5, were 0.2 e/Å^3 and were not within bonding distance to any atom in the molecule). Final refinement included these peaks as "hydride" ligands in which their positional and thermal parameters were refined. Selected bond distances and angles are given in Table IV.

(η^5-C_9H_{10})ReH(PPh_3)$_2$ (6). A yellow crystal of **6** with approximate dimensions 0.1 × 0.3 × 0.2 mm^3 was mounted on a glass fiber and placed on the diffractometer at 25 °C. Data collection and reduction were as for **1** with a monoclinic crystal system, in accord with the parameters in Table IX. The space group was uniquely assigned as $P2_1/n$. Anisotropic refinement of all non-hydrogen atoms was carried out with hydrogen atoms attached to carbon included in fixed, idealized positions (thermal parameters set to 1.2 × B_{iso}(carbon)). A difference Fourier map was now calculated using only data with sin $\theta/\lambda < 0.34$ ($\theta < 14°$). The largest peak (0.5 e/Å^3) was in a position corresponding to that expected for the hydride ligand on the basis of the geometry of the other ligands. (The next largest peaks, nos. 2-5, were 0.1-0.2 e/Å^3 and were not within bonding distance to any atom in the molecule.) Final refinement included this peak as a "hydride" ligand in which the positional and thermal parameters were refined. Selected bond distances and angles are given in Table V.

(η^4-C_9H_{12})ReH_3(PPh_3)$_2$ (7). A yellow crystal of **7** with approximate dimensions 0.15 × 0.25 × 0.15 mm^3 was mounted on a glass fiber and placed on the diffractometer at 25 °C. Data collection and structure refinement were as for **1** with a monoclinic crystal system. Data were collected in accord with the parameters in Table IX. The space group was uniquely assigned as $P2_1/n$. The isotropically refined model showed evidence for disorder of C38 between two possible locations, and consequently a second carbon (C38B) was introduced and refined isotropically, allowing the populations of C38A and C38B to vary together. One of the phenyl groups was also refined as a rigid group with isotropic thermal parameters as anisotropic refinement led to nonpositive definite values. Anisotropic refinement of all remaining non-hydrogen atoms was carried out with hydrogen atoms attached to carbons in fixed, idealized positions (thermal parameters set to 1.2 × B_{iso}(carbon); disordered hydrogens omitted on atoms C37-C39). A difference Fourier map was then calculated using only data with sin $\theta/\lambda < 0.34$ ($\theta < 14°$). Three peaks among the top eight peaks (0.4-0.6 e/Å^3) were in locations corresponding to the expected locations for the three hydride ligands on the basis of the geometry of the other ligands. (The other largest peaks, nos. 1, 2, and 5-7, were all in between the carbon atoms of the rigid phenyl group.) Final refinement included these peaks as "hydride" ligands in which their positional and thermal parameters were refined. The isotropic thermal parameter for the central hydride went slightly negative and was consequently fixed at 1.0. Selected bond distances and angles are given in Table VI.

(η^5-C_9H_{11})ReH_2(PPh_3)$_2$ (8). A yellow crystal of **8** with approximate dimensions 0.15 × 0.2 × 0.25 mm^3 was mounted on a glass fiber and placed on the diffractometer under a stream of nitrogen at 0 °C. Data collection and structure refinement were as for **1** with a primitive triclinic crystal system. Data were collected in accord with the parameters in Table IX. The space group was assigned as $P\bar{1}$. The hydrogens attached to the Re atom were not located. Selected bond distances and angles are given in Table VII.

[(η^6-C_9H_{10})ReH_2(PPh_3)$_2$][ReO_4] (9). A yellow crystal of **9** with approximate dimensions 0.2 × 0.1 × 0.2 mm^3 was mounted on a glass fiber and placed on the diffractometer at 25 °C. Data collection and structure refinement were as for **1** with a monoclinic crystal system, in accord with the parameters in Table IX. The space group was uniquely assigned as $P2_1/n$. The hydrogens attached to the Re atom were not located. Selected bond distances and angles are given in Table VIII.

Acknowledgement is made to the U.S. Department of Energy (Grant FG02-86ER-13569) and to NATO for a travel grant.

Supplementary Material Available: Tables of fractional atomic coordinates, bond distances and angles, and thermal parameters (80 pages); tables of calculated and observed structure factors (129 pages). Ordering information is given on any current masthead page.

Equilibrium Acidities of Some Transition-Metal Acyl Compounds

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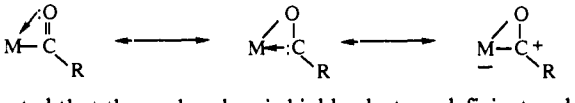
Abstract: There is readily available a series of stable niobium acyl and iminoacyl compounds of the general formula [(η^5-$C_5H_4SiMe_3$)$_2$Nb(X)(η^2-CECHR$_2$)][BF_4] (E = O, NR; X = H, Cl); these are prepared by protonation of their conjugate bases, the corresponding ketene, or ketene imine complexes. These proton-transfer equilibria have been studied in dimethyl sulfoxide or acetonitrile with organic acids of known pK_a, allowing for the determination of enolization pK_as for the η^2-acyl and -iminoacyl ligands. The acyls are appreciably more acidic than are the corresponding phenyl ketones (those in which a phenyl group replaces niobium), with pK_a differences of ca. 18-24 pK units. The acyls are somewhat less sensitive to changes in substituents at the ionizing position than are the ketones, but they are surprisingly sensitive to the electronic properties of the neighboring ligand. A few representative η^1-acyl compounds have been studied, and these are substantially less acidic than are the organic ketones. The enhanced acidity of the η^2-acyls is thus attributed to the interaction of the cationic niobium center with the acyl heteroatom, and the data contribute to a semiquantitative understanding of the influence of the metal on the solution chemistry of the acyl ligand.

Introduction

The η^2-acyl ligand was first identified in 1971,[1] and it has been the subject of extensive study ever since.[2] The interest in this ligand stems primarily from its role in the reduction of carbon monoxide, a process that has been shown to involve many reactions that are unavailable to η^1-acyls.[3] Since these include a variety of insertion, C-C coupling, and hydrogen migration reactions, η^2-acyls were originally considered to possess a substantial oxycarbene character. However, recent theoretical studies have



indicated that the acyl carbon is highly electron-deficient and is therefore better described as a carbenium ion center.[4] The

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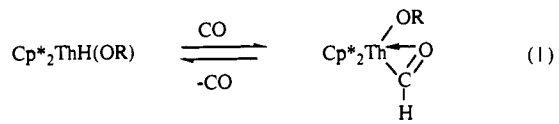
Table I. Acidities of Metal Acyls[a]

	compound $[Cp'_2Nb(X)(C(O)CHR^1R^2)]^+$			Me_2SO		MeCN	
	R^1	R^2	X	pK_a	*HA*[b]	pK_a	*HA*[b]
1	Me	$CH_2{}^tBu$	H	7.0 (5)	$4\text{-}NO_2C_6H_4CO_2H$		
2	Me	$CH_2{}^tBu$	Cl	2.0 (3)	$PhNH_3^+$	13.4 (3)	pyH^+
3	Me	Me	Cl	1.8 (2)	$PhNH_3^+$	12.8 (2)	pyH^+
4	Et	Ph	Cl			10.4 (3)	$4\text{-}CF_3C_6H_4NH_3^+$
5	Et	Ph	H	1.6 (1)	$PhNH_3^+$		
6	Ph	Ph	Cl			9.0 (2)	$4\text{-}CNC_6H_4NH_3^+$
7	$CpFe(CO)(PPh_3)COCHMe_2$			>35	^tBuOH		
8	$Cp_2Mo(H)(COCH_3)$			>35	^tBuOH		
9	$[Cp'_2Nb(Cl)(CNPhCHPh_2)]^+$			4.7 (2)	$2,4\text{-}(NO_2)_2C_6H_3OH$	14.6 (2)	$2,4\text{-}(NO_2)_2C_6H_3OH$
10	$[Cp'_2Nb(Cl)(CNEtCHPh_2)]^+$					18.0 (3)	$PhCH_2NH_3^+$
11	$PhC(O)CHMe_2$			26.25 (10)[c]			
12	$PhC(O)CHPh_2$			18.7 (1)[c]			

[a] Numbers in parentheses represent the uncertainty in the final digit, quoted on the basis of the range of data obtained. [b] Reference acid used (see Table II). [c] Data from ref 21.

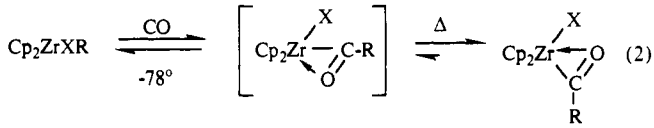
unusual electronic properties of this carbon center are presumably the result of the metal–oxygen interaction, but it has proved difficult to gather quantitative or semiquantitative data to substantiate this. In view of the fundamental importance of this interaction, further characterization of the metal–acyl bond is clearly warranted.

There are thermodynamic data on the insertion of carbon monoxide into metal–carbon and metal–hydride bonds, and Marks has suggested that the production of a thorium η^2-formyl (eq 1) is rendered exothermic by the metal–oxygen bond that is formed.[5]



(1)

However, the consideration of bond dissociation energies in this reaction leads to the conclusion that the Th–O bond is worth only ca. 5 kcal/mol; it was noted that this estimate is probably too low.[5a] Another possible approach to the determination of the M–O bond strength involves a study of the barrier to rotation exhibited by the acyl ligand. Unfortunately, this too is prone to difficulties. First, dynamic NMR studies on the related iminoacyl ligand are consistent with a process involving spinning about the midpoint of the C=N bond;[6] in particular, the data are *not* consistent with a process which involves the η^2–η^1–η^2 pathway. Theoretical studies *are* consistent with the operation of such a process in acyl rotations,[4,7] but they predict relatively low barriers ranging from 3 kcal/mol for molybdenum acyls to ca. 18.5 kcal/mol for zirconocene systems. Indeed, Erker has studied the isomerization of zirconocene acyl derivatives from O-outside to O-inside isomers (eq 2), and the barriers range from 11 to 15 kcal/mol.[8] Curtis



(2)

has suggested that these low barriers arise from the fact that the loss of the M–O bond is accompanied by the strengthening of the M–C bond during the η^2–η^1 isomerization process.[7] Others have also noted the difficulties associated with partitioning such effects between the M–C and M–O bonds,[5] so isomerization barriers do not represent a direct measure of the M–O bond strength. Likewise, there are some acyl compounds that exhibit an interconversion between η^2 and η^1 bonding modes, but these reactions are usually induced by the formation of a new metal–ligand bond; this has been seen in the intermolecular addition of, e.g., a carbonyl ligand to various group VI acyl compounds[9] and also in the tautomerization of a molybdenum η^2-acyl to an isomeric η^1-acyl with an agostic C–H ligand.[10] Although it is possible, in principle, to separate out the contribution due to the new metal–ligand bond, no thermodynamic analyses have been carried out on such systems.

Curtis has advocated the use of structural data in the study of η^2-acyls, and an independent consideration of the M–O and M–C bonds is explicit in this approach.[7] The parameter Δ is defined as the quantity d(M–O)-d(M–C), where d is the crystallographically-determined length of the indicated bond. A more significant M–O interaction should give rise to a smaller value of Δ and would be predicted for highly electron-deficient metal centers. Indeed, it has been shown that there is a reasonable correlation between Δ and metal d-electron count, with d^0 compounds (usually containing metals from Group III, IV, or V or the lanthanide or actinide series) showing the lowest Δ values.[11] However, there is at least one interesting exception to this general trend. The d^6 system Fe(dippe)(Br)(CO)(η^2-C(O)mesityl) (dippe = bis(diisopropylphosphino)ethane) has been found to exhibit an anomalously low Δ value (0.14 Å) and the shortest M–O bond length yet observed in a η^2-acyl compound.[12] Nonetheless, it is not yet clear whether there are any chemical ramifications associated with this structural irregularity.

In the present work we have chosen to study some cationic niobium η^2-acyl and -iminoacyl compounds, one each of which ($[Cp'_2Nb(Cl)(\eta^2\text{-}C(O)CHEtPh)][BF_4^-]$[13] and $[Cp'_2Nb(Cl)(\eta^2\text{-}CNPhCHEtPh)][BF_4^-]$,[14] Cp′ = η^5-$C_5H_4SiMe_3$) has been structurally characterized. The resulting metrical parameters indicate significant Nb–O and Nb–N interactions, with respective Δ values of 0.112 and −0.022 Å; these values are both near the low end of the ranges known for the two classes of compounds, as would be expected for a cationic d^0 system. However, the current work is based on determinations of solution reactivity rather than on aspects of the solid-state structures. Specifically, we have utilized equilibrium methods to determine the pK_as of protons α to the carbonyl or imino group. The advantage of this approach is that we can study a number of compounds containing various ligands and substituents with different electronic and steric properties, allowing for a systematic comparison of their effects. We are unaware of any previous determination of metal acyl

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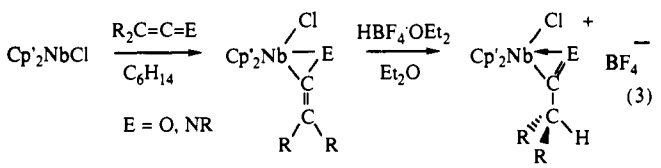
enolization pK_as, in spite of the established synthetic utility of the metallaenolates.[15] Indeed, we have found that (a) these compounds exhibit extremely low pK_as, much lower than the corresponding ketones, (b) pK_as are sensitive to the electron density at the metal center, and (c) we can utilize some semiquantitative comparisons to suggest that this effect results primarily from the Nb–O or Nb–N interaction.

Results

Synthesis. The syntheses of the niobium compounds have been reported recently.[13,14] The general route involves the addition of the appropriate heterocumulene (ketene or ketene imine) to the electron-rich fragment Cp'$_2$NbCl, resulting in the preparation of the O- and N-inside η^2-(C,O) and η^2-(C,N) complexes. We have reported that the complexed ketenes are susceptible to protonation at the ketene β-carbon and that the result is the production of cationic η^2-acyls (eq 3, compound numbers are indicated in Table I);[13] a similar strategy was subsequently applied to the synthesis



of the corresponding iminoacyl compounds.[14] This chemistry is part of our general strategy to use the reactivity of the complexed heterocumulene in the synthesis of organometallic molecules.[16] Note that free ketenes are characterized by the electrophilic nature of the central carbon and are extremely susceptible to attack by a wide range of nucleophiles;[17] this can be moderated by the formation of the η^2-(C,O) complexes, which are largely unreactive toward nucleophiles. The current route to acyls is particularly valuable since niobocene and tantalocene systems are not normally susceptible to migratory insertion of carbon monoxide.[18]

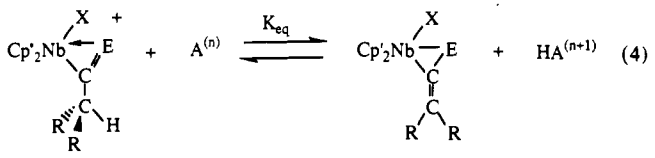
A number of significant aspects of the acyl syntheses have a bearing on the current work. First, the reaction involves the interconversion of compounds constituting a conjugate acid/base pair. Moreover, in most cases both are stable, diamagnetic, crystalline solids that are readily differentiated by common spectroscopic techniques, facilitating the equilibrium measurements to be described below. Finally, convenient synthesis of the acyl complexes requires the use of diethyloxonium tetrafluoroborate ($Et_2OH^+BF_4^-$); this is a strong acid, the aqueous pK_a of which has recently been reported as −2.39.[19] The utility of this acid may in part derive from effective packing of the tetrafluoroborate anion in the resulting salts, all of which precipitate out of ether immediately after the addition of acid. However, trifluoroacetic acid was ineffective in the preparations of **4** and **6**, apparently because it led to equilibrium mixtures rather than complete conversion to the desired acyl. These observations suggested that the niobocene acyls are quite acidic at the position α to the carbonyl. Our access to a variety of stable conjugate acid/base pairs provided an opportunity to determine the acyl pK_as.

Table II. Reference Acid Data[a]

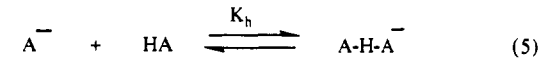
	Me_2SO		MeCN	
acid	pK_a	K_h	pK_a	K_h
4-nitrobenzoic	9.0	(50)[b]		
anilinium	3.6	0		
pyridinium[c]			12.33	3.98
benzylammonium			16.76	15.85
4-(trifluoromethyl)anilinium[c]			8.6	0
4-cyanoanilinium[c]			7.6	0
2,4-dinitrophenol	5.12	0	16.0	100
tert-butyl alcohol[c]	32.2			

[a] Data are from refs 20–23. [b] Estimated from 3,5-dinitrobenzoic acid (pK = 7.4, K_h = 23) and benzoic acid (pK = 11, K_h = 79) as discussed in text. [c] In these cases the conjugate base of the indicated acid was used to establish equilibrium (see Experimental Section).

Experimental Approach. The immediate aim here is to establish equilibrium with a ketene–acyl system and an acid–base pair in which the acid pK_a is known (eq 4, n = −1, 0). This requires



an acid with a pK_a within ca. 2 pK units of the unknown acyl. Again, the ready access to either acyl or ketene complex allows us to enter the equilibrium from either side, depending on whether the known acid or its conjugate base is more readily available in sufficient purity. The initial plan was to utilize dimethyl sulfoxide (Me_2SO) in all pK_a determinations. This solvent is readily available in high purity, it has a high dielectric constant, and it functions as a good hydrogen-bond acceptor but a poor hydrogen-bond donor.[20] Further, Bordwell and co-workers have determined the pK_as of hundreds of organic compounds, including many ketones, in this solvent,[21] and we wished to be able to compare our acyl pK_as with these ketone data. The solvent characteristics minimize the effects due to ion pairing and homohydrogen bonding (eq 5); unfortunately, Me_2SO is sufficiently



basic that it exhibits leveling of strong acids (those with pK_as below ca. 1.5), and it thus proved inappropriate for some of the acyls studied herein. As an alternative, acetonitrile was used in many cases. This solvent has been recommended for the determination of metal hydride pK_as because it too has a high dielectric constant, minimizes ion pairing, and is effective in solvating transition-metal compounds (especially ionic salts of transition metals).[22] It is a very weak acid and base and is thus appropriate for the study of some acids which are leveled in Me_2SO.[20a] For some of the known acid–base pairs utilized herein, homohydrogen bonding (eq 5) was known to occur to a significant extent. Many of the homohydrogen-bonding equilibrium constants (K_h) have been reported in the literature,[20a,23] but we were unable to locate such

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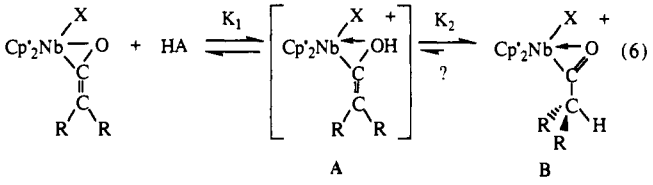
data for 4-nitrobenzoic acid (see Table II). Bordwell has noted that the tendency to engage in homohydrogen bonding tends to track acid pK_a;[23b,c] hence, we used the available Me_2SO data for benzoic acid (pK_a = 11.0, K_h = 79)[23b] and 3,5-dinitrobenzoic acid (pK_a = 7.4, K_h = 23)[23a] to estimate a K_h of 50 for 4-nitrobenzoic acid (pK_a = 9.0). In general, homohydrogen bonding is more significant in MeCN since this solvent is a poorer hydrogen bond acceptor than is Me_2SO.[20] For the acids exhibiting significant homohydrogen bonding, this second equilibrium (eq 5) would be expected to alter the equilibrium concentrations of HA and A–, neither of which is measured directly. However, the concentrations of these two species can be determined by considering both equilibria (eqs 4 and 5) and solving simultaneous equations; the method has been explained in detail by Norton, and the presentation need not be repeated here.[22a]

The desired equilibria were established using stock solutions of the known and unknown acids and bases. Of the various spectroscopic techniques tested, ^1H NMR was the most useful for determining the equilibrium concentrations of acyl and ketene complexes. The UV–visible spectra were frequently complicated by the overlap of various bands, and the acyls exhibit IR bands that are too weak to be reliable for quantitative determinations. Long pulse delays (several seconds in some cases) were utilized in the NMR experiments, and there was no evidence that the integrations were affected by these. Clearly the experiments required the use of deuterated MeCN and Me_2SO. Since neither compound is an effective hydrogen-bond donor, there is no reason to anticipate any discrepencies arising from the use of the deuterated analogues. Although no kinetic measurements were carried out, there were no apparent complications arising from extremely fast or slow reactions. The desired equilibria were typically established within minutes of mixing (usually sooner). In addition, and crucial to the approach used here, there was no evidence for acyl complex/ketene complex exchange that was rapid on the NMR time scale at 25 °C (i.e., no exchange-averaged signals). This simplified the quantitation of equilibrium concentrations and also suggests there is no significant involvement of the enol-like tautomer **A** depicted in eq 6. A significant population of species



(6)

A would be expected to enable rapid exchange in equilibrium process 1, since the acids (HA) we used are all oxygen or nitrogen acids. While enol **A** may be involved in the initial proton transfer from HA, it has no detrimental effect on the rate; moreover, both solution spectral data and X-ray data show that tautomer **B** is the only observable component of hypothetical equilibrium 2.[13]

Acyl and Iminoacyl pK_a Data. Table I contains pK_as for the seven niobium compounds studied here. Each determination was based on the measurement of four or five separate equilibria, and the uncertainities quoted represent the spread in all determinations for the indicated compound with the indicated known acid. In most cases the unknown pK_a was first bracketed with one of two trial acids before an appropriate acid could be identified, so this bracketing process represents an alternate semiquantitative confirmation of the data presented. We also studied two η^1-acyl compounds (**7** and **8**) for comparison but were only able to determine lower bounds for these pK_as. Liebeskind has reported that the iron metallaenolates (derivatives of the conjugate base of **7**) are unstable toward metal-to-ring migration of the enolate moiety at room temperature,[15b] and we were also unable to prepare and characterize a stable molybdenum metallaenolate; hence equilibria of the sort presented in eq 4 are inaccessible. In both cases, we confirmed that the acyl compounds failed to react with various alkoxides (including *tert*-butoxide) in Me_2SO; since the corresponding alcohols have pK_as of 30–32 in Me_2SO,[21] we estimate a lower limit of ca. 35 for the η^1-acyls **7** and **8**. Finally, Table I also contains data for two comparable ketones, the pK_as of which were determined by Bordwell and co-workers.[21] Some of the niobium compounds were studied in MeCN, some in Me_2SO, and some (**2**, **3**, and **9**) in both solvents. The choice of solvents was predicated on two factors. First, some of the acyl chlorides (**4** and **6**) proved to be too acidic for study in Me_2SO, while **3** and **5** are very close to the leveling limit of this solvent. Indeed, the overall range observed in Me_2SO is ca. 1.6–7.0, indicating that the acyls are appreciably acidic. The leveling problem prompted the search for another solvent system, and MeCN was chosen for the reasons noted above. However, the ketene hydride compounds (**1** and **4**) undergo a reaction with MeCN, the nature of which has not been determined (it does *not*, however, appear to involve simple insertion of MeCN into the Nb-H bond). Hence, all of these compounds were studied in Me_2SO only. For the compounds studied in MeCN solution, the pK_as ranged from 9.0 to 14.6. Since compounds **2**, **3**, and **9** proved amenable to study in both solvent systems, the two data sets can be anchored with some confidence. In all cases the compounds proved to be ca. 11 pK units less acidic in MeCN solution, suggesting that the pK_as of **4** and **6** would be −1 and −2, respectively, in Me_2SO solution.

Discussion

Data Trends. In comparing the data for the two solvent systems, the values of ca. 11 for the ΔpK_as (defined as $pK_a(MeCN) - pK_a(Me_2SO)$ for a given compound) compare reasonably well with those seen for several other compounds; a series of carboxylic acids and ammonium compounds taken from the literature shows an average ΔpK_a of ca. 9–10 in these two solvents.[20a] It has been shown that the proton is solvated more effectively in DMSO (vs MeCN) and that the difference in solvation energy corresponds to a difference of 11.4 pK units.[20c] Hence, it seems that the pK differences in the two solvents observed for compounds **2**, **3**, and **9** are *not* related to any differential solvation of the ketene and acyl complexes in the two solvents but can rather be explained solely on the basis of proton solvation differences. This interpretation is entirely consistent with Norton's conclusions on the transferability of metal hydride pK_as between water and MeCN.[22c]

A comparison of some of the data in Table I yields an understanding of the influences of various substituents. The effect of substituents at the ionizing position is clear from the pK_as for compounds **2**, **3**, **4**, and **6**. The first two in this series contain α,α-dialkylacyl ligands, **4** contains an α-alkyl-α-arylacyl, and **6** contains an α,α-diarylacyl. Predictably, dialkyl compounds **2** and **3** exhibit similar acidities in both solvents used here. The effect of replacing an electron-releasing alkyl with an electron-withdrawing aryl (**4**) is to lower the pK_a by ca. 2.4–3 pK units. A further such replacement corresponds to diphenyl compound **6**, in which the pK_a drops by another 1.4 pK units (MeCN solution). The replacement of two alkyls with two aryls thus results in a total change of ca. 4 pK units. One can compare this trend with that exhibited by ketones **11** and **12** in Me_2SO solution.[21] Here a similar situation results in a difference of 7.55 pK units, suggesting that the organic analogues are appreciably more sensitive to the nature of the α substituents than are the η^2-acyl compounds.

The availability of acyl chloride and acyl hydride compounds also allows for a determination of the effect of these two cis ancillary ligands on acyl and iminoacyl pK_as. Since these ligands are a full four bonds removed from the ionizing site, one might a priori anticipate small differences. However, comparison of chloride derivative **2** with hydride analogue **1** shows that the acidity difference is 5 pK units, with the strong σ-donor hydride ligand giving rise to decreased acidity. Clearly the donor/acceptor properties of hydride and chloride ligand are very different, with differences much greater than those existing between the alkyl and aryl groups in the α position; nonetheless, it is surprising to observe such a sensitivity to a substituent this far removed from the reactive site. It should be noted that the ancillary ligand set has also been shown to have a substantial effect on the pK_as of various metal hydrides[22,24] and metal η^2-H_2 complexes,[25] molecules

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in which the ionizing proton is within two bonds of the ligand of interest. Since we are seeing the effects of ancillary ligands transmitted well out onto the ligand, we invoke the metal–oxygen (or metal–nitrogen) bond as the carrier and infer that the interaction between the cationic metal center and the acyl heteroatom is a strong one. These substantial differences can also be utilized to estimate the significance of chloride-to-niobium π-donation in the acyl compounds, a phenomenon that would tend to diminish the pK_a difference between acyl chloride and acyl hydride by making the acyl chloride less acidic. One may compare the current data to those gathered in the carbonylation of various $Cp_2Zr(X)(Me)$ (as in eq 2; note that the O-outside intermediate is *not* observed at room temperature), where the equilibrium constant was seen to decrease on varying X from Me > Cl > OR; since the tendency of the X substituents to engage in π-donation decreases as OR > Cl > Me, the trend in equilibrium constant was ascribed to competition by X for the metal orbital that would otherwise support the acyl O–Zr interaction.[26] The substantial pK_a difference between **1** and **2** leads us to conclude that Cl–Nb π-donation is relatively unimportant here.

The results for compounds **6**, **9**, and **10** provide for a close comparison between acyl and iminoacyl compounds and for an evaluation of the effects of substituents on the iminoacyl nitrogen. The iminoacyls are considerably less acidic than the acyls, with a difference of ca. 6–9 pK units in MeCN (e.g., for **6** vs **9** or **10**). This difference is understandable on the basis of relative electronegativities, since the conversions from acyl to ketene and iminoacyl to ketenimine involve a reduction in the formal charge on the heteroatom (+1 to 0). In addition, this observation is consistent with tendencies reported previously. Rothwell has noted that iminoacyl Δ values correlate with the degree of metal electron deficiency in a manner similar to that of the acyls.[2] However, iminoacyls show considerably less variation in this parameter than do the corresponding acyl compounds. Further, iminoacyls show a greater tendency to undergo facile rotation; Lappert showed that the η^2-iminoacyl compound $Cp_2Zr(Cl)(\eta^2\text{-}N(p\text{-}Tol){=}CCH(SiMe_3)_2)$ participates in an equilibrium involving interconversion of N-inside and N-outside isomers and that this is facile at room temperature.[27] In contrast, the corresponding zirconium acyls show a distinct thermodynamic preference for the O-inside isomer.[8] This suggests that the M–N bond is less significant than is the M–O bond in these two classes of compounds. However, the different nitrogen substituents (Ph vs Et) in compounds **9** and **10** exert a substantial effect on the pK_a of the iminoacyls; the difference is greater than 3 pK units (14.6 vs 18.0 in MeCN), showing that these compounds are more sensitive to these electronic differences (aryl vs alkyl) at the heteroatom than the acyl compounds are at the ionizing position. Taken together, the forgoing observations suggest that the metal–heteroatom bond is responsible for the enhancement in acyl acidity and that oxygen is more effective in this regard than is nitrogen.

Thermodynamic Consequences of the Lewis Acid Interaction. To understand the magnitude of the effect induced by the cationic niobium center, we sought to compare our data with those for organic systems. In particular, we wished to contrast the pK_a of a ketone to that of a Lewis-acid-complexed ketone, and data are available for protonated ketones (in aqueous solution). The aqueous pK_a of acetone (eq 7) is 19.3,[28] and the direct comparison

$$H_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \xrightleftharpoons{pK_a = 19.3} H_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2^- + H^+ \qquad (7)$$

$$H_3C\text{-}\overset{+OH}{\overset{\|}{C}}\text{-}CH_3 \xrightleftharpoons{pK_a = ?} H_3C\text{-}\overset{OH}{\overset{|}{C}}{=}CH_2 + H^+ \qquad (8)$$

would involve measuring the C–H acidity for protonated acetone (eq 8); obviously this cannot be measured directly, since the O-bound proton is more acidic. One can, however, utilize the pK_a of protonated acetone[19] with Kresge's data[29] on keto-enol equilibria to construct the relevant thermodynamic cycle (eqs 9, 10), from

$$H_3C\text{-}\overset{+OH}{\overset{\|}{C}}\text{-}CH_3 \xrightleftharpoons{pK_a = -3.06} H_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + H^+ \qquad (9)$$

$$H_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \xrightleftharpoons{pK = 8.33} H_3C\text{-}\overset{OH}{\overset{|}{C}}{=}CH_2 \qquad (10)$$

which it is clear that the C–H pK_a of protonated acetone is ca. 5.3. This indicates that the effect of the proton on oxygen is to increase the carbon acidity by 14 pK units, a dramatic effect. Note that a similar analysis has been reported for metalloenzyme systems, and the results suggest that just such an interaction provides the thermodynamic driving force necessary to render the critical proton transfer steps (involving enolization of carbonyl derivatives) kinetically competent.[30]

The niobium acyls may be compared to the ketones listed in Table I. In Me_2SO the ketones exhibit pK_as of 18–26, depending on the nature of the substituents at the ionizing site.[21] Clearly the acyls differ dramatically, since they exhibit a range of pK_as that is roughly 20 pK units below that of the organic systems. Taking specific examples, the diphenyl derivative **6** is ca. 21 pK units more acidic than **12** (assuming a Me_2SO pK_a of −2 for **6**), while dialkyl derivatives **2** and **3** are roughly 24 pK units more acidic than **11**. The effects are slightly less dramatic in the case of ketene hydrides, yet the difference between **1** and **11** is still a substantial 19 pk units. In each of these cases, it is clear that the cationic metal center exerts a dramatic effect on the proton-transfer equilibrium.

The forgoing comparison of organic ketones and metal acyls is complicated by the fact that it does not allow for incorporation of the difference between C–C and Nb–C_{acyl} bonds. This is related to another problem, that of apportioning the chemical consequences of η^2-acyl ligand bonding between M–C and M–O bonds. In order to gain some insight into the effect of the M–C bond, we have attempted to measure pK_as for η^1-acyl compounds **7** and **8**. The latter in particular constitutes a reasonable structural model for niobium compounds **1** and **5**; although the d^2 Mo(IV) center is not isoelectronic with the d^0 Nb(V) center, this concession must be made to achieve the η^1 bonding mode. Indeed, we estimate the lower limit of 35 for the pK_a of both **7** and **8** on the basis of the lack of reaction with KO^{t}Bu in Me_2SO; ^{t}BuOH has a pK_a of 32.2 in this solvent.[21] Bases more powerful than *tert*-butoxide were avoided, since Me_2SO itself has a pK_a of 35. Enolization of iron acyls analogous to **7** is typically carried out with lithium alkyls or amides, in solvents less acidic than Me_2SO;[15] the pK_as of representative alkanes in Me_2SO have been estimated by extrapolation methods, and they range from 43 for toluene to 56 for methane.[21] Ammonia has a pK_a of 41 in Me_2SO,[21] and those of dialkylamines should be slightly higher; hence, our lower bound for **7** is not inconsistent with the synthetic results. Our data suggest that the effect of the M–C bond in η^1-acyls is to raise the pK_a of the α-hydrogen by at least 10–12 pK units relative to that of an organic ketone, even with a high-valent metal center like Mo(IV).

Another fruitful comparison derives from the consideration of an acylsilane, since this will exhibit the η^1 bonding mode in the absence of nonbonding electron density on silicon. The pK_a of $Me_3SiC(O)Me$ has been determined as 16.42 in aqueous solution, while that of acetophenone is 18.31 under similar conditions.[29] While this shows that the metal (or semimetal, in this case) causes an enhancement in the carbon acidity of the acyl, the effect is rather small. This is again consistent with the suggestion that the effect of the cationic niobium center in our compounds is transmitted primarily through the acyl oxygen or nitrogen.

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Conclusions

We have measured the pK_as of various acyl- and (iminoacyl)niobocenium compounds in Me_2SO and MeCN solutions. These compounds are found to exhibit substantial acidities, with pK_as 18–24 pK units below those of the corresponding phenyl ketones. This enhancement in the tendency toward enolization is attributed to the O–Nb and N–Nb interactions, all of which are more effective in this regard than is a proton residing on a ketone oxygen. Variations in the substituents at the ionizing site exert predictable effects on the pK_as, although the acyls are less sensitive to these effects than are the analogous phenyl ketones. Conversely, the cis ancillary ligand exhibits a more significant effect, one which operates over a greater distance from the reacting site. Although there is no direct quantitative correlation between these pK_as and chemical transformations of the acyl ligand, the large effects are consistent with the small values of Δ observed in the structurally-characterized derivatives.[13,14] In addition, the ready availability of cationic niobium acyls and their conjugate bases will allow for systematic studies of other substituent effects in the future.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of nitrogen gas that was purified by passage through Linde 4-Å molecular sieves and activated BTS catalysts. Solids were handled in a Vacuum Atmospheres Corporation glovebox filled with purified nitrogen. Solutions for pK_a determinations were prepared volumetrically in the glovebox and then transferred to NMR tubes for analysis. Solvents were distilled from a drying agent appropriate to each under a nitrogen atmosphere, and solutions were prepared and manipulated using standard Schlenk techniques.[31]

Materials. The necessary ketene complexes were synthesized from the appropriate ketene and Cp'_2NbCl, and the chemistry has been described elsewhere.[16] Aryl-substituted ketenes were prepared from the corresponding acyl chlorides by using triethylamine-induced dehydrohalogenation.[32] Dialkylketenes were prepared from the α-bromoacyl bromides by using zinc reduction in THF solution.[33] Diethyloxonium tetrafluoroborate was purchased from Aldrich and used as received under nitrogen atmosphere. 2,4-Dinitrophenol (Aldrich) was recrystallized from hexane/ethyl acetate, and pyridine (Aldrich) was distilled from barium oxide under nitrogen, while anilinium chloride (Aldrich), *tert*-butyl alcohol (Baker), 4-nitrobenzoic acid (Aldrich), 4-(trifluoromethyl)aniline (Pfalz & Bauer), benzylamine (Aldrich), and 4-cyanoaniline (Aldrich) were used under nitrogen as received. Me_2SO-d_6 (Aldrich) was stirred over barium oxide and distilled under vacuum. MeCN-d_3 (Aldrich) was stirred over calcium hydride and distilled under vacuum.

Acyls **1–6** were prepared from the corresponding ketene complexes and diethyloxonium tetrafluoroborate in diethyl ether; synthetic and spectroscopic details are available elsewhere.[16] Compound **9** and its ketenimine precursor were prepared according to the method of Antiñolo et al.[14] Acyls **7**[34] and **8**[35] were also prepared according to literature procedures.

pK_a Determinations. Entry into the requisite equilibrium (eq 4) was determined by the availability of the known acids or bases, all of which are listed above; preliminary experiments were carried out to establish an appropriate acid, one that could be used to establish a mixture of acyl and ketene complexes amenable to accurate integration (the minor component always constituted at least 20% of the mixture). Once identified, this acid was used for accurate determinations. A typical procedure (used for **2**) follows: a stock solution containing 0.0253 M pyridine in MeCN-d_3 was prepared. Four samples of **2** were weighed out in the glovebox and dissolved in the pyridine stock solution; the various initial concentrations of **2** ranged from 1.265 to 5.06 mM. The resulting solutions were transferred to 5-mm NMR tubes, and spectra were recorded promptly using a 45° pulse, 1-s pulse delay, and 500 transients to insure a high signal-to-noise ratio; longer pulse delays were tried but found to have no effect on integrations. Cyclopentadienyl signals for **2** and its conjugate base were well-resolved, and these were integrated to determine the equilibrium concentrations. A similar procedure was utilized for compounds **3** (in MeCN), **4**, **6**, **7**, **8**, and **10** with the conjugate bases of the acids indicated in Table I. NMR integrations were applied in some cases to signals for the ketene/acyl substituents; this choice depended on the resolution of various signals in the spectrum, and care was taken to insure that the signals used were not saturated during data collection. For the remaining determinations, the approach was modified to utilize the acids indicated in Table I and the conjugate bases (ketene complexes) corresponding to acyls **1**, **2** (in Me_2SO), **3** (in Me_2SO), **5**, and **9** (both solvents). For acids known to exhibit homohydrogen bonding, the method of Norton[22] was used to calculate equilibrium concentrations of HA and A^-. In all cases the pK_a of the niobium acyl or iminoacyl was determined from the expression $pK_a(Nb) = -(pK_{eq} - pK_a(HA))$.

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