

Activity of Mo–Mo and Mo–P multiple bonds at the phosphinidene complex $[\text{Mo}_2\text{Cp}_2\{\mu\text{-P}(2,4,6\text{-C}_6\text{H}_2^t\text{Bu}_3)\}(\mu\text{-CO})_2]$ in reactions with isocyanides and phosphine ligands [☆]

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ABSTRACT

The title complex reacted with the aryl isocyanides CNXyl and CN(*p*-tol) rapidly at room temperature to yield the corresponding derivatives $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_2(\text{CNR})_2]$ (Cp = $\eta^5\text{-C}_5\text{H}_5$; R = Xyl, *p*-tol; R* = 2,4,6- $\text{C}_6\text{H}_2^t\text{Bu}_3$) even when using 1 equiv of reagent. In contrast, reactions with 1 equiv of CN^tBu yielded the isocyanide-bridged derivatives *cis*- or *trans*- $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\mu\text{-}\eta^1\text{:}\eta^2\text{-CN}^t\text{Bu})(\text{CO})_2]$ depending on reaction conditions (Mo–Mo = 3.0818(3) and 3.1453(8) Å, respectively). The *cis* isomer was computed to be 16 kJ/mol more stable than the *trans* isomer, and could be also prepared by heating petroleum ether solutions of the latter at 333 K, while reaction of excess CN^tBu with the *trans* isomer yielded $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_2(\text{CN}^t\text{Bu})_2]$. The title complex reacted with Me₂PCH₂PMe₂ (dmpm) to give the corresponding diphosphine-bridged derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_2(\mu\text{-dmpm})]$ or its chelate isomer $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_2(\kappa^2\text{-dmpm})]$, depending on reaction conditions (Mo–Mo = 3.342(1) and 3.176(1) Å, respectively), whereas its room-temperature reaction with PH₂Cy involved a H-shift to the phosphinidene ligand, to give the bis(phosphide) derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-PHCy})(\mu\text{-PHR}^*)(\text{CO})_2]$. Photolysis of the latter induced decarbonylation, C–H bond cleavage, and dehydrogenation, to eventually yield the triply-bonded phosphinidene derivative $[\text{Mo}_2\text{Cp}_2\{\mu\text{-P}(\text{CH}_2\text{CMe}_2)\text{C}_6\text{H}_2^t\text{Bu}_2\}(\mu\text{-PHCy})(\mu\text{-CO})]$ (Mo–Mo = 2.511(2) Å). Density functional theory analysis of the bonding in the title complex revealed a substantial mixing of one of the δ components of the intermetallic triple bond with the p_π orbital of the phosphinidene ligand. As a result of this, the LUMO of the molecule is mainly centered at the P atom, but leads to little reactivity because of the steric protection provided by the *ortho*-^tBu groups of the phosphinidene substituent. The electron-acceptor reactivity of the molecule is then dominated by the close LUMO+1 orbital, which has Mo–Mo antibonding character and is well suited for interaction with donors approaching the dimetal site from the less congested side of the molecule, located between the carbonyl ligands.

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1. Introduction

Since the pioneering study [1] on the quadruple bond at the dirhenium anion $[\text{Re}_2\text{Cl}_2]^{2-}$ there has been much interest in the structure, bonding and chemical behavior of complexes having multiple bonds between metal atoms [2,3]. These molecules display a low HOMO–LUMO gap which, added to the low coordination

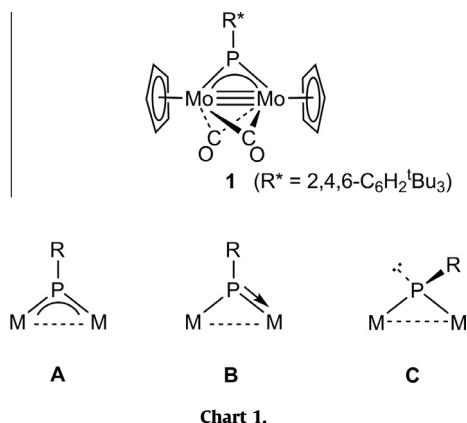
numbers of the metal atoms involved in the multiple bond, provides them with a high reactivity towards a great variety of reagents under mild conditions, thus allowing the formation and isolation of novel derivatives unavailable through more conventional synthetic routes (i.e. involving electron-precise substrates). Yet, after more than four decades of extensive research in this field, the seminal report in 2005 by Power and co-workers on the first isolable complex featuring a quintuple metal–metal bond [4] triggered a renewed interest in the area, which is currently focused at exploring the reactivity of these highly unsaturated molecules [5].

Within the realm of organometallic complexes, most of the reactivity studies on molecules featuring metal–metal multiple bonds has been carried out so far on complexes having cyclopentadienyl and related ancillary ligands, with the most extensively

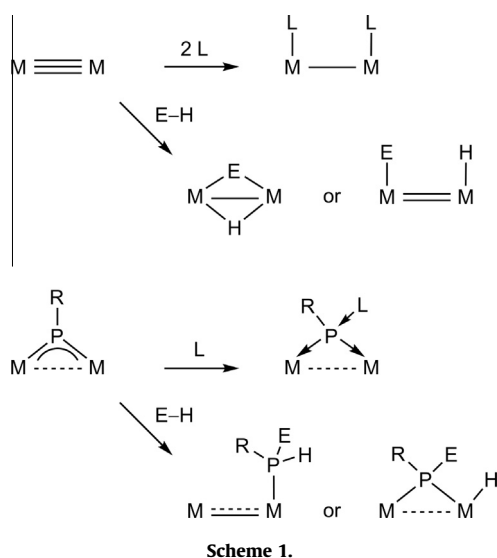
[☆] This work is dedicated to Prof. F.A. Cotton in recognition for his outstanding contribution to modern Inorganic Chemistry, on occasion of the 50th anniversary of its seminal description of the quadruple metal–metal bond.

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studied substrates being different 30-electron complexes having intermetallic triple bonds [6,7]. A few years ago we reported the preparation of a peculiar member of this family, the dimolybdenum complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\mu\text{-CO})_2]$ (**1**) (Chart 1, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{R}^* = 2,4,6\text{-C}_6\text{H}_2\text{tBu}_3$) [8], which stands as the unique phosphinidene-bridged complex featuring an intermetallic bond of order 3 reported so far. Actually, only two other unsaturated phosphinidene complexes appear to have been reported, these being the 32-electron complexes $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)\text{I}_2(\text{CO})_2]$ [9], and $[\text{V}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_4]$ [10], for which metal–metal double bonds should be formulated according to the EAN formalism, although their chemical behavior has not been explored. Phosphinidene-bridged complexes are themselves quite reactive species, even at electron-precise dimetal substrates, due to the presence of multiple M–P bonding (and their associated low HOMO–LUMO gap) or lone electron-pairs in the different coordination modes that the $\mu\text{-PR}$ ligand can adopt (A–C in Chart 1) [11–13]. Thus complex **1** provides us with a unique opportunity to explore the reactivity of a metal–metal multiple bond in the presence of a metal–phosphorus multiple bond. In this paper we explore the reactions of **1** with donors such as CO, isocyanides and phosphines. From the known behavior of organometallic complexes having M–M triple bonds we can expect a rapid addition of two donor units (L) to yield electron-precise derivatives [6,7]. However, simple donors might also add to the P atom of a phosphinidene-bridged complex of type A [11,14] (Scheme 1). Moreover, when the donor atom has an hydrogen atom attached to it (E–H donors, with $\text{E} = \text{O}, \text{S}, \text{P}$, etc.), then the

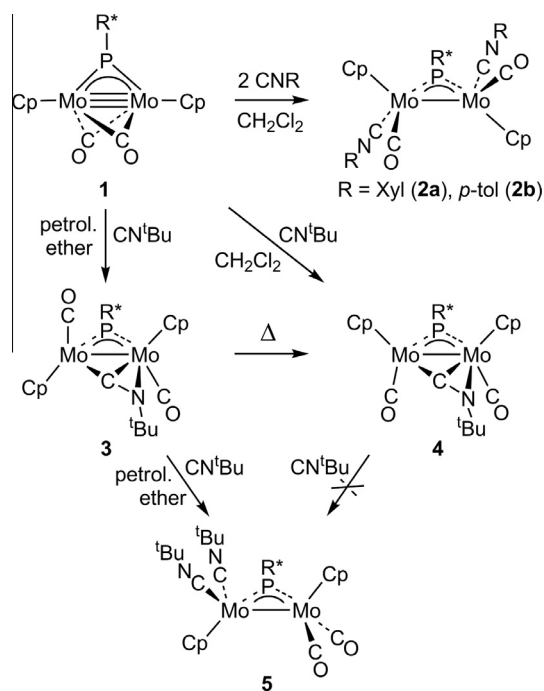


unsaturated M–M or M–P functionalities are likely to induce the cleavage of E–H bonds, to give products strongly dependent on the particular substrate under study (Scheme 1, only some possible outputs shown) [6,7,14,15]. As it will be discussed below, the reactivity of **1** towards isocyanides and tertiary phosphines is dominated by the intermetallic bond due to the steric protection of the P site provided by the bulky substituent of the phosphinidene ligand, whereas reactions with the primary phosphine PH_2Cy involve the active participation of both Mo–Mo and Mo–P multiple bonds.

2. Results and discussion

2.1. Reactions with isocyanides

We have reported previously that compound **1** reacts rapidly with CO (1 atm) at room temperature to give the electron-precise Cowley's complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_4]$ (actually, the latter is the precursor of **1**) [8]. In an analogous way, reactions of **1** with the aryl isocyanides CNXyl and $\text{CN}(p\text{-tol})$ proceed rapidly at room temperature to yield related bis(isocyanide) derivatives $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_2(\text{CNR})_2]$ ($\text{R} = \text{Xyl}$ (**2a**), $p\text{-tol}$ (**2b**)) even when using 1 equiv of isocyanide or a lower reaction temperature. In contrast, the reactions with CN^tBu turned to be somewhat slower and strongly dependent on stoichiometry and reaction conditions (Scheme 2). When using 1 equiv of reagent, the isocyanide-bridged derivatives *trans*- $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\mu\text{-}\eta^1\text{:}\eta^2\text{-CN}^t\text{Bu})(\text{CO})_2]$ (**3**) and *cis*- $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\mu\text{-}\eta^1\text{:}\eta^2\text{-CN}^t\text{Bu})(\text{CO})_2]$ (**4**) were obtained in relative ratios strongly dependent on the solvent. Thus, compound **3** was formed almost as the unique product when carrying this reaction in petroleum ether, while the use of tetrahydrofuran or dichloromethane as solvent led to a mixture of isomers **3** and **4** in comparable amounts, along with significant decomposition. Fortunately, compound **4** could be selectively prepared by heating petroleum ether solutions of **3** at 333 K for 30 min, which allowed its satisfactory preparation and full characterization. Thus, it is clear that the *cisoid* isomer **4** is thermodynamically favoured over its *transoid* isomer **3**, a finding unusual in comparison to the



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