

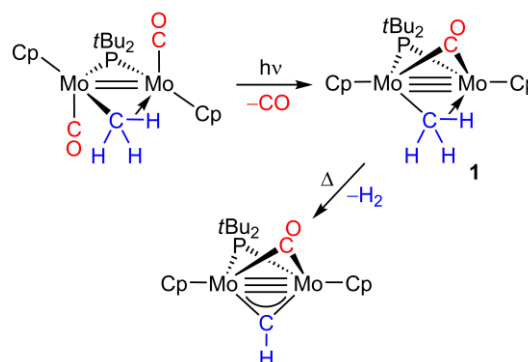
Dehydrogenation, Methyl Elimination and Insertion Reactions of the Agostic Methyl-Bridged Complex $[\text{Mo}_2\text{Cp}_2(\mu-\kappa^1:\eta^2\text{-CH}_3)(\mu\text{-PtBu}_2)(\mu\text{-CO})]$

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Abstract: The high unsaturation of the title complex enabled it to react with a wide variety of molecules under mild conditions, whereby the agostic methyl ligand underwent unusual or unprecedented processes. Methane elimination occurred in the reactions with PPh_2H and SiPh_2H_2 , this being followed in the latter case by Si–H bond oxidative addition to give the hydride silylene derivative $[\text{Mo}_2\text{Cp}_2\text{H}(\mu\text{-PtBu}_2)(\mu\text{-SiPh}_2)(\text{CO})]$. Dehydrogenation, however, was the dominant process in the room temperature reaction with $[\text{Fe}_2(\text{CO})_9]$, to give the unsaturated methylidyne cluster $[\text{Mo}_2\text{FeCp}_2(\mu_3\text{-CH})(\mu\text{-PtBu}_2)(\text{CO})_5]$ ($\text{Mo}\text{--}\text{Mo} = 2.6770(8) \text{ \AA}$). In contrast, PMe elimination took place in the reaction with P_4 , to give the unsaturated triphosphorus complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\eta^3\text{-}\eta^3\text{-P}_3)(\mu\text{-PtBu}_2)]$ ($\text{Mo}\text{--}\text{Mo} = 2.6221(3) \text{ \AA}$). Yet a most remarkable reaction occurred with $\text{BH}_3\cdot\text{THF}$, this involving insertion of two BH_3 units and dehydrogenation to yield $[\text{Mo}_2\text{Cp}_2(\mu\text{-B}_2\text{H}_4\text{Me})(\mu\text{-PtBu}_2)(\text{CO})]$, with the novel methylboranyl ligand acting as a 5-electron donor due to the presence of two 3-centre, 2-electron B–H–Mo interactions, according to spectroscopic data and DFT calculations ($\text{Mo}\text{--}\text{Mo}$ ca. 2.65 \AA).

Alkyl complexes are a most important class of compounds within organometallic chemistry, and the reactivity of the corresponding σ M–C bonds is a central matter of the discipline, extensively studied in the case of mononuclear complexes.^[1] The chemistry of binuclear complexes featuring bridging alkyl ligands, however, is comparatively less developed, even if such complexes might serve as models for the intermediate species involved in several processes of interest, these including olefin oligomerization and polymerization, alkyl transfer reactions, and heterogeneously catalyzed CO hydrogenation.^[2,3] When compared to electron-precise analogues, it is expected that the reactivity of alkyl-bridged complexes might be further increased in molecules bearing multiple metal-metal bonds, because of the coordinative and electronic unsaturation of the dimetal centre in such species. However, complexes displaying alkyl ligands bridging over metal-metal multiple bonds are scarce, and their reactivity has been little explored.^[3,4,5] This situation changed upon our synthesis of the dimolybdenum complexes $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1:\eta^2\text{-CH}_2\text{R})(\mu\text{-PCy}_2)(\text{CO})_2]$ ($\text{R} = \text{H}, \text{Ph}$), which feature agostic alkyl ligands over shortened Mo–Mo double bonds,^[6] and turned to be highly reactive, they being able to undergo coupling reactions to CO, CNR and Cp ligands, as well as photochemical dehydrogenation and more complex processes.^[7,8] It was then of

interest to examine the reactivity of related agostic complexes at even more unsaturated centres, as it is the case of the monocarbonyl derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1:\eta^2\text{-CH}_3)(\mu\text{-PCy}_2)(\mu\text{-CO})]$, which features an agostic methyl ligand bridging over an intermetallic triple bond,^[8d] but these studies were hampered by the high air-sensitivity of this molecule. Recently, however, we found that the stability of this type of complexes could be significantly improved by using the bulkier PtBu_2 ligand as support of the dimetal centre.^[9] Indeed we found that the targeted methyl complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1:\eta^2\text{-CH}_3)(\mu\text{-PtBu}_2)(\mu\text{-CO})]$ (**1**) could be conveniently prepared in situ upon photolysis of the corresponding dicarbonyl precursor $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1:\eta^2\text{-CH}_3)(\mu\text{-PtBu}_2)(\text{CO})_2]$ (Scheme 1), and this gave us the opportunity to explore in detail its chemical behaviour. At the time, it was clear that compound **1** was significantly activated with respect to C–H bond cleavage, since it undergoes clean intramolecular dehydrogenation upon gentle heating at 353 K to yield the corresponding methylidyne derivative, in contrast to the behaviour of dicarbonyl complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1:\eta^2\text{-CH}_3)(\mu\text{-PCy}_2)(\text{CO})_2]$, which only yielded methylidyne derivatives under photochemical activation.^[8b] In this paper we report our preliminary results on the general reactivity of **1** which involves, *inter alia*, several unusual or unprecedented transformations of the methyl ligand, such as room temperature dehydrogenation, reductive elimination with phosphorus, and migratory insertion of borane.



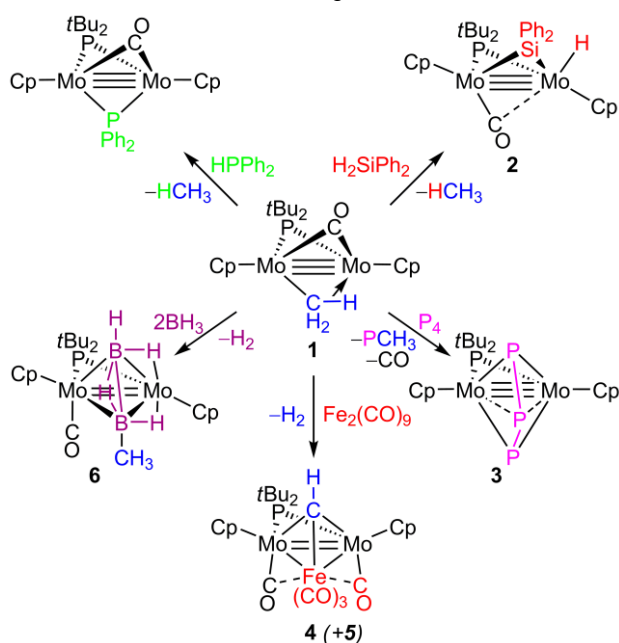
Scheme 1. Synthesis and thermal dehydrogenation of compound **1**.

The unsaturated nature of compound **1** enables the addition of a variety of donor molecules under mild conditions, with the methyl ligand being actively involved in all cases (Scheme 2). For instance, **1** reacts rapidly with PPh_2H at room temperature, with concomitant methane elimination, to give the known phosphanide complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-PPh}_2)(\mu\text{-PtBu}_2)(\mu\text{-CO})]$ in high yield.^[10,11] Even a weak donor molecule as diphenylsilane adds to compound **1** upon moderate heating (343 K). Methane elimination again takes place in this case, but also the oxidative addition of the second Si–H bond, to give the hydride silylene

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derivative $[\text{Mo}_2\text{Cp}_2\text{H}(\mu\text{-P}t\text{Bu}_2)(\mu\text{-SiPh}_2)(\text{CO})]$ (**2**) in high yield.^[11] Spectroscopic data for **2** denote the presence of a terminal hydride ($\delta_{\text{H}} -5.20$ ppm), a semibridging carbonyl ($\nu(\text{CO})$ 1776 cm^{-1} , δ_{C} 282 ppm) and a bridging silylene ligand (δ_{Si} 214 ppm), and suggest that the structure of this complex is related to that of the hydride benzylidene complex $[\text{Mo}_2\text{Cp}_2\text{H}(\mu\text{-P}t\text{Bu}_2)(\mu\text{-CHPh})(\text{CO})]$, an intermediate species detected in the photochemical dehydrogenation of the agostic benzyl complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\eta^2\text{-CH}_2\text{Ph})(\mu\text{-P}t\text{Bu}_2)(\text{CO})_2]$ and studied by DFT methods.^[9] Interestingly, compound **2** undergoes a fluxional process, fast on the NMR timescale, that renders equivalent metal centres down to 173 K, likely involving the reversible formation and cleavage of a Si–H bond, which would be analogous to the process computed for the mentioned hydride benzylidene complex. We note that the Ru_2 complexes $[\text{Ru}_2\text{Cp}^*_2(\mu\text{-H})_2(\mu\text{-SiRR}')]$ (δ_{Si} 265–310 ppm),^[12] seem to be the only other complexes identified previously as having silylene ligands bridging over (formally) triple intermetallic bonds. Interestingly, **1** also reacts with primary silanes, and these reactions are under current investigation.



Scheme 2. Reactivity of compound **1**.

Compound **1** reacts rapidly with P_4 at 333 K to give the blue triphosphorus complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-P}_3)(\mu\text{-P}t\text{Bu}_2)]$ (**3**) in high yield,^[11] a process involving decarbonylation and an unprecedented methylphosphinidene elimination (Scheme 2). The crystal structure of **3** (Figure 1) confirms the symmetrical coordination of a P_3 chain (P-P ca. 2.15 Å) to the dimetal centre, with the external atoms tightly bound to the metals (Mo-P ca. 2.40 Å) and the central atom involved in a much weaker interaction (Mo-P ca. 2.63 Å). These parameters are comparable to those measured in the trinuclear complex $[\text{Mo}_2\text{CrCp}^*_2(\mu_3\text{-P}_3)(\mu_2\text{-PS})(\text{CO})_5]$ ($\text{Mo}=\text{Mo}$), which seems to be the only other complex featuring a comparable P_3 ligand bridging over a multiple metal-metal bond.^[13] As a first approach, the P_3 ligand in **3** might be viewed as providing the dimetal centre with 5 electrons, which would lead to the formulation of an intermetallic triple bond for **3**, according to the 18-electron rule. However, this might be an oversimplification, as the external

Mo-P lengths are shorter than anticipated (ca. 2.51 Å in the diphosphorus complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-P}_2)(\text{CO})_4]$,^[14] while the intermetallic length of 2.6221(3) Å is somewhat longer than expected (cf. 2.515(2) Å in the 30-electron complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-PPh}_2)_2(\mu\text{-CO})]$,^[15] all of it might be indicative of some involvement of the P lone pairs in Mo-P bonding, a matter to be analyzed through future studies. In solution, the P_3 ligand of **3** gives rise to a strongly deshielded resonance at 412 ppm corresponding to the terminal atoms, while the internal P atom gives rise to a dramatically shielded resonance at –626.5 ppm, which appears to be the lowest ^{31}P chemical shift reported to date.^[16]

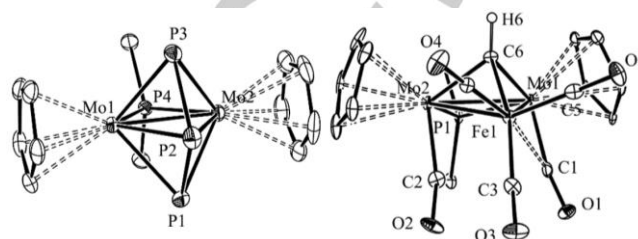


Figure 1. ORTEP diagrams (30% probability) of compounds **3** (left) and **4** (right, only one of the three independent molecules shown), with most H atoms and $t\text{Bu}$ groups (except their C^1 atoms) omitted. Selected bond lengths (Å) for **3**: $\text{Mo1-Mo2} = 2.6221(3)$, $\text{Mo1-P1} = 2.3952(8)$, $\text{Mo2-P1} = 2.3952(8)$, $\text{Mo1-P2} = 2.6308(8)$, $\text{Mo2-P2} = 2.6255(8)$, $\text{Mo1-P3} = 2.3988(8)$, $\text{Mo2-P3} = 2.3909(8)$, $\text{P1-P2} = 2.156(1)$, $\text{P2-P3} = 2.144(1)$. Compound **4**: $\text{Mo1-Mo2} = 2.6770(8)$, $\text{Mo1-Fe1} = 2.742(1)$, $\text{Mo2-Fe1} = 2.811(1)$, $\text{Mo1-C6} = 2.078(7)$, $\text{Mo2-C6} = 2.087(8)$, $\text{Fe1-C6} = 1.934(7)$, $\text{Fe1-C1} = 2.401(8)$.

Compound **1** reacts readily with $[\text{Fe}_2(\text{CO})_9]$ at room temperature to give the methylidyne cluster $[\text{Mo}_2\text{FeCp}_2(\mu_3\text{-CH})(\mu\text{-P}t\text{Bu}_2)(\text{CO})_5]$ (**4**) as major product (Scheme 2), along with a small amount of the acyl-bridged cluster $[\text{Mo}_2\text{FeCp}_2(\mu_3\text{-}\kappa^1\text{:}\eta^2\text{:}\kappa^1\text{-C(O)Me})(\mu\text{-P}t\text{Bu}_2)(\text{CO})_5]$ (**5**).^[11] The formation of **4** follows from addition of a $\text{Fe}(\text{CO})_4$ fragment to the unsaturated dimolybdenum centre of **1**, along with CO transfer and a very unusual room temperature dehydrogenation of the methyl group that renders the methylidyne ligand (δ_{C} 304.3, δ_{H} 14.44 ppm at 213 K). In contrast, **5** follows from an alternative reaction pathway involving CO insertion into the Mo-Me bond, and a rearrangement of the resulting acyl ligand into the $\mu_3\text{-}\kappa^1\text{:}\eta^2\text{:}\kappa^1$ coordination mode (δ_{C} 196.3 ppm), to give an electron-precise cluster.^[17] However, **4** is an unsaturated (46 electron) trinuclear cluster, a circumstance reflected in intermetallic separations (Mo-Mo ca. 2.68 Å, Mo-Fe ca. 2.72 and 2.82 Å) below the reference single-bond lengths (Figure 1).^[18] Other simple carbonyl compounds react with compound **1**, and the potential of the latter in the synthesis of heterometallic methylidyne-bridged clusters is under further investigation. This strategy builds up on extensive previous work by F. G. A. Stone and others on the isolobal-guided synthesis of heterometallic clusters starting from unsaturated precursors.^[19]

A most remarkable reaction of **1** takes place at room temperature upon addition of an excess of the borane adduct $\text{BH}_3\text{-THF}$, which yields a mixture of three isomers (A to C) of the methylidboranyl complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-B}_2\text{H}_4\text{Me})(\mu\text{-P}t\text{Bu}_2)(\text{CO})]$ (**6**) in a ratio of ca. 10:1:3 (Scheme 2).^[11] Compound **6** follows from the unprecedented insertion of two BH_3 units into a M-Me bond and dehydrogenation, to give the unreported methylidboranyl ligand. Spectroscopic data for these isomers are similar to each other, thus indicating a similar coordination of the $\text{B}_2\text{H}_4\text{Me}$ ligand in each case, which retains a terminal BH group (δ_{H} ca 4 ppm),

while one H atom likely bridges the B atoms (δ_{H} ca. 2 ppm) and the other two H atoms are clearly involved in 3-centre, 2-electron B–H–Mo interactions (δ_{H} ca. –9 and –19 ppm). The binding of the former methyl ligand to boron is readily apparent from the high shielding and broadness of the corresponding ^{13}C NMR resonance (ca. 0 ppm). The proposed coordination of the $\text{B}_2\text{H}_4\text{Me}$ ligand in **6** is based on the one crystallographically determined for the diboranyl complex $[\text{FeIr}(\mu\text{-B}_2\text{H}_5)(\text{CO})_4(\text{PPh}_3)_2]$,^[20] and is further supported by DFT calculations on two of the possible isomers (likely A and C, just differing in the relative positioning of the BH and BMe units),^[11] which turned to be of very similar energy as expected (Figure 2). Overall, the $\text{B}_2\text{H}_4\text{Me}$ ligand in **6** can be viewed as a 5-electron donor group, which leads to the formulation of an intermetallic double bond for this molecule, according to the 18-electron rule, in agreement with the short intermetallic lengths of ca. 2.65 Å computed for these isomers (cf. 2.699 Å computed for the isoelectronic carbyne-bridged complex $[\text{Mo}_2\text{Cp}_2\{\mu\text{-C}(\text{CO}_2\text{Me})\}(\mu\text{-PCy}_2)(\text{CO})_2]$).^[21]

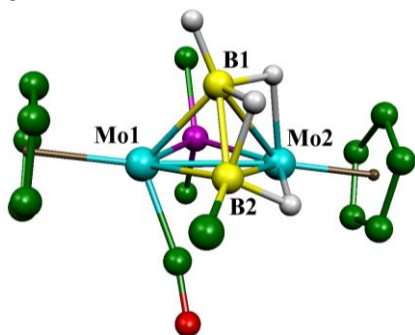


Figure 2. B3LYP-DFT optimized structure of the most stable isomer of compound **6**, with most H atoms and *t*Bu groups (except their C1 atoms) omitted. Selected bond lengths (Å): Mo1–Mo2 = 2.672, Mo1–B1 = 2.258, Mo1–B2 = 2.348, Mo2–B1 = 2.418, Mo2–B2 = 2.488, B1–B2 = 1.729, B1H–Mo2 = 1.812, B2H–Mo2 = 1.939. A second isomer with exchanged B–Me and B–H groups was computed to be just 1.7 kJ/mol less stable in the gas phase.

In summary we have shown that the high unsaturation of compound **1** enables its reactions with very diverse p-block molecules and transition metal complexes under mild conditions, whereby unusual or unprecedented transformations of the bridging methyl ligand take place, these including room temperature dehydrogenation, methylphosphinidene elimination and borane insertion, which lead to new unsaturated complexes bearing uncommon ligands. Further studies on the reactivity of **1** and some of the above derivatives are now in progress in our laboratory.

Acknowledgements

We thank the Gobierno del Principado de Asturias (Project GRUPIN14-011) and the MINECO of Spain and FEDER (Project CTQ2015-63726-P) for financial support, and the X-ray diffraction and CMC units of the Universidad de Oviedo for acquisition of diffraction data and access to computing facilities.

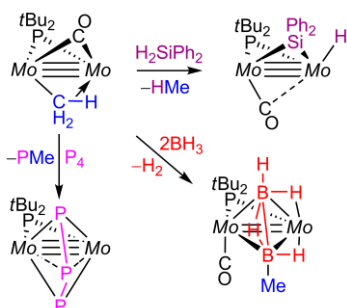
Keywords: alkyl ligands • agostic complexes • molybdenum • phosphorus • metal-metal interactions

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- [18] In the three independent molecules present in the crystals of **4**, one of the Mo-bound carbonyls is involved in a semibringing interaction of variable strength to the Fe atom ($\text{Fe}\cdots\text{C} = 2.11$ to 2.40 Å), which is balanced with slightly different Mo–Fe and M–CH separations in each case. In solution, however, only one molecule with equivalent Mo-bound carbonyls is apparent from the NMR data, as observed for the related cluster $[\text{Mo}_2\text{RuCp}_2(\mu_3\text{-CH})(\mu\text{-PCy}_2)(\text{CO})_3]$ (see reference 8b). These data also reveal restricted rotation of one of the *t*Bu groups, likely due to steric congestion.
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Entry for the Table of Contents

COMMUNICATION

The high unsaturation of the title compound enables the addition of very diverse p-block molecules and transition metal complexes under mild conditions, whereby unusual or unprecedented transformations of the bridging methyl ligand take place, such as room temperature dehydrogenation, methane or methylphosphinidene elimination, and borane insertion, to give unsaturated derivatives bearing uncommon ligands.



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Dehydrogenation, Methyl Elimination and Insertion Reactions of the Agostic Methyl-Bridged Complex [Mo₂Cp₂(μ-κ¹:η²-CH₃)(μ-P^tBu₂)(μ-CO)]