Activation of Niobocene–Ketene Complexes: Ligand-Centered Syntheses of Hydrides and Acyls

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The title compounds $(C_5H_4R)_2Nb(X)(\eta^2\text{-}C,O\text{-}OCCR^1R^2)$ (R = H, $SiMe_3$; X = Cl) were prepared from electron-rich Nb(III) compounds of formula $(C_5H_4R)_2NbCl$ and the free ketenes. One such derivative (**3b**, R = $SiMe_3$, R^1 = Et, R^2 = Ph) was studied crystallographically (monoclinic, $P2_1/c$, with a = 7.938(5) Å, b = 15.81(2) Å, c = 21.61(1) Å, β = 95.41(6)°, and Z = 4) and was found to exhibit the exo-*E* geometry in the solid state. General use was made of unsymmetrically-substituted ketenes to demonstrate mechanistic aspects of the chemistry. For instance, the ligated ketenes were found to undergo an intramolecular isomerization involving the *E* and *Z* ketene isomers, which is postulated to proceed via a slipped-ketene intermediate. The unsaturated ligands also function as a source of synthetic potential, since the complexes are susceptible to protonation at the ketene β-carbon or reduction involving the ketene π system. The metallaenolates resulting from the latter process have been converted to ketene–hydride analogues (X = H) by way of a multistep process involving acyl β-hydride elimination, while protonation generates highly-substituted cationic η^2-acyl compounds. Reduction of the latter constitutes another entry into the sequence resulting in ketene–hydrides and serves to corroborate the mechanistic claims. Finally, the hydride ligands in the ketene–hydrides are unusually resistant to strong acids, since the compounds react instead at the ketene terminus to form highly electron-deficient acyl hydride cations which show no tendency to eliminate aldehyde.

Introduction

Much of the current interest in the chemistry of metal-complexed ketenes is derived from two facets of their synthetic potential, those being the role of such compounds in the reduction of carbon monoxide and their use in synthetic organic applications. Early evidence for the intermediacy of ketenes in the reduction of carbon monoxide was provided by Schrauzer,[1] who showed that ketenes resulted from the coupling of metal carbonyls and alkylidene sources. Since that time, product distributions resulting from some catalytic systems have been interpreted in this context;[2] in particular, it has been suggested that processes yielding significant fractions of oxygen-containing end products may proceed through ketene intermediates. In addition, there is recent evidence from studies of molecular systems suggesting that carbon monoxide conversion does indeed proceed through cumulated systems such as ketenides[3] and ketenylidenes.[4] The other important aspect of metal–ketene chemistry is based on the rich potential such compounds have for the production of organic molecules such as β-lactams,[5] cyclic ketones,[6] highly-functionalized phenols,[7] and lactones.[8] These processes typically involve cycloaddition of various substrates with short-lived metal–ketene intermediates, and it is clear that the reactions can be rendered stereoselective under the proper circumstances.[5b]

Although synthetic applications of metal–ketene complexes have been developed recently, the similar potential of free ketenes has been recognized for nearly a century.[9] The cumulated structure and extensive unsaturation provide the potential for construction of up to four new bonds. Additionally, free ketenes are highly susceptible to cycloadditions with dienes, alkenes, and related species,[9] as well as to reactions with nucleophilic reagents.[10] Indeed, reactions between unsymmetrically-substituted ketenes and nucleophiles have been shown to produce enolates with high levels of stereoselectivity.[10]

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Complexed ketenes have been prepared by a variety of routes, including the coupling of alkylidene and carbonyl moieties[11] and deprotonation of metal acyls.[12] In light of the considerations discussed above, however, the present work was begun with the aim of preparing such complexes from unsaturated metal systems and free ketenes. Indeed, our goal was to utilize the synthetic potential of the complexed ketene in the preparation of new organometallic compounds, while also using the stereochemical properties of the unsymmetrically-substituted ketene to understand compound structures and reaction mechanisms. Herein we describe the preparation of a series of niobium–ketene complexes and their use in the preparation of new and otherwise inaccessible molecules. Most of the reactions are mediated by the ketene ligand, they often exhibit unusual regiochemistry, and they can be used to effect changes in both the ligand and adjacent metal coordination sites.[13]

Results

Synthesis of Precursors. The preparation of the desired ketene complexes involved the use of the electron-rich Nb(III) compounds Cp'_2NbCl (**1**, $Cp' = \eta^5$-$C_5H_4SiMe_3$) and Cp_2NbCl (**2**). The former has been prepared by using the sequence outlined in eq 1,[14-16] a process involving two

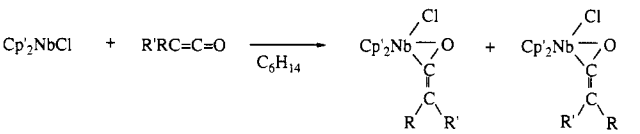
$$NbCl_5 \xrightarrow[2.\ THF]{1.\ Al,\ MeCN} NbCl_4(THF)_2 \xrightarrow{2LiCp'} Cp'_2NbCl_2 \xrightarrow{Na/Hg} Cp'_2NbCl \quad (1)$$

single-electron reductions. This sequence is time-consuming (Cp'_2NbCl_2 must be sublimed), and the overall yield is only ca. 50–60%. We have developed a new synthetic scheme (eq 2) based on the two-electron reduc-

$$NbCl_5 \xrightarrow[DME]{2Bu_3SnH} NbCl_3(DME) \xrightarrow{2LiCp'} Cp'_2NbCl \quad (2)$$

tion of $NbCl_5$ to the Nb(III) reagent $NbCl_3$(DME), which is routinely prepared in >95% yield on a 10–20-g scale.[17] Reaction of this with 2 equiv of LiCp′ gives the desired compound **1** as a red-brown solid in 55–60% yield; thus the yields for the two sequences (eqs 1 and 2) are similar and the new route is considerably more convenient. A similar reaction of $NbCl_3$(DME) and NaCp gives brown analogue **2**, which appears to undergo an oligomerization reaction upon attempted isolation. This limits the use of the isolated reagent, since it is not very soluble in organic solvents. Hence **2** must be generated and used in situ for the chemistry to be described below; yields suffer, apparently due to the presence of impurities in crude **2**. These difficulties are not encountered with **1**, which remains soluble in most solvents; hence, most of the work described below involves the use of **1**, complexes of which are also more highly crystalline and isolable in higher purity. We have attempted to use the methodology of eq 2 to prepare $(C_5Me_5)_2NbCl$ without success, but have not made a detailed study of this.

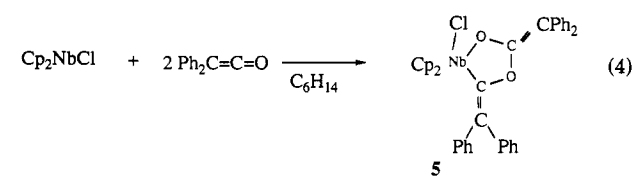
Preparation of Ketene Complexes. These were prepared from either **1** or **2** and the desired free ketene. Reactions of **1** and the appropriate ketene were carried out at room temperature in hexane solution, from which the desired complexes precipitated as yellow solids over a period of several hours (eq 3). Compounds **3a–f** are



3a R=Me, R'=Ph
3b R=Et, R'=Ph
3c R=R'=Me
3d R=R'=Ph
3e R=Me, R'=CH_2CMe_3
3f R=Me, R'=Et

(3)

soluble in most organic solvents, with the exception of diethyl ether and acetonitrile; most can be recrystallized from toluene–hexane mixtures. The compounds are air-stable in the the solid state, but solutions must be handled under inert atmosphere. A similar reaction with **2** has been used to prepare analogous compounds **4a–c**; however, because **2** must be generated and used in situ, the ketene complexes are often impure. Although purification has proved difficult, the compounds can be successfully carried on in some of the chemistry described below. In addition, the reaction of **2** with diphenylketene does not lead to successful preparation of a ketene complex. Instead, **2** takes up 2 equiv of ketene to form a compound tentatively identified as **5**, resulting from the reductive coupling of two ketene ligands (eq 4); a similar compound has been



5 (4)

observed in related titanocene chemistry.[18] We suspect that diphenylketene is more susceptible to such a reaction

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Table I. Equilibrium Ratios of Ketene Complexes $L_2Nb(X)(OCCRR')$ in C_6D_6 Solution (25 °C)[a]

compd	X	R	R'	*E*:*Z*
3a	Cl	Me	Ph	81:19
3b	Cl	Et	Ph	77:23
3e	Cl	Me	Np[b]	>95:5[c]
3f	Cl	Me	Et	52:48
4b	Cl	Et	Ph	73:27
4f	Cl	Me	Et	65:35
6a	H	Me	Ph	50:50
6b	H	Et	Ph	50:50
6e	H	Me	Np[b]	>95:5[c]

[a] For compounds **3** and **6**, L = Cp'; for compounds **4**, L = Cp. [b] Np = CH_2CMe_3. [c] No *Z* isomer was observed.

because the two electron-withdrawing phenyl groups render it more susceptible to reduction; this process is not observed in the reaction with **1**, where the approach of the second ketene moiety is probably precluded by the bulky $SiMe_3$ substituents.

The ketene complexes are readily identified by a combination of infrared and NMR techniques. Each compound exhibits one set of NMR signals for the cyclopentadienyl ligands, while the ketene ligands give rise to IR bands in the region 1620–1640 cm^{-1} (aryl-substituted ketenes) or 1650–1695 cm^{-1} (dialkyl ketenes). Both of these observations are consistent with the η^2-C,O ketene binding mode. Aryl-substituted η^2-C,O ketene ligands are known[19] to exhibit an IR band with predominant C=C stretching character in this range; moreover, this would place the ketene substituents in the equatorial mirror plane of the compounds and render the cyclopentadienyl ligands chemically equivalent. This bonding mode is readily distinguished from the C=C ketene bonding mode, since the latter exhibits a C=O stretch at higher frequency (≥1750 cm^{-1}).[11] Of particular interest are the complexes **3a,b,e,f** containing unsymmetrically-substituted ketene ligands. The ^1H NMR spectra for these compounds give clear evidence for the presence of two complex isomers, observed in the ratios given in Table I; these *E* and *Z* isomers arise from formal isomerization about the C=C bond, but the spectral data do not constitute a sufficient basis for identifying the major isomer or for establishing exo versus endo ketene ligation. For this reason, crystallographic characterization was deemed appropriate.

Compound **3b** was crystallized (yellow parallelepipeds) by slow cooling of a saturated toluene–hexane solution and subjected to crystallographic analysis. The resulting data are summarized in Tables II and III and Figure 1. The compound crystallized in space group $P2_1/c$ with four molecules of **3b** per unit cell; there are no significant intermolecular contacts. The ketene ligand is complexed through the C=O bond (as suggested by the solution spectral data), and these atoms and the adjacent Cl ligand constitute the equatorial plane in the bent metallocene. Indeed, they are coplanar, as evidenced by the Cl—Nb—O—C_1 dihedral angle of 0(1)°. Moreover, the ketene ligand adopts the O-inside (exo) configuration typically seen for early transition metal metallocene complexes of heteroatom-containing ligands (e.g., CO_2, CS_2, and acyls).[12,20]

Table II. Crystallographic Data for 3b

formula	$C_{24}H_{33}NbClOSi_2$
fw	522.05
space group	$P2_1/c$
cryst dimens, mm	0.50 × 0.37 × 0.37
cell dimens (25 °C, 25 reflns)	
a, Å	7.938(5)
b, Å	15.81(2)
c, Å	21.61(1)
α, γ, deg	90
β, deg	95.41(6)
Z (molecules/cell)	4
vol, Å^3	2700(7)
d(calcd), g cm^{-3}	1.28
wavelength, Å	0.710 69
abs coeff., cm^{-1}	6.25
R	0.046
R_w	0.059

Table III. Selected Bond Lengths (Å) and Angles (deg) for Ketene Complex 3b and Acyl Complex 7b

	3b	**7b**	diff
Nb–C_1	2.135(4)	2.121(5)	–0.014
Nb–O	2.093(3)	2.233(4)	0.140
Nb–Cl	2.507(2)	2.446(2)	–0.061
C–O	1.302(5)	1.242(5)	–0.060
C_1–C_2	1.346(6)	1.506(8)	0.160
Nb–C_1–O	70.3(2)	78.3(4)	8.0
O–C_1–C_2	135.3(4)	127.1(5)	–8.2
Et–C_2–Ph	119.3(4)	113.2(4)	–6.1
Nb–O–C_1–C_2	–178.4(5)	–179.7(6)	1.3

The ketene phenyl group is located trans to the niobium center, establishing the *E* alkene geometry. Although the cyclopentadienyl ligands are slightly staggered with respect to each other, both are oriented in the solid state so as to place the bulky $SiMe_3$ substituent out over the equatorial plane. Although presumably linear in the free (uncomplexed) state, the ketene moiety in **3b** exhibits considerable bending and an O—C_1—C_2 angle of 135.3(4)°. The C_1—O and C_1—C_2 bond lengths are 1.302(5) and 1.346(6) Å, respectively. The structure of free dimesityl ketene has been determined recently, and it exhibits C=O and C=C bond lengths of 1.18(1) and 1.29(1) Å, respectively.[21] A comparison of the free and complexed ketenes thus indicates that the C=C bond is lengthened by ca. 0.06 Å upon complexation, and the C=O bond is lengthened by 0.12 Å; these tendencies have been observed in related ketene complexes.[12b,c,16c] The metrical data provide evidence of considerable metallaoxirane character in the bonding of **3b**, which is best characterized as a compound of Nb(V).

When the synthetic reaction (eq 3) was monitored using ^1H NMR (0 °C in toluene-d_8 solution), resonances for both isomers were seen to appear in a ratio approximating that seen in the isolated mixture. However, when crystals of **3b** were dissolved in C_6D_6 and studied immediately with ^1H NMR, the spectrum showed evidence for only that isomer identified as the major isomer in Table I. This subsequently equilibrates to the typical 77:23 mixture. This illustrates that the exo-*E* isomer in the crystal is the major solution component, and the minor isomer is thus the exo-*Z* isomer; note that exo–endo isomerism is not responsible for the presence of two compounds, since the

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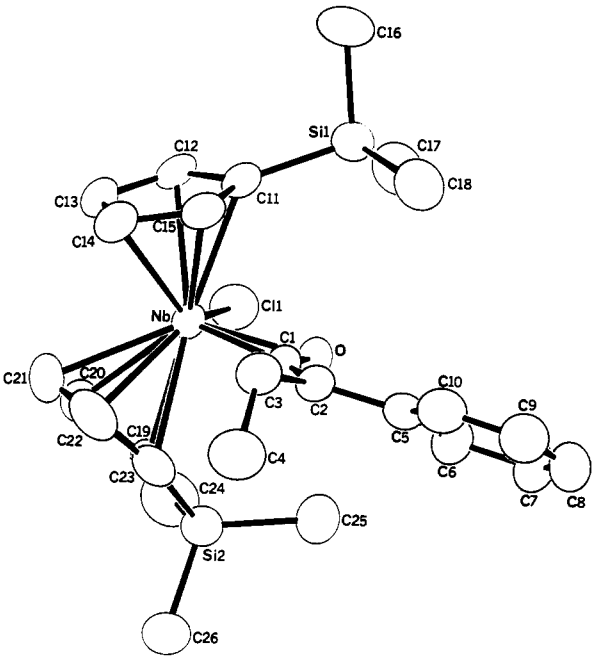
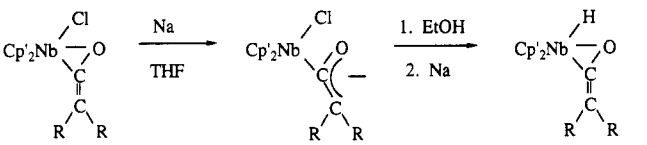


Figure 1. Structure of compound **3b** showing the atom numbering scheme.

symmetrically-substituted ketene complexes (which could support the exo–endo process) only show one isomer under similar conditions. The data do not rule out parallel synthetic reactions leading to *E* and *Z* isomers, but they do establish the operation of an exchange equilibrium interconverting the two. Indeed, if **3a** is heated in C_6D_6 solution, the *E*:*Z* ratio decreases from 81:19 at 17 °C to 68:32 at 56 °C; a van't Hoff plot of three points in this range is linear ($r^2 = 0.993$) and gives an enthalpy difference ($\Delta H°$) of −2.2 kcal/mol for the *Z*–*E* conversion. We have not executed kinetic studies because of the relatively small differences in isomer population. However, if the warmed C_6D_6 solution is cooled to room temperature, it is clear that the new equilibrium is established within a few hours. With this information, crossover studies were carried out by mixing **3a** with 1 equiv of free EtPhC=C=O; after 4 h at room temperature (ample time to ensure equilibration of complex isomers) the NMR indicated that no **3b** had resulted from intermolecular exchange. The experiment was done in the reverse direction (i.e., with **3b** and free MePhC=C=O) with the same result. Clearly, the ligated ketenes are undergoing a facile *E*–*Z* isomerization that does not involve ligand labilization.

Preparation of Ketene–Hydride Complexes. In an attempt to activate the ketene complexes and probe the synthetic utility of the ketene ligand, compounds **3a–d** were subjected to sodium amalgam reduction. THF solutions of compounds **3** turn green-brown under these conditions, and the reaction of **3b** was studied by use of cyclic voltammetry, coulometry, infrared spectroelectrochemistry, and ESR spectroscopy. The results of these studies have been published elsewhere,[22] and will not be discussed in detail here. The data are wholly consistent with the operation of a redox process giving rise to an anionic Nb(IV) metallaenolate complex; in particular, coulometry was consistent with a single-electron reduction, infrared spectroelectrochemistry showed evidence for the conversion of the ketene ligand (1623 cm^{-1}) to the metallaenolate (1530 cm^{-1}), and ESR confirmed the Nb(IV) formulation. The metallaenolate was obtained as a brown-green oil that was too reactive for further purification; nonetheless, there is ample evidence to suggest it is involved in the chemistry described below. The metallaenolate was quenched with ethanol in ether solution with the expectation that a neutral Nb(IV) acyl compound would result. However, the infrared spectrum of the resulting species contained overlapping bands at ca. 1625 cm^{-1}, consistent with the regeneration of ketene ligands. ^1H NMR confirmed the presence of a mixture of starting ketene complex **3b** and a new ketene complex **6b**; the latter comprised roughly half of the total present. Compound **6b** exhibited resonances for the Cp′ and ketene ligands, as well as a slightly broadened singlet at 1.41 ppm. The latter is due to a metal hydride ligand, the presence of which was also indicated by an IR band at 1731 cm^{-1}; the compound was thus formulated as one isomer of Cp'_2-Nb(H)(OCCEtPh). Equation 5 represents the general



3 6 (5)

process, which proceeds for all analogues of **3b**. If the metal hydride results from the ethanol added, the conversion of **3b** to **6b** constitutes a two-electron process; the use of MeOD in the quench does lead to substantial incorporation of deuterium in the Nb–H(D) site. Indeed, the synthesis can be driven to completion if use is made of 2 equiv of sodium amalgam *and* the proton source is added in the presence of the reducing agent. Though the alcohol might be expected to react with the reducing reagent, this reaction is relatively slow and does not compete successfully with the formation of product **6b**; we have noted previously that preparative electrolyses with added ethanol result in ketene–hydride complexes as the only niobium-containing products, even though there is substantial gas evolution at the cathode due to the reduction of alcohol to alkoxide and dihydrogen.[22]

If isolated **6a** is dissolved in THF solution, it equilibrates over a period of hours to an equimolar mixture of two isomers. Thus, when carried out in ether solution the synthesis is specific for one isomer of **6a**, even though an *E*–*Z* equilibrium mixture of reactant **3a** was utilized; however, the thermodynamic stabilities of the two ketene–hydride isomers are virtually identical. The kinetic isomer of **6a** was identified by the use of NOE experiments. Irradiation of the ketene methyl signal (2.44 ppm, C_6D_6) resulted in an enhancement of the signals due to the phenyl ortho protons (8.2 ppm) and two of the Cp′ protons (5.57 and 5.18 ppm); there was no observable enhancement of the metal hydride signal. These observations are consistent with the exo-*E* geometry, with the ketene methyl in close proximity to the Cp′ ligands. If the methyl signal of the second isomer of **6a** is irradiated, only the phenyl ortho protons exhibit any enhancement; this is consistent with the exo-*Z* formulation. Again, the hydride derivatives containing symmetrically-substituted ketene ligands fail to exhibit isomerism.

The conversion of the ketene–chloride compounds to the ketene–hydride compounds requires a sequence of reduction, protonation, and reduction, with both reduc-

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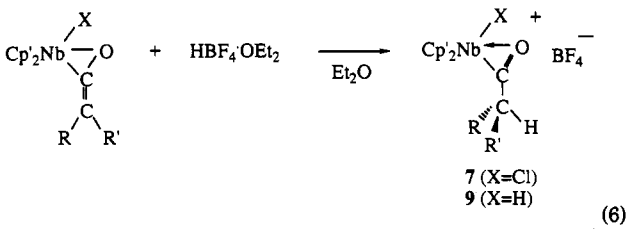
tions consisting of single-electron events. Overall, this is formally equivalent to the substitution of the chloride ligand with a hydride. We thus attempted such a displacement with lithium aluminum hydride. This reacted immediately with **3a** in THF solution, but the resulting compound showed no spectral evidence for the presence of a ketene ligand. Instead, the orange product of this reaction was identified as $Cp'_2Nb(\mu\text{-}H)_2AlH_2$, an analogue of the known cyclopentadienyl derivative;[23] subsequent hydrolysis led to production of the known Cp'_2NbH_3.[24] Since the LAH reagent was too reactive, **3a** was reacted with lithium borohydride in THF solution; after several hours it was apparent from infrared and NMR studies that no reaction had occurred. Hence, LAH is too reactive and removes the ketene ligand while borohydride is insufficiently reactive; since the reaction noted above (eq 5) is convenient and efficient, we have not pursued the use of other hydride sources in the synthesis of ketene–hydrides. In this context, it is also worth noting that the Cp′ derivatives also fail to react with alkyllithium reagents such as BuLi and MeLi. In contrast, the Cp analogues **4a–c** fail to undergo conversion to ketene–hydride compounds under any conditions we have tried, but they will react with alkyllithiums to produce alkyl–ketene compounds such as $Cp_2Nb(R)(OCCMePh)$ (R = Me, Et); we have not determined the reason for these differences, although the $SiMe_3$ groups in the Cp′ derivatives may constitute a steric impediment to the reactions of the alkyllithium reagents.

Preparation of Cationic Acyl Compounds. The initial reaction of the metallaenolate anion with a proton source would be expected to generate a paramagnetic acyl compound, but we were unable to gather any evidence for the intermediacy of an acyl in the conversion to ketene–hydride. Alternatively, the neutral ketene–chloride compounds were subjected to protonation with acids stronger than ethanol. An initial attempt with trifluoroacetic acid (aqueous $pK_a = 0.52$)[25] was unsuccessful in that it failed to effect complete conversion. However, if an ether suspension of ketene complex **3a** is treated with a slight excess of $HBF_4{\cdot}Et_2O$ under nitrogen (eq 6), the yellow



7 (X=Cl)
9 (X=H) (6)

compound dissolves and turns colorless immediately. Within several seconds a colorless precipitate (**7a**) is deposited and isolated by filtration. The other Cp′ derivatives behave similarly (yielding **7b–d**), while the Cp analogue **4b** yields beige **8** under similar conditions. For the latter this reaction proceeds well even if the ketene complex is not entirely pure; it thus represents the preferred method for carrying the Cp complexes on to pure derivatives. The compounds exhibit clear evidence for η^2-acyl formation resulting from protonation at the ketene β-carbon; the added proton (α to the acyl carbonyl) exhibits an NMR resonance in the region 4.5–6.5 ppm (depending on the nature of the other substituents), compounds with alkyl substituents exhibit the expected couplings between alkyl protons and the α-proton, and unsymmetrically-substituted ketene complexes give rise to acyls in which the Cp ligands are inequivalent due to the asymmetry of the carbon center α to the acyl carbonyl. The η^2-acyl formulation is also supported by the low energy infrared band observed in the region 1590–1620 cm^{-1},[26] and the presence of the tetrafluoroborate anion is clear from the strong, broad band at ca. 1080 cm^{-1}. Finally, **7b** has been crystallized from methylene chloride–ether and characterized crystallographically. The structural data have been published[13b] and details will not be presented here, but the metrical data will be considered in the Discussion section. The acyl does exhibit the expected O-inside (exo) conformation in the solid state.[27]

If the synthesis of ketene–hydride compounds involves a sequence of reduction, protonation, and reduction as postulated above, the preparation of cationic acyls (eq 6) constitutes the beginning of an alternate synthetic sequence. To complete the sequence, the acyls were treated with 2 equiv of amalgamated sodium. Indeed, the only observed niobium-containing product is the ketene–hydride complex, supporting the prospect of any acyl intermediate in the synthesis (eq 5). The reaction was further studied through the use of a deuterium labeling experiment. Ketene–chloride complex **3b** was treated with sulfuric acid-d_2 and sodium tetrafluoroborate in a methanol-*O*-*d*–ether mixed solvent system (methanol was required to dissolve the sodium tetrafluoroborate). The resulting acyl salt was isolated in the usual manner, and NMR confirmed the presence of a deuteron in the α-position (≥95% deuterium incorporation). This compound was then reduced with amalgamated sodium, and the resulting ketene complex **6b**-d_1 was studied by proton and deuterium NMR. The latter confirmed that the deuterium appeared only in the Nb–D site, while the former confirmed that the level of deuterium incorporation remained high (≥90%). This corroborates the notion that an acyl is on the mechanistic path leading to the ketene–hydride compounds.

Having established that the ketene–chloride compounds reacted cleanly with strong acid, we subjected the ketene–hydride compounds to a similar reaction. With the expectation that the acid would react with the metal hydride to liberate dihydrogen, we were surprised to discover that treatment of **6a** with $HBF_4{\cdot}Et_2O$ led cleanly to the production of the cationic acyl hydride **9a** (eq 6, X = H, R = Me, R′ = Ph); this salt is readily isolated as a colorless, microcrystalline solid, and compounds **9b–d** are prepared similarly. These compounds exhibit NMR properties similar to those of the acyl chlorides (**7**), but they also exhibit a metal hydride resonance in the range 1.3–2.8 ppm (depending on solvent). Although both the ketene–chlorides and ketene–hydrides react with strong acid at the β-carbon, we have been unable to add other strong electrophiles. Hence, there is no addition reaction with methyl trifluoromethanesulfonate, trimethylsilyl trifluoromethanesulfonate, or trimethyloxonium tetraflu-

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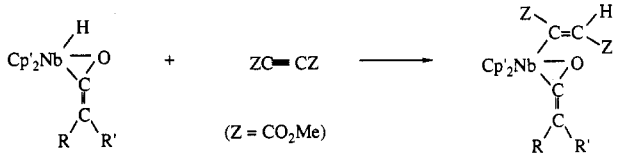
oroborate; at very long reaction times these reagents ultimately lead to protonation, presumably resulting from trace hydroxylic species present in the solvent or on the glass surface.

The resistance of the niobium–hydride linkage in **6** to strong acid might be interpreted as evidence for unusual metal–hydride bonding character in the ketene–hydrides. We thus attempted reactions typical of other niobocene hydrides. Many compounds of general formula Cp_2-Nb(L)H are known to undergo insertion of alkynes into the Nb–H bond via a process referred to as nonmigratory insertion (i.e., not involving prior coordination of the alkyne to the saturated metal center);[28] the process is often not stereospecific, and mixtures of *E* and *Z* alkenyl compounds have been obtained. Thus ketene–hydrides **6a–d** were treated with activated alkynes such as phenylacetylene, diphenylacetylene, and dimethyl acetylenedicarboxylate (DMAD). The first two of these failed to react at ambient temperature and pressure, but the latter did react cleanly at room temperature to give yellow alkenyl compounds **10** (eq 7). In studies of related reactions for $Cp_2Nb(L)H$ and



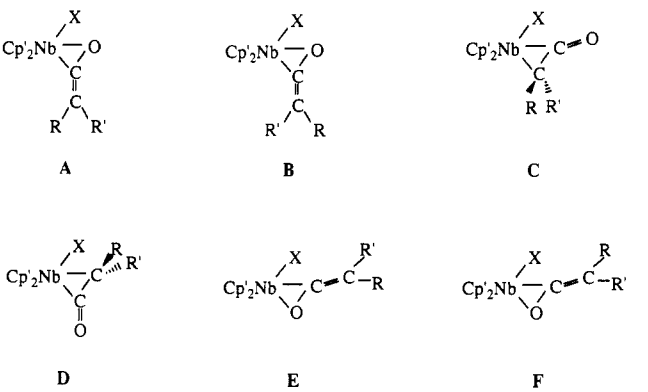
10 (7)

similar metal hydrides, Herberich has established that the couplings between the vinyl proton and the α-carbonyl carbon ($^3J_{C-H}$) and the terminal alkenyl carbon ($^1J_{C-H}$) are useful in determining alkenyl geometry.[29] The *Z* isomers typically exhibit $^3J_{C-H}$ and $^1J_{C-H}$ values in the ranges 6–8 and 146–156 Hz, while the *E* isomers exhibit similar data in the ranges 12–15 and 166–167 Hz. Compounds **10** exhibit values of ca. 6 and 156 Hz, clearly establishing the *Z* alkenyl geometry. A comparison of derivatives **10a** (R = Me, R′ = Ph) and **10d** (R = R′ = Ph) establishes that ketene isomers are accessible in **10a**, since the equilibrium *E*:*Z* ratio in benzene is 64:36; however, we have seen no evidence for isomerization of the alkenyl ligand in either compound. Ultraviolet irradiation of **10d** (medium pressure mercury lamp, benzene solution) for 2 h led to some decomposition of the alkenyl compound, but there was no evidence for any new diamagnetic compounds.

Discussion

Ketene–Chloride Complexes. The reactions between free ketenes and compounds **1** and **2** (eq 3) must compete with the dimerization and/or oligomerization of the ketenes themselves. Complexes result with a variety of disubstituted ketenes, but we have been unable to prepare such compounds with the parent ketene (CH_2=C=O) or any monosubstituted derivatives. The latter are particularly unstable toward dimerization,[9] and this would be expected to preempt complex synthesis. As such, we also tried to prepare a complex of the monosubstituted derivative *tert*-butylketene, which is long-lived in solution (as shown by infrared spectroscopy); however, this compound failed to result in an observable niobium complex. In general, the successful syntheses constitute a good match between the highly air-sensitive (electron-rich) Nb(III) nucleophiles and the moisture-sensitive ketene electrophiles, since the resulting complexes are fairly resistant to oxidation, nucleophiles, and most protic reagents.

The use of free ketenes in the syntheses was predicated on the selectivity usually observed in their reactions with nucleophilic reagents. Although unsymmetrically-substituted ketenes could in principle result in any of six possible complex isomers (A–F), many of these were



deemed to be unlikely. First, electron-rich early transition metals have been observed to favor ketene C=O complexation,[12,19] and a variety of heteroatom-containing ligands have been observed to favor the exo geometry in bent metallocene complexes.[12a–c,20] Furthermore, the ketene LUMO is known to lie in the plane containing the two substituents, and Tidwell and Seebach have shown that ketenes exhibit a high degree of facial selectivity in reactions with nucleophilic reagents.[10] The nucleophile attacks from within the plane containing the substituents, which therefore exert a strong influence favoring the formation of the *Z* enolate derived from attack on the side of the smaller ketene substituent. Although this work involved the use of alkyllithium and Grignard reagents, we subsequently showed that vanadocene behaved similarly and gave exclusively *E* isomers of the η^2-C,O ketene complexes.[19c] On this basis the observation of two facial isomers of the niobocene–ketene complexes **3a,b,d,f** was unexpected; however, the equilibrium data suggest that the two isomers result from isomerization *after* complex formation, rather than from parallel synthetic pathways. Since complexes of the symmetrically-substituted ketenes exhibit no such isomerism, we can rule out exo–endo interconversion as the equilibrium process. The isomerization therefore involves a formal twist about the ketene C=C bond, and though we have established with the unsuccessful trapping reactions that ketene labilization is not important, various intramolecular mechanisms remain viable. These include a conducted tour mechanism[30] involving intermediate complexation of the ketene C=C bond (as shown in isomer C above), linkage isomerism to the σ-bound ketene (G) which spins about the Nb—O

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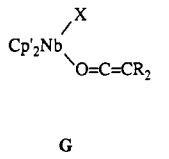
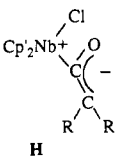


G



H

bond,[31] and zwitterionic intermediates such as H, in which the formal carbon—carbon bond order is reduced. We tried to model the conducted tour mechanism by preparing allene complexes that would undergo a degenerate rearrangement of the same type, but the necessary allene complexes proved elusive. We have established that the ketene isomerization reaction depends on the nature of the adjacent ligand and on the solvent, since (a) the ketene–hydride and ketene–alkyl complexes isomerize more slowly than do the ketene–chlorides and (b) isomerism is qualitatively faster in polar solvents such as THF and methylene chloride than it is in benzene. For the kinetic (*E*) isomer of $Cp_2Nb(Me)(OCCEtPh)$ the approach to the 1:1 *E*:*Z* equilibrium took nearly 10 days in C_6D_6 and less than 1 day in THF-d_8. This suggests that some charge separation is involved in the isomerism and argues against a conducted tour mechanism. However, the observation that hydride and alkyl coligands hinder the process (relative to the compounds containing chloride coligands) is inconsistent with the intermediacy of zwitterion H; from studies of the Bronsted basicities of the ketene compounds[32] it was clear that chloride functions as a stronger acceptor than do hydride or alkyl ligands, i.e., σ inductive effects are more important than any hypothetical chloride π donor effects. Hence the greater ease with which ketene–chlorides undergo isomerization implicates a process involving net transfer of electron density *to* the metal center; we thus suggest that π–σ isomerization is the most viable pathway for ketene *E*–*Z* isomerization, since the σ-bound isomer G formally contains a Nb(III) center. Related η^1-O ketone and aldehyde complexes are known.[31] Gladysz has reported that σ and π isomers of cationic rhenium complexes may interconvert and that polar solvents stabilize the isomer exhibiting the greater degree of charge separation;[31d-f] in the rhenium complexes this is the π isomer, but in our neutral niobium–ketene complexes the σ isomer G would exhibit greater charge separation (electron-rich Nb(III), electron-deficient ketene) and stabilization by a polar solvent.

Reactions and Properties of Ketene–Chloride Complexes. The complexation of other heterocumulenes has been shown to increase the nucleophilicity of the unbound terminus,[33] and this suggested that the bound ketene ligand would be susceptible to electrophiles. In fact, this is only true of very strong proton donors, since the pK_a's of the resulting acyls have been shown to range from ca. −2 (estimated) to +7 in DMSO solution;[32] these compare to the pK_a's measured for trifluoroacetic acid (3.45) and dichloroacetic acid (6.4) in the same solvent.[34] The conversion of **3** to **7** consists only of the addition of a proton to the terminal carbon of the ketene ligand, and the atomic frameworks of the two molecules are otherwise identical. Since both **3b** and **7b**[13b] have been crystallographically characterized, they present an opportunity to compare metrical data (Table III) for two compounds with similar atomic composition and very different canonical bonding pictures. Although most of the changes brought about in the ligand structure by protonation are consistent with these valence bond pictures, some of the metal—ligand bond lengths respond in unexpected ways. As a starting point, it is clear that both the ketene and acyl ligands are planar (Nb—O—C—C dihedral angles of 178.4(5) and 179.7(6)°, respectively) and that the Nb—C bond lengths are experimentally indistinguishable (differing by only 2.8σ) for the two compounds. Although this carbon center is formally sp^2 hybridized in both compounds, one might have expected the acyl compound to exhibit a shorter bond by virtue of the formal positive charge; this is clearly the case for the chloride ligand, since the Nb—Cl distance decreases by 0.061 Å (corresponding to 31σ here) upon protonation. Conversely, the Nb—O distance increases by a substantial 0.14 Å upon protonation; although this linkage is converted from a formal single bond to a formal dative bond, an increase of this magnitude is surprising and might have been expected to be offset by the development of the positive charge. We have shown elsewhere[32] that the Nb—O interaction in this η^2-acyl compares well with those seen in other η^2-acyls (as judged by the structural Δ parameter[35a]) and that it exerts a substantial effect on the pK_a of the acyl α-proton. As a consequence of the Nb—O bond lengthening, the Nb—C—O angle opens from 70.3(2) to 78.3(4)° and the O—C—C angle decreases from 135.3(4) to 127.1(5)°. The intraligand changes reflect the canonical structures to varying degrees. The C—O bond length decreases from 1.302(5) to 1.242(5) Å; although this change reflects the development of double bond character, the magnitude (0.06 Å) is considerably less than the typical 0.2-Å difference between organic carbon—oxygen single and double bonds.[36] This undoubtedly reflects the importance of the oxycarbene or oxycarbenium formulations (both with formal C—O single bonds) used to describe η^2-acyls.[35] The C—C distance changes from 1.346(6) to 1.506(8) Å upon protonation; the former is quite typical for a carbon—carbon double bond, while the latter is close to the length expected for the carbon—carbon single bond length in a C—C=O system (1.53 Å).[36] Thus, while the changes in the Nb—C_1 distances are somewhat unpredictable, the C_1—C_2 distances behave as expected for a similar organic moiety. In summary, then, protonation leads to a lengthening of the Nb—O bond, a shortening of the Nb—Cl bond, and intraligand changes in the directions suggested by the canonical bonding pictures.

The redox chemistry of the ketene complexes (Scheme I) was initially undertaken so as to generate metallaenolates, which have been shown to be versatile nucleophiles

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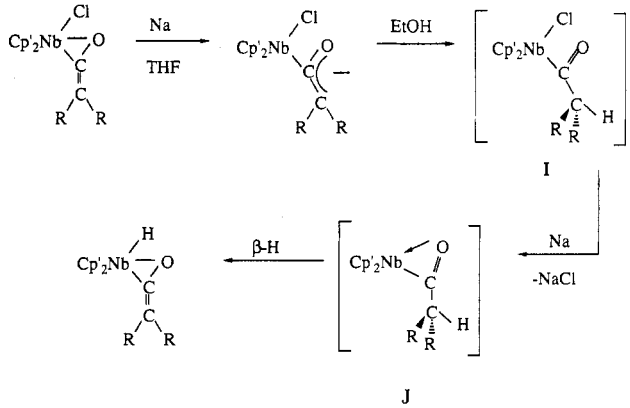
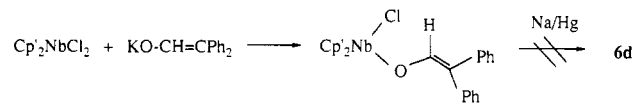
Scheme I. Proposed Mechanism for Ketene–Hydride Formation



in many other systems.[37] As noted previously,[22] we have gathered ample evidence for the formation of the metallaenolate anion in the reduction of **3b**. However, salts of this complex are extremely difficult to work with, since the anion is extremely sensitive to oxidation and it suffers slow loss of chloride in solution. For these reasons we sought to trap the enolate with a proton source, thereby generating a neutral Nb(IV) acyl which we expected to be less sensitive to both of the degradation pathways noted for the metallaenolate. Also, there would be a synthetic benefit from acyl formation; niobocene and tantalocene species do not support migratory insertion of carbon monoxide, and hence trivalent acyls have been unavailable.[38] Although kinetic factors have been implicated, it appears that insertion is in fact endothermic; Brintzinger showed that treatment of $[Cp_2Nb(CO)_2]^+$ with alkyllithium reagents gives rise to $Cp_2Nb(R)(CO)$, undoubtedly through the intermediacy of an acyl that is unstable toward migratory deinsertion.[38c] In any case, our redox chemistry showed no evidence for a Nb(IV) acyl intermediate (I). Indeed, the addition of the proton apparently facilitates a second reduction; if insufficient sodium is present the metallaenolate itself serves as the reducing agent, and this gives rise to the mixture (eq 5) seen when one reducing equivalent is employed.

After addition of the proton, a second reduction results in chloride loss and formation of the Nb(III) acyl J. Again, our spectroelectrochemistry studies confirmed that the loss of chloride after the first reduction is very slow and would not be expected to compete with proton addition.[22] Once the empty coordination site is available, intermediate J is postulated to undergo β-hydride elimination to generate ketene–hydride. Fortunately, the ready access to Nb(V) acyl salts **7** provides an alternate entrance into this reaction pathway leading to the ketene–hydrides. Reduction of the acyl chlorides should generate a neutral Nb(IV) acyl, the same compound (I, Scheme I) thought to result from protonation of the metallaenolate. The deuterium labeling experiment involved conversion of acyl $Cp'_2Nb(Cl)[\eta^2\text{-}C,O\text{-}C(O)CDEtPh)]^+$ (**7b-*d***) to the deuteride $Cp'_2Nb(D)(O{=}C{=}CEtPh)$ (**3b-*d***) and provides compelling evidence for the viability of β-CH(D) elimination. It is worth noting that direct elimination from an acyl (whether bound in a η^1 or η^2 fashion) to generate the η^2-C,O ketene ligand cannot be a concerted process; a coplanar arrangement of the Nb—C—C—H system would not allow for formation of the C=C π bond which is orthogonal to the equatorial plane. However, there exist other mechanistic possibilities proceeding by way of hydrogen shifts and/or ketene linkage isomerizations. The first involves the intermediacy of a η^2-C,C ketene–hydride (D above, with X = H) which then undergoes isomerism of the ketene to the more stable η^2-C,O isomer. Alternatively, the η^2-acyl could undergo a 1,2-hydrogen shift to give an enolate, which could then suffer the 1,3-migration of C—H to Nb—H. Precedents exist for each of these paths. Baird has shown that ruthenium acyls may be used to generate the ruthenium hydride and free ketene, establishing that acyl β-H elimination can be facile.[39] There are also many examples of tautomerization of η^2-acyls to enolates (a 1,2-hydrogen shift),[40] and Bergman and Andersen have shown that ruthenium enolates generate hydrides and free ketene upon thermolysis (a 1,3 shift).[41] To test for the latter possibility, we prepared the Nb(IV)–diphenylacetaldehyde enolate[42] complex shown in eq 8



(8)

and reduced it with sodium amalgam under conditions used in the preparation of **6** (eq 5); although we have yet to identify the resulting product, it is not **6d** and it exhibits no evidence for the presence of a hydride ligand. For this reason we are inclined to discount the enolate elimination mechanism. Curtis has also shown that closely related titanocene enolates do not yield ketenes after prolonged thermolysis.[43] Hence we propose that the formation of **6** involves β-hydride elimination and subsequent ketene isomerization; while we cannot preclude the intermediacy of a metallaenol intermediate along this pathway, we have seen no spectroscopic evidence of such a species. Although similar in principle to Baird's ruthenium chemistry,[39] the current work constitutes the only example in which such an elimination proceeds so as to retain ketene and hydride ligands within the coordination sphere of the metal.

In the mechanism described above (Scheme I) we propose that the chloride coligand is labilized during the

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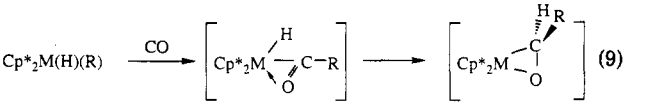
second reduction event. This provides an interesting contrast with the chemistry of analogous iminoacyl compounds of general formula $[Cp'_2Nb(Cl)(\eta^2\text{-}C,N\text{-}N(Ph)=C\text{—}CHR_2)][BF_4]$.[44] For these compounds reduction has been shown to result in loss of the iminoacyl α-proton and regeneration of the precursor ketenimine complex; subsequent reduction labilizes the chloride ligand, and trapping with ethanol then generates the Nb(III) iminoacyl compounds of formula $Cp'_2Nb(\eta^2\text{-}C,N\text{-}N(Ph)=C\text{—}CHR_2)$.[44] This sequences is clearly not operating for the acyls described herein, since (a) we have seen no evidence for the production of Nb(III) acyls and (b) it would have resulted in loss of the deuterium label in the α-deuterioacyl compounds. The Nb(III) acyls *are* thought to be the precursors to the ketene–hydrides, however, and the iminoacyl chemistry provides an indication of the viability of such compounds; we have no explanation for the failure of reduced iminoacyls to proceed on to ketenimine–hydrides.

Hydride Complexes. Quite apart from the mechanism by which they are formed, the ketene–hydride compounds contain an unusual combination of ligands. The niobium–hydride linkage in related compounds has been shown to insert the unsaturated coligand, and this insertion can be driven by the addition of another potential ligand.[45] The present compounds contain a highly unsaturated ketene ligand and yet appear to favor deinsertion in some of the chemistry described herein. We have attempted to induce insertion through the addition of phosphine ligands, but no such process is evident. We ascribe this to the strong niobium–oxygen interaction and the fact that the oxygen resides in the inside coordination position. However, attempts to prepare ketene–hydrides by reaction of the free ketene with precursors such as $Cp'_2Nb(H)(PPh_3)$ were unsuccessful, apparently resulting in ketene polymerization induced by the metal hydride. This demonstrates the synthetic value of the metal-complexed ketenes; altough various synthetic pathways are still available, the ketene moiety is clearly stabilized by complexation.

One of the reactivity pathways remaining for the ketene–hydrides involves protonation with strong acid. The process exhibits remarkable regiochemistry, in that the ketene rather than the metal–hydride linkage is protonated. As noted above, this could be construed as evidence for an unusual metal–hydride bond with excessive protic character; we have thus attempted to deprotonate the ketene–hydrides with Grignard reagents and alkyllithiums, the approach Green used in the successful deprotonation of Cp_2MH_2 (M = Mo, W).[46] The lack of any such reaction for the ketene–hydrides argues against appreciable protic character. Moreover, the insertion of activated alkynes such as DMAD is entirely typical of niobocene hydrides of general formula $Cp_2Nb(L)(H)$.[28] For L = CO, Herberich has seen that insertion of DMAD (−80 °C) gives a 3:1 mixture of *Z* and *E* isomers, and this isomerizes to a 1:5 ratio of *Z*:*E* at room temperature.[28b] Conversely, for sterically crowded compounds with L = diphenylacetylene or bis(trimethylsilyl)acetylene, only the (*E*)-alkenyl isomer is observed.[28a] In general, the *Z* isomer is the kinetic one and the *E* isomer is the thermodynamic product, and observation of the *Z* isomer (derived from trans M–H addition) shows convincingly that the insertion is not a concerted process. The current example with the ketene–hydride is unusually stereospecific, giving only *Z* insertion product even at room temperature. Mechanistic proposals for related reactions have involved radical intermediates, arising from either hydrogen atom transfer or an electron transfer–proton transfer scheme;[47] mechanistic studies on the niobium systems have not been reported. The fact that this DMAD adduct fails to isomerize under thermal conditions can be attributed to the properties of the ketene ligand. First, the ketene is not sterically demanding in that the oxygen has no substituents; this minimizes the thermodynamic driving force for *Z*–*E* isomerization. In addition, metal vinyl isomerizations are presumed to proceed through alkylidene intermediates derived from donation of electron density from the metal center to the α-carbon;[48] inasmuch as the ketene is a strong acceptor ligand, the niobium center effectively resembles a d^0 Nb(V) ion and is therefore unable to provide the electron density normally required for isomerization.

The protonation of the ketene–hydrides gives rise to cationic acyl hydrides, and the latter compounds also contain an interesting combination of ligand types. Acyl hydrides are typically made by way of oxidative addition of an aldehyde to a low-valent late transition metal center.[49] In very few cases such a compound has been accessed by migratory insertion of CO into the metal–alkyl bond of an alkyl hydride, and the acyl hydride was observed only at low temperature;[50] similar reactions on related systems proceed directly to the aldehyde products,[51] suggesting that the acyl hydrides represent an important intermediate in the reduction of carbon monoxide. The general sequence (eq 9, M = Zr, Hf) involves migratory insertion



(9)

to form the unstable acyl hydride and subsequent for-

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mation of the transient unsaturated aldehyde complex; depending on conditions, the latter may undergo either (a) subsequent β-hydride elimination to the enolate–hydride[40a] or (b) trapping with excess carbon monoxide.[50] Our isoelectronic acyl hydrides **9** have the O-inside (exo) conformation by virtue of their synthesis, and their failure to form aldehydes under ambient conditions constitutes additional evidence favoring the intermediacy of O-outside (endo) acyls in subsequent CO reduction chemistry (eq 9).[50] Reductive elimination of the aldehyde or the corresponding alkane (following acyl decarbonylation) is expected to predominate if the metal center is overly electron deficient. In this context, the stability of **9a**-*d* is remarkable; these compounds contain cis acyl and hydride ligands bound to a cationic d^0 Nb(V) center yet show no obvious tendency toward elimination at room temperature. Again, this stability is logically attributed to the favored O-inside geometry in both this compound and its ketene–hydride precursor; this constitutes another example of the use of the synthetic potential of the ketene ligand in the preparation of unusual organometallics.

Conclusions

The reactions of electron-rich niobocene derivatives with disubstituted ketenes lead to the formation of the η^2-C,O ketene complexes. Although organic nucleophiles exhibit kinetic addition on the side of the smaller ketene substituent,[10] little can be said about the approach of the metal nucleophile to the ketene electrophile since the isomerization of the ligated ketene results in loss of stereochemical information. Nonetheless, it is clear that the ketene–chloride systems exhibit the *E* isomer as the thermodynamic one. Conversely, the ketene–hydride systems offer a clear indication that the *E* isomer is the kinetic one in the syntheses utilized, but the *E* and *Z* isomers exhibit virtually identical thermodynamic stability. Although the origin of these differences is not understood, it is clear that the bound ketene still has a rich synthetic chemistry. This is largely due to the availability of the uncomplexed C=C system, since reduction to the metallaenolate proceeds so as to add electron density to the ligand π* orbital. In addition, protonation at the ketene terminus utilizes the remaining π electron density, but this process is aided by the donation of electron density from the adjacent oxygen atom. Indeed, the ketene system as a whole mediates the operation of several processes, including the first example of ketene–hydride synthesis by way of acyl β-hydride elimination; we have proposed a mechanism consistent with deuterium labeling and iminoacyl model studies.[44] The hydride elimination process clearly dominates the chemistry, to the virtual exclusion of the more typical acyl migratory deinsertion to alkyl–carbonyl; we have shown elsewhere that this latter process can be induced only in the presence of added Lewis acids.[22] This tendency toward hydride transfer probably reflects the highly-substituted nature of the acyls; presumably these do not undergo deinsertion because of steric problems associated with α-branched metal alkyls. As a consequence, the chemistry described herein provides access to acyls that are more highly substituted than those available from normal migratory insertion processes. The conversion of the ligated ketenes to highly branched acyls, ketene–hydride complexes, and acyl hydride complexes is rendered possible by the strong niobium–oxygen interaction and O-inside geometry favored in these compounds. Further work in this area will be devoted to developing new synthetic methods based on the ketene ligands.

Experimental Section

General Considerations. All manipulations involving ketenes or ketene complexes were carried out under an atmosphere of nitrogen which was first passed through activated BTS catalyst and molecular sieves. Standard Schlenk techniques were used to handle solutions,[52] and solids were transferred in a Vacuum Atmospheres Corp. glovebox under purified nitrogen. Solvents toluene, benzene, hexane, tetrahydrofuran, dimethoxyethane, and diethyl ether (J. T. Baker) were distilled from sodium benzophenone ketyl under nitrogen. Acetonitrile and methylene chloride (Baker) were distilled from phosphorus pentoxide under nitrogen.

NMR spectra were obtained on a Varian XL-400 FT-NMR instrument, infrared spectra were obtained on a Perkin-Elmer Model 1600 FT-IR spectrophotometer, and elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Phenyl-substituted ketenes were prepared from the appropriate acid chlorides, which were deprotonated with triethylamine.[53] Dialkylketenes were prepared from the α-bromoacyl bromides, which were prepared using the literature procedure[54] and then reduced with either activated zinc or potassium dicarbonylcyclopentadienylferrate(II).[55] (Trimethylsilyl)cyclopentadiene (Cp′H) was prepared using the literature method,[56] with the exception that the THF solution of sodium cyclopentadienide was added in dropwise fashion to the Me_3SiCl 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. $NbCl_3(DME)$[17] was prepared using literature methods.

Syntheses. Cp'_2NbCl (1). In a typical procedure, $NbCl_3$(DME) (4 g, 13.8 mmol) was dissolved in 100 mL of THF, and 2 equiv (3.98 g, 27.6 mmol) of Cp′Li were added via an addition tube under nitrogen purge. The resulting brown solution was stirred at room temperature for 1 h, solvent was removed in vacuo, and 60 mL of toluene was added. Subsequent filtration gave a light brown filtrate and a colorless powder (LiCl); the latter was discarded. The solvent was removed in vacuo, and 20 mL hexane was added. The solution was cooled to 0 °C, and a light brown powder precipitated and was filtered and dried in vacuo; yield 4.12 g (74%). ^{1}H NMR (C_6D_6): 5.79 (4H, br m, C_5H_4), 4.51 (4H, br m, C_5H_4), 0.05 ppm (s, $Si(CH_3)_3$). **Cp_2NbCl (2)** was prepared similarly but was used in situ since subsequent reactions were hampered by the low solubility of the isolated solid.

$Cp'_2Nb(Cl)(OCCMePh)$ (3a). A 2.0-g sample of Cp'_2NbCl (1, 5.0 mmol) was suspended in 25 mL of hexane. A solution containing 8 mmol of methylphenylketene was added and the resulting solution stirred at room temperature overnight. The desired product formed a heavy yellow precipitate and was filtered out at 0 °C. This crude material was dissolved in a minimum volume of toluene, and the toluene solution was filtered to remove a small amount of insoluble impurity and concentrated in vacuo. Hexane was added to precipitate the product, which was isolated by filtration and dried in vacuo (1.78 g, 56%). The compound prepared in this way was sufficiently pure for subsequent use but could be recrystallized by slow cooling of a saturated toluene–hexane solution. IR (THF): 1639 (m), 1592 (m), 1260 (s), 840 cm^{-1} (vs). ^{1}H NMR (C_6D_6), *E* isomer: 8.18 (2H, d), 7.56 (2H, t),

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6.48, 6.27, 5.27, 4.86 (2H each, br s, Cp′–H), 2.22 (3H, s), 0.35 (18 H, s). $^{13}C\{^1H\}$ (CD_2Cl_2): 141.5 (ketene β), 128.5 (overlapping phenyls), 125.5, 124.3, 119.3, 104.7, 101.8 (Cp′), 17.1 (Me), –0.66 ppm (SiMe). ^1H NMR (CD_2Cl_2), *Z* isomer: 6.62, 6.52, 5.22, 4.88 (2H each, br s, Cp′–H), 2.66 (3H, s), 0.34 (18 H, s). The remaining phenyl signals overlapped. Compounds **3b–f** were prepared in analogous fashion.

Cp′$_2$Nb(Cl)(O=C=CEtPh) (3b). Yellow solid, 65%. IR (THF): 1623 (m), 1590 (m), 1249 (m), 842 (s). ^1H NMR (CD_2Cl_2), *E* isomer: 7.71 (2H, d), 7.32 (2 H, t), 7.01 (1H, t), 6.56, 6.32, 6.01, 5.60 (2 H each, br s, Cp′—H), 2.64 (2H, q, J = 8 Hz), 1.38 (3H, t, J = 8), 0.20 (18H, s). $^{13}C\{^1H\}$ (CD_2Cl_2): 140.9 (ketene β), 128.8, 125.8, 125.6, 123.2 (phenyls), 119.6, 105.6, 102,3 (Cp′), 25.7 (CH_2), 14.7 (Me), –0.01 (SiMe). ^1H NMR (CD_2Cl_2), *Z* isomer: 6.51, 6.40, 6.05, 5.52 (2H each, br s, Cp′—H), 2.84 (2H, q, J = 7), 1.18 (3H, t, J = 7), 0.25 (18H, s) and unresolved phenyl signals at ca. 7.4.

Cp′$_2$Nb(Cl)(OCCMe$_2$) (3c). Yellow solid, 58% yield. IR (Nujol): 1413 (w), 1246 (m), 1214 (w), 1176 (m), 1042 (m), 904 (m), 840 (s, br), 756 (m). ^1H NMR (C_6D_6): 6.41, 6.23, 5.070, 4.60 (2H each, br s), 2.20, 1.75 (3H each, s), 0.31 (18H, s).

Cp′$_2$Nb(Cl)(O=C=CPh$_2$) (3d). Yellow solid, 72%. IR (THF): 1614 (m), 1585 (m), 1249 (m), 842 (s). ^1H NMR (C_6D_6): 8.05 (2H, d), 7.50 (2H, t), 7.32 (4H, t), 7.25 (1H, t), 7.03 (1H, t), 6.49, 5.98, 4.88, 4.59 (2H each, br s, Cp′—H), 0.29 (18 H, s). $^{13}C\{^1H\}$ (CD_2Cl_2): 197.2 (ketene α), 142.4 (ketene β), 131.6, 128.9, 128.1, 126.2, 126.1 (phenyls), 123.9, 123.1, 120.4, 105,8, 103.0 (Cp′), –0.44 (SiMe). Anal. Calcd for $C_{30}H_{36}Si_2ONb$: C, 60.34; H, 6.07. Found: C, 60.29; H, 6.03.

Cp′$_2$Nb(Cl)(O=C=CMeCH$_2$CMe$_3$) (3e). IR (THF): 1666 (m), 1248 (s), 842 (s). ^1H NMR ($CDCl_3$), *E* isomer: 6.48, 6.02, 5.97, 5.50 (2H each, br s, Cp′—H), 2.26 (2H, s), 1.90 (3H, s), 0.99 (9H, s), 0.29 (18 H, s). $^{13}C\{^1H\}$ (CD_2Cl_2): 122.0, 119.3, 114.4, 107.2, 102.2 (Cp′), 34.0 (CH_2), 30.5 (Me_3), 20.8 (Me), –0.57 (SiMe).

Cp′$_2$NbCl(O=C=CMeEt) (3f). Yellow powder, 70% yield. IR (CH_2Cl_2): 2958 (s), 1692 (m, br), 1461 (m, br), 1378 (m), 1316 (w), 1249 (s), 1174 (m), 1043 (s), 901 (s), 842 (vs), 634 (s). ^1H NMR ($CDCl_3$), *E* and *Z* isomers are present in a 1:1 ratio: 6.52 (2H, d, Cp′), 6.50 (2H, d, Cp′), 6.17 (2H, d, Cp′), 6.12 (2H, d, Cp′), 5.88 (2H, d, Cp′), 5.86 (2H, d, Cp′), 5.42 (2H, d, Cp′), 5.39 (2H, d, Cp′), 2.34 (q, CH_2), 2.13 (q, CH_2), 1.86 (s, CH_3), 1.79 (s, CH_3), 1.21 (t, CH_3), 1.05 (t, CH_3), 0.28 (s, $SiMe_3$), 0.23 (s, $SiMe_3$).

Cp$_2$NbCl(O=C=CPhEt) (4b). $NbCl_2$(DME) (3 g, 10.36 mmol) was dissolved in 90 mL of THF; to this was added 2 equiv (1.83 g, 20.79 mmol) of sodium cyclopentadienide via an addition tube. The resulting solution (dark brown) was stirred for 1 h at 25 °C. Cp_2NbCl (**2**) was formed in ca. 65% yield (1.74 g, 6.73 mmol), and the reaction solution was treated with a 0.05 M benzene solution containing 0.98 g (6.73 mmol) of ethyl phenyl ketene. The solution showed no immediate color change and was stirred at 25 °C for 5 h, during which time the color changed gradually to brownish-olive-green. Solution IR showed the disappearance of the ketene stretch at 2100 cm^{-1}, which indicated the completion of the reaction. The solution was concentrated to ca. 20 mL in vacuo; to this was added 40 mL of toluene, and the resulting solution was filtered. The filtrate volume was reduced to ca. 10 mL in vacuo and then 20 mL hexane added. An olive-green powder precipitated and was filtered and dried in vacuo: yield 1.91 g (70%). IR (THF): 1632 (m), 1591 (s), 1492 (m), 1463 (m), 1263 (s), 1184 (m), 1019 (s), 823 (vs), 764 (w). ^1H NMR (C_6D_6): (a) *E* isomer 8.14 (d, 2 *o*-H), 7.48 (t, 2 *m*-H), 7.37 (t, 1 *p*-H), 5.26 (s, C_5H_5), 2.43 (q, CH_2, J = 7), 1.36 (t, CH_3, J = 7); (b) *Z* isomer 7.28 (d, 2 *o*-H), 5.32 (s, C_5H_5), 3.22 (q, CH_2, J = 7), 1.13 (t, CH_3, J = 7); peaks due to the other phenyl protons (2 *m*-H and 1 *p*-H) were not resolved. Derivatives **4c** and **4f** were prepared similarly.

Cp$_2$NbCl(O=C=CMe$_2$) (4c). Olive-green powder; yield 73%. IR (THF): 1707 (br, m), 1432 (s), 1286 (m), 1167 (s), 822 (vs), 734 (m). ^1H NMR ($CDCl_3$): 5.9 (s, C_5H_5), 1.91 (s, CH_3), 1.80 (s, CH_3).

Cp$_2$NbCl(O=C=CMeEt) (4f). Olive-green powder; yield 64%. IR (THF): 1693 (br, m), 1466 (w), 1384 (m), 1325 (m), 1245 (s), 1181 (m), 1041 (s), 906 (s), 847 (vs), 639. ^1H NMR (C_6D_6): (a) *E* isomer 5.28 (s, C_5H_5), 2.72 (q, CH_2), 1.68 (s, CH_3), 1.32 (t, CH_3); (b) *Z* isomer 5.31 (s, C_5H_5), 2.27 (s, CH_3), 2.03 (q, CH_2), 1.24 (t, CH_3).

Cp′$_2$Nb(H)(O=C=CMePh) (6a). A sample of **3a** (160 mg, 0.29 mmol) was dissolved in 20 mL of tetrahydrofuran. The resulting solution was added to a sodium amalgam containing 15 mg of sodium (0.6 mmol) and stirred for 10 min at room temperature, during which time the solution turned green-brown in color. Degassed absolute ethanol (2 mL) was added, and the solution was stirred for additional 10 min and then filtered through dried Celite. The volume of the resulting yellow solution was reduced in vacuo, eventually yielding a yellow oily solid. IR (TRF): 1730 (br, w), 1631 (s), 1590 (s), 1494 (s), 1249 (s), 1173 (m), 841 (vs), 757 (m), 722 (m). ^1H NMR (C_6D_6): *E* isomer 8.20 (2H, d), 7.46 (2H, t), 7.09 (1H, t), 5.57, 5.30, 5.18, 4.25 (2H each br s, Cp′H), 2.44 (3H, s, Me), 1.41 (1H, s Nb—H), 0.23 (18H, s, SiMe). $^{13}C\{^1H\}$ (DMSO-d_6): 133.1 (ketene β), 128.9, 128.7, 128.1, 127.9, 127.7, 127.6, 125.0, 122.9, 121.2 (Ph and Cp′), 18.3 (Me), 0.26 ($SiMe_3$). ^1H NMR (C_6D_6): *Z* isomer 7.82 (2H, d), 7.52 (2H, t), 7.25 (1H, t), 5.62, 5.55, 5.39, 4.26 (2H each, br s, Cp′H), 2.57 (3H, s, Me), 1.52 (1H, s, Nb—H), 0.20 (18H, s, SiMe). Anal. Calcd for $C_{25}H_{35}Si_2ONb$: C, 59.74; H, 7.42. Found: C, 59.71; H, 7.35. Analogues **6b–e** were prepared similarly.

Cp′$_2$Nb(H)(O=C=CEtPh) (6b). Pale yellow oily solid. IR (THF): 1731 (s, Nb—H), 1623 (m), 1589 (m), 806 (s). ^1H NMR (C_6D_6), *E* isomer: 8.30 (2H, d, J = 7), 7.43 (2H, t, J = 7), 7.05 (1H, t, J = 7), 5.60, 5.30, 5.25, 4.20 (2H each, br s, Cp′—H), 2.95 (2H, q, J = 7), 1.58 (3H, t, J = 7), 1.41 (1H, br s, Nb—H), 0.20 (18H, s). $^{13}C\{^1H\}$ (DMSO-d_6): 140.0 (ketene β), 128.7, 128.0, 127.6, 127.4 (Ph), 126.9, 126.5, 122.7 (Cp′), 17.7 (Me), 1.7 ($SiMe_3$). ^1H NMR (C_6D_6); *Z* isomer: 7.82 (2H, d, J = 7), 7.49 (2H, t, J = 7), 7.23 (1H, t, J = 7), 5.65, 5.36, 5.20, 4.31 (2H each, br s, Cp′—H), 3.09 (2H, q, J = 7), 1.51 (1H, br s, Nb—H), 1.35 (3H, t, J = 7), 0.25 (18H, s).

Cp′$_2$Nb(H)(O=C=CMe$_2$) (6c). Colorless oil, 52%. IR (THF): 1731 (w, Nb—H), 1642 (m), 1249 (s), 832 (s). ^1H NMR (C_6D_6): 5.48 (4H), 5.42 (2H), 4.13 (2H) (all br s, Cp′—H), 2.26, 2.09 (3H each, s, Me), 1.29 (1H, br s, Nb—H), 0.26 (18H, s, SiMe).

Cp′$_2$Nb(H)(O=C=CPh$_2$) (6d). Colorless solid is obtained by taking the crude oil up in benzene, which is then slowly removed in vacuo; product precipitates in 75% yield. IR (THF): 1740 (w, Nb—H), 1582 (m), 1248 (s), 840 (vs). ^1H NMR (C_6D_6): 8.08 (d, J = 8), 7.81 (d, J = 8), 7.47 (t), 7.36 (t), 7.06 (m), 5.52 (2H), 5.32 (4H), 4.20 (2H), 1.60 (1H, br s, Nb—H), 0.27 (18H, s). $^{13}C\{^1H\}$ (DMSO-d_6): 143.8 (ketene β), 132.8, 129.7, 128.8, 128.7, 127.6, 127.3, 127.1, 126.9, 125.3 (overlapping Ph and Cp′), 0.23 ($SiMe_3$).

Cp′$_2$Nb(H)(O=C=C(Me)CH$_2$CMe$_3$) (6e). IR (THF): 1737 (w, Nb—H), 1668 (m), 1247 (s), 847 (vs). ^1H NMR (C_6D_6), *E* isomer: 5.86, 5.09, 5.01, 4.30 (2H each, br s, Cp′—H), 2.53 (2H, s), 2.19 (3H, s), 1.16 (9H, s), 0.31 (18 H, s).

[Cp′$_2$Nb(Cl)(η^2-C(O)CHMePh)][BF$_4$] (7a). Compound **3a** (0.37 g, 0.64 mmol) was suspended in 20 mL of diethyl ether, and 110 μL of diethyloxonium tetrafluoroborate was added using a syringe. The solid turned colorless and dissolved immediately, and a colorless solid precipitated within several seconds. The solid was filtered, washed with cold diethyl ether, and dried in vacuo (58%). IR (THF): 1617 (m), 1592 (m), 1261 (s), 1015 (s, br), 843 (s). ^1H NMR (C_6D_6): 7.62 (2H, d), 7.16 (2H, t), 7.04 (1H, t), 6.82, 6.69, 6.67, 6.52, 6.44, 6.40, 6.08, 5.65 (1H, each, br s, Cp′–H), 5.92 (1H, q, C*H*MePh), 1.71 (3H, d), 0.22, 0.08 (9H each, SiMe). A similar procedure was used to prepare **7b–d**.

[Cp′$_2$Nb(Cl)(η^2-C(O)CHEtPh)][BF$_4$] (7b). Colorless crystals, 60%. IR (Nujol): 1615 (m), 1252 (s), 1171 (m), 1080 (s, br), 847 (s), 763 (m), 739 (s). ^1H NMR ($CDCl_3$): 7.69 (2H, d, J = 7), 7.47 (1H, t, J = 7), 7.39 (2H, pseudo-t), 6.64, 6.61, 6.50, 6.48, 6.45, 5.85, 5.75 (each 1H, br s, Cp′–H), 5.91 (1H, d of d, J = 4.2 and 12), 2.19 (2H, m), 1.03 (3H, apparent t, J = 7), 0.29, 0.11 (9H each). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 287.2, 134.5, 130.0 (2C), 129.4 (2 C), 126.4, 125.2, 124.3, 122.7, 121.4, 120.8, 110.2, 107.7, 107.5, 60.9, 28.0, 11.6, –0.05 (3C), –0.07 (3C). Anal. Calcd for $C_{26}H_{37}Si_2OClBF_4Nb$: C, 49.03; H, 5.86. Found: C, 48.98; H, 5.63.

[Cp′$_2$Nb(Cl)(η^2-C(O)CHMe$_2$)][BF$_4$] (7c). Colorless solid, 52%. IR (Nujol): 1612 (w), 1060 (br s). ^{1}H NMR ($CDCl_3$): 6.71 (2H), 6.61 (2H), 6.33 (4H), 3.92 (1H, septet, C*H*Me$_2$, J = 7), 1.63 (6H, d), 0.21 (18H, SiMe).

[Cp′$_2$Nb(Cl)(η^2-C(O)CHPh$_2$)][BF$_4$] (7d). Colorless crystals, 60%. IR (THF): 1613 (m), 1585 (m), 1248 (s), 842 (s). ^{1}H NMR (C_6D_6): 8.08 (4H, d), 7.38 (4H, d), 6.98 (2H, d), 6.41 (1H, s, C*H*Ph$_2$), 6.93 (2H), 6.57 (2H), 6.20 (4H) (all br s, Cp′–H), 0.01 (18H, s, SiMe).

[Cp$_2$NbCl(η^2-C(O)CHPhEt)][BF$_4$] (8). Beige powder, yield 82%. IR (CH_3CN): 3116 (s), 1613 (m), 1446 (vs), 1376 (vs), 1061 (vs), 1039 (vs), 853 (s), 825 (s), 745 (m). ^{1}H NMR (CD_3CN): 7.55 (s, 2 phenyl protons), 7.54 (s, 3 phenyl protons), 6.34 (5H, s, Cp), 6.00 (5H, s, Cp), 5.25 (dd, C*H*PhEt, J_{app} = 5), 2.37 (m, CHH′), 2.28 (m, CHH′), 0.98 ppm (t, CH_3, J = 7).

[Cp′$_2$Nb(H)(η^2-C(O)CHMePh)][BF$_4$] (9a). Colorless microcrystals, 55%. IR (THF): 1592 (m), 1260 (s), 1092 (br, s), 840 (s). ^{1}H NMR (C_6D_6): 7.48 (2H, d), 7.20 (2H, t), 7.05 (1H, t), 6.58, 6.54, 6.47, 6.40, 6.29 (2H), 5.92, 5.58 (1H each except as noted br s, Cp′–H), 5.78 (1H, q, C*H*MePh, J = 7), 1.62 (1H, s Nb–H), 0.97 (3H, d, Me, J = 7), 0.14, 0.07 (9H each, SiMe).

[Cp′$_2$NbH(η^2-C(O)CHPhEt)][BF$_4$] (9b). Colorless microcrystals, 70%. IR (Nujol): 1610 (w), 1593 (w), 1251 (m), 1162 (m), 1055 (br, s), 898 (m), 845 (s). ^{1}H NMR (CD_2Cl_2): 7.4–7.8 (5H, overlapping multiplets), 6.58, 6.18, 5.75, 5.69, 5.59, 5.52, 4.81, 4.12 (1H, each, Cp′–H), 5.13 (1H, pseudo-t, C*H*EtPh), 2.79 (1H, singlet, Nb–H), 2.16 (2H, multiplet, CH_2Me), 0.98 (3H, pseudo-t, CH_2CH_3, J_{app} = 7), 0.24, 0.32 (9H each, singlets, SiMe). ^{13}C{^{1}H} ($CDCl_3$): 294.4, 136.2, 135.1, 134.5, 133.6, 132.9, 129.9, 128.6, 128.0, 126.0, 114.6, 113.3, 111.6, 109.7, 106.6, 62.3, 27.5, 11.6, 1.0, –1.1. Anal. Calcd for $C_{26}H_{38}Si_2OBF_4Nb$: C, 51.83; H, 6.36. Found: C, 51.82; H, 6.29.

[Cp′$_2$NbH(η^2-C(O)CHMe$_2$)][BF$_4$] (9c). Colorless solid, 60%. IR (THF): 1737 (w), 1590 (m), 1251 (s), 843 (s). ^{1}H NMR (C_6D_6): 6.58, 5.59, 5.46, 4.54 (2H, each, br s, Cp′–H), 5.87 (1H, septet, J = 7), 1.38 (1H, s, Nb–H), 1.27 (6H, d, J = 7), 0.035 (18H, s).

[Cp′$_2$NbH(η^2-C(O)CHPh$_2$)][BF$_4$] (9d). Colorless solid, 68%. IR (THF): 1735 (w), 1582 (m), 1249 (s), 1092 (s, br), 841 (s). ^{1}H NMR (C_6D_6): 8.02 (1H, s, C*H*Ph$_2$), 7.85 (4H, d), 7.09 (4H, t), 6.97 (2H, t), 7.03, 6.39, 5.65, 4.38 (2H, each, br s, Cp′–H), 2.70 (1H, s, Nb–H), 0.03 (18H, s, SiMe).

Cp′$_2$Nb((*E*)-O=C=CMePh)[(*Z*)-C(CO$_2$Me)=CH(CO$_2$Me)] (10a). A 40-mg (0.080-mmol) sample of **6a** was dissolved in 20 mL of toluene and 10 μL (0.013 g, 0.089 mmol) of dimethyl acetylenedicarboxylate (DMAD) was added. The solution turned orange and was stirred at room temperature overnight. The toluene was removed in vacuo and the residue taken up in hexane. This solution was filtered and the hexane removed. The compound did not crystallize and was obtained as a yellow oil; this did not give acceptable analytical data, but appeared reasonably pure by NMR. IR (toluene): 1714 (s, with shoulder, CO_2Me), 1635 (m), 1592 (m), 807 (s), ^{1}H NMR (C_6D_6): 8.05 (2H, d), 7.49 (2H, t), 7.28 (1H, s, vinyl), 7.06 (1H, t), 6.38 (2H, m, Cp′H), 6.12 (2H, m, Cp′H), 5.50 (4H, m, Cp′H), 3.80, 3.48 (3H each, s, CO_2Me), 2.25 (3H, s), 0.08 (18H, s). ^{13}C{^{1}H} (THF-d_8): 194.2 (ketene α), 177.4 (α-CO), 170.2 (α-vinyl), 169.5 (β-CO), 142.4 (ketene β-C), 131.9 (β-vinyl, $^1J_{CH}$ = 156.5), 128.4, 125.0, 122.8, 121.4 (phenyls), 119.5, 110.2, 104.9, 104.1, 94.4 (Cp′), 51.7, 50.7 (CO_2Me), 19.2 (Me), 0.5 (SiMe). A similar procedure was used to prepare **10b,d**.

Cp′$_2$Nb((*E*)-O=C=CEtPh)[(*Z*)-C(CO$_2$Me)=CH(CO$_2$Me)] (10b). Pale yellow solid from hexane. IR (toluene): 1712 (s, with shoulder, CO_2Me), 1629 (m), 1590 (m), 806 (s). ^{1}H NMR (C_6D_6): 7.98 (2H, d), 7.45 (1H, t), 7.25 (1H, s, vinyl), 7.08 (1H, t), 7.05 (1H, t), 6.40, 6.20, 5.62, 5.42 (2H, each, m, Cp′H), 3.78, 3.48 (3H each, s, CO_2Me), 2.70 (2H, q, J = 8), 1.45 (3H, t, J = 8), 0.08 (18H, s). ^{13}C{^{1}H} (THF-d_8): 193.9 (ketene α), 177.0 (α-CO), 169.8 (α-vinyl), 168.8 (β-CO), 140.9 (ketene β-C), 128.1, 125.6, 122.5, 120.6 (phenyls), 117.9, 109.1, 105.2, 104.3, 100.9 (Cp′), 131.6 (β-vinyl, $^1J_{CH}$ = 157.6), 51.4, 50.3 (CO_2Me), 26.1 (CH_2), 14.6 (Me), –0.9 (SiMe).

Cp′$_2$Nb(O=C=CPh$_2$)[(*Z*)-C(CO$_2$Me)=CH(CO$_2$Me)] (10d). Pale yellow oil. IR (THF): 1713 (s), 1613 (m), 1566 (m), 808 (s). ^{1}H NMR (C_6D_6): 7.82, 7.53, 7.34, 7.05 (10H, overlapping multiplets), 7.22 (1H, s, vinyl-H), 6.35, 6.29, 5.54, 5.42 (2H, each, br s, Cp′H), 3.72, 3.45 (3H, each, s, CO_2Me), 0.03 (18H, s). ^{13}C{^{1}H} (C_6D_6): unresolved phenyl signals at ca. 125, 194 (ketene α), 177.6 (α-CO), 172.4 (vinyl α) 170.4 (β-CO), 144.6, 144.1, 132.4 (vinyl β), 131.7 (Ph), 119.7, 119.4, 110.4, 106.5, 106.0 (Cp′), 51.9, 51.4 ($COCH_3$), 0.07 (Si—C).

X-ray Crystallography. Compound **3b** was crystallized by cooling a saturated toluene–hexane solution slowly to –30 °C. A crystal measuring 0.50 × 0.37 × 0.37 mm was mounted in a capillary and the capillary sealed. Diffraction data were obtained on an Enraf-Nonius CAD4 fully automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Preliminary indications of the unit cell based on 25 randomly selected reflections revealed monoclinic symmetry. The data were processed with the following lattice parameters: a = 7.938(2) Å, b = 15.81(2) Å, c = 21.61(1) Å, and β = 95.41(6)°. The space group, based on the systematic absences, was uniquely assigned as $P2_1/c$ (No. 14) with one molecule of composition $C_{24}H_{33}NbClOSi_2$ comprising the asymmetric unit. The cell volume was 2700(7) Å^3, and the calculated density was 1.22 g/cm^3. There were 5548 unique reflections collected in the range $2\theta \leq 52°$, of which 3796 (68%) with $I \geq 3\sigma(I)$ were adjudged observed. The data set was corrected for the Lorentz factor, polarization, and adsorption using three suitable reflections to obtain ψ scans and subsequently corrected by the empirical absorption correction method.

The structure was solved by locating the position of the niobium atom using the Patterson function. Iterative use of the WFOURIER option in DIRDIF revealed the entire non-hydrogen structure. Several hydrogen positions were located and the remaining were input at calculated positions. The full matrix refinement of the non-hydrogen atoms and input of the hydrogen scattering factors resulted in convergence of the crystallographic reliability factor to an unweighted residual of 0.046 and a weighted residual of 0.059. Data are collected in Table II.

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Supplementary Material Available: Crystal data for **3b**, including a textual summary of X-ray analysis, tables of crystal data, bond lengths and angles, atomic coordinates, and thermal parameters, and a structure (11 pages). Ordering information is given on any current masthead page.

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