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Syntheses and structures of the first terminal phosphanylphosphido complexes of molybdenum(IV)

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ABSTRACT

The reactions of $R_2P{-}P(SiMe_3)Li$ (R = ^{t}Bu, ^{i}Pr$_2$N) with [Cp_2MoCl_2] yield terminal phosphanylphosphido complexes formally via the insertion of the phosphinidene P-atom into the C—H bond of a cyclopentadienyl ring and the migration of the hydrogen atom or $SiMe_3$ moiety to the molybdenum centre. Solid state structures of [$Cp(C_5H_4P{-}P^tBu_2)MoH$], [$Cp(C_5H_4P{-}P^tBu_2)Mo(SiMe_3)$] and [$Cp\{C_5H_4P{-}P(N^iPr_2)_2\}Mo(SiMe_3)$] were established by single crystal X-ray diffraction. The proposed reaction path is supported by the results of NMR studies and DFT calculations.

1. Introduction

Though interest in phosphinidene complexes has grown enormously in recent years, the synthesis of isolable mononuclear nucleophilic phosphinidene complexes of transition metals still represents a significant challenge [1]. Phosphinidene complexes of the molybdenum group can be divided into four categories: (i) phosphinidene bridged electrophilic dimolybdenum complexes [2], (ii) terminal bent nucleophilic [$Cp_2Mo(PMes^*)$], which was obtained in the reaction of [$(MoCp_2HLi)_4$] with Mes^*PCl_2 [3], (iii) terminal bent cationic electrophilic [$Cp^*(CO)_3Mo(PN^iPr_2)$]$^+$ [4] and (iv) unstable neutral [$Cp^*_2Mo(P{-}NHMes^*)$] [5].

The main target of our group is the incorporation of phosphanylphosphinidene groups, R_2PP, into transition metal complexes via methathesis reactions of lithiated diphosphanes, $R_2P{-}P(SiMe_3)Li$ (R = ^{t}Bu, ^{i}Pr, Et_2N and ^{i}Pr$_2$N), with dichlorido complexes of transition metals. These precursors, similarly to lithiated phosphanes, can act as a source of both phosphanylphosphido [6a,b] and terminal phosphanylphosphinidene ligands [6c]. Reactions leading to diphosphorus complexes [6d] or to complexes with side-on bonded phosphanylphosphinidene ligands of Pt(0) [6e] or W(IV) [6f] have no equivalents in the case of lithiated phosphanes.

Recently we have reported the reactions of $R_2P{-}P(SiMe_3)Li$ (R = ^{t}Bu, ^{i}Pr, ^{i}Pr$_2$N and Et_2N) with [Cp_2WCl_2]. These metathesis reactions yield a new type of tungsten(IV) phosphanylphosphido complexes, [$Cp(C_5H_4P{-}PR_2)WH$] and [$Cp(C_5H_4P{-}PR_2)W(SiMe_3)$] [7], and resemble the rearrangement leading to [$(C_5H_4Me)\{C_5H_3Me(PMes^*)\}WH$] observed by Cowley and co-workers in the reaction of $Mes^*(Me_3Si)PLi$ with [$(C_5H_4Me)_2WCl_2$]. This result was rationalized by assuming the formation of the "transient" [$(C_5H_4Me)_2W(PMes^*)$] followed by a P-atom insertion into a Cp ring and H → W transfer [8]. Contradictory to this finding, the related similar complex [$Cp_2Mo(PMes^*)$] was obtained in a different way and proved to be a stable "bent" phosphinidene complex [3]. Thus a mechanism proposed by Cowley should probably be revised.

Now we present the results of our studies on the reactivity of $R_2P{-}P(SiMe_3)Li$ (R = ^{t}Bu, ^{i}Pr$_2$N) towards [Cp_2MoCl_2]. The aim of our work was to get more insight into the art of binding of a R_2PP moiety to the Cp_2Mo centre and to compare the outcomes of the reactions with those reported for [Cp_2WCl_2] [7]. Some of the described results were presented in a preliminary form at the 8th European Workshop on Phosphorus Chemistry [9].

2. Results and discussion

[Cp_2MoCl_2] reacts with $R_2P{-}P(SiMe_3)Li$ yielding phosphanylphosphido complexes by the formal insertion of the phosphinidene P-atom into the C—H bond of a cyclopentadiene ring and migration of a hydrogen atom in the case of [$Cp(C_5H_4P{-}P^tBu_2)MoH$] (**1H**) or a $SiMe_3$ group in the case of [$Cp(C_5H_4P{-}P^tBu_2)Mo(SiMe_3)$] (**1Si**) and [$Cp\{C_5H_4P{-}P(N^iPr_2)_2\}Mo(SiMe_3)$] (**2Si**) to the Mo atom (Scheme 1).

Table 1 shows the results of ^{31}P NMR spectra of solutions from the reactions of [Cp_2MoCl_2] with ^{t}Bu$_2P{-}P(SiMe_3)Li{\cdot}2THF$ and with $(^iPr_2N)_2P{-}P(SiMe_3)Li{\cdot}1.1THF$. The molar ratio of compounds (**1H**)/(**1Si**) was established by the integration of the $^{31}P\{^1H\}$ resonances of the P1 atoms (connected to the Mo atom). The contents of side products were estimated from the heights of the $^{31}P\{^1H\}$ NMR resonances of the R_2P group.

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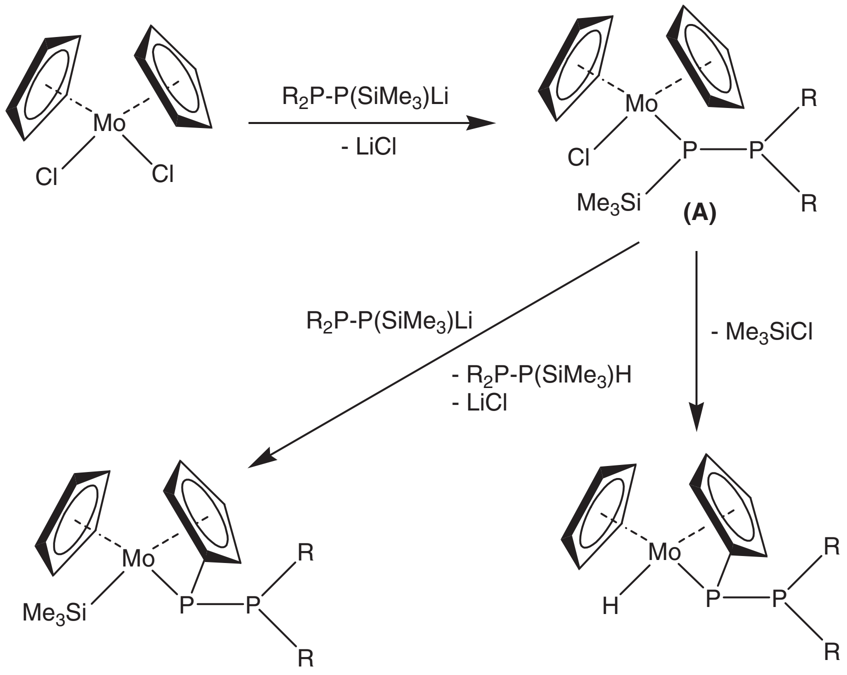

(1Si) R=^{t}Bu **(2Si)** R=N^{i}Pr$_2$ **(1H)** R=^{t}Bu

Scheme 1. The formation of phosphanylphosphido complexes **1Si**, **2Si** and **1H**.

Table 1
The results of NMR studies for the reactions of $R_2P{-}P(SiMe_3)Li$ with $[Cp_2MoCl_2]$.

No.	Substrates (mmol)		Solvent	Products (%), side-products (intensity of signal) s – strong, m – medium, w – weak
	R = ^{t}Bu	**Cp_2MoCl_2**		
1	0.37	0.69	DME	**1H**(61%) **1Si**(39%), $^{t}Bu_2P{-}P(SiMe_3)H$ (w), $^{t}Bu_2PH$ (m)
2	0.60	0.27	DME	**1H**(13%) **1Si**(87%), $^{t}Bu_2P{-}P(SiMe_3)H$ (s)
3	0.66	0.69	Toluene	**1H**(3%) **1Si**(97%), $^{t}Bu_2P{-}P(SiMe_3)H$ (s)
	R = $^{i}Pr_2N$	**Cp_2MoCl_2**		
4	0.79	0.59	DME	**2S**i(100%), $(^{i}Pr_2N)_2P{-}PH{-}P(N^{i}Pr_2)_2$ (m), $(^{i}Pr_2N)_2PH$ (w), $(^{i}Pr_2N)_2P{-}P(SiMe_3)H$ (m)
5	1.19	0.60	DME	**2Si**(100%), $(^{i}Pr_2N)_2P{-}P(SiMe_3)H$ (m)
6	0.75	0.69	Toluene	**2Si**(100%), $(^{i}Pr_2N)_2P{-}P(SiMe_3)H$ (s)

$(^{i}Pr_2N)_2P{-}P(SiMe_3)Li$ reacts with $[Cp_2MoCl_2]$ yielding solely $[Cp\{C_5H_4P{-}P(N^{i}Pr_2)_2\}Mo(SiMe_3)]$ (a pair of enantiomers) (**2Si**) – similarly to the reaction of $[Cp_2WCl_2]$ [7]. **2Si** decomposes slowly in solution. Runs 1, 2 and 3 (see Table 1) indicate that mixtures of $[Cp(C_5H_4P{-}P^{t}Bu_2)MoH]$ (**1H**) and $[Cp(C_5H_4P{-}P^{t}Bu_2)Mo(SiMe_3)]$ (**1Si**) form in toluene as well as in DME. The formation of **1Si** is clearly favoured, the amount of **1H** is significant only if an excess of $[Cp_2MoCl_2]$ is present (run 1, Table 1).

A comparison of the reactivity of $^{t}Bu_2P{-}P(SiMe_3)Li$ towards $[Cp_2MoCl_2]$ versus $[Cp_2WCl_2]$ indicates that the tendency to form hydrido $[Cp(C_5H_4P{-}P^{t}Bu_2)MH]$ versus silyl complexes $[Cp(C_5H_4P{-}P^{t}Bu_2)M(SiMe_3)]$ is favoured if M = W, moreover for M = W four isomers (two pairs of enantiomers) of the hydrido complex $[Cp(C_5H_4P{-}PR_2)WH]$ (R = ^{t}Bu or ^{i}Pr) are formed [2b].

The ^{1}H NMR spectrum of the reaction solution for the run of $^{t}Bu_2P{-}P(SiMe_3)Li$ with $[Cp_2MoCl_2]$ indicates an unresolved triplet at −9.245 ppm (Mo—H). According to our earlier results [7], it points to the formation of only two isomers (one pair of enantiomers) in which the Mo—H and $P{-}P^{t}Bu_2$ bonds are placed on the same side of the three-membered Mo1—P1—C10-ring (Fig 2). The calculated DFT [10–12] structure of **1H** (Fig. 3) properly locates the Mo—H bond.

The formation of the phosphido complex **D** via the rearrangement of a transient phosphinidene complex **C** and hydrogen migration to the tungsten atom was postulated by Cowley and co-workers [8] (Scheme 2).

The phosphido complex **B** losses Me_3SiCl to afford the transient phosphinidene complex **C**. In the next step compound **C** rearranges to the phosphido complex **D**. Lappert and co-workers [3] had, however, isolated phosphinidene complexes $[Cp_2M(PMes^{*})]$ (M = Mo, W) very similar to **C** in the reaction of $[\{MCp_2HLi\}_4]$ with $Mes^{*}PCl_2$. These complexes are stable at room temperature in solution and there is no evidence for a rearrangement to complexes similar to **D**. Thus the step **C** → **D** is not very likely. We have performed DFT [10–12] calculations in order to get more insight into the stability of possible transient compounds in the reaction of $[Cp_2MoCl_2]$ with $^{t}Bu_2P{-}P(SiMe_3)Li$ in a 1:1 M ratio. The results of our calculations are shown in Scheme 3.

Our calculations indicate that the phosphanylphosphido complex **A** is thermodynamically unstable. In order to get more insight into the origin of the high reactivity of $[Cp_2(Cl)Mo\{(Me_3Si)P{-}P^{t}Bu_2\}]$, we have performed DFT calculations on its structure (Fig. 1).

The Cl1—Mo1—P1—Si1 dihedral angle of 15.26° in $Cp_2MoCl\{(Me_3Si)P{-}P^{t}Bu_2\}$ (**A**) is nearly ideal for intramolecular Me_3SiCl elimination via a cyclic transition state leading to $[Cp_2Mo(\eta^1\text{-}P{-}P^{t}Bu_2)]$, so that the tendency of **A** to rearrange yielding the transient $[Cp_2Mo(\eta^1\text{-}P{-}P^{t}Bu_2)]$ or **1H** is obvious. We suggest that the phosphido complexes **A** (Scheme 1) and **B** (Scheme 2) are responsible for the formation of **1H** and **1Si** (Scheme 1) or **D** (Scheme 2) and a phosphinidene complex of the **C** type is not formed at all. This assumption is strongly supported by the stability of $[Cp_2M(PMes^{*})]$ (M = Mo, W) [3], by the lack of $[Cp_2Mo(\eta^1\text{-}P{-}P^{t}Bu_2)]$ in the reaction solutions and by the formation of **1Si**, which is hard to explain by considering the step **1H** → **1Si**. We have calculated the enthalpy change for this hypothetical reaction (not included in Scheme 3):