C_6F_5XeCl and $[(C_6F_5Xe)_2Cl][AsF_6]$: The First Isolated and Unambiguously Characterized Xenon(II) Chlorine Compounds[**]

Hermann-Josef Frohn,[*] Thorsten Schroer, and Gerald Henkel

$Xe^{II}-F$ compounds such as XeF_2 and salts with $[XeF]^+$ and $[Xe_2F_3]^+$ ions are thermally stable compounds.[1] However, the $Xe^{II}-Cl$ compounds $XeCl_2$ and XeClF have not been isolated. They have been synthesized under special low-temperature conditions such as in matrices. The matrix species $XeCl_2$ has been characterized by IR,[2] Raman,[2b, 3] and Mössbauer spectroscopy,[4] and the compound XeClF[5] by its IR and Raman spectra. In 1966 Meinert[6] obtained a sublimable solid from the high-frequency excitation (25 MHz, 150–350 mA, −80 °C) of a 1:1:1 mixture of Xe, F_2, and $SiCl_4$ or CCl_4. The negative-ion mass spectrum revealed the presence of, among others, a $[XeCl]^-$ fragment. On the basis of this information he assigned the constitution $XeCl_2$ to the product which was stable to 80 °C.

The results of our investigations on compounds containing the C_6F_5Xe fragment indicated that there was a realistic chance of obtaining thermally stable $Xe^{II}-Cl$ compounds with the C-Xe-Cl triad, since the $[C_6F_5Xe]^+$ ion **1** displays a smaller electrophilicity and a lower oxidation potential as, for example, $[FXe]^+$ in XeClF. Furthermore, our working hypothesis was supported by the observation that FXeOAc and $Xe(OAc)_2$ (OAc = acyloxy) are thermally less stable than the corresponding Xe–C compounds, that is $C_6F_5XeO_2CC_6F_5$ (**2**).[7]

Of the syntheses investigated for C-Xe-Cl compounds, only the two preparatively most significant are presented here. All synthesis concepts began not from Xe–Cl substrates, but from the electrophilic cation **1**, which was treated with Cl^- sources of reduced nucleophilicity. C_6F_5XeCl (**3**) is obtained in good yields (85 %) from the reaction of $[C_6F_5Xe][AsF_6]$ (**4**) with $4\text{-}ClC_5H_4N\cdot HCl$ (**5**) in CH_2Cl_2 at −78 °C [Eq. (1)].

$$\underset{\mathbf{4}}{[C_6F_5Xe][AsF_6]} + \underset{\mathbf{5}}{4\text{-}ClC_5H_4N\cdot HCl} \xrightarrow[-78\,^\circ C]{CH_2Cl_2} \underset{\mathbf{3}}{C_6F_5XeCl} + [4\text{-}ClC_5H_4N\cdot H][AsF_6]\downarrow \qquad (1)$$

The advantage of this method is that both substrates and the coproduct $[4\text{-}ClC_5H_4N\cdot H][AsF_6]$ are virtually insoluble in CH_2Cl_2, whereas the desired product **3** is soluble and can be isolated from the mother liquor in pure form. Compound **3** is obtained as a colorless solid and decomposes vigorously without melting at 36 °C with the formation of C_6F_5Cl and Xe gas. Solutions of **3** in the polar aprotic solvent CD_2Cl_2 are stable at −40 °C and decompose slowly at 0 °C. In the acidic solvent SO_2 a noticeable decomposition begins at −20 °C and is nearly complete after two hours at room temperature. The stability of **3** in the basic solvent MeCN is similar, in that after 2.5 h at 35 °C only 18 mol % **3** is still remaining in the solution.

Reaction of **4** with three equivalents of Me_3SiCl in CH_2Cl_2 at −40 to −30 °C results in $[(C_6F_5Xe)_2Cl][AsF_6]$ **6** in 91 % yield as an insoluble product (by-products: Me_3SiF, $AsCl_3$, and Cl_2) [Eq. (2)].

$$2\underset{\mathbf{4}}{[C_6F_5Xe][AsF_6]} + 6\,Me_3SiCl \xrightarrow[-78\,^\circ C]{CH_2Cl_2} \underset{\mathbf{6}}{[(C_6F_5Xe)_2Cl][AsF_6]}\downarrow + 6\,Me_3SiF + AsCl_3 + Cl_2 \qquad (2)$$

$[AsF_6]^-$ salts with a less electrophilic cation such as $Cs[AsF_6]$ in MeCN do not react with Me_3SiCl under analogous conditions. The reactivity of **4** according to Equation (2) is caused by the polarizing effect of **1** on the $[AsF_6]^-$ ion.[8] In the presence of bases such as MeCN a reaction with a different stoichiometry occurs [Eq. (3)].

$$2\underset{\mathbf{4}}{[C_6F_5Xe][AsF_6]} + Me_3SiCl + MeCN \xrightarrow[-78\,^\circ C]{CH_2Cl_2} \underset{\mathbf{6}}{[(C_6F_5Xe)_2Cl][AsF_6]} + Me_3SiF + AsF_5\cdot MeCN \qquad (3)$$

Use of excesses of Me_3SiCl with respect to the stoichiometries given in Equations (2) and (3) do not lead to the conversion of **6** into **3**.

Compound **6** is a colorless solid that decomposes vigorously at 100 °C. The decomposition product contains 44 mol % C_6F_5Cl (expected: 50 mol %), 32 mol % C_6F_6, and 24 mol % **4** [Eq. (4), (5)[8]].

$$\underset{\mathbf{6}}{[(C_6F_5Xe)_2Cl][AsF_6]} \xrightarrow{\triangle} C_6F_5Cl + Xe + \underset{\mathbf{4}}{[C_6F_5Xe][AsF_6]} \qquad (4)$$

$$\underset{\mathbf{4}}{[C_6F_5Xe][AsF_6]} \xrightarrow{\triangle} C_6F_6 + Xe + AsF_5 \qquad (5)$$

Compound **6** is insoluble in CH_2Cl_2 and soluble in MeCN. The thermal stability of **6** in MeCN is higher than that of **3**. After 16 h at 35 °C 95 mol % **6** have decomposed with formation of 24 mol % C_6F_5Cl and 71 mol % C_6F_5H. During the decomposition no individual ^{19}F NMR shift values could be detected for **6** and the MeCN-coordinated cation **1**. The decrease of **6** with simultaneous increase in **1** occurs with a high frequency shift of the signals of the F atoms bonded to the arene (see Table 1).

The crystal structure of $\mathbf{6}\cdot CH_2Cl_2$[9] was determined from colorless crystals, which were obtained by cooling a cold solution (−20 °C) of **6** in $MeCN/CH_2Cl_2$ to −40 °C. Compound $\mathbf{6}\cdot CH_2Cl_2$ crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell. The dichloromethane molecules have no relevant contacts to **6**. The $[(C_6F_5Xe)_2Cl]^+$ ion in $\mathbf{6}\cdot CH_2Cl_2$ shows no strong electrophile–nucleophile interactions with the $[AsF_6]^-$ ion—in contrast to the situations in **4**[8] and **2**.[7] The cation in **6** consists of two C_6F_5Xe fragments bridged through a chloride ion. The two linear C-Xe-Cl triads can be considered as asymmetric hypervalent three-center–four-electron bonding sequences and differ only marginally in terms of their overall bond lengths (Figure 1). Thus, a shorter C–Xe distance

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[*] Prof. Dr. H.-J. Frohn, Dr. T. Schroer, Prof. Dr. G. Henkel
Fachgebiet Anorganische Chemie der Universität
D-47048 Duisburg (Germany)
Fax: (+49) 203-379-3310
E-mail: frohn@uni-duisburg.de

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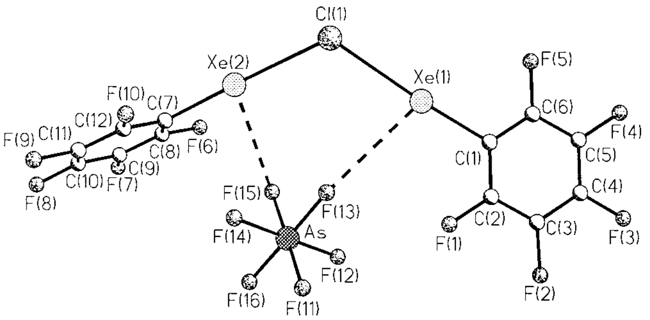

Figure 1. Structure of $\mathbf{6}\cdot CH_2Cl_2$ in the crystal. Selected distances [Å] and angles [°]: Xe(1)–Cl(1) 2.847(2), Xe(1)–C(1) 2.111(9), Xe(2)–Cl(1) 2.784(2), Xe(2)–C(7) 2.116(9); C(1)-Xe(1)-Cl(1) 176.0(3), C(7)-Xe(2)-Cl(1) 178.8(2), Xe(1)-Cl(1)-Xe(2) 116.96(8); selected intermolecular distances [Å]: Xe(1)–F(13) 3.372(7), Xe(2)–F(15) 3.158(7).

occurs with a longer Xe–Cl distance and vice versa. The two Xe–Cl distances are 2.847(2) and 2.784(2) Å, respectively, and are significantly shorter than the values reported for isoelectronic iodine–chlorine distances, for example, the 1:1 donor–acceptor complex from p-$C_6F_4I_2$ and $[NMe_4]Cl$ (3.153 and 3.134 Å)[10] and the intermolecular I–Cl distances in α-ICl (3.00 Å)[11] and β-ICl (2.939 Å).[12] The Xe-Cl-Xe angle in $\mathbf{6}\cdot CH_2Cl_2$ of 116.96(8)° is larger than that of the corresponding I-Cl-I angle in the above-mentioned complex (77.2°).[10] Weak Xe–F contacts occur between the $[AsF_6]^-$ ion and Xe(1) and Xe(2) in **6**, with the most significant (3.158(7) Å) being 9% shorter than the sum of the van der Waals radii (Xe–F) according to Bondi[13] (3.47 Å).

The multinuclear NMR data of **3** and **6** are given in Table 1. The comparison of the ^{19}F NMR spectroscopic data of the F atoms bonded to the arene in **3**, **6**, and **4** shows the effect of nucleophiles of varying strength (Cl^-, $ClXeC_6F_5$, and MeCN) on the C_6F_5Xe fragment. The stronger the nucleophile interacts with Xe^{II}, the weaker is the polarizing effect that is exerted from the Xe center onto the fluoroaromatic moiety. As the nucleophile–electrophile interaction becomes stronger, the $^{3}J_{\mathrm{F,Xe}}$ coupling constant increases. The influence of the solvent, both on the chemical shifts and on the $^{3}J_{\mathrm{F,Xe}}$ coupling constant, can be shown by changing to acidic solvents. Compounds **3**, **6**, and **4**, also differ significantly in terms of the ^{13}C NMR shift values of C(1) as well as in terms of the $^{1}J_{\mathrm{C,Xe}}$ and $^{2}J_{\mathrm{C(1),F}}$ coupling. The ^{129}Xe shift values reveal a systematic change in the shielding from **4** to **6** to **3** in accord with the increasing interaction with the nucleophile.

Table 1. ^{129}Xe, ^{19}F, and ^{13}C NMR data of **3**, **6**, and **4**.[a]

^{129}Xe	**3**	CD_2Cl_2/ – 60 °C	– 4116.5 (t, $^{3}J_{\mathrm{Xe,F}} = 95$, $\tau_{1/2} = 58$ Hz)
	6	CD_3CN/ – 40 °C	– 3937.6 (s, $\tau_{1/2} = 196$ Hz)
	4	CD_3CN/ – 40 °C*	– 3807.8 (t, $^{3}J_{\mathrm{Xe,F}} = 69$ Hz)
^{19}F	**3**	CD_2Cl_2/ – 60 °C	– 130.84 (m,[b] $^{3}J_{\mathrm{F,Xe}} = 94.2$ Hz, o-F), – 146.21 (tt, $^{3}J_{\mathrm{F,F}} = 21.0$, $^{4}J_{\mathrm{F,F}} = 3.1$ Hz, p-F), – 155.49 (m, m-F)
	3	EtCN/MeCN(3/1)/ – 60 °C*	– 131.03 (m,[b] $^{3}J_{\mathrm{F,Xe}} = 94.1$ Hz, o-F), – 147.51 (tt, $^{3}J_{\mathrm{F,F}} = 20.3$, $^{4}J_{\mathrm{F,F}} = 3.5$ Hz, p-F), – 156.97 (m, m-F)
	3	SO_2/ – 70 °C*	– 129.84 (m,[b] $^{3}J_{\mathrm{F,Xe}} = 86.4$ Hz, o-F), – 146.21 (t, $^{3}J_{\mathrm{F,F}} = 18.5$, $^{4}J_{\mathrm{F,F}} = 3.1$ Hz, p-F), – 155.70 (m, m-F)
	6	CD_3CN/ – 40 °C	– 128.57 (m,[b] $^{3}J_{\mathrm{F,Xe}} = 81.4$ Hz, o-F), – 144.28 (tt, $^{3}J_{\mathrm{F,F}} = 20.2$, $^{4}J_{\mathrm{F,F}} = 3.8$ Hz, p-F), – 155.50 (m, m-F), – 64.27 (1:1:1:1-q, $^{1}J_{\mathrm{F,As}} = 927.0$ Hz, $[AsF_6]^-$)
	4	CD_3CN/ – 40 °C*	– 125.45 (m,[b] $^{3}J_{\mathrm{F,Xe}} = 67.8$ Hz, o-F), – 141.83 (tt, $^{3}J_{\mathrm{F,Xe}} = 20.2$, $^{4}J_{\mathrm{F,F}} = 5.4$ Hz, p-F), – 154.69 (m, m-F), – 64.29 (1:1:1:1-q, $^{1}J_{\mathrm{F,As}} = 929.7$ Hz, $[AsF_6]^-$)
^{13}C	**3**	CD_2Cl_2/ – 60 °C	101.57 (t,[b] $^{1}J_{\mathrm{C,Xe}} = 208.1$, $^{2}J_{\mathrm{C,F}} = 29.1$ Hz, C(1)), 137.62 (dm, $^{1}J_{\mathrm{C,F}} = 260.7$ Hz, C(3,5)), 142.62 (dm, $^{1}J_{\mathrm{C,F}} = 250.3$ Hz, C(2,6)), 143.26 (dtt, $^{1}J_{\mathrm{C,F}} = 259.6$, $^{2}J_{\mathrm{C,F}} = 13.4$, $^{3}J_{\mathrm{C,F}} = 4.6$ Hz, C(4))
	6	CD_3CN/ – 40 °C	92.91 (t,[b] $^{1}J_{\mathrm{C,Xe}} = 194.6$, $^{2}J_{\mathrm{C,F}} = 27.2$ Hz, C(1)), 138.49 (dm, $^{1}J_{\mathrm{C,F}} = 256.4$ Hz, C(3,5)), 143.68 (dm, $^{1}J_{\mathrm{C,F}} = 253.0$ Hz, C(2,6)), 144.84 (dtt, $^{1}J_{\mathrm{C,F}} = 254.2$, $^{2}J_{\mathrm{C,F}} = 13.5$, $^{3}J_{\mathrm{C,F}} = 3.1$ Hz, C(4))
	4	CD_3CN/ – 40 °C*	82.16 (t,[b] $^{1}J_{\mathrm{C,Xe}} = 117.4$, $^{2}J_{\mathrm{C,F}} = 25.6$ Hz, C(1)), 137.79 (dm, $^{1}J_{\mathrm{C,F}} = 258.3$ Hz, C(3,5)), 143.37 (dm, $^{1}J_{\mathrm{C,F}} = 257.2$ Hz, C(2,6)), 144.82 (dtt, $^{1}J_{\mathrm{C,F}} = 260.7$, $^{2}J_{\mathrm{C,F}} = 13.2$, $^{3}J_{\mathrm{C,F}} = 4.1$ Hz, C(4))

[a] Measured with a Bruker-AVANCE-DRX-500 instrument, the measurements marked with an asterisk were recorded with a Bruker-WP-80-SY instrument; δ(Xe) relative to $XeOF_4$, 24 °C, δ(F) relative to CCl_3F with C_6F_6 as internal standard and δ(C) relative to TMS with the respective solvent as internal standard. In parentheses after the δ values, information on the signal multiplicity, the coupling constant J [Hz], and the signal assignment. [b] With ^{129}Xe satellites.

Experimental Section

Pentafluorophenylxenon(II) chloride **3**: Compound **4** (223 mg, 0.46 mmol) was suspended at – 78 °C in CH_2Cl_2 (1 mL) and treated under vigorous stirring with **5** (69 mg, 0.46 mmol). After 3 h the suspension was centrifuged at – 78 °C, the mother liquor was decanted and the colorless residue was washed with CH_2Cl_2 (1 mL). Both CH_2Cl_2 phases were combined, CCl_3F (3 mL) was added, and the mixture was stored for 12 h at – 78 °C. This led to the precipitation of a small amount of the originally dissolved coproduct $[4\text{-}C_5H_4NH][AsF_6]$. The mother liquor was decanted and evaporated to dryness at – 60 to – 50 °C and 0.1 hPa. Compound **3** (130 mg, 0.39 mmol) was isolated in 85% yield. M.p. 36 °C (decomp). NMR: see Table 1.

μ-Chlorobis[pentafluorophenylxenon(II)]hexafluoroarsenate **6**: Compound **4** (216 mg, 0.44 mmol) was suspended at – 40 °C in CH_2Cl_2 (5 mL) and treated with Me_3SiCl (144 mg, 1.33 mmol). The suspension was stirred for 4.5 h at – 40 to – 30 °C. The mother liquor turned yellow and the originally pale yellow solid became colorless. The suspension was centrifuged at – 78 °C, the mother liquor was decanted, and the colorless solid was washed with cold CH_2Cl_2 (– 78 °C, 3 × 2 mL) and then dried at – 40 °C and 0.1 hPa. Yield of **6**: 166 mg (0.20 mmol, 91%). M.p. 100 °C (decomp). NMR: see Table 1; Raman (glass capillary): $\tilde{\nu} = 1418$ (22.6), 1286 (11.1), 1085 (20.6), 784 (63.5), 490 (58.4), 278 (12.8), 197 (100) (ν_{as}(Xe–C)), 181 (82.4) (ν_s(Xe–C)), 128 cm^{-1} (13.5).

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[9] Crystal structure analysis: Siemens P4RA four-circle diffractometer, $Mo_{K\alpha}$ irradiation ($\lambda = 0.71073$ Å), graphite monochromator, rotating anode generator, scintillation counter, 150 K, empirical absorption corrections, SHELX97 programs, direct methods, least-squares refinement (F^2), a scaling factor, an isotropic extinction parameter. $C_{13}H_2F_{16}Cl_3AsXe_2$, formula weight 906.02, monoclinic, space group $P2_1/c$, $a = 8.391(2)$, $b = 20.588(5)$, $c = 13.541(3)$ Å, $\beta = 96.55(2)^\circ$, $V = 2323.99$ Å^3, $Z = 4$, $\rho_{calcd} = 2.589$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 4.804$ mm^{-1}, transmission range 0.280–0.229, crystal dimensions ca. $0.52 \times 0.24 \times 0.19$ mm, ω scan, $2\Theta_{max} = 52^\circ$ ($+h,+k,\pm l$), 4602 symmetry-independent reflections, $R1 = 0.0513$ for 3536 observed reflections ($I > 2\sigma(I)$), $wR2(F^2) = 0.1238$ (all data), 318 variables, all heavy atoms anisotropic, H atoms on idealized positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-121788. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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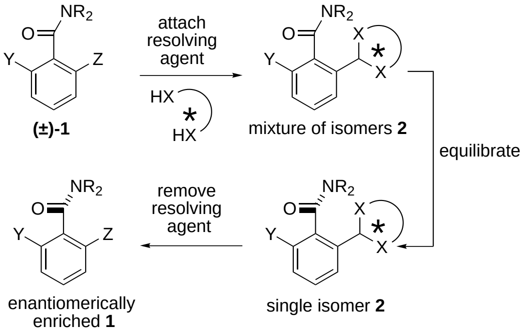
Enantioselective Synthesis of Atropisomeric Amides by Dynamic Resolution: Thermodynamic Control with a Proline-Derived Diamine Resolving Agent**

Jonathan Clayden* and Lai Wah Lai

Enantiomerically pure atropisomers, widely used as chiral ligands for metal-promoted asymmetric reactions, have generally been obtained for practical purposes by resolution and not by enantioselective synthesis.[1, 2] While there are a number of useful enantioselective routes to atropisomeric biaryls,[3] the enantioselective synthesis of non-biaryl atropisomers[4] is an unexplored area. Enantiomerically pure anilides have been derived from the chiral pool,[5, 6] and other enantiomerically pure non-biaryl atropisomers have been resolved—classically,[7, 8] by chromatography on a chiral stationary phase,[9–11] or kinetically.[12, 13] The only truly enantioselective synthesis of non-biaryl atropisomers is that of Koide and Uemura,[14] who used the desymmetrization of an arene–tricarbonylchromium complex to make aromatic amides related to **1** (see Scheme 1) in enantiomerically pure form.

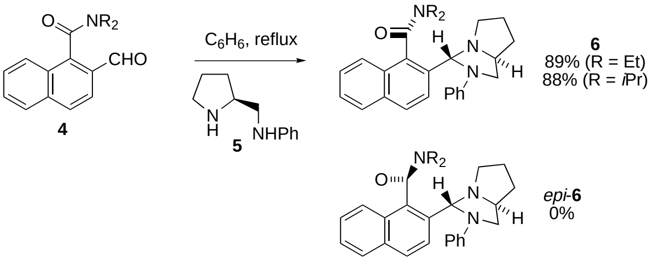
Here we describe our own enantioselective synthesis of atropisomeric aromatic amides **1**, which we have already shown to be powerful tools for the diastereoselective synthesis of racemic compounds.[15] Our strategy is outlined in Scheme 1. We aimed to start with the racemic amide (±)-**1**, to which we would attach an enantiomerically pure resolving agent to give a mixture of atropisomeric diastereoisomers **2**. We would then exploit the thermal instability of the conformation of the Ar–CO bond of **2**, equilibrating the mixture of diastereoisomers to a single isomer in a thermodynamically controlled process. The resolving agent would then be removed, leaving **1** in enantiomerically enriched form.



Scheme 1. Dynamic resolution of atropisomeric amides.

In the event, this approach proved highly successful. We chose to start with two naphthamides **4** (see Scheme 2) bearing CHO as the group Z, which led to problems later, as described below, but which allowed us to make the starting material by ortholithiation/DMF quench of the parent naphthamides.[16, 17] Furthermore, it allowed us to use, as the resolving agent, diamine **5**,[18] which is available from proline in four steps.

Refluxing **4** with **5** in benzene or toluene for 24 h gave the aminals **6** in excellent yield (Scheme 2), and quite remarkably both were formed with greater than 90:10 diastereoselectivity (by NMR spectroscopy). After chromatography on neutral alumina, pure diastereoisomers **6** were isolated in 88% (R = *i*Pr) and 89% yield (R = Et). The stereochemistry of **6** (R = *i*Pr) was proved by X-ray crystallography (see Figure 1).



Scheme 2. Atroposelective formation of aminals.

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[*] Dr. J. P. Clayden, L. W. Lai
Department of Chemistry
University of Manchester
Oxford Road, Manchester M13 9PL (UK)
Fax: (+44) 161-275-4939
E-mail: j.p.clayden@man.ac.uk

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