Hydride and Proton Transfer Reactions of Niobium-Bound Ligands. Synthetic and Thermodynamic Studies of Ketene, Enacyl, and Vinylketene Complexes

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The niobium ketene complexes $Cp'_2Nb(Cl)(O{=}C{=}C(R')CH_2R)$ (**1**; $Cp' = \eta^5\text{-}C_5H_4SiMe_3$) exhibit complexation of the ketene C=O bond. Upon treatment with an appropriate triarylcarbenium tetrafluoroborate they donate a hydride, a process constituting a useful synthesis of the η^2-enacyl salts $[Cp'_2Nb(Cl)(\eta^2\text{-}OCC(R'){=}CHR)][BF_4]$ (**3**). The reactions involve transfer of a γ-hydride and are specific for the generation of the (*E*)-enacyl isomers; one derivative (**3b**, R′ = Ph, R = Me) was the subject of an X-ray diffraction study. The cationic enacyls are strong electrophiles and are susceptible to conjugate addition reactions and [4 + 2] cycloadditions. If the substituent R contains allylic protons, the enacyl complex is also very acidic; treatment with a suitable base converts these enacyls to the $\eta^2(C,O)$-vinylketene complexes $Cp'_2Nb(Cl)(\eta^2\text{-}O{=}C{=}C(R')CH{=}CH_2)$ (**7**). These compounds are relatively electron-rich, and the vinyl terminus constitutes a site for addition of electrophiles. The overall conversion of ketene ligand to vinylketene ligand constitutes an ionic dehydrogenation reaction, and thermodynamic data have been determined for the individual hydride and proton transfer reactions. These show that the metal contributes ca. 30 kcal/mol to the individual steps; since it impedes hydride transfer and facilitates proton transfer, these effects cancel and the free energies of the overall dehydrogenation process are similar to those calculated for uncomplexed organic species.

Introduction

Metal-complexed enacyls (acryloyls) and vinylketenes are highly unsaturated and therefore provide considerable opportunity for functionalization.[2] Free vinylketenes have also proved useful in a variety of cycloaddition reactions, many of which have been applied to the synthesis of highly substituted phenols or quinones.[3] These reactions are formally [4 + 2] cycloadditions in which the vinylketene serves as the diene component. However, some have been shown to proceed instead by way of a cascade of pericyclic processes,[3f] the first of which is a [2 + 2] reaction involving the ketene C=C bond. Indeed, the vinylketenes are often generated via an intramolecular retrocycloaddition reaction involving the tautomeric cyclobutenone.[3]

Because of the high reactivity of vinylketenes, they are often prepared within the coordination sphere of a metal center. Common approaches include the reaction of metal carbonyls with cyclopropenes,[4] addition of carbon monoxide to metallacyclobutenes,[2u,5] and coupling of vinylalkylidene and carbon monoxide ligands.[2j,k,6] It should be noted that low-valent metal centers are usually thought to insert into the carbon−carbon single bond of cyclopropenes to generate metallacyclobutenes,[4] and the latter are tautomers of vinylalkylidenes.[7] As such, these synthetic routes are closely related, even though they originate from different starting materials; all involve the combination of a doubly unsaturated organic fragment with carbon monoxide. Alternatively, cyclobutenone precursors may also be used to prepare

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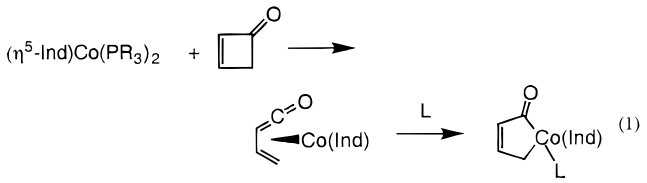
metal-complexed vinylketenes.[2g,n,o] Liebeskind has used this approach with several metal complexes, and an example is shown in eq 1.[8] The electron-rich cobalt



(1)

complex provides the (η^5-indenyl)Co moiety, which generates the vinylketene complex. Although this process could involve trapping of a transient vinylketene, it has been suggested that complexation of the cyclobutenone precedes the retrocycloaddition.[8] The metal center binds to the diene part of the vinylketene, and it is important to note that this η^4 binding mode is observed for the overwhelming majority of vinylketene complexes. Indeed, the cobalt complex is unusual in that addition of a ligand causes the vinylketene to adopt the indicated η^2 binding mode, but this still involves an interaction of the metal center with the diene portion of the vinylketene. This complex is ideally suited for metal-mediated cycloaddition when the added ligand is an alkyne.[8]

Metal enacyls are closely related to vinylketenes, and these two functional groups may (in principle) be interconverted by a single conjugate addition reaction. Enacyl complexes are typically made via the migratory insertion of carbon monoxide into a metal−vinyl bond,[9] the addition of electron-rich metal centers to acryloyl halides or acroleins (the latter is a C−H oxidative addition),[10] or aldol-type condensation of metallaenolates with free aldehydes or ketones.[11] We have discovered an alternate synthesis of niobium-complexed enacyls,[12] a process which involves an unusual abstraction of a γ-hydride from a ketene complex precursor. This results in a cationic η^2-enacyl, which is the conjugate acid of a niobium−vinylketene complex.[13] The overall conversion of complexed ketene to complexed vinylketene constitutes a stepwise ionic dehydrogenation. We are interested in gathering quantitative data on the effect of a transition metal on ligand-centered reactions, and we have previously reported the hydride-acceptor powers of a series of compounds;[14] we will make use of these data to ascertain the thermodynamics of the hydride transfer reactions involving the ketene complexes. We report herein, therefore, the results of a synthetic, structural, and thermodynamic study on the use of niobium ketene complexes in the synthesis of enacyl and vinylketene complexes.

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of nitrogen, which was purified by passage through a column of Linde 4A molecular sieves and activated BTS catalyst. Solutions were handled using standard Schlenk methods,[15] and solids were transferred in a Vacuum Atmospheres Corp. glovebox. The solvents toluene, hexane, tetrahydrofuran, benzene, and diethyl ether were purchased from J. T. Baker and distilled from sodium benzophenone ketyl under nitrogen. Methylene chloride (J. T. Baker) was distilled under nitrogen from P_2O_5. The NMR solvents C_6D_6 and THF-d_8 were freeze−thaw-degassed and vacuum-distilled from sodium amalgam, while $CDCl_3$ and CD_3CN were freeze−thaw-degassed and vacuum-distilled from P_2O_5. Tetrafluoroboric acid diethyl ether complex (diethyloxonium tetrafluoroborate) was purchased from Aldrich Chemical Co. and used as received. Triphenylcarbenium tetrafluoroborate (Aldrich) was recrystallized from a 5:1 solvent mixture of methylene chloride and ethyl acetate prior to use. Substituted derivatives were

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prepared according to literature procedures[16] and purified similarly. The preparations of the niobium ketene complexes $Cp'_2Nb(Cl)(\eta^2\text{-}OCCRR')$ ($Cp' = \eta^5\text{-}C_5H_4SiMe_3$; **1a**, R = R′ = Me; **1b**, R=Ph, R′ = Et; **1c,** R = R′ = Et; and **1d**, R = Me, R′ = Et) and the corresponding acyl salts $[Cp'_2Nb(Cl)(\eta^2\text{-}OCCHRR')][BF_4]$ (**2**) have been described previously.[17]

Proton NMR spectra were obtained on a Varian 300 FT-NMR, and IR spectra were determined using either 0.05 mm path length liquid cells or Nujol mulls on a Perkin-Elmer Model 1600 FT-IR. 2D-NOESY studies were done using a Varian 400 FT-NMR. Chemical shifts are in ppm relative to internal TMS, and infrared frequencies are in cm^{-1}. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY. As a class of compounds, the vinylketene complexes exhibited limited stability in solution and were not amenable to crystallization; these compounds were characterized by FAB mass spectrometry (spectra were obtained at the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois), and NMR spectra are included as Supporting Information.

$[Cp'_2NbCl(O{=}CC(Ph){=}CHMe]^+[BF_4]^-$ (3b). $Cp'_2NbCl(O{=}C{=}CPhEt)$ (0.50 g, 0.91 mmol) was dissolved in 15 mL of freshly distilled methylene chloride. The resulting yellow solution was treated with 0.30 g (0.91 mmol) of $Ph_3C^+BF_4^-$; the color changed immediately to orange. After the reaction solution was stirred for 2 h, the solvent was removed in vacuo and 20 mL of freshly distilled diethyl ether was added to the pink-orange residue. The resulting precipitate was filtered, washed with two 5 mL portions of diethyl ether, and dried in vacuo (0.50 g, 86.3% yield). It was recrystallized from $CDCl_3$ by allowing slow evaporation of the solvent at room temperature. Well-formed yellow (orange in chloroform) hexagonal crystals of **3b**·$CHCl_3$ were isolated. IR (CH_2Cl_2): 3114 (m), 2958 (m), 1615 (vw), 1600 (vw), 1565 (s), 1496 (w), 1411 (m), 1378 (m), 1317 (w), 1228 (s), 1170 (m), 1063 (vs), 1040 (vs), 961 (w), 900 (m), 843 (vs), 799 (w), 834 (m). ^1H NMR ($CDCl_3$): 8.43 (t, CH), 7.44 (m, 3H, Ph), 7.20 (m, 2H, Ph), 6.71 (d, 2H, Cp′), 6.59 (d, 2H, Cp′), 6.53 (d, 2H, Cp′), 6.49 (d, 2H, Cp′), 2.49 (d, CH_3), 0.14 (s, $SiMe_3$). Anal. Calcd for $C_{26}H_{35}NbBClF_4OSi_2$: C, 49.17; H, 5.51. Found: C, 49.42; H, 5.22. The derivatives $[Cp'_2Nb(Cl)(\eta^2\text{-}C(O)C(Me){=}CH_2)][BF_4]$ (**3a**) and $[Cp'_2Nb(Cl)(\eta^2\text{-}C(O)C(Et){=}CHMe)][BF_4]$ (**3c**) were prepared similarly in 84% and 78% yields, respectively. Data for **3a** are as follows. IR (Nujol): 1573 (w), 1248 (m), 1038 (s, br). ^1H NMR ($CDCl_3$): 7.52 (br s, 1H, vinyl), 7.32 (br s, 1H, vinyl), 6.79 (br s, 2H, Cp′), 6.58 (br s, 4H, Cp′), 6.45 (br s, 2H, Cp′), 2.23 (s, 3H, Me), 0.22 (s, 18H, SiMe). Data for **3c** are as follows. ^1H NMR ($CDCl_3$): 8.15 (q, J = 15, vinyl), 6.68, 6.48, 6.44, 6.32 (br s, 2H, Cp′), 2.71 (t, CH_2), 2.65 (d, J = 15, C=CHCH_3), 1.25 (t, 3H, Me), 0.20 (s, 18 H, SiMe). The derivatives $[Cp'_2NbCl(O{=}CC(Et){=}CH_2)][BF_4]$ (**3d**) and $[Cp'^2NbCl(O{=}CC(Me){=}CHMe]$-$[BF_4]$ (**3d′**) were obtained as an isomeric mixture from $Cp'_2Nb{-}Cl(O{=}C{=}CMeEt)$ (**1d**) and $Ph_3C^+BF_4^-$ via a procedure similar to that used to prepare compound **3b**; this resulted in a pale yellow powder in 92% yield. IR (CH_2Cl_2): 3116 (s), 2958 (s), 2900 (w), 1627 (w), 1566 (s), 1411 (s), 1376 (m), 1318 (w), 1256 (s), 1063 (vs), 1040 (vs), 98 (w), 899 (s), 843 (vs), 633 (m), 522 (w). ^1H NMR ($CDCl_3$): (a) **3d**, 7.50 (CHH′), 7.30 (s, CHH′), 2.54 (q, CH_2), 1.25 (t, CH_3); (b) **3d′**, 8.20 (q, CH), 0.44 (d, CH_3), 2.13 (s, CH_3). It was not possible to identify the chemical shift for the Cp′ ligands of the two separate isomers. The peaks due to the Cp′ ligands of both isomers are 6.75 (d, s H), 6.50 (d, 2 H), 6.48 (d, 2 H), 6.39 (d, 2 H), 6.36 (d, 2 H), and 0.16, 0.15 (s, $Si(CH_3)_3$).

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$Cp'_2Nb(Cl)(\eta^2\text{-}OCC(Me)CH_2OMe)$ (4a). A Schlenk flask was charged with 0.2 g (0.36 mmol) of **3a** and 0.05 g (0.844 mmol) of NaOMe. To this was added 40 mL of THF via syringe, and a yellow solution resulted. After 30 min at ambient temperature, the solvent was removed in vacuo. The residue was extracted with hexanes, and the product was isolated as a yellow oil following evacuation of the hexanes (yield 46%). IR (Nujol): 1676.6 (w), 1260.1 (vs), 1081.7 (vs, br), 800.1 (vs). ^1H NMR (C_6D_6): 6.73, 6.21, 5.10, 4.69 (each 2H, br s Cp′ H), 3.92 (2H, s, CH_2OMe), 3.35 (3H, s, OCH_3), 2.32 (3H, s, CH_3), 0.28 (18H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): 130.4, 129.7, 127.6, 127.0, 117.6, 102.4, 101.1, 84.0, 74.1, 1.8.

$Cp'_2Nb(Cl)(\eta^2\text{-}OCC(Me)CH_2NEt_2)$ (4b). A 0.2 g (0.36 mmol) sample of **3a** was dissolved in 40 mL of THF, and 2 equiv (74 μL, 0.71 mmol) of diethylamine was added via syringe. The yellow solution was stirred for 45 min at room temperature and the solvent removed in vacuo. The crude product was dissolved in toluene, this solution was filtered to remove diethylammonium salts and concentrated in vacuo. Hexane was added to precipitate a yellow solid, which was isolated by filtration and dried in vacuo (0.11 g, 56%). IR (Nujol): 1653 (m), 1248 (s), 1042 (vs, br), 835 (vs). ^1H NMR (C_6D_6): 6.29, 6.06, 5.8113, 5.79 (each 2H, br s, Cp′ H), 3.44 (2H, s, CH_2NEt_2), 2.45 (4H, br m, N(CH_2CH_3)$_2$), 2.25 (3H, s, CH_3), 0.85 (6H, t, N(CH$_2$CH_3)$_2$), 0.22 (18H, s, $SiMe_3$).

$[Cp'_2Nb(Cl)(\eta^2\text{-}OCC(Me){=}CHNEt_2)][BF_4]$ (5b). A 0.1 g (0.18 mmol) sample of aminoketene **4b** and 0.06 g (0.18 mmol) of triphenylcarbenium tetrafluoroborate were dissolved in 40 mL of CH_2Cl_2. The solution was stirred at room temperature for 2 h, and the solvent was removed in vacuo. A brownish red precipitate containing a mixture of the product and enacyl **3a** (ca. 50:50) was filtered from diethyl ether. The product **5b** was isolated as a white precipitate by recrystallization from CH_2Cl_2/Et_2O in 35% yield. IR (neat): 1599.0 (s, C=O), 1575.5 (s, C=C), 1446.8 (s), 1411.5 (s), 1255.7 (vs), 1084.6 (vs, br) 836.3 (s). ^1H NMR ($CDCl_3$): 7.78 (1H, s, CHNEt_2), 6.73, 6.68, 6.58, 6.45 (each 2H, br s, Cp′ H), 3.20 (4H, br m, N(CH_2CH_3)$_2$), 1.77 (3H, s, CH_3), 1.42 (6H, t, N(CH$_2$CH_3)$_2$), 0.27 (18H, s, $SiMe_3$). ^{13}C NMR ($CDCl_3$): 201.1, 143.5, 129.9, 128.5, 127.9, 127.6, 44.2, 26.3, 11.5, 0.09. High-resolution FAB-MS: calcd for $C_{24}H_{40}OClNbSi_2$, 542.140 07; found, 542.140 11.

$Cp'_2Nb(Cl)(\eta^2\text{-}OCC(Ph)CH{=}CH_2)$ (7b). KO^{t}Bu (0.12 g, 0.105 mmol) was weighed in air, added to a Schlenk flask, and evacuated. Enacyl **3b** (0.22 g, 0.35 mmol) was weighed out in the nitrogen glovebox and loaded into a separate flask. Using a nitrogen purge, 40 mL of THF was added to the flask containing **3b**, and 20 mL of THF was added to the flask containing KO^{t}Bu. Both flasks were cooled to 0 °C. The THF solution of **3b** was added quickly via cannula to the KO^{t}Bu solution. The yellow-orange color of the enacyl gave way to a dark yellow. The solution was stirred for 30 min at ambient temperature and then filtered through Celite. The THF was removed in vacuo, and toluene (ca. 20 mL) was added. Some dark brown precipitate formed along with a yellow solution. This was filtered, and the toluene was removed in vacuo. Addition of hexanes produced a yellow solid, which was filtered and dried in vacuo; yield 0.15 g (0.28 mmol, 80%). ^1H NMR (C_6D_6): 7.98 ppm (d, 2H, *o*-Ph), 7.42 (t, 2H, *m*-Ph), 7.13 (1H, *p*-Ph), 6.47 (m, 2H, Cp′), 6.45 (d of d, J = 11, 18 Hz, 1H, vinyl), 6.00 (m, 2H, Cp′), 5.59 (d, J = 18 Hz, 1H, vinyl), 5.21 (d, J = 11 Hz, 1H, vinyl), 5.14 (m, 2H, Cp′), 4.77 (m, 2H, Cp′), 0.22 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 138 (ketene), 128, 128, 125, 123, 121 (phenyl), 118, 107, 106, 102, (Cp′), −0.9 ($SiMe_3$). IR (Nujol): 1601 (m), 1584 (m), 1246 (m), 1073 (br, s), 840 (s). High-resolution FAB-MS: calcd for $C_{26}H_{35}OClNbSi_2$, 547.097 88; found, 547.097 90. **$Cp'_2Nb(Cl)(\eta^2\text{-}OCC(Et)CH{=}CH_2)$ (7c)** was prepared in a similar fashion but proved to be soluble in hexanes. Hence, at the completion of the reaction, the THF was removed in vacuo and hexane (ca. 20 mL) was added. The solution was filtered through Celite, giving a yellow filtrate. Removal of solvent in vacuo gave a yellow oil; yield 52%. ^1H

NMR (C_6D_6): 6.41 (m, 2H, Cp′), 6.29 (d of d, 1H, J = 17, 11 Hz, vinyl), 5.99 (m, 2H, Cp′), 5.20 (d, J = 17 Hz, 1H, vinyl), 5.10 (d, J = 11 Hz, 1H, vinyl), 5.06 (m, 2H, Cp′), 4.69 (m, 2H, Cp′), 2.86 (q, 2H, J = 7 Hz, CH_2), 1.41 (t, 3H, J = 7, Me), 0.31 (s, 18H, $SiMe_3$). **7c** was only stable for ca. 1 h in solution. IR (neat): 3086 (m), 1626 (s), 1598 (m), 1248 (s), 1174 (m), 1043 (s), 838 (s).

Diels−Alder Adduct 6. Enacyl **3a** (0.3 g, 0.536 mmol) was added to a Schlenk flask in the nitrogen glovebox. Under nitrogen purge, 40 mL of THF was added. The yellow solution was cooled to 0 °C. Dicyclopentadiene was cracked by distillation under nitrogen and collected in an ice-cooled flask. The cyclopentadiene (35 μL, 0.107 mmol) was added via syringe to the solution of **3a**. The solution was stirred and allowed to come to room temperature as the ice in the bath melted. After 3 h, the solution had turned from yellow to greenish yellow. The THF was removed in vacuo, and hexanes was added. A green-beige precipitate formed and was filtered out and dried under vacuum. Purification of this product by recrystallization from hexane/toluene produced a white precipitate; yield 0.23 g (0.375 mmol, 70%). ^{1}H NMR ($CDCl_3$): 6.79 (m, 1H, Cp′), 6.71 (m, 3H, Cp′), 6.50 (overlapping doublets, 2H, vinyls), 6.39 (m, 3H, Cp′), 6.20 (m, 1H, Cp′), 3.21 (br s, 1H, bridgehead), 3.03 (br s, 1H, bridgehead), 2.21 (d, J = 9 Hz, bridge), 2.06 (d of d, J = 8, 3 Hz, 1H, *exo* H), 1.78 (s, 3H, Me), 1.60 (d, 1H, bridge), 1.53 (d of d, J = 11, 3 Hz, 1H, *endo* H), 0.29 (overlapping singlets, 18 H total, $SiMe_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): 141.1, 134.8, 128.7, 128.3, 128.0, 127.4, 126.0, 108.8, 104.1, 58.9, 55.9, 48.8, 45.7, 44.8, 23.9, 0.06, 0.03. IR (Nujol): 1596 (w), 1252 (m), 1060 (br, s), 842 (s). High-resolution FAB-MS: calcd for $C_{25}H_{37}OClNbSi_2$, 537.113 528; found, 537.113 60.

Acylvinylketene 9a. Vinylketene **7b** (0.100 g, 0.183 mmol) was weighed into a Schlenk flask in the glovebox. Under a nitrogen purge, 40 mL of THF was added by syringe. The yellow solution was cooled on an ice bath prior to addition of ketene. A hexane solution of ethylphenylketene (0.55 mL of a 1 M solution, 0.55 mmol ketene) was added, and the solution was allowed to come to room temperature and stirred for 3 h. The color changed over this time from yellow to a darker yellow-brown. After the mixture was stirred, the THF was removed in vacuo and 20 mL of hexanes was added. A small amount of colorless precipitate (ketene dimer) was removed by filtration. The solvent was removed from the filtrate by vacuum, leaving a dark yellow oil; this was purified using column chromatography. The oil was dissolved in C_6H_6 and loaded onto a neutral alumina column that had been degassed and was under a nitrogen atmosphere. It was eluted using 15−20% THF in hexanes. An orange layer (which contained no Nb-derived product) came through immediately with the solvent, followed by the yellow product layer. The solvent was removed from this fraction in vacuo, giving a yellow oil; yield 38%. ^{1}H NMR (C_6D_6): 7.90 (d, 1H, J = 15 Hz, vinyl), 7.78 (2H, d, J = 8 Hz, Ph), 7.39 (m, 6H, Ph), 7.2 (m, 2H, Ph), 6.82 (d, J = 15 Hz, 1H, vinyl), 6.35 (m, 1H, Cp′), 6.19 (m, 1H, Cp′), 5.91, 5.87, 5.21, 5.13 (m, 1H each, Cp′), 5.08 (m, 2H, Cp′), 3.61 (d of d, 1H, C*H*EtPh), 2.48 (m, 1H, C*H*HMe), 2.03 (m, 1H, CH*H*Me), 0.97 (d of d, 3H, Me), 0.14 (s, 9H, $SiMe_3$), 0.09 (s, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR (C_6D_6): 139.6, 127.9, 126.6, 125.5, 121.2, 121.0, 119.6, 105.4, 105.2, 103.9, 103.5, 30.72, 26.97, 13.25, 1.927, −0.088. IR (Nujol): 1744 (m), 1650 (m), 1590 (m), 1514 (s), 1440 (s), 1251 (s), 1042 (s), 838 (s). High-resolution FAB-MS: calcd for $C_{36}H_{45}O_2ClNbSi_2$, 693.171 043; found, 693.171 100. Derivative **9b** was prepared similarly; dimethylketene (1.65 mmol) was prepared according to the method of Sorensen[18] and vacuum-distilled as an ether solution. The dimethylketene/ether was transferred to a cooled (0 °C) solution of **7b** (0.100 g, 0.183 mmol) in 40 mL of THF. The reaction proceeded as for **9a**, and the compound was chromatographed in an identical fashion to give a yellow oil (yield 33%). ^{1}H NMR (C_6D_6): 8.05 (d, J = 15 Hz, 1H, vinyl), 7.89 (d, 2H, J = 8 Hz, Ph), 7.41 (t, J = 8 Hz, 2H, Ph), 7.03 (m, 1H, Ph), 6.79 (d, J = 15 Hz, 1H, vinyl), 6.38, 5.93, 5.28, 5.18 (m, 2H each, Cp′), 2.57 (septet, J = 7 Hz, 1H, C*H*Me$_2$), 1.21 (d, J = 7 Hz, 6H, Me), 0.18 (s, 18H, $SiMe_3$). ^{13}C{^{1}H} NMR (C_6D_6): 149.0, 139.8, 132.6, 130.7, 126.6, 125.8, 120.9, 119.6, 115.1, 105.3, 103.7, 41.3, 30.7, 19.7, 0.02. IR (Nujol): 1747 (m), 1519 (w), 1260 (s), 1020 (br, s), 789 (s).

Vinylketene Dimer 11. A 0.7 g (1.1 mmol) sample of **3b** was dissolved in 40 mL of THF. To this yellow solution was added 165 μL (1.1 mmol) of DBU via syringe. The bright orange solution was stirred for 30 min at room temperature, and the solvent was removed in vacuo. The crude product was run through a neutral alumina column using 30% THF/hexane under nitrogen. The orange fraction was collected and precipitated as a yellow solid from hexanes in 35% yield. IR (Nujol): 1605.8 (s), 1588.8 (s), 1246.9 (vs), 1172.5 (s) 1040.7 (s), 900.2 (m), 834.7 (vs). ^{1}H NMR (C_6D_6): 8.49 (2H, d, J = 8.49 Hz), 8.07 2H, d, J = 8.19 Hz), 7.41 (m), 6.92 (t), 6.62, 6.57, 6.52, 6.45, 6.40, 6.31, 6.05, 5.93, 5.73, 5.64, 5.40, 5.21, 5.15, 5.12, 4.95, 4.65 (1H each, m, Cp′ *H*), 3.55 (1H, br m, C*H*CH$_3$), 1.86 (3H, d, CHC*H*$_3$), 0.31, 0.28, 0.27, 0.24 (9H each, $SiMe_3$). ^{13}C{^{1}H} NMR (C_6D_6): 130.4, 129.7, 129.4, 127.6, 125.7, 123.4, 119.8, 105.4, 102.8, 102.1, 93.4, 2.0, 0.08, −0.40. High-resolution FAB-MS: calcd for $C_{52}H_{69}O_2Si_4Cl_2Nb_2$, 1093.187 932; found, 1093.187 399.

Acidity Determinations of the Niobium−Enacyl Complexes. The bracketing technique was used for the determination of the pK_a values of the enacyl complexes **3b** and **3c**. In a typical procedure, the pK_a value was determined by adding excess base to an NMR sample (MeCN-d_3) of the enacyl. The acid and base were either dissolved together in the nitrogen glovebox, if the base was a solid, or the base was added via microliter syringe through a rubber septum capping the NMR tube, if it was a liquid. NMR spectra were recorded within 5−10 min after the addition of the base. Bracketing was accomplished when one base caused no reaction, and the next base in the series caused a full reaction. Enacyl **3b** was determined to have a pK_a between that of *p*-toluidine (pK_a = 11.25, full reaction by NMR as monitored by loss of **3b** and appearance of the dimer **11**) and aniline (pK_a = 10.56, no reaction by NMR). The pK_a value of enacyl **3c** was determined by using the base 2,4-lutidine (pK_a = 14.0, no reaction by NMR) with the enacyl and using malonic acid (pK_a = 15.3) with the conjugate base **7c**. This was monitored by NMR, showing loss of **7c** and the appearance of **3c**.

X-ray Crystallography. Compound **3b** was prepared as described above and was crystallized from chloroform as yellow hexagons. A well-formed crystal of dimensions 0.50 mm × 0.33 mm × 0.25 mm was selected and mounted in a random orientation in a capillary. Diffraction measurements were made on a four-circle Enraf-Nonius CAD-4 fully automated diffractometer using graphite-monochromated Mo Kα (λ = 0.710 69 Å). The cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 23 carefully centered reflections in the range 14.46 ≤ 2θ ≤ 21.89°. These corresponded to a monoclinic cell with dimensions a = 14.796(1) Å, b = 11.884(2) Å, c = 19.801(2) Å, and β = 96.515(7)°.

The space group, on the basis of systematic absences of $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$) and the successful solution and refinement of the stucture, was determined to be $P2_1/c$ (No. 14), Z = 4, with one molecule of $C_{26}H_{34}ONbSi_2ClBF_4$ and one molecule of chloroform forming the asymmetric unit. The volume was 3501(1) Å^3, and the calculated density was 1.429 g/cm^3. There were 6489 unique reflections collected (R_{int} = 0.038) with 2θ ≤ 50°, of which 3937 (61%) with $I \geq 3\sigma(I)$ were adjudged observed. The structure was solved using the PHASE

(18) Masters, A. P.; Sorenson, T. S.; Ziegler, T. *J. Org. Chem.* **1986**, *51*, 3558.

Table 1. Crystallographic Data for 3b

empirical formula	$C_{27}H_{34}ONbSi_2ClBF_4$
fw	753.27
cryst dimens, mm	0.50 × 0.30 × 0.25
space group	$P2_1/c$ (No. 14)
cell dimens	
a, Å	14.976(1)
b, Å	11.884(2)
c, Å	19.801(2)
β, deg	96.515(1)
temp, °C	25
V, Å^3	3501(1)
Z (molecules/cell)	4
calcd density, g/cm^3	1.429
wavelength, Å	0.710 69
linear abs coeff, mm^{-1}	0.744
R	0.059
R_w	0.069

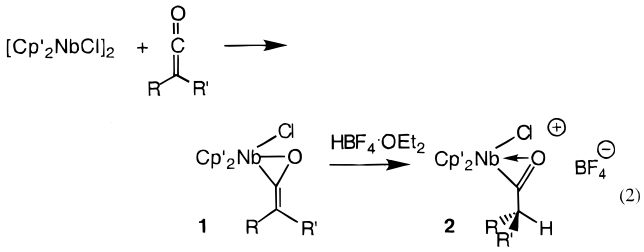
Table 2. Selected Bond Lengths and Angles for 3b

Bond Lengths (Å)			
Nb−Cl2	2.446(2)	Nb−C22	2.445(7)
Nb−C25	2.421(8)	Nb−C28	2.430(8)
Nb−C31	2.409(7)	C5−C6	1.33(1)
Nb−O	2.199(5)	Nb−C23	2.416(7)
Nb−C26	2.418(8)	Nb−C29	2.418(8)
O−C4	1.218(8)	C5−C8	1.49(1)
Nb−C4	2.118(8)	Nb−C24	2.410(8)
Nb−C27	2.443(7)	Nb−C30	2.429(8)
C4−C5	1.47(1)	C6−C7	1.49(1)
Bond Angles (deg)			
O−C4−C5	128.4(7)	Nb−C4−C5	154.1(6)
C5−C6−C7	127.2(7)	C4−Nb−O	32.7(2)
C4−C5−C6	117.1(7)	Nb−C4−O	77.3(5)
Cl−Nb−O	79.8(1)	Nb−O−C4	70.0(4)
C4−C5−C8	117.2(7)		

option of DIRDIF.[19] Two iterations of the WFOUR option resulted in the solution of the entire asymmetric unit. All hydrogens were calculated and assigned isotropic thermal parameters which were 20% greater than the equivalent value of the atom to which they were bonded. The maximum and minimum peaks on the final Fourier map corresponded to 1.31 and −0.82 e/Å^3. The other electron densities were associated with the BF_4 unit; this exhibited some disorder, which was not modeled. Crystal data are collected in Table 1**,** and key bond lengths and angles are in Table 2.

Results

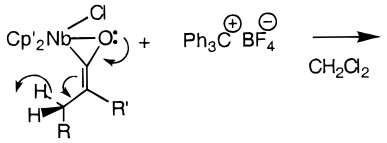
We have previously described the preparation of a series of niobium ketene complexes of general formula $Cp'_2Nb(X)(\eta^2\text{-}OCCRR')$ ($Cp' = \eta^5\text{-}C_5H_4SiMe_3$; X = Cl, H).[17] These compounds were prepared from the free ketenes and the niobium(III) reagent $[Cp'_2Nb(\mu\text{-}Cl)]_2$ (eq 2). In this way, the yellow crystalline solids **1** may be



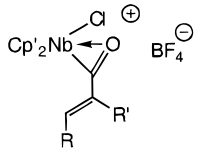
(2)

obtained in satisfactory yields. Although there are several isomeric structures involving ketene C═C binding and/or rotation about the metal−ligand vector,[20] the isolated materials always exhibit the indicated (eq 2) C,O binding mode and the "O-inside" conformation. However, when R and R′ differ, this reaction usually gives rise to a mixture of *E* and *Z* isomers. We have shown that these isomers are equilibrating via intramolecular processes, the equilibria are all slow on the NMR time scale, and the *E*−*Z* ratio at equilibrium depends on the sizes of R and R′ and on the coligand X. The ketene complexes are weakly basic, and protonation with $HBF_4{\cdot}OEt_2$ converts them to the η^2-acyl cations **2** (eq 2).[17] This is an important synthetic route to the acyls, since the niobium compounds are not susceptible to migratory CO insertion. Although acyl synthesis does not always require the use of $HBF_4{\cdot}OEt_2$, the acyls *are* relatively acidic. In a study of the thermodynamic acidities of these compounds, we found that they exhibited pK_a's that were ca. 18−20 p*K* units lower than those of the corresponding organic ketones.[21] We proposed that this acidity resulted from the strong influence of the metal center on the ligand chemistry, and we have since reported other thermodynamic studies of the influence of the metal on ligand-centered reactions.[22] Despite the ease with which the ketene ligand adds protons, we have been unable to induce reaction with other electrophiles. For this reason, we have pursued other means for functionalization of the ketene ligand.

Formation of η^2-Enacyls. Although we have reported an instance in which triphenylcarbenium ion adds to a niobium-bound ligand,[23] it more typically serves as a reagent for the abstraction of hydride. Indeed, treatment of the ketene complexes **1** with 1 equiv of Ph_3CBF_4 gave smooth conversion to the enacyl cations, which were isolated as the tetrafluoroborate salts in good yield (eq 3). The reaction was readily



1 a R = H, R' = Me
b R = Me, R' = Ph
c R = Me, R' = Et
d R = H, R' = Et



(3)

3 a R = H, R' = Me
b R = Me, R' = Ph
c R = Me, R' = Et
d R = H, R' = Et; R = R' = Me

carried out in methylene chloride at ambient tempera-

(19) (a) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42−46. (b) Beurkens, P. T. Technology Report; Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands, 1984.

(20) (a) Bleuel, E.; Laubender, M.; Weberndorfer, B.; Werner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 156−157. (b) Grotjahn, D. B.; Lo, H. C. *Organometallics* **1995**, *14*, 5463−5465. (c) Lo, H. C.; Grotjahn, D. B. *J. Am. Chem. Soc.* **1997**, *119*, 2958−2959.

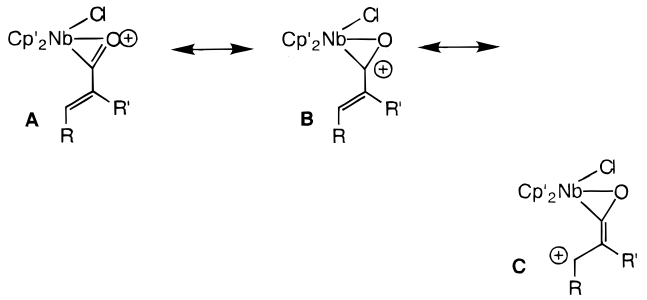
(21) Fermin, M. C.; Thiyagarajan, B.; Bruno, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 974−979.

(22) Kerr, M. E.; Zhang, X.-M.; Bruno, J. W. *Organometallics* **1997**, *16*, 3249−3251.

(23) Thiyagarajan, B.; Kerr, M. E.; Bollinger, J. C.; Young, V. G., Jr.; Bruno, J. W. *Organometallics* **1997**, *16*, 1331−1334.

ture. The yellow-orange solution turned pink within several minutes, and the reactions were run for a few hours to ensure complete conversion. Removal of the solvent in vacuo gave an oily solid, which was extracted with diethyl ether; this dissolved the triphenylmethane byproduct and allowed isolation (by filtration) of the solid, off-white salts **3**. Compounds **3** were sufficiently pure for most purposes but can be recrystallized from chloroform with some loss of yield. The isolated solids are stable for short periods in air, and the compounds are indefintely stable in the absence of air. It is important to avoid the introduction of protic impurities in these syntheses, since they will react with trityl cation to form strong acids. This leads to protonation of the ketenes (eq 2) and formation of the saturated acyls **2**; normally this problem is circumvented by the use of freshly recrystallized trityl reagent.

The enacyl products were identified on the basis of their spectral data sets. All of the derivatives exhibit an infrared band at ca. 1600 cm^{-1}, which is consistent with the presence of the η^2-acyl functional group.[24] The salts also show a broad absorption at ca. 1040 cm^{-1}, as would be expected for a tetrafluoroborate anion. The NMR spectrum provides evidence for mirror symmetry, since the Cp′ groups are equivalent; protonation of an unsymmetrically substituted ketene (eq 2) generates a stereocenter and removes the equivalence of the Cp′ rings. As such, acyls and enacyls are typically distinguished by the observation of eight or four Cp′ resonances, respectively. The unsaturation in the organic ligand was clearly evident from the resonances of the vinylic hydrogens, which were typically observed at ca. 8.4 ppm. This is near the downfield end of the range commonly exhibited by vinylic hydrogens and is reminiscent of enones and other α,β-unsaturated carbonyl compounds.[25] It suggests the importance of a resonance contributor in which the positive charge is located on the vinyl terminus (e.g., **C**).



Although **3a** could only exist as one isomer, some of the other ketene substrates in eq 3 were chosen to probe the stereochemistry and regiochemistry of the hydride transfer process. For example, **3b** could exhibit isomerism about the C=C bond, but only a single isomer was detected. This compound was subjected to NOE studies, which indicated that the vinyl C−H was in close proximity to one of the Cp′ hydrogens and that the

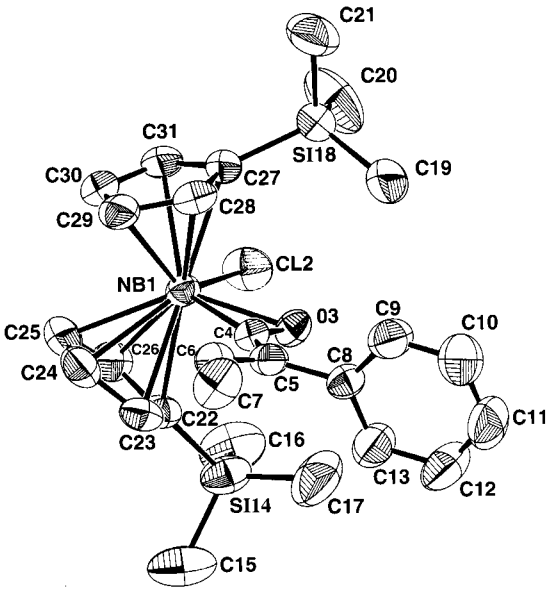


Figure 1. ORTEP drawing demonstrating the atom-labeling system of the cation in **3b**.

methyl group was near the phenyl substituent. Both of these observations suggest the (*E*)-alkene formulation shown in eq 3. A similar situation was evident for compound **3c**. Conversely, **1d** has both ethyl and methyl substituents, either of which could yield a hydride. We observed formation of both regioisomers, which were produced in nearly equal amounts; this indicates a statistical preference for attack at the ethyl substituent (which has only two available hydrogens), but it is not a synthetically useful reaction. It is noteworthy that the reaction involving ethyl C−H abstraction exhibited only the (*E*)-alkene product isomer. These reactions indicate that the hydride abstraction process is highly stereoselective, giving only *E* stereoisomers. When both ketene substituents are susceptible to hydride transfer, there is a preference for formation of the more highly substituted vinyl substituent; however, the level of regioselectivity is not high enough to be synthetically useful. Our subsequent discussion (below) will focus on enacyls **3a**−**c**, for which a single product isomer is readily available.

Crystallographic Study of 3b. To corroborate the conclusions derived from NOE studies and to gather data on the structure of the enacyl compound, enacyl **3b** was subjected to a crystallographic study. The salt was crystallized from chloroform, from which it formed yellow hexagonal crystals. These diffracted satisfactorily, and the results of the X-ray study are depicted in Figure 1. Crystal data and key bond lengths and angles are collected in Tables 1 and 2, and full details are included as Supporting Information. Compound **3b** crystallized in the monoclinic space group $P2_1/c$, with four molecules per unit cell. As crystallized, the compound contained one molecule of chloroform per asymmetric unit. There was some disorder in the positions of the fluorides of the tetrafluoroborate, but this did not prevent structure solution and was not modeled. The closest cation−anion contact was between one of these fluorides and one of the Cp′ ring carbons (C24), but this distance was greater than 3 Å. As is clear from Figure 1, the cation of **3b** exhibits the expected bent-metal-

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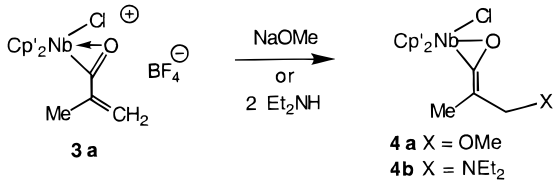
locene structure, in which the equatorial plane is occupied by the enacyl and chloride ligands. A view from above the symmetry plane confirms that the Cp′ rings are virtually eclipsed, and the trimethylsilyl groups reside above and below the cleft inside the O−Nb−Cl angle. The Nb−Cp′ bonding is normal, with Nb−C bond lengths ranging from 2.409(7) to 2.445(7) and averaging 2.424 Å. The Nb−Cl bond length is 2.446(2) Å, consistent with the presence of a cationic Nb(V) center; the related Nb−Cl bond lengths in $[Cp'_2Nb(Cl)(\eta^2\text{-}C(O)CHEtPh)][BF_4]$[17c] and $[Cp'_2Nb(Cl)(OCH_2CPh_3)][BF_4]$[23] were 2.446(2) and 2.3880(6) Å, respectively. Conversely, the neutral compounds **1b**[17a] and $Cp'_2Nb(Cl)(\eta^2\text{-}CH_2{=}O)$[26] exhibited longer Nb−Cl bond lengths of 2.507(2) and 2.5253(11) Å, respectively. The remainder of the coordination sphere is occupied by the η^2-enacyl ligand. The structure is consistent with that derived from NOE studies in solution, and the vinyl hydrogen on C6 is in close proximity to the Cp′ ring hydrogens. The enacyl does exhibit the (*E*)-alkene geometry, with a C=C (C5−C6) bond length of 1.33(1) Å and a C=C−C angle (C5−C6−C7) of 127.2(8)°. For comparison, the C−C single bonds are longer, with C4−C5 and C6−C7 bond lengths of 1.47(1) and 1.49(1) Å. The acyl functional group exhibits C−O, Nb−C, and Nb−O distances of 1.218(8), 2.118(8), and 2.199(5) Å and an O−C4−C5 angle of 128.4(7)°. The enacyl backbone is largely planar, with intraligand torsion angles (O−C4−C5−C6, C4−C5−C6−C7, and O−C4−C5−C8) of 178.1(8), 178.9(8), and −2(1)°. Interestingly, the phenyl substituent is nearly orthogonal to the backbone of the enacyl ligand, with torsion angles (C4−C5−C8−C9 and C6−C5−C8−C9) of 109.4(9) and −70(1)°. A view from above the molecular symmetry plane indicates that there is ample room for the phenyl group to reside in this plane; thus, there is no obvious explanation for this solid-state conformation. Finally, we note that the difference Δ between Nb−O and Nb−C bond lengths is 0.081 Å. This parameter is often used to characterize the magnitude of the metal−oxygen interaction in η^2-acyls,[24] and typical values for transition metals range from ca. 0 to 0.5 Å (although the actinide compound $Cp^*_2Th(Cl)(\eta^2\text{-}OCCH_2tBu)$ exhibits a Δ value of −0.07 Å[27]). By this criterion, **3b** shows a strong Nb−O interaction, and this has a decided influence on the chemistry described below.

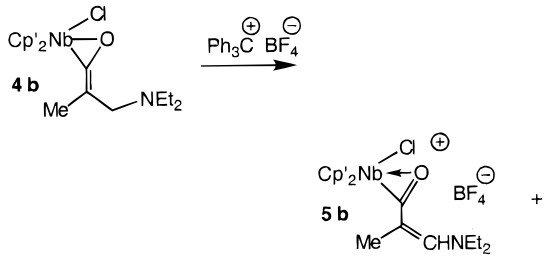
Reactions of η^2-Enacyls. Derivative **3a** was used to carry out a study of the reactions of enacyls with potential nucleophiles. This particular substrate was chosen because it is derived from a symmetrical ketene and is available as a single isomer, it has a relatively accessible vinyl group, and there are no obvious sources of acidic hydrogens (vide infra). Since **3a** is an obvious candidate for conjugate addition, it was first treated with carbon-based nucleophiles such as alkyllithiums, Grignard reagents, and lithium dialkylcuprates. In all cases, redox chemistry ensued, leading to the production of unidentified paramagnetic (presumably Nb(IV)) derivatives. Subsequent efforts were directed to the use of nonreducing nucleophilic reagents, including alkoxides and amines. As shown in eq 4, reaction of **3a** and sodium methoxide or diethylamine (2 equiv) in THF



(4)

gave rise to the heteroatom-substituted ketene complexes **4**. These were isolated by extraction from the solid byproducts $NaBF_4$ or $[NEt_2H_2][BF_4]$. The methoxy derivative **4a** was isolated as a yellow oil, and the yellow amino derivative **4b** was precipitated from toluene upon addition of hexane. Both of these proved to be too unstable for purification, and they decomposed during attempts to collect NOE data. As such, the ketene geometry is not established conclusively, but the NMR spectra do confirm that both compounds are formed stereoselectively.

In an attempt to probe the reactivity of the heteroatom-substituted ketenes in compounds **4**, they were treated with 1 equiv of triphenylcarbenium ion. Not unexpectedly, compound **4a** reverted exclusively to **3a** and Ph_3COMe under these conditions. However, similar reaction with **4b** gave a ca. 50:50 mixture of products (eq 5) derived from amide abstraction and hydride



(5)

abstraction. The new product is an aminoenacyl, and it was separated from coproduct **3a** by precipitation from a methylene chloride/ether mixture. The formulation is consistent with the NMR spectrum, which exhibits resonances at 7.78 (=C*H*NEt_2), 3.21 (NCH_2CH_3), 1.78 (allylic Me), and 1.42 ppm (NCH_2CH_3). In addition, the IR spectrum contains the expected bands for the η^2-acyl (1599 cm^{-1}) and the BF_4 counterion (1084 cm^{-1}). We are continuing our efforts to assign the stereochemistry of this compound, a process made difficult by facile proton relaxation due to the quadropolar nitrogen.

The conjugate additions described above suggest that the enacyls are electron-deficient, and we suspected they would serve as dienophiles in the Diels−Alder reaction. To this end, **3a** was treated with freshly distilled cyclopentadiene in THF solution. Over a period of ca. 2 h at room temperature, the solution color turned from yellow to green-yellow. The solvent was removed in vacuo, and a green-beige solid was produced upon addition of hexane; this was isolated by filtration. This compound was identified as the substituted norbornene derivative (eq 6). The NMR spectrum ($CDCl_3$) exhibited overlapping Cp′ and vinyl resonances in the range 6−7 ppm, singlets for the two bridgehead hydrogens at 3.0 and 3.2 ppm, a methyl signal at 1.8 ppm, and four methylene signals in the range 1.5−2.2 ppm. These data suggested that only one cycloaddition product results, and NOESY spectroscopy was used to identify that

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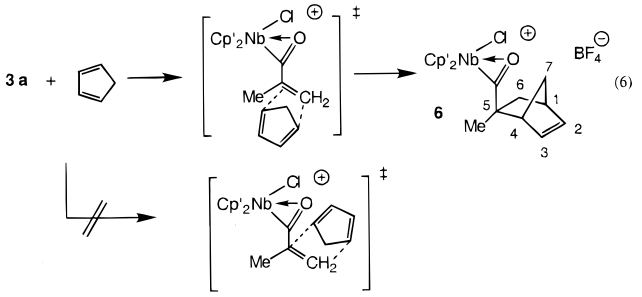
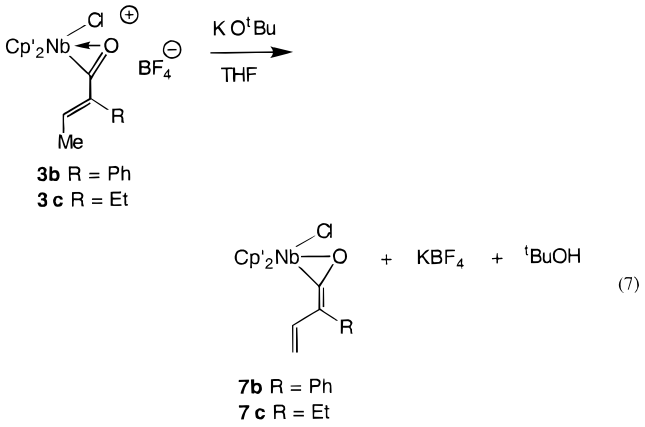


product. From those studies it was possible to assign all resonances except those (2.21 and 1.60 ppm) for the hydrogens on the bridging carbon (C-7); in particular, the signal at 3.2 ppm may be assigned to the methine hydrogen on the bridgehead carbon C-1. This proton showed an interaction with the proton resonating at 2.1 ppm, which is assigned as the *exo* hydrogen on C-6. This, in turn, allows us to identify the C-6 *endo* hydrogen, which appears at 1.5 ppm. Since this *endo* hydrogen (but not the *exo* hydrogen) showed an interaction with the methyl group, we conclude that the methyl group is endo on C-5 and the acyl−niobium system is the *exo* substituent on C-5.

In most cases, enone cycloaddition processes yield the *endo* product preferentially, and metal-complexed systems have been observed to exhibit a similar preference.[28] This is commonly attributed to secondary orbital interactions between the diene and C=O π systems.[29] When this is prevented by the bulk of the metal and its coordination sphere, *exo* products may result.[30] The current process gives exclusively the *exo* product, presumably via the transition state shown in eq 6. The alternative would involve an approach by the diene over the center of the equatorial plane, a region occupied by the Cp′ silyl groups. Even without this stabilizing interaction, the enacyls are clearly electrophilic and capable of [4 + 2] cycloadditions under extremely mild conditions. This is due, in part, to the enforced *S-cis* conformation of cyclopentadiene. We have studied the reactions of unconstrained dienes such as 2,3-dimethoxybutadiene and 2,3-dimethylbutadiene. The first of these reacts smoothly with **3a**, but the product proved difficult to isolate in acceptably pure form. The second fails to react with **3a** under comparable conditions.

Synthesis of Vinylketenes. The enacyl chemistry described above shows compound **3a** to be highly electrophilic, suggesting that derivatives **3b**−**d** would exhibit appreciable acidity. The saturated acyls **2** (eq 2) were highly susceptible to enolization,[21] and the enacyls **3** should exhibit a comparable acidity based on the vinylogous relationship of the allylic hydrogens with the carbonyl. To this end, compounds **3b**,**c** were treated with potassium *tert*-butoxide at 0 °C in THF solution (eq 7).



The yellow-orange color of **3** gave way immediately to a darker yellow. After 30 min, the solution was filtered to remove potassium tetrafluoroborate, the solvent removed in vacuo, and the residue extracted with toluene. In the case of **3b**, addition of hexane gave rise to the yellow precipitate **7b**, but the corresponding derivative **7c** was isolated as a yellow oil. These compounds exhibited limited lifetimes in solution and could not be recrystallized, but the extraction workup yielded samples that were spectroscopically pure. Compounds **7** are identified as η^2(C,O) complexes of vinylketenes. For example, **7b** exhibits three phenyl and four Cp′ resonances, consistent with the presence of a mirror plane bisecting the Cp′-Nb−Cp′ angle. The presence of this mirror plane and the absence of an IR band for uncomplexed carbonyl confirms the vinylketene complexation mode, since isomerization to a C=C complex (either possibility) would lower the symmetry. There are three resonances due to vinylic hydrogens, a doublet of doublets for the internal vinyl hydrogen at 6.45 ppm, and two doublets for the terminal vinyls at 5.59 and 5.21 ppm (the geminal coupling is too small to observe). These data confirm that there is only one vinylketene isomer present in solution, and NOESY spectroscopy was used to identify that isomer. This indicated an interaction between the vinyl hydrogens and a Cp′ hydrogen, confirming that the vinyl substituent is *cis* to the metal center. We would expect this to be the thermodynamic isomer,[17] and the only observable one for **7b**. Here the phenyl group is much larger and would reside in the position *trans* to the metal center. However, the similar sizes of the ethyl and vinyl substituents would have led us to predict that **7c** would exhibit appreciable populations of both isomers at equilibrium; we have seen no evidence for this.

Reactions of Vinylketene Complexes. Although there is one previous report of a C,O-complexed vinylketene,[5a] little is known about the synthetic potential of this class of ligand. This binding mode leaves the diene portion of the molecule uncomplexed, and it is worth noting that the NMR signals for the vinyl protons are shifted 2−3 ppm upfield of those seen in enacyls **3**. This increased shielding is consistent with the resonance descriptions **D**−**F**, from which we expect nucleophilic character at the terminal carbon. To compare the chemistry of **7** with that of enacyls **3**, the former was treated with cyclopentadiene. Predictably, there was no reaction, and eventually the diene formed the dimer from which it is produced. The zwitterionic

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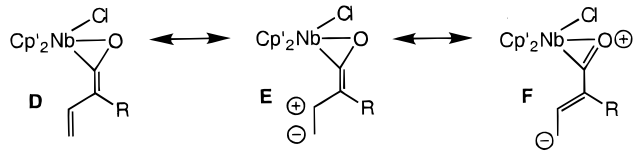
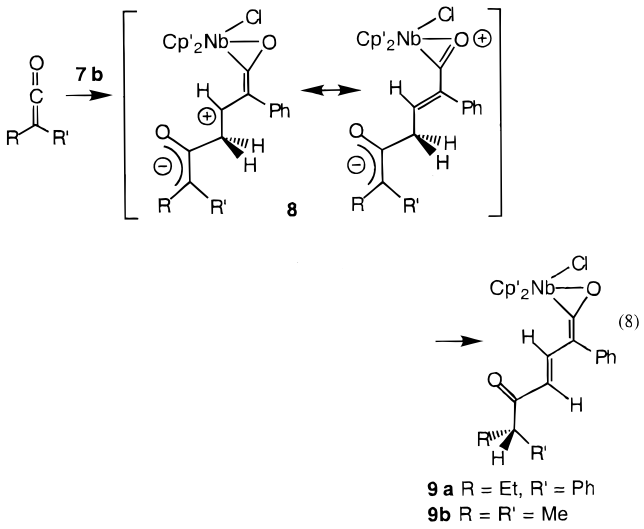


character of **7** (note that the positive charge is delocalized throughout the ligand) suggested that it might be susceptible to an ionic [2 + 2] cycloaddition process; therefore, this possibility was tested via reactions with free ketenes. Compound **7b** was treated with ethylphenylketene or dimethylketene (eq 8), but there was no

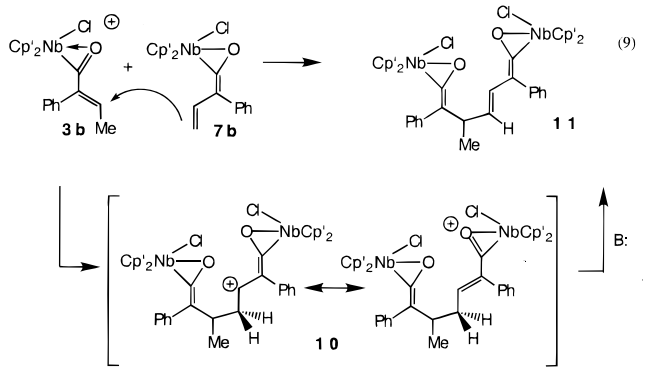


9 a R = Et, R' = Ph
9b R = R' = Me

evidence for formation of a [2 + 2] product. Instead, the isolated products were the acylvinylketenes **9**. Adducts **9** were contaminated by ketene dimers and polymers, but **9** was stable to chromatrography on neutral alumina and was separated from these organic byproducts. These compounds showed a pair of vinyl resonances, and the coupling constants were sufficiently large ($^3J_{HH}$ = 15 Hz) as to require the (*E*)-alkene geometry.[25] The ketone carbonyl was indicated by an infrared absorption at ca. 1745 cm^{-1}, and NOESY studies confirmed the indicated geometry. Product identification was particularly straightforward for **9b**, since the isopropyl group constitutes an obvious NMR marker.

We surmise that the reaction proceeds as indicated in eq 8. Initially the vinylketene terminus gave the expected nucleophilic attack at the sp-hybridized carbon of the free ketene. This presumably resulted in zwitterionic intermediate **8**, which would be highly stabilized by resonance. The enolate anion should exhibit the normal delocalization of the electron pair, and it is worth noting that the positive charge is also delocalized throughout the rest of the ligand; this latter point is emphasized in the two canonical structures given for **8**. Zwitterion **8** might be expected to close up the four-membered ring by forming an oxygen−carbon or carbon−carbon bond. Instead, a proton transfer ensues so as to regenerate the vinyl group and protonate the enolate base to give the acyl. Note that the initial vinylketene synthesis (eq 7) involved deprotonation of an enacyl by *tert*-butoxide, and the conversion of **8** to **9** constitutes an intramolecular deprotonation of an enacyl by an enolate anion; the mechanistic parallels are obvious. The interesting aspect of this reaction is that the vinylketene is used for the addition of the free ketene, but the proton transfer reaction regenerates a functionalized version of this useful functional group. Future studies will involve further elaboration of the new acylvinylketenes **9**.

We noted above that *tert*-butoxide was used to deprotonate enacyls **3** in the synthesis of vinylketene complexes **7**. However, η^2-acyls **2** were very acidic; therefore, we surmised that weaker bases would suffice to deprotonate **3** in this reaction. In fact, however, reactions with, for example, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) failed to convert **3b** to **7b** but led instead to the new compound **11** with a very complex NMR spectrum. This compound was stable to column chromatography, which was used to separate **11** from byproducts. The presence of 16 Cp′ signals in the NMR suggested a dimeric structure, and leads us to propose the structure in eq 9. The compound consists of a niobocene vi-



nylketene and a niobocene ketene, with the molecules linked by a carbon−carbon single bond. As with the other vinylketenes **7**, compound **11** decomposes in solution over a period of hours and single crystals are unavailable. The carbon bearing the methyl substituent is a stereocenter; thus, the molecule has no symmetry element. As a result, all of the Cp′ hydrogens are unique. With the 2 phenyl groups, the 2 vinyl protons, and the Cp′ rings, there are a total of 28 resonances in the region 5−8.5 ppm; this makes it impossible to perform NOE studies or identify the vinyls clearly, and so the C=C geometries are not established firmly. Fortunately, the unique methyl group gives a doublet at 1.86 ppm and the doubly allylic methine proton appears as a multiplet at 3.55 ppm; this part of the spectrum confirms that **11** is produced as a single geometric isomer. Finally, high-resolution FAB mass spectrometry provided convincing evidence in support of this dimeric structure.

We suggest that **11** is formed via the mechanism shown in eq 9. Vinylketene **7b** initiates a conjugate nucleophilic addition on enacyl **3b**, generating cation **10**. This is consistent with the established nucleophilicity of the vinylketene and the electrophilicity of the enacyl. In cation **10**, the original enacyl ligand has been converted back to a ketene ligand, while the vinylketene has been converted into a new enacyl cation. This is emphasized by the two resonance pictures for **10**. For this reason, the two indicated hydrogens should be acidic (as in **3**; eq 3), and reaction with base converts **10** into vinylketene **11**. This explains the importance of the *tert*-butoxide base in vinylketene synthesis; this

base is known to undergo especially rapid proton transfer processes[31] and is capable of converting **3** to **7** before it condenses to form **11**. Conversely, slower bases generate mixtures of the two compounds, and condensation occurs. We have confirmed this hypothesis by mixing isolated samples of **3b** and **7b** in the absence of any added base; this does produce **11** as the only observable niobium-containing product.

Thermodynamic Considerations. We have initiated a program designed to determine the effect of the metal center on the thermodynamics of ligand-centered reactions. This involves studies on the energetics of proton and hydride transfer processes, both of which figure in the chemistry described herein. The conversion of **1** to **3** requires hydride donation by **1**, and we[14] and others[32] have recently established a series of hydride acceptors that may be used as indicators for this process. Ideally, one would establish an equilibrium involving hydride transfer. Since this process is slow for **1**, bracketing studies were required to estimate the energy of the process. For this purpose we used the hydride acceptors $[Ph_3C]^+$ (99), $[(p\text{-}MeOC_6H_4)CPh_2]^+$ (93), $[(p\text{-}MeOC_6H_4)_2CPh]^+$ (89), $[(p\text{-}MeOC_6H_4)_3C]^+$ (86), $[(p\text{-}Me_2NC_6H_4)CPh_2]^+$ (83), and $[(p\text{-}Me_2NC_6H_4)_2CPh]^+$ (77), for which the hydride acceptor free energies (kcal/mol in acetonitrile) are indicated in parentheses.[14,32] For **1b**, there was no reaction with $[(p\text{-}Me_2NC_6H_4)CPh_2][BF_4]$ or $[(p\text{-}MeOC_6H_4)_3C][BF_4]$ and clean conversion to **3b** with $[(p\text{-}MeOC_6H_4)_2CPh][BF_4]$, $[(p\text{-}MeOC_6H_4)CPh_2][BF_4]$, or $[Ph_3C][BF_4]$. From these data we estimate that loss of a hydride from **1b** requires 88 ± 3 kcal/mol in acetonitrile. Derivative **1c** fails to react with $[(p\text{-}Me_2NC_6H_4)_2CPh][BF_4]$ but is converted to **3c** by $[(p\text{-}Me_2NC_6H_4)CPh_2][BF_4]$. In a similar fashion, we assign a hydride donor energy of 81 ± 3 kcal/mol to **1b**.

Studies on the acidity of **3** were complicated by the condensation of **3** and **7** to **11**, as described above. Again, we made use of bracketing studies to determine the pK_a of **3**. The following bases have conjugate acids with the acetonitrile pK_a values given in parentheses;[33] pyridine (12.33), *p*-toluidine (11.25), aniline (10.56), 2,4-lutidine (14.0), monosodium malonate (15.3), benzylamine (16.76), and triethylamine (18.46). Compound **3b** failed to react with aniline or 2,4-lutidine but was converted to **11** by *p*-toluidine or pyridine. From this we estimate its pK_a value as 11 ± 2 in acetonitrile. Similarly, **3c** failed to react with 2,4-lutidine or aniline but was converted to the corresponding dimer by benzylamine. Malonic acid converted **7c** to **3c**, and this reaction occurred more quickly than did the dimerization; hence, **7c** could be driven completely to **3c** in the presence of excess malonic acid. This suggests that **3c** has a pK_a of 15 ± 2 in acetonitrile.

Discussion

Synthetic Aspects. The work described herein was begun in an attempt to utilize the synthetic potential of the multiply unsaturated ketene ligand. While free ketenes are even more reactive, they are also susceptible to polymerization and dimerization reactions that can supersede the desired reactions.[3] For this reason, the metal center provides a means of anchoring the ketene while still providing access to its synthetic potential. In addition, the metal center provides a location for sequestering or releasing electron density as required by the individual reactions. In this sense the process is functionally similar to the stepwise ionic hydrogenation of nitriles bound to molybdenum. Templeton has suggested that an alkyne coligand facilitates this process by functioning as either a four- or a two-electron donor, as required.[34] This allows the sequential addition of two hydrides and two protons, which serve to convert the nitrile to an amine. The niobium ketene chemistry is functionally similar in that the ketene in **1** is subjected to a stepwise ionic *de*hydrogenation process during the conversion to vinylketene **7**. It differs, however, in that the reactive site is never bound to the metal center during the process. Indeed, the hydride transfer step is unusual. The trityl cation and various derivatives have frequently been used in reactions with metal alkyls, metal alkenes, and metal alkynes. In the first case, the hydride abstraction may involve the α C−H bond, in which case the result is a metal alkylidene.[35] Conversely, abstraction of a β-hydride serves to convert the alkyl ligand into a π-complexed alkene.[36] Finally, abstraction of an allylic or propargylic hydrogen serves to convert an alkene or alkyne into the corresponding η^3-allyl or -propargyl complex.[37] The common thread in all of these processes is that loss of the ligand C−H is always accompanied by formation of a new metal−carbon bond. Conversely, the synthesis of **3** from **1** generates no new metal−carbon bond and is a rare example of a γ-C−H activation. The only previous examples of which we are aware involve the hydride transfer reactions of the cyclopropylmethyl compound $FpCH_2CH(CH_2)_2$, and the allyl compound $FpCH_2CH{=}CMe_2$ (Fp = $CpFe(CO)_2$).[38]

The X-ray structure of **3b** confirms that no new niobium−carbon bond results when a γ-hydride is abstracted from **1b**. At first sight, the process appears

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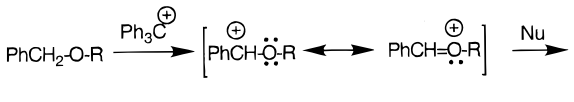
to involve abstraction of an allylic hydride, but this should be a highly endothermic process with trityl cation. As noted above, trityl has a hydride affinity of 99 kcal/mol in acetonitrile, and benzyl cation has been suggested to have a hydride affinity of 113 kcal/mol;[14a] the hydride affinity of an allylic cation should be even higher than that of benzyl cation. However, while niobium fails to assist in this reaction, it is clear that the ketene oxygen is donating a lone pair. In this sense the reaction is reminiscent of the well-known protocol for deprotecting benyzl ethers with trityl cation, a process resulting in the loss of benzaldehyde (eq 10).[39]



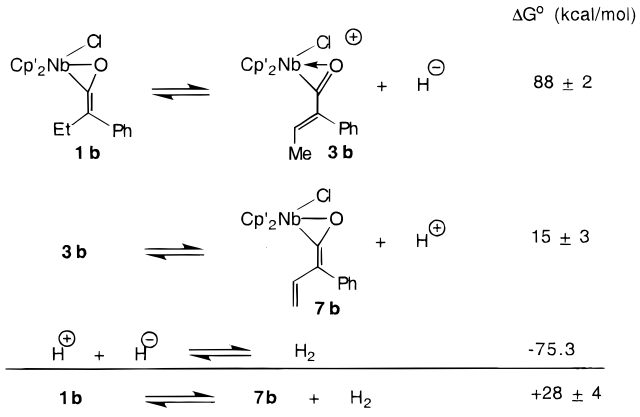
(10)

The initial step involves abstraction of a benzylic hydride, and the resulting carbenium ion is stabilized by the adjacent oxygen lone pair. In the reaction with **1**, there exists a vinylogous interaction between the ketene oxygen and the γ-position. Thus, the conversion of **1** to **3** does involve heteroatom stabilization, and this operates so as to lower the energy of the hydride transfer step.

Thermodynamic Aspects. The enacyl cations **3b**,**c** exhibit pK_a's of 11 and 15 in acetonitrile. This may be compared to the saturated acyls **2**, all of which are more highly substituted at the ionizing position. For example, $[Cp'_2Nb(Cl)(\eta^2\text{-}OCCHMe_2)]^+$ exhibited a pK_a of 12.8 in acetonitrile,[21] roughly 2 pK units higher than that of **3b**. From the pK_a's (in DMSO) of $PhC(O)CH_3$ (24.7) and $PhC(O)CHMe_2$ (26.3),[40] we can estimate that the effect of two alkyl groups is ca. 2 pK units. We can predict that the unsubstituted acyl derivative $[Cp'_2Nb(Cl)(\eta^2\text{-}OCCH_3)]^+$ (for which no synthetic route is yet available) would exhibit a pK_a of 11 in acetonitrile. Clearly, then, the enacyls exhibit pK_a's quite similar to those seen for the saturated acyls, once the substitution pattern at the ionizing position is considered.

As noted above, the chemistry described herein constitutes a stepwise ionic dehydrogenation of the ketene substituent. Since we have thermodynamic data for both steps, we can construct a thermodynamic cycle for the entire process (Scheme 1). This is done by converting the pK_a of the enacyl to a free energy for deprotonation ($\Delta G° = 1.37$ pK_a), incorporating the hydride affinity determined by the bracketing studies on **3b**, and noting that these two processes release a hydride and a proton. Using standard electrochemical potentials and thermodynamic data,[41] we can establish that the free energy of their combination to solvated dihydrogen is −75 kcal/mol. The three steps combine to give the overall free

Scheme 1



energy for dehydrogenation of the ketene ethyl group, which is calculated to be 28 ± 4 kcal/mol when all species are in acetonitrile solution. A similar analysis on **1c** leads to the same conclusion. Here the ethyl substituent facilitates the hydride donation, so that this step has an energy of 81 ± 3 kcal/mol; this is 7 kcal/mol below the energy for **1b**. Conversely, the donor substituent makes **3c** a weaker acid than **3b**, and the pK_a (15) corresponds to a free energy change of 21 ± 3 kcal/mol. The overall conversion of **1c** to **7c** and dihydrogen has a free energy of 27 ± 4 kcal/mol, within experimental error of that of **1b**. To ascertain the impact of the metal on this process, we may compare this with the related reactions for free alkanes/alkenes. Using literature thermodynamic data[42] and making the reasonable assumption that the solvation free energies of the alkane and alkene are similar and liable to cancel, we calculate a dehydrogenation free energy of 26 kcal/mol for the conversion of butane to butene. Noting that **7** resembles a conjugated diene, we have also calculated the free energy for the conversion of butene to butadiene. This value is 25 kcal/mol; thus, all four of the dehydrogenation free energies are within the estimated uncertainty of our experimental determinations. From this we conclude that neither the metal center nor the ketene substituent (Et vs Ph) have any impact on the *overall* dehydrogenation process. This is reasonable, since the vinyl group in **7** is never bound to the metal, and the substituent (Et or Ph) is not directly bound to the vinyl group being formed. At the same time, our knowledge of the free energies for the individual steps allows us to calculate the impact of the metal center on each of them. Both the acyls **2** and the enacyls **3** exhibit pK_a's of ca. 11−15 in acetonitrile; from the known difference in proton solvation, we have estimated (and in a few cases demonstrated)[21] that the same compounds exhibit pK_a's of ca. 0−4 in DMSO. The corresponding phenyl ketones exhibit pK_a's of 19−26, depending on substitution patterns.[40] The 22 pK unit difference corresponds to a free energy of 30 kcal/mol, which is the

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driving force the niobium center contributes to the deprotonation of acyl and enacyl ligands; this may be compared to the effect of BF_3 on the pK_a of complexed acetaldehyde, for which the pK_a enhancement is ca. 33 kcal/mol.[43] Since the overall niobium contribution is zero, and since the metal makes no contribution to the third step (hydrogen formation), this means that the niobium center must also disfavor the hydride transfer by ca. 30 kcal/mol. As shown in eq 3, the oxygen lone pair is used to help release a hydride; the process is thus a vinylogous analogue of the hydride transfer depicted in eq 10. In contrast to the situation prevailing in nitrile reduction,[34] the niobium centers in **1** and **3** have no ancillary ligand to accept and release electron density. The chemistry is dictated instead by the ability of the oxygen atom to release or recapture lone pairs, and the formal metal−oxygen bond order does not change during the process. However, the tendency of the oxygen center to hold or release electron density is strongly influenced by the metal center, as indicated by the 30 kcal/mol contribution.

Conclusions

Ketene complexes have been prepared with the expectation that the unsaturated ligands would incorporate substantial reactivity to the resulting complexes. This has been observed, and the ketenes are susceptible to a variety of proton and hydride transfer reactions. A two-step sequence has been used in an ionic dehydrogenation of ketene substituents, and the new synthetic routes provide facile access to enacyl and vinylketene complexes. These exhibit substantial differences in reactivity, with the enacyls functioning as strong electrophilies and the vinylketenes serving as strong nucleophiles. With the ligands suitably anchored to the niobium center, it is possible to utilize these tendencies in the synthesis of new types of compounds. At the same time, care must be taken, since the two compounds are ideally suited for a condensation reaction involving the conjugate acid/base pair. Fortunately, this can be managed with the proper choice of base, so that both classes of compounds are accessible. Future work will center on the liberation of the elaborated ligands from the metal center and on studies of their use in the synthesis of useful heterocyclic compounds.

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Supporting Information Available: Crystal data for **3b**, including a textual summary of the analysis, tables of crystal data, bond lengths and angles, and atomic coordinates and thermal parameters, and structure drawings and NMR spectra for compounds **4**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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