Synthesis and characterization of \( \eta^5 \)-cyclopentadienyl–silylallyl niobium and tantalum complexes

Pilar Nicola´s, Pascual Royo *

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Alcalá, Campus Universitario, E-28871 Alcalá de Henares, Spain

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Dedicated to Professor F.G.A. Stone in recognition of his outstanding contribution to organometallic chemistry

Abstract

Reaction of the disilylcyclopentadiene 1,1-\([\text{SiMe}_2(\text{CH}_2\text{CH} \equiv \text{CH}_2)\])_2\text{C}_5\text{H}_4\) with \(\text{NbCl}_5\) gave the new allylsilyl-substituted monocyclopentadienyl niobium complex \([\text{Nb}\{\eta^5-\text{C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH} \equiv \text{CH}_2)\}\text{Cl}_4]\). This compound was reacted with \(\text{LiNH}_2\text{Bu}\) or \(\text{NH}_2\text{Bu}\) to give the imido derivative \([\text{Nb}\{\eta^5-\text{C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH} \equiv \text{CH}_2)\}(\text{N}_2\text{Bu})\text{Cl}_2]\), which was further alkylated to the imido alkyl complexes \([\text{Nb}\{\eta^5-\text{C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH} \equiv \text{CH}_2)\}(\text{N}_2\text{Bu})\text{R}_2]\) (\(\text{R} = \text{Me}, \text{CH}_2\text{Ph}\)). Reaction of the imido complexes with the corresponding lithium cyclopentadienides gave the dicyclopentadienyl-imido complexes \([\text{M}\{\eta^5-\text{C}_5\text{R}_5\}\{\eta^5-\text{C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH} \equiv \text{CH}_2)\}(\text{N}_2\text{Bu})\text{Cl}\]\) (\(\text{M} = \text{Nb}, \text{Ta}; \text{R} = \text{H}, \text{Me}\)). Metallocene dichlorides \([\text{M}\{\eta^5-\text{C}_5\text{R}_5\}\{\eta^5-\text{C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH} \equiv \text{CH}_2)\}\text{Cl}_2]\) (\(\text{M} = \text{Nb}, \text{Ta}; \text{R} = \text{H}, \text{Me}\)) were easily prepared by reduction with \(\text{Na/Hg}\) and simultaneous transmetallation of \([\text{Ta}\{\eta^5-\text{C}_5\text{R}_5\}\text{Cl}_4]\) with \(\text{Li}\{\text{C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH} \equiv \text{CH}_2)\}\) and of \([\text{Nb}\{\eta^5-\text{C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH} \equiv \text{CH}_2)\}\text{Cl}_4]\) with \(\text{Li}\{\text{C}_5\text{R}_5\}\). All of the new compounds have been characterized by elemental analysis, and IR and NMR spectroscopy.

Keywords: Niobium; Tantalum; Imido; Cyclopentadienyl

1. Introduction

Important efforts have been made to elucidate the behavior of the alkene-alkyl cationic species responsible for the catalytic activity of group 4 metallocene complexes in Ziegler–Natta type polymerization of \(\alpha\)-olefins [1]. With this aim, we synthesized olefin-tethered group 4 metallocene complexes [2] containing the allylsilylcyclopentadienyl ligand and studied the coordination of its olefinic moiety. The metal–olefin interaction in these \(d^0\) metal compounds is essentially due to the weak \(\sigma\)-donation from the olefin \(\pi\)-bonding MO to the cationic metal center strengthened by a significant electrostatic contribution from the polarized olefinic system. These results encouraged us to prepare similar group 5 metal derivatives, which would allow comparison of the nature of the metal–olefin interaction of the related \(d^0\) and \(d^2\) metal complexes. The weakly coordinating properties reported [3] for the dicyclopentadienyl \([\text{MC}_5\text{R}_5]^+\) cations, which are stabilized by strong \(\alpha\)-agostic interactions [4], recommended the isolobal analogs [5–8], cyclopentadienyl imido compounds (a), as better models for \(d^0\), whereas the neutral dicyclopentadienyl metal(III) (b) derivatives were the most suitable models for \(d^2\) species, as shown in Scheme 1. The results of these studies have been reported [9] separately.

Both (a)– and (b)–type complexes may be easily accessible from the half-sandwich niobium and tantalum complexes \([\text{M}\{\eta^5-\text{C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH} \equiv \text{CH}_2)\}\text{Cl}_4]\) through...
conversion into the imido derivatives [M\{η⁵-SiMe₂(CH₂CH=CH₂)\}Cl₂(NBu)] and into the dicyclopentadienyl metal(IV) compounds [M(η⁵-C₅H₅)\{η⁵-SiMe₂(CH₂CH=CH₂)\}Cl₂], followed by further reduction by alkylation and reductive elimination of alkane. Here, we report the synthesis and structural characterization of these precursor chloro complexes and their alkylated derivatives.

2. Results and discussion

2.1. Synthetic results

Desilylation of silylcyclopentadienes by reaction with electrophilic metal halides is a convenient method [10] to prepare silylcyclopentadienyl niobium [11], tantalum [12] and group 6 metal [13] complexes. The selectivity of this reaction, when two different silyl groups are bound to the ring, is not only dependent on the nature of the silyl substituents but also on the metal halide.

The reaction of NbCl₅ with [1-SiMe₂(CH₂CH=CH₂)] [2] gave a mixture containing a 1:1 molar ratio of the already reported [Nb(η⁵-C₅H₅)\{η⁵-SiMe₂(CH₂CH=CH₂)\}Cl₂] [14] and [Nb(η⁵-SiMe₂(CH₂CH=CH₂)\}Cl₂] 1 regardless of the solvent or the reaction conditions used. Compound 1 could be separated by repeated recrystallization from toluene but always in low yield (< 30%) and containing small amounts of the other component. The same reaction with TaCl₅ took place with two different silyl groups of alkane. Here, we report the synthesis and structural characterization of these precursor chloro complexes and their alkylated derivatives.
unique component in 90% yield by a redistribution reaction when an equimolar mixture of 5 and 7 was heated in toluene at 120 °C. The alkyl complexes 6–8 were isolated as waxy brown air sensitive solids, very soluble in all organic solvents including hexanes. They were characterized by elemental analyses and NMR spectroscopy.

Similar alkylation using 1 equiv of Li(C5R5) (R = H, Me) gave the dicyclopentadienyl imido complexes [Nb(η5-C5R5)(η5-C5H4SiMe2(CH2CH=CH2)](NBu)Cl] (R = H 9, Me 10) isolated in 75% yield as yellow and waxy brown solids, respectively. The related tantalum complex 11 was isolated as a brown waxy solid in 70% yield by a similar reaction of the corresponding [Ta(η5-C5Me5)(NBu)Cl]2 with the lithium salt of the allylsilylcyclopentadienyl ligand. Complexes 9–11 were very soluble in all usual organic solvents including hexanes. They were identified by elemental analyses and NMR spectroscopy.

2.2. Structural studies

The metal(IV) complexes 2–4 are paramagnetic compounds with effective magnetic moments \( \mu_{\text{eff}} = 1.7–1.8 \) BM at 298 K similar to those found for related compounds.

All of the other metal(V) compounds were studied by \(^1\)H and \(^{13}\)C NMR spectroscopy and selected data are shown in Section 3. The tetrachloro (1), dichloro-imido (5) and dialkyl-imido (6–7) complexes are \( \pi \) donating molecules which show the expected \(^1\)H NMR spectra corresponding to an AA'BB' spin system for the ring protons. The typical spectral pattern of the allyl–dimethylsilyl group consists of two high field signals observed as one singlet for both equivalent silicon methyl groups and one doublet for the methylene silicon-bound group, together with three low field signals appearing as two doublets for the olefinic methylene group and one multiplet due to the internal olefinic proton. The ring proton resonances are shifted upfield for imido complexes (5–8) compared with the tetrachloro niobium derivative 1, whereas the resonances due to SiMe2, Si–CH2 and olefinic CH=CH2 protons of the dimethylsilyl-allyl group are shifted low field, the Si–CH2 being the most sensitive signals. These displacements are related to the stronger \( \sigma-\pi \) donating character of the imido ligand, causing the metal to require less electron density from the aromatic ring. The same behavior can be observed in the \(^{13}\)C NMR spectra, although smaller differences are found. The electron donating capacity of the imido ligand can be inferred from the \( \Delta \delta = \delta(\text{methyl C}) - \delta(\text{methyl C}) \) differences observed for the tert-butyl group in the \(^{13}\)C NMR spectra which are between 33.0 (6) and 39.7 (5), in the range accepted for a substantial \( \pi \) donating contribution (see Table 1). The \(^1\)H and \(^{13}\)C NMR spectra of complex 8 show similar resonances for the tert-butyl and olefin groups although the chiral character of the metal center makes all of the other substituents non-equivalent. Therefore, it shows two singlets for the methyl-silyl groups, two overlapped doublets for the methylene–silyl protons and two doublets for the methylene–benzyl protons. Consequently, there are four \(^1\)H multiplets and five \(^{13}\)C resonances for the silyl-substituted ring.

All of the dicyclopentadienyl imido complexes 9–11 are chiral asymmetric molecules which show the expected similar pattern observed for 8 in their \(^1\)H and \(^{13}\)C NMR spectra. The nature of these apparently 20-electron compounds has been reported previously for similar group 5 and 6 metal derivatives, which show nearly linear M–N–R imido ligands with the \( sp^2 \) hybridized nitrogen acting as a four-electron donor ligand. Theoretical investigation of the bonding in compounds of this type showed that the surplus electron pair is located in an essentially cyclopentadienyl-based orbital. We were not able to isolate single crystals appropriate for X-ray diffraction studies. Nevertheless, the \( \pi \) donating capacity of the imido ligand in complexes 9–11 can be estimated by the \( \Delta \delta \) values observed in their \(^{13}\)C NMR spectra for the tert-butyl substituent.

As shown in Table 1, complex 9 shows a value of \( \Delta \delta \) (40.0), even higher than that found for complex 5, indicating the strong \( \pi \) bonding contribution of the imido ligand. As expected, this contribution is lower for the niobium complex 10 (\( \Delta \delta = 38.5 \)) and even lower for the tantalum complex 11 (\( \Delta \delta = 33.7 \)) with its more donating Cp* ligand.

3. Experimental

Standard Schlenk procedures were used for all syntheses and sample manipulations. The solvents were
dried by standard methods (hexane over Na/K alloy, toluene and THF over sodium) and distilled under argon before use. Na, Hg, C6H6, SiMe2(CH2CH=CH2)Cl, SiMe2Cl, LinBu (1.6 M in hexane), TaCl5, NbCl5, NH2Bu, NEt3, MgCl(CH2Ph) (2 M in THF) and MgCuMe (3 M in THF) were obtained from Aldrich and used without further purification. Na(C5H5) [21], SiMe3Cl, Li[NH2]tBu, NEt3, MgCl(CH2Ph) (2 M in THF) and Li(C5H5) [24], [Ta(C5H5)Cl4] [25] and [Ta(N(C5H5)Cl2)3(C5Me5)]CI4 [23] were prepared as described previously. IR spectra were recorded on a Perkin-Elmer 583 spectrophotometer (4000–200 cm−1) as Nujol mulls between CsI pellets. 1H and 13C{1H} NMR spectra were recorded on a Varian VXR-300 Unity instrument in C6D6 solution at 300 K and chemical shifts are reported in δ units relative to the solvent signals (δH, 7.15, δC 128.00). C, H and N analyses were performed with a Perkin-Elmer 240 microanalyzer.

### 3.2. Preparation of [Nb[η5-C5H4SiMe2(CH2CH=CH2)]Cl2] (2)

Toluene (150 ml) was added to a mixture of I (1.38 g, 3.4 mmol) and Li(C6H5)2 (0.25 g, 3.4 mmol). This suspension was added to a 10% sodium amalgam (0.08 g, 3.4 mmol). The mixture was stirred for 16 h at room temperature. The resulting brown suspension was decanted and filtered through Celite, and the filtrate was concentrated to ca. 15 ml and cooled to −40 °C to give 2 as a dark brown solid. Yield: 0.93 g, 2.37 mmol (70%). IR (cm−1): 3074w, 1461m, 1050s, 804m, 1251s, 576m, 1627s, 960w, 489s, 285s. Elemental Anal. Calc. for C15H20Cl2SiTa (480.26): C, 37.51; H, 4.20. Found: C, 45.78; H, 5.10%.

### 3.3. Preparation of [Ta[η5-C5H4SiMe2(CH2CH=CH2)]Cl2] (R = H, 3; Me, 4)

Toluene (150 ml) was added to a mixture of [Ta[η5-C5H4SiMe2(CH2CH=CH2)]Cl2] (R = H, 1.68 g, 4.35 mmol; R = Me, 2.0 g, 4.35 mmol) and Li[C5H4SiMe2(allyl)] (0.74 g, 4.35 mmol). This suspension was added to a 10% sodium amalgam (0.1 g, 4.35 mmol). The mixture was stirred for 16 h at room temperature. The resulting brown or green suspension was decanted and filtered through Celite, and the filtrate was concentrated to ca. 15 ml and cooled to −40 °C to give 3 as a dark brown solid or 4 as dark green crystals.

Data for compound 3: Yield: 1.46 g, 3.04 mmol (70%). IR (cm−1): 3095w, 1461m, 1017s, 824s, 1250s, 1627s, 989m, 400w, 274s. Elemental Anal. Calc. for C15H20Cl2SiTa (480.26): C, 37.51; H, 4.20. Found: C, 37.65; H, 4.32%.

Data for compound 4: Yield: 1.79 g, 3.25 mmol (75%). IR (cm−1): 3080w, 1461s, 1029s, 812m, 1243s, 574w, 1628s, 918m, 444m, 274s. Elemental Anal. Calc. for C20H30Cl2SiTa (550.40): C, 43.64; H, 5.49. Found: C, 43.68; H, 5.65%.

### 3.4. Preparation of [Nb[η5-C5H4SiMe2(CH2CH=CH2)]Cl2(NtBu)] (5)

A hexane solution (50 ml) of LiNHtBu (0.3 g, 3.7 mmol) was added at −78 °C to a toluene suspension (50 ml) of I (1.5 g, 3.7 mmol) and NEt3 (0.52 ml, 3.7 mmol). The mixture was stirred for 15 h at room temperature. The resulting brown suspension was concentrated under reduced pressure and hexane (50 ml) was added. The suspension was filtered through Celite and the filtrate was concentrated to ca. 10 ml and cooled to −40 °C to give 5 as a yellow solid. Yield: 1.00 g, 2.51 mmol (70%). 1H NMR (C6D6): δ 0.29 (s, 6H, SiMe2), 1.06 (s, 9H, CMe3), 1.66 (d, 3J = 8.0 Hz, 2H, SiCH2), 4.85 (m, 2H, CH=CH2), 5.62 (m, 1H, CH=CH2), 6.09 (m, 2H, C5H4), 6.35 (m, 2H, C5H4);

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1 Quantitative yield by reaction of NH3tBu with LinBu.

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### Table 1

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13C NMR (C6D6): δ-2.8 (SiMe2), 24.1 (SiCH2), 30.4 (CMe2), 70.1 (CMe3), 114.3 (CH=CH2), 134.1 (CH=CH2), 110.3 (C6H4), 122.6 (C6H4), 124.5 (C6H4, C). IR (cm⁻¹): 2964m, 1450m, 1036s, 824m, 1256s, 1368s, 570m, 1626s, 925w, 425w, 374w. Elemental Anal. Calc. for C16H30NNbSi (357.41): C, 53.77; H, 8.46; N, 3.52. Found: C, 42.26; H, 6.07; N, 3.67%.

3.5. Preparation of [Nb(η³-C5H5)3]2CH=CH2]R2(NtBu) R = Me, 6; CH2Ph, 7

A THF solution of MgClR (R = Me, 2.3 ml, 6.8 mmol) was added at −78 °C to a hexane solution (50 ml) of 5 (1.37 g, 3.4 mmol). The mixture was stirred for 2 h at room temperature. The resulting brown suspension was decanted and filtered through Celite, and the filtrate was concentrated under reduced pressure to give 6 (reddish) and 7 (brown) as viscous products.

Data for compound 6: Yield: 0.85 g, 2.38 mmol (70%). 1H NMR (C6D6): δ 0.19 (s, 6H, SiMe2), 0.55 (s, 6H, NbMe2), 1.32 (s, 9H, CMe3), 1.63 (d, J = 7.3 Hz, 2H, SiCH2), 4.88 (s, 2H, CH=CH2), 5.73 (m, 1H, CH=CH2), 5.75 (m, 2H, C6H4), 6.05 (m, 2H, C6H4).

13C NMR (C6D6): δ-2.4 (SiMe2), -2.5 (SiMe2), 24.8 (SiCH2), 31.1 (CMe3), 68.0 (CMe3), 51.6 (NbCH2Ph), 113.7 (CH=CH2), 106.3 (C6H4), 143.7 (CH=CH2), 109.7 (C6H4), 111.8 (C6H4), 119.7 (C6H4), 118.5 (C6H4, C), 128.5; 127.8, 129.9; 131.5 (C6H4) IR (cm⁻¹): 3074s, 1449m, 1046m, 819m, 1247s, 1356s, 548m, 1620s, 929m, 431m, 353w, 375w. Elemental Anal. Calc. for C22H27ClNbSi (447.90): C, 59.00; H, 6.08. Found: C, 59.14; H, 6.21%.

3.7. Preparation of [Nb|η³-C5H5|3]2CH=CH2]R2(NtBu) (9)

Hexane (50 ml) was added to a mixture of 5 (0.4 g, 1.0 mmol) and LiC5H5 (0.072 g, 1.0 mmol) cooled to −78 °C. After stirring overnight at room temperature, the yellow suspension was decanted and filtered through Celite. The filtrate was concentrated to ca. 10 ml and cooled to −40 °C to give 9 as a yellow solid. Yield: 0.32 g, 0.75 mmol (75%). 1H NMR (C6D6): δ 0.33 (s, 3H, SiMe2), 0.40 (s, 3H, SiMe2), 0.97 (s, 9H, CMe3), 1.74 (m, 2H, SiCH2), 4.95 (m, 2H, CH=CH2), 5.76 (m, 1H, C6H4), 5.80 (m, 1H, CH=CH2), 5.84 (m, 1H, C6H4), 5.90 (s, 5H, CH3), 6.22 (m, 1H, C6H4), 6.28 (m, 1H, C6H4); 13C NMR (C6D6): δ-2.3 (SiMe2), -2.2 (SiMe2), 25.0 (SiCH2), 29.9 (CMe3), 69.9 (CMe3), 114.6 (CH=CH2), 105.3 (C6H4), 135.0 (CH=CH2), 113.6 (C6H4), 111.9 (C6H4), 121.7 (C6H4), 125.6 (C6H4), 118.9 (C6H4, C). IR (cm⁻¹): 3078m, 1450m, 1046s, 805w, 1243s, 1357s, 575w, 1628s, 897m, 433m, 319w. Elemental Anal. Calc. for C19H29ClNbSi (427.89): C, 53.33; H, 6.83; N, 3.27. Found: C, 53.51; H, 6.97; N, 3.41%.

3.8. Preparation of [Nb|η³-C5H5|3]2CH=CH2]R2(NtBu) (10)

THF (30 ml) was added to a mixture of 5 (0.5 g, 1.3 mmol) and Li(C5Me3) (0.18 g, 1.3 mmol) cooled to −78 °C. The mixture was stirred for 15 h at room temperature and the solution was filtered and concentrated under vacuum to give 10 as a brown viscous solid. Yield: 0.45 g, 0.90 mmol (70%). 1H NMR (C6D6): δ 0.42 (s, 3H, SiMe2), 0.50 (s, 3H, SiMe2), 1.09 (s, 9H, CMe3), 1.80 (d, J = 8.0 Hz, 2H, SiCH2), 1.80 (s, 15 H, C5Me3), 4.95 (m, 2H, CH=CH2), 5.54 (m, 1H, C6H4), 5.86 (m, 1H, C6H4), 5.86 (m, 1H, CH=CH2), 6.14 (m, 1H, C6H4), 6.39 (m, 1H, C6H4);
$^{13}$C NMR (C$_6$D$_6$): δ 2.5 (SiMe$_2$), −2.4 (SiMe$_2$), 12.7 (C$_5$Me$_5$), 25.3 (SiCH$_2$), 31.3 (CMe$_3$), 69.8 (CMe$_5$), 120.5 (C$_5$Me$_5$), 113.5 (CH$_3$CH$_2$), 108.8 (C$_5$H$_4$), 110.0 (C$_5$H$_4$), 135.5 (CH$_2$CH$_2$), 112.6 (C$_5$H$_4$), 114.3 (C$_5$H$_4$), 130.1 (C$_5$H$_4$). IR (cm$^{-1}$): 3075 vs, 1447 m, 1049 s, 1082 m, 1248 s, 1545 s, 572 w, 1629 s, 942 m, 432 m, 377 w.

Elemental Anal. Calc. for C$_{24}$H$_{39}$ClNNbSi (498.03): C, 30.70; H, 4.85; N, 2.86. Found: C, 30.72; H, 4.85; N, 2.86.

3.9. Preparation of $[Ta\{\eta^5-C_5H_4SiMe_2(CH_2CH=CH_2)\}Cl(NiBu)]$ (II)

A THF solution (10 ml) of LiC$_{5}$H$_{4}$SiMe$_2$(allyl) (0.18 g, 1.09 mmol) was added at −78 °C to a hexane solution (50 ml) of $[Ta\{\eta^5-C_5H_3Cl(NBu)\}]$ (0.50 g, 1.09 mmol). After stirring overnight, the orange suspension was decanted and filtered through Celite. The filtrate was concentrated under vacuum to give II as a brown viscous product. Yield: 0.42 g, 0.72 mmol (70%).

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References


    (c) M.V. Galakhov, M. Gómez, G. Jiménez, P. Royo, Organometallics 14 (1995) 2843;


    (d) A. Antiño, P. Espinosa, M. Fajardo, P. Gómez-Sal, C.


