▌ **Coordination Chemistry**

Cationic Niobium-Sandwich and Piano-Stool Complexes

Wiebke Unkrig, Fu Zhe, Razan Tamim, Friederike Oesten, Daniel Kratzert, and
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Abstract: The syntheses of the homoleptic bis(arene) niobium cations $[Nb(arene)_2]^+$ (arene = $C_6H_3Me_3$, C_6H_5Me) with 16 valence electrons and heteroleptic arene-carbonyl cations $[(CO)Nb(arene)_2]^+$ (arene = $C_6H_3Me_3$, C_6H_5Me) and $[(arene)M(CO)_4]^+$ (arene = $C_6H_3Me_3$, C_6H_6) obeying 18 valence electrons are described. Stabilization of these complexes was achieved by using the weakly coordinating anions $[Al(OR^F)_4]^-$ or $[F\{Al(OR^F)_3\}_2]^-$ (R^F = $C(CF_3)_3$). The limits of two synthesis routes starting from neutral Nb(arene)$_2$ (arene = $C_6H_3Me_3$, C_6H_5Me) or $[NEt_4][M(CO)_6]$ (M = Nb, Ta) were investigated. All compounds were analyzed by single crystal X-ray determination, vibrational and NMR spectroscopy. DFT calculations were executed to support the experimental data.

Introduction

In 1955, Fischer and Hafner published the first transition metal bis(arene) complex bis(benzene)chromium[1] and established one of the still most important synthesis routes for transition metal bis(arene) complexes. The Fischer–Hafner reduction of metal halides by Al/AlX$_3$ in presence of arene, as solvent and reactant, allowed for the synthesis of a variety of products. One example is the preparation of the first neutral Nb^0 derivative $[Nb(C_6H_3Me_3)_2]$,[2] which was previously only accessible using a vapor-metal technique.[3,4] Niobium derivates with weaker coordinating arenes like toluene, benzene or even aryl halides or the analogous tantalum derivates were inaccessible from the Fischer–Hafner procedure, but obtainable by the methodologically and experimentally very demanding vapor-metal method.[4]

Soon after the discovery of $[Cr(C_6H_6)_2]$, the cationic $[Cr(C_6H_6)_2]^+$ was published.[1,5] It appeared, that bis(arene) complexes are easily oxidized, but depending on the metal, in some cases loss of the arene ligands was observed.[5] Further cationic bis(arene) complexes, like $[Fe(arene)_2]^+$ (arene = C_6H_6, 1,3,5-Me$_3$C$_6$H$_3$, C_6Me$_6$), the paramagnetic 20 valence electron complex $[Co(Me_6C_6)_2]^+$[6] or $[Ti(MeC_6H_5)_2]^+$ containing a well-defined M^I (M = Fe, Co, Ti), were synthesized and their properties

investigated. The salt $[Nb(C_6H_3Me_3)_2][BPh_4]$ was also reported as product of the oxidation of $[Nb(C_6H_3Me_3)_2]$ with $[FeCp_2][BPh_4]$, but was only identified by further reaction with CO as $[Nb(C_6H_3Me_3)_2(CO)][BPh_4]$ shown by single crystal X-ray diffraction (SC-XRD).[7,8]

As a result of the possible applications of salts including homoleptic bis(arene) cations $[M(arene)_n]^+$ (n = 1–3) in arene functionalization, olefin oligomerization (M = Ga)[9] and as building blocks for organometallic pharmaceuticals (M = Re, Tc),[10] they are an important part of current research. The replacement of an arene ligand is the key for their application in the synthesis of organometallic compounds and the use as precursors for catalysts.[11] Recently, a variety of bis(arene) cobalt complexes (arene = $C_6H_3Me_3$, C_6H_6, FC_6H_5, $F_2C_6H_4$) were obtained from the homoleptic carbonyl salt $[Co(CO)_5][F\{Al(OR^F)_3\}_2]$ (R^F = $C(CF_3)_3$) as easily accessible Co^I source.[12]

The ligand exchange of CO for arenes often results in heteroleptic piano-stool complexes of their own interest. For example, $[Cr(arene)(CO)_3]$ occurs as intermediate of organic transformations at the chromium-coordinated aromatic ring[13] and $[(arene)Mn(CO)_3]^+$ salts are used in arene-functionalization of the coordinated arenes.[14]

Mass and IR spectra of piano-stool complexes $[(arene)M(CO)_4]^+$ of the group 5 metals niobium and tantalum, which are one topic of this work, were already published with the methylated arene ligands toluene, mesitylene, tetra- and hexamethylbenzene and with the counterion $[Al_2Br_6Cl]^-$.[7,15] However, the recently as a side project communicated cations $[(F_2C_6H_4)M(CO)_4]^+$ (M = Nb, Ta)[16] remain the only reported structurally characterized examples.

Here we present the structural investigations and spectroscopic analyses of the first fully characterized homoleptic bis(arene) niobium cations $[Nb(arene)_2]^+$ (arene = $C_6H_3Me_3$, C_6H_5Me), stabilized by the weakly coordinating anion $[F\{Al(OR^F)_3\}_2]^-$ (R^F = $C(CF_3)_3$). Attempts to synthesize bis(arene)

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niobium or tantalum cations with weaker coordinating arenes, led to the parent piano-stool complexes $[(C_6H_6)M(CO)_4]^+$ (M = Nb, Ta), which were analyzed by SC-XRD, NMR spectroscopy and vibrational analysis and are discussed in context with the data of $[(arene)M(CO)_4]^+$ (arene = $C_6H_3Me_3$, $F_2C_6H_4$, M = Nb, Ta).

Results and Discussion

Syntheses and molecular structures of 1–4

$Nb(C_6H_3Me_3)_2$,[7] $[NEt_4][M(CO)_6]$ (M = Nb, Ta),[17] $Ag[Al(OR^F)_4]$,[18] and $Ag[F\{Al(OR^F)_3\}_2]$[19] were synthesized according to literature. $Nb(C_6H_5Me)_2$, which was hitherto only obtained by metal vapor synthesis,[3,4] was likewise prepared based on the Fischer–Hafner synthesis.[1]

Oxidation of the isolated dark red powders of $Nb(arene)_2$ by Ag[A] in an o-dfb solution at room temperature led to the hitherto unknown salts $[Nb(arene)_2][A]$ (arene = $C_6H_3Me_3$, C_6H_5Me, A = $Al(OR^F)_4$, $F\{Al(OR^F)_3\}_2$) (Figure 1).

The products were crystallized by gas phase diffusion of n-pentane into an o-dfb solution at room temperature. The obtained yellow-brown crystals (Figure S49, Figure S51) were suitable for SC-XRD (Figure 3a, b). However, the crystal structures of the salts with the anion $[Al(OR^F)_4]^-$ were heavily disordered and are therefore not further discussed. Less disordered structures could be obtained from crystals of $[Nb(arene)_2][F\{Al(OR^F)_3\}_2]$ (arene = $C_6H_3Me_3$ (1), C_6H_5Me (2)). 1 crystallized in the orthorhombic space group Pbca, whereas crystals of 2 were triclinic in the space group $P\bar{1}$. Both cations 1^+ and 2^+ adopt an anti-configuration and are C_i symmetric. The arene ligands are aligned in parallel with a Ct-Nb-Ct angle (Ct = centroid) of 180° (Figure 2a, b).

Attempts to obtain the parent bis(benzene) complex $[Nb(C_6H_6)_2][F\{Al(OR^F)_3\}_2]$ on this route unfortunately failed due to the inaccessibility of the starting material $Nb(C_6H_6)_2$. Although a modified Fischer–Hafner synthesis resulted in an intense red solution, which was analogous to the synthesis of

$Nb(C_6H_3Me_3)_2$ and $Nb(C_6H_5Me)_2$, the product could not be isolated. All attempts of low-temperature crystallization or solvent removal resulted in decomposition to a brown solid. The direct addition of $Ag[F\{Al(OR^F)_3\}_2]$ to the red reaction solution also led to decomposition. Tantalum bis(arene) complexes of any kind were also inaccessible so far.

When the reactions were carried out under CO atmosphere, $[(CO)Nb(arene)_2][F\{Al(OR^F)_3\}_2]$ (arene = $C_6H_3Me_3$ (3), C_6H_5Me (4)) salts formed. This formation was instantly noticeable by a color change of the suspensions from brown to dark green (Figure S55). The products 3 and 4 were isolated by precipitation with n-pentane after the separation of the solution from Ag^0 (Figure 1). While 3 and 4 could only be crystallized when the excess CO gas was completely removed, in presence of CO the piano-stool complexes $[(arene)Nb(CO)_4][F\{Al(OR^F)_3\}_2]$ (arene = $C_6H_3Me_3$, C_6H_5Me) formed instead. These compounds are discussed in the next section. 3 and 4 were obtained as yellow-green crystals (Figure S53, Figure S55), which were suitable for SC-XRD. 3 crystallized in the monoclinic space group P_2/c and 4 in the triclinic space group $P\bar{1}$. The cations 3^+ and 4^+ are almost C_2 symmetric and adopt an anti-configuration with a Ct-Nb-Ct angle of 153.30(16) (3^+) or 157.20(12) (4^+) (Figure 2c, d). 1, 2, 3 and 4 were additionally analyzed by IR and NMR spectroscopy (Figure S1, Figure S2, Figure S8–Figure S30). IR and NMR spectra of 3 and 4 were measured from precipitated products.

Syntheses and molecular structures of 5a, b and 6a, b

We recently reported the synthesis of the piano-stool complexes $[(F_2C_6H_4)M(CO)_4][Al(OR^F)_4]$ (M = Nb, Ta),[16] prepared by the reaction of $[NEt_4][M(CO)_6]$ with two equivalents of $Ag[Al(OR^F)_4]$ in o-dfb. As expected, this synthesis route could be used to prepare further piano-stool complexes, like the hitherto unknown parent compounds $[(C_6H_6)M(CO)_4][Al(OR^F)_4]$ (M = Nb (6a), Ta (6b)), by adding an excess of the respective arene C_6H_6 or $C_6H_3Me_3$ (Figure 3, Figure 4). Suitable crystals for SC-XRD of $[(C_6H_3Me_3)M(CO)_4][Al(OR^F)_4]$ (M = Nb (5a), Ta (5b))
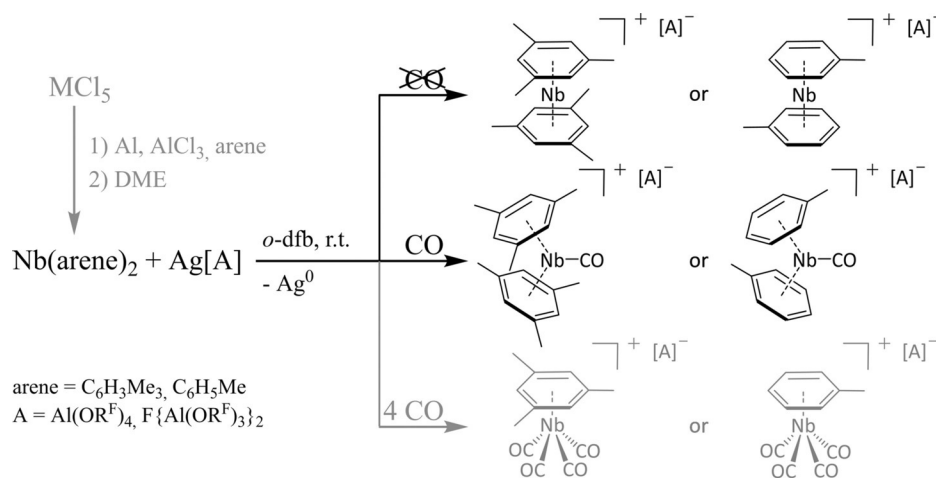

Figure 1. Synthesis route to $[Nb(arene)_2]^+[A]^-$, $[(CO)Nb(arene)_2]^+[A]^-$ (arene = $C_6H_3Me_3$, C_6H_5Me; A = $Al(OR^F)_4$, $F\{Al(OR^F)_3\}_2$) or $[(arene)Nb(CO)_4]^+[A]^-$. The synthesis of the starting material $Nb(arene)_2$ is included in grey.
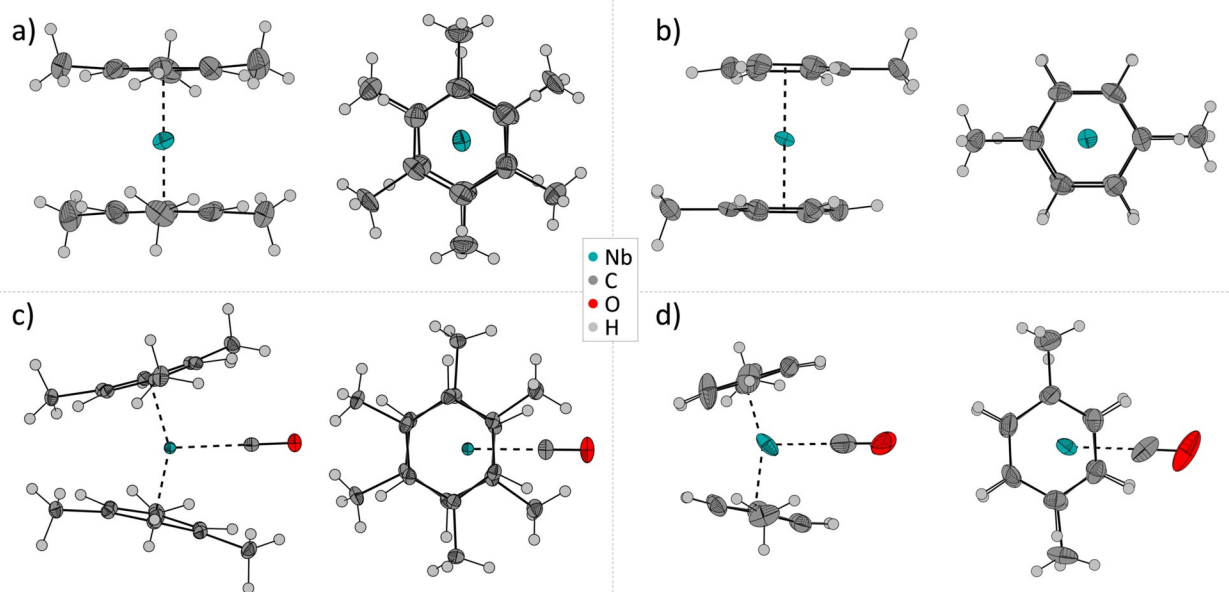
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Figure 2. Side and top view of the molecular structures of the cations 1^+ (a), 2^+ (b), 3^+ (c) and 4^+ (d). Ellipsoids are drawn at a 50% probability level. The counterions $[F\{Al(OR^F)_3\}_2]^-$ are omitted for clarity. Cation 1^+ and 4^+ include disordered $C_6H_3Me_3/C_6H_5Me$ ligands with 0.5:0.3:0.2 (1^+) / 0.6:0.4 (4^+) occupancy; only the main orientations are shown. The distance Nb-Ct (Ct = centroid) is included with dashed lines. Selected bond lengths [Å] and angles [°] $1^+/2^+$: Nb-Ct 1.840(3)/1.8395(15), av. Nb-C$_{(arene)}$ 2.317/2.317, Ct-Nb-Ct 180.00(13)/180.0(2); $3^+/4^+$: av. Nb-Ct 1.915/1.939, av. Nb-C$_{(arene)}$ 2.382/2.319, Ct-Nb-Ct 153.30(16)/157.20(12), Nb-C$_{(CO)}$ 2.1363(17)/ 2.153(4), C-O 1.137(2)/1.138(5). For full details, see Supporting Information (Table S8).
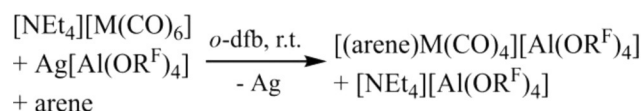
Figure 3. Synthesis route to $[(arene)M(CO)_4]^+[Al(OR^F)_4]^-$ (arene = $C_6H_3Me_3$ (**5**), C_6H_6 (**6**)).

and **6a**, **b** were obtained by gas phase diffusion of *n*-pentane into an *o*-dfb solution at room temperature. Compounds **5a**, **b** and **6a**, **b** crystallized in the orthorhombic space group *Pbca* (**5a**, **b** and **6a**) or *Pbcm* (**6b**). All cations are almost C_s symmetric, which is consistent with the density functional theory (DFT) calculations (BP86-D3(BJ)/def2-SVP). Note, that one equivalent of the co-product $[NEt_4][Al(OR^F)_4]$ also formed (Figure S62), which could not be separated from the products completely, due to very similar solubility and crystallization properties. The non-reactive, air- and water-stable $[NEt_4][Al(OR^F)_4]$ has previously been characterized in detail.[20] All spectroscopic signatures could be assigned with certainty and complexes **5a**, **b** and **6a**, **b** were unambiguously characterized. However, a great advantage of this synthesis route was the easily exchangeable arene ligand that allowed the synthesis of a variety of niobium and additionally tantalum piano-stool complexes.

[1] The compounds $[(F_2C_6H_4)M(CO)_4][Al(OR^F)_4]$ (M = Nb, Ta) were already published.[16] To simplify the following discussion with a clear assignment, they were included with the following numbering Scheme: **7** $[(F_2C_6H_4)M(CO)_4]$ $[Al(OR^F)_4]$, M = Nb (**7a**), Ta (**7b**).

However, our primary aim was the synthesis of niobium and tantalum bis(arene) cations, preferably with weaker coordinating arenes than $C_6H_3Me_3$ or C_6H_5Me. Therefore, **5**, **6** and the recently published[1] $[(F_2C_6H_4)M(CO)_4][Al(OR^F)_4]$ (**7**)[16] were dissolved in *o*-dfb and refluxed for two hours with an excess of the respective arene. The bright orange colored solutions turned darker, but the analysis only showed the starting materials and a small amount of a brown decomposition product. Ultra-sonication overnight and UV-irradiation for four hours led to the same result.

Vibrational characterization

Attenuated total reflection (ATR) FT-IR spectra of the isolated complexes **1**, **2**, **3** and **4** were measured (Figure S1, Figure S2). Bands of the cations 1^+ and 2^+ could not be unambiguously assigned, since the bands of the anion $[F\{Al(OR^F)_3\}_2]^-$ either lay in the same region or are much more intense. For **3** and **4** one CO vibration was detected at 2007 cm^{-1} (**3**, calc. 2009 cm^{-1} (a, 100%)) or 2034 cm^{-1} (**4**, calc. 2039 (a, 100%)), which was in good agreement with the calculated spectra at the BP86-D3(BJ)/def2-SVP level of theory (Figure S2). As expected, the toluene ligands donate less electron density than mesitylene, which is reflected in the blue shift of 27 cm^{-1} of the CO vibration band in **4** compared to **3**.

FT-IR and FT-Raman spectra of the isolated four-legged piano-stool complexes **5a**, **b**, **6a**, **b** and **7a**, **b** showed the same effect (Figure 5). The shift to higher wavenumbers of the all-symmetrical CO stretching frequency of **5** to **6** to **7** ($C_6H_3Me_3 \rightarrow C_6H_6 \rightarrow F_2C_6H_4$) is about 10 cm^{-1} for each substitution (Figure 5, Table 1). The exchange of the metal from

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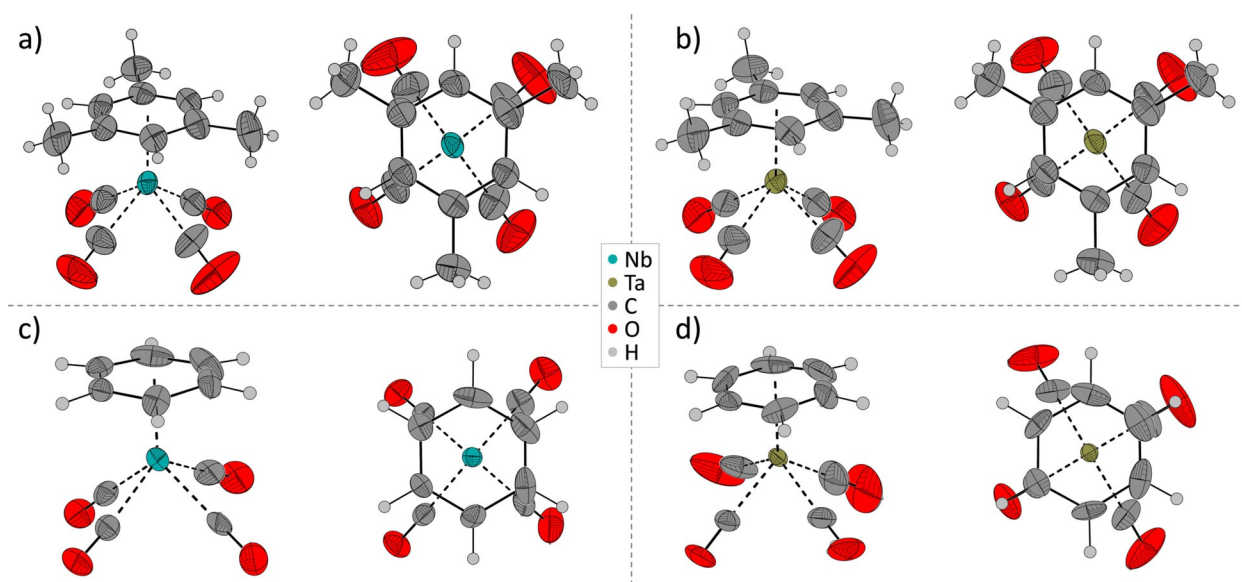**Chemistry
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Figure 4. Side and top view of the molecular structures of the cations **5a⁺** (a), **5b⁺** (b), **6a⁺** (c) and **6b⁺** (d). Ellipsoids are drawn at 50% probability level. The counterions [Al(OR^F)₄]⁻ are omitted for clarity. The distance Nb-Ct (Ct = centroid) is included with dashed lines. Selected experimental and calculated (BP86-D3(BJ)/def2-SVP, written in *italics*) bond lengths [Å]: **5a⁺**: Nb-Ct 2.032(2) (*2.041*), av. Nb-C(arene) 2.470 (*2.490*), av. Nb-C(CO) 2.089 (*2.091*), C-O 1.126 (*1.167*); **5b⁺**: Ta-Ct 2.0113(14) (*2.060*), av. Ta-C(arene) 2.454 (*2.506*), av. Ta-C(CO) 2.069 (*2.097*), C-O 1.134 (*1.158*); **6a⁺**: Nb-Ct 2.028(5) (*2.048*), av. Nb-C(arene) 2.460 (*2.493*), av. Nb-C(CO) 2.107 (*2.095*), C-O 1.136 (*1.155*); **6b⁺**: Ta-Ct 1.992(3) (*2.065*), av. Ta-C(arene) 2.436 (*2.508*), av. Ta-C(CO) 2.084 (*2.102*), C-O 1.134 (*1.156*). For full details, see Supporting Information (Table S9).
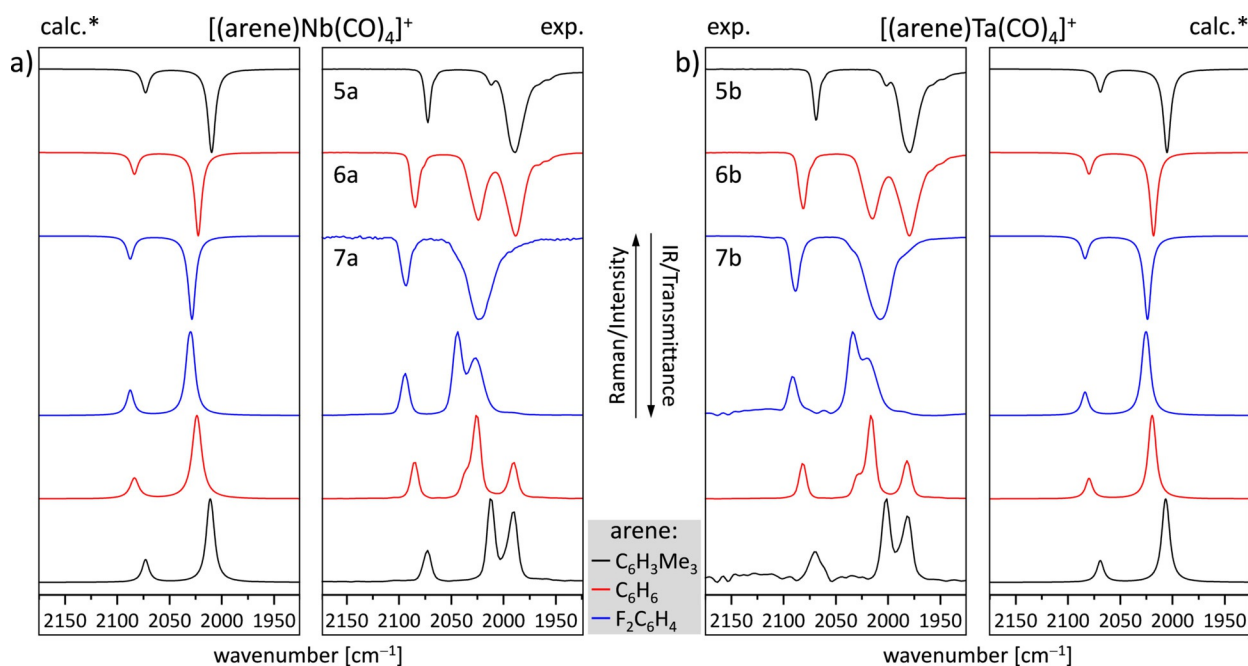

Figure 5. Experimental and calculated (*BP86-D3(BJ)/def2-SVP, scaling factor 0.9947) IR and Raman frequencies in the v(CO) [cm⁻¹] range of **5a**, **6a** and **7a** (a) and **5b**, **6b** and **7b** (b).

niobium to tantalum has only a small but consistent effect on the CO stretching frequencies, which can be noticed by a shift to lower wavenumbers of the all-symmetrical CO stretching frequency by about 4 cm⁻¹ (Figure 5, Table 1). Higher fluorinated arenes than *o*-dfb are not able to serve as ligands. We recently published a ⁹³Nb NMR investigation of an equilibrium between the piano-stool complex **7a** and [Nb(CO)₇][Al(OR^F)₄],

which showed that *o*-dfb is equally strong bound to niobium as CO ligands.[16]

All obtained vibrations were IR and Raman active and virtually at the same wavenumbers. IR and Raman spectra were calculated for all cations in C_s symmetry at the BP86-D3(BJ)/def2-SVP level of theory. With a line width of 10 cm⁻¹, two visually intense vibrations were obtained for each cation, whereas the

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Table 1. Experimental and calculated (*BP86-D3(BJ)/def2-SVP, scaling factor of 0.9947) IR and Raman frequencies of 5–7 in the $\nu(CO)$ [cm^{-1}] range. The relative intensities refer only to the CO vibration range. Thus, the most intensive CO band was set to 100%. All listed calculated CO vibrations are IR and Raman active. The intensities of the calculated vibrations refer to IR.

	IR	Raman	Calc.* C_s		IR	Raman	Calc.* C_s	Assign.
5a	2072 (s)	2073 (w)	2073 (a', 53%)	**5b**	2069 (s)	2069 (w)	2069 (a', 53%)	ν_s(CO)
	2012 (vw)	2012 (vs.)	2012 (a', 7%)		2001 (w)	2002 (vs.)	2007 (a', 3%)	ν_{as}(CO)
	1989 (vs.)	1991 (vs.)	2010 (a'', 100%)		1979 (vs.)	1981 (s)	2006 (a'', 100%)	ν_{as}(CO)
			2009 (a', 92%)				2004 (a', 96%)	ν_{as}(CO)
6a	2085 (s)	2085 (m)	2084 (a', 51%)	**6b**	2081 (s)	2082 (m)	2080 (a', 50%)	ν_s(CO)
		2035 (w, sh)	2025 (a'', 0%)		2015 (vs.)	2028 (w, sh)	2020 (a'', 0%)	ν_{as}(CO)
	2024 (vs.)	2026 (vs.)	2023 (a'', 99%)		1980 (vs.)	2016 (vs.)	2018 (a', 100%)	ν_{as}(CO)
	1988 (vs.)	1990 (m)	2022 (a', 100%)			1982 (m)	2018 (a'', 99%)	ν_{as}(CO)
7a	2093 (m)	2094 (m)	2088 (a', 52%)	**7b**	2089 (vs.)	2091 (m)	2084 (a', 51%)	ν_s(CO)
		2044 (vs.)	2032 (a'', 13%)			2034 (vs.)	2027 (a'', 10%)	ν_{as}(CO)
	2024 (vs.)	2027 (s)	2029 (a', 100%)		2007 (vs.)	2020 (s)	2024 (a', 100%)	ν_{as}(CO)
			2028 (a'', 85%)				2023 (a'', 88%)	ν_{as}(CO)

spectra of the experimentally investigated compounds show at least three vibration bands (Figure 5). Packing effects in the solid state, where the symmetry of the cations slightly deviates from the point group C_s, could account for this. The deviations were investigated with the program *Chemcraft* (Table S3). Compared to the experiment, the wavenumbers of the calculated all-symmetrical CO stretching frequency are constantly blue shifted by about 10 cm^{-1} with the exception of **7a** and **b**. Therefore, a scaling factor of 0.9947 was applied to all calculated CO vibrations, which was determined by the shift of the all-symmetrical vibration in **5a** (Table 1).

Theoretical investigation of 1 and 2

In the experimental crystal structures of **1** and **2**, the arene ligands of the cations **1$^+$** and **2$^+$** are oriented in parallel with a Ct-Nb-Ct angle of 180°. DFT calculated minimum structures with a singlet spin state of these cations showed an angle of 162.87° (**1$^+$**) or 162.52° (**2$^+$**), whereas the calculation of the cations with a triplet spin state resulted in minimum structures with almost parallel ligands (177.96° (**1**), 179.55 (**2**), Figure 6).

However, the triplet minimum structures lay energetically higher than the tilted singlet ones ($\Delta G^0 = +12.42$ kJ mol^{-1} (**1$^+$**), $+18.67$ kJ mol^{-1} (**2$^+$**), Table 2). The calculated formation thermodynamics collected in Table 2 appears reasonable, since all trends noticed from the experiments leading to the title compounds as described with Figure 2 and 3 were reproduced.

Thus, to estimate the required energy to tilt the ligands, the energetically lowest reaction path between the optimized singlet and triplet structure of the parent [Nb(C$_6$H$_6$)$_2$]$^+$ was determined by the woelfling module at the BP86-D3(BJ)/def2-SVP level of theory (Figure S64). [Nb(C$_6$H$_6$)$_2$]$^+$ was used as model molecule to exclude any influence of the degree of methylation of the arene ligands. Starting from the singlet minimum structure with a Ct-Nb-Ct angle of 162.24°, it was widened stepwise up to 179.91°, being the angle of the triplet minimum structure. After each step a single point calculation was executed. This reaction path was determined for the singlet and triplet spin state and the relative energy was plotted against the Ct-Nb-Ct angle (Figure S64). All obtained structures along the path with a singlet spin state were energetically lower than the structures with a triplet spin state. The structure with almost parallel arene ligands showed the lowest energy difference between the singlet and triplet spin state with less than 1 kJ mol^{-1} (Figure S63, Table S13).

These results led to the assumption, that **1** and **2** adopt a singlet spin state in solution, what was supported by experimental NMR measurements (cf. next section). The modest energy required to tilt the arenes suggests, that packing effects in the solid state are sufficient to achieve a parallel arrangement of the arenes. With this geometry, it might be assumed that cations with both a singlet and triplet spin state might be present. Yet, the comparison of experimental and calculated Nb-Ct distances (1.840 Å (XRD) vs. 1.834/36 Å (singlet) vs. 1.919/06 Å (triplet)) would contradict noticeable triplet contributions. Unfortunately, this could not be experimentally confirmed due to the insufficient stability of the complexes **1** and **2** that decompose at room temperature with formation of niobium metal, which would contaminate any magnetic measurements.

NMR spectroscopy

^{1}H and ^{13}C NMR measurements of the complexes **1**, **2**, **3** and **4** in *o*-dfb show significant shifts for the aromatic proton and carbon atoms to higher fields in comparison to the free arenes (Table S4). For the piano-stool complexes **5a** and **b** a moderate shift of these signals was obtained (Table S4) and in **6a** and **b**, and **7a** and **b** the peaks cannot be differentiated from the solvent signals. The ^{13}C, ^{19}F and ^{27}Al NMR spectra (cf. Supporting Information) show the intact anion [F{Al(OR^F)$_3$}$_2$]$^-$ (**1–4**) or [Al(OR^F)$_4$]$^-$ (**5–7**). In addition, ^{93}Nb NMR measurements were performed. In the spectra of **1** and **2** no signal was detected. A very broad peak was obtained for **3** (-2068 ppm, FWHM = 22171 Hz, whereas the spectrum of **4** only shows a weak but sharp signal at -1547 ppm (Figure S24)). Because of the chemical shift and nature, this signal can rather be assigned to the piano-stool complex [(C$_6$H$_5$Me)Nb(CO)$_4$]$^+$ than to **4$^+$**, which supports the previous discussion that a slight excess of CO gas

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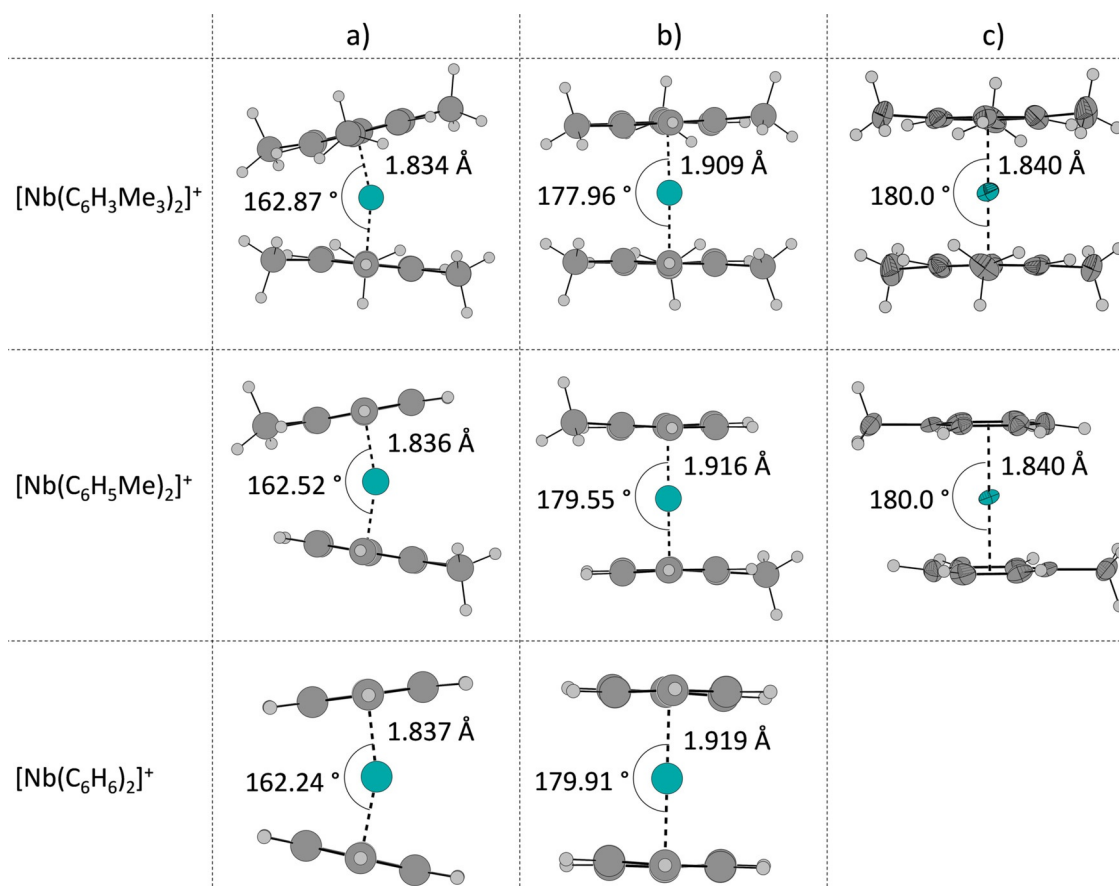doi.org/10.1002/chem.202003748

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Figure 6. Calculated singlet (a) and triplet (b) minimum structures of $[Nb(arene)_2]^+$ (arene = $C_6H_3Me_3$, C_6H_5Me, C_6H_6) at the BP86-D3(BJ)/def2-SVP level and experimental crystal structures (c) of $[Nb(arene)_2]^+$ (arene = $C_6H_3Me_3$, C_6H_5Me). Ellipsoids are drawn at 50 % probability level.

Table 2. Calculated reaction enthalpies (@BP86-D3(BJ)/def2-SVP) to estimate the relative stability of the reported products.

Reaction	$\Delta_r H^0_{(gas)}$ [kJ mol^{-1}]	$\Delta_r G^0_{(gas)}$ [kJ mol^{-1}]
$[Nb(C_6H_3Me_3)_2]^+$ singlet $(C_1) \rightarrow [Nb(C_6H_3Me_3)_2]^+$_triplet (C_1)	+15	+12
$[Nb(C_6H_5Me)_2]^+$ singlet $(C_1) \rightarrow [Nb(C_6H_5Me)_2]^+$_triplet (C_1)	+21	+19
$[Nb(C_6H_5Me)_2]^+$ singlet $(C_1) \rightarrow [Nb(C_6H_5Me)_2]^+$_triplet (C_2)	+21	+21
$[Nb(C_6H_6)_2]^+$_singlet $(C_1) \rightarrow [Nb(C_6H_6)_2]^+$_triplet (C_1)	+28	+28
$[Nb(C_6H_3Me_3)_2]^+$_singlet $(C_1) + CO (C_{6v}) \rightarrow [(CO)Nb(C_6H_3Me_3)_2]^+ (C_2)$	−140	−88
$[Nb(C_6H_5Me)_2]^+$_singlet $(C_1) + CO (C_{6v}) \rightarrow [(CO)Nb(C_6H_5Me)_2]^+ (C_2)$	−134	−85
$[(CO)Nb(C_6H_3Me_3)_2]^+ (C_2) + 3 CO (C_{6v}) \rightarrow [(C_6H_3Me_3)Nb (CO)_4]^+ (C_s) + C_6H_3Me_3 (C_1)$	−227	−173
$[(F_2C_6H_4)Nb(CO)_4]^+ (C_s) + C_6H_6 (C_s) \rightarrow [(C_6H_6)Nb(CO)_4]^+ (C_s) + F_2C_6H_4 (C_{2v})$	−35	−26
$[(C_6H_6)Nb(CO)_4]^+ (C_s) + C_6H_3Me_3 (C_1) \rightarrow [(C_6H_3Me_3)Nb(CO)_4]^+ (C_s) + C_6H_6 (C_s)$	−60	−54
$[(F_2C_6H_4)Nb(CO)_4]^+ (C_s) + C_6H_3Me_3 (C_1) \rightarrow [(C_6H_3Me_3)Nb(CO)_4]^+ (C_s) + F_2C_6H_4 (C_{2v})$	−95	−80
$[(F_2C_6H_4)Nb(CO)_4]^+ (C_s) + F_3C_6H_3 (C_s) \rightarrow [(F_3C_6H_3)Nb(CO)_4]^+ (C_1) + F_2C_6H_4 (C_{2v})$	+18	+19

in the reaction is sufficient to form the energetically more stable complex $[(C_6H_5Me)Nb(CO)_4]^+$ ($\Delta_r G^0 = -85.29$ kJ mol^{-1}, Table S12). This is also consistent with the sharp signals, which were obtained in a similar range for the piano-stool complexes **5 a$^+$** (−1512 ppm, Figure S31), **6 a$^+$** (−1555 ppm, Figure S40) and **7 a$^+$** (−1426 ppm, Figure S7).

^{93}Nb NMR calculations (@ BP86-D3(BJ)/x2c-TZVPPall) were executed using the experimental chemical shift of the stable **5 a$^+$** (−1512 ppm) as reference and compared with the experimentally obtained data. The calculated ^{93}Nb NMR shifts of the piano-stool complexes support the experimental data with a

maximum deviation of 58 ppm for **7 a$^+$** (Figure 7, Figure S7, Table S6).

Contrary to what is expected from the basicity of the arene ligands, the signal of **5 a$^+$** is shifted to lower field compared to $[(C_6H_5Me)Nb(CO)_4]^+$ and **6 a$^+$**. The same trend was obtained for **1$^+$**, **2$^+$** and $[Nb(C_6H_6)_2]^+$ and **3$^+$** and **4$^+$**. The shifts for the aromatic proton and carbon atoms compared to free mesitylene or toluene also follow this counterintuitive trend (Table S5). The niobium metal seems to have a stronger influence on the arenes with lower degree of methylation, whereas the bond lengths d_{Nb-Ct} are almost identical within the mole-
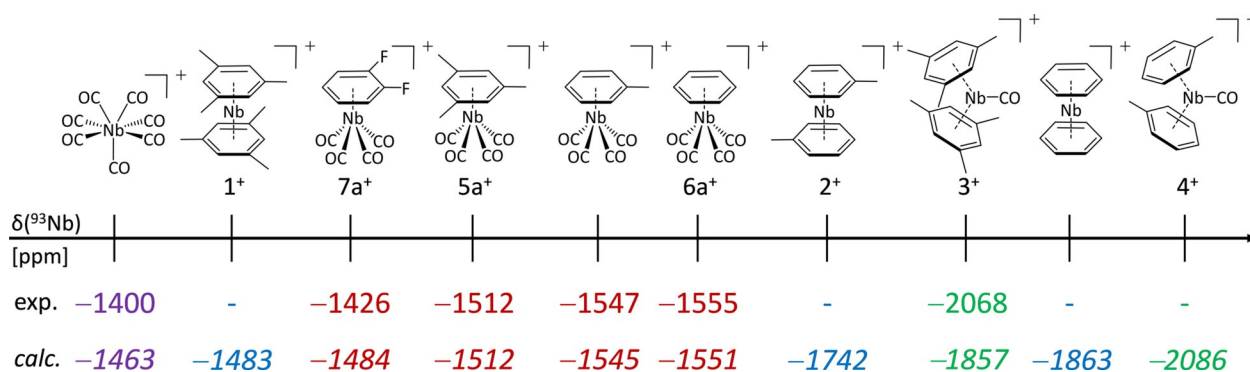
Figure 7. Experimental and calculated (BP86-D3(BJ)/x2c-TZVPPall) ^{93}Nb NMR chemical shifts plotted on a relative NMR scale in ppm.

cule groups. The effect of the ring current on such organometallic complexes is not trivial as has already been shown, for example, by theoretical investigations of complexes containing the Cr(CO)$_3$ fragment and bis(arene) chromium compounds.[21]

A further aspect might be a synergistic effect through the ligands, which was evident from the previously discussed vibrational spectra. Mesitylene donates the most electron density, which allows a stronger π-back-bonding from the niobium metal to the CO ligands. From toluene to benzene, less electron density is provided, so the π-back-bonding is decreased and the signals are shifted to higher field. When exchanging three CO for one mesitylene ligand (**5a** → **3**), the niobium atom is more strongly shielded and the electron density is only compensated by one CO ligand. The weaker synergistic effect reduces the stability of the complex (supported by DFT calculations, see Table S12) and shifts the ^{93}Nb NMR signal to a significantly higher field (−2068 ppm, Figure S19). The o-dfb ligand in **7a**, on the other hand, provides hardly any electron density, so that almost no back-bonding can be expected. As discussed before, o-dfb and CO ligands are equally strong bound to the niobium atom and therefore it is reasonable that the chemical shifts of [(F$_2$C$_6$H$_4$)Nb(CO)$_4$]$^+$ (−1426 ppm) and the previously published [Nb(CO)$_7$]$^+$ (−1400 ppm)[16] are quite similar (Figure S7).

^{1}H and ^{19}F signal integration in the spectra of **1** and **2** of the respective cation, anion and solvent signals resulted in an anion to cation ratio of 1:0.93 (**1**) and 1:0.75 (**2**). Due to the low concentration of sample **2**, partly decomposition of the product, noticeable by minor metal deposition and the imprecision of the signal integration, it can be assumed that **1$^+$** and **2$^+$** are only present in a detectable singlet spin state in solution.

Conclusions

The synthesis, structural and spectroscopic investigation of the homoleptic bis(arene) niobium cations [Nb(arene)$_2$]$^+$ (arene = C$_6$H$_3$Me$_3$, C$_6$H$_5$Me), stabilized by the weakly coordinating anion [F{Al(OR^F)$_3$}$_2$]$^-$ (R^F = C(CF$_3$)$_3$) were reported. DFT calculations showed a deviation of the Ct-Nb-Ct angle (Ct = centroid) of the experimental and calculated minimum structure in the singlet spin state. It turned out, that the calculation of the triplet

state resulted in a geometry, which matched the experimental data. A further investigation of the energy difference and required energy to tilt the arene ligands led to the conclusion that the molecules exist in the singlet state in solution. In the solid state, however, both the singlet and triplet state might be present as a consequence of packing effects.

The further reaction of [Nb(arene)$_2$][F{Al(OR^F)$_3$}$_2$] with CO resulted in the complexes [(CO)Nb(arene)$_2$][F{Al(OR^F)$_3$}$_2$], which were analyzed by SC-XRD, NMR spectroscopy and vibrational analysis.

The parent piano-stool complexes [(C$_6$H$_6$)M(CO)$_4$]$^+$ (M = Nb, Ta) were discussed in context with the data of [(arene)M(CO)$_4$]$^+$ (arene = C$_6$H$_3$Me$_3$, F$_2$C$_6$H$_4$, M = Nb, Ta). Experimental and calculated ^{93}Nb NMR data were investigated, which provides comparative values for further investigation of niobium compounds in solution.

In addition, the here reported complexes are probably excellent precursors for catalysts, since they already allow ligand exchange under mild conditions at room temperature in non-coordinating solvents. Using the presented synthesis route, the molecules can also be easily modified to suit the required properties. The 16 valence electron complexes **1$^+$** and **2$^+$** even directly provide a coordination site and are therefore also interesting candidates for the activation of small molecules. This, however, certainly needs to be further investigated.

Experimental Section

General methods

Full details of the employed methods and additional information are given in Supporting Information: synthesis, crystal structures and spectra of all compounds; DFT (density functional theory) calculated geometries, simulated spectra, calculated DFT and ab initio total energies.

Data availability

Atomic coordinates and structure factors for the crystal structure of all compounds: Deposition Numbers 2009845 (**1**), 2009843 (**2**), 2009849 (**3**), 2009846 (**4**), 2009844 (**5a**), 2009850 (**5b**), 2009847 (**6a**), 2009848 (**6b**) contain the supplementary

crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Conflict of interest

The authors declare no conflict of interest.

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