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# A Thiophosphinidene Complex as a Vehicle in Phosphinidene Transmetalation: Easy Formation and Cleavage of a P–S Bond

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Supporting Information

**ABSTRACT:** A method for the generation of transition metal–phosphorus multiple bonds has been developed using the reactions of a novel thiophosphinidene-bridged dimolybdenum complex with different metal carbonyls. The overall process could be considered as a transmetalation of the phosphinidene ligand involving the activation of P–S and P–Mo bonds.

Compounds with multiple bonds between a transition metal and an element of the groups 14 and 15 constitute an important class of organometallic reagents and have attracted the attention of both the experimental and theoretical communities.[1] Over the past few years, our group has been interested in the chemistry of complexes with multiple Mo–P bonds, such as the phosphinidene complexes $[Mo_2Cp(\mu\text{-}\kappa^1\!:\!\kappa^1,\eta^5\text{-}PC_5H_4)(CO)_2(\eta^6\text{-}HMes^*)]$ and $[Mo_2Cp_2(\mu\text{-}\kappa^1\!:\!\kappa^1,\eta^6\text{-}PMes^*)(CO)_2]$ (**1**) or the oxophosphinidene complex $[MoCp\{\kappa^1\text{-}P(O)Mes^*\}(CO)_2]^-$ (Cp = $\eta^5\text{-}C_5H_5$; Mes* = 2,4,6-$C_6H_2{}^tBu_3$).[2] These species are particularly reactive toward different electrophilic metal complexes, to give heterometallic derivatives often displaying unprecedented structures.[3] We report here preparation of the novel thiophosphinidene complex $[Mo_2Cp_2\{\mu\text{-}\kappa^2{}_{P,S}\!:\!\kappa^1{}_P,\eta^6\text{-}SPMes^*\}(CO)_2]$ (**2**) and a preliminary analysis of its use as a reagent in cluster-building reactions. We should note that only a few P(S)R complexes have been reported so far[4] and that their chemistry remains unexplored, if we except the reactions of $[Mn_2(CO)_9\{\mu\text{-}\kappa^2{}_{P,S}\!:\!\kappa^1{}_P\text{-}SP(Me)\}]$ with alkynes.[5] Rather unexpectedly, we have now found that the P–S bond of the P(S)R ligand in **2** is easily cleaved in the reactions with different metal carbonyls, to give new complexes displaying a $\mu_2$-PR ligand attached to different metals (Scheme 1), a circumstance rarely met in the chemistry of PR complexes.[6] As a result, the thiophosphinidene complex **2** effectively behaves as a synthetic intermediate for new phosphinidene complexes, thus opening the way to future studies on molecules displaying multiple bonds between P and a variety of transition-metal atoms. Additional interest for this chemistry stems from the fact that heterometallic complexes and clusters bridged by S-donor ligands might be useful as models for the active sites of several natural enzymes as hydrogenases and nitrogenases (the so-called biomimetic approach)[7] and as models or precursors of the heterogeneous catalysts used in different industrial reactions, particularly hydrodesulfurization processes.[8]

The addition of $S_8$ to compound **1** gives complex **2** in 64% yield (Scheme 1). This formal [2 + 1] addition can be compared to that described previously by Malisch and co-workers on related phosphide complexes.[4e] It implies the addition of the S atom perpendicularly to the $Mo_2P$ plane of **1**, thus removing the symmetry plane of the molecule, as revealed by the NMR spectra [see the Supporting Information (SI)]. The $^{31}P$ chemical shift of **2** ($\delta$ 124.2 ppm) is much lower than that of the phosphinidene **1** as expected, but still higher than the values of ca. 50–85 ppm measured for the related thiophosphinidene complexes previously described, even if these involve lighter metal atoms.[4a,c,d]

Compound **2** is quite reactive toward simple metal carbonyls such as $[Co_2(CO)_8]$, $[W(CO)_5(THF)]$, and $[Fe_2(CO)_9]$, thus becoming a versatile reagent for the building of heterometallic species and clusters. However, P–S bond cleavage occurs easily, to give phosphinidene complexes having multiple bonds between phosphorus and the added metal. For instance, **2** reacts rapidly at room temperature with $[Co_2(CO)_8]$ to give the heterobimetallic derivative $[CoMoCp(\mu\text{-}\kappa^1\!:\!\kappa^1,\eta^6\text{-}PMes^*)(CO)_3]$ (**3**) as the major product, along with small amounts of other, yet uncharacterized species. Interestingly, we note that other carbonyl dimers such as $[Mn_2(CO)_{10}]$ or $[W_2Cp_2(CO)_6]$ seem to react with **2** in an analogous way under photolytic conditions, and we are currently exploring the generality of this synthetic route to heterobinuclear complexes, as well as the fate of the "SMoCp(CO)$_n$" fragment lost on the way. The reaction of **2** with $[W(CO)_5(THF)]$ at room temperature is more selective but still involves an intermediate species, which is eventually transformed at 333 K into the final tetranuclear product $[Mo_2W_2Cp_2(\mu\text{-}\kappa^1\!:\!\kappa^1,\eta^6\text{-}PMes^*)(\mu_3\text{-}S)(CO)_9]$ (**4**). The formation of compounds **3** and **4** requires at least cleavage of the P–Mo and P–S bonds and the formation of a new multiple P–M′ bond (M′ = Co, W), and it must obviously be a multistep process. Fortunately, the reaction of **2** with $[Fe_2(CO)_9]$ proceeded at a lower rate, and we were able to isolate a product preceding the P–S bond cleavage step, with this providing a hint on the nature of some of the intermediate species involved in these complex events. Thus, when this reaction was carried out at 313 K, then the trinuclear thiophosphinidene complex $[FeMo_2Cp_2(\mu_3\text{-}\kappa^2{}_{P,S}\!:\!\kappa^1{}_S\!:\!\kappa^1{}_P,\eta^4\text{-}SPMes^*)(CO)_6]$ (**5**) was obtained. Further heating of **5** with excess $[Fe_2(CO)_9]$ at 373 K gave the phosphinidene derivative $[Fe_2Mo_2Cp_2(\mu\text{-}\kappa^1\!:\!\kappa^1,\eta^6\text{-}PMes^*)(\mu_3\text{-}S)(CO)_7]$ (**6**), which is structurally related to the tungsten compound **4**.

The heterobimetallic compound **3** displays a structure comparable to that of the precursor **1**,[2c] with an asymmetric phosphinidene ligand bridging the Mo and Co atoms and $\eta^6$-bound to the Mo center through its aryl ring (Figure 1).

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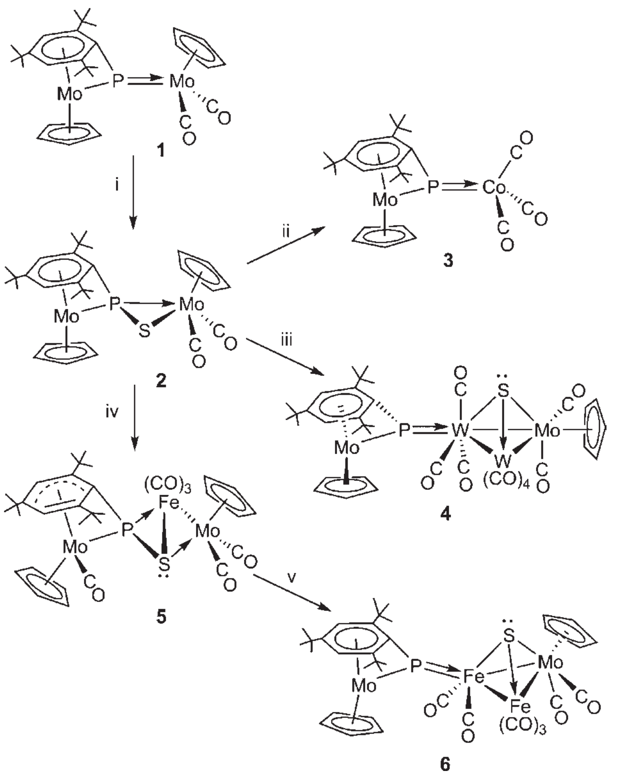
**Scheme 1**[a]



[a] Reagents and conditions: (i) $S_8$, $CH_2Cl_2$, 290 K, 2 h; (ii) $[Co_2(CO)_8]$, $CH_2Cl_2$, 290 K, 1 h; (iii) $[W(CO)_5(THF)]$, toluene, 290 K, 30 min, then 30 min at 333 K; (iv) $[Fe_2(CO)_9]$, THF, 290 K, 40 min; (v) $[Fe_2(CO)_9]$, toluene, 373 K, 1.5 h.

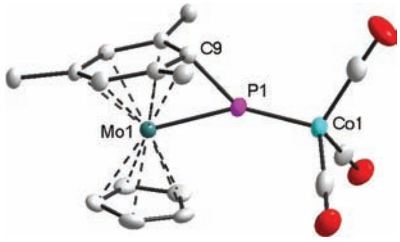


**Figure 1.** *Diamond* plot (50% probability) of compound **3**, with H atoms and Me groups omitted for clarity. Selected bond lengths [Å] and angles [deg]: Mo1−P1 2.326(1), Co1−P1 2.054(2), P1−C9 1.818(5); Mo1−P1−Co1 151.1(1), C9−P1−Co1 145.1(2), C9−P1−Mo1 62.7(2).

The environment around the P atom is trigonal-planar, and the M−P lengths are shorter than the reference single-bond lengths, thus indicating a significant delocalization of the $\pi$(M−P) interaction along the Mo−P−Co chain (not reflected in the drawings of Scheme 1). This has been previously discussed by us for **1** and related $Mo_2$ complexes.[2c,3a] The Mo−P length of 2.326(1) Å in **3** is even shorter than the corresponding value in **1** [2.3630(6) Å],[2c] while the P−Co length of 2.054(2) Å is comparable to that measured in the homobimetallic complex $[Co_2(CO)_6(\mu\text{-PMes*})]$ [2.047(6) Å, formal Co−P bond order of 1.5][9] and only a bit longer than that in the mononuclear phosphide complex $[Co\{P(2,4,6\text{-}OC_6H_2{}^tBu_3)(C_5Me_5)\}(CO)_3]$ [2.010(2) Å, formal Co−P bond order of 2].[10] The spectroscopic data in solution for **3** are consistent with the structure in the crystal (see the SI).

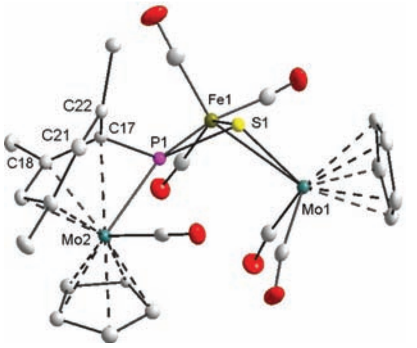


**Figure 2.** *Diamond* plot (50% probability) of compound **5**, with H atoms and Me groups omitted for clarity. Selected bond lengths [Å] and angles [deg]: Mo1−Fe1 2.9204(3), Mo1−S1 2.4358(5), Fe1−S1 2.2923(5), Fe1−P1 2.2150(5), P1−S1 2.111(1), C21−C22 1.333(3); S1−P1−Mo2 129.79(2), Fe1−P1−Mo2 152.24(2), P1−S1−Mo1 102.11(2).

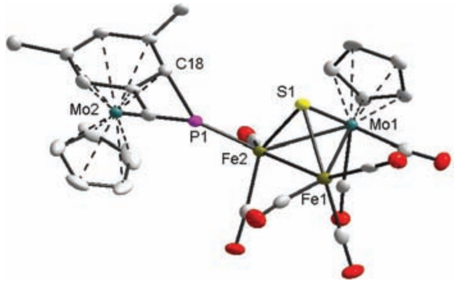


**Figure 3.** *Diamond* plot (50% probability) of compound **6**, with H atoms and Me groups omitted for clarity. Selected bond lengths [Å] and angles [deg]: Mo2−P1 2.325(1), Fe2−P1 2.087(1), Fe1−Fe2 2.615(1), Mo1−Fe2 2.782(1), Mo1−Fe1 2.801(1); Fe2−P1−Mo2 150.8(1), P1−Fe2−Fe1 124.7(1), P1−Fe2−Mo1 140.9(1).

The structure of **5** (Figure 2) can be viewed as resulting from the insertion of a $Fe(CO)_3$ fragment into a Mo−P bond of **2**, while a CO molecule is incorporated into the metallocene center, then forcing a change in the hapticity of the arene ring, from $\eta^6$ to the $\eta^4$ mode.[2c] The thiophosphinidene ligand in **5** bridges three metal atoms in an unprecedented way, with the P−S moiety nearly at its maximun donor ability (6e). Overall, the P(S)R ligand in **5** provides the metal centers with a total of 10 electrons, with P−S, S−Fe, and Mo−S lengths of 2.1112(7), 2.2923(5), and 2.4358(5) Å, respectively, being consistent with the formulation of single bonds between the corresponding atoms.[7d,4c,11] This coordination mode is presumably retained in solution, as indicated by the pertinent spectroscopic data (see the SI).

When heated at 373 K in the presence of excess $[Fe_2(CO)_9]$, compound **5** adds a further iron fragment to give the tetranuclear compound **6**. This complex follows from an obviously multistep reaction that involves cleavage of the P−S bond, an $\eta^4$ to $\eta^6$ back-rearrangement of the arene ring, and the formation of new Fe−X bonds (X = Fe, Mo, S), as the most significant steps. Presumably, analogous steps might be involved in the formation of the ditungsten compound **4**. Actually, the intermediate detected in the formation of the latter displays a $^{31}P$ NMR resonance ($\delta_P$ 94.5 ppm) not far from that of **5** ($\delta_P$ 167.4 ppm), if we allow for the different metals involved, and thus might have a comparable structure.

The structures of **4** and **6** are comparable to each other in that they both show a tetrahedral $MoM_2(\mu_3\text{-}S)$ core, with a

MoCp($\eta^6$-PMes*) metallocene fragment comparable to those present in compounds **1** and **3**, but now terminally bound to W or Fe atoms, with a planar environment around the P atom (see Figure 3 and the SI). The phosphinidene ligand bridges Mo and W (or Fe) atoms much in the same way as that found for **1** and **3**, with significant delocalization of the $\pi$(M−P) bonding interaction along the Mo−P−M chain (not shown in Scheme 1). Indeed, the Mo−P length of ca. 2.33 Å is comparable to the corresponding length in **3**, and the P−W and P−Fe lengths of 2.284(1) and 2.087(1) Å, respectively, are significantly shorter than the reference single-bond lengths and not far from the values for the corresponding double bonds.[12] In contrast, the interatomic distances within the tetrahedral $MoM_2(\mu_3\text{-}S)$ core are comparable to those previously measured for other S-capped clusters.[7d,13] The major differences between the structures of **4** and **6** concern the relative conformation of the ligands surrounding the tetrahedral $MoM_2S$ core (see the SI). Interestingly, the ditungsten compound **4** exists in solution as an equilibrium mixture of two isomers, most likely differing just in the orientation of the $MoCp(CO)_2$ fragment relative to the central $MoW_2(\mu_3\text{-}S)$ core. We must note that compounds **4** and **6** are the first clusters having exocyclic PR ligands to be structurally characterized. Moreover, the multiple M−P bonding connecting the tetrahedral $MoM_2(\mu_3\text{-}S)$ core with the metallocene fragment provides a novel communication channel between these redox-active centers, a matter to be studied in the future.

In summary, we have described an efficient synthesis of the thiophosphinidene complex **2**, a molecule displaying an unprecedented coordination mode for an arylthiophosphinidene ligand. More interestingly, the P−S bond in this ligand is easily cleaved in the reactions of **2** with different metal carbonyls under mild conditions, this enabling the formation of new multiple P−M bonds with the added metal. Further work is now in progress to extend the above methodology as a synthetic route to new heterometallic complexes having $\mu_2$-phosphinidene ligands that are not accessible through more conventional routes.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Experimental procedures and spectroscopic data for new compounds and a crystallographic CIF file for compounds **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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