

Nucleophilic Character of a Charge Neutral, High Oxidation State d^0 Zirconium Trimethylenemethane Complex

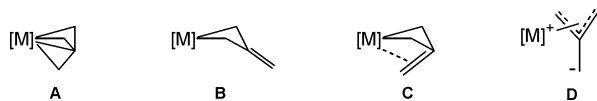
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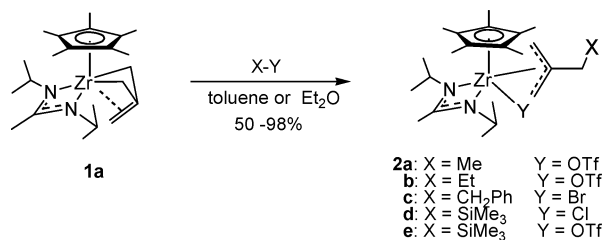
Organozirconium chemistry, as applied to organic synthesis, has become synonymous with bis(cyclopentadienyl)zirconium(IV) and -zirconium(II) complexes (also known as zirconocenes), and after nearly 50 years of development,¹ its value to the synthetic chemist continues to grow at a constant pace.² With respect to carbon-carbon bond-forming reactions, however, organozirconocene derivatives are still principally limited to insertion of $X=Y$ or $X\equiv Y$ species (e.g., alkenes, alkynes, carbon monoxide, and isonitriles) into preexisting Zr-C bonds, and as recently pointed out by Negishi and Huo,³ this state of affairs represents "a stifflingly severe restriction, which must nevertheless be dealt with by synthetic chemists." One strategy by which to achieve this goal is to look for new patterns of reactivity among nonzirconocene complexes that might then expand the range of synthetic possibilities. Herein, we present the nucleophilic behavior of charge neutral, high oxidation state d^0 zirconium trimethylenemethane (TMM) complexes of the general formula $Cp^*Zr(TMM)[N(R^1)C(Me)N(R^2)]$ ($Cp^* = \eta^5-C_5Me_5$) (**1**) that can engage in carbon-carbon bond-forming reactions with organic electrophiles, including unactivated ones. While knowledge of this reactivity may now lead to the development of new classes of bifunctional TMM reagents for the construction of complex organic molecules,⁴ perhaps the more important extension of these findings is that the monocyclopentadienyl/amidinate ligand combination upon which **1** is based may prove complementary to zirconocenes for developing a range of new synthetic methodologies.⁵

To date, only four early transition-metal TMM complexes have been reported, but within this group, three strongly differing bonding schemes between the metal and the TMM fragment, which is a formal -2 charged, six-electron donor ligand, have been described.⁶⁻¹⁰ More specifically, the η^4 -TMM bonding mode (A) has been invoked for neutral $Cp^*Ta(TMM)Me_2$ ⁶ and anionic $[Cp^*Zr(TMM)(\mu-Cl)_2Li-(TMEDA)]^-$ (TMEDA = *N,N,N',N'*-tetramethylethylenediamine), whereas the zirconocene complex, $Cp^*_2Zr(TMM)$,⁸ clearly adopts the σ^2 -TMM structure (B) in both solution and the solid state.



On the basis of crystallographic information, we previously reported that derivatives of **1** where $R^1 = R^2 = i\text{-Pr}$ (**1a**) and $R^1 = t\text{-Bu}$, $R^2 = Et$ (**1b**), are best represented as supporting the σ^2, π -TMM interaction (C) in the solid state because of the large observed difference in Zr-C distances between two sets of this geometric parameter involving the metal center and the three carbon termini of the TMM fragment (cf. Zr-C: 2.3774(17) and 2.3888(17) Å (bonded) and 2.642 Å (nonbonded) in **1a**). As depicted, all of these structures, A-C, conform to generally accepted conventions, and none are particularly suggestive of any unusual physical property or reactivity. However, subsequent observation of a significantly

Scheme 1



low ΔG_c^\ddagger value of 10.1 kcal mol⁻¹ ($T_c = 273$ K) for the barrier to rotation of the TMM fragment in **1a**, coupled with a facile reaction between **1b** and electrophilic $B(C_6F_5)_3$ to produce the charge-neutral zwitterion, $\{Cp^*Zr[\eta^3-CH_2C(CH_2)CH_2B(C_6F_5)_3][N(t-Bu)C(Me)N(Et)]\}^{0b}$, led us to speculate that the TMM fragment in **1** might possess significant zwitterionic ground state character due to a contribution from a resonance structure in which the TMM fragment can be represented as a resonance-delocalized coordinated allyl anion as in structure D. Preliminary theoretical support for this hypothesis was provided by DFT methods, as implemented by the Jaguar 3.5 computational package, which not only provided an optimized equilibrium structure for **1a** that closely mirrored that of the experimentally determined solid-state structure, but which further revealed that the electrostatic potential of this complex as mapped onto the overall density surface possesses a high concentration of negative charge on the TMM fragment that gives rise to an associated molecular dipole of 3.5 D.¹¹ This latter finding then led to a further hypothesis that compounds such as **1a** and **1b** ought to be reactive toward various electrophiles and, perhaps, even unactivated ones at that. To probe this idea, the nucleophilic character of **1a** was tested with a wide range of organic and silyl electrophiles, and as Scheme 1 reveals, it was quickly discovered that apparent nucleophilic attack by the TMM moiety proceeded with alkyl triflates, benzyl bromide, trimethylsilylchloride and -triflate to produce the corresponding substituted allyl complexes **2a-e** in nearly quantitative yields as determined by ¹H NMR spectroscopy (50-98% isolated yields).¹¹ To the best that we can establish, these reactions represent the first examples of the uncatalyzed direct nucleophilic substitution of organohalides or organotriflates by an early transition-metal organometallic complex, and they are more significant given both the d^0 high oxidation state and formal electron deficiency of the metal center in **1**, which suggests that, similar to organozirconocenes, these complexes should possess very little, if any, intrinsic nucleophilicity.¹² It is further important to distinguish these nucleophilic substitution reactions from the well-known insertion of C-X multiple bonds ($X = O$ and N) into early transition-metal alkyl and metal allyl bonds, including TMM complexes,^{8,10b} as these most likely proceed through a mechanistically different path involving prior coordination of the X atom to the metal center.^{2,3} In fact, compound **1a**, not surprisingly, was found to readily react with benzaldehyde and benzophenone to

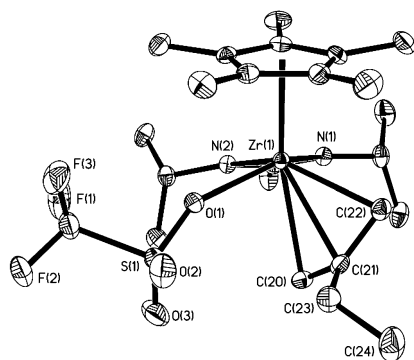
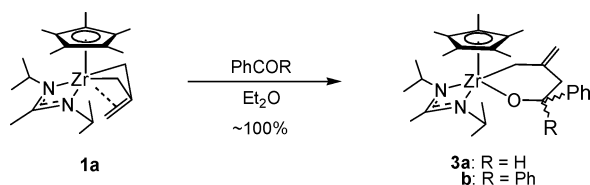


Figure 1. Molecular structure (30% thermal ellipsoids) of **2a**. Hydrogen atoms have been removed for the sake of clarity.

Scheme 2

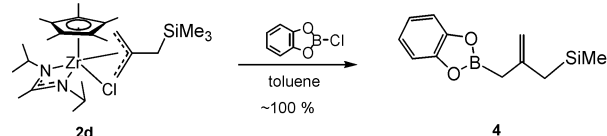


provide the heterocyclic insertion products **3a** and **3b**, respectively, shown in Scheme 2.

As proof of structure, crystallographic analyses of **2a** and **3b** were conducted, which revealed a molecular structure for the former compound in which the new C_5H_9 moiety can best be described as a distorted σ,π -allyl ligand (cf. Zr(1)–C(22) 2.371(3) Å vs Zr(1)–C(20) 2.619(3) Å and Zr(1)–C(21) 2.559(3) Å) (see Figure 1).^{11,13} It is possible, however, that this deviation from a symmetric η^3 -allyl ligation might be enforced more by nonbonded steric interactions, as suggested by a space-filling representation of the molecular structure, rather than a consequence of any electronic factors. Finally, in the solid-state structure of **3b** (not shown), the allyl moiety is clearly bound in an η^1 -fashion with the metal center.¹¹

To further probe the nucleophilic behavior of this class of TMM complex, the reaction of **1a** with benzyl bromide was studied in more detail. To begin, this reaction is clearly facilitated by more polar solvents (cf. $k_{\text{obs}} = 0.0026(3) \text{ s}^{-1}$ (C_6D_6) vs $0.0075(3) \text{ s}^{-1}$ (THF- d_8) in formation of **2c** under pseudo-first-order conditions at 30 °C using a 10-fold excess of benzyl bromide).¹¹ Further, a detailed kinetic analysis of the formation of **2c** in THF- d_8 over the temperature range of 10–40 °C (five points) yielded the thermodynamic parameters, $\Delta H^\ddagger = 12.1(9) \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -28.0(9) \text{ esu}$, which are consistent with a classic associative nucleophilic substitution (i.e., S_N2 -like) mechanism. Finally, with the reactivity established of **1a** toward a variety of electrophiles, including unactivated ones such as ethyl triflate, it was of interest to explore the potential synthetic utility of this chemistry. In this regard, symmetric and unsymmetric bifunctional TMM reagents are important building blocks for the construction of complex organic molecules.⁴ Hence, it was gratifying to find that reaction of compound **2d** with *B*-chlorocatecholborane proceeded in a near quantitative yield as determined by ¹H NMR spectroscopy to provide the new unsymmetric bifunctional TMM compound **4** as a colorless oil (see Scheme 3). Alternatively, **4** could be prepared in a similar high yield by carrying out the two reactions with **1a** in a

Scheme 3



“one-pot” fashion. Further studies are currently under investigation to explore the utility of **2** for the palladium-catalyzed zirconium–Negishi coupling with electrophiles.¹²

In summary, this report presents the nucleophilic behavior of a charge neutral, high oxidation state zirconium TMM complex that, based upon standard conventions, would not have been readily expected. However, with the availability of computational methods that includes new means by which to analyze the nature of metal–ligand bonding interactions,¹⁴ the precise origin of this novel behavior should be forthcoming. Additional investigations of unique reaction paths involving **1** and other Zr(IV) and Zr(II) complexes based on the monocyclopentadienyl/amidinate ligand combination are also currently in progress.

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Supporting Information Available: Experimental details (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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