Arene Radical Cations

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Long-Lived Radical Cations of Monocyclic Arenes at Room Temperature Obtained by NbF_5 Acting as an Oxidizing Agent and Counterion Precursor**

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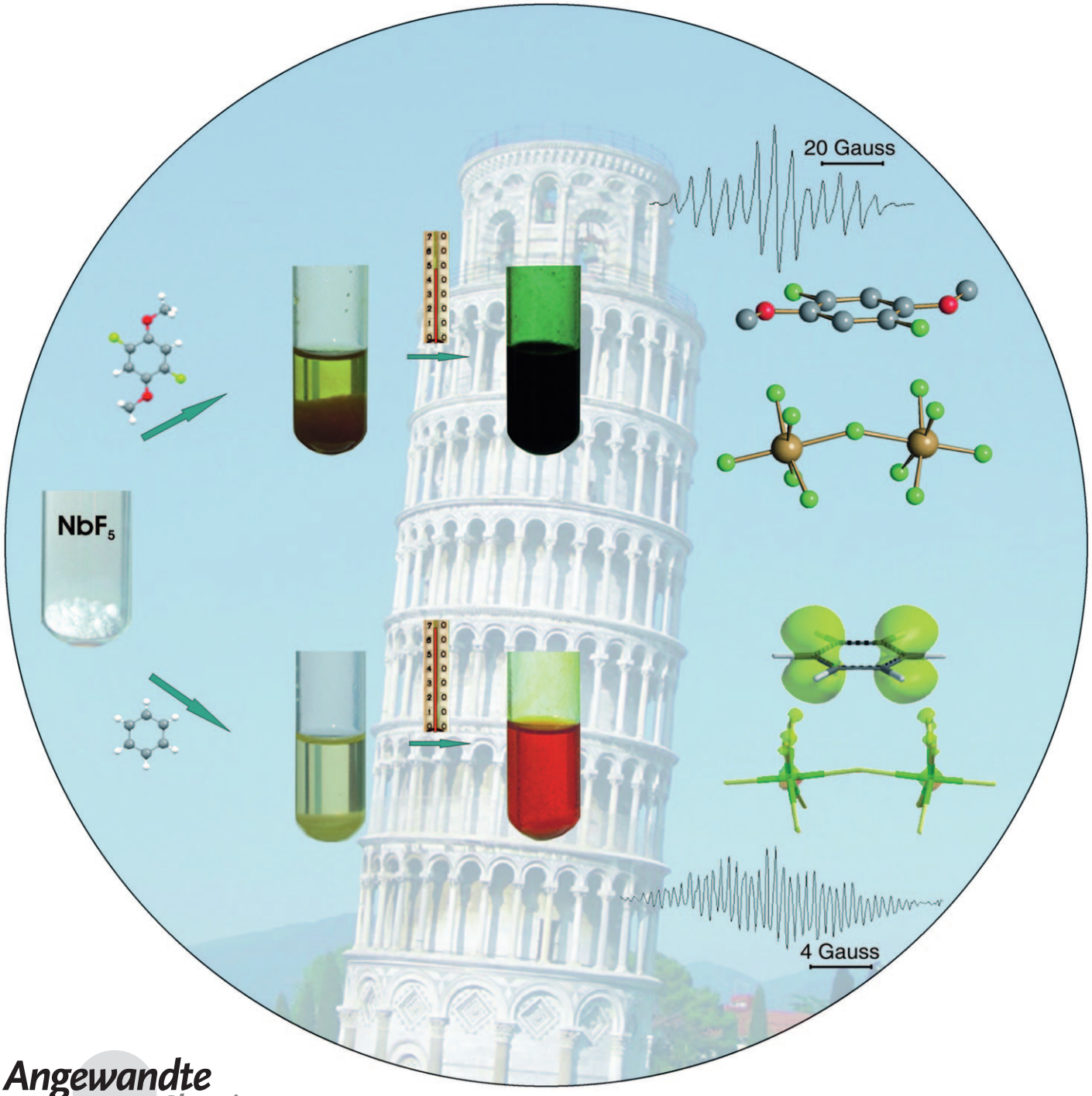


Radical carbocationic species have been intensively studied on account of the impressive number of fields in which they are involved.[1] In this context, the preparation of room-temperature long-lived radical cations by one-electron oxidation of monocyclic aromatic molecules, $[Arene]^+$, is still a difficult task. As a matter of fact, examples are not lacking of $[Arene]^+$ species that are fairly stable at room temperature,[2] yet their isolation in the solid state has remained an elusive goal.

It appears that the choice of the counterion represents a critical point for the detection of monocyclic arene radical cations, in view of their high susceptibility to undergo nucleophilic attack. The anions $[AsF_6]^-$, $[SbF_6]^-$, and $[Sb_2F_{11}]^-$ have been successfully used for this purpose,[3] while $[Os_2F_{11}]^-$ has been recently added to the list.[4]

In the framework of our research dealing with the chemistry of the pentahalides of Group 5 metals,[5] we have recently proved that niobium(V) halide anions are efficient for the stabilization at room temperature of crystalline salts containing unusual organic cations.[6] Herein, we describe the synthesis and the characterization of long-lived $[Nb_2F_{11}]^-$ salts at room temperature of radical cations of monocyclic arenes, including benzene. Our discovery started with a serendipitous event: we noticed that a yellow chloroform solution of $(NbF_5)_2[\mu\text{-}\kappa^2\text{-}1,4\text{-}F_2\text{-}2,5\text{-}(OMe)_2C_6H_2]$,[7] in the presence of excess NbF_5, turned emerald green on a hot summer day (temperature in the laboratory was ca. 30 °C). Then, a large crop of X-ray quality crystals consisting of $[1,4\text{-}F_2\text{-}2,5\text{-}(OMe)_2C_6H_2][Nb_2F_{11}]$, **1**, precipitated after some hours at −30 °C. Compound **1** (Figure 1)[8] represents a rare example of crystallographic characterization of a radical cation of a simple benzene derivative.

Short intermolecular contacts are present between the $[1,4\text{-}F_2\text{-}2,5\text{-}(OMe)_2C_6H_2]^+$ cation and the $[Nb_2F_{11}]^-$ anion, involving the fluorine atoms of the latter and, respectively, the $H\text{–}C_{sp^2}$ [2.254(3) Å], $H\text{–}C_{sp^3}$ [2.504(3)–2.561(3) Å], and C_{sp^2} [2.988(3)–3.159(3) Å] atoms of the former. The distance between the bridging fluoride F6 and the centroid of the six-membered ring of the nearest cation is 3.724(2) Å. Moreover, the Nb-F-Nb bridge is bent [Nb1-F6-Nb2 154.77(9)°], the bending angle resembling that observed in $[SeF_3][Nb_2F_{11}]$ of 166.3(2)°.[9]

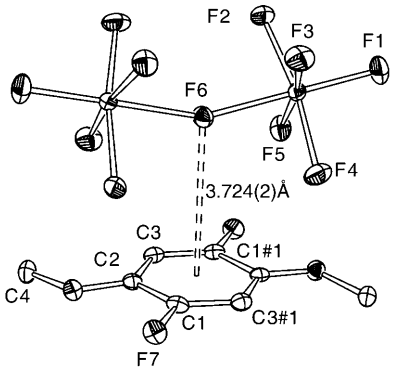
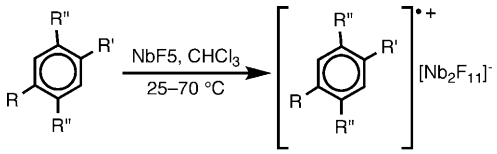


Figure 1. View of the molecular structure of **1** with key atoms labeled. Displacement ellipsoids are at the 50% probability level. Symmetry transformation used to generate equivalent atoms: #1 $-x+1/2,-y+1/2,z$. Selected bond lengths [Å] and angles [°]: C1–C2 1.432(2), C2–C3 1.405(2), C1–C3#1 1.358(2), C1–F7 1.3310(18), C2–O1 1.313(2), C4–O1 1.454(2); C3-C2-C1 118.53(16), C1#1-C3-C2 118.07(16), C3#1-C1-C2 123.38(15).

Deeply-colored chloroform solutions of **1** and of the radical cation containing species $[1,4\text{-}(OMe)_2C_6H_4][Nb_2F_{11}]$, **2**, and $[2,5\text{-}(OEt)_2(Me)C_6H_3][Nb_2F_{11}]$, **3**, could be obtained by treatment of the appropriate arene with a three-fold excess of NbF_5, see Scheme 1. Compounds **1**–**3** have been detected in



Compd.	R	R'	R''
1	F	F	OMe
2	H	H	OMe
3	H	Me	OEt
4	H	H	H

Scheme 1. Synthesis of compounds **1**–**4**.

good yields (ca. 70%) and survive in solution at 20 °C for days, under an argon atmosphere.[2a–c,e,f] Remarkably, the crystalline compound **1** lives at 20 °C for several days and represents a rare example of a radical cation salt of a monocyclic arene isolated at room temperature in the solid state.[10] By contrast with **1**, the salts **2** and **3** rapidly decompose in the solid state at 20 °C.

Compounds **1**–**3** have been characterized by spectroscopic and analytical techniques (see the Experimental Section). The ^{19}F NMR spectrum of **1** ($CDCl_3$, 213 K) shows broad peaks attributable to the $[Nb_2F_{11}]^-$ anion,[11] in accordance with the solid state features. The ^{19}F NMR spectra of **2** and **3** exhibit analogous peak patterns. Molar conductivities measured for **2** and **3** fall in the range typical of ionic niobium(V) derivatives.[5c] Furthermore, unambiguous EPR characterization of **1**–**3** has been carried out (see the Supporting Information).

To extend our scope to include non-alkoxy-substituted arenes, we studied the thermal reaction of benzene with NbF_5

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(1:3 molar ratio) in $CHCl_3$: an orange solution was obtained in a few minutes at about 70 °C. Then, EPR spectroscopy at room temperature indicated the formation of $[C_6H_6][Nb_2F_{11}]$, **4**, in small amounts, see Scheme 1. All attempts to increase the yield by tuning the reaction conditions (i.e. time and temperature) were unsuccessful.[12] Like **1**–**3**, compound **4** has been unambiguously characterized by EPR spectroscopy, see Figure 2. The formation of the $[C_6H_6]^+$ cation at 70 °C, albeit

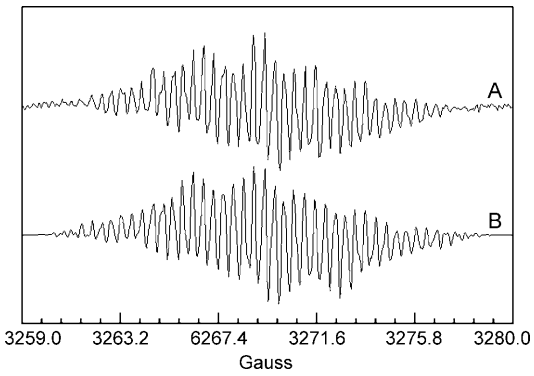

Figure 2. EPR spectrum ($CHCl_3$, 25 °C) of $[C_6H_6][Nb_2F_{11}]$, **4**. A: experimental; B: computer simulated.

in low yields, and its clear identification by EPR spectroscopy as a nontransient species in solution at room temperature,[13] is novel in the field of radical carbocation chemistry. In fact up to now, the benzene radical cation has been generated either by irradiation (γ, X-ray, UV) of Freon solid matrices at very low temperatures,[14] or within solid supports (e.g. alumina, zirconia, zeolites, and silica).[15]

The well-resolved EPR spectra of **1**–**4** in $CHCl_3$ solution (see Table 1SI, given as Supporting Information) are consistent with radical species that exhibit spin delocalization extended over the skeletons of the cation and the anion. The structures of compounds **1**–**4** have been optimized for the gas phase by DFT calculations at the B3LYP/6-31G** level.[16] Hence, the spin density distributions and the isotropic hyperfine coupling constants have been calculated by using the parallel Linux version of the Spartan '08 Program (the calculated spin density distribution for compound **4** is given in Figure 1SI in the Supporting Information,).[17] The calculated isotropic hyperfine coupling constants agree well with those obtained by computer simulation of the experimental EPR spectra in $CHCl_3$ solution.[18]

According to the computational analysis for compounds **1**–**4**, an interaction between the π-electron density of the cation and the bridging fluorine of the $[Nb_2F_{11}]^-$ anion exists. Furthermore, the ring···μ-F distance appears correlated to the Nb-F-Nb bending: more precisely, the latter increases on shortening the former. The ring···μ-F distances and Nb-F-Nb angles calculated for **1**–**4** in the gas phase are reported in Table 1, together with the corresponding experimental values found for **1** in the solid state (X-ray analysis).

The formation of arene radical cations by reaction of NbF_5 with monocyclic aromatic compounds must involve some reductive process. We have found that the oxidations take place with concomitant $NbF_5 \rightarrow NbF_4$ reduction [Eq. (1)].

Table 1: Cation–anion distance and Nb-F-Nb angle in compounds **1**–**4**.

Compound	$F_{bridging}$···ring distance [Å]		Nb-F-Nb angle [°]	
	exp.[a]	calcd.	exp.[a]	calcd.
1	3.724(2)	3.748	154.77(9)[a]	163.41
2	–	3.811	–	166.73
3	–	4.440	–	165.23
4	–	3.531	–	161.82

[a] Determined by X-ray analysis.

$$3\,NbF_5 + Arene \rightarrow [Arene][Nb_2F_{11}] + NbF_4 \quad (1)$$

We were successful in the identification of the Nb^{IV} product in the form of a bisphosphine adduct: the unprecedented compound $NbF_4(PEt_3)_2$, **5**,[19] was obtained upon addition of an excess of PEt_3 to the reaction mixtures containing **1**–**4**. The EPR spectrum of **5** (not shown) consists of a ten-line hyperfine pattern ($g_{iso} = 2.93114$, $A_{iso} = 64.2$ G), characterized by a strong linewidth alternation and by a dynamic frequency shift effect, in addition to a second- and third-order contribution.

It is noteworthy that the reported preparations of NbF_4 from NbF_5 require very drastic conditions,[20] likewise the one-electron oxidations of monocyclic arenes generally involve strong oxidizing systems.[2,4] In other words, the synthesis of **1**–**4** [Eq. (1)] is an unexpected redox process who's driving force is probably supplied by the formation of the dinuclear anion $[Nb_2F_{11}]^-$ and by the interaction established between this anion and the π-electron density of the cation. The presence of cation–anion interactions in **1**–**4** is clearly supported by both experimental (EPR spectroscopy and X-Ray analysis) and computational (DFT calculations) evidence, see above.

A further point which deserves comment is that NbF_5 plays a dual role in the synthesis of **1**–**4**, that is, it acts both as oxidant, by converting into NbF_4, and as Lewis acid by adding one fluoride ion [Eq. (1)]. The resulting $[NbF_6]^-$ combines with the third equivalent of NbF_5[21,22] to afford the counterion $[Nb_2F_{11}]^-$.[23]

Studies are in progress to extend the applicability of niobium and tantalum pentahalides as oxidizing agents of organic substrates, and to exploit further the capability of the $[M_2F_{11}]^-$ anions (M = Nb, Ta) to stabilize uncommon cationic species.

Experimental Section

Preparation and characterization of $[1,4\text{-}F_2\text{-}2,5\text{-}(OMe)_2C_6H_2]$-$[Nb_2F_{11}]$, **1**: A suspension of NbF_5 (0.140 g, 0.745 mmol) in chloroform (3 mL) was treated with $1,4\text{-}F_2\text{-}2,5\text{-}(OMe)_2C_6H_2$ (0.043 g, 0.247 mmol). The mixture was heated at about 40 °C for 20 min. The formation of an emerald green solution was noticed. The solution was maintained at −30 °C for 12 h, then **1** precipitated as a microcrystalline green solid. Yield: 0.045 g, 32 %. The microcrystalline compound partially degraded to brown solid after 10 days at 20 °C. Elemental analysis calcd for $C_8H_8F_{13}Nb_2O_2$: C 16.89, H 1.42; found: C 16.71; H 1.48; IR (solid state): $\tilde{\nu}$ = 3081w, 2985vw, 2942vw, 1620w,

1513vs, 1453m, 1412m, 1364w, 1269w, 1220s, 1187m, 1143m, 1017w, 946s, 894s, 865s, 839s, 741m, 705s cm^{-1}.

NMR characterization: $CDCl_3$ (1.0 mL), NbF_5 (0.050 g, 0.27 mmol) and 1,4-F_2-2,5-$(OMe)_2C_6H_2$ (0.016 g, 0.092 mmol) were mixed in a NMR tube. The tube was sealed, then the mixture was shaken to be homogenized. The tube was heated at ca. 45 °C (temperature of the external oil bath) for 10 min. Progressive dissolution of solid NbF_5 into an emerald green solution was observed. The ^1H NMR spectrum showed non-attributed broad signals. The ^{19}F NMR spectra appeared as follows: ^{19}F NMR ($CDCl_3$, 298 K): $\delta = 168.7$ (brs, $\Delta\nu_{1/2} = 1.5 \times 10^3$ Hz, $Nb_2F_{11}^-$), −135.5 ppm (brs, $\Delta\nu_{1/2} = 250$ Hz, *arom* C–F). ^{19}F NMR ($CDCl_3$, 213 K): $\delta = 189.2$ (br, $\Delta\nu_{1/2} = 1.7 \times 10^3$ Hz, 2F, $Nb_2F_{11}^-$), 160.0 (br, $\Delta\nu_{1/2} = 1.5 \times 10^3$ Hz, 8F, $Nb_2F_{11}^-$), −42.1 (br, 1.6×10^3 Hz, μ-F, $Nb_2F_{11}^-$), −136.7 ppm (br, $\Delta\nu_{1/2} = 250$ Hz, *arom* C–F). UV/VIS ($CHCl_3$): $\lambda_{max} = 610$ nm. X-ray quality crystals of **1** formed in 12 h on storage the tube at −30 °C.

EPR characterization: the synthesis of **1** was performed by the same procedure indicated for the NMR characterization, by using $CHCl_3$ as solvent. An aliquot (0.08 mL) of the resulting solution was transferred into an EPR tube; subsequent EPR integration analysis indicated formation of **1** in 75% yield.

Preparation and characterization in solution of [1,4-$(OMe)_2C_6H_4$][Nb_2F_{11}] **2**, and [2,5-$(OEt)_2(Me)C_6H_3$][Nb_2F_{11}] **3**: Solutions of **2** and **3** were prepared by procedures analogous to that described for **1**, that is, by reacting suspensions of NbF_5 (0.50 mmol) in chloroform (1.0 mL) with the appropriate arene (0.17 mmol), inside sealed NMR tubes. The preparation of green solutions of **2** required heating at 50 °C (temperature of the external oil bath) for 20 min, while red solutions of **3** were obtained at 25 °C in about 30 min. Compound **2**: yield (EPR, $CHCl_3$) = 72%; Λ_M($CHCl_3$, 298 K) = 2.6 $S\,cm^2\,mol^{-1}$; UV/VIS ($CHCl_3$): $\lambda_{max} = 589$ nm. Compound **3**: yield (EPR, $CHCl_3$) = 66%; Λ_M($CHCl_3$, 298 K) = 4.0 $S\,cm^2\,mol^{-1}$; UV/VIS ($CHCl_3$): $\lambda_{max} = 523$ nm. ^{19}F NMR spectra of **2** and **3** ($CDCl_3$, 213 K) exhibit broad resonances corresponding to $[Nb_2F_{11}]^-$, analogous to what was described for **1**.

Reactivity of NbF_5 with benzene: solution characterization of $[C_6H_6][Nb_2F_{11}]$, **4.** An orange solution containing **4** was obtained by reacting NbF_5 (0.60 mmol) with benzene (0.20 mmol) in $CHCl_3$ (0.70 mL), in a sealed NMR tube at 70 °C for 5 min. Yield (EPR, $CHCl_3$) = 9%.

Preparation and EPR characterization of $NbF_4(PEt_3)_2$, **5**: The addition of PEt_3 (0.60 mmol) to the reaction mixtures formed from NbF_5 (0.75 mmol)/arene (0.25 mmol) in $CHCl_3$ (0.60 mL) gave colorless solutions containing $NbF_4(PEt_3)_2$. The latter was identified by EPR analysis.

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