Structure of Nitrile-Functionalized Alkyltrifluoroborate Salts

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Two nitrile-functionalized alkyltriflouroborate anion based complexes $[(Ph_3P)_2N][CH_3CH(BF_3)CH_2CN]$ and $[K(18\text{-crown-}6)][CH_3CH(BF_3)CH_2CN]$ were synthesized and characterized by spectroscopic methods and single X-ray diffraction analysis. In the former complex no direct cation-anion (F→N or F→P) interactions are observed although F···H–C hydrogen bonds are present. In the later complex all three fluorine atoms interact with the potassium cation and C–H···F hydrogen bonds are also present. The ESI-MS spectra in methanol solution of the potassium complex show similar anion-cation aggregation to that observed for ionic liquids, and comparisons between the two complexes and ionic liquid systems are made.

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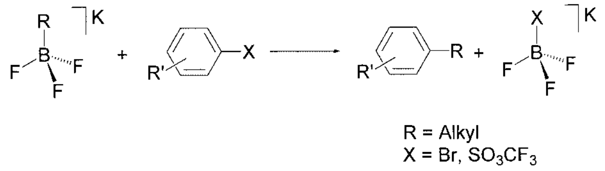
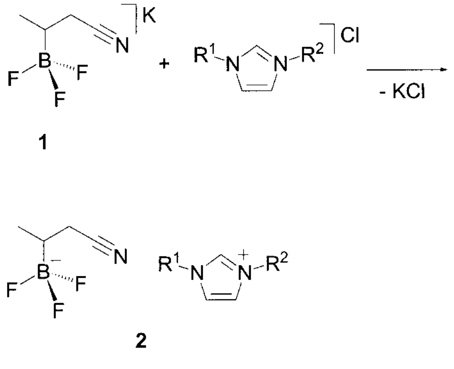
Introduction

Alkyltrifluoroborates are valuable substrates for Suzuki–Miyaura coupling reactions.[1,2] The relatively mild reaction conditions under which they react with arylhalides have made this synthetic approach a highly popular route for the generation of new C–C bonds in organic synthesis, see Scheme 1. Alkyltrifluoroborates are easily prepared on a moderate scale by the addition of KHF_2 to a variety of organoboron intermediates such as boronic acids and esters, organodihaloboranes and organodiaminoboranes, which makes them particularly attractive reagents.[1,2]



Scheme 1

Being structurally and electronically closely related to the BF_4^- anion they can be regarded as potential precursors for the formation of low-melting ionic liquids. The design and synthesis of functionalized ionic liquids is currently attracting a great deal of interest.[3,4,5] In these ionic liquid systems the emphasis lies in the modification of the cationic component, whereas the nature of the anion remains usually unchanged; typically BF_4^- and PF_6^- and to a lesser extent $SO_3CF_3^-$ and $N(SO_2CF_3)^-$ are employed. Recently, we reported on the synthesis of the first imidazolium-based ionic liquids with nitrile-functionalized alkylfluoroborate anions, see Scheme 2.[6] Even in the presence of functional groups on the imidazolium cation, these salts exhibit significantly lower melting points and viscosities relative to the well-established BF_4^- ionic liquids, an effect that has also been noted with the $CF_3BF_3^-$ anion.[7]



Scheme 2

Despite the fact that numerous alkyltrifluoroborate salts have been prepared over the years solid state structural studies of such compounds are extremely sparse. As far as we are aware, only three structures with a sp^3-carbon bound to a BF_3-fragment exist.[8] Apart from these, structures of BF_3-olefin,[9] -aryl,[10] -carbene[11] and -cyclopentadienyl[12] anions are also known.

Structural information of such alkylated trifluoroborates may help to estimate the physical properties of ionic liquids based on such anions. Thus far, efforts to gain insight into

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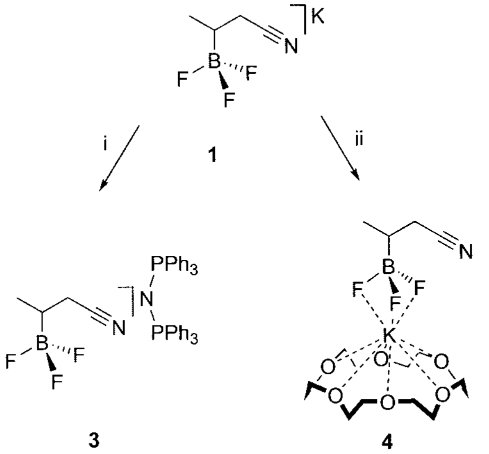
their structural characteristics have been made using IR and NMR techniques on imidazolium tetrafluoroborate systems,[13]partly because the imidazolium salts with the BF_4^- anion of most interest are liquid at room temperature, which has made it difficult to obtain crystals for X-ray studies. In this paper we present structural investigations on two novel compounds based on the alkylfluoroborate anion $CH_3CH(BF_3)CH_2CN^-$, which provide clues as to how it may interact with imidazolium cations in the liquid phase. This study also illustrates the utility of crown ethers as reagents to facilitate crystallization of anions with small metal counterions which are usually difficult to crystallize.

Results and Discussion

The potassium salt $K[CH_3CH(BF_3)CH_2CN]$, **1**, prepared as a racemic mixture using the literature protocol, crystallized as thin needles which proved unsuitable for single-crystal X-ray diffraction analysis (several attempts to give useful data failed).[6] However, exchange of the potassium cation for $[(Ph_3P)_2N]^+$ or complexation with 18-crown-6 affords compounds **3** and **4**, respectively, as crystalline products that are amenable to X-ray analysis, see Scheme 3.



Scheme 3. Synthesis of compounds **3** and **4**; (i): $[N(PPh_2)_2]Cl$, CH_2Cl_2; (ii): 18-crown-6, THF

Both salts are obtained in essentially quantitative yield. In the case of **3**, the potassium chloride formed from the reaction was separated by filtration and the product obtained after removal of the solvent. This approach, viz. metathesis of a small cation for a large cation is a widely used method to facilitate crystallization of large anions and in some cases is referred to as crystal engineering.[14] For compound **4**, the product was easily obtained by mixing the potassium salt with stoichiometric amounts of 18-crown-6. This strategy essentially converts the small potassium cation into a larger entity by combining it with the crown moiety (rather than replacing it for another anion altogether), and it could prove to be an important way of generating good quality crystals as an alternative to the metathesis approach.

In this manner, the alkyltrifluoroborate anion is obtained either as the "free" anion or in the form of an ion-pair: In **3**, the charge on the cation $[(Ph_3P)_2N]^+$ is delocalized along the P–N–P unit while at the same time beingprotected by six phenyl groups, excluding direct cation-anion charge transfer, F→N or F→P. In contrast, in **4**, complexation by the 18-crown-6 macrocycle leaves the potassium cation accessible enough to interact with the fluorine atoms to form a tight ion-pair. Such potassium 18-crown-6 borate complexes are very rare, the synthesis of the BH_4-analog has been published[15] and the BF_4-salt appears in the patent literature as flame retardant for polycarbonates.[16]

The nitrile stretching frequency, υ_{CN}, is observed at 2233 cm^{-1} in **3** and at 2237 cm^{-1} in **4** [cf. **1** $\upsilon_{CN} = 2247\ cm^{-1}$. The ^1H NMR spectra of both **3** and **4** is of routine nature in that there are no noteworthy differences for protons belonging to the anion relative to the potassium salt **1** and the ionic liquid **2**. In [D$_6$]acetone, the ^{19}F chemical shift stemming from the BF_3-moiety in **3** and **4** is identical, with $^1J_{FB}$ coupling constants being also very similar, indicating that in this solvent, the cation and anion are solvolysed and do not interact significantly with each other. The electrospray ionisation (ESI) mass spectrum of **3** in methanol shows a parent peak at *m*/*z* 538 in positive ion mode for the $[(PPh_3)_2N]^+$ cation and *m*/*z* 136 in the negative ion mode for the $[CH_3CH(BF_3)CH_2CN]^-$ anion. Anion-cation aggregations were observed in neither the positive nor negative spectra in the concentration range of 5–50 ppm. In contrast, the ESI mass spectrum of **4** exhibits some concentration dependence, see Figure 1. At low concentration, ca. 5 ppm, a peak at *m*/*z* = 303 corresponding to the monomeric cation [K(18-crown-6)]$^+$ dominates, whereas at higher concentration, ca. 50 ppm, the aggregate [K(18-crown-6)]$_2$-$[CH_3CH(BF_3)CH_2CN]$ gives rise to the base peak at *m*/*z* 742.

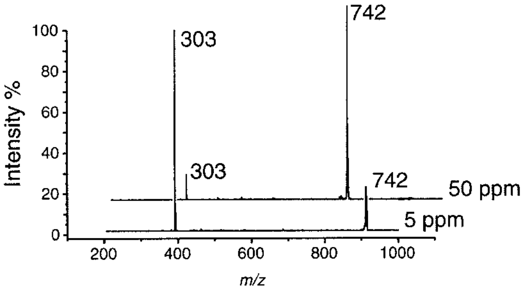


Figure 1. ESI-MS spectrum of **4** in methanol at concentrations of 5 and 50 ppm

Structural Characterization of 3 and 4

The few known structures for alkyltrifluoroborates comprise the potassium salts $K[CF_3BF_3]$[8a] and $K[CH_3BF_3]$[8b] which exhibit extensive potassium-fluorine interactions with K–F distances as short as 2.678(1) Å. The structure of the zwitterionic compound $BF_3CH_2S(O)(CH_3)_2$ has also been reported.[8c]

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Single crystals of **3** and **4** suitable for X-ray diffraction studies were grown at –21 °C from dichloromethane-diethyl ether and THF-diethyl ether solution, respectively. The structures of **3** and **4** are illustrated in Figure 2 and Figure 3, respectively, with key bond parameters in the captions. Details of the data collection and the structure determination are provided in the Experimental. There is negligible disorder in the anion of **3**, involving carbon atoms C2 and C3, whereas in **4** there is considerable disorder in the anion, where carbon atoms C2 and C4 are split over two positions with almost identical occupation factors.

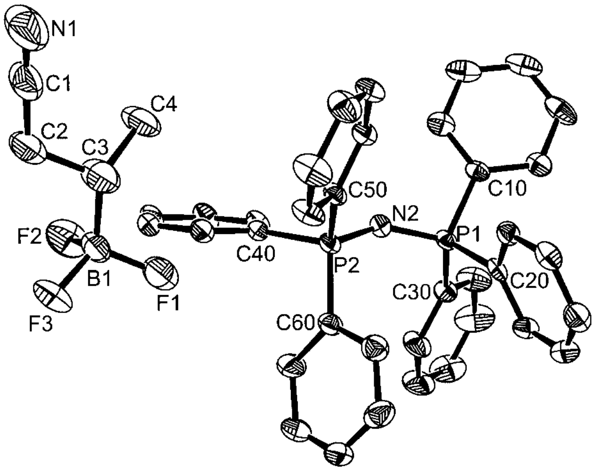


Figure 2. ORTEP-plot of **3** with ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: F1–B1 1.385(5), F2–B1 1.427(5), F3–B1 1.412(5), B1–C3 1.585(6), P1–N2 1.574(3), P2–N2 1.570(3), C1–N1 1.112(6); F1–B1–C3 110.7(3), F2–B1–C3 112.0(3), F3–B1–C3 110.9(4), C2–C3–C4 109.9(4), P1–N2–P2 142.8(2)

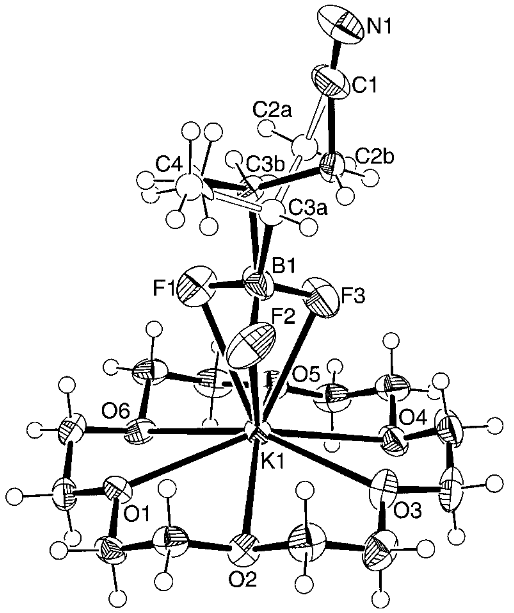


Figure 3. ORTEP-plot of **4** showing the disorder in the alkane moiety; ellipsoids drawn at the 50% probability level. Selected bond lengths [Å]: F1–B1 1.401(3), F2–B1 1.407(3), F3–B1 1.422(3), K1–F1 2.782(1), K1–F2 2.929(1), K1–F3 2.766(1), K1–O1 2.843(1), K1–O2 2.939(1), K1–O3 2.792(2), K1–O4 2.929(2), K1–O5 2.802(2), K1–O6 2.912(1)

In compound **3** the anion adopts a staggered conformation about the B1–C3 bond with an alignment of F1 *anti* to the C3–C2 bond and F3 *anti* to the C3–C4 bond. This conformation influences the B–F distances, which are shorter for F1 and F3 [1.385(5) and 1.412(5) Å, respectively], than for F2 [1.427(5) Å]. In addition, the F2–B1–C3 angle is slightly larger, 112.0(3)°, but all bonding angles around B1 are within 5° of the ideal tetrahedral angle. All fluorine atoms are engaged in intra- and intermolecular hydrogen bonding with H–F distances as short as 2.386 Å (to F1). The B1–C3 distance of 1.585(6) Å is of the same order as in $K[CH_3BF_3]$, viz. 1.575(3) Å,[8b] and markedly shorter than in $BF_3CH_2S(O)(CH_3)_2$, 1.650(2) Å,[8c] reflecting the presence of a localized negative charge on the boron atom. The nitrile moiety, which exhibits a somewhat short C≡N distance of 1.112(6) Å, points away from the fluorine atoms, being almost parallel to the B1–C3 bond. This alignment is probably due to both electrostatic repulsion from the electronegative fluorine atoms and to interactions with phenyl-hydrogen atoms, which come as close as 2.567 Å to N1. The structure of the $[PPN]^+$ cation agrees well with the data reported elsewhere.[17,18] The P–N distances, 1.574(3) Å and 1.570(3) Å, are as expected; the P–N–P angle, 142.8(2)°, is slightly larger than frequently observed but still within the normal range. No close intermolecular contacts to N2 are present.

Only few structures exist in which a potassium cation is complexed to both a crown ether and fluorine atoms. Most of these salts contain perfluorated silicates as anions,[19] but structures with, for example, hexafluorophosphate[20] and pentafluoroalkyne tungstenate[21] are also known. In addition, a KF adduct of a 21-membered crown ether containing six oxygen atoms and a tethered boronic acid moiety has also been reported.[22] Yet, complex **4** represents the first example of a structure in which a perfluorated boron moiety interacts with a potassium crown ether complex.

Due to the above mentioned disorder, which affects carbon atoms C2 and C4 in the anion in **4**,no quantitative comparison of the anionic structure with **3** is possible. As in **3**, F3 is *anti* to the C3–C4 bond, but the orientation of the C3–C2 bond relative to the fluorine atoms in not unambiguously clear. Despite interaction of the fluorine atoms with the potassium ion, no significant elongation of the B–F bond distances are observed, which range from 1.401(3) to 1.422(3) Å.

The potassium ion lies 0.450 Å above the mean plane defined by the three oxygen atoms O1, O3 and O5 and 0.844 Å above the mean plane defined by the three oxygen atoms O2, O4 and O6. The K–O bonds can accordingly be divided into two groups of three with shorter distances to O1, O3 and O5 [range 2.792(2) to 2.843(2) Å], and longer distances to O2, O4 and O6 [range 2.912(1) to 2.939(1) Å], which is in good agreement with a comparable structure.[23]

The fluorine atoms interact with both intra- and intermolecular hydrogen atoms. Yet, as a result of the bulky crown ether moiety only five intermolecular hydrogen bonds below 3 Å to the fluorine atoms are present, see Figure 4. Such F→H–C hydrogen bonding is very common in imidazolium based systems, where it has been probed by IR and NMR spectroscopic methods, but seldom by single-crystal X-ray analysis.[13] The cation and anion in **4** are held in place by potassium-fluorine interactions with two shorter bonds [2.766(1) and 2.782(1) Å], and one longer bond [2.929(1) Å]. These distances are of the same order as in crystals of potassium tetrafluoroborate[24] and the asymmetry of the bonding is comparable to a related fluorosilicate complex.[19a]

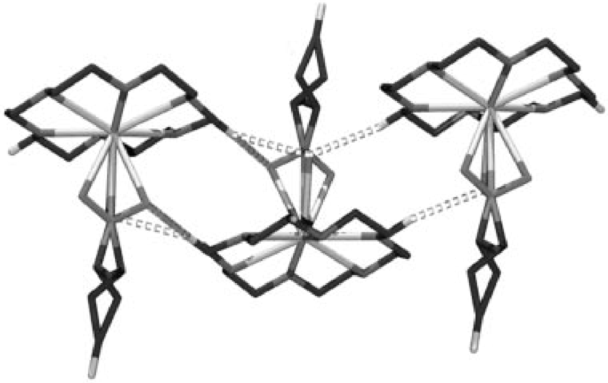
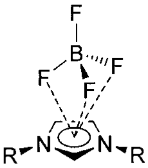


Figure 4. Crystal packing in compound **4**, showing intramolecular hydrogen bonding interactions below 3 Å to the fluorine atoms. For clarity, only those hydrogen atoms involved in the H-bonding are shown

In the context of ionic liquid chemistry it is not unreasonable to propose a similar interaction e.g. with the fluoroborate straddling the face of the imidazolium ring as shown in Scheme 4. This kind of interaction might provide additional rational for the low melting points observed in such compounds in that the intermolecular van-der-Waals forces and C–H···F hydrogen bonding interactions would be reduced.[25]



Scheme 4

In conclusion, the structural studies reported herein provide insight into the bonding characters and substitution effect of one of the F atoms in the BF_4^- anion by a functional group. The information gained is relevant to the Suzuki–Miyaura reaction and to the functionalization of ionic liquid anions. Crown ethers have been used as competitors for ion immobilization in ionic liquids[26] and to increase the solubility of amino acids in ionic liquid,[27]but their function herein was as a crystallization aid, an approach that has been used for some time in crystal engineering.[28]

Experimental Section

The potassium salt **1** was prepared following a published method.[6] Bis(triphenylphosphanyl)iminium chloride and 18-crown-6 were purchased from Aldrich and were used as received. The synthesis of compound **3** was carried out in an inert atmosphere of dry nitrogen and the synthesis of **4** was performed without precautions to exclude air or moisture. IR spectra were recorded on a Perkin–Elmer FT-IR 2000 system. NMR spectra were measured on a Bruker DMX 400 spectrometer. Chemical shifts, δ, are given in ppm and coupling constants, *J*, in Hz. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ™ Deca XP Plus quadrupole ion trap instrument on samples diluted in methanol. Samples were infused directly into the source at 5 µL min^{-1} using a syringe pump, the spray voltage was set at 5 kV and the capillary temperature at 50 °C.[29] Elemental analysis were carried out at the Institute of Molecular and Biological Chemistry at the EPFL.

Synthesis of [$(PPh_3)_2N$][$CH_3CH(BF_3)CH_2CN$] (3): A mixture of the potassium salt **1** (175 mg, 1.0 mmol) and bis(triphenylphosphanyl)iminium chloride (574 mg, 1.0 mmol) in dichloromethane (10.0 mL) was stirred at room temperature for 24 hours. The reaction mixture was filtered and the solid washed with dichloromethane (2 × 5.0 mL). The filtrates were combined and the solvent removed under reduced pressure to give the pure product. Yield: 654 mg, 97%, m.p. 140 °C. ESI-MS (MeOH) positive ion *m/z*, 538, $[(PPh_3)_2N]^+$; negative ion, 136, $[CH_3CH(BF_3)CH_2CN]^-$. IR (cm^{-1}) 3060 (m), 2938 (m), 2864 (m), 2233 (m), 1588 (m), 1482 (m), 1438 (str.), 1281 (m), 1243 (str.), 1209 (m), 1110 (str.), 1050 (m), 995 (str.), 933 (m),, 910 (m), 802 (m), 721 (str.). ^1H NMR (400 MHz, [D_6]acetone): δ = 7.85–7.68 (m, 18 H), 7.64 –7.55 (m, 12 H); 2.38 (dd, 1 H, $^2J($H,H) = 17.2, $^3J_{H,H}$ = 3.0), 1.85 (dd, 1 H, $^2J_{H,H}$ = 17.0, $^3J_{H,H}$ = 12.0), 0.92 (d, 3 H, $^3J_{H,H}$ = 6.8), 0.59 (m, 1 H).[31] P NMR (161 MHz, [D_6]acetone): δ = 21.1 (s). ^{19}F NMR (282 MHz, [D_6]acetone): δ = –151.5 (q, $^1J_{FB}$ = 60). $C_{40}H_{36}BF_3N_2P_2$ (674.48): C 71.23, H 5.38, N 4.15; found: C 71.31, H 5.41, N 4.13.

Synthesis of [K(18-crown-6)][$CH_3CH(BF_3)CH_2CN$] (4): A mixture of potassium salt **1** (175 mg, 1.0 mmol) and 18-crown-6 (264 mg, 1.0 mmol) in THF (10.0 mL) was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure to give the product in pure form. Yield: 435 mg, 99%, m.p. 145 °C. ESI-MS (MeOH) positive ion, *m/z* 303 $[C_{12}H_{24}O_6K]^+$; negative ion, 136, $[CH_3CH(BF_3)CH_2CN]^-$. IR (cm^{-1}) 2899 (str.), 2826 (w), 2237 (m), 1589 (w), 1479 (str.), 1458 (m), 1438 (m), 1351 (str.), 1286 (m), 1249 (str.), 1100 (str.), 1008 (str.), 962 (str.). 931 (m), 838 (m), 720 (m). ^1H NMR (400 MHz, [D_6]acetone): δ = 3.62 (s, 24 H, OCH_2), 2.38 (dd, 1 H, $^2J_{H,H}$ = 17.1, $^3J_{H,H}$ = 3.3), 1.93 (dd, 1 H, $^2J_{H,H}$ = 17.0, $^3J_{H,H}$ = 12.1), 0.93 (d, 3 H, $^3J_{H,H}$ = 6.9), 0.59 (m, 1 H). ^{19}F NMR ([D_6]acetone, 282 MHz): δ = –151.5 (q, $^1J_{FB}$ = 59). $C_{16}H_{30}BF_3KNO_6$ (439.32) (%): C 43.74, H 6.88, N 3.19; found: C 43.80, H 6.91, N 3.18.

Structural Characterisation of 3 and 4: Crystals of **3** suitable for X-ray diffraction studies were obtained at –21 °C from in dichloromethane/diethyl ether (1:1) solution, those of **4** (Table 1) under similar conditions from THF/diethyl ether (1:5). Single crystals were mounted on a KUMA KM4/Sapphire CCD diffractometer. Data reduction was performed using CrysAlis RED.[30] Structure solution and refinement was performed using the SHELX97 software package,[31] graphical representations of the structures were made with ORTEP32.[32] Structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against F^2). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were

Table 1. Crystal data and details of the structure determination for **3** and **4**

	3	**4**
Formula	$C_{40}H_{36}BF_3N_2P_2$	$C_{16}H_{30}BF_3KNO_6$
M	674.46	439.32
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P21/n$
a [Å]	9.8205(13)	13.0764(12)
b [Å]	11.0284(15)	8.5112(8)
c [Å]	17.220(2)	19.7499(18)
α [°]	107.184(11)	90
β [°]	94.231(10)	95.013(7)
γ [°]	99.666(11)	90
V [Å^3]	1741.3(4)	2189.7(4)
Z	2	4
Density [Mg/m^3]	1.286	1.333
T [K]	140	140
Θ range [°]	$3.02 \leq \Theta \leq 25.02$	$2.86 \leq \Theta \leq 25.03$
μ/mm^{-1}	0.173	0.297
Reflections measured	10233	12166
Unique reflections [$I > 2\sigma(I)$]	5378 (R_{int} = 0.0465)	3687 (R_{int} = 0.0398)
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0711, 0.2066	0.0375, 0.0809

placed in their geometrically generated positions and refined using a riding model. In **4**, carbon atoms C2 and C3 were split over two positions with almost identical occupancy factors and the structure refined without restraints. CCDC-250726 and CCDC-250727 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.

Acknowledgments

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[1] a) G. A. Molander, T. Ito, *Org. Lett.* **2001**, *3*, 393; b) G. A. Molander, M. Rodriguez Rivero, *Org. Lett.* **2002**, *4*, 107; c) G. A. Molander, C. R. Bernardi, *J. Org. Chem.* **2002**, *67*, 8424; d) G. A. Molander, B. W. Katona, F. Machrouhi, *J. Org. Chem.* **2002**, *67*, 8416; e) G. A. Molander, C.-S. Yun, M. Ribagorda, B. Biolatto, *J. Org. Chem.* **2003**, *68*, 5534.

[2] a) H.-J. Frohn, N. Y. Adonin, V. V. Bardin, V. F. Starichenko, *Tetrahedron Lett.* **2002**, *43*, 8111; b) J.-P. Tremblay-Morin, S. Raeppel, F. Gaudette, *Tetrahedron Lett.* **2004**, *45*, 3471; c) N. Y. Adonin, V. V. Bardin, U. Flörke, H.-J. Frohn, *Organometallics* **2004**, *23*, 172; d) N. Y. Adonin, V. V. Bardin, H.-J. Frohn, *Organometallics* **2004**, *23*, 535.

[3] a) L. C. Branco, J. N. Rosa, J. J. Moura Ramos, C. A. M. Alfonso, *Chem. Eur. J.* **2002**, *8*, 3671; b) Z. Fei, D. Zhao, T. J. Geldbach, R. Scopelliti, P. J. Dyson, *Chem. Eur. J.* **2004**, *10*, 4886.

[4] a) H. Schottenberger, K. Wurst, U. E. I. Horvath, S. Cronje, J. Lukasser, J. Polin, J. M. McKenzie, H. G. Raubenheimer, *J. Chem. Soc., Dalton Trans.* **2003**, 4275; b) Z. Fei, D. Zhao, R. Scopelliti, P. J. Dyson, *Organometallics* **2004**, *23*, 1622.

[5] a) C. Ye, J. M. Shreeve, *J. Org. Chem.* **2004**, *69*, 6511; b) Y. Gao, J. M. Shreeve, *Synthesis* **2004**, *7*, 1072; c) J. Kim, R. P. Singh, J. M. Shreeve, *Inorg. Chem.* **2004**, *43*, 2960; d) O. D. Gupta, B. Twamley, J. M. Shreeve, *Tetrahedron Lett.* **2004**, *45*, 1733; e) H. Xue, B. Twamley, J. M. Shreeve, *J. Org. Chem.* **2004**, *69*, 1397; f) Y. R. Mirzaei, H. Xue, J. M. Shreeve, *Inorg. Chem.* **2004**, *43*, 361.

[6] D. Zhao, Z. Fei, C. A. Ohlin, G. Laurenczy, P. J. Dyson, *Chem. Commun.* **2004**, 2500.

[7] a) Z.-B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Lett.* **2004**, *33*, 680; b) Z.-B. Zhou, M. Takeda, M. Ue, *J. Fluorine Chem.* **2004**, *125*, 471.

[8] a) D. J. Brauer, H. Bürger, G. Pawelke, *Inorg. Chem.* **1977**, *16*, 2305; b) D. J. Brauer, H. Bürger, G. Pawelke, *J. Organomet. Chem.* **1982**, *238*, 267; c) J. M. Stoddard, K. J. Shea, *Organometallics* **2003**, *22*, 1124.

[9] A. N. Thadani, R. A. Batey, D. V. Smil, A. J. Lough, *Acta Crystallogr. Sect. E* **2001**, *57*, m333.

[10] a) T. D. Quach, R. A. Batey, A. J. Lough, *Acta Crystallogr. Sect. E* **2001**, *57*, o688; b) E. Vedejs, R. W. Chapman, S. Lin, M. Müller, D. R. Powell, *J. Am. Chem. Soc.* **2000**, *122*, 3047; c) G. Conole, A. Clough, A. Whiting, *Acta Crystallogr. Sect. C* **1995**, *51*, 1056.

[11] a) X. Cattoën, H. Gornitzka, D. Bourissou, G. Bertrand, *J. Am. Chem. Soc.* **2004**, *126*, 1342; b) D. J. Nielsen, K. J. Cavell, B. W. Skelton, A. H. White, *Inorg. Chim. Acta* **2003**, *352*, 143; c) A. J. Arduengo III, F. Davidson, R. Krafczyk, W. J. Marshall, R. Schmutzler, *Monatsh. Chem.* **2000**, *131*, 251; d) N. Kuhn, R. Fawzi, H. Kotowski, M. Steimann, *Z. Kristallogr.* **1997**, *212*, 259.

[12] a) J. W. Bats, M. Scheibitz, M. Wagner, *Acta Crystallogr. Sect. C* **2003**, *59*, m355; b) T. Quach, R. A. Baley, A. J. Lough, *Acta Crystallogr. Sect. E* **2001**, *57*, 320.

[13] a) P. Bonhote, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, *35*, 1168; b) A. Noda, K. Hayamizu, M. Watanabe, *J. Phys. Chem. B* **2001**, *105*, 4603; c) J.-F. Huang, P.-Y. Chen, I-W. Sun, S. P. Wang, *Inorg. Chim. Acta* **2001**, *32*, 7.

[14] D. Braga, *Chem. Commun.* **2003**, 2751.

[15] Y. N. Shevchenko, K. B. Yatsimirskii, S. A. Minkov, *Z. Neorg. Khim.* **1985**, *30*, 1705.

[16] L. S. Thomas, US-Patent US 4439566 A 19840327.

[17] R.-Y. Liau, H. Ehlich, A. Schier, H. Schmidbaur, *Z. Naturforsch., Teil B* **2002**, *57*, 1085.

[18] a) T. S. Cameron, M. E. Peach, *J. Chem. Crystallogr.* **1998**, *28*, 919; b) S. H. Lawrence, S. G. Shore, T. F. Koetzle, J. C. Huffman, C.-Y. Wei, R. Bau, *Inorg. Chem.* **1985**, *24*, 3171.

[19] a) N. Kano, F. Komatsu, T. Kawashima, *J. Am. Chem. Soc.* **2001**, *123*, 10778; b) S. E. Johnson, J. S. Payne, R. O. Day, J. M. Holmes, R. R. Holmes, *Inorg. Chem.* **1989**, *28*, 3190.

[20] A. Zaeni, F. T. Edelmann, F. Olbrich, private communication in 2004; see also CCDC-231012 (Cambridge Crystallographic Data Centre, www.ccdc.cam.ac.uk/data_request/cif).

[21] P. Neumann, K. Dehnicke, D. Fenske, G. Baum, *Z. Naturforsch. Teil B* **1991**, *46*, 999.

[22] M. T. Reetz, C. M. Niemeyer, K. Harms, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1472.

[23] D. G. Gusev, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **1998**, *120*, 13138.

[24] G. Brunton, *Acta Crystallogr. Sect. B* **1969**, *B25*, 2161.

[25] A. R. Katritzky, R. Jain, A. Lomaka, R. Petrukhin, U. Maran, M. Karelson, *Cryst. Growth Des.* **2001**, *1*, 261.

[26] S. Chun, S. V. Dzyuba, R. A. Bartsch, *Anal. Chem.* **2001**, *73*, 3737.

[27] S. V. Smirnova, I. I. Torocheshnikova, A. A. Formanovsky, I. V. Pletnev, *Anal. Bioanal. Chem.* **2004**, *378*, 1369.

[28] a) H. Zhang, X. Wang, B. K. Teo, *J. Am. Chem. Soc.* **1996**, *118*, 11813; b) J. A. Manskaya, K. V. Domasevitch, V. Konstantin, V. V. Ponomareva, J. Sieler, V. N. Kokozay, *Z. Naturforsch. Teil B* **1998**, *53*, 683.

[29] P. J. Dyson, J. S. McIndoe, D. Zhao, *Chem. Commun.* **2003**, 508.

[30] Oxford Diffraction Ltd., 68 Milton Park, Abingdon, OX14 4 RX, UK, **2003**.

[31] G. M. Sheldrick, *SHELX-97. Structure Solution and Refinement Package*, University of Göttingen, **1997**.

[32] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

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