Effects of the Niobium(V) Center on the Energetics of Ligand-Centered Proton and Hydrogen Atom Transfer Reactions in Acyl and Alkoxide Complexes

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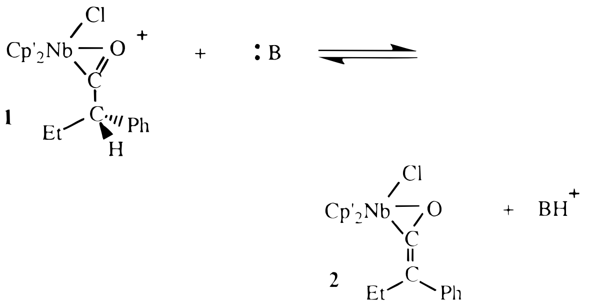
*Summary: Cationic niobium η^2-acyl (**1**) and alkoxide (**3**) compounds are relatively strong C−H acids which give stable η^2-ketene (**2**) and η^2-formaldehyde (**4**) complexes upon deprotonation. Determinations of the C−H bond dissociation enthalpies (BDEs) show that $\mathbf{2}^{\bullet+}$ gains little stabilization from radical delocalization but that generation of a Nb−C σ bond facilitates the homolytic conversion of **3** to $\mathbf{4}^{\bullet+}$.*

The catalytic reduction of carbon monoxide is a process through which readily available synthesis gas can be converted to hydrocarbons or oxygenated derivatives. The mechanistic proposals forwarded for the latter include (a) a sequence of insertion reactions in which CO is converted to a formyl group, a formaldehyde ligand, and ultimately methanol[1] and (b) scission of the C−O bond, hydrogenation of the carbide to a methylene, reaction with CO to make ketene, and subsequent conversion of the ketene to alcohols, esters, etc.[2] Some of these processes have model chemistries involving the free organic moieties, but many can only proceed within the coordination sphere of a metal. While a complete understanding of these reactions requires detailed information on the energetics of the key reactions, this is rarely available for the metal-induced reactions. We have begun a program designed to study the energetics of ligand-centered organometallic reactions, with the specific goal of determining the energetic contribution of the metal center to these processes. Herein we report a comparative study on niobium-bound acyl and alkoxide ligands, including an assessment of the C−H bond strength and thermodynamic acidity. These data will show that the metal may have a profound effect on the energetics of these proton and/or hydrogen atom transfer reactions.

We have previously reported the pK_a's of a series of cationic niobium η^2-acyls, including the ethyl-phenyl derivative **1** (Cp′ = η^5-$C_5H_4SiMe_3$).[3] This compound was originally prepared by protonation of the corresponding ketene complex **2**, and both conjugate acid **1** and conjugate base **2** have been characterized by X-ray diffraction.[4] A study of **1** in acetontrile indicated that it has a pK_a value of 10.4 ± 0.3; since structurally similar acyls exhibited a DMSO pK_a ca. 11 units lower than the MeCN pK_a,[5] we can estimate that **1** would exhibit a DMSO pK_a of ca. −1. For comparison, a series of phenyl ketones exhibit enolization pK_a's ranging from ca. 17 to 24 in DMSO; specific examples include $PhC(O)CH_2Ph$ (pK_a = 17.65), $PhC(O)CHPh_2$ (pK_a = 18.7), and $PhC(O)CH_3$ (pK_a = 24.7).[6] Clearly, the metal center in **1** exerts a considerable effect on the enolization acidity of the bound η^2-acyl; the 20 pK unit contribution corresponds to 27 kcal/mol.



(1)

Several previous studies have illustrated the use of solution acidity data with an appropriate thermodynamic cycle to establish gas-phase bond dissociation energies (BDE's; eq 2).[7] The conversion requires thermodynamic information on the oxidation of the conju-

$$\mathrm{BDE} = 1.37[\mathrm{p}K_a(\mathbf{1})] + 23.1\,[E_{ox}(\mathbf{2})] + C \qquad (2)$$

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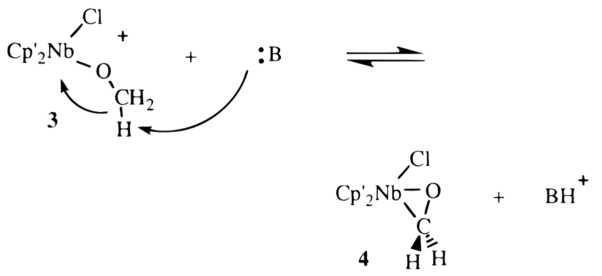
gate base and the reduction of the proton, and the latter is included in the term *C* (as are solvation energies and entropy contributions); this has been evaluated as 59.5 kcal/mol when the solution work is carried out in MeCN, and the redox potentials are referenced to ferrocene/ferrocenium (Fc/Fc$^+$).[8] Voltammetric determination of the thermodynamic oxidation potential ($E°$) formally requires a reversible redox process. The voltammetric oxidation of **2** is wholly irreversible, and we have used infrared spectroelectrochemistry to verify that the associated chemical process involves ketene labilization; this was obvious from the strong ketene band at 2100 cm^{-1}.[9] In some instances it is acceptable to use the peak potential as a reasonable estimate of $E°$,[10] although this depends on the kinetics of the following reaction.[8] In the case of **2**, we have obtained voltammetric data at two scan rates and simulated the data (see the Supporting Information) so as to confirm that a mechanism involving first-order ligand loss is consistent with the voltammetric data. The lack of a return (reduction) wave requires a first-order rate constant for ligand loss $k \geq 10$ s^{-1} at this sweep rate; this would indicate that $E° = 0.243$ V, and the use of eq 2 leads to a C−H BDE of 79 kcal/mol. This is a lower limit, but a first-order rate constant as high as 10^{10} s^{-1} requires $E° = 0.495$ and leads to a calculated BDE of 85 kcal/mol;[8b,11] we thus report a value of 82 ± 3 kcal/mol for the C−H BDE in **1**. This value may be compared with data for the following phenyl ketones: $PhC(O)CH_3$ (BDE 93 kcal/mol), $PhC(O)CH_2Ph$ (BDE 82.3 kcal/mol), and $PhC(O)CH_2Me$ (BDE 88.6 kcal/mol).[12] The α-phenyl group stabilizes the radical by ca. 12 kcal/mol, and the α-methyl stabilizes the radical by ca. 5 kcal/mol; although the degree to which these are additive is not known, it is nonetheless clear that the BDE for **1** is entirely within the range expected for a comparably substituted ketone. Further, the value for acetophenone shows that the carbonyl moiety lends little stabilization to the adjacent radical, presumably because there is little delocalization due to the instability of the oxygen-centered radical.[13]

The cationic methoxy−niobium compound **3** was prepared by protonation of the known η^2-formaldehyde complex **4**.[14] Mixtures of **3** and **4** were readily identified in $CDCl_3$ solution, but their interconversion was rapid (on the NMR time scale) in MeCN. This was confirmed by dissolving **3** and adding aliquots of $[Et_2OH][BF_4]$; this allowed us to establish the chemical shift limits for the formaldehyde ligand in **4** (3.46 ppm) and the methoxide ligand in **3** (3.91 ppm) and to verify that the protonation process is reversible. Conjugate acid **3** again proved too acidic for study in DMSO, but titration with pyridine in MeCN led to the determination of the pK_a of 10.1 ± 0.3 for **3**.[15] Again, the corresponding DMSO pK_a should be ca. 0 ± 1; this may be compared with the organic model compound methyl phenyl ether ($PhOCH_3$), for which the DMSO pK_a has been estimated to be 49.[6] From this we conclude that the metal center has exerted an effect corresponding to ca. 50 pK units (68 kcal/mol) on the C−H acidity. The oxidation of **4** proved to be quasi-reversible; therefore, the data allow us to identify an $E_{ox}°$(**4**) value of −0.072 (vs Fc/Fc$^+$). Use of eq 2 indicates that the C−H bond in **3** has a BDE of 72 ± 2 kcal/mol. The C−H bond of methanol has a BDE of 94 ± 2 kcal/mol,[16] suggesting that the niobium center in **3** has weakened the C−H bond by a substantial 22 kcal/mol.



(3)

In comparing acyl **1** and methoxide **3**, we note that the metal center enhances the acidity of both ligands (in **3** more so than **1**) and exerts a significant effect on the ligand C−H bond strength of **3**, but not of **1**. The latter difference may be understood by comparing the processes involved, and this is done in eqs 4 and 5. The positive charge in **1** is shared by the oxygen and carbon atoms of the η^2-acyl ligand; loss of the hydrogen atom gives a tertiary radical center that gains little stabilization from delocalization onto oxygen or the metal. For **3**, however, the positive charge is shared by the oxygen and the niobium center;[17] loss of hydrogen atom does not give a carbon-centered radical but leads to formation of a Nb-C bond. This is an elimination reaction, and Nb−C bond formation contributes a significant thermodynamic component to the C−H homolysis; a similar contribution assists in deprotonation (eq 3) and is presumably responsible for the acidity of **3**. A recent calorimetric study has shown that the Nb^{IV}−Me bonds in Cp_2NbMe_2 have an average BDE of 60 kcal/mol,[18] and a Nb^V−C bond should be ca. 10 kcal/mol weaker.[19] Organic epoxides are known to have ring strain of 27−28 kcal/mol.[20] It is not clear if the same value applies

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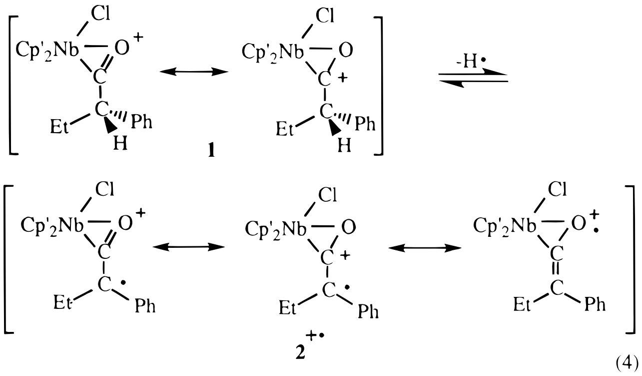
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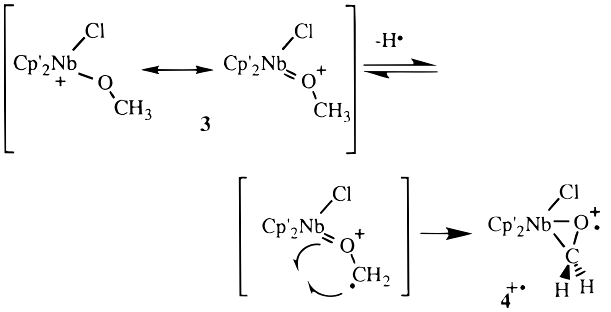
(5)

to metal-containing three-membered rings such as that in **4**; if it does, however, 22 kcal/mol is a very reasonable estimate for the thermodynamic contribution of the Nb−C bond in $\mathbf{4}^{+}$. It is also possible to depict the products in eqs 4 and 5 as metal-centered radical cations, and this serves to remove unpaired spin density from the organic ligand. While this could provide a stabilizing contribution for $\mathbf{4}^{\bullet +}$, we do not consider this a major factor; a similar resonance structure is available for $\mathbf{2}^{\bullet +}$, for which no apparent stabilization is evident from the C−H BDE. In any case, it is clear that Nb−C σ bond formation constitutes a significant driving force in the reactions in eqs 3 and 5.

In summary, the presence of an electron-deficient metal center (as would be present in an oxide-supported metal catalyst) has a substantial effect on the thermodynamics of intraligand hydrogen and proton transfers. Proton and hydrogen atom loss from a β-carbon center (in **3**) is facilitated by formation of the M−C σ bond, and **3** is slightly more acidic than is compound **1**; in the latter, the ionizing center does not bind to the metal center and must rehybridize to gain stabilization of the incipient radical or carbanion. The use of the appropriate thermodynamic cycle promises to yield considerable information on ligand thermodynamics, and future work will be designed to probe the thermodynamics of related intraligand reactions.

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Supporting Information Available: A figure giving experimental and simulated voltammetric data for the oxidation of **2** (1 page). Ordering information is given on any current masthead page.

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