Functionalization of Complexed N\textsubscript{2}O in Bis(pentamethylcyclopentadienyl) Systems of Zirconium and Titanium

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ABSTRACT: Methyl triflate reacts with the metastable azoxymetallacyclopentene complex Cp\textsuperscript{\#}Zr(N(O)NC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5})\textsubscript{2}, generated in situ from nitrous oxide insertion into the Zr–C bond of Cp\textsuperscript{\#}Zr(r\textsuperscript{2}-PhC\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5}) at −78 °C, to afford the salt [Cp\textsuperscript{\#}Zr(N(O)(N(Me)C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5}))][O\textsubscript{3}SC\textsubscript{6}H\textsubscript{5}] (1) in 48% isolated yield. A single-crystal X-ray structure of 1 features a planar azoxymetallacycle with methyl alkylation taking place only at the β-nitrogen position of the former Zr(N(O)NC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5}) scaffold. In addition to 1, the methoxy-triflate complex Cp\textsuperscript{\#}Zr(OMe)(O\textsubscript{3}SC\textsubscript{6}H\textsubscript{5}) (2) was also isolated from the reaction mixture in 26% yield and fully characterized, including its independent synthesis from the alkylation of Cp\textsuperscript{\#}Zr(Oi\textsubscript{2}C\textsubscript{6}H\textsubscript{5}) with MeO\textsubscript{3}SC\textsubscript{6}H\textsubscript{5}. Complex 2 could also be observed, spectroscopically, from the thermolysis of 1 (80 °C, 2 days). In contrast to Cp\textsuperscript{\#}Zr(N(O)NPhCC\textsubscript{6}H\textsubscript{5}), the more stable titanium N\textsubscript{2}O-inserted analogue, Cp\textsuperscript{\#}Ti(N(O)NC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5}), reacts with MeO\textsubscript{3}SC\textsubscript{6}H\textsubscript{5} to afford a 1:1 mixture of regioisomeric salts, [Cp\textsuperscript{\#}Ti(N(O)(N(Me)C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5}))][O\textsubscript{3}SC\textsubscript{6}H\textsubscript{5}] (3) and [Cp\textsuperscript{\#}Ti(N(OMe)NC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5})][O\textsubscript{3}SC\textsubscript{6}H\textsubscript{5}] (4), in a combined 65% isolated yield. Single-crystal X-ray diffraction studies of a cocrystal of 3 and 4 show a 1:1 mixture of azoxymetallacylates salts resulting from methyl alkylation at both the β-nitrogen and the β-oxygen of the former Ti(N(O)NC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5}) ring. As opposed to alkylation reactions, the one-electron reduction of Cp\textsuperscript{\#}Ti(N(O)NC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5}) with KC\textsubscript{8}, followed by encapsulation with the cryptand 2,2,2-Krypto\textsubscript{2}, resulted in the isolation of the discrete radical anion [K(2,2,2-Krypto\textsubscript{2})][Cp\textsuperscript{\#}Ti(N(O)NC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5})] (5) in 68% yield. Complex 5 was studied by single-crystal X-ray diffraction, and its solution X-band EPR spectrum suggested a nonbonding σ-type wedge hybrid orbital on titanium, d(\(x^{2}\))/d(\(y^{2}\)–\(z^{2}\)), houses the unpaired electron, without perturbing the azoxymetallacycle core in Cp\textsuperscript{\#}Ti(N(O)NC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5})PPh\textsubscript{3}(O\textsubscript{3}SC\textsubscript{6}H\textsubscript{5}). Theoretical studies of Ti and the Zr analogue are also presented and discussed.

INTRODUCTION

Due to the thermodynamic oxidizing power of nitrous oxide (\(\Delta \textit{G}^\circ = 25 \text{ kcal/mol}\)) and its kinetic inertness in the absence of a suitable activating metal center, the development of systems capable of catalyzing the oxidation of organic or inorganic substrates using this greenhouse feedstock represents a paradigm in inorganic chemistry.\textsuperscript{1,2} Unlike most common powerful oxidants, nitrous oxide is cheap and very soluble in organic solvents such as toluene, alcohols, ethers, oils, water, and acids, with the advantage of such a chemical being resourceful, nonflammable, and essentially harmless. Therefore, it is not surprising that there has been considerable interest in employing N\textsubscript{2}O for oxygen-atom transfer reactions.\textsuperscript{3–21} Unfortunately, and as noted before, this molecule is kinetically inert due to its poor properties as a ligand,\textsuperscript{22–24} consequently resulting in only a handful of systems being capable of complexing N\textsubscript{2}O without the entropic and enthalpic driving force to N\textsubscript{2}O ejection and metal oxo formation.\textsuperscript{1,12,18,22–31} Thus, the use of N\textsubscript{2}O as an oxidizing substrate in transition metal chemistry is often hampered by a combination of kinetic inertness and inevitable oxidation of the metal center, concomitant with entropy-assisted loss of a thermodynamically stable molecule such as dinitrogen.\textsuperscript{22}

Given the disposition of nitrous oxide as being a poor ligand in the realm of coordination chemistry, our group and others are pursuing the use of nitrous oxide in O atom transfer systems for the purpose of oxidation catalysis. Previously, we reported that group 4 transition metals (Ti and Zr) can insert nitrous oxide into a strained M–C bond without oxidation of the metal center to form bis(pentamethylcyclopentadienyl) systems, having coordinated N\textsubscript{2}O as part of the ligand scaffold (Scheme 1).\textsuperscript{11,12} As a result, N\textsubscript{2}O functionalizes the ligand (e.g, tolane) \textit{without immediate extrusion} of N\textsubscript{2}. Although N\textsubscript{2} extrusion can in one case occur, affording an oxametallacycle, this process depends heavily on the metal in question (zirconium vs titanium, Scheme 1).\textsuperscript{12} The fact that the azoxymetallacycle complex Cp\textsuperscript{\#}Ti(N(O)NC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5}) was not prone to dinitrogen elimination under ambient conditions (unlike its Zr derivative), to give a hypothetical oxametallacylobutene system Cp\textsuperscript{\#}Ti(OCP\textsubscript{3}CH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5}), led us to speculate that such a system could be ideal for O atom and/or functionalization reactions stemming from N\textsubscript{2}O complexation (Scheme 1).\textsuperscript{11} In addition, the azoxymetallacylobutene moiety in complexes of the type Cp\textsuperscript{\#}M(N(O)NC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5}) (M = Ti or Zr)
Organometallics

Scheme 1. Nitrous Oxide Insertion into a Strained Metal–Carbon Bond of an η²-Tolane Bis(pentamethylocyclopentadienyl) Complex and N₂ Extrusion to Form an Oxytetracacylobutene

Scheme 2. Proposed Canonical Forms for the Azoxytetracacylobutene Framework in Complexes of the Type Cp*₂M(N(O)NCPCHP) (M = Ti and Zr)

structures A and B represent zwiternionic forms with negative charge being localized on β-O and the β-N, respectively, resonance form C can be best represented as an ylide, having more nucleophilic character on O (Scheme 2). Another probable form in Cp*₂M(N(O)NCPCHP) is the formation of an N-nitroso ketimine tethered alkyldiene moiety, resonance D, where most of the nucleophilic charge is presumed to reside at the hindered alkyldiene carbon (Scheme 2). Hence, examining the reactivity of Cp*₂M(N(O)NCPCHP) with an electrophile could provide some clues as to which site is likely most nucleophilic, but also allow us to further functionalize the N(O)N motif resulting from N₂O insertion into a strained M–C bond. Surprisingly, examples of homogenous catalytic oxidation reactions using N₂O as an O atom transfer reagent are exceedingly rare, and examples include the oxidation with N₂O of PPh₃ using a cobalt(I) complex and the oxidation of styrene by a ruthenium porphyrin system. Unfortunately, the latter reaction has yet to be developed into an efficient catalytic cycle. This lackluster situation in homogeneous catalysis is rather unanticipated given the popular usage of N₂O in heterogeneous catalytic reactions such as the oxidation of benzene to phenol over supported metals or Fe and Ru/ZSM-5 zeolites and the oxidation of methane on silica-molybdate catalyst.

Herein, we report comparative studies of the reaction of an electrophile, such as MeO₂SCF₃ with the oxyzotetracylobutene scaffold in the compounds Cp*₂M(N(O)NCPCHP) (M = Ti or Zr). Thermoconductibility of the salt and the fate of coordination of the methyl cation were found to be highly dependent on the nature of the metal. In addition, it was also observed that the oxyzotetracylobutene scaffold of complex Cp*₂Ti(N(O)NCPCHP) can be resistant to reducing conditions and house one unpaired electron, in the form of the radical anion titanium(III) species [Cp*₂Ti(N(O)-NCPCHP)]⁻, without significant perturbation of the oxozometalliclobutene core.

### EXPERIMENTAL SECTION

**General Considerations.** Unless stated otherwise, all operations were performed in an M. Braun Lab Master drybox under an atmosphere of purified nitrogen or using high-vacuum and standard Schlenk techniques under an argon atmosphere. HPLC grade or anhydrous solvents such as benzene, toluene, diethyl ether, n-hexane, pentane, and CH₂Cl₂ were purchased from Acros Chemicals or EM Science and were further dried by passage through activated alumina and/or Q-S columns. THF was distilled from purple benzophenone ketyl solution under an inert atmosphere. C₆D₆, THF-d₈, and CDCl₃ were purchased from Cambridge Isotope Laboratory (CIL), degassed and dried under vacuum to afford a white powder. All other chemicals were used as received. Elemental analysis was performed by Desert Analytics (Tucson, AZ, USA).

**Preparation of Cp*₂Zr(N(O)N(Me)CPCHP)O₂SCF₃ (1).** Toluene (ca. 20 mL) was vacuum transferred into a Schlenk flask equipped with a stir bar and Cp*₂Zr(p^²-PhCPCHP) [554 mg, 1.027 mmol]. The solution was placed under an N₂O atmosphere at -78 °C, causing a rapid color change from green-brown to orange. The orange solution was stirred under an atmosphere of N₂O at -78 °C for 1 h and then degassed. To the orange solution was added via cannula a similarly cold (~ -78 °C) toluene solution (ca. 8 mL) of MeO₂SCF₃ [171 mg, 1.042 mmol] under an argon atmosphere. The mixture was allowed to stir for 2 h at -78 °C, and the mixture was then slowly warmed to ~42 °C and stirred for an additional 0.5 h, upon which an orange microcrystalline solid was observed to precipitate. Slow warming of the solution to room temperature afforded a yellow-orange solution with an orange precipitate. The reaction mixture was transferred into the glovebox and cooled to ~35 °C. The cold solution was then filtered to remove the orange crystalline solid, which was washed with cold toluene followed by cold pentane. The solid was dried under vacuum to afford pure 1 [373 mg, 0.499 mmol, 48% yield in one crop].

**31H NMR (22 °C, 500.1 MHz, CDCl₃):** δ 1.57 (s, 1H).
C_{19}(CH_{3})_{3}, 30 H), 3.05 (s, NCH_{3} H), 3.52 (d, 6-OH, 2 H), 6.75 (m, Ph, 3 H), 7.08 (m, Ph, 2 H), 7.24 (m, Ph, 3 H). 1^1C NMR (22 °C, 125.8 MHz, CDCl_{3}); δ 11.91 (q, C_{1}(CH_{3})), 37.20 (q, NCH_{3}), 127.3 (s, C_{2}(CH_{3})), 128.3, 128.8, 130.4, 130.5, 130.7, 133.4 (s), 137.5 (s), 190.8 (s). 2^1F NMR (22 °C, 470.6 MHz, CDCl_{3}); δ −81.7 (s, O_{2}SCF_{3}). Anal. Calcd for C_{21}H_{22}F_{3}O_{4}SZr: C, 48.77; H, 6.14; N, 0.00. Found: C, 48.90; H, 6.03; N, <0.09.

Preparation of C_{2}Zr(MeO)(OSCF_{3}) (2). Method A. The analogous procedure and scale reported for 1 was followed, and after separation of the toluene insoluble salt, 1, the filtrate was dried under vacuum and extracted with pentane, the solution filtered through Celite, the filtrate concentrated to ∼2 mL, and then the solution cooled to −35 °C for 3–4 days under N_{2}. The yellow solid was collected via filtration and dried under vacuum to afford pure 2 as evidenced by 1H NMR spectroscopy [143 mg, 0.264 mmol, 26% yield in two crops]. Examination of the pentane filtrate (after separation of 2) revealed a mixture of free toluene (PhCHCPh) along with compound 2, as well as some other minor intractable products. Complex 2 is highly soluble in hydrocarbon solvents, but analytically pure complex can be obtained from recrystallization of the solid from a saturated solution in diethyl ether at −35 °C over 5–6 days. 1H NMR (22 °C, 500.1 MHz, CDCl_{3}); δ 1.80 (s, C_{2}(CH_{3})), 30.43 (s, OCH_{2}H), 3.03 (s, OCH_{2}H). 1^1C NMR (22 °C, 125.8 MHz, CDCl_{3}); δ 10.99 (q, C_{1}(CH_{3})), 59.31 (s, OCH_{2}), 123.2 (s, C_{2}(CH_{3})), 128.3 (s, O_{2}SCF_{3}). 2^1F NMR (22 °C, 470.6 MHz, CDCl_{3}); δ −78.7 (s, O_{2}SCF_{3}). Anal. Calcd for C_{21}H_{22}F_{3}O_{4}SZr: C, 48.77; H, 6.14; N, 0.00. Found: C, 48.90; H, 6.03; N, <0.09.

Preparation of C_{2}Zr(MeO)(OSCF_{3}) (2). Method B. In a vial loaded with a stir bar C_{2}Zr(0)(NCCH_{3}) [100 mg, 0.219 mmol] was partially dissolved in toluene (ca. 5 mL), and the suspension cooled to −35 °C. A cold toluene solution (−35 °C, ca. 5 mL) containing MeO_{2}SCF_{3} [38 mg, 0.236 mmol] was added dropwise, and the brown-yellow mixture was allowed to stir for 1 h. The volatiles were removed under reduced pressure, the yellow-brown residue was extracted with pentane and filtered through Celite, and the filtrate was dried under vacuum to afford pure 2 as a light yellow powder [106 mg, 0.196 mmol, 89% yield]. 1H NMR spectroscopy of the crude reaction mixture confirmed clean formation of 2 by comparison with authentic samples reported by method A.

Preparation of [C_{2}ZrTi(NOMe)(NCPhCPh)][O_{2}SCF_{3}] (3) and [C_{2}ZrTi(N(NOMe)(NCPhCPh))(OSCF_{3})] (4). In a Schlenk flask equipped with a stir bar C_{2}ZrTi(0)(NOMe)(NCPhCPh) [180 mg, 0.333 mmol] was dissolved in toluene (ca. 30 mL), and the orange solution was cooled to −78 °C. To the cold solution was added via cannula a solution of MeO_{2}SCF_{3} [58 mg, 0.353 mmol] dissolved in cold toluene (ca. 10 mL, −78 °C), causing a rapid color change to yellow-brown followed by immediate formation of a brown oil. The reaction mixture was slowly warmed to room temperature, and the solution transferred into the glovebox. The yellow mother liquor was decanted with a pipet, and the brown oil rinsed with toluene (1–2 mL) by diethyl ether (3 mL) and then n-hexanes (2 × 5 mL). The remaining oil was dried under reduced pressure, extracted with 2 mL of CH_{2}Cl_{2}, and filtered through a small pad of Celite, and the filtrate was concentrated to ∼1 mL. Subsequently, the solution was carefully layered with diethyl ether until a fine mist formed at the interface. Cooling the CH_{2}Cl_{2}/EtOAc layer solution to −35 °C for 6 days afforded dark-brown blocks. Decanting of the solution and washing of the crystals with 2–3 mL of Et_{2}O/pentane (1:1) afforded pure 3 and 4 in a 1:1 cocystal mixture, as evidenced by 1H and 1^1C NMR spectroscopy [160 mg, 0.227 mmol, 68% yield combined from two crops]. Note: The solution obtained after separating the crystals can be cooled for further several days to afford a second crop of 3 and 4. 1H NMR (22 °C, 500.1 MHz, CDCl_{3}); δ 7.56 (m, Ph), 7.47 (m, Ph), 7.37 (m, Ph), 7.04 (m, Ph), 6.91 (s, Ph), 6.02 (br s, Ph), 5.58 (d, Ph), 5.93 (s, OCH_{2}), 3.56 (s, NCH_{3}), 2.93 (s, CH_{3}), 3.00 (s, CH_{3}). 1^1C NMR (22 °C, 125.8 MHz, CDCl_{3}); δ 225.8 (s, Ti-C), 204.3 (s, Ti-C), 141.3, 140.2, 139.0, 138.2, 133.9, 131.8, 131.6, 131.3, 130.7 (br s, O_{2}SCF_{3}), 130.4 (m), 130.2, 129.7, 129.6, 129.4, 129.1, 128.9, 128.7, 128.0, 127.7, 60.0 (q, OCH_{2}).
space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set. A "hemisphere" data set was obtained, which samples approximately 1.2 hemispheres of reciprocal space to a resolution of 0.84 Å using 0.3 degree steps in ø and using 10 s interval times for each frame. Absorption corrections were applied using SADABS (references of all software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library, G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI, USA). The space group was determined based on systematic absences and intensity statistics. Direct or Patterson methods were used to locate the heavy atoms, C atoms, and all other heteroatoms from the E-map. Repeated difference Fourier maps allowed recognition of all expected H atoms. Prior to location of H, other atoms were converted to and refined anisotropically. Hydrogen atoms were refined isotropically and were placed in calculated positions. Structures were collected at 100 K. Crystal data and structure analysis results are shown in the Supporting Information.

Crystal Structure of 1. An orange thin plate of 1 grown from slow evaporation of a CH₂Cl₂ solution was selected under a stereomicroscope while immersed in Paratone oil (Exxon) to avoid minimal contact with air. The crystal was removed from the oil using a tapered fiber, which also served to hold the crystal for data collection. The structure was solved by direct methods in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically, and hydrogens were placed in calculated positions. The least-squares refinement converged normally.

Crystal Structure of Complex 3 and 4. A dark red-brown block of 3 and 4 grown from a CH₂Cl₂ solution layered with Et₂O at −35 °C was selected under a stereomicroscope while immersed in Paratone oil (Exxon) to avoid minimal contact with air. The crystal was removed from the oil using a tapered fiber, which also served to hold the crystal for data collection. The structure was solved by Patterson methods. Considerable electron density was confined next to O1. To account for this, the peak was selected as C1B and refined at nearly 1/2 occupancy with C1A. No anomalous bond lengths or thermal parameters were noted except for the methyl carbons C1a and C1b. Both atoms suffer from disorder and were fixed at approximately 0.52889 and 0.47111 occupancies using the second variable in the FVAR card, respectively. The thermal parameter was fixed for both atoms such that it would not change during refinement. Both C1a and C1b were refined anisotropically, but no hydrogens were placed at calculated positions for each of these atoms. All other non-hydrogen atoms were refined anisotropically, and hydrogens were placed in calculated positions. An absorption correction was applied in the refinement using semi-empirical methods from psi-scans (max. and min. transmission 0.8953 and 0.8639). The least-squares refinement converged normally. No extinction coefficient was applied.

Crystal Structure of Complex 5. A dark green block of 5 grown from a THF solution layered with a few drops of pentane/Et₂O at −35 °C was selected under a stereomicroscope while immersed in Paratone oil (Exxon) to avoid minimal contact with air. The crystal was removed from the oil using a tapered fiber, which also served to hold the crystal for data collection. The structure was solved by direct methods in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically, and hydrogens were placed in calculated positions. No absorption correction was applied in the refinement. The least-squares refinement converged normally, and no extinction coefficient was applied.

Computational Details. All calculations were performed with the Gaussian 09 package at the B3PW91 level of theory. Basis sets used included LANL2DZ for Ti and Zr and 6-31G(d) for H, C, N, and O. All non-hydrogen atoms were refined anisotropically, and hydrogens were placed in calculated positions. The initial geometry of Cp₂Ti(N(O)N(Me)CPhCPh) was adapted from a refined crystal structure of (Cp*₂)²Ti(N(O)NCPhCPh)11 with all methyl groups on the Cp* replaced with H and phenyl groups on the metallacycle replaced by methyls.

RESULTS AND DISCUSSION

Reaction of Zr(N(O)NCPH) and Cp*-Zr(O)(NC₅H₄) with MeOTf. As reported in earlier work,11,12 treatment of a toluene solution of Cp*-Zr(η3-P₃PhC₆H₄C) with N₂O at −78 °C results in insertion of nitrous oxide into the Zr−C(alkyne) bond to afford the orange and thermally unstable complex Cp*-Zr(N(O)NCPH), which was not characterized.11 Upon generation of metastable Cp*-Zr(N(O)NCPH), we found that addition of a cold toluene solution of Me₂SCF₃ to a solution of the reaction mixture, and, unlike its predecessor Cp*-Zr(N(O)NCPH), compound 1 is relatively stable as a solid when stored at −35 °C. The most salient spectroscopic feature associated with 1 is the observation of a singlet in the ¹H NMR spectrum at 3.05 ppm, which corresponds to the methyl resonance derived from addition of the electrophile to the N(O)N motif. Complex 1 also exhibits a singlet at 1.57 ppm for the methyl protons of the ancillary Cp* as well as multiplets ranging from 5.3 to 7.3 ppm, arising from the two inequivalent phenyl groups (10 hydrogens total). The insoluble nature of 1 in nonprotic and nonpolar solvents such as pentane, ether, and arenes suggests this system to be a discrete salt, while the ¹⁹F NMR spectrum also implies an OTf⁻ counterion to be present in this species (−81.7 ppm). The canonical forms, which are possible in the azoxymetallacyclobutene moiety in Cp*-Zr(N(O)NPPhCCPh) (vide supra, Scheme 2), suggest the β-O and β-N atoms to be the most exposed nucleophilic sites. In order to unambiguously
address the site of alkylation, a single-crystal X-ray diffraction study was undertaken. Accordingly, a single crystal was grown, and the molecular structure of 1 is shown in Figure 1, illustrating one of the two chemically equivalent, but crystallographically independent molecules in the asymmetric unit. One interesting feature associated with the molecular structure of 1 is the retention of an azoxymetallacyclobutene ring in Cp*Zr(N(O)NPhCCPh), a previously reported unstable complex that eluded crystallographic analysis due to its propensity to eject N₂ and subsequently form the oxygen-metalliclobutene compound (Scheme 1). In addition, the solid-state structure confirms methylation of the β-N position of the metallacycle (N(2)−C(1), 1.457(8) Å). For comparison, the N(1)−N(2) distance of 1.318(7) Å in the azoxymetallacyclobutene fragment is relatively elongated from that of the titanium and neutral analogue, Cp*Ti(N(O)NPhCCPh). Likewise, the N−O distance is shorter than in Cp*Ti(N(O)NPhCCPh), implying a canonical structure such as the one depicted in Scheme 3. The metrical parameters of 1 are overall consistent with an approximately planar five-membered metallacycle (Table 2) with a long N−N bond when compared to the

Table 2. Selected Bond Lengths (Å) and Dihedral Angles (deg) for Complex 1

<table>
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<th>Bond/Angle</th>
<th>Length (Å)</th>
<th>Dihedral Angle (deg)</th>
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<tr>
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<tr>
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<td>Zr(1)−C(31)−C(41)−N(2)</td>
<td>1.0(7)</td>
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</table>

similar functional group in p-azoxyanisole, p-MeOC₆H₄N-(O)≡NC₆H₄-p-OMe (N−N = 1.218(5) Å). As a result, complex 1 could also possess canonical forms A and C, as shown in Scheme 2, thereby forming a salt by positive charge at the β-nitrogen atom. The trapping and isolation of a discrete salt, 1, undoubtedly implies that the thermally unstable intermediate Cp*Zr(N(O)NPhCCPh) must be the species reacting with the electrophile, since such an intermediate undergoes thermal extrusion of N₂ to generate the oxygen-metalliclobutene complex Cp*Zr(OCPHCCPh).12

The moderate to low yield associated with the preparation of 1 suggested that other products could be formed from this reaction. Accordingly, it was found that the filtrate resulting from the separation of 1 contained another Zr(IV) material, namely, the alkoxide complex Cp*Zr(OOMe)(O3SCF₃) (2) in 26% yield, subsequent to recrystallization from pentane at −35 °C (Scheme 3). The low isolated yield of the substance can be attributed to its high lipophilicity in most common organic solvents, including pentane and hexane, in addition to complex 1 being the major product. Compound 2 displays ¹H NMR spectral resonances consistent with two equivalent Cp* rings (1.80 ppm), and a downfield singlet shift, which is diagnostic of a methoxide ligand (4.03 ppm). In addition, formation of a triflate complex was evidenced by a singlet at −78.7 ppm in the ¹³C NMR spectrum. Intuitively, the high solubility of 2 in most common organic solvents suggests the triflate anion to be coordinating to the coordinatively unsaturated zirconium(IV) center, especially when similar Cp*Zr(OR)(X) (R = SiMe₃, X = Cl; R = Me, X = I) have been reported. To substantiate the connectivity of 2, an independent and more convenient route to its formation was undertaken. It was found that complex 2 could be prepared in quantitative yield by alkylation of Parkin’s terminal oxo species Cp*Zr(O)(NC₅H₅) with MeO₃SCF₃ (Scheme 4). The formation of 2 from the alkylation of metastable Cp*Zr(N(O)NPhCCPh) suggested that 1, or the byproduct resulting from N₂ extrusion in Cp*Zr(N(O)NPhCCPh), could be reacting with MeO₃SCF₃. It was observed by ¹H NMR spectroscopy that complex 1 slowly decays in solution at −35 °C (several days) to afford a complicated mixture of products, one of which was indeed 2. In fact, thermolysis of complex 1 in chlorobenzene affords 2 and tolane among many other byproducts, but isolation of any zirconium complexes from the reaction mixture was hampered by their high solubility as well as their formation in low yield (Scheme 4). Independently, it was found that Cp*Zr(OCPHCCPh) does not react with MeO₃SCF₃ under similar conditions. Without going through 1, followed by analogous transformation steps such as ring expansion as well as N₂ and tolane elimination by retrocycloadditions. Another process could be a concerted addition of the methyl cation directly to the β-O atom of Cp*Zr(N(O)NPhCCPh) (without going through 1), followed by analogous transformation steps such as ring expansion as well as N₂ and tolane elimination or retrocycloaddition. Regardless, methyl alkylation at the β-N intuitively implies complex 1 to be a kinetic product. The hypothesis of whether alkylation takes place at the β-oxygen or β-nitrogen was further investigated by using a more stable analogue of 1, namely, the complex Cp*Ti(N(O)NPhCCPh), prepared analogously from the reaction of Cp*Ti(η²-PhCPh) with N₂O.13

Alkylation of Cp*Ti(N(O)NPhCCPh) with MeOTf. When a toluene solution of Cp*Ti(N(O)NPhCCPh) was treated with one equivalent of MeO₃SCF₃ at −78 °C, an

Figure 1. Perspective view of the molecular structure of only the cation component in complex 1 (and one crystallographically independent molecule), depicting the atom-labeling ellipsoid plot at the 50% probability level. H atoms have been omitted for clarity.
immediate precipitation of a brown oil was observed. Decanting the solution and extraction of the oil with CH$_2$Cl$_2$ followed by layering with Et$_2$O afforded dark maroon single crystals of a mixture of two salts, [Cp$_2^*_{2}$Ti(N(OMe)NCPhCPh)][O$_3$SCF$_3$] (3) and [Cp$_2^*_{2}$Ti(N(O)N(Me)CPhCPh)][O$_3$SCF$_3$] (4), in 68% combined isolated yield (Scheme 5). The $^1$H NMR spectrum of the salts revealed a nearly 1:1 ratio of compounds with characteristic resonances for the methyl protons on the Cp* rings as well as multiplets for a total of four different phenyl environments (two per complex). The most definitive evidence for formation of two complexes was the observation of two singlets residing at 3.93 (O-methyl moiety in 4) and 3.36 (N-methyl moiety in 3) ppm. We tentatively assign the latter resonances on the basis of electron-withdrawing effects of O vs N as well as comparison with the observed resonance for the N-bound methyl analogue, 1 (vide supra, 4.03 ppm). In addition, the $^{13}$C NMR spectrum corroborates formation of a mixture of salts via the observation of two distinct Ti−C resonances at 225.8 and 204.3 ppm, as well as the methyl carbon resonances (formally from Me$^+$ in MeOTf) at 60.0 and 37.2 ppm, respectively.

Single-crystal X-ray diffraction studies revealed not only that both 4 and 5 cocrystallize (one molecule per asymmetric unit) but that the methyl group is both observed at the $\beta$-O and $\beta$-N with nearly half-occupancies (Figure 2). Although our molecular structure (and NMR spectroscopy) provides concrete evidence for methylation taking place at both the $\beta$-O and $\beta$-N, the metrical parameters about the Cp$_2^*_{2}$Ti(N(O)-NCPHCPH) scaffold represent the average of the two systems, therefore limiting our discussion of resonances from the metrical parameters (Table 3 lists selected metrical parameters for the average of the core structures of 3 and 4 and comparison to the neutral species Cp$_2^*_{2}$Ti(N(O)NCPhCPh).11 As anticipated, multiple attempts to separate complexes 3 from 4 were hindered by their similar solubilities.

**Synthesis of the Ti(III) Radical Anion Salt [K(2,2,2-Kryptofix)][Cp$_2^*_{2}$Ti(N(O)NCPhCPh)] (6) and Theoretical Analysis of the Azoxytitanacyclobutene Fragment.** Our studies have demonstrated that the “N(O)N” moiety (derived from N$_2$O) in systems of the type Cp$_2^*_{2}$M(N(O)NCPhCPh) (M = Zr and Ti) can be further functionalized with an electrophile to form a metal-bound dialkylnitrosoamine, and in the case of titanium, the O-methylated regioisomer can be obtained as a mixture with the N-methylated product. Having studied the reactivity of complexed nitrous oxide with an electrophile, we inquired if the azoxymetallacyclobutane motif would be stable to reducing conditions. Since N$_2$O is by itself a thermodynamically powerful oxidant, one would anticipate systems such as Cp$_2^*_{2}$M(N(O)NCPhCPh) to also be good oxidants. Accordingly, complex Cp$_2^*_{2}$Ti(N(O)NCPhCPh) was examined by cyclic voltammetry to reveal an irreversible one-electron anodic event at 0.30 V (vs FeCp$_2^{2+}$/0 referenced at 0.0 V). A cathodic scan showed a reversible one-electron process for the average of the core structures of 3 and 4 and comparison to the neutral species Cp$_2^*_{2}$Ti(N(O)NCPhCPh).11

**Table 3. Selected Bond Lengths (Å) for Complexes Cp$_2^*_{2}$Ti(N(O)NCPhCPh) and 5**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Complex 3</th>
<th>Complex 4</th>
<th>Complex 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti−N(1)</td>
<td>2.088(4)</td>
<td>2.132(3)</td>
<td>2.185(4)</td>
</tr>
<tr>
<td>Ti−C(31)</td>
<td>2.210(5)</td>
<td>2.187(3)</td>
<td>2.208(5)</td>
</tr>
<tr>
<td>N(1)−N(2)</td>
<td>1.294(7)</td>
<td>1.270(4)</td>
<td>1.275(7)</td>
</tr>
<tr>
<td>N(1)−O(1)</td>
<td>1.281(6)</td>
<td>1.321(3)</td>
<td>1.295(5)</td>
</tr>
<tr>
<td>N(2)−C(41)</td>
<td>1.435(7)</td>
<td>1.441(4)</td>
<td>1.430(6)</td>
</tr>
<tr>
<td>C(31)−C(41)</td>
<td>1.344(7)</td>
<td>1.357(4)</td>
<td>1.349(7)</td>
</tr>
<tr>
<td>O(1)C(1B)</td>
<td>n/a</td>
<td>1.647(8)</td>
<td>n/a</td>
</tr>
<tr>
<td>N(2)C(1A)</td>
<td>n/a</td>
<td>1.449(6)</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Figure 2. Perspective view of the molecular structure of the cationic component for a cocrystal for the average of complexes 3 and 4, depicting the atom-labeling ellipsoid plot at the 50% probability level. Both $\beta$-N and $\beta$-O methyl alkylated sites are shown.
centered at −1.80 V, thus implying that complex Cp*2Ti(N-O)NCPhCPh is not a good oxidant given such a highly negative potential. Chemical reduction of Cp*2Ti(N-O)NCPhCPh with one equivalent of KC8 in benzene afforded an extremely air-sensitive green solution, from which the Ti(III) radical anion \([K(2,2,2-Kryptofix)][Cp*2Ti(N-O)NCPhCPh]\) (5) has been isolated as an encrypted dark green crystalline material in 68% yield (Scheme 6).

Scheme 6. Reduction of Cp*2Ti(N(O)NCPhCPh) with KC8 to Form the Ti(III) Complex Salt 5

\[
\begin{align*}
\text{Cp*}^2\text{Ti}^+ & \quad \text{1. KC8, C6H6} \\
\text{- C8} & \quad \text{2. Kryptofix} \\
\text{Cp*2Ti}^+ & \quad \text{[K(Kryptofix)]} \\
\text{KCp*2Ti(N-O)NCPhCPh} & \quad \text{[Cp*2Ti(N-O)NCPhCPh]} \\
\text{5} & \quad \text{(5)} \\
\end{align*}
\]

*H atoms have been omitted for clarity purposes.

Complex 5 is paramagnetic, therefore displaying only a couple of extremely broad resonances in the 1H NMR spectrum (2.20 and 7.50 ppm), while relatively sharp resonances for the cryptand cationic portion (1.95, 2.73, and 3.70 ppm) are clearly visible. At room temperature, a solution magnetic moment measurement of complex 5 in THF solution was consistent with this complex having one unpaired electron (\(\mu_{eff} = 2.28 \mu_B\) for clarity purposes). In addition, the room-temperature X-band EPR spectrum of 5 in THF revealed the unpaired electron to reside primarily on titanium (\(g_{iso} = 1.9846\)) with \(A_{iso} = 8.55\ G\) (\(^{4}T_{1g}, I = 5/2, 7.4\%\); \(^{4}T_{1g}, I = 7/2, 5.4\%\)), in addition to some superhyperfine coupling to the \(\alpha-N\) with \(A_{iso} = 2.0\ G\) (\(^{14}N, I = 1, 99.64\%\), and coupling to the more distant \(\beta-N\) (\(A_{iso} = 0.5\ G, ^{14}N, I = 1, 99.64\%\)) composing the azoxymetallacycle ring (Figure 3). Although the coupling constant of the unpaired electron with titanium is characteristic for Cp*2Ti(III)L or Cp*2V(IV)L systems studied previously, \(^{4}T_{1g}\) complex 5 represents the first example of a stable transition metal radical species derived from N2O complexation. Unfortunately, multiple attempts to prepare the zirconium analogue of 5 were unsuccessful, even when performing the reaction at −78 °C and in the presence of cryptand as a trap.\(^{51}\)

Single crystals of 5 reveal a discrete salt with an essentially intact azoxymetallacylobutene ligand, grossly similar to that of its precursor Cp*2Ti(N-O)NCPhCPh.\(^{11}\) The only significant perturbation is the Ti–N(1) bond distance of 2.185(4) Å, which reflects slight elongation from that of its neutral counterpart (Figure 4). Table 2 lists selected metrical parameters for Cp*2Ti(N(O)NCPhCPh)\(^{11}\) and the radical anion core of 5. Intuitively, inclusion of an unpaired electron should not deform the core structure in Cp*2Ti(N-O)NCPhCPh, but only permute the Ti–N distance slightly, since the orbital housing the unpaired electron should be a nonbonding metal d orbital. Surprisingly though, the N–O and N–N distances are relatively unperturbed when compared to Cp*2Ti(N(O)NCPhCPh), even though the X-band EPR spectrum implies some delocalization of the unpaired electron onto these sites.

In order to understand the chemistry of the azoxymetallacylobutene moiety toward electrophiles or reductants, we relied on theoretical studies using the Gaussian 09 package\(^{44}\) at the B3PW91 level of theory to dissect the molecular picture of the complexes Cp*2M(N(O)NCPhCPh) (M = Ti and Zr). When inspecting the molecular representation of the simplified models of Cp*2M(N(O)NCPhCPh), namely, Cp*2M(N(O)NCMeCMe), it can be observed how the azoxymetallacylobutene moiety dominates the frontier orbital picture. For example, the HOMOs for each metal complex are nearly identical and expose the N=N \(\pi\)-bond, which is out of phase with the \(\beta-O\) atom (Figure 5), and thus consistent with resonance structures A or C depicted in Scheme 2 (vide supra).

From the HOMO, the most obviously exposed nucleophilic site is the \(\alpha-O\) and \(\beta-O\). This pattern well explains why Me+ addition occurs at both the \(\beta-N\) and \(\beta-O\) for \(M = Ti\). However, it does not explain why alkylation occurs only (based on our observations) at the \(\beta-N\) for \(M = Zr\). In fact, close inspection of the orbital populations for each individual atom do not reflect any notable discrepancies in the atomic contributions from the \(\beta-N\) and \(\beta-O\) atoms. For \(M = Ti\), the LUMO and LUMO+1 illustrate a titanium d\((\alpha^2-\alpha^2)\) orbital that interacts in a “slipped” \(\sigma\) fashion with the \(\alpha-N\). In contrast to the HOMO orbitals, the
activated N\textsubscript{2}O is further functionalized at both the $\beta$-O and $\beta$-N moieties. At this end, the apparent variation in reactivity of the electrophile with each azoxymetallacycle remains unclear. However, we suggest that the observed divergent reactivity is due to the Zr—O versus Ti—O bond strengths and relates to the thermodynamic stability of the titanium azoxymetallacycle precursors relative to that of zirconium, which spontaneously extrudes N\textsubscript{2}O to yield the oxometallacyclobutene complex. Using Cp\textsuperscript{*} Ti(N(O)NCPhCPh) however, we are able to trap the O-methylated intermediate, resulting in N\textsubscript{2}O and tolane extrusion in the case of Zr. The regioselectivity for Me$^+$ addition suggests the HOMO in Cp\textsuperscript{*} Zr(N(O)NCPhCPh) to be predominantly dominated by the lone pairs in the $\beta$-O and $\beta$-N positions. In contrast, the LUMO for M = Ti represents a slipped nonbonding metal-based $\sigma$ orbital. This feature contrasts M = Zr where there is more azoxymetallacycle character in the LUMO. Despite our shortcoming to use N\textsubscript{2}O as a catalytic O atom transfer source, complexes of the type Cp\textsuperscript{*} Zr(N(O)NCPhCPh) represent attractive synthetic targets since N\textsubscript{2}O can be a reagent for the preparation of the nitrosimine functionality, which can be further functionalized with Me$^+$ to a dialkynitrosamine. Given the fact that N\textsubscript{2}O binding to metal complexes has been predicted and shown to occur preferentially at the terminal nitrogen atom,\textsuperscript{24b,32} other systems can potentially harness the oxidizing power of this resourceful, but underutilized reagent.

**ASSOCIATED CONTENT**

Supporting Information
CIF files for the structures of compounds 1, 3/4, and 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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This paper is dedicated to the memory of Prof. Gregory L. Hillhouse, a terrific chemist, advisor, and beloved friend. In order to pay our last respects to a great and unique scientist, we voice both mentally and physically that a sad day has come, one where we wish a fond farewell to a wonderful man, a man whom we were all so very privileged to have known and worked with. We thank the National Science Foundation for financial support, Professor M. D. Hopkins and Dr. Daniel E. Haines for access to a BAS potentiosat and software, and Dr. Ian Steele for some assistance with X-ray crystallography. D.J.M. acknowledges postdoctoral fellowship support from the Ford Foundation and the National Institutes of Health.
Organometallics

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(51) It was observed that reduction of the metastable complex Cp₅Zr(N(C=NPh)CPh) with KC₈ at −78 °C resulted in a green solution, which rapidly decayed to a myriad of products even if the reaction was conducted in the presence of 222-KryptoFix at low temperatures.