Multifunctional Ligands. Phosphinimine-Substituted Cyanofluoroaromatics Including X-ray Molecular Structures of Three Representative Ligands 4,6-$(CN)_2C_6F_2$-1,3-$(N{=}PPh_3)_2$, 4,6-$(CN)_2C_6F_2$-1,3-$(N{=}PPh_2Me)_2$ and 4,6-$(CN)_2C_6F_2$-1-$(N{=}PPh_3)$-3-$(N{=}PPh_2Me)$. Formation of Rhodium(I) Complexes

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Reaction of 1,3-dicyanotetrafluorobenzene with 2 equiv of (trimethylsilyl)iminophosphoranes gave the disubstituted derivatives 4,6-$(CN)_2C_6F_2$-1,3-AB: **1**, A = B = $(N{=}PPh_3)$; **2**, A = B = $(N{=}PPh_2Me)$; and **3**, A = $(N{=}PPh_3)$, B = $(N{=}PPh_2Me)$. Monosubstituted compounds of the type 2,4-$(CN)_2C_6F_3$-1-A; notably **4**, A = $(N{=}PPh_3)$, and **5**, A = $(N{=}PPh_2Me)$, were readily obtained by reaction of 1 molar equiv of the silylated iminophosphorane with the cyanofluoro aromatic. Substitution of the fluorine *para* to the CN group(s) occurs in all cases. Reactions of 1,2- and 1,4-dicyanotetrafluorobenzene with (trimethylsilyl)iminophosphoranes gave only monosubstituted derivatives 3,4-$(CN)_2C_6F_3$-1-A (**6**, A = $(N{=}PPh_3)$, and **7**, A = $(N{=}PPh_2Me)$) and 2,5-$(CN)_2C_6F_3$-1-A (**8**, A = $(N{=}PPh_3)$, and **9**, A = $(N{=}PPh_2Me)$), respectively, as the result of electronic deactivation of the second substitutional point. **1**, 4,6-$(CN)_2C_6F_2$-1,3-$(N{=}PPh_3)$, **2**, 4,6-$(CN)_2C_6F_2$-1,3-$(N{=}PPh_2Me)_2$, and **3**, 4,6-$(CN)_2C_6F_2$-1-$(N{=}PPh_3)$-3-$(N{=}PPh_2Me)$ have been structurally characterized. For **1** (at 21 °C), monoclinic, $C2/_c$ (No. 15), a = 15.289(2) Å, b = 10.196(1) Å, c = 23.491(6) Å, β = 91.63(2)°, V = 3660(2) Å^3, and Z = 4. The P═N bond length is 1.579(2) Å and the P^V−N−C(phenyl) angle is 134.0(2)°. For **2**, (at 21 °C) monoclinic, $C2/_c$ (No. 15), a = 18.694(2) Å, b = 8.576(1) Å, c = 40.084(4) Å, β = 94.00(1)°, V = 6411(2) Å^3, and Z = 8. The P(1)═N(1) bond length is 1.570(4) Å, the P(2)═N(2) bond length is 1.589(3) Å, the P(1)−N(1)−C(14) angle is 131.6(3)°, and the P(2)−N(2)−C(16) angle is 131.3(3)°. For **3**, (at −80 °C) monoclinic, $P2_1/c$ (No. 14), a = 9.210(1) Å, b = 18.113(2) Å, c = 20.015(2) Å, β = 100.07(1)°, V = 3287(2) Å^3, and Z = 4. The P(1)═N(1) bond length (PPh_3 group) is 1.567(4) Å, the P(2)═N(2) bond length (PPh_2Me group) is 1.581(5) Å, the P(1)−N(1)−C(1) angle is 140.4(4)°, and the P(2)−N(2)−C(3) angle is 129.4(4)°. These new multifunctional chelating ligands readily react with $[Rh(cod)Cl]_2$ and $AgClO_4$ to give cationic Rh(I) complexes in which the imine and/or the nitrile groups are coordinated to the Rh center.

Introduction

There has been considerable interest in metal-nitrile complexes since the 1960s. Nitrile ligands are relatively good σ-donors of moderate basic strength but are relatively poor π-acceptors toward transition metals. As a result, organonitrile complexes contain weakly bound, easily displaced ligands, and these complexes are often used as convenient synthetic precursors.

In principle, the RCN group may coordinate to metals in two ways: either *via* the lone pair of the nitrogen in an "end-on" fashion or *via* the CN triple bond to form a "side-on" π complex. Most nitrile complexes show the former, end-on, style of coordination. Such complexes may be characterized by the IR stretching frequencies arising from the CN triple bond, and these values in general increase by small amounts upon coordination.[3] In this model, donation of the lone pair of the RCN ligand (which is an orbital with some antibonding character) to the metal to form the RCN→ML_n complex leads to the situation in which the antibonding character in the lone pair orbital decreases upon coordination. As a result, the CN bond order is increased and therefore the stretching frequencies increase. In the cases summarized in a comprehensive review[3] the average increase observed was approximately 33 cm^{-1}.

Although rare, a few side-on coordination compounds have been reported.[4−20] When π or side-on coordination occurs, the CN stretching frequency is very substantially reduced as a result

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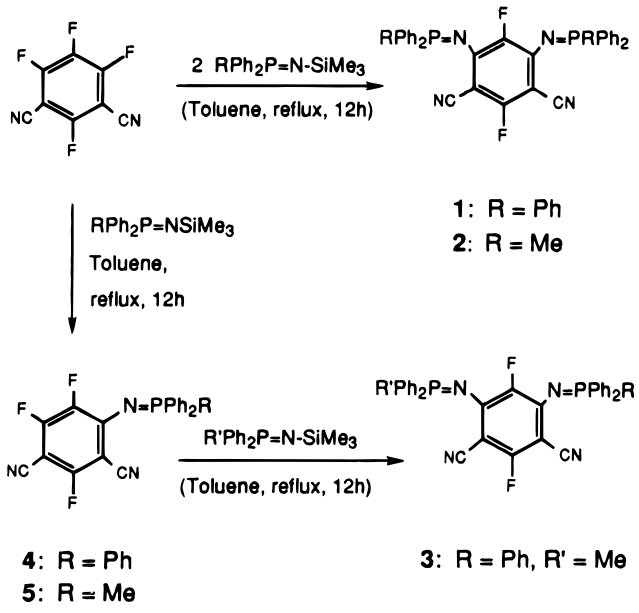
Scheme 1



of the perturbation of the CN π-bond structure. Complexes of this type wherein this mode of bonding has been invoked show an average CN stretching frequency shift on complex formation of approximately -190 cm^{-1}.[3]

We have previously shown that reactions of 1,2- and 1,4-dicyanotetrafluorobenzene with (trimethylsilyl)iminophosphoranes gives only monosubstituted derivatives.[21] Herein we show that reaction of 1,3-dicyanotetrafluorobenzene with a variety of (trimethylsilyl)iminophosphoranes gives both mono- and disubstituted derivatives through smooth and sequential reactions. Differently disubstituted cyanofluorobenzene derivatives can be formed by carrying out the substitution using one molar equivalent of reagent at each step, changing the silyliminophosphorane reagent between steps. The imine retains significant basicity so these multifunctional ligands are good complexing agents. Herein we also describe the preparation of a series of Rh(I) complexes of cyanoaromatics carrying simple iminophosphorane substituents. Metal complexation involves imine and/or nitrile groups and all interactions appear to be the usual σ donor type although the geometrical relationships between the imine and the CN center could be expected to facilitate the "side-on" type of interaction.

Results and Discussion

Synthesis, Properties, and Structures of the Ligands. Refluxing 1,3-dicyanotetrafluorobenzene with 2 equiv of (trimethylsilyl)iminophosphoranes in toluene gave the disubstituted cyanofluoroaromatic derivatives **1**−**3** in good yields. The reaction is stepwise and use of 1 equiv of the silyliminophosphorane gave only the monosubstituted product. This product can then be treated with a second equivalent of the same or a different phosphinimine to yield either symmetrically or asymmetrically substituted ligands. (Scheme 1). Both the mono- and disubstituted compounds are crystalline, air stable solids which are soluble in most common organic solvents. The disubstituted compounds are in general less soluble than the monosubstituted species. The reactions shown in Scheme 1 demonstrate that in 1,3-$(CN)_2C_6F_4$, the two fluorine atoms which are *para* to the electron-withdrawing, activating groups, CN, are the most reactive, and it is these fluorines which are

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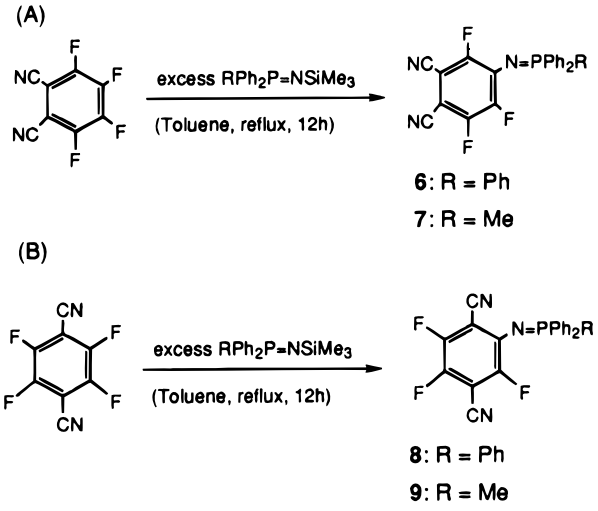
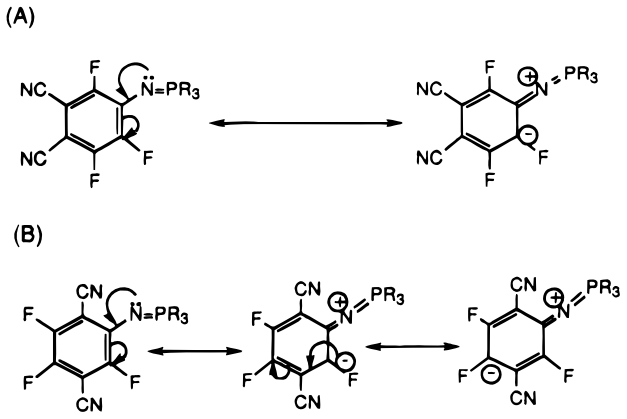
Scheme 2



Scheme 3



sequentially replaced. In contrast, only one of the fluorine atoms which are *para* to CN groups in 1,2-$(CN)_2C_6F_4$ could be eliminated to form the imine (Scheme 2A), and second substitution was not obtained.[21] This difference is in keeping with the expected electronic influence of the electron rich iminophosphorane. The introduction of the first substituent on the *para* site electronically deactivates both of the *ortho* positions required for second substitution (Scheme 3A) and the remaining *meta* fluorine is not active.

The isomeric compound, 1,4-$(CN)_2C_6F_4$, which can only react via *ortho* (or *meta*) fluorine substitution shows similar behavior to 1,2-$(CN)_2C_6F_4$. Only one fluorine in this 1,4-precursor can be eliminated to form the imine (Scheme 2B). Second substitution was not obtained for reasons similar to those advanced for 1,2-$(CN)_2C_6F_4$, Again the first imine substituent electronically deactivates the remaining *ortho* and *para* positions, and further nucleophilic substitution does not occur at neither of these positions (Scheme 3B).

The identification and molecular constitution of all the compounds follows from the analytical data, mass spectra and ^{1}H, ^{31}P, and ^{19}F NMR spectroscopy. Molecular ions for each of the compounds were observed in the mass spectra. Phosphorus-31 NMR data of the disubstituted ligands **1** and **2** (given in Table 1) showed chemical shifts to high fields compared with the monosubstituted analogs, and the observation of only one chemical shift signal indicated that the imine groups are symmetry related. The disubstituted compound **3**, with different phosphinimine substituents, shows two ^{31}P chemical shifts each of which are individually similar to those observed for **1** and **2**.

Table 1. Phosphorus-31 NMR[a] Data and the IR Data of the CN Groups for Ligands **1**−**9**

compoud[b]	no.	δ_P (ppm)	ν_{CN} (cm^{-1})
4,6-$(CN)_2C_6F_2$-1,3-$(N{=}PPh_3)_2$	**1**	8.75	2217
4,6-$(CN)_2C_6F_2$-1,3-$(N{=}PPh_2Me)_2$	**2**	10.03	2208
			2224
4,6-$(CN)_2C_6F_2$-1-$(N{=}PPh_3)$-3-$(N{=}PPh_2Me)$	**3**	9.30 (in PPh_3) 10.20 (in PPh_2Me)	2214
2,4-$(CN)_2C_6F_3$-1-$(N{=}PPh_3)$	**4**	13.50	2237
2,4-$(CN)_2C_6F_3$-1-$(N{=}PPh_2Me)$	**5**	14.60	2233
3,4-$(CN)_2C_6F_3$-1-$(N{=}PPh_3)$	**6**	12.60	2229
3,4-$(CN)_2C_6F_3$-1-$(N{=}PPh_2Me)$	**7**	14.40	2230
2,5-$(CN)_2C_6F_3$-1-$(N{=}PPh_3)$	**8**	10.81	2230
			2240
2,5-$(CN)_2C_6F_3$-1-$(N{=}PPh_2Me)$	**9**	11.60	2213
			2225

[a] Spectra obtained in $CDCl_3$ solution; ppm vs 85% H_3PO_4. Positive values indicate resonance to low field standard. [b] The imine-substituted fluoroaromatics are numbered starting from one at the imine attachment point. The numbers associated with the substituents may therefore be different from those used for the systematic name of the original fluoroaromatic.

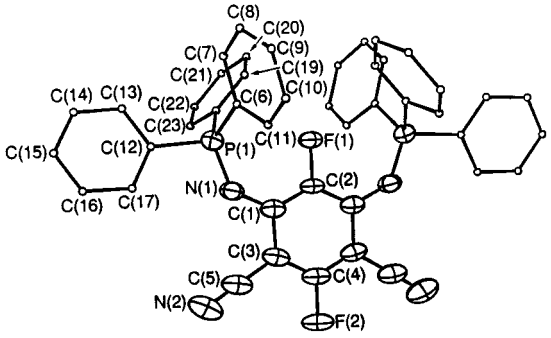


Figure 1. ORTEP perspective view of **1** showing the atom numbering scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Phenyl carbon atoms are shown with reduced probabilities for clarity. Hydrogen atoms are not shown.

The different iminophosphorane environments are readily distinguished by their different ^{31}P NMR shifts.

X-ray crystal and molecular structures (illustrated as ORTEP[22] plots in Figures 1−3) have been determined for **1**, **2** and **3**, as representative examples of these new compounds. The X-ray crystallographic data and selected bonding parameters are given in Tables 2−6. As expected the structures show similar characteristics. The P−N bond lengths (1.579(2) Å for **1**, 1.570(4) and 1.589(3) Å for **2**, and 1.567(4) (to the PPh_3 group) and 1.581(5) Å (to the PPh_2Me group) for **3**) fall within the range observed for similar phosphinimine and phosphazene compounds with P−N double bonds.[23−26] The P−N bond lengths are substantially longer than the P═N bond length in $Ph_2PCH_2P(Ph)_2NSiMe_3$ (1.529(3)Å).[27] The P−N−C(phenyl)angles (134.0(2)° in **1**, 131.6(3) and 131.3(3)° in **2** and 140.4(4) (to the PPh_3 group) and 129.4(4)° (to the PPh_2Me group) in **3**) are substantially smaller than those exhibited by other structures in which entities are bound to $P{=}NSiMe_3$,[28] but are comparable

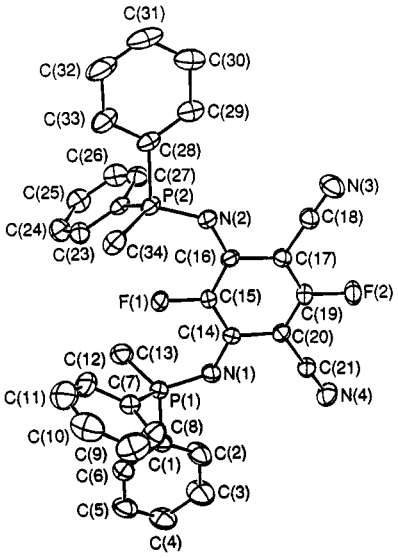


Figure 2. ORTEP perspective view of **2** showing the atom numbering scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 30% probability level. Hydrogen atoms are not shown.

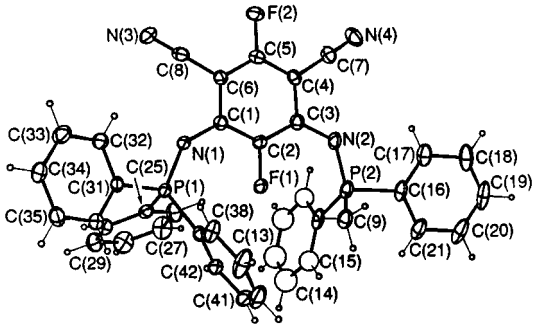


Figure 3. ORTEP perspective view of **3** showing the atom numbering scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 30% probability level. One poorly defined phenyl ring is shown with isotropic carbon atoms. Hydrogen atoms are shown with reduced probabilities for clarity.

to other structures which we have obtained for fluoroaromatic phosphinimine ligands.[21,29]

Formation of (cod)Rh(I) Cationic Complexes. Complexation reactions with Rh(I) are illustrated in Schemes 4−7. The products appear to differ in their degree of polymerization according to the structure of the ligand. For example reactions of **8** or **9**, the monoiminocyanoaromatics, with $^1/_2[Rh(cod)Cl]_2$ and $AgClO_4$ in acetone at 25 °C gave **10**, (R = Ph) or **11** (R = Me), [2,5-$(CN)_2C_6F_3$-1-$(N{=}PPh_2R)$Rh(cod)](ClO_4), respectively (Scheme 4). The ligand **5**, also a monoiminocyanoaromatic (but in this case there is one CN group *meta* and one *para* to the iminophosphorane substituent) gave, with the same reagents and conditions, complex, **12**, [2,4-$(CN)_2C_6F_3$-1-$(N{=}PPh_2Me)$Rh(cod)](ClO_4) (Scheme 5). The mass spectra (FAB) of all three complexes, **10**, **11**, and **12**, indicated the presence of a metal complex corresponding to the illustrated cations. The $^{31}P\{^1H\}$ NMR spectra (Table 7) showed singlets shifted by 3.1, 5.7, and 5.4 ppm downfield, respectively, relative to the corresponding ligands. The ^{19}F NMR spectra of the complexes showed no pronounced differences relative to the ligands. A solution molecular weight determination of **10** gave a value of 590, slightly smaller than the molecular weight of the monomer, and likewise the molecular weight value of 654 obtained for **11** is slightly smaller than that of the monomer. In contrast **12** was

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Table 2. Summary of Crystallographic Data for Compounds **1**−**3**

	1	**2**	**3**
formula	$C_{44}H_{30}F_2N_4P_2$	$C_{34}H_{26}F_2N_4P_2 \cdot 0.5C_2H_3N$	$C_{42}H_{29}F_2N_4P_2$
fw	714.70	611.09	689.67
cryst size (mm)	0.45 × 0.40 × 0.10	0.34 × 0.30 × 0.16	0.31 × 0.28 × 0.22
cryst syst	monoclinic	monoclinic	monoclinic
space group[a]	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	$P2_1/c$ (No. 14)
unit cell parameters			
a (Å)	15.289(2)	18.694(2)	9.210(1)
b (Å)	10.196(1)	8.576(1)	18.113(2)
c (Å)	23.491(6)	40.084(4)	20.015(2)
β (deg)	91.63(2)	94.00(1)	100.07(1)
V (Å^3)	3660(2)	6411(2)	3287(2)
Z	4	8	4
ρ_{calcd} (g cm^{-3})	1.30	1.27	1.39
μ (cm^{-1})	1.6	1.7	1.76
diffractometer[b]	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation (λ [Å])	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp (°C)	21	21	−80
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-\theta$
max 2θ (deg)	52.0	52.0	52.0
tot no. of data collcd	4610	6966	7430
no. of independent reflcns (NR)	4420	6289	6454
no. of observns (NO)	2524[c]	3653[c]	3605[c]
structure solution method	direct methods[d]	direct methods[e]	direct methods[d]
refinement method	full-matrix of F[f]	full-matrix on F[f]	full-matrix on F[f]
abs cor method	empirical	empirical	empirical
range of abs cor factors	0.951−0.998	0.916−0.995	0.949−0.999
parameters (*NV*)	237	383	399
goodness-of-fit (*S*)[g]	1.95	1.79	2.34
final *R* indices[h]			
R_1	0.042	0.063	0.056
R_2	0.051	0.093	0.047

[a] *International Tables for X-Ray Crystallograpy*; Kynoch Press: Birmingham England, 1974 (Present distributor, Kluwer Academic Publishers: Dordrecht, The Netherlands). [b] University of Toledo. [c] $F_o^2 > 3.0\sigma(F_o^2)$. [d] MULTAN: Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; DeClerq, J. P.; Woolfson, M. M., University of York, 1980. [e] SIR: Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389. [f] MOLEN: Fair, C. K., Enraf-Nonius, Delft, The Netherlands, 1990. [g] $S = [\sum w_1(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ ($w_1 = 4F_o^2/\sigma^2(F_o^2)$). [h] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w_1(|F_o| - |F_c|)^2/\sum w_1F_o^2]^{1/2}$; $I \geq 3\sigma(I)$.

Table 3. Table of Positional Parameters and Their Estimated Standard Deviations for **1**[a]

atom	*x*	*y*	*z*	*B* (Å^2)
P(1)	0.05652(4)	0.22559(6)	0.37178(2)	2.81(1)
F(1)	0.000	0.2168(2)	0.250	3.55(4)
F(2)	0.000	−0.3146(2)	0.250	5.03(5)
N(1)	0.0528(1)	0.0791(2)	0.35007(8)	3.28(4)
N(2)	0.0811(2)	−0.2482(2)	0.3874(1)	5.83(6)
C(1)	0.0265(1)	0.0215(2)	0.30063(9)	2.82(4)
C(2)	0.000	0.0823(3)	0.250	2.74(6)
C(3)	0.0265(1)	−0.1191(2)	0.2994(1)	3.18(5)
C(4)	0.000	−0.1820(3)	0.250	3.44(7)
C(5)	0.0559(2)	−0.1903(2)	0.3485(1)	4.01(5)
C(6)	0.1404(1)	0.3221(2)	0.33905(9)	2.88(4)
C(7)	0.1551(2)	0.4526(2)	0.3528(1)	4.11(5)
C(8)	0.2270(2)	0.5174(3)	0.3312(1)	5.03(6)
C(9)	0.2827(2)	0.4536(3)	0.2960(1)	4.95(6)
C(10)	0.2676(2)	0.3254(3)	0.2814(1)	4.58(6)
C(11)	0.1967(1)	0.2602(2)	0.3026(1)	3.59(5)
C(12)	0.0878(1)	0.2160(2)	0.4460(1)	3.54(5)
C(13)	0.0828(2)	0.3258(3)	0.4802(1)	5.85(7)
C(14)	0.1113(2)	0.3209(4)	0.5364(1)	7.51(9)
C(15)	0.1442(2)	0.2090(4)	0.5585(1)	7.8(1)
C(16)	0.1494(3)	0.0995(4)	0.5256(1)	8.3(1)
C(17)	0.1203(2)	0.1015(3)	0.4688(1)	5.98(7)
C(18)	−0.0450(1)	0.3159(2)	0.36868(9)	3.03(4)
C(19)	−0.0616(2)	0.4183(2)	0.3313(1)	3.88(5)
C(20)	−0.1423(2)	0.4788(3)	0.3291(1)	4.77(6)
C(21)	−0.2070(2)	0.4373(3)	0.3638(1)	5.30(7)
C(22)	−0.1919(2)	0.3365(3)	0.4008(1)	5.69(7)
C(23)	−0.1110(2)	0.2760(3)	0.4042(1)	4.71(6)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

not sufficiently soluble for molecular weight determination suggesting much more extensive polymerization in this case, perhaps as a result of the fact that the phosphinimine and one of the CN groups are mutually *para* to each other. The CN stretching frequencies of all three complexes **10**, **11**, and **12** (Table 7) appeared at 2253, 2245, and 2253 cm^{-1}, all slightly larger than the CN stretching frequency in the parent ligands (**8** has two peaks at 2240 and 2230 cm^{-1}, **9** has two peaks at 2225 and 2213 cm^{-1}, and **5** has only one peak at 2233 cm^{-1} (which is probably an overlapped pair of peaks)). The CN stretches in these metal complexes are broad with an appearance of an unresolved shoulder as would be expected for different environments for the CN groups. There are no definitive bands which could be attributed to the "side-on" bonding mode although these complexes do have the appropriate geometry to facilitate such interaction.

The reaction of the doubly imine-substituted ligand **2** with $[Rh(cod)Cl]_2$ and 2 equiv of $AgClO_4$ in acetone at 25 °C gave complex, **13**, which we formulate as a dimer (Scheme 6). We propose a symmetric structure in which one phosphine imine and one CN of the ligand act as the connecting links. In this case both the CN groups possess a mutual *para* relationship. This proposed complex structure is based on the following evidence: the elemental analysis is consistent with the $[LRh_2(cod)_2](ClO_4)_2$ formula, and the mass spectrum (FAB) showed peaks corresponding to [(cod)RhLRh(cod)], [RhLRh(cod)], $[L_2Rh(cod)]$, $[L_2Rh]$, and [LRh(cod)] species. The ^{31}P NMR showed a broad singlet at 16.4 ppm (a downfield shift of about 6.0 ppm compared with the values in the ligand (10.4 ppm)) which indicates that the two phosphinimine groups are related by symmetry and that the phosphinimine centers coordinate to the metal. The ^{19}F NMR spectrum showed two broad peaks at −102.1 and −143.2 ppm respectively with no significant

Table 4. Table of Positional Parameters and Their Estimated Standard Deviations for **2**[a]

atom	*x*	*y*	*z*	B_{eq}[b] (Å^2)
P(1)	0.59645(5)	0.4121(1)	0.67608(3)	3.71(2)
P(2)	0.44979(5)	0.3583(1)	0.54557(3)	3.49(2)
F(1)	0.5300(1)	0.3837(3)	0.60939(6)	5.23(6)
F(2)	0.7652(1)	0.1143(3)	0.56337(6)	4.91(5)
N(1)	0.6496(2)	0.3228(4)	0.65418(8)	4.30(8)
N(2)	0.5289(2)	0.2974(4)	0.54138(8)	3.97(7)
N(3)	0.6565(2)	0.1493(5)	0.48977(9)	5.60(9)
N(4)	0.8181(2)	0.1546(5)	0.64713(9)	5.23(9)
N(5)	0.1230(5)	0.500(1)	0.2905(4)	13.2(4)*
C(1)	0.6418(2)	0.4239(5)	0.7174(1)	4.17(9)
C(2)	0.7006(3)	0.3369(7)	0.7255(1)	6.9(1)
C(3)	0.7347(4)	0.3439(9)	0.7577(1)	8.7(2)
C(4)	0.7066(3)	0.4372(7)	0.7815(1)	6.9(1)
C(5)	0.6473(3)	0.5246(7)	0.7728(1)	6.3(1)
C(6)	0.6147(3)	0.5181(6)	0.7413(1)	5.3(1)
C(7)	0.5771(2)	0.6099(5)	0.6632(1)	4.04(9)
C(8)	0.6330(3)	0.7060(6)	0.6576(1)	6.3(1)
C(9)	0.6213(3)	0.8553(7)	0.6459(2)	8.0(2)
C(10)	0.5539(3)	0.9105(7)	0.6404(2)	7.8(2)
C(11)	0.4966(3)	0.8162(7)	0.6453(2)	7.8(2)
C(12)	0.5076(2)	0.6641(6)	0.6569(1)	5.8(1)
C(13)	0.5135(2)	0.3150(6)	0.6826(1)	5.6(1)
C(14)	0.6465(2)	0.2894(5)	0.62076(9)	3.14(7)
C(15)	0.5893(2)	0.3154(5)	0.59777(9)	3.43(8)
C(16)	0.5853(2)	0.2780(5)	0.56386(9)	3.26(8)
C(17)	0.6494(2)	0.2115(5)	0.55205(9)	3.30(7)
C(18)	0.6527(2)	0.1761(5)	0.5175(1)	3.92(9)
C(19)	0.7061(2)	0.1825(5)	0.57446(9)	3.44(8)
C(20)	0.7073(2)	0.2169(5)	0.60827(9)	3.23(7)
C(21)	0.7685(2)	0.1823(5)	0.63001(9)	3.64(8)
C(22)	0.4007(2)	0.2535(5)	0.57565(9)	3.49(8)
C(23)	0.3705(2)	0.3247(6)	0.6024(1)	4.42(9)
C(24)	0.3329(2)	0.2374(6)	0.6241(1)	5.3(1)
C(25)	0.3244(3)	0.0767(6)	0.6193(1)	5.4(1)
C(26)	0.3539(3)	0.0093(6)	0.5932(1)	5.3(1)
C(27)	0.3922(2)	0.0940(5)	0.5711(1)	4.32(9)
C(28)	0.4021(2)	0.3232(5)	0.50558(9)	3.86(8)
C(29)	0.4286(2)	0.2189(6)	0.4836(1)	4.8(1)
C(30)	0.3923(3)	0.1926(7)	0.4530(1)	6.1(1)
C(31)	0.3287(3)	0.2728(8)	0.4447(1)	7.4(1)
C(32)	0.3015(3)	0.3752(8)	0.4668(1)	7.4(1)
C(33)	0.3386(2)	0.3991(7)	0.4972(1)	5.8(1)
C(34)	0.4426(2)	0.5618(5)	0.5538(1)	4.9(1)
C(35)	0.097	0.505	0.263	13.2*
C(36)	0.064	0.511	0.230	13.2*

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Starred values belong to a disordered solvent molecule which was constrained to have an ideal geometry and identical thermal parameters.

Table 5. Table of Positional Parameters and Their Estimated Standard Deviations for **3**[a]

atom	*x*	*y*	*z*	B_{eq}[b] (Å^2)
P(1)	0.0431(1)	0.17153(6)	0.48570(5)	2.28(2)
P(2)	−0.5353(1)	0.20624(7)	0.31003(5)	3.10(2)
F(1)	−0.2516(2)	0.1887(1)	0.3888(1)	3.90(6)
F(2)	−0.0641(3)	0.0133(1)	0.2025(1)	3.99(6)
N(1)	0.0300(3)	0.1258(2)	0.4185(2)	2.74(7)
N(2)	−0.4473(3)	0.1545(2)	0.2672(2)	3.48(8)
N(3)	0.2471(4)	0.0199(2)	0.3296(2)	4.26(9)
N(4)	−0.4052(4)	0.0642(2)	0.1151(2)	4.4(1)
C(1)	−0.0639(4)	0.1147(2)	0.3595(2)	2.40(8)
C(2)	−0.2066(4)	0.1431(2)	0.3422(2)	2.61(9)
C(3)	−0.3067(4)	0.1296(2)	0.2825(2)	2.69(9)
C(4)	−0.2528(4)	0.0845(2)	0.2343(2)	2.55(9)
C(5)	−0.1134(4)	0.0559(2)	0.2494(2)	2.70(9)
C(6)	−0.0183(4)	0.0689(2)	0.3097(2)	2.47(9)
C(7)	−0.3407(4)	0.0725(2)	0.1685(2)	3.1(1)
C(8)	0.1291(4)	0.0408(2)	0.3212(2)	2.93(9)
C(9)	−0.5666(4)	0.1727(2)	0.3907(2)	3.5(1)
C(10)	−0.4596(4)	0.2982(3)	0.3232(2)	3.7(1)
C(11)	−0.3820(5)	0.3251(3)	0.2739(3)	5.1(1)*
C(12)	−0.3201(6)	0.3955(3)	0.2844(3)	6.9(1)*
C(13)	−0.3323(6)	0.4341(4)	0.3382(3)	7.3(2)*
C(14)	−0.4041(6)	0.4108(3)	0.3890(3)	7.3(2)*
C(15)	−0.4719(5)	0.3399(3)	0.3799(3)	5.2(1)*
C(16)	−0.7181(4)	0.2136(3)	0.2600(2)	3.5(1)
C(17)	−0.7624(5)	0.1689(2)	0.2048(2)	4.1(1)
C(18)	−0.9084(5)	0.1718(3)	0.1708(2)	5.1(1)
C(19)	−1.0064(4)	0.2190(3)	0.1931(2)	5.4(1)
C(20)	−0.9622(5)	0.2648(3)	0.2478(2)	5.7(1)
C(21)	−0.8174(4)	0.2624(3)	0.2814(2)	4.6(1)
C(25)	0.1116(4)	0.2640(2)	0.4761(2)	2.54(9)
C(26)	0.0370(5)	0.3086(3)	0.4248(2)	3.9(1)
C(27)	0.0830(5)	0.3802(3)	0.4168(2)	5.1(1)
C(28)	0.2044(5)	0.4077(3)	0.4590(3)	5.1(1)
C(29)	0.2806(5)	0.3641(3)	0.5097(2)	4.4(1)
C(30)	0.2344(4)	0.2924(2)	0.5188(2)	3.1(1)
C(31)	0.1749(4)	0.1217(2)	0.5464(2)	2.30(8)
C(32)	0.2579(4)	0.0666(2)	0.5241(2)	2.95(9)
C(33)	0.3562(5)	0.0262(2)	0.5701(2)	3.6(1)
C(34)	0.3728(4)	0.0406(2)	0.6384(2)	3.3(1)
C(35)	0.2907(4)	0.0950(2)	0.6612(2)	3.4(1)
C(36)	0.1918(4)	0.1355(2)	0.6154(2)	3.01(9)
C(37)	−0.1174(4)	0.1838(2)	0.5256(2)	2.40(8)
C(38)	−0.1749(4)	0.1221(3)	0.5522(2)	3.9(1)
C(39)	−0.3031(5)	0.1269(3)	0.5796(2)	5.5(1)
C(40)	−0.3733(5)	0.1943(3)	0.5795(2)	5.0(1)
C(41)	−0.3186(4)	0.2558(3)	0.5537(2)	4.1(1)
C(42)	−0.1895(4)	0.2510(2)	0.5263(2)	2.96(9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Starred values are for are poorly defined atoms which were refined isotropically.

difference exhibited by the peak at −143.2 ppm compared with the associated peak in the free ligand (−142.3 ppm), but the peak at −102.1 ppm in the complex (due to the fluorine located between two CN groups) was shifted 5 ppm downfield relative to the value in the ligand (−107.1 ppm). The IR data showed only one strong peak (2238 cm^{-1}) between 1700 and 2700 cm^{-1} whereas the free ligand showed two peaks at 2208 and 2224 cm^{-1}. These slightly increased CN stretching frequencies (14−30 cm^{-1}) are consistent with, but do not definitively prove, that the CN is σ coordinated to the Rh center. As the geometry of the ligand does not allow the same Rh center to form a complex with σ-coordinate links with both the imine nitrogen and the CN of the same ligand, we propose that the material which is formed is a polymer, and this is consistent with the very poor solubility of the complex, so poor that solution molecular weight measurements were impossible. The difference in the behavior of the two apparently symmetric F substituents is also consistent with the proposed polymer structure which generates two different F environments. Thus **2** which contains an *ortho* CN−phosphinimine unit similar to that in **8** and **9** but also provides mutually *para*-related phosphinimine−CN units forms a chain polymer with σ-bonded ligands, a propensity which also seems to be demonstrated by **5**. We may speculate (without definitive proof) that polymeric association arises from the interaction of the phosphinimine and *para* CN groups, perhaps because of the augmentation of the nitrile basicity in this position (but it is also possible that the effect may arise from the bulk of the iminophosphorane substituent).

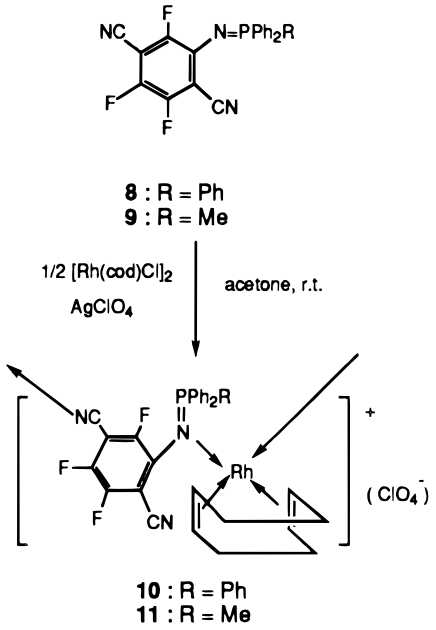
The proposition seems to be supported by the behavior of **6** and **7** in which there is one CN *para* and one *ortho* to the iminophosphorane. Complexes, **14** (R = Ph) or **15**, (R = Me), $[(3,4\text{-}(CN)_2C_6F_3\text{-}1\text{-}(N{=}PRPh_2)Rh(cod)]_2(ClO_4)_2$, are obtained by reaction of **6** and **7** respectively with $^1/_2[Rh(cod)Cl]_2$ and $AgClO_4$ in acetone (Scheme 7). Ions of mass indicating [L_2-Rh(cod)] and [LRh(cod)] were observed for both **15** and **16** in the mass spectra (FAB), suggesting that the units are metal dimers. The ^{31}P NMR showed downfield shifts of only 2.0 and 2.8 ppm respectively for **15** and **16** compared with the shift values for the parent ligands and there were no significant

Table 6. Selected Bond Distances (Å) and Angles (deg) in Compounds **1**−**3**

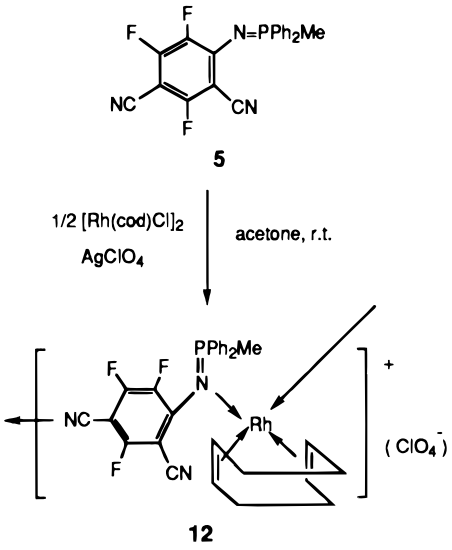
1		**2**		**3**	
		Distances			
P(1)−N(1)	1.579(2)	P(1)−N(1)	1.570(4)	P(1)−N(1)	1.567(4)
N(1)−C(1)	1.352(3)	P(2)−N(2)	1.589(3)	P(2)−N(2)	1.581(5)
N(2)−C(5)	1.146(4)	N(1)−C(14)	1.367(5)	N(1)−C(1)	1.350(6)
C(3)−C(5)	1.426(3)	N(2)−C(16)	1.348(4)	N(2)−C(3)	1.359(6)
		N(3)−C(18)	1.140(5)	N(3)−C(8)	1.134(6)
		N(4)−C(21)	1.139(5)	N(4)−C(7)	1.135(6)
		N(5)−C(35)	1.16(1)	C(6)−C(8)	1.435(7)
		C(17)−C(18)	1.425(5)	C(4)−C(7)	1.439(7)
		C(20)−C(21)	1.420(5)		
		Angles			
P(1)−N(1)−C(1)	134.0(2)	P(1)−N(1)−C(14)	131.6(3)	P(1)−N(1)−C(1)	140.4(4)
N(1)−P(1)−C(6)	113.5(1)	P(2)−N(2)−C(16)	131.3(3)	P(2)−N(2)−C(3)	129.4(4)
N(12)−P(1)−C(12)	105.5(1)	N(1)−P(1)−C(1)	105.3(2)	N(1)−P(1)−C(25)	112.0(2)
N(1)−P(1)−C(18)	116.5(1)	N(1)−P(1)−C(7)	114.9(2)	N(1)−P(1)−C(31)	104.8(2)
		N(1)−P(1)−C(13)	116.2(2)	N(1)−P(1)−C(37)	119.7(2)
		N(2)−P(2)−C(22)	115.3(2)	N(2)−P(2)−C(9)	117.8(3)
		N(2)−P(2)−C(28)	104.9(2)	N(2)−P(2)−C(10)	113.7(3)
		N(2)−P(2)−C(34)	115.1(2)	N(2)−P(2)−C(16)	104.9(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Scheme 4



Scheme 5



differences in the ^{19}F NMR spectra between ligand and complex. The solution molecular weight value (918) for **15** is about 1.2 times of the molecular weight of monomer, [LRh(cod)](ClO_4), which suggests that the dimer unit may be partly broken up upon dissolution. Finally, only one ν_{CN} was observed in each case; at 2252 cm^{-1} for **15** and 2253 cm^{-1} for **16**. This corresponds to an increase of 23 cm^{-1} for both **15** and **16** compared with the corresponding free ligands (2229 cm^{-1} for **6** and 2230 cm^{-1} for **7**). Therefore we conclude that both the CN groups are coordinated to a Rh center *via* a σ bond. Since the given ligand geometry does not allow two CN groups to form σ bonds to the same Rh center, we propose that this compound is a dimer with the structure illustrated in Scheme 7.

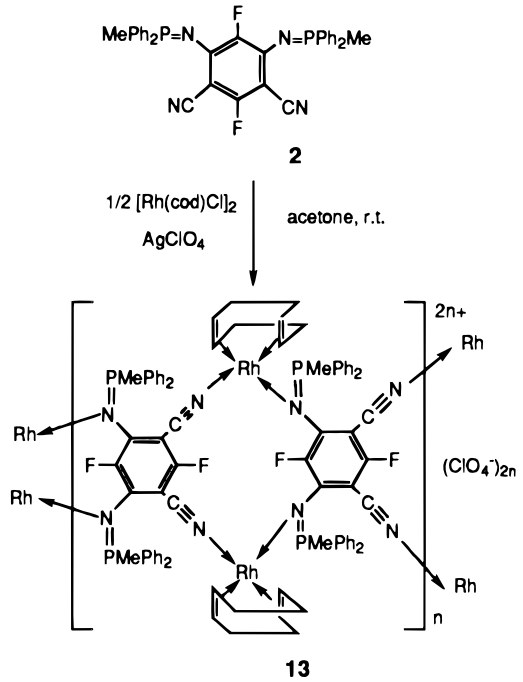
Conclusions

Reaction of 1,3-dicyanotetrafluorobenzene with (trimethylsilyl)phosphinimine gives both mono- and disubstituted derivatives *via* sequential elimination reactions. In contrast, reactions of 1,2- and 1,4-dicyanotetrafluorobenzene give only monosubstituted derivatives. Complexes of Rh(I) are readily formed by all ligands formed from the substitution of iminophosphoranes on the cyano−flororaromatic rings; however, those in which the CN group is *para* to the iminophosphorane center appear to favor more extensive intramolecular asociation which in some cases results in polymeric complexes.

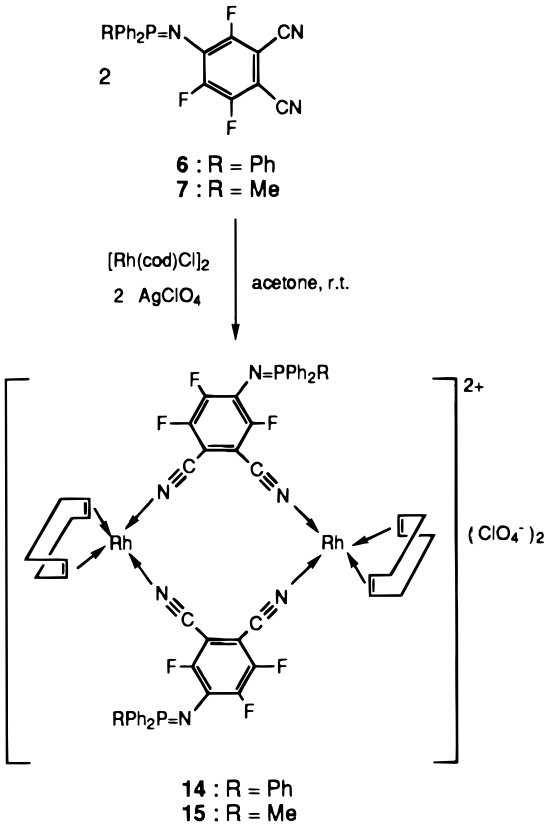
Experimental Section

All experimental manipulations were performed under an atmosphere of dry argon using Schlenk techniques. Solvents were dried and distilled prior to use. Toluene, acetonitrile, and dichloromethane were distilled from Na, CaH_2, and P_4O_{10}, respectively. These solvents were purged with dry argon for at least 0.5 h before use. Commercial (Aldrich) supplies of 1,4-dicyanotetrafluorobenzene, 1,3-dicyanotetrafluorobenzene, and 1,2-dicyanotetrafluorobenzene were used as obtained. Nuclear magnetic resonance spectra were recorded on Bruker WH-200 and WH-400 spectrometers locked on and referenced to the deuterium signal of the solvent employed. The ^{1}H chemical shifts are reported in parts per million downfield from external Me_4Si, the ^{31}P NMR spectra in ppm downfield from external 85% H_3PO_4, and the ^{19}F NMR spectra in ppm downfield from external $CFCl_3$. Low-resolution mass spectra were recorded at 16 or 70 eV on an AEI MS50 spectrometer. Positive ion fast atom bombardment mass spectra (FAB−MS) were recorded by using Xe fast atom bombardment on a customized AEI MS9 spectrometer. Infrared spectra were recorded

Scheme 6



Scheme 7



on a Nicolet 7199 infrared spectrometer. Melting points were ascertained by visual methods in unsealed capillaries. Osmometry measurements were made in CH_2Br_2 solutions on a Corona Wescan vapor pressure osmometer by the University of Alberta Microanalytical Services. Microanalysis was also done by the University of Alberta Microanalytical Services.

Synthesis of 4,6-$(CN)_2C_6F_2$-1,3-$(N{=}PPh_3)_2$ (1). To a solution of $Me_3SiN{=}PPh_3$ (0.699 g; 2.00 mmol) in dry toluene (20 mL) was added dropwise a solution of 1,3-dicyanotetrafluorobenzene (0.200 g; 1.00 mmol) also in toluene (20 mL). The reaction mixture was refluxed for 12 h before the solvent was removed *in vacuo* to leave a yellow crystalline solid. This crude product was recrystallized from acetonitrile to obtain the pure compound **1** (yield 0.61 g; 85%; cubic crystals, suitable for diffraction studies; mp 329 °C). Anal. Calcd for $C_{44}H_{30}N_4F_2P_2$: C, 73.95; H, 4.23; N, 7.84. Found: C, 73.37; H, 4.04; N, 7.73. MS (EI, *m*/*z*): 714 (M^+, 100%). ^{19}F NMR ($CDCl_3$): δ (F_2 (adjacent to CN)) −107.4 ppm (a doublet of triplets, 1F, $^5J_{F_1F_2} = 11$ Hz, $^5J_{PF_2} = 4.5$ Hz); δ (F_1) −135.3 ppm (a doublet of triplets, 1F, $^5J_{F_1F_2} = 11$ Hz, $^4J_{PF_1} = 10.8$ Hz). ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.35, 7.50 ppm (m, 30H).

Synthesis of 4,6-$(CN)_2C_6F_2$-1,3-$(N{=}PPh_2Me)_2$ (2). To a solution of $Me_3SiN{=}PPh_2Me$ (1.437 g; 5.00 mmol) in dry toluene (20 mL) was added dropwise a solution of 1,3-dicyanotetrafluorobenzene (0.500 g; 2.50 mmol) also in toluene (20 mL). The reaction mixture was refluxed for 12 h before the solvent was removed *in vacuo* to leave a yellow crystalline solid. This crude product was recrystalized from acetonitrile to obtain the pure compound **2** (yield 1.32 g; 89%; cubic crystals, suitable for diffraction studies; mp 270 °C). Anal. Calcd for $C_{34}H_{26}N_4F_2P_2$: C, 69.15; H, 4.44; N, 9.49. Found: C, 68.33; H, 4.48; N, 9.60. MS (EI, *m*/*z*): 590 (M^+, 100 %). ^{19}F NMR ($CDCl_3$): δ (F_2 (adjacent to CN)) −107.1 (a doublet of triplets, 1F, $^5J_{F_1F_2} = 11$ Hz, $^5J_{PF_2} = 4.6$ Hz); δ (F_1) = −142.3 (a doublet of triplets, 1F, $^5J_{F_1F_2} = 11$ Hz, $^4J_{PF_1} = 13.5$ Hz). ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.30, 7.45, 7.70 ppm (m, 20H); two methyl groups δ 1.80 ppm (d, 6H, $J = 13$ Hz).

Synthesis of 4,6-$(CN)_2C_6F_2$-1-$(N{=}PPh_3)$-3-$(N{=}PPh_2Me)$ (3). To a solution of $Me_3SiN{=}PPh_2Me$ (0.200 g; 0.70 mmol) in dry toluene (20 mL) was added dropwise a solution of 2,4-$(CN)_2C_6F_3N{=}PPh_3$, **4** (0.279 g; 0.61 mmol), also in toluene (50 mL). The reaction mixture was refluxed for 12 h before the solvent was removed *in vacuo* to leave a light yellow crystalline solid. This crude product was recrystallized from acetontrile to obtain the pure compound **3** (yield 0.31 g; 78%; cubic crystals, suitable for diffraction studies; mp 264 °C). Anal. Calcd for $C_{39}H_{28}N_4F_2P_2$: C, 71.78; H, 4.32; N, 8.58. Found: C, 71.52; H, 4.26; N, 8.57. MS (EI, *m*/*z*): 652 (M^+, 100 %). ^{19}F NMR ($CDCl_3$): δ (F_2 (adjacent to CN)) = 107.3 ppm (ddd, 1F, $^5J_{F_1F_2} = 11.3$ Hz, $^5J_{P_1F_2} = 4.5$ Hz, $^5J_{P_2F_2} = 4.7$ Hz); δ (F_1) −139.0 ppm (ddd, 1F, $^5J_{F_1F_2} = 11$ Hz, $^4J_{P_1F_1} = 10.7$ Hz, $^4J_{P_2F_1} = 13.8$ Hz). ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.5 ppm (m, 20H), methyl group δ 1.7 ppm (dd, 3H).

Synthesis of 2,4-$(CN)_2C_6F_3$-1-$(N{=}PPh_3)$ (4). To a solution of $Me_3SiN{=}PPh_3$ (0.874 g; 2.50 mmol) in dry toluene (20 mL) was added dropwise a solution of 1,3-dicyanotetrafluorobenzene (0.500 g; 2.50 mmol) also in toluene (20 mL). The reaction mixture was refluxed for 12 h before the solvent was removed *in vacuo* to leave a yellow crystalline solid. This crude product was recrystalized from acetonitrile to obtain the pure compound **4** (yield 1.00 g; 88%; mp 228 °C). Anal. Calcd for $C_{26}H_{15}N_3F_3P$: C, 68.28; H, 3.31; N, 9.19. Found: C, 68.22; H, 3.15; N, 9.23. MS (EI, *m*/*z*): 457 (M^+, 100%). ^{19}F NMR ($CDCl_3$): δ (F_3 (between two CN)) −104.80 ppm (a doublet of doublets, 1F, $^5J_{F_1F_3} = 11.3$ Hz, $^5J_{PF_3} = 4.0$ Hz); δ (F_1 (close to P)) −150.64 ppm (ddd, 1F, $^3J_{F_1F_2} = 22.6$ Hz, $^5J_{F_1F_3} = 11.3$ Hz, $^4J_{PF_1} = 7.9$ Hz); δ (F_2) −125.78 ppm (a doublet, 1F, $^3J_{F_1F_2} = 22.6$ Hz). ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.25, 7.55, 7.75 ppm (m, 15H).

Synthesis of 2,4-$(CN)_2C_6F_3$-1-$(N{=}PPh_2Me)$ (5). To a solution of $Me_3SiN{=}PPh_2Me$ (0.600 g; 2.09 mmol) in dry toluene (20 mL) was added dropwise a solution of 1,3-dicyanotetrafluorobenzene (0.418 g; 2.09 mmol) also in toluene (20 mL). The reaction mixture was refluxed for 12 h before the solvent was removed *in vacuo* to leave a yellow crystalline solid. This crude product was recrystallized from acetonitrile to obtain the pure compound **5** (yield 0.67 g; 81%; mp 176 °C). Anal. Calcd for $C_{21}H_{13}N_3F_3P$: C, 63.80; H, 3.31; N, 10.63. Found: C, 64.30; H, 3.27; N, 10.30. MS (EI, *m*/*z*): 395 (M^+, 100 %). ^{19}F NMR ($CDCl_3$): δ (F_3 (between two CN)) −104.75 ppm (a doublet of doublets, 1F, $^5J_{F_1F_3} = 7.5$ Hz, $^5J_{PF_3} = 4.2$ Hz); δ (F_1 (close to P)) −153.67 ppm (ddd, 1F, $^3J_{F_1F_2} = 22.6$ Hz, $^5J_{F_1F_3} = 7.5$ Hz, $^4J_{PF_1} = 9.9$ Hz); δ (F_2) −126.15 ppm (a doublet, 1F, $^3J_{F_1F_2} = 22.6$ Hz). ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.25, 7.55, 7.85 ppm (m, 10H), methyl group δ 2.30 ppm (dd, 3H).

Synthesis of 3,4-$(CN)_2C_6F_3$-1-$(N{=}PPh_3)$ (6). To a solution of $Me_3SiN{=}PPh_3$ (0.350 g; 1.00 mmol) in dry toluene (20 mL) was added dropwise a solution of 1,2-$(CN)_2C_6F_4$ (0.200 g; 1.00 mmol) also in toluene (20 mL). The reaction mixture was refluxed for 12 h before

Table 7. ^{31}P NMR[a] Data and the ν_{CN} region IR[b] data for complexes **10**−**15**

compounds[c]	no.	δ_P (ppm)	ν_{CN} (cm^{-1})
[2,5-(CN)$_2$C$_6$F$_3$-1-(N═PPh$_3$)Rh(cod)](ClO$_4$)	**10**	13.9 (s)	2253
[2,5-(CN)$_2$C$_6$F$_3$-1-(N═PPh$_2$Me)Rh(cod)](ClO$_4$)	**11**	17.3 (s)[d]	2245
[2,4-(CN)$_2$C$_6$F$_3$-1-(N═PPh$_2$Me)Rh(cod)](ClO$_4$)	**12**	20.0 (br)	2253
[4,6-(CN)$_2$C$_6$F$_2$-1,3-(N═PPh$_2$Me)$_2$Rh(cod)](ClO$_4$)	**13**	16.4 (br)	2238
[3,4-(CN)$_2$C$_6$F$_3$-1-(N═PPh$_3$)Rh(cod)]$_2$(ClO$_4$)$_2$	**14**	14.6 (s)[d]	2252
[3,4-(CN)$_2$C$_6$F$_3$-1-(N═PPh$_2$Me)Rh(cod)]$_2$(ClO$_4$)$_2$	**15**	17.2 (s)[d]	2253

[a] Spectra obtained in $CDCl_2$ solution; ppm vs 85% H_3PO_4. Positive values indicate resonance to low field standard. [b] All IR spectra were obtained via the microscope attachment, not as casts or mulls. [c] The imine-substituted fluoroaromatics are numbered starting from one at the imine attachment point. The numbers associated with the substituents may therefore be different from those used for the systematic name of the original fluoroaromatic. [d] Spectra were obtained in $CDCl_3$ solution.

the solvent was removed *in vacuo* to leave a yellow crystalline solid. This crude product was recrystallized from acetonitrile to obtain the pure compound **6** (yield 0.42 g; 92%; mp 196 °C). Anal. Calcd for $C_{26}H_{15}N_3F_3P$: C, 68.28; H, 3.31; N, 9.19. Found: C, 67.84; H, 3.24; N, 9.27. MS (EI, *m*/*z*): 457 (M^+, 100 %). ^{19}F NMR ($CDCl_3$): δ (F_1 (para to one (CN)) −137.0 ppm (ddd, 1F, $^3J_{F_1F_3}$ = 22.6 Hz, $^4J_{F_1F_2}$ = 22.6 Hz, $^3J_{PF_1}$ = 4.0 Hz); δ (F_2 (close to P and para to F_3)) −116.0 ppm (ddd, 1F, $^4J_{F_1F_2}$ = 22.6 Hz, $^5J_{F_2F_3}$ = 7.5 Hz, $^3J_{PF_2}$ = 7.0 Hz); δ (F_3) −146.0 ppm (dd, 1F, $^3J_{F_1F_3}$ = 22.6 Hz, $^5J_{F_2F_3}$ = 7.5 Hz). ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.30, 7.60 ppm (m, 15H).

Synthesis of 3,4-(CN)$_2$C$_6$F$_3$-1-(N═PPh$_3$) (7). To a solution of Me_3-SiN═PPh_2Me (0.700 g; 2.44 mmol) in dry toluene (20 mL) was added dropwise a solution of 1,2-$(CN)_2C_6F_4$ (0.487 g; 2.44 mmol) also in toluene (20 mL). The reaction mixture was refluxed for 12 h before the solvent was removed *in vacuo* to leave an orange yellow crystalline solid. This crude product was recrystallized from acetonitrile to obtain the pure compound **7** (yield 0.54 g; 56%; mp 160 °C). Anal. Calcd for $C_{21}H_{13}N_3F_3P$: C, 63.80; H, 3.31; N, 10.63. Found: C, 63.93; H, 3.30; N, 10.63. MS (EI, *m*/*z*): 395 (M^+, 100 %). ^{19}F NMR ($CDCl_3$): δ (F_1 (para to one CN)) −139.0 ppm (ddd, 1F, $^3J_{F_1F_3}$ = 22.6 Hz, $^4J_{F_1F_2}$ = 22.6 Hz, $^3J_{PF_1}$ = 4.0 Hz). δ (F_2 (close to P and para to F_3)) −117.8 ppm (ddd, 1F, $^4J_{F_1F_2}$ = 22.6 Hz, $^5J_{F_2F_3}$ = 7.5 Hz, $^3J_{PF_2}$ = 7.0 Hz), δ F_3 −32.8 ppm (dd, 1F, $^3J_{F_1F_3}$ = 22.6 Hz, $^5J_{F_2F_3}$ = 7.5 Hz). ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.25, 7.55, 7.75 ppm (m, 10H), methyl group δ 2.25 ppm (d, 3H).

Synthesis of 2,5-(CN)$_2$C$_6$F$_3$-1-(N═PPh$_3$) (8). To a solution of Me_3-SiN═PPh_3 (0.250 g; 0.715 mmol) in dry toluene (20 mL) was added dropwise a solution of 1,4-$(CN)_2C_6F_4$ (0.143 g; 0.715 mmol) also in toluene (20 mL). The reaction mixture was refluxed for 12 h before the solvent was removed *in vacuo* to leave a yellow crystalline solid. This crude product was recrystallized from acetonitrile to obtain the pure compound **8** (yield 0.28 g; 86%; mp 181 °C). Anal. Calcd for $C_{26}H_{15}N_3F_3P$: C, 68.28; H, 3.31; N, 9.19. Found: C, 68.07; H, 3.12; N, 9.06. MS (EI, *m*/*z*): 457 (M^+, 100%). ^{19}F NMR ($CDCl_3$): δ (F_1 (close to P)) −118.1 ppm (ddd, 1F, $^5J_{F_1F_2}$ = 13 Hz, $^4J_{F_1F_3}$ = 8 Hz, $^4J_{PF_1}$ = 7.0 Hz); δ (F_2 (para to P)) −133.7 ppm (ddd, 1F, $^3J_{F_2F_3}$ = 21 Hz, $^4J_{F_1F_2}$ = 13 Hz, $^6J_{PF_2}$ = 3.0 Hz); δ (F_3) −146.0 ppm (dd, 1F, $^3J_{F_2F_3}$ = 21 Hz, $^5J_{F_1F_3}$ = 8 Hz). ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.30, 7.55, 7.75 ppm (m, 15H).

Synthesis of 2,5-(CN)$_2$C$_6$F$_3$-1-(N═PPh$_2$Me) (9). To a solution of Me_3SiN═PPh_2Me (0.300 g; 1.04 mmol) in dry toluene (20 mL) was added dropwise a solution of 1,4-$(CN)_2C_6F_4$ (0.200 g; 1.00 mmol) also in toluene (20 mL). The reaction mixture was refluxed for 12 h before the solvent was removed *in vacuo* to leave an orange yellow crystalline solid. This crude product was recrystallized from acetonitrile to obtain the pure compound **9** (yield 0.22 g; 56%; mp 125 °C). Anal. Calcd for $C_{21}H_{13}N_3F_3P$: C, 63.80; H, 3.31; N, 10.63. Found: C, 64.02; H, 3.22; N, 10.63. MS (EI, *m*/*z*): 395 (M^+, 100%). ^{19}F NMR ($CDCl_3$): δ (F_1 (close to P)) −121.5 ppm (ddd, 1F, $^5J_{F_1F_3}$ = 11.3 Hz, $^4J_{F_1F_2}$ = 7.5 Hz, $^4J_{PF_1}$ = 9.4 Hz). $^3J_{F_2F_3}$ = 22.6 Hz, δ (F_2 (para to P)) −133.7 ppm (ddd, 1F, $^3J_{F_2F_3}$ = 22.6 Hz, $^4J_{F_1F_2}$ = 7.5 Hz, $^6J_{PF_2}$ = 3.9 Hz), δ (F_3) −146.5 ppm (dd, 1F, $^3J_{F_2F_3}$ = 22.6 Hz, $^5J_{F_1F_3}$ = 11.3 Hz). ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.25, 7.55, 7.80 ppm (m, 10H), methyl group δ 2.25 ppm (dd, 3H).

Synthesis of [2,5-(CN)$_2$C$_6$F$_3$-1-(N═PPh$_3$)Rh(cod)](ClO$_4$) (10). To a 100 mL flask were added $[Rh(cod)Cl]_2$ (0.049 g; 0.100 mmol), $AgClO_4$ (0.042 g; 0.200 mmol), and 15 mL of acetone. The solution was stirred for 15 min, and then the solution was filtered and transferred to a flask which contained 2,5-$(CN)_2C_6F_3$-1-(N═PPh_3), **8** (0.092 g; 0.200 mmol), in 15 mL of acetone. The resultant yellow solution was stirred at room temperature for about 2 h before the solvent was removed *in vacuo* to leave a yellow solid. This crude product was washed with hexane (3 × 15 mL) and dried *in vacuo* to obtain **10** (yield 0.10 g; 64%; mp >165 °C dec). Anal. Calcd for $C_{34}H_{27}N_3F_3PRhClO_4$: C, 53.18; H, 3.54; N, 5.47; Cl, 4.62. Found: C, 52.38; H, 3.53; N, 5.11; Cl, 6.01. MS (FAB): 668 (monocation). ^{19}F NMR (CD_2Cl_2) (F ortho, meta, or para relative to the imino substituent): δ (F_o) −116.8 ppm (singlet, 1F); δ (F_p) −133.6 ppm (singlet, 1F); δ (F_m) −146.7 ppm (singlet, 1F). ^{1}H NMR (CD_2Cl_2): phenyl rings, δ 7.7 ppm (m, 15H); cod group: δ 4.5 ppm (broad, 4H, HC═), δ 2.55 ppm (broad, 4H, H_2C), δ 1.95 ppm (broad, 4H, H_2C). Molecular weight determination: 590 (solvent: CH_2Br_2).

Synthesis of [2,5-(CN)$_2$C$_6$F$_3$-1-(N═PPh$_2$Me)Rh(cod)](ClO$_4$) (11). To a 100 mL flask were added $[Rh(cod)Cl]_2$ (0.022 g; 0.044 mmol), $AgClO_4$ (0.018 g; 0.089 mmol), and 15 mL of acetone. The solution was stirred for 15 min, and then the solution was filtered and transferred to a flask which contained 2,5-$(CN)_2C_6F_3$-1-(N═PPh_2Me) **9** (0.035 g; 0.089 mmol) in 15 mL of acetone. The resultant yellow solution was stirred at room temperature for about 2 h before the solvent was removed *in vacuo* to leave a yellow solid. This crude product was washed with hexane (3 × 15 mL) and dried *in vacuo* to obtain the pure compound **11** (yield 0.04 g; 64%; mp >150 °C dec). Anal. Calcd for $C_{29}H_{25}N_3F_3PRhClO_4$: C, 49.35; H 3.57; N, 5.95; Cl, 5.02. Found: C, 49.47; H, 3.55; N, 5.60; Cl, 5.06. MS (FAB): 606 (monocation). ^{19}F NMR (CD_2Cl_2): (F ortho, meta, or para relative to the imino substituent): δ (F_o) −118.9 ppm (singlet, 1F); δ (F_p) −132.6 ppm (singlet, 1F); δ (F_m) −146.2 ppm (singlet, 1F). ^{1}H NMR (CD_2Cl_2): phenyl rings, δ 7.6, 7.8 ppm (m, 10H); cod group, δ 4.50 ppm (broad, 4H, HC═), δ 2.50 ppm (broad, 4H, H_2C), δ 1.95 ppm (broad, 4H, H_2C); methyl group: 2.30 ppm (d, 3H, $^2J_{PH}$ = 13 Hz). Molecular weight determination: 654 (solvent; CH_2Br_2).

Synthesis of [2,4-(CN)$_2$C$_6$F$_3$-1-(N═PPh$_2$Me)Rh(cod)](ClO$_4$) (12). To a 100 mL flask were added $[Rh(cod)Cl]_2$ (0.049 g; 0.100 mmol), $AgClO_4$ (0.042 g; 0.200 mmol), and 15 mL of acetone. The solution was stirred for 15 min, and then the solution was filtered and transferred to a flask which contained 2,4-$(CN)_2C_6F_3$-1-(N═PPh_2Me) **5** (0.079 g; 0.200 mmol), in 15 mL of acetone. The resultant yellow solution was stirred at room temperature for about 2 h before the solvent was removed *in vacuo* to leave a yellow solid. This crude product was washed with hexane (3 × 15 mL) and dried *in vacuo* to obtain the pure compound **12** (yield 0.075 g; 53%; mp 204−206 °C). Anal. Calcd for $C_{29}H_{25}N_3F_3PRhClO_4$: C, 49.35; H, 3.57; N, 5.95; Cl, 5.02. Found: C, 49.49; H, 3.34; N, 5.72; Cl, 5.39. MS (FAB): 606 ([LRh-(cod)]. ^{19}F NMR (CD_2Cl_2): δ (F_3 (between two CN)) −100.4 ppm (s, 1F); δ (F_1 (close to P) −152.1 ppm (broad, 1F); δ (F_2) −123.8 ppm (d, J = 20 Hz, 2F). ^{1}H NMR (CD_2Cl_2): phenyl rings, δ 7.55, 7.60, 7.75 ppm (m, 10H); methyl group, δ 2.35 ppm (d, $^2J_{PH}$ = 12 Hz) cod group; δ 4.55 ppm (s, 4H, HC═), δ 2.50 ppm (broad doublet, 4H, H_2C−), δ 1.95 ppm (broad 4H, H_2C−). The compound was not sufficiently soluble for a molecular weight determination.

Synthesis of [4,6-(CN)$_2$C$_6$F$_2$-1,3-(N═PPh$_2$Me)$_2$Rh(cod)](ClO$_4$) (13). To a 100 mL flask were added $[Rh(cod)Cl]_2$ (0.049 g; 0.100 mmol), $AgClO_4$ (0.042 g; 0.200 mmol), and 15 mL of acetone. The solution was stirred for 15 min, and then the solution was filtered and transferred to a flask which contained 4,6-$(CN)_2C_6F_2$-1,3-(N═PPh_2-$Me)_2$, **2** (0.059 g; 0.100 mmol), in 15 mL of acetone. The resultant

yellow solution was stirred at room temperature for about 2 h before the solvent was removed *in vacuo* to leave a yellow solid. This crude product was washed with hexane (3 × 15 mL) and dried *in vacuo* to obtain the pure compound **14** (yield 0.08 g; 66%; mp >170 °C dec). Anal. Calcd for $C_{50}H_{50}N_4F_2P_2Rh_2(ClO_4)_2$: C, 49.57; H, 4.14; N, 4.62; Cl, 5.85. Found: C, 50.11; H, 4.26; N, 4.51; Cl, 5.83. MS (FAB): 801 ([LRh(cod)]), 903 ([RhLRh(cod)]), 1012 ([LRh_2(cod)$_2$]), 1283 ([L_2-Rh]), and 1391 ([L_2Rh(cod)]). ^{19}F NMR (CD_2Cl_2): δ (F_1 (between two imines)) −143.2 ppm (broad, 1F); δ (F_2) −102.06 ppm (broad, 1F). ^{1}H NMR (CD_2Cl_2): phenyl rings, δ 7.50 ppm (m, 20H); methyl group, δ 1.90 ppm (broad, 6H); cod group, δ 4.45 ppm (broad, 8H, HC═), δ 2.55 ppm (broad, 8H, H_2C−), δ 1.95 ppm (broad, 8H, H_2C−). The compound was not sufficiently soluble for a molecular weight determination.

Synthesis of [3,4-$(CN)_2C_6F_3$-1-(N═PPh_3)Rh(cod)]$_2$(ClO_4)$_2$ (14). To a 100 mL flask were added [Rh(cod)Cl]$_2$ (0.049 g; 0.100 mmol), $AgClO_4$ (0.042 g; 0.20 mmol), and **15** mL of acetone. The solution was stirred for 15 min, and then the solution was filtered and transferred to a flask which contained 3,4-$(CN)_2C_6F_3$-1-(N═PPh_3), **6** (0.092 g; 0.200 mmol), in 15 mL of acetone. The resultant yellow solution was stirred at room temperature for about 2 h before the solvent was removed *in vacuo* to leave a yellow solid. This crude product was washed with hexane (3 × 15 mL) and dried *in vacuo* to obtain the pure compound **15** (yield 0.085 g; 55%; mp >140 °C dec). Anal. Calcd for $C_{68}H_{54}N_6F_6P_2Rh_2Cl_2O_8$: C, 53.18; H, 3.54; N, 5.47; Cl, 4.62. Found: C, 53.11; H, 3.48; N, 5.14; Cl, 5.08. MS (FAB): 668 (monocation). ^{19}F NMR ($CDCl_3$): δ (F_1 (between imine and F_3)) −135.0 ppm (broad, 2F): δ (F_2 (between imine and and one CN) −113.1 ppm (broad doublet, J = 21 Hz, 2F); δ (F_3 (between F_1 and one CN)) −129.9 ppm (broad doublet, J = 21 Hz, 2F). ^{1}H NMR (CD_2Cl_2): phenyl rings, δ 7.45, 7.55 ppm (m, 30H); δ 4.5 ppm (s, 8H, HC═), δ 2.45 ppm (broad, 8H, H_2C−), δ 1.90 ppm (broad, 8H, H_2C−). Molecular weight determination: 918 (solvent: CH_2Br_2).

Synthesis of [3,4-$(CN)_2C_6F_3$-1-(N═PPh_2Me)Rh(cod)]$_2$(ClO_4)$_2$ (15). To a 100 mL flask were added [Rh(cod)Cl]$_2$ (0.049 g; 0.100 mmol), $AgClO_4$ (0.042 g; 0.20 mmol), and 15 mL of acetone. The solution was stirred for 15 min, and then the solution was filtered and transferred to a flask which contained 3,4-$(CN)_2C_6F_3$-1-(N═PPh_2Me) **7** (0.079 g; 0.200 mmol) in 15 mL of acetone. The resultant yellow solution was stirred at room temperature for about 2 h before the solvent was removed *in vacuo* to leave a yellow solid. This crude product was washed with hexane (3 × 15 mL) and dried *in vacuo* to obtain the pure compound **16** (yield 0.10 g; 81%; mp >150 °C dec). Anal. Calcd for $C_{58}H_{50}N_6F_6P_2Rh_2Cl_2O_8$: C, 49.35; H, 3.57; N, 5.95; Cl, 5.02. Found: C, 49.65; H, 3.71; N, 5.55; Cl, 5.44. MS (FAB): 1001, [L_2-Rh(cod)], 668 [LRh(cod)]. ^{19}F NMR ($CDCl_3$): δ (F_1 (between imine and F_3)) −137.3 ppm (broad, 2F); δ (F_2 (between imine and one CN)) −114.5 ppm (broad doublet, J = 22 Hz, 2F), δ (F_3 (between F_1 and one CN)) −130.5 ppm (broad doublet, J = 22 Hz, 2F). ^{1}H NMR ($CDCl_3$): phenyl rings, δ 7.50, 7.75 ppm (m, 20H); δ 4.65 ppm, (s, 8H, HC═), δ 2.60 ppm (broad, 8H, H_2C−), δ 2.00 ppm (broad, 8H, H_2C−), methyl groups: δ 2.30 ppm (d, 6H, $^2J_{PH}$ = 13 Hz). Molecular weight determination: 828 (sovlent: CH_2Br_2).

Crystallography. Crystal structure studies of compounds **1**−**3** were done at the University of Toledo. The relevant data are given in Table 2. The hydrogen atoms were generated at idealized calculated positions by assuming a C−H bond length of 0.95 Å and the appropriate sp^2 or sp^3 geometry. All hydrogen atoms were than included in the calculations with fixed, isotropic Gaussian displacement parameters 1.3 times those of the attached atoms, and were constrained to "ride" on the attached atoms. Final *R* values are given in Table 2, and final difference peaks were small and without chemical significance.

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Supporting Information Available: Tables of experimental crystallographic data, bond lengths and angles, positional and displacement parameters and displacement parameter expressions are given for **1**, **2**, and **3**, and a least-squares plane table is also given for **2** (36 pages). Ordering information is given on any current masthead page.

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