Organometallics **2006,** *25,* 5374−5380

Dimolybdenum−Tin Derivatives of the Unsaturated Hydride $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ and $HSnR_3$ (R = Ph, Bu): Bridging versus Terminal Coordination of the Triorganostannyl Group

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Received June 5, 2006

Reaction of the 30-electron hydride $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ with $HSnR_3$ (Cp = $\eta^5\text{-}C_5H_5$; R = Ph, Bu) leads to the unsaturated dimolybdenum−tin derivatives $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}SnR_3)(CO)_2]$ (R = Ph, Bu), which display a triorganostannyl ligand unusually bridging two metal atoms, and to the phosphine-hydride complex $[Mo_2Cp_2(\mu\text{-}H)(SnPh_3)(CO)_2(PCy_2H)]$, which has a formally triple Mo−Mo bond bridged by only one hydride ligand. The structures of the triphenylstannyl compounds were determined by single-crystal X-ray diffraction studies, which revealed the presence of short Mo−Mo separations (<2.6 Å), consistent with the presence of metal−metal multiple bonding in these 30-electron derivatives. The phosphine-hydride complex experiences spontaneous dehydrogenation at room temperature to give $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}SnPh_3)(CO)_2]$, whereby the terminal $SnPh_3$ group moves into a bridging position. In contrast, carbonylation of the latter stannyl-bridged compound gives an unstable tricarbonyl derivative, $[Mo_2Cp_2(\mu\text{-}PCy_2)(SnPh_3)(CO)_3]$, and then the stable tetracarbonyl $[Mo_2Cp_2(\mu\text{-}PCy_2)(SnPh_3)(CO)_4]$ (Mo−Mo = 3.202(1) Å), both of which display a terminal stannyl group.

Introduction

During our preliminary study of the reactivity of the unsaturated dinuclear hydride $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ (**1**) we found that this complex reacted readily with $HSnPh_3$ to give the stannyl-bridged derivative $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}SnPh_3)(CO)_2]$ (**2a**).[1] There are several aspects of interest in this result. In the first place, we note that there are only two previous reports on the reactivity of unsaturated polynuclear hydride compounds toward organotin hydrides, none of them leading to the formation of triorganostannyl-bridged species.[2,3] Thus, the dimanganese dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ (L_2 = $Ph_2PCH_2PPh_2$, $(EtO)_2POP(OEt)_2$) were reported to react with $HSnPh_3$ to give the compounds $[Mn_2(\mu\text{-}H)(\mu\text{-}\kappa^1\text{:}\,\kappa^2\text{-}HSnPh_2)(CO)_6(\mu\text{-}L_2)]$, which display σ coordination of a Sn−H bond to one of the Mn centers, and the stannylene-bridged derivatives $[Mn_2(\mu\text{-}SnPh_2)_2(CO)_6(\mu\text{-}L_2)]$.[2] On the other hand, the unsaturated triosmium cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ has been reported to react with an excess of $HSnMe_3$ to give the bis-stannyl cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}(SnMe_3)_2]$, in which the triorganotin groups are terminally bound to the osmium atoms.[3] Terminal binding to transition metal centers is the most common coordination mode for triorganostannyl groups, whereas diorganotin groups (SnR_2) usually adopt bridging positions by establishing two M−Sn bonds.[4] In contrast, compounds having triorganostannyl groups bridging two metal atoms are very unusual, and we can quote just two other examples in the literature apart from **2a**, these being the recently reported manganese−tin compounds $[Mn_2\{\mu\text{-}Sn\text{:}Sn,P\text{-}SnR_2OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6L]$ (R = Bu, Ph; L = CO, tertiary phosphine)[5] and the tin−germanium compound [K(2,2,2-crypt)]$[Ge_9(\mu\text{-}SnPh_3)]$.[6] Other related examples are the platinum−tin clusters $[Pt_3(\mu\text{-}Ph_2PCH_2PPh_2)_3(\mu_3\text{-}SnMe_2X)]PF_6$ (X = H, $OPOF_2$),[7] in which the stannyl group triply bridges the metal triangle, and the ruthenium−tin cluster $[Ru_6C(CO)_{16}(\mu\text{-}SnCl_3)]^-$, in which the trichlorostannyl group bridges two ruthenium atoms.[8] Apart from their structures and reactions,[4] heterometallic clusters combining tin and transition metals are of interest because of their potential use in catalysis, either as catalysts themselves[4a] or as precursors of bimetallic nanoparticles.[9] In this paper we report full details of our study of the reactions of the unsaturated hydride **1** toward the organotin hydrides $HSnPh_3$ and $HSnBu_3$, as well as some complementary experiments. These have revealed a facile shift of the stannyl group between terminal and bridging positions in these molybdenum−tin derivatives.

Results and Discussion

Reactions of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ (1) with Triorganotin Hydrides. Compound **1** reacts with $HSnR_3$ (R =

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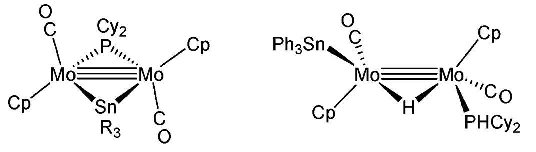
10.1021/om060495m CCC: $33.50

Chart 1



R = Ph (**2a**), Bu (**2b**)

3

Ph, Bu) in toluene at room temperature to give, after stirring for 3 h (R = Ph) or 24 h (R = Bu), the corresponding unsaturated stannyl derivatives $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}SnR_3)(CO)_2]$ [R = Ph (**2a**), Bu (**2b**)] in good yield (Chart 1). The formation of compounds **2** requires the elimination of H_2 at some intermediate stage, and indeed we have detected the new unsaturated hydride $[Mo_2Cp_2(\mu\text{-}H)(SnPh_3)(CO)_2(PCy_2H)]$ (**3**) as an intermediate species in the reactions with $HSnPh_3$ (but not in the case of the $HSnBu_3$ reaction, despite its lower rate). In fact, a 4:3 mixture of compounds **2a** and **3** is obtained after stirring a solution of **1** with $HSnPh_3$ for just 10 min. Unfortunately, we have not been able to find more selective conditions for the preparation of **3** since no significant changes in the above product distribution were obtained when carrying out the reaction under a H_2 atmosphere at 0 °C. On the other hand, in a separate experiment we observed that the complete transformation of toluene solutions of **3** into **2** was a relatively slow process, requiring ca. 2 h at room temperature. This proves the presence of at least two different pathways in these reactions, to be discussed later on. Compound **3**, along with **1**, is one of the few examples of organometallic compounds bearing hydride ligands bridging a metal−metal (formally) triple bond. Previous complexes of this type are the iridium complexes $[Ir_2Cp^*_2(\mu\text{-}H)_2]$,[10] $[Ir_2Cp^*_2(\mu\text{-}H)_3]^+$,[11] and the low-yield *N*-methylpyrrole derivative $[Ir_2Cp^*_2\{\mu\text{-}C_4H_3N(Me)\}(\mu\text{-}H)]$,[12] the group 8 polyhydrides $[M_2Cp^*_2(\mu\text{-}H)_4]$ (M = Fe, Ru; Cp*= η^5-C_5Me_5),[13] studied in detail for M= Ru,[13c] the monocarbonyls $[M_2Cp^*_2(\mu\text{-}H)_2(\mu\text{-}CO)]$ (M = Ru,[14] Os[15]), the trihydride cations $[Ru_2(\eta^6\text{-}C_6Me_6)_2(\mu\text{-}H)_3]^+$ [16] and $[Os_2(Mes)_2(\mu\text{-}H)_3]^+$ (Mes = 1,3,5-$C_6H_3Me_3$),[17] and the ditungsten monohydride cations $[W_2Cp_2(\mu\text{-}H)(CO)_2(\mu\text{-}L_2)]^+$ (L_2 = $R_2PCH_2PR_2$; R= Ph, Me).[18] In most of the above examples the intermetallic bond order (BO) is not very clear, ranging from 0 to 3 according to the views of the different authors, the number of bridging hydride ligands, and the consideration given to the corresponding three-center−two-electron (3c-2e) interactions. For instance, a theoretical study on $[Ru_2Cp^*_2(\mu\text{-}H)_4]$ (BO = 3 according to the EAN formalism) suggested the presence of negligible direct metal−metal interaction.[19] In all the above compounds, however, there are either several hydride bridges or other groups bridging the dimetal center, thus complicating the analysis of the intermetallic interaction. In this respect, compound **3** is unique in having just one ligand (the hydrogen atom) bridging its triple metal−metal bond.

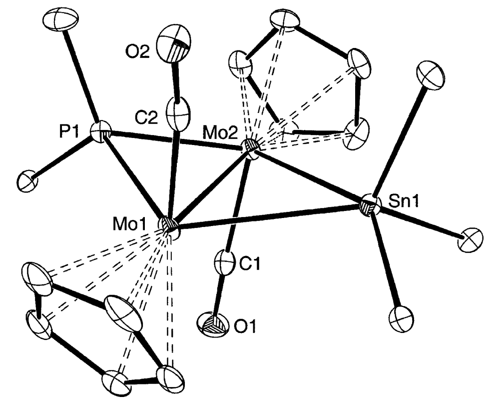


Figure 1. ORTEP diagram (30% probability) of compound **2a**, with H atoms and Cy and Ph rings omitted for clarity, except the C^1 atoms.[1] Selected bond lengths (Å) and angles (deg): Mo(1)−Mo(2) = 2.5743(7), Mo(1)−P(1) = 2.385(1), Mo(2)−P(1) = 2.368(1), Mo(1)−Sn(1) = 2.9139(7), Mo(2)−Sn(1) = 2.9244(7), Mo(1)−C(2) = 1.946(6), Mo(2)−C(1) = 1.922(5); C(1)−Mo(2)−Mo(1) = 71.2(2), C(2)−Mo(1)−Mo(2) = 90.5(1).

Structural Characterization of Compounds 2a,b and 3. The structure of compound **2a** was confirmed by a single-crystal X-ray diffraction study (Figure 1).[1] The molecule displays two MoCp(CO) moieties placed in a slightly distorted transoid arrangement and joined by two bridging groups: dicyclohexylphosphide and triphenylstannyl. The short Mo−Mo distance, 2.5743(7) Å, is consistent with the presence of a metal−metal triple bond, and it is only ca. 0.05 Å longer than that measured in the hydride precursor **1**,[1] surely as a result of the steric pressure introduced by the bulky triphenylstannyl group. The presence of multiple bonding in **2a** is also consistent with its reactivity toward carbon monoxide (see below). The conformation of the molecule is asymmetric, which is denoted by the distinct bending of the carbonyl ligands over the intermetallic vector (C(1)−Mo(2)−Mo(1) = 71.2(2)°; C(2)−Mo(1)−Mo(2) = 90.5°) and the puckering of the PMo_2Sn ring (ca. 158°). Yet, the C(1)−O(1) ligand has a relatively large separation from the second metal atom [C(1)···Mo(1) = 2.671(6) Å] and must be described at most as a very weakly semibridging ligand (see below). In contrast, compound **1** displays an essentially flat PMo_2H ring,[1] and this conformational difference has surely a steric origin too. On the other hand, the $SnPh_3$ group displays a pseudotetrahedral geometry, with C−Sn−C angles ranging from 99.6(2)° to 103.6(2)°, these values being not very different from those found in mononuclear group 6 complexes having terminal $SnPh_3$ groups, such as the pentacarbonyl $[W(SnPh_3)(CO)_5]^-$, (99−104°)[20] or the tricarbonyls $[M\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(CO)_3(SnPh_3)]$ (M = Mo, W) (106−108°).[21] The Sn−Mo lengths in **2a** (ca. 2.92 Å), however, are substantially larger than those measured in the above mononuclear complexes (ca. 2.82 Å), and all this is therefore consistent with a description of this heterometallic interaction as a three-center (Mo_2Sn) two-electron bond.

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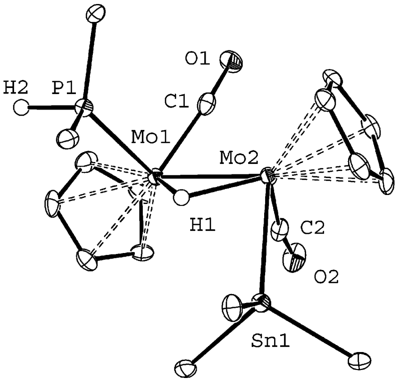

Figure 2. ORTEP diagram (30% probability) of compound **3**, with H atoms and Cy and Ph rings omitted for clarity, except the C^1 atoms, the hydride ligand, and the H atom bonded to phosphorus.

The structure of compound **3** in the crystal displays MoCp($SnPh_3$)(CO) and MoCp(CO)(PCy_2H) moieties bridged only by a hydride ligand, with the Cp rings on opposite sides of the Mo_2H plane and the carbonyl ligands arranged in a transoid position with respect to the hydride atom (Figure 2 and Table 2). According to the EAN formalism, a Mo−Mo triple bond can be formulated for this 30-electron complex, which is consistent with the short intermetallic length of 2.5730(6) Å, comparable to the value found in the stannyl complex **2a**. The Mo(2)−Sn(1) distance, 2.7340(6) Å, is now much shorter than the average metal−tin distance in **2a** (ca. 2.92 Å), as expected for a terminal stannyl ligand, and even shorter than the single-bond lengths measured in the saturated mononuclear compounds [M{η^5-$C_5H_4(CH_2)_2NMe_2$}$(CO)_3(SnPh_3)$] (ca. 2.82 Å) mentioned above.[21] An unexpected feature of the structure of **3** is the essentially terminal coordination of the two carbonyl ligands. In fact, these ligands can be at most described as very weak linear semibridging, as deduced from the relatively high C−Mo−Mo angles (69.1(1)° and 76.0(1)°) and C···Mo lengths (2.605(5) and 2.815(6) Å). In contrast, the linear semibridging carbonyls present in the triply bonded complexes [$Mo_2Cp_2(CO)_4$],[22a] [$W_2Cp_2(CO)_2$(μ-dppm)],[22b] and [W_2Cp_2(μ-CO)(CO){$P(OMe)_3$}(μ-dppm)](BAr'_4)$_2$[22c] display lower C−M−M angles (58.0−68.7°) and much shorter M···C separations (2.28−2.49 Å). We note that the presence of linear semibridging carbonyls is a common structural feature for carbonyl complexes having triple metal−metal bonds[23] and that this feature can be justified on theoretical grounds.[23b,24]

Spectroscopic data in solution for compound **2a** are consistent with its solid state structure, but suggest dynamic behavior. The IR spectrum is itself consistent with the slightly distorted transoid arrangement of the CO ligands, and the chemical shift for the phosphorus nucleus, 248.5 ppm, is in good agreement with those shifts found for other 30-electron compounds related to **2a**, such as the dicarbonyls [Mo_2Cp_2(μ-PCy_2)(μ-X)$(CO)_2$] [X = H (**1**), AuP(p-tol)$_3$][25] or the monocarbonyls [Mo_2Cp_2(μ-PCy_2)(μ-PRR′)(μ-CO)] (R = R′ = Cy, Ph; R = Cy, R′ = H).[26] However, the ^1H and $^{13}C\{^1H\}$ NMR spectra are not consistent with the asymmetric structure found in the crystal. In fact, both spectra exhibit just one resonance for the Cp ligands, which suggests the presence of an apparent C_2 symmetry axis, probably generated by a dynamic process taking place in solution. This is also consistent with the six-resonance pattern exhibited by the cyclohexyl groups in the ^{13}C spectrum. Low-temperature NMR experiments were carried out in order to slow the rate of this process, but no significant changes were detected in these spectra down to 193 K. Therefore, we propose that there is a quite low energy fluxional process involving a slight rotation of both MoCp(CO) fragments in opposite directions, thus causing a flip oscillation of the puckered PMo_2Sn ring (Scheme 1). This would imply a transition state (and average structure) with a geometry similar to the one found for **1**,[1] that is, with equivalent MoCp(CO) moieties and a flat central ring. As for compound **2b**, spectroscopic data obtained in solution are very similar to those just discussed for **2a** and need then no further analysis.

IR and NMR spectra for compound **3** are fully consistent with the structure found in the crystal. Thus, two C−O stretching bands are observed in the IR spectrum with intensities (strong and very strong, in order of decreasing frequency) indicative of two CO ligands defining an angle somewhat higher than 90°,[27] in good agreement with the solid structure. The ^{31}P NMR spectrum displays a quite shielded resonance (45.4 ppm), as expected for a coordinated phosphine, and the inequivalent Cp ligands give rise to separate resonances in the ^1H NMR spectrum, one of them exhibiting $^{119/117}Sn$−H coupling (7 Hz), which is consistent with the terminal coordination of the $SnPh_3$ group. The signal due to the hydrogen directly bonded to phosphorus (4.78 ppm) exhibits a large P−H coupling (325 Hz), as expected for one-bond interactions between these nuclei. Finally, the bridging hydride gives rise to a resonance exhibiting strong two-bond coupling to phosphorus (30 Hz) and tin (131 Hz), as expected. Its chemical shift (δ_H −1.98 ppm) is unusually high for a bridging hydride, it being comparable only to the values found for other 30-electron hydride-bridged compounds such as **1** (δ_H −6.94 ppm)[25] or the cations [W_2Cp_2(μ-H)$(CO)_2$(μ-L_2)]$^+$ ($L_2 = R_2PCH_2PR_2$; R = Ph, Me) with chemical shifts of ca. −2.5 ppm.[18] In contrast, the chemical shifts for bridging hydrides in electron-precise compounds related to the latter ones, such as [Mo_2Cp_2(μ-H)(μ-PCy_2)$(CO)_4$][26] and [W_2Cp_2(μ-H)$(CO)_4$(μ-L_2)][BF_4],[18] are much lower (−13.2 and ca. −20 ppm, respectively). We trust that the unusual deshielding exhibited by the bridging hydrides in our 30-electron complexes is mainly a negative-shielding effect caused by the strongly anisotropic metal−metal multiple bonds present in these unsaturated species.[28]

Reaction Pathways. To account for the formation of the tin derivatives **2a**,**b** and **3**, at least two competing pathways must be proposed (Scheme 2). In the first place, it is expected that the reaction is initiated in any case by coordination of the organotin hydride through its σ Sn−H bond to one of the metal centers of **1** (intermediate **A**). This type of interaction is well known for mononuclear complexes,[29] although it is perhaps less common than σ coordination of Si−H bonds. The next step would be the oxidative addition of the Sn−H bond to form the

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Table 1. Selected IR[a] and $^{31}P\{^1H\}$ NMR[b] Data for New Compounds

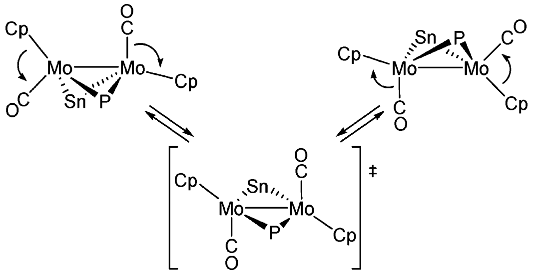
compound	ν(CO)	δ_P, $[J_{PSn}]^c$
$[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}SnPh_3)(CO)_2]$ (**2a**)	1865 (m), 1809 (vs)	248.5 [85][d]
$[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}SnBu_3)(CO)_2]$ (**2b**)	1848 (m), 1801 (vs)	235.8 [79]
$[Mo_2Cp_2(\mu\text{-}H)(SnPh_3)(CO)_2(PHCy_2)]$ (**3**)	1834 (s), 1799 (vs)	45.4[e]
$[Mo_2Cp_2(\mu\text{-}PCy_2)(SnPh_3)(CO)_3]$ (**4**)	1892 (m), 1828 (s, sh), 1812 (vs)	194.9 [66]
$[Mo_2Cp_2(\mu\text{-}PCy_2)(SnPh_3)(CO)_4]$ (**5**)	1936 (m), 1886 (s), 1836 (vs), 1821 (s, sh)	223.7 [70]

[a] Recorded in dichloromethane solution, unless otherwise stated, ν in cm^{-1}. [b] Recorded in CD_2Cl_2 solutions at 290 K and 121.50 MHz, unless otherwise stated, δ in ppm relative to external 85% aqueous H_3PO_4. [c] J_{PSn} (in Hz) refers to the average coupling between ^{31}P and the ^{119}Sn and ^{117}Sn isotopes. [d] At 162.00 MHz. [e] In $CDCl_3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 3

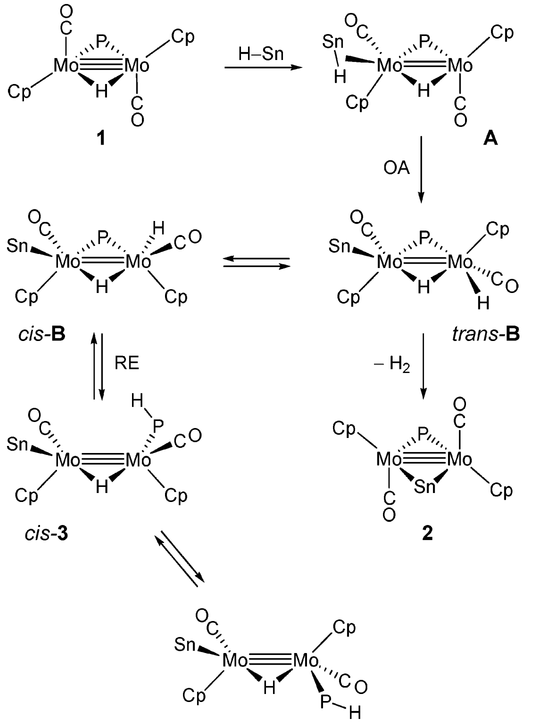
Mo(1)−Mo(2)	2.5730(6)	Mo(1)−C(2)	2.815(6)
Mo(1)−C(1)	1.924(5)	Mo(1)−P(1)	2.450(1)
Mo(2)−C(2)	1.927(5)	Mo(2)−Sn(1)	2.7340(6)
Mo(2)−C(1)	2.605(5)	Mo(1)−H(1)	1.82(5)
Mo(2)−H(1)	1.84(5)		
O(1)−C(1)−Mo(1)	169.0(4)	Sn(1)−Mo(2)−Mo(1)	98.75(2)
O(1)−C(1)−Mo(2)	122.3(4)	Sn(1)−Mo(2)−H(1)	67(1)
O(2)−C(2)−Mo(2)	170.7(4)	Sn(1)−Mo(2)−C(2)	83.0(2)
C(1)−Mo(1)−Mo(2)	69.1(1)	C(19)−Sn(1)−C(25)	103.6(2)
C(2)−Mo(2)−Mo(1)	76.0(1)	C(19)−Sn(1)−C(13)	105.0(2)
P(1)−Mo(1)−Mo(2)	101.28(3)	C(25)−Sn(1)−C(13)	104.4(2)
P(1)−Mo(1)−C(1)	91.7(1)	Mo(1)−H(1)−Mo(2)	89(1)
P(1)−Mo(1)−H(1)	74(1)		

Scheme 1. Fluxional Process Proposed for Compound 2a in Solution (substituents on phosphorus and tin omitted for clarity)



dihydride intermediate *trans*-**B**. This is likely to be a low-energy process, since Sn−H bonds are relatively weak and can undergo oxidative addition more easily than, for example, Si−H or H−H bonds.[29] Besides, this oxidative addition would push the former bridging hydride into a terminal position to yield a structure (*trans*-**B**) having the Cp ligands on opposite sides of the average Mo_2HP plane, but keeping both the $SnPh_3$ group and the terminal hydride positioned close to the bridging hydride. This allows one of the possible evolutions of this intermediate, that is, the reductive elimination of H_2 to give the stannyl-bridged complexes **2**. Alternatively, the intermediate *trans*-**B** might undergo an isomerization process to give *cis*-**B**, this having now the Cp ligands on the same side of the average Mo_2PH plane. A related cis/trans equilibrium in solution has been recently reported by us for the structurally related tetracarbonyl species $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHMes)(CO)_4]$,[30] and it has been also described for the thiolate-bridged complexes $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_4]$.[31] In our case, the isomerization proposed would involve the rearrangement of the less congested MoCp(CO)H moiety, and it would render a cis disposition of the terminal hydride with respect to the phosphide ligand, thus enabling the reductive elimination of the P−H bond to give the intermediate phosphine complex *cis*-**3**. A new cis/trans isomerization would finally give the isolable compound **3**. Since compounds **2a** and **3** are both formed rapidly, it is concluded that the required reductive eliminations (formation of P−H and H−H bonds) and cis/trans rearrangements must have quite low energy barriers. However, to explain the slow transformation of **3** into **2a**, we propose that the reaction pathway leading to **3** is reversible. Thus, compound **3** would be in equilibrium with tiny amounts of dihydrides **B**, which, after irreversible loss of H_2, would slowly transform **3** into **2a**. The irreversible character of the dehydrogenation step is consistent with the absence of any measurable effect when the reaction of **1** and $HSnPh_3$ was carried out under a H_2 atmosphere (1 atm). Despite this, the existence of a different and independent reaction pathway leading to **2a** from **3** cannot be completely ruled out.

Scheme 2. Proposed Reaction Pathways in the Reactions of 1 with $HSnPh_3$ (substituents on phosphorus and tin omitted for clarity; OA = oxidative addition; RE = reductive elimination)



Reaction of Compound 2a with Carbon Monoxide. To check the unsaturated nature of **2a**, as well as the stability of the unusual coordination position (bridging) of the stannyl group, we examined the reaction of this complex with CO. In fact, a solution of **2a** in CH_2Cl_2 reacts instantaneously with CO to give first the still unsaturated tricarbonyl derivative $[Mo_2Cp_2(\mu\text{-}PCy_2)(SnPh_3)(CO)_3]$ (**4**), which, after stirring for 2 h under a CO atmosphere, yields the saturated tetracarbonyl $[Mo_2Cp_2(\mu\text{-}$

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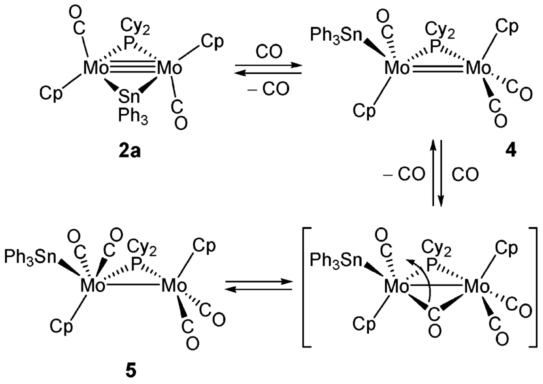
(30) Alvarez, C. M.; Alvarez, M. A.; García-Vivó, D.; García, M. E.; Ruiz, M. A.; Sáez, D.; Falvello, L. R.; Soler, T.; Herson, P. *Dalton Trans.* **2004**, 4168.

(31) Schollhammer, P.; Pétillon, F. Y.; Pichon, R.; Poder-Guillou, S.; Talarmin, J.; Muir, K. W.; Guirdwood, S. E. *J. Organomet. Chem.* **1995**, *486*, 183.

Scheme 3. Carbonylation Reaction for Compound 2a



$PCy_2)(SnPh_3)(CO)_4]$ (**5**) quantitatively (Scheme 3). This process is reversible, and the irradiation of a toluene solution of **5** with visible−UV light for 30 min gives back the dicarbonyl precursor **2a**. Unfortunately, compound **4** is rather unstable and decomposes progressively to give a mixture of the dicarbonyl **2a** and the tetracarbonyl **5** when CO is removed from the reaction environment or upon the usual purification procedures (crystallization, filtration, etc.), so full structural characterization was not possible for this complex.

Structural Characterization of Compounds 4 and 5. The structure of compound **5** was determined by a single-crystal X-ray study (Figure 3 and Table 3). The molecule displays $MoCp(CO)_2$ and $MoCp(CO)_2(SnPh_3)$ fragments bridged by a dicyclohexylphosphide ligand, with the Cp ligands positioned on opposite sides of the Mo_2P plane, as found in **2a**, and the $SnPh_3$ group arranged trans with respect to the phosphide bridge (Sn−Mo−P = 132.21(6)°). The relatively large intermetallic distance, 3.203(1) Å, is consistent with the formulation of a metal−metal single bond, as expected under the EAN formalism, and is similar to the values found for the structurally related and isoelectronic tetracarbonyl complexes $[Mo_2ClCp_2(\mu\text{-}PHPh)(CO)_4]$ (3.2315(3) Å)[30] and $K[Mo_2Cp_2(\mu\text{-}PH_2)(GaCl_3)(CO)_4]$ (3.206(3)Å).[32] The Mo(1)−Sn(1) distance, 2.826(1) Å, is now very close to those found for the above-mentioned complexes $[M\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(CO)_3(SnPh_3)]$,[21] as expected for a normal Mo−Sn single bond. The difference in the coordination numbers around the molybdenum atoms is compensated for by a strongly asymmetric coordination of the phosphide bridge, placed ca. 0.1 Å closer to Mo(2). This is not unusual for PR_2 ligands bridging inequivalent metal centers, and it can lead to M−P bond lengths differing by as much as 0.2 Å, as it is the case of the tricarbonyl complex $[Mo_2Cp_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(Me){=}CHMe\}(\mu\text{-}PMe_2)(CO)_3]$.[33] The CO ligands in **5** clearly can be regarded as terminal, except for one of the carbonyls cis to the $SnPh_3$ group (C(1)−O(1)), which can be viewed as a very weak semibridging ligand (C(1)···Mo(2) = 2.77 Å). A similar effect can be appreciated in the anion $[Mo_2Cp_2(\mu\text{-}PH_2)(GaCl_3)(CO)_4]^-$, a complex with a structure similar to that of **5**, with the $GaCl_3$ group trans to the PH_2 bridge.[32] In contrast, the chloride and phosphide ligands in $[Mo_2ClCp_2(\mu\text{-}PHPh)(CO)_4]$ are arranged cis,[30] perhaps due to the much smaller steric demands of a chlorine atom (compared to $GaCl_3$ or $SnPh_3$ groups), and there are no semibridging carbonyls, which then appear to have a steric origin.

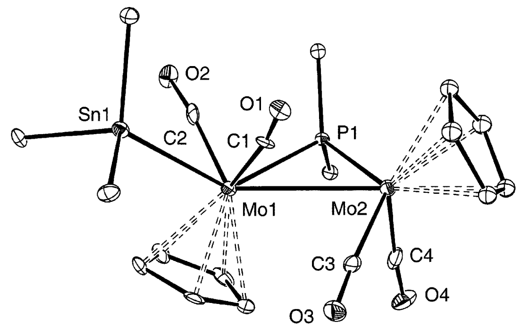


Figure 3. ORTEP diagram (30% probability) of compound **5**, with H atoms and Cy and Ph rings omitted for clarity, except the C^1 atoms.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 5

Mo(1)−C(1)	1.961(9)	Mo(1)−Mo(2)	3.203(1)
Mo(1)−C(2)	1.95(1)	Mo(1)−Sn(1)	2.826(1)
Mo(2)−C(3)	1.99(1)	Mo(1)−P(1)	2.505(2)
Mo(2)−C(4)	1.92(1)	Mo(2)−P(1)	2.399(2)
C(2)−Mo(1)−C(1)	100.8(4)	O(3)−C(3)−Mo(2)	175.6(8)
C(4)−Mo(2)−C(3)	82.9(4)	O(4)−C(4)−Mo(2)	174.8(9)
C(2)−Mo(1)−Sn(1)	72.0(3)	C(1)−Mo(1)−Mo(2)	59.3(3)
C(1)−Mo(1)−Sn(1)	67.7(3)	C(2)−Mo(1)−Mo(2)	117.8(3)
P(1)−Mo(1)−Sn(1)	132.21(6)	C(3)−Mo(2)−Mo(1)	73.7(3)
Mo(2)−Mo(1)−Sn(1)	162.92(3)	C(4)−Mo(2)−Mo(1)	90.7(3)
Mo(2)−P(1)−Mo(1)	81.51(7)	C(33)−Sn(1)−C(27)	102.8(4)
O(1)−C(1)−Mo(1)	171.2(8)	C(33)−Sn(1)−C(39)	112.0(3)
O(2)−C(2)−Mo(1)	173.2(9)	C(27)−Sn(1)−C(39)	102.6(3)

The single crystals of **5** analyzed by X-ray diffraction were grown by slow diffusion of petroleum ether into a brown toluene solution of the complex at −20 °C and were surprisingly of a dark green color. In contrast, fast precipitation of the complex using the same solvents yielded a dark brown powder. However, the IR spectra of both types of solids exhibited a similar pattern for the C−O stretching bands, although their frequencies were somewhat different (see Experimental Section). Thus we conclude that the conformations of the molecules in both the green crystals and the brown powder are essentially identical, with the differences in the IR frequencies possibly arising from their distinct packing in the solid. In fact, the spectroscopic data for the brown solutions of **5** are fully consistent with the structure of the green crystals just discussed. In the first place, the IR spectra exhibit four C−O stretching bands with a pattern similar to that of the spectra recorded in Nujol mulls. This pattern, however, is different from those observed in related phosphide-bridged tetracarbonyl complexes, such as $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_4]$ (M = Mo, W; R = alkyl, aryl)[26] or $[Mo_2ClCp_2(\mu\text{-}PHR)(CO)_4]$.[30] This can be attributed to the presence of a transoid $M(CO)_2$ oscillator in **5**, whereas the mentioned tetracarbonyls have only cisoid $M(CO)_2$ oscillators. The asymmetry of the metal centers in **5** is reflected in its ^1H NMR spectrum, which exhibits two distinct resonances for the Cp ligands as expected. Finally, the ^{31}P NMR spectrum exhibits a singlet at 223.7 ppm, a typical shift for a dicyclohexylphosphide ligand bridging two molybdenum centers connected through a single metal−metal bond.[26]

The structure proposed for the unstable tricarbonyl **4** is based only on the spectroscopic data obtained from solutions in which this complex is the major species present (Table 1). Its IR spectrum exhibits three C−O stretching bands with a pattern different from that found for other tricarbonyl dimolybdenum compounds in which $MoCp(CO)_2$ and $MoCp(CO)$ moieties are joined by two bridging ligands, such as $[Mo_2Cp_2(\mu\text{-}PEt_2)_2(CO)_3]$,[26] $[Mo_2Cp_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(Me){=}CHMe\}(\mu\text{-}PMe_2)(CO)_3]$,[33] $[Mo_2Cp_2\text{-}$

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[32] Vogel, U.; Scheer, M. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1491.

[33] Connole, G.; Henrick, K.; McPartlin, M.; Horton, A. D.; Mays, M. J. *New J. Chem.* **1988**, *12*, 559.

$(\mu\text{-H})(\mu\text{-PPh}_2)(\text{CO})_3(\text{PR}_3)]$,[34] and $[\text{Mo}_2(\mu\text{-}\eta{:}^5\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_5\text{H}_4)(\mu\text{-PMe}_2)_2(\text{CO})_3]$[35] (the last three structures confirmed by X-ray diffraction). All the above compounds exhibit three strong C−O stretching bands in their IR spectra, with the strongest band being that highest in frequency. In contrast, the most intense C−O stretching band in **4** is that lowest in frequency, which suggests that the arrangement of the CO groups in **4** is quite different from that found in the above-mentioned tricarbonyls. On the basis of this difference, we propose that compound **4** has a single bridge (the PCy_2 ligand) joining MoCp(CO)_2 and MoCp(CO)SnPh_3 moieties, these probably arranged in a transoid configuration if we take into account the fact that both the dicarbonyl **2a** and the tetracarbonyl **5** display Cp groups on opposite sides of the Mo_2P plane. In any case, a double metal−metal bond must be formulated for this complex according to the EAN formalism. The available NMR data for compound **4** are consistent with this structural proposal. For example, its ^{31}P NMR spectrum exhibits a relatively shielded phosphide resonance (194.3 ppm), as generally observed for 32-electron phosphide-bridged dimolybdenum species,[26] while the inequivalent Cp ligands give rise to separate resonances in the ^1H NMR spectrum. The latter are significantly broader than usual, which can be indicative of the presence of a dynamic process in solution, which we have not studied.

Reaction Pathways in the Carbonylation of 2a. As deduced from the data discussed above, the carbonylation of compound **2a** occurs stepwise and essentially with retention of the transoid arrangement of the MoCp moieties relative to the Mo_2P plane (Scheme 3). In the first step compound **2a** would incorporate a CO molecule at one of the metal centers as a terminal ligand, whereby the stannyl group would shift from bridging into a terminal position at the adjacent metal center, thus yielding the tricarbonyl **4**, for which a double Mo−Mo bond can be formulated. The next CO molecule is then likely to be added to this double bond, then becoming a bridging ligand, as observed in the carbonylation of the isoelectronic tetracarbonyls $[\text{Mo}_2\text{Cp}_2(\mu\text{-PHR})(\text{CO})_4]^+$ (R = Cy, Ph) to give the pentacarbonyl derivatives $[\text{Mo}_2\text{Cp}_2(\mu\text{-PHR})(\mu\text{-CO})(\text{CO})_4]^+$.[30] In a final step, the new CO ligand would rearrange by moving into a terminal position possibly due to steric effects, since this allows the stannyl group to be placed further away from the bridging dicyclohexyl ligand. It should be noted that this last rearrangement leads in a natural way to a transoid arrangement of the carbonyl ligands close to the tin atom, as observed in the structure of **5**. Finally, since these carbonylation reactions are reversible, we conclude that, even when the SnPh_3 group is usually found terminally bound to metal centers, it appears to shift in a relatively easy way into a bridging position, thus resembling the isoelectronic hydride ligand. The transformation of the hydride complex **3** into **2a** is just another example of this rearrangement. Consideration of this unexpected ability of the SnPh_3 group to shift between terminal and bridging positions might be of use when analyzing the reactions of triorganotin hydrides with polynuclear transition metal complexes.

Experimental Section

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures and distilled prior to use.[36] Compound $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_2]$ (**1**) was prepared as described previously,[25] and all other reagents were obtained from the usual commercial suppliers and used as received, unless otherwise stated. Petroleum ether refers to that fraction distilling in the range 65−70 °C. Photochemical experiments were performed using jacketed quartz Schlenk tubes, cooled by tap water (ca. 288 K). A 400 W mercury lamp (Applied Photophysics) placed ca. 1 cm away from the Schlenk tube was used for these experiments. Chromatographic separations were carried out using jacketed columns cooled by tap water. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity desired. IR stretching frequencies of CO ligands were measured either in solution (using CaF_2 windows) or in Nujol mulls (using NaCl windows) and are referred to as ν(CO). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (^{1}H), 121.50 ($^{31}\text{P}\{^1\text{H}\}$), or 75.47 MHz ($^{13}\text{C}\{^1\text{H}\}$) at 290 K in CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 solutions (^{31}P). Coupling constants (J) are given in hertz.

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-SnPh}_3)(\text{CO})_2]$ (2a). Compound **1** (0.030 g, 0.05 mmol) and HSnPh_3 (0.025 g, 0.07 mmol) were stirred in toluene (10 mL) for 3 h to give a brown solution. Solvent was then removed from the solution under vacuum, and the residue was dissolved in petroleum ether and chromatographed on an alumina column (activity IV) at 15 °C. Elution with dichloromethane−petroleum ether (1:8) gave a brown fraction. Removal of solvents from the latter under vacuum gave compound **2a** as a brown powder (0.044 g, 92%). The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a concentrated toluene solution of the complex at −20 °C. Anal. Calcd for $\text{C}_{42}\text{H}_{47}\text{Mo}_2\text{O}_2\text{PSn}$: C, 54.51; H, 5.12. Found: C, 54.79; H, 5.42. ^{1}H NMR (400.13 MHz): δ 7.80−7.10 (m, 15H, Ph), 4.64 (s, 10H, Cp), 2.80−1.10 (m, 22H, Cy). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, 213 K): δ 247.1 (d, $J_{\text{CP}} = 11$, CO), 145.5 (s, C^1-Ph), 137.6 (s, C^2-Ph), 128.2 (s, C^3-Ph), 127.5 (s, C^4-Ph), 89.3 (s, Cp), 48.8 (d, $J_{\text{CP}} = 16$, C^1-Cy), 33.6, 31.2 (2 × s, $\text{C}^{2,6}$-Cy), 27.8 (d, $J_{\text{CP}} = 11$, $\text{C}^{3,5}$-Cy), 27.6 (d, $J_{\text{CP}} = 14$, $\text{C}^{5,3}$-Cy), 26.1 (s, C^4-Cy).

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-SnBu}_3)(\text{CO})_2]$ (2b). Compound **1** (0.030 g, 0.05 mmol) and HSnBu_3 (30 μL, 0.11 mmol) were stirred in toluene (10 mL) for 24 h to give a brown solution. Solvent was then removed from the solution under vacuum, and the residue was dissolved in petroleum ether and chromatographed on an alumina column (activity IV) at 15 °C. Elution with the same solvent gave a brown fraction. Removal of the solvent from the latter under vacuum gave compound **2b** as a highly air-sensitive brown powder (0.044 g, 92%). ^{1}H NMR: δ 4.98 (s, 10H, Cp), 2.70−1.20 (m, 22H, Cy), 1.40−1.25 (m, 18H, CH_2), 0.94 (t, $J_{\text{HH}} = 7$, 9H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 245.6 (d, $J_{\text{CP}} = 14$, CO), 88.1 (s, Cp), 49.8 (d, $J_{\text{CP}} = 17$, C^1-Cy), 33.9, 32.5 (2 × s, br, $\text{C}^{2,6}$-Cy), 30.5 (s, $J_{\text{C}-117\text{Sn}} \approx J_{\text{C}-119\text{Sn}} = 19$, C^1-Bu), 28.2 (d, $J_{\text{CP}} = 11$, $\text{C}^{3,5}$-Cy), 28.1 (s, C^2-Bu), 26.5 (d, $J_{\text{CP}} = 1$, C^4-Cy), 14.8 (s, C^3-Bu), 14.0 (s, C^4-Bu).

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\text{SnPh}_3)(\text{CO})_2(\text{PHCy}_2)]$ (3). Compound **1** (0.030 g, 0.05 mmol) and HSnPh_3 (0.025 g, 0.07 mmol) were stirred in toluene (10 mL) for 10 min to give an orange-brown solution containing a mixture of compounds **2a** and **3** in a 4:3 ratio. Solvent was then removed from the solution under vacuum, and the residue was dissolved in petroleum ether and chromatographed on an alumina column (activity IV) at 15 °C. Elution with dichloromethane−petroleum ether (1:9) gave a brown fraction, yielding, after removal of solvents, 0.024 g (50%) of compound **2a**. Elution with a 1:3 solvent mixture gave an orange fraction,

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[34] Henrick, K.; McPartlin, M.; Horton, A. D.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1083.

[35] (a) Heck, J. *J. Organomet. Chem.* **1986**, *311*, C5. (b) Abriel, W.; Baum, G.; Burdorf, H.; Heck, J. *Z. Naturforsch.* **1991**, *46b*, 841.

[36] Armarego, W. L. F.; Chai, C. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: Oxford, UK, 2003.

yielding, after removal of solvents, compound **3** as an orange solid (0.020 mg, 41%). This complex is thermally unstable, and complete transformation into complex **2a** occurs by just stirring a toluene solution of **3** for 2 h at room temperature. The crystals used in the X-ray study of **3** were grown by slow diffusion of a layer of petroleum ether into a concentrated toluene solution of the complex at −20 °C. Anal. Calcd for $C_{42}H_{49}Mo_2O_2PSn$ (**3**): C, 54.39; H, 5.33. Found: C, 54.58; H, 5.75. ^1H NMR ($CDCl_3$): δ 7.90−7.20 (m, 15H, Ph), 4.78 (d, br, $J_{PH} = 325$, 1H, HPCy$_2$), 4.76 (s, $J_{H-119Sn} \approx J_{H-117Sn} = 7$, 5H, Cp), 4.31 (d, $J_{PH} = 2$, 5H, Cp), 2.40−1.00 (m, 22H, Cy), −1.98 (dd, $J_{PH} = 30$, $J_{HH} = 1$, $J_{H-119Sn} \approx J_{H-117Sn} = 131$, 1H, μ-H).

Preparation of Solutions of [$Mo_2Cp_2(\mu\text{-}PCy_2)(SnPh_3)(CO)_3$] (4). In a typical experiment, compound **2a** (0.044 g, 0.05 mmol) was stirred in toluene (5 mL) or CD_2Cl_2 (1 mL) under a CO atmosphere for 1 min to give a purple solution containing compound **4** as the major product. Compound **4** is highly unstable, and it decomposes upon the usual workup (removal of solvents, crystallization, etc.) to give a mixture of the starting dicarbonyl **2a** and the tetracarbonyl derivative **5**. ^1H NMR: δ 7.40−7.10 (m, 15H, Ph), 5.51, 5.09 (2 × s, br, 2 × 5H, Cp), 3.05−0.10 (m, 22H, Cy).

Preparation of [$Mo_2Cp_2(\mu\text{-}PCy_2)(SnPh_3)(CO)_4$] (5). Compound **2a** (0.044 g, 0.05 mmol) was stirred in toluene (5 mL) under CO atmosphere during 2 h to give a brown solution. Solvent was then removed from the solution under vacuum, and the residue was washed with petroleum ether (5 mL) to give compound **5** as a brown powder (0.045 g, 96%). The green crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a concentrated toluene solution of the complex at −20 °C. Anal. Calcd for $C_{44}H_{47}Mo_2O_4PSn$: C, 53.84; H, 4.83. Found: C, 53.63; H, 4.75. IR ν(CO) (Nujol mull/green crystals): 1939 (s), 1879 (s), 1840 (vs), 1798 (s) cm^{-1}. IR ν(CO) (Nujol mull/brown powder): 1938 (s), 1888 (s), 1847 (vs), 1824 (s) cm^{-1}. ^1H NMR: δ 7.75−7.25 (m, 15H, Ph), 5.32, 5.06 (2 × s, 2 × 5H, Cp), 2.40−1.00 (m, 22H, Cy).

X-ray Structure Determination of Compound 3. The X-ray intensity data were collected on a Smart-CCD-1000 Bruker diffractometer using graphite-monochromated Mo Kα radiation at 120 K (Table 4). Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in three sets of 30 exposures collected in three different ω regions and eventually refined against all reflections. The software SMART[37] 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,[37] and a multiscan absorption correction was applied with SADABS.[38] The structure was solved by Patterson interpretation and phase expansion using DIRDIF[39] and refined with full-matrix least-squares on F^2 using SHELXL97.[40] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the Fourier map in the last least-squares refinements, but all the methylenic hydrogen atoms were fixed at calculated geometric positions, to reach a satisfactory convergence. All hydrogen atoms were given an overall isotropic thermal parameter.

Table 4. Crystal Data for Compounds 3 and 5

	3	5
mol formula	$C_{42}H_{49}Mo_2O_2PSn$	$C_{44}H_{47}Mo_2O_4PSn$
mol wt	927.35	981.36
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
radiation (λ, Å)	0.71073	0.71073
a, Å	11.427(2)	11.7278(19)
b, Å	18.567(3)	14.627(2)
c, Å	18.542(3)	22.860(4)
α, deg	90	90
β, deg	105.488(3)	97.054(3)
γ, deg	90	90
V, Å^3	3791.1(11)	3891.8(11)
Z	4	4
calcd density, gcm^{-3}	1.625	1.675
absorp coeff, mm^{-1}	1.382	1.355
temperature, K	120	120
θ range (deg)	1.58 to 28.27	1.66 to 28.28
index ranges (h, k, l)	−15, 14; 0, 24; 0, 24	−15, 15; 0, 19; 0, 29
no. of reflns collected	31 998	36 644
no. of indep reflns	9184 [$R_{int} = 0.0555$]	9421 [$R_{int} = 0.1317$]
no. of reflns with $I > 2\sigma(I)$	6104	5056
R indexes ($I > 2\sigma(I)$)[a]	$R_1 = 0.0383$, $wR_2 = 0.0710$[b]	$R_1 = 0.0608$, $wR_2 = 0.1156$[c]
R indexes (all data)[a]	$R_1 = 0.0848$, $wR_2 = 0.0899$[b]	$R_1 = 0.1584$, $wR_2 = 0.1581$[c]
GOF	1.073	1.016
no. of restraints/ params	0/549	0/465
$\Delta\rho$(max, min), e Å^{-3}	1.091, −1.094	1.168, −1.566

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] $a = 0.0157$, $b = 17.1043$. [c] $a = 0.0230$, $b = 55.2232$.

X-ray Structure Determination of Compound 5. Collection of data, structure solution, and refinements were done as described for **3** (Table 4). For compound **5** the Cp ligand bonded to Mo(1) was found disordered over two positions related by rotation about the Mo−Cg vector, in which Cg represents the center of the Cp ring; the almost equal occupancy factors given (0.52 and 0.48) provided satisfactory refinement. All non-hydrogen atoms were refined anisotropically, with the exception of those C atoms of the disordered Cp ring, which were refined isotropically because they were persistently nonpositive definite. Because of the low quality of the diffraction data, only some hydrogen atoms could be found on difference maps, so all were fixed at calculated geometric positions in the last cycles of refinement, and they were given an overall isotropic thermal parameter.

Acknowledgment. We thank the MEC of Spain for a Ph.D. grant (to A.R.) and the MCYT for financial support (BQU2003-05471).

Supporting Information Available: Crystallographic data for the structural analysis of compounds **3** and **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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