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Reactivity of a dichlorophosphido complex. Nucleophilic substitution reactions at metal coordinated phosphorus

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ABSTRACT

Reaction of the dichlorophosphido complex $[Cp^*Mo(CO)_3(PCl_2)]$ (**1**) with $AlCl_3$ leads to the bimetallic bridging P_2Cl_3 complex $[\{Cp^*Mo(CO)_3\}_2(\mu\text{-}P_2Cl_3)][AlCl_4]$ (**2**), which is formed via a Lewis-acid assisted nucleophilic substitution reaction, and not via a chlorophosphinidene intermediate. A similar reaction with external nucleophile PPh_3 leads to $[Cp^*Mo(CO)_3(P(Cl)PPh_3)][AlCl_4]$ (**3**), which can be viewed as a phosphine coordinated chlorophosphinidene complex. Addition of two equivalents each of PPh_3 and $AlCl_3$ leads a double chloride displacement, and formation of the known triphosphenium salt $[Ph_3PPPPh_3][AlCl_4]$. In this reaction the dichlorophosphido complex effectively act as a source of P^+. Reaction of **1** with alkoxides leads to alkoxyphosphido complexes $[Cp^*Mo(CO)_3\{P(OR)Cl\}]$ (R = p-*t*-butyl phenoxy, menthoxy). These complexes serve as precursors to transient alkoxy phosphinidenes $[Cp^*Mo(CO)_3\{POR\}]^+$, which can be trapped with alkynes. A computational study on the chloro, alkoxy, and related amino and alkyl phosphinidenes shows that chloro and alkoxy phosphinidenes have minimal π-donation to P from Cl or OR, in contrast to stable aminophosphinidenes, which have significant N to P π-donation.

Introduction

Chloride abstraction is now a well established route to cationic terminal phosphinidene complexes, but phosphinidene complexes formed via this route are thus far limited to stable amino-phosphinidenes [1–3] and a transient alkyl phosphinidene [4]. In contrast, transient neutral terminal phosphinidene complexes have been described with a much wider variety of substituents on phosphorus, including alkyl and aryl [5], amino [6], alkoxy [7], chloro [8], and fluoro [9] substituents. Pikies has also made extensive studies of phosphanylphosphinidenes, however, these ligands most frequently bind in a side-on fashion, and are classified as nucleophilic [10]. The cationic electrophilic phosphinidene complexes show similar reactivity to transient neutral electrophilic phosphinidene [4,11], with some exceptions [12]. However, they have the advantages of shorter synthetic routes and can be generated at lower temperatures. We were interested in expanding the range of possible P substituents. Of particular interest to us is a simple route to P–Cl phosphinidenes, because they can directly provide products, such as P-heterocycles and C–H activation products, containing a P–Cl bond ready for further substitution. This led us to explore the chemistry of dichlorophosphido complexes, which are potential precursors to cationic chloro–phosphinidene complexes. Terminal dichlorophosphido complexes are relatively rare [13–15], however the reactivity of the known complexes has been well explored, and typical reactions include oxidation of the lone pair, coordination to Lewis acids, and reductive coupling [16]. Iron PCl_2 complexes have also been used to form phospha-alkenes via nucleophilic substitution-dehydrohalogenation sequences [15]. As far as we know, direct halide abstraction as a route to chlorophosphinidene complexes has not been attempted, although a neutral transient chlorophosphinidene has been prepared by a different route [8]. Of known PCl_2 complexes, we were drawn to $[Cp^*Mo(CO)_3(PCl_2)]$, reported by Malisch [13], because the synthesis is straightforward, and because it is analogous to the well studied phosphinidene precursor $[Cp^*Mo(CO)_3\{P(Cl)N\text{-}i\text{-}Pr_2\}]$. Here we describe the reaction chemistry of this complex with respect to chloride abstraction and substitution, and its utility as a precursor to phosphinidene complexes.

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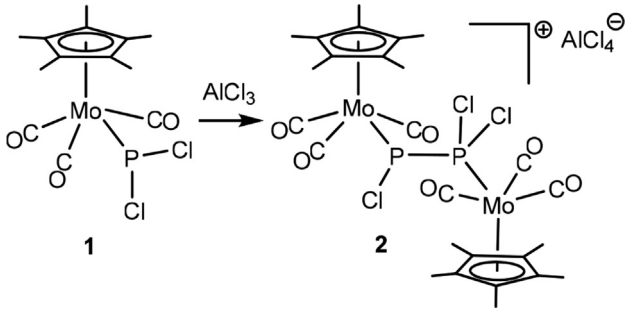
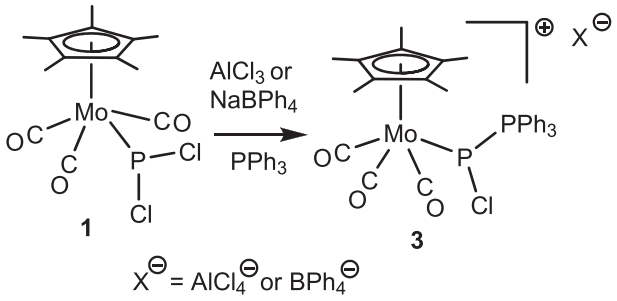


Scheme 1.



Scheme 3.

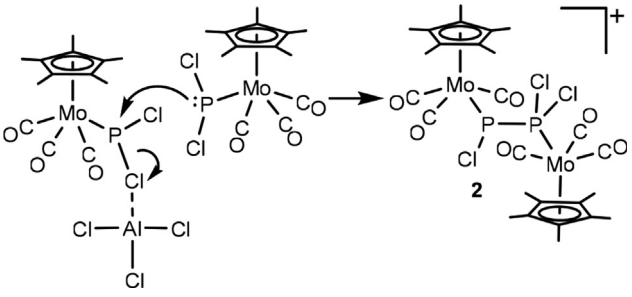
Results

Compound synthesis and characterization

The dichlorophosphido complex [Cp*Mo(CO)$_3$(PCl$_2$)] (**1**) was synthesized from Cp*Mo(CO)$_3^-$ and PCl$_3$ using a modification of the published procedure [13]. The IR spectrum of **1** shows carbonyl stretching bands at 2018, 1951 and 1931 cm^{-1} and ^{31}P NMR spectrum shows a singlet at δ 408, matching reported values.

Abstraction of chloride from **1** was attempted using AlCl$_3$, AgBF$_4$ and NaBPh$_4$. All reagents led to the same metal complex **2** as the sole phosphorus containing product, with only the counterions differing. The ^{31}P NMR spectrum of **2** shows doublets at δ 318 and 258, each having a coupling constant of 528 Hz. The large P–P coupling constant indicates a direct P–P bond between two chemically inequivalent P atoms. The IR spectrum shows three carbonyl stretches at 2020, 1932 and 1953 cm^{-1}, in a pattern consistent with a Cp*Mo(CO)$_3$X unit. The ^{1}H NMR spectrum shows peaks at δ 1.95 and 1.89 for two chemically different Cp* groups. The ^{13}C NMR spectrum shows six carbonyls, and two Cp* groups, confirming that there are two chemically non-equivalent Cp*Mo(CO)$_3$ units. The electrospray mass spectrum shows an isotope pattern (m/z = 780–809) that corresponds to the predicted masses for $C_{26}H_{30}O_6P_2Cl_3Mo_2^+$. Based on these data, the structure of **2** is assigned as a bimetallic complex containing a bridging P_2Cl_3 ligand and an overall +1 charge, which results from the displacement of chloride from one molecule of the dichlorophosphido ligand of **1** by a second equivalent of **1** (Scheme 1).

The observed product could indicate formation of a transient chlorophosphinidene, followed by its coordination by a second equivalent of **1**. In order to test this possibility, the chloride abstraction reaction was carried out in the presence of an alkyne trapping reagent. Reaction with alkynes to form phosphirenes is considered a characteristic reaction of terminal phosphinidene complexes [17]. However, in this attempted trapping reaction, compound **2** was the only observed product, and no phosphirene complex was detected, even with a large excess of alkyne and high dilution. This suggests that **2** does not form via a phosphinidene intermediate, but by another mechanism. We suggest that **2** forms via a Lewis acid assisted nucleophilic substitution mechanism (Scheme 2).



Scheme 2.

In order to provide support for this mechanism, the reaction was carried out in the presence of an external nucleophile. Abstraction of chloride from **1** in the presence of one equivalent of triphenylphosphine leads to the triphenylphosphine coordinated chlorophosphinidene complex [Cp*Mo(CO)$_3${P(Cl)(PPh$_3$)}][X] (**3**) (Scheme 3). Note that PPh$_3$ does not react with **1** in the absence of a chloride abstractor. The ^{31}P NMR spectrum of **3** shows two doublets at δ 179 and δ 37.9, both of which show a coupling constant of 454 Hz. The large coupling constant indicates a direct P–P bond. The IR spectrum of **3** shows three carbonyl stretches at 2019, 1972 and 1934 cm^{-1}, which indicate that the molybdenum center has retained three carbonyl ligands. Compound **3** has been structurally characterized, and an ORTEP diagram of the cation is shown in Fig. 1. The structure of the cation consists of a four legged piano stool, with three legs occupied by carbonyls and the fourth by the P(Cl)(PPh$_3$) unit. The metal bound P is trigonal pyramidal. The PPh$_3$ is coordinated to the metal bound P, and is directed away from the Cp* ring, while the chloro group is directed such that the P–Cl bond is nearly parallel to the Cp* ring. In this position, the Cl atom lies directly between the bulky Cp* and PPh$_3$ groups. The reactivity of **1** towards nucleophiles, but not towards alkynes, supports the proposed Lewis acid assisted nucleophilic substitution mechanism.

Interestingly, the nucleophilic substitution reaction that leads to **3** can be repeated a second time, leading to the displacement of the second chloride with PPh$_3$ (Scheme 4). However, the formation of

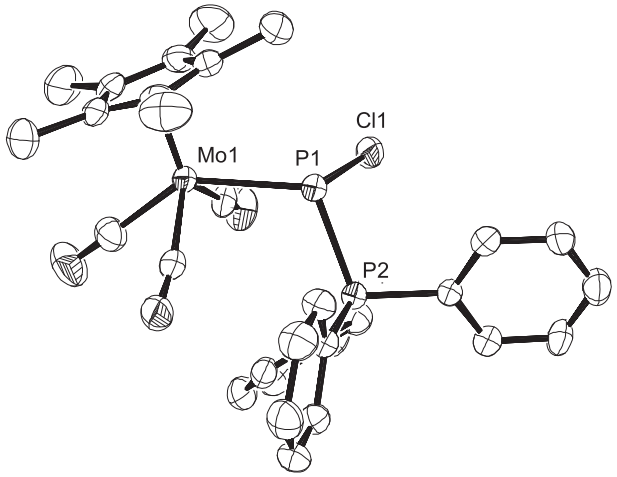


Fig. 1. ORTEP diagram showing one of two crystallographically non-equivalent cations of **3**. Hydrogen atoms and the counterion have been omitted for clarity. Selected distances and angles: Mo1–P1 = 2.531(1), P1–P2 = 2.196(1), P1–Cl(1) = 2.102(1), Mo1–P1–P2 = 112.51(5), Mo1–P1–Cl1 = 108.94(5), Cl(1)–P(1)–P(2) = 94.41(5).