61.6 [d, J_{CP} = 35, $C^1(C_6H_2)$], 57.7 [s, CNC$(CH_3)_3$], 39.4, 35.3, 35.2 [3s, C(^{t}Bu)], 34.1, 32.8, 31.7, 30.8 [4s, CH(^{t}Bu)].

Reaction of Compound 4 with Sulfur. A dichloromethane solution of S_8 (1 mL of a 0.150 M solution, 0.150 mmol) was added to a dichloromethane solution (3 mL) of compound **4** (0.100 g, 0.142 mmol), and the mixture was stirred at room temperature for 20 min to give an orange solution containing a 1:1 mixture of the isomers ***syn*-** and ***anti*-10b**. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/9) and the extracts were chromatographed on alumina. Elution with the same solvent mixture gave a yellow fraction yielding, after removal of solvents, compound ***anti*-10b** as a yellow-orange microcrystalline solid (0.045 g, 41%). Elution with a 1/2 solvent mixture gave an orange fraction yielding analogously compound ***syn*-10b** as an orange solid (0.047 g, 43%).

*Data for Compound **anti-10b**.* Anal. Calcd for $C_{35}H_{48}Mo_2O_2NPS$: C, 54.62; H, 6.29; N, 1.82. Found: C, 54.85; H, 6.37; N, 1.91.^{1}H NMR: δ 5.81 (d, J_{PH} = 5, 1H, C_6H_2), 5.76 (d, J_{PH} = 1, 1H, C_6H_2), 5.26 (s, 5H, Cp), 4.79 (d, J_{PH} = 2, 5H, Cp), 1.81, 1.27, 1.07, 0.94 (4s, 4 × 9H, ^{t}Bu). ^{1}H NMR (400.13 MHz, CD_2Cl_2): δ 5.86 (d, J_{PH} = 2, 1H, C_6H_2), 5.77 (d, J_{PH} = 5, 1H, C_6H_2), 5.43 (s, 5H, Cp), 4.80 (d, J_{PH} = 2, 5H, Cp), 1.60, 1.55, 1.01, 0.98 (4s, 4 × 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ 257.9 (d, J_{CP} = 29, CO), 244.0 (s, CO), 171.2 (d, J_{CP} = 14, MoCN), 152.4 [d, J_{CP} = 4, $C^6(C_6H_2)$], 130.1 [d, J_{CP} = 6, $C^5(C_6H_2)$], 102.2 [s, $C^2(C_6H_2)$], 95.3 [s, $C^4(C_6H_2)$], 93.4, 91.1 (2s, Cp), 90.3 [d, J_{CP} = 4, $C^3(C_6H_2)$], 57.9 [d, J_{CP} = 43, $C^1(C_6H_2)$], 57.9 [s, CNC$(CH_3)_3$], 32.2, 35.0, 34.5 [3s, C(^{t}Bu)], 36.5, 31.9, 30.9, 30.6 [4s, CH(^{t}Bu)].

Preparation of *syn*-[$Mo_2Cp_2(\mu$-$\kappa^2_{P,Se}$:κ^1_P,η^4-SePMes*)(CN^{t}Bu)(CO)$_2$] (*syn*-10c). Neat CN^{t}Bu (35 μL, 0.41 mmol) and gray selenium (0.020 g, 0.253 mmol) were added to a tetrahydrofuran solution (5 mL) of compound **2** (0.075 g, 0.107 mmol) and the mixture was stirred for 8 h at 333 K to give an orange solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/1) and the extracts were chromato-

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Table 4. Crystal Data for New Compounds

compound	6c	7a	*syn*-8b·0.5C_6H_{14}	*anti*-8b·0.25C_7H_8	*syn*-8c·CH_2Cl_2	*syn*-10b	12
mol formula	$C_{30}H_{41}Mo_2O_2PSe$	$C_{30}H_{39}Mo_2O_3P$	$C_{34}H_{46}Mo_2O_3PS$	$C_{131}H_{164}Mo_8O_{12}P_4S_4$	$C_{32}H_{41}Cl_2Mo_2O_3PSe$	$C_{35}H_{48}Mo_2NO_2PS$	$C_{30}H_{39}Mo_2O_2PS_2$
mol wt	735.44	670.46	757.62	2950.30	846.36	769.66	718.58
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_12_12_1$	$P2_1/c$	$P-1$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P-1$
radiation (λ, Å)	1.54180	0.71073	0.71073	0.71073	0.71073	0.71073	1.54180
a, Å	11.30200(10)	9.6372(19)	10.678(3)	18.9423(3)	10.54060(10)	17.154(5)	9.5281(6)
b, Å	17.7376(2)	16.773(3)	11.279(3)	9.69810(10)	16.6907(2)	11.003(5)	12.5563(10)
c, Å	29.4278(3)	17.553(3)	14.708(4)	36.6486(5)	19.3623(2)	18.268(5)	14.4321(11)
α, deg	90	90	94.632(5)	90	90	90	64.355(8)
β, deg	90	93.209(4)	104.006(4)	97.3710(10)	100.242(4)	90.066(5)	77.855(6)
γ, deg	90	90	97.960(4)	90	90	90	87.777(6)
V, Å^3	5899.40(10)	2832.9(9)	1690.1(8)	6676.87(16)	3352.13(6)	3448(2)	1519.02(19)
Z	8	4	2	2	4	4	2
calcd density, gcm^{-3}	1.656	1.572	1.489	1.467	1.677	1.483	1.571
absorpt. coeff., mm^{-1}	9.074	0.971	0.883	0.892	2.072	0.865	8.736
temperature, K	100(2)	100(2)	100(2)	100(2)	100(2)	100(1)	123(1)
θ range (deg)	2.91 to 73.97	2.12 to 26.44	1.84 to 27.48	1.46 to 25.62	2.14 to 25.24	2.16 to 26.01	3.48 to 74.45
index ranges (h, k, l)	−12, 13; −22, 20; −35, 35	−11, 11; 0, 21; 0, 21	−13, 13; −14, 14; 0, 19	−22, 22; 0, 11; 0, 44	−12, 13; 0, 20; 0, 23	−21, 21; 0, 13; 0, 22	−11, 10; −15, 12; −17, 14
no. of reflns collected	27799	39947	30246	60725	42521	67491	11339
no. of indep reflns (R_{int})	11371 (0.0576)	5807 (0.0759)	7704 (0.0347)	12426(0.0474)	6020 (0.0346)	6792(0.0388)	5892(0.0505)
reflns with $I > 2\sigma(I)$	9175	4385	6389	10156	5171	5773	4497
R indexes [data with $I > 2\sigma(I)$][a]	R1 = 0.0378	R1 = 0.0342	R1 = 0.0288	R1 = 0.0382	R1 = 0.0299	R1 = 0.0369	R1 = 0.079
	wR2 = 0.0752[b]	wR2 = 0.0659[c]	wR2 = 0.0674[d]	wR2 = 0.1350[e]	wR2 = 0.0807[f]	wR2 = 0.0819[g]	wR2 = 0.1962[h]
R indexes (all data)[a]	R1 = 0.0549	R1 = 0.0527	R1 = 0.0377	R1 = 0.0487	R1 = 0.0397	R1 = 0.0472	R1 = 0.1006
	wR2 = 0.0823[b]	wR2 = 0.0695[c]	wR2 = 0.0704[d]	wR2 = 0.1419[e]	wR2 = 0.1045[f]	wR2 = 0.0885[g]	wR2 = 0.215[h]
GOF	0.954	1.081	1.056	1.111	1.255	1.028	1.022
no. of restraints/ params	0/655	0/334	0/445	28/744	0/387	2/403	0/338
$\Delta\rho$(max, min), e Å^{-3}	1.312, −0.838	0.619, −0.672	1.803, −0.666	1.357, −1.472	1.913, −1.041	1.873, −1.763	5.094, −1.347

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] $a = 0.0363$, $b = 0.0000$. [c] $a = 0.0259$, $b = 0.9708$. [d] $a = 0.0303$, $b = 1.5577$. [e] $a = 0.0888$, $b = 5.1822$. [f] $a = 0.0572$, $b = 3.0288$. [g] $a = 0.0281$, $b = 12.2848$. [h] $a = 0.1033$, $b = 13.0408$.

graphed on alumina. Elution with the same solvent mixture gave an orange fraction yielding, after removal of solvents, compound ***syn*-10c** as an orange microcrystalline solid (0.068 g, 83%). Anal. Calcd for $C_{35}H_{48}Mo_2O_2NPSe$: C, 51.49; H, 5.93; N, 1.72. Found: C, 51.36; H, 6.01; N, 1.80. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 5.99 (s, 1H, C_6H_2), 5.56 (d, J_{PH} = 4, 1H, C_6H_2), 5.38, 5.01 (2s, 2 × 5H, Cp), 1.58, 1.40 (2s, 2 × 9H, ^{t}Bu), 1.03 (s, 18H, ^{t}Bu). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ 255.9 (d, J_{CP} = 26, CO), 243.2 (s, CO), 171.9 (d, J_{CP} = 11, MoCN), 151.7 [s, $C^6(C_6H_2)$], 133.5 [s, $C^5(C_6H_2)$], 100.3 [d, J_{CP} = 12, $C^2(C_6H_2)$], 95.9 [s, $C^4(C_6H_2)$], 92.5, 89.4 (2s, Cp), 84.6 [d, J_{CP} = 5, $C^3(C_6H_2)$], 64.9 [d, J_{CP} = 38, $C^1(C_6H_2)$], 57.9 [s, $CNC(CH_3)_3$] 39.4, 35.4, 35.1 [3s, C(^{t}Bu)], 34.2, 33.1, 31.8, 30.8 [4s, CH(^{t}Bu)].

Preparation of [$Mo_2Cp(\mu$-$\kappa^2_{P,S}$:κ^1_P,η^5-$SPC_5H_4)(\eta^6$-HMes*)-$(CO)_2$] (11b). A dichloromethane solution of S_8 (1 mL of a 0.054 M solution, 0.054 mmol) was added at 263 K to a dichloromethane solution (4 mL) containing ca. 0.053 mmol of compound **5** prepared in situ, and the mixture was stirred and allowed to reach room temperature for 20 min to give a yellow-brown solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/5) and the extracts were chromatographed on alumina. Elution with the same solvent mixture gave a brown fraction yielding, after removal of solvents, compound **11b** as a red-brown solid (0.028 g, 76%). In solution, this product was shown by NMR to exist as an equilibrium mixture of cis and trans isomers, with the cis/trans ratio in CD_2Cl_2 solution being 1/1 at 293 K and 2/3 at 233 K (4/1 in C_6D_6 solution at 293 K). Anal. Calcd for $C_{30}H_{39}Mo_2O_2PS$: C, 52.48; H, 5.73. Found: C, 52.35; H, 5.69.

Data for cis Isomer. ^{1}H NMR (CD_2Cl_2, 233 K): δ 5.43 (s, 5H, Cp), 5.33 (m, br, 1H, C_5H_4), 5.12 (m, br, 2H, C_5H_4), 5.08 (d, J_{HP} = 7, 3H, C_6H_3), 4.48 (m, br, 1H, C_5H_4), 1.17 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.63 MHz, CD_2Cl_2, 233K): δ 251.8 (d, J_{CP} = 25, CO), 243.8 (s, CO), 111.0 [s, $C(C_6H_3)$], 92.4 (s, Cp), 90.2 (d, J_{CP} = 4, C_5H_4), 87.1 (d, J_{CP} = 7, C_5H_4), 86.7 (d, J_{CP} = 3, C_5H_4), 79.6 (d, J_{CP} = 16, C_5H_4), 78.8 [d, J_{CP} = 42, $C^1(C_5H_4)$], 74.3 [s, $CH(C_6H_3)$], 34.8 [s, C(^{t}Bu)], 31.2 [s, CH(^{t}Bu)].

Data for trans Isomer. ^{1}H NMR (CD_2Cl_2, 233K): δ 5.47 (s. 5H, Cp), 5.25 (m, br, 2H, C_5H_4), 5.01, 4.95 (2 m, br, 2 × 1H, C_5H_4), 4.89 (d, J_{HP} = 7, 3H, C_6H_3), 1.22 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.63 MHz, CD_2Cl_2, 233K): δ 249.6 (d, J_{CP} = 22, CO), 244.0 (s, CO), 108.3 [s, $C(C_6H_3)$], 89.5 (d, J_{CP} = 8, C_5H_4), 89.0 (d, J_{CP} = 5, C_5H_4), 86.7 (d, J_{CP} = 3, C_5H_4), 80.4 (d, J_{CP} = 14, C_5H_4), 77.6 [d, J_{CP} = 32, $C^1(C_5H_4)$], 92.7 (s, Cp), 76.8 [s, $CH(C_6H_3)$], 34.5 [s, br, C(^{t}Bu)], 31.5 [s, CH(^{t}Bu)].

Preparation of [$Mo_2Cp(\mu$-$\kappa^2_{P,Se}$:κ^1_P,η^5-$SePC_5H_4)(\eta^6$-HMes*)-$(CO)_2$] (11c). The procedure is identical to that described for the preparation of **11b**, but using gray selenium instead (0.004 g, 0.051 mmol) and a reaction time of 30 min at room temperature. After chromatographic workup [elution with dichloromethane/petroleum ether (1/2)] compound **11c** was obtained as a brown microcrystalline solid (0.015 g, 67%). In solution, this product was shown by NMR to exist as an equilibrium mixture of *cis* and trans isomers, with their ratio being 1/1 at 253 K. Anal. Calcd for $C_{30}H_{39}Mo_2O_2PSe$: C, 49.14; H, 5.36. Found: C, 49.05; H, 5.30. ^{1}H NMR (CD_2Cl_2, 253 K, mixture of isomers): δ 5.42 (s, 5H, Cp), 5.41 (s, 5H, Cp), 5.35, 5.29, 5.25, 5.14 (4 m, 4 × 1H, C_5H_4), 5.10 (d, J_{HP} = 6, 3H, C_6H_3), 4.97 (m, 1H, C_5H_4),

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4.89 (d, J_{HP} = 6, 3H, C_6H_3), 4.85, 4.82, 4.49 (3 m, 3 × 1H, C_5H_4), 1.19 (s, 27H, ^{t}Bu), 1.15 (s, 27H, ^{t}Bu).

Preparation of [$Mo_2Cp(\mu$-$\kappa^2_{P,Te}$:κ^1_P,η^5-$TePC_5H_4)(\eta^6$-HMes*)$(CO)_2$] (11d). The procedure is identical to that described for the preparation of **11c**, but using tellurium instead (0.008 g, 0.063 mmol) and a reaction time of 3 h at 313 K. After chromatographic workup at 253 K [elution with dichloromethane/petroleum ether (1/1)] compound **11d** was obtained as a brown solid (0.017 g, 71%). In solution, this product was shown by NMR to exist as an equilibrium mixture of cis and trans isomers, with their ratio being 3/2 at 213 K. Microanalytical data could not be obtained for this quite air-sensitive product due to its rapid decomposition upon manipulation.

Data for cis Isomer. ^{1}H NMR (CD_2Cl_2, 213 K): δ 5.38 (s, 5H, Cp), 5.24 (m, 1H, C_5H_4), 5.15 (d, J_{HP} = 6, 3H, C_6H_3), 5.06 (m, 1H, C_5H_4), 4.60 (m, 1H, C_5H_4), 4.52 (m, 1H, C_5H_4), 1.17 (s, 27H, ^{t}Bu).

Data for anti Isomer. ^{1}H NMR (CD_2Cl_2, 213 K): δ 5.40 (s, 5H, Cp), 5.37 (m, 2H, C_5H_4), 5.30 (m, 1H, C_5H_4), 4.93 (d, J_{HP} = 6, 3H, C_6H_3), 4.54 (m, 2H, C_5H_4), 1.21 (s, 27H, ^{t}Bu).

Preparation of [$Mo_2Cp(\mu$-$\kappa^2_{P,S}$:$\kappa^1_{S'}$,η^5-$S_2PC_5H_4)(\eta^6$-HMes*)$(CO)_2$] (12). The procedure is analogous to that described for **11b**, but using 2 mL of the sulfur solution instead (0.108 mmol). After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/2) and the extracts were chromatographed on alumina at 253 K. Elution with the same solvent mixture gave a yellow-brown band yielding, after removal of solvents, compound **12** as brown-yellowish solid (0.024 g, 62%). This product could be also obtained upon reaction of **11b** with a stoichiometric amount of sulfur. The tiny crystals used in the X-ray analysis were grown by the slow diffusion of layers of diethyl ether and petroleum ether into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{30}H_{39}Mo_2O_2S_2P$: C, 50.13; H, 5.47. Found: C, 49.90; H, 5.69. ^{1}H NMR (300.13 MHz): δ 6.02 (m, 1H, C_5H_4), 5.48 (m, 1H, C_5H_4), 5.08 (s, 5H, Cp), 4.68 (s, 3H, C_6H_3), 4.31, 4.16 (2 m, 2 × 1H, C_5H_4), 1.12 (s, 27H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 102.6 [s, $C(C_6H_3)$], 94.1 (s, Cp), 88.7 [d, J_{CP} = 6, $CH(C_5H_4)$], 88.5 [d, J_{CP} = 8, $CH(C_5H_4)$], 86.0 [d, J_{CP} = 12, $CH(C_5H_4)$], 83.1 [d, J_{CP} = 18, $CH(C_5H_4)$], 79.6 [s, $CH(C_6H_3)$], 34.8 [s, $C(^tBu)$], 31.9 [s, $CH(^tBu)$]. The CO and $C^1(C_5H_4)$ resonances could not be identified in the spectrum.

X-ray Structure Determination for Compound 6c. Data collection was performed at 100 K on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using CuK_α radiation. Images were collected at a 65 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (10−50 s). Data collection strategy was calculated with the program CrysAlis Pro CCD.[35] Data reduction and cell refinement was performed with the program CrysAlis Pro RED.[35] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED. Using the program suite WinGX,[36] the structure was solved using Patterson interpretation and phase expansion and refined with full-matrix least-squares on F^2 using SHELXL97.[37] Two molecules of the complex were present in the asymmetric unit. During the refinement stages, one ^{t}Bu group was found disordered over two positions and it was satisfactorily modeled with occupancy factors of 0.7 and 0.3. Some disorder was present in all Cp ligands, but it could not be modeled satisfactorily. During the final stages of the refinement, all the positional parameters and temperature factors of all non-H atoms were refined anisotropically, except atoms C(3), C(10), C(11), C(40) and the carbon atoms involved in the disorder, which were refined isotropically to prevent their temperature factors from becoming nonpositive definite. Hydrogen atoms were geometrically placed riding on their parent atoms, except for H(1) and H(1B), which were located in the Fourier map and refined isotropically. Crystallographic data and structure refinement details for compound **6c** are collected in the Table 4.

X-ray Structure Determination for Compounds 7a and *syn*-8b. The X-ray intensity data were collected on a Smart-CCD-1000 Bruker diffractometer using graphite-monochromated MoK_α radiation at 100 K. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in 3 sets of 30 exposures collected in 3 different ω regions and eventually refined against all reflections. The software SMART[38] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The collected frames were then processed for integration by the software SAINT,[38] and a multiscan absorption correction was applied with SADABS.[39] Using the program suite WinGX,[36] the structure was solved by Patterson interpretation and phase expansion, and refined with full-matrix least-squares on F^2 using SHELXL97.[37] All non-hydrogen atoms were refined anisotropically. For compound **7a** all hydrogen atoms were fixed at calculated positions and were given an overall isotropic thermal parameter. For compound ***syn*-8b**, half a molecule of *n*-hexane was found in the asymmetric unit, placed at an inversion center, with a two-site disorder involving two of the three independent C atoms, which was satisfactorily refined with occupancy factors of 0.70 and 0.30 for each part. All hydrogen atoms were located in the Fourier map in the last least-squares refinements, except for the methyl and methylenic hydrogen atoms, which were fixed at calculated positions. All of them were given an overall isotropic thermal parameter.

X-ray Structure Determination for Compounds *anti*-8b and *syn*-8c. The X-ray intensity data were collected at 100 K on a Nonius KappaCCD single crystal diffractometer, using graphite-monochromated MoK_α radiation. Images were collected at a fixed crystal-detector distance (50 mm for ***anti*-8b**, 29 mm for ***syn*-8c**), using the oscillation method, with 1° oscillations and 50 and 60 s exposure time per image respectively. Data collection strategies were calculated with the program Collect.[40] Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.[41] A semiempirical absorption correction was applied using the program SORTAV.[42] Using the program suite WinGX,[36] the structures were solved by Patterson interpretation and phase expansion using SHELXL97, and refined with full-matrix least-squares on F^2 using SHELXL97.[37] For compound ***syn*-8c**, all non-hydrogen atoms were refined anisotropically and all hydrogen atoms were fixed at calculated positions except for H(16) and H(18), which were located in the Fourier map and refined; all them were given an overall isotropic thermal parameter. For compound ***anti*-8b** two independent molecules were present in the asymmetric unit along with a molecule of toluene placed on the symmetry operation −x+1,−y,−z. Another molecule of a disordered and unidentified solvent was also present. Moreover, one carbonyl ligand and one ^{t}Bu group were found to be disordered and the corresponding disorders were satisfactorily modeled. A slight disorder was found to be present on the atom C23, but this could not be modeled satisfactorily. All non-hydrogen atoms were refined anisotropically, except for the atoms involved in disorder, which were refined isotropically to prevent their temperature factors from becoming nonpositive definite. All hydrogen atoms were geometrically placed and refined using a riding model, except for H(16), H(18), H(53) and H(55), which were located in the Fourier Map and refined isotropically. Finally, the SQUEEZE program,[43] as implemented in PLATON,[44] was used to model the electron density corresponding to the unidentified solvent molecule. After convergence, the strongest residual peaks (1.36−1.05 e A^{-3}) were located around the ^{t}Bu groups.

X-ray Structure Determination for Compound *syn*-10b. The X-ray intensity data were collected on a Kappa-Appex-II Bruker diffractometer using graphite-monochromated MoK_α radiation at 100 K. The software APEX was used for collecting frames with the ω/ϕ scans measurement method.[45] The Bruker SAINT software was used for the data reduction,[38] and a multiscan absorption correction was applied with SADABS.[39] Using the program suite WinGX,[36] the structure was solved by direct methods using SIR92,[46] and refined with full-matrix least-squares on F^2 using SHELXL97.[37] The $MoCp(CO)_2$ moiety of the complex was disordered over two positions that could be satisfactorily modeled with occupancy factors of 0.5, as it was the case of the other cyclopentadienyl ligand. Two of the ^{t}Bu groups were also disordered over two positions but the disorder was satisfactorily solved with occupancy factors of 0.55/0.45. A restraint on the distances C(10)−C(11) and C(11)−C(12) had to be applied for satisfactory refinement. All non-hydrogen atoms were refined anisotropically, except for the carbon atoms involved in disorder, which were refined

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isotropically to prevent their temperature factors from becoming nonpositive definite. All hydrogen atoms were geometrically placed and refined using a riding model, except for H(20) and H(22), which were located in the Fourier map and refined isotropically.

X-ray Structure Determination for Compound 12. Data collection and reduction, absorption correction, structure solution and refinements were carried out on a very tiny crystal as described for **6c** (images collected at a 63 mm crystal-detector distance, with 1° oscillation and 20−45 s exposure time). All non-hydrogen atoms were refined anisotropically, except for C(1); attempts to refine anisotropically that atom even in combination with the instructions DELU and SIMU gave no satisfactory results, so it was eventually refined isotropically. All hydrogen atoms were geometrically placed and refined using a riding model. After convergence the strongest residual peak (5.09 e $Å^{-3}$) was placed at 1.055 Å from the phosphorus atom.

Computational Details. Computations for compound ***syn*-8b** were carried out using the GAUSSIAN03 package,[47] in which the hybrid method B3LYP was applied with the Becke three parameters exchange functional[48] and the Lee−Yang−Parr correlation functional.[49] Effective core potentials (ECP) and their associated double-ζ LANL2DZ basis set were used for the metal atoms.[50] The light elements (S, P, O, C, and H) were described with 6-31G* basis.[51] Geometry optimization was performed under no symmetry restrictions, using initial coordinates derived from the X-ray data of the complex, and frequency analysis were performed to ensure that a minimum structure with no imaginary frequencies was achieved. For interpretation purposes, Mulliken charges were computed as usually,[52] and natural population analysis (NPA) charges were derived from the natural bond order (NBO) analysis of the data.[53] Molecular orbitals and vibrational modes were visualized using the Molekel program.[54]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A pdf file containing tables of data from the DFT calculations of ***syn*-8b**, and a CIF file giving the crystallographic data for the structural analysis of compounds **6c**, **7a**, ***syn*-** and ***anti*-8b**, ***syn*-8c**, ***syn*-10b**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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