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Article

Synthesis and Reactivity of Fluoro Complexes: Part 2.[1] Rhodium(I) Fluoro Complexes with Alkene and Phosphine Ligands. Synthesis of the First Isolated Rhodium(I) Bifluoride Complexes. Structure of [Rh$_3$(μ_3-OH)$_2$(COD)$_3$](HF$_2$) by X-ray Powder Diffraction

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The reaction between [Rh(μ-OH)(COD)]$_2$ (COD = 1,5-cyclooctadiene) and 73% HF in THF gives [Rh$_3$(μ_3-OH)$_2$(COD)$_3$](HF$_2$) (**1**). Its crystal structure, determined by ab initio X-ray powder diffraction methods (from conventional laboratory data), contains complex trimetallic cations linked together in 1D chains by a μ_3-OH···F–H–F···HO-μ_3 sequence of strong hydrogen bonds. The complex [Rh(μ-F)(COE)$_2$]$_2$ (COE = cyclooctene; **2**), prepared by reacting [Rh(μ-OH)(COE)$_2$]$_2$ with NEt$_3$·3HF (3:2), has been characterized. Complex **1** reacts with PR$_3$ (1:3) to give [RhF(COD)(PR$_3$)] [R = Ph (**3**), C$_6$H$_4$OMe-4 (**4**), ^{i}Pr (**5**), Cy (**6**)] that can be prepared directly by reacting [Rh(μ-OH)(COD)]$_2$ with 73% HF and PR$_3$ (1:2:2). The reactions of **1** with PPh$_3$ or Et$_3$P have been studied by NMR spectroscopy at different molar ratios. Complexes [RhF(PEt$_3$)$_3$] (**7**), [RhF(COD)(PEt$_3$)] (**8**), and [RhF(PPh$_3$)$_3$] (**9**) have been detected. The complex [Rh(F)(NBD)(^{i}Pr$_3$P)] (NBD = norbornadiene; **10**) was prepared by the sequential treatment of [Rh(μ-OMe)(NBD)]$_2$ with 1 equiv of NEt$_3$·3HF and ^{i}Pr$_3$P. The first isolated bifluoride rhodium(I) complexes [Rh(FHF)(COD)(PR$_3$)] [R = Ph (**11**), ^{i}Pr (**12**), Cy (**13**)], obtained by reacting fluoro complexes **3**, **5**, and **6** with NEt$_3$·3HF (3:1), have been characterized. The crystal structures of **3** and **11** have been determined.

Introduction

The fluoro complexes of the late transition metals in low oxidation states[2,3] show several singular features that have attracted growing attention during the last few years. The first is their stability,[4] which goes against the prediction of the hard and soft acids and bases principle.[5] In addition, they show singular reactivity, being much more reactive than the analogous chloro, bromo, and iodo complexes.[1,6−8] Finally, their potential as homogeneous catalysts has still not been fully exploited,[9] in particular, in metal-catalyzed fluorination reactions.[10]

Rhodium(I) phosphine or olefin−phosphine complexes have been intensively studied because of their important

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(1) Vicente, J.; Gil-Rubio, J.; Bautista, D. *Inorg. Chem.* **2001**, *40*, 2636 (Part 1).

(2) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Rev.* **1997**, *97*, 3425. Roesky, H. W.; Haiduc, I. *J. Chem. Soc., Dalton Trans.* **1999**, 2249. Roesky, H. W. *Inorg. Chem.* **1999**, *38*, 5934. Holloway, J. H.; Hope, E. G. *J. Fluorine Chem.* **1996**, *76*, 209.

(3) Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553.

(4) Mezzetti, A.; Becker, C. *Helv. Chim. Acta* **2002**, *85*, 2686. Caulton, K. G. *New. J. Chem.* **1994**, *18*, 25.

(5) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581. Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(6) Huang, D.; Koren, P. R.; Folting, K.; Davidson, E. R.; Caulton, K. G. *J. Am. Chem. Soc.* **2000**, *122*, 8916. Huang, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 3185. Doherty, N. M.; Critchlow, S. C. *J. Am. Chem. Soc.* **1987**, *109*, 7906. Grushin, V. V. *Angew. Chem., Int. Ed.* **1998**, *37*, 994. Braun, T.; Parsons, S.; Perutz, R. N.; Voith, M. *Organometallics* **1999**, *18*, 1710. Veltheer, J. E.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 12478. Gil-Rubio, J.; Laubender, M.; Werner, H. *Organometallics* **2000**, *19*, 1365.

(7) Gil-Rubio, J.; Weberndörfer, B.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1999**, 1437.

(8) Grushin, V. V.; Marshall, W. J. *J. Am. Chem. Soc.* **2004**, *126*, 3068.

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applications in catalysis.[11] The majority of these complexes contain chloro ligands or have been prepared from Rh(I) olefin−chloro complexes, which are the usual starting materials in Rh(I) chemistry.[12] In contrast, a very small number of Rh(I)−fluoro complexes containing only phosphine or alkene ligands have been reported, and their catalytic properties are virtually unexplored.[1,7,8,13−16]

Most Rh(I)−fluoro complexes have been prepared by Cl/F exchange from the corresponding chloro complexes by using AgF or by sequential treatment with a silver salt and a fluoride-donor reagent.[7,13,14,16,17] A few have been prepared by reacting hydroxo complexes with HF or $NEt_3{\cdot}3HF$.[1,7,8] To the best of our knowledge, only two olefin−fluoro complexes of Rh(I) have been reported. The first was the product of the reaction between $[Rh(\mu\text{-}Cl)(COE)_2]_2$ and AgF (COE = cyclooctene), which was tentatively formulated as $[Rh(\mu\text{-}F)(COE)_2]_2$ by analogy to the known $[Rh(\mu\text{-}Cl)(COE)_2]_2$ and remains insufficiently characterized.[14] The second was the tetramer $[Rh(\mu_3\text{-}F)(C_2H_4)(C_2F_4)]_4$, which was prepared by successive treatment of $[Rh(\mu\text{-}Cl)(C_2H_4)(C_2F_4)]_2$ with $AgBF_4$ and the fluoride-donor reagent $[(Me_2N)_3S]^+[Me_3SiF_2]^-$ and fully characterized by X-ray crystallography.[16]

We have recently reported that the reaction between $[Rh(\mu\text{-}OH)(COD)]_2$ (COD = 1,5-cyclooctadiene) and 73% hydrofluoric acid gives a fluorine-containing Rh(I) complex in good yield that can be used as a starting material for the synthesis of Rh(I)−fluoro complexes.[1] On the basis of its C and H elemental analyses and reactivity, a $[RhF(COD)]_n$ composition was proposed for this compound. All of our attempts to grow single crystals for an X-ray diffraction structure determination were unsuccessful, and owing to its low solubility, the NMR spectra of this compound gave little information about its structure in solution. In this paper, we report the structure determination of this compound by X-ray powder diffraction (XRPD), which, together with additional spectroscopic, analytical, and chemical evidence, shows that in this complex fluorine is not bonded to Rh but appears as the bifluoride anion in the $[Rh_3(\mu_3\text{-}OH)_2(COD)_3](HF_2)$ salt. Several methodological aspects of this rather complex structure determination, as well as the subsequent reinterpretation of experimental data, have already been extensively discussed at the thematic SSPD '03 meeting[18] and fully agree with the model very recently presented by Grushin and coworkers who, independently, were able to obtain a suitable single crystal from the reaction of $[Rh(\mu\text{-}OH)(COD)]_2$ with $NEt_3{\cdot}3HF$ for conventional diffraction analysis.[19]

In addition, we have explored the synthesis of Rh(I) fluoro complexes by neutralization reactions of hydroxo or methoxo complexes with hydrofluoric acid or $NEt_3{\cdot}3HF$. This method avoids the use of silver salts to remove chloro ligands and allows the synthesis of a wide variety of Rh(I) fluoro complexes with considerable synthetic potential. Finally, the synthesis and characterization of the first isolated Rh(I) complexes containing a coordinated HF_2^- anion are reported.

Results and Discussion

Olefin Fluoro and Hydroxo Complexes. The reaction of $[Rh(\mu\text{-}OH)(COD)]_2$ with an equivalent amount of 73% hydrofluoric acid (Scheme 1) gave rise to the precipitation of a yellow, microcrystalline solid in good yield. In a previous communication, we formulated this solid as $[RhF(COD)]_n$ on the basis of (a) its C and H analyses and (b) the formation of $[RhF(COD)(PPh_3)]$ as the main product of its reaction with triphenylphosphine. After several unsuccessful attempts to obtain single crystals for an X-ray crystal structure determination, we carried out a complete powder diffraction analysis, showing it to be $[Rh_3(\mu_3\text{-}OH)_2(COD)_3](HF_2)$ (**1**).

This "formally ionic" species crystallizes as neutral chains originating from the presence of strong OH···F−H−F···HO

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(9) Bode, J. W.; Gauthier, D. R., Jr.; Carreira, E. M. *Chem. Commun.* **2001**, 2560. Duthaler, R. O.; Hafner, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 43. Pagenkopf, B. L.; Carreira, E. M. *Tetrahedron Lett.* **1998**, *39*, 9593. Pagenkopf, B. L.; Carreira, E. M. *Chem.−Eur. J.* **1999**, *5*, 3437. Fagnou, K.; Lautens, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 26. Burckhardt, U.; Baumann, M.; Togni, A. *Tetrahedron: Asymmetry* **1997**, *8*, 155. Dorta, R.; Egli, P.; Zürcher, F.; Togni, A. *J. Am. Chem. Soc.* **1997**, *119*, 10857. Krüger, J.; Carreira, E. M. *J. Am. Chem. Soc.* **1998**, *120*, 837.

(10) Barthazy, P.; Togni, A.; Mezzetti, A. *Organometallics* **2001**, *20*, 3472. Barthazy, P.; Hintermann, L.; Stoop, R. M.; Wörle, M.; Mezzetti, A.; Togni, A. *Helv. Chim. Acta* **1999**, *82*, 2448. Barthazy, P.; Stoop, R. M.; Wörle, M.; Togni, A.; Mezzetti, A. *Organometallics* **2000**, *19*, 2844. Togni, A.; Mezzetti, A.; Barthazy, P.; Becker, C.; Devillers, I.; Frantz, R.; Hintermann, L.; Perseghini, M.; Sanna, M. *Chimia* **2001**, *55*, 801. Sakakura, T.; Chaisupakitsin, M.; Hayashi, T.; Tanaka, M. *J. Organomet. Chem.* **1987**, *334*, 205. Okano, T.; Harada, N.; Kiji, J. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1741. Hamashima, Y.; Yagi, K.; Takano, H.; Tamás, L.; Sodeoka, M. *J. Am. Chem. Soc.* **2002**, *124*, 14530. Mikami, K.; Ohba, S.; Ohmura, H. *J. Organomet. Chem.* **2002**, *662*, 77. Muñiz, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 1653. Hintermann, L.; Togni, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 4359. Yanagisawa, A.; Kageyama, H.; Nakatsuka, Y.; Asakawa, K.; Matsumoto, Y.; Yamamoto, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 3701.

(11) Tkatchenko, I.; James, B. R.; Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8, p 101. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(12) Jardine, F. H.; Sheridan, P. S. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McLeverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 4, p 901. Hughes, R. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 5, p 277.

(13) van Gaal, H. L. M.; van den Bekerom, F. L. A. *J. Organomet. Chem.* **1977**, *134*, 237.

(14) van Gaal, H. L. M.; van den Bekerom, F. L. A.; Verlaan, J. P. J. *J. Organomet. Chem.* **1976**, *114*, C35.

(15) Fryzuk, M. D.; Piers, W. E. *Polyhedron* **1988**, *7*, 1001.

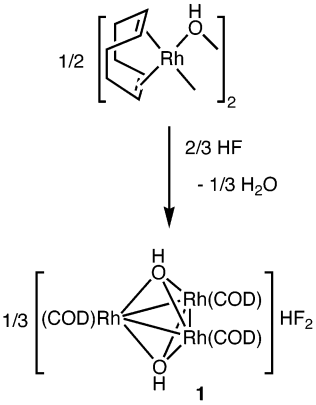
(16) Burch, R. R.; Harlow, R. L.; Ittel, S. D. *Organometallics* **1987**, *6*, 982.

(17) Vaska, L.; Peone, J. J. *Inorg. Synth.* **1974**, *15*, 64. Cairns, M. A.; Dixon, K. R.; McFarland, J. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1159. Sakakura, T.; Sodeyama, T.; Sasaki, K.; Wada, K.; Tanaka, M. *J. Am. Chem. Soc.* **1990**, *112*, 7221. Grinberg, A. A.; Singh, M. M.; Varshavskii, Y. S. *Russ. J. Inorg. (Engl. Transl.) Chem.* **1968**, *13*, 1399. Goswami, K.; Singh, M. M. *J. Indian Chem. Soc.* **1979**, *56*, 477. Vaska, L.; Peone, J. J. *J. Chem. Soc., Chem. Commun.* **1971**, 418.

(18) Masciocchi, N.; Sironi, A. In *Book of Abstracts*, Structure Solution from Powder Diffraction Data 2003, Stara Lesna, Slovakia, September 13−19, 2003.

(19) Grushin, V. V. Private communication. The refined cell parameters measured from single-crystal X-ray diffraction [a = 12.2685(8) Å, b = 15.9849(10) Å, c = 12.7070(8) Å, β = 95.6150(16)°] closely match, upon permutation, those reported in this paper, determined by XRPD. A similar match also occurs on the structural model retrieved by the two different techniques.

Scheme 1



(the O···F distance is near 2.50 Å) hydrogen bonds between the trinuclear complex cation (Figure 1) and the bifluoride anion. The very same cation has been previously observed in the SbF_6^- salt.[20] Interestingly, besides having a similar molecular stereochemistry, the two species also share some analogies at the supramolecular level. Indeed, despite crystallizing in different unit cells and space groups, they consist of parallel chains, packed in a square lattice and built upon strong OH−F contacts (with HF_2^- or SbF_6^-). However, in **1**, the hydrogen-bonded chains of $[Rh_3(OH)_2]^+$ complexes and HF_2^- ions wind up about a 2_1 axis, whereas in the closely related SbF_6^- salt, "similar" chains are generated by simple lattice translations.

The structure of the trinuclear complex is definitely distorted from its idealized D_{3h} symmetry because the refined intermetallic bond distances are 2.79, 2.86, and 3.08 Å (typical esd's 0.02 Å). Although the first one is rather short (with the caveats inherent in the XRPD method), this effect should not be surprising because the few known structures containing the $Rh_3(\mu_3\text{-}OX)_2$ core show a large variability in the Rh−Rh contacts (2.87−3.12), which are then to be considered rather flexible.[20,21] In particular, the closely related SbF_6^- salt, cited above, shows an isosceles triangle metal core with similar distances.

The analytical and spectroscopic data support the formulation of complex **1**. Thus, the C, H, and F elemental analyses serve to discard alternative formulations with the general formula $Rh_3(OH)_x(F_2H)_yF_{3-y-x}(COD)_3$, where x or $y = 0$, 1, 2, or 3, except for $x = 2$, $y = 1$ ($x + y \leq 3$). In its IR spectrum, no bands corresponding to the O−H stretching vibrations (above 3000 cm^{-1}) were detected; however, a broad band at 1954 cm^{-1}, which is assigned to the F−H−F stretching mode, was present. The broadening of this band and the absence of the $\nu(OH)$ bands may be motivated by hydrogen-bond interactions between the OH groups and the HF_2^- anions in the lattice.

The room-temperature ^1H NMR spectra, recorded in D_8-THF, CD_2Cl_2, $CDCl_2-CDCl_2$, or $CDCl_3$, show three multiplets with the same relative integral, which are typical of a symmetrical COD ligand, and no signals for the OH and HF_2^- protons. On lowering the temperature (to −80 °C in D_8-THF or CD_2Cl_2), the spectra are of low quality, and on raising the temperature (to 85 °C in $CDCl_2-CDCl_2$), a broad resonance appears at 2.08 ppm in addition to the three multiplets of COD, which could be due to OH and/or HF_2^- protons. The ^{19}F NMR spectra (D_8-THF, CD_2Cl_2, $CDCl_3$) at room or higher temperatures ($CD_2Cl_2-CDCl_3$ at 58 and 85 °C or D_8-THF at 60 °C) do not show absorptions. However, on lowering the temperature to −40 °C in CD_2Cl_2, a unique, weak, broad signal was observed at −149.8 ppm, which is in the expected chemical shift range for the HF_2^- anion.[22−24] Fast proton exchange between the OH and HF_2^- groups is probably responsible for the broadening and temperature dependence of the ^{19}F and ^1H NMR solution spectra. Complex **1** is very soluble in D_4-methanol, giving a broad singlet in the ^{19}F NMR spectrum at −177.4 ppm, but because the ^1H NMR spectrum shows two types of COD signals, we believe that **1** reacts with methanol, giving new species that

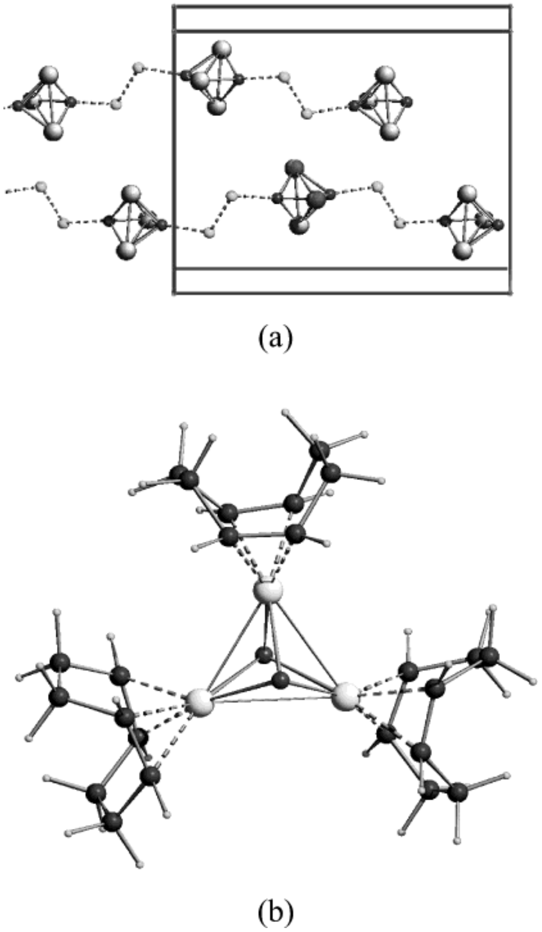


Figure 1. (a) Hydrogen-bonded chains of the $[Rh_3(OH)_2]^+$ complex (COD ligands are omitted) and HF_2^- ions in **1**, winding up about a 2_1 axis. (b) Drawing of the $[Rh_3(COD)_3(OH)_2]^+$ cation. This species, of idealized D_{3h} symmetry, is actually distorted toward C_{2v}, with Rh···Rh contacts in the 2.79−3.08-Å range.

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(20) Kuhn, N.; Grathwohl, M.; Nachtigal, C.; Steimann, M.; Henkel, G. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2039.

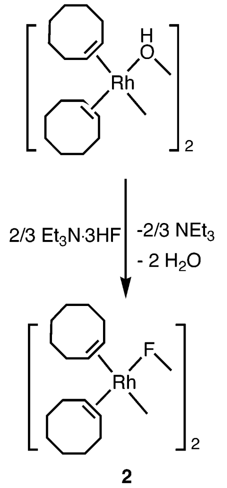
(21) Yamagata, T.; Kani, K.; Tatsuno, Y.; Saito, T. *J. Chem. Soc., Chem. Commun.* **1988**, 466. Churchill, M. R.; Barkan, M. D.; Atwood, J. R.; Ziller, J. W. *Acta Crystallogr., Sect. C* **1990**, *46*, 2462.

(22) Shenderovich, H. G.; Limbach, H.-H.; Smirnov, S. N.; Tolstoy, P. M.; Denisov, G. S.; Golubev, N. S. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5488.

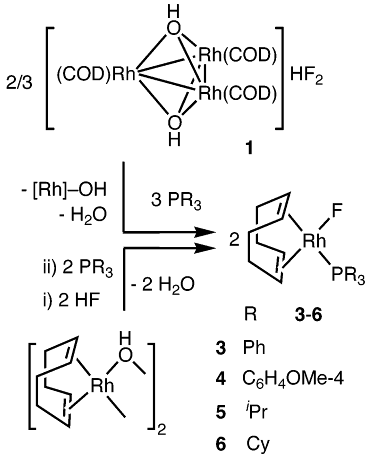
(23) Fujiwara, F. Y.; Martin, J. S. *J. Am. Chem. Soc.* **1974**, *96*, 7625.

(24) Gouin, L.; Cousseau, J.; Smith, J. A. S. *J. Chem. Soc., Faraday Trans.* **1977**, *73*, 1878.

Scheme 2



Scheme 3



could result from OH^-/MeO^- exchange. In agreement with that, the ESI-MS spectrum of **1** dissolved in methanol gave a high relative abundance peak with $m/z = 695$ Da, which can be assigned to the $[Rh_3(OMe)_2(COD)_3]^+$ cation. The CP MAS ^{19}F spectrum shows a broad singlet at −144.1 ppm, which is in agreement with the presence of only one type of fluorine in the solid state.

We could not isolate a well-defined product from the reaction of $[Rh(\mu\text{-}OMe)(NBD)]_2$ (NBD = norbornadiene)[25] with the equivalent amount of $NEt_3 \cdot 3HF$ or 73% HF in THF. The solid isolated after precipitation with either *n*-hexane or *n*-pentane gave broad NMR spectra, which were different from one preparation to another and, when $NEt_3 \cdot 3HF$ was used, contained variable amounts of NEt_3 that could not be completely removed under vacuum.

Because an optimal starting material to prepare Rh(I) fluoro complexes should contain easily replaceable ligands, we turned our attention to the complex $[Rh(\mu\text{-}F)(COE)_2]_2$ (COE = cyclooctene; **2**), which was prepared by van Gaal et al. by the reaction of $[Rh(\mu\text{-}Cl)(COE)_2]_2$ with AgF in acetone.[14] The product obtained in this way was impure, and only its analytical data were given to support the proposed composition. We have prepared pure **2** in good yield (Scheme 2) by the reaction of $[Rh(\mu\text{-}OH)(COE)_2]_2$ with an equivalent amount of $NEt_3 \cdot 3HF$. It is soluble in most organic solvents, but it slowly decomposes to metallic rhodium in solution at room temperature. Its room-temperature ^{19}F NMR spectrum in C_6D_6 shows a broad triplet (−292.9 ppm, $^1J_{RhF} = 55.5$ Hz), which agrees with the presence of fluoro ligands bridging two rhodium atoms as shown in Scheme 2.

In a new attempt to obtain a compound containing both COD and fluoro ligands, we treated a solution of **2** in C_6D_6 with an equimolar amount of COD. A yellow solution was obtained whose ^1H NMR spectrum showed the signals of free COE and another set of signals, similar to those of **1**. The ^{19}F NMR spectrum showed no signals. The addition of 1 equiv of PPh_3 to the yellow solution gave rise to the formation of **3** (Scheme 3). When the reaction of **2** with COD was carried out in THF to isolate the product, a yellow, partially soluble solid was obtained that was identified as **1** by ^1H NMR. This suggests that a complex of composition $[RhF(COD)]_n$, which may be formed by the substitution of COE by COD, is unstable under these conditions and reacts with traces of H_2O present in the solvent to give **1**.

Fluoro Rhodium(I) Complexes Containing Phosphine Ligands. To explore the chemical behavior of complex **1**, we have studied its reactivity toward phosphines. Thus, when a suspension of **1** in THF was treated with PPh_3, $P(C_6H_4\text{-}OMe\text{-}4)_3$, P^iPr_3, or PCy_3 in 1:3 stoichiometry (Scheme 3), complexes of the general composition $[RhF(COD)(PR_3)]$ (**3**−**6**) were obtained.

The formation of complexes **3**−**6** from **1** probably occurs through cleavage of the hydroxo bridges by the phosphine ligand to give a somewhat more basic hydroxo rhodium complex, which reacts with the acidic HF_2^- anion to afford complexes **3**−**6** and H_2O. However, the adjustment of the equation relating **1** to complexes **3**−**6** requires the formation of some hydroxo rhodium complexes: $[Rh_3(\mu_3\text{-}OH)_2(COD)_3](HF_2) + 3PR_3 \Rightarrow 2[RhF(COD)(PR_3)] + Rh(OH)(COD)(PR_3) + H_2O$. To test this hypothesis, we carried out the reactions of **1** with PR_3, R = Ph, 4-MeO−C_6H_4, ^{i}Pr, and Cy in C_6D_6 in an NMR tube. Under these conditions, compounds **3**−**6** were the main reaction products, but other species were observed. These secondary products do not contain fluorine because only the signals corresponding to the fluoro ligands of **3**−**6** were observed in the ^{19}F NMR spectra of the reaction mixtures. One of these products was identified in the reaction mixture of **1** with PPh_3 (1:1**)** as the hydroxo complex $[Rh(\mu\text{-}OH)(PPh_3)_2]_2$ by the comparison of its ^1H and $^{31}P\{^1H\}$ NMR data [^1H: $\delta = -2.17$ (OH); $^{31}P\{^1H\}$: $\delta = 57.4$ (d, $^1J_{RhP} = 188.7$ Hz)] with those reported in the literature.[26] Apart from **3**, $[Rh(\mu\text{-}OH)(PPh_3)_2]_2$, and free COD, there was another species in the reaction mixture that was tentatively formulated as the dinuclear complex $[(COD)Rh(\mu\text{-}OH)_2Rh(PPh_3)_2]$ on the basis of the following data: (a) in the ^{31}P NMR spectrum, a doublet was observed at 57.7 ppm ($^1J_{RhP} = 191.8$ Hz), which is similar to the signal of $[Rh(\mu\text{-}OH)$-

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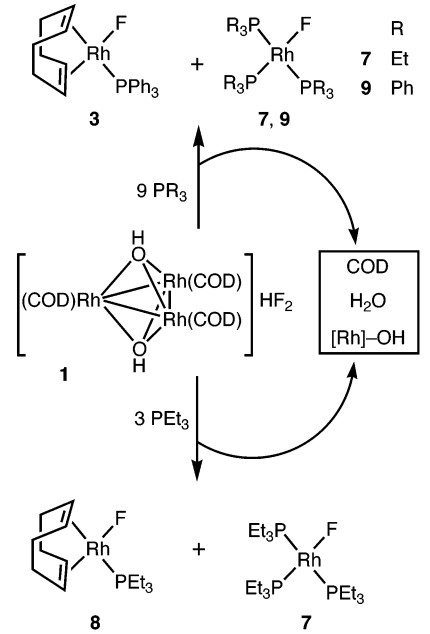
(25) Connelly, N. G.; Loyns, A. C.; Fernández, M. J.; Modrego, J.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1989**, 683.

(26) Grushin, V. V.; Kuznetsov, V. F.; Bensimon, C.; Alper, H. *Organometallics* **1995**, *14*, 3927.

Scheme 4



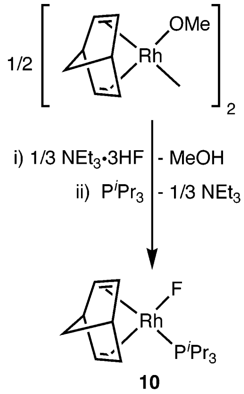
$(PPh_3)_2]_2$ and (b) in the ^1H NMR spectrum, a characteristic OH signal was observed at −1.71 ppm as a broad singlet, and three multiplets corresponding to a coordinated COD ligand were observed at 3.40 (olefinic protons), 2.39, and 1.59 ppm (methylenic protons).

Because only $^2/_3$ of the total amount of Rh in **1** is used to prepare complexes **3**−**6** (they were isolated in 59−65% yield on rhodium and 89−98% on F), a more direct method for their synthesis is the reaction of $[Rh(\mu\text{-}OH)(COD)]_2$ with 73% HF and PR_3 (1:2:2 molar ratio; Scheme 3). This method has been tested for R = Ph, 4-MeO−C_6H_4, and ^{i}Pr, giving **3**−**5** in 50−89% yield without the need to isolate **1**.

PEt_3 behaves differently than the other phosphines. Thus, treatment of **1** with PEt_3 (1:3 molar ratio) gave a mixture of $[RhF(PEt_3)_3]$ (**7**)[27] and, likely, $[RhF(COD)(PEt_3)]$ (**8**) [selected NMR data (C_6D_6): $\delta(^{19}F)$ −251.9 (br s); $\delta(^{31}P\{^1H\})$ 59.2 (br d, $^1J_{RhP}$ = 157.9 Hz)], which was the main product, together with nonfluorinated products at a lower concentration as deduced from the ^1H, $^{31}P\{^1H\}$, and ^{19}F NMR spectra of the reaction mixture (Scheme 4).

When **1** was reacted with PPh_3 in a 1:9 ratio, complex **3**, $[RhF(PPh_3)_3]$ (**9**),[8,14] COD, and $[Rh(\mu\text{-}OH)(PPh_3)_2]_2$ were detected by ^1H, $^{31}P\{^1H\}$, and ^{19}F NMR spectroscopy (Scheme 4). The addition of an additional 9 equiv of PPh_3 (PPh_3:**1** = 18:1) gave rise to a nearly complete transformation of **3** into **9**. A similar result, except for the lack of the presence of the hydroxo complex, was obtained by reacting **3** with PPh_3 (1:2 and 1:8 molar ratios). When the ratio of PEt_3:**1** was 9:1, complex **7** was formed as the only fluorine-containing product. Because the nonfluorinated products were also observed in the ^1H and $^{31}P\{^1H\}$ spectra in C_6D_6 of mixtures of $[Rh(\mu\text{-}OH)(COD)]_2$ and PEt_3 (Rh:PEt_3 = 1:3), we assume that they are hydroxo complexes. One of them was tentatively formulated as $[Rh(OH)(PEt_3)_3]$ on the basis of its $^{31}P\{^1H\}$ NMR data (C_6D_6): δ 37.8 (dt, PEt_3 trans to OH, $^1J_{RhP}$ = 161.9 Hz, $^2J_{PP}$ = 40.2 Hz), 22.6 (dd, PEt_3 trans to PEt_3, $^1J_{RhP}$ = 143.9 Hz).

Scheme 5



Complex $[Rh(F)(NBD)(^iPr_3P)]$ (**10**) was prepared by the sequential treatment of $[Rh(\mu\text{-}OMe)(NBD)]_2$[25] with $NEt_3{\cdot}3HF$ and $^iPr_3P$ (Scheme 5). The analogous reactions of $[Rh(\mu\text{-}OMe)(NBD)]_2$ with PPh_3 in 1:2 or 1:4 molar ratios gave mixtures of compounds that could not be separated and characterized.

The ^{19}F NMR spectra of complexes **3**−**6** and **10** show resonances in the range of −230.2 to −259.6 ppm, which are typical for a metal-bound fluorine.[3] In complexes **5** and **6**, they appear as doublets of doublets because of the coupling of ^{19}F with ^{103}Rh and ^{31}P and as broad singlets for complexes **3**, **4**, and **10**. On lowering the temperature, **4** and **10** gave broad doublets while **3** showed the expected doublets of doublets. The room-temperature $^{31}P\{^1H\}$ NMR spectra showed the expected doublets of doublets for **5** and **6** but a broad singlet for **3**, a broad doublet for **4**, and a doublet for **10**, all of which split into the expected doublets of doublets on lowering the temperature. This behavior could arise from fast phosphine and fluoride dissociation processes on the NMR time scale at room temperature.

The crystal structure of **3** (Figure 2) was determined by X-ray diffraction analysis and reported in a preliminary communication.[1] The metal is in a distorted square-planar coordination environment. The Rh−F distance (2.0214(12) Å) is similar to the distances found in other mononuclear Rh(I) fluoro complexes: *trans*-$[RhF(CO)(PPh_3)_2]$ (2.046(2) Å),[28] *trans*-$[RhF(\eta^2\text{-}CH_2{=}CH_2)(P^iPr_3)_2]$ (2.060(3) Å),[7] and $[RhF(PPh_3)_3]$ (2.070(2) Å).[8]

Bifluoride Complexes of Rhodium(I). There are few examples of late-transition-metal complexes in which the bifluoride anion acts as a ligand.[29−35] Because recent studies have shown that fluoro complexes of Ni,[33,34] Pd[32], and Pt[30]

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[27] Braun, T.; Noveski, D.; Neumann, B.; Stammler, H.-G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2745.

[28] Wierzbicki, A.; Salter, E. A.; Hoffman, N. W.; Stevens, E. D.; Van Do, L.; VanLoock, M. S.; Madura, J. D. *J. Phys. Chem.* **1996**, *100*, 11250.

[29] Roesky, H. W.; Sotoodeh, M.; Xu, Y.; Schrumpf, F.; Noltemeyer, M. *Z. Anorg. Allg. Chem.* **1990**, *580*, 131. Coulson, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 3111. Grushin, V. V. *Organometallics* **2000**, *19*, 1888. Murphy, V. J.; Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1995**, *117*, 9762. Bentrup, U.; Harms, K.; Massa, W.; Pebler, J. *Solid State Sci.* **2000**, *2*, 373. Holzbock, J.; Sawodny, W.; Walz, L. *Z. Kristallografiya* **1997**, *212*, 115.

[30] Jasim, N. A.; Perutz, R. N. *J. Am. Chem. Soc.* **2000**, *122*, 8685.

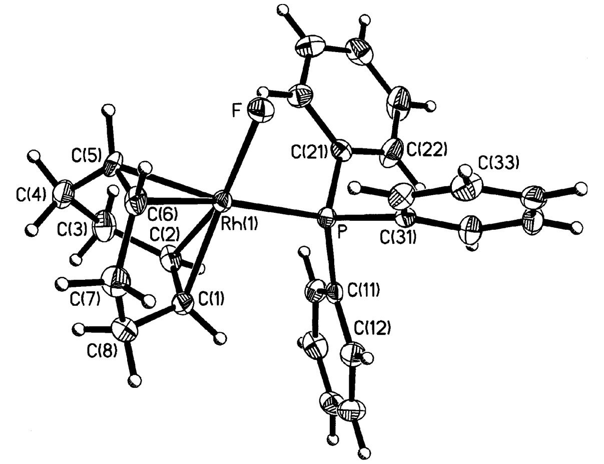
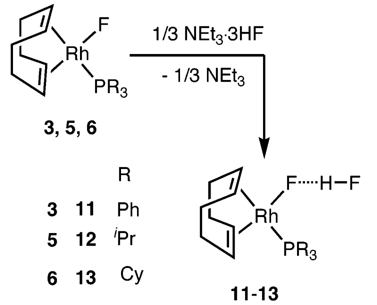


Figure 2. Molecular structure of **3** with 50% probability ellipsoids and the labeling scheme. Selected bond lengths (Å) and angles (deg): Rh−F 2.0214(12), Rh−C(1) 2.115(2), Rh−C(2) 2.097(2), Rh−C(5) 2.197(2), Rh−C(6) 2.189(2), C(1)−C(2) 1.399(3), C(5)−C(6) 1.379(3), Rh−P 2.3229(5); F−Rh−C(5) 89.06(7), F−Rh−C(6) 87.24(7), C(1)−Rh−P 96.92(6), C(2)−Rh−P 92.86(6), F−Rh−P 89.40(4).

Scheme 6



are able to trap a molecule of HF when they are treated with $NEt_3 \cdot 3HF$ to generate a coordinated bifluoride unit and reported NMR studies have suggested that the formation of observable amounts of a bifluoride complex when the fluoro vinylidene complex *trans*-$[RhF(=C=CHPh)(P^iPr_3)_2]$ was treated with acetic acid,[7] we attempted the synthesis of Rh(I) bifluoride complexes by treating fluoro complexes **3**, **5**, and **6** with $NEt_3 \cdot 3HF$ (3:1 molar ratio). Under these conditions, compounds $[Rh(FHF)(COD)(PR_3)]$ [R = Ph (**11**), ^{i}Pr (**12**), Cy (**13**)] were obtained in 67−92% yield (Scheme 6). These are the first isolated Rh(I) bifluoride complexes.

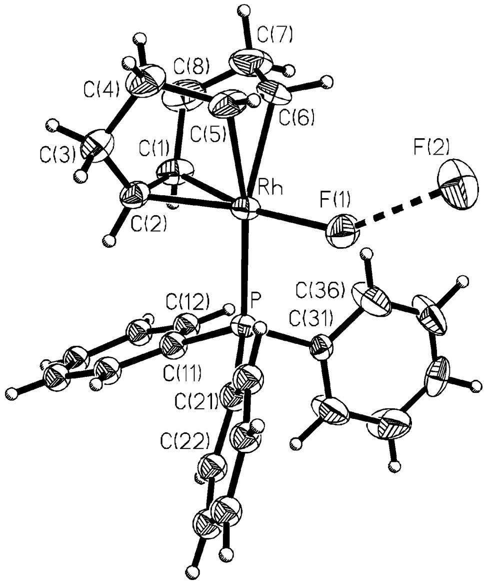


Figure 3. Molecular structure of **11** with 50% probability ellipsoids and the labeling scheme. Selected bond lengths (Å) and angles (deg): Rh−F(1) 2.083(2), F(1)−F(2) 2.3310 (34), Rh−C(2) 2.098(4), Rh−C(1) 2.107(4), Rh−C(6) 2.190(4), Rh−C(5) 2.207(4), Rh−P 2.3211(10), C(1)−C(2) 1.391(5), C(5)−C(6) 1.378(6), F(2)−F(3)−Rh 147.23 (14), F(1)−Rh−C(2) 158.17(12), F(1)−Rh−C(1) 162.70(13), F(1)−Rh−C(6) 88.52(14), C(2)−Rh−C(6) 97.4(2), C(1)−Rh−C(6) 81.8(2), F(1)−Rh−C(5) 91.24(13), C(2)−Rh−C(5) 81.5(2), C(1)−Rh−C(5) 89.4(2), F(1)−Rh−P 88.34(7), C(2)−Rh−P 92.73(11), C(1)−Rh−P 95.96(11), C(6)−Rh−P 160.26(12), C(5)−Rh−P 163.08(12).

The crystal structure of **11** was determined by X-ray diffraction to confirm the presence of a coordinated bifluoride anion (Figure 3). In addition, the availability of the structures of both analogous fluoride and bifluoride complexes **3** and **11** gave us the opportunity to compare the bonding properties of both fluoride and bifluoride anions coordinated to rhodium.

The metal is in a slightly distorted square-planar coordination. The F−F distance, 2.3310(34) Å, is shorter than twice the van der Waals radius of fluorine (1.4 Å),[36] is in the range found for other bifluoride complexes (2.276−2.400 Å),[31,33,35] and is similar to the F−F distance found for the ion in the gas phase (2.304432(52) Å)[37] or in bifluoride salts (2.233−2.342 Å).[38] The Rh−F−F angle, 147.23(14)°, is in the range found for terminal bifluoride complexes (128.5−156.7°).[31,33,35] The hydrogen atom was not unambiguously located, which is also the case in all previous X-ray structure determinations of other bifluoride complexes. The Rh−F distance, 2.083(2) Å, is longer than that in complex **3** (2.0214(12) Å), which suggests a weakening of the Rh−F bond in the bifluoride complex due to the F···H hydrogen bond. As is observed in the structure of **3**, the Rh−C distances are longer for the C=C of the COD ligand trans to the phosphine than for the C=C trans to the bifluoride ligand. Because the Rh−C distances are not significantly different from the distances found in **3**, we can conclude that the fluoride and bifluoride ligands have similar trans influences, which are in both cases lower than those of PPh_3.

The IR spectra of complexes **11**−**13** (Nujol mulls) show bands at 2630 and 1842 (**11**), 2580 and 1866 (**12**), and 2634 and 1842 (**13**) cm^{-1}, which can be assigned to the ν(FHF)

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(31) Roe, D. C.; Marshall, W. J.; Davidson, F.; Soper, P. D.; Grushin, V. V. *Organometallics* **2000**, *19*, 4575. Jasim, N. A.; Perutz, R. N.; Foxon, S. P.; Walton, P. H. *J. Chem. Soc., Dalton Trans.* **2001**, 1676.

(32) Pilon, M. C.; Grushin, V. V. *Organometallics* **1998**, *17*, 1774.

(33) Braun, T.; Foxon, S. P.; Perutz, R. N.; Walton, P. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 3326.

(34) Archibald, S. J.; Braun, T.; Gaunt, J. A.; Hobson, J. E.; Perutz, R. N. *J. Chem. Soc., Dalton Trans.* **2000**, 2013.

(35) Murphy, V. J.; Hascall, T.; Chen, J. Y.; Parkin, G. *J. Am. Chem. Soc.* **1996**, *118*, 7428. Whittlesey, M. K.; Perutz, R. N.; Greener, B.; Moore, M. H. *Chem. Commun.* **1997**, 187. Kirkham, M. S.; Mahon, M. F.; Whittlesey, M. K. *Chem. Commun.* **2001**, 813. Murphy, V. J.; Rabinovich, D.; Hascall, T.; Klooster, W. T.; Koetzle, T. F.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 4372.

(36) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(37) Kawagushi, K.; Hirota, E. *J. Chem. Phys.* **1986**, *84*, 2953.

(38) Ramos Silva, M.; Paixao, J. A.; Matos Beja, A.; Alte da Veiga, L. *J. Fluorine Chem.* **2001**, *107*, 117.

modes.[30,31,35] In compounds containing a hydrogen-bonded HF molecule, a decrease of the ν(FH) wavenumber is observed with respect to that of free HF (3960 cm^{-1}) as the hydrogen bond interaction becomes stronger.[39] For compounds **11**−**13**, the values are much higher than those found in various HF_2^- salts (1284−1450 cm^{-1}),[39,40] and the bands at higher wavenumber are close to the values found for the mixed XHF^- anions (X = Cl: 2491 and Br: 2803 cm^{-1}).[39] This suggests that the bifluoride ligand in **11**−**13** is highly unsymmetrical.

The ^{19}F NMR resonance of bridging fluoro complex **2** appears upfield (−292.9 ppm) with respect to the terminal ones in complexes **3**−**6** and **10** (−230.2 to −259.1 ppm). The values of $^1J_{RhF}$ are higher for the latter (70−79 Hz) than for **2** (55.5 Hz). These relationships have been found previously.[8] The *F*−Rh resonance in bifluoride complexes **11**−**13** appears in the upper limit of the above range, whereas the *F*−H resonance appears in the range of −180.5 to −190 ppm, which is close to that found in FHF^- salts (−144 to −155 ppm).[22,24,41] At room temperature, the ^{19}F NMR resonances of the bifluoride complexes appear very broad, but at −80 °C, the *F*−H signals transform into doublets of doublets, whereas the *F*−Rh resonance appears as an unresolved multiplet. The proton F−*H* resonance appears, as expected, highly deshielded (around 12 ppm) as a broad signal that resolves into a broad doublet of doublets at low temperature. A singular feature of this signal, which has also been observed in the low-temperature ^1H NMR spectra of *trans*-$[Pt(FHF)H(P\textit{i}Pr_3)_2]$[30] and $(FH)_xF^-$ anions ($x = 2$ or 3),[22] is the larger line width of the inner signals of the doublet of doublets. The values of $^1J_{FH}$ for the terminal fluorine are substantially higher (360−375 Hz) than those for the fluorine bound to Rh (32−41 Hz). Both differ considerably from the $^1J_{FH}$ in the HF_2^- anion (120 Hz).[23] The larger coupling is smaller than the $^1J_{FH}$ in HF (476 Hz in MeCN) and closer to the value found for $FHCl^-$ (404 Hz).[23] Both are similar to the FH coupling constants observed in $[(F{-}H\cdots)_xF]^-$ anions ($^1J_{F-H}/^1J_{F\cdots H} = 354.3/{-24.5}$ Hz for $x = 2$ and 430/−45 Hz for $x = 3$).[22] All of these data are in agreement with the formulation Rh−F···H−F, that is, a hydrogen bond between a fluoro complex and a HF molecule. This conclusion is supported by a comparison with the structural and spectroscopic data reported for other bifluoride complexes in which a similar situation has been observed.[30,31,34]

Conclusions

$[Rh_3(\mu_3\text{-}OH)_2(COD)_3](HF_2)$ (**1**) is the product of the reaction between $[Rh(\mu\text{-}OH)(COD)]_2$ and 73% hydrofluoric acid in THF. Its structure, determined by XRPD, shows the presence of trimetallic complexes linked together in 1D chains by a μ_3-OH···F−H−F···HO-μ_3 sequence of strong hydrogen bonds. It is interesting that XRPD has allowed the discarding of a strong chemical belief (the existence of a $[Rh(COD)F]_n$ polymer) in favor of a completely new structural model, absolutely unforeseen on the basis of the originally available analytical and spectroscopic data. Obviously, the XRPD technique cannot afford geometrical parameters of the accuracy normally obtained by conventional single-crystal diffraction methods. More importantly, the fortunate occurrence of a single crystal of the very same species, prepared and characterized independently in another laboratory, confirmed our structural assignment, and thus, it should be taken as a strengthening factor for our study, showing that, if suitably employed, XRPD can, whenever necessary, substitute or complement conventional diffraction analyses. We have isolated and characterized the fluoro−olefin rhodium(I) complex, $[Rh(\mu\text{-}F)(COE)_2]_2$, new fluoro−olefin−phosphino rhodium(I) complexes, $[RhF(COD)(PR_3)]$ (R = Ph, 4-MeO−C_6H_4, ^{i}Pr, and Cy) and $[RhF(NBD)(PP^ir_3)]$, and the first bifluoride rhodium(I) complexes, $[Rh(FHF)(COD)(PR_3)]$ (R = Ph, ^{i}Pr, and Cy). The reactions between **1** and different phosphines have been studied by NMR spectroscopy. Additional studies aimed at determining the solid-state structure of **2** and its reactivity are in progress

Experimental Section

General Considerations. Compounds $[Rh(\mu\text{-}OH)(COD)]$,[42] $[Rh(\mu\text{-}OH)(COE)_2]_2$,[43] and $[Rh(\mu\text{-}OMe)(NBD)]_2$[25] were prepared as described previously. Hydrofluoric acid (73%) and $NEt_3{\cdot}3HF$ were purchased from Fluka and Aldrich, respectively. Infrared spectra were recorded in the range of 4000−200 cm^{-1} on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets. Melting points were determined on a Reichert apparatus in the open atmosphere and were corrected. C and H analyses were carried out with a Carlo Erba 1108 microanalyzer. F analysis of complex **1** was carried out at the Servei de Microanàlisi IIQAB (CSIC), Barcelona. NMR spectra were measured at room temperature, unless otherwise stated, on Bruker Avance 200, 300, and 400 and Varian Unity 300 instruments. The CP MAS ^{19}F spectrum was measured in a 400-MHz instrument with a 25-kHz spin rate. ^1H chemical shifts were referenced to residual C_6D_5H (7.15 ppm) or $CDHCl_2$ (5.29 ppm). $^{13}C\{^1H\}$ spectra were referenced to C_6D_6 (128.0 ppm) or D_8-toluene (21.4 ppm for the CD_3 carbon). ^{19}F and $^{31}P\{^1H\}$ NMR spectra were referenced to external $CFCl_3$ and H_3PO_4 (0 ppm), respectively. Electrospray mass spectra (ESI-MS) were measured in an Agilent HPLC-MS 1100 spectrometer. All operations were carried out under an inert atmosphere of nitrogen by using standard Schlenk techniques. Tetrahydrofurane, toluene, and Et_2O were distilled with sodium benzophenone and stored over 4-Å molecular sieves. *n*-Hexane and *n*-pentane were dried with basic alumina, deoxygenated, and stored over 4-Å molecular sieves. C_6D_6 was distilled over CaH_2 and stored under nitrogen. D_8-Toluene and CD_2Cl_2 were dried over 4-Å molecular sieves.

$[Rh_3(\mu_3\text{-}OH)_2(COD)_3](HF_2)$ (1). A Schlenk tube equipped with a PTFE liner was charged with $[Rh(\mu\text{-}OH)(COD)]_2$ (1113 mg, 2.44 mmol) and THF (15 mL). The suspension was treated with a solution of HF in THF prepared from 73% hydrofluoric acid (5.1 mmol of HF). The mixture was stirred for 2 h, and the resulting suspension was filtered. The yellow solid was washed with THF (3 × 5 mL) and dried in vacuo. Yield: 920 mg, 80%. Dec pt 150 °C. ^1H NMR (299.9 MHz, D_8-THF): δ 4.01 (br m, 4 H, CH), 2.66

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[39] Ault, B. S. *Acc. Chem. Res.* **1982**, *15*, 103.
[40] Tuck, D. G. *Prog. Inorg. Chem.* **1968**, *9*, 161.
[41] Christe, K. O.; Wilson, W. W. *J. Fluorine Chem.* **1990**, *46*, 339.
[42] Usón, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126.
[43] Werner, H.; Bosch, M.; Schneider, M. E.; Hahn, C.; Kukla, F.; Manger, M.; Windmüller, B.; Weberndörfer, B.; Laubender, M. *J. Chem. Soc., Dalton Trans.* **1998**, 3549.

(br m, 4 H, CH$_2$), 1.90 (br m, 4 H, CH$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, D$_8$-THF): δ 76.2 (br m, CH), 32.7 (s, CH$_2$). ^{19}F NMR (188.3 MHz, CD$_2$Cl$_2$, −40 °C): δ −149.8 (br s). ^{19}F NMR CP MAS: δ −144.1. IR (Nujol, cm^{-1}): 1954 (m, br) (FHF). Anal. Calcd for $C_{24}H_{39}F_2O_2Rh_3$: C, 40.81; H, 5.57; F, 5.38. Found: C, 41.20; H, 5.77; F, 5.66.

[Rh(μ-F)(COE)$_2$]$_2$ (2). A solution of [Rh(μ-OH)(COE)$_2$]$_2$ (113 mg, 0.17 mmol) in THF (7 mL) was treated with NEt$_3$·3HF (18 μL, 0.11 mmol) at room temperature. The mixture was stirred for 1 h and then filtered to give a yellow solution that was concentrated to dryness and kept in vacuo for 2 h. The resulting yellow solid was washed with *n*-hexane (3 mL) and dried in vacuo. Yield: 91 mg, 81%. Dec pt 142 °C. ^{1}H NMR (200.1 MHz, C$_6$D$_6$): δ 2.35 (br m, 8 H, CH), 1.96 (br m, 16 H, CH$_2$), 1.58−1.24 (br m, 32 H, CH$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, C$_6$D$_6$): δ 71.9 (m, CH), 29.6, 27.3, 26.8 (all s, CH$_2$). ^{19}F NMR (188.3 MHz, C$_6$D$_6$): δ −292.9 (t, $^{1}J_{\mathrm{RhF}}$ = 55.5 Hz). Anal. Calcd for $C_{32}H_{56}F_2Rh_2$: C, 56.14; H, 8.25. Found: C, 56.05; H, 8.16.

[RhF(COD)(PPh$_3$)] (3). Method A. A suspension of complex **1** (425 mg, 0.60 mmol) in THF (20 mL) was treated with PPh$_3$ (484 mg, 1.85 mmol) at room temperature. The mixture was stirred for 15 min, concentrated to ca. 4 mL in vacuo, and Et$_2$O (12 mL) was added. The yellow precipitate was filtered, washed with Et$_2$O (4 × 2 mL), and dried in vacuo. Yield: 538 mg, 61%. Mp 120−122 °C. ^{1}H NMR (299.9 MHz, C$_6$D$_6$): δ 7.98−7.93 (m, 6 H, Ph), 7.07−6.99 (m, 9 H, Ph), 5.77 (m, 2 H, CH, COD), 2.80 (m, 2 H, CH, COD), 2.22 (m, 4 H, CH$_2$), 1.63 (m, 4 H, CH$_2$). ^{13}C{^{1}H} NMR (75.4 MHz, C$_6$D$_6$): δ 135.0 (d, Ph, J_{PC} = 12.1 Hz), 132.5 (d, *C*−P, $^{1}J_{\mathrm{PC}}$ = 39.0 Hz), 130.2 (s, Ph), 128.5 (d, Ph, J_{PC} = 9.7 Hz), 105.9 (d, CH, COD, $^{1}J_{\mathrm{RhC}}$ = 8.9 Hz), 64.8 (d, CH, COD, $^{1}J_{\mathrm{RhC}}$ = 13.7 Hz), 33.8, 28.5 (both s, CH$_2$). ^{19}F NMR (188.3 MHz, CD$_2$Cl$_2$, 23 °C): δ −259.1 (br s); (−60 °C): δ −256.4 (dd, $^{1}J_{\mathrm{RhF}}$ = 72.3 Hz, $^{2}J_{\mathrm{PF}}$ = 12.3 Hz). ^{31}P{^{1}H} NMR (81.0 MHz, CD$_2$Cl$_2$, 23 °C): δ 24.7 (br d, $^{1}J_{\mathrm{RhP}}$ = 162.2 Hz); (−60 °C): δ 25.8 (dd, $^{1}J_{\mathrm{RhP}}$ = 158.9 Hz, $^{2}J_{\mathrm{PF}}$ = 17.0 Hz). Anal. Calcd for $C_{26}H_{27}FPRh$: C, 63.42; H, 5.53. Found: C, 63.71; H, 6.05.

Method B. A Schlenk tube equipped with a PTFE liner was charged with [Rh(μ-OH)(COD)]$_2$ (198 mg, 0.43 mmol) and THF (15 mL). The suspension was treated sequentially with PPh$_3$ (228 mg, 0.88 mmol) and a solution of HF in THF prepared from 73% hydrofluoric acid (0.9 mmol of HF). The resulting yellow solution was stirred at room temperature for 30 min and then concentrated in vacuo to ca. 1 mL. On addition of Et$_2$O (5 mL), a yellow solid precipitated, which was filtered, washed with Et$_2$O (4 × 5 mL), and dried in vacuo. Yield: 262 mg, 61%.

[RhF(COD){P(C$_6$H$_4$OMe-4)$_3$}] (4). A suspension of complex **1** (131 mg, 0.19 mmol) in THF (10 mL) was treated with P(C$_6$H$_4$-OMe-4)$_3$ (201 mg, 0.57 mmol) at room temperature. The mixture was stirred for 20 min, concentrated to ca. 2 mL, and treated with Et$_2$O (10 mL). A yellow powder formed, which was washed with Et$_2$O (4 × 4 mL) and dried in vacuo. Yield: 196 mg, 59%. Mp 120−123 °C. ^{1}H NMR (299.9 MHz, C$_6$D$_6$): δ 7.99 (virtual t, 6 H, C$_6$H$_4$, J = 9.0 Hz), 6.73 (virtual dd, 6 H, C$_6$H$_4$, J = 9.0 and 1.5 Hz), 5.82 (m, 2 H, CH, COD), 3.20 (s, 9 H, MeO), 2.92 (m, 2 H, CH, COD), 2.32 (m, 4 H, CH$_2$), 1.73 (m, 4 H, CH$_2$). ^{13}C{^{1}H} NMR (75.4 MHz, C$_6$D$_6$): δ 161.6 (*C*−OMe), 136.5 (d, CH, aryl, J_{PC} = 13.3 Hz), 124.1 (d, *C*−P, $^{1}J_{\mathrm{PC}}$ = 44.0 Hz), 114.3 (d, CH, aryl, J_{PC} = 10.4 Hz), 105.2 (d, CH, COD, $^{1}J_{\mathrm{RhC}}$ = 6.8 Hz), 64.4 (d, CH, COD, $^{1}J_{\mathrm{RhC}}$ = 14.5 Hz), 54.7 (s, MeO), 33.9, 28.6 (both s, CH$_2$). ^{19}F NMR (188.3 MHz, D$_8$-toluene, 25 °C): δ −253.8 (br s); (−60 °C): δ −252.1 (br d, $^{1}J_{\mathrm{RhF}}$ = 71.6 Hz); (−80 °C): δ −251.6 (br s). ^{31}P{^{1}H} NMR (81.0 MHz, D$_8$-toluene, 25 °C): δ 20.3 (br d, $^{1}J_{\mathrm{RhP}}$ = 158.5 Hz); (−60 °C): δ 20.5 (br d, $^{1}J_{\mathrm{RhP}}$ = 160.6 Hz); (−80 °C): δ 20.6 (br dd, $^{1}J_{\mathrm{RhP}}$ = 160.2 Hz, $^{2}J_{\mathrm{PF}}$ = 10.3 Hz). Anal. Calcd for $C_{29}H_{33}FO_3PRh$: C, 59.80; H, 5.71. Found: C, 59.58; H, 5.91.

Method B. A suspension of [Rh(μ-OH)(COD)]$_2$ (406 mg, 0.89 mmol) in THF (12 mL) was treated with a solution of HF in THF prepared from 73% hydrofluoric acid (1.9 mmol of HF) in a Schlenk tube equipped with a PTFE liner. The yellow solution was stirred at room temperature for 2 h and then treated with P(C$_6$H$_4$OMe-4)$_3$ (628 mg, 1.78 mmol). The solution was stirred at room temperature for 15 min and evaporated in vacuo to dryness, and then the yellow oily residue was stirred with Et$_2$O (5 mL) until a yellow powder precipitated. The ethereal solution was removed by means of a pipet, and the precipitate was washed with Et$_2$O (4 × 5 mL) and dried in vacuo. Yield: 922 mg, 89%.

[RhF(COD)(P^{i}Pr$_3$)] (5). Method A. A suspension of complex **1** (138 mg, 0.20 mmol) in THF (7 mL) was treated with P^{i}Pr$_3$ (115 μL, 0.60 mmol) at room temperature. The resulting yellow solution was stirred for 15 min, and then the solvent was removed in vacuo. The yellow oily residue was stirred with *n*-hexane (ca. 3 mL) until a yellow powder formed. The resulting suspension was concentrated to ca. 1.5 mL and cooled at −18 °C to complete the precipitation of the solid, which was then washed with cold *n*-hexane (−40 °C, 2 × 1.5 mL) and dried in vacuo. Yield: 152 mg, 65%. Mp 92−96 °C. ^{1}H NMR (299.9 MHz, C$_6$D$_6$): δ 5.44 (m, 2 H, CH, COD), 3.17 (m, 2 H, CH, COD), 2.32−2.10 (m, 4 H, CH$_2$), 2.05−1.88 (d of sept, 3 H, PC*H*, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, $^{2}J_{\mathrm{PH}}$ = 9.3 Hz), 1.81−1.58 (m, 4 H, CH$_2$), 1.18 (dd, 18 H, Me, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, $^{3}J_{\mathrm{PH}}$ = 13.2 Hz). ^{13}C{^{1}H} NMR (50.3 MHz, D$_8$-toluene): δ 104.1 (dd, CH, COD, $^{1}J_{\mathrm{RhC}}$ and $^{1}J_{\mathrm{PC}}$ = 7.8 and 10.6 Hz), 63.0 (d, CH, COD, $^{1}J_{\mathrm{RhC}}$ = 14.4 Hz), 35.1, 29.6 (both s, CH$_2$), 23.8 (d, P*C*H, $^{1}J_{\mathrm{PC}}$ = 17.1 Hz), 20.9 (s, Me). ^{19}F NMR (282.2 MHz, C$_6$D$_6$): δ −255.2 (dd, $^{1}J_{\mathrm{RhF}}$ = 78.7 Hz, $^{2}J_{\mathrm{PF}}$ = 14.7 Hz). ^{31}P{^{1}H} (121.4 MHz, C$_6$D$_6$): δ 39.1 (dd, $^{1}J_{\mathrm{RhP}}$ = 154.3 Hz, $^{2}J_{\mathrm{PF}}$ = 16.0 Hz). Anal. Calcd for $C_{17}H_{33}FPRh$: C, 52.31; H, 8.52. Found: C, 51.91; H, 8.69.

Method B. A suspension of [Rh(μ-OH)(COD)]$_2$ (241 mg, 0.53 mmol) in THF (15 mL) was treated with a solution of HF in THF prepared from 73% hydrofluoric acid (1.1 mmol of HF) in a Schlenk tube equipped with a PTFE liner. The yellow solution was stirred at room temperature for 1 h and then treated with P^{i}Pr$_3$ (225 μL, 1.18 mmol). The solution was stirred at room temperature for 15 min and then treated with KF (excess) to remove traces of unreacted HF. The suspension was filtered and evaporated to dryness in vacuo, and then the yellow oily residue was stirred with *n*-hexane (3 mL) at 0 °C until a yellow powder formed. The *n*-hexane solution was removed by means of a pipet, and the precipitate was washed with *n*-hexane (2 × 2 mL) and dried in vacuo. Yield: 205 mg, 50%.

[RhF(COD)(PCy$_3$)] (6). A suspension of complex **1** (145 mg, 0.21 mmol) in THF (10 mL) was treated with PCy$_3$ (177 mg, 0.63 mmol) at room temperature. The mixture was stirred for 30 min and evaporated to dryness in vacuo, and then the yellow oily residue was stirred with *n*-hexane (4 mL) at 0 °C until a yellow powder formed, which was washed with *n*-hexane (2 × 4 mL) at 0 °C and dried in vacuo. Small amounts of water, which could not be completely removed by an oil pump vacuum at 60 °C, were present in all obtained samples. Yield: 195 mg, 60%. Mp 142−144 °C. ^{1}H NMR (200.1 MHz, C$_6$D$_6$): δ 5.45 (m, 2 H, CH, COD), 3.28 (m, 2 H, CH, COD), 2.34−1.18 (several m, 41 H, CH$_2$, COD and Cy protons). ^{13}C{^{1}H} NMR (50.3 MHz, C$_6$D$_6$): δ 102.8 (m, CH, COD), 62.2 (d, CH, COD, $^{1}J_{\mathrm{RhC}}$ = 14.7 Hz), 34.1 (d, CH$_2$, COD, $^{2}J_{\mathrm{RhC}}$ = 2.2 Hz), 32.7 (d, C−P, $^{1}J_{\mathrm{PC}}$ = 16.9 Hz), 30.6, 28.1, 27.9, 26.9 (all s, CH$_2$, COD and Cy). ^{19}F NMR (188.3 MHz, C$_6$D$_6$): δ −255.7 (dd, $^{1}J_{\mathrm{RhF}}$ = 77.2 Hz, $^{2}J_{\mathrm{PF}}$ = 18.9 Hz). ^{31}P{^{1}H} NMR (81.0 MHz, C$_6$D$_6$): δ 27.9 (dd, $^{1}J_{\mathrm{RhP}}$ = 152.7 Hz, $^{2}J_{\mathrm{PF}}$ = 18.9 Hz). The

C and H analyses of different samples were in agreement with the amount of water determined by integration of the ^{1}H NMR spectra. Anal. Calcd for $[RhF(COD)(PCy_3)]\cdot 0.4H_2O$, $C_{26}H_{45.8}FO_{0.4}PRh$: C, 60.32; H, 8.92. Found: C, 60.61; H, 9.30.

NMR Data of 7. ^{19}F NMR (282.2 MHz, C_6D_6): δ −280.2 (ddt, $^{1}J_{RhF}$ = 56.7 Hz, $^{2}J_{PFtrans}$ = 176.9 Hz, $^{2}J_{PFcis}$ = 28.8 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 44.9 (ddt, P trans to F, $^{1}J_{RhP}$ = 179.7 Hz, $^{2}J_{PP}$ = 41.6 Hz), 24.8 (ddd, P trans to P, $^{1}J_{RhP}$ = 141.4 Hz).

NMR Data of 9. ^{19}F NMR (188.3 MHz, C_6D_6): δ −277.0 (ddt, $^{1}J_{RhF}$ = 74.6 Hz, $^{2}J_{PFtrans}$ = 174.4 Hz, $^{2}J_{PFcis}$ = 29.8 Hz). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6): δ 56.8 (ddt, P trans to F, $^{1}J_{RhP}$ = 173.1 Hz, $^{2}J_{PP}$ = 39.5 Hz), 32.1 (ddd, P cis to P, $^{1}J_{RhP}$ = 153.4).

[RhF(NBD)(P^{i}Pr$_3$)] (10). A suspension of $[Rh(\mu\text{-}OMe)(NBD)]_2$ (194 mg, 0.43 mmol) in THF (12 mL) was treated with $NEt_3\cdot 3HF$ (47 μL, 0.29 mmol) at room temperature. The yellow solution was stirred for 1 h and 40 min, and then P^{i}Pr$_3$ (164 μL, 0.86 mmol) was added. The mixture was stirred for 30 min, and the volatiles were removed in vacuo. The residue was stirred with Et_2O (3 mL) to give a yellow solid, which was washed with Et_2O (2 × 3 mL) and dried in vacuo, giving spectroscopically pure **10**. Yield: 210 mg, 65%. Dec pt 122−124 °C. ^{1}H NMR (200.1 MHz, C_6D_6): δ 5.19 (m, 2 H, CH═CH), 3.45 (m, 2 H, aliphatic CH, NBD), 3.05 (m, 2 H, CH═CH), 1.77 (m, 3 H, P−CH), 1.14 (dd, 18 H, Me, $^{3}J_{PH}$ = 13.4 Hz, $^{3}J_{HH}$ = 7.0 Hz), the signals of the CH_2 protons are overlapped with the Me signal. ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6): δ 84.2 (dd, CH═CH, J_{RhC} and J_{PC} = 10.6 and 5.8 Hz), 62.8 (dd, CH_2, NBD, J_{RhC} and J_{PC} = 5.1 and 1.5 Hz), 51.1 (dd, aliphatic CH, NBD, J_{RhC} and J_{PC} = 2.6 and 1.5 Hz), 42.8 (d, CH═CH, $^{1}J_{RhC}$ = 12.1 Hz), 23.0 (dd, C−P, $^{1}J_{PC}$ = 17.9 Hz, $^{2}J_{RhC}$ = 1.1 Hz), 19.8 (d, Me, $^{2}J_{PC}$ = 1.1 Hz). ^{19}F NMR (188.3 MHz, C_6D_6, 22 °C): δ −230.2 (br s); (D_8-toluene, −80 °C): δ −224.7 (br d, $^{1}J_{RhF}$ = 69.7 Hz). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 22 °C): δ 42.4 (d, $^{1}J_{RhP}$ = 177.0 Hz); (D_8-toluene, −80 °C): δ 42.2 (dd, $^{1}J_{RhP}$ = 177.8 Hz, $^{2}J_{PF}$ = 9.4 Hz). Anal. Calcd for $C_{16}H_{29}FPRh$: C, 51.34; H, 7.81. Found: C, 50.79; H, 7.54. Combustion analysis were performed on a spectroscopically pure, crystalline (recrystallized from $CH_2Cl_2/Et_2O/n$-hexane) sample. In our opinion, the difference in %C (0.55; 1% relative error) is due to a combustion problem and not to the impurity of the sample.

[Rh(FHF)(COD)(PPh$_3$)] (11). A solution of complex **3** (177 mg, 0.36 mmol) in THF (12 mL) was treated with $NEt_3\cdot 3HF$ (25 μL, 0,15 mmol) at room temperature. The mixture was stirred for 1 h, and the volatiles were removed in vacuo for 2 h. The yellow residue was dissolved in THF (3 mL) in a Schlenk tube, and a layer of *n*-hexane (13 mL) was added slowly to minimize the mixing with the THF solution. The tube was not moved until the diffusion of both solvents was complete. Yellow crystals grew that were washed with *n*-pentane (3 × 3 mL) and dried in vacuo. Yield: 123 mg, 67%. Dec pt 138−141 °C. ^{1}H NMR (200.1 MHz, C_6D_6, 24 °C): δ 11.7 (very br s, 1 H, FHF), 7.84−7.74 (m, 6 H, Ph), 7.02 (m, 9 H, Ph), 5.76 (m, 2 H, CH, COD), 2.83 (m, 2 H, CH, COD), 2.20 (m, 4 H, CH_2), 1.59−1.39 (m, 4 H, CH_2); (CD_2Cl_2, −80 °C): δ 12.24 (dd, 1 H, FHF, $^{1}J_{FH}$ = 375.3 and 41.0 Hz). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 24 °C): δ 134.7 (d, Ph, J_{PC} = 11.8 Hz), 131.4 (d, *C*−P, $^{1}J_{PC}$ = 39.0 Hz), 130.8 (d, Ph, J_{PC} = 2.2 Hz), 128.7 (d, Ph, J_{PC} = 10.0 Hz), 106.6 (dd, CH, COD, $^{1}J_{RhC}$ and $^{2}J_{RhP}$ = 9.6 and 7.5 Hz), 65.6 (d, CH, COD, $^{1}J_{RhC}$ = 15.0 Hz), 33.4, 28.2 (both s, CH_2). ^{19}F NMR (188.3 MHz, C_6D_6, 77 °C): δ −225 (br s); (CD_2Cl_2, 25 °C): δ −190 (very br s, Rh−FH*F*), −260 (very br s, Rh−*F*HF); (CD_2Cl_2, −80 °C): δ −177.3 (dd, Rh−FH*F*, $^{1}J_{FH}$ = 372.8 Hz, $^{1}J_{FF}$ = 124.3 Hz), −258.3 (m, Rh−*F*HF). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 25 °C): δ 26.1 (d, $^{1}J_{RhP}$ = 154.9 Hz); (−80 °C): δ 27.0 (dd, $^{1}J_{RhP}$ = 154.1 Hz, $^{2}J_{PF}$ = 17.2 Hz). IR (Nujol, cm^{-1}): 2630, 1842 (both s) (FHF). Anal. Calcd for $C_{26}H_{28}F_2PRh$: C, 60.95; H, 5.51. Found: C, 60.91; H, 5.81.

[Rh(FHF)(COD)(P^{i}Pr$_3$)] (12). A solution of complex **5** (180 mg, 0.46 mmol) in THF (10 mL) was treated with $NEt_3\cdot 3HF$ (26 μL, 0.16 mmol) at room temperature. The mixture was stirred for 50 min, and the volatiles were removed in vacuo. The residue was extracted with Et_2O (15 mL), the extract was filtered, and the solvent was evaporated to dryness in vacuo. The residue was washed with *n*-pentane (3 × 2 mL) at 0 °C and dried in vacuo to give **12** as a yellow solid. Yield: 174 mg, 92%. Mp 87−92 °C. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 21 °C): δ 11.7 (v br s, 1 H, FHF), 5.02 (m, 2 H, CH, COD), 3.42 (m, 2 H, CH, COD), 2.47−2.24 (m, 4 H, CH_2), 2.13−1.79 (m, 7 H, P−CH and CH_2), 1.29 (dd, 18 H, Me, $^{3}J_{PH}$ = 13.4 Hz, $^{3}J_{HH}$ = 7.2 Hz); (−80 °C): δ 12.5 (br dd, 1 H, FHF, $^{1}J_{FH}$ = 366.2 and 32.0 Hz). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 24 °C): δ 104.3 (dd, CH, COD, $^{1}J_{RhC}$ and $^{2}J_{PC}$ = 10.9 and 3.5 Hz), 62.9 (dd, CH, COD, $^{1}J_{RhC}$ and $^{2}J_{PC}$ = 15.3 and 1.6 Hz), 33.6 (d, CH_2, $^{2}J_{RhC}$ = 2.6 Hz), 27.7 (d, CH_2, $^{2}J_{RhC}$ = 1.6 Hz), 22.6 (d, P−C, $^{1}J_{PC}$ = 17.1 Hz), 19.7 (s, Me). ^{19}F NMR (188.3 MHz, CD_2Cl_2, 21 °C): δ −180.7 (br s, Rh−FH*F*), −259.6 (br s, Rh-*F*HF); (−80 °C): δ −176.3 (dd, Rh−FH*F*, $^{1}J_{FH}$ = 363.8 Hz, $^{2}J_{FF}$ = 133.9 Hz), −256.7 (m, Rh-*F*HF). ^{31}P{^{1}H} NMR (81 MHz, CD_2Cl_2, 21 °C): δ 39.1 (d, $^{1}J_{RhP}$ = 147.7 Hz); (−80 °C): δ 38.3 (dd, $^{1}J_{RhP}$ = 146.6 Hz, $^{2}J_{PF}$ = 12.7 Hz). IR (Nujol, cm^{-1}): 2580, 1866 (both s) (FHF). Anal. Calcd for $C_{17}H_{34}F_2PRh$: C, 49.76; H, 8.53. Found: C, 49.59; H, 8.74.

[Rh(FHF)(COD)(PCy$_3$)] (13). A solution of complex **6** (147 mg, 0.29 mmol) in THF (7 mL) was treated with $NEt_3\cdot 3HF$ (16 μL, 0.098 mmol) at room temperature. The mixture was stirred for 1 h, and then the volatiles were removed in vacuo at 40 °C for 2 h. The residue was extracted with Et_2O (15 mL). The extract was filtered, concentrated up to ca. 3 mL in vacuo, and stored at −20 °C for 24 h. A yellow solid crystallized, which was washed with cold (−20 °C) Et_2O (2 × 2 mL) and dried in vacuo. Yield: 120 mg, 78%. Dec pt 102−105 °C. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 24 °C): δ ca. 12 (very broad s, FHF), 4.99 (m, 2 H, CH, COD), 3.31 (m, 2 H, CH, COD), 2.37, 1.93−1.61, 1.26−1.15 (all m, 41 H, COD CH_2 and Cy). ^{1}H NMR (200.1 MHz, CD_2Cl_2, −80 °C): δ 12.50 (br dd, $^{1}J_{FH}$ = 364.2 and 32.0 Hz, FHF). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6): δ 104.0 (dd, COD CH, $^{1}J_{RhC}$ and $^{2}J_{PC}$ = 7.4 and 10.7 Hz), 63.1 (dd, COD CH, $^{1}J_{RhC}$ and $^{2}J_{PC}$ = 1.5 and 15.3 Hz), 33.7 (d, COD CH_2, $^{2}J_{RhC}$ = 2.4 Hz), 32.6 (d, C−P, $^{1}J_{PC}$ = 17.3 Hz), 30.5 (s, Cy), 28.0, 27.8, 26.8 (all s, COD CH_2 and Cy). ^{19}F NMR (188.3 MHz, CD_2Cl_2, 24 °C): δ −180.5 (br s, Rh−FH*F*), −261.2 (br s, Rh−*F*HF); (−80 °C): δ −176.2 (dd, $^{1}J_{FH}$ = 359.7, $^{2}J_{FF}$ = 137.5 Hz, Rh−FH*F*), −258.3 (m, Rh−*F*HF). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 24 °C): δ 28.0 (d, $^{1}J_{RhP}$ = 146.7 Hz); (−80 °C): δ 27.7 (dd, $^{1}J_{RhP}$ = 145.3 Hz, $^{2}J_{PF}$ = 12.9 Hz). IR (Nujol, cm^{-1}): 2634 and 1842 (FHF). Anal. Calcd for $C_{26}H_{46}F_2PRh$: C, 58.86; H, 8.74. Found: C, 58.13; H, 9.00. Small amounts of $NEt_3\cdot 3HF$ that could not be completely removed in vacuo are likely responsible for the difference in the C percentage.

Single-Crystal X-ray Structure Determinations of Complexes 3 and 11. The crystals were mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment) as summarized in Table 1. The structures were solved by the heavy-atom method and were refined anisotropically on F^2 (program SHELX-93, G. M. Sheldrick, University of Göttingen). For complex **3**, unit cell parameters were determined from a least-squares fit of 88 accurately centered reflections ($10.82 < 2\theta < 2\ 5.00$). Maximum $\Delta/\sigma = -0.003$, maximum $\Delta\rho = 0.372$ e Å^{-3}. Hydrogen atoms were included using a riding method. For complex **11**, unit cell parameters were determined from a least-

Table 1. Crystal Data and Details of Structure Refinements (from Powders or Single Crystals)

species	**1**	**3**	**11**
method	powder diffraction	single-crystal diffraction	single-crystal diffraction
formula	$C_{24}H_{39}F_2O_2Rh_3$	$C_{26}H_{27}FPRh$	$C_{26}H_{28}F_2PRh$
fw	706.29	492.36	512.36
T(K)	298(2)	173(2)	173(2)
λ(Å)	1.5418	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	12.7740(3)	12.7652(7)	13.8193(14)
b, Å	16.1518(4)	11.3795(7)	11.0201(14)
c, Å	12.2803(3)	14.6419(8)	15.018(2)
β, deg	95.601(2)	95.728(4)	101.083(5)
V(Å^3)	2521.6(1)	2116.3(2)	2244.5(5)
Z	4	4	4
ρ(calcd) (Mg m^{-3})	1.860	1.545	1.516
μ(mm^{-1})	16.0	0.901	0.859
F(000)	1408	1008	1048
sample size (mm^3)	20 × 10 × 1 (powders)	0.60 × 0.32 × 0.30	0.34 × 0.24 × 0.18
θ range (deg)	8 to 57.5	3.08 to 25.00	3.00 to 25.00
hkl collected	n.a.	$-15 \Leftarrow h \Leftarrow 15$	$-16 \Leftarrow h \Leftarrow 16$
		$-13 \Leftarrow k \Leftarrow 1$	$-13 \Leftarrow k \Leftarrow 1$
		$-17 \Leftarrow l \Leftarrow 0$	$0 \Leftarrow l \Leftarrow 17$
no. of reflns measd	n.a.	3891	4383
indep		3720 [R(int) = 0.0140]	3934 [R(int) = 0.0352]
abs. corr	none	ψ scans	ψ scans
max. and min. transmission	n.a.	0.79798 and 0.75555	0.79230 and 0.76985
refinement method	full-matrix least-squares on y_i	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data (restraints/params)	4851	3720/208/262	3931/78/241
$S(F^2)$	2.00 (χ^2 [c])	1.057	1.009
R1[a]	0.054 (R_{Bragg}[c])	0.0205	R1 = 0.0339, wR2 = 0.0708
wR2[b]	0.083 (R_p[c]) 0.105 (R_{wp}[c])	0.0498	R1 = 0.0553, wR2 = 0.0836
max $\Delta\rho$(e Å^{-3})	n.a.	0.372 and −0.331	0.477 and −0.394

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program. [c] For the XRPD analysis, $R_p = \sum_i|y_{i,o} - y_{i,c}|/\sum_i|y_{i,o}|$; $R_{wp} = [\sum_i w_i(y_{i,o} - y_{i,c})^2/\sum_i w_i(y_{i,o})^2]^{1/2}$; $R_{\mathrm{Bragg}} = \sum_n||F_{n,o}|^2 - |F_{n,c}|^2|/\sum_i|F_{n,o}|^2$; $\chi^2 = \sum_i w_i(y_{i,o} - y_{i,c})^2/(N_{\mathrm{obs}} - N_{\mathrm{par}})$, where $y_{i,o}$ and $y_{i,c}$ are the observed and calculated profile intensities, respectively, and $|F_{n,o}|$ and $|F_{n,c}|$ the observed and calculated structure factors. The summations run over i data points or n independent reflections. Statistical weights w_i are normally taken as $1/y_{i,o}$.

squares fit of 83 accurately centered reflections ($9.62 < 2\theta < 24.92$). Maximum $\Delta/\sigma = -0.001$, maximum $\Delta\rho = 0.477$ e Å^{-3}. The hydrogen atom in the bifluoride was not located, but the other hydrogen atoms were included using a riding method. Two phenyl rings are disordered over two sites (ca. 51:48).

Ab Initio X-ray Powder Diffraction Analysis of [Rh$_3$(μ_3-OH)$_2$(COD)$_3$](HF$_2$) (1). The gently ground yellow powder was cautiously deposited in the hollow of an aluminum holder equipped with a quartz zero-background plate (supplied by The Gem Dugout, State College, PA). Diffraction data (Cu Kα, $\lambda = 1.5418$ Å) were collected on a θ:θ vertical scan Bruker AXS D8 diffractometer equipped with parallel (Soller) slits, a secondary beam curved graphite monochromator, a Na(Tl)I scintillation detector, and pulse height amplifier discrimination. The generator was operated at 40 kV and 40 mA. The slits used had divergence 0.5°, antiscatter 0.5°, and receiving 0.2 mm. The nominal resolution for the present setup is 0.07° 2θ (fwhm) for the Si(111) peak at 28.44° (2θ). A long scan was performed with $5 < 2\theta < 105°$, $t = 24$ s step^{-1}, and $\Delta 2\theta = 0.02°$.

The indexing, using TREOR,[44] of the low-angle diffraction peaks suggested a primitive monoclinic cell of approximate dimensions $a = 12.783$, $b = 16.157$, and $c = 12.292$ Å and $\beta = 95.6°$ [M(20)[45] = 35; F(20)[46] = 117 (0.005, 32)]. Systematic absences indicated $P2_1/n$ as the probable space group, later confirmed by successful solution and refinement. The computation of the Patterson map clearly showed the oligomeric, trinuclear nature of the complex, thus allowing us to discard the original hypothesis of a polymeric species. The Rh$_3$(COD)$_3$ moiety was eventually obtained by the simulated annealing technique implemented in TOPAS[47] upon adopting two different starting models: free Rh(COD) fragments or independent Rh and COD fragments. No matter what starting model was chosen, we found the COD ligands to be radially distributed with the conformation described above. The remaining light atoms were detected by difference Fourier methods; obviously, XRPD cannot easily distinguish nearly isoelectronic atoms (such as O and F); however, simple considerations of their connectivity and charge-balancing requirements made their interpretation as triple-bridging hydroxyls and [HF$_2$]$^-$ anions held together by strong hydrogen bonds possible. The final structural model for **1** is also in agreement with a number of spectroscopic and analytical data, some of which were reinterpreted on the basis of these new findings.

The final refinement was performed by the Rietveld method with the aid of TOPAS. In the final cycles, the peak shapes were carefully described by the fundamental parameters approach.[48] The background level was modeled by a polynomial function, and systematic errors were corrected with the aid of a sample displacement angular shift and a preferred orientation correction along the [010] pole. Each of the three Rh(COD) fragments was eventually treated as an independent rigid body, whereas, to assist convergence to a chemically reasonable model, Rh−O and F···F distances were assigned soft restraints. A (single isotropic) displacement parameter

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(44) Werner, P. E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, *18*, 367.

(45) de Wolff, P. M. *J. Appl. Crystallogr.* **1968**, *1*, 108.

(46) Smith, G. S.; Snyder, R. L. *J. Appl. Crystallogr.* **1979**, *12*, 60.

(47) Bruker AXS 2003: *Topas V3.0: General Profile and Structure Analysis Software for Powder Diffraction Data*.

(48) Cheary, R. W.; Coelho, A. A. *J. Appl. Crystallogr.* **1992**, *25*, 109.

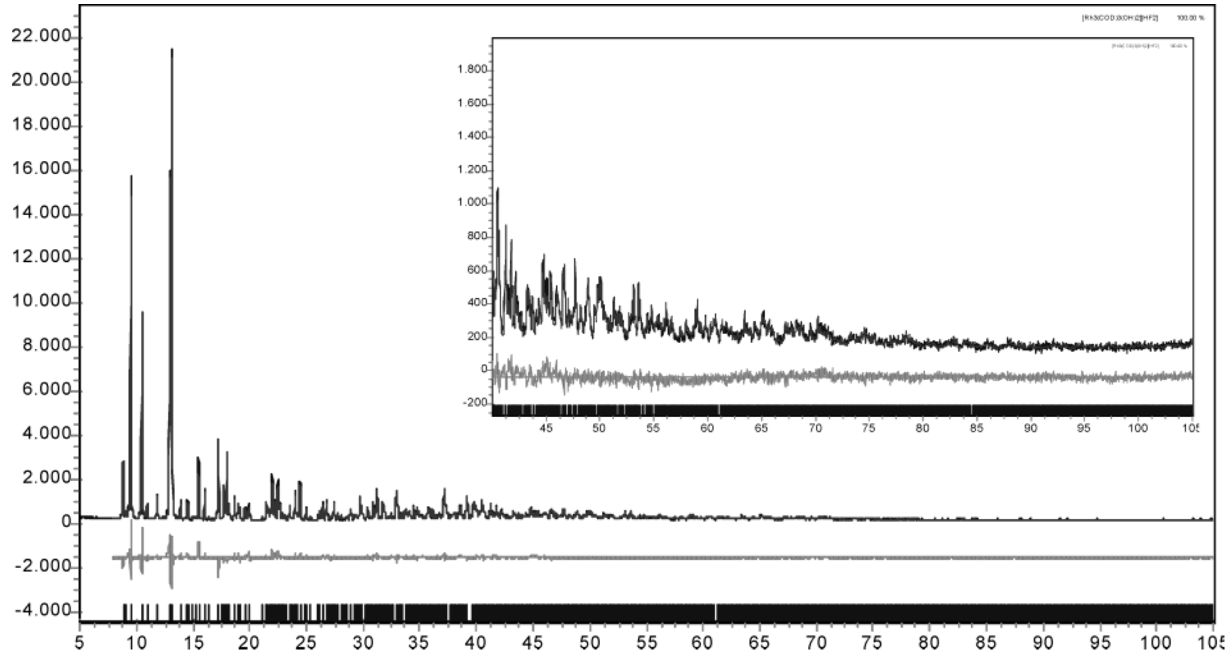

Figure 4. Rietveld refinement plot for species **1**. Horizontal scale, 2θ; vertical scale, counts. Difference plot and peak markers at the bottom. The inset shows the magnified (10×) high-angle region.

for Rh atoms was refined ($B_{Rh} = 2.7(1)$ Å^2); lighter atoms were given $B_{iso} = B_{Rh} + 2.0$ Å^2). Scattering factors were taken from the internal library of TOPAS. The final R_p, R_{wp}, and R_{Bragg} agreement factors, together with details of the data collections and analysis, can be found in Table 1. Figure 4 shows the final Rietveld refinement plot for **1**.

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Note Added in Proof: During the correction of the galley proof of this article, the work mentioned in reference 19 has appeared (Marshall, W. J.; Grushin, V. V. *Organometallics* **2004**, *23*, 3343). Details of the X-ray crystal structure determination of **1** and the synthesis of complex **5**, using the method we call B, are given.

Supporting Information Available: Crystallographic data for compounds **1**, **3**, and **11**, CIF files for **3** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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