



Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Double insertion of benzophenone into thorium-phosphorus bonds

Sean P. Vilanova, Michael L. Tarlton, Charles L. Barnes, Justin R. Walensky*

Department of Chemistry, University of Missouri, Columbia, MO 65211, USA

ARTICLE INFO

Article history:

Received 31 August 2017

Received in revised form

18 October 2017

Accepted 19 October 2017

Available online xxx

Keywords:

Thorium

Phosphorus

Insertion

Benzophenone

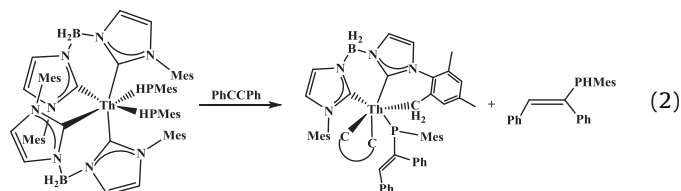
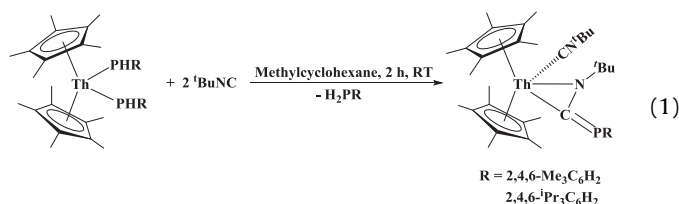
ABSTRACT

The reactivity of thorium-phosphorus bonds was investigated with benzophenone. The insertion of two equivalents of benzophenone into both thorium-phosphorus bonds in $(C_5Me_5)_2Th[PH(2,4,6-R_3C_6H_2)]_2$, $R = Me$ or iPr , was observed. In addition, a new thorium polyphosphido complex, $(C_5Me_5)_2Th(P_3Ph_3)$ is reported from the reaction of $(C_5Me_5)_2ThCl_2$ with $Na_2(P_4Ph_4)(DME)_3$.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Historically, the reactivity of actinide-phosphorus bonds has been relatively unexplored [1–3], and only recently have actinide-phosphorus coordination complexes received greater attention [4–6]. For example, the reaction of iBuNC with $(C_5Me_5)_2Th[PH(2,4,6-R_3C_6H_2)]_2$, $R = Me$ or iPr , reacts to form phosphazaaallene moieties, eq (1). Additionally, the Arnold group has reported the reaction of a bis(phosphido) thorium complex with $PhCCPh$ to produce a mono(phosphido) thorium metallacycle, eq (2) [3]. However, due to being soft donor ligands, the chemistry of actinide-phosphorus bonds have been understudied compared to its harder, more Lewis basic, nitrogen congener.



Benzophenone displays a variety of reactivity as it can be reduced to the ketyl form [7,8], undergo reductive coupling [9,10], or 1,2-migratory insertion [11–14]. While reduction of benzophenone is unlikely, reductive coupling of phosphido-ligands has been recently observed, which could lead to redox chemistry [2]. However, migratory insertion is more probable as thorium is not a redox-active metal, and would prefer the hard oxygen atom of benzophenone, and the formation of a phosphorus-carbon bond is thermodynamically favorable. Herein, we report the reactivity of benzophenone with $(C_5Me_5)_2Th[PH(2,4,6-R_3C_6H_2)]_2$, $R = Me$ (Mes) or iPr (Tipp), as well as the synthesis of a new polyphosphido thorium complex [15,16]. However, the reactivity of

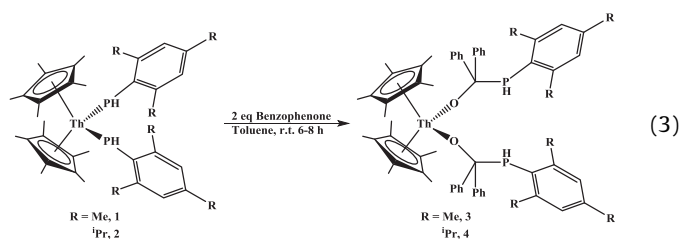
* Corresponding author.

E-mail address: walenskyj@missouri.edu (J.R. Walensky).

$(C_5Me_5)_2Th(P_3Ph_3)$ with benzophenone was found to be more complex.

2. Results and discussion

The synthesis and isolation of benzophenone insertion products was achieved via the addition of two equivalents of benzophenone to either $(C_5Me_5)_2Th(PHMes)_2$, **1**, or $(C_5Me_5)_2Th(PHTipp)_2$, **2**, eq (3). Reaction of one equivalent of benzophenone does not produce the double insertion product and further analysis is ongoing. At room temperature, the reaction proceeds to completion in under 8 h, yielding the new products, **3** and **4**. Both compounds were characterized by 1H , $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^{31}P NMR spectroscopy. Analysis of the room temperature NMR spectra for both **3** and **4** indicated that two species are present in solution. Initially, it was thought that this was due to the steric properties of the insertion products, and two rotational isomers were observed. In that case, only one product would be observed by increasing the temperature of the NMR measurements. However, in both cases, as the temperature was increased to 340 K, there was a clear sharpening of the resonances belonging to each species in solution. For **3**, two doublets were observed in the proton NMR spectrum, each representing a P-H proton. One was found at 5.30 ppm and the other at 5.41 ppm (both with $^1J_{P-H} = 222$ Hz). A NOESY experiment was performed, at 340 K, in order to determine whether or not the two P-H protons interact at all in solution. In the spectrum, the doublets only correlated to themselves, not each other. This indicates that the resonances are not part of the same molecule, and likely belong to two different isomers. Similar results were found for **4** with doublets representing the P-H protons being found at 5.64 ($^1J_{P-H} = 222$ Hz) and 5.34 ($^1J_{P-H} = 228$ Hz) ppm for each of the isomers. The NOESY experiment for this compound also showed that the two P-H protons do not couple to one another. Unfortunately, the compounds begin to decompose at these higher temperatures, making their characterization via $^{13}C\{^1H\}$ NMR spectroscopy not possible. At lower temperatures, only one of the two isomers is found in solution, so low temperature NMR experiments were performed to fully characterize the major isomer via 1H and $^{13}C\{^1H\}$ NMR spectroscopy.

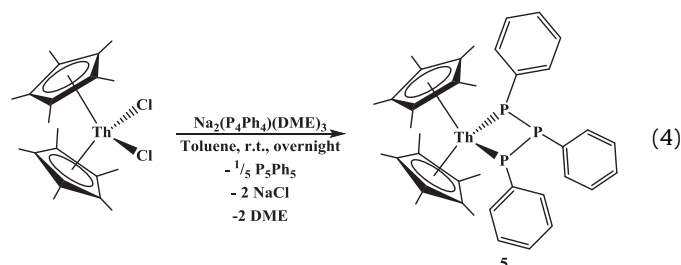


The $^{31}P\{^1H\}$ NMR spectra lent further support to the idea that there are potentially two isomeric species in solution, as the spectra for both compounds contained one singlet resonance, representing the isolated product, as well as a second, smaller broad resonance at similar chemical shifts. For **3**, a broad singlet was observed for the major product at -15.76 ppm ($^1J_{P-H} = 222$ Hz), while for **4**, the analogous resonance was located at -27.38 ppm ($^1J_{P-H} = 224$ Hz). The new sp^3 carbon formed upon insertion was found in the $^{13}C\{^1H\}$ NMR spectra at 92.53 ppm or 93.17 ppm, for the Mes and Tipp analogues, respectively.

Both products were characterized in the solid-state, via single crystal X-ray diffraction, Fig. 1, and showed that one benzophenone

had inserted into each thorium-phosphorus bond. Similar to the starting material, the geometry about the Th(IV) metal center is pseudo-tetrahedral. The insertion product results in the formation of two new Th-O bonds and two new C-P bonds. The bond lengths for the Th-O bonds are similar to other Th-O bonds found in the literature, being 2.165(3) and 2.171(3) Å for the Mes and Tipp species, respectively. For example, the Th-O bond had distances of 2.1769(18) and 2.1771(19) Å in $(C_5Me_5)_2Th[O(2,6-Me_2C_6H_3)]_2$ [5] and 2.189(6) Å in $Th[O-(2,6-tBu_2C_6H_3)]_4$ [17]. The O-Th-O bond angles are 99.71(15) and 102.49(16)° for **3** and **4**, respectively. An analysis of the C-O bonds of 1.420(5) and 1.426(5) Å for **3** and **4**, respectively, shows a significant elongation of the C=O bond from free benzophenone (1.23 Å) [18].

The reaction of $(C_5H_5)_2MCl_2$, $M = Ti, Zr, Hf$, with $Na_2P_4Ph_4(DME)_3$ has been reported to produce a $(P_3Ph_3)^{2-}$ ligand [19–21], and a similar result was observed with thorium. Reaction of $(C_5Me_5)_2ThCl_2$ with $Na_2P_4Ph_4(DME)_3$ [22], eq (4), yielded an orange-red colored solution. The $^{31}P\{^1H\}$ NMR spectrum showed two resonances: a doublet located at 55.3 ppm and a triplet at -121.5 ppm, each with $^1J_{P-P}$ of 295 Hz. In addition, the $^{31}P\{^1H\}$ NMR spectrum showed the presence of P_5Ph_5 as a byproduct that could not be easily separated. However, a satisfactory elemental analysis could be obtained. This coupling constant is smaller than that observed for the $(C_5H_5)_2Zr(P_3Ph_3)$ ($^1J_{P-P} = 349.9$ Hz) analog as well as the cyclohexyl derivatives, $(C_5H_5)_2Zr(P_3Cy_3)$ ($^1J_{P-P} = 346.0$ Hz) and $(C_5H_5)_2Hf(P_3Cy_3)$ ($^1J_{P-P} = 319.4$ Hz) [21]. When moving to the pentamethylcyclopentadienyl derivative, $(C_5Me_5)_2Zr(P_3Cy_3)$, the coupling constant decreased to 308.5 Hz [21].



Single crystal X-ray diffraction analysis confirmed the product as $(C_5Me_5)_2Th(P_3Ph_3)$, **5**, Fig. 2. Complex **5** shows a pseudo-tetrahedral geometry about thorium with coordination with the two centroids of the cyclopentadienyl rings and two phosphido bonds. The phenyl group on each phosphorus alternates between above and below the Th-P-P-P plane. The thorium-phosphorus bond distances of 2.8546(17) and 2.8693(17) Å are similar to the 2.861(7) and 2.887(8) Å seen in $(C_5Me_5)_2Th(PPh_2)_2$ [23]. The P1-Th1-P3 bond angle of 80.33(5)° is more acute than those seen in bis(phosphido) complexes. For example, the P-Th-P bond angle in $(C_5Me_5)_2Th(PPh_2)_2$ is 94.2(2)° [21].

A mixture of **5** with benzophenone resulted in a color change from orange to dark red, indicating a reaction occurred. Unfortunately, the 1H NMR spectrum showed multiple products from which only P_5Ph_5 [24] and P_4Ph_4 [25] could be identified and isolated, so the reactivity of this molecule was not as straight forward as that of **1** and **2**.

3. Conclusion

We have demonstrated the facile migratory insertion of benzophenone into the thorium-phosphido bonds of metallocene thorium complexes. This reactivity differs from the reaction with $tBuNC$ which produced the phosphine, H_2PMes or H_2PTipp , as a

Download English Version:

<https://daneshyari.com/en/article/7756255>

Download Persian Version:

<https://daneshyari.com/article/7756255>

[Daneshyari.com](https://daneshyari.com)