Journal of Organometallic Chemistry, 429 (1992) C33–C37
Elsevier Sequoia S.A., Lausanne
JOM 22596PC

Preliminary communication

Facile synthesis of α,β-unsaturated niobium acyls via γ-hydride abstraction

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(Received September 17, 1991)

Abstract

The niobocene ketene complexes $[C_5H_4(SiMe_3)]_2Nb(Cl)(\eta^2\text{-}C,O\text{-}O{=}C{=}C(R)CH_2R')$ (**1**) undergo a facile reaction with $Ph_3C^+BF_4^-$ to give the cationic α,β-unsaturated metal acyls of general formula $[[C_5H_4(SiMe_3)]_2Nb(Cl)(\eta^2\text{-}C(O)CR{=}CHR')][BF_4]$. The reaction is stereospecific for the production of *E*-alkenes, but these undergo slow isomerization to a mixture of *E* and *Z* isomers. If both ketene substituents contain accessible allylic hydrogens, the reaction shows little regioselectivity. Preliminary mechanistic studies are consistent with a direct hydride abstraction rather than an electron-transfer/H atom transfer sequence.

Recent work by Davies [1], Liebeskind [2], and others [3] has established that α,β-unsaturated metal acyls are extremely useful in the construction of new carbon-carbon bonds via Michael addition reactions. These reactions are often highly stereospecific, as shown via the use of chiral-at-metal species. The acryloyl-metal derivatives have been prepared (i) from metal acyls via a sequence of enolization, Aldol condensation, and elimination [3b,4], (ii) via addition of acryloyl halides or acroleins to electron-rich metal centers [5], (iii) in the reductive coupling of carbon monoxide by oxophilic organoactinide compounds [6], and (iv) via migratory insertion of carbon monoxide in metal-vinyl compounds [7]. Routes (ii) and (iii) have obvious limitations since they require specific types of metal centers, and route (iv) is undependable; insertion has been reported to fail in one case [4c], and de-insertion has been used as a synthetic route to metal-vinyl species in another [8]. For these reasons, and in view of the usefulness of α,β-unsaturated metal acyls, alternate synthetic avenues are of interest. We have been pursuing the synthetic utility of metal-ketene complexes of the general formula $[C_5H_4(SiMe_3)]_2$-$Nb(Cl)(\eta^2\text{-}C,O\text{-}O{=}C{=}CR_2)$ [9] and herein we report their conversion to α,β-unsaturated acyls via hydride abstraction.

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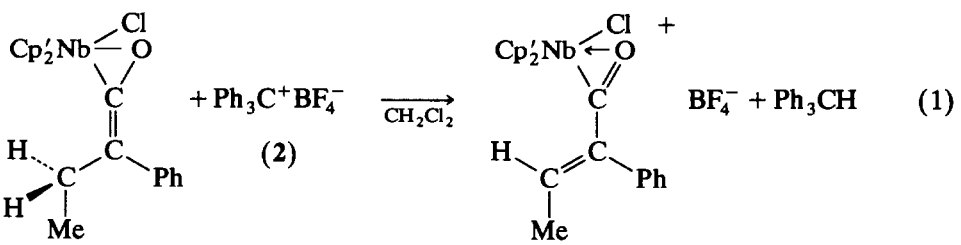
In a typical synthetic experiment, *ca.* 15 mL of dry, degassed CH_2Cl_2 is added (via vacuum distillation) to an equimolar mixture of ketene complex $[C_5H_4(SiMe_3)]_2Nb(Cl)(O{=}C{=}CEtPh)$ (**1**, which exists as an equilibrating mixture of *E* and *Z* isomers with $E/Z = 2.5$ in C_6D_6 [9]) and $Ph_3C^+BF_4^-$ (**2**). The resulting yellow-orange solution is allowed to stir at room temperature for *ca.* 1–2 hours, after which time solvent is removed *in vacuo*. Dry ether is added to extract the triphenylmethane by-product and triturate the pale orange oil. The resulting off-white solid can be isolated via filtration (yields are typically 85–90%) and is sufficiently pure for most uses, but it may be recrystallized from chloroform with loss of yield. Similar results are obtained for other alkylarylketene- and dialkylketene-complexes. We note the importance of excluding protic impurities, the presence of which leads to the formation of known saturated acyls via protonation of the ketene β-carbon [9b].

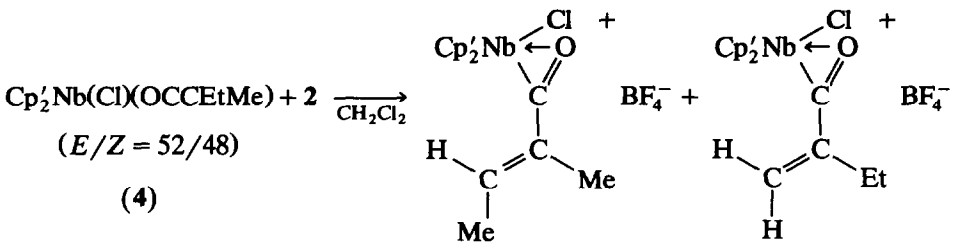
The products are identified as the α,β-unsaturated η^2-C,O-acyl complexes (**3**, eq. 1; only the *E* isomer of **1** is shown, *vide infra*). This formulation is consistent with the spectral data set and with elemental analysis. There are no infrared absorptions between 1600 and 2900 cm^{-1}, and the compounds exhibit bands in the region 1490–1550 cm^{-1} which are assigned to the acyl C–O stretch. The NMR spectra ($CDCl_3$) obtained for freshly-prepared samples of **3** contain only one set of resonances [10], indicating that one isomer of **3** results from the synthetic reaction;



(1) (1)

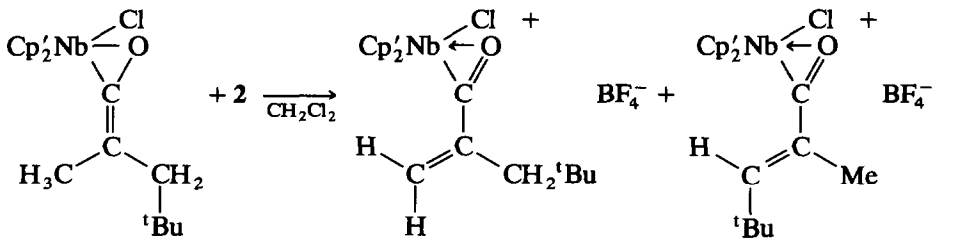
this is true even though **1** exists as a 70:30 mixture of the *E* and *Z* isomers. The synthetic product **3** was identified as the *E*-isomer using NOE experiments. These showed interactions between the allylic methyl hydrogens and the vinyl and *ortho*-phenyl hydrogens. There was also an interaction between the vinyl hydrogen and two of the Cp′ hydrogens, but there was no evidence for an interaction between the vinyl hydrogen and any phenyl hydrogens. After several hours in chloroform solution NMR data indicate that the *Z* isomer begins to form, ultimately constituting *ca.* 10% of the mixture present.

The synthesis of the α,β-unsaturated acyls is a highly stereospecific process favoring the formation of *E*-alkenes. In order to probe the regioselectivity of the process, we carried out similar reactions on dialkylketene complexes, in which both ketene substituents would be susceptible (in principle) to a reaction with **2**. As such, we utilized **4**, which exists as a 52:48 mixture of *E* and *Z* isomers, and **7**, which exists almost exclusively (≥ 95%) as the *E* isomer. In the former case, the resulting product consisted of *ca.* equimolar amounts of regioisomers **5** and **6** (eq. 2), with isomer **5** again exhibiting the *E* geometry; there was no evidence for the *Z*



(2)

analogue of **5**. For compound **7** a reaction with equimolar **2** results in an 8:1 ratio of **8**:**9**, favoring the less substituted alkene isomer (eq. 3). This suggests that the



(3)

abstraction reaction is slow relative to the ketene isomerization (*E*-**7** ⇌ *Z*-**7**); we sought to prove this by using an excess of reagent **2**, since the isomerization is a unimolecular process while the reaction with **2** is presumably bimolecular in nature. Indeed, with a 10-fold excess of **2** (vs. **7**), we observe that the ratio of **8** to **9** is reduced to 4:1. Thus, we conclude that (i) ketene isomerization is indeed faster than abstraction, (ii) the trityl reagent **2** adopts an approach from the exterior of the complex, and (iii) the regiochemical ratios are determined, not by starting material geometry, but by a combination of steric and product stability effects.

The use of **2** as a hydride abstracting agent is well known in organic [11] and organometallic [12,13] chemistry. With metal alkyls the reaction has been shown to result in either β-hydride abstraction (giving alkene complexes) [12] or α-hydride abstraction (giving alkylidene complexes) [13]. In addition, there are three reported examples in which **2** reacts with η^2-propene complexes to give η^3-allyl complexes [14]. In each case the loss of the C–H bond is formally accompanied by the formation of a new M–C bond. Conversely, the reaction described herein represents a rare example of a γ-H abstraction (we are aware of only one previous report [15]), and no new ligand-metal bonds result. In this sense, the reaction is reminiscent of the organic examples [11] in which **2** is used to de-protect benzyl ethers (R–OCH_2Ph) by abstracting the benzylic hydride; the eventual result is either hydrolysis of the benzyl cation or displacement of benzaldehyde and production of trapping product. The hydride abstraction process is facilitated by the resonance interactions with the arene and the adjacent heteroatom; the ketene complexes **1**, **4**, and **7** do not require arene stabilization, but the reaction may be facilitated by a vinylogous interaction with the ketene oxygen.

Organometallic hydride abstractions may proceed directly or via a sequence of electron transfer-hydrogen atom transfer [13]. Preliminary mechanistic experiments on **1** suggest that an electron transfer mechanism is precluded; cyclic voltammetry indicates that oxidation is completely irreversible, and infrared spectroelectrochemical studies show the immediate production of a band for free ketene (*ca.* 2100 cm^{-1}) upon oxidation. These results suggest that the radical cation $\mathbf{1}^{+\cdot}$ is too short-lived to engage in bimolecular hydrogen atom transfer, but this possibility is still under investigation.

In conclusion, the C=O-complexed ketene ligands in **1**, **4**, and **7** present a synthetic avenue to highly electron-deficient η^2-C,O-acryloylmetal systems via an unusual γ-hydride abstraction. The process occurs in high yield under mild conditions and exhibits a high degree of stereoselectivity, but little or no regioselectivity; in addition, the resulting species undergo a facile *E*–*Z* isomerization reaction. Further studies will be devoted to understanding the reactivity of the acyl compounds.

Acknowledgments. We thank Professor Ronald Halterman for helpful discussions and NSF for financial support of this work.

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