trans-[$Ru^{II}Cl(MeCN)_5$][$Ru^{III}Cl_4(MeCN)_2$]: A Reactive Intermediate in the Homogeneous Catalyzed Hydrosilylation of Carbon Dioxide†

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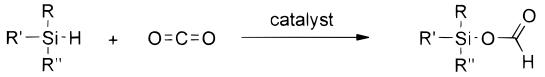
$RuCl_3 \cdot nH_2O$ in MeCN catalyzes the hydrosilylation of carbon dioxide with *n*-Hex_3SiH into *n*-$Hex_3SiOOCH$ and, with Me_2PhSiH, into $Me_2PhSiOOCH$. The initial catalyst formed is *trans*-[$Ru^{II}Cl(MeCN)_5$][$Ru^{III}Cl_4(MeCN)_2$], the synthesis and structural characterization of which are described. With [$Ru^{II}Cl(MeCN)_5$][$Ru^{III}Cl_4(MeCN)_2$] as a catalyst, $Me_2PhSiOOCH$ is produced at 313 K. Analogously, Et_2SiH_2, Ph_2SiH_2, and *p*-C_6H_4-$(Me_2SiH)_2$ yield $Et_2Si(OOCH)_2$, $Ph_2Si(OOCH)_2$, and *p*-C_6H_4-$(Me_2SiOOCH)_2$, respectively. When exposed to air, the latter compounds hydrolyze spontaneously into mixtures of silanediols, linear siloxane oligomers and polymers, and cyclic siloxane oligomers with the release of formic acid.

Introduction

One research area recently attracting increasing attention is the use of carbon dioxide as a C_1-building block.[1] The main criteria favoring this use are the conservation of organic resources and the availability of carbon dioxide. Catalytic hydrosilylation of multiple bonds is an important route to functionalized organic compounds.[2] Independently, two groups in 1981 reported the hydrosilylation of carbon dioxide into formoxysilanes of the type $R_2R'SiOOCH$ (R,R′: alkyl) catalyzed by transition metal complexes, preferably based on ruthenium.[3] The general reaction type is provided in eq 1. Fourteen catalytic cycles at a turnover frequency (TOF) of 0.7 h^{-1} were achieved with $RuCl_2(PPh_3)_3$.[3a] Recently, some initial results were published concerning hydrosilylations in supercritical carbon dioxide used as the solvent and substrate.[4]



(1)

Little is known about possible uses of formoxysilanes, which are available from stoichiometric conversion of chlorosilanes with suitable formic acid derivatives.[5] Applications discussed include the precipitation of thin SiO_x layers by controlled thermal decomposition of $Si(OOCH)_4$.[6] Another potential application is the use of multiply formoxy-functionalized silanes, $R_nSi(OOCH)_{4-n}$ (*n*: 0−2) as a cross-linking component in RTV silicones.[7]

This study focuses on the development of a powerful and economically efficient catalyst system for the synthesis of singly and multiply formoxy-functionalized silanes.

Results and Discussion

We started our studies with investigations on the catalytic activity of $RuCl_3 \cdot nH_2O$ (**1**) in MeCN as a low-cost commercially available ruthenium compound.[8] A summary of the results of the catalytic reactions is provided in Table 1. At 373 K, 1 mol % of **1** achieves a nearly complete conversion of Hex_3SiH (**2a**) within 62 h (Table 1, entry 1). Distillation of the crude product affords 84% $Hex_3SiOOCH$ (**3a**). Me_2PhSiH (**2b**) reacts more rapidly to afford $Me_2PhSiOOCH$ (**3b**) (Table 1,

† This work is dedicated to Prof. Dr. Dirk Walther (Jena, Germany) on the occasion of his 60th birthday.

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Table 1. Hydrosilylation of Carbon Dioxide[d]

entry	substrate	catalyst (mol % Ru)	reaction time (h)	temp (K)	product (%)
1[a]	*n*-Hex_3SiH **2a**	**1** (1.0)	62	373	**3a** (84)
2[a]	Me_2PhSiH **2b**	**1** (0.2)	20	353	**3b** (90)
3[a]		**1** (0.2)	20	313	no conversion
4[a]		**4** (0.2)	20	353	**3b** (91)
5[a]		**4** (0.2)	2	353	**3b** (93)
6[a,b]		**4** (0.2)	20	333	**3b** (33)
7[a,b]		**4** (0.2)	20	313	**3b** (15)
8[c]	Et_2SiH_2 **5a**	**4** (0.5)	6	333	**6a** (80)
9[a]	Ph_2SiH_2 **5b**	**4** (0.5)	20	343	**6b** (39)
10[a]	*p*-C_6H_4-$(Me_2SiH)_2$ **5c**	**4** (0.5)	4	333	**6c** (87)

[a] Reaction performed in MeCN solution. [b] Yield determined by ^1H NMR. [c] Reaction performed in 3-phenylpropionitrile solution. [d] For Details of the procedure refer to the Experimental Section.

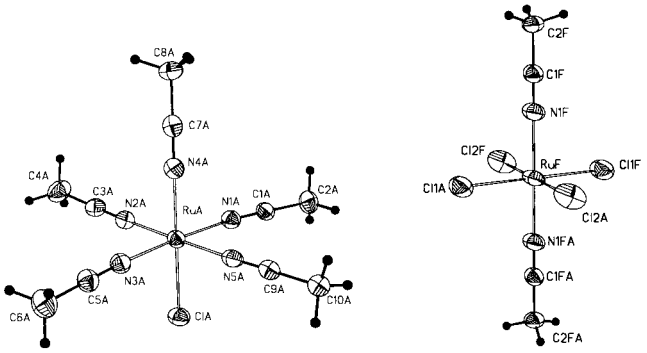

Figure 1. ORTEP plot of **4** showing 50% probability ellipsoids for non-H atoms (see Experimental Section). Selected bond distances (Å): RuA−N1A 2.035(3), RuA−N4A 2.024(3), RuF−N1F 2.020(4), RuA−ClA 2.3984(11), RuF−Cl1F 2.3550(13). Selected bond angles (deg): RuA−N1A−C1A 166.7(3), RuA−N4A−C7A 172.2(3), RuF−N1F−C1F 179.0(4), N4A−RuA−ClA 177.20(10), N1A−RuA−N2A 95.20(14), N1F−RuF−Cl1F 90.04(11), Cl1F−RuF−Cl2F 90.51(6).

entry 2). The rate increase of **2b** compared to **2a** is probably steric in origin. The reaction of **2b** is the first example of the reaction of carbon dioxide with an aryl hydrosilane. Consequently, it should be possible to produce a multitude of functionalized formoxysilane derivatives in a similar way. As secondary products which were identified by NMR spectroscopy and gas chromatography, the respective disiloxanes are formed by hydrolysis of **3a**,**b** with the water contained in **1**.

When the reaction temperature is 313 K, no conversion of silane takes place (Table 1, entry 3). This finding may be related to the observation that the initially intensely dark reaction solution does not begin to brighten until 353 K. This prompted us to consider whether a reduction is the initiating reaction in the formation of the active catalyst. For this purpose, we reacted **1** with 1 equiv of **2b** in MeCN in the absence of carbon dioxide. The characteristic brightening encountered under conditions of catalysis was also observed at 353 K for this stoichiometric reaction of **1**. With a yield of 79%, a complex of the composition of $Ru_2Cl_5(MeCN)_7$ (**4**) was isolated. No further products were obtained using a 10-fold excess of **2b** and longer reaction times. Also, no reaction took place by refluxing **4** with **2b** in MeCN. The constitution of **4** was determined by single-crystal X-ray structural analysis (Figure 1). The ionic compound **4** crystallizes in the $P\bar{1}$ space group and is made up of one Ru(III) anion and one Ru(II) cation, both of octahedral symmetry (refer to the Experimental Section). The cation of **4** has the constitution $[RuCl(MeCN)_5]^+$. The average Ru−N bond distance value, 2.03(3) Å, is similar to that bond in the anion. The Ru−N bond distance of the MeCN ligand trans to the chloro ligand is not extended. In the anion *trans*-$[RuCl_4(MeCN)_2]^-$, which has a C_i-symmetry, two MeCN ligands in the axial positions are coordinated linearly at the ruthenium center [average angle for N−C−C 178.8(5)°, average angle Ru−N−C 176.3(3)°]. Average bond distances Ru−Cl [2.36(1) Å] and Ru−N [2.02(4) Å] are as expected.

The same anion has been reported in the complexes *n*-$Bu_4N[RuCl_4(MeCN)_2]$[9] and $Et_4N[RuCl_4(MeCN)_2]$.[10] The synthesis of **4**·H_2O as a byproduct of the synthesis of $RuCl_3[MeCN)_3$·H_2O and studies on its physical and electronic properties were described by Dehand et al.[11]

4 is moderately soluble in MeCN and chloroform, insoluble in hydrocarbons, and gradually decomposes in water, releasing MeCN. We suspect that the comparatively weak coordination of the MeCN ligands in **4** plays a key role in the formation of the active catalyst.

The easy preparation of **4**, even in large quantities, suggests its use as an anhydrous single-component catalyst. It is shown that **4**, at 353 K, is just as active as **1** in the conversion of **2b** to **3b** (Table 1, entry 4). Multiple replications at different reaction times led to an optimized yield (93%) of **2b** within 2 h, corresponding to a TON of 465 and a TOF of 233 h^{-1} (Table 1, entry 5). To date, **4** is the most active catalyst for the hydrosilylation of carbon dioxide yet reported. Unlike the case with **1**, hydrosilylation with **4** as a catalyst is possible at temperatures of 333 and 313 K (Table 1, entries 6 and 7). This allows the conclusion that the reaction temperature of 353 K required for the use of **1** is needed to generate **4**.

4 also catalyzes the conversion of Et_2SiH_2 **5a**, Ph_2SiH_2 **5b**, and *p*-C_6H_4-$(Me_2SiH)_2$ **5c** to the bis(formoxy)silanes $Et_2Si(OOCH)_2$ **6a**, $Ph_2Si(OOCH)_2$ **6b**, and *p*-C_6H_4-$(Me_2SiOOCH)_2$ **6c** with isolated yields between 39% and 87% (Table 1, entries 8−10). Purification, especially of **6b**, by distillation is aggravated by thermal decomposition. The yields as determined by NMR spectroscopy are above 90% in each case. The ^1H NMR spectrum of a raw product solution of **6b** (Table 1, entry 9) shows a complete conversion of **3b**. Unreacted **3b** would give a singlet for the Si,H protons at 4.96 ppm. A small resonance at 8.70 ppm probably corresponds to condensation products of **6b** such as $[Ph_2Si(OOCH)]_2O$, which could not be isolated.

6a−**c**, when in contact with atmospheric humidity, very quickly condense into linearly and cyclically crosslinked silicone oligomers and polymers, respectively, in a manner similar to the hydrolysis of Ph_2SiCl_2.[12] The characteristic odor of formic acid disappears after only

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a few minutes. The hydrolysis products, $HOSiR_2OH$, $HOSiR_2O(SiR_2O)_nSiR_2OH$ (n = 0, 1, ...) and $(SiR_2O)_n$ (n = 2, 3, ...) with R = Et, Ph and $HOSiMe_2C_6H_4SiMe_2O(SiMe_2C_6H_4SiMe_2O)_nSiMe_2C_6H_4SiMe_2OH$ (n = 0, 1, ...) consist of a mixture of monomeric, oligomeric, and polymeric compounds. The molar mass distributions were determined by GPC and had molecular weights of up to 80 000 g/mol.[13] Single crystals of $(SiPh_2O)_3$ were isolated from the hydrolysis product of **6b** and identified by their cell parameters.[14] Thus, the basic suitability of this class of compounds for use in single-component RTV silicones is demonstrated. Continuing studies of the elementary steps of the reaction mechanism and of the possibilities of catalyst recycling are currently underway.

Experimental Section

All manipulations were carried out under an atmosphere of dry argon by standard Schlenk techniques except the hydrolyses of **6a**−**c**. Reactions under CO_2 pressure were performed in 80 cm^3 stainless steel reactors equipped with manometer, thermoelement, and magnetic stirrer. Isolated yields of formoxysilanes were based on the corresponding starting silanes.

Solvents were distilled prior to use using standard methods. Commercially available reagents were used as received and freshly degassed.

NMR spectra were acquired on a Bruker AC 200 spectrometer (^{1}H NMR, 200.13 MHz; ^{13}C NMR, 50.32 MHz; ^{29}Si NMR, 39.76 MHz). Chemical shifts (δ) are given in ppm and were referenced to internal or external $SiMe_4$ (^{1}H, ^{13}C, ^{29}Si), respectively. Assignments were confirmed by ^{13}C-DEPT experiments. Elemental analyses were measured by the Microanalytical Laboratory Kolbe (Mülheim a. d. R., Germany). The molecular weight measurements (refer to ref 13) were performed on a GPC JASCO equipped with three columns (PSSSDV 10^2 nm, PSS 10^3 nm, PSS 10^5 nm) calibrated with polystyrene standard; eluent THF; flow rate 1 cm^3 min^{-1}.

Syntheses of Formoxysilanes 3a,b and 6a−c. Formoxytri-*n*-hexylsilane, (n-C_6H_{13})$_3$Si(OOCH), 3a. $RuCl_3 \cdot nH_2O$ **1** (0.0990 g, 0.4 mmol) was dissolved in 30 cm^3 of MeCN. The solution was transferred to a reactor equipped with a magnetic stirrer and an internal thermometer. (n-C_6H_{13})$_3$SiH **2a** (11.38 g, 40.0 mmol) and CO_2 (26.4 g, 0.6 mol) were added, and the mixture was vigorously stirred at 373 K for 62 h. Unreacted CO_2 was carefully removed by stirring at 298 K. Volatile components were removed in a vacuum of less than 8 mbar. Purification was performed by vacuum distillation, affording 11.02 g (83.3%) of **3a** (bp: 388 K at 1.0 10^{-5} mbar). ^{1}H NMR data ($CDCl_3$): 8.08 (s, 1H, O_2CH), 1.29 (complex pattern, 24H, CH_2), 0.82 (complex pattern, 15H, CH_2/CH_3).^{13}C NMR data ($CDCl_3$): 160.9 (O_2CH), 33.0 (CH_2), 31.4 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 13.1 (CH_3), 13.4 ($SiCH_2$).^{29}Si NMR data ($CDCl_3$): 25.2. Anal. Calcd (%) for $C_{19}H_{40}SiO_2$ (M_r = 328.61): C, 69.45; H, 12.27; Si, 8.55. Found: C, 69.53; H, 12.36; Si, 8.47. IR ν_{CO}(film/NaCl): 1714 (vs) cm^{-1}. MS (EI): m/z (%) = 243 (45) [$M^+ - C_6H_{13}$], 197 (9) [$M^+ - C_6H_{13} - HCOOH$], 157 (48) [$M^+ - C_6H_{14} - C_6H_{13}$], 113 (58) [$M^+ - 2\,C_6H_{13} - COOH$], 101 (21), 85 (54), 75 (100), 61 (34), 41 (77).

Dimethylformoxyphenylsilane, Me_2PhSi(OOCH), 3b. Analogous to the procedure described for the synthesis of **3a**, $Ru_2Cl_5(MeCN)_7$ **4** (0.0269 g, 0.0401 mmol), Me_2PhSiH **2b** (5.45 g, 40 mmol), and CO_2 (3.5 g, 80 mmol) were reacted at 353 K for 20 h to afford 6.53 g (90.6%) of **3b** (bp: 367 K at 23 mbar). ^{1}H NMR data ($CDCl_3$, 298 K): 8.12 (s, 1H, O_2CH), 7.65 (complex pattern, 2H, *Ph*), 7.43 (complex pattern, 3H, *Ph*), 0.63 (s, 6H, CH_3). ^{13}C NMR data ($CDCl_3$, 298 K): 160.8 (O_2CH), 134.8 (C_i), 133.5 (C_o), 130.4 (C_p), 128.0 (C_m), −1.7 (CH_3). ^{29}Si NMR data ($CDCl_3$, 298 K): 14.2. Anal. Calcd (%) for $C_9H_{12}SiO_2$ (M_r = 180.28): C, 59.96; H, 6.71; Si, 15.58. Found: C, 59.86; H, 6.79; Si, 15.46. IR ν_{CO}(film/NaCl): 1709 (vs) cm^{-1}. MS (EI): m/z (%) = 180 (6) [M^+], 165 (100) [$M^+ - CH_3$], 152 (6) [$M^+ - 2\,CH_2$], 137 (99) [$MH^+ - CO_2$], 103 (10) [$M^+ - Ph$], 91 (13), 77 (11), 51 (7), 45 (19).

Diethyldiformoxysilane, Et_2Si(OOCH)$_2$, 6a. Analogous to the procedure described for the synthesis of **3a**, **4** (0.1345 g, 0.202 mmol), Et_2SiH_2 **5a** (3.52 g, 40 mmol), and CO_2 (7.0 g, 160 mmol) were reacted in 30 cm^3 of 3-phenylpropionitrile at 333 K for 6 h to afford 5.64 g (80.1%) of **6a** (bp: 343 K at 10 mbar). ^{1}H NMR data ($CDCl_3$, 298 K): 8.06 (s, 2H, O_2CH), 0.98 (complex pattern, 10H, CH_2,CH_3).^{13}C NMR data ($CDCl_3$, 298 K): 159.3 (O_2CH), 5.2 (CH_3), 4.9 (CH_2).^{29}Si NMR data ($CDCl_3$, 298 K): 6.7. Anal. Calcd (%) for $C_{12}H_{12}Si_2O_4$ (M_r = 276.39): C, 40.89; H, 6.86; O, 36.31; Si, 15.94. Found: C, 40.78; H, 6.81; Si, 15.99. IR ν_{CO}(film/NaCl): 1714 (vs) cm^{-1}. MS (EI): m/z (%) = 147 (28) [$M^+ - C_2H_5$], 131 (2) [$M^+ - COOH$], 119 (43) [$MH^+ - 2\,C_2H_5$], 102 (7) [$M^+ - HCOOH - C_2H_4$], 91 (48) [$C_3H_{11}OSi^+$], 75 (11) [$(CH_3)_2SiOH^+$], 63 (100), 45 (58).

Diformoxydiphenylsilane, Ph_2Si(OOCH)$_2$, 6b. Analogous to the procedure described for the synthesis of **3a**, **4** (0.1345 g, 0.202 mmol), Ph_2SiH_2 **5b** (3.69 g, 20 mmol), and CO_2 (3.5 g, 80 mmol) were reacted in 30 cm^3 of MeCN at 343 K for 20 h to afford 2.13 g (39.1%) of **6b** (bp: 378 K at 1.0 10^{-5} mbar). ^{1}H NMR data ($CDCl_3$, 298 K): 8.24 (s, 2H, O_2CH), 7.82 (complex pattern, 4H, *Ph*), 7.52 (complex pattern, 6H, *Ph*). ^{13}C NMR data ($CDCl_3$, 298 K): 158.7 (O_2CH), 134.9 (C_o), 131.9 (C_p), 128.2 (C_m), 127.5 (C_i). ^{29}Si NMR data ($CDCl_3$, 298 K): −26.8. Anal. Calcd (%) for $C_{14}H_{10}Si_2O_4$ (M_r = 298.40): C, 61.75; H, 4.44; Si, 10.31. Found: C, 61.78; H, 4.41; Si, 10.37. IR ν_{CO}(film/NaCl): 1719 (vs) cm^{-1}. MS (EI): m/z (%) = 272 (66) [M^+], 243 (13) [$M^+ - CHO$], 227 (52) [$M^+ - COOH$], 195 (64) [$M^+ - C_6H_5$], 167 (61) [$M^+ - C_7H_5O$], 150 (14) [$M^+ - C_6H_5 - COOH$], 139 (100), 121 (14), 105 (3) [$C_7H_5O^+$], 94 (8) [$C_6H_6O^+$], 77 (42), 51 (19), 45 (25).

1,4-Bis(dimethylformoxysilyl)benzene, p-C_6H_4-(Me_2SiOOCH)$_2$, 6c. Analogous to the procedure described for the synthesis of **3a**, **4** (0.1345 g, 0.202 mmol), p-C_6H_4-$(Me_2SiH)_2$ **5c** (7.78 g, 40 mmol), and CO_2 (7.0 g, 160 mmol) were reacted in 30 cm^3 of MeCN at 333 K for 4 h to afford 9.88 g (87.4%) of **6c** (bp: 390 K at 2.0 10^{-5} mbar). ^{1}H NMR data ($CDCl_3$, 298 K): 8.10 (s, 2H, O_2CH), 7.69 (s, 4H, *Ph*), 0.62 (s, 12H, CH_3). ^{13}C NMR data ($CDCl_3$, 298 K): 160.6 (O_2CH), 137.2 (C_i), 132.8 (C_o), −1.9 (CH_3). ^{29}Si NMR data ($CDCl_3$, 298 K): 14.0. Anal. Calcd (%) for $C_{12}H_{12}Si_2O_4$ (M_r = 276.39): C, 51.03; H, 6.42; Si, 19.89. Found: C, 50.91; H, 6.48; Si, 19.92. IR ν_{CO}(film/NaCl): 1709 (vs) cm^{-1}. MS (EI): m/z (%) = 282 (0.2) [M^+], 267 (17) [$M^+ - CH_3$], 237 (3) [$M^+ - COOH$], 223 (1) [$M^+ - HCOOH - CH_3$], 193 (4) [$M^+ - HCOOH - COOH$], 133 (10) [$M^+ - HCOOH - COOH, -4CH_3$], 121 (14 [$C_6H_5SiHCH_3^+$], 103 (40 [$(CH_3)_2Si(O_2CH)^+$], 91 (25), 75 (100) [$(CH_3)_2SiOH^+$], 45 (83).

Synthesis of *trans*-[$Ru^{II}Cl(MeCN)_5$][$Ru^{III}Cl_4(MeCN)_2$], 4. A mixture of $RuCl_3 \cdot nH_2O$ **1** (4.95 g, 20 mmol) and Me_2PhSiH **2a** (2.73 g, 20 mmol) in 100 cm^3 of MeCN was refluxed for 4 h. After an initial period, the color of the reaction mixture changed from dark purple to yellow, and a yellow precipitate was formed. The precipitate was filtered off, washed four times with diethyl ether and pentane, and dried in high vacuum to yield 5.29 g (79.3%) of **4** (>443 K decomp). Anal. Calcd (%) for $C_{14}H_{21}N_7Cl_5Ru_2$ (M_r = 666.77): C, 25.22; H, 3.17, Cl, 26.59, N, 14.70. Found: C, 25.09; H, 3.18; Cl, 25.83; N, 14.79. IR

(13) Gel permeation chromatography (refer to Experimental Section) of a THF solution of the products derived from hydrolysis of **6a**−**c** reveals (relative to polystyrene): (from **6a**) M_w 580, M_n 390, M_w/M_n = 1.5. (from **6b**) M_w 320, M_n 220, M_w/M_n = 1.5. (from **6c**) M_w 14 000, M_n 5600, M_w/M_n = 2.5.

(14) Crystal structures of 2,2,4,4,6,6-hexaphenylcyclotrisiloxane in: (a) Ovchinnikov, Yu. E.; Struchkov, Yu. T.; Buzin, M. T.; Papkov, V. S. *Vysokomol. Soyed. A* **1997**, *39*, 430. (b) Tomlins, P. S.; Lydon, J. E.; Akrigg, D.; Sheldrick, E. *Acta Crystallogr. Sect. C* **1985**, *11*, 591.

Table 2. Crystal Data, Data Collection, and Refinement Parameters for Complex 4

empirical formula	$C_{14}H_{21}N_7Cl_5Ru_2$
molecular weight	666.77
temp (K)	183(2)
wavelength (Å)	0.71073
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, b, c (Å)	12.2606(3), 14.3523(3), 17.035(3)
α, β, γ (deg)	103.705(1), 91.841(1), 113.451(1)
V (Å^3)	2644.7(5)
Z	4
d_{calcd} (g cm^{-3})	1.675
abs coeff (mm^{-1})	1.661
F_{000}	1308
cryst size (mm^3)	0.20 × 0.20 × 0.10
θ for data collection (deg)	3.29−26.34
limiting indices	$-15 \le h \le 15$, $-17 \le k \le 17$, $-21 \le l \le 21$
no. of reflns collected	18 342
no. of ind reflns	10 704 ($R_{int} = 0.0378$)
completeness to $\theta = 26.34°$ (%)	99.1
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	10 704/0/511
goodness of fit on F^2	1.020
final R indices [$I > 2\sigma(I)$]	R1 = 0.0393, wR2 = 0.0884
R indices (all data)	R1 = 0.0563, wR2 = 0.0954
largest diff peak and hole	2.213 and −0.879 e Å^{-3}

(KBr): 2969 (vs), 2912 (vs), 2275 (s), 1625 (m), 1425 (s), 1362 (s), 1262 (m), 1040 (s), 944 (s) cm^{-1}.

X-ray Crystallographic Analysis of 4. Orange crystals of $[Ru^{II}Cl(MeCN)_5][Ru^{III}Cl_4(MeCN)_2]$ **4** were grown from a MeCN solution (see Table 2). The intensity data for the compound were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz, polarization, and absorption effects.[15]

The structure was solved by direct methods (SHELXS)[16] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[17] The hydrogen atoms of the structure were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically. The asymmetric unit of the cell contains two cations on general and four half-anions on special positions ($\bar{1}$). The different cations and anions, respectively, showed no significant differences. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.[18]

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Supporting Information Available: Crystal Data of compound **4**; ^{1}H NMR of **6b** (raw product). This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Further details of the crystal structure investigations are available on request from the director of the Cambridge Crystallographic Data Center, 12 Union Road, GB-Cambridge CB2 1 EZ, on quoting the depository number CCSD-133097, the names of the authors, and the journal citation.