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

Preliminary Communication

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The 16-electron, five-coordinate fluoro complex $[RuF(dppp)_2]PF_6$ (**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 $[RuBr(dppp)_2]^+$ 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 F → 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 $[RuF(dppp)_2]^+$ (**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 $[RuF(dppp)_2]PF_6$ (**1a**·PF_6), containing the unprecedented FP_4 donor set, by the reaction of $[RuCl(dppp)_2]PF_6$ (**1b**·PF_6) with TlF in CH_2Cl_2 (*Eqn. 1*)[1]).

$$[RuCl(dppp)_2]^+ + TlF \rightarrow [RuF(dppp)_2]^+ + TlCl \quad (1)$$

1b **1a**

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 δ −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 $[RuF(dppp)_2]^+$ (*Fig.*)[2]), similar to that of the chloro analogues $[MCl(P-P)_2]^+$ (M=Ru or Os, P−P = diphosphine) [16]. This geometry is known to optimize the X → 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

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[1]) Fluorobis{propane-1,3-diylbis[diphenylphosphine-κP]}ruthenium(1+) hexafluorophosphate ($[RuF(dppp)_2]$-PF_6; **1a**·PF_6): A suspension of $[RuCl(dppp)_2]PF_6$ (817 mg, 0.74 mmol) and TlF (200 mg, 0.90 mmol) in CH_2Cl_2 (20 ml) was stirred for 3 h at r.t. TlCl was filtered off, and a second portion of TlF (100 mg, 0.45 mmol) was added. After 2 h, TlCl was filtered off, ^{i}PrOH (50 ml) was added, and CH_2Cl_2 was evaporated: 725 mg (90%) of **1a**·PF_6. Red precipitate. ^{1}H-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(P,F) = 47, J(P,P′) = 32); −7.1 (*td*, J(P,F) = 15.2, J(P,P′) = 32); −143 (sept., J(P,F) = 710, PF_6). ^{19}F-NMR ($CDCl_3$, $CFCl_3$ reference): −74.5 (*d*, J(P,F) = 710, PF_6); −203.6 (*tt*, J(P,F) = 47, J(P′,F) = 15, RuF). FAB-MS (pos.): 945 (100, M^+), 511 (35, $[M - dppp]^+$). Anal. calc. for $C_{54}H_{52}F_7P_5Ru \cdot 0.5\ CH_2Cl_2$: C 57.81, H 4.72: found: C 57.81, H 4.82.

[2]) Crystals of **1a** were obtained by slow evaporation from concentrated CH_2Cl_2/^{i}PrOH solutions of the complex. Crystal data: crystal size 0.50 × 0.32 × 0.22 mm^3, red platelets, $C_{56}H_{56}Cl_4F_7P_5Ru$, M 1268.80, T 213 K; monoclinic, $P2_1/n$, a = 11.925(2) Å, b = 14.798(2) Å, c = 31.644(5) Å, β = 99.59(2)°, V = 5505.8(14) Å^3, F(000) = 2604, Z = 4, D_c = 1.531 Mg m^{-3}; μ(Mo$K\alpha$) = 0.686 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° < θ < 29.94° (14 217 unique, R_{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(F(1A)) + f(F(1B)) + f(Cl) = 1 and U(F(1A)) = U(F(1B)) gave f(F(1A)) = 0.458, f(F1B) = 0.396, and f(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 eÅ^{-3}, largest and mean were Δ/σ = 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).

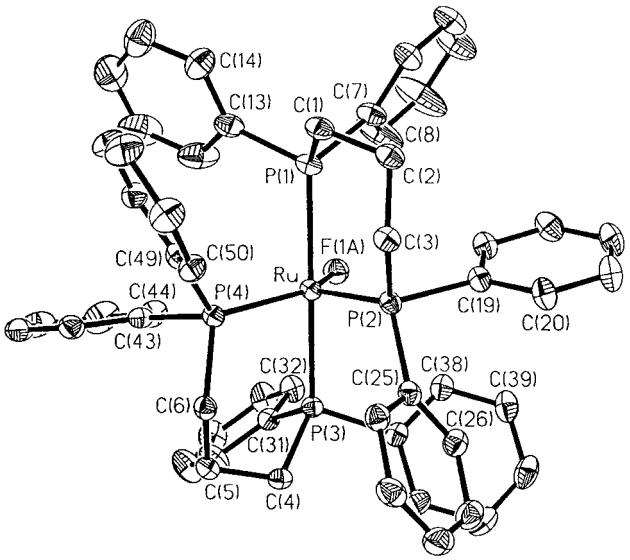

Figure. *ORTEP View of [RuF(dppp)$_2$]$^+$*. 30% Probability ellipsoids. Only F(1A) is shown. Selected interatomic distances [Å] and angles [deg]: Ru–F(1A) 2.030(7), Ru–F(1B) 2.033(9), Ru–P(1) 2.423(1), Ru–P(3) 2.408(1), Ru–P(2) 2.261(1), Ru–P(4) 2.254(1), F(1A)–Ru–P(1) 88.8(2), F(1B)–Ru–P(1) 85.8(2), 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]). [RuF(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 [RuCl(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 F$\cdots$H–C distances have been observed in other fluoro complexes [14]. Interestingly, the positional disorder in **1a** appears to minimize the F$\cdots$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

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[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].

^{1}H- 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 $[RuBr(dppp)_2]^+$ (**1c**) (*Scheme*), which may be recovered from the reaction mixture[4]). 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 TBAT[5]) [22] or KF in DMF [23] yielded samples of **3** sufficiently pure for unambiguous identification[6]). Under similar conditions, bromide (or chloride)/fluoride exchange also occurred with chlorotriphenylmethane (=1,1′,1″-(chloromethylidyne)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 NMR[7]) [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 elecrophile 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

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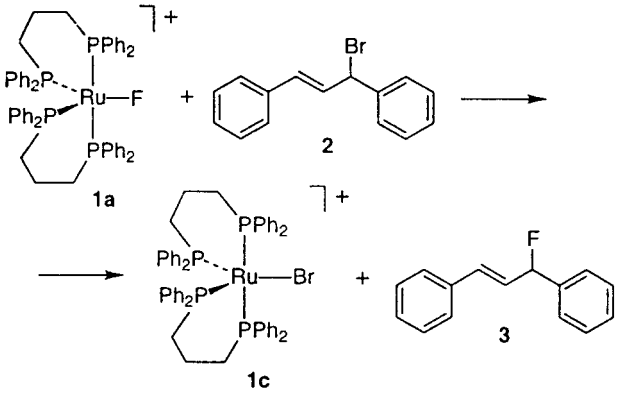
4) $[RuBr(dppp)_2]^+$ (**1c**): ^{31}P-NMR ($CDCl_3$): −1.0 (*t*, *J*(P,P′) = 31.3); 38.6 (*t*, *J*(P,P′) = 31.3). FAB-MS (pos.) 1007 (100, M^+), 926 (6, $[M-Br]^+$).

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 ^{1}H-NMR). ^{1}H-NMR ($CDCl_3$): 7.45–7.26 (*m*, 10 arom. H); 6.72 (*ddd*, *J*(F,H) = 15.9, 4.0, 0.9, 1 H, H–C(1″)); 6.38 (*ddd*, *J*(F,H) = 15.9, 11.7, 6.7, H–C(2″)); 6.02 (*ddd*, *J*(F,H) = 47.5, 6.7, 0.9, H–C(3″)). ^{13}C-NMR ($CDCl_3$): 138.9 (*d*, *J*(F,C) = 22, 1 C); 135.7 (*d*, *J*(F,C) = 2, 1 C); 133.0 (*d*, *J*(F,C) = 12, 1 CH); 128.5–128.4 (several CH); 128.3 (*d*, *J*(F,C) = 15, 1 CH); 127.0 (*d*, *J*(F,C) = 22, 1 CH); 126.7 (*d*, *J*(F,C) = 1.5, 1 CH); 126.1 (*d*, *J*(F,C) = 6, 1 CH); 93.8 (*d*, *J*(F,C) = 169, 1 CH). ^{19}F-NMR ($CDCl_3$): −165.4 (*ddd*, *J*(F,C) = 47.5, 11.7, 4.0). EI-MS: 212 (100, M^+), 192 (20, $[M-F]^+$), 133 (48).

7) Reactions of **1a** with other substrates: $[RuF(dppp)_2]PF_6$ (**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 ^{1}H-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*(H,F) = 21) ([24b]: −132 (10 lines, *J*(H,F) = 21)); ^{1}H-NMR: 1.39 (*d*, *J*(H,F) = 21) ([24b]: 1.30 (*d*, *J*(H,F) = 20))). Diphenylmethyl bromide gave diphenylmethyl fluoride (85%) after 1 d at r.t. ^{19}F-NMR: −167 (10, *J*(H,F) = 49) ([24a]: −169 (10, *J*(H,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.

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