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Communications

A New Phosphinite Chelate, (aryl)$_2$POBF$_2$OH, Complexed to Ruthenium(II). HBF$_4$-Induced P−C Bond Cleavage in Chiral MeO-Biphep Complexes

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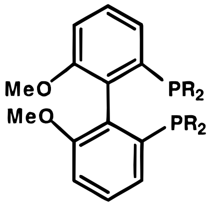
Summary: Reaction of Ru(OAc)$_2$(MeO-Biphep) (MeO-Biphep = 6,6′-dimethoxybiphenyl-2,2′-diylbis(diarylphosphine)) with 2 equiv of HBF$_4$ in CH$_2$Cl$_2$ cleaves the MeO-Biphep. Products contain the exotic chelate ligand (aryl)$_2$POB(OH)F$_2$ (aryl = phenyl, p-tolyl, 3,5-di-tert-butylphenyl) together with an (aryl)$_2$P−η^6-arene, 8e donor chelate. The reaction involves a fluorophosphine intermediate.

There has been increased study in the area of enantioselective homogeneous catalysis,[1] due to the fact that relatively small quantities of chiral catalytic materials can produce substantial amounts of enantiopure product. Although there are examples of successful chiral nitrogen chelates,[2,3] many auxiliaries are based on chelating tertiary phosphines,[4] e.g. MeO-Biphep (**1**).[5] We report here a series of reactions originating from Ru(OAc)$_2$(**1**) (**2**), which leads to an unprecedented coordinated phosphinite ligand derived from the BF$_4$ anion and potentially destroys the axial chirality of the auxiliary.



1 a, R = 3,5-di-t-Bu-phenyl

b, R = Ph

c, R = 4-tolyl

Reaction of the Ru complex **2a** with 2 equiv of HBF$_4$ in methylene chloride affords the product[6] **3a** in 78% yield.

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[1] Trost, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 70−79.

[2] Tanner, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 599−619.

[3] Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1−45. Pfaltz, A. *Acta Chim. Scand.* **1996**, *50*, 189−194.

[4] Corey, E. J.; Guzman-Perez, A. *Angew. Chem.* **1998**, *110*, 402−415.

[5] Schmid, R.; Broger, E. A.; Cereghetti, M.; Crameri, Y.; Foricher, J.; Lalonde, M.; Mueller, R. K.; Scalone, M.; Schoettel, G.; Zutter, U. *Pure Appl. Chem.* **1996**, *68*, 131. Heiser, B.; Broger, E. A.; Crameri, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 51.

[6] Complete conversion to **3a** takes several weeks; however, P−C bond breaking can be relatively rapid on the basis of ^{31}P NMR measurements (for **3a**, within the time needed to arrive at the NMR spectrometer). The appearance of **3** can be accelerated by controlled addition of water. **Synthesis of 3a.** A solution of Ru(OAc)$_2$(**1a**) (42.3 mg, 0.034 mmol) in 2 mL of CD$_2$Cl$_2$ in an NMR tube was treated with 2.1 equiv of HBF$_4$·Et$_2$O (0.07 mmol, 10 μL of a 7.3 M solution in diethyl ether). After 18 days at 30 °C the reaction mixture was transferred to a Schlenk tube. Washing three times with 5 mL of water and drying over MgSO$_4$ was followed by evaporation to dryness. Drying under vacuum afforded a pale yellow powder in 78% yield. A yellow crystal of **3b** was grown by slow diffusion of diethyl ether into a CH$_2$Cl$_2$ solution.

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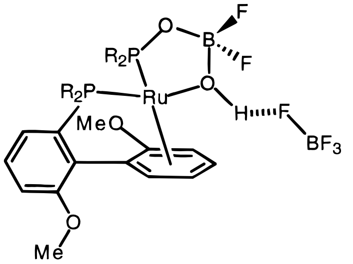
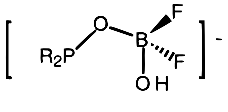


3 a, R = 3,5-di-t-Bu-phenyl

b, R = Ph

c, R = 4-tolyl

The complexes **3** contain new P−O and B−O bonds in addition to an η^6 Ru−arene interaction stemming from complexation of the biaryl ring, which loses the P-donor. The bis-phosphine bidentate ligand has been cleaved to afford two different chelating ligands. Although P−C bond cleavage in complexes is known,[7−10] it is a relatively rare reaction and is normally not induced by protonation.[8−10] Formally, **3** contains the phosphinite anion **4** ($C_{12}H_{11}BF_2O_2P$), which, to our knowledge, is as yet unknown. The ligand **4** arises via a slow hydrolysis reaction.[6] The second BF_4^- is held close to **4** via a hydrogen bond.



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The major features of the structure of **3** were determined via one- and two-dimensional multinuclear NMR spectroscopy.[11] (i) **3a** shows an AX ^{31}P NMR spectrum with one *unexpectedly high frequency ^{31}P signal*, δ 119.9 ($^2J(P,P) = 57$ Hz).[12] Normally Ru(II) complexes of **1** have their signals in the region 30−70 ppm. (ii) The *boron-decoupled* ^{19}F NMR spectrum reveals an ABX spin system ($X = {}^{31}P$) for the two nonequivalent fluorine signals (without decoupling these signals are quite broad) plus the BF_4^- anion. The presence of ^{31}P coupling to the ^{19}F signals is consistent with the proposed new phosphinite fragment (Figure 1 shows both the ^{31}P and routine ^{19}F spectra for **3a**). (iii) The ^{11}B spectrum shows the signals for the new ligand plus "uncomplexed" BF_4. (iv) In both the ^1H and ^{13}C spectra one observes *four* relatively low frequency absorptions, due to the four CH types in the η^6-arene moiety. For **3a** these four carbon signals, C3−C6, appear at 78.6, 95.4, 101.7, and 76.0 ppm, respectively, exactly where one expects ^{13}C resonances of arenes complexed to Ru(II).[13−15]

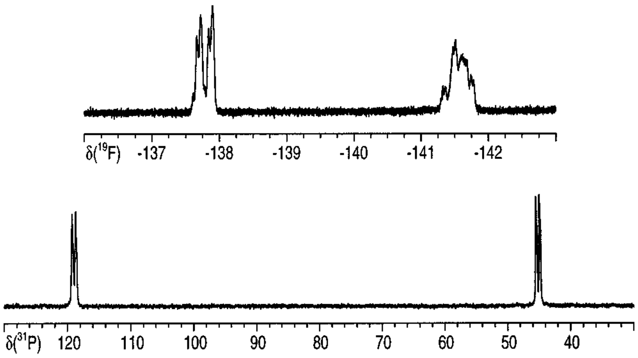

Figure 1. ^{31}P NMR spectrum (bottom) of **3a** showing the relatively high frequency signal, arising from the phosphinite donor. A second isomer is just resolved at the low-frequency position. (The ^{31}P spectrum was measured in CD_2Cl_2, since in this solvent, as opposed to acetone-d_6, the resolution of the second isomer, at the low-frequency end, is somewhat better. Solvent-dependent chemical shift differences are small.) The upper trace represents the conventional ^{19}F spectrum with the two nonequivalent ^{19}F resonances from the $POBF_2O$ fragment. The fluorine spectrum is broadened by the boron atom. With boron decoupling two ABX spin systems are observed (see text).

Apart from its surprising structure, **3** is noteworthy in that it demonstrates an undesirable side reaction: potential loss of its axial chirality. One might expect diastereomers (the metal is a stereogenic center); indeed, the boron-decoupled ^{19}F spectra all show that two closely related species are formed in unequal quantities. Since the complexes $Ru(OAc)_2$(MeO-Biphep) give very high ee's in hydrogenation reactions in alcoholic solvents,[5] the solvation of the acid and/or substrate complexation, in these media, must compete favorably with the decomposition to **3**.

A rather poor crystal of **3b** (R = Ph) was obtained.[16] Although it was sufficient to confirm that the solid-state structure corresponds to that found in solution (see Figure 2, which shows the two nonequivalent molecules

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(7) Chan, A. S. C. Laneman, S. A. Miller, R. E. In *Selectivity in Catalysis*; ACS Symp. Ser. 517; American Chemical Society: Washington, D.C., 1993; p 27.

(8) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441−12453.

(9) Morita, D. K.; Stille, J. K.; Norton, J. R. *J. Am. Chem. Soc.* **1995**, *117*, 8576−8581. Kong, K. C.; Cheng, C. H. *J. Am. Chem. Soc.* **1991**, *113*, 6313.

(10) Herrmann, W. A.; Thiel, W. R.; Brossmer, C.; Oefele, K.; Priermeier, T.; Scherer, W. *J. Organomet. Chem.* **1994**, *461*, 51−60.

(11) For the use of 2-D NMR in determining structures of chiral complexes, see: Pregosin, P. S.; Trabesinger, G. *J. Chem. Soc., Dalton Trans.* **1998**, 727−734. For **3a** (acetone-d_6): ^{31}P NMR δ 119.9 ($^2J(P,P) = 57$ Hz), δ 47.3 ($^2J(P,P) = 57$ Hz); ^{19}F NMR δ −137.8 ($^2J(F,F) = 66$ Hz; $^3J(P,F) = 5$ Hz), δ −141.6 ($^2J(F,F) = 66$ Hz; $^3J(P,F) = 5$ Hz), δ −152.2 (BF_4); ^{11}B NMR δ 6.5 (broad, complexed **4**), δ 2.2 (BF_4). ^1H NMR (δ) for the four protons of the η^6 aromatic moiety: H3, 6.10 (d); H4, 6.36 (m); H5, 4.49 (m); H6, 5.78 (m). ^{13}C NMR data are given in the text.

(12) The ^{31}P chemical shift of 119.9 ppm is consistent with a complexed P−O phosphinite; see: Roucoux, A.; Carpentier, J.; Devocelle, M.; Agboussou, F.; Mortreux, A *Synlett* **1995**, 358. Agboussou, F.; Carpentier, J.; Hatat, C.; Mortreux, A.; Betz, P.; Goddard, R.; Krüger, C. *Organometallics* **1995**, *14*, 2480. Roucoux, A.; Thieffry, L.; Carpentier, J.; Devocelle, M.; Meliet, C.; Agboussou, F.; Mortreux, A.; Welch, A. J. *Organometallics* **1996**, *15*, 2440.

(13) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981.

(14) Bennett, M. A.; McMahon, I. J.; Pelling, S.; Brookhart, M.; Lincoln, D. M. *Organometallics* **1992**, *11*, 127.

(15) Adams, C. M.; Hafner, A.; Koller, M.; Marcuzzi, A.; Prewo, R.; Solan, I.; Vincent, B.; von Philipsborn, W. *Helv. Chim. Acta* **1989**, *72*, 1658.

(16) The most salient aspects of the solution structures of **3** were apparent early on from detailed 2-D NMR studies; however, due to its unusual nature several months were taken for crystal growing to confirm that the solid-state structure was in agreement with the solution results.

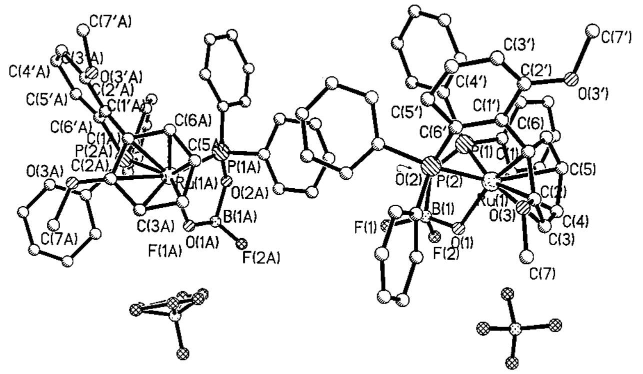
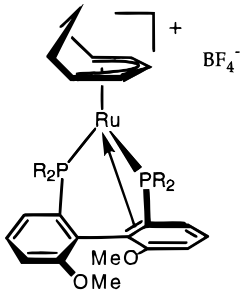


Figure 2. View of the two independent molecules of **3b**. The view for the molecule on the left readily displays the coordinated arene as well as the new phosphinite.

in the unit cell), the data are just sufficient for a qualitative analysis. The view shows the aryl η^6-arene bonding as well as the new phosphinite. Given the unusual nature of the product **3**, a third derivative, with R = 4-tolyl, was also prepared.

The η^6 bonding in **3** is not completely unexpected.[17−19] Ligand **1a** is known to complex individual biaryl double bonds,[17] as shown in **5**. Moreover, in Ru−dialkyl complexes of **1a**,[18] the η^6 mode, pictured in **6**, is found. The molecule achieves this structure by dissociating one tertiary phosphine donor. We believe that this propensity for Ru to complex one face of the biaryl is connected with the appearance of **3**.



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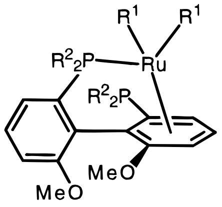
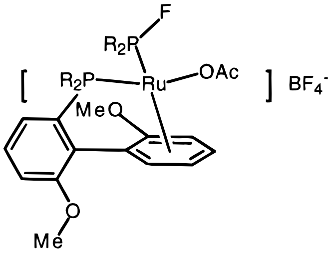


6, R^1 = Me, CH_2SiMe_3

R^2 = 3,5-di-t-Bu-phenyl

The P−C bond-breaking reactions can be shown to involve monofluorophosphine intermediates, whose structures we tentatively assign as **7**. The ^{31}P and ^{19}F NMR spectra of the PFR_2 ligand in **7** clearly show the expected large one-bond ^1J(P,F) values as well as a very high frequency ^{31}P chemical shift due to the strongly electronegative F. Obviously, this chemistry produces species which are reactive enough to extract fluoride from the BF_4^- anion. The observed concentration[20] of intermediate **7** varies with the aryl group; however, **7** always disappears during the course of the reaction. Aspects of these details along with experiments designed to isolate **4** will be described shortly.



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[17] Feiken, N.; Pregosin, P. S.; Trabesinger, G. *Organometallics.* **1997**, *16*, 537. Feiken, N.; Pregosin, P. S.; Trabesinger, G. *Organometallics* **1997**, *16*, 5756.

[18] Feiken, N.; Pregosin, P. S.; Trabesinger, G. *Organometallics* **1997**, *16*, 3735.

[19] Winter, R. F.; Hornung, F. M. *Inorg. Chem.* **1997**, *36*, 6197−6204.

[20] Complex **7** can be as much as 40−50% of the total, although it also seems to exist in several isomeric forms. In addition to **3** and **7**, there are additional species in solution. We do not know whether the P−C bond-breaking and P−F bond-making steps are separate or concerted.