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Synthesis and Reactivity of Niobium−Vinylketene Complexes Exhibiting Ketene η^2-C,O Complexation

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Vinylketenes have proven to be extremely useful substrates for cycloaddition reactions in which they typically function as the diene component of a [4 + 2] reaction.[1] After aromatization, the result is often a highly-substituted phenol. This chemistry usually requires the generation of the free vinylketene in the presence of the intended dienophile, since vinylketenes are often reactive toward dimerization and/or polymerization. However, a variation involves the generation of the vinylketene within the coordination sphere of a metal, and several methods have been developed for this purpose.[2] When the vinylketene complex is stable toward isolation, it typically exhibits the η^4-diene complexation mode.[3] We have previously reported the preparation of a series of niobium−ketene complexes in which the ketene is complexed via the C=O π system.[4] This stabilizes the ketene considerably, and the complexes are indefinitely stable in the absence of air. With the ketenes thus suitably anchored, we have pursued synthetic strategies aimed at converting them to vinylketenes; this has proved successful, and herein we report the preparation and reactions of these complexes. These are the first vinylketenes observed to adopt the η^2-C,O binding mode, which serves to isolate the electron-rich vinyl substituent from the remainder of the ketene molecule.

Our synthetic approach involves the use of cationic enacyls, which are derived from the ketene complexes. We have previously reported that the complexed ketenes react smoothly with triphenylcarbenium tetrafluoroborate, and that this reaction involves abstraction of a γ-hydrogen and stereospecific formation of the E-enacyls (eq 1; Cp′ = η^5-C₅H₄SiMe₃, **2a**, R = Ph,

2b, R = Et).[5] This process is not aided by the simultaneous
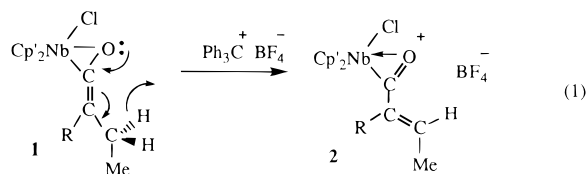
formation of a metal-carbon bond, as is typically true in the abstraction of α-hydrides (to make alkylidenes)[6] or of β-hydrides (to make π-complexed alkenes).[7] Hydride abstraction is used in organic applications to deprotect benzyl ethers,[8] in which case the resulting carbenium ion is stabilized by the adjacent oxygen; we suggest that the ketene oxygen fills this same role in eq 1, by engaging in a vinylogous stabilization of the incipient carbenium ion. We have further noted that a series of saturated acyls of general formula [Cp′₂Nb(Cl)(η^2-COCHR₂)][BF₄] exhibit substantial driving force for removal of the indicated proton,[9] a process which yields ketene complexes **1**. This acidity is clearly the result of the electron-deficiency in the cationic metal acyls, and they exhibit DMSO pK_a values some 18−24 pK units below those of similarly-substituted organic ketones. We thus reasoned that the conjugated methyl groups in **2** would contain acidic protons as well and sought the use of bases suitable for preparation of the vinylketenes.

Treatment of **2** with a slight excess of KO^{t}Bu in THF resulted in the development of a yellow color due to the vinylketenes **3**. These were isolated by toluene extraction; **3a** (R = Ph) is a yellow solid that precipitates upon addition of hexane, but **3b** (R = Et) is a yellow oil.[10] The vinyl substituent in each is
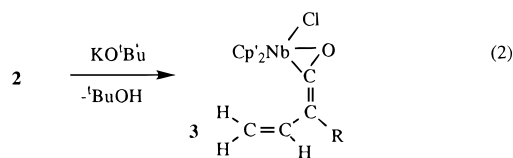
clearly indicated by the downfield NMR signals for the vinyl hydrogens, and the IR spectra show bands at ca. 1600 cm^{-1} for the η^2-C,O-bound ketene; isomerization would have been evident from the strong band for the uncomplexed carbonyl group and from the presence of inequivalent Cp′ substituents. Both reactions are stereospecific, with 2D-NOESY studies on **3a** indicating the formation of the E-ketene isomer shown. This contains the smaller ketene substituent near the metal center,

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(10) Synthetic procedures and spectral data for all compounds are available as Supporting Information.

and would therefore be predicted to be the thermodynamic isomer. Unlike our complexes with saturated ketenes,[4] compounds **3** show no tendency to isomerize to the Z-ketene isomer under ambient conditions.

We subsequently sought a comparison of the reactivity patterns of the conjugate acid−base pair, **2** and **3**. Since the enacyls contain a vinyl substituent conjugated with a strong withdrawing group, we expected they would function as useful dienophiles. Indeed, treatment of **4** (an analogue of **2** with smaller vinyl substituents) with cyclopentadiene for 3 h at 25 °C gave the [4 + 2] cycloaddition product **5** (eq 3), which may be precipitated with hexane and isolated as an off-white solid.
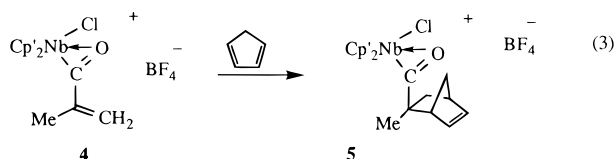

Although the enforced *S-cis* conformation of cyclopentadiene makes it a reactive Diels−Alder diene, these conditions are still quite mild and attest to the reactivity of the enacyls as dienophiles. We were interested to note that this reaction is completely stereospecific, giving only the indicated *exo* product (as verified with 2D-NOESY spectroscopy); Diels−Alder reactions usually favor the *endo* path, and this is normally attributed to secondary orbital overlap between the diene π system and that of the carbonyl substituent on the dienophile.[11] In **4** this would require an interaction of the diene with the niobium acyl, which resides in a crowded region of the molecule. Even though this secondary interaction is unavailable, the electron-deficient enacyl is clearly a powerful dienophile.

The vinylketenes **3** fail to react with excess cyclopentadiene within 6 h at ambient temperature; this suggested that they are more electron-rich than are enacyls. We thus sought to use them in cycloaddition reactions involving free ketenes, since the latter are known to engage in dipolar cycloadditions leading to cyclobutanone derivatives.[12] In fact, however, treatment of **3a** with either Me$_2$C=C=O or EtPhC=C=O led to the carbonyl derivatives **7** shown in eq 4 (**7a**, R = Et, R′ = Ph, **7b**, R = R′ = Me). We propose that **7** results from the expected zwitter-ionic intermediate **6**, which undergoes proton transfer rather than closure to a strained 4-membered ring; note that the positive charge in **6** is stabilized, since the cationic fragment could equally well be described as an enacyl. The niobium products are formed in the presence of ketene-derived byproducts, but **7** is stable to chromatography on neutral alumina and may be
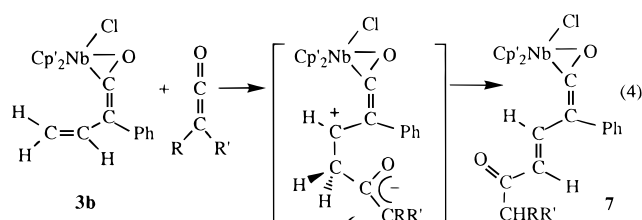
purified by elution (under nitrogen) with ca. 15% THF/hexane. NMR data are consistent with the E-alkene geometry,[13] since the vinyl hydrogens exhibit large couplings (ca. 15 Hz); the addition of the ketene moiety is confirmed, since **7b** shows the expected iso-propyl group and **7a** shows the ABX pattern associated with the C*H*(Ph)C*H$_2$*Me subsituent on the carbonyl. Both compounds show carbonyl IR bands at ca. 1750 cm^{-1}. Once again, 2D-NOESY studies were used to confirm the stereochemistry about both C=C bonds.

The results described herein constitute the first synthesis of η^2-C,O-bound vinylketenes via a sequence involving sequential hydride and proton loss, a strategy reported recently in the preparation of bound imines.[13] Compounds **3** show nucleophilic behavior involving the remote terminus of the ketene vinyl substituent, and this stands in contrast to the electrophilic behavior exhibited by the enacyl precursors. The enacyls are susceptible to [4 + 2] reactions with activated dienes, but the vinylketenes are potentially capable of a much wider range of carbon−carbon bond-forming reactions. As seen here, these can lead to the introduction of functional groups not compatible with free ketenes. We have previously shown that the ketene ligands can be liberated from the metal center upon mild oxidation.[5] While we have yet to pursue this with these vinylketenes, this work constitutes a synthetic approach to ketene functionalization involving the "isolated" ketene vinyl substituent. Further studies on the chemistry of enacyls and vinyl-ketenes are in progress.

Supporting Information Available: Synthetic details and spectral data for compounds **3**, **5**, and **7** (5 pages). See any current masthead page for ordering and Internet access instructions.

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