



Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Dual reactivity pattern of Mn(I) carbyne complexes $\text{Cp}(\text{CO})_2\text{Mn}^+\equiv\text{C}-\text{R}$ (R = Ar, Alk) vs. dppm: Subtle balance between double intramolecular nucleophilic addition and nucleophilic addition followed by migratory CO insertion

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ARTICLE INFO

Article history:

Received 3 November 2017

Received in revised form

21 December 2017

Accepted 23 December 2017

Available online xxx

The authors dedicate this paper to Prof. Irina P. Beletskaya, a famous expert in organometallic chemistry and catalysis.

Keywords:

Manganese

Fischer carbenes

CO insertion

Ketene complexes

Phosphorus ylides

ABSTRACT

The Mn(I) cationic carbyne complexes $[\text{Cp}(\text{CO})_2\text{Mn}^+\equiv\text{C}-\text{R}]\text{BX}_4$ (R = Ph, Tol, Me, Bn; X = F, Cl, Ph) react with bis(diphenylphosphino)methane to afford selectively either cyclic λ^5 -1,3-diphosphetium semiylides $[\text{RC}-\text{P}^+\text{Ph}_2\text{CH}_2\text{P}^+\text{Ph}_2]\text{BPh}_4$ ($[\text{R}^4]\text{BPh}_4$; R = Ph, Tol), or Mn(I) complexes $[\text{Cp}(\text{CO})\text{Mn}(\eta^3\text{-}(\text{P},\text{C},\text{C})\text{-Ph}_2\text{PCH}_2\text{P}^+\text{Ph}_2\text{C}(\text{R})=\text{C}=\text{O})]\text{BX}_4$ ($[\text{R}^5]\text{BX}_4$; R = Me, X = Ph; R = Bn, X = F) featuring unprecedented phosphonioketene ligands depending on the nature of the carbyne substituent, aryl or alkyl, respectively. The selective formation of these products is tentatively rationalized through the key formation of a transient cationic Mn(I) phosphoniocarbene complexes $[\text{Cp}(\text{CO})_2\text{Mn}=\text{C}(\text{R})\text{PPh}_2\text{CH}_2\text{PPh}_2]\text{BX}_4$ bearing a pendent phosphine moiety. The molecular structures of semi-ylide $[\text{P}^{\text{h}}4]\text{BPh}_4$ and complex $[\text{B}^{\text{n}}5]\text{BF}_4$ were elucidated by single-crystal X-ray diffraction.

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1. Introduction

In contrast to conventional heteroatom-substituted Fischer carbenes, transition metal carbene complexes bearing phosphorus-containing groups at the α -position relative to the carbene carbon, **A–D** (Fig. 1) have been little studied [1–5] and until recently did not afford any significant applications in organic synthesis and homogeneous catalysis.

This situation started to change in 2004 after the seminal work by Piers and coll. showing that cationic 14-electron Ru(II) phosphinocarbene complexes (**A**) can be extremely active initiators in olefin metathesis [1d–g]. Later, Mezailles, Le Floch and coll. showed

that nucleophilic carbene complexes **B** and **D** of early transition metals can efficiently perform the stoichiometric olefination of aldehydes, ketones, isocyanates and carbodiimides to afford the corresponding alkene and ketenimine derivatives [2c,5c,5f]. Finally, we have recently shown that Mn(I) phosphonio- (**A**) and η^1 -phosphinocarbene (**B**) compounds serve as key reaction intermediates for the Mn-mediated synthesis of backbone decorated diphosphinomethanes [6] and precursors of novel NHC core pincer-type ligands [7], respectively.

Despite incontestable advances in this research area, a deeper insight into the reactivity of α -P-substituted carbene species is still necessary to facilitate further development of their applications. In this contribution, we present our investigations on the reactions of Mn(I) carbyne complexes $[\text{Cp}(\text{CO})_2\text{Mn}^+\equiv\text{C}-\text{R}]$ with a tertiary diphosphine, namely bis(diphenylphosphino)methane (dppm), which revealed an unexpected dual reactivity pattern, resting on the transient formation of Mn(I) phosphinocarbenes $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}(\text{R})$

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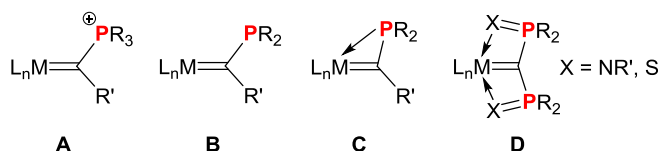


Fig. 1. Main types of transition metal α -P-substituted carbene complexes.

$\text{PPh}_2\text{CH}_2\text{PPh}_2$ (A) bearing a pendant phosphine moiety.

2. Results and discussion

We have initially observed that the reaction of the arylcarbyne complex $[\text{Cp}(\text{CO})_2\text{Mn}^+\equiv\text{C}-\text{Ph}]\text{BPh}_4$ ($[\text{Ph}^1]\text{BPh}_4$) [2h] with one equivalent of dppm leads to the formation of the cyclic λ^5 -1,3-diphosphetium semi-ylide compound $[\text{Ph}^4]\text{BPh}_4$ (Scheme 1) in 83% yield [6]. A similar result was obtained starting from the arylcarbyne complex $[\text{Cp}(\text{CO})_2\text{Mn}^+\equiv\text{C}-\text{Tol}]\text{BPh}_4$, now generated *in situ* from the alkoxycarbene precursor $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}(\text{Tol})\text{OEt}$ upon treatment with BCl_3 , and dppm to afford *in fine* $[\text{Tol}^4]\text{BPh}_4$ via the formation of $[\text{Tol}^4]\text{BPh}_4$ and anion exchange with NaBPh_4 .

Both compounds were fully characterized by the usual spectroscopic methods, complemented in the case of $[\text{Ph}^4]\text{BPh}_4$ by an X-ray diffraction study. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{Ph}^4]\text{BPh}_4$ show a sharp singlet at δ 11.6 for $\text{R} = \text{Ph}$ and δ 10.7 for $\text{R} = \text{Tol}$. The ylidic and methylene carbon atoms give rise to two triplets in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, which appear at δ 34.5 ($^1J_{\text{PC}} = 93.0$ Hz) and δ 34.5 ($^1J_{\text{PC}} = 53.0$ Hz) for $[\text{Ph}^4]\text{BPh}_4$ and at δ 33.6 ($^1J_{\text{PC}} = 93.6$ Hz) and δ 24.8 ($^1J_{\text{PC}} = 53.0$ Hz) for $[\text{Tol}^4]\text{BPh}_4$, respectively.

Compound $[\text{Ph}^4]\text{BPh}_4$ crystallized in the orthorhombic space group $\text{Pca}2_1$ with two independent molecules per unit cell featuring identical metrical parameters within the experimental uncertainty. The perspective view of one of cations (cation A) is shown in Fig. 2. The four-membered PCPC cycle, which is essentially planar (maximum deviations from the mean planes of 0.006(2) Å and 0.016(2) Å associated with C1a and C2b in their respective four-membered cycles), and the phenyl ring attached to the ylidic C1 atom are basically coplanar ($\{\text{P1a}-\text{C1a}-\text{C11a}-\text{C12a}\} = 3.9(4)$; $\{\text{P1b}-\text{C1b}-\text{C11b}-\text{C12b}\} = 1.1(4)^\circ$).

The P–C bonds involving the methylene bridge are significantly longer than those involving the ylidic carbon ones, thereby reflecting the partial P=C bond character of the latter. As compared to similar λ^5 -1,3-diphosphetium compounds bearing NMe_2 groups at the phosphorus atoms and alkyl substituents at the ylidic carbon [8], the present phenyl-substituted semi-ylide $[\text{Ph}^4]\text{BPh}_4$ displays, generally, slightly longer C–P distances and slightly wider P–C_{ylidic}–P valence angle [9].

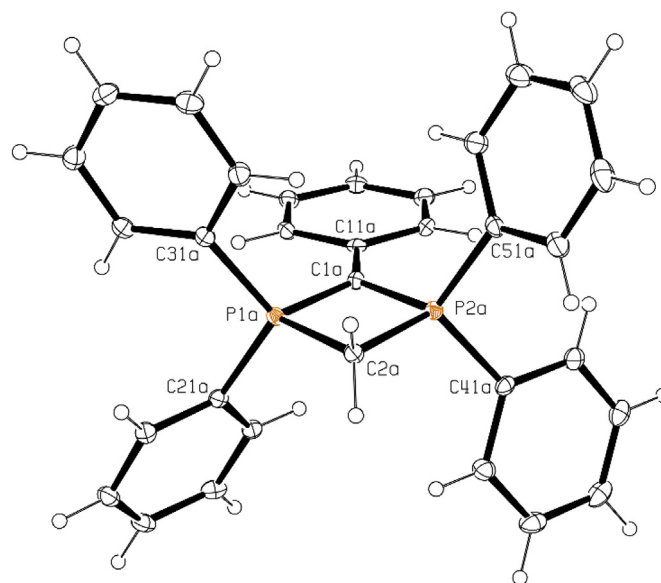
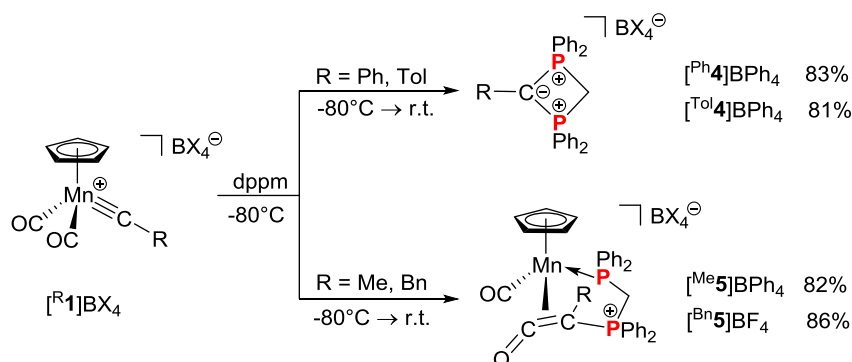


Fig. 2. A perspective view of one of the independent cation (cation A) within the structure of λ^5 -1,3-diphosphetium semi-ylide tetraphenylborate chloroform solvate $[\text{Ph}^4]\text{BPh}_4 \cdot \text{CHCl}_3$. Selected bond lengths (Å) and angles ($^\circ$): C1a–P1a 1.730(2), C1a–P2a 1.727(2), C2a–P1a 1.832(2), C2a–P2a 1.830(2), P1a–C1a–P2a 94.46(10), P1a–C2a–P2a 87.72(10) [C1b–P1b 1.727(2), C1b–P2b 1.822(2), C2b–P1b 1.832(2), C2b–P2b 1.829(2), P1b–C1b–P2b 94.78(10), P1b–C2b–P2b 87.78(10)].

To our surprise, the reaction between the alkyl-substituted carbyne complex $[\text{Cp}(\text{CO})_2\text{Mn}^+\equiv\text{C}-\text{Me}]\text{BPh}_4$, generated *in situ* from $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}(\text{Me})\text{OEt}$ upon treatment with BCl_3 , and dppm proceeded in a quite different manner to yield the complex $[\text{Cp}(\text{CO})\text{Mn}(\eta^3-(\text{P},\text{C},\text{C})\text{-Ph}_2\text{PCH}_2\text{P}^+\text{Ph}_2\text{C}(\text{Me})=\text{C}=\text{O})]$, $[\text{Me}^5]^+$ (Scheme 1) featuring an unprecedented bidentate phosphonio-substituted ketene/phosphine ligand. This compound was isolated as its tetraphenylborate salt in 82% yield after the $\text{BCl}_4^-/\text{BPh}_4^-$ anion exchange. The identity of $[\text{Me}^5]\text{BPh}_4$ was established by IR and NMR spectroscopy and high-resolution mass spectrometry. Its IR spectrum exhibits a strong band at 1932 cm^{-1} attributable to the stretching ν_{CO} frequency of one carbonyl ligand and a set of broad medium-intensity bands in the region of $1785\text{--}1695\text{ cm}^{-1}$ corresponding to the stretching vibrations of η^2 -coordinated phosphoniosubstituted ketene moiety, as it has been observed earlier for the neutral analogues $\text{Cp}(\text{CO})\text{Mn}(\eta^3-(\text{P},\text{C},\text{C})\text{-R}_2\text{P}(\text{Ph})\text{C}=\text{C}=\text{O})$ [2f, 2h, 7a]. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of $[\text{Me}^5]\text{BPh}_4$ shows two doublets at δ 90.6 and δ 45.6 with a characteristic $^2J_{\text{PP}}$ coupling constant of 56.0 Hz corresponding to the phosphine moiety bound to manganese and to the phosphonium moiety, respectively. Due to the



Scheme 1. Dual reactivity pattern of the Mn(I) cationic carbyne complexes $[\text{R}^1]\text{BX}_4$ with dppm.

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