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Symmetrization in a Phosphinidene-Bridged Complex To Give a Diphosphanediyl Derivative with Metal-Centered Reactivity

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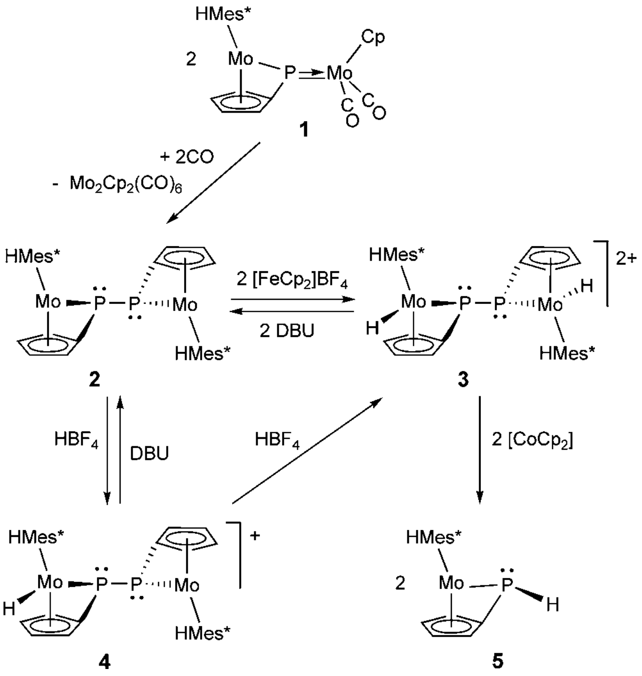
Supporting Information

ABSTRACT: The phosphinidene complex $[Mo_2Cp(\mu\text{-}\kappa^1:\kappa^1,\eta^5\text{-}PC_5H_4)(CO)_2(\eta^6\text{-}HMes^*)]$ reacts with CO to give the diphosphanediyl derivative $[Mo_2\{\mu\text{-}\kappa^1,\eta^5:\kappa^1,\eta^5\text{-}(C_5H_4)PP(C_5H_4)\}(\eta^6\text{-}HMes^*)_2]$. The latter compound features unreactive lone electron pairs at phosphorus, which instead contribute to the electronic communication between metal centers via a weak π(PP)-bonding interaction. As a result, this complex displays metal-centered acid−base and redox behavior.

The synthesis of molecules having novel bonding and reactivity features or unprecedented structures is a classical goal of the chemical research. Many of these targets have been achieved by using bulky substituents and ligands, providing kinetic stabilization, which enables the isolation of transition-metal and main-group species displaying unusually low coordination environments[1] or molecules featuring bonds otherwise unaffordable.[2] In recent years, we have used the bulky Mes* group (Mes* = $2,4,6\text{-}C_6H_2{}^tBu_3$) to stabilize different phosphinidene-bridged complexes, allowing a study of the reactivity of the multiple M−P bonds present in these molecules. This is the case of the dimolybdenum complexes $[Mo_2Cp_2(\mu\text{-}\kappa^1:\kappa^1,\eta^6\text{-}PMes^*)(CO)_2]$ and $[Mo_2Cp(\mu\text{-}\kappa^1:\kappa^1,\eta^5\text{-}PC_5H_4)(CO)_2(\eta^6\text{-}HMes^*)]$ (**1**; Cp = $\eta^5\text{-}C_5H_5$), which display unusual structures and reactivity patterns.[3]

Recently, we reported that complex **1** undergoes a dramatic increase of its nucleophilic power in the presence of CO or CNXyl (Xyl = $2,6\text{-}C_6H_3Me_2$) ligands, enabling it to react rapidly at room temperature with several alkynes and alkenes.[4] In this paper, we report that the reaction of **1** with CO in the absence of any other substrate induces a fast symmetrization of the Mo−P bond to yield the corresponding diphosphanediyl derivative $[Mo_2\{\mu\text{-}\kappa^1,\eta^5:\kappa^1,\eta^5\text{-}(C_5H_4)PP(C_5H_4)\}(\eta^6\text{-}HMes^*)_2]$ (**2**) and $[Mo_2Cp_2(CO)_6]$ (Scheme 1). The formation of P_2R_2 complexes through P−P coupling between coordinated phosphinidene ligands is not a new process itself.[5] What is remarkable in the formation of **2** is that it provides a novel $\mu\text{-}\kappa^1:\kappa^1$-coordination mode for a diphosphanediyl ligand in a transition-metal complex. Moreover, this compound does not behave with the P-centered reactivity expected for a dimetalladiphosphane. Instead, **2** displays a metal-centered acid−base and redox behavior that can be interpreted as derived, in part, from the presence of a certain diphosphene character in its bridging P_2R_2 ligand, with this, in turn, providing a novel channel for the electronic communication between the metal centers.

Scheme 1. Formation and Reactions of Compound 2



Compound **1** reacts smoothly with CO (1 atm) in tetrahydrofuran (1 h at 290 K or 15 min at 313 K) to give quantitatively **2** and $[Mo_2Cp_2(CO)_6]$, presumably via homolysis of a P−Mo bond in the pyramidal intermediate following coordination of CO to **1**.[4] This is in strong contrast with the reaction of its isomer $[Mo_2Cp_2(\mu\text{-}\kappa^1:\kappa^1,\eta^6\text{-}PMes^*)(CO)_2]$ with CO to give the addition product $[Mo_2Cp_2(\mu\text{-}\kappa^1:\kappa^1,\eta^4\text{-}PMes^*)(CO)_3]$,[3b] a difference possibly derived from the reluctance of the PC_5H_4 ligand to modify its hapticity, thus driving coordination of CO to the $MoCp(CO)_2$ center.

The structure of the centrosymmetric complex **2** in the crystal (Figure 1 and Table 1) displays a disorder of the P atoms and three $CH(C_5H_4)$ groups that was satisfactorily refined with 80/20 occupancies. We note that this sort of disorder has been previously found in different diphosphenes[6a] and diphosphanes.[6b] The $\mu\text{-}\kappa^1:\kappa^1$-coordination mode of the P_2

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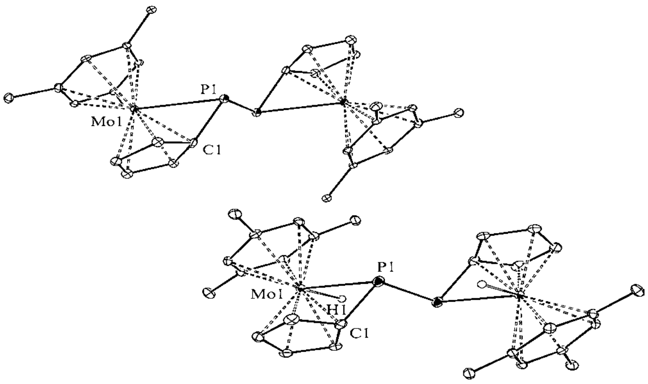


Figure 1. ORTEP plots (30% probability) of complex **2** (upper) and the cation of **3** (lower), with H atoms (except H1 in **3**) and Me groups omitted for clarity.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for 2 and 3

	P−P	Mo−P	Mo−P−C	C−P−P	Mo−P−P
2	2.202(9)	2.608(1)	55.5(1)	98.1(2)	104.6(1)
3	2.224(2)	2.600(1)	56.1(1)	98.6(1)	105.6(1)

ligand connecting the metal fragments in **2** appears to have no precedent in the chemistry of transition-metal diphosphanediyl complexes, although it is known for diphoshene complexes.[2j,7] The P−P separation of 2.202(9) Å in **2** has a value expected for a single bond (cf. 2.211(2) Å in the diphosphane complex $[Ru_2Cp_2(\mu\text{-}H_2PPH_2)(PPh_3)_4]^{2+})^{8}$ and is significantly longer than the values of ca. 2.00−2.05 Å reported for P═P double bonds in either free or coordinated organophosphorus ligands[2b,7] and even longer than the values measured for complexes having κ^2- or μ-κ^2:κ^2-P_2R_2 ligands.[2j,7c,9] At the same time, the large Mo−P separation of 2.608(1) Å is also consistent with the presence of single Mo−P bonds.[10] All of these geometrical features point to a description of the P_2R_2 moiety in **2** as a diphosphanediyl ligand, also in agreement with its relatively low ^{31}P chemical shift in solution (δ_P 54.3 ppm), much closer to the shift of a diphosphane (e.g., −64 ppm for Mes*(H)P−P(H)Mes*)[11] than to the value expected for a diphosphene complex (ca. 350−500 ppm).[2j] The chemical behavior of **2**, however, suggests that the actual situation is somewhat more complex.

The electron-rich complex **2** is easily protonated by $HBF_4{\cdot}OEt_2$. Surprisingly, however, protonation does not take place at the P sites but at the metal sites, to give the dihydride $[Mo_2\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^5\text{-}(C_5H_4)PP(C_5H_4)\}(H)_2(\eta^6\text{-HMes*})_2](BF_4)_2$ (**3**) in high yield, a reaction that can be fully reversed upon the addition of a base such as 1,8- diazabicyclo[5.4.0]-undec-7-ene. The formation of **3** can be accomplished stepwise via the monohydride $[Mo_2\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^5\text{-}(C_5H_4)PP(C_5H_4)\}(H)(\eta^6\text{-HMes*})_2](BF_4)$ (**4**), a complex that can also be isolated in good yield.

The structure of the cation in **3** (Figure 1) is little perturbed with respect to **2**, except for some opening of the angle between the metallocene rings (from ca. 16 to 25°) to accommodate the hydride ligands. Although the latter were not located directly on the difference map, their positions could be satisfactorily refined at ca. 1.8 Å from the metal centers and cis to the P atom (H−Mo−P ca. 84°). Moreover, their binding to the Mo atoms was clearly established by the appearance of a strongly shielded resonance in the ^{1}H NMR spectrum (δ_H −7.10 ppm) showing no coupling to the P atoms. As expected, the spectroscopic properties of the monohydride **4** share features with both **2** and **3**. Thus, **4** displays a hydride resonance at −6.35 ppm and two strongly coupled ^{31}P resonances (J_{PP} = 272 Hz), at 130.9 and 40.0 ppm, which compare well with those of **3** (112.5 ppm) and **2** (54.3 ppm), respectively.

The removal of two electrons from **2** could be easily accomplished with $[FeCp_2](BF_4)$ in a CH_2Cl_2 solution; however, this did not render a stable cation $\mathbf{2}^{2+}$, but the dihydride **3**, following from a fast hydrogen-abstraction reaction with traces of water present in the solvent.[12] In turn, the reduction of **3** with $[CoCp_2]$ did not give back **2** but instead resulted in cleavage of the P−P bond, along with a H shift from Mo to P, to give the phosphanyl complex $[Mo\{\kappa^1,\eta^5\text{-}PH(C_5H_4)\}(\eta^6\text{-HMes*})]$ (**5**) in high yield. The presence of a terminal and pyramidal PRH ligand in **5** was revealed by its shielded ^{31}P resonance (δ_P −49.6 ppm) exhibiting a relatively low one-bond coupling to a H atom (δ_H 2.07 ppm, J_{HP} = 144 Hz).[13]

A cyclic voltammetry (CV) experiment on **2** revealed that its oxidation takes place in two quasi-reversible steps, with the observed waves being assigned to the $\mathbf{2}/\mathbf{2}^+$ ($E_{1/2}$ = −0.78 V) and $\mathbf{2}^+/\mathbf{2}^{2+}$ couples ($E_{1/2}$ = −0.32 V vs $[Cp_2Fe]^{0/+}$). The large separation of 0.46 V between waves (ΔE) reflects a strong electronic communication between the redox centers,[14] which is somewhat unexpected for metal centers connected through a M−P−P−M chain of σ bonds. For instance, ΔE for the diphosphane complex $[Cr_2(\mu\text{-}\eta^6{:}\eta^6\text{-}PhCH_2Ph)(CO)_4(\mu\text{-}Me_2PPMe_2)]$ is only 0.29 V.[15]

To rationalize the unusual behavior of **2**, we carried out a density functional theory (DFT) calculation on this molecule. The four highest occupied molecular orbitals (MOs; −4.00 to −4.39 eV) represent nonbonding electron pairs essentially located at the Mo atoms, which also bear higher negative charges than the P atoms, thus accounting for the preferential protonation and oxidation of **2** at the metal sites. However, the most salient feature is that the expected lone pairs (LPs) at the P atoms are significantly mixed with the P−Mo and P−C σ-bonding orbitals, thus accounting for the low chemical activity of these electrons. This is a very unusual behavior for trivalent P centers,[16] including the metallophosphanes,[5a,13,17] and it is dramatically represented by the HOMO−4/HOMO−5 couple, which illustrates LP/Mo−P mixing (Figure 2). As a result, a certain π(PP)-bonding interaction is developed, thus accounting for the strong intermetallic communication deduced from the CV measurements. To our knowledge, this sort of P−P-bonding interaction has not been recognized previously in related diphosphorus molecules, and it represents a new mechanism for communication between redox centers connected by single P−P bonds, adding to the known through-bond coupling (mixing with σ and σ* P−P orbitals),[18] recognized recently in different biphospholes.[19] In simple

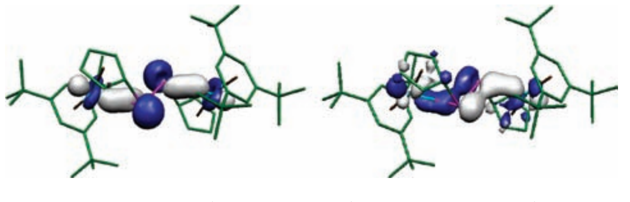
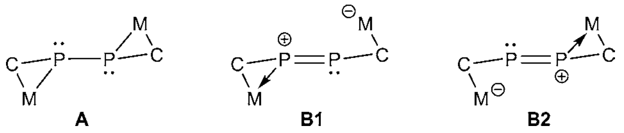


Figure 2. HOMO−4 (−4.96 eV, left) and HOMO−5 (−5.97 eV, right) orbitals of **2**.

valence-bond terms, we can describe the above orbital interaction by considering a small contribution of the zwitterionic diphosphene forms **B** to the electronic structure of **2**, to be added to the main diphosphanediyl form **A** (Chart 1). It remains to be seen to which extent the above interaction is facilitated by the geometrical constraints imposed by the bifunctional PC_5H_4 moiety present in **2**, and further work to synthesize analogues of **2** via symmetrization reactions of asymmetric phosphinidene complexes isoelectronic with **1** is now in progress. The latter reactions are themselves of interest because they provide a novel method to induce the formation of P−P bonds, to be added to the more classical procedures relying on elimination reactions, nucleophilic addition, or photochemical activation, among others.

Chart 1



In summary, we have reported the first example of a P−P coupling reaction via symmetrization in an asymmetric phosphinidene-bridged precursor under mild conditions. This leads to a dimetalladiphosphane derivative displaying a novel μ-κ^1,κ^1-coordination mode for a P_2R_2 ligand in transition-metal complexes. The latter provides a strong communication between the metal centers derived from involvement of the LPs at phosphorus in a π(PP)-bonding interaction. As a result, the P_2R_2-bridged complex displays a metal-centered acid−base and redox chemistry.

■ ASSOCIATED CONTENT

Supporting Information

Preparative procedures, analytical and spectroscopic data for complexes **2**−**5**, tables of data from the DFT calculations, and crystallographic files for **2** and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Attempts to isolate the cation $\mathbf{2}^{2+}$ have been unsuccessful so far. A control reaction of **2** with excess $[FeCp_2]BF_4$ carried out in a CD_2Cl_2 solution within an NMR tube revealed the initial formation of a single species identified by a broad ^{31}P NMR resonance at 25.1 ppm, presumably corresponding to $\mathbf{2}^{2+}$, with this resonance being replaced by that of the dihydride **3** progressively.

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