The Acetonitrile Adduct [MoReCp(μ-H)(μ-PCy2)(CO)5(NCMe)]: A Surrogate of an Unsaturated Heterometallic Hydride Complex

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Supporting Information Placeholder

ABSTRACT: The title compound was prepared in excellent yield upon irradiation of acetonitrile solutions of the readily available hexacarbonyl [MoReCp(μ-H)(μ-PCy2)](CO)3. The acetonitrile ligand in this compound could be replaced easily by donor molecules or displaced upon two-electron reduction. In most cases, the substitution step was followed by additional processes such as insertion into the M–H bonds (alkynes), E–H bond cleavage (thiols), H2 elimination (aldehydes and phosphines) and other transformations.

Multimetallic complexes hold the potential to display a captivating chemical behavior due to cooperative effects between metal centers which are not possible in mononuclear compounds. The reactivity of these systems can be significantly increased by the presence of M–M multiple bonds, due to their inherent electronic and coordinative unsaturation, or heterometallic M–M’ bonds, due to their intrinsic bond polarity. However, until recent years the combination of both factors in the same molecule remained largely undeveloped, this being mainly a consequence of the lack of effective synthetic routes leading to sufficiently stable complexes. However, recent work from the groups of Thomas, Lu and Tonks provided a systematic access to several dinuclear complexes featuring M–M’ multiple bonds between different transition metals, and also highlighted the potential of these species in several stoichiometric and catalytic processes. Then, it is not surprising that the synthesis of new compounds of this type has emerged as an attractive target in the area. In this context, we reported recently the high yield synthesis of the unsaturated heterometallic anions [MoMCp(μ-PR2)](CO)3 (M = Mn, Re), which turned out to be effective precursors of several compounds having single and double Mo–M bonds. However, the attempted preparation of the related unsaturated hydrides [MoMCp(μ-H)(μ-PR2)](CO)3 by protonation of the above anions was unsuccessful due to rapid coordination of external molecules at the group 7 metal, as nicely exemplified by the formation of the ammonia complexes [MoMCp(μ-H)(μ-PR2)](CO)3(NH3)] upon protonation with NH4PF6. Yet, the study of the chemical behavior of unsaturated hydrides is itself an attractive topic, as their reactivity can be taken as a model for the elemental steps involved in hydrogen transfer reactions taking place in several transition-metal catalyzed industrial processes (i.e. Fischer–Tropsch reaction), and even more in the case of heterometallic hydrides, for which synergistic effects between two different metals might lead to unique reactivity. Keeping in mind the easy formation of several complexes bearing potentially labile ligands in the reactions of the unsaturated anions with electrophiles, we decided to explore the possibility to prepare stable surrogates of the mentioned unsaturated hydrides bearing sufficiently labile ligands so that they could be displaced easily by suitable reagents, then opening the possibility to explore the chemical behavior of these compounds. Herein we report a straightforward route for the preparation of the acetonitrile complex [MoReCp(μ-H)(μ-PCy2)](CO)3(NCCH3)] (2) and a preliminary study of its reactivity, which revealed that the NCMe ligand can be replaced easily by even weak donors or displaced upon reduction. The substitution reactions are typically followed by H2 loss, insertion into M–H bonds or more complex processes. We also found that, under certain conditions, compound 2 can act as a source of unsaturated heterometallic radicals.

The synthesis of the acetonitrile adduct 2 was accomplished in two steps starting from the readily available hexacarbonyl [MoReCp(μ-H)(μ-PCy2)](CO)3 (I) (Scheme 1). First, irradiation with visible-UV light of acetonitrile solutions of I led to the formation of a mixture of the coordination isomers [MoReCp(μ-H)(μ-PR2)](CO)3]1+x(NCMe)] (1) and [MoReCp(μ-H)(μ-PR2)](CO)3]2x(NCMe)] (2), following from replacement of a CO ligand at either the Mo or Re atoms, respectively. Although these isomers could not be separated by conventional techniques, we found that the Mo–substituted compound 1 isomerizes spontaneously (2 h in NCMe or 5 min in CH3Cl) to give the Re–substituted isomer 2, a process which is more conveniently achieved on a preparative scale by gentle heating (353 K, 5 min) the acetonitrile solutions. Remarkably, compound 2 is relatively stable and can be handled in solution using common organic solvents without decomposition, and stored for long periods at low temperature under argon. The available spectroscopic data for these isomers are consistent with the replacement of a CO ligand in 1 by NCMe at different metal sites. Isomer 1 displays C=O stretching bands in the IR spectra (see Supporting Information -SI-), indicative of the retention of a Mo(CO)5 fragment, while isomer 2 displays bands displaced to lower frequencies and with a pattern consistent with the presence of a fac-M(CO)5 fragment. Both isomers display strongly shielded resonances (ca. –12 ppm) in their 1H NMR spectrum in
agreement with the retention of bridging hydrides, while the coordinated NCMe molecules give rise to the expected signals around 2 ppm.

To examine the chemical behavior of compound 2, we first evaluated its thermal and photochemical stability, and found that either the photolysis or heating of toluene solutions of 2 yielded mixtures of the hexacarbonyl 1 (carbonylation product) and the new tetranuclear cluster [Mo,Re,Cp,μ-PCy,](CO), (3) in a ratio of 1:2 (Scheme 2). The latter product formally follows from dimerization of the radical fragment [MoReCp(μ-PCy,)](CO), resulting from loss of NCMe, CO and dehydrogenation, a type of process which does not take place under similar conditions for the hexacarbonyl 1. It is also worth noting that similar dimerizations have never been observed for the related homonuclear hydrides [M,CP,μ-H](μ-PCy,)](CO), (M = Mo, W), then highlighting the potential of compound 2 to act as precursor of dinuclear heterometallic radicals. An X-ray diffraction study of 3 (Figure 1) revealed the presence of a tetrahedral Mo-Re core with two PCy, ligands bridging Mo-Re edges and the Mo-bound carbonyls involved in semibridging interactions. Electron count in this cluster yields 58 valence electrons, two below the required number for an electron-precise tetrahedral cluster. This is reflected in the observation of relatively short Mo-Re separations, which span a range of 2.82–2.92 Å, some 0.3–0.4 Å shorter than the single-bond distance in [MoReCp(μ-H)(μ-PPPh,)](CO), (3.19 Å), while the two homometallic distances (Mo–Mo 2.960(8) Å and Re–Re 3.1703(3) Å) are close to the reference values for single bonds, hence suggesting that the electronic unsaturation of the cluster is largely delocalized over the heterometallic edges.

The acetonitrile ligand in 2 is also displaced upon two-electron reduction with Na(Hg) to give the unsaturated anion [MoReCp(μ-PCy,)](CO),, a complex prepared recently in our laboratory through a multi-step route. This new synthetic method provides a much more convenient access to this unsaturated MoRe anion, a situation which will facilitate the study of its chemical behavior.

![Scheme 1. Synthesis of acetonitrile complexes 1 and 2.](image1)

![Scheme 2. Reactions of compound 2.](image2)

![Figure 1. ORTEP diagram (30 % probability) of 3 with H atoms and Cy groups (except C atoms) omitted.](image3)
[\text{MoReCp}\{\mu^{-}\eta^{2}:\eta^{1}:\eta^{1}:\text{C}(\text{CO},\text{Me})\text{CH}(-\text{CO},\text{Me})\}{\mu^{-}\text{PCy}}_{2}\{\eta^{2}-\text{C}(\text{CO},\text{Me})\text{CH}(-\text{CO},\text{Me})\}] \quad (6) \text{ and } [\text{MoReCp}\{\mu^{-}\eta^{2}:\eta^{1}:\eta^{1}:\text{C}(\text{CO},\text{Me})\text{CH}(-\text{CO},\text{Me})\}{\mu^{-}\text{PCy}}_{2}\{\eta^{2}-\text{C}(\text{CO},\text{Me})\text{CH}(-\text{CO},\text{Me})\}] \quad (7) \] in a ca. 6:1 ratio (Scheme 2). These products differ in the coordination sphere at the Re center, with four carbonyls in 6 but three plus an O-bound carboxylate group (from the Cp atom of the alkenyl) in 7. However, their formation likely follow from different pathways as the decarbonylation $6 \rightarrow 7 + CO$ could only be achieved after prolonged reflux in toluene. In the solid state (Figure 3), both compounds display almost perfectly planar  

Figure 2. ORTEP diagram (30% probability) of 5 with H atoms and Cy groups (except C' atoms) omitted.

Figure 3. ORTEP diagram of compounds 6 (left) and 7 (right) with H atoms and Cy groups (except C' atoms) omitted.

MoReC2P rings with the alkenyl ligands displaying strong $\sigma$-binding to the Re center [Re–C = 2.244(3) Å and 2.288(6) Å (7)] and $\pi$-coordination to the Mo atom [Mo–C = 2.110(3) Å (6) and 2.137(7) Å (7)]. The three (6) and five-electron (7) coordination of the alkenyl ligands makes these compounds electron-precise species for which Mo–Re single bonds should be formulated, in agreement with the intermetallic separations of ca. 2.99 Å measured for both compounds.

The reactions of compound 2 with molecules having E–H bonds of moderate acidity may involve the activation of the latter bond. For instance, S–H bond activation takes place under mild conditions (333 K) in the reaction with HSPh to give [MoReCp(2–H)(S–PH2)PH2(2–C(=O)–CO)] (8) (Scheme 2), a poorly stable molecule which could be characterized only through spectroscopic methods. Quite surprisingly, compound 8 displays a terminal Re-bound hydride as indicated by the modest shielding of the corresponding resonance in the $^1H$ NMR spectra, which appears at $-6.37$ ppm, almost 6 ppm above the positions expected for a bridging coordination (cf. $-13.5$ ppm in 1). The presence of a phosphane ligand, presumably generated after reductive elimination of phosphanyl and hydride ligands, is clearly evidenced by the low chemical shift of the $^3P$ resonance of 8 and its large P–H coupling ($\delta_P = 53$ ppm, $J_{HP} = 321$ Hz). The disposition of ligands around the Re atom is deduced from the IR spectrum, which displays bands consistent with the presence of a face-Re(CO)$_3$ fragment, also indicated by the large coupling to P of one of these carbonyls ($\delta_C = 193.7$ ppm, $J_{PC} = 31$ Hz), this leaving the terminal hydride positioned cis to the PHCy ligand. It is worth noting that the outcome of this reaction is in contrast with the usual elimination of H$_2$ and replacement of the hydride by the SR fragment observed in the reactions of unsaturated hydride-bridged complexes with thiols. However, we can quote that the reactions of complexes [Mo$_2$(μ-H)(μ-PCy$_3$)(CO)$_2$] (M = Mo, W) with thionylidines involve intermediates resulting from related bond cleavage (Sn–H) and formation (P–H) steps.

Another possible outcome in the reactions of 2 with molecules having E–H bonds is the direct elimination of dihydrogen between the hydride and a suitable hydrogen atom of the incoming reagent. This is exemplified by the reaction of 2 with the aldehyde (p-tol)C(O)H (383 K in toluene), although in this case the product isolated is not the expected acyl derivative, but the carboxylate [MoReCp(μ-κ:C=O,p-C(p-tol))(HPCp)(μ-κ:C(O)=CO)(2–C(=O)–CO)] (9), which incidentally seems to be the first Mo–Re carboxylate complex to be ever reported. The possibility of 9 as being formed through reaction of 2 with the carboxylic acid (p-tol)CO$_2$H (which might be present at trace levels in the commercial aldehyde) can be ruled out because a separated experiment revealed that 2 does not react with benzoic acid under the same conditions. However, the actual source of the extra oxygen atom in compound 9 is yet unclear. The solid state structure of 9 (Figure 4) reveals the presence of MoCp(CO)$_2$ and Re(CO)$_5$ fragments bridged by two ligands: dicyclohexylphosphanyl and a bidentate carboxylate. It is worth noting the different arrangement of carbonyls in 9 if compared to that found in the isostructural bis(phosphanyl) 5 (with Re(CO)$_5$ and MoCp(CO) fragments). This difference is accompanied by a strong puckering of the central skeleton in 9 ($\theta_{PPh}_{1} \approx 85^\circ$), although this has little effect on the Mo–Re separation ($3.033(2)$ Å vs. $3.0970(5)$ in 5).

In summary, we have described the synthesis of a new bimetallic MoRe hydride complex bearing a coordinated acetonitrile molecule easy to be displaced even by weak donors. The outcome of these reactions depends on the nature of the added reagent, and generally involves the hydride ligand through processes such as insertion into the M–H bonds, H$_2$ elimination, deprotonation, or more complex reactions. In the absence of added ligands, the complex exhibits an interesting thermal decomposion process likely involving the participation of heterometallic radicals, which eventually yields an unsaturated Mo$_2$Re$_2$ cluster. It can be concluded...
then that the newly reported acetonitrile complex effectively behaves as a surrogate of the unstable unsaturated hydride [MoReCp(μ-H)(μ-PCy3)(CO)2].

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI 10.1021/acs.inorgchem.xxx.xxxxxx X-ray crystallographic data in CIF format for compounds 3, 5, 6, 7 and 9 (CCDC 1982358-1982362) (CIF) Synthetic details, NMR and IR spectroscopic data (PDF)

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The authors declare no competing financial interests.

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REFERENCES
(12) The spectroscopic data for this compound denote the presence of dynamic behavior in solution. Thus, room temperature 1H and 13C NMR signals are relatively broad and low temperature NMR data collected in the slow exchange regime allowed for the identification of a minor isomer (see the SI) which also displays a terminally coordinated hydride ligand (δH = 5.67 ppm). Hence, the difference between isomers might arise from an inverted configuration of the bridging thiolate or from a different arrangement of the terminal ligands at the Re center, a point currently under study.
An efficient synthetic route to the title acetonitrile complex has been developed, this allowing the study of its reactivity towards different molecules, which typically involved processes such as insertion into the M–H bonds, H₂ elimination, deprotonation, or more complex transformations, a behavior equivalent to the one expected for the unstable unsaturated hydride [MoReCp(μ-H)(μ-PCy₂)(CO)₅].