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Synthesis and Reactivity of (Dialkylacetylene)niobium(III) Complexes and Derivatives. Contrast between Protonation and Methylation Pathways

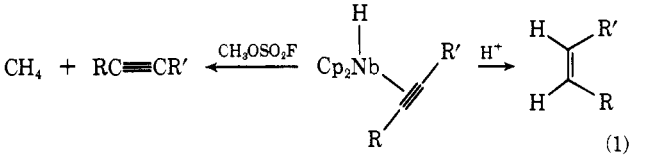
Sir:

We have previously reported[1] the preparation and characterization of the stable complexes $[\eta^5\text{-}(CH_3)C_5H_4]_2TaX$(dialkylacetylene) (X = H, I). We now find that similar Nb(III) species can be prepared under reaction conditions milder than those required for their Ta(III) analogs and that the Nb(III) compounds undergo a variety of transformations which are of interest from the standpoints of both mechanistic considerations and potential utility for organic synthesis.

Acetylene complexes and derivatives were prepared employing Cp_2NbH_3 (Cp = η^5-C_5H_5) as starting material. The published preparation[2] of the trihydride, **1**, requires extremely high pressures of hydrogen. We found the following modification of a 1 atm procedure[3] to be a convenient one. A suspension of Cp_2NbCl_2[4] in toluene[5] was stirred with an excess of "Vitride" until all solids dissolved. After hydrolysis with aqueous NaOH, separation, drying, and evaporation of the organic layer, **1** was obtained in up to 55% yield as yellow crystals. Treatment of **1** with a dialkylacetylene in refluxing benzene for 15 min afforded an hydrido(acetylene) complex $Cp_2NbH(RC{\equiv}CR')$, **2** (Table I). The ir and ^1H NMR spectra for **2** are similar to those observed[1] for the analogous Ta(III) complexes (for **2a**, $\nu_{Nb\text{-}H}$ 1720 cm^{-1}; $\nu_{C\equiv C}$ 1815 cm^{-1}; $\tau_{Nb\text{-}H}$ 10.8). In contrast to $Cp_2NbH(C_2H_4)$ which readily forms an insertion product, $Cp_2Nb(C_2H_5)(C_2H_4)$, in the presence of excess ethylene,[2] no such reaction of **2** with excess acetylene was observed, even after several hours in refluxing toluene.

The ^1H NMR spectra of complexes **2** are consistent with the structure proposed for the Ta(III) analogs[1] and established crystallographically for the related olefin complex $Cp_2Nb(C_2H_5)(C_2H_4)$;[6] viz., the acetylenic C≡C bond lies in a plane that contains the Nb and H atoms. Thus, for an unsymmetrically substituted acetylene, two isomers for the hydrido(acetylene) complex are possible which are due to the two orientations of the acetylene ligand in the Nb-H-(C≡C) plane. Models suggest that, in the complex, the sterically bulkier substituent on the triple bond will be oriented preferentially toward the small hydride ligand. This supposition is supported by ^1H NMR evidence obtained for a series of hydrido(acetylene) complexes (see Table I). For the mixture of isomeric complexes of a methyl-substituted unsymmetrical acetylene, the major component in this mixture is the one displaying the methyl group resonance at higher field (i.e., the sterically smaller substituent group of the acetylene preferentially occupies the site in the coordination pocket of the metal that gives rise to an upfield shift and the larger group prefers the site that gives rise to a downfield shift). For **3b**, only the lower field resonance displays coupling to the Nb-H ($J_{CH_3\text{-}H}$ = ca. 1 Hz) which indicates that the site associated with the low field resonance (and, hence, the one preferred by the larger substituent group) is the one spatially closest to the hydride ligand.

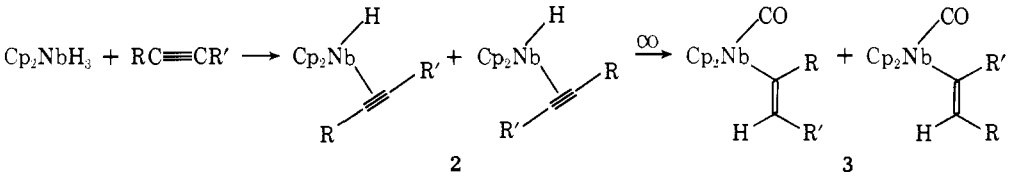
Hydrido(acetylene) complexes **2** are rapidly converted by CH_3I to the orange, crystallize iodo(acetylene) analogs, $Cp_2NbI(RC{\equiv}CR')$, **3**, which were characterized by elemental analysis, ir (for **3a** $\nu_{C\equiv C}$ 1825 cm^{-1}), and ^1H NMR. The hydrido(acetylene) complexes also react rapidly with acid to yield, nearly quantitatively, the corresponding cis olefin. Treatment of **2** with methyl fluorosulfonate also causes rapid reaction, but no methylated olefin is obtained; instead, methane is evolved and the original acetylene is liberated. For these complexes, methylation presumably occurs at niobium as does protonation,[7] but reductive elimination of CH_4 from the resulting cationic species is too fast to allow acetylene insertion into the Nb-H bond to compete (reaction 1).



(1)

The above results suggest that alkylation of a coordinated

Table I



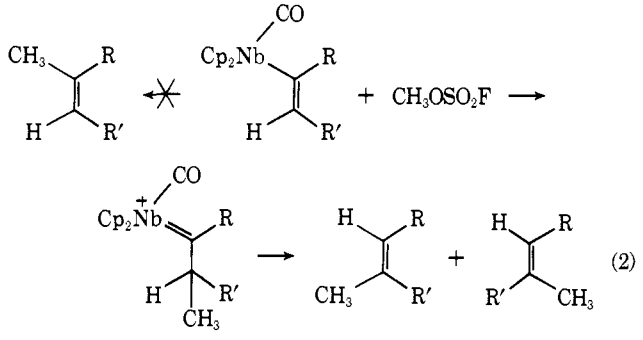
2 3

RC≡CR'	τ_R	$\tau_{R'}$ (Rel intens)	τ_R	$\tau_{R'}$ (Rel intens)
a, R = $CH_3CH_2CH_2$– R' = $CH_3CH_2CH_2$–	7.25	7.20	7.55	7.95
b, R = CH_3– R' = CH_3–	7.58	7.43	8.27	8.30
c, R = CH_3– R' = *i*-C_3H_7–	7.55 (80)	7.37 (20)	8.22 (>95)	(<5)[a]
d, R = CH_3– R = *n*-C_3H_7–	7.53 (60)	7.38 (40)	8.23 (75)	(25)[b]

[a] Not observable within limits of detection. [b] Hidden by other resonances. Determined from relative intensities of C_5H_5 peaks.

acetylene, without concomitant side reactions associated with the Nb-H group, requires that M-H insertion to give an alkenyl complex be effected prior to treatment of the organometallic species with alkylating agent. Isoelectronic hydrido(ethylene) complexes $Cp_2MH(C_2H_4)^+$ (M = Mo, W) undergo insertion to yield the ethyl complex on heating with triphenylphosphine;[8] however, prolonged treatment of **2** with excess PMe_2Ph at 110° caused no hydride insertion, and only very slow replacement of the acetylene by the phosphine was observed. In contrast, heating **2** under CO (50 psi, 75°, 15 min) caused smooth conversion to alkenyl(carbonyl) complexes **3** (Table I) which were characterized by ir (for **3a**, ν_{CO} 1900 cm^{-1}) and ^1H NMR (Table I). Apparently, the relative stability of noninserted (π-acetylene hydride) and inserted (alkenyl) forms of the Nb complexes is largely determined by the availability of electron density on Nb for back-bonding which is required to stabilize the (π-acetylene)-metal bond. Thus an electron donor ligand (PMe_2Ph) does not favor insertion whereas ligands which are electron acceptors (CO, H^+) do. For complexes of unsymmetrically substituted acetylenes, high regiospecificity for insertion is observed in which the niobium atom attaches preferentially to the vinylic carbon atom bearing the sterically smaller substituent. This insertion occurs with (C=C) cis stereochemistry.

As expected, complexes **3** react rapidly with acid to give the corresponding cis olefins. Reaction of **3c** with D_2SO_4 gives $CH_3C(D)=C(H)CH(CH_3)_2$, reinforcing the contention that protonation occurs at Nb followed by reductive elimination of olefin. Reaction of the vinylic complexes with CH_3OSO_2F is considerably slower than protonation (several hours at room temperature),[9] but methylated olefins are eventually formed. Surprisingly, however, treatment of **3c** with CH_3OSO_2F yielded none of the expected trisubstituted olefin $(CH_3)_2C=CHCH(CH_3)_2$; instead, *cis*- and *trans*-$CH_3C(H)=C(CH_3)CH(CH_3)_2$ were formed (in 75% yield based on Nb; see reaction 2). Thus alkylation proceeds



(2)

regiospecifically by attack of the electrophilic reagent on that vinylic carbon atom to which the Nb atom is *not* attached. We suggest that this unusual reaction results from an inability of the methyl group to attack at the metal center for steric reasons; instead, alkylation occurs "allylically" at the β-vinylic carbon.[10] The resulting intermediate, which may be represented as a cationic (alkylcarbene)Nb(III) complex,[11] undergoes proton migration followed by reductive elimination of the olefinic product (reaction 2).

Parallels between protonation and alkylation of low-valent transition metal complexes have previously been emphasized.[7a] As demonstrated by the contrasting results described herein, it must now be recognized that these two types of reactions may indeed proceed by *dissimilar* pathways in complexes which possess several potential sites of electrophilic attack, especially in cases where steric crowding exists at one such site.

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(10) In agreement with this view, $Cp_2Nb(C_2H_5)(CO)$ (prepared by carbonylation of $Cp_2NbH(C_2H_4)$[2]), which has no reactive site alternative to the metal center, is not methylated by CH_3OSO_2F.
(11) A stable (alkylcarbene)Ta(III) complex has been recently reported.[12] Furthermore, the anions formed by metalation of carbene complexes have been shown to be best represented as vinyl complexes, and these are alkylated by reagents such as CH_3OSO_2F in a reaction closely paralleling that proposed herein.[13]
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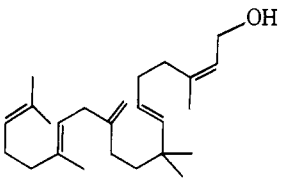
Sesterterpenes. I. Stereospecific Total Synthesis of Moenocinol

Sir:

The C_{25} acyclic lipid moenocinol has been obtained from the antibiotics moenomycin[1] and prasinomycin[2] by hydrolysis and shown to possess structure **1**.[2,3] This communication describes the first stereospecific synthesis of moenocinol employing nerol and geraniol as trisubstituted olefin precursors.



1

The key intermediate ester **10** was synthesized from pure nerol.[4] Ozonolysis[5] of nerol benzyl ether (**2**) (prepared from nerol (sodium hydride followed by benzyl bromide in glyme, 95%)) at −78° in methylene chloride-pyridine afforded after reduction with zinc in acetic acid, aldehyde **3** in 55% yield[6,7] (ir(neat)5.80 μ; NMR 9.65 (t, J = 1.5 Hz, 1