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From Coordinated Oxophosphinidene to O,O,P-Bound Arylhypophosphite(2−) To Build a Singular $Mo_2Sn_2O_4P_2$ Metallocycle

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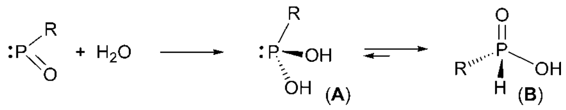
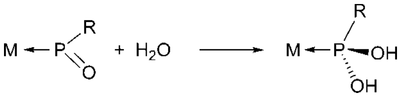
P-bound derivatives of the hypophosphorous acids can be prepared from complexed phosphinidene oxides. The anion $[MoCp(CO)_2\{P(O)R^*\}]^-[(H\text{-DBU})^+$ salt ($R^* = 2,4,6\text{-}C_6H_2{}^tBu_3$; $Cp = \eta^5\text{-}C_5H_5$) reacts with $SnCl_2Ph_2$ to give the neutral oxophosphinidene complex $[MoCp\{P(O)R^*\}(CO)_2(SnPh_2Cl)]$ in high yield. Basic hydrolysis of the latter complex occurs readily to yield the novel Mo−Sn metallocyclic derivatives $[MoSn\{\mu\text{-}O,P\text{-}OP(OH)R^*\}CpPh_2(CO)_2]$ and $[MoSn\{\mu\text{-}O,O,P\text{-}O_2PR^*\}CpPh(CO)_2]_2$. These products display respectively hydrogenhypophosphite(1−) and hypophosphite(2−) anions coordinated through all of their O (to Sn) and P (to Mo) atoms.

Organic hypophosphorous acids and their derivatives are important intermediates in the syntheses of biologically active compounds[1] and are also valuable intermediates in the synthesis of other organophosphorus compounds.[2a] Out of the two possible tautomers, with either pyramidal [$RP(OH)_2$ (**A**)] or tetrahedral [$RHP(O)(OH)$ (**B**)] structures, the latter is generally the most stable one, as found for other oxoacids of phosphorus.[2b] Actually, the pyramidal structure **A** is only stable when R is an extremely bulky group.[3] As a result of this preference, the coordination chemistry of the hypophosphorous acids and their derived anions has been dominated by their binding to metals via the O atoms. In fact, even when the involvement of P-bound derivatives of these acids as intermediate species in some Pd-catalyzed reactions has been proposed,[2a] only recently have the first complexes containing P-bound $RP(OH)_2$ acids (R = H, Ph) been isolated.[4] In this paper, we report a novel rational route to these P-donor ligands starting from a coordinated oxophosphinidene ligand.



(1)



(2)

The formation of hypophosphorous acids might be conceived as resulting from the addition of water to the double bond of a phosphinidene oxide molecule (eq 1). The latter, however, are unstable species thought to be generated in the decomposition of several organophosphorus compounds.[5] Interestingly, these transient species undergo processes related to eq 1, such as insertion into O−H and S−S bonds.[5a] As an alternative approach to this chemistry, one could then study the reactivity of P(O)R species when coordinated to metal centers (eq 2). However, only a few oxophosphinidene complexes have been reported so far,[6] and their reactivity has not been explored. Herein we report the synthesis of the neutral oxophosphinidene complex $[MoCp\{P(O)R^*\}$-

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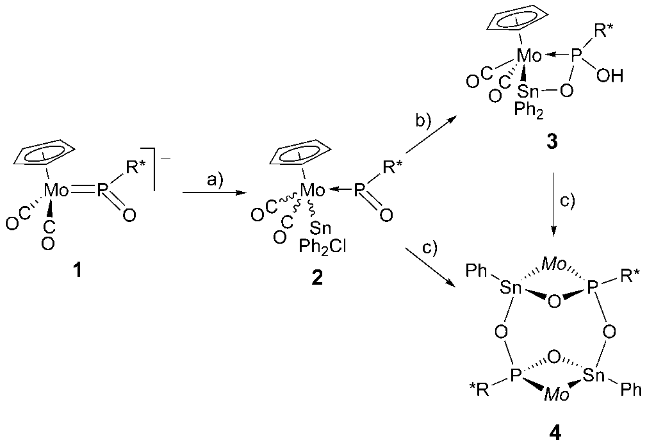
Scheme 1. Synthesis of Complexes **2**–**4** [R* = 2,4,6-$C_6H_2{}^tBu_3$; Cp = η^5-C_5H_5; Mo = $MoCp(CO)_2$]: (a) $SnCl_2Ph_2$, CH_2Cl_2, 0 °C; (b) KOH, THF, 0 °C; (c) KOH, petroleum ether, 0 °C

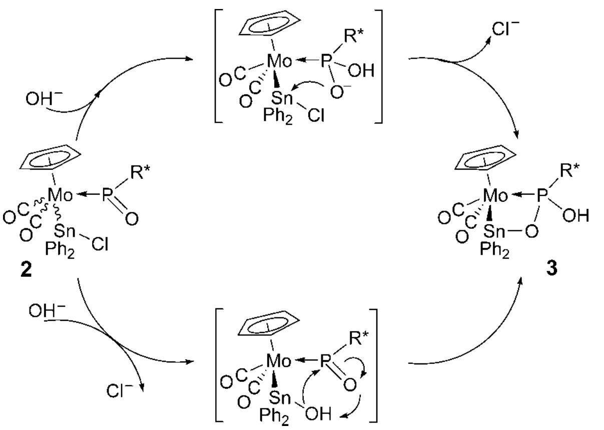


(CO)$_2$(SnPh$_2$Cl)] (**2**; R* = 2,4,6-$C_6H_2{}^tBu_3$; Cp = η^5-C_5H_5) and its remarkable hydrolytic behavior, which involves both the P and Sn sites to build novel MoSnPO rings. The resulting products provide the first examples of *O*,*P*-hydrogenhypophosphite(1−) and *O*,*O*,*P*-hypophosphite(2−) ligands (Scheme 1), and they can be also of interest in the rapidly expanding field of the clusters, cages, rings, and coordination polymers containing oxoorganotin building blocks.[7]

Complex **2** can be prepared by the reaction of the anion $[MoCp(CO)_2\{P(O)R^*\}]^-$ (**1**) $[(H\text{-}DBU)^+$ salt; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene][8] with $SnCl_2Ph_2$ (Scheme 1), and it displays cis and trans isomers in solution (see the Supporting Information).[9] The trans to cis ratio is both solvent- and temperature-dependent, with the cis isomer being favored in low-polarity solvents and at low temperatures. The presence of the cis isomer is revealed not only by the characteristic C−O stretching bands in the IR spectra but also by the dramatic increase in the $^{31}P-^{119/117}Sn$ couplings (ca. 530 Hz, compared to 149 Hz in the trans isomer) derived from the acute Sn−Mo−P angle in this isomer.

The presence of the cis isomer is critical to the formation of the metallocyclic species [MoSn{μ-*O*,*P*-OP(OH)R*}CpPh$_2$(CO)$_2$] (**3**) and [MoSn{μ-*O*,*O*,*P*-O$_2$PR*}CpPh(CO)$_2$]$_2$ (**4**) upon hydrolysis of **2**. This reaction takes place slowly upon manipulation of **2** in wet solvents but much faster in the presence of KOH, with the product being strongly dependent on the solvent (Scheme 1). Thus, the reaction with KOH in tetrahydrofuran (THF) gives the unprecedented hydrogenhypophosphite complex **3**,[10] which could be isolated as a yellow powder. In contrast, the reaction with KOH in petroleum ether gives the metallocyclic compound **4**,[11] which can be viewed as having two hypophosphite(2−) anions bound through all of their P and O atoms. A separate experiment showed that **3** also transforms into **4** upon reaction with KOH in petroleum ether, which makes it a likely intermediate in the formation of **4**. The latter requires a dearylation process in **3**, which is unexpected for an organotin compound, where such a reaction is usually promoted by acidic reagents.[7d]

Scheme 2. Reaction Pathways in the Formation of Complex **3**



The formation of **3** might occur following the attack of the OH^- anion to either the P and Sn sites in **2** (Scheme 2). In the first route, a P-bound hydrogenhypophosphite complex would be formed and then undergoing displacement of Cl^- to yield **3**. Alternatively, Cl^- could be first displaced by the direct attack of OH^- at the Sn site, followed by the intramolecular addition of the O−H bond to the P═O bond of the P(O)R* ligand. We note that the hydrolysis of $SnClR_3$ to give the corresponding organotin hydroxides and/or their condensed products is well established.[7d]

The IR spectra of complexes **3** and **4** denote a cis arrangement of the CO ligands in each case, which is also consistent with the large $^{119/117}Sn-^{31}P$ couplings observed for **3** ($^2J_{PSn}$ = ca. 550 Hz). Incidentally, the ^{31}P NMR shift for **3** (δ_P = 154.4 ppm) is similar to those for classical Mo complexes having $P(OR)_3$ ligands and is also comparable to those found for the few hypophosphorous acid complexes reported so far.[4] The ^{31}P NMR shift for **4** is similar to that of **3** (δ_P = 149.2 ppm), but the Sn−P couplings yield now a more complex pattern, taking the values of ca. 660 and 55 Hz. This is in agreement with its solid-state structure (see

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(9) Selected data for **2**. IR [ν(CO), CH_2Cl_2]: 2001 (m), 1960 (s), 1899 (vs) cm^{-1}.^1H NMR (CD_2Cl_2): δ 5.26 (s, 5H, C_5H_5, cis isomer), 4.96 (s, 5H, C_5H_5, trans isomer), 1.64 (s, 18H, CH_3, trans isomer), 1.61, 1.28, 1.17 (3 × s, 3 × 9H, CH_3 cis isomer), 1.35 (s, 9H, CH_3 trans isomer), trans/cis = 3.5.$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 475.3 [s, $J(^{119}SnP) = J(^{117}SnP)$ = 149 Hz, trans isomer], 438.5 [s, $J(^{119}SnP)$ = 540 Hz, $J(^{117}SnP)$ = 516 Hz, cis isomer].$^{119}Sn\{^1H\}$ NMR (CD_2Cl_2): δ 216.9 [s, J(SnP) = 149 Hz, trans isomer].

(10) Selected data for **3**. IR [ν(CO), THF]: 1935 (vs), 1856 (s) cm^{-1}.^1H NMR (C_6D_{12}): δ 5.16 (s, 5H, C_5H_5), 2.81 (s, 1H, OH), 1.52, 1.25, 1.22 (3 × s, 3 × 9H, CH_3).$^{31}P\{^1H\}$ NMR (THF-d_8): δ 154.4 [s, $J(^{119}SnP)$ = 563 Hz, $J(^{117}SnP)$ = 538 Hz].$^{119}Sn\{^1H\}$ NMR (C_6D_{12}): δ 136.8 [s, J(SnP) = 563 Hz].

(11) Selected data for **4**. IR [ν(CO), THF]: 1941 (vs), 1863 (s) cm^{-1}.^1H NMR (CD_2Cl_2): δ 5.12 (s, 5H, C_5H_5), 1.43, 1.24, 1.21 (3 × s, 3 × 9H, CH_3).$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 149.2 [s, $J(^{119}SnP)$ = 674 Hz, $J(^{117}SnP)$ = 646 Hz, $J(^{119}SnP) = J(^{117}SnP)$ = 55 Hz].$^{119}Sn\{^1H\}$ NMR (CD_2Cl_2): δ 19.3 [s, J(SnP) = 674 Hz].

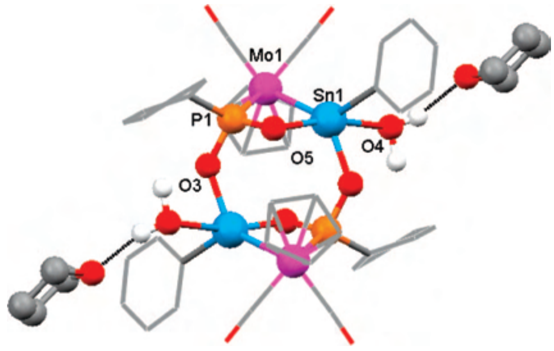

Figure 1. Crystal structure of **4**·$2H_2O$·$2C_4H_8O$, with ^{t}Bu groups and H atoms not involved in hydrogen bonding omitted.

below), revealing that the P and Sn atoms are connected through acute (P−Mo−Sn ca. 65°) and obtuse (P−O−Sn ca. 100 and 130°) two-bond pathways.

The structure of **4** has been studied in two different crystalline forms (see the Supporting Information). Crystals of **4**·$2C_7H_8$ were obtained by diffusion of petroleum ether into a toluene solution of the complex.[12] In contrast, the use of a toluene−wet THF solution of the complex yielded crystals of **4**·$2H_2O$·$2C_4H_8O$.[13] Both crystals display essentially the same tricyclic metallocycle resulting from the dimerization of two Cp(CO)$_2$Mo(PR*O$_2$)SnPh moieties (with almost flat PMoSnO rings) so that the terminal O atom of the hypophosphite(2−) ligand in one fragment binds to the unsaturated Sn atom of the second fragment and vice versa, thus creating an inversion center (Figure 1). Such a heterometallocyclic arrangement is extremely rare and can be compared to that in the tin(II) phosphinidene anions $[\{Sn(\mu\text{-}PR)\}_2(\mu\text{-}PR)]_2^{4-}$.[14] Besides, the solvent molecules are involved in significant interactions modifying both the overall crystal structure and also the coordination environment of the Sn atom.

In the crystals of **4**·$2C_7H_8$, the Sn atoms exhibit an unusual trigonal-pyramidal (rather than tetrahedral) environment, which changes to trigonal bipyramidal in **4**·$2H_2O$·$2C_4H_8O$ because of the weak coordination of a water molecule [Sn−O 2.517(4) Å] in an axial position (Figure 1). This causes a slight lengthening of ca. 0.06 Å in the axial Sn−O bond trans to this ligand, but otherwise the interatomic lengths are little modified. In both crystals, the hypophosphite(2−) ligands are strongly bound to the Sn atoms through their O atoms (P−O lengths ca. 1.57 Å; Sn−O lengths ca. 2.05–2.15 Å) and bound to Mo via the P atom (P−Mo ca. 2.56 Å). In the THF solvate, there is strong hydrogen bonding[15] between THF and the Sn-bound water molecule (H···O = 1.88 Å; O···O = 2.71 Å). In addition, there are substantial intermolecular interactions between Cp and CO ligands (C−H···O = 2.54 Å) tailoring a one-dimensional chain (Figure 2); the latter are of strength comparable to those found in other organometallic crystals.[15b,16]

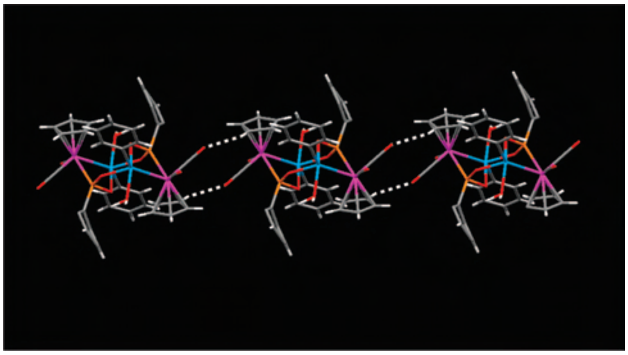

Figure 2. Crystal packing in **4**·$2H_2O$·$2C_4H_8O$, emphasizing the (Cp)C−H···O−C interactions, with solvent molecules and ^{t}Bu groups omitted.

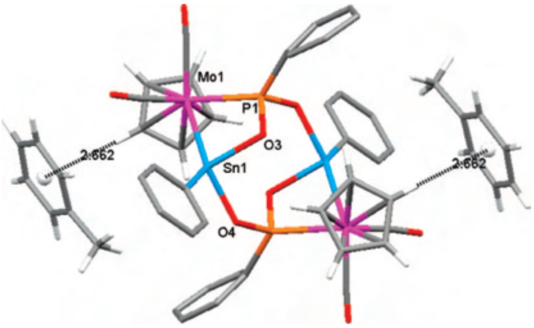

Figure 3. Crystal structure of **4**·$2C_7H_8$, emphasizing the (Cp)C−H···π-(toluene) interactions, with ^{t}Bu groups omitted.

In the case of **4**·$2C_7H_8$, the crystal packing is controlled by the presence of strong C−H···π interactions between the Cp ligands and the toluene molecules (Figure 3). In each case, one of the cyclopentadienyl H atoms points to the centroid of the toluene ring. The short distance involved in this interaction (H···centroid = 2.66 Å) and the perpendicular positioning of the C−H bond with respect to the ring are indicative of a considerably strong interaction.[15b,17]

In this paper, we have shown for the first time that oxophosphinidene complexes can be used as rational precursors for complexes having P-bound derivatives of the hypophosphorous acids, with this, in turn, allowing for the buildup of novel metallocyclic structures. Further research to extend the scope of these transformations is currently underway.

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Supporting Information Available: Preparative and spectroscopic data for new complexes (PDF) and crystallographic data for compounds **4**·$2H_2O$·$2C_4H_8O$ and **4**·$2C_7H_8$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) X-ray data for **4**·$2C_7H_8$: orange crystals, triclinic ($P\bar{1}$), a = 12.1377(1) Å, b = 13.0674(1) Å, c = 13.2949(1) Å, α = 111.897(1)°, β = 102.987(1)°, γ = 104.300(1)°, V = 1774.30(4) Å^3, T = 100 K, Z = 1, R = 0.0248 [observed data with $I > 2\sigma(I)$], GOF = 1.333.

(13) X-ray data for **4**·$2H_2O$·$2C_4H_8O$: yellow crystals, monoclinic ($C2/c$), a = 19.449(7) Å, b = 14.367(5) Å, c = 27.400(10) Å, β = 101.748(6)°, V = 7496(5) Å^3, T = 120 K, Z = 4, R = 0.0499 [observed data with $I > 2\sigma(I)$], GOF = 1.02.

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