The First Stable Zirconium Alkylidene Complex Formed via α-Hydrogen Abstraction: Synthesis and X-ray Crystal Structure of $[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2CH_2PPr^i{}_2)_2]Zr{=}CHPh(Cl)$

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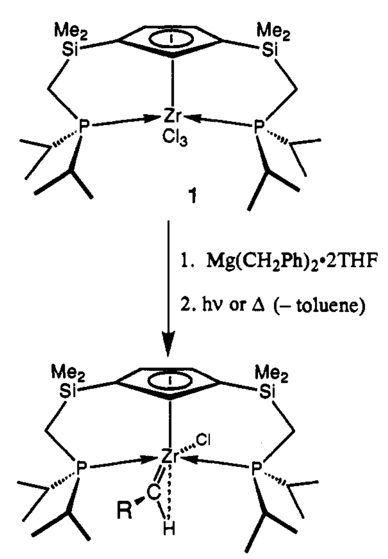
Alkylidene complexes of the general formula $L_nM{=}CHR$ are now recognized as key derivatives used to initiate olefin metathesis reactions[1] and ring-opening metathesis polymerization (ROMP) processes.[2-7] In addition, such complexes can be employed in stoichiometric reactions as "Wittig-type" reagents to produce olefins from ketones and esters.[8-12] One of the preparative routes to generate an alkylidene unit on a metal is via α-hydrogen abstraction, whereby a bis(hydrocarbyl) precursor eliminates alkane either photochemically or thermally.[13-15] While this process is common for the synthesis of group 5 and 6 alkylidene derivatives,[13,14] it is quite uncommon for group 4 derivatives.[16,17] For example, $Cp^*{}_2TiMe_2$ does eliminate CH_4, but the final product is not a methylidene derivative.[18] Attempts to prepare alkylidene derivatives of zirconium via α-hydrogen abstraction of bis(neopentyl)-type complexes led to disproportionation and Zr–C bond homolysis to give Zr(III) dimers.[16] In fact, the only reports of alkylidene complexes of Zr involve the in situ detection of thermally labile $Cp_2Zr{=}CH_2(PMePh_2)$ via reaction of $H_2C{=}PPh_3$ with a zirconocene phosphine complex[19] and the preparation of $Cp_2Zr{=}CHCH_2R(L)$-type complexes as thermally labile oils by HMPA-induced bridge cleavage of alkylidene-bridged zirconocene–aluminum precursors.[20] In this report we present the synthesis and solid-state structure of the first authentic example of a stable alkylidene complex of zirconium formed via an α-hydrogen abstraction process.

Scheme I



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4 R = Ph

The starting zirconium complex, $[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2CH_2PPr^i{}_2)_2]ZrCl_3$ (**1**, $[P_2Cp]ZrCl_3$), prepared by addition of $[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2CH_2PPr^i{}_2)_2]Li$[21] to $ZrCl_4(THT)_2$ (THT = tetrahydrothiophene) in toluene, reacts with 1 equiv of $Mg(CH_2Ph)_2{\cdot}2THF$[22] to generate a 1:1 mixture of the corresponding monobenzyl derivative, $[P_2Cp]ZrCH_2Ph(Cl)_2$ (**2**) and the tris(benzyl) complex $[P_2Cp]Zr(CH_2Ph)_3$ (**3**); none of the expected bis(benzyl) derivative could be detected by either $^{31}P\{^1H\}$ or ^1H NMR spectroscopy. However, when this mixture of **2** and **3** was photolyzed or thermolyzed, a smooth reaction was observed and the benzylidene complex $[P_2Cp]Zr{=}CHPh(Cl)$ (**4**) was isolated in 85% yield after crystallization from pentane (Scheme I).[23]

Particularly diagnostic of the benzylidene unit is the presence of a resonance at 8.1 ppm in the ^1H NMR spectrum for the benzylidene proton ($Zr{=}C\mathit{H}Ph$) and a doublet of triplets at 229.4 ppm in the coupled ^{13}C NMR spectrum due to the benzylidene carbon ($Zr{=}CHPh$); the rather low carbon–hydrogen coupling constant, $^1J_{HC}$, of 86.8 Hz, can be ascribed to evidence of an agostic interaction with the Zr center.[24]

The structural assignment of the benzylidene complex based on solution data has been confirmed by an X-ray crystal structure

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(21) The preparation of the ancillary ligand $[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2CH_2PPr^i{}_2)_2]Li$ is via the reaction of 3 equiv of $LiPPr^i{}_2$ with $5,5\text{-}C_5H_4\text{-}(SiMe_2CH_2Cl_2)$ prepared according to the method of Pribytkova, I. M.; Kisin, A. V.; Luzikov, Yu. N.; Makoveyeva, N. P.; Torocheshnikov, V. N.; Ustynyuk, Yu. A. *J. Organomet. Chem.* **1971**, *30*, C57.

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(23) For **4**: ^1H NMR (C_6D_6, 500 MHz) δ 8.08 (s, 1H, CHPh), 7.54 (t, J = 1.6 Hz, 1H, C_5H_3), 7.34 (d, J_{o-m} = 7.5 Hz, 2H, $o\text{-}C_6H_5$), 7.22 (t, J_{m-o} = 7.4 Hz, J_{m-p} = 7.3 Hz, 2H, $m\text{-}C_6H_5$), 6.77 (t, J_{p-m} = 7.1 Hz, 1H, $p\text{-}C_6H_5$), 6.20 (d, J = 1.6 Hz, 2H, C_5H_3), 2.56 (sept, J = 7.0 Hz, 2H, $CHMe_2$), 1.75 (d of sept, J_{H-H} = 7.0 Hz, J_{H-P} = 3.3 Hz, 2H, $CHMe_2$), 1.31 (d of d, J_{H-H} = 7.0 Hz, J_{H-P} = 13.7 Hz, 6H, $CH(C\mathit{H}_3)_2$), 1.07 (d of d, J_{H-H} = 7.1 Hz, J_{H-P} = 15.4 Hz, 6H, $CH(C\mathit{H}_3)_2$), 1.00 (d of d, J_{H-H} = 6.9 Hz, J_{H-P} = 10.6 Hz, 6H, $CH(C\mathit{H}_3)_2$), 0.87 (d of d, J_{H-H} = 6.8 Hz, J_{H-P} = 9.7 Hz, 6H, $CH(C\mathit{H}_3)_2$), 0.62 (d of d, J_{H-P} = 5.0 Hz, J_{H-H} = 4.3 Hz, 2H, $SiCH_2P$), 0.55 (d of d, J_{H-P} = 5.0 Hz, J_{H-H} = 4.3 Hz, 2H, $SiCH_2P$), 0.36 (s, $SiCH_3$, 6H), 0.20 (s, $SiCH_3$, 6H); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 229.4 (t, J_{P-C} = 8.0 Hz), 148.9 (t, J = 2.0 Hz), 128.3, 125.8 (t, J = 1.4 Hz), 122.5, 121.7 (t, J = 1.0 Hz), 115.6 (t, J = 2.9 Hz), 112.2 (t, J = 1.0 Hz), 34.4, 30.2, 27.8 (t, J = 5.4 Hz), 22.8 (t, J = 3.3 Hz), 22.7, 20.3 (t, J = 3.0 Hz), 19.2 (t, J = 2.3 Hz), 18.8 (t, J = 2.4 Hz), 16.6 (t, J = 2.3 Hz), 14.2, 7.2 (t, J = 4.1 Hz), 1.5 (t, J = 2.9 Hz), –1.8; ^{13}C NMR 229.4 (d of t, J_{H-C} = 86.8 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6, 405 MHz) δ 18.81.

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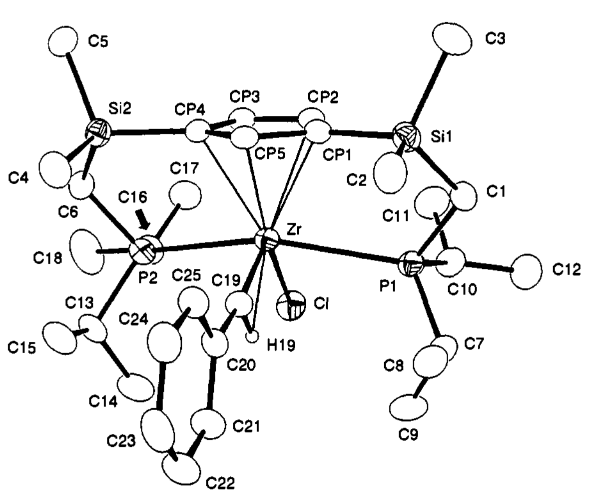

Figure 1. Labeled ORTEP view of **4**. Important bond distances (angstroms) and angles (degrees): Zr–Cl 2.5418(13), Zr–P1 2.8299(16), Zr–P2 2.8425(17), Zr–Cp1 2.564(4), Zr–Cp2 2.521(4), Zr–Cp3 2.499(4), Zr–Cp4 2.544(4), Zr–Cp5 2.575(4), Zr–C19 2.024(4), C19–C20 1.456(5), C19–H19 0.93(4), Zr···H19 2.07(4), Zr–Cp(cent) 2.234, P1–Zr–P2 153.58(4), Cl–Zr–P1 77.23(4), Cl–Zr–P2 76.35(4), Cl–Zr–C19 110.11(11), P1–Zr–C19 94.47(12), P2–Zr–C19 94.20(12), Zr–C19–C20 169.2(3), Zr–C19–H19 79.8(23), C20–C19–H19 111.0(23).

determination;[25] the results are summarized in Figure 1 along with some selected bond lengths and bond angles. The critical feature is the benzylidene unit with a Zr-C bond distance of 2.024(4) Å and the presence of an agostic C—H···Zr interaction; this hydrogen was located and refined. The Zr···H distance is 2.07(4) Å and the Zr–C19–C20 angle is 169.2(3)°; the Zr–C19–H angle is 79.8(23)°. A series of NOEDIFF ^{1}H NMR experiments confirms that the solid-state structure is maintained in solution. For example, irradiation of the unique cyclopentadienyl proton (CP5–H) results in significant enhancement of both ortho protons of the phenyl group but no enhancement of the benzylidene hydrogen; irradiation of the remaining two equivalent cyclopentadienyl protons (CP2-H and CP3-H) leads to no enhancement of any protons on the benzylidene unit. That the benzylidene fragment is found *syn* to the unique cyclopentadienyl carbon (CP5) is surprising, and thus far we cannot explain the stereoselectivity of this reaction. Variable-temperature NMR studies show that phosphine dissociation is slow (undetectable) on the NMR time scale, and, in addition, no rotation of the benzylidene unit about the Zr=C double bond is observed.

The mechanism of this reaction is under investigation. However, the evidence for an α-abstraction process comes from some simple stoichiometry experiments. If the starting trichloride **1** is allowed to react with 0.5 equiv of $Mg(CH_2Ph)_2{\cdot}2THF$, the monobenzyl complex **2** can be prepared cleanly; similarly, the reaction of 1.5 equiv of $Mg(CH_2Ph)_2{\cdot}2THF$ generates the tris(benzyl) derivative **3**, free of other species. Neither of these two species is thermally sensitive or reacts with light as a separate species. However, if they are mixed in equimolar amounts and thermolyzed at 65 °C for 3 h, the benzylidiene complex is generated quantitatively by NMR spectroscopy. Therefore, we presume that the bis(benzyl) complex $[P_2Cp]Zr(CH_2Ph)_2Cl$, although undetectable, is being formed in equilibrium with the mono- and tris(benzyl) derivatives, but it is the bis(benzyl) derivative that is photochemically and thermally labile. Experiments are in progress to test this hypothesis as well as to examine the generality of this process by the attempted preparation of other zirconium bis(hydrocarbyl) complexes stabilized by this new ancillary ligand.

Preliminary reactivity studies of the benzylidene complex **4** show that it is very reactive. For example, addition of acetone results in the formation of the corresponding olefin, $Me_2C{=}CHPh$, quantitatively (by GC-MS); other reactions include adduct formation with ethylene, while reactions with H_2 and $PhSiH_3$ generate hydride Zr derivatives. Investigations into the nature of these reaction products are currently in progress.

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Supplementary Material Available: Full experimental details and spectroscopic data for the preparation of the zirconium complexes **1–4**; details of the X-ray analysis; atomic and hydrogen positional parameters for **4**; anisotropic temperature factors; tables of bond lengths and bond angles (10 pages); observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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(25) Crystal data for **4**: $C_{30}H_{53}ClP_2Si_2Zr{\cdot}0.5C_6H_{14}$, triclinic, $P\bar{1}$, a = 11.882(3) Å, b = 12.435(4) Å, c = 14.112(8) Å, α = 98.74(4)°, β = 95.50(3)°, γ = 110.68(3)°, V = 1902.7(13) Å^3, Z = 2, D_{calc} = 1.22 g cm^{-3}, T = 298 K, μ(Mo Kα) = 0.52 mm^{-1}. Data were collected on a Nonius diffractometer using the ω scan mode ($2\theta_{max}$ = 45°); of the 4978 reflections measured, 4967 were unique and 3912 had $I_{net} > 3\sigma I_{net}$. After anisotropic refinement of all non-hydrogen atoms, H19 was located via difference Fourier map inspection and refined with a fixed temperature factor; the remaining hydrogens were idealized. $R(F)$ = 3.3%; $R(wF)$ = 3.2% (all data 3.2%). All crystallographic calculations were conducted with the PC version of the NRCVAX program package locally implemented on an IBM compatible 80486 computer, see: Gabe, E. J.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.