

Carbon–Fluorine Bond Formation *via* a Five-Coordinate Fluoro Complex of Ruthenium(II)

Preliminary Communication

by Peter Barthazy, Lukas Hintermann, Robert M. Stoop, Michael Wörle, Antonio Mezzetti*,
and Antonio Togni*

Laboratory of Inorganic Chemistry, Swiss Federal Institute of Technology, ETH Zentrum, CH-8092 Zürich (Tel: 01 632 6121/2236; e-mail: mezzetti@inorg.chem.ethz.ch; togni@inorg.chem.ethz.ch)

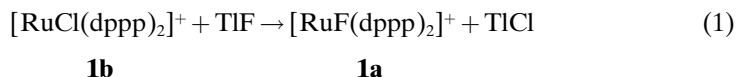
The 16-electron, five-coordinate fluoro complex $[\text{RuF}(\text{dppp})_2]\text{PF}_6$ (**1a**; dppp = propane-1,3-diylbis[diphenylphosphine]) smoothly reacts with 1,3-diphenylallyl bromide (= 1,1'-(3-bromoprop-1-ene-1,3-diyl)bis[benzene]) in dry CDCl_3 to give 1,3-diphenylallyl fluoride and $[\text{RuBr}(\text{dppp})_2]^+$ in nearly quantitative yield. Under similar conditions, bromide (or chloride)/fluoride exchange also occurs with chlorotriphenylmethane, bromodiphenylmethane, and *tert*-butyl bromide. The crystal structure of **1a** is reported.

Introduction. – F-Containing organic molecules find extensive use in biochemistry and medicinal chemistry. Therefore, selective fluorination (C–F bond formation) has to be regarded as one of the new frontiers in organic synthesis [1]. By contrast, organometallic chemists have directed more efforts toward stoichiometric [2–5] or catalytic [6][7] C–F bond cleavage, and metal-assisted fluorination is essentially restricted to the formation of fluoroacyl complexes [8] and to the use of metal fluoride salts [9]. Driven by the interest in C–F activation, studies of the coordination chemistry of fluoride have recently progressed from the stage of serendipity to systematic investigation [10–14].

Fluoride is known to stabilize early- or middle-transition-metal complexes with fewer than six valence electrons by $\text{F} \rightarrow \text{M}$ π -donation [10], whereas the four-electron repulsion between the filled π -orbitals on the metal and the F π -orbitals is thought to account for the paucity of fluoro complexes of the late-transition-metal ions [15]. Interestingly, this interaction can be exploited to stabilize ‘operationally unsaturated’ complexes with a formal 16-electron count [11][15]. However, five-coordinate fluoro complexes with such an electron configuration are exceedingly rare [11], and most of the reported complexes combining fluoride and phosphine ligands contain strong π -acceptor co-ligands, generally as part of a *trans*-[F–M–CO] fragment featuring push-pull interactions [11][14][15].

Results and Discussion. – We report herein the 16-electron species $[\text{RuF}(\text{dppp})_2]^+$ (**1a**; dppp = propane-1,3-diylbis[diphenylphosphine]) and its use as a fluorinating agent for selected organic bromides. Thus, we prepared the dark-red five-coordinate

complex $[\text{RuF}(\text{dppp})_2]\text{PF}_6$ (**1a** · PF_6), containing the unprecedented FP_4 donor set, by the reaction of $[\text{RuCl}(\text{dppp})_2]\text{PF}_6$ (**1b** · PF_6) with TIF in CH_2Cl_2 (Eqn. 1).¹⁾



The ^{31}P -NMR spectrum of **1a** consists of the $AA'MM'$ part of a $AA'MM'X$ spin system, with resolved couplings between the F-atom and the two pairs of axial and equatorial P-atoms. The ^{19}F -NMR spectrum features the F-ligand as tt (X part of $AA'MM'X$) at $\delta -203.4$. As already observed for a number of fluoro complexes [4], the P,F coupling is not observed in CDCl_3 that contains traces of H_2O .

The crystal structure of **1a** displays a pseudo trigonal-bipyramidal structure (Y-shaped) for the cation $[\text{RuF}(\text{dppp})_2]^+$ (Fig. 2), similar to that of the chloro analogues $[\text{MCl}(\text{P}-\text{P})_2]^+$ ($\text{M}=\text{Ru}$ or Os , $\text{P}-\text{P}$ = diphosphine) [16]. This geometry is known to optimize the $X \rightarrow \text{M}$ π -donation in π -stabilized 16-electron complexes [17]. The F-ligand is disordered between two positions (at 0.728(9) Å from each other) approximately lying in the equatorial plane and with similar occupancies (46 and

1) Fluorobis[propane-1,3-diylbis[diphenylphosphine- κ P]]ruthenium(1+) hexafluorophosphate ($[\text{RuF}(\text{dppp})_2]\text{PF}_6$; **1a** · PF_6): A suspension of $[\text{RuCl}(\text{dppp})_2]\text{PF}_6$ (817 mg, 0.74 mmol) and TIF (200 mg, 0.90 mmol) in CH_2Cl_2 (20 ml) was stirred for 3 h at r.t. TiCl was filtered off, and a second portion of TIF (100 mg, 0.45 mmol) was added. After 2 h, TiCl was filtered off, $^i\text{PrOH}$ (50 ml) was added, and CH_2Cl_2 was evaporated: 725 mg (90%) of **1a** · PF_6 . Red precipitate. ^1H -NMR (CDCl_3): 7.82 (*m*, 8 arom. H); 6.8–7.5 (*m*, 32 arom. H); 2.62 (*m*, 4 H, PCH_2); 2.0–2.5 (*m*, 2 PCH_2); 1.58 (*m*, 2 H, CH_2); 0.80 (*m*, 2 H, CH_2). ^{31}P -NMR (CDCl_3): 49.0 (*dt*, $J(\text{P,F})=47$, $J(\text{P,P'})=32$); –7.1 (*td*, $J(\text{P,F})=15.2$, $J(\text{P,P'})=32$); –143 (*sept.*, $J(\text{P,F})=710$, PF_6). ^{19}F -NMR (CDCl_3 , CFCl_3 reference): –74.5 (*d*, $J(\text{P,F})=710$, PF_6); –203.6 (*tt*, $J(\text{P,F})=47$, $J(\text{P',F})=15$, RuF). FAB-MS (*pos.*): 945 (100, M^+), 511 (35, $[\text{M}-\text{dppp}]^+$). Anal. calc. for $\text{C}_{54}\text{H}_{52}\text{F}_7\text{P}_5\text{Ru} \cdot 0.5 \text{CH}_2\text{Cl}_2$: C 57.81, H 4.72; found: C 57.81, H 4.82.

2) Crystals of **1a** were obtained by slow evaporation from concentrated $\text{CH}_2\text{Cl}_2/^i\text{PrOH}$ solutions of the complex. Crystal data: crystal size $0.50 \times 0.32 \times 0.22 \text{ mm}^3$, red platelets, $\text{C}_{56}\text{H}_{56}\text{Cl}_4\text{F}_7\text{P}_5\text{Ru}$, M 1268.80, T 213 K; monoclinic, $P2_1/n$, $a = 11.925(2) \text{ Å}$, $b = 14.798(2) \text{ Å}$, $c = 31.644(5) \text{ Å}$, $\beta = 99.59(2)^\circ$, $V = 5505.8(14) \text{ Å}^3$, $F(000) = 2604$, $Z = 4$, $D_c = 1.531 \text{ Mg m}^{-3}$; $\mu(\text{MoK}\alpha) = 0.686 \text{ mm}^{-1}$, Siemens-Smart-Platform diffractometer with CCD detector, normal focus molybdenum-target X-ray tube, graphite monochromator, ω -scans, $h - 16$ to 15, $k - 19$ to 15, $l - 41$ to 44; 38 839 reflections for $1.31^\circ < \theta < 29.94^\circ$ (14 217 unique, $R_{\text{int}} 0.0576$). Unit cell dimensions determination and data reduction were performed by standard procedures, and an empirical absorption correction (SADABS) was applied. The structure was solved with SHELXS-96 by direct methods, and refined by full-matrix least squares on F^2 with anisotropic displacement parameters for all non-H-atoms except disordered atoms, which were refined isotropically. Analysis of the electron-density contour map showed that the F-ligand is disordered between two positions (F(1A) and F(1B)), and that a small amount of Cl-atom (Cl) is present. Refinement of the occupancy factors f of these three atoms with the restraints $f(\text{F}(1\text{A})) + f(\text{F}(1\text{B})) + f(\text{Cl}) = 1$ and $U(\text{F}(1\text{A})) = U(\text{F}(1\text{B}))$ gave $f(\text{F}(1\text{A})) = 0.458$, $f(\text{F}(1\text{B})) = 0.396$, and $f(\text{Cl}) = 0.146$. The latter value was confirmed independently by integration of the ^{31}P -NMR spectrum of crystals taken from the same batch. Positional and thermal parameters, but not occupancies, were refined in the last cycles. Two CH_2Cl_2 molecules were found, one of which is disordered. H-Atoms were introduced at calculated positions on non-disordered C-atoms of the cation and refined with the riding model and individual isotropic thermal parameters. $R_1 0.0598$ and $wR_2 = 0.1259$ (9196 unique reflections with $I > 2\sigma(I)$), $R_1 = 0.1097$ and $wR_2 = 0.1473$ (all data), $S = 1.042$. Max. and min. difference peaks +0.969 and –0.894 e Å^{-3} , largest and mean were $\Delta/\sigma = 2.470$ and 0.029. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 134839 (**1a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

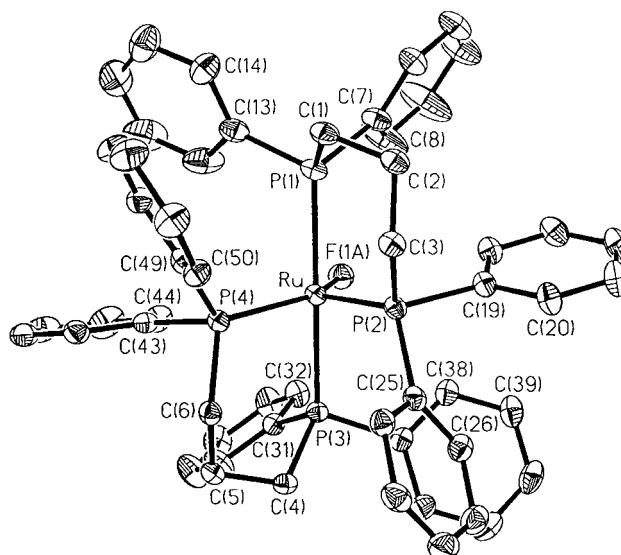


Figure. ORTEP View of $[\text{RuF}(\text{dppp})_2]^+$. 30% Probability ellipsoids. Only F(1A) is shown. Selected interatomic distances [Å] and angles [deg]: Ru–F(1A) 2.030(7), Ru–F(1B) 2.033(9), Ru–P(1) 2.423(1), Ru–P(3) 2.408(1), Ru–P(2) 2.261(1), Ru–P(4) 2.254(1), F(1A)–Ru–P(1) 88.8(2), F(1B)–Ru–P(1) 85.8(2), F(1A)–Ru–P(2) 125.3(2), F(1B)–Ru–P(2) 145.5(2), F(1A)–Ru–P(3) 82.9(2), F(1B)–Ru–P(3) 85.5(2), F(1A)–Ru–P(4) 139.6(2), F(1B)–Ru–P(4) 119.7(2), P(1)–Ru–P(2) 89.41(4), P(2)–Ru–P(3) 97.40(4), P(1)–Ru–P(3) 171.26(4), P(2)–Ru–P(4) 94.85(4), P(1)–Ru–P(4) 96.51(4), P(3)–Ru–P(4) 88.39(4).

40% for F(1A) and F(1B), respectively)³. $[\text{RuF}(\text{dppp})_2]^+$ is nearly isostructural with the chloro analogue **1b**, the main differences being due to the smaller size of the F-ligand. Thus, six Ph rings form a pocket around the halide ligand in both **1a** and **1b**, but in the fluoro complex, a twist of the axial Ph groups C(7)–C(12) and C(31)–C(36) reduces the nonbonded distances between F and the H_o atoms (calculated positions) from values in the range 2.99–2.49 Å in $[\text{RuCl}(\text{dppp})_2]^+$ (**1b**) to 2.17–2.59 Å in **1a**, clearly shorter than the sum of the *Van der Waals* radii (2.67 Å). Short nonbonded $\text{F} \cdots \text{H} \cdots \text{C}$ distances have been observed in other fluoro complexes [14]. Interestingly, the positional disorder in **1a** appears to minimize the $\text{F} \cdots \text{H}$ nonbonded distances. The Ru–F distances (2.030(7) and 2.033(9) Å) in **1a** are very close to 2.02 Å, the value calculated from the Ru–Cl distance of 2.371(5) Å in **1b** by subtracting the difference of the atomic radii of F and Cl (0.35 Å), suggesting that the π -effects on the bonding are similar in **1a** and **1b**.

With the aim of assessing the reactivity of complex **1a**, we found that the F-ligand is smoothly transferred to selected organic electrophiles. Thus, when equivalent amounts of the five-coordinate **1a** and 1,3-diphenylallyl bromide (**2**) [19] were mixed in an NMR tube in dry CDCl_3 , an immediate color change from red to brown was observed. The

³) The crystal contains 14% of **1b** as impurity due to partial reaction with the CH_2Cl_2 solvent upon crystallization, as confirmed by ^{31}P -NMR. Attempts to grow suitable crystals in other solvents were unsuccessful. The related Ru–Cl distance (2.315(11) Å) is close to the value found in **1b** (2.371(5) Å); see [18].

^1H - and ^{19}F -NMR spectra of the resulting solution indicated that the starting material **2** was converted to 1,3-diphenylallyl fluoride **3** in nearly quantitative yield ($> 80\%$). Although the reaction between **1a** and **2** was carried out in a glove-box in dry solvents, a small amount ($> 10\%$) of bis(1,3-diphenylallyl) ether was also formed. This side reaction was completely suppressed when the experiment was carried out in a *Teflon* tube. The ^{31}P -NMR spectrum of the reaction solution shows the quantitative formation of $[\text{RuBr}(\text{dppp})_2]^+$ (**1c**) (*Scheme*), which may be recovered from the reaction mixture⁴). The synthesis of an authentic sample of the allyl fluoride derivative **3** proved to be far from trivial. When 1,3-diphenylprop-2-en-1-ol was reacted with (diethylamino)sulfur trifluoride (DAST) [20] or *Olah's* reagent (HF/pyridine) [21], bis(1,3-diphenylallyl) ether was the only product isolated. Thus, rigorous exclusion of O_2 and H_2O is imperative, and, indeed, the reaction of **2** with soluble, dry fluoride sources such as TBAT⁵) [22] or KF in DMF [23] yielded samples of **3** sufficiently pure for unambiguous identification⁶). Under similar conditions, bromide (or chloride)/fluoride exchange also occurred with chlorotriphenylmethane ($=1,1',1''$ -(chloromethylidene)tris[benzene], bromodiphenylmethane ($=1,1'$ -(bromomethylene)bis[benzene], and *tert*-butyl bromide ($=2$ -bromo-2-methylpropane), and the corresponding fluorinated products were identified spectroscopically by NMR⁷) [24]. The reaction of the latter substrate was quite sluggish. However, no elimination of HBr to afford 2-methylprop-1-ene could be observed.

Conclusions. – The C–F bond-forming process observed is still a rare example of a reaction of an organic electrophile with a fluoro complex. Derivative **1a** acts as a donor of 'naked' fluoride [25] as well as a *Lewis* acid and bromide scavenger. Although similar reactions have been reported previously by *Bergman* and co-workers with an Ir^{III} 18-electron system [12], we believe that a coordinatively unsaturated complex such as **1a** offers advantages in terms of reactivity. Although the use of a fluoro complex is not strictly necessary for the above type of reaction to occur, the use of well-defined fluoro

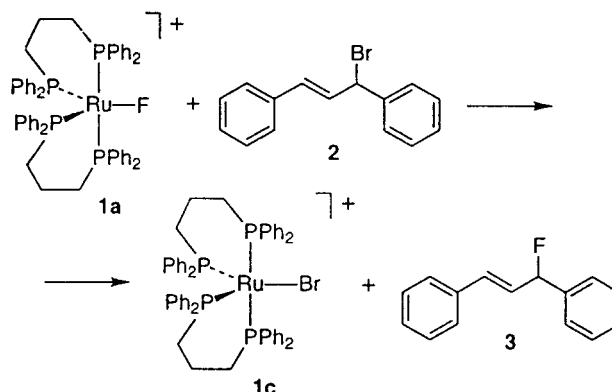
⁴) $[\text{RuBr}(\text{dppp})_2]^+$ (**1c**): ^{31}P -NMR (CDCl_3): -1.0 (t , $J(\text{P},\text{P}') = 31.3$); 38.6 (t , $J(\text{P},\text{P}') = 31.3$). FAB-MS (pos.) 1007 (100, M^+), 926 (6, $[M - \text{Br}]^+$).

⁵) TBAT = tetrabutylammonium difluorotriphenylsilicate.

⁶) $1,1'$ -[(1*E*)-3-Fluoroprop-1-ene-1,3-diyl]bis[benzene] (**3**): In freshly distilled (CaH_2) DMF (10 ml), $1,1'$ -[(1*E*)-3-bromoprop-1-ene-1,3-diyl]bis[benzene] (206 mg, 0.85 mmol) and KF (90 mg, 1.55 mmol) were stirred for 2 d at r.t. in the dark. Filtration and evaporation of the solvent yielded a brownish oil containing some DMF and bis(1,3-diphenylallyl) ether (less than 3% by ^1H -NMR). ^1H -NMR (CDCl_3): 7.45–7.26 (m , 10 arom. H); 6.72 (ddd , $J(\text{F},\text{H}) = 15.9$, 4.0, 0.9, 1 H, $\text{H}-\text{C}(1'')$); 6.38 (ddd , $J(\text{F},\text{H}) = 15.9$, 11.7, 6.7, $\text{H}-\text{C}(2'')$); 6.02 (ddd , $J(\text{F},\text{H}) = 47.5$, 6.7, 0.9, $\text{H}-\text{C}(3'')$). ^{13}C -NMR (CDCl_3): 138.9 (d , $J(\text{F},\text{C}) = 22$, 1 C); 135.7 (d , $J(\text{F},\text{C}) = 2$, 1 C); 133.0 (d , $J(\text{F},\text{C}) = 12$, 1 CH); 128.5–128.4 (several CH); 128.3 (d , $J(\text{F},\text{C}) = 15$, 1 CH); 127.0 (d , $J(\text{F},\text{C}) = 22$, 1 CH); 126.7 (d , $J(\text{F},\text{C}) = 1.5$, 1 CH); 126.1 (d , $J(\text{F},\text{C}) = 6$, 1 CH); 93.8 (d , $J(\text{F},\text{C}) = 169$, 1 CH). ^{19}F -NMR (CDCl_3): -165.4 (ddd , $J(\text{F},\text{C}) = 47.5$, 11.7, 4.0). EI-MS: 212 (100, M^+), 192 (20, $[M - \text{F}]^+$), 133 (48).

⁷) Reactions of **1a** with other substrates: $[\text{RuF}(\text{dppp})_2]\text{PF}_6$ (**1a**· PF_6 ; 22 mg, 20 μmol) and the appropriate substrate (20 μmol) were dissolved in CDCl_3 (2 ml) in an *Young*-valve NMR tube equipped with a *Teflon* liner. Yields were determined by ^{19}F -NMR and ^1H -NMR. Triphenylchloromethane gave triphenylfluoromethane (90%) after 1 min at r.t. (^{19}F -NMR: -126.4 (s) ([24a]: -126.5)). *tert*-Butyl bromide gave *tert*-butyl fluoride (20%) after 1 d at 50° (^{19}F -NMR: -131 (10 lines, $J(\text{H},\text{F}) = 21$) ([24b]: -132 (10 lines, $J(\text{H},\text{F}) = 21$)); ^1H -NMR: 1.39 (d , $J(\text{H},\text{F}) = 21$) ([24b]: 1.30 (d , $J(\text{H},\text{F}) = 20$))). Diphenylmethyl bromide gave diphenylmethyl fluoride (85%) after 1 d at r.t. (^{19}F -NMR: -167 (10, $J(\text{H},\text{F}) = 49$) ([24a]: -169 (10, $J(\text{H},\text{F}) = 48$)).

Scheme



complexes in fluorination reactions clearly offers advantages in terms of transport of F-ions in organic solvents and may open new avenues for asymmetric C–F bond formation.

In conclusion, we have shown that fluoride can be used to stabilize 16-electron species of relatively soft metal ions such as Ru^{II}, and that the resulting complexes react with activated organic halides to form a new C–F bond. We are currently extending our investigation to less reactive organic substrates, as well as toward the development of a catalytic fluorination process.

Novartis Services Ltd., Basel, is gratefully acknowledged for financial support to L. H.

REFERENCES

- [1] See, e.g., 'Houben-Weyl, Methods of Organic Chemistry', 'Organo-Fluorine Compounds', Vol. E10a, Eds. B. Baasner, H. Hagemann, and J. C. Tatlow, Thieme, Stuttgart, 1999, and refs. cited therein; 'Enantiocontrolled Synthesis of Fluoro-Organic Compounds', Ed. V. A. Soloshonok, Wiley, Chichester, 1999; 'Chemistry of Organic Fluorine Compounds II', Eds. M. Hudlicky, A. E. Pavlath, ACS Monograph 187, American Chemical Society, Washington, DC, 1995; J. A. Wilkinson, *Chem. Rev.* **1992**, 92, 505; 'Selective Fluorination in Organic and Bioinorganic Chemistry', Ed. T. J. Welch, ACS Symposium Series 456, American Chemical Society, Washington, DC, 1990.
- [2] J. L. Kiplinger, T. G. Richmond, C. E. Osterberg, *Chem. Rev.* **1994**, 94, 373.
- [3] J. Burdeniuc, P. E. Siegbahn, R. H. Crabtree, *New J. Chem.* **1998**, 503; J. Burdeniuc, B. Jedlicka, R. H. Crabtree, *Chem. Ber./Recl.* **1997**, 130, 145.
- [4] S. L. Fraser, M. Y. Antipin, V. N. Khroustsl'yov, V. V. Grushin, *J. Am. Chem. Soc.* **1997**, 119, 4769; M. C. Pilon, V. V. Grushin, *Organometallics* **1998**, 17, 1774; V. V. Grushin, *Angew. Chem., Int. Ed.* **1998**, 37, 994.
- [5] L. Cronin, C. L. Higgitt, R. Karch, R. N. Perutz, *Organometallics* **1997**, 16, 4920.
- [6] M. Aizenberg, D. Milstein, *Science (Washington, D.C.)* **1994**, 265, 359; M. Aizenberg, D. Milstein, *J. Am. Chem. Soc.* **1995**, 117, 8674.
- [7] J. L. Kiplinger, T. G. Richmond, *J. Chem. Soc., Chem. Commun.* **1996**, 1115; J. L. Kiplinger, T. G. Richmond, *J. Am. Chem. Soc.* **1996**, 118, 1805.
- [8] S. A. Brewer, K. S. Coleman, J. Fawcett, J. H. Holloway, E. G. Hope, D. R. Russell, P. G. Watson, *J. Chem. Soc., Dalton Trans.* **1995**, 1073, A. J. Blake, R. W. Cockman, E. A. V. Ebsworth, J. H. Holloway, *J. Chem. Soc., Chem. Commun.* **1988**, 529.
- [9] For a recent application, see S. J. Taverner, P. A. Heath, J. H. Clark, *New J. Chem.* **1998**, 655.
- [10] E. F. Murphy, R. Murugavel, H. W. Roesky, *Chem. Rev.* **1997**, 97, 3425; N. M. Doherty, N. W. Hoffman, *ibid.* **1991**, 91, 553.

- [11] J. T. Poulton, M. P. Sigalas, O. Eisenstein, K. G. Caulton, *Inorg. Chem.* **1993**, 32, 5490; J. T. Poulton, M. P. Sigalas, K. Folting, W. Streib, O. Eisenstein, K. G. Caulton, *ibid.* **1994**, 33, 1476; A. C. Cooper, K. Folting, J. C. Huffman, K. G. Caulton, *Organometallics* **1997**, 16, 505; M. Ogasawara, D. Huang, W. E. Streib, J. C. Huffman, N. Gallego-Planas, F. Maseras, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1997**, 119, 8642.
- [12] J. E. Veltheer, P. Burger, R. G. Bergman, *J. Am. Chem. Soc.* **1995**, 117, 12478.
- [13] M. K. Whittesley, R. N. Perutz, B. Greener, M. H. Moore, *J. Chem. Soc., Chem. Commun.* **1997**, 187.
- [14] K. S. Coleman, J. Fawcett, J. H. Holloway, E. G. Hope, D. R. Russell, *J. Chem. Soc., Dalton Trans.* **1997**, 3557.
- [15] K. G. Caulton, *New J. Chem.* **1994**, 18, 25.
- [16] See, e.g., M. Bressan, P. Rigo, *Inorg. Chem.* **1975**, 14, 2286; A. Mezzetti, A. Del Zotto, P. Rigo, N. Bresciani Pahor, *J. Chem. Soc., Dalton Trans.* **1989**, 1045; B. Chin, A. J. Lough, R. H. Morris, C. T. Schweitzer, C. D'Agostino, *Inorg. Chem.* **1994**, 33, 6278.
- [17] J.-F. Riehl, Y. Jean, O. Eisenstein, M. Pélicissier, *Organometallics* **1992**, 11, 729; T. J. Johnson, K. Folting, W. E. Streib, J. D. Martin, J. C. Huffman, S. A. Jackson, O. Eisenstein, K. G. Caulton, *Inorg. Chem.* **1995**, 34, 488 and refs. cited therein.
- [18] A. A. Batista, L. A. Centeno Cordeiro, G. Oliva, *Inorg. Chim. Acta* **1993**, 203, 185.
- [19] R. Lespieau, R. L. Wakeman, *Bull. Soc. Chim. Fr.* **1932**, 51, 384.
- [20] W. J. Middleton, *J. Org. Chem.* **1975**, 40, 574.
- [21] G. A. Olah, J. T. Welch, Y. D. Vankar, M. Nojima, I. Kerekes, J. A. Olah, *J. Org. Chem.* **1979**, 44, 3872.
- [22] A. S. Pilcher, H. L. Ammon, P. DeShong, *J. Am. Chem. Soc.* **1995**, 117, 5166.
- [23] For the use of CsF in similar substitution reactions, see, e.g., E. Fritz-Langhals, *Tetrahedron Lett.* **1994**, 35, 1851.
- [24] a) C. W. Lai, Y. I. Kim, C. M. Wang, T. E. Mallouk, *J. Org. Chem.* **1993**, 58, 1393; b) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, I. J. Bastien, *J. Am. Chem. Soc.* **1964**, 86, 1360.
- [25] K. Seppelt, *Angew. Chem.* **1992**, 104, 299; *ibid.*, *Int. Ed.* **1992**, 31, 292; see also B. K. Bennett, R. G. Harrison, T. G. Richmond, *J. Am. Chem. Soc.* **1994**, 116, 11165.

Received September 22, 1999