Autoxidation of an Electron-Rich Organometallic. Mechanism of the Reaction of a Substituted Niobocene Compound with Dioxygen

B. Thiyagarajan, Margaret E. Kerr, and Joseph W. Bruno*

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459

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The subsituted niobocene compound $[Cp'_2NbCl]_x$ (**1**, $Cp' = \eta^5\text{-}C_5H_4SiMe_3$) is an electron-rich Nb(III) system that reacts readily with oxygen and other potential oxygen atom donors. The ultimate product of these processes is the known Nb(V) oxo compound $Cp'_2Nb(=O)(Cl)$ (**2**), which obviously arises by way of a multistep mechanism. We have investigated the mechanism of the autoxidation using a series of alternate syntheses and/or modified reaction conditions and provide direct evidence for a sequence involving the sequential formation of the η^2-peroxide $Cp'_2Nb(O_2)Cl$, its reaction with excess **1** to generate **2**, the subsequent conproportionation of **2** and **1** to make the μ-oxo compound $[Cp'_2NbCl]_2(O)$ (**3**), and the further oxidation of this compound to **2**. The reaction of **1** and **2** is postulated to involve the intermediacy of a peroxide-bridged system $[Cp'_2NbCl]_2(O_2)$ (**5**); although this compound has not been observed directly, attempted synthesis of **5** using superoxide lead directly to **3**. These individual reactions are kinetically competent, and the results thus constitute a four-step mechanism for the production of **3**. In addition, studies on the reactions of **3** with $PMePh_2$ illustrate that **3** disproportionates to **2** and **1** and that the latter is trapped rapidly. Conversely, reaction of **3** with additional dioxygen does not require dissociation and may proceed via a direct redox pathway. Finally, the oxygen atom transfer process involved in dioxygen reduction is compared to reactions involving nitrosoarenes and carbon dioxide, processes that yield azoxyarene (or azoarene) and carbon monoxide, respectively; mechanistic features differ, even though the overall process involves X=O scission in all cases.

Introduction

The longstanding interest in the redox interactions of metal-containing compounds with dioxygen derives from the mechanistic complexity of the process and its importance in a variety of synthetic and biological applications. Suitably designed compounds have been used to model the active sites of oxidase[1] and oxygenase[2] enzymes, of key importance in biochemical oxidation and oxygen transfer. Other systems, typically containing iron or copper centers, have been prepared to model biochemical oxygen transport proteins such as hemoglobin,[3] myoglobin,[4] and hemocyanin.[5] In addition, related compounds are sought to function as reversible oxygen carriers,[6] often for the purposes of oxygen purification and/or removal from gas mixtures.[7] Finally, a number of important industrial processes involve metal-catalyzed oxidation of organic substrates,[8] and
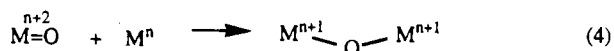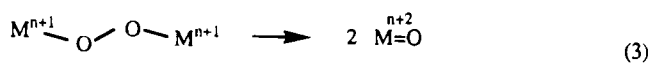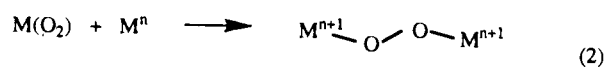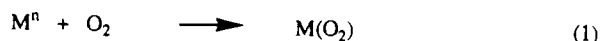
mechanistic information on the role of the metal center and its interactions with the oxidant is of obvious utility. For the latter purpose, the use of dioxygen as the actual oxidant (vs, e.g., peroxides) has a number of obvious advantages related to cost and handling ease. Indeed, the key role of metal catalysts is well recognized to arise from the kinetic limitations involved in the reactions of triplet oxygen with diamagnetic organic substrates.[9]

The complete reduction of dioxygen to hydroxide ion or metal oxide constitutes a four-electron process. Since most metal centers are constrained to function as one- or two-electron reductants, it is clear that the full redox sequence must be comprised of a number of sequential steps involving various partially-reduced oxygen species. Studies on a variety of metal-containing systems[1-7] have provided evidence for superoxo, peroxo, μ-peroxo, oxo, and μ-oxo species arising from reactions with dioxygen. A typical sequence for the process is outlined

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in eqs 1–4,[6a] in which the metal-containing starting material is

$$M^n + O_2 \longrightarrow M(O_2) \tag{1}$$

$$M(O_2) + M^n \longrightarrow M^{n+1}\diagdown_O\diagup^{O}\diagdown M^{n+1} \tag{2}$$

$$M^{n+1}\diagdown_O\diagup^{O}\diagdown M^{n+1} \longrightarrow 2 \ \overset{n+2}{M=O} \tag{3}$$

$$\overset{n+2}{M=O} + M^n \longrightarrow M^{n+1}\diagdown_O\diagdown M^{n+1} \tag{4}$$

represented generically as M^n. The initial reaction (eq 1) involves the formation of an adduct for which the metal oxidation state is left unspecified. This may be either an η^2-peroxide or an η^1-superoxide, depending on the oxidation states available to the metal center.[10] A reaction with a second metal center (eq 2) provides additional reducing power and leads to the μ-peroxide. This may adopt the μ-1,2 bridging mode[11] shown or the $\mu,\eta^2{:}\eta^2$ mode,[12] but the former appears more susceptible to O–O cleavage and is usually invoked in dioxygen reduction schemes. This homolysis (eq 3) gives rise to an oxometal species, which may react with starting material to generate the μ-oxo species shown in eq 4. Clearly many of the details of these processes depend critically on the available oxidation states and coordination sites of the metal centers involved, and manipulation of the ligand sphere can enhance or diminish the relative stabilities of various intermediates.

Although the sequence in eqs 1–4 is generally invoked, it has been formulated from studies on a variety of systems in which the metal and coligand set have often been chosen to stabilize certain species along the path. For example, the peroxide product in eq 2 has been observed in copper systems,[11] and low-temperature NMR evidence is availabe for a (μ-peroxo)bis[(porphyrin)iron(III)] species.[13] The (porphyrin)iron-(IV) oxide complexes (e.g., eqs 3 and 4) are quite reactive and typically convert rapidly to the μ-oxo iron(III) compound;[14] related (porphyrin)chromium(IV) oxide compounds can proceed to the μ-oxo species but are themselves readily isolable.[15] Indeed, the μ-oxo Cr(III) derivatives are sufficiently reducing as to react with additional dioxygen to give chromium(IV) oxide in a subsequent step. This may be contrasted to the aqueous chemistry of Cr(II); here the superoxide complex $[(H_2O)_5Cr(O_2)]^{2+}$ has been observed to react with additional Cr(II) to give the μ-1,2-peroxide $\{[(H_2O)_5Cr^{III}]_2(O_2)\}^{4+}$, which apparently does *not* cleave to the Cr(IV) oxide.[16] These examples indicate the influence of metal center and ligand sphere on the individual steps in the overall sequence.

We recently reported some oxygen atom transfer reactions that occur at substituted niobocene centers,[17] and others have noted that peroxoniobocene compounds can function as catalysts of alkene epoxidation with hydrogen peroxide.[18] All of the compounds involved are formally derived from the Nb(III) species "Cp$_2$NbCl", and niobium also exhibits stable +4 and +5 oxidation states. We have carried out a detailed study of the dioxygen chemistry of $[Cp'_2NbCl]_x$ (1, $Cp' = \eta^5$-C$_5$H$_4$-SiMe$_3$), since (a) the d^2 trivalent species is highly reactive toward dioxygen, (b) the niobocene moiety has a rich redox chemistry available, and (c) the derivatives noted above are active in catalytic oxygen atom transfer reactions. We have isolated a number of intermediates along the redox pathway, demonstrated their kinetic viability in the overall scheme for dioxygen reduction, and related these dioxygen reduction processes to reactions involving other oxygen atom sources such as nitrosoarenes and carbon dioxide. These results yield an unusually detailed overview of the processes involved in oxidation of an organometallic compound.

Experimental Section

General Considerations. All manipulations except oxygenation reactions were carried out under an atmosphere of nitrogen which was first passed through activated BTS catalyst and molecular sieves. Standard Schlenk techniques[19] were used to handle solutions, and solids were transferred in a Vacuum Atmospheres Corp. glovebox under purified nitrogen. Oxygenation reactions were carried out on a synthetic high-vacuum line using a mercury-filled manometer to establish oxygen pressure. Solvents toluene, benzene, hexane, and tetrahydrofuran (J. T. Baker) were distilled from sodium benzophenone ketyl under nitrogen.

NMR spectra, infrared spectra, UV–vis spectra, and mass spectra were obtained on commercial instruments. For FAB-MS determinations, the compound of interest was suspended in a glycerol or 3-nitrobenzyl alcohol matrix.[20]

(Trimethylsilyl)cyclopentadiene (Cp'H) was prepared using the literature method,[21] with the exception that the THF solution of sodium cyclopentadienide was added in dropwise fashion to the Me$_3$SiCl solution; this ensures that the latter is always present in excess and minimizes the formation of disilyl byproducts. Cp'H was metalated with butyllithium and cyclopentadiene was metalated with sodium metal, both in THF. NbCl$_3$(DME),[22] Cp'$_2$NbCl$_2$,[23] [Cp'$_2$NbCl]$_x$ (1),[24] Cp'$_2$NbCl(O) (2),[25] Cp'$_2$Nb(Cl)(η^2-O$_2$) (6),[18a] Cp'$_2$Nb(Cl)(CO),[26] and Cp'$_2$Nb(Cl)(PMePh$_2$)[26] were synthesized according to literature methods.

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Synthesis of [Cp′₂NbCl]₂(μ-O) (3). In the preferred method, equimolar amounts of **1** (0.50 g, 1.24 mmol) and **2** (0.52 g, 1.24 mmol) were added to a gas-inlet flask in the glovebox. Under a purge of nitrogen, ca. 15 mL of toluene was added via syringe and the resulting solution stirred at ca. 0 °C for 15 min. The resulting violet solution was filtered under nitrogen and the solvent removed in vacuo. The violet solid was taken up in 5−10 mL of hexane and the mixture cooled to 0 °C to precipitate **3**, which was then isolated via filtration; yield 0.65 g (0.79 mmol, 64%). Alternatively, 1.0 g (2.48 mmol) of **1** was added to a 250 mL gas-inlet flask and then dissolved in 15 mL of toluene under nitrogen. The flask was evacuated on a vacuum line and cooled to 0 °C, whereupon a limited quantity (60 Torr) of oxygen was admitted. The rate of this process is sensitive to experimental conditions, and the reaction was most effectively monitored visually by observing the intensity of the violet color. When the reaction was judged complete by this criterion, the solvent and atmosphere were removed in vacuo. The solid residue was extracted with hexane as above and the violet solid isolated by filtration; yield 0.69 g (0.73 mmol, 30%). NMR (C₆D₆): 6.57, 5.99, 5.75, 5.56 ppm (4 H each, broad singlets, Cp′H), 0.29 ppm (36 H, singlet, SiMe₃). IR (Nujol): 1247 cm⁻¹ (m), 1164 (w), 1051 (w), 903 (w), 839 (s, br), 668 cm⁻¹ (m). The 668 cm⁻¹ band shifts to 632 cm⁻¹ if ¹⁸O is incorporated. FAB-MS (3-nitrobenzyl alcohol): *m/e* 402 (100%), 404 (40%), 517 (5%), 664 (4%), 801 (3%), 820 (5%). The 801 mass shows an isotopic envelope consisting of *m/e* 801, 802, 803, and 804 in relative intensities 3:2:2.2:1. The 820 mass shows an isotopic envelope consisting of *m/e* 820, 821, 822, 823 and 824 with approximate relative intensities 3.3: 2:3.2:1.5:1.

Kinetics Determinations. These were carried out using UV−vis instrumentation and a 1 cm square quartz cell with a gas-inlet valve attached. A 10⁻³ M stock solution of **3** in toluene was prepared volumetrically in the glovebox, removed promptly from the glovebox, and cooled while being maintained under nitrogen. A separate toluene solution of PMePh₂ was also prepared under nitrogen atmosphere. The cell holder in the instrument was cooled or heated using a circulating bath, and the desired amounts of stock solutions of **3** and phosphine were added to the quartz cell via syringe; the resulting solution was equilibrated briefly, and the solution absorbance at 550 nm was determined at appropriate time intervals. The reaction was allowed to reach its end point so as to determine A_∞, and the quantity $\ln(A_t - A_\infty)$ was plotted vs time to determine first-order rate constants.
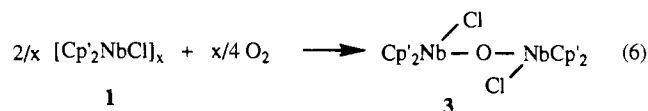
Results

The substituted niobocene compound [Cp′₂NbCl]ₓ (**1**, Cp′ = η^5-C₅H₄SiMe₃) was originally reported by Antiñolo et al., who prepared it by sodium amalgam reduction of Cp′₂NbCl₂.[26] We subsequently reported that reaction of the known NbCl₃(DME)[22] with Cp′Li afforded an alternate route to **1**.[24] The molecularity of **1** in solution has not been established, in part because of its extreme air and moisture sensitivity.[26c] Indeed, long-term exposure of **1** to air leads to the production of the Nb(V) oxide **2** (eq 5), which also results similarly from a number of

$$1/x\ [Cp'_2NbCl]_x\ +\ x/2\ O_2\ \longrightarrow\ Cp'_2Nb\overset{Cl}{\underset{O}{\diagdown}} \qquad (5)$$

1   **2**
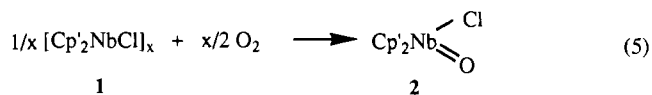
derivatives Cp′₂NbCl(L).[25] Compound **2** is a yellow solid that is only sparingly soluble in most organic solvents; it is highly crystalline, forming pale yellow needles readily. It shows an

IR band for the Nb=O moiety at 864 cm⁻¹ (nujol), and in the ¹⁸O-labeled compound (made with labeled O₂) this band shifts to a point at which it is masked by a strong, broad Cp′ band at 835 cm⁻¹.

In handling **1**, we have noted that brief exposure of its solutions to limited quantities of air generates an intense violet color. As suggested above, this ultimately gives way to **2**. Compound **1** has been used to prepare a variety of complexes of general formula Cp′₂NbCl(L), in which L may be a σ donor or η^2-bonded π acceptor.[26] Some of these synthetic processes proceed after the appearance of the violet color, albeit with reduced yield (vide infra); however, the presence of the violet compound precludes isolation of the ketene complexes we have reported previously.[24] In an effort to identify the source of this violet color, we have deliberately exposed toluene solutions of **1** to limited amounts of dry O₂ using a synthetic high-vacuum line; the molar ratio of O₂ to **1** in these reactions was slightly greater than 0.25, and the reactions are best carried out at 0 °C. Under these conditions it proved possible to generate the violet color while still minimizing the conversion to **2**. The solution was evacuated to dryness, leaving a violet solid; this was subsequently extracted with hexane at 0 °C and cooled to precipitate a violet solid **3** (eq 6). The crude solid always

$$2/x\ [Cp'_2NbCl]_x\ +\ x/4\ O_2\ \longrightarrow\ Cp'_2Nb\overset{Cl}{\underset{Cl}{\diagup}}-O-NbCp'_2 \qquad (6)$$

1   **3**

contains either some unreacted **1** or some **2**, and the reaction temperature and dioxygen concentration determine which impurity results. Fortunately **3** is intermediate in solubility and may be extracted away (in hexane) from largely insoluble **2** or precipitated from cooled hexane solutions containing **1**. It is significant that **3** is never contaminated with *both* **1** and **2** (vide infra).

We have identified **3** as the μ-oxo compound shown in eq 6, and isolated **3** has been characterized by a variety of spectroscopic probes. The ¹H NMR spectrum (C₆D₆) exhibits four cyclopentadienyl signals in the range 5.55−6.57 ppm and one signal for the SiMe₃ groups at 0.29 ppm. These patterns indicate that each Nb center contains a plane of symmetry rendering the Cp′ ligands equivalent *and* that the two Nb centers are magnetically equivalent. The aromatic signals are slightly broadened by the unresolved coupling with other aromatic hydrogens, as is typical for Cp′−Nb compounds. These observations are consistent with the μ-oxo formulation for **3** but do not require it. The infrared spectrum shows bands typical of the Cp′₂Nb moiety, as well as an additional band at 668 cm⁻¹. If the reaction in eq 6 is run with ¹⁸O₂, the resulting violet solid (**3**-¹⁸O) exhibits a shift in this band to 632 cm⁻¹. Perhaps more convincing is the result of a FAB-MS study, carried out with either *m*-nitrobenzyl alcohol or glycerol as the matrix material. The spectrum exhibits a peak at *m/e* 820, as would be expected for a bimolecular compound of formula C₃₂H₅₂Si₄Cl₂Nb₂O. The spectrum also contains an envelope of signals from *m/e* 820 to 824, indicating the presence of two chlorine atoms; we have simulated the spectrum for the formula given above, and the simulation is virtually identical to the experimental spectrum. If a similar spectrum is obtained for **3**-¹⁸O, the expected increase

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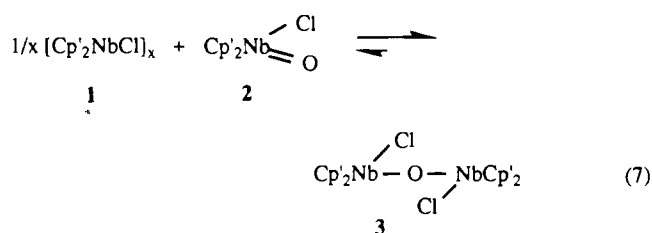
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of 2 mass units is observed. The NMR data cited above show no evidence of line broadening or paramagnetic shifts, even though the compound nominally contains two Nb(IV) centers with the d^1 electron configuration. This is not surprising, however, in that the oxo bridge has a degenerate set of π-symmetry orbitals and can facilitate antiferromagnetic coupling between metal centers via a M—O—M π^* system;[27] indeed, the iron and chromium systems described in the Introduction exhibit strong antiferromagnetic coupling and exchange integrals (*J*) ranging from -130 to -200 cm^{-1}.[15, 27]

The UV—visible spectrum of **3** contains useful information as well. Toluene solutions exhibit strong bands at 286 and 360 nm with extinction coefficients 5400 and 1500 M^{-1} cm^{-1}, respectively; the latter is a shoulder on the more intense 286 nm band. We believe these absorptions are due, at least in part, to LMCT transitions involving the Cp$'$ and chloride ligands, since we see similar bands in related niobocene complexes. There is also a weaker band at 548 nm with an extinction coefficient of 800 M^{-1} cm^{-1}. This is responsible for the violet color of **3** and is doubtless derived from a transition involving the μ-oxo ligand; this transition has LMCT character in that it involves a transition coupling the M—O—M π system with a π^* antibonding orbital. Indeed, a variety of early transition metal μ-oxo compounds exhibit a violet color, and there is no obvious correlation with d electron count or metal oxidation state.[28]
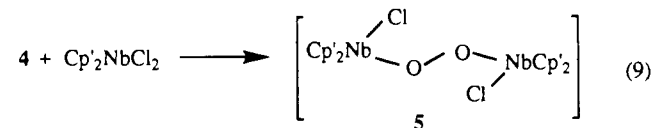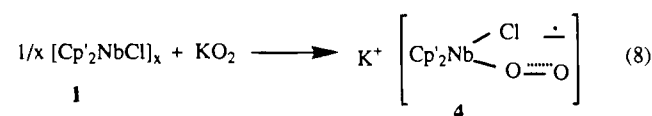
Alternate Synthetic Routes to 3. The foregoing observations are consistent with the μ-oxo structure for **3**. However, we also attempted to characterize this compound by relating it to known compounds via predictable chemical processes. In the first of these, equimolar quantities of isolated **1** and **2** were mixed in toluene solution under anaerobic conditions (eq 7).

$$1/x \ [Cp'_2NbCl]_x \ + \ Cp'_2Nb\overset{Cl}{\underset{O}{\diagdown}} \ \rightleftharpoons$$
$$\quad\quad \mathbf{1} \quad\quad\quad\quad \mathbf{2}$$

$$Cp'_2Nb - O - NbCp'_2 \quad\quad (7)$$
$$\quad\quad\quad\quad \mathbf{3}$$

The solution immediately developed the characteristic violet color, and **3** was readily isolated as described above; this conproportionation reaction generates two Nb(IV) centers from a Nb(V) and Nb(III) and constitutes the preferred synthetic route to **3**.[15,29] The crude solid typically contains a small amount of either **1** or **2**, reflecting the accuracy with which the equimolar condition was approached. Pure samples of **3** are realized from the extraction protocol described above; there is no evidence for dissociation of **3** yielding any detectable amounts of **1** or **2**, and neither compound exhibits alterations in its NMR spectrum in the presence of **3**. This proves that the equilibrium in eq 7

rests well to the right as written and that any equilibration is slow on the NMR time scale.

The formation of **3** from isolated **1** and **2** suggests a pathway for its synthesis from **1** and O_2. This would require the initial preparation of **2**, which would then couple quickly with unreacted **1**. Obviously the preparation of **2** from O_2 requires O—O cleavage, a process facilitated by reduction to the peroxide stage. Indeed, we noted earlier the facility with which dimeric μ-1,2-peroxides cleave to oxides (eq 3). We have no direct evidence for the intermediacy of such a species here, so we sought indirect evidence. This involved the use of a strategy that has been applied to the synthesis of related copper and palladium complexes,[30] and potassium superoxide was added to a mixture of the Nb(III) and Nb(IV) compounds **1** and Cp$'_2$-NbCl$_2$ in THF. This reaction again proceeds to **3** over a period of 6 h at ambient temperature, presumably by way of an initially-formed superoxide complex. To probe for this, we treated the two niobium compounds with KO$_2$ in separate reactions in THF solvent. The Cp$'_2$NbCl$_2$ failed to react and was isolated intact. However, **1** reacted over a period of 3—4 h at room temperature to generate a yellow-orange solution. We attempted to isolate the niobium-containing species by evaporating the solvent in vacuo, whereupon the solid ignited and decomposed violently. We thus discontinued this line of inquiry, which nonetheless suggests the sequence in eqs 8 and 9. Here, the initial reaction

$$1/x \ [Cp'_2NbCl]_x \ + \ KO_2 \ \longrightarrow \ K^+ \left[Cp'_2Nb\overset{Cl}{\underset{O\cdots\cdots O}{\diagdown}}\right]^{\cdot -} \quad (8)$$
$$\quad \mathbf{1} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \mathbf{4}$$

$$\mathbf{4} \ + \ Cp'_2NbCl_2 \ \longrightarrow \ \left[Cp'_2Nb\overset{Cl}{\underset{O}{\diagdown}}O\diagdown\overset{}{\underset{Cl}{NbCp'_2}}\right] \quad (9)$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \mathbf{5}$$

with diamagnetic **1** would lead to a superoxide radical anion **4** (eq 8). This would then undergo a subsequent reaction with Cp$'_2$NbCl$_2$, displacing a chloride and generating an intermediate μ-1,2-peroxide **5** (eq 9). Subsequent O—O cleavage in **5** would generate 2 equiv of **2**, which would result in **3** as in eq 7. This sequence would consume 3 equiv of 1/equiv of Cp$'_2$NbCl$_2$; formation of **5** requires 1 equiv of each, but **5** yields 2 equiv of **2** that must be scavenged by **1** to make **3**. Indeed, we have confirmed that this 3:1 stoichiometric ratio consumes virtually all of the **1** used. Moreover, the use of substoichiometric amounts of **1** fails to produce observable quantities of oxide **2**, suggesting that the chemistry in eqs 8 and 9 is slow relative to cleavage of **5** and the subsequent coupling of **1** and **2** to give μ-oxide **3** (eq 7).

In the previous sequence, KO$_2$ failed to react with Cp$'_2$NbCl$_2$, and we are proposing that a superoxide intermediate **4** does react successfully. In this context, we note that **4** is a d^2 Nb(III) anion prepared by adding an anion radical to what was already an extremely electron-rich center in **1**. Moreover, superoxide complexes typically have excess unpaired spin density on the superoxide ligand.[9b,10] As a result, **4** may well be more nucleophilic than is the uncomplexed anion.[31]
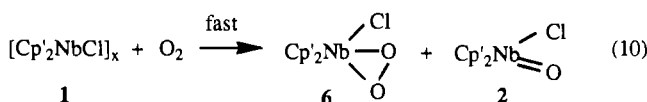
Toney, G. E.; Gold, A.; Mewborn, T. D.; Pemberton, J. R. *Inorg. Chem.* **1986**, *25*, 2334—2337. (f) Gamelin, D. R.; Kirk, M. L.; Stemmler, T. L.; Pal, S.; Armstrong, W. H.; Penner-Hahn, J. E.; Solomon, E. I. *J. Am. Chem. Soc.* **1994**, *116*, 2392—2399.

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(30) (a) Napa, M.; Valentine, J. S.; Mitsztal, A. R.; Schugar, H. J.; Isied, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 7744—7746. (b) Suzuki, H.; Mizutani, K.; Moro-oka, Y.; Ikawa, T. *J. Am. Chem. Soc.* **1979**, *101*, 748—749.

(31) (a) San Fillipo, J., Jr.; Chern, C.-I.; Valentine, J. S. *J. Org. Chem.* **1975**, *40*, 1678—1680. (b) Johnson, R. A.; Nidy, E. G. *J. Org. Chem.* **1975**, *40*, 1680—1681. (c) Corey, E. J.; Nicolaou, K. C.; Shibasaki, M.; Machida, Y.; Shiner, C. S. *Tetrahedron Lett.* **1975**, 3183—3186.

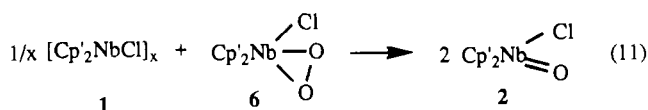**Table 1.** Rate Constants for the Reaction of **3** with PMePh$_2$

temp, °C	$10^3 k$, s^{-1}	temp, °C	$10^3 k$, s^{-1}
5	0.926	20	5.50
10	2.54	25	9.47
15	3.38	30	16.9

The results described above suggest that compounds **2** and **3** interconvert in complex ways during the sequence of reactions initiated by the reaction of **1** with O$_2$. In order to establish the relative rates of such processes, we sought to speed the initial reaction of **1** with O$_2$ so as to determine if subsequent reactions would alter their course if **1** was depleted. To this end, a toluene solution of **1** was prepared and evacuated to remove the inert atmosphere. The flask was attached directly to a tank of pure dioxygen, which was rapidly admitted into the evacuated flask. This solution failed to show the violet color associated with **3**, and subsequent workup and NMR analysis revealed the presence of **2** and the monomeric peroxide **6** (eq 10). A series of

$$[\text{Cp}'_2\text{NbCl}]_x + \text{O}_2 \xrightarrow{\text{fast}} \text{Cp}'_2\text{Nb} \overset{\text{Cl}}{\underset{\text{O}}{\diagup}} \text{O} + \text{Cp}'_2\text{Nb} \overset{\text{Cl}}{\underset{\text{O}}{\diagdown}} \quad (10)$$

$$\mathbf{1} \qquad\qquad\qquad \mathbf{6} \qquad\qquad \mathbf{2}$$

inorganic Nb(V) peroxide complexes containing one, two, or three η^2-peroxide ligands have been structurally characterized,[32] and the analogue $(C_5H_5)_2\text{Nb(Cl)}(\eta^2\text{-}O_2)$ was first prepared from Cp$_2$NbCl$_2$ and hydrogen peroxide by Sala-Pala et al.[18a] This is a typical synthetic strategy, which is presumably successful because the Nb(IV) compound can provide only a single electron for reduction; this inhibits susequent further reduction of O$_2$ and halts the reaction at the peroxide stage. In a similar vein, a few isonitrile complexes Cp$'_2$Nb(Cl)(CNR) react directly with oxygen to produce the peroxide in a reaction that may also be initially controlled by the electron-withdrawing character of the isonitrile.[25] These results notwithstanding, it is surprising that **1** forms the peroxide complex, since **1** is so electron-rich and can readily form oxo complex **2**. Indeed, Drago has noted that early metal compounds in the +3 or +4 oxidation state invariably react with O$_2$ to yield the oxide and that peroxide complexes are rarely observed.[9b,33]

The rapid reaction with excess oxygen (eq 10) suggests that **6** is the first-formed product, since it only results under these conditions. Indeed, while **6** is the major component, it is impossible to avoid the appearance of some **2**. This suggested that **6** is on the path to **2**. This possibility was probed using clean **6**, prepared from Cp$'_2$NbCl$_2$ and peroxide. Indeed, reaction of **6** and equimolar **1** resulted in immediate conversion to oxide **2** (eq 11). This explains the utility of the rapid reaction

$$1/x \ [\text{Cp}'_2\text{NbCl}]_x + \text{Cp}'_2\text{Nb} \overset{\text{Cl}}{\underset{\text{O}}{\diagup}} \text{O} \longrightarrow 2 \ \text{Cp}'_2\text{Nb} \overset{\text{Cl}}{\underset{\text{O}}{\diagdown}} \quad (11)$$

$$\mathbf{1} \qquad\qquad \mathbf{6} \qquad\qquad\qquad \mathbf{2}$$

condition described above (eq 10), in that this depletes **1** quickly and largely precludes the subsequent reaction between **6** and **1** (eq 11).
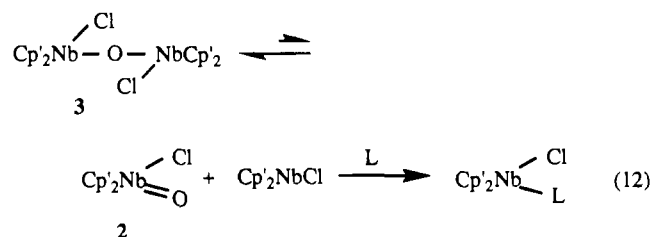
Chemistry of μ-Oxo Complex 3. The results described thus far provide a mechanistic rationale for the conversion of **1** to **3**, a multistep process in which **2** is prepared and consumed. However, we noted that exhaustive oxygenation of **1** leads

(32) (a) Mathern, B.; Weiss, R. *Acta Crystallogr., Sect. B* **1971**, *27*, 1572–1581. (b) Mathern, B.; Weiss, R. *Acta Crystallogr., Sect. B* **1971**, *27*, 1582–1597. (c) Mathern, B.; Weiss, R. *Acta Crystallogr., Sect. B* **1971**, *27*, 1598–1609.

(33) MacDonnell, F. M.; Fackler, M. L. P.; Stern, C.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1994**, *116*, 7431–7433.
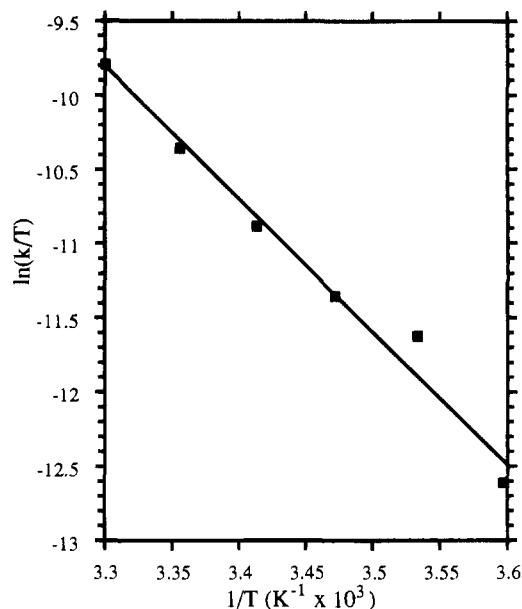

Figure 1. Eyring plot for the reaction of **3** with PMePh$_2$.

finally to **2**, so we sought to characterize the chemistry of μ-oxo compound **3**. If solid **3** is heated to ca. 100 °C in a dynamic vacuum and the resulting solid dissolved in C$_6$D$_6$ and probed by NMR, it is readily identified as **1**. This is further evidence of the dissociative chemistry of **3**, which is clearly losing a molecule of **2** to sublimation in the solid state. In addition, the reactions of **3** with potential donor ligands such as CO, PMePh$_2$, or paraformaldehyde result in complexes of these ligands (eq 12), and these are readily prepared from **1**. The first two of

$$\text{Cp}'_2\text{Nb} \overset{\text{Cl}}{\diagup} \text{O} - \text{NbCp}'_2 \rightleftharpoons$$

$$\mathbf{3}$$

$$\text{Cp}'_2\text{Nb} \overset{\text{Cl}}{\underset{\text{O}}{\diagdown}} + \text{Cp}'_2\text{NbCl} \xrightarrow{\text{L}} \text{Cp}'_2\text{Nb} \overset{\text{Cl}}{\underset{\text{L}}{\diagdown}} \quad (12)$$

$$\mathbf{2}$$

these are known,[26] but the light brown formaldehyde complex is a new compound. Antiñolo et al. reported the generation of a benzaldehyde complex of **1** in an electrochemical study,[26b] but this decomposed during attempted workup; other aldehydes were noted to be unreactive with **1**. To probe the mechanism of these substitutions, we carried out kinetic studies on the reaction of **3** with PMePh$_2$. These were facilitated by the obvious conversion of violet **3** to the green phosphine complex, and the process was studied using UV–vis spectrophotometry in toluene solution. Reactions using 10^{-3} M **3** and phosphine concentrations ranging from 0.22 to 0.88 M exhibited first-order loss of **3**, as judged by linear plots of ln($A_t - A_\infty$) vs time (*A* is the absorbance at 548 nm, the wavelength at which **3** absorbs). In addition, these four reactions gave rate constants ranging from 0.011 to 0.012 s^{-1} at 29 °C, virtually identical in spite of the 4-fold variation in phosphine concentration. The first order rate law is thus of the form $-d[\mathbf{3}]/dt = k[\mathbf{3}]$, the reaction does involve the dissociation depicted in eq 12, and the subsequent reaction with L is fast relative to dissociation of **3**. A series of six kinetic runs over the temperature range 5–30 °C yielded the rate constants shown in Table 1. The resulting Eyring plot (Figure 1) indicates that $\Delta H^\ddagger = 17 \pm 3$ kcal mol^{-1} and $\Delta S^\ddagger = -9 \pm 4$ cal mol^{-1} deg^{-1}.

We have also initiated relative rate studies on the reaction of **3** with excess dioxygen in toluene solution, a process that indeed
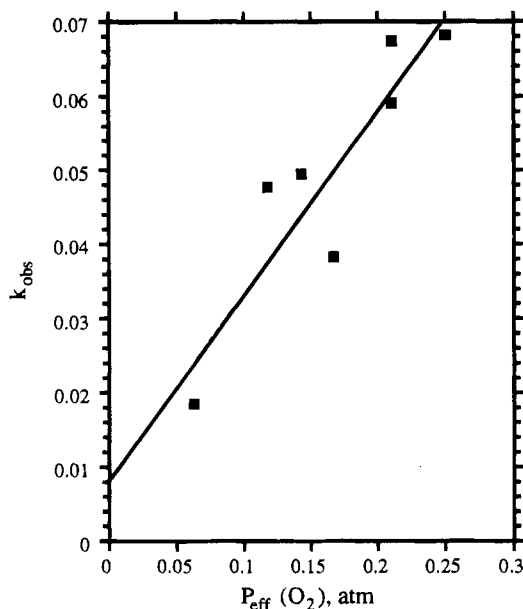
Figure 2. Plot of k_{obs} (s^{-1}) for the reactions of **3** and dioxygen as a function of effective oxygen partial pressure (see text).
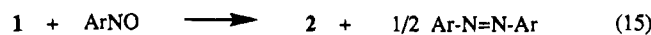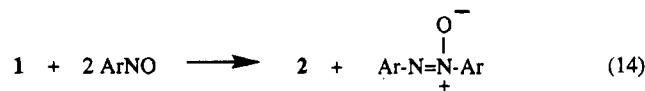
leads to **2** with no detectable intermediates. These reactions were carried out in the presence of excess oxygen, and pseudo-first-order conditions would be expected to apply. The reaction of **3** and O$_2$ is more rapid than is diffusion, so the addition of oxygen was accomplished by adding various quantities of an oxygen-saturated toluene solution to a toluene solution of **3** at 29 °C. By considering the volume added and the resulting total solution volume, we can define an effective oxygen pressure P_{eff} and plot k_{obs} vs this quantity (Figure 2); this assumes that the reaction is quicker than is the establishment of equilibrium by diffusion of oxygen *out* of solution, and the scatter in Figure 2 probably results from some differential loss of dissolved oxygen prior to consumption of **3**. This effect is nonetheless relatively minor, and it can be seen that variation in the dioxygen partial pressure now has a strong effect on the rate. The plot is apparently linear with an intercept of 0.0088; this is consistent with the operation of a two-term rate law containing both oxygen-dependent and -independent terms (eq 13). The latter

$$- \frac{d[3]}{dt} = k_1[3] + k_2[3][O_2] \qquad (13)$$

is most likely due to dimer dissociation prior to oxygenation, and the k_1 value of 0.0088 s^{-1} is in reasonable agreement with the value determined in the phosphine experiments discussed above ($k_1 = 0.011-0.012$ s^{-1}). The slope of the plot indicates that k_2 has a value of 0.25 ± 0.05 atm^{-1} s^{-1}, and we emphasize that the units reflect the effective oxygen concentration so as to eliminate diffusion problems; the comparison suggests that the second-order process dominates the reaction at all but the lowest accessible oxygen concentrations. This also explains the low synthetic yields obtained in the preparation of **3** from **1** and O$_2$; during the course of the reaction unreacted O$_2$ serves to convert **3** on to **2**. This is partially prevented by using stoichiometric quantities of oxygen, but the production and consumption of **3** occur at competitive rates.

Reactions of 1 with Other Oxo Sources. We noted earlier the key role of peroxide **6** in the chemistry of **1** with oxygen. As a further probe of the potential of this compound for oxygen atom transfer processes, we also sought to understand the chemistry of related nitrosoarene complexes. Our initial synthetic attempt involved the reaction of peroxide **6** with aniline

derivatives, by analogy with the preferred process in related molybdenum chemistry;[34] this resulted in no reaction for aniline, 4-methoxyaniline, or 4-(trifluoromethyl)aniline. Conversely, the direct reaction between **1** and nitrosobenzene in hexane proceeded immediately to **2**, and the nature of the organic products depended on the stoichiometry of the reactants. If the ratio of nitrosoarene to **1** was 2 or greater, the reaction proceeded to azoxyarene (eq 14). If a 1:1 stoichiometry was employed, the resulting organic product was azoarene (eq 15). In neither case

$$\mathbf{1} + 2\text{ArNO} \longrightarrow \mathbf{2} + \underset{+}{\overset{\overset{\displaystyle O^-}{\vert}}{\text{Ar-N=N-Ar}}} \qquad (14)$$

$$\mathbf{1} + \text{ArNO} \longrightarrow \mathbf{2} + 1/2\ \text{Ar-N=N-Ar} \qquad (15)$$

was there any evidence for a stable nitrosoarene complex of niobocene, although this is undoubtedly a reactive intermediate in the process. We propose the sequence depicted in eq 16 to
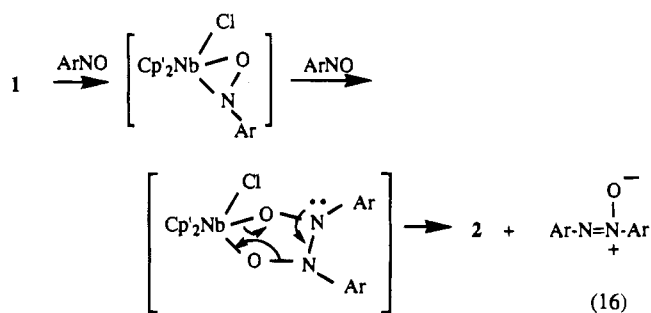
account for the processes observed here. Initially, complexation gives rise to the η^2-nitrosoarene intermediate. This compound is susceptible to reaction with another equivalent of nitrosarene, a process that generates the metallacyclic intermediate. Fragmentation of this ring generates the azoxyarene and oxide **2**. This chemistry differs from that seen for (dipic)(HMPA)Mo-(=O)(η^2-ArNO) (dipic is pyridine-2,6-dicarboxylate), since, in the molybdenum case, the initial complex is stable and isolable;[34] this precludes oxygen atom transfer under the 1:1 stoichiometric condition we utilized for niobocene in eq 15. The molybdenum complex may be driven to form azoxyarene by addition of another equivalent of nitrosoarene at elevated temperature or by thermal dissociation from the first complex, but there is no obvious route to azoalkene. The enhanced reactivity of the niobium center in **1** allows for the immediate incorporation of a second nitrosoarene equivalent; this generates azoxyarene in the presence of unreacted **1** and allows the observation of the second oxygen atom transfer between the azoxyarene product and **1**. We verified that this process is rapid using commercial 4,4'-azoxyanisole and **1**. There is no obvious requirement for a metallacycle intermediate in the latter reaction. The zwitterionic azoxyarene is presumably activated for oxygen atom transfer, and **1** is wholly unreactive with pure azoarene; there is thus no indication of a useful interaction with the azoarene nitrogen.

We[24,35] and others[36] have noted the **1** forms stable complexes with heterocumulenes such as ketenes, ketenimines, and carbon disulfide. In addition, we have reported herein the reducing power **1** exhibits in some reactions with unsaturated heteroatom-

(34) Møller, E. R.; Jørgensen, K. A. *J. Am. Chem. Soc.* **1993**, *115*, 11814−11822.

(35) (a) Halfon, S. E.; Fermin, M. C.; Bruno, J. W. *J. Am. Chem. Soc.* **1989**, *111*, 5490−5491. (b) Bruno, J. W.; Fermin, M. C.; Halfon, S. E.; Schulte, G. K. *J. Am. Chem. Soc.* **1989**, *111*, 8738−8740.

containing substrates. Lappert[37] and Nicholas[38] have reported η^2-C,O complexes of carbon dioxide with derivatives of **1**, formed either from free CO_2 or from oxidation of a bound carbonyl ligand. As such, we have probed the direct chemistry of **1** and carbon dioxide, which we find also yields oxygen atom transfer arising from CO_2 reduction.

Treatment of a toluene solution of **1** (10^{-3} M) with excess oxygen-free carbon dioxide (bubbled into solution through a long syringe needle) ultimately converts all of the compound to oxide **2**. This clearly represents a series of reactions, the nature of which was probed by adding limited amounts (1 atm) of carbon dioxide to a C_6D_6 solution of **1** in a 5 mm NMR tube; although excess CO_2 is present, the small head space and slow diffusion into solution allow us to monitor the process at intermediate stages. After ca. 5 min at ambient temperature, we find that **1** is consumed and that the niobium-containing products are **3** and Cp'$_2$NbCl(CO). These products are readily explained by the sequence presented in eq 17. The initial

$$1 + CO_2 \longrightarrow Cp'_2Nb\underset{CO}{\overset{Cl}{<}} + 2 \overset{1}{\longrightarrow} 3 \quad (17)$$
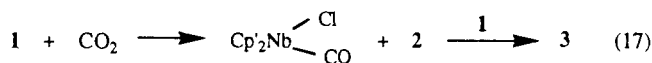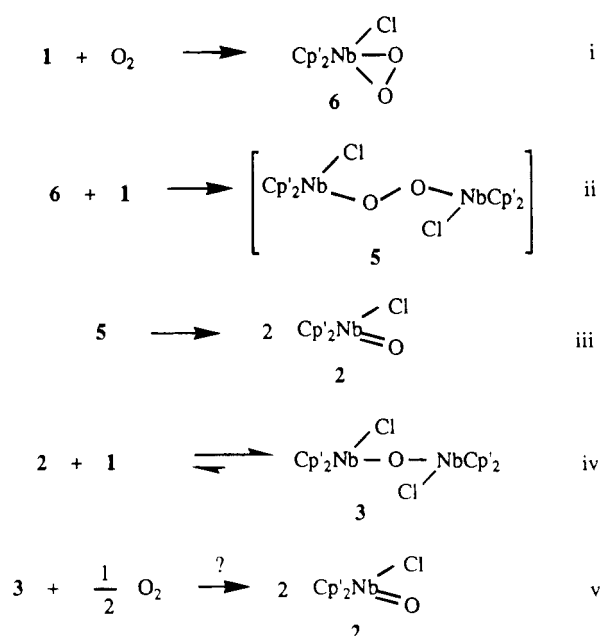
reduction of CO_2 is envisioned to yield oxide **2**, which subsequently reacts with **1** to yield the observed **3**; again, the equilibrium in eq 7 precludes the observation of **2** in the presence of unreacted **1**. If the reaction is allowed to proceed for an additional 5 min under these conditions, NMR monitoring indicates the loss of **3** and shows only **2** and carbonyl complex. This indicates that **3** has been consumed by added CO_2, undoubtedly generating **2** and additional carbonyl complex. At this point it is not clear if this requires the dissociation of **3** into **1** and **2** (eq 7) or if CO_2 reacts directly with the intact oxo dimer. If the same reacting solution is probed by NMR after ca. 1 h, it is clear that all of the carbonyl complex has been consumed and **2** is the only significant product. The carbonyl compound liberates the CO ligand when treated with O_2 or CO_2 but does not appear to undergo exchange with other added ligands; hence we favor a direct redox reaction between CO_2 and the intact carbonyl complex rather than prior dissociation to **1** and CO.

Discussion

Dioxygen Reduction and Preparation of 3. The results obtained to this point are best accommodated by the autoxidation sequence shown in Scheme 1. The overall process is depicted in five steps because the final step is not yet understood; clearly this last transformation will itself involve a multistep pathway. The initial interaction between **1** and dioxygen (step i) is depicted to involve the two-electron complexation event, and we have confirmed this by working under conditions in which step i is rendered rapid relative to step ii. Further reduction of the peroxide ligand requires an additional equivalent of reducing agent **1**, and this reaction between **6** and **1** has been seen to result promptly in **2**. We maintain that this conversion proceeds as indicated in steps ii and iii, even though direct evidence for the intermediacy of **5** is lacking. It is not surprising that **5** should be unstable and short-lived, inasmuch as it represents a point

Scheme 1

$$1 + O_2 \longrightarrow Cp'_2Nb\overset{Cl}{\underset{O}{\overset{\diagup}{-}}O} \quad i$$
$$\underset{\mathbf{6}}{}$$

$$6 + 1 \longrightarrow \left[Cp'_2Nb\overset{Cl}{\underset{O}{\diagdown}}\overset{}{O}\overset{}{\diagup}O\overset{}{\diagdown}NbCp'_2 \right] \quad ii$$
$$\underset{\mathbf{5}}{}$$

$$5 \longrightarrow 2 \; Cp'_2Nb\overset{Cl}{\underset{O}{\Longleftarrow}} \quad iii$$
$$\underset{\mathbf{2}}{}$$

$$2 + 1 \underset{\longrightarrow}{\overset{\longrightarrow}{\longleftarrow}} Cp'_2Nb\overset{Cl}{\underset{Cl}{-}}O\overset{}{-}NbCp'_2 \quad iv$$
$$\underset{\mathbf{3}}{}$$

$$3 + \frac{1}{2}O_2 \overset{?}{\longrightarrow} 2 \; Cp'_2Nb\overset{Cl}{\underset{O}{\Longleftarrow}} \quad v$$
$$\underset{\mathbf{2}}{}$$

at which the internal redox chemistry is arrested; **5** contains partially-reduced dioxygen (peroxide) and partially-oxidized Nb-(IV) centers. In the absence of direct evidence, we have used the superoxide chemistry (eqs 8 and 9) as an alternate entry into the sequence, and the result is consistent with both steps iii and iv. Indeed, we can also separate out step iv and have noted that this process constitutes the preferred route to **3**. Hence, the first four steps are extremely rapid in the direct reaction of **1** with dioxygen, and violet **3** is proposed to result within the time of mixing at room temperature. In this context it is worth noting that Struchkov and co-workers have reported the X-ray structure of an analogue of **3**, [(C$_5$H$_4$Me)$_2$NbCl]$_2$O.[39] This resulted from attempts to prepare Nb$-$Ga compounds and precipitated upon cooling a refluxing mixture of (C$_5$H$_4$Me)$_2$Nb-(μ-H)$_2$BH$_2$, BuLi, Et$_3$N, and GaCl$_3$ in THF. The solid state structure exhibited short Nb$-$O bonds (1.924(3) Å) and a Nb$-$O$-$Nb angle of 172.7(7)°, indicating partial multiple-bond character. These authors did not report extensively on the chemistry of their compound, which nonetheless clearly differs from that of **3**; the latter is extremely reactive above ca. 0 °C (vide infra). In fact, we have been unable to crystallize **3**, even at low temperatures. Several attempts at temperatures between -78 and -30 °C led to crystallization of **2**, sometimes contaminated with crystals of **1**. We noted earlier the facility with which **2** crystallizes, and this drives the equilibrium in eq

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7 to the left and precludes crystallization of **3**. Thus, even though we are unable to observe dissociation products by NMR, this process is clearly facile for **3**. We attribute this to the bulky SiMe$_3$ groups, which are typically located over the equatorial plane of the bent niobocene in solid state structures.

There remains the question of step v (Scheme 1), the process-(es) by which **3** ultimately generates **2**. The occurrence of this process has also been verified independently using isolated **3** and O$_2$, and we have kinetic data showing a two-term rate law and a dominant process exhibiting a dependence on dioxygen concentration. We thus believe that **3** reacts directly with O$_2$ and that prior dissociation (as in eq 12) is unnecessary for the primary event. An initial redox reaction between **3** and O$_2$ would yield **3$^+$** and superoxide, and Richman and co-workers have shown that diiron μ-oxo compounds fragment readily upon photochemical excitation to a distorted charge transfer excited state;[40] by analogy, formation of **3$^+$** may result in expulsion of **2** directly. We note, however, that Douglas and Green reported that oxidation of Cp$_2$NbCl$_2$ in concentrated hydrochloric acid and subsequent addition of tetrafluoroboric acid resulted in crystallization of the Nb(V) salt [(Cp$_2$NbCl)$_2$(μ-O)](BF$_4$)$_2$.[41] This compound is the Cp analogue of **3^{2+}**, and there is no indication of dissociation here. We have yet to probe the redox links among **3**, **3$^+$**, and **3^{2+}**, but these processes (particularly the possible conproportionation of **3** and **3^{2+}**) may lend valuable information regarding the mechanism of oxidation of **3**. The studies are pending, but we note that the fragmentation of **3$^+$** would generate **2**, **1$^+$**, and superoxide; a reaction between the last two would generate **6**. Since we have direct evidence for dissociation of **3** (discussed next) to **2** and **1**, the latter would be available to trap **6** and re-initiate the sequence proposed in steps i–iv (Scheme 1) for autoxidation.

Dissociation of 3. The reactions with PMePh$_2$ and the solid state degradation of **3** indicate the proclivity of the compound for dissociation. The activation entropy (-9 eu) determined in the phosphine substitution reaction (eq 12) is rather low for a dissociative process and suggests there is little or no bond breaking in the transition state. Matsuda et al. have studied a series of Mo(V) dimers [L$_2$Mo(O)]$_2$(μ-O) (L is a η^2-dithio- or η^2-diselenocarbamate) for which the dissociative disproportion-ation to L$_2$Mo^{IV}=O and L$_2$Mo^{VI}(=O)$_2$ is readily observed;[42] their values for $\Delta S^{\ddagger}$ are also rather low (ranging from $+7$ to -9 eu), from which they also conclude that the dimeric structure is maintained in the transition state. Their diselenocarbamate compound [(Et$_2$NCSe$_2$)$_2$Mo(O)]$_2$(μ-O) exhibits the lowest of their observed values for $\Delta S^{\ddagger}$ (-9 eu) and $\Delta H^{\ddagger}$ (12.7 kcal/mol), and a relatively low intensity ($\epsilon = 8100$ M^{-1} cm^{-1}) for the oxo-derived LMCT band; all of this is attributed to some combination of bending/twisting, which necessitates a structural change before dissociation can occur. We have been unable to gather structural information on **3**, but it too exhibits a low LMCT intensity. We are tempted again to invoke the SiMe$_3$ substituents; this requires that they provide the steric driving force for dissociation, while also causing a ground state distortion to be eliminated on the way to the dissociative geometry.

Nitrosoarene and Dioxygen Reduction. These substrates are thought to form niobocene complexes of varying stability, and the comparison in their reactivity is an interesting one. We noted above that Møller and Jørgenson recently reported the

reactions of molybdenum complexes of general formula (dipic)-(HMPA)Mo(=O)(η^2-L), in which dipic is pyridine-2,6-dicar-boxylate and L is either O$_2$ or ArNO;[34] they also developed a theoretical rationale for the comparison of the isoelectronic η^2-ArNO and η^2-peroxide ligands. They find that the N–O σ^* orbital is higher in energy than is the O–O σ^*, from which they predict that the nitroso compound will be less susceptible to reactions with donors (reductants) and that N–O cleavage will be more difficult than O–O cleavage. In view of this theoretical prediction, it is initially surprising that **1** forms a stable peroxide (**6**) with O$_2$ when N–O breaking precludes the observation of a stable nitrosoarene complex. However, it should be remembered that complex formation is a two-electron process (i.e., niobium serves as a two-electron donor in the backbonding formalism) while bond breaking presumably requires two additional electrons. In the case of O–O scission this requires a second equivalent of **1**, as depicted in eq 11 and Scheme 1, step ii. For the case of nitrosoarene, however, formation of a stable complex is not observed because a second equivalent of nitrosoarene itself serves to provide the additional reducing equivalents (eq 16); it would thus prove impossible to preclude N–O scission by using excess nitrosoarene to consume **1** rapidly, the strategy we used to prepare **6** from O$_2$. This involvement of the second nitrosoarene presumably results because the formation of the N–N bond renders the metallacycle accessible, while the weak O–O single bond would not accommodate an analogous Nb(O)$_4$ metallacycle. Thus the reducing (second) equivalent of nitrosoarene is formally oxidized in the azoxyarene product. This also points to the mechanistic importance of metallacyclic intermediates, which may provide avenues that can be unavailable to other redox systems with greater thermodynamic driving force.

Carbon Dioxide Reduction. It is of interest to compare the reactivity of **1** with that seen for related titanocene and zirconocene compounds. The trivalent dimer [Cp$_2$TiCl]$_2$ has been observed to undergo a reaction with CO$_2$ only under forcing conditions, involving temperatures of 90 °C and CO$_2$ pressures of 100 atm.[43] The resulting products are free CO and [Cp$_2$TiCl]$_2$O, with no evidence for additional reaction of the latter with excess CO$_2$. Although related systems have been observed to result in carbonate intermediates,[43,44] we see no evidence for carbonates in the current work. This is presumably true because **2** is insufficiently basic to react with CO$_2$. The divalent Cp$_2$Zr(CO)$_2$ or Cp$_2$Zr(PMe$_3$)$_2$ reacts more readily with CO$_2$,[43,45] converting at ambient temperature and pressure to CO and [Cp$_2$ZrO]$_3$. These processes have been proposed to proceed via initial formation of the η^2-CO$_2$-*C,O* complex, reaction with a second metal center to give a μ^2:η^1-*C*,η^1-*O* intermediate, and subsequent C–O cleavage to generate a carbonyl complex and an oxo complex. In fact, however, none of these proposed intermediates was observed. In the chemistry of **1**, the CO complex is observed, as is its subsequent reactivity with additional CO$_2$. Since the CO$_2$ complexes are well established in closely-related derivatives, we propose the sequence of events depicted in eq 18. Again, **1** supplies the two electrons necessary for complexation, whereupon a second equivalent of **1** is required to complete C–O bond scission; this presumably requires a bridged intermediate, although we have no direct proof of this. However, this may reveal why **1** reduces CO$_2$ so

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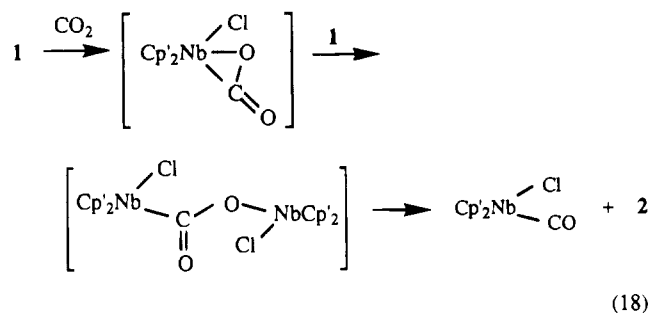(41) Douglas, W. E.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1796–1800.

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$$1 \xrightarrow{CO_2} \left[Cp'_2Nb \overset{Cl}{\underset{O}{\overset{|}{-}}} O \overset{|}{\underset{C}{\diagdown}} O \right] \xrightarrow{1}$$

$$\left[Cp'_2Nb \overset{Cl}{\underset{C}{\diagdown}} \overset{O}{\underset{\overset{||}{O}}{\diagup}} \overset{O}{\underset{Cl}{\diagdown}} NbCp'_2 \right] \longrightarrow Cp'_2Nb \overset{Cl}{\underset{CO}{\diagdown}} + \mathbf{2}$$

(18)

readily when $(C_5H_4Me)_2Nb(R)$ derivatives (which are apparently more electron-rich and reducing) form stable complexes;[37,38] if the $SiMe_3$ groups in **1** slow the rate of CO_2 complex formation, there will always be sufficient unreacted **1** present for further reduction. This is consistent with the observation that η^2-peroxide is only observable when the complexation step is rendered rapid relative to subsequent reduction and O—O scission (eq 10).

Summary. The present work illustrates that the autoxidation of **1** proceeds rapidly, as would be predicted for the electron-rich Nb(III) center. The first four mechanistic steps (Scheme 1) occur within the time of mixing **1** and excess dioxygen, but the use of suitable experimental controls has allowed for the observation of most of the individual steps. The comparison between this niobocene center and the more typical inorganic systems described in the Introduction is informative, in that **1** has accessible two orbitals, only one coordination site, and two higher oxidation states. Although there is similarity in some of these respects to Fe(II) and Cr(II), the availability of the empty π-symmetry orbital and the greater inherent stability of the Nb(V) oxide would be expected to bias the chemistry dramatically in favor of **2**. Although **2** does, in fact, represent the resting state for this system, the diamagnetic character of **1** and most of its oxygenated derivatives facilitates the identification of intermediates, and hence the mechanistic features, on the path to this compound. There is considerable literature evidence indicating the importance of ligand design, and the cyclopentadienyl ligands in **3** afford the opportunity to protect the niobium coordination site at which the oxygen chemistry occurs.

In spite of these apparent similarities, the chemistry described herein differs from the oxygen chemistry of many of the aforementioned metal complexes. Most notable is the electron deficiency of the oxide ligand in **2**; although related oxides have been used as nucleophiles in reactions with organic electrophiles or metal complexes,[29] it seems that **2** serves as the electrophile in its reactions with **1**. These differences do not manifest themselves after **3** is formed, and **3** shows magnetic and spectroscopic properties typical of μ-oxo compounds. Indeed, the strong interaction between oxo ligand and electron-deficient niobium center is typical of high-valent early transition metals and makes the ready observation of peroxides surprising; this reaffirms the importance of bimolecular processes in oxygen reductions and shows the utility of the blocking group ($SiMe_3$) on the coligands. In addition, the Cp' ligand exhibits a strong link to the niobium center; in this context it is worth comparing the oxygenations seen here with hydrolyses of related niobium compounds.[39h−l] Reactions of this type with $Cp'NbCl_4$, (C_5-Me_5)$NbCl_4$, and (C_5Me_5)$_2NbCl_2$ have been shown to proceed to μ-oxo compounds such as [$Cp'NbCl_2$]$_2(\mu$-Cl)$_2(\mu$-O), [(C_5-Me_5)$NbCl_2$]$_2(\mu$-Cl)(μ-OH)(μ-O), and [(C_5Me_5)$NbCl$]$_3(\mu$-Cl)(μ_3-O)(μ-O)$_3$. This synthetic approach is thus susceptible to ligand hydrolysis and product mixtures that depend critically on the specific reaction conditions, but it also leads to a rich structural chemistry.[46] The oxygenation of **1** shows no apparent susceptibility to ligand oxidation, and the limited number of accessible structure types has allowed for the stepwise characterization of oxidation sequences. The information available here is thus, to an extent, complementary to that from the hydrolyses, and future work will compare the degree to which these synthetic approaches share mechanistic features.

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