Synthesis and Characterization of the Stable Cationic d^2 Metal Acetylene Complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}RC{\equiv}CR')(NCMe)]^+$. X-ray Crystal Structures of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}MeO_2CC{\equiv}CMe)(NCMe)][BPh_4]$ and $[(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)Nb{=}C{=}C(CH_3)(CH_3)\text{-}C{=}C{=}Nb(CO)(\eta^5\text{-}C_5H_4SiMe_3)_2][BPh_4]_2$

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*Summary: Treatment of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}RC{\equiv}CR')$ (2) with 1 equiv of $[Cp_2Fe][BPh_4]$ in acetonitrile leads to the cationic acetylene complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}RC{\equiv}CR')(CH_3CN)][BPh_4]$. The same reaction for **2d** (R = Me, R′ = CO_2Me) under different experimental conditions affords a divinylidene binuclear d^2 niobocene complex, $[(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)Nb{=}C{=}C(CH_3)(CH_3)C{=}C{=}Nb(CO)(\eta^5\text{-}C_5H_4SiMe_3)_2][BPh_4]_2$. The molecular geometries of both this complex and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}MeC{\equiv}CCO_2Me)(CH_3CN)][BPh_4]$ have been determined by X-ray diffraction studies.*

Most d-block transition metals form well-defined compounds with acetylenes.[1] However, while η^2-acetylene complexes of group 6 metals are extensively known, the scope of acetylene complexes of group 5 metals is much less developed.[2] Our recent isolation of Lewis-base-containing niobocene ketenimine cationic complexes[3] led us to believe that analogous acetylene complexes could be obtained. As part of our program to develop synthetic applications of niobocene complexes, we report here the outcome of our recent studies with acetylene ligands. These have resulted in the synthesis and solid-state structure of stable cationic acetylene complexes of a d^2 metal. The starting niobium complexes $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}RC{\equiv}CR')$ (**2**), prepared by reduction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}RC{\equiv}CR')$ (**1**) with 1 equiv of Na(Hg),[4] react with 1 equiv of $[FeCp_2][BPh_4]$ to generate the corresponding cationic acetylene niobocene complexes **3** (Scheme 1). These compounds were isolated in high yield (70−90%) as pure air-stable crystalline solids after recrystallization from acetonitrile/diethyl ether.[5] Particularly diagnostic of the coordinated acetylene unit is the presence of a $\nu_{C{\equiv}C}$ (1750−1850 cm^{-1}) characteristic band in the IR spectra and resonances at ca. δ 140.5 and 145 ppm (**3a**) due to the nonequivalent acetylene carbon atoms in the ^{13}C NMR spectra. To unequivocally confirm the proposed structure for compounds **3**, an X-ray crystal structure determination of complex **3d** was undertaken.[6] The results are summarized in Figure 1 along with some selected bond lengths and bond angles. The complex shows a typical bent-sandwich structure. The critical feature is the acetylenic unit, which adopts an endo conformation with respect to the acetonitrile ligand. In

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(4) Antiñolo, A.; Fajardo, M.; Gil-Sanz, R.; López-Mardomingo, C.; Otero, A.; Lucas, D.; Chollet, H.; Mugnier, Y. *J. Organomet. Chem.* **1994**, *481*, 27.

(5) Synthesis of **3**: To an equimolar mixture of **2** and $[Cp_2Fe][BPh_4]$ (0.60 mmol) was added 30 mL of CH_3CN at −20 °C. The solution was stirred at this temperature for 5 min and then warmed to room temperature for 2 h. The solvent was removed, and the resulting oily solid was washed with diethyl ether and then recrystallized (CH_3CN/Et_2O, 70−90%). Key data for some complexes **3** are as follows. **3a**: IR (Nujol mull) 2280, 2310 ($\nu_{C{\equiv}N}$), 1769 cm^{-1} ($\nu_{C{\equiv}C}$); ^{1}H NMR (300 MHz, CD_3CN) δ 0.09 (s, 18H, $SiMe_3$), 2.31 (s, 3H, CH_3CN), 5.90 (2H), 5.96 (2H), 6.30 (2H), 6.35 (2H) (m, $C_5H_4SiMe_3$), 6.84 (m, 4H, *p*-C_6H_5), 6.99 (m, 8H, *m*-C_6H_5), 7.28 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-), 7.30−7.56 (m, 10H, phenyl groups of acetylene); $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN) δ −1.54 ($SiMe_3$), 4.92 (CH_3CN coordinated), 103.31, 112.02, 115.80, 125.12, 126.65 ($C_5H_4SiM_3$), 125.23, 125.30, 128.35, 128.48, 128.55, 128.78, 129.49, 135.44 (C phenyl groups of acetylene ligand), 121.44, 125.27, 135.46 (C phenyl groups of BPh_4^-), 140.47, 144.86 (Ph*C*≡*C*Ph), 163.51 (C_{ipso} of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.7 Hz). Anal. Calcd for $C_{56}H_{59}NNbSi_2B$: C, 74.28; H, 6.52; N, 1.54. Found: C, 74.30; H, 6.48; N, 1.49. **3d**: IR (Nujol mull) 2323, 2296 ($\nu_{C{\equiv}N}$), 1774 ($\nu_{C{\equiv}C}$), 1679 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR (300 MHz, CD_3CN) δ 0.14 (s, 18H, $SiMe_3$), 2.49 (s, 3H, CH_3CN), 2.69 (s, 3H, ≡CCH_3), 3.72 (s, 3H, ≡CCO_2CH_3), 5.84−5.87 (4H), 5.94 (2H), 6.23 (2H) (m, $C_5H_4SiMe_3$), 6.84 (m, 4H, *p*-C_6H_5), 6.99 (m, 8H, *m*-C_6H_5), 7.27 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-); $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN) δ −0.69 ($SiMe_3$), 5.82 (CH_3CN coordinated), 21.70 (≡CCH_3), 52.34 (≡CCO_2CH_3), 104.40, 111.76, 112.51, 116.93, 120.02 ($C_5H_4SiMe_3$), 122.76, 126.55, 136.72 (C phenyl groups of BPH_4^-), 140.85 (≡CCO_2CH_3), 167.17 (CH_3C≡), 164.78 (q, C_{ipso} of BPh_4^-, $J_{^{13}C-^{11}B}$ = 49.7 Hz), 170.48 (≡CCO_2CH_3). Anal. Calcd for $C_{47}H_{55}O_2NNbSi_2B$: C, 68.40; H, 6.66; N, 1.70. Found: C, 68.45; H, 6.62; N, 1.68. Detailed synthetic procedures and key data for complexes **3b**,**c** are provided in the supplementary material.

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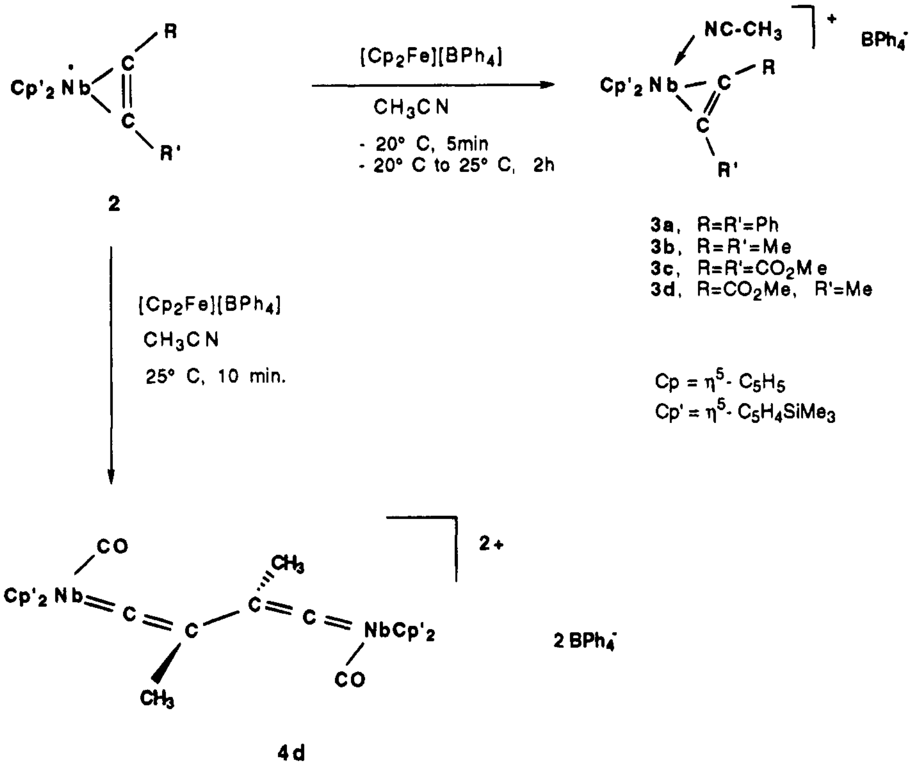
Scheme 1



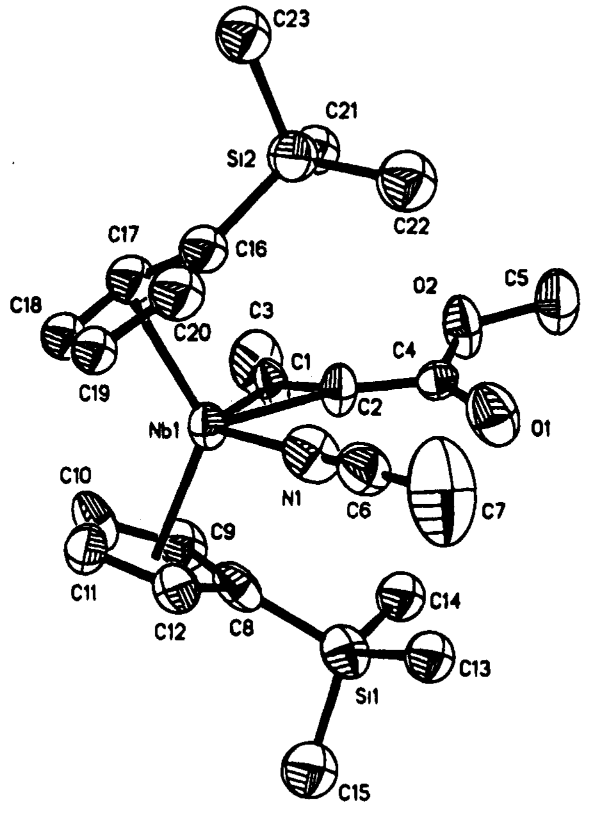


Figure 1. Structure of **3d** showing the atom-labeling scheme (anion omitted for clarity). Selected bond distances (Å) and angles (deg): Nb1−C1, 2.15(1); Nb1−C2, 2.180(8); C1−C2, 1.30(1); Nb1−N1, 2.221(8); C2−C1−C3, 141.0(10); C1−C2−C4, 140.0(9); Nb1−C1−C3, 145.2(8); Nb1−C2−C4, 148.8(7); Nb1−N1−C6, 177.4(9); N1−C6−C7, 177.0(10).

view of the thermal stability displayed by compounds **3**, the endo isomer seems to be thermodynamically favored over the exo alternative.[7] The values of angles formed by C1 and C2 with Nb1, C3, and C4 are clear evidence of near- sp^2 hybridization at those acetylenic carbon atoms. Further proof of this hybridization is provided by the bond distance C1−C2, 1.30(1) Å, which is slightly shorter than a typical carbon−carbon double bond.[2e,g,h] ^{13}C NMR data (vide supra) support this result, indicating that the acetylene ligand in **3** behaves as a two-electron ligand.[8] In accordance with these results complexes **3** may be described either as d^2 acetylene complexes or as d^0 niobacyclopropene complexes. They are isoelectronic with a wide range of neutral group 4 species, Cp_2M(acetylene)(Lewis base),[9] and closely related to both base-free group 4 species, Cp_2M(acetylene)[10] and neutral group 5 species, Cp_2M(acetylene or olefin)X (X = anionic ligand).[2] In contrast to the aforementioned behavior, the reaction of **2d** with 1 equiv of the ferrocenium salt in acetonitrile at room temperature did not afford **3d** but rather a yellow

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(6) Crystal data for **3d**: $C_{47}H_{55}BNO_2Si_2Nb$, orthorhombic, $Pna2_1$, $a = 21.166(7)$ Å, $b = 16.127(6)$ Å, $c = 12.893(8)$ Å, $V = 4401.7(34)$ Å^3, $Z = 4$, $D_{calc} = 1.246$ g cm^{-3}, μ(Mo Kα) = 3.50 cm^{-1}, 23 °C, Enraf-Nonius CAD4 diffractometer, graphite monochromator, colorless crystal (0.38 × 0.33 × 0.25 mm) sealed in a glass capillary. Of 5321 reflections collected (4° ≥ 2θ ≥ 54°; ω−θ scan), 2833 with $F_o \geq 4\sigma(F_o)$ were unique observed data. No corrections for linear decay and for absorption were necessary for the intensity data. The structure was solved by a combination of direct methods and Fourier synthesis and then refined by full-matrix least-squares calculations. Carbon atoms from the $SiMe_3$ and BPh_4 groups were isotropic and the rest of non-hydrogen atoms were anisotropic (hydrogen atoms were included in calculated positions with fixed thermal and positional parameters). $R = 0.062$, $R_w = 0.060$, data/parameters = 8.4, GOF = 1.567, highest peak 1.03 e Å^{-3}.

(7) We have previously described several neutral haloketene, ketenimine, and cationic ketenimine niobocene complexes where the exo isomer (the bulkier substituent in an outside position) is always favored over the endo isomer: (a) Antiñolo, A.; Fajardo, M.; López-Mardomingo, C.; Otero, A.; Mugnier, Y.; Mourad, Y.; Sanz-Aparicio, J.; Fonseca, I.; Florencio, F. *Organometallics* **1990**, *9*, 2919. (b) Antiñolo, A.; Fajardo, M.; López-Mardomingo, C.; Gil-Sanz, R.; Martín-Villa, P.; Otero, A.; Kubicki, M. M.; Mugnier, Y.; El Krami, S.; Mourad, Y. *Organometallics* **1993**, *12*, 381. (c) Antiñolo, A.; Otero, A.; Fajardo, M.; López-Mardomingo, C.; Lucas, D.; Mugnier, Y.; Lanfranchi, M.; Pellinghelli, H. A. *J. Organomet. Chem.* **1992**, *435*, 55.

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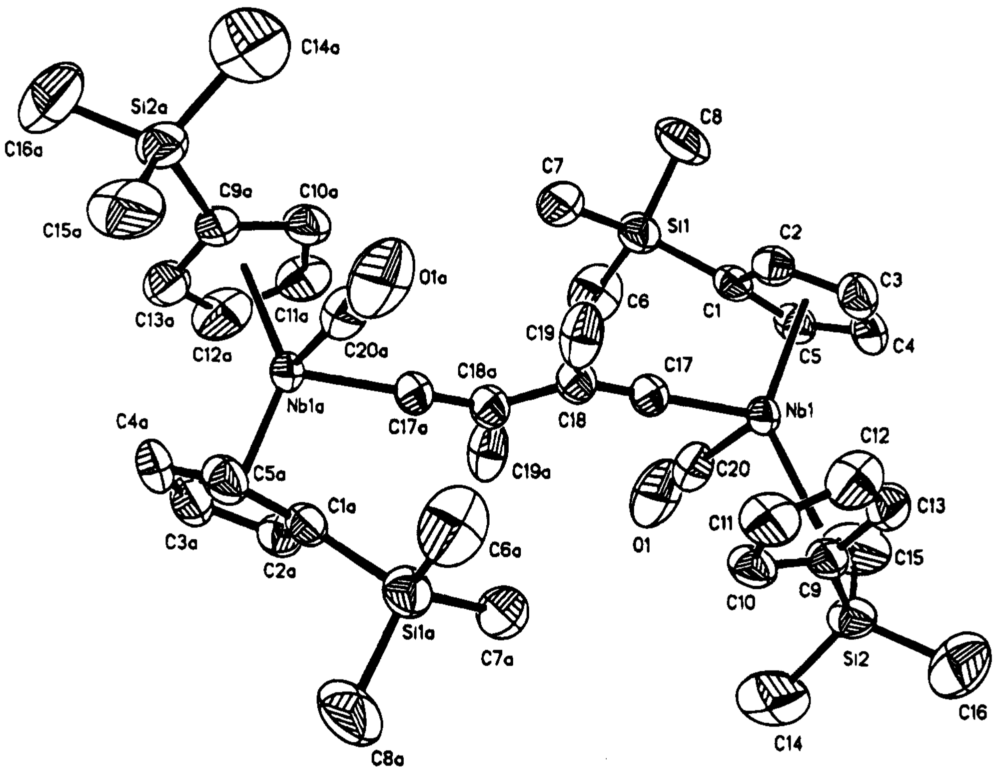

Figure 2. Labeled ORTEP view of **4d** (anion omitted for clarity). Important bond distances (Å) and angles (deg): Nb1–C20, 2.110(3); O1–C20, 1.123(4); Nb1–C17, 2.001(2); C17–C18, 1.320(3); C18–C18a, 1.468(3); Nb1–C20–O1, 177.5(3); Nb1–C17–C18, 173.0(2); C17–C18–C18a, 122.9(2); C17–C18–C19, 119.3(2); C17–Nb1–C20, 87.5(1).

precipitate of **4d** was obtained in good yield (60–70%) which was recrystallized from hot acetonitrile (Scheme 1). The compound was unambiguously characterized by spectroscopy[11] as the binuclear vinylidene derivative $[(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)Nb{=}C{=}C(CH_3)(CH_3)\text{-}C{=}C{=}Nb(CO)(\eta^5\text{-}C_5H_4SiMe_3)_2][BPh_4]_2$. Both concentration and temperature have been established as limiting factors in the chemoselectivity of the reaction of **2d** with the ferrocenium salt. No conversion of **3d** to **4d** was observed even on refluxing in THF. Similar efforts to prepare **4d** analogously from complex **2** (R = R′ = CO_2Me) proved unsuccessful. **4d** constitutes an unusual d^2 niobocene complex exhibiting simultaneously both carbonyl and C_4 chain 2,3-dimethyl-1,3-butadien-1,4-diylidene ligands. Particularly diagnostic of the carbonyl ligand is the presence of a band at 2081 cm^{-1} in the IR spectrum. The position of the band could be ascribed to a slight back-donation from the Nb=C=C– bonding orbital to the in-plane CO π^* orbital, in a manner similar to that previously described[3,12] for the cationic d^2 carbonyl complexes $[Cp_2Nb(CO)_2]^+$. However, the signal expected for the ^{13}C resonance from the carbonyl ligand attached to the metal is observed in neither solution nor the solid state. This could be attributed to the quadrupolar moment of the ^{93}Nb nucleus (spin $I = {}^9/_2$, natural abundance 100%) which could cause such broadening of the signal that it becomes undetectable at room temperature.[13] The vinylidene α- and β-carbons exhibited resonances at 378.2 and 138.5 ppm, respectively, in the ^{13}C NMR spectrum which are entirely consistent with the presence of a vinylidene complex.[14] Related mononuclear vinylidene tantalocene and niobocene complexes have been described,[15] and some divinylidene complexes for late transition metals have also been reported.[16] The structural assignment of complex **4d** based on data taken in solution has been confirmed by an X-ray crystal structure determination.[17] Figure 2 shows an ORTEP diagram of the molecule, illustrating its binuclear bent-sandwich structure. The molecular structure consists of two crystallographically

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(9) Leading references: (a) Fachinetti, G.; Floriani, C.; Marchetti, F.; Mellini, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1799. (b) Demerseman, B.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1981**, 665. (c) Demerseman, B.; Mahé, R.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1984**, 1394. (d) Alt, H. G.; Herrmann, G. S.; Rausch, M. D.; Mallin, D. T. *J. Organomet. Chem.* **1988**, *356*, C53. (e) Alt, H. G.; Herrmann, G. S. *J. Organomet. Chem.* **1990**, *390*, 159. (f) Rosenthal, U.; Ohff, A.; Michalik, M.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Angew. Chem.* **1993**, *105*, 1228.

(10) See, for example: (a) Vaughan, G. A.; Sofield, C. D.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 5491. (b) Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7994.

(11) Synthesis of **4d** (in CH_3CN): To an equimolar mixture of **2d** (450 mg, 0.97 mmol) and $[Cp_2Fe][BPh_4]$ (490 mg, 0.97 mmol) was added 2 mL of CH_3CN at room temperature. The solution was stirred for 10 min, and immediately a yellow precipitate was formed. The solid was isolated by filtration, washed with diethyl ether, and then recrystallized from hot acetonitrile (530 mg, 0.35 mmol, 70%). Key data for **4d**: IR (Nujol mull) 2081 cm^- (ν_{CO}); ^1H NMR (300 MHz, CD_3CN) δ 0.30 (s, 36H, $SiMe_3$), 1.68 (s, 6H, CH_3), 6.02 (8H), 6.06 (4H), 6.15 (4H) (m, C_5H_4-$SiMe_3$), 6.85 (m, 8H, *p*-C_6H_5), 6.99 (m, 16H, *m*-C_6H_5), 7.28 (m, 16H, *o*-C_6H_5) (phenyl groups of BPh_4^-); $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN, 40 °C) δ −0.20 ($SiMe_3$), 19.43 (=C=CCH_3), 103.60, 106.54, 106.79, 108.37, 111.37 ($C_5H_4SiMe_3$), 122.81, 126.61, 136.86 (C phenyl groups of BPh_4^-), 164.98 (q, C_{ipso} of BPh_4^-, $J_{^{13}C-^{11}B} = 49.7$ Hz), 138.50 (Nb=C=*C*), 378.25 (Nb=*C*=C); FAB MS *m/e* (relative intensity) 868 (5) (M^{2+}), 840 (76) ($M^{2+} - CO$), 812 (12) ($M^{2+} - 2CO$), 434 (68) ($M^{2+}/2$), 406 (45) ($[M^{2+}/2] - CO$) 391 (87) ($[M^{2+}/2] - CO - Me$), 366 (100) ($Nb[C_5H_4SiMe_3]_2^+$). Anal. Calcd for $C_{88}H_{98}O_2Nb_2Si_4B_2$: C, 70.10; H, 6.50. Found: C, 70.24; H, 6.55.

(12) Eckart, E. H. O.; Brintzinger, H. H. *J. Organomet. Chem.* **1978**, *148*, 29.

(13) See: (a) Green, M. L. H.; Hughes, A. K.; McGowan, P. C.; Mountford, P.; Scott, P.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1992**, 1591. (b) Green, M. L. H.; O'Hare, D.; Watkin, J. G. *J. Chem. Soc., Chem. Commun.* **1989**, 698.

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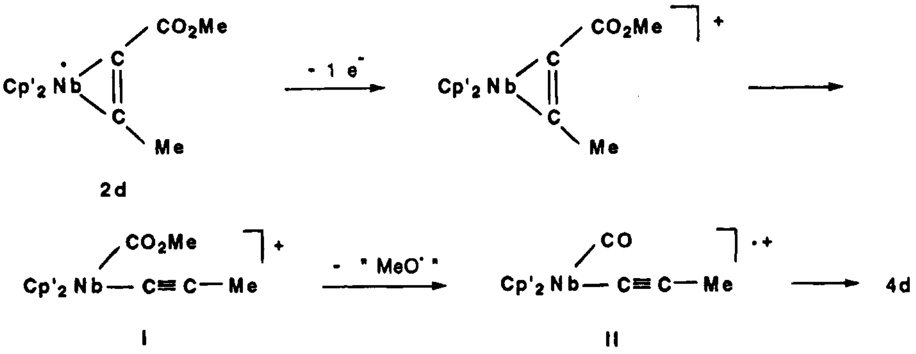
Scheme 2. Proposed Mechanism for the Formation of 4d



equivalent moieties related by a center of symmetry, located in the middle of the divinylidene ligand. The CO ligands are practically linear and are located in a trans disposition with respect to the C_4 chain-divinylidene ligand, avoiding adverse steric interactions with the methyl groups on C18 and C18a carbon atoms. The Nb=C=C–linkage is almost linear, 173.0(2)°, which implies that the vinylidene α-carbon is sp hybridized. The value of 122.9(2)° observed for the C17–C18–C18a angle is clear evidence of sp^2 hybridization at the vinylidene β-carbon. A final feature to be emphasized is that the =C=C–C=C= moiety is practically planar, being located in the reflection plane of the bent-sandwich structure.

Although this study has unambiguously established the structure of **4d**, the precise mechanism of the reaction leading to this complex remains to be clarified. Remarkably, the nature of the products resulting from the reaction of **2d** with the ferrocenium salt depends dramatically upon the choice of both values of temperature and concentration of reactants. Thus, to isolate **4d**, values of temperature and concentration higher than those required for **3d** are needed. Liberation of CO does not take place in the formation of the dimeric product, since when the reaction was carried out under a ^{13}CO atmosphere the corresponding labeled compound is not obtained, suggesting that the methoxycarbonyl group of **2d** is the only source of the CO ligand in **4d**. When the synthetic reaction is monitored using ^1H NMR (20 °C in THF-d_8 solution), no resonance attributable to a methoxy group or methanol appear and GC experiments to identify the organic products derived from the "MeO•" evolution have so far been unsuccessful. Taking into consideration the well-known conversion of terminal acetylene to metal vinylidene *via* alkynyl intermediates,[18] it is tempting to speculate on the possible participation of an alkynyl radical cation intermediate, $[(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)NbC{\equiv}CMe]^+$ (**II**), which might lead to **4d** by ligand–ligand coupling (Scheme 2). The formation of divinylidene ligands bridging two metal atoms has been described both by ligand–ligand coupling of the unstable radical alkynyl species[16b] and by oxidatively induced coupling of vinylidene species.[16a] We assume in this proposal that the first step in the mechanism would be the one-electron oxidation of **2d** followed by an intramolecular rearrangement of the acetylene to alkynyl species **I**[19] which would lead to the proposed alkynyl radical cation **II**. A critical point to resolve is the evolution of the 2 equiv of "MeO•" formally formed in the reaction from the CO_2Me moiety. Work aimed at ascertaining the evolution of the "MeO•" and the role of both temperature and concentration and other mechanistic aspects of the process are under investigation.

It may be concluded that cationic acetylene d^2 niobocene complexes can be easily prepared in one step by an oxidation process, and efforts to broaden the scope and develop synthetic applications are currently in progress.

Acknowledgment. We gratefully acknowledge financial support from the Dirección General de Investigación Científica Técnica (Grant No. PB92-0715) and thank Dr. Mariano Laguna from the University of Zaragoza (Spain), who recorded the mass spectra.

Supplementary Material Available: Text giving full details of the syntheses of complexes **3** and key data for **3b,c** and tables giving X-ray crystal structure analysis data, atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters for the non-hydrogen atoms, selected bond distances and angles, and least-squares planes and deviations therefrom for **3d** and **4d** (21 pages). Ordering information is given on any current masthead page.

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(16) Leading references: (a) Iyer, R. S.; Selegue, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 910. (b) Le Narvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 357. (c) Rappert, T.; Nürnberg, O.; Werner, H. *Organometallics* **1993**, *12*, 1359.

(17) Crystal data for **4d**: $C_{88}H_{98}B_2O_2Si_4Nb_2$, monoclinic, $P2_1/c$, a = 13.714(2) Å, b = 15.193(9) Å, c = 19.606(3) Å, β = 100.54(1)°, V = 4016.1(24) Å^3, Z = 2, D_{calc} = 1.248 g cm^{-3}, μ(Mo Kα) = 3.75 cm^{-1}, 23 °C, Enraf-Nonius CAD4 diffractometer, graphite monochromator, yellow prism (0.48 × 0.30 × 0.30 mm). Of 7632 reflections collected (4° ≥ 2θ ≥ 50°; ω–2θ scan) 6990 unique and 5838 with $F_o \geq 4\sigma(F_o)$ were considered observed. No corrections for linear decay and for absorption were necessary to apply to the intensity data. The structure was solved by a combination of direct methods and Fourier synthesis and then refined by full-matrix least-squares calculations. Non-hydrogen atoms were anisotropic (hydrogen atoms were included in calculated positions with fixed thermal and positional parameters). R = 0.033, R_w = 0.044, data/parameters = 13.2, GOF = 1.582, highest peak 1.00 e Å^{-3}.

(18) Leading references: (a) García Alonso, F. J.; Höhn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 406 and references therein. (b) Birdwhistle, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474. (c) Schneider, D.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 700.

(19) It has been recently described[18c] that not only terminal alkynes but also internal alkynes can undergo intramolecular rearrangement.