poor (ca. 18% of the initial intensity). This result can be ascribed to the smaller stability of $[Pd^{IV}Cl_2(en)_2]$ at elevated temperatures, with the complex being readily reduced to a $Pd^{II}(en)_2$ species by oxidation of the coordinating chloride ion.[8]

In the case of $[Ni(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ in chloroform (3×10^{-4} M), the recovery of intervalence electron transfer absorption after heating was inferior to that observed for $[Pd(en)_2][PdCl_2(en)_2](\mathbf{1})_4$. Only approximately 50% of the initial intensity was recovered after cooling the 60 °C solution to room temperature,. However, reversible thermochromism was observed for $[Pd(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ in chloroform (4×10^{-4} M). When a solution of this complex was heated to 60 °C (Figure 4b), the UV absorption decreased to 17% of the initial intensity without changing the peak position. The original intensity was restored upon cooling to room temperature, and this reversible change was possible even after three thermal cycles. Figure 1e shows an electron micrograph of $[Pd(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ after cooling. Rectangular nanocrystals (length: ca. 1400–2000 nm, width: ca. 80–200 nm) are abundant. These nanostructures are more developed than those before the heat treatment (Figure 1b). It is clear that this regular supramolecular structure is formed by self-assembly of thermally dissociated component complexes.

In conclusion, it is established that formation of amphiphilic supramolecular assemblies is a general route to stabilize one-dimensional, halogen-bridged mixed-valent complexes in organic media. The combination of metal ions significantly alters their spectral properties and morphologies, which gives rise to a wide spectrum of one-dimensional electronic systems in the solution phase. These new findings offer a new basis for research on molecular wires.

Experimental Section

The synthesis of sodium dihexadecyl sulfosuccinate (Na-**1**) was described previously.[9] Ethylenediamine complexes and chloro-bridged mixed-valence complexes were prepared according to the literature.[10] Elemental analyses (calcd (found)): $[Pd(en)_2][Pt(en)_2Cl_2](\mathbf{1})_4$ ($C_{152}H_{308}N_8O_{28}S_4Cl_2$-PdPt): C 57.11 (56.80), H 9.71 (9.68), N 3.51 (3.45); $[Ni(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ ($C_{152}H_{308}N_8O_{28}S_4Cl_2NiPt$): C 57.97 (57.31), H 9.86 (9.81), N 3.56 (3.45); $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ ($C_{152}H_{308}N_8O_{28}S_4Cl_2Pt_2$): C 55.57 (55.06), H 9.45 (9.38), N 3.41 (3.32); $[Pd(en)_2][Pd(en)_2Cl_2](\mathbf{1})_4$ ($C_{152}H_{308}N_8O_{28}S_4Cl_2Pd_2$): C 58.74 (58.11), H 9.99 (10.09), N 3.61 (3.52). UV/Vis absorption spectra were obtained using a JASCO V-570 spectrophotometer. Transmission electron microscopy (TEM) was conducted on a Hitachi H-600 instrument. Samples were readily dispersed in chloroform (0.3 mM) by ultrasonication (Branson Sonifier Model 185) for 0.5–1 min at 0 °C, and were dropped on a carbon-coated Cu grid. The Cu meshes were subjected to TEM observation with an acceleration voltage of 75 kV and magnifications of 5000–20000.

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The First Organoxenon(IV) Compound: Pentafluorophenyldifluoroxenonium(IV) Tetrafluoroborate**

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The preparative chemistry of the noble gases is based on their binary fluorides. Of the compounds derived from the three known xenon fluorides XeF_2, XeF_4, and XeF_6, relatively few Xe^{IV} species have been prepared to date.[1] The bonding systems that have been observed are limited to Xe^{IV}–F and Xe^{IV}–O compounds (XeF_4, $[XeF_3]^+$, $[XeF_5]^-$, $XeOF_2$, $[XeOF_3]^-$, $Xe(OTeF_5)_4$, $XeF_3(OIOF_4)$). Important aspects of the reactivity of the parent compound XeF_4 are its fluoride-donor and -acceptor and oxidative-fluorinating abilities. The latter is intermediate to those of the other xenon fluorides: $XeF_6 > XeF_4 > XeF_2$. The fluoride-donor ability of XeF_4 is much lower than that of either XeF_2 or XeF_6.

Since 1989 an increasing number of organoxenon(II) compounds have been prepared, mainly in the form of cationic xenonium compounds [OrgXe][X] (Org = aryl,[2] alkenyl,[3] and alkynyl[4]) but also as molecular species such as C_6F_5XeCl.[5] In most cases the Xe^{II}–C bond formation occurs through nucleophilic substitution with organoboranes [xenodeborylation: Eq. (1)] and in some specific cases through electrophilic substitution on electron-poor aromatic compounds [xenonylation: Eq. (2)].[6]

$$XeF_2 + Org{-}BX_2 \rightarrow [Org{-}Xe][BF_2X_2] \quad (1)$$

$$X{-}Xe{-}Y + C_6H_x(CF_3,F)_{6-x} \rightarrow [(C_6H_{x-1}(CF_3,F)_{5-x})Xe][X] + HY \quad (2)$$

We have now been able to apply an optimized form of the xenodeborylation procedure successfully to XeF_4. Because of

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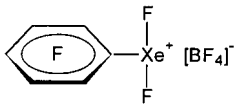
the increased oxidation potential of XeF_4 compared to XeF_2, oxidatively resistant reactants and by-products with electron-poor organic groups were required. The use of $B(C_6F_5)_3$, which was successful in the fluoroaryl substitution of XeF_2,[7] had to be ruled out because the nucleophilic and easily oxidizable anion $[(C_6F_5)_2BF_2]^-$ results from the aryl transfer. The problem of oxidizable by-products was overcome by using the recently accessible $C_6F_5BF_2$,[8] which yields $[BF_4]^-$ as the by-product. Furthermore the Lewis acidity of $C_6F_5BF_2$ is appropriate for the fluoroaryl substitution on XeF_4 (sufficient polarization of the hypervalent F-Xe-F bond, but no complete abstraction of a fluoride ion). If the reaction conditions are too acidic, oxidation of the aromatic system takes place. In addition to using the right aryl transfer reagent the solvent also had to be carefully selected. The basic solvent MeCN hindered the nucleophilic substitution to the point that no product **1** could be observed. Dichloromethane is a suitable solvent for strongly oxidizing nonmetal fluorides, based on previous work on fluoroaryl substitution on BrF_3[9] and BrF_5.[10] Additionally CH_2Cl_2 greatly facilitates the isolation of insoluble saltlike products. Pentafluorophenylboron difluoride (**3**) reacts smoothly with a suspension of xenon tetrafluoride (**2**) in CH_2Cl_2 at $-55\,^\circ C$ to yield the first organoxenon(IV) compound, pentafluorophenyldifluoroxenonium(IV) tetrafluoroborate (**1**), in nearly quantitative yield [Eq. (3)]. Salt **1** is a yellow solid which decomposes above about $-20\,^\circ C$. It is insoluble in CH_2Cl_2 and dissolves well in MeCN, forming a bright yellow solution.

$$\underset{\mathbf{3}}{C_6F_5BF_2} + \underset{\mathbf{2}}{XeF_4} \xrightarrow[CH_2Cl_2]{-55\,^\circ C} \underset{\mathbf{1}}{[C_6F_5XeF_2][BF_4]} \qquad (3)$$

The Xe atom in the $[C_6F_5XeF_2]^+$ cation is surrounded by two nonbonding and three bonding electron pairs, for which the VSEPR model predicts a φ-trigonal-bipyramidal arrangement resulting in a T-shaped molecular geometry (Scheme 1). The cation is isoelectronic with neutral $C_6F_5IF_2$. A comparison of the ^{19}F NMR spectroscopic data of the two species shows a significant high-frequency shift for the *p*- and *m*-F atoms in the aromatic part of the cation, even in basic solution (Table 1).



Scheme 1. Salt **1** with the T-shaped arylxenon-ium(IV) cation.

The ^{19}F NMR spectrum of salt **1** in a 1:1 mixture of CH_3CN and CD_3CN at $-40\,^\circ C$ consists of resonances at -29.54 (XeF_2), -125.51 (*o*-F), -134.97 (*p*-F), -153.44 (*m*-F), and -149.01 ppm ($[BF_4]^-$). The XeF_2 resonance shows satellites corresponding to one-bond scalar coupling to ^{129}Xe (26.44% natural abundance; $I = 1/2$) with $^1J(^{19}F,^{129}Xe) = 3893$ Hz. This ^1J value is comparable to that of XeF_4 itself ($^1J(^{19}F,^{129}Xe) = 3908$ Hz); however, the resonance of **1** is more shielded than that of **2** in MeCN at $-40\,^\circ C$ ($\delta = -19.08$). The ^{129}Xe NMR spectrum of **1** (CH_3CN/CD_3CN 1/1) consists of a triplet at $\delta = -1706.5$ ($^1J(^{129}Xe,^{19}F) = 3892$ Hz), which is significantly shielded compared to that of XeF_4 ($\delta = 316.9$, $^1J(^{129}Xe,^{19}F) = 3895$ Hz; MeCN, $24\,^\circ C$).[11] This difference in chemical shifts between **1** and **2** is consistent with that observed between $[C_6F_5Xe]^+$ ($\delta = -3807.8$) and XeF_2 ($\delta = -1784.5$). The

Table 1. ^{129}Xe, ^{19}F, ^{13}C, and ^{11}B NMR data of **1**.[a]

^{129}Xe NMR: $\delta = -1706.5$ (t, $\tau_{1/2} = 206$ Hz, $^1J(^{129}Xe\text{-}^{19}F) = 3892$ Hz)

^{19}F NMR: $\delta = -29.54$ (s, $\tau_{1/2} = 20$ Hz, 2F, XeF_2 with ^{129}Xe satellites, $^1J(^{19}F\text{-}^{129}Xe) = 3893$ Hz), -125.51 (m,[b] 2F, *o*-F), -134.97 (m,[b] 1F, *p*-F), -153.44 (m, 2F, *m*-F), -149.01 (s, $\tau_{1/2} = 82$ Hz, 4F, $[BF_4]^-$)

^{13}C NMR: $\delta = 121.86$ (m, C-1), 143.28 (dd, $^1J(^{13}C\text{-}^{19}F) = 268.5$ Hz, $^2J(^{13}C\text{-}^{19}F) = 16.2$ Hz, C-2,6) 138.25 (dm, $^1J(^{13}C\text{-}^{19}F) = 267.8$ Hz), 148.54 (dm, $^1J(^{13}C\text{-}^{19}F) = 273.8$ Hz)

^{11}B NMR: $\delta = -1.21$ (s, $\tau_{1/2} = 18$ Hz)

for comparison:

$[C_6F_5Xe]^+$:[c]

^{19}F NMR: $\delta = -125.15$ (2F, *o*-F), -141.86 (1F, *p*-F), -154.69 (2F, *m*-F)

$C_6F_5IF_2$:[c]

^{19}F NMR: $\delta = -123.02$ (2F, *o*-F), -144.55 (1F, *p*-F), -156.87 (2F, *m*-F), -161.24 (2F, IF_2)

[a] Measured with a Bruker AVANCE-DRX-500 instrument; δ(Xe) relative to $XeOF_4$, $24\,^\circ C$; δ(F) relative to CCl_3F with C_6F_6 as internal standard; δ(C) relative to TMS with the respective solvent as a internal standard; δ(B) relative to $BF_3 \cdot OEt_2$. Information on the signal multiplicity, the coupling constant *J* [Hz], and the signal assignment are given in parentheses after the δ values. [b] Unresolved signal. [c] Data from the conversion of **1** with C_6F_5I, measured with a Bruker WP-80-SY instrument.

^{13}C NMR spectrum of the same solution of **1** at $-40\,^\circ C$ shows resonances at $\delta = 121.86$ (C-1), 143.28 (C-2,6), 138.25 (C-3,5), and 148.54 (C-4). A singlet at $\delta = -1.21$ ($\tau_{1/2} = 18$ Hz) was observed in the ^{11}B NMR spectrum.

The preliminary data on the reactivity of the $[C_6F_5XeF_2]^+$ cation in salt **1** clearly show the oxidative-fluorinating power of the XeF_2 fragment. The phosphane $P(C_6F_5)_3$ was oxidized by $[C_6F_5XeF_2]^+$ to the phosphorane $(C_6F_5)_3PF_2$ [Eq. (4)]. Oxidation of the iodine atom in C_6F_5I requires strong oxidizing agents such as F_2,[12] XeF_2,[13], ClF, $ClOCF_3$, Cl_2O,[14] or $HNO_3/(CF_3CO)_2O$.[15] C_6F_5I reacts with **1** in MeCN to form $C_6F_5IF_2$ [Eq. (5)].

$$P(C_6F_5)_3 + [C_6F_5XeF_2]^+ \xrightarrow[MeCN]{-40\,^\circ C} (C_6F_5)_3PF_2 + [C_6F_5Xe]^+ \qquad (4)$$

$$[C_6F_5XeF_2]^+ + C_6F_5I \xrightarrow[MeCN]{-40\,^\circ C} [C_6F_5Xe]^+ + C_6F_5IF_2 \qquad (5)$$

$$5[C_6F_5XeF_2]^+ + I_2 \xrightarrow[MeCN]{-40\,^\circ C} 2IF_5 + 5[C_6F_5Xe]^+ \qquad (6)$$

The oxidative-fluorinating ability of $[C_6F_5XeF_2]^+$ under moderate conditions (coordinating solvent MeCN) is so large that the molecule I_2 was oxidized to IF_5 [Eq. (6)].

Experimental Section

All experiments were carried out under careful exclusion of moisture (dry argon atmosphere) in FEP traps (FEP = tetrafluoroethylene–hexafluoropropylene copolymer).

A solution of **3** (140 μmol) in CH_2Cl_2 (400 μL) at $-78\,^\circ C$ was added to a cold suspension of **2** (117 μmol) in CH_2Cl_2 (400 μL) at $-78\,^\circ C$. The mixture was then warmed to $-55\,^\circ C$ while stirring, resulting in the formation of a yellow solid. After 45 min at $-55\,^\circ C$ the mother liquor was decanted and the solid dissolved in CH_3CN/CD_3CN (1/1, 400 μL, $-45\,^\circ C$; Table 1).

Reactions of **1**: Yellow solutions of **1** in MeCN (approx. 30 μmol) were treated at $-40\,^\circ C$ with excess amounts of reagent ($P(C_6F_5)_3$ as a solution in MeCN, C_6F_5I as a liquid, and I_2 as a solid). The course of the reaction was followed by ^{19}F NMR spectroscopy. The main product of the reaction with I_2 was IF_5, observed as a doublet ($I(F_{eq})_4$) at $\delta = 4.10$ and a quintet (IF_{ax}) at $\delta = 52.80$ with a coupling constant $^2J(F,F)$ of 83.5 Hz.

The NMR data from the reaction with C_6F_5I show the presence of the excess of C_6F_5I as well as equimolar amounts of $C_6F_5IF_2$ and $[C_6F_5Xe]^+$ (Table 1).

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After the reaction with the phosphane the solvent was distilled off at $-30\,^{\circ}C$ under vacuum, the molecular organic compounds were extracted with CH_2Cl_2 at $-30\,^{\circ}C$, and the solid residue was dissolved in MeCN (main product: $[C_6F_5Xe][BF_4]$ (Table 1)). The extract of the reaction with the phosphane was characterized by ^{19}F NMR spectroscopy: $\delta = 1.32$ (d hept., $^1J(F,P) = 694.5$, $^4J(F,F) = 16.3$, 2F; PF_2), -132.73 (6F, *o*-F), -146.50 (3F, *p*-F), -159.48 (6F, *m*-F); GC-MS (70 eV): *m*/*z* (%): 570 (5) $[M^+]$, 551 (3) $[M^+ - F]$, 403 (100) $[M^+ - C_6F_5]$.

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Methylcorrinoids Methylate Radicals—Their Second Biological Mode of Action?**

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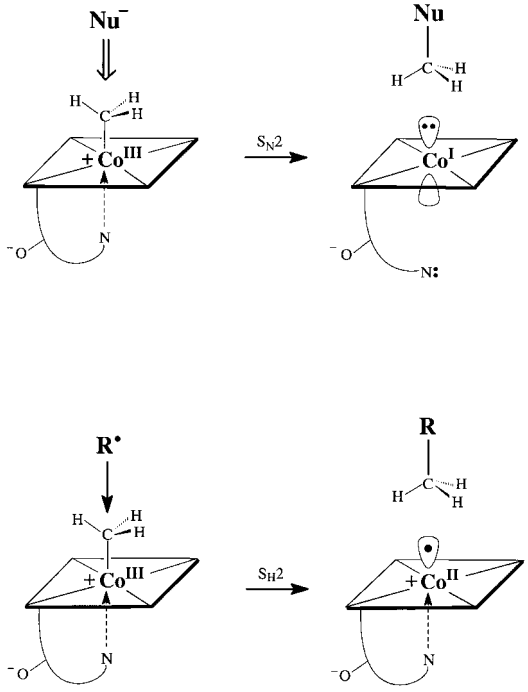
Dedicated to Professor Rolf Thauer on the occasion of his 60th birthday

The vitamin B_{12} derivative methylcobalamin (**1**), as well as related methylcorrinoids, are fundamentally important organometallic cofactors of methylation reactions.[1] The known enzymatic reactions with **1** depend on the heterolytic organometallic reactivities of methyl-Co^{III}-corrins and Co^{I}-corrins and the methylations proceed by nucleophilic substitution steps (Scheme 1, top).[2, 3] Extensive investigations of the B_{12}-dependent methionine synthase have indeed shown that the methyl transfer reactions occur by two nucleophilic substitution steps and convert homocysteine and N^5-methyltetrahydrofolate (with net retention) into methionine and tetrahydrofolate.[4]



Scheme 1.

Recent biosynthetic investigations on archaebacterial lipids[5a] and the antibiotics bottromycin,[5b] thienamycin,[6a] and thiostrepton[6b] provided evidence for unprecedented biological methylation reactions (and other alkylations) at saturated and inactivated carbon centers. In these methylation reactions methyl groups that originate from methionine are incorporated with net retention into the products.[5, 6] Arigoni and coworkers have considered a radical mechanism involving methylcorrin cofactors for these methylation reactions.[5a] Herein we report the first experiments that establish the (very efficient!) methylation of alkyl radicals by **1** (see Scheme 1, bottom).

Heating an oxygen-free aqueous solution of 2′-bis(ethoxycarbonyl)propylcobalamin (**2**)[7] and methylcobalamin (**1**)[1, 8] (**1**:**2** = 1.6:1) at 70 °C for about 5 h (at pH 7, with protection from light) completely decomposed the organocobalamin **2**. The organic decomposition products obtained after oxidation of the reaction mixture with air (in the dark and with the addition of potassium cyanide) were analyzed after extraction with deuterochloroform.[9] The 200 MHz ^1H NMR spectrum of the product exhibited signals for a 4.6:1 mixture of 2-ethyl-2-methylmalonic acid diethyl ester (**3**) and of 2,2-dimethylmalonic acid diethyl ester (**4**), with a combined yield amounting to approximately 70% (Scheme 2). In an analogous experiment using trideuteromethylcobalamin ([D_3]**1**) instead of **1** a combined yield of approximately 70% of [D_3]**3** and **4** was obtained as a 4.7:1 mixture (degree of deuteration of [D_3]**3**: 95 ± 5% from NMR studies). Storage of a deoxy-

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