Mixed-Metal Complexes

Heterobimetallic Main-Group–Transition-Metal Paddle-Wheel Carboxylates**

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> *“Main group elements and transition metal fragments interact with one another in interesting and often unexpected fashions”*
>
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Heterometallic carboxylates along with alkoxides are of great interest as they can be used as single-source precursors for binary or multimetallic oxides.[1] Bismuth-containing oxide materials cover a broad range of high-technology applications, including high T_c superconductivity,[2] oxide-ion conductivity,[3] nonlinear optics,[4] catalysis,[5] and ferroelectrics.[6] Of all heavy metals, bismuth has the greatest potential for applications within the context of green chemistry.[7] The first heterometallic precursor for bismuth-containing inorganic materials was reported only in 1996[8] and several others have been isolated since then.[9] However, none of these materials are homoleptic carboxylates. Recently we described a rational synthesis of the first bismuth(II) carboxylate, $[Bi_2(O_2CCF_3)_4]$, which forms a dimeric tetrabridged structure (Figure 1 a).[10] Owing to the high reactivity of this unusual complex and its potential Lewis base character, we decided to study its reactions with Lewis acidic transition-metal carboxylates to obtain mixed-metal complexes of the general formula $[BiM(O_2CR)_4]$. Heterometallic carboxylates can assemble in two different ways: 1) through formation of Lewis acid–base adducts (Figure 1, b and c) to give an ordered arrangement of homonuclear units in infinite chains, and 2) through formation of a “true” heterobimetallic unit bridged by carboxylate ligands and further supported by direct metal–metal bonding (Figure 1 d) to provide homogenization at the molecular level. Herein we report the synthesis and characterization of the first two bismuth-containing heterobimetallic carboxylates that indeed adopt the paddle-wheel structure shown in Figure 1 d, $[BiRh(O_2CCF_3)_4]$ (**1**) and $[BiRu(O_2CCF_3)_4]$ (**2**).

Compounds **1** and **2** were obtained by heating stoichiometric mixtures of $[Bi_2(O_2CCF_3)_4]$ and unligated $[M_2(O_2CCF_3)_4]$ (**1**: M = Rh; **2**: M = Ru) in the solid state in a sealed ampoule. While the formation of **1** proceeds well, the yield of **2** is far from quantitative. Our attempts to prepare these heterometallic compounds by heating in toluene at reflux failed. The use of Bi^{III} trifluoroacetate instead of Bi^{II} results in the same products with lower yields; this finding can be explained by our previous observation[10] that Bi^{III} trifluoroacetate partially disproportionates in the vapor phase to give Bi^{II} species.

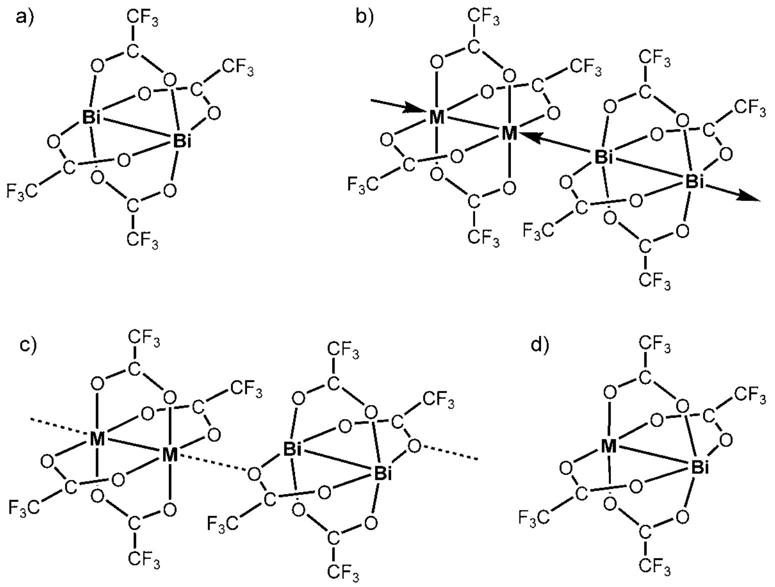

Figure 1. a) Dimeric tetrabridged structure of $[Bi_2(O_2CCF_3)_4]$; b), c) Lewis acid–base adducts formed by homonuclear units; d) paddle-wheel structure of “true” heterobimetallic unit $[BiM(O_2CCF_3)_4]$.

Bismuth rhodium tetra(trifluoroacetate) (**1**) is volatile and can be quantitatively resublimed upon heating. It shows fair thermal stability in a sealed ampoule, decomposing at around 250 °C. In open air, crystals of **1** are more stable than both parent homometallic species. Compound **1** is soluble in anhydrous, deoxygenated toluene, acetone, ether, ethyl alcohol, and THF and can be kept in these solutions for prolonged times. It is also partially soluble in $CHCl_3$, CH_2Cl_2, and DMSO. The infrared and mass spectra indicate that the dimeric molecules remain intact in solution.

The structures of **1** and **2**[11] consist of heterobimetallic paddle-wheel units (Figure 2). Each bismuth atom maintains a distorted square-pyramidal coordination geometry composed of one Rh(Ru) and four O atoms. In contrast, the similar coordination around the transition-metal ion is less distorted. The distances between the bismuth and transition-metal atoms are 2.5493(3) and 2.5487(4) Å for **1** and **2**, respectively. Table 1 shows that these distances are significantly shorter than the average values of metal–metal

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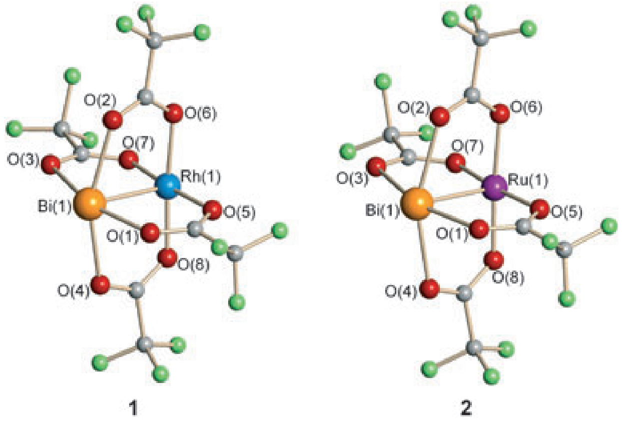

Figure 2. Paddle-wheel heterobimetallic carboxylates [BiM(O_2CCF_3)$_4$] (**1**: M = Rh; **2**: M = Ru). **1**: Bi–Rh 2.5493(3), Bi–O 2.315(3)–2.575(3), Rh–O_{av} 2.018(3) Å; **2**: Bi–Ru 2.5487(4), Bi–O 2.347(3)–2.691(3), Ru–O_{av} 2.022(3) Å.

Table 1: Metal–metal bond distances [Å] in homo- and heterometallic paddle-wheel carboxylates

metal–metal bonds	M = Rh	M = Ru
Bi-Bi[a]	2.9462(3)	2.9462(3)
M-M[b]	2.3813(8)	2.2645(6)
1/2Σ	2.664	2.606
Bi-M	2.5493(3)	2.5487(4)

[a] See Reference [10]. [b] See Reference [12].

distances in the corresponding homometallic trifluoroacetates. Importantly, the M–O (M = Bi, Rh, Ru) distances in heterometallic units **1** and **2** are essentially the same as the corresponding distances in the homometallic molecules [M_2^{II}(O_2CCF_3)$_4$].[10,12]

The bimetallic molecules **1** and **2** act as one-end Lewis acids. In the solid state they form extended chain structures (Figure 3 a) through axial coordination of the transition-metal center to one of the Bi-bound carboxylate oxygen atoms from a neighboring unit. When **1** was treated with excess $(C_2H_5)_2O\cdot BF_3$, the monoadduct [BiRh(O_2CCF_3)$_4$]·$O(C_2H_5)_2$ (**3**) was the only product isolated from the solution. The structure of **3** reveals that the ether molecule is coordinated to the Rh end of the heterometallic unit (Figure 3 b), while the Bi end exhibits neither Lewis acidic nor basic properties.

The examples of heterobimetallic carboxylates with direct metal–metal bonding are by far limited to quadruply-bonded Group 6 transition metals,[13] [MoM(O_2CR)$_4$] (M = Cr, R = Me; M = W, R = *t*Bu). Several other heterometallic carboxylates,[14] that also contain main group–transition-metal species, [PdTl(O_2CCH_3)$_5$], [Au_2M(O_2CCH_3)$_8$] (M = Pb, Sr), and [M_2Ca(O_2CR)$_6$] (M = Zn, R = Et; M = Co, R = *t*Bu), are reported to maintain no metal–metal bonding interactions. To understand better the bonding character between bismuth and transition metals,[15] scalar relativistic density functional theory calculations were carried out for **1** and **2**. The rhodium complex, which is experimentally diamagnetic, was calculated in a spin-restricted manner; the calculation for the ruthenium compound was spin-unrestricted. As metal–metal bond lengths are especially sensitive to crystal-packing effects,[16] all calculations were run on the experimental geometries.

Figure 4 shows a diagram of the calculated energies of one-electron (Kohn–Sham) orbitals that display significant d-metal character. Images of selected orbitals are inset. Irreducible representations of the metal d orbitals in C_{4v} symmetry are indicated; however, the crystallographic structure departs from this idealized symmetry, and d_{xz} and d_{yz} orbitals (i.e. in C_{4v}) are only approximately degenerate. In both complexes, the Bi–M bonding combination lies below the frontier in energy and is doubly occupied. The highest-occupied molecular orbitals (HOMOs) are predominantly transition-metal d orbitals (d_{xy}, **1**; d_{yz}, **2**) that are effectively nonbonding with respect to bismuth. One consequence is that

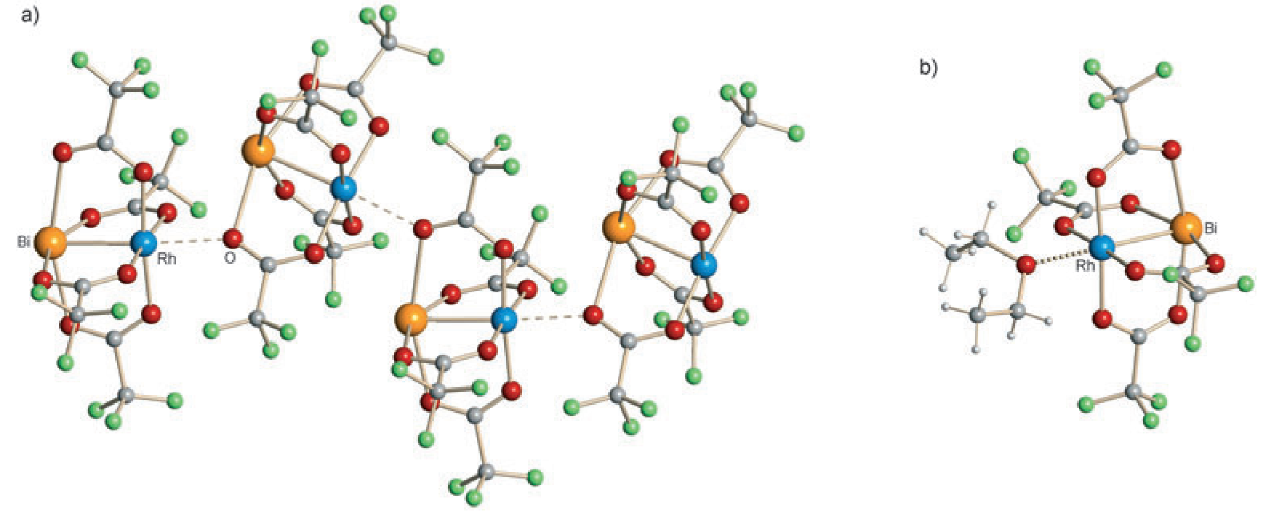

Figure 3. a) A fragment of a 1D infinite chain in the structure of **1**. Intermolecular contacts Rh···O 2.413(3) Å, Bi-Rh···O 175.83(7)°. For **2** (chain structure not shown): Ru···O 2.369(3) Å, Bi-Ru···O 176.34(8)°. b) Crystal structure of the [BiRh(O_2CCF_3)$_4$]–ether adduct **3**. Bi–Rh 2.5519(3), Rh···O 2.291(3) Å, Bi-Rh···O 179.60(8)°.

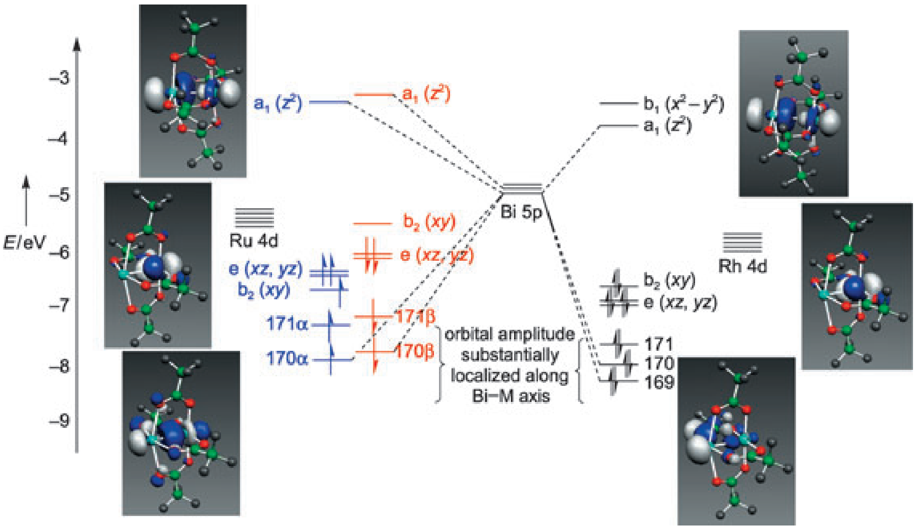

Figure 4. Calculated Kohn–Sham orbital energy-level diagrams for **1** and **2**. Transition-metal d and bismuth p orbitals, from atomic fragment calculations, are indicated. Images of selected orbitals are inset. For **2**, spin-α orbitals appear in blue; spin-β orbitals, in red. Irreducible representations within C_{4v} are indicated for orbitals of predominantly metal d character; note, however, that the complexes were calculated in C_1 symmetry and the degeneracy of the transition-metal d_{xz}/d_{yz} pair is broken.

one-electron oxidation from these HOMOs would leave the metal–metal bond order unchanged if the HOMO is the electroactive orbital. The LUMOs of **1** and **2** are the respective bismuth–metal σ* orbitals. The net result is that a direct metal–metal bond joins the metal centers. The Mayer bond order[17] of the Bi–Rh bond in **1** is 1.0, whereas that of the Bi–Ru bond in **2** is 1.2. The p_x and p_y orbitals of bismuth contribute almost exclusively to the higher energy virtuals, precluding metal–metal multiple bonding.

The observation that rhodium and ruthenium coordinate intermolecularly to carboxylate oxygens, rather than to neighboring bismuth centers, is explicable in terms of atomic charge. Table 2 lists the calculated Mulliken atomic charges for bismuth, ruthenium, and rhodium, along with average values for the carboxylate oxygen atoms. In both compounds, the positive charge on bismuth exceeds that of the transition-metal ion, which is also positively charged. The carboxylate oxygen atoms bear partial negative charges, and electrostatic interactions with either metal are attractive.

Table 2: Mulliken atomic charges calculated for **1** and **2**.

1		2	
Bi	1.3137	Bi	1.1671
Rh	0.5201	Ru	0.6573
O_{av}	−0.5675	O_{av}	−0.5734

In summary, bismuth(II) trifluoroacetate has been found to act as a metalloligand toward transition-metal fragments to afford heterobimetallic homoleptic carboxylates $[BiM(O_2CCF_3)_4]$ (**1**: M = Rh; **2**: M = Ru). The formation of heterometallic units **1** and **2** is clearly a very complex process that involves cleavage of the Bi–Bi and M–M bonds as well as rearrangement of carboxylate ligands. The coordination of the bismuth unit to the axial position of the Lewis acidic transition-metal dimer is likely an initial step in the above reaction. Heterometallic species have not been obtained with dimolybdenum(II) tetra(trifluoroacetate), which is known to feature a strong Mo–Mo quadruple bond[18] and weak Lewis acidic properties.

Experimental Section

All manipulations were performed under an anhydrous and oxygen-free atmosphere (N_2) using Schlenk-line and glove-box techniques.

1: A stoichiometric mixture of $[Bi_2(O_2CCF_3)_4]$ (0.044 g, 0.05 mmol) and $[Rh_2(O_2CCF_3)_4]$ (0.034 g, 0.05 mmol) was sealed under vacuum in a small glass ampoule and this was placed in an electric furnace that allowed a small temperature gradient along the length of the tube. The temperature was set at 120 °C. In three days, light brown crystals of **1** were deposited in the cold part of the ampoule where the temperature was set approximately 6–8 °C lower and these crystals were collected (yield ≈ 50–55 %). ^{13}C NMR (75.4 MHz, [D$_8$]toluene, 22 °C): $\delta = 116.0$ (q, $J_{CF} = 286.1$, CF_3); $\delta = 173.0$ ppm (q, $J_{CF} = 41.1$, OCO); ^{19}F NMR (282.2 MHz, [D$_8$]toluene, 22 °C): $\delta = -73.35$ (s); IR (KBr): $\tilde{\nu} = 1683$s, 1652sh (ν_{asym}(COO)), 1438m (ν_{sym}(COO)), 1209s, 1193sh, 1135s, 842m, 810m, 726m, 740s, 677m, 668w cm^{-1}; IR ($CHCl_3$): $\tilde{\nu} = 1654$s (ν_{asym}(COO)), 1453w (ν_{sym}(COO)), 1219s, 1192s, 809w, 736m cm^{-1}; UV/Vis (toluene, 22 °C): λ_{max} (ε) = 280sh (1533), 294 (2931), 326 (3314); UV/Vis ($CHCl_3$, 22 °C): λ_{max} (ε) = 260 (1658), 296 (1651), 360br (617). ESI-MS (+ mode, $CHCl_3$, m/z): 765 ($[BiRh(O_2CCF_3)_4]^+$). The compound was found to be diamagnetic over the temperature range 300–1.8 K.

2: Maroon crystals of **2** were obtained by a similar procedure using a stoichiometric mixture of $[Bi_2(O_2CCF_3)_4]$ and $[Ru_2(O_2CCF_3)_4]$ (yield ≈ 10–15 %). IR (KBr): $\tilde{\nu} = 1682$s, 1652sh (ν_{asym}(COO)), 1436w (ν_{sym}(COO)), 1209s, 1193sh, 1135s, 854m, 790m, 732s, 624vw, 530w cm^{-1}; UV/Vis (toluene, 22 °C): λ_{max} (ε) = 280sh (1462), 296 (3170), 345br (1759); UV/Vis ($CHCl_3$, 22 °C): λ_{max} (ε) = 268 (1241), 292 (1578), 338br (928).

3: Crystals of **1** were dissolved in $(C_2H_5)_2O{\cdot}BF_3$ in an NMR tube to give a saturated solution. The tube was then placed in a freezer, and orange crystals of **3** were collected after one week.

Calculations were executed with the Amsterdam Density Functional package (ADF2003.01).[19] The local density functional is that of Vosko, Wilk, and Nusair.[20] The exchange function of Becke[21] and the correlation function of Perdew[22] were applied to introduce gradient corrections. Atomic orbitals of ruthenium, rhodium, and bismuth were constructed from a triple-ζ Slater-orbital basis set (ADF database T2ZP). Triple-ζ Slater-orbital bases (TZP) were applied to carbon, oxygen, and fluorine. Core electronic shells (one or more principle quantum numbers below the valence level) were frozen for all atoms. Scalar relativistic effects were incorporated within the zero-order regular approximation (ZORA).[23] The electron density was fitted with sets of auxiliary s, p, d, f, and g functions, centered on all nuclei, along with the Coulomb and exchange potentials, in every SCF cycle. Kohn–Sham orbitals were imaged with the program MOLEKEL;[24] default isodensity values were applied. Mayer bond orders were calculated with the program MAYER.[17a,25]

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[1] a) L. G. Hubert-Pfalzgraf, *Inorg. Chem. Commun.* **2003**, *6*, 102; b) V. G. Kessler, *Chem. Commun.* **2003**, 1213; c) K. G. Caulton, L. G. Hubert-Pfalzgraf, *Chem. Rev.* **1990**, *90*, 969.

[2] a) P. Majewski, *J. Mater. Res.* **2000**, *15*, 854; b) M. L. Norton in *Chemistry of Superconductor Materials* (Ed.: T. A. Vanderah), Noyes, New Jersey, **1992**, pp. 347–379.

[3] a) J. H. Thurston, T. Ould-Ely, D. Trahan, K. H. Whitmire, *Chem. Mater.* **2003**, *15*, 4407; b) N. M. Sammes, G. A. Tompsett, H. Nafe, F. Aldinger, *J. Eur. Ceram. Soc.* **1999**, *19*, 1801.

[4] A. Sharan, I. An, C. Chen, R. W. Collins, J. Lettieri, Y. Jia, D. G. Schlom, V. Gopalan, *Appl. Phys. Lett.* **2003**, *83*, 5169.

[5] a) E. M. Slavinskaya, S. A. Veniaminov, P. Notte, A. S. Ivanova, A. I. Boronin, Yu. A. Chesalov, I. A. Polukhina, A. S. Noskov, *J. Catal.* **2004**, *222*, 129; b) B. Mazumder, J. C. Vedrine, *Appl. Catal. A* **2003**, *245*, 87; c) R. Rangel, P. Bartolo-Perez, A. Gomez-Cortes, G. Diaz, S. Fuentes, D. H. Galvan, *J. Mater. Synth. Process.* **2001**, *9*, 207; d) E. Mamedov, *Catal. Rev. Sci. Eng.* **1994**, *36*, 1.

[6] a) R. C. Mehrotra, A. Singh, *Chemtracts* **2003**, *16*, 734; b) L. E. Cross, R. C. Pohanka, *Mater. Res. Bull.* **1971**, *6*, 939.

[7] P. C. Andrews, G. B. Deacon, W. R. Jackson, M. Maguire, N. M. Scott, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.* **2002**, 4634.

[8] J. W. Pell, W. C. Davis, H. C. zur Loye, *Inorg. Chem.* **1996**, *35*, 5754.

[9] a) J. H. Thurston, D. Trahan, T. Ould-Ely, K. H. Whitmire, *Inorg. Chem.* **2004**, *43*, 3299; b) J. H. Thurston, K. H. Whitmire, *Inorg. Chem.* **2003**, *42*, 2014; c) R. E. Bachman, K. H. Whitmire, J. H. Thurston, A. Gulea, O. Stavila, V. Stavila, *Inorg. Chim. Acta* **2003**, *346*, 249; d) J. H. Thurston, K. H. Whitmire, *Inorg. Chem.* **2002**, *41*, 4194; e) M. Hunger, C. Limberg, E. Kaifer, P. Rutsch, *J. Organomet. Chem.* **2002**, *641*, 9.

[10] E. V. Dikarev, B. Li, *Inorg. Chem.* **2004**, *43*, 3461.

[11] X-ray crystal data for **1**: $BiRhC_8F_{12}O_8$, $M_r = 763.97$, light brown block, $0.26 \times 0.11 \times 0.07$ mm^3, orthorhombic, space group *Pbca*, $a = 9.7378(4)$, $b = 16.8545(8)$, $c = 20.9850(10)$ Å, $V = 3444.2(3)$ Å^3, $Z = 8$, $T = 173(2)$ K, $\rho_{calcd} = 2.947$ g cm^{-3}, $2\theta_{max} = 56.62°$. For **2**: $BiRuC_8F_{12}O_8$, $M_r = 762.13$, red block, $0.15 \times 0.08 \times 0.08$ mm^3, orthorhombic, space group *Pbca*, $a = 9.7061(5)$, $b = 16.8655(9)$, $c = 21.1527(12)$ Å, $V = 3462.7(3)$ Å^3, $Z = 8$, $T = 173(2)$ K, $\rho_{calcd} = 2.924$ g cm^{-3}, $2\theta_{max} = 56.48°$. For **3**: $BiRhC_{12}F_{12}O_9H_{10}$, $M_r = 838.09$, orange plate, $0.19 \times 0.19 \times 0.04$ mm^3, monoclinic, space group *C2/c*, $a = 31.0308(19)$, $b = 10.0341(6)$, $c = 16.2637(10)$ Å, $\beta = 116.7220(10)°$, $V = 4523.1(5)$ Å^3, $Z = 8$, $T = 173(2)$ K, $\rho_{calcd} = 2.461$ g cm^{-3}, $2\theta_{max} = 56.56°$. Bruker SMART APEX CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined using the Bruker SHELXTL (version 6.1) Software Package. Data were corrected for absorption effects using the empirical methods SADABS (min./max. apparent transmission are 0.311, 0.608, and 0.401 for **1**, **2**, and **3**, respectively). All non-hydrogen atoms were refined anisotropically except the disordered fluorine atoms. Hydrogen atoms in **3** were included in idealized positions for structure factor calculations. The fluorine atoms of some CF_3 groups were disordered over two or three different rotational orientations. This disorder was modeled individually in each case. In the structure of **3** both ethyl groups of ether were found to be disordered over two orientations. For **1** full-matrix refinement on F^2 converged at $R1 = 0.0225$ and $wR2 = 0.0511$ for 310 parameters and 72 restraints and 3785 reflections with $I > 2\sigma(I)$ ($R1 = 0.0257$, $wR2 = 0.0523$ for 4171 unique reflections) and a goodness-of-fit of 1.056. For **2** full-matrix refinement on F^2 converged at $R1 = 0.0266$ and $wR2 = 0.0626$ for 298 parameters and 54 restraints and 3570 reflections with $I > 2\sigma(I)$ ($R1 = 0.0342$, $wR2 = 0.0653$ for 4179 unique reflections) and a goodness-of-fit of 1.039. For **3** full-matrix refinement on F^2 converged at $R1 = 0.0215$ and $wR2 = 0.0527$ for 325 parameters and 25 restraints and 4926 reflections with $I > 2\sigma(I)$ ($R1 = 0.0237$, $wR2 = 0.0536$ for 5310 unique reflections) and a goodness-of-fit of 1.051. CCDC 252670, CCDC 252671, and CCDC 252672 (**1**, **2**, and **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] a) F. A. Cotton, E. V. Dikarev, X. Feng, *Inorg. Chim. Acta* **1995**, *237*, 19; b) E. V. Dikarev, A. S. Filatov, M. A. Petrukhina, unpublished results.

[13] a) C. D. Garner, R. G. Senior, T. J. King, *J. Am. Chem. Soc.* **1976**, *98*, 3526; b) V. Katovic, R. E. McCarley, *J. Am. Chem. Soc.* **1978**, *100*, 5586.

[14] a) S. Adam, A. Bauer, O. Timpe, U. Wild, G. Mestl, W. Bensch, R. Schlogl, *Chem. Eur. J.* **1998**, *4*, 1458; b) A. L. Balch, B. J. Davis, E. Y. Fung, M. M. Olmstead, *Inorg. Chim. Acta* **1993**, *212*, 149; c) P. G. Jones, R. Schelbach, E. Schwarzmann, C. Thone, A. Vielmader, *Z. Naturforsch. B* **1988**, *43*, 807; d) P. G. Jones, *Acta Crystallogr. Sect. C* **1984**, *40*, 804; e) Y. Cui, X. Zhang, F. Zheng, J. Ren, G. Chen, Y. Qian, J. Huang, *Acta Crystallogr. Sect. C* **2000**, *56*, 1198.

[15] T. R. Cundari, *Chem. Rev.* **2000**, *100*, 807.

[16] A. Martin, A. G. Orpen, *J. Am. Chem. Soc.* **1996**, *118*, 1464.

[17] a) A. J. Bridgeman, G. Cavigliasso, L. R. Ireland, J. Rothery, *J. Chem. Soc. Dalton Trans.* **2001**, 2095; b) I. Mayer, *Chem. Phys. Lett.* **1983**, *97*, 270.

[18] F. A. Cotton, R. A. Walton, *Multiple Bonds between Metal Atoms*, Oxford University Press, New York, **1993**.

[19] a) G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931; b) C. Fonseca Guerra, J. G. Snijders, G. te Velde, E. J. Baerends, *Theor. Chem. Acc.* **1998**, *99*, 391; c) ADF2003.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

[20] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200.

[21] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.

[22] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.

[23] a) E. van Lenthe, E. J. Baerends, J. G. Snijders, *J. Chem. Phys.* **1993**, *99*, 4597; b) E. van Lenthe, E. J. Baerends, J. G. Snijders, *J. Chem. Phys.* **1994**, *101*, 9783; c) E. van Lenthe, J. G. Snijders, E. J. Baerends, *J. Chem. Phys.* **1996**, *105*, 6505; d) E. van Lenthe, R. van Leeuwen, E. J. Baerends, J. G. Snijders, *Int. J. Quantum Chem.* **1996**, *57*, 281.

[24] a) MOLEKEL 4.3, P. Flükiger, H. P. Lüthi, S. Portmann, J. Weber, Swiss Center for Scientific Computing, Manno (Switzerland), **2000–2002**; b) S. Portmann, H. P. Lüthi, *Chimia* **2000**, *54*, 766.

[25] A. J. Bridgeman, C. J. Empson, MAYER, The University of Hull, Hull, UK, **2003**.