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Communications

ansa-Niobocene Complexes: Synthesis and Characterization of Novel Complexes $[Me_2Si(\eta^5\text{-}C_5H_4)_2]NbCl_2$ and $[Me_2Si(\eta^5\text{-}C_5H_4)_2]NbCl(RC{\equiv}CR)$ (R = Me, Ph). X-ray Crystal Structure of $[Me_2Si(\eta^5\text{-}C_5H_4)_2]NbCl(MeC{\equiv}CMe)$

Antonio Antiñolo,[†] Martín Martinez-Ripoll,[‡] Yves Mugnier,[§] Antonio Otero,*,[†]
Sanjiv Prashar,[†] and Ana M. Rodriguez[†,‡]

Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Químicas,
Campus Universitario, Universidad de Castilla-La Mancha, 13071-Ciudad Real, Spain,
Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, CNRS URA 1685, Faculté des
Sciences Gabriel, 6 bd Gabriel, 21000 Dijon, France, and Departamento de Cristalografía,
Instituto Rocasolano-CSIC, Serrano 119, 28006, Madrid, Spain

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Summary: The ansa-niobocene(IV) dichloride complex $[Me_2Si(\eta^5\text{-}C_5H_4)_2]NbCl_2$ *(**1**) has been prepared by the reaction of* $NbCl_4(THF)_2$ *and* $[Me_2Si(C_5H_4)_2]Tl_2$ *in THF. The reduction of **1** by sodium amalgam in the presence of an alkyne (2-butyne or diphenylacetylene) yielded the ansa-niobocene(III) monochloride alkyne complexes* $[Me_2Si(\eta^5\text{-}C_5H_4)_2]NbCl(RC{\equiv}CR)$ *(R = Me (**2**), Ph (**3**)). Compounds **1**−**3** were characterized by IR, ESR, and NMR spectroscopy. In addition, the structure of **2** was determined by single-crystal X-ray diffraction.*

The use of *ansa*-cyclopentadienyl ligands has recieved wide attention in the chemistry of group 4 metals,[1] due mainly to its ability to impart on its complexes a high and selective degree of catalytic activity.[2]

The synthesis of other metal complexes containing *ansa*-cyclopentadienyl ligands has also been reported; however, to date these are few and include *ansa* ligands of chromium,[3] molybdenum,[4] tungsten,[4] iron,[5] and ytterbium[6] complexes.

For group 5 metals, few such compounds are known. The first *ansa* compounds, reported in 1980, contained $Me_2Si{-}O{-}SiMe_2$ or CMe_2CMe_2 bridging groups.[7] An *ansa*-vanadocene complex has also been described.[8] Recently, *ansa* complexes of niobium with a CMe_2 bridging group[9] and a monocyclopentadienyl−amido system[10] were reported.

The known niobocene complexes have in most cases been restricted to conventional cyclopentadienyl ligands such as C_5H_5, C_5Me_5, or $C_5H_4SiMe_3$,[11] and the chemistry

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[†] Universidad de Castilla-La Mancha.

[‡] Instituto Rocasolano-CSIC.

[§] Laboratoire de Synthèse et d'Electrosynthèse Organométalliques.

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of the $C_5H_4SiMe_3$ niobocene complexes has been developed by our group.[12] We report here our first studies on the synthesis and reactivity of new *ansa*-niobocene complexes with the $Me_2Si(C_5H_4)_2$ ligand.

$[Me_2Si(\eta^5\text{-}C_5H_4)_2]NbCl_2$ (**1**) was prepared by the reaction of $NbCl_4(THF)_2$[13] and $[Me_2Si(C_5H_4)_2]Tl_2$[14] in THF at room temperature,[15] in a synthesis similar to that previously used for the complexes $(\eta^5\text{-}C_5H_5)_2NbCl_2$, $(\eta^5\text{-}C_5H_4Me)_2NbCl_2$, and $(\eta^5\text{-}C_5H_4SiMe_3)_2NbCl_2$.[16] In the present case a thallium reagent rather than a lithium reagent was used, since use of the latter usually gives diminished yields as a result of reduction processes. The poor solubility of **1** in organic media required extraction of the crude product several times with dichloromethane in order to separate pure **1** from the thallium chloride salt. Complex **1** was characterized by IR and ESR[17] spectroscopy. Electrochemical studies gave results similar to those obtained with the corresponding η^5-C_5H_5 or η^5-$C_5H_4SiMe_3$ derivatives.[18] One oxidation (0.54 V) and one reduction (−1.00 V) peak were observed due to the practically reversible processes shown in eq 1.

$$[(cp\text{^}cp)NbCl_2]^+ \underset{-\,\mathrm{le}}{\overset{+\,\mathrm{le}}{\rightleftarrows}} [(cp\text{^}cp)NbCl_2] \underset{-\,\mathrm{le}}{\overset{+\,\mathrm{le}}{\rightleftarrows}} [(cp\text{^}cp)NbCl_2]^- \qquad (1)$$

$$cp\text{^}cp = Me_2Si(\eta^5\text{-}C_5H_4)_2$$

The niobium(III) complexes $[Me_2Si(\eta^5\text{-}C_5H_4)_2]NbCl(MeC{\equiv}CMe)$ (**2**) and $[Me_2Si(\eta^5\text{-}C_5H_4)_2]NbCl(PhC{\equiv}CPh)$ (**3**) were prepared[19] by the reduction of **1** by sodium amalgam in the presence of the respective alkyne as previously reported for $(\eta^5\text{-}C_5H_4SiMe_3)_2NbCl(L)$ (L = alkyne) complexes.[18] Both complexes were only slightly soluble in hexane but highly soluble in toluene. Crystals of **2** and **3** were obtained by recrystallization from either hexane or a diethyl ether/toluene mixture. The complexes were characterized by IR and ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectra showed the expected signals for the $SiMe_2$ group of the *ansa*-bridge (two singlets at *ca.* 0.0 ppm). The symmetry of the molecule in solution is such that there is only one plane of symmetry and the methyl groups of $SiMe_2$ become inequivalent as do the cyclopentadienyl protons (H_a, H_b, $H_{a'}$, and $H_{b'}$) (see Figure 1) and the alkyne protons (i.e., two singlets for $MeC{\equiv}CMe$ and two multiplets for $PhC{\equiv}CPh$).

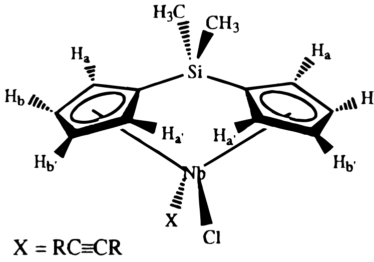

Figure 1.

In order to gain more insight into the structures of these complexes the X-ray crystal structure of **2** was carried out.[20] The molecular structure, atomic numbering scheme, and selected bond lengths and angles for **2** are shown in Figure 2.

The structure shows the $Me_2Si(C_5H_4)_2$ *ansa* ligand chelating the niobium center and is the first to be determined of a group 5 *ansa* complex where both cyclopentadienyl rings of the *ansa* ligand are bound to the metal in an η^5-mode only as opposed to the previ-

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(15) Synthesis of **1**: THF (*ca.* 400 mL) was added to a mixture of $NbCl_4(THF)_2$ (13.05 g, 34.44 mmol) and $[Me_2Si(\eta^5\text{-}C_5H_4)_2]Tl_2$ (20.49 g, 34.44 mmol). The reaction mixture was stirred at room temperature for 16 h, after which the suspension was filtered. Solvent was removed *in vacuo* from the filtrate to give the title complex **1**. In order to maximize the yield, the residue from the filtration was extracted several times with dichloromethane, solvent was removed from the extracts under reduced pressure, and the resulting brown solid was dried under vacuum (7.78 g, 65%). Key data for **1**: IR (Nujol mull) 1261 (ν_{Si-Me}), 1159, 1070, 824 ($\nu_{C-C(Cp)}$), 263 (ν_{Nb-Cl}); Anal. Calcd for $C_{12}H_{14}Cl_2NbSi$: C, 41.27; H, 4.04. Found: C, 40.93; H, 4.20.

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(17) (a) The ESR spectra for the paramagnetic niobium(IV) complex **1** gives a value of $g_{iso} = 2.0034$ with a hyperfine splitting $\langle a_{^{93}Nb} \rangle$ of 100.0 G, analogous to other niobocene(IV) complexes, with the unpaired electron mainly located at the metal center. (b) Antiñolo, A.; Fajardo, M.; de Jesús, E.; Mugnier, Y.; Otero, A. *J. Organomet. Chem.* **1994**, *470*, 127.

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(19) (a) Synthesis of **2**: $[Me_2Si(\eta^5\text{-}C_5H_4)_2]NbCl_2$ (**1**) (0.60 g, 1.71 mmol) was added to sodium amalgam (0.039 g, 1.71 mmol of Na). To this mixture was added THF (*ca.* 100 mL). To this stirred solution was added via microsyringe $MeC{\equiv}CMe$ (0.13 mL, 1.71 mmol), and the reaction mixture was allowed to stir at room temperature for 3 h. The solvent was removed under reduced pressure, and toluene (*ca.* 50 mL) was added. The suspension was filtered and solvent removed *in vacuo* from the filtrate yielding a yellow/green solid. This solid was recrystallized from a diethyl ether/toluene to give yellow crystals of the title compound (0.44 g, 70%). Key data for **2**: IR (Nujol mull) 1697 ($\nu_{C\equiv C}$); ^1H NMR (300 MHz, C_6D_6) δ 0.02 (s, 3H, $SiMe_2$), 0.08 (s, 3H, $SiMe_2$), 2.22 (s, 3H, $MeC{\equiv}CMe$), 2.50 (s, 3H, $MeC{\equiv}CMe$), 4.73 (2H), 5.16 (2H), 5.31 (2H), 6.13 (2H) (m, $(C_5H_4)_2(\mu\text{-}SiMe_2)$); $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6) δ −6.34, −5.52 ($SiMe_2$), 11.83, 18.86 (${\equiv}CMe$), 98.36, 99.51 (C^1), 100.40, 118.88, 125.80 $(C_5H_4)_2(\mu\text{-}SiMe_2)$, 126.71, 149.98 (${\equiv}CMe$). Anal. Calcd for $C_{16}H_{20}ClNbSi$: C, 52.17; H, 5.48. Found: C, 51.83; H, 5.35. (b) Synthesis of **3**: This was carried out in a similar manner to the synthesis of **2** [$PhC{\equiv}CPh$ (0.28 g, 1.57 mmol), **1** (0.55 g, 1.57 mmol), sodium amalgam (0.036 g, 1.57 mmol of Na), yield of **3** (0.58 g, 75%)]. Key data for **3**: IR (Nujol mull) 1738 ($\nu_{C\equiv C}$); ^1H NMR (300 MHz, C_6D_6) δ 0.03 (s, 3H, $SiMe_2$), 0.06 (s, 3H, $SiMe_2$), 5.22 (2H), 5.51 (2H), 5.59 (2H), 6.05 (2H) (m, $(C_5H_4)_2(\mu\text{-}SiMe_2)$), 6.95−7.74 (m, 10H, $PhC{\equiv}CPh$)); $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6) δ −5.78, −5.38 ($SiMe_2$), 98.50, 101.82 (C^1), 108.35, 121.78, 122.07 $(C_5H_4)_2(\mu\text{-}SiMe_2)$, 141.03, 159.68 (${\equiv}CPh$), 140.08 ($C^1$), 139.20 ($C^1$), 131.82, 128.35, 128.94, 128.20, 128.06, 127.74, 127.56, 126.24 (${\equiv}CPh$). Anal. Calcd for $C_{26}H_{24}ClNbSi$: C, 63.41; H, 4.92. Found: C, 62.93; H, 4.94.

(20) Crystal data for **2**: $C_{16}H_{20}ClNbSi$, monoclinic, $P2_1/c$; $a = 11.5690(10)$, $b = 10.9508(7)$, $c = 14.3790(10)$ Å; $\beta = 108.910(11)°$; $V = 1723.4(12)$ Å^3; $Z = 4$; $D_{calc} = 1.421$ g·cm^{-3}; λ(Mo Kα) = 0.7107 Å; μ(Mo Kα) = 0.91 mm^{-1}; 293 K; Phillips PW 1100 diffractometer, graphite monochromator, yellowish crystal (0.18 × 0.15 × 0.20 mm); 2833 collected reflections ($2 \le \theta \le 25$), 2217 with $I > 2\sigma(I)$. No absorption correction was applied. The structure was solved by a combination of direct methods and Fourier synthesis and then refined by full-matrix least-squares (SHELXL-93). Non-hydrogen atoms were anisotropic, and hydrogen atoms were included in their calculated positions as fixed isotropic contributors. $R = 0.0666$, $R_w = 0.1320$, ratio data/parameters = 2833/188, GOF = 1.158, and largest difference peak and hole = 0.605 and −0.581 e/Å^3.

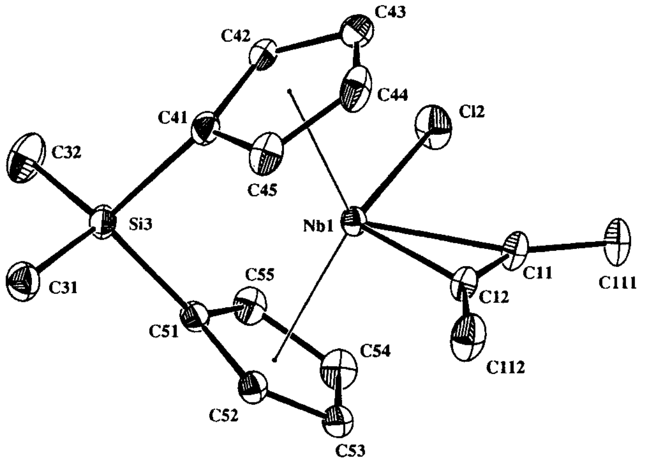

Figure 2. Structure of **2**, showing the atom-labeling scheme. Selected bond distances (Å) and angles (deg): Nb(1)–cent(1), 2.225(12); Nb(1)–cent(2), 2.272(12); average Nb(1)–C(41–45), 2.5326; average Nb(1)–C(51–55), 2.572; Nb(1)–Cl(2), 2.552(2); Nb(1)–C(11), 2.168(8); Nb(1)–C(12), 2.156(8); C(11)–C(12), 1.271(11); cent(1)–Nb(1)–cent(2), 130.0(5); cent(1)-Nb(1)–Cl(2), 100.7(3); cent(2)–Nb(1)–Cl(2), 105.7(3); cent(1)–Nb(1)–C(11), 115.1(5); cent(1)–Nb(1)–C(12), 103.1(5); cent(2)–Nb(1)–C(11), 110.6(5); cent(2)–Nb(1)–C(12), 103.0(5); C(11)–Nb(1)–Cl(2), 81.0(2); C(12)–Nb(1)–Cl(2), 114.9(2); C(11)–Nb(1)–C(12), 34.2(3); C(112)–C(12)–C(11), 146.1(8); C(111)–C(11)–C(12), 145.6(8); cent(1)–C(41)–Si(3), 160.3(11); cent(2)–C(5)–Si(3), 160.9(10); C(41)–Si(3)–C(51), 96.5(4) (cent(1) is the centroid of C(41)–C(45), and cent(2) is the centroid of C(51)–C(55)).

ously reported structures of *ansa*-niobocene complexes where the cyclopentadienyl rings also exhibit σ bonding to the metal.[7,9] The cent(1)–Nb–cent(2) angle of 130.0(5)° (cent(1) is the centroid of C(41)–C(45), and cent(2) is the centroid of C(51)–C(55)) is slightly greater than that observed for (η^5-$C_5H_4SiMe_3$)$_2$NbCl(PhC≡CPh) (cent(1)–Nb–cent(2) angle of 128.4°).[18] This indicates that bridging the cyclopentadienyl rings of the *ansa* ligand does not greatly affect their disposition with respect to the metal center. In addition, a lengthening of the C≡C bond of the alkyne (C(11)–C(12) bond length of 1.271(11) Å) and a significant deviation from linearity of the C–C≡C angles (C(111)–C(11)–C(12) angle of 145.6(8)° and C(112)–C(12)–C(11) angle of 146.1(8)°) with respect to the free alkyne are observed similar to that reported for (η^5-$C_5H_4SiMe_3$)$_2$NbCl(PhC≡CPh).[18] This reflects the effect of π-back-donation and indicates that the ligand MeC≡CMe behaves as a two-electron donor.

In conclusion, we describe in this paper a straightforward method for the preparation of a useful starting material, an *ansa*-niobocene complex, and the first determined X-ray structure of such a complex in which the cyclopentadienyl rings are bound only in an η^5-mode. Work in order to develop this chemistry is presently in progress.

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Supporting Information Available: Tables giving X-ray crystal structure and 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 **2** (8 pages). Ordering information is given on any current masthead page.

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