Reactivity of a *trans*-[H-Mo≡Mo-H] Unit Towards Alkenes and Alkynes. Bimetallic Migratory Insertion, H-Elimination and Other Reactions

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Complex [$Mo_2(H)_2\{\mu$-HC(NDipp)$_2\}_2$(THF)$_2$], (1·THF), reacts with C_2H_4 and PhCH=CH$_2$ to afford hydrido-hydrocarbyl and bis(hydrocarbyl) derivatives of the Mo≡Mo bond. Reversible migratory insertion and β-hydrogen elimination, as well as reductive elimination and other reactions, have been uncovered. PhC≡CH behaves instead as a Brönsted-Lowry acid towards the strongly basic Mo-H bonds of 1·THF.

More than thirty-five years ago, Chisholm proposed[1a] that "all the types of reactions which have been studied for mononuclear transition metal complexes will also occur for dinuclear transition metal complexes". Although the first complex with a metal-metal quadruple bond was discovered by Cotton and coworkers in 1964,[2] intense research in recent years has brought about a remarkable strengthening of the chemistry of M-M single and multiple bonds,[3] particularly with the discovery of high bond orders beyond the quadruple limit,[4] and with the recognition that many important stoichiometric and catalytic reactions require the concerted action of pairs of directly bonded active metal sites.[5-9]

Despite this progress, developing useful catalytic transformations is still at an early stage,[7a] particularly for catalysis by metal-metal multiple bonds.[8,10] Though knowledge of elementary reactions on multiply bonded dimetal entities has accumulated steadily[3,10] since Chisholm's studies,[1] there is a surprising scarcity of information on some of these transformations, as for instance oxidative addition and reductive elimination of H-H and C-H bonds.[11,12] Similarly, well-defined examples of hydride eliminations and of migratory insertions on M-M multiple bonds are scant.[13]

With the perception that alkyl complexes of the Mo≡Mo bond are important research objectives,[14] we studied recently the unsaturated compound [$Mo_2Me_2\{\mu$-HC(NDipp)$_2\}_2$] (Dipp=2,6-^{i}Pr$_2$C$_6$H$_3$), which features a fourteen-electron count and three-coordinate (plus the Mo≡Mo bond) metal atoms.[15] We next envisioned that longer chain hydrocarbyl analogues, [R-Mo≡Mo-R], would also be attractive targets as models for the study of elementary reactions involving the formation and cleavage of C-H and H-H bonds. Herein we discuss the interaction of the bis(hydride) complex [$Mo_2(H)_2\{\mu$-HC(NDipp)$_2\}_2$(THF)$_2$] (**1·THF**)[12a,b] with the unsaturated hydrocarbons RCH=CH$_2$ and the RC≡CH (R=H, Ph) as archetypes for alkene and alkyne reactivity, respectively. Besides the formation of novel, unsaturated bis(hydrocarbyl) and hydrido-hydrocarbyl complexes, we describe concomitant bimetallic migratory insertion, reductive elimination and other reactions of the central *trans*-[H-Mo≡Mo-H] unit of **1·THF**.

An immediate, albeit temporary, colour change from red-brown to green, took place when a toluene solution of **1·THF** was placed under 1 bar of C_2H_4 at room temperature. Upon further reaction (5-6 hours) the solution became again red-brown. ^{1}H NMR monitoring (C_6D_6, 25°C, 400 MHz; see Figure S1 in the Supporting Information) revealed complete consumption of **1·THF** after only 5 min and appearance of two complexes, namely a green intermediate species **A** and a red-brown complex **2**, which became the only reaction product after a period of 5-6 hours (Scheme 1). The NMR spectra of complex **2** strongly

supported formulation as the bis(ethyl) derivative [Mo$_2$Et$_2${μ-HC(NDipp)$_2$}$_2$], resulting from migratory insertion of ethylene into the Mo-H bonds of **1·THF**. The Mo-CH$_2$CH$_3$ units of **2** give rise to characteristic triplet and quartet ^{1}H resonances at 2.25 and 2.61 ppm ($^3J_{HH}$= 7.3 Hz), corresponding to the methyl and the methylene hydrogen atoms, respectively. Associated ^{13}C signals can be found at 31 and 17.4 ppm, with $^1J_{CH}$ values of 120 and 123 Hz (determined by 2D HSQC NMR experiments), in accordance with terminal ethyl coordination void of agostic interactions.[16] The structure of **2** is therefore similar to that found previously for the bis(methyl) complex analogue.[15]

Complex **2** possesses poor thermal stability in solution, but in the presence of ethylene decomposition is retarded, allowing its crystallization from concentrated toluene solutions at 0°C. Figure 1 shows an ORTEP view of the molecules of **2** that contain a *trans*-[Et-Mo≡Mo-Et] central group characterized by d(Mo-Mo)=2.083(5) Å and d(Mo-C)=2.154(2) Å, which are comparable to corresponding values in [Mo$_2$Me$_2${μ-HC(NDipp)$_2$}$_2$].[15] For each Mo atom the shortest Mo⋯H distances to the other Mo-*CH$_2$*CH$_3$ and Mo-CH$_2$*CH$_3$* groups are of *ca*. 3.26 and 2.93 Å, thereby too long for significant agostic interactions.[16] Thus, as shown in Scheme 1 and Figure 1, complex **2** is best represented in solution and in the solid state as featuring four - coordinate Mo atoms (including the Mo≡Mo bond) with a fourteen-electron count.

We next centred attention on the nature of the green intermediate **A**. This species was generated in more than 90 % yield (by ^{1}H NMR) either from **1·THF** and a large excess of C$_2$H$_4$ in C$_7$D$_8$ at -30°C, or alternatively by the room temperature reaction of **1·THF** and C$_2$H$_4$ in a 1:4 molar ratio (Scheme 1). This allowed full spectroscopic characterization at the said temperatures. Its lower symmetry in comparison with **2** explains the observation of four septets and eight doublets (instead of two and four for **2**), attributable to the methyne and methyl protons, respectively, of the eight amidinate isopropyl substituents (Figure S2). Moreover, a singlet at 3.15 ppm (relative intensity 1H) can be assigned to the Mo-H bond (5.67 ppm in **1·THF**), whereas a quartet resonance at 1.92 ppm and a triplet at 0.70 ppm (2H:3H relative intensities) convincingly point at the presence of a Mo-CH$_2$CH$_3$ bond, therefore indicating that **A** is the product of the first C$_2$H$_4$ migratory insertion into the Mo-H bonds of **1·THF** (Scheme 1). In the presence of C$_2$H$_4$, **A** converts into the bis(ethyl) complex **2**, while in its absence it decomposes quickly liberating ethane as demonstrated by GC-MS analysis (see the SI). Thus, it is clear that: (a) bimetallic ethylene migratory insertion and β-H elimination are, as expected, reversible; and (b) the *trans*-to-*cis* isomerization of the H-Mo≡Mo-C$_2$H$_5$ core of **A** required for bimetallic reductive elimination of C$_2$H$_6$ is facile under our experimental conditions.[12c] Computational studies (see the SI) reveal that the first migratory insertion leading to **A** needs surmounting an energy barrier of ca. 14.4 kcal·mol^{-1} whereas its microscopic reverse β-H elimination is much less costly, with ΔG‡ ≈ 6.8 kcal·mol^{-1}.

At variance with C$_2$H$_4$, PhCH=CH$_2$ yields only a monoinsertion hydrido-phenetyl product [Mo$_2$(H)(CH$_2$CH$_2$Ph){μ-HC(NDipp)$_2$}$_2$], (**B**), under similar reaction conditions. Given the high steric hindrance exerted by the two HC(NDipp)$_2$ ligands in the coordination environment of the Mo≡Mo bond, failure to reach a bis-insertion complex analogous to **2** is most probably due to steric reasons. Like **A**, **B** has meagre thermal stability and could not be isolated as a pure solid. NMR data are, however, in full agreement with the proposed formulation (see the SI).

Toluene or benzene solutions of complex **2** kept under C$_2$H$_4$, underwent a slow rearrangement (4-5 days) that led to a new organometallic complex of the Mo≡Mo bond (complex **3** in Scheme 2). Besides signals due to the amidinate ligands, its ^{1}H NMR spectrum contains several multiplets spanning a wide chemical shift range of nearly 10 ppm (from 11.20 to 1.33), hinting at the existence of two different hydrocarbyl ligands. ^{1}H and ^{13}C NMR studies allowed their recognition as Mo-CH$_2$CH$_3$ and Mo-CH=CH$_2$, the vinyl being responsible for three ^{1}H resonances at 11.20 (dd, $^3J_{HH}$=15.7 and 9.8 Hz), 6.26 (dd, $^3J_{HH}$=15.7 and 1.8 Hz) and 6.9 ppm. The latter is underneath some amidinate aromatic signals and was only detectable with the aid of a COSY experiment. These resonances are associated with ^{13}C signals at 207.4 and 113.4 ppm that present one-bond ^{13}C-^{1}H couplings of 145-150 Hz.

Formulation of **3** as an ethyl-vinyl complex was unequivocally confirmed by X-ray diffraction studies (Figure 2). The $Mo_2(CH_2CH_3)(CH=CH_2)$ half of **3** is characterized by Mo-Mo, $Mo-CH_2CH_3$ and $Mo-CH=CH_2$ bond distances of 2.110(4) Å, 2.174(3) Å and 2.124(3) Å, respectively. Once more, the ethyl ligand is terminal and does not seem to participate in agostic interactions with the other Mo atom (Mo1 in Figure 2), because the shortest $Mo1\cdots CH_3$ contact is of around 3.48 Å. Nevertheless, the Mo1-bonded vinyl carbon atom C53 might be engaged in a non-classical, 3c-2e bond,[17] but since the $Mo2\cdots C53$ contact is rather long at 2.519(3) Å, if at all, this interaction must be weak. Although a detailed mechanistic investigation of the **2** to **3** transformation is beyond the scope of this work, it is worth detailing some experimental observations made during its progress. In the absence of C_2H_4, decomposition of **2** was rapid and generated C_2H_6 and C_2H_4, similar to Chisholm's finding for the triply bonded $[Mo_2(CH_2CH_3)_2(NMe_2)_4]$ complex.[18] Additionally, the reaction of the quintuply bonded $[Mo_2\{\mu\text{-}HC(NDipp)_2\}_2]$ complex[19] with C_2H_4 formed **3** as the main reaction product (Figure S7). These findings suggest that in its way to **3**, complex **2** experiences β-H elimination with generation of C_2H_4 and formation of the hydride-ethyl intermediate **A**, followed by reductive elimination of C_2H_6. In the presence of sufficient amounts of C_2H_4, the resulting Mo-Mo quintuple bond promotes oxidative addition of an ethylene C-H bond. Subsequent isomerization of the resulting $cis\text{-}[H\text{-}Mo\equiv Mo\text{-}(CH=CH_2)]$ moiety[12c] and migratory insertion of C_2H_4 into the Mo-H bond would render complex **3**.

In an NMR tube reaction performed in C_6D_6, complex **1·THF** reacted immediately with C_2H_2 (1 bar) forming a black precipitate of polyacetylene.[20] $PhC\equiv CH$ behaved differently. Once more, reaction was fast at room temperature, and as represented in Scheme 3, it gave rise to a bright red solution of the alkynyl complex $[Mo_2(C\equiv CPh)_2\{\mu\text{-}HC(NDipp)_2\}_2(THF)_2]$, **(4)**, in ≥90 % yield by ^1H NMR. Formation of dihydrogen was demonstrated by ^1H and ^2H NMR studies with the detection of HD when $PhC\equiv CH$ was allowed to react with the bis(deuteride) isotopologue of **1·THF** (Scheme 3 and SI). Full characterization of **4** was attained by microanalysis, IR and NMR spectroscopy and by X-ray studies (Figure S10). An IR band due to ū (C≡C) was recorded at 2057 cm^{-1}, while the ^{13}C {^1H} NMR spectrum showed two resonances at 134.2 and 113.7 ppm due to the alkynyl carbon atoms, in agreement with literature values.[21] Formation of complex **4** as in Scheme 3 can therefore be viewed as a Brönsted-Lowry acid-base reaction involving strongly basic Mo- H bonds (for $PhC\equiv CH$ in DMSO pKa=28.7).[22] At this stage, however, no mechanistic information is available. As can be seen in Figure S10, complex **4** contains two coordinated molecules of THF, short Mo-C bonds to the alkynyl ligands (2.113(3) Å), and also short C≡C distances of 1.217(4) Å. The Mo- Mo bond has a normal length for a quadruple bond at 2.122(3) Å, being nonetheless slightly longer than in **1·THF**,[12a,b] possibly because of the bulkiness of phenylacetylide compared to hydride.

In conclusion, the bis(hydride) complex **1·THF** experiences facile bimetallic reversible migratory insertion of C_2H_4 to afford the bis(ethyl) complex **2**. Well-known β-H elimination in mononuclear complexes is thermodynamically favoured for the Mo≡Mo bond, at least when driven by concomitant dissociation of the resulting ethylene molecule and subsequent irreversible reductive elimination of ethane. When **2** is allowed to rearrange under C_2H_4, the reaction end-product is the ethyl-vinyl complex **3**, that can also be reached from the Mo-Mo quintuple bond and ethylene, in a complex reaction that most likely involves oxidative addition of an ethylene C_{sp2}-H bond to the Mo-Mo quintuple bond.[12]

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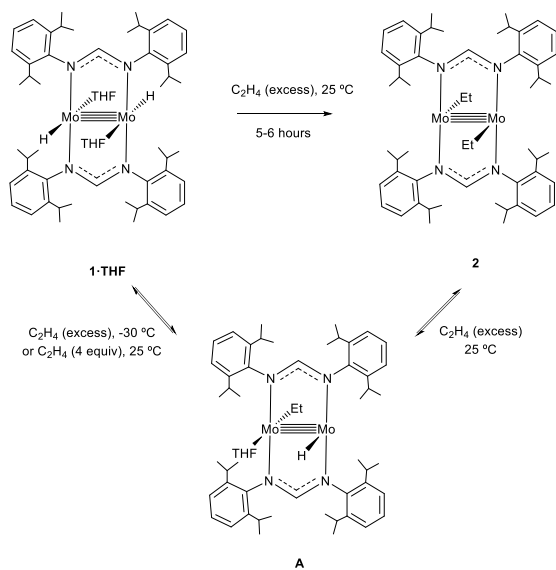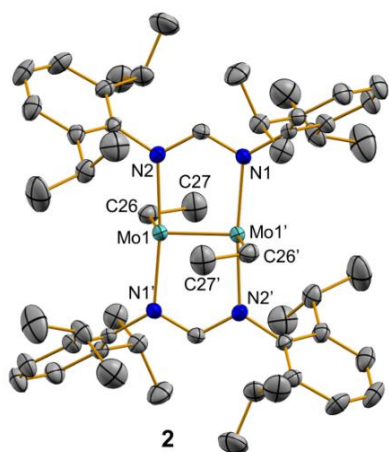
Scheme 1. Reaction of complex **1·THF** with C_2H_4.

Figure 1. Solid-state molecular structure of complex **2**.

Scheme 2. Rearrangement of complex **2** in the presence of C$_2$H$_4$.

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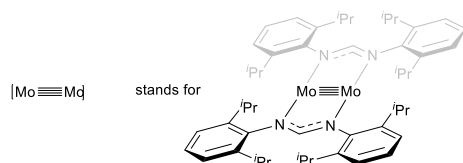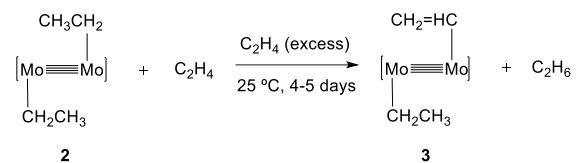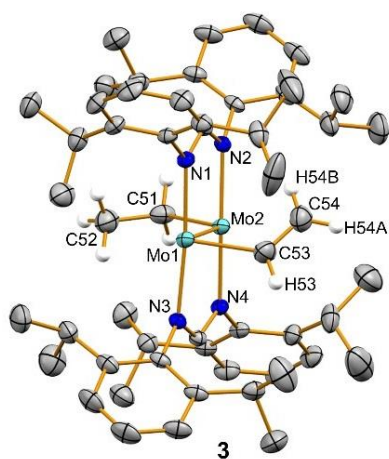

Figure 2. Solid-state molecular structure of complex **3**.

Scheme 3. Reaction of complex **1·THF** with PhC≡CH.