Synthesis of the First Family of Rhodium(I) Perfluoroalkyl Complexes from Rhodium(I) Fluoro Complexes[1]

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The rhodium(I) fluoro complexes [RhF(COD)(PR_3)] (R = Ph (**1a**), C_6H_4OMe-4 (**1b**), *i*-Pr (**1d**), Cy (**1e**); COD = 1,5-cyclooctadiene) react with Me_3SiR_F to afford the rhodium(I) perfluoroalkyl complexes [Rh(R_F)(COD)(PR_3)] (R_F = CF_3, R = Ph (**2a**), C_6H_4OMe-4 (**2b**), *i*-Pr (**2d**), Cy (**2e**); R_F = *n*-C_3F_7, R = Ph (**2c**)), of which **2a**,**c** were isolated as pure solids. [Rh(CF_3)(NBD)(PPh_3)] (**3**) was prepared by reaction of **2a** with norbornadiene. The reactions of **2a**−**c** with 2,6-dimethylphenyl isocyanide (XyNC) or *t*-BuNC, in a 1:2 molar ratio, gave the compounds *trans*-[Rh(R_F)(CNR′)$_2$(PR_3)] (R_F = CF_3, R′ = Xy, R = Ph (**4a**), C_6H_4OMe-4 (**4b**); R_F = CF_3, R′ = *t*-Bu, R = Ph (**4a′**); R_F = *n*-C_3F_7, R′ = Xy, R = Ph (**4c**)). The reactions of **2a**−**c** with an equimolar amount of XyNC gave mixtures containing complexes **4a**−**c** as the major products. The peroxo complexes [Rh(CF_3)(η^2-O_2)(CNXy)$_2$(PR_3)], (R = Ph (**7a**), C_6H_4OMe-4 (**7b**)) were isolated by reacting O_2 with **4a**,**b**, respectively. The complexes [Rh(R_F)(CNR′)$_3$(PR_3)] (R_F = CF_3, R′ = Xy, R = Ph (**8a**), C_6H_4OMe-4 (**8b**); R_F = *n*-C_3F_7, R′ = Xy, R = Ph (**8c**)) were obtained by reaction of **2a**−**c** with 3 equiv of XyNC. Formation of [Rh(CF_3)(PPh_3)(CO)$_3$] (**9**) in the reaction of complex **2a** with CO was spectroscopically observed. The crystal structures of complexes **4a**, **7a**, and **8a** have been determined by single-crystal X-ray diffraction studies. The dynamic behavior in solution of the prepared complexes was studied by variable-temperature NMR.

Introduction

The selective functionalization of perfluoroorganic compounds is a major challenge in chemistry and, particularly, in organometallic and coordination chemistry.[2] Transition-metal perfluoroalkyl complexes are relevant in this context, due to the higher reactivity of the C−F bond in a position α to the metal with respect to perfluorocarbons.[3−7] Hence, the study of the reactivity of perfluoroalkyl complexes may play an important role in the development of new reactions which allow the substitution of fluorine by different functional groups in perfluorocarbons.[3,8]

The classical methods for the synthesis of perfluoroalkyl complexes are (a) oxidative addition of perfluoroalkyl iodides or bromides to low-valent metal complexes, (b) decarbonylation of perfluoroacyl complexes, and (c) transmetalation reactions.[6,9,10] Method a is not suitable for the synthesis of complexes in low oxidation states, and method b is quite specific and frequently requires heating at high temperatures.[9] A limitation of method c is the instability of the (perfluoroalkyl)lithium and -magnesium reagents,[11] especially for the trifluoromethyl derivatives, which has been solved by the use of toxic (trifluoromethyl)cadmium or -mercury compounds.[6,10]

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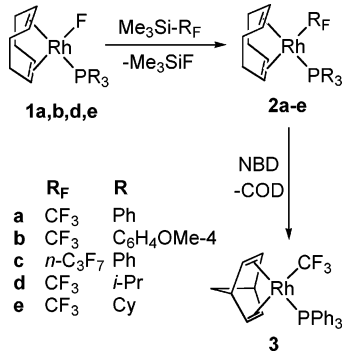
The reactions between fluoro complexes and silanes of general formula Me_3SiR allow the substitution of fluorine by a wide variety of R groups under very mild conditions.[12,13] In particular, Me_3SiCF_3 has been successfully used to transfer a CF_3 group to Ru[7] and Ti[14] centers by reaction with the corresponding fluoro complexes. We have preliminarily reported its use, for the first time, to prepare a Rh(I) trifluoromethyl complex.[15]

Despite the fact that numerous examples of Rh(III) perfluoroalkyl complexes have been reported,[4,9,16−19] the chemistry of Rh(I) perfluoroalkyls has been virtually unexplored. To the best of our knowledge, the only reported example is *trans*-$[Rh(CF_3)(CO)(PPh_3)_2]$, which was prepared by Roper and co-workers by reaction of $[RhH(CO)(PPh_3)_3]$ with $Hg(CF_3)_2$.[16] Related complexes are *trans*-$[Rh(CF_2CF_2H)L(PPh_3)_2]$ (L = CO,[20] PF_3[21]) which were obtained by reaction of $[RhH(CO)(PPh_3)_3]$ with tetrafluoroethylene. We have preliminarily reported that the reaction between [RhF(COD)(PPh_3)] and Me_3SiCF_3 afforded cleanly the trifluoromethyl complex $[Rh(CF_3)(COD)(PPh_3)]$.[15] Herein, we describe the synthesis of a series of Rh(I) perfluoroalkyl complexes by using the same method and their reactivity toward isocyanides and CO.

Results and Discussion

Synthesis. The complexes $[RhF(COD)(PR_3)]$,[1] where R = Ph (**1a**), C_6H_4OMe-4 (**1b**), *i*-Pr (**1d**), Cy (**1e**), react at room temperature with Me_3SiR_F to give the perfluoroalkyl derivatives $[Rh(R_F)(COD)(PR_3)]$ ($R_F = CF_3$, R = Ph (**2a**), C_6H_4OMe-4 (**2b**), *i*-Pr (**2d**), Cy (**2e**); R_F = *n*-C_3F_7, R = Ph (**2c**)) (Scheme 1). While the reactions leading to **2a**−**c** were complete after a few minutes, the reactions of the trialkylphosphine complexes **1d**,**e** with Me_3SiCF_3 were remarkably slower (the **2d**:**1d** and **2e**:**1e** ratios determined by ^{19}F NMR were 2 and 1.5, respectively, after 24 h), probably due to the steric hindrance of P(*i*-Pr)$_3$ and PCy_3. In addition, owing to the instability of **2d**,**e** in solution, decomposition products were formed from which **2d**,**e** could not be separated. Treatment of **2a** with excess of norbornadiene (NBD) gave $[Rh(CF_3)(NBD)(PPh_3)]$ (**3**).

Scheme 1



Complexes **2a**,**c** and **3** were isolated as orange solids in good yields and characterized by analytical and spectroscopical methods. In addition, compound **2a** was also characterized by a single-crystal X-ray diffraction study.[15] Complex **2b** could be characterized only by NMR spectroscopy in solution, because it was always isolated along with tris(4-methoxyphenyl)phosphine oxide. Nevertheless, in situ prepared solutions of **2b** as well as of **2a**,**c** were used successfully in further reactions (see below).

To synthesize a family of Rh(I) trifluoromethyl complexes and to study the reactivity of the Rh−C bond toward unsaturated organic molecules that could lead to new C−C bond formation reactions involving the R_F group, the reactions of **2a**−**c** with isocyanides and CO were studied.

The products of the reactions with 2,6-dimethylphenyl isocyanide (XyNC) were dependent on the isocyanide/Rh complex molar ratio used. Thus, when complexes **2a**−**c** were treated with an equimolar amount of XyNC (Scheme 2), the main reaction products were *trans*-$[Rh(R_F)(CNXy)_2(PR_3)]$ ($R_F = CF_3$, R = Ph (**4a**), C_6H_4OMe-4 (**4b**); R_F = *n*-C_3F_7, R = Ph (**4c**)), together with unreacted starting complexes. In addition, in the reaction with **2a**,**b**, complexes $[Rh(CF_3)(CNXy)(COD)]$ (**5**) and *trans*-$[Rh(CF_3)(CNXy)(PR_3)_2]$ (R = Ph (**6a**) and R = C_6H_4-OMe-4 (**6b**), respectively), were detected in minor amounts. Despite the fact that these mixtures could not be separated, the presence of **4a**−**c** could be unambiguously determined, because these complexes were isolated by reaction of **2a**−**c** with XyNC in a 1:2 molar ratio (see below). The structures of complexes **5** and **6a**,**b** were proposed on the basis of their NMR signals in the reaction mixture (see NMR and IR Spectroscopy). To obtain additional support for the assignation of the structures of compounds **6a**,**b**, the synthesis of **6a** was attempted by reaction of **2a** with equimolar amounts of XyNC and PPh_3. However the reaction gave a mixture which could not be separated.

The reactions of **2a**−**c** with XyNC or *t*-BuNC in a 1:2 molar ratio gave the compounds *trans*-$[Rh(R_F)(CNR')_2(PR_3)]$ ($R_F = CF_3$, R′ = Xy, R = Ph (**4a**), C_6H_4OMe-4 (**4b**); $R_F = CF_3$, R′ = *t*-Bu, R = Ph (**4a′**); R_F = *n*-C_3F_7, R′ = Xy, R = Ph (**4c**)), which were the result of the substitution of the COD ligand by two XyNC ligands (Scheme 2). Complexes **4a**,**a′**,**c** were isolated in good yields and spectroscopically and analytically character-

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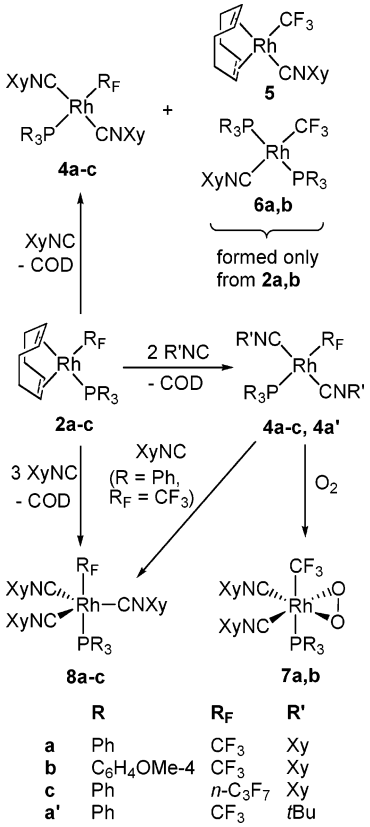
Scheme 2



	R	R_F	R'
a	Ph	CF_3	Xy
b	C_6H_4OMe-4	CF_3	Xy
c	Ph	n-C_3F_7	Xy
a'	Ph	CF_3	*t*Bu

ized. In addition, the structure of compound **4a** was established by a single-crystal X-ray diffraction study (Figure 1). Owing to the elevated oxygen sensitivity of complex **4b**, it could be characterized only by NMR spectroscopy. Thus, despite the the fact that the NMR spectra of the reaction mixture showed that the reaction of **2b** with XyNC to give **4b** is nearly quantitative, the isolated solid after concentrating and adding *n*-pentane always contained considerable amounts of tris(4-methoxyphenyl)phosphine oxide and the peroxo complex [Rh(CF$_3$)(η^2-O$_2$)(CNXy)$_2${P(C$_6$H$_4$OMe-4)$_3$}] (**7b**), both impurities arising from the reaction of **4b** with residual oxygen during its isolation. Complex **7b** and the analogous triphenylphosphine-containing complex **7a** were isolated by exposing THF solutions of **4b** and **4a**, respectively, to air and were characterized by spectroscopical and analytical means. A single-crystal X-ray diffraction analysis of complex **7a** (see Figure 2) revealed unambiguously the presence of the peroxo ligand. The formation of this complex seems to be irreversible,[22] because it did not appreciably lose O$_2$ in CDCl$_3$ solution under vacuum to regenerate compound **4a**.

When compounds **2a**−**c** were treated with XyNC using a 3:1 molar ratio of isocyanide to starting complex, complexes [Rh(R_F)(CNXy)$_3$(PR$_3$)] (R_F = CF$_3$, R = Ph (**8a**), C$_6$H$_4$OMe-4 (**8b**); R_F = n-C$_3$F$_7$, R = Ph (**8c**)) were obtained. Formation of **8a** was also observed by NMR when a C$_6$D$_6$ solution of complex **4a** was treated with 1 equiv of XyNC. Compounds **8a**−**c** were isolated in good yields and characterized by spectroscopical and analytical means and, in the case of **8a**, also by a single-crystal X-ray diffraction study (see Figure 3). No further reactions were observed on treatment of **8a** with 1 equiv of XyNC or when complex **2a** was treated with 4 equiv of XyNC.

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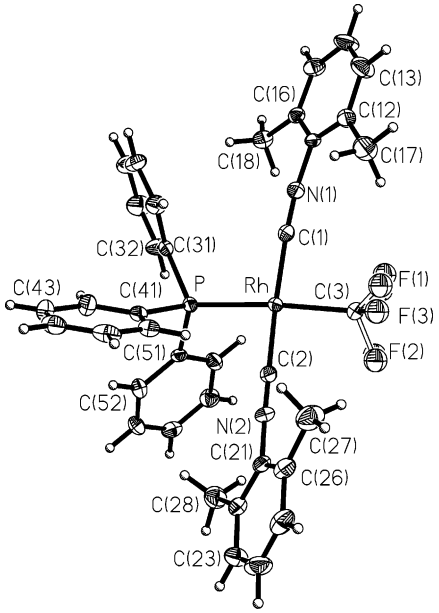


Figure 1. Molecular structure of **4a** (50% thermal ellipsoids). Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): Rh−C(1) = 1.939(4), Rh−C(2) = 1.946(4), Rh−C(3) = 2.076(3), Rh−P = 2.3023(8), N(1)−C(1) = 1.164(4), N(2)−C(2) = 1.152(4), C(3)−F(3) = 1.350(5), C(3)−F(2′) = 1.365(6), C(3)−F(3′) = 1.373(6), C(3)−F(2) = 1.391(6), C(3)−F(1) = 1.396(6), C(3)−F(1′) = 1.413(6); F(2′)−C(3)−F(3′) = 104.7(4), F(3)−C(3)−F(2) = 104.4(4), F(3)−C(3)−F(1) = 104.0(3), F(2)−C(3)−F(1) = 98.7(3), F(2′)−C(3)−F(1′) = 101.4(4), F(3′)−C(3)−F(1′) = 100.5(3), C(1)−Rh−C(2) = 168.55(14), C(1)−Rh−C(3) = 87.43(14), C(2)−Rh−C(3) = 88.42(14), C(1)−Rh−P = 95.25(10), C(2)−Rh−P = 90.37(10), C(3)−Rh−P = 171.59(10), N(1)−C(1)−Rh = 173.8(3), N(2)−C(2)−Rh = 173.9(3), F(3)−C(3)−Rh = 117.3(3), F(2′)−C(3)−Rh = 116.8(3), F(3′)−C(3)−Rh = 117.8(3), F(2)−C(3)−Rh = 113.2(3), F(1)−C(3)−Rh = 117.0(3), F(1′)−C(3)−Rh = 113.2(3).

In the reaction of complex **2a** with 3 equiv of *t*-BuNC, the room-temperature ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR spectra were consistent with the formation of [Rh(CF$_3$)(CN-*t*-Bu)$_3$(PPh$_3$)] (see Experimental Section). Unfortunately, the attempts to isolate this complex gave an oily impure material that could not be characterized, because its ^{19}F and ^{31}P{^{1}H} spectra showed broad signals even at low temperatures.

Clean formation of [Rh(CF$_3$)(PPh$_3$)(CO)$_3$] (**9**) and COD in the reaction of complex **2a** with CO in C$_6$D$_6$ was observed by ^{1}H, ^{19}F, and ^{31}P NMR and IR spectroscopy (Scheme 3). However, the attempts to isolate **9** led to mixtures of products that could not be separated nor identified. The presence of three equivalent CO ligands in **9** was confirmed by the ^{13}C, ^{19}F, and ^{31}P{^{1}H} NMR spectra of its ^{13}CO-containing analogue **9*** (see below).

Crystallographic Studies. The crystal structures of complexes **4a**, **7a**, and **8a** have been solved by single-crystal X-ray diffraction studies. The crystal structure of **2a** has been preliminarily reported.[15] These are the first crystal structure determinations carried out on Rh(I) perfluororalkyl complexes.

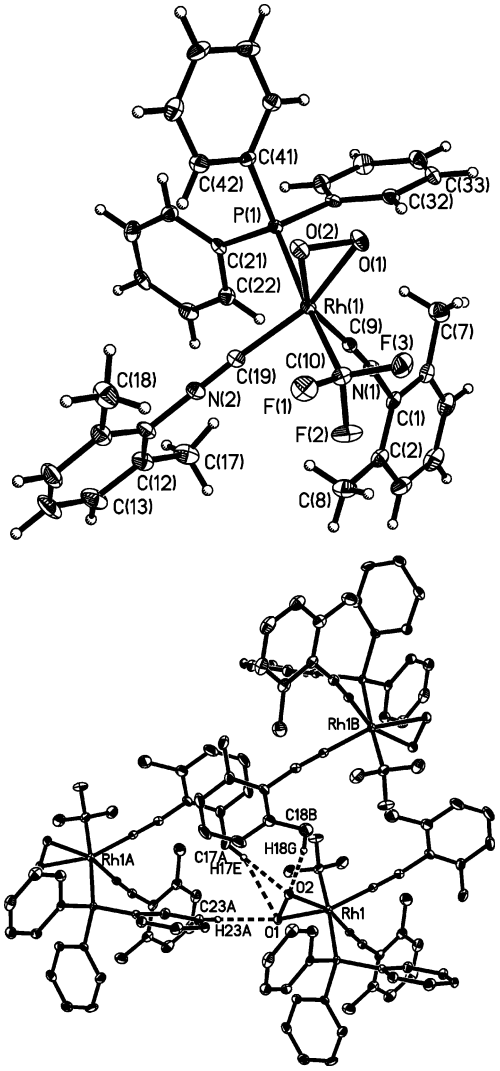


Figure 2. Molecular structure of **7a** (top) (50% thermal ellipsoids, hydrogen atoms are omitted) and packing diagram showing the O···H−C interactions (bottom). Selected bond lengths (Å) and angles (deg): Rh(1)−C(9) = 1.961(3), Rh(1)−C(19) = 1.968(3), Rh(1)−O(2) = 2.010(2), Rh(1)−O(1) = 2.015(2), Rh(1)−C(10) = 2.051(3), Rh(1)−P(1) = 2.3920(7), F(1)−C(10) = 1.368(3), F(2)−C(10) = 1.365(3), F(3)−C(10) = 1.357(3), N(1)−C(9) = 1.158(4), N(2)−C(19) = 1.152(4), O(1)−O(2) = 1.438(3), C(18)···O(2) = 3.354(4), C(17)···O(2) = 3.519(4), C(17)···O(1) = 3.649(4), C(23)···O(1) = 3.263(4); F(3)−C(10)−F(2) = 103.9(2), F(3)−C(10)−F(1) = 104.2(2), F(2)−C(10)−F(1) = 103.6(2), C(9)−Rh(1)−C(19) = 90.86(11), C(9)−Rh(1)−C(10) = 89.53(11), C(19)−Rh(1)−C(10) = 87.49(12), O(2)−Rh(1)−C(10) = 87.88(10), O(1)−Rh(1)−C(10) = 91.13(10), C(9)−Rh(1)−P(1) = 92.01(8), C(19)−Rh(1)−P(1) = 95.92(8), O(2)−Rh(1)−P(1) = 89.30(6), O(1)−Rh(1)−P(1) = 85.10(6), C(10)−Rh(1)−P(1) = 176.22(9), N(1)−C(9)−Rh(1) = 177.2(2), F(3)−C(10)−Rh(1) = 114.37(19), F(2)−C(10)−Rh(1) = 115.43(19), F(1)−C(10)−Rh(1) = 113.96(19), N(2)−C(19)−Rh(1) = 177.1(3).

The mean C−F bond lengths are similar in the four complexes (**2a**, 1.369(3) Å;[15] **4a**, 1.381(6) Å; **7a**, 1.363(3) Å; **8a**, 1.376(3) Å) and are slightly longer than the mean C−F bond distances reported in compounds containing trifluoromethyl groups bonded to nonmetallic atoms (1.322[23] and 1.33 Å[24]). In agreement with the VSEPR model,[24,25] the F−C−F and Rh−C−F angles in the four complexes are smaller (98.7−104.7°) and larger (113.2−117.8°), respectively, than the ideal tetrahedral angle, as has been observed for other perfluoroalkyl complexes.[17,26]

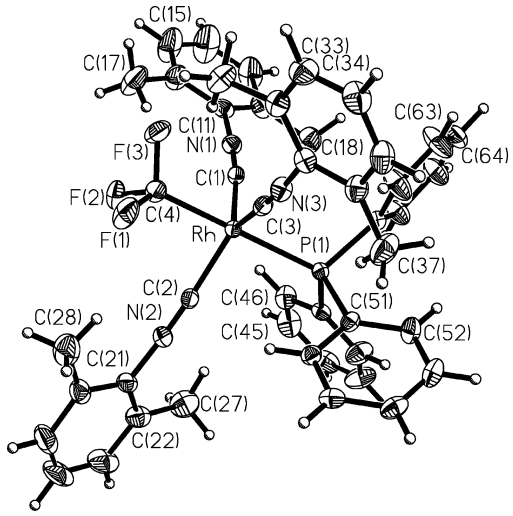
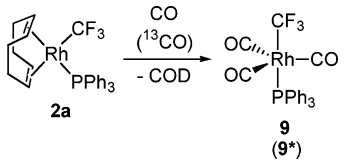


Figure 3. Molecular structure of **8a** (50% thermal ellipsoids). Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): P(1)−Rh = 2.3310(6), Rh−C(3) = 1.965(2), Rh−C(2) = 1.986(2), Rh−C(1) = 1.995(2), Rh−C(4) = 2.051(2), F(1)−C(4) = 1.378(3), F(2)−C(4) = 1.371(3), F(3)−C(4) = 1.379(3), C(1)−N(1) = 1.165(3), C(2)−N(2) = 1.166(3), C(3)−N(3) = 1.169(3); F(2)−C(4)−F(1) = 102.8(2), F(2)−C(4)−F(3) = 102.9(2), F(1)−C(4)−F(3) = 102.8(2), C(3)−Rh−C(2) = 127.48(9), C(3)−Rh−C(1) = 120.38(9), C(2)−Rh−C(1) = 111.55(9), C(3)−Rh−C(4) = 87.55(9), C(2)−Rh−C(4) = 87.85(9), C(1)−Rh−C(4) = 86.88(9), C(3)−Rh−P(1) = 90.22(7), C(2)−Rh−P(1) = 92.87(7), C(1)−Rh−P(1) = 94.96(6), C(4)−Rh−P(1) = 177.62(7), N(1)−C(1)−Rh = 173.0(2), N(2)−C(2)−Rh = 176.5(2), N(3)−C(3)−Rh = 177.8(2), F(2)−C(4)−Rh = 116.1(2), F(1)−C(4)−Rh = 114.9(2), F(3)−C(4)−Rh = 115.5(2).

Scheme 3



In complex **4a**, the metal is in a distorted-square-planar environment (Figure 1), with C(1)−Rh−C(2) (168.55(14)°) and C(3)−Rh−P (171.59(10)°) bond angles appreciably lower than 180°. The CF_3 group is disordered between two positions, with a 50% probability for each one. The Rh−CF_3 and Rh−P bond distances (2.076(3) and 2.3023(8) Å, respectively) are shorter than those found in **2a** (Rh−CF_3, 2.097(2) and 2.112(2) Å; Rh−P, 2.3245(5) and 2.3259(5) Å).[15]

Complex **7a** has a distorted-octahedral geometry (see Figure 2) in which the CF_3 and PPh_3 ligands are placed trans to each other. The O−O (1.438(3) Å) and Rh−O (2.010(2) and 2.015(2) Å) bond distances are typical values for a Rh(III) peroxo complex.[22,27−31] The Rh−

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Table 1. Selected NMR Data of the New Complexes[a]

compd	$\delta(^{19}F)$ (ppm)	$\delta(^{31}P)$ (ppm)	$^1J_{RhP}$ (Hz)	$^2J_{RhF}$ (Hz)	$^3J_{PF}$ (Hz)
[Rh(CF$_3$)(COD)(PPh$_3$)] (**2a**)	−17.3 dd	33.3 dq	177.9	19	21.4
[Rh(CF$_3$)(COD)(P{C$_6$H$_4$OMe-4}$_3$)] (**2b**)	−18.6 dd	28.7 dq	175.7	20	20.8
[Rh(C$_3$F$_7$)(COD)(PPh$_3$)] (**2c**)	−86.9 m (F1), −116.4 br s (F2), −79.3 t (F3)[b]	31.2 dtt	175.7		38.5[c]
[Rh(CF$_3$)(COD)(P*i*-Pr$_3$)] (**2d**)	−17.8 dd	26.7 dq	159.1	17.9	9.9
[Rh(CF$_3$)(COD)(PCy$_3$)] (**2e**)	−17.9 dd	37.9 dq	161.4	19.2	10.6
[Rh(CF$_3$)(NBD)(PPh$_3$)] (**3**)[d]	−22.4 dd	33.2 dq	186.3	22.0	13.4
trans-[Rh(CF$_3$)(CNXy)$_2$(PPh$_3$)] (**4a**)[d]	−5.7 dd	36.7 dq	102.3	26.0	46.2
trans-[Rh(CF$_3$)(CNXy)$_2$(P{C$_6$H$_4$OMe-4}$_3$)] (**4b**)[e]	−5.1 dd	31.7 dq	102.2	25.2	45.9
trans-[Rh(C$_3$F$_7$)(CNXy)$_2$(PPh$_3$)] (**4c**)	−82.3 br m (F1), −117.2 s (F2), −77.9 t (F3)[f]	34.1 dt	103.7		20.3
trans-[Rh(CF$_3$)(CN*t*-Bu)$_2$(PPh$_3$)] (**4a′**)	−8.7 dd	36.2 dq	146.1	27.4	45.5
[Rh(CF$_3$)(CNXy)$_2$(η^2-O$_2$)(PPh$_3$)] (**7a**)	−18.9 dd	19.5 dq	68.3	10.4	68.9
[Rh(CF$_3$)(CNXy)$_2$(η^2-O$_2$)(P{C$_6$H$_4$OMe-4}$_3$)] (**7b**)	−19.1 dd	15.8 dq	71.1	10.7	70.0
[Rh(CF$_3$)(CNXy)$_3$(PPh$_3$)] (**8a**)[g]	3.1 dd	42.5 dq	76.5	8.1	60.1
[Rh(CF$_3$)(CNXy)$_3$(P{C$_6$H$_4$OMe-4}$_3$)] (**8b**)[e]	4.6 dd	38.3 dq	76.1	7.5	61.4
[Rh(C$_3$F$_7$)(CNXy)$_3$(PPh$_3$)] (**8c**)[h]	−62.8 br m (F1), −112.6 s (F2), −76.9 s (F3)	44.8 dt	75.9		37.8
[Rh(CF$_3$)(^{13}CO)$_3$(PPh$_3$)] (**9***)[i]	8.2 ddq	31.7 dqq	68.9	8.0	60.9

[a] Legend: s = singlet, d = doublet, t = triplet, q = quadruplet. The values correspond to room temperature unless the temperature is given. [b] $^4J_{FF}$ = 11.1 Hz. [c] $^4J_{PF}$ = 4.6 Hz. [d] T = −20 °C. [e] T = −60 °C. [f] $^4J_{FF}$ = 11.3 Hz. [g] T = −80 °C. [h] T = −84 °C. [i] T = −70 °C.

CNXy (1.961(3) and 1.968(3) Å) bond distances are slightly longer than that found in [Rh(CN)(η^2-O$_2$)(CNXy)(PPh$_3$)$_2$][31] (1.935(4) Å), while the C≡NXy bond distances are close for both compounds (1.158(4) and 1.152(4) Å vs 1.159(5) Å). Short intermolecular C−H···O contacts were detected (i) between one oxygen atom and methylic hydrogens of two neighboring molecules and (ii) between the other oxygen atom and C−H groups of PPh$_3$ and a methyl group of an adjacent molecule. The C···O distances are in the range 3.263−3.649 Å. These contacts give rise to the formation of layers of reciprocally interacting molecules.[32] Hydrogen bonding between a peroxo ligand and a N−H, O−H, or C−H group in Rh(III) peroxo complexes has already been reported.[28,30,31] Whether the intermolecular contacts observed for **7a** originate from hydrogen bonding or they are imposed by the packing of molecules cannot be distinguished.

Complex **8a** has a trigonal-bipyramidal structure with the XyNC ligands placed in the equatorial plane (Figure 3). The XyNC ligands are bent toward the CF$_3$ ligand (the C−Rh−CF$_3$ angles are 87.55(9), 87.85(9), and 86.88(9)°), probably due to the steric repulsions with the phosphine phenyl groups. Concerning the conformation of the molecule, the CF$_3$ and PPh$_3$ groups are nearly eclipsed with each other and alternated with respect to the Rh(CNXy)$_3$ unit. The C(2)−Rh−C(1) and C(3)−Rh−C(2) (111.55(9) and 127.48(9)°, respectively) bond angles are notably deviated from 120°. The Rh−CNXy bond distances are longer for **8a** (1.995(2), 1.986(2), and 1.965(2) Å) than for **4a** (1.939(4) and 1.946(4) Å) and, as for the C≡N (1.165(3)−1.169(3) Å) bond distances, are similar to the values found in other Rh(I) complexes containing terminal isocyanide ligands.[33]

NMR and IR Spectroscopy. The ^{1}H NMR spectra of the diene complexes **2a**−**e** show two multiplets at 5.36−5.81 and 3.37−4.37 ppm corresponding to the olefinic protons in positions trans to the phosphine[34] and CF$_3$ ligands, respectively. The presence of only one methyl resonance in the ^{1}H NMR of complexes **4a**−**c**, **4a′**, **7a**,**b**, and **8a**−**c** is in agreement with the proposed geometries (Scheme 2) and with those observed in the crystal structures of **4a**, **7a**, and **8a**.

Especially useful for the characterization of the complexes in solution were the ^{19}F and ^{31}P{^{1}H} NMR spectra (Table 1). The ^{19}F NMR spectra of all trifluoromethyl complexes except **5** and **6a**,**b** gave doublets of doublets by coupling with ^{103}Rh and ^{31}P, and the ^{31}P{^{1}H} NMR spectra gave doublets of quadruplets by coupling with ^{103}Rh and the three ^{19}F atoms. In some cases, the couplings were not observed at room temperature due to ligand dissociation processes (see below), but when the temperature was lowered, the expected splitting patterns were observed in all cases. The ^{19}F NMR spectra of the *n*-heptafluoropropyl complexes **2c**, **4c**, and **8c** gave three signals which were assigned by means of a ^{19}F,^{19}F-COSY measurement for complex **8c** and by considering the usual order of magnitude of the

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F−F coupling constants in *n*-perfluoropropyl groups: $^3J_{FF} < {}^4J_{FF}$.[35] Thus, the triplets observed from −78.1 to −79.3 ppm were assigned to the CF_3 fluorines, which are coupled with the α-CF_2 groups ($^4J_{FF}$ = 11.1−11.3 Hz), the multiplets observed from −81.8 to −86.9 ppm were assigned to the α-CF_2 groups, and the broad singlets appearing from −112.6 to −117.2 ppm were assigned to the *β*-CF_2 groups. The room-temperature $^{31}P\{^1H\}$ NMR spectra gave a doublet of triplets of triplets for **2c**, due to coupling with ^{103}Rh and the α- and *β*-CF_2 fluorine nuclei, a doublet of triplets for **4c**, due to coupling with ^{103}Rh and the α-CF_2 groups, and a broad singlet for **8c**, which was transformed into a doublet of triplets at −84 °C.

The structures of complexes **5** and **6a**,**b** were proposed on the basis of the ^{19}F NMR spectra in the reaction mixtures. Compounds **6a**,**b** gave doublets of triplets,[36] which implies the presence of two equivalent phosphine ligands, and **5** gave a doublet,[37] which suggests the absence of the phosphine ligand. The value of $^2J_{RhF}$, which is similar to that found for **2a**,**b**, suggests the presence of the COD ligand in a position trans to the CF_3 group.

All complexes containing isocyanide ligands gave intense IR bands in the range 2028−2177 cm^{-1} corresponding to the *ν*(C≡N) vibrational mode. The carbonyl complex **9** gave the *ν*(CO) band at 2012 cm^{-1}. The O−O stretching bands of peroxo complexes **7a**,**b** appear at 882 and 881 cm^{-1}, respectively, which fall in the range reported for Rh(III) peroxo complexes (833−893 cm^{-1}).[22,27,28,38] In the IR spectra of all isolated complexes, several intense bands were observed in the region where the C−F stretching modes of transition-metal perfluoroalkyl complexes usually appear (900−1350 cm^{-1}).[19,39] However, the unambiguous assignment of these bands was complicated by the presence of absorptions in the same region belonging to other ligands. For the trifluoromethyl complex **2a**, several bands in the region 914−1059 cm^{-1}, which are typical of metal-bound CF_3 groups,[14,16,19,40] were assigned to *ν*(C−F) modes by comparison with the IR spectrum of the related fluoro complex **1a**. The lowering of the C−F stretching wavenumbers for transition-metal trifluoromethyl complexes with respect to the values found in CF_3X, where X = Cl, Br, I (1058−1104 and 1117−1217 cm^{-1} for the A_1 and E modes, respectively), has been taken as an indication of the weakening of the C−F bond.[6,41] The perfluoropropyl complex **2c** showed several bands in the same region as for **2a** which are assignable to the α-CF_2 *ν*(C−F) modes, along with bands at higher wavenumbers (1143−1325 cm^{-1}), which can be assigned to the CF_2CF_3 group.[42]

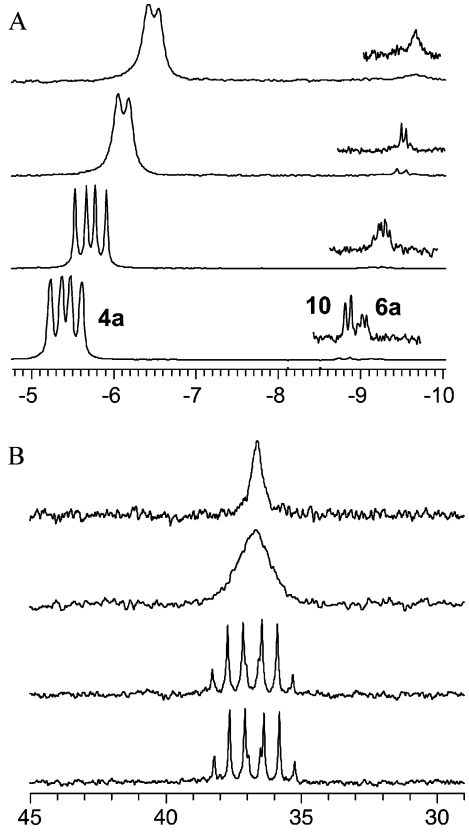

Figure 4. Variable-temperature ^{19}F NMR (A) and $^{31}P\{^1H\}$ NMR (B) spectra of **4a** in d_8-toluene measured at (from top to bottom) 82, 23, −20, and −60 °C.

Variable-Temperature NMR Studies. The ^{19}F and $^{31}P\{^1H\}$ NMR spectra of complexes **3**, **4a**,**b**, **8**, and **9** show at low temperatures the expected doublet of doublets and doublet of quadruplets, respectively. At room and higher temperatures, they show singlets or broad doublets, suggesting that dynamic processes involving phosphine dissociation take place. In addition, the ^{19}F NMR spectra of **4a** and **8b** show additional small peaks (Figures 4 and 5). For **4a** (−60 °C) they appear as a doublet at −8.8 ppm ($^2J_{RhF}$ = 26.0 Hz), which we assign to $[Rh(CF_3)(CNXy)_3]$ (**10**), and a poorly resolved multiplet at −9.2 ppm, assigned to complex **6a** on the basis of its chemical shift value (Scheme 4). Both signals collapse at higher temperatures into a broad singlet, indicating that the ligand exchange rates of the processes shown in Scheme 4 are fast enough to average these signals, which are close in frequency, but not fast enough to average also the signal of **4a**, which is far away in the spectrum. Complex **4b** shows a similar behavior. In contrast, complexes **4c** and **4a′** show sharp

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(36) NMR data of **6a** and **6b** (C_6D_6). **6a**: ^{19}F NMR *δ* −10.4 (dt, $^2J_{RhF}$ = 17.9 Hz, $^3J_{PF}$ = 22.0 Hz). **6b**: ^{19}F NMR *δ* −10.4 (dt, $^2J_{RhF}$ = 17.9 Hz, $^3J_{PF}$ = 22.0 Hz). The $^{31}P\{^1H\}$ NMR spectra could not be assigned due to overlapping with signals of other components of the mixture.

(37) NMR data of **5** (C_6D_6): ^{19}F NMR *δ* −17.6 (d, $^2J_{RhF}$ = 22.2 Hz).

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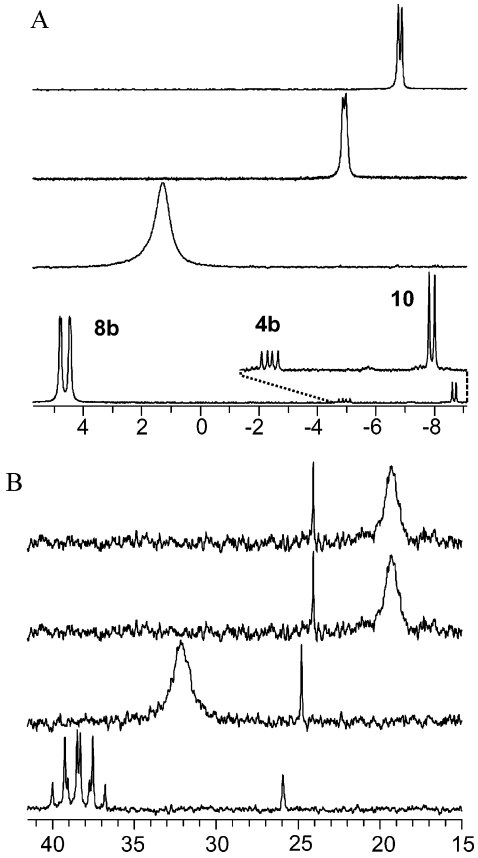
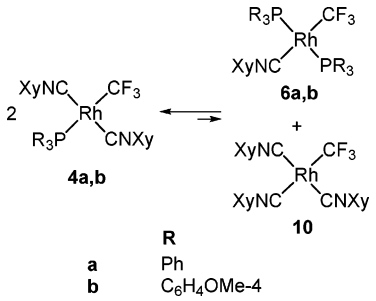


Figure 5. Variable-temperature ^{19}F NMR (A) and $^{31}P\{^1H\}$ NMR (B) spectra of **8b** in d_8-toluene measured at (from top to bottom) 77, 58, 23, and −60 °C. The peak around 25 ppm in the ^{31}P spectra corresponds to $OP(C_6H_4OMe\text{-}4)_3$.

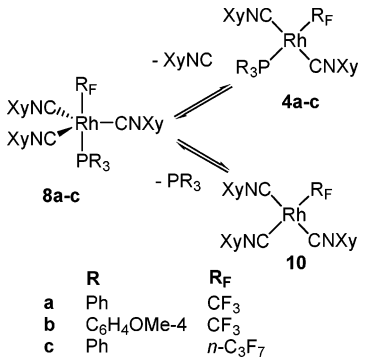
Scheme 4



signals with the expected coupling patterns at room temperature. We do not have an explanation for this difference.

For **8b**, the small signals appear (−60 °C) as a doublet at −8.7 ppm ($^2J_{RhF}$ = 24.5 Hz) that we assigned to **10**, as we did in the low-temperature ^{19}F NMR spectrum of **4a**, and a doublet of doublets at −4.9 ppm ($^3J_{PF}$ = 46.0 Hz, $^2J_{RhF}$ = 25.7 Hz), corresponding to **4b**, indicating that not only phosphine but also isocyanide dissociation takes place (Scheme 5). In addition, both ^{19}F and $^{31}P\{^1H\}$ signals of **8a** shift at higher temperatures toward the signal of **10** and that of the free phosphine (−9.5 ppm for $P(C_6H_4OMe\text{-}4)_3$ in C_6D_6), respectively, suggesting that the phosphine dissociation degree becomes higher when the temperature increases. A similar behavior is shown by **8a**. The heptafluoropropyl complex **8c** shows in its room-temperature ^{19}F NMR spectrum a broad multiplet for the α-fluorine nuclei, which is not resolved in the temperature range from +80 to −84 °C,

Scheme 5



and, in the $^{31}P\{^1H\}$ NMR spectrum, a broad singlet which is converted into the expected doublet of triplets at low temperature. A shift to higher field of the ^{31}P NMR signal from low to high temperature is also observed, suggesting the temperature dependence of the PPh_3 dissociation as in **8a**,**b**.

The ^{19}F and $^{31}P\{^1H\}$ NMR spectra of compound **9** show a broad doublet and a doublet of quadruplets, respectively, with $^1J_{RhP}$ = 69.3 Hz and $^3J_{PF}$ = 62.0 Hz, which is in agreement with the presence of the CF_3 and PPh_3 groups bonded to Rh, but did not allow us to determine the number of CO ligands or the structure of the complex. However, the coupling patterns of the ^{19}F and $^{31}P\{^1H\}$ NMR spectra of the ^{13}CO-containing analogue **9*** at −70 °C (a doublet of doublets of quadruplets and a doublet of quadruplets of quadruplets, respectively) and the values of coupling constants ($^3J_{PF}$ = 60.8 Hz, $^3J_{CF}$ = 10.3 Hz, $^2J_{RhF}$ = 8.0 Hz, $^1J_{RhP}$ = 68.9 Hz, $^2J_{PC}$ = 15.4 Hz), similar to those found in the pentacoordinate complexes **8a** and **8b**, were in full agreement with the presence of three equivalent ^{13}CO ligands in a trigonal-bipyramidal structure. Because the room-temperature ^{19}F and $^{31}P\{^1H\}$ NMR spectra of **9*** are similar to those of **9** (i.e., couplings of ^{13}CO with ^{103}Rh, ^{19}F, and ^{31}P are not observed), fast ^{13}CO dissociation on the NMR time scale takes place in solution, as does that of isocyanide in **8a**,**b**. However, since the $^{31}P-^{103}Rh$ and $^{31}P-^{19}F$ couplings in **9*** were observed at all temperatures, dissociation of the PPh_3 does not occur noticeably.

Conclusions

We report the synthesis of the perfluoroalkyl complexes $[Rh(R_F)(COD)(PR_3)]$ prepared by reacting the corresponding fluoro complexes with (perfluoroalkyl)trimethylsilanes. This work represents the first application of this synthetic method to the chemistry of Rh(I). We have also studied the reactivity of some of these perfluoroalkyl complexes toward norbornadiene, isocyanides, and carbon monoxide. Depending on the molar ratio of complex to isocyanide used, tetra- or pentacoordinated complexes containing diolefin, isocyanide, or/and triarylphosphine ligands, in addition of the R_F group, have been isolated or detected in solution. The reaction of $[Rh(CF_3)(COD)(PPh_3)]$ with CO gives the tricarbonyl complex $[Rh(CF_3)(PPh_3)(CO)_3]$. All of the above compounds form the first family of rhodium(I) perfluoroalkyl complexes reported so far. *trans*-$[Rh(CF_3)(CNXy)_2(PR_3)]$ are very reactive species, giving the rhodium(III) peroxo complexes $[Rh(CF_3)(\eta^2\text{-}O_2)(CNXy)_2$-

(PR_3)] when in contact with O_2. Fast phosphine, isocyanide, or CO ligand dissociation and exchange processes in solution have been observed by variable-temperature NMR in most of the reported complexes. We also describe the first crystal structure determinations carried out on Rh(I) perfluoroalkyl complexes. Current work in our laboratories is aimed at more studies on the reactivity of these and other rhodium perfluoroalkyl complexes. Given the growing number of transition-metal fluoro derivatives which are being described in the literature, and the lack of general synthetic methods for the synthesis of perfluoroalkyl derivatives of transition metals in low oxidation states, the reported synthetic approach is promising for the preparation of these complexes, including those with $R_F \neq CF_3$. These perfluoroalkyl derivatives are promising substrates for the development of new C−F activation and C−C bond formation reactions.

Experimental Section

General Considerations. The preparation of compounds **1a**,**b**,**d**,**e** was carried out as we described previously.[1] Other reagents were obtained from commercial sources and used without further purification: Me_3SiCF_3, norbornadiene, XyNC, and *t*-BuNC from Fluka and $Me_3SiC_3F_7$ and ^{13}CO (99% ^{13}C) from Aldrich.. All manipulations were carried out under an inert atmosphere of nitrogen by using standard Schlenk techniques. Tetrahydrofuran, toluene, and Et_2O were distilled over sodium−benzophenone, *n*-hexane was passed through a basic alumina column and deoxygenated, and *n*-pentane was distilled over CaH_2. All solvents were stored under nitrogen over 4 Å molecular sieves.

Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets. C, H, S analyses were carried out with Carlo Erba 1108 and Perkin-Elmer 2400 microanalyzers. NMR spectra were measured on Bruker Avance 200, 300, and 400 instruments. ^1H chemical shifts were referenced to residual C_6D_5H (7.15 ppm), $C_6D_5-CD_2H$ (2.09 ppm), $CHDCl_2$ (5.29 ppm), or $CHCl_3$ (7.26 ppm). $^{13}C\{^1H\}$ NMR spectra were referenced to C_6D_6 (128.0 ppm), $CDCl_3$ (77.1 ppm), or external $(CD_3)_2SO$ (40.4 ppm). ^{19}F NMR spectra were referenced to external $CFCl_3$ (0 ppm). $^{31}P\{^1H\}$ NMR spectra were referenced externally to H_3PO_4 (0 ppm). In cases where ^{19}F and $^{31}P\{^1H\}$ NMR spectra were measured in nondeuterated THF, a external CD_3COCD_3 capillary was used for locking and referencing. The temperature values in NMR experiments were not corrected. Melting points were determined on a Reichert apparatus under an air atmosphere.

[Rh(CF$_3$)(COD)(PPh$_3$)] (2a). A solution of **1a** (180 mg, 0.37 mmol) in THF (12 mL) was treated with Me_3SiCF_3 (0.20 mL of a 2.0 M solution in THF, 0.40 mmol) and stirred for 10 min at room temperature. The resulting orange solution was concentrated under reduced pressure to ca. 1 mL. On addition of *n*-hexane (5 mL), an orange solid precipitated. The solution was removed by means of a pipet, and the solid was washed with *n*-hexane (2 × 5 mL) and dried under vacuum. Yield: 152 mg, 76%. Mp: 124−128 °C dec. Anal. Calcd for $C_{27}H_{27}F_3PRh$: C, 59.79; H, 5.02. Found: C, 59.42; H, 5.00. IR (Nujol, cm^{-1}): ν(C−F) 1059 (vs), 948, 935, 928, 914 (s). IR (CH_2Cl_2, cm^{-1}): 1065, 963, 921. ^1H NMR (200.1 MHz, C_6D_6): δ 7.84−7.74 (m, 6 H, Ph), 7.06−7.02 (m, 9 H, Ph), 5.81 (m, 2 H, CH, COD), 3.87 (m, 2 H, CH, COD), 2.16−1.73 (several m, 8 H, CH_2). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 143.7 (qdd, CF_3, $^1J_{RhC}$ = 62.7 Hz, $^2J_{PC}$ = 8.7 Hz, $^1J_{FC}$ = 366.4 Hz), 134.9 (d, C2, Ph, $^2J_{PC}$ = 12.8 Hz), 134.1 (d, C1, Ph, $^1J_{PC}$ = 39.0 Hz), 130.1 (d, C4, Ph, $^4J_{PC}$ = 1.7 Hz), 128.3 (d, C3, Ph, $^3J_{PC}$ = 9.8 Hz), 97.4 (tq, CH, COD, $^1J_{RhC} = {}^2J_{PC}$ = 9 Hz, $^3J_{FC}$ = 2.3 Hz), 88.9 (dq, CH, COD, $^1J_{RhC}$ = 7.0 Hz, $^3J_{FC}$ = 1.7 Hz), 30.8 (d, CH_2, $^2J_{RhC}$ = 1.7 Hz), 30.8 (s, CH_2).^{19}F NMR (188.3 MHz, C_6D_6): δ −17.3 (t, $^2J_{RhF} = {}^3J_{PF}$ = 19 Hz). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ 33.3 (dq, $^1J_{RhP}$ = 177.9 Hz, $^3J_{PF}$ = 21.4 Hz).

The presence of Me_3SiF in the reaction mixture was confirmed by NMR-tube reactions (C_6D_6). ^1H NMR: δ 0.02 (d, $^3J_{FH}$ = 6.9 Hz). ^{19}F NMR: δ −157.6 (decaplet).[12,43]

[Rh(CF$_3$)(COD){P(C$_6$H$_4$OMe-4)$_3$}] (2b). A solution of **1b** (76 mg, 0.13 mmol) in THF (5 mL) was treated with Me_3SiCF_3 (0.13 mL of a 2.0 M solution in THF, 0.26 mmol) and stirred for 5 min at room temperature. Due to the oxygen and moisture sensitivity of **2b**, we were unable to isolate it in pure form. Nevertheless, solutions of **2b** obtained by this method were used successfully in subsequent reactions. ^1H NMR (200.1 MHz, C_6D_6): δ 7.54 (m, 6 H, H2, C_6H_4), 6.88 (m, 6 H, H3, C_6H_4), 5.36 (m, 2 H, CH, COD), 3.78 (s, 9 H, OMe), 3.76 (m, 2 H, CH, COD), 2.34, 2.18, 2.02 (3 m, 8 H, CH_2). $^{13}C\{^1H\}$ NMR (100.8 MHz, CD_2Cl_2): δ 161.4 (s, C4, C_6H_4), 136.2 (d, C2, C_6H_4, $^2J_{PC}$ = 13.6 Hz), 125.3 (d, C1, C_6H_4, $^1J_{PC}$ = 44.4 Hz), 113.9 (d, C3, C_6H_4, $^3J_{PC}$ = 11.1 Hz), 96.9 (t, CH, COD, $^1J_{RhC} = {}^2J_{PC}$ = 9.2 Hz), 89.0 (d, CH, COD, $^1J_{RhC}$ = 7.4 Hz), 55.7 (s, OMe), 31.0, 30.9 (2s, CH_2); the signal of the CF_3 carbon was not observed. ^{19}F NMR (188.3 MHz, C_6D_6): δ −18.6 (t, $^2J_{RhF} = {}^3J_{PF}$ = 20 Hz). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ 28.7 (dq, $^1J_{RhP}$ = 175.7 Hz, $^3J_{PF}$ = 20.8 Hz).

[Rh(C$_3$F$_7$)(COD)(PPh$_3$)] (2c). A solution of **1a** (149 mg, 0.30 mmol) in THF (5 mL) was treated with $Me_3SiC_3F_7$ (0.13 mL, 0.26 mmol) and stirred for 15 min at room temperature. The resulting orange solution was concentrated under reduced pressure to ca. 0.5 mL, and by addition of *n*-pentane (3 mL), an orange solid precipitated. The solution was removed by means of a pipet, and the solid was washed with *n*-pentane (3 × 1 mL) and dried under vacuum. Yield: 181 mg, 93.1%. Mp: 102 °C. Anal. Calcd for $C_{29}H_{27}F_7PRh$: C, 54.22; H, 4.24. Found: C, 53.97; H, 4.31. IR (CH_2Cl_2, cm^{-1}): ν(C−F) 1325, 1219, 1184 (vs), 1143, 1071, 1009, 943 (s). ^1H NMR (200.1 MHz, C_6D_6): δ 7.82−7.72 (m, 6 H, Ph), 7.05−7.02 (m, 9 H, Ph), 5.73 (m, 2 H, CH, COD), 3.82 (m, 2 H, CH, COD), 2.20−1.60 (several m, 8H, CH_2). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 134.9 (d, C2, Ph, $^2J_{PC}$ = 12.2 Hz), 134.0 (d, C1, Ph, $^1J_{PC}$ = 38.6 Hz), 130.0 (d, C4, Ph, $^4J_{PC}$ = 2.2 Hz), 128.2 (d, C3, Ph, $^3J_{PC}$ = 9.4 Hz), 95.8 (m, CH, COD), 88.4 (d, CH, COD, $^1J_{RhC}$ = 7.3 Hz), 30.9 (s, CH_2), 30.5 (d, CH_2, $^2J_{RhC}$ = 1.7 Hz); the signals of the C_3F_7 carbons were not observed. ^{19}F NMR (188.3 MHz, C_6D_6): δ −79.3 (t, 3 F, CF_3, $^4J_{FF}$ = 11.1 Hz), −86.9 (m, 2 F, α-F), −116.4 (br s, 2 F, *β*-F). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ 31.2 (dtt, $^1J_{RhP}$ = 175.7 Hz, $^3J_{PF}$ = 38.5 Hz, $^4J_{PF}$ = 4.6 Hz).

[Rh(CF$_3$)(NBD)(PPh$_3$)] (3). A solution of **1a** (134 mg, 0.27 mmol) in THF (3 mL) was treated with Me_3SiCF_3 (0.27 mL of a 2.0 M solution in THF, 0.54 mmol) and stirred for 5 min at room temperature. The volatiles were removed in vacuo, and Et_2O (10 mL) and norbornadiene were added (0.22 mL, 2.22 mmol) to give, after 1 h of stirring, a red solution containing a small amount of a fine solid in suspension. The suspension was concentrated under reduced pressure to ca. 0.5 mL, and addition of *n*-pentane (5 mL) gave a precipitate of an orange solid. The solution was removed by means of a pipet, and the solid was washed with *n*-pentane (4 × 5 mL) and dried under vacuum. Yield: 121 mg, 84.5%. Mp: 128 °C dec. Anal. Calcd for $C_{26}H_{23}F_3PRh$: 59.33; H, 4.40. Found: C, 58.98; H, 4.21. ^1H NMR (200.1 MHz, C_6D_6): δ 7.64 (m, 6 H, H2, PPh_3), 7.01 (s, 9 H, H3 and H4, PPh_3), 5.51 (m, 2 H, CH=CH, NBD), 3.72 (m, 2 H, CH, NBD), 3.37 (m, 2 H, CH=CH, NBD), 1.17, 1.00 (AB system, 2 H, CH_2, $^2J_{HH}$ = 7.8 Hz). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6): δ 134.6 (d, C2, PPh_3, $^2J_{PC}$ = 12.8 Hz), 133.7 (d, C1, PPh_3, $^1J_{PC}$ = 39.1 Hz), 130.3 (s, C4, PPh_3), 128.7 (d, C3, PPh_3, $^3J_{PC}$ = 11.0 Hz), 81.6, 77.8 (2 br s, C=C, NBD), 68.0 (s,

(43) Bassindale, A. R.; Baukov, Y. I.; Borbaruah, M.; Glynn, S. J.; Negrebetsky, V. V.; Parker, D. J.; Taylor, P. G.; Turtle, R. *J. Organomet. Chem.* **2003**, *669*, 154−163.

CH_2), 53.0 (s, CH, NBD); the signal of the CF_3 carbon was not observed. ^{19}F NMR (188.3 MHz, C_6D_6, 22 °C): δ −22.7 (br d, $^2J_{RhF}$ = 21.3 Hz). ^{19}F NMR (188.3 MHz, d_8-toluene, −20 °C): δ −22.4 (dd, $^2J_{RhF}$ = 22.0 Hz, $^3J_{PF}$ = 13.4 Hz). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 22 °C): δ 32.8 (br d, $^1J_{RhP}$ = 182.6 Hz). ^{31}P{^{1}H} NMR (81.0 MHz, d_8-toluene, −20 °C): δ 33.2 (dq, $^1J_{RhP}$ = 186.3 Hz, $^3J_{PF}$ = 13.1 Hz).

***trans*-[Rh(CF$_3$)(CNXy)$_2$(PPh$_3$)] (4a).** A solution of **2a**, obtained from **1a** (168 mg, 0.34 mmol), THF (7 mL), and Me_3SiCF_3 (0.30 mL of a 2.0 M solution in THF, 0.60 mmol), was treated with XyNC (89 mg, 0.68 mmol) at room temperature and stirred for 1 h. The resulting yellow-orange solution was concentrated under reduced pressure (ca. 0.5 mL), and Et_2O (5 mL) was added to give a yellow-orange precipitate. The solution was removed by means of a pipet, and the solid was washed with Et_2O (3 × 2 mL) and dried under vacuum. Yield: 156 mg, 65.6%. Mp: 116−118 °C dec. Anal. Calcd for $C_{37}H_{33}N_2F_3PRh$: C, 63.80; H, 4.78; N, 4.02. Found: C, 63.76; H, 4.51; N, 4.05. IR (cm^{-1}): ν(C≡N) 2087 (vs). ^{1}H NMR (400.9 MHz, CD_2Cl_2): δ 7.64 (m, 6 H, H2, Ph_3P), 7.28 (m, 9 H, H3 and H4, Ph_3P), 7.00 (AB_2 m, 6 H, Xy), 1.95 (s, 12 H, Me). ^{13}C{^{1}H} NMR (100.8 MHz, THF/d_6-DMSO (ext)): δ 162.5 (br d, C≡N, $^1J_{RhC}$ = 59.7 Hz), 136.4 (d, C1, Ph, $^1J_{PC}$ = 37.3 Hz), 135.3 (s, C2, Xy), 134.8 (d, C2, Ph, $^2J_{PC}$ = 13.1 Hz), 129.9 (s, C4, Ph), 128.4 (d, C3, Ph, $^3J_{PC}$ = 9.9 Hz), 128.0 (s, C4, Xy), 127.8 (s, C3, Xy), 17.1 (s, Me); the signals corresponding to the CF_3 and Xy C1 carbons were not observed. ^{19}F NMR (188.3 MHz, d_8-toluene): 23 °C, δ −6.1 (br d, $^2J_{RhF}$ = 24 Hz); −20 °C, δ −5.7 (dd, $^3J_{PF}$ = 45.9 Hz, $^2J_{RhF}$ = 26.0 Hz). ^{31}P{^{1}H} NMR (162.3 MHz, d_8-toluene): 23 °C, δ 36.6 (br s); −20 °C, δ 36.7 (dq, $^1J_{RhP}$ = 102.3 Hz, $^3J_{PF}$ = 46.2 Hz).

***trans*-[Rh(CF$_3$)(CN-*t*-Bu)$_2$(PPh$_3$)] (4a′).** A solution of **2a**, prepared from **1a** (161 mg, 0.33 mmol) and Me_3SiCF_3 (0.33 mL of a 2.0 M solution in THF, 0.66 mmol) in THF (5 mL), was treated with *t*-BuNC (74 μL, 0.68 mmol) at room temperature and stirred for 1 h. The resulting yellow-orange solution was concentrated under reduced pressure (ca. 0.5 mL), and an oil precipitated, which was converted into a yellow solid upon stirring for 30 min at 0 °C. The solution was removed by means of a pipet, and the solid was washed with *n*-pentane (2 × 5 mL) and dried under vacuum. Yield: 176 mg, 96.8%. Mp: 92 °C. Anal. Calcd for $C_{29}H_{33}N_2F_3PRh$: C, 58.01; H, 5.54; N, 4.67. Found: C, 57.74; H, 5.21; N, 4.56. IR (cm^{-1}): ν(C≡N) 2123 (vs). ^{1}H NMR (300.1 MHz, C_6D_6): δ 7.78 (m, 6 H, H2, Ph_3P), 7.03 (m, 9 H, H3 + H4, Ph_3P), 0.74 (s, 18 H, *t*-Bu). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 150.1 (d, C≡N, $^1J_{RhC}$ = 49.2 Hz), 138.2 (d, C1, PPh_3, $^1J_{PC}$ = 35.4 Hz), 135.4 (d, C2, PPh_3, $^2J_{PC}$ = 12.2 Hz), 130.0 (s, C4, PPh_3), 128.4 (d, C3, PPh_3, $^3J_{PC}$ = 5.0 Hz), 56.4 (s, *C*Me$_3$), 30.2 (s, Me). ^{19}F NMR (282.4 MHz, C_6D_6): δ −8.7 (dd, $^2J_{RhF}$ = 27.4 Hz, $^3J_{PF}$ = 39.5 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 36.2 (dq, $^1J_{RhP}$ = 146.1 Hz, $^3J_{PF}$ = 45.5 Hz).

***trans*-[Rh(CF$_3$)(CNXy)$_2${P(C$_6$H$_4$OMe-4)$_3$}] (4b).** A solution of **2b**, prepared from **1b** (190 mg, 0.33 mmol) and Me_3SiCF_3 (0.33 mL of a 2.0 M solution in THF, 0.66 mmol) in THF (4 mL), was treated with XyNC (85 mg, 0.65 mmol) at room temperature and stirred for 1 h. The orange solution was concentrated under reduced pressure (ca. 0.5 mL), and *n*-pentane (10 mL) was added. An oil precipitated, which was converted into a yellow-orange solid upon stirring for 1 h at 0 °C. The solution was removed by means of a pipet, and the solid was washed with *n*-pentane (3 × 5 mL) and dried under vacuum. The isolated solid was a mixture of **4b**, **7b**, and OP(C$_6$H$_4$OMe-4)$_3$, which could not be separated. The ratio between the two first species, determined by integration of the ^{19}F NMR spectrum, was aproximately 8:1. Data for **4b** are as follows. ^{1}H NMR (200.1 MHz, C_6D_6): δ 7.83 (m, 6 H, H2, C_6H_4), 6.60 (m, 12 H, H3, C_6H_4 + CH, Xy), 3.14 (s, 9 H, OMe), 2.04 (s, 12 H, Me, Xy). ^{13}C{^{1}H} NMR (100.8 MHz, THF/d_6-DMSO (ext)): δ 162.4 (br d, C≡N, $^1J_{RhC}$ ≈ 70 Hz, overlapped with an impurity peak), 161.1 (s, C4, C_6H_4), 135.6 (d, C2, C_6H_4, $^2J_{PC}$ = 14.2 Hz), 134.9 (s, C2, Xy), 127.9 (d, C1, C_6H_4, $^1J_{PC}$ = 41.3 Hz), 127.7 (s, C4, Xy), 127.5 (s, C3, Xy), 113.5 (d, C3, C_6H_4, $^3J_{PC}$ = 9.9 Hz), 54.6 (s, OMe), 17.7 (s, Me); the signals corresponding to the CF_3 and Xy group C1 carbons were not observed. ^{19}F NMR (188.3 MHz): C_6D_6, 22 °C, δ −5.6 (br s); d_8-toluene, −60 °C, δ −5.1 (dd, $^3J_{PF}$ = 45.9 Hz, $^2J_{RhF}$ = 25.2 Hz). ^{31}P{^{1}H} NMR (81.0 MHz): C_6D_6, 22 °C, δ 30.7 (br s); d_8-toluene, −60 °C, δ 31.7 (dq, $^1J_{RhP}$ = 102.2 Hz, $^3J_{PF}$ = 46.1 Hz).

***trans*-[Rh(C$_3$F$_7$)(CNXy)$_2$(PPh$_3$)] (4c).** A solution of **2c**, prepared from **1a** (152 mg, 0.31 mmol) and $Me_3SiC_3F_7$ (0.13 mL, 0.62 mmol) in THF (6 mL), was treated with XyNC (81 mg, 0.62 mmol) at room temperature and stirred for 1 h. The resulting yellow solution was concentrated under reduced pressure to 0.5 mL; addition of Et_2O (2 mL) gave a suspension containing a yellow solid. The solution was removed by means of a pipet, and the solid was washed with Et_2O (3 × 1 mL) and dried under vacuum. Yield: 137 mg, 55.7%. Mp: 97 °C dec. Anal. Calcd for $C_{39}H_{33}N_2F_7PRh$: C, 58.81; H, 4.18; N, 3.52. Found: C, 58.52; H, 3.96; N, 3.52. IR (cm^{-1}): ν(C≡N) 2097 (vs). ^{1}H NMR (300.1 MHz, C_6D_6): δ 7.82 (m, 6 H, H2, Ph_3P), 6.87 (m, 9 H, H3 + H4, Ph_3P), 6.57 (AB_2 m, 6 H, CH, Xy), 1.89 (s, 12 H, Me). ^{13}C{^{1}H} NMR (100.8 MHz, C_6D_6): δ 162.6 (br d, C≡N, $^1J_{RhC}$ = 65.6 Hz), 137.5 (d, C1, PPh_3, $^1J_{PC}$ = 37.6 Hz), 135.7 (s, C2, Xy), 135.3 (d, C2, PPh_3, $^2J_{PC}$ = 12.5 Hz), 130.3 (d, C4, PPh_3, $^4J_{PC}$ = 1.5 Hz), 128.9 (d, C3, PPh_3, $^3J_{PC}$ = 8.8 Hz), 128.2 (s, C3, Xy), 18.9 (s, Me). The signals of the C_3F_7 carbons and C1 and C4 of Xy were not observed. ^{19}F NMR (282.4 MHz, C_6D_6): δ −77.9 (t, 3 F, CF_3, $^4J_{FF}$ = 11.3 Hz), −82.3 (br m, 2 F, α-F), −117.2 (s, 2 F, *β*-F). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 34.1 (dt, $^1J_{RhP}$ = 103.7 Hz, $^3J_{PF}$ = 20.3 Hz).

***trans*-[Rh(CF$_3$)(η^2-O$_2$)(CNXy)$_2$(PPh$_3$)] (7a).** A solution of **2a**, prepared from **1a** (129 mg, 0.26 mmol) and Me_3SiCF_3 (0.26 mL of a 2.0 M solution in THF, 0.52 mmol) in THF (5 mL), was treated with XyNC (68 mg, 0.52 mmol) at room temperature and stirred for 1 h. The volatiles were removed in vacuo, the resulting residue was redissolved in THF (5 mL), and air was bubbled through the solution for 30 min. A colorless solid precipitated, which was filtered, washed with Et_2O (4 × 10 mL), and dried under vacuum. Yield: 104 mg, 54.5%. Mp: 110 °C. Anal. Calcd for $C_{37}H_{33}N_2O_2F_3PRh$: C, 60.95; H, 4.57; N, 3.62. Found: C, 61.00; H, 4.57; N, 3.85. IR (cm^{-1}): ν(C≡N) 2170 (s), 2145 (s), ν(O−O) 882 (s). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.54 (m, 6 H, H2, Ph_3P), 7.34 (m, 9 H, H3 + H4, Ph_3P), 7.14 (AB_2 m, 6 H, CH, Xy), 2.06 (s, 12 H, Me). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 150.3 (br d, C≡N, $^1J_{RhC}$ = 60.6 Hz), 136.0 (s, C2, Xy), 134.7 (d, C2, PPh_3, $^2J_{PC}$ = 11.0 Hz), 131.2 (d, C1, PPh_3, $^1J_{PC}$ = 43.1 Hz), 130.9 (s, C4, PPh_3), 129.6 (s, C4, Xy), 128.8 (d, C3, PPh_3, $^3J_{PC}$ = 9.4 Hz), 128.3 (s, C3, Xy), 127.4 (s, C1, Xy) 18.5 (s, Me); the signal of the CF_3 carbon was not observed. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −18.9 (dd, $^2J_{RhF}$ = 10.4 Hz, $^3J_{PF}$ = 68.9 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 19.5 (quintuplet, $^1J_{RhP}$ = $^3J_{PF}$ = 68.3 Hz).

***trans*-[Rh(CF$_3$)(η^2-O$_2$)(CNXy)$_2${P(C$_6$H$_4$OMe-4)$_3$}] (7b).** This compound was prepared as for **7a** from **1b** (109 mg, 0.19 mmol), Me_3SiCF_3 (0.20 mL of a 2.0 M solution in THF, 0.40 mmol) in THF (4 mL), and XyNC (49 mg, 0.38 mmol). Yield: 85 mg, 55.5%. Mp: 116 °C. Anal. Calcd for $C_{40}H_{39}N_2O_5F_3PRh$: C, 58.69; H, 4.80; N, 3.42. Found: C, 58.43; H, 4.77; N, 3.23. IR (cm^{-1}): ν(C≡N) 2177 (s), 2151 (vs), ν(O−O) 881 (m). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.45 (m, 6 H, H2, C_6H_4), 7.14 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, H4, Xy), 7.02 (d, 4 H, H3, Xy), 6.83 (m, 6 H, H3, C_6H_4), 3.76 (s, 9 H, OMe, Xy), 2.09 (s, 12 H, Me, Xy). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 161.7 (d, C4, C_6H_4, $^4J_{PC}$ = 2.2 Hz), 150.9 (br d, C≡N, $^1J_{RhC}$ = 54.4 Hz), 136.1 (d, CH, C_6H_4, J_{PC} = 12.5 Hz), 136.0 (s, C2, Xy), 129.5 (s, C4, Xy), 128.3 (s, C3, Xy), 127.5 (br s, C1, Xy), 122.9 (d, C1, C_6H_4, $^1J_{PC}$ = 43.5 Hz$_3$), 114.4 (d, J_{PC} = 11.1 Hz, CH, C_6H_4), 55.6 (s, OMe), 18.6 (s, Me). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −19.1 (dd, $^2J_{RhF}$ = 10.7 Hz, $^3J_{PF}$ = 70.0 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 15.8 (quintuplet, $^1J_{RhP}$ = $^3J_{PF}$ = 71.1 Hz).

Table 2. Crystal Data for Complexes 4a, 7a, and 8a

	4a	7a	8a
formula	$C_{37}H_{33}F_3N_2PRh$	$C_{38}H_{35}Cl_2F_3N_2O_2PRh$	$C_{46}H_{42}F_3N_3PRh$
M_r	696.53	813.46	827.71
cryst size (mm)	0.46 × 0.37 × 0.18	0.19 × 0.16 × 0.10	0.60 × 0.52 × 0.37
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
cell constants			
a (Å)	15.9615(9)	17.8190(8)	11.4854(6)
b (Å)	11.1136(9)	9.5009(5)	12.1920(5)
c (Å)	19.4852(12)	21.6317(10)	15.3971(6)
α (deg)	90	90	107.118(3)
β (deg)	112.700(4)	103.809(1)	93.460(4)
γ (deg)	90	90	101.193(4)
V (Å^3), Z	3188.7(4), 4	3556.3(3), 4	2005.4(2), 2
λ (Å)	0.710 73	0.710 73	0.710 73
ρ(calcd) (Mg m^{-3})	1.424	1.519	1.371
F(000)	2404	1656	852
T (K)	173(2)	100(2)	173(2)
μ (mm^{-1})	0.632	0.728	0.515
transmissn	0.843−0.821	0.931−0.874	0.851−0.827
θ range (deg)	3.14−25.00	1.94−28.17	3.14−25.00
limiting indices	$-17 \le h \le 18$	$-22 \le h \le 22$	$0 \le h \le 13$
	$-13 \le k \le 4$	$-12 \le k \le 12$	$-13 \le k \le 13$
	$-23 \le l \le 0$	$-27 \le l \le 27$	$-18 \le l \le 18$
no. of rflns			
measd	7818	39 930	7335
indep	5591	8153	6957
R_{int}	0.0296	0.0277	0.0110
abs cor	ψ scans	semiempirical from equivalents	ψ scans
refinement method		full-matrix least squares on F^2	
no. of data/restraints/params	5591/43/394	8153/40/446	6957/465/487
S (F^2)	0.999	1.214	1.061
R1[a]	0.0361	0.0476	0.0283
wR2[b]	0.0868	0.1023	0.0796
largest diff peak (e Å^{-3})	1.159	0.907	0.504
max Dr (e Å^{-3})	−0.618	−0.996	−0.525

[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.

[Rh(CF$_3$)(CNXy)$_3$(PPh$_3$)] (8a). A solution of **2a**, prepared from **1a** (119 mg, 0.24 mmol) and Me_3SiCF_3 (0.18 mL of a 2.0 M solution in THF, 0.36 mmol) in THF (5 mL), was treated with XyNC (97 mg, 0.74 mmol) at room temperature and stirred for 1 h. The resulting orange solution was concentrated (ca. 1 mL), *n*-hexane (5 mL) was added, and a yellow solid precipitated. The solution was removed by means of a pipet, and the solid was washed with *n*-hexane (2 × 5 mL) and dried in vacuo. Yield: 170 mg, 85%. Mp: 104−106 °C. Anal. Calcd for $C_{46}H_{42}N_3F_3PRh$: C, 66.73; H, 5.11; N, 5.10. Found: C, 66.69; H, 5.30; N, 5.15. IR (cm^{-1}): ν(C≡N) 2038 (vs). ^{1}H NMR (300.1 MHz, C_6D_6): δ 7.67 (m, 6 H, H2, Ph$_3$P), 6.97 (m, 9 H, H3 + H4, Ph$_3$P), 6.70 (AB$_2$ m, 9 H, CH, Xy), 2.12 (s, 18 H, Me). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6): δ 163.6 (br s, C≡N), 137.2 (d, C1, Ph, $^1J_{PC}$ = 25.9 Hz), 134.8 (s, C2, Xy), 134.5 (d, C2, Ph, $^2J_{PC}$ = 14.2 Hz), 129.5 (s, C4, Ph), 129.2 (s, C1, Xy), 128.4 (d, C3, Ph, $^3J_{PC}$ = 8.8 Hz), 127.8 (s, C4, Xy), 127.2 (s, C3, Xy), 18.7 (s, Me). The signal corresponding to the CF$_3$ carbon was not observed. ^{19}F NMR (188.3 MHz, d_8-toluene): 77 °C, δ −8.4 (d, $^2J_{RhF}$ = 23.3 Hz); 58 °C, δ −7.1 (d, $^2J_{RhF}$ = 21.5 Hz); 22 °C, δ −1.2 (br s); CD_2Cl_2, −80 °C, δ 3.1 (dd, $^2J_{RhF}$ = 8.1 Hz, $^3J_{PF}$ = 59.8 Hz). ^{31}P{^{1}H} NMR (81.0 MHz, d_8-toluene): 77 °C, δ 2.3 (br s); 58 °C, δ 4.1 (br s); 22 °C, δ 20.1 (v br s); CD_2Cl_2, −80 °C, δ 42.5 (dq, $^1J_{RhP}$ = 76.5 Hz, $^3J_{PF}$ = 60.1 Hz).

[Rh(CF$_3$)(CNXy)$_3${P(C$_6$H$_4$OMe-4)$_3$}] (8b). This compound was prepared as for **8a** from **1b** (115 mg, 0.22 mmol), Me_3SiCF_3 (0.22 mL of a 2.0 M solution in THF, 0.44 mmol) in THF (7 mL), and XyNC (89 mg, 0.66 mmol). *n*-Pentane was used instead of *n*-hexane to precipitate the complex. Yield: 191 mg, 94.5%. Mp: 106−108 °C dec. Anal. Calcd for $C_{49}H_{48}O_3N_3F_3PRh$: C, 64.12; H, 5.27; N, 4.58. Found: C, 63.98; H, 5.67; N, 4.60. IR (cm^{-1}): ν(C≡N) 2028 (vs). ^{1}H NMR (200.1 MHz, d_8-toluene, 23 °C): δ 7.84−7.69 (m, 6 H, H2, C_6H_4), 6.78−6.56 (m, 15 H, CH, Xy, H3, C_6H_4), 3.22 (s, 9 H, OMe), 2.13 (s, 18 H, Me, Xy). ^{13}C{^{1}H} NMR (100.8 MHz, THF/d_6-DMSO (ext)): δ 164.0 (br s, C≡N), 161.1 (s, C4, C_6H_4), 135.5 (d, $^2J_{PC}$ = 14.2 Hz, C2, C_6H_4), 134.2 (s, C2, Xy), 129.1 (s br, C1, Xy), 128.2 (br d, C1, C_6H_4, $^1J_{PC}$ = 38.8 Hz), 127.4 (s, C3, Xy), 126.7 (s, C4, Xy), 113.5 (d, C3, C_6H_4, $^3J_{PC}$ = 9.9 Hz), 54.6 (s, OMe), 17.9 (s, Me). The signal corresponding to the CF$_3$ carbon was not observed. ^{19}F NMR (188.3 MHz, d_8-toluene): 23 °C, δ 1.3 (br s); −60 °C, δ 4.6 (dd, $^2J_{RhF}$ = 7.5 Hz, $^3J_{PF}$ = 61.4 Hz). ^{31}P{^{1}H} NMR (81.0 MHz, d_8-toluene): 23 °C, δ 32.3 (br s); −60 °C, δ 38.3 (dq, $^1J_{RhP}$ = 76.1 Hz, $^3J_{PF}$ = 61.0 Hz).

[Rh(C$_3$F$_7$)(CNXy)$_3$(PPh$_3$)] (8c). A solution of **2c**, prepared from **1a** (128 mg, 0.26 mmol) and $Me_3SiC_3F_7$ (0.11 mL, 0.52 mmol) in THF (5 mL), was treated with XyNC (102 mg, 0.78 mmol) at room temperature and stirred for 1 h. The resulting orange solution was concentrated to ca. 0.5 mL, and *n*-pentane (5 mL) was added. An oil precipitated, which was converted into a yellow solid by stirring for 10 min at 0 °C. The solution was removed by means of a pipet, and the solid was washed with *n*-pentane (2 × 5 mL) and dried under vacuum. Yield: 199 mg, 82.5%**.** Mp: 78 °C. Anal. Calcd for $C_{48}H_{42}N_3F_7PRh$: C, 62.14; H, 4.56; N, 4.53. Found: C, 62.02; H, 4.47; N, 4.54. IR (cm^{-1}): ν(C≡N) 2035 (vs). ^{1}H NMR (200.1 MHz, C_6D_6): δ 7.51 (m, 6 H, H2, PPh$_3$), 7.00 (m, 9 H, H3 + H4, PPh$_3$), 6.64 (AB$_2$ m, 9 H, CH, Xy), 2.12 (s, 18 H, Me). ^{13}C{^{1}H} NMR (100.8 MHz, C_6D_6): δ 160.9 (br s, C≡N), 137.9 (br s, C1, PPh$_3$), 135.7 (s, C2, Xy), 134.9 (d, $^2J_{PC}$ = 16.2 Hz, C2, PPh$_3$), 129.8 (s, C4, PPh$_3$), 129.1 (d, $^3J_{PC}$ = 8.1 Hz, C3, PPh$_3$), 128.9 (s, C3, Xy), 128.5 (s, C4, Xy), 19.1 (s, Me); the signals of C_3F_7 group and C1 Xy group carbons were not observed. ^{19}F NMR (188.3 MHz, d_8-toluene): 80 °C, δ −78.3 (t, 3 F, CF$_3$, $^4J_{FF}$ = 10.3 Hz), −84.8 (br m, 2 F, α-F), −117.7 (s, 2 F, β-F); 25 °C, δ −78.1 (t, 3 F, CF$_3$, $^4J_{FF}$ = 10.4 Hz), −81.8 (br m, 2 F, α-F), −116.7 (s, 2 F, β-F); −84 °C, δ −62.8 (br m, 2 F, α-F), −76.9 (s, 3 F, CF$_3$),

−112.6 (s, 2 F, β-F). $^{31}P\{^1H\}$ NMR (81.0 MHz, d_8-toluene): 80 °C, δ 12.4 (br s); 25 °C, δ 9.8 (br s); −84 °C, δ 44.8 (dt, $^1J_{RhP}$ = 75.9 Hz, $^3J_{PF}$ = 37.8 Hz).

Reaction of 2a with *t*-BuNC in a 1:3 Molar Ratio. A solution of **2a**, prepared from **1a** (11 mg, 0.022 mmol) and Me_3SiCF_3 (0.040 mmol) in d_8-toluene or THF (0.5 mL), was treated with *t*-BuNC (0.066 mmol) at room temperature, and the NMR spectra were measured after 30 min. ^1H NMR (200.1 MHz, d_8-toluene, 25 °C): δ 7.46 (m, 6 H, H2, Ph), 7.05 (m, 9 H, H3 + H4, Ph), 0.97 (s, 27 H, *t*-Bu). ^{19}F NMR (188.3 MHz): d_8-toluene, 25 °C, δ −9.9 (d, $^2J_{RhF}$ = 24.6 Hz); d_8-toluene, −70 °C, δ 3.7 (very broad), −7.9 (very broad); THF, 22 °C, δ −12.9 (d, $^2J_{RhF}$ = 24.5 Hz); THF, −84 °C, δ 0.8 (br d, $^2J_{RhF}$ = 60.1 Hz), −12.8 (very broad). $^{31}P\{^1H\}$ NMR (81.0 MHz): d_8-toluene, 25 °C, δ 10.8 (br s); d_8-toluene, −70 °C, δ 49.3 (very broad); THF, 22 °C, δ 3.9 (br s); THF, −84 °C, δ 47.3 (br m).

$[Rh(CF_3)(CO)_3(PPh_3)]$ (9) and $[Rh(CF_3)(^{13}CO)_3(PPh_3)]$ (9*). Complex **1a** (10 mg, 0.020 mmol) was placed in a NMR tube fitted with a Young valve, and d_8-toluene (0.5 mL) was added. The yellow solution was treated with Me_3SiCF_3 (20 μL of a 2.0 M solution in THF, 0.040 mmol) at room temperature, the NMR tube was connected to the vacuum line, the solution was frozen with N_2(l), and the tube was then evacuated, thawed, and then filled with CO (1 atm). The same steps were repeated two times more to give an orange solution. Compound **9*** was prepared in the same way using ^{13}CO. Data for **9** are as follows. IR (toluene, cm^{-1}): ν(CO) 2012 (s). ^1H NMR (200.1 MHz, C_6D_6, 25 °C): δ 7.34−7.25 (m, 6 H, H2, PPh_3), 6.90 (m, 9 H, H3 + H4, PPh_3). ^{19}F NMR (188.3 MHz, C_6D_6, 25 °C): δ 7.7 (br d, $^3J_{PF}$ = 61.8 Hz). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): δ 31.9 (dq, $^1J_{RhP}$ = 69.3 Hz, $^3J_{PF}$ = 62.0 Hz). Data for **9*** are as follows. $^{13}C\{^1H\}$ NMR (50.3 MHz): C_6D_6, 25 °C, δ 188.5 (br s, CO); d_8-toluene, −70 °C, δ 184.3 (ddq, *CO; $^1J_{RhC}$ = 71.1 Hz, $^2J_{PC}$ = 14.0 Hz, $^3J_{CF}$ = 10.7 Hz). ^{19}F NMR (188.3 MHz, d_8-toluene): 25 °C, δ 7.8 (br d, $^3J_{PF}$ = 61.7 Hz); −70 °C, δ 8.2 (ddq, $^3J_{PF}$ = 60.8 Hz, $^3J_{CF}$ = 10.3 Hz, $^2J_{RhF}$ = 8.0 Hz). $^{31}P\{^1H\}$ NMR (81.0 MHz, d_8-toluene): 25 °C δ 32.2 (dq, $^1J_{RhP}$ = 69.8 Hz, $^3J_{PF}$ = 61.8 Hz); −70 °C, δ 31.7 (dqq, $^1J_{RhP}$ = 68.9 Hz, $^3J_{PF}$ = 60.9 Hz, $^2J_{PC}$ = 15.4 Hz).

Crystallography. Data for compounds **4a** and **8a** were measured on a Siemens P4/LT2 machine and for **7a** on a Bruker Smart Apex CCD machine. Data were collected using monochromated Mo Kα radiation in ω-scan mode. The structures were solved by the heavy-atom method, and all were refined anisotropically on F^2. Restraints to local aromatic ring symmetry or light atom displacement factor components were applied in some cases. Methyl groups were refined using rigid groups, for compounds **4a** and **7a**. Other hydrogens were refined using a riding mode. The fluorine atoms are disordered over two sites in compound **4a**. Crystal data for compounds **4a**, **7a**, and **8a** are given in Table 2.

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Supporting Information Available: Crystallographic files in CIF format and crystallographic tables for compounds **4a**, **7a**, and **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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