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Methylidene Complexes **Hot Paper**

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Mononuclear and Terminal Zirconium and Hafnium Methylidenes**

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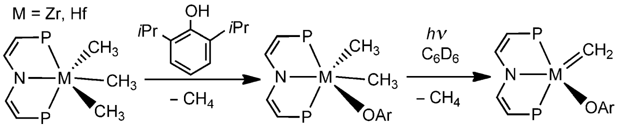
Abstract: *The dimethyl aryloxide complexes [(PNP)M(CH_3)$_2$(OAr)] (M = Zr or Hf; PNP$^-$ = N[2-P($CHMe_2$)$_2$-4-methylphenyl]$_2$); Ar = 2,6-iPr$_2$$C_6H_3$), which were readily prepared from [(PNP)M(CH_3)$_3$] by alcoholysis with HOAr, undergo photolytically induced α-hydrogen abstraction to cleanly produce complexes [(PNP)M = CH_2(OAr)] with terminal methylidene ligands. These unique systems have been fully characterized, including the determination of a solid-state structure in the case of M = Zr.*

Although the first transition-metal complex possessing a methylidene ligand, [$Cp_2Ta{=}CH_2(CH_3)$], was prepared nearly 40 years ago,[1] the isolation and complete characterization of Group 4 transition-metal complexes was not possible thus far, presumably given their reactive nature.[2–13] The only reported example of a zirconium methylidene complex, [$Cp_2Zr{=}CH_2(PPh_2Me)$],[13] was reported over 30 years ago by Schwartz, but the unstable nature of such species eluded detailed study. To diffuse some of the nucleophilic character in such an unhindered ligand, Lewis acid stabilized methylidene complexes of Ti and Zr (Tebbe-like reagents) have been isolated,[4] and in some cases these species have been structurally characterized.[14,15] In fact, even substituted alkylidene complexes of Zr and Hf are quite rare,[16–20] with the only reports including structural details being documented by Fryzuk.[16,19] A bridging carbene-type moiety (Zr=CHO-Zr) has been also documented by Bercaw.[21] In this work we describe a simple synthetic route to stable zirconium and hafnium complexes that bear the parent and terminal alkylidene ligand, a methylidene. In addition to providing complete solution NMR spectroscopic characterization, we also present a solid-state structure and theoretical studies (for Zr).

Our approach to install a stable methylidene ligand relied on the use of the stable starting materials [(PNP)M(CH_3)$_3$] (M = Zr, Hf; PNP$^-$ = N[2-P($CHMe_2$)$_2$-4-methylphenyl]$_2$) reported by Ozerov.[18,20] Attempts to promote α-hydrogen abstraction thermally, photolytically, or chemically by using Lewis acids or bases were thwarted by the presence of multiple products. Similar reactivity was also noted by Ozerov.[18,20] Despite these trials, we were encouraged by the observation of downfield ^{1}H and ^{13}C NMR spectroscopic resonances, which were signatures of what we hypothesized to be methylidene species. However, given the reactive nature of what we reasoned could be [(PNP)M=CH_2(CH_3)], we suspected that subsequent side reactions were taking place.

To kinetically block possible decomposition pathways that involved what we proposed to be putative [(PNP)M=CH_2(CH_3)], we surmised that the replacement of one methyl group with a more robust and sterically encumbering ligand such as an aryloxide would result in a more kinetically stable product. Accordingly, treatment of [(PNP)M(CH_3)$_3$] with an equal molar amount of HOAr (Ar = 2,6-*i*Pr$_2$$C_6H_3$) in toluene at −35 °C resulted in the extrusion of CH_4 with concurrent formation of [(PNP)M(CH_3)$_2$(OAr)] (M = Zr (**1**); Hf (**2**)) in yields of 60–70 % (Scheme 1).[22] NMR spectroscopic features for **1** and **2** were clearly indicative of the presence of two equivalent methyl ligands (6*H*; ^{1}H NMR: 0.76 ppm for **1**, 0.55 ppm for **2**), while ^{31}P{^{1}H} NMR spectra revealed only one isomer formed, thereby implying a highly fluxional environment for these complexes. The ^{31}P{^{1}H} NMR spectra showed only one singlet resonance at 2.51 ppm for **1** and 2.94 ppm for **2**.



Scheme 1. Synthesis of the parent methylidene complexes of Zr and Hf. For clarity the *i*Pr groups on P and the tolyl backbone bridging the N and P groups have been omitted from the PNP ligand.

The solid-state structure of **1** (Figure 1, top) depicts a highly distorted octahedral complex, in which the phosphine moieties of the PNP ligand do not adopt a *transoid* orientation (P-Zr-P = 122.708(13)°).[22] Zr-P distances are also not isometric (Zr-P = 2.8441(4) and 2.9886(4) Å) presumably as a result of the congested environment about the metal center. In fact, the aryloxide ligand is nearly in *trans* position to P2, at 155.92(3)°. The two methyl ligands are quite proximal with an acute C-Zr-C angle of 99.69(7)° and Zr-C distances of 2.2370(16) and 2.2916(16) Å, analogous to those observed

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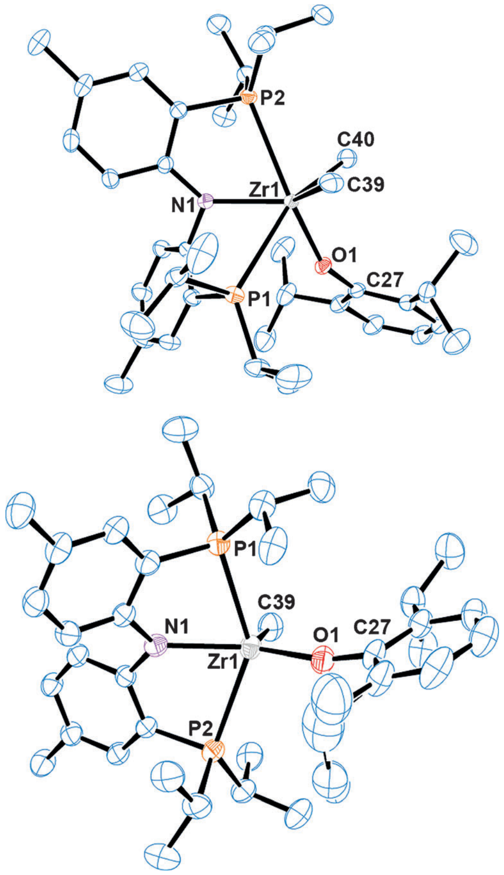

Figure 1. Solid-state structures of complexes **1** (top) and **3** (bottom) displaying thermal ellipsoids at 50% probability level. All hydrogen atoms have been omitted for clarity.

for the precursor [(PNP)Zr(CH_3)$_3$] (Zr-C average distance of 2.264 Å).[18] The proximity of the methyl ligands in **1** is encouraging if one plans to promote α-hydrogen abstraction.

Unlike complex [(PNP)M(CH_3)$_3$], which undergoes degeneration to a myriad of products under thermal or photolytic conditions, photolysis of **1** or **2** with 254–355 nm fluorescent light in benzene resulted in the gradual formation of the methylidene complexes [(PNP)M=CH_2(OAr)] (M = Zr (**3**); M = Hf (**4**)) along with methane. We chose this wavelength range, given that **1** and **2** absorb at 310 and 302 nm, respectively.[22] Complex **3** formed rather sluggishly over a period of 16 hours, whereas complex **4** was much faster, reaching nearly 95% conversion after only 3 hours. Thermolysis of **1** or **2** at 60°C resulted in the formation of only a fraction of the methylidene complexes accompanied by decomposition products, suggesting the precursor to be the thermodynamic product, whereas the methylidene is the kinetic product. Rothwell and co-workers observed similar phenomena in phototriggered reactions to form tantalum-methylidenes.[23]

Diagnostic spectroscopic features for **3** and **4** include a highly downfield shifted ^{1}H NMR resonance at 9.08 and 8.09 ppm, respectively. Judging from the ^{1}H NMR spectra recorded at room temperature, we cannot resolve coupling of methylidene hydrogen atoms to the inequivalent phosphine moieties. Irrespective of this observation, performing a

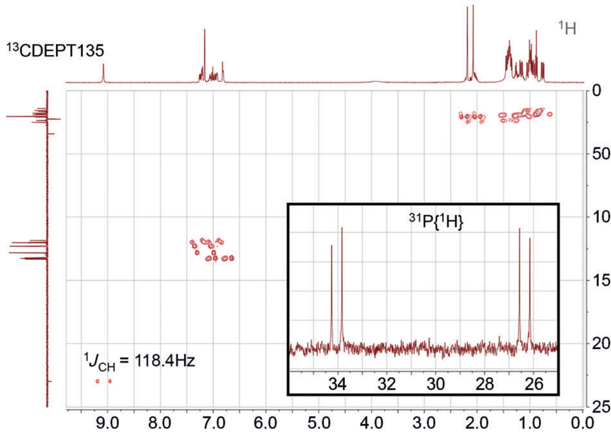

Figure 2. ^{1}H–^{13}C HSQC NMR spectrum of complex **3**. Inset shows the resonances (^{31}P{^{1}H} NMR) of inequivalent phosphorus atoms with their respective coupling.

^{1}H-^{13}C HSQC NMR spectroscopic experiment, we unquestionably correlated the highly downfield shifted ^{1}H NMR resonance to a highly downfield ^{13}C NMR spectroscopic resonance at 230.2 (**3**) and 224.3 ppm (**4**), while the negative DEPT-135 trace is consistent with this ligand being a CH_2 moiety (Figure 2). The highly deshielded resonances in the ^{13}C NMR spectrum reveal small coupling to the two inequivalent phosphine moieties of the PNP ligand ($^2J_{CP} = 3.8$ Hz for **3**, 3.5 Hz for **4**), whereas the $^1J_{CH}$ was found to be 118.4 Hz for **3** and 118.2 Hz for **4**. For comparison, the unstable methylidene complex [$Cp_2Zr{=}CH_2(PPh_2Me)$] displays an alkylidene ^{13}C NMR spectroscopic resonance at 248.6 ppm with a $^1J_{CH}$ of 121 Hz.[13] The ^{31}P{^{1}H} NMR spectra for **3** and **4** also show two doublets with $^2J_{PP}$ values of 61.5 and 68.2 Hz, respectively, in accord with a non-C_2 but C_s-like symmetric species. Apart from these salient spectroscopic features, the ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR spectra for these methylidene complexes are quite uniform.

Small single crystals of **3** can be grown from a saturated pentane solution cooled to −35°C.[22] Using a synchrotron source, we were able to collect reliable data on a single crystal and the solid-state structure is shown in Figure 1 (bottom). The molecular structure reveals the first example of a mononuclear Group 4 complex having a terminal methylidene ligand with a short Zr=C bond of 2.038(6) Å, comparable to Fryzuk's benzylidene (2.024(4) Å).[16] Slightly shorter Zr=C distances ranging from 1.95–1.99 Å have been calculated for $Zr{=}CH_2(H)_2$ molecules generated at 5 K by laser-ablated zirconium atoms and methane.[24] The overall geometry at the Zr^{IV} ion is square pyramidal with a τ value of 0.03, where the methylidene ligand occupies the axial site. The aryloxide ligand is *transoid* to the PNP amide at 141.33(15)°, akin to the P-Zr-P angle of 143.36(4)°. Although we were unable to locate the hydrogen atoms on the methylidene ligand in the E-map, the *transoid* nature of the PNP nitrogen and aryloxide oxygen atoms suggests the methylidene π bond to be oriented along the P-Zr-P vector.

To conclusively establish the correct orientation of the methylidene π bond in **3** (hence the location of the hydrogen

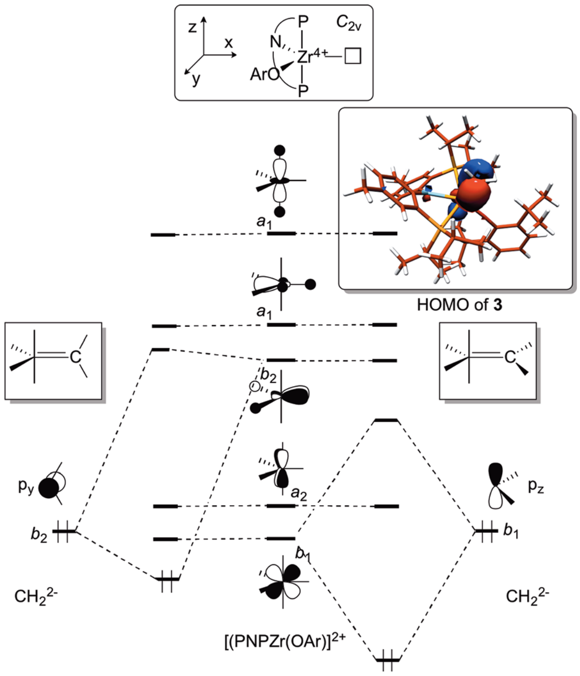

Figure 3. Molecular orbital diagram for the two plausible conformers of complex **3** with a differently oriented methylidene unit. Above, the HOMO orbital of **3** illustrates the orientation of the methylidene hydrogen atoms.

atoms), we relied on theoretical studies to understand both the geometry and the most important molecular orbitals by using coordinates obtained from the solid-state structure.[22] The computational result clearly shows the plane defined by the atoms in the CH_2^{2-} ligand in **3** to be perpendicular to the P-Zr-P axis, as depicted in the solid-state structure shown at the bottom of Figure 1. As shown in Figure 3 (right), the HOMO (b_1) is based on the interaction of the filled p_z orbital of the methylidene fragment with the lowest and unoccupied d_{xz} orbital of the $[(PNP)Zr(OAr)]^{2+}$ fragment. Rotating the methylidene by 90° (Figure 3, left) would also result in formation of a π bond (b_2) involving the filled p_y and an empty but hybridized $d_{xy}+p_x$ orbital for the $[(PNP)Zr(OAr)]^{2+}$ fragment. Although hybridization of the latter two orbitals should stabilize this molecular orbital, the antibonding combination with the PNP nitrogen and alkoxide oxygen counterfeits this feature, hence raising its overall energy. Consequently, there is a disparity of the energies between the b_2 orbitals involving the filled p orbital of the methylidene moiety and the metal fragment, resulting in an overall less-stabilized HOMO (Zr=C π bond) and more stabilized Zr=C π* (Figure 3, left side).

Thus far, all attempts to expand this methodology to the lighter congener titanium have failed, in part because of the thermal and photosensitive nature of the $[(PNP)Ti(CH_3)_3]$ precursor.[25] After almost four decades, we have shown that the right combination of geometry and ligand scaffold can allow the stabilization of zirconium and hafnium complexes with terminal methylidene units.

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[22] See the Supporting Information. CCDCs 1000695 (**1**) and 1000696 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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