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Oxygen Atom Transfer Reactions in the Interconversion of Niobocene Ketene and Vinylidene Compounds

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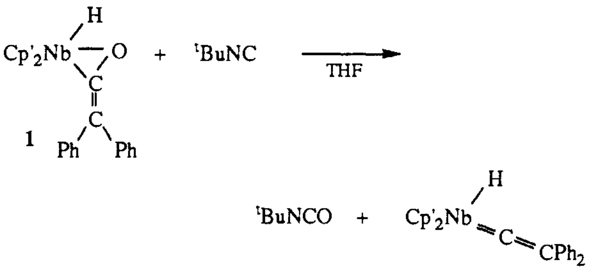
In the past several years, a variety of mechanisms have been postulated to account for CO reduction processes.[1] Model studies have led to the identification of several potential intermediates, including alkylidenes,[2] ketenes,[3] carbides,[4] and vinylidenes.[5] Although compelling evidence for each is available, few mechanistic schemes account for all possibilities *or* accommodate interconversions between potential intermediates. In the course of our studies on metal–ketene complexes, we have discovered the facile interconversion of vinylidene and ketene ligands via novel processes involving oxygen atom transfer, and these are described herein.

The niobium ketene hydrides of formula $Cp'_2Nb(H)(\eta^2\text{-}C,O\text{—}O{=}C{=}CR_2)$[6] were found to be unstable in acetonitrile solution. To probe the chemistry involved, diphenylketene derivative **1** was subsequently reacted with ᵗbutylisocyanide or acetonitrile at room temperature in THF (eqs 1 and 2). Both reactions resulted in the same niobium compound **2** (isolated as an off-white powder), inconsistent with chemistry involving insertion of the organics into the Nb–H bond.[7] The organic products were isolated and identified as ᵗbutylisocyanate and methylisocyanate, respectively, by comparison of spectral data with those of authentic materials; the use of ^{18}O-labeled $\mathbf{1}^{8a}$ in eq 1 resulted in ᵗbutylisocyanate exhibiting an IR band at 2230 cm^{-1} (vs 2258 in the unlabeled compound), thus confirming that the ketene ligand is the source of the oxygen atom in the isocyanate products.



1 **2** (1)

$$\mathbf{1} + \text{MeCN} \xrightarrow[\text{THF}]{} \mathbf{2} + \text{MeNCO} \qquad (2)$$

The ^{1}H NMR spectrum of **2** contained resonances for equivalent Cp′ groups, two unique phenyl groups, and a metal hydride (1.59 ppm). Compound **2** also gave ^{13}C NMR data consistent with the vinylidene formulation, since the vinylidene α-carbon exhibited a resonance at 326.8 ppm and coupling to the metal hydride ($^2J_{CH}$ = 6 Hz); this assignment was confirmed by a ^{13}C-labeling experiment involving the use of a sample of **1** labeled selectively at the ketene α-carbon (169 ppm).[8b,c] These data, and particularly the diagnostic downfield ^{13}C resonance,[5,9] are entirely consistent with the presence of a vinylidene complex. Related vinylidene compounds $Cp^*_2Ta(H)({=}C{=}CHR)$ have been prepared by thermolysis of allyl or vinyl precursors, and these show similar ^{13}C data (346–348 ppm, $^2J_{CH}$ = ca. 5 Hz).[5a]

To verify further the vinylidene formulation and characterize the reactivity of **2**, we sought means by which it could be converted back to **1**. In the course of these studies, it became clear that **2** was largely unreactive toward a number of traditional oxidants, including oxiranes,[10] hydrogen peroxide, MCPBA, iodosobenzene,[11] and dioxygen.[12] Adam *et al.* have recently described the facile synthesis of dry, ketone-free ether solutions of methyl(trifluoromethyl)dioxirane (**3**).[13a] Dioxiranes have been utilized in organic applications and found to function as powerful, yet often selective, oxidants.[13] Indeed, treatment of **2** with an ethereal solution of **3** for a few hours at room temperature led to the smooth production of **1** (eq 3). Compound **3** is known to decompose to ketone and dioxygen by way of a process involving

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[12] In a related reaction, dioxygen *does* convert a carbon monoxide ligand to a carbon dioxide ligand: Fu, P.-F.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 6579–6580.

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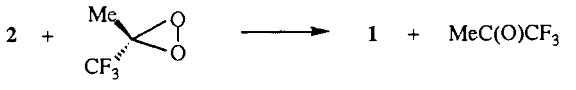

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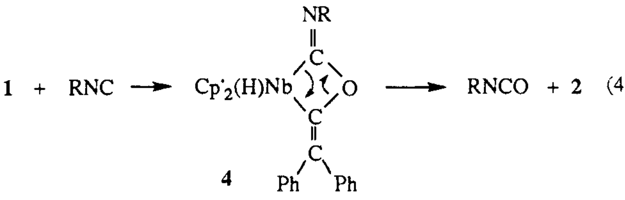
(3)

intermediate superoxide in a reaction catalyzed by mild reductants:[13b] hence, we have treated **2** with potassium superoxide and seen no conversion to **1**, so we attribute the oxygen transfer reaction to **3** itself. Dioxiranes have been used as decomplexing agents in (arene)Cr(CO)$_3$ chemistry,[14a,b] to decarbonylate metal carbonyls,[14c] and to oxidize thioalkyl ligands at sulfur.[14d] We believe that their reactivity and selectivity profiles bode well for other organometallic applications, and we are surveying this prospect.

Isocyanides have been converted to isocyanates by metal–dioxygen complexes[15] and by sulfoxides[16] via processes involving heterolysis of the M–O or S–O bond; the latter are known to require both electrophilic and nucleophilic activation at the isonitrile carbon (sulfoxide adds only in the presence of acid, and the process is initiated by addition of the electrophile to the isonitrile carbon).[16] In addition, isonitriles are well known to undergo migratory insertions at carbon[17] and to form organic cycloaddition products in which they incorporate only the carbon atom into the ring.[16c] On this basis we propose a metallacyclic species (**4**) as the intermediate in the oxo-transfer chemistry (eq 4). The related conversion of nitriles (eq 2) is unprecedented and



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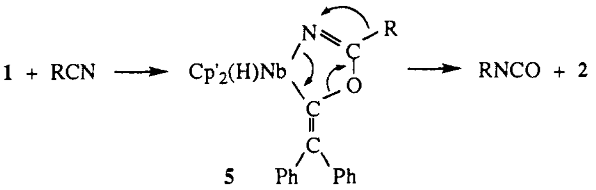
(4)

must involve 1,2 (C to N) migration of the alkyl group. Precisely such a process is known in the Hofmann and Curtius rearrangements (both of which yield isocyanates from amides) and in the Beckmann rearrangement.[18] All of these organic reactions involve 1,2 migration of an alkyl group to an electron-deficient nitrogen; the rearrangement in eq 2 also constitutes evidence in favor of a metallacyclic intermediate here, since open-chain zwitterionic species (which have been demonstrated in the chemistry of low-valent tungsten compounds[19]) would not provide the electrophilic nitrogen normally required for migration. For this reason, we propose species **5** as the key intermediate (eq 5) and note that



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(5)

related metallacyclic compounds have been identified in the reactions of zirconocene oxides with nitriles.[20a] We discount the involvement of nitrile oxides ($RCN^+\!-\!O^-$) in the chemistry described herein, since these are known to form cycloaddition products (furoxans) or polymers that rearrange to isocyanates only at elevated tempertures.[21]

The reactions reported herein are indicative of electron-rich systems, in spite of the high formal niobium oxidation states in **1** and **2**. Vinylidenes typically react with nucleophiles at the α-carbon (to make vinyls) and with electrophiles at the β-carbon (to make alkylidynes).[9,22] However, electron-rich metal centers will support reactions with electrophiles at the M=C bond; this has been seen in the reactions of a few vinylidenes with sulfur or selenium to make thio- or selenoketenes.[9k–m] The reaction of the niobium vinylidenes at the Nb=C bond with electrophilic dioxirane suggests that the Nb(V) center is more electron-rich than would be predicted on the basis of the d^0 electron configuration.

The conversion of ketene to vinylidene is noteworthy in two additional respects. First, there are reports of the reactions of free ketenes with polynuclear metal carbonyls proceeding to μ-vinylidenes, with concomitant liberation of a carbonyl ligand as carbon dioxide.[23] However, there are no observations of such an interconversion for a bound ketene, even though complexation of the C=O bond would be envisioned to activate it toward cleavage. It is also surprising that cleavage of the Nb(V)–oxygen bond is so facile. However, the isomerization of tantalaoxetanes $\mathrm{Cp^*_2(H)\overline{TaOCH_2CH_2CH_2}}$ from the O-inside to O-outside derivatives is thought to proceed via Ta–O heterolysis, and the process is indeed acid-catalyzed.[24] Ring strain in **1** (a methylene metallaoxirane) may be important in facilitating niobium–oxygen heterolysis and insertion reactions with nitriles or isonitriles.

In summary, the ketene hydride complex **1** serves as an oxo-transfer reagent under mild conditions. Related reactions with sulfoxides involve the polar nature of the S–O bond ($S^+\!-\!O^-$),[16] and we believe that **1** can generate zwitterionic character via formal heterolysis of the Nb–O bond. This process and the reaction with dioxirane constitute a cycle by which ketene and vinylidene ligands may be interconverted, and these conversions can be coupled with unusual oxidations of nitriles. Further organic and organometallic applications and mechanistic features are currently under investigation.

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