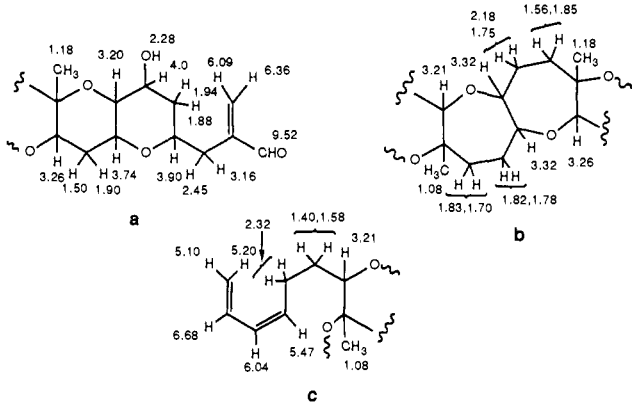
quaternary carbons bearing methyl groups and oxygen.

The information obtained from ^1H–^1H COSY plot, difference decoupling, *J*-resolved 2D NMR, and chemical shifts led to the connectivities shown in the partial structures, **a**, **b**, and **c**. The structure **a** contains an α-vinyl aldehyde moiety, which was found in all brevetoxins. The *J*-resolved spectrum was particularly useful in assigning the methylene proton signal in the partial structure **b**, which have close chemical shifts due to the near symmetricity



of the partial structure. The geometry of the diene in the partial structure **c** was determined as *Z* in comparison with proton–proton coupling constants and carbon chemical shifts in similar structures.[13-15]

The three partial structures, whose connectivities in NMR are disrupted by quaternary carbons, were combined together on the basis of the difference NOE and long-range coupling COSY spectral data. The methyl protons (H-27, δ 1.18) showed long-range couplings with protons, δ 3.20 (H-7), 3.26 (H-10), 1.85 (H-12a), and 1.56 (H-12b). The other methyl group (H-26, δ 1.08) showed couplings with protons, δ 3.21 (H-19) and 1.70 (H-17) (Figure 4 of Supplementary Material). NOE was observed between the methyl protons, H-27, and two methine protons, δ 3.32 (H-14) and 3.20 (H-7). Similarly, NOE was observed between the methyl protons, δ 1.08 (H-26), and two methylene protons, δ 1.83 and 1.70 (H-17). The oxygen function at C-6 is a hydroxyl group, because, in some spectra, the OH proton at C-6 was observable (δ 2.28) and showed two-bond and three-bond couplings with H-6 and H-5a,b, respectively. This structural arrangement, A/B ring and the side chain, is identical with the right terminus of all brevetoxin series. In fact the NMR data of the moiety are in good agreement with those of brevetoxin-A.[1] Therefore the all-trans–syn-trans structure was also assumed for **3**. The 18α configuration of the 18-hydroxyl group was also assumed from the biosynthetic consideration. We previously reported that hemibrevetoxin-A (GB-M) has also a terminal diene and a conjugated aldehyde.[10] Hemibrevetoxin-C (GB-4) has a conjugated aldehyde but no diene. Both compounds are considered to be closely related to hemibrevetoxin-B.

The structure **3** constitutes essentially the right half of brevetoxin molecules. It was speculated that brevetoxins are biosynthesized through a cascade of epoxide ring openings triggered by protonation on the carbonyl group at the left terminus of the carbon chain (**A**).[16] In view of the structures of the hemibrevetoxins, however, the cyclization may be better explained by an alternate mechanism (**B**),[16,17] in which the cascade is initiated from the right hand by the opening of *cis*-epoxide followed by a hydride ion transfer and consecutive *trans*-epoxide openings. Moreover, the structures of hemibrevetoxins with alkene tails affirm the polyene origin of brevetoxins.

Hemibrevetoxin-B causes the characteristic rounding of cultured mouse neuroblastoma cells as brevetoxin-A and -B and shows cytotoxicity at a concentration of 5 μmol.

Acknowledgment. This research was supported by NIH Grants, GM28754 and GM24425, which are greatly appreciated. We are also grateful to Claudia Walker for the bioassay.

Supplementary Material Available: Figures of the ^1H–^1H COSY and ^1H and ^{13}C NMR spectra of **3** (6 pages). Ordering information is given on any current masthead page.

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Stepwise Reduction of Acetonitrile in [Tp′(CO)(PhC≡CMe)W(N≡CCH$_3$)][BF$_4$]

S. G. Feng and J. L. Templeton*

Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27599

Received March 13, 1989

Reduction of nitriles to amines with either hydrogen or hydride reagents is a common reaction,[1] but characterization of intermediates in nitrile reduction promoted with metal monomers has proved elusive.[2] Conversion of acetonitrile to ethylamine results when [(triars)Ru(NCMe)$_3$]$^{2+}$ is treated with NaBH$_4$ in methanol as [(triars)HRu(NH$_2$CH$_2$CH$_3$)$_2$]$^+$ forms.[3] Reduction of acetonitrile on metal clusters has yielded isolable intermediates.[4]

We report here stepwise reduction of coordinated acetonitrile by sequential hydride and proton addition reactions (Scheme I). Intermediate metal complexes have been isolated and characterized at each stage of the reduction (Table I).

Oxidation of K[Tp′W(CO)$_3$][5] with iodine followed by addition of MeC≡CPh yields Tp′W(CO)(I)(PhC≡CMe) [Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate]. Abstraction of I$^-$ with [Ag][BF$_4$] in acetonitrile produces a royal blue cationic Tp′(CO)(PhC≡CMe)W(N≡CCH$_3$)$^+$ complex. The ^{13}C chemical shifts of the two alkyne carbons (215, 213 ppm) indicate that the alkyne $\pi_\perp$ orbital is donating into the vacant d_π orbital of this six-coordinate d^4 monomer.[6]

Low-temperature addition of Li[HBEt$_3$] to a THF solution of the cationic acetonitrile complex causes a color change, and orange crystals of Tp′(CO)(PhC≡CMe)W—N̈=CHMe were isolated in 70% yield. Salient ^1H data for the major isomer include a quartet at 6.26 ppm (1 H, J = 6 Hz) and a doublet at 1.78 ppm (3 H, J = 6 Hz), while ^{13}C NMR revealed alkyne carbons at 160 and 159 ppm, with the azavinylidene carbon[7] at 145 ppm exhibiting a $^1J_{CH}$ value of 167 Hz. The shift in ν_{CO} from 1940 cm^{-1} in the reagent to 1885 cm^{-1} is consistent with formation of a neutral product. A second isomer with similar spectroscopic

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Scheme I

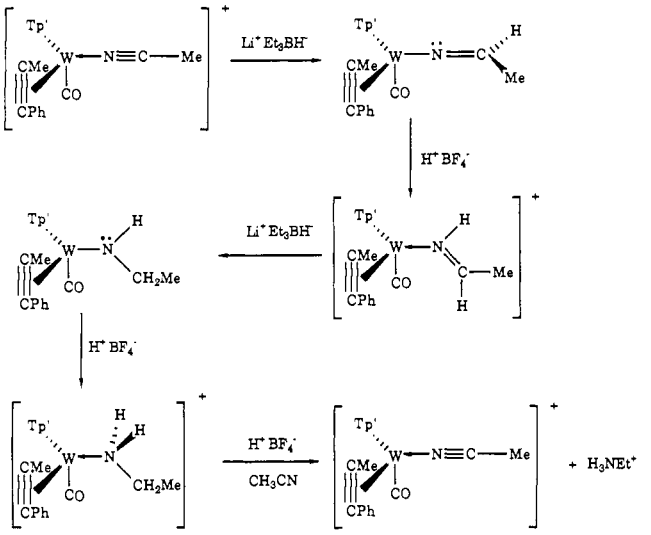

Table I. Selected Data for Intermediates in the Reduction of Coordinated Acetonitrile

complex	color	ν_{CO}, cm^{-1}	alkyne ^{13}C, ppm
$[Tp'(CO)(PhC_2Me)W{\leftarrow}N{\equiv}CCH_3][BF_4]$	blue	1940	215, 213
$Tp'(CO)(PhC_2Me)W{-}N{=}CHCH_3$	orange	1885	160, 159
$[Tp'(CO)(PhC_2Me)W{\leftarrow}NH{=}CHCH_3][BF_4]$	blue	1920	215, 214
$Tp'(CO)(PhC_2Me)W{-}NHCH_2CH_3$	orange	1854	169, 167
$[Tp'(CO)(PhC_2Me)W{\leftarrow}NH_2CH_2CH_3][BF_4]$	blue	1909	215, 213

properties constitutes about 20% of the product.

Protonation at the azavinylidene nitrogen in CH_2Cl_2 solution generates a blue cationic imine complex, [Tp'(CO)(PhC≡CMe)W(NH=CHMe)][BF_4] (90% yield). The ^{13}C NMR spectrum indicates that formation of the imine has returned the alkyne to a four-electron-donor role (alkyne carbons: 215, 214 ppm). Coupling information from ^1H NMR is informative (10.86 ppm, 1 H, broad d, $^3J_{HH}$ = 20 Hz, N*H*; 6.38 ppm, 1 H, dq, $^3J_{HH}$ = 20 Hz, 6 Hz, NH=C*H*CH_3; 2.22 ppm, dd, 3 H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, NH=CHC*H*$_3$).

The coordinated imine is activated for further reduction. Hydride addition at carbon with Li[H**B**Et_3] in THF forms an ethylamido ligand in the neutral orange $Tp'(CO)(PhC{\equiv}CMe)W{-}NHCH_2CH_3$ product (75% yield). Again the nitrogen lone pair competes with the alkyne $\pi_\perp$ orbital for donation into the lone vacant metal d_π orbital (alkyne carbons at 169 and 167 ppm). The methylene protons of the amidoethyl group are diastereotopic since the metal is chiral, and assignment of the ^1H NMR is straightforward. As in the neutral azavinylidene product, two isomers are evident in the ^1H and ^{13}C NMR in a 4:1 ratio. We believe these isomers result from restricted rotation about the metal-nitrogen bond.

Protonation of the neutral amido complex in 1:5 CH_2Cl_2/Et_2O completes reduction of the nitrile as the blue cationic ethylamine complex forms. The ^1H NMR properties of the ethylamine ligand are very similar to those of the ethylamine ligand in [(triars)$HRu(NH_2CH_2CH_3)]^+$.[3] The amine ligand can be removed as the ethylammonium salt by addition of excess acid to the amine complex in acetonitrile to regenerate the starting acetonitrile adduct.

We have no mechanistic information. Nucleophilic attack on four-electron-donor alkyne ligands is known to form η^2-vinyl products in other d^4 monomers.[8] Indeed we have isolated η^2-vinyl products from hydride addition to [$Tp'(CO)_2W(PhC{\equiv}CH)$][$BF_4$],[9] so initial attack at the alkyne is a possibility in the acetonitrile reduction reactions. Nitrile insertion into metal-alkyl bonds has been reported,[10] and we cannot rule out initial nucleophilic attack at the metal by the hydride reagent. Given the steric bulk of the Tp' ligand, which is known to inhibit metal-based reactions in related systems,[11] we favor direct attack at the acetonitrile carbon by Li[H**B**Et_3]. Protonation at the nitrogen lone pair also seems more attractive than metal protonation followed by hydrogen migration to the α-nitrogen position.

Regardless of the mechanism, this system illustrates one sequence of reactions that converts metal-bound nitriles to amines. The stepwise reduction of the acetylide triple bond in Fp'—C≡CH to form Fp'—CH_2CMe_3 capitalized on the nucleophilicity of C_α and the electrophilicity of C_β in unsaturated η^1 carbon ligands.[12] Such reactions reflect the ability of the metal to house lone pairs or form π bonds while adhering to the 18-electron rule.[13] The reactivity pattern in the acetonitrile reduction is reversed, as expected, since it is the nitrogen that alternates between accommodating a lone pair and forming a covalent bond. No doubt the flexible electron-donor capability of the alkyne $\pi_\perp$ orbital in this system is important in accounting for the stability of these nitrile reduction intermediates.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Supplementary Material Available: Experimental procedures, complete ^1H and ^{13}C NMR data, and elemental analyses for $Tp'(CO)(PhC_2Me)WI$ and **1–5** (5 pages). Ordering information is given on any current masthead page.

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Nickel(0)-Catalyzed Cyclization of 1,7-Diynes via Hydrosilation: One-Step Synthesis of 1,2-Dialkylidenecyclohexanes with a (*Z*)-Vinylsilane Moiety

Kohei Tamao,* Kenji Kobayashi, and Yoshihiko Ito*

Department of Synthetic Chemistry, Faculty of Engineering Kyoto University, Kyoto 606, Japan

Received December 27, 1988

1,2-Dialkylidenecycloalkanes are useful building blocks for the synthesis of polycyclic molecules.[1] Three methodologies have recently been developed: (1) Cyclization of 1,*n*-diynes with stoichiometric amounts of titanium or zirconium complexes[2] or with palladium catalysts,[3] (2) palladium[4] or nickel-chromium-

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