Organometallics **2005,** *24,* 5634−5643

Synthesis and Reactivity of Trifluoromethyl Isocyanide Rhodium(I) Complexes[§]

José Vicente,[*,†] Juan Gil-Rubio,[*,†] Juan Guerrero-Leal,[†] and Delia Bautista[‡]

Grupo de Química Organometálica, Departamento de Química Inorgánica,
Facultad de Química, and SACE, Universidad de Murcia, Apartado de correos 4021,
E-30071 Murcia, Spain

Received July 8, 2005

The complex *trans*-$[Rh(CF_3)(CNXy)_2(PPh_3)]$ (**1**) reacts with SO_2, tetracyanoethylene (TCNE), or maleic anhydride (MA) to give the complexes $[Rh(CF_3)(CNXy)_2(PPh_3)L]$ (L = SO_2 (**2**), TCNE (**3**), MA (**4**)) and with CO or CF_3CO_2H to give, respectively, mixtures containing mainly $[Rh(CF_3)(CNXy)_2(CO)(PPh_3)]$ or *trans*-$[Rh(CNXy)_2(PPh_3)_2]CF_3CO_2$, which is prepared in better yield by reaction of *trans*-$[RhCl(PPh_3)_2(CO)]$ with XyNC and $NaCF_3CO_2$. $[Rh(CF_3)(CNXy)_3]$ (**6**) is prepared by reaction of $[Rh(CF_3)(CNXy)_3(PPh_3)]$ (**7**) with 35% H_2O_2 or, better, by reaction of $[Rh(\mu\text{-}OH)(COD)]_2$ with XyNC and Me_3SiCF_3. The reaction of **6** with tetracyanoethylene (TCNE) or maleic anhydride (MA) gives the complexes $[Rh(CF_3)(CNXy)_3L]$ (L = TCNE (**8**), MA (**9**)). The oxidative addition reaction of MeI or *n*-C_4F_9I with complex **6** gives the octahedral Rh(III) complexes $[Rh(CF_3)(R)I(CNXy)_3]$ (R = Me (**10**), *n*-C_4F_9 (**11**)). In an attempt to obtain single crystals of complex **11**, a few crystals of $[\{Rh(CF_3)(n\text{-}C_4F_9)(CNXy)_2\}_2(\mu\text{-}I)_2]$ (**12**) were obtained. The crystal structures of complexes **2**−**4** and **12** have been determined by X-ray diffraction studies.

Introduction

There is a demand for selective synthetic methods of highly fluorinated organic compounds.[1] In recent years, transition-metal perfluoroorganometallic chemistry has emerged as a promising alternative for the synthesis and functionalization of fluoroorganic compounds. In this context, C−F bond activation by metal complexes[2] is a major goal that has been achieved in stoichiometric[3] or catalytic reactions.[4] The use of perfluoroorganometallic compounds for C−C coupling reactions is also a desirable goal, but it is limited by the thermodynamic stability and kinetic inertness of the M−R_F bond (M = transition metal, R_F = highly fluorinated alkyl, aryl, or alkenyl) with respect to its nonfluorinated analogues.[5−8] Despite this limitation, C−R_F bond formation has been reported in highly fluorinated aryl, alkenyl, or alkyl complexes[9,10] or in transition-metal-catalyzed coupling reactions.[9,11]

In consequence, the synthesis and reactivity of new types of perfluoroorganometallic complexes are of interest, especially for complexes of low-oxidation-state metals, which cannot be prepared by oxidative addition reactions with perfluoroalkyl halides.[5,6] Recent studies have shown that perfluoroalkyl complexes can be obtained under very mild conditions by reaction of (perfluoroalkyl)trimethylsilanes with fluoro complexes[12−14] or with chloro or bromo complexes in the presence of

---

[§] Dedicated to Dr. José Antonio Abad, with best wishes, on the occasion of his retirement.

[*] To whom correspondence should be addressed. Tel and fax: (34) 968 364143. Web address: http://www.um.es/gqo/. E-mail: jvs1@um.es (J.V.), jgr@um.es (J.G.-R.).

[†] Departamento de Química Inorgánica, Universidad de Murcia.

[‡] SACE, Universidad de Murcia.

(1) Ritter, S. K. *Chem. Eng. News* **2005**, *83*, 35. Langlois, B. R.; Billard, T.; Roussel, S. *J. Fluorine Chem.* **2005**, *126*, 173. Ma, J.-A.; Cahard, D. *Chem. Rev.* **2004,** *104*, 6119. Umemoto, T. *Chem. Rev.* **1996**, *96*, 1757.

(2) Richmond, T. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 3241. Richmond, T. G. *Top. Organomet. Chem.* **1999**, *3*, 243. Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber./Recl.* **1997**, *130*, 145. Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373.

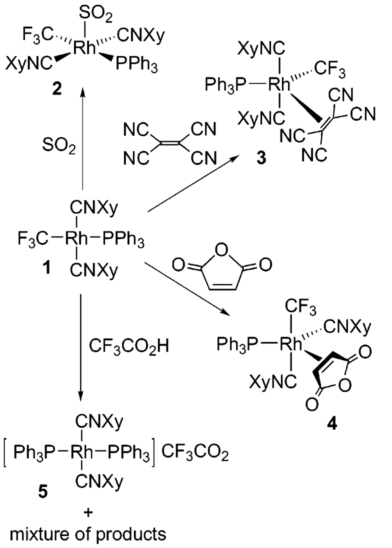
(3) Jasim, N. A.; Perutz, R. N.; Whitwood, A. C.; Braun, T.; Izundu, J.; Neumann, B.; Rothfeld, S.; Stammler, H.-G. *Organometallics* **2004**, *23*, 6140. Braun, T.; Rothfeld, S.; Schorlemer, V.; Stammler, A.; Stammler, H.-G. *Inorg. Chem. Commun.* **2003**, *6*, 752. Sladek, M. I.; Braun, T.; Neumann, B.; Stammler, H.-G. *Dalton Trans.* **2002**, 297. Braun, T.; Foxon, S. P.; Perutz, R. N.; Walton, P. H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3326. Braun, T.; Blöcker, B.; Schorlemer, V.; Neumann, B.; Stammler, A.; Stammler, H.-G. *Dalton Trans.* **2002**, 2213. Braun, T.; Cronin, L.; Higgit, C. L.; McGrady, J. E.; Perutz, R. N.; Reinhold, M. *New J. Chem.* **2001**, *25*, 19. Bach, I.; Pörschke, K.-R.; Goddard, R.; Kopiske, C.; Krüger, C.; Rufinska, A.; Seevogel, K. *Organometallics* **1996**, *15*, 4959. Reinhold, M.; McGrady, J. E.; Perutz, R. N. *J. Am. Chem. Soc.* **2004**, *126*, 5268. Whittlesey, M. K.; Perutz, R. N.; Moore, M. H. *Chem. Commun.* **1996**, 787. Noveski, D.; Braun, T.; Schulte, M.; Neumann, B.; Stammler, A. *Dalton Trans.* **2003**, 4075. Bellabarba, R. M.; Nieuwenhuyzen, M.; Saunders, G. C. *Organometallics* **2002**, *21*, 5726. Edelbach, B. L.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 7734. Kraft, B. M.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 10973. Kraft, B. M.; Jones, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 8681. Hughes, R. P.; Willemsen, S.; Williamson, A.; Zhang, D. *Organometallics* **2002**, *21*, 3085. Hughes, R. P.; Smith, J. M.; Incarvito, C. D.; Lam, K.-C.; Rhatigan, B.; Rheingold, A. L. *Organometallics* **2002**, *21*, 2136. Hughes, R. P.; Smith, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 6084. Hughes, R. P.; Laritchev, R. B.; Zakharov, L. N.; Rheingold, A. L. *J. Am. Chem. Soc.* **2004**, *126*, 2308. Clot, E.; Mégret, C.; Kraft, B. M.; Eisenstein, O.; Jones, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 5647. Watson, P. L.; Tulip, T. H.; Williams, I. *Organometallics* **1990**, *9*, 1999. Weydert, M. W.; Andersen, R. A.; Bergman, R., G. *J. Am. Chem. Soc.* **1993**, *115*, 8837. Deacon, G. B.; Harris, S. C.; Meyer, G.; Stellfeldt, D.; Wilkinson, D. L.; Zelesny, G. *J. Organomet. Chem.* **1998**, *552*, 165. Albietz, P. J., Jr.; Houlis, J. F.; Eisenberg, R. *Inorg. Chem.* **2002**, *41*, 2001.

(4) Kim, Y. M.; Yu, S. *J. Am. Chem. Soc.* **2003**, *125*, 1696. Böhm, V. P. W.; Gstöttmayr, W. K.; Weskamp, T.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 3387. Dankwardt, J. W. *J. Organomet. Chem.* **2005**, *690*, 932. Widdowson, D. A.; Wilhelm, R. *Chem. Commun.* **1999**, 2211. Wilhelm, R.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3808. Terao, J.; Ikumi, A.; Kuniyasu, H.; Kambe, N. *J. Am. Chem. Soc.* **2003**, *125*, 5646. Kiso, Y.; Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1973**, *50*, C12. Kiplinger, J. L.; Richmond, T. G. *J. Am. Chem. Soc.* **1996**, *118*, 1805. Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 8674.

10.1021/om050573q CCC: $30.25

fluoride ions.[8,15] Thus, we have reported the synthesis of a series of new perfluoroalkyl rhodium(I) complexes, $[RhR_F(COD)(PR_3)]$ ($R_F = CF_3$, *n*-C_3F_7; R = Ph, C_6H_4-OMe-4), and their reactions with isocyanides, to give $[RhR_F(CNR')_x(PR_3)]$ ($x = 2, 3$, R′ = 2,6-dimethylphenyl (Xy), *t*-Bu, $R_F = CF_3$, *i*-C_3F_7).[13,14] Previous studies have shown that these complexes are fairly reactive. For example, the complexes *trans*-$[Rh(CF_3)(CNXy)_2(PR_3)]$ react at room temperature with atmospheric O_2 or with XyNC to give the peroxo complex $[Rh(CF_3)(\eta^2\text{-}O_2)(CNXy)_2(PR_3)]$ or the pentacoordinate complex $[Rh(CF_3)(CNXy)_3(PR_3)]$. Despite the fact that the low reactivity of the metal−trifluoromethyl bond is well known,[5−8] the electron-rich Rh(I) center may increase the reactivity of the Rh−C and α-C−F bonds. In the search for new rhodium(I)-mediated C−C bond formation processes involving perfluoroorganic substrates, we have explored the chemical behavior of the complexes *trans*-$[Rh(CF_3)(CNXy)_2L]$ (L = PPh_3 (**1**),[13] XyNC (**6**)) toward different types of reagents, including the results of oxidative addition reactions which gave trifluoromethyl isocyanide Rh(III) complexes.

Scheme 1



Most Rh(III) perfluoroalkyl complexes have been prepared by oxidative addition of R_F−I to Rh(I) precursors,[16−20] but they have also been prepared by oxidative addition of an Ar−CF_3 compound to a Rh(I) complex[21] or by the reaction of $[RhHCl_2(PPh_3)_2]$ with $Hg(CF_3)_2$, which gave a mixture of $[RhCl_2(CF_3)(PPh_3)_2]$ and $[RhCl_2(CF_2H)(PPh_3)_2]$.[22] Some of them undergo interesting selective C−F activation reactions under very mild conditions.[19,21−23] Despite the fact that the oxidative addition reactions to Rh(I) complexes have been intensively studied, the oxidative additions to Rh(I) perfluoroalkyl complexes are very rare. We are only aware of reactions of *trans*-$[Rh(CF_3)(CO)(PPh_3)_2]$ with X_2 (X = Cl, Br, I), HCl, and MeI. The last compound gave $[Rh(CF_3)\{C(O)Me\}I(PPh_3)_2]$ instead of the methyl complex.[22] In this context, the synthesis of mixed alkyl−perfluoroalkyl or bis(perfluoroalkyl) complexes of Rh(III) is of particular interest, because no examples of such compounds have been described and they are potential candidates for the observation of C−C bond formation and C−F bond activation processes.

Results and Discussion

Synthesis. The reaction of *trans*-$[Rh(CF_3)(CNXy)_2(PPh_3)]$ (**1**) with excess SO_2 gave $[Rh(CF_3)(CNXy)_2(PPh_3)(SO_2)]$ (**2**) as the main reaction product, which was isolated in 91% yield (Scheme 1). A single-crystal X-ray diffraction analysis showed that the SO_2 ligand in **2** is coordinated by the S atom and possesses a pyramidal geometry (see Figure 1; for a detailed description of the structures see Crystallographic Studies).

Complex **1** did not react with ethylene and norbornene at room temperature, but it did react with olefins containing electron-withdrawing groups such as tetracyanoethylene (TCNE) and maleic anhydride (MA) to give the pentacoordinate complexes $[Rh(CF_3)(CNXy)_2(PPh_3)L]$ (L = TCNE (**3**), MA (**4**)), which were isolated in good yields and characterized by single-crystal X-ray diffraction analyses (Figures 2 and 3). Complexes **3** and

---

(5) Bruce, M. I.; Stone, F. G. A., Fluorocarbon Complexes of Transition Metals. In *Preparative Inorganic Reactions*; Jolly, W. L., Ed.; Interscience: Bristol, U.K., 1968; Vol. 4, p 177. Morrison, J. A. *Adv. Organomet. Chem.* **1993**, *35*, 211.

(6) Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293.

(7) Hughes, R. P. *Adv. Organomet. Chem.* **1990**, *31*, 183. Saddei, D.; Freund, H.-J.; Hohlneicher, G. *J. Organomet. Chem.* **1980**, *186*, 63.

(8) Culkin, D. A.; Hartwig, J. F. *Organometallics* **2004**, *23*, 3398.

(9) Burton, D. J.; Lu, L. *Top. Curr. Chem.* **1997**, *193*, 45.

(10) Braun, T.; Perutz, R. N. *Chem. Commun.* **2002**, 2749. Braun, T.; Noveski, D.; Braun, T.; Neumann, B.; Stammler, A.; Stammler, H.-G. *Dalton Trans.* **2004**, 4106. Hughes, R. P.; Zhang, D.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2002**, *21*, 4902.

(11) Anilkumar, R.; Burton, D. J. *J. Fluorine Chem.* **2005**, *126*, 835. Kitazume, T.; Nakajima, S. *J. Fluorine Chem.* **2004**, *125*, 1447. Frohn, H.-J.; Adonin, N. Y.; Bardin, V. V.; Starichenko, V. F. *J. Fluorine Chem.* **2002**, *117*, 115. Casado, A. L.; Espinet, P.; Gallego, A. M.; Martínez-Ilarduya, J. M. *Chem. Commun.* **2001**, 339. Albéniz, A. C.; Espinet, P.; Martín-Ruiz, B.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 11504. Albéniz, A. C.; Espinet, P.; Martín-Ruiz, B.; Milstein, D. *Organometallics* **2005**, *24*, 3679. Perutz, R. N.; Sladek, M. I. *Chem. Commun.* **2001**, 2254. Edelbach, B. L.; Kraft, B. M.; Jones, W. D. *J. Am. Chem. Soc.* **1999,** *121*, 10327.

(12) Taw, F. L.; Scott, B. L.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 14712. 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. Tyrra, W.; Naumann, D. *J. Fluorine Chem.* **2004**, *125*, 823.

(13) Vicente, J.; Gil-Rubio, J.; Guerrero-Leal, J.; Bautista, D. *Organometallics* **2004**, *23*, 4871.

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

(15) Naumann, D.; Kirij, N. V.; Maggiarosa, N.; Tyrra, W.; Yagupolskii, Y. L.; Wickleder, M. S. *Z. Anorg. Allg. Chem.* **2004**, *630*, 746.

(16) Hughes, R. P.; Lindner, D. C.; Smith, J. M.; Zhang, D.; Incarvito, C. D.; Lam, K.-C.; Liable-Sands, L. M.; Sommer, R. D.; Rheingold, A. L. *Dalton Trans.* **2001**, 2270.

(17) Bowden, A. A.; Hughes, R. P.; Lindner, D. C.; Incarvito, C. D.; Liable-Sands, L. M.; Rheingold, A. L. *Dalton Trans.* **2002**, 3245.

(18) Hughes, R. P.; Lindner, D. C.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 5678. Hughes, R. P.; Le Husebo, T. *Organometallics* **1997**, *16*, 5. Dart, J. W.; Lloyd, M. K.; McCleverty, J. A.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1971**, 1197. Dart, J. W.; Lloyd, M. K.; Mason, R.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2039. Clark, H. C.; Reimer, K. J. *Can. J. Chem.* **1976**, *54*, 2077. Hyde, E. M.; Kennedy, J. D.; Shaw, B. L.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1977**, 1571. McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1964**, 4200. McCleverty, J. A.; Williams, J. *Transition Met. Chem.* **1978**, *3*, 205. Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 1165.

(19) Hughes, R. P.; Lindner, D. C. *J. Am. Chem. Soc.* **1997**, *119*, 11544.

(20) Dart, J. W.; Lloyd, M. K.; Mason, R.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2046.

(21) Van der Boom, M. E.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 6652.

(22) Burrell, A. K.; Clark, G. R.; Jeffrey, J. G.; Rickard, C. E. F.; Roper, W. R. *J. Organomet. Chem.* **1990**, *388*, 391.

(23) Hughes, R. P.; Lindner, D. C.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **2001**, *20*, 363.

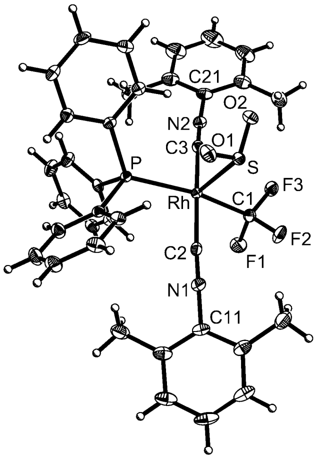


Figure 1. Molecular structure of **2** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Rh−C(2) = 1.975(2), Rh−C(3) = 1.978(2), Rh−C(1) = 2.066(2), Rh−P = 2.3605(5), Rh−S = 2.3763(5), S−O(1) = 1.4655(16), S−O(2) = 1.4679(15), F(1)−C(1) = 1.378(2), F(2)−C(1) = 1.357(2), F(3)−C(1) = 1.368(2), N(1)−C(2) = 1.156(3), N(2)−C(3) = 1.157(3); C(2)−Rh−C(3) = 168.24(8), C(2)−Rh−C(1) = 84.07(8), C(3)−Rh−C(1) = 88.68(8), C(2)−Rh−P = 93.50(6), C(3)−Rh−P = 91.43(6), C(1)−Rh−P = 166.68(6), C(2)−Rh−S = 93.54(6), C(3)−Rh−S = 95.86(6), C(1)−Rh−S = 91.24(6), P−Rh−S = 101.996(18), O(1)−S−O(2) = 113.19(9), O(1)−S−Rh = 103.64(6), O(2)−S−Rh = 104.24(6), C(2)−N(1)−C(11) = 174.4(2), C(3)−N(2)−C(21) = 176.8(2), F(2)−C(1)−F(3) = 103.30(16), F(2)−C(1)−F(1) = 103.96(16), F(3)−C(1)−F(1) = 103.37(16), F(2)−C(1)−Rh = 117.16(14), F(3)−C(1)−Rh = 117.68(14), F(1)−C(1)−Rh = 109.70(13), N(1)−C(2)−Rh = 170.69(18), N(2)−C(3)−Rh = 174.96(18).

4 were not affected by the presence of an excess of olefin or by heating at 70 °C overnight. No significant reaction took place when complex **1** was treated with phenylacetylene or bis(trimethylsilyl)acetylene at room temperature. The reactions of **1** with alkynes containing electron-withdrawing groups, such as dimethyl acetylenedicarboxylate, methyl propiolate, or methyl 2-phenylpropiolate, gave mixtures which could not be characterized.

When the reaction of complex **1** with CO was carried out in a NMR tube, a single set of broad signals was observed in the ^{19}F and ^{31}P{^{1}H} NMR spectra at 25 °C. When the temperature was lowered to −60 °C, the signals became sharp and the ^{19}F NMR spectrum revealed the presence of four signals in the range where Rh−CF_3 groups usually appear, suggesting the presence of a mixture of four trifluoromethyl complexes which are in fast exchange at room temperature on the NMR time scale. These complexes could not be isolated, because they easily lost CO when the solvent was removed under vacuum. The major component (its abundance was 86%, as determined by integration of the ^{19}F NMR spectrum) gave a doublet of doublets and a doublet of quadruplets in the ^{19}F and ^{31}P{^{1}H} NMR spectra, respectively, which are typical of the Rh(CF_3)(PPh_3) unit. In addition, the ^{1}H NMR spectrum showed two equivalent XyNC ligands, and the IR spectrum showed intense bands in the range where the ν(CN) (2116 and 2086 cm^{-1}) and ν(CO) (1958 cm^{-1}) modes of the XyNC and CO ligands appear in similar complexes.[13] These data suggest that the main component could be [Rh(CF_3)$(CNXy)_2$(CO)(PPh_3)]. In addition, the values of δ, $^1J_{RhP}$, $^2J_{RhF}$, and $^3J_{PF}$ are very similar to those observed in [Rh(CF_3)$(CNXy)_3$(PPh_3)] (**7**),[13] which suggests that the structure of the carbonyl complex may be trigonal bipyramidal, as for **7**. An unambiguous assignment of the minor trifluoromethyl complexes could not be carried out because of their low abundances (9%, 4%, and 1%). We temptatively propose the composition [Rh(CF_3)(CNXy)$(CO)_2$(PPh_3)] only for the most abundant of them on the basis of their NMR data (^{19}F, doublet of doublets; ^{31}P{^{1}H}, doublet of quadruplets, with $^1J_{RhP}$, $^2J_{RhF}$ and $^3J_{PF}$ values similar to those of [Rh(CF_3)$(CNXy)_2$(CO)(PPh_3)]). The IR spectrum showed two lower intensity bands at 2018 and 1976 cm^{-1}, which could correspond to ν(CO) modes of the minor components.

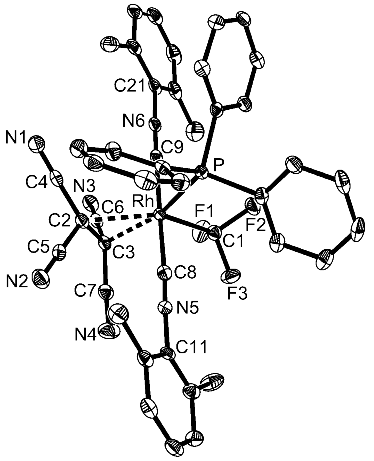


Figure 2. Molecular structure of **3** (50% thermal ellipsoids; hydrogen atoms are omitted). Selected bond lengths (Å) and angles (deg): Rh−C(9) = 1.974(4), Rh−C(8) = 1.981(4), Rh−C(1) = 2.065(3), Rh−C(3) = 2.122(3), Rh−C(2) = 2.216(3), Rh−P = 2.3717(9), N(1)−C(4) = 1.148(5), N(2)−C(5) = 1.137(5), N(3)−C(6) = 1.141(5), N(4)−C(7) = 1.145(5), N(5)−C(8) = 1.148(4), N(6)−C(9) = 1.151(4), F(1)−C(1) = 1.365(4), F(2)−C(1) = 1.365(4), F(3)−C(1) = 1.364(4), C(2)−C(4) = 1.434(5), C(2)−C(5) = 1.446(5), C(2)−C(3) = 1.509(5), C(3)−C(7) = 1.443(5), C(3)−C(6) = 1.448(5); C(9)−Rh−C(8) = 177.02(14), C(9)−Rh−C(1) = 87.57(14), C(9)−Rh−C(2) = 92.92(13), C(8)−Rh−C(1) = 93.59(14), C(9)−Rh−C(3) = 91.29(13), C(8)−Rh−C(3) = 91.19(14), C(8)−Rh−C(2) = 87.89(13), C(9)−Rh−P = 89.62(10), C(8)−Rh−P = 87.47(10), C(1)−Rh−P = 100.07(10), C(8)−N(5)−C(11) = 175.4(3), C(9)−N(6)−C(21) = 177.8(3), F(3)−C(1)−F(2) = 103.5(3), F(3)−C(1)−F(1) = 103.6(3), F(2)−C(1)−F(1) = 103.3(3), F(3)−C(1)−Rh = 115.7(2), F(2)−C(1)−Rh = 117.6(2), F(1)−C(1)−Rh = 111.5(2), C(4)−C(2)−C(5) = 113.0(3), C(4)−C(2)−C(3) = 117.5(3), C(5)−C(2)−C(3) = 117.2(3), C(4)−C(2)−Rh = 115.9(2), C(5)−C(2)−Rh = 119.5(2), C(7)−C(3)−C(6) = 113.5(3), C(7)−C(3)−C(2) = 118.9(3), C(6)−C(3)−C(2) = 116.3(3), C(7)−C(3)−Rh = 113.8(2), C(6)−C(3)−Rh = 115.4(2), N(5)−C(8)−Rh = 176.4(3), N(6)−C(9)−Rh = 179.2(3).

Complex **1** was reacted with CF_3CO_2H in order to test if protonolysis of the C−F bonds would take place. Thus, when **1** was treated with an equimolar amount of CF_3CO_2H in C_6D_6, the ^{19}F NMR spectrum of the reaction mixture showed after a few minutes a singlet at −75.2 ppm (assigned to $CF_3CO_2^-$), which was the main signal. In addition, in the range from 24.2 to −17.7 ppm, where the Rh−CF_3 groups usually appear, no less than 25 signals were observed, which could not be identified. After 1 h, a yellow solid had crystallized out from the reaction mixture. The ^{31}P NMR spectrum ($CDCl_3$) of this

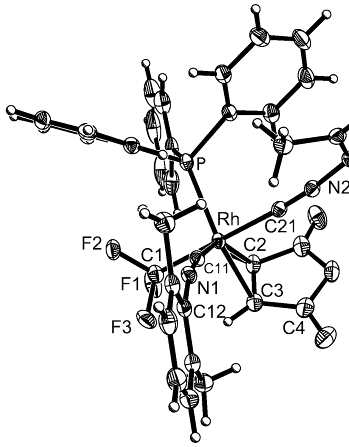
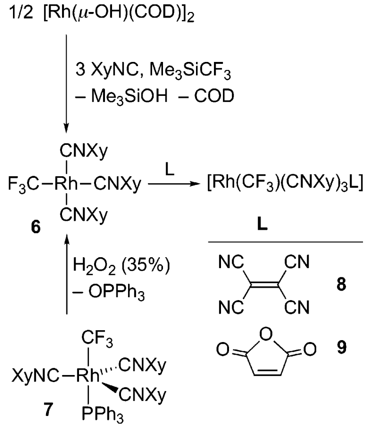


Figure 3. Molecular structure of **4** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Rh−C(1) = 2.0654(18), Rh−C(11) = 1.9846(18), Rh−C(21) = 2.0034(17), Rh−C(2) = 2.1536(18), Rh−C(3) = 2.1491(18), Rh−P = 2.3810(5), F(1)−C(1) = 1.372(2), F(2)−C(1) = 1.366(2), F(3)−C(1) = 1.378(2), C(2)−C(3) = 1.430(3), N(1)−C(11) = 1.160(2), N(2)−C(21) = 1.155(2); C(11)−Rh−C(21) = 87.43(7), C(11)−Rh−C(1) = 86.34(7), C(21)−Rh−C(1) = 173.76(7), C(11)−Rh−C(3) = 107.50(7), C(21)−Rh−C(3) = 96.51(7), C(1)−Rh−C(3) = 85.68(7), C(11)−Rh−C(2) = 146.32(7), C(21)−Rh−C(2) = 95.37(7), C(1)−Rh−C(2) = 90.00(7), C(3)−Rh−C(2) = 38.82(7), C(11)−Rh−P = 105.37(5), C(21)−Rh−P = 88.93(5), C(1)−Rh−P = 92.42(5), C(11)−N(1)−C(12) = 165.21(17), C(21)−N(2)−C(22) = 173.73(17), F(2)−C(1)−F(1) = 102.82(14), F(2)−C(1)−F(3) = 102.65(14), F(1)−C(1)−F(3) = 102.10(14), F(2)−C(1)−Rh = 115.91(11), F(1)−C(1)−Rh = 117.65(12), F(3)−C(1)−Rh = 113.65(12), C(2)−C(3)−C(4) = 107.39(17), C(3)−C(2)−C(5) = 106.79(16), C(4)−C(3)−Rh = 112.34(12), C(5)−C(2)−Rh = 112.17(12).

solid showed only the presence of the cationic complex *trans*-$[Rh(CNXy)_2(PPh_3)_2]^+$, whose identity was confirmed by spectroscopy as well as by an independent synthesis of the salt *trans*-$[Rh(CNXy)_2(PPh_3)_2]CF_3CO_2$ (**5**), which was prepared by a modification of a reported method.[20] Thus, despite the fact that all starting material disappeared after a few minutes, the reaction is quite complex and unselective and only complex **5** could be identified and isolated in a low yield (18%). The ^{19}F NMR spectrum of the isolated yellow solid showed, apart from the signal of $CF_3CO_2^-$, two smaller signals at −140.7 and −154.7 ppm corresponding to the anions SiF_5^- [24] and BF_4^-,[25] respectively, which are likely to arise from the attack of the borosilicate glass of the flask by HF generated in the reaction.[24] In addition, we note that no CF_3H was detected in the reaction mixture by ^1H and ^{19}F NMR spectroscopy and that no signals of metal-bound fluorine were observed in the high-field region of the ^{19}F NMR spectrum, which, as one of the rewievers pointed out, would indicate an initial migration of fluorine to the metal. Therefore, C−F protonolysis seems to take place in the reaction of **1** with CF_3CO_2H to a detectable extent; however, given the complexity of the reaction, its mechanism was not further investigated.

Scheme 2



The reactions of **1** with $NOBF_4$ or Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) gave complex mixtures which could not be characterized. The treatment of **1** with bases such as NH_3, pyridine, and NaOMe did not produce any significant reaction at room temperature.

When complex **1** was treated with 35% H_2O_2 in an NMR tube, Ph_3PO and $[Rh(CF_3)(CNXy)_3]$ (**6**) were the main products detected by NMR (Scheme 2), together with **1** and other unidentified products. We have reported that in d_8-toluene solution, complex **1** is in equilibrium with traces of complexes **6** and *trans*-$[Rh(CF_3)(CNXy)(PPh_3)_2]$ resulting from the dissociation and recoordination of PPh_3 or XyNC ligands of **1**.[13] Therefore, the presence of H_2O_2 inhibits the formation of *trans*-$[Rh(CF_3)(CNXy)(PPh_3)_2]$, because the dissociated PPh_3 transforms into Ph_3PO and contributes to the formation of **6**.

Because $[Rh(CF_3)(CNXy)_3(PPh_3)]$ (**7**) contains three XyNC ligands and we have shown that it is partially dissociated in solution to give PPh_3 and **6**,[13] the reaction of **7** with H_2O_2 was carried out in order to prepare pure **6**. However, formation of **6** and Ph_3PO was observed, but the yields were moderate to low and were sometimes not reproducible.

To find a better method for the synthesis of **6**, the reaction of $[Rh(\mu\text{-}OH)(COD)]_2$[26] with XyNC and Me_3SiCF_3 was studied (Scheme 2). Under these conditions, complex **6** was formed as the main product together with small amounts of other unidentified isocyanide-containing products, which could be separated by crystallization to give pure **6** in moderate yields. It is noteworthy that, in contrast to the previously reported synthesis of trifluoromethyl complexes by using Me_3SiCF_3,[12−15] the formation of **6** took place without the need of fluoride ions to activate this reagent.[27] The stability of complex **6** is remarkable, because the Rh−CF_3 group is not significantly affected by the presence of H_2O and H_2O_2 during its synthesis. In addition, it is air stable, in contrast to **1** and **7**, which are easily oxidized to the peroxo Rh(III) complex $[Rh(CF_3)(\eta^2\text{-}O_2)(CNXy)_2(PPh_3)]$ in contact with air.[13]

When the reaction was carried out in an NMR tube (C_6D_6), two new signals at 0.12 and 0.10 ppm were

---

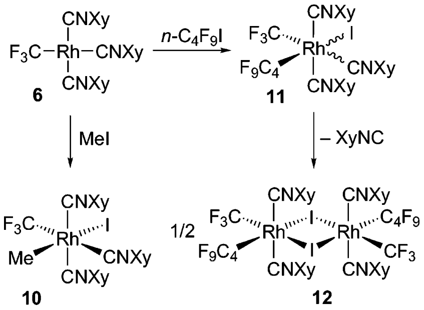
(24) Gorol, M.; Mösch-Zanetti, N. C.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Eur. J. Inorg. Chem.* **2004**, 2678.

(25) Gandelmann, M.; Konstantinovski, L.; Rozenberg, H.; Milstein, D. *Chem. Eur. J.* **2003**, *9*, 2595. Padelidakis, V.; Tyrra, W.; Naumann, D. *J. Fluorine Chem.* **1999**, *99*, 9. Plakhotnik, V. N.; Ernst, L.; Sakhaii, P.; Tovmash, N. F.; Schmutzler, R. *J. Fluorine Chem.* **1999**, *98*, 133.

(26) Usón, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126.

(27) Maggiarosa, N.; Tyrra, W.; Naumann, D.; Kirij, N. V.; Yagupolskii, Y. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 2252. Kolomeitsev, A.; Bissky, G.; Lork, E.; Movchun, V.; Rusanov, E.; Kirsch, P.; Röschenthaler, G.-V. *Chem. Commun.* **1999**, 1017. Prakash, G. K. S.; Yudin, A. K. *Chem. Rev.* **1997**, *97*, 757.

Scheme 3



observed in the ^{1}H NMR spectrum which were assigned to Me_3SiOH and $(Me_3Si)_2O$. GC/MS analysis of the reaction mixture confirmed the presence of both. Formation of $(Me_3Si)_2O$ can be explained by condensation of Me_3SiOH with another molecule of Me_3SiOH or by reaction with Me_3SiCF_3, which was added in excess.

The reaction of **6** with TCNE or MA gave the pentacoordinate complexes $[Rh(CF_3)(CNXy)_3L]$ (L = TCNE (**8**), MA (**9**)) (Scheme 2). Although we could not grow suitable single crystals to determine the geometry of these complexes, their NMR spectra are compatible with structures resulting from substitution of PPh_3 by XyNC in complexes **3** and **4**, respectively. The reaction of **6** with SO_2 or dimethyl acetylenedicarboxylate gave mixtures of products which could not be characterized.

Oxidative addition reactions with complexes **1** and **6** were studied. Unfortunately, the reactions of **1** with I_2, MeI, or n-C_4F_9I were not clean and the resulting complexes could not be isolated in pure form and characterized. In contrast, **6** reacted with MeI or n-C_4F_9I to afford $[Rh(CF_3)(R)I(CNXy)_3]$ (R = Me (**10**), n-C_4F_9 (**11**)) (Scheme 3) in good yield. The result of the reaction of **6** with MeI is in contrast with that of the analogous reaction of *trans*-$[Rh(CF_3)(CO)(PPh_3)_2]$, which gives $[Rh(CF_3)\{C(O)Me\}I(PPh_3)_2]$. This acyl complex results from oxidative addition of MeI, followed by CO insertion into the Rh–Me bond.[22] In our case, the insertion of XyNC to give an iminoacyl complex did not occur. A related result is the reaction of *trans*-$[Ir(CF_3)(CO)(PPh_3)_2]$ with MeI to give $[Ir(CF_3)(Me)I(CO)(PPh_3)_2]$.[28]

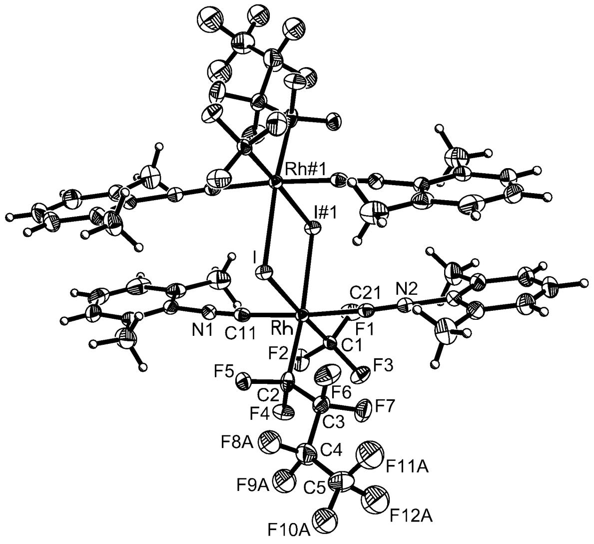


Figure 4. Molecular structure of **12** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Rh–C(21) = 1.976(5), Rh–C(11) = 1.978(5), Rh–C(1) = 2.075(5), Rh–C(2) = 2.090(5), Rh–I#1 = 2.7620(4), Rh–I = 2.7648(4), I–Rh#1 = 2.7620(4), N(1)–C(11) = 1.149(6), N(2)–C(21) = 1.152(6), F(1)–C(1) = 1.341(5), F(2)–C(1) = 1.336(5), F(3)–C(1) = 1.344(5), F(4)–C(2) = 1.358(5), F(5)–C(2) = 1.382(5); C(21)–Rh–C(11) = 173.76(18), C(21)–Rh–C(1) = 87.19(18), C(11)–Rh–C(1) = 90.50(18), C(21)–Rh–C(2) = 97.28(18), C(11)–Rh–C(2) = 88.54(18), C(1)–Rh–C(2) = 90.55(18), C(21)–Rh–I#1 = 86.98(13), C(11)–Rh–I#1 = 87.37(13), C(1)–Rh–I#1 = 93.23(12), C(2)–Rh–I#1 = 174.44(12), C(21)–Rh–I = 92.00(13), C(11)–Rh–I = 90.10(13), C(1)–Rh–I = 177.77(13), C(2)–Rh–I = 91.61(12), I#1–Rh–I = 84.647(13), Rh#1–I–Rh = 95.353(13), F(2)–C(1)–F(1) = 106.3(4), F(2)–C(1)–F(3) = 106.4(4), F(1)–C(1)–F(3) = 104.9(4), F(2)–C(1)–Rh = 113.7(3), F(1)–C(1)–Rh = 111.5(3), F(3)–C(1)–Rh = 113.3(3), F(4)–C(2)–F(5) = 104.9(4), F(4)–C(2)–C(3) = 107.2(4), F(5)–C(2)–C(3) = 106.2(4), F(4)–C(2)–Rh = 112.0(3), F(5)–C(2)–Rh = 108.0(3), C(3)–C(2)–Rh = 117.7(3).

Both **10** and **11** were characterized by spectroscopy as well as by elemental analysis. In addition, an X-ray diffraction analysis was carried out on single crystals of **10**. Despite the fact that the structural model could be crudely refined and its qualitative nature unambiguously established, iodine atom disorder over the two mutually trans sites precluded satisfactory refinement. The observed arrangement of the ligands around the metal is as shown in Scheme 3, with the XyNC ligands in a mer disposition and the Me and I ligands placed mutually in trans positions. This configuration results after a trans addition of MeI to complex **6**. The ^{1}H NMR spectra of **10** and **11** agree with the mer disposition of the XyNC ligands observed in the crystal structure of **10**. In addition, the presence of the Rh–Me bond was confirmed by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy (see Spectroscopic Characterization). The ^{19}F NMR spectrum of **11** showed the presence of the Rh-bound CF_3 and n-C_4F_9 groups, which were coupled with ^{103}Rh and with each other (see Spectroscopic Characterization). The attempts to grow single crystals of **11** by liquid diffusion were unsuccessful; however, by slow evaporation of a $CDCl_3$ solution of **11** in an NMR tube, single crystals grew after several days, which were used for an X-ray diffraction analysis. Surprisingly, the determined structure was that of the dinuclear complex $[\{Rh(CF_3)(n\text{-}C_4F_9)(CNXy)_2\}_2(\mu\text{-}I)_2]$ (**12**) (Figure 4 and Scheme 3) instead of that of complex **11**. The formation of **12** from **11** may be explained by dissociation of one XyNC ligand followed by dimerization through iodo bridging. However, all our attempts to synthesize **12** were unsuccessful. Thus, the ^{1}H and ^{19}F NMR spectra of **11** in $CDCl_3$ solution do not change significantly after 6 days at room temperature, and on heating the solution to 60 °C for 75 min a mixture of products was formed. Treatment of **11** with $[AuCl(SMe_2)]$ in order to remove a XyNC ligand by formation of [AuCl(CNXy)] did not give complex **12**. Assuming that the relative disposition of the ligands in **11** is not altered during the formation of **12**, the crystal structure of the latter suggests that in complex **11** the CF_3 and n-C_4F_9 groups are disposed cis to each other; however, it does not establish whether in **11** the iodo ligand is placed trans to the CF_3 or to the n-C_4F_9 group and, thus, if the oxidative addition occurred in a cis or trans fashion.

---

(28) Brothers, P. J.; Burrell, A. K.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R. *J. Organomet. Chem.* **1990**, *394*, 615.

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

compd	$\delta(^{19}F)$ (ppm)	$\delta(^{31}P)$ (ppm)	$^{1}J_{RhP}$ (Hz)	$^{2}J_{RhF}$ (Hz)	$^{3}J_{PF}$ (Hz)
$[Rh(CF_3)(CNXy)_2(PPh_3)(\eta^1\text{-}SO_2)]$ (**2**)	−9.5 dd	2.45 dq	92.1	19.8	50.6
$[Rh(CF_3)(CNXy)_2(PPh_3)(\eta^2\text{-TCNE})]$ (**3**)	3.6 d	28.5 d	99.8	14.4	*c*
$[Rh(CF_3)(CNXy)_2(PPh_3)(\eta^2\text{-MA})]$ (**4**)	−11.6 dd	28.9 dq	127.5	10.2	21.2
trans-$[Rh(CNXy)_2(PPh_3)_2]CF_3CO_2$ (**5**)	−74.9 s	31.0 d	122.9		
$[Rh(CF_3)(CNXy)_3]$ (**6**)	−9.6 d			24.3	
$[Rh(CF_3)(CNXy)_3(\eta^2\text{-TCNE})]$ (**8**)	1.7 d			14.2	
$[Rh(CF_3)(CNXy)_3(\eta^2\text{-MA})]$ (**9**)	−11.9 d			9.3	
$[Rh(CF_3)(Me)I(CNXy)_3]$ (**10**)	−11.2 d			15.8	
$[Rh(CF_3)(n\text{-}C_4F_9)I(CNXy)_3]$ (**11**)	−8.1 dtt[b]			13.6	

[a] Legend: s = singlet, d = doublet, t = triplet, q = quadruplet. [b] Rh−CF_3. [c] The $^{31}P-^{19}F$ coupling was not observed.

Spectroscopic Characterization. Complexes **2**, **3**, and **5** show in their ^1H NMR spectra a singlet corresponding to the Me groups of the equivalent XyNC ligands, while complex **4** showed two singlets corresponding to the axial and equatorial XyNC ligands. This is in agreement with its crystal structure and suggests that the solid-state structure is not altered in solution. Complexes **6**−**8** and **11** show two Me singlets in their ^1H NMR spectra of 2:1 intensity ratio, which suggest that two XyNC ligands are in a trans disposition. The Rh−Me group of complex **10** appears in the $^{13}C\{^1H\}$ NMR spectrum as a doublet of quadruplets at −8.1 ppm ($^1J_{RhC} = 20.6$ Hz and $^3J_{CF} = 5.5$ Hz) and in the ^1H NMR spectrum as a doublet at 1.41 ppm, with $^2J_{RhH} = 3.3$ Hz.

The ^{19}F NMR spectra of complexes **2** and **4** show doublets of doublets by coupling with ^{103}Rh and ^{31}P (Table 1), and their $^{31}P\{^1H\}$ NMR spectra show doublets of quadruplets, as expected. The ^{19}F and $^{31}P\{^1H\}$ NMR spectra of complex **3** show a doublet which is not split or broadened by lowering the temperature to −64 °C, suggesting that $^3J_{PF}$ is very small. Complexes **6**−**8** and **11** show a doublet in their ^{19}F NMR spectra, and **11** shows five multiplets, which were assigned by means of a $^{19}F,^{19}F$-COSY measurement. The Rh−CF_3 group appears as a doublet of triplets of triplets by coupling with ^{103}Rh and the α- and β-CF_2 groups; the latter groups give three complex multiplets, and the terminal CF_3 gives a triplet of triplets.

In the IR spectra, the $\nu(C{\equiv}N)$ bands of the XyNC and TCNE ligands appear in the ranges 2102−2204 and 2204−2218 cm^{-1}, respectively. The MA ligand in complexes **4** and **9** gives two $\nu(C{=}O)$ bands at 1808 and 1746 cm^{-1}. The $\nu(S{=}O)$ and $\nu(C-F)$ bands could not be assigned because of the presence of intense bands in the expected regions belonging to other ligands.

Crystallographic Studies. The molecular structures of complexes **2**−**4** and **12** have been determined by single-crystal X-ray diffraction studies. In compounds **2**−**4** the Rh−CF_3 bond distances (**2**, 2.066(2) Å; **3**, 2.065(3) Å; **4**, 2.0654(18) Å) and the mean C−F distances (**2**, 1.368 Å; **3**, 1.365 Å; **4**, 1.372 Å) are similar to those previously reported for Rh(I) trifluoromethyl complexes (Rh−CF_3, 2.051−2.112 Å; C−F, 1.369−1.381 Å).[13] The mean C−F distances are longer than those observed in compounds containing CF_3 groups bonded to nonmetallic atoms (1.322[29] and 1.33[30] Å). In complex **12**, the Rh−CF_2 distance (2.090(5) Å) is not significantly different from the Rh−CF_3 distance (2.075(5) Å), and it is close to the Rh−CF_2 distances reported in Rh(III) pentafluoroethyl or heptafluoropropyl complexes (2.052−2.086 Å).[16,17,19,31] The mean C−F distance observed in the CF_3 group of **12** (1.340 Å) is shorter than that of the CF_2 group (1.37 Å), which is in the range of mean C−F distances reported in the α-CF_2 groups of Rh(III) pentafluoroethyl or heptafluoropropyl complexes (1.34−1.395 Å). As has been noted previously,[13,17] the mean Rh−C−F angles in complexes **2**−**4** and **12** (**2**, 114.85°; **3**, 114.93°; **4**, 115.74°; **12**, 112.8° (CF_3) and 110.0° (α-CF_2)) are larger and the F−C−F angles (**2**, 103.54°; **3**, 103.47°; **4**, 102.52°; **12**, 105.9° (CF_3) and 104.9° (α-CF_2)) are smaller than the ideal tetrahedral angle, in agreement with the VSEPR model.

The geometry of complex **2** is pseudo square pyramidal. The SO_2 ligand is placed in the apical position, and the isocyanide ligands are disposed trans to each other. The C(1)−Rh−P and C(2)−Rh−C(3) angles are 166.68(6) and 168.24(8)°, respectively, and the angles between the sulfur atom and the Rh-bonded carbon and phosphorus atoms are in the range 91.24(6)−101.996(18)°. The SO_2 ligand is η^1 coordinated through the sulfur atom and has a pyramidal geometry. The Rh−S and S−O distances (Rh−S, 2.3763(5) Å; S−O, 1.4655(16) and 1.4679(15) Å) and the O−S−Rh and O−S−O angles (O−S−Rh, 103.64(6) and 104.24(6)°; O−S−O, 113.19(9)°) fall in the range of values reported for Rh(I) complexes containing a pyramidal SO_2 ligand coordinated through the S atom.[32] The S−O bonds of the SO_2 ligand are bent away from the CF_3 group and toward the PPh_3 and an XyNC ligand.

Complex **3** possess a distorted-trigonal-bipyramidal geometry, with the isocyanide ligands placed in axial positions (C(8)−Rh−C(9), 177.02(14)°). Concerning the equatorial ligands, the CF_3−Rh−P angle is 100.07(10)°, and the *C*′−Rh−P and *C*′−Rh−CF_3 (*C*′ is the centroid of the TCNE olefinic carbons) angles are 138.60 and 121.41°, respectively. The olefinic carbons of the TCNE ligand are approximately coplanar with Rh, the CF_3 carbon, and the phosphorus atoms. As expected, the TCNE ligand is significantly distorted from planarity (the distances between the average plane of C(4), C(5), C(6), and C(7) carbon atoms and the olefinic carbons C(2) and C(3) are 0.437 and 0.428 Å, respectively). The Rh−C (2.122(3) and 2.216(3) Å) and C=C (1.509(5) Å) distances are comparable to the previously reported

---

(29) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(30) Yokozeki, A.; Bauer, S. H. *Top. Curr. Chem.* **1973**, *53*, 71.

(31) Churchill, M. R. *Inorg. Chem.* **1965**, *4*, 1734. Hughes, R. P.; Kovacik, I.; Lindner, D. C.; Smith, J. M.; Willemsen, S.; Zhang, D.; Guzei, I. A.; Rheingold, A. L. *Organometallics* **2001**, *20*, 3190.

(32) Kubas, G. J.; Ryan, R. R. *Inorg. Chim. Acta* **1981**, *47*, 131. Lindner, E.; Keppeler, B.; Fawzi, R.; Steinmann, M. *Chem. Ber.* **1996**, *129*, 1103. Muir, K. W.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 1921. Eller, P. G.; Ryan, R. R. *Inorg. Chem.* **1980**, *19*, 142. Doux, M.; Mézailles, N.; Ricard, L.; Le Floch, P. *Organometallics* **2003**, *22*, 4624.

values for Rh(I) TCNE complexes.[33] The C═C bond distance is considerably larger than in the free ligand (1.355(2) Å)[34] and is in the range of single C−C bond distances.[29]

In complex **4**, the geometry around the metal is distorted trigonal bipyramidal. In contrast to **2** and **3**, where the isocyanide ligands are mutually trans, in complex **4** an isocyanide and the CF_3 ligand are placed in axial positions (C−Rh−C, 173.76(7)°). The angles between the metal atom and the axial and equatorial donor atoms are close to 90° (85.68(7)−96.51(7)°). The rhodium atom, the olefinic and CF_3 carbons, and the phosphorus atom are roughly coplanar, and the bond angles in the equatorial plane are 105.37(5)° (P−Rh−CN) and 126.93 and 127.56° (*C*′−Rh−CN and *C*′−Rh−P, where *C*′ is the centroid of the MA olefinic carbons). The maleic anhydride ligand is oriented toward the isocyanide, probably in order to reduce the steric repulsion with the CF_3 group fluorine atoms. The distance between the olefinic carbons (1.430(3) Å) is significantly longer than in the free molecule (1.332 Å).[35] According to a Cambridge Structural Database search,[36] this is the first crystal structure determination on a Rh complex with MA. The Rh−C(alkene) distances (2.1536(18) and 2.1491(18) Å) are slightly longer than the values found in **3** and are within the range of Rh−C distances found in Rh(I) complexes with $MeO_2CCH═CHCO_2Me$ (2.092−2.193 Å).[37] The C═C distance is within the range of distances reported in transition-metal MA complexes (1.396−1.514 Å).[36]

In complex **12**, both metal centers are equivalent and show a distorted-octahedral coordination, with the isocyanide ligands in a mutually trans disposition. The phenyl rings of the isocyanide ligands bonded to different Rh atoms of the same molecule are nearly parallel (the angle between the mean planes defined by the rings is 5.8°) and the Rh−C≡N−Xy chains are bent,[38] giving rise to a parallel offset disposition of the rings (Figure 5), which probably is adopted in order to minimize steric repulsion and favor stabilizing interactions between the π-electron densities.[39] The distance between the centroids of the phenyl rings is 3.978 Å, and the angles between the vector defined by the centroids of the rings and the mean planes of the rings are 64.6 and 64.3°. The Rh−I distances (2.7620(4) and 2.7648(4) Å) are similar to the values reported in Rh(III) containing μ-iodo ligands.[40]

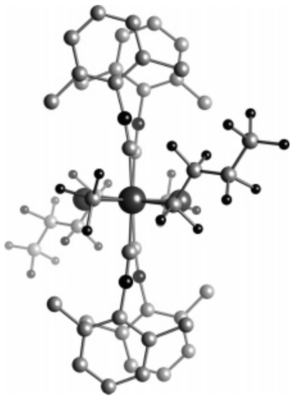


Figure 5. Drawing of the structure of **12** down the Rh−Rh axis, showing the arrangement of the phenyl rings.

Conclusions

The reactivities of the square-planar trifluoromethyl Rh(I) complexes *trans*-$[Rh(CF_3)(CNXy)_2(PPh_3)]$ (**1**) and $[Rh(CF_3)(CNXy)_3]$ (**6**) have been studied. They react with SO_2, TCNE, or MA to give formally Rh(I) pentacoordinate adducts which are the first examples of Rh(I) perfluoroalkyl complexes containing SO_2, TCNE, and MA ligands. No CO, isocyanide, or olefin insertion reactions into the Rh−CF_3 bond have been observed. This lack of reactivity toward insertion of unsaturated molecules is in line with the reported behavior of transition-metal trifluoromethyl complexes, which has been attributed to thermodynamic and kinetic factors.[5−8] Complex **6** has been prepared by a fluoride-free method using the reaction of $[Rh(\mu\text{-}OH)(COD)]_2$ with XyNC and Me_3SiCF_3. Given that the hydroxo complex is easily available, this method could be a simpler way to prepare Rh(I) perfluoroalkyl complexes starting from the desired Me_3SiR_F reagent. Work on the synthesis of new Rh(I) perfluoroalkyl complexes by this method is currently in progress. The reactions of **6** with MeI or n-C_4F_9I gave the octahedral complexes $[Rh(CF_3)(R)I(CNXy)_3]$ (R = Me, n-C_4F_9) resulting from oxidative addition reactions, the latter being a rare example of a Rh(III) complex containing two perfluoroalkyl ligands. We are currently working on the synthesis of new Rh(III) complexes containing different R_F groups and on the study of their reactivity.

Experimental Section

General Considerations. The preparation of compounds **1**,[13] **7**,[13] *trans*-$[RhCl(CO)(PPh_3)_2]$,[41] and $[Rh(\mu\text{-}OH)(COD)]_2$[26] was carried out as previously described. SO_2 was produced by dropwise addition of H_2SO_4 (98%) to anhydrous Na_2SO_3 in a previously deoxygenated system and dried through a $CaCl_2$ tube. Other reagents were obtained from commercial sources and used without further purification: Me_3SiCF_3, 2,6-dimethylphenyl isocyanide (XyNC), and maleic anhydride (MA) from Fluka, tetracyanoethylene (TCNE) and n-C_4F_9I from Aldrich, and MeI from Panreac. All manipulations were carried out under an inert atmosphere of nitrogen by using standard Schlenk techniques. THF, toluene, and Et_2O were distilled over sodium−benzophenone, n-hexane and $CDCl_3$ were passed through a basic alumina column and deoxygenated, and n-pentane, CH_2Cl_2, and C_6D_6 were 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

---

[33] Bruce, M. I.; Ellis, B. G.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000**, *607*, 137. Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, G. *J. Organomet. Chem.* **1982**, *235*, 105.

[34] Becker, P.; Coppens, P.; Ross, F. K. *J. Am. Chem. Soc.* **1973**, *95*, 7604.

[35] Lutz, M. *Acta Crystallogr., Sect. E* **2001**, *57*, o1136.

[36] Cambridge Structural Database, version 5.26, May 2005.

[37] Yoshida, T.; Okano, T.; Otsuka, S.; Miura, I.; Kubota, T.; Kafuku, K.; Nakatsu, K. *Inorg. Chim. Acta* **1985**, *100*, 7. Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F. *Organometallics* **1990**, *9*, 2283. Mantovani, L.; Ceccon, A.; Gambaro, A.; Santi, S.; Ganis, P.; Venzo, A. *Organometallics* **1997**, *16*, 2682.

[38] The torsion angles between the vectors defined by Rh and the para carbon of the CNXy ligands are 17.4°.

[39] Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 2* **2001**, 651. Magistrato, A.; Pregosin, P. S.; Albinati, A.; Rothlisberger, U. *Organometallics* **2001**, *20*, 4178.

[40] Adamson, G. W.; Daly, J. J.; Forster, D. *J. Organomet. Chem.* **1974**, *71*, C17. Rizkallah, P. J.; Maginn, S. J.; Harding, M. M. *Acta Crystallogr., Sect. B* **1990**, *46*, 193. Moloy, K. G.; Petersen, J. L. *Organometallics* **1995**, *14*, 2931. Dilworth, J. R.; Morales, D.; Zheng, Y. F. *Dalton Trans.* **2000**, 3007. Thomas, C. M.; Neels, A.; Staeckli-Evans, H.; Suss-Fink, G. *Eur. J. Inorg. Chem.* **2001**, 3005.

[41] Evans, D.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1968**, *11*, 99.

mulls between polyethylene sheets. C, H, N, S analyses were carried out with Carlo Erba 1108 and LECO CHS-932 microanalyzers. NMR spectra were measured on Bruker Avance 200, 300, and 400 instruments. ^{1}H 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{^{1}H} 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{^{1}H} NMR spectra were referenced externally to H_3PO_4 (0 ppm). In cases where ^{13}C, ^{19}F, or ^{31}P{^{1}H} NMR spectra were measured in nondeuterated solvent, an external CD_3SOCD_3 capillary was used for locking and referencing. Abreviations used: vt = virtual triplet; br = broad; sh = shoulder; $N = {}^1J_{PC} + {}^3J_{PC}$. The temperature values in NMR experiments were not corrected. Melting points were determined on a Reichert apparatus under an air atmosphere.

[Rh(CF$_3$)(CNXy)$_2$(PPh$_3$)(η^1-SO$_2$)] (2). A solution of [RhF(COD)(PPh$_3$)] (106 mg, 0.22 mmol) in THF (5 mL) was treated with Me_3SiCF_3 (0.20 mL of a 2.0 M solution in THF, 0.40 mmol) at room temperature. After 5 min of stirring, XyNC (57 mg, 0.43 mmol) was added and the mixture was stirred for 1 h and evaporated to dryness under vacuum. The residue (complex **1**) was dissolved in THF (5 mL), and a stream of SO_2 was bubbled through the solution for 1 min. When the bubbling was stopped, the tube containing the reaction mixture was sealed and the solution was stirred for 30 min. The resulting solution was evaporated to dryness and, by addition of *n*-pentane (5 mL), a yellow greenish solid precipitated. The mother liquor was removed, and the solid was washed with *n*-pentane (2 × 5 mL) and dried under vacuum. Yield: 149 mg, 91%. Mp: 113 °C dec. Anal. Calcd for $C_{37}H_{33}N_2F_3O_2PRhS$: C, 58.43; H, 4.37; N, 3.68; S, 4.22. Found: C, 58.37; H, 4.61; N, 3.86; S, 4.12. IR (Nujol, cm^{-1}): ν(C≡N) 2151 (s). ^{1}H NMR (300.1 MHz, C_6D_6): δ 7.87 (m, 6 H, H2, Ph), 6.91 (m, 9 H, H3 and H4, Ph), 6.66−6.46 (AB$_2$ m, 6 H, Xy), 2.00 (s, 12 H, Me). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ 136.0 (C2, Xy), 134.0 (d, J_{PC} = 12.1 Hz, Ph), 133.2 (d, $^1J_{PC}$ = 41.3 Hz, C1, Ph), 130.6 (C4, Ph), 129.3 (C4, Xy), 128.7 (d, J_{PC} = 10.0 Hz, Ph), 127.8 (C3, Xy), 126.5 (C1, Xy), 18.2 (Me); the signals of CF$_3$ and C≡N carbons were not observed. ^{19}F NMR (282.4 MHz, C_6D_6): δ −9.5 (dd, $^3J_{PF}$ = 50.6 Hz, $^2J_{RhF}$ = 19.8 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 24.5 (dq, $^1J_{RhP}$ = 92.1 Hz, $^3J_{PF}$ = 50.4 Hz).

[Rh(CF$_3$)(CNXy)$_2$(PPh$_3$)(η^2-TCNE)] (3). A solution of **1** in THF (5 mL) was prepared as for **2** from [RhF(COD)(PPh$_3$)] (77 mg, 0.16 mmol), Me_3SiCF_3 (0.32 mmol), and XyNC (43 mg, 0.33 mmol). TCNE (21 mg, 0.16 mmol) was added to this solution to give a green solution which turned brown in about 5 min. After it was stirred for 30 min, it was evaporated to dryness and Et$_2$O (5 mL) was added to give a beige precipitate. The mother liquor was removed, and the solid was washed with Et$_2$O (2 × 5 mL) and dried under vacuum. Yield: 121 mg, 94%. Mp: 154 °C. Anal. Calcd for $C_{41}H_{35}N_2F_3O_3PRh$: C, 62.63; H, 4.03; N, 10.19. Found: C, 62.40; H, 3.93; N, 9.90. IR (Nujol, cm^{-1}): ν(C≡N, XyNC) 2188 (s), ν(C≡N, TCNE) 2218 (m), 2212, 2204 (m). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.58 (m, 6 H, H2, Ph), 7.46−7.36 (m, 9 H, H3 and H4, Ph), 7.20−6.98 (AB$_2$ m, 6 H, Xy), 2.11 (s, 12 H, Me). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 137.3 (C2, Xy), 133.5 (d, J_{PC} = 11.1 Hz, Ph), 131.5 (d, J_{PC} = 3.0 Hz, C4, Ph), 130.9 (d, $^1J_{PC}$ = 45.0 Hz, C1, Ph), 130.5 (C4, Xy), 129.0 (d, J_{PC} = 11.1 Hz, Ph), 128.1 (C3, Xy), 125.2 (C1, Xy), 117.6, 116.6, 116.5 (three s, C−*C*N), 18.3 (s, Me); the signals of CF$_3$, Rh−CN, and C=C carbons were not observed. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ 3.6 (d, $^3J_{RhF}$ = 14.4 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 28.5 (d, $^1J_{RhP}$ = 99.8 Hz).

[Rh(CF$_3$)(CNXy)$_2$(PPh$_3$)(η^2-MA)] (4). A solution of **1** in THF (5 mL) was prepared as for **2** from [RhF(COD)(PPh$_3$)] (96 mg, 0.19 mmol), Me_3SiCF_3 (0.40 mmol), and XyNC (52 mg, 0.40 mmol). Maleic anhydride (22 mg, 0.22 mmol) was added to give an orange solution, which was stirred for 1 h and then evaporated to dryness. Et$_2$O (5 mL) was added to precipitate an oil, which was converted into a yellow solid by stirring for 15 min at 0 °C. The mother liquor was removed, and the solid was washed with Et$_2$O (2 × 3 mL) and dried under vacuum. Yield: 79 mg, 51%. Mp: 168−171 °C dec. Anal. Calcd for $C_{41}H_{35}F_3N_2O_3PRh$: C, 61.97; H, 4.44; N, 3.35. Found: C, 62.09; H, 4.51; N, 3.58. IR (Nujol, cm^{-1}): ν(C≡N) 2164 (s), 2136 (s), ν(C=O) 1808 (s), 1746 (s). ^{1}H NMR (300.1 MHz, C_6D_6): δ 7.87 (m, 6 H, H2, Ph), 6.99 (m, 6 H, H3, Ph), 6.88 (m, 3 H, H4, Ph), 6.76−6.37 (two AB$_2$ m, 6 H, Xy), 4.79 (m, 1 H, C*H*=CH), 4.23 (m, 1 H, CH=C*H*), 2.25 (s, 6 H, Me), 1.91 (s, 6 H, Me). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 176.0 (C=O), 175.4 (C=O), 155.5 (C≡N), 152.7 (C≡N), 135.5 (C2, Xy), 134.4 (C2, Xy), 134.7 (d, $^1J_{PC}$ = 37.3 Hz, C1, Ph), 133.7 (d, J_{PC} = 11.5 Hz, Ph), 129.9 (s, C4, Ph), 129.2 (both C4, Xy), 128.3 (d, J_{PC} = 9.7 Hz, Ph), 128.1 (C3, Xy), 127.7 (C3, Xy), 127.5 (C1, Xy), 126.4 (C1, Xy), 44.4 (dm, $^1J_{RhC}$ = 31.5 Hz, C=C), 42.4 (m, C=C), 18.9 (Me), 18.5 (Me); the signal of CF$_3$ carbon was not observed. ^{19}F NMR (282.4 MHz, C_6D_6): δ −11.6 (dd, $^3J_{PF}$ = 21.2 Hz, $^2J_{RhF}$ = 10.2 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 28.9 (dq, $^1J_{RhP}$ = 127.5 Hz, $^3J_{PF}$ = 20.7 Hz).

Reaction of 1 with CO. A solution of **1** (15 mg, 0.022 mmol) in d_8-toluene (0.5 mL) was placed into an NMR tube sealed with a septum cap. Then, a stream of CO was bubbled through the solution by means of a needle for 1 min. The color of the solution changed from yellow-orange to yellow. The spectroscopic data for the obtained solution are as follows. IR (CH_2Cl_2, cm^{-1}): ν(C≡N) 2116, 2086 (s, [Rh(CF$_3$)(CNXy)$_2$(CO)(PPh$_3$)]), ν(CO) 2018 (m), 1976 (sh), 1958 (s, [Rh(CF$_3$)(CNXy)$_2$(CO)(PPh$_3$)]). ^{1}H NMR (200.1 MHz, d_8-toluene): 25 °C, δ 7.68 (m, 6 H, H2, Ph), 6.97 (m, 9 H, H3 and H4, Ph), 6.76−6.58 (AB$_2$ m, 6 H, Xy), 2.01 (s, 12 H, Me). ^{19}F NMR (188.3 MHz, d_8-toluene): 25 °C, δ 3.9 (br s); −60 °C, δ 6.8 (dd, relative intensity = 9%, $^3J_{PF}$ = 61.1 Hz, $^2J_{RhF}$ = 7.6 Hz, [Rh(CF$_3$)(CNXy)(CO)$_2$(PPh$_3$)]), 5.7 (dd, relative intensity 86%, $^3J_{PF}$ = 61.0 Hz, $^2J_{RhF}$ = 8.0 Hz, [Rh(CF$_3$)(CNXy)$_2$(CO)(PPh$_3$)]), 4.7 (dd, relative intensity 4%, $^3J_{PF}$ = 60.8 Hz, $^2J_{RhF}$ = 8.0 Hz), 3.9 (d, relative intensity 1%, $^2J_{RhF}$ = 9.1 Hz). ^{31}P{^{1}H} NMR (81.0 MHz, d_8-toluene): 25 °C, δ 35.5 (br s); −60 °C (162.3 MHz, d_8-toluene), δ 40.9 (dq, $^1J_{RhP}$ = 74.9 Hz, $^3J_{PF}$ = 60.9 Hz, [Rh(CF$_3$)(CNXy)$_2$(CO)(PPh$_3$)]), 36.4 (dq, $^1J_{RhP}$ = 71.9 Hz, $^3J_{PF}$ = 60.8 Hz, [Rh(CF$_3$)(CNXy)(CO)$_2$(PPh$_3$)]).

Reaction of 1 with CF$_3$CO$_2$H. A solution of **1** (17 mg, 0.024 mmol) in C_6D_6 (0.5 mL) was treated with CF_3CO_2H (2 μL, 0.026 mmol). After 10 min, the NMR spectrum of the resulting solution showed a complex mixture of compounds. After 30 min, a yellow solid started to precipitate in the NMR tube, and 1 h later, the solution was removed and the solid washed with Et$_2$O (1 mL) and dried under vacuum. Larger amounts of the yellow solid were obtained in the following way: a solution of **1** was prepared as for **2** from [RhF(COD)(PPh$_3$)] (147 mg, 0.30 mmol), Me_3SiCF_3 (0.6 mmol), and XyNC (79 mg, 0.60 mmol) in THF (5 mL). The volatiles were removed in vacuo, the residue was disolved in toluene (3 mL), and CF_3CO_2H (23 μL, 0.31 mmol) was added. The solution was stirred for a few seconds and stored for 4 h without stirring. A yellow microcrystalline solid precipitated, which was filtered, washed with *n*-pentane (3 × 5 mL), and dried in vacuo. Yield: 55 mg, 18% (calcd as trifluoroacetate). IR (Nujol): ν(C≡N) 2126 (s), ν(C=O) 1696 (m). The ^{1}H and ^{31}P NMR spectra of this solid were identical with those of complex **5** (see below). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −75.9 (s, $CF_3CO_2^-$), −140.7 (s, SiF_5^-), −154.68 (br s, $^{10}BF_4^-$), −154.73 (br s, $^{11}BF_4^-$). MS (+FAB): *m/z* 889 ([Rh(CNXy)$_2$(PPh$_3$)$_2$]$^+$), 758 ([Rh(CNXy)(PPh$_3$)$_2$]$^+$), 627 ([Rh(CNXy)$_2$(PPh$_3$)]$^+$), 496 ([Rh(CNXy)(PPh$_3$)]$^+$). MS (−ESI): *m/z* 123 (SiF_5^-), 113 ($CF_3CO_2^-$), 87 (BF_4^-), 69 (CF_3^-).

***trans*-[Rh(CNXy)$_2$(PPh$_3$)$_2$]CF$_3$CO$_2$ (5).** Complex **5** was prepared by a modification of the procedure reported by Dart and co-workers.[20] A suspension of *trans*-[RhCl(CO)(PPh$_3$)$_2$] (140 mg, 0.20 mmol) in CH_2Cl_2/MeOH (1:1, 30 mL) was treated with XyNC (53 mg, 0.40 mmol) and $NaCF_3CO_2$ (28 mg, 0.21

Table 2. Crystal Data for Complexes 2−4 and 12

	2	**3**	**4**	**12**
formula	$C_{37}H_{33}F_3N_2O_2PRhS$	$C_{44}H_{35}Cl_2F_3N_6PRh$	$C_{47}H_{35}D_6F_3N_2O_3PRh$	$C_{48}H_{38}Cl_6F_{24}I_2N_4Rh_2$
M_r	760.59	909.56	878.70	1799.14
cryst size (mm)	0.36 × 0.29 × 0.18	0.26 × 0.14 × 0.14	0.35 × 0.32 × 0.20	0.33 × 0.12 × 0.10
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$C2/c$
cell constants				
a, Å	11.9599(6)	18.6130(8)	9.4633(4)	29.9171(14)
b, Å	18.4790(9)	10.1753(4)	14.5730(6)	16.2557(7)
c, Å	15.7470(7)	21.6122(11)	14.9666(6)	12.9824(6)
α, deg	90	90	86.404(2)	90
β, deg	92.871(2)	95.826(2)	83.216(2)	95.397(2)
γ, deg	90	90	81.008(2)	90
V, Å^3; Z	3475.8(3); 4	4072.1(3); 4	2022.32(14); 2	6285.7(5); 4
λ, Å	0.710 73			
ρ(calcd), Mg m^{-3})	1.453	1.484	1.443	1.901
F(000)	1552	1848	896	3472
T, K	100(2)	100(2)	100(2)	100(2)
μ (mm^{-1})	0.649	0.644	0.520	1.871
transmissns	0.8922 and 0.8000	0.9152 and 0.8504	0.9032 and 0.8390	0.8350 and 0.5772
θ range, deg	1.70−26.37	1.89−26.37	1.93−28.17	2.08−26.37
limiting indices	$-14 \leq h \leq 14$	$-23 \leq h \leq 23$	$-12 \leq h \leq 12$	$-37 \leq h \leq 37$
	$-23 \leq k \leq 23$	$-12 \leq k \leq 12$	$-18 \leq k \leq 18$	$-20 \leq k \leq 20$
	$-19 \leq l \leq 19$	$-27 \leq l \leq 27$	$-19 \leq l \leq 18$	$-16 \leq l \leq 16$
no. of rflns				
measd	37 871	44 003	23 736	34 138
indep	7106	8303	9081	6429
R_{int}	0.029	0.0615	0.0201	0.0213
abs cor	semiempirical from equivalents			
refinement method	full-matrix least-squares on F^2			
no. of data/restraints/params	7106/40/431	8303/40/518	9081/48/518	6429/21/386
$S(F^2)$	1.157	1.103	1.084	1.030
R1^a	0.0294	0.0490	0.0290	0.0443
wR2^b	0.0709	0.1147	0.0724	0.1069
largest diff peak, e Å^{-3}	0.572	1.296	0.568	2.157
max Δr, e Å^{-3}	−0.263	−0.823	−0.618	−2.109

[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.

mmol). The mixture was stirred for 30 min and evaporated to dryness under vacuum, and the residue was extracted with CH_2Cl_2 (5 mL). The yellow extract was filtered and concentrated up to ca. 0.5 mL, and Et_2O (5 mL) was added to precipitate a yellow solid. The solution was removed, and the solid was washed with Et_2O (2 × 5 mL) and dried under vacuum. Yield: 130 mg, 65%. Mp: 153−156 °C dec. Anal. Calcd for $C_{56}H_{48}N_2F_3O_2P_2Rh$: C, 67.07; H, 4.82; N, 2.79. Found: C, 66.89; H, 4.88; N, 2.65. IR (Nujol, cm^{-1}): ν(C≡N) 2132 (s), ν(C═O) 1696 (m). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 7.65 (m, 12 H, H2, Ph), 7.34 (m, 18 H, H3 and H4, Ph), 7.07−6.82 (AB_2 m, 6 H, Xy), 1.62 (s, 12 H, Me). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 161.0 (q, $^2J_{FC}$ = 34.6 Hz, CO_2CF_3), 156.1 (br d, $^1J_{RhC}$ = 52 Hz, Rh−CN), 134.1 (s, Xy), 133.7 (vt, N = 12.5 Hz, C2, Ph), 132.6 (vt, N = 46.4 Hz, C1, Ph), 131.0 (s, C4, Ph), 128.9 (s, Xy), 128.7 (s, C3, Ph), 127.6 (s, Xy), 125.2 (s, Xy), 117.0 (q, $^1J_{FC}$ = 293.4 Hz, CF_3), 17.8 (s, Me). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −74.9 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 31.0 (d, $^1J_{RhP}$ = 122.9 Hz).

[Rh(CF_3)(CNXy)$_3$] (6). Method A. A solution of [RhF(COD)(PPh_3)] (251 mg, 0.51 mmol) in THF (6 mL) was treated with Me_3SiCF_3 (0.51 mL of a 2.0 M solution in THF, 1.02 mmol) at room temperature and stirred for 5 min. XyNC (207 mg, 1.58 mmol) was added, and after the mixture was stirred for 45 min, the volatiles were removed under vacuum. The residue was dissolved in THF (5 mL) and the solution treated with H_2O_2 (44 μL, 35%, 0.51 mmol). After it was stirred for 30 min at room temperature, the solution was concentrated to dryness under vacuum and the residue treated with EtOH (2 mL) to give a yellow solid, which was filtered, washed with EtOH (2 × 2 mL), and dried under vacuum. Yield: 159 mg, 55%.

Method B. Solid [Rh(μ-OH)(COD)]$_2$ (100 mg, 0.22 mmol) was added in small portions for a period of 3 min to a solution of XyNC (179 mg, 1.36 mmol) and Me_3SiCF_3 (0.6 mL of a 2.3 M THF solution, 1.38 mmol) in THF (7 mL). The brown solution was stirred for 15 min and concentrated under vacuum to about 1 mL; Et_2O (5 mL) was added, and the flask was stored at −30 °C overnight. A yellow microcrystalline solid formed. The mother liquor was removed, and the solid was washed with cold Et_2O (−20 °C, 3 × 3 mL) and dried under vacuum. Yield: 140 mg, 56%. Mp: 149−152 °C dec. Anal. Calcd for $C_{28}H_{27}N_3F_3Rh$: C, 59.48; H, 4.81; N, 7.43. Found: C, 59.33; H, 4.67; N, 7.33. IR (Nujol, cm^{-1}): ν(C≡N) 2118 (s), 2102 (s). ^{1}H NMR (300.1 MHz, C_6D_6): δ 6.80−6.55 (two AB_2 m, 9 H, Xy), 2.22 (s, 12 H, Me), 2.14 (s, 6 H, Me). $^{13}C\{^1H\}$ NMR (50.3 MHz, THF/CD_3SOCD_3(ext)): δ 135.5 (C2, 2 Xy), 134.7 (C2, Xy), 128.7 (CH, Xy), 128.2 (CH, Xy), 128.13 (CH, Xy), 128.08 (CH, Xy), 18.4 (Me, Xy), 18.2 (Me, 2 Xy); the signals of CF_3, C1 of Xy, and C≡N carbons were not observed. ^{19}F NMR (282.4 MHz, C_6D_6): δ −9.6 (d, $^2J_{RhF}$ = 24.3 Hz).

[Rh(CF_3)(CNXy)$_3$(η^2-TCNE)] (8). A solution of **6** (85 mg, 0.15 mmol) in THF (4 mL), was treated with TCNE (20 mg, 0.16 mmol) at room temperature. The resulting yellow solution was stirred for 1 h and concentrated to dryness under vacuum. Et_2O (5 mL) was added to precipitate a pale yellow solid, which was washed with Et_2O (2 × 5 mL) and dried under vacuum. Yield: 97 mg, 93%. Mp: 168−170 °C dec. Anal. Calcd for $C_{34}H_{27}N_7F_3Rh$: C, 58.88; H, 3.92; N, 14.14. Found: C, 59.00; H, 4.21; N, 13.73. IR (Nujol, cm^{-1}): ν(C≡NXy) 2182 (s), ν(C≡N, TCNE) 2206 (s). ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.37−7.09 (two AB_2 m, 9 H, Xy), 2.522 (s, 6 H, Me), 2.515 (s, 12 H, Me). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 137.1, 135.9 (C2 Xy), 130.9, 128.5, 128.3 (C3 + C4 Xy), 117.3, 116.2 (C1 Xy), 18.6 (Me); the signals of CF_3 and C≡N carbons were not observed. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ 1.7 (d, $^2J_{RhF} = 14.2$ Hz).

[Rh(CF_3)(CNXy)$_3$(η^2-MA)] (9). A solution of **6** (72 mg, 0.13 mmol) in THF (10 mL) was treated with MA (14 mg, 0.14 mmol) at room temperature. The resulting pale yellow solution was stirred for 1 h and evaporated to dryness under vacuum. Et_2O (3 mL) was added to precipitate a pale yellow solid which was washed with Et_2O (3 mL) and dried under vacuum. Yield: 60 mg, 71%. Mp: 166−168 °C dec. Anal. Calcd for $C_{32}H_{29}N_3F_3O_3Rh$: C, 57.93; H, 4.41; N, 6.33. Found: 58.16; H, 4.49; N, 6.33. IR (Nujol, cm^{-1}): ν(C≡N) 2188 (s), 2162 (s), 2146 (s), ν(C=O) 1808 (s), 1746 (s). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.23−7.06 (two AB_2 m, 9 H, Ar, Xy), 4.26 (br s, 2 H, CH=CH), 2.48 (s, 12 H, Me), 2.39 (s, 6 H, Me). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 175.6 (s, C=O), 151.8 (br d, $^1J_{RhC} = 49$ Hz, XyN*C*), 150.0 (br s, XyN*C*), 135.5 (s, Xy), 135.4 (s, Xy), 129.7 (s, Xy), 129.3 (s, Xy), 128.0 (s, Xy), 127.2 (s, Xy), 126.3 (s, Xy), 18.63 (s, Me), 18.58 (s, Me); the signal of CF_3 carbon was not observed. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −11.9 (d, $^2J_{RhF} = 9.3$ Hz).

[Rh(CF_3)(Me)I(CNXy)$_3$] (10). A solution of **6** (72 mg, 0.13 mmol) in THF (10 mL) was treated with MeI (12 μL, 0.19 mmol) at room temperature. The resulting pale yellow solution was stirred for 1 h and then evaporated to dryness under vacuum. *n*-Pentane (5 mL) was added to precipitate an oil, which was converted into a pale yellow solid by stirring for 15 min at 0 °C. The solid was washed with *n*-pentane (2 × 5 mL) and dried under vacuum. Yield: 89 mg, 79%. Mp: 226−228 °C dec. Anal. Calcd for $C_{29}H_{30}N_3F_3IRh$: C, 49.24; H, 4.27; N, 5.94. Found: C, 49.57; H, 4.48; N, 5.86. IR (Nujol, cm^{-1}): ν(C≡N) 2178 (s). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.23−7.10 (two AB_2 m, 9 H, Xy), 2.52 (s, 12 H, Me, Xy), 2.51 (s, 6 H, Me, Xy), 1.41 (d, 3 H, $^2J_{RhH} = 3.3$ Hz, Me−Rh). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ 136.0 (C4, 2 Xy), 135.7 (C4, Xy), 129.8 (C2, Xy), 129.7 (C2, 2 Xy), 128.2 (C3, Xy), 128.0 (C3, 2 Xy), 126.4 (br s, C1, 2 Xy), 18.9 (Me, Xy), 18.8 (Me, 2 Xy), −8.1 (dq, Me-Rh, $^1J_{RhC} = 20.6$ Hz, $^3J_{CF} = 5.5$ Hz); the C1 signal of the equatorial Xy group is probably overlapped with other signals; the CF_3 and C≡N signals were not observed. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −11.2 (d, $^2J_{RhF} = 15.8$ Hz).

[Rh(CF_3)(*n*-C_4F_9)I(CNXy)$_3$] (11). A solution of **6** (101 mg, 0.18 mmol) in THF (5 mL) was treated with *n*-C_4F_9I (34 μL, 0.20 mmol) at room temperature. The resulting yellow solution was stirred for 1 h and then evaporated to dryness under vacuum. *n*-Pentane (5 mL) was added to precipitate an oil, which was converted into a yellow solid by stirring for 15 min at 0 °C. The solid was washed with *n*-pentane (2 × 5 mL) and dried under vacuum. Yield: 145 mg, 89%. Mp: 191−195 °C. Anal. Calcd for $C_{32}H_{27}N_3F_{12}IRh$: C, 42.17; H, 2.99; N, 4.61. Found: C, 42.25; H, 3.20; N, 4.80. IR (Nujol, cm^{-1}): ν(C≡N) 2204 (s). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.27−7.11 (two AB_2 m, 9 H, Xy), 2.54 (s, 12 H, Me, Xy), 2.51 (s, 6 H, Me, Xy). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 136.8 (C2, 2 Xy), 136.5 (C2, Xy), 130.3 (C4, 2 Xy), 128.3 (C3, Xy), 128.2 (C3, 2 Xy), 126.0 (C1, 2 Xy), 18.9 (Me, Xy), 18.7 (Me, 2 Xy); the C1 and C4 signals of the single Xy group are probably overlapped with others; those of the C≡N, CF_3, and C_4F_9 carbons were not observed. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −8.1 (dtt, $^2J_{RhF} = 13.6$, $^4J_{FF} = 7.3$, $^5J_{FF} = 3.7$ Hz, Rh−CF_3), −66.3 (m, Rh−CF_2), −81.3 (tt, $^4J_{FF} = 9.3$, $^5J_{FF} = 4.6$ Hz, CF_3), −113.2 (m, β-CF_2), −125.2 (m, γ-CF_2).

Crystallography. Compounds **2**−**4** and **12** were measured on a Bruker Smart Apex CCD machine. Data were collected using monochromated Mo Kα radiation in ω-scan mode. The structures of compounds **2** and **3** were solved by the heavy-atom method and the structures of **4** and **8** were solved by the direct method, and all were refined anisotropically on F^2. Methyl groups were refined using rigid groups. Other hydrogens were refined using a riding mode.

Complex **12** contains an ill-resolved $CHCl_3$ molecule which is disordered over two positions with a ca. 61:39 distribution. The highest residual electron density (2.16 e Å^{-3}) is near one of its chlorine atoms. The CF_3−CF_2 group of the *n*-C_4F_9 ligand is disordered over two positions; therefore, appropriate similarity restraints were employed.

Crystal data for complexes **2**−**4** and **12** are given in Table 2.

Acknowledgment. We thank the Dirección General de Investigación/FEDER for financial support (Grant CTQ2004-05396 and a "Ramón y Cajal" contract to J.G.-R.) and Fundación Séneca for a grant to J.G.-L.

Supporting Information Available: Crystallographic files in CIF format for compounds **2**−**4** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050573Q