extinction coefficients, M^{-1} cm^{-1}): 470 (72.1), 330 (94.1).

The conjugate base of the carboxamido complex (II) was prepared by alkaline hydrolysis[24] of I. A solution containing 0.64 g of I in 25 mL of water was treated with 2.2 mL of 0.68 M NaOH. The solution immediately changed from yellow to pink, and after 20 s, solid $NaClO_4$ was added to precipitate the product, which was collected by filtration after cooling for 1 h at 5 °C. The product was recrystallized from warm water at pH 9.5 by addition of $NaClO_4$ as before. The proton NMR spectrum in DMSO-d_6 has the expected features: 6.72 τ (trans NH_3), 6.55 τ (cis NH_3), 5.40 τ (HNC=O), 5.25 τ (-CH_2Br), 2.45, 2.40, 2.20, 2.13 τ (-C_6H_4 multiplet). The electronic spectrum shows maxima at 485 (99.5) and 340 nm (146).

For the homolysis study, the oxidizing agents were $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ and $CuSO_4 \cdot 5H_2O$ from commercial sources, and $[Co(NH_3)_5Br](ClO_4)_2$ was prepared by standard methods.[25]

Other reagents and procedures have been described previously.[26]

Product Analysis. The ion exchange separations were done on Sephadex SP-C25 resin at 5 °C in a cold room. The amount of cobalt was determined spectrophotometrically[12] after alkaline decomposition of the cobalt(III) complexes when appropriate. Chromium was determined as chromate after oxidation with alkaline hydrogen peroxide.

Instrumentation. The electronic spectra for species characterization were done on a Cary 219 spectrophotometer while the kinetic measurements were on a Hewlett-Packard diode-array system as described previously.[26] The NMR spectra were recorded on a Bruker AM-300 spectrometer.

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(24) Pinnel, D.; Wright, G. B.; Jordan, R. B. *J. Am. Chem. Soc.* **1972**, *94*, 6104.
(25) Diehl, H.; Clark, H.; Willards, H. H. *Inorg. Synth.* **1939**, *1*, 186.
(26) Sharma, P.; Jordan, R. B. *Inorg. Chem.* **1988**, *27*, 168.

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Convenient Synthesis of $[(n\text{-Bu})_4N]_3[Ru^{III}(CN)_6]$: First Access to a Pure Salt of the Hexacyanoruthenate(III) Anion and to a Coordination Polymer Thereof

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The preparation of pure salts of the hexacyano*ruthenate(III)* anion, $[A]_3[Ru^{III}(CN)_6]$, is, in contrast to corresponding Fe and Os homologues, still poorly documented. Actually, as late as 1984, i.e. more than three decades after first systematic attempts by DeFord and Davidson to oxidize alkali-metal salts of the $[Ru^{II}(CN)_6]^{4-}$ anion,[1] Crean and Schug have repeated the longstanding statement that the $[Ru^{III}(CN)_6]^{3-}$ anion is intrinsically unstable in water.[2] In 1979 Vogler et al. demonstrated that, in $CHCl_3$ solution, in situ prepared $[Et_4N]_4[Ru^{II}(CN)_6]$[3a] may be successfully photooxidized to $[Ru^{III}(CN)_6]^{3-}$ ions; however, a solid product described as "analytically pure" $[Et_4N]_3[Ru^{III}(CN)_6]$ has never been characterized in any detail.[3b]

In view of the evidently greater chances to oxidize $[R_4N]_4[Ru^{II}(CN)_6]$ systems (with R = alkyl) in *nonaqueous* solvents, we have reexamined some early findings by Gray et al. according to which $[(n\text{-Bu})_4N]_3[Os^{III}(CN)_6]$ results spontaneously from $[(n\text{-Bu})_4N]_4[Os^{II}(CN)_6]$ in $EtOH/Et_2O$.[4] Apparently, even the attempted preparation of $[(n\text{-Bu})_4N]_4[Fe^{II}(CN)_6]$ (**1b**) from $H_4Fe^{II}(CN)_6$ and $[(n\text{-Bu})_4N]OH$ in MeOH had led exclusively to $[(n\text{-Bu})_4N]_3[Fe^{III}(CN)_6]$ (**2b**).[4,5] We have reproduced this facile (i.e. in the presence of air!) access to **2b** and prepared, moreover, both pure $[Et_4N]_4[Fe^{II}(CN)_6]$ (**1d**), from $H_4Fe^{II}(CN)_6$ and $[Et_4N]OH$ under a strict N_2 atmosphere, and $[Et_4N]_3[Fe^{III}(CN)_6]$ (**2d**),[6c] from **1d**/EtOH in the presence of air. However, all attempts to also oxidize the salts $[R_4N]_4[Ru^{II}(CN)_6]$ (R = *n*-Bu (**1a**); R = Et (**1c**)) in a corresponding manner simply by air were unsuccessful in EtOH and MeOH as well as in numerous other solvents. Yet, as we wish to emphasize here, the above route becomes also viable for $[Ru^{II}(CN)_6]^{4-}$ when (a) the solvent is dimethylformamide (DMF) and (b) the countercation is $[(n\text{-Bu})_4N]^+$.

$$\underset{\mathbf{1a}}{[n\text{-Bu}_4N]_4[Ru^{II}(CN_6)]} \xrightarrow[\text{(b) Et}_2\text{O}]{\text{(a) DMF, air}} \underset{\mathbf{2a}}{[n\text{-Bu}_4N]_3[Ru^{III}(CN)_6]} + \text{other products} \quad (1)$$

Again, complete and quick oxidation by air takes place in DMF, while in H_2O oxidants stronger than O_2 are required.[1] Attempts to also prepare pure $[Et_4N]_3[Ru^{III}(CN)_6]$ (**2c**) from $[Et_4N]_4[Ru^{II}(CN)_6]$ (**1c**) remained unsatisfactory even in DMF due to incomplete reaction. A sensitive synergism, reminiscent of the well-known influence of the nature of both the solvent and the countercation $[R_4N]^+$ (R = Et or *n*-Bu) on the half-wave potential $E_{1/2}$ of the reduction of the $[Fe^{III}(CN)_6]^{3-}$ ion,[6d] seems to govern the oxidation of $[Ru^{II}(CN)_6]^{4-}$, too, and might be best described by Gutmann's concept of the "acceptor number" (AN).[6] Actually, the AN values of H_2O (54.8), MeOH (41.3), and EtOH (37.1) exceed appreciably the AN value of DMF (16.0),[6a] suggesting, in view of the notable change of $E_{1/2}$ of the couple $[Fe^{III}(CN)_6]^{3-}/[Fe^{II}(CN)_6]^{4-}$ from +0.24 V (solvent EtOH) to −0.61 V (solvent DMF),[6d] a correspondingly large reduction of the redox potential of the couple $[Ru^{III}(CN)_6]^{3-}/[Ru^{II}(CN)_6]^{4-}$ when EtOH is replaced by DMF.[7] The availability of **2a** and the facile tunability of its rather high reduction potential (ca. +0.86 V in H_2O[1]) might make this compound an interesting oxidant in organic, organometallic, and inorganic chemistry.

The brilliant yellow salt **2a** is thermally stable up to 220 °C and soluble in e.g. MeCN, CH_2Cl_2, and $CHCl_3$ but not in hexane, toluene, and CCl_4. Solutions even in N_2-conditioned H_2O display spontaneous decomposition accompanied by a color change toward green. The reappearance of the ν(CN) absorption bands of the $[Ru^{II}(CN)_6]^{4-}$ ion in the IR spectra of KBr pellets, but not of Nujol mulls, of initially pure **2a** suggests partial oxidation of Br^- ions in the pellet.

Like its Fe^{III} homologue, **2a** is a paramagnetic low-spin system ($\mu_{\text{eff}}^{\text{cor}}$(25 °C) = 2.00 μ_B). The electronic absorption maxima and extinction coefficients between 20 000 and 40 000 cm^{-1} compare well with corresponding literature data for both $[Ru^{III}(CN)_6]^{3-}$ and $[Os^{III}(CN)_6]^{3-}$.[3,4,8] In Table I, the ν(CN) vibrational bands of **2a** are compared with e.g. those of **1a**, **1d**, **2a**, and **2b**.

Not quite unexpectedly (vide supra), **2a** may be applied as an effective solid-state oxidant by simple grinding at room temperature with various solid reductants (eq 2).

$$[(n\text{-Bu})_4N]_3[M^{III}(CN)_6] \xrightarrow[\text{or } x\text{AI; } -(x/2)\text{I}_2]{x\text{A}} [A^+]_x[(n\text{-Bu})_4N]_3[M^{II}{}_xM^{III}{}_{1-x}(CN)_6] \quad (2)$$

$$M = Fe, Ru;\ 0 < x \leq 1$$

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(1) DeFord, D. D.; Davidson, A. W. *J. Am. Chem. Soc.* **1951**, *73*, 1469.
(2) Crean, F. M.; Schug, K. *Inorg. Chem.* **1984**, *23*, 853.
(3) (a) By reacting $Ag_4[Ru(CN)_6]$ with $[Et_3NH]Cl$ (!) in $CHCl_3$. (b) Vogler, A.; Losse, W.; Kunkely, H. *J. Chem. Soc., Chem. Commun.* **1979**, 187.
(4) Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 4260.
(5) Das, B.; Carlin, R.; Osteryoung, R. A. *Inorg. Chem.* **1989**, *28*, 421. These authors have apparently overlooked ref 4 and describe another, but not the first, route to compound **2b**.
(6) (a) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: Cambridge, U.K., 1983; see also references therein. (b) Gutmann, V. *Chimia* **1977**, *31*, 1. (c) Gutmann, V.; Gritzner, G.; Danksagmüller, K. *Inorg. Chim. Acta* **1976**, *17*, 81. (d) Gritzner, G.; Danksagmüller, K.; Gutmann, V. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *72*, 177.
(7) Electrochemical studies of the variation of $E_{1/2}$ of the redox reaction $[Ru^{II}(CN)_6]^{4-} - e^- \rightleftharpoons [Ru^{III}(CN)_6]^{3-}$ as a function of the AN of the solvent are presently underway.
(8) Waltz, W.; Akhtar, S.; Eager, R. *Can. J. Chem.* **1973**, *51*, 2525.

Table I. Comparison of the ν(CN) Spectra of the $M(CN)_6$ Group

sample	no.	ν(CN)(IR), cm^{-1}			ν(CN)(Raman), cm^{-1}		
$[(n\text{-}Bu)_4N]_4[Ru^{II}(CN)_6]$	**1a**	2040 m, sh	2060 s	2070 w, sh	2043 s	2083 m	
$[Et_4N]_4[Fe^{II}(CN)_6]$	**1d**[b]	2030 s	2050 vs	2080 m	2035 s	2072 m	
$[(n\text{-}Bu)_4N]_3[Ru^{III}(CN)_6]$	**2a**[a]		2090 m		2098 m	2111 m	
$[(n\text{-}Bu)_4N]_3[Fe^{III}(CN)_6]$	**2b**		2095 vs		2108 m, sh	2112 s	
$[(Me_3Sn)_3Fe^{III}(CN)_6]$	**3b**		2145/2159 vs[c]		2154 w	2167 w[d]	
$[(n\text{-}Bu)_4N]_{0.5}(Me_3Sn)_3[Ru^{II}{}_{0.5}Ru^{III}{}_{0.5}(CN)_6]$	**3a′**[a]	2070 m, br	2140 m		not observable[d]		
$[(Et_4N)(Me_3Sn)_3Ru^{II}(CN)_6]_\infty$[e]			2060 s	2080 m, sh	2080 m, sh	2091 s	2135 m

[a] IR spectrum of Nujol mull. [b] ν(CN) bands identical with those of **1b**. [c] Doublet under high resolution. [d] Very poor Raman scattering. [e] Cf. ref 10.

From the relative intensities of the ν(CN) bands of **2a** and of the resulting $[Ru^{II}(CN)_6]^{4-}$ anion (cf. Table I), the relative efficiency of slightly different reductants may be estimated, e.g. NaI, NH_4I, KI > $[Me_4N]I$ > KBr, $[Et_4N]I$, Cp_2Fe > $[(n\text{-}Pr)_4N]I$ > $[(n\text{-}Bu)_4N]I$.

Interestingly, **2b** oxidizes under the strictly repeated standard conditions only the iodides of Na^+–Me_4N^+, while e.g. the novel coordination polymer $[(Me_3Sn)_3Fe^{III}(CN)_6]_\infty \triangleq [Fe^{III}(\mu\text{-}CN\text{–}Me_3Sn\text{–}NC)_3]_\infty$ (**3b**)[9] is about as efficient as the Ru(III) system **2a**. This feature agrees with the view that the nitrogen-bonded Me_3Sn^+ units could be considered as fixed counterions of a particularly large AN.

In contrast to the facile formation of **3b**,[9] attempts to also prepare the Ru homologue **3a** of **3b**, which is expected to be an even stronger oxidant than **2a** and **3b**, did not afford any precipitate when solutions of **2a** and Me_3SnCl were combined in H_2O, EtOH, THF, MeCN, and DMF, respectively. So far, only in CH_2Cl_2 could an initially orange-yellow, insoluble product **3a′** be obtained, which turns light brown even after strict manipulation under N_2 and exclusion of light. The vibrational spectra of **3a′** in the ν(CN) range display equally intense bands typical of both $[Ru^{III}(CN)_6]$ *and* $[Ru^{II}(CN)_6]$ units, probably with bridging CN ligands (cf. Table I). The IR spectrum is diagnostic not only of Me_3Sn groups but also of minor amounts of $[(n\text{-}Bu)_4N]^+$ ions, while short grinding of **3a′**, e.g. with KI, affords again elemental iodine. The elemental analysis is consistent with the formulation $[(n\text{-}Bu)_4N]_x(Me_3Sn)_3[Ru^{II}{}_xRu^{III}{}_{1-x}(CN)_6]$ with $x \approx 0.5$. A similar cation intercalate (with Fe instead of Ru and $x \approx 0.2$) was obtained by exhaustive grinding of **3b** with $[(n\text{-}Bu)_4N]I$.[10]

Recently, Osteryoung et al.[5] have noted that the salt **2b** dissolves in an acidic 1-methyl-3-ethylimidazolium chloride/aluminum chloride melt probably under partial reduction of $[Fe^{III}(CN)_6]^{3-}$ to $[Fe^{II}(CN)_6]^{4-}$ by Cl^- anions. The authors consider the formation of CN-bridged adducts of $[Fe^{III}(CN)_6]^{3-}$ and $AlCl_3$ responsible for a notable increase of the ferrocyanide/ferricyanide redox potential that would even allow the oxidation of Cl^-. These findings strongly resemble our own observation that **3b** behaves as a notably stronger oxidant than **2b** (vide supra) and suggest that the formation of pure **3a** might be likewise impeded by the oxidation of Cl^- ions owing to the formation of adducts of $[Ru^{III}(CN)_6]^{3-}$ and Me_3SnCl species.[11]

In view of the particularly interesting properties of pure **3a** as a strongly oxidizing zeolite-like material, our efforts to develop suitable conditions for its successful preparation are being continued.

Experimental Section

The following instruments were used to characterize the products: Perkin-Elmer Model 577 (infrared spectroscopy), Ramanov U-1000 of Jobin Yvon (Raman spectroscopy), Cary Model 17 I (UV/vis spectroscopy), and a Johnson Matthey susceptometer after D. F. Evans (magnetic susceptibility). Only the preparation and spectroscopy of **1d** and **3a′** as well as all grinding experiments were carried out under a N_2 atmosphere.

A. Preparation of $[(n\text{-}C_4H_9)_4N]_4[Ru^{II}(CN)_6]$ (1a) and Related Salts. $K_4[Ru(CN)_6]$[12] was converted into $H_4Ru(CN)_6$[13] by reaction with aqueous HCl and Et_2O, and the latter into $[R_4N]_4[Ru(CN)_6]$ by titration with $[R_4N]OH$ (R = C_2H_5 or $n\text{-}C_4H_9$), solvent removal, and drying.[4]

B. Preparation of $[(n\text{-}C_4H_9)_4N]_3[Ru^{III}(CN)_6$ (2a). A solution of 0.25 g (0.20 mmol) of $[(n\text{-}C_4H_9)_4N]_4[Ru(CN)_6]$ in 10 cm^3 of anhydrous DMF was stirred at room temperature in a flask protected against moisture by a $CaCl_2$ tube. After 3 h, 50 cm^3 of absolute Et_2O was added, and the resulting suspension was kept overnight in the refrigerator. Finally, after filtration, a brilliant yellow solid was isolated, washed with Et_2O, and dried under vacuum for a few hours: 0.18 g (90%). Anal. Calcd for $C_{54}H_{108}N_9Ru$: C, 65.88; H, 11.06; N, 12.80. Found: C, 65.42; H, 10.88; N, 12.61. UV/vis absorptions (MeCN), cm^{-1}: 35 700, 33 700, 30 400, 28 100, 21 500 (ϵ_0, $cm^2\ mol^{-1}$: 1090, 2340, 2410, 1720, 830).

C. Solid-State Redox Reactions with 2a, "Standard" Procedure. A 0.02-g sample (0.02 mmol) of **2a** was mixed with 0.06 mmol of the respective reductant. After intense grinding of this mixture under an atmosphere of N_2 for 5 min, washing with several portions of toluene to remove all iodine, and final drying, the spectra of the KBr pellets were recorded.

D. Reaction of 2a with $(CH_3)_3SnCl$. Under an N_2 atmosphere and in the absence of light, solutions of 0.040 g (0.041 mmol) of $[(n\text{-}C_4H_9)_4N]_3[Ru(CN)_6]$ and 0.025 g (0.125 mmol) of $(CH_3)_3SnCl$ in 10 cm^3 CH_2Cl_2 were combined under stirring. The orange-yellow precipitate formed after several seconds was separated out by filtration, washed with a small amount of CH_2Cl_2, and dried in vacuo (room temperature): 0.043 g. Selected bands (cm^{-1}): Me_3Sn^+, 550 m (IR), 518 s (Ra); $[(n\text{-}Bu)_4N]^+$, 1490 m, 1380 w, 1155 m (IR). Anal. Calcd for $(Me_3Sn)_3Ru(CN)_6 \triangleq C_{15}H_{27}N_6RuSn_3$: C, 26.63; H, 4.02; N, 12.42; Sn, 52.63. Calcd for $[(n\text{-}Bu)_4N]_{0.5}(Me_3Sn)_3[Ru^{II}{}_{0.5}Ru^{III}{}_{0.5}(CN)_6] \triangleq C_{23}H_{45}N_{6.5}RuSn_3$: C, 31.76; H, 5.21; N, 10.47; Sn, 40.94. Found: C, 34.53; H, 5.83; N, 10.02; Sn, 40.32.

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[9] Brandt, P.; Brimah, A. K.; Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1988**, *100*, 1521.

[10] Eller, S.; Brandt, P.; Brimah, A. K.; Schwarz, P.; Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1263.

[11] Even the ν(CN) spectra of **3b** obtained from pure $K_3[Fe^{III}(CN)_6]$ and Me_3SnCl in H_2O are not always fully devoid of ν(CN) absorptions of $[Fe^{II}(CN)_6]^{4-}$ units: Yünlü, K. Ph.D. Thesis, Universität Hamburg, FRG, 1983.

[12] Krause, R. A.; Violette, C. *Inorg. Chim. Acta* **1986**, *113*, 161.

[13] Ginsberg, A. P.; Koubek, E. *Inorg. Chem.* **1965**, *4*, 1186.

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Further Studies on Dirhenium Complexes That Contain the Bridging Ligand 2-(Diphenylphosphino)pyridine. Isolation and Characterization of *cis*-$[Re_2(O_2CR)_2X_2(Ph_2Ppy)_2]^{n+}$ (R = CH_3, C_2H_5; X = Cl, Br; n = 0, 1)

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During the course of our studies on the reactions of the dirhenium(III) carboxylate complexes $Re_2(O_2CR)_2X_4L_2$ (R = CH_3, C_2H_5; X = Cl, Br; L = H_2O, py, 4-Mepy) with the phosphines PPh_3 and Ph_2Ppy, we isolated and characterized several complexes of the type $Re_2(\mu\text{-}O_2CR)X_4(PPh_3)_2$ and $Re_2(\mu\text{-}O_2CR)X_4(Ph_2Ppy)_2$ that are derivatives of the paramagnetic $Re_2{}^{5+}$ core.[1] In one