Synthesis and Reactivity of Phosphametallacyclobutenes: Sterically Induced [4 + 2] Retrocycloadditions

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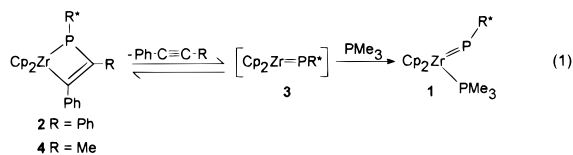*University of Windsor, Windsor, ON, Canada N9B 3P4*

The cycloaddition of alkynes to metal carbene complexes is an established reaction in organometallic chemistry,[1] yet analogous reactions with metal−heteroatom multiple bonds are much less common. The resulting metallacyclobutenes often undergo further reaction and consequently have been proposed as intermediates.[2−5] Nonetheless, the synthesis and structural characterization of stable aza-,[6] oxa-,[7] and sulfametallacyclobutenes,[7] prepared through [2 + 2] cycloadditions of alkynes with the appropriate metal−ligand multiply bonded species, have been dominated by the research of Bergman et al. Although the preparation and structural studies of several terminal phosphinidenes and arsinidenes have been reported in the literature,[8] the chemistry of these highly reactive species is just beginning to emerge. Herein we describe the first examples of phosphametallacyclobutenes, prepared by the [2 + 2] cycloaddition of an alkyne with a terminal zirconium phosphinidene. The subsequent chemistry of these metallacycles differs from their imido counterparts since insertion of aldehyde or ketone, as well as ring opening of epoxide into the Zr−P bond, affords new phosphaoxametallacycles which undergo [4 + 2] retrocycloadditions under steric duress.

We have previously described the synthesis of the terminal zirconium phosphinidene $Cp_2Zr(PR^*)(PMe_3)$ ($R^* = C_6H_2$-2,4,6-t-Bu_3) **1**.[8e,h] Reaction of **1** with 1 equiv of diphenylacetylene proceeded slowly. As the released trimethylphosphine was successively removed from solution under vacuum, the formation of **2** was indicated by the observation of a singlet at 55 ppm in the ^{31}P NMR. This signal was initially attributed to phosphametallacycle $Cp_2Zr(P(R^*)CPh{=}CPh)$ **2**, the product of a [2 + 2] cycloaddition between Zr=PR* and PhC≡CPh. A more expeditious route to **2** parallels the previously reported[8h] synthesis of **1**. Spontaneous loss of methane from Cp_2Zr-$(PR^*H)Me$ to generate the reactive terminal phosphinidene intermediate **3**, followed by a cycloaddition reaction with diphenylacetylene, provided an 87% yield of **2**. Similarly, the use of 1-phenylpropyne as a trapping agent gave a 68% yield of $Cp_2Zr(P(R^*)CMe{=}CPh)$ **4**.

^1H and ^{13}C NMR data[9] indicate that complexes **2** and **4** are best described as phosphametallacyclobutenes. For both compounds only a single resonance is observed for the cyclopentadienyl ligands, indicating that these groups are equivalent on the NMR time scale and the metallacycles are either planar[10] or rapidly undergoing inversion at phosphorus. However, these alternatives could not be distinguished, as cooling solutions of **2** or **4** to −80 °C merely resulted in the observation of line broadening.

The reversible formation of metallacycles **2** and **4** was illustrated by the addition of trimethylphosphine, which rapidly resulted in the quantitative conversion to **1** along with the release of alkyne (eq 1). Similarly, addition of 1 equiv of 1-phenyl-propyne to **2** resulted in alkyne exchange to give an equilibrium mixture of **2** and **4** ($K_{eq} = 1.1$ at 25 °C). Comparable to related oxa-,[7a] aza-,[6b−d] and sulfametallacyclobutenes,[7b,c] these reactions are thought to occur through [2 + 2] retrocycloadditions to generate transient phosphinidene intermediate **3**, which then reacts with either PMe_3 or alkyne.

Acetone reacts with metallacycle **2** over a 10 min period to produce a 51% yield of the insertion product $Cp_2Zr(OCMe_2P$-$(R^*)CPh{=}CPh)$ **5**. In contrast to reactions of related aza-[11] and oxametallacyclobutenes[7e] where insertions occur exclusively at the Zr−C bond, ^1H, ^{13}C, and ^{31}P NMR spectra of **5** were consistent with acetone insertion into the Zr−P bond. An X-ray crystallographic study[12] of **5** confirmed the formulation of the phosphaoxametallacyclohexene, in which the geometry at phosphorus is pyramidal and the supermesityl substituent adopts an equatorial position relative to the ring. The inequivalence of the cyclopentadienyl rings and methyl groups indicated by the solid state structure is consistent with the ^1H NMR spectrum at −80 °C. However, the fluxional nature of this compound

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(9) Full details of the ^1H and $^{13}C\{^1H\}$ NMR spectra of compounds **2−6** are reported as supporting information. $^{31}P\{^1H\}$ NMR (25 °C, C₆D₆): δ **2**, 55.3; **3**, 70.1; **4**, 36.1; **5**, 13.9; **6**, −2.4; **7a,b**, 46.3 and 37.0.

(10) Planarity at phosphorus in a phosphametallacyclobutene formulation seems unlikely, as orthogonality of the lone pair of electrons on phosphorus and the LUMO of the metallocene fragment precludes the stabilization of M−P multiple bonding.

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(12) Mo Kα radiation λ = 0.71069 Å and a Rigaku AFC5-R diffracto-meter were used to collect the data (4.5° < 2θ < 50°) for each compound. **5**: Triclinic space group P1̄ (No. 2), a = 13.26(1) Å, b = 15.414(6) Å, c = 11.085(8) Å; α = 101.75(5)°, β = 112.10(5)°, γ = 94.96(5)°. **6**: Monoclinic space group Cc (No. 9), a = 31.835(6) Å, b = 16.316(4) Å, c = 16.685(4) Å; β = 95.86(2)°. **7**: Monoclinic space group P2₁/c (No. 14), a = 9.944(4) Å, c = 41.12(2) Å; β = 106.37(3)°. The solution was obtained and refined employing the TEXSAN software from MSC. Refinements (data I > 3σ(I), variables, R, R_w): **5**, 2495, 208, 0.0799, 0.0668; **6**, 1540, 248, 0.0777, 0.0634; **7**, 2707, 229, 0.0953, 0.0761. Full details are deposited as supporting information.

Scheme 1
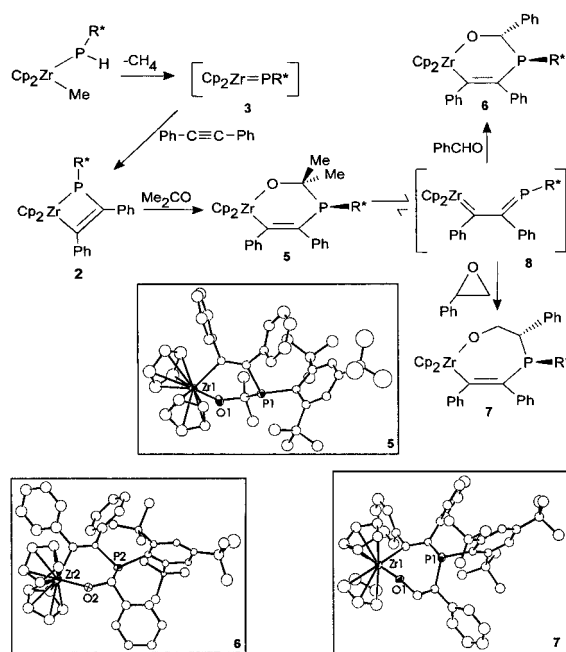
was indicated by the single broad resonances observed in the room temperature ^{1}H and ^{13}C NMR spectra ($\Delta G_c^{\ddagger} = 13.4$ kcal/mol).

Reactivity studies of **5** reveal a process involving a [4 + 2] retrocycloaddition (Scheme 1). For example, addition of 1 equiv of benzaldehyde to **5** resulted in the liberation of free acetone and the formation of metallacycle Cp$_2$Zr(OCHPhP(R*)CPh=CPh) **6**. This species could also be synthesized directly through the reaction of benzaldehyde with **2**, which afforded **6** in 61% yield. The observation of one ^{31}P NMR resonance for **6** indicates that the insertion reaction is diastereoselective. An X-ray crystallographic study[12] of **6** confirmed the selective formation of the RR/SS pair of enantiomers, in which the supermesityl group on phosphorus and the ketonic phenyl group both adopt equatorial positions and thus are *trans* with respect to the metallacyclic ring. Similar reactions of either **2** or **5** with 1 equiv of styrene oxide resulted in the formation of phosphaoxametallacycloheptene Cp$_2$Zr(OCH$_2$CHPhP(R*)CPh=CPh) **7** in 68% yield. X-ray crystallography[12] again confirmed that the RR/SS enantiomeric pair was selectively formed. In contrast to **5**, neither **6** nor **7** are fluxional species, as the solution ^{1}H and ^{13}C NMR data are temperature invariant and in accord with the solid state structure.

Kinetic studies of the reactions of **5** with either benzaldehyde or styrene oxide show that the rates of formation of metallacycles **6** and **7** are first order in the concentration of **5** but independent of changes in the concentration of either benzaldehyde or styrene oxide.[13] This indicates a rate-limiting loss of acetone from **5** through a [4 + 2] retrocycloaddition, comparable to organic retro-Diels−Alder reactions, which generates a zirconocene alkylidene intermediate. A subsequent [4 + 2] cycloaddition with benzaldehyde leads to the formation of **6**. Similarly, the ring opening of styrene oxide results in the production of **7**. Both reactions are irreversible; addition of excess acetone to solutions of either **6** or **7** does not produce metallacycle **5**. The reactive nature of **5** may be attributed to

steric congestion in the six-membered ring. Close contacts between both methyl groups and supermesityl *tert*-butyl fragments (five H···H distances ranging from 2.098 to 2.234 Å) are observed in the solid state structure of **5**. Replacement of one of the offending methyl groups with a hydrogen atom (as in metallacycle **6**) stabilizes the complex, and [4 + 2] retrocycloadditions are not observed.

Related [4 + 2] retrocycloadditions have been reported for azaoxametallacyclohexenes[11] and oxatitanacyclohexenes.[14] In these cases, preferential insertion of the ketone into the metal−vinyl bond results in retrocycloadditions that furnish (Cp$_2$M=O)$_n$ along with either α,β-unsaturated imines or conjugated dienes. Because the exclusive insertion of ketone into the Zr−P bond of **5** precludes this reaction path, the retrocycloaddition yields acetone and the alkylidene intermediate. Attempts to trap this intermediate with excess PMe$_3$, or pyridine or by [4 + 2] cycloaddition with 1-phenylpropyne were unsuccessful. Nonetheless, the related work of Doxsee et al.[15] on vinylimido complexes of titanocene and the recent trapping of a related imido−phosphaalkene complex Cp$_2$Zr(NC(Ph)=PR*)(PMe$_3$)[8h] give credence to the elusive alkylidene−phosphaalkene intermediate.

While the above kinetic data provide mechanistic insight into the reactivity of **5**, the lack of a rapid equilibrium between **5** and zirconocene alkylidene intermediate **8** indicates that this process is not responsible for the fluxionality of **5**. Consistent with this, the NMR data do not suggest fragmentation of the six-membered metallacycle; however, the value of $\Delta G_c^{\ddagger}$ indicates a lowered barrier to inversion at phosphorus. We propose that conjugation of the phosphorus lone pair with the metal-lavinylic fragment accounts for the observed fluxionality (eq 2). Steric congestion in the six-membered ring of **5** encourages this behavior. Further increases of the steric demands result in greater instability. For example, reaction of **2** with 2-butanone resulted in the formation of both diastereomers of the fluxional and unstable metallacycle Cp$_2$Zr(OCMeEtP(R*)CPh=CPh) **9** (eq 2).

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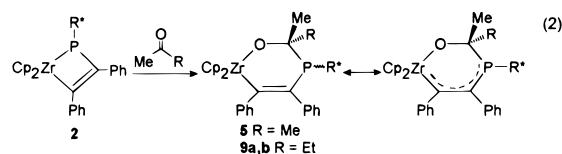
In summary, the first examples of phosphametallacyclobutenes exhibit intriguing chemistry, readily reacting with ketones, aldehydes, and epoxides by insertion into the Zr−P bond. The high P/C diastereoselectivity observed for these insertions augurs well for future development of enantioselective syntheses. In addition, our results demonstrate that steric factors can destabilize the resulting phosphaoxametallacyclohexenes and induce [4 + 2] retrocycloadditions. Studies of the nature, reactivity, and synthetic utility of these products are ongoing.

Supporting Information Available: Text describing the experimental procedures, tables giving crystallographic data, positional parameters, *U* values, and bond distances and angles of **5**-**7**, and figures showing diagrams of **5**-**7** (38 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

(13) While we were able to determine that the rate of reaction did not depend on concentrations of either benzaldehyde or styrene oxide, rate constants have not been included due to unavoidable problems with decomposition in these reactions.

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