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Azavinylidene and Azavinylidene-Bridged Compounds of Iridium and Rhodium

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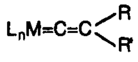
The synthesis of the azavinylidene and azavinylidene-bridged compounds Ir(=N=CPh$_2$)(diolefin)(PCy$_3$) (**5**, diolefin = tetrafluorobenzobarrelene (TFB); **6**, diolefin = 1,5-cyclooctadiene (COD)) and [Ir(μ-N=CPh$_2$)(diolefin)]$_2$ (**7**, diolefin = COD; **8**, diolefin = TFB) is described. The azavinylidene derivatives **5** and **6** were prepared by reaction of the corresponding square-planar methoxy complex Ir(OMe)(diolefin)(PCy$_3$) with benzophenone imine, whereas the azavinylidene-bridged **7** and **8** were similarly obtained from [Ir(μ-OMe)(diolefin)]$_2$ (diolefin = COD, TFB). The complexes **7** and **8** react with CO to give [Ir(μ-N=CPh$_2$)(CO)$_2$]$_2$ (**9**), which affords [Ir(μ-N=CPh$_2$)(CO)(PCy$_3$)]$_2$ (**10**) in the presence of PCy$_3$. The preparation of the related compounds [Rh(μ-N=CPh$_2$)(diolefin)]$_2$ (diolefin = COD (**13**), TFB (**14**)), [Rh(μ-N=CPh$_2$)(CO)$_2$]$_2$ (**15**), Rh$_2$(μ-N=CPh$_2$)$_2$(CO)$_3$PCy$_3$ (**16**), and [Rh(μ-N=CPh$_2$)(CO)(PCy$_3$)]$_2$ (**17**) is also reported. The structure of **14** was determined by an X-ray investigation. **14** crystallizes in the space group $P\bar{1}$ with a = 16.468(5) Å, b = 16.569(5) Å, c = 18.139(5) Å, α = 66.03(1)°, β = 74.32(2)°, γ = 89.71(2)°, and Z = 4. The molecular structure reveals that the core of the molecule is formed by a Rh$_2$N$_2$ skeleton in a bent configuration.

Introduction

In contrast to the well-documented vinylidene (I) and vinylidene-bridged (II) complexes, which have been the subject of intensive studies in recent years,[1] little is known about the related azavinylidene (III) and azavinylidene-bridged (IV) compounds with nitrogen instead of carbon in the α-position of the unsaturated ligands.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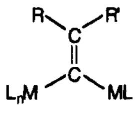
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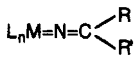
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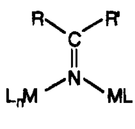
IV

The azavinylidene compounds previously reported are Sc,[2] Ti,[3] Zr,[4] Cr,[5] Mo,[6] W,[7] Re,[8] Ru,[9] and Os[10] complexes, which have been prepared in some of the following ways:[3−10] (i) reaction of halogenhydridometal compounds with oximes in the presence of AgPF$_6$, (ii) deprotonation of imine complexes, (iii) treatment of halogeno compounds with ketenimino derivatives such as LiN=CRR′, NaN=CRR′, and Me$_3$Si−N=CRR′, (iv) exchange of an oximato ligand by reaction with an imine, (v) insertion of nitriles into M−H, M−C, and M−Si bonds, (vi) deprotonation of an imido ligand at a C$_\beta$ atom, (vii) nucleophilic attack at a coordinated nitrile carbon, (viii) addition of CN$^-$ and H$^+$ to carbene compounds, and (ix) isomerization of azaallyl complexes.

The formation of azavinylidene-bridged compounds has only been described in a few cases for Ti,[11] Mn,[12] Fe,[13] and Co.[14] In general, these compounds have been synthesized by reaction of dinuclear complexes with diazirines.

[⊛] Abstract published in *Advance ACS Abstracts,* July 1, 1994.

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We have previously reported that the reaction of the dimer [Ir(μ-OMe)(COD)]$_2$ (COD = 1,5-cyclooctadiene) with PCy$_3$ leads to the mononuclear Ir(OMe)(COD)(PCy$_3$), which is a useful starting material for the synthesis of σ-alkynyl, dihydrido silyl, and new alkoxy compounds.[15]

We have now observed that the reactions of Ir(OMe)(COD)(PCy$_3$) and the related tetrafluorobenzobarrelene (TFB) derivative Ir(OMe)(TFB)(PCy$_3$) with benzophenone imine afford unusual iridium(I) compounds of formula Ir(=N=CPh$_2$)(diolefin)(PCy$_3$). Similarly, the reactions of the dimers [M(μ-OMe)(diolefin)]$_2$ (M = Ir, Rh) with benzophenone imine lead to [M(μ-N=CPh$_2$)(diolefin)]$_2$ (M = Ir, Rh).

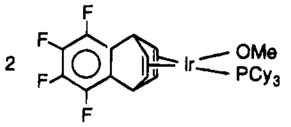
The present paper describes the preparation and characterization of these unusual azavinylidenes and azavinylidene-bridged compounds.

Results and Discussion

Synthesis and Characterization of (Azavinylidene)iridium(I) Compounds. Similarly to the reaction of [Ir(μ-OMe)(COD)]$_2$ (**1**) with PCy$_3$ to give Ir(OMe)(COD)(PCy$_3$) (**2**), the reaction of [Ir(μ-OMe)(TFB)]$_2$ (**3**) with the stoichiometric amount of PCy$_3$ in methanol, after 30 min, leads to Ir(OMe)(TFB)(PCy$_3$) (**4**), which was isolated as an orange solid in 85% yield (eq 1).

$[Ir(\mu\text{-}OMe)(TFB)]_2 + 2\,PCy_3 \longrightarrow$

3

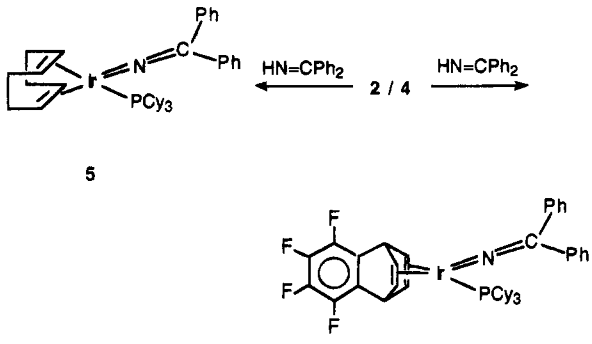


(1)

4

The ^{1}H NMR spectrum of **4** is compatible with a square-planar structure, analogous to that of **2**. It shows a singlet at 4.12 ppm due to the methoxy protons. The characteristic resonances of the diolefin are two broad signals at 5.29 and 3.59 ppm. The first signal is attributable to the tertiary CH protons and the second signal to the olefinic protons *trans* to the PCy$_3$ group. The resonance due to the olefinic protons *trans* to the methoxy group is masked by the complex aliphatic resonances (2.00–1.10 ppm) of the tricyclohexylphosphine ligand. The presence of the methoxy group is also supported by the IR spectrum in Nujol, which shows a band at 1035 cm^{-1} assignable to ν(CO). The ^{31}P{^{1}H} spectrum contains a singlet at 19.2 ppm.

The easy synthesis and stability of **2** and **4** allow the preparation of the azavinylidenes **5** and **6** (eq 2). Thus, treatment of **2** and **4** with benzophenone imine in hexane at room temperature affords orange solids in 36% and 60% yields, respectively. With regard to the spectroscopic data, there is no doubt that **5** and **6** have



5

(2)

6

a square-planar geometry. The ^{1}H NMR spectrum of **5** shows two broad resonances at 4.43 and 2.99 ppm, assigned to the vinyl protons of the 1,5-cyclooctadiene ligand *trans* to PCy$_3$ and N=CPh$_2$, respectively. In agreement with this, the ^{13}C{^{1}H} NMR spectrum of **5** also shows two resonances due to the vinyl carbon atoms. The carbon atoms of the olefinic bond *trans* to PCy$_3$ appear at 83.39 ppm as a doublet with a P—C coupling constant of 12.9 Hz, whereas the olefinic carbon atoms *trans* to N=CPh$_2$ appear at 48.41 ppm as a singlet. The *C*=N carbon atom of the azavinylidene ligand was found at 156.28 ppm as a doublet with a P—C coupling constant of 1.8 Hz. In the ^{1}H NMR spectrum of **6** the resonance due to the vinyl protons *trans* to N=CPh$_2$ is masked by the aliphatic resonances of PCy$_3$. However, in the ^{13}C{^{1}H} NMR spectrum, the resonance attributable to the corresponding olefinic carbon atoms can clearly be observed as a singlet at 16.15 ppm. The olefinic carbon atoms *trans* to PCy$_3$ appear at 56.70 ppm as a doublet with a P—C coupling constant of 11.9 Hz. Similarly to the ^{13}C{^{1}H} NMR spectrum of **5**, the ^{13}C{^{1}H} NMR spectrum of **6** shows the *C*=N carbon atom of the azavinylidene ligand at 157.90 ppm as a doublet with a P—C coupling constant of 1.4 Hz.

In addition, it should be noted that the resonances due to the olefinic carbon atoms *trans* to the azavinylidene ligand appear at unusually high field. This is in agreement with the great π-donor power of the azavinylidene groups, which are generally viewed as three-electron-donor ligands.[6a,16,17]

The presence of the azavinylidene ligand in **5** and **6** is also supported by the IR spectra of both compounds, which show a band at 1625 (**5**) and 1640 (**6**) cm^{-1} assignable to ν(C=N). Singlets at 12.02 (**5**) and 15.84 (**6**) ppm, in the ^{31}P{^{1}H} NMR spectra, are also characteristic of the new species.

To the best of our knowledge, the only iridium–azavinylidene complex described so far is the pentamethylcyclopentadienyl–iridium(III) derivative [Ir(η^5-C$_5$Me$_5$)(=N=CPh$_2$)(PMe^{t}Bu$_2$)]PF$_6$ obtained by Werner *et al.* by reaction of Ir(η^5-C$_5$Me$_5$)Cl$_2$(PMe^{t}Bu$_2$) with benzophenone imine in the presence of AgPF$_6$.[10b] Therefore, our compounds are the first iridium(I) azavinylidene complexes, and the first examples of neutral iridium azavinylidene derivatives.

Synthesis and Characterization of Azavinylidene-Bridged Iridium Compounds. The methoxy dimer complexes **1** and **3** react with the stoichiometric

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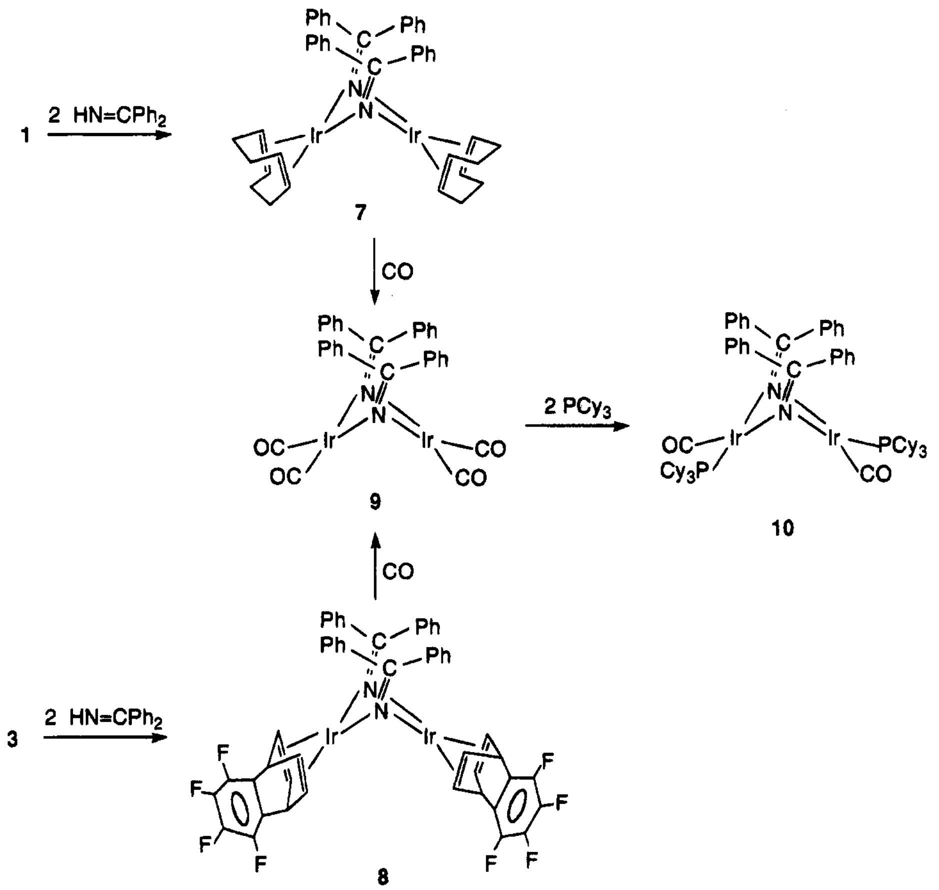
Scheme 1



amount of benzophenone imine to give the azavinylidene-bridged compounds **7** and **8** (Scheme 1), which were isolated as green solids in 82% and 81% yield, respectively.

In agreement with the bent configuration shown in Scheme 1, the ^{1}H NMR spectrum of **7** (Figure 1a) contains two olefinic resonances at 4.20 and 3.12 ppm and three aliphatic resonances at 2.45, 1.95, and 1.78 ppm. These signals were assigned to the protons a, b, c, and d of the coordinated 1,5-cyclooctadiene, by comparison of the spectrum shown in Figure 1a with that recently reported by Shapley and co-workers for the trifluoroacetato dimer $[Ir(\mu\text{-}\eta^2\text{-}O_2CCF_3)(COD)]_2$.[18] In accordance with the ^{1}H NMR spectrum, the $^{13}C\{^1H\}$ NMR spectrum of **7** shows in the δ 70–25 ppm region four signals (Figure 1b), two olefinic resonances at 64.25 and 63.54 ppm and two aliphatic resonances at 32.76 and 32.40 ppm.

The ^{1}H NMR spectrum of **8** is temperature dependent. At room temperature it shows two signals due to the tetrafluorobenzobarrelene diolefin at 5.39 and 2.50 ppm, whereas at −60 °C the spectrum contains four resonances, two aliphatic at 5.74 and 5.14 ppm and two olefinic at 3.05 and 1.90 ppm. This behavior suggests a slow (on the NMR time scale) intramolecular exchange process that interconverts the inequivalent (up/down) diolefin protons. This equilibration could be due to rotation of the tetrafluorobenzobarrelene ligand about the diene coordination axis or to inversion of the folded structure at the position of the bridging ligands.

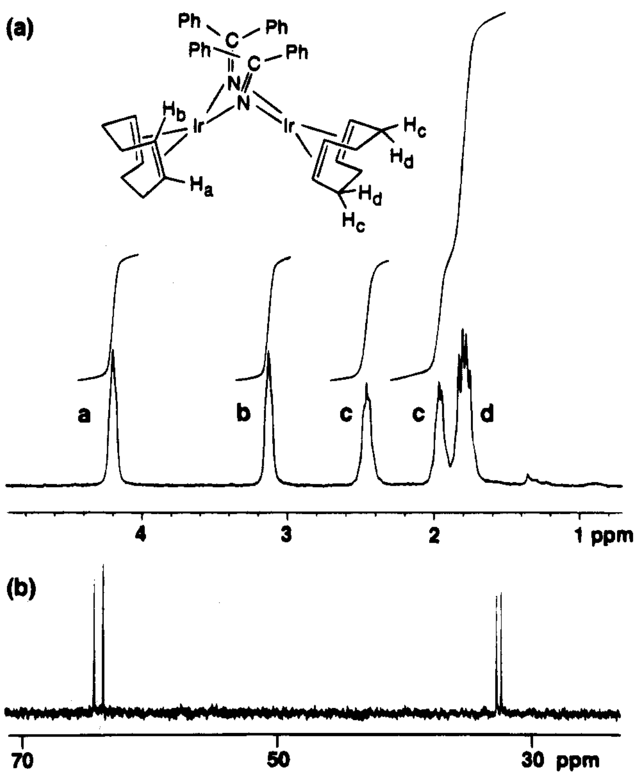


Figure 1. (a) ^{1}H NMR (benzene-d_6) spectrum of **7** in the 5.00–1.00 ppm region. (b) $^{13}C\{^1H\}$ NMR (benzene-d_6) spectrum of **7** in the 70–25 ppm region.

Bubbling CO through a dichloromethane solution of **7** or **8** results in the displacement of the coordinated diolefin and formation of the tetracarbonyl derivative **9**, which was isolated as a brown solid in 40% yield. The IR and $^{13}C\{^1H\}$ NMR spectra of this compound are in

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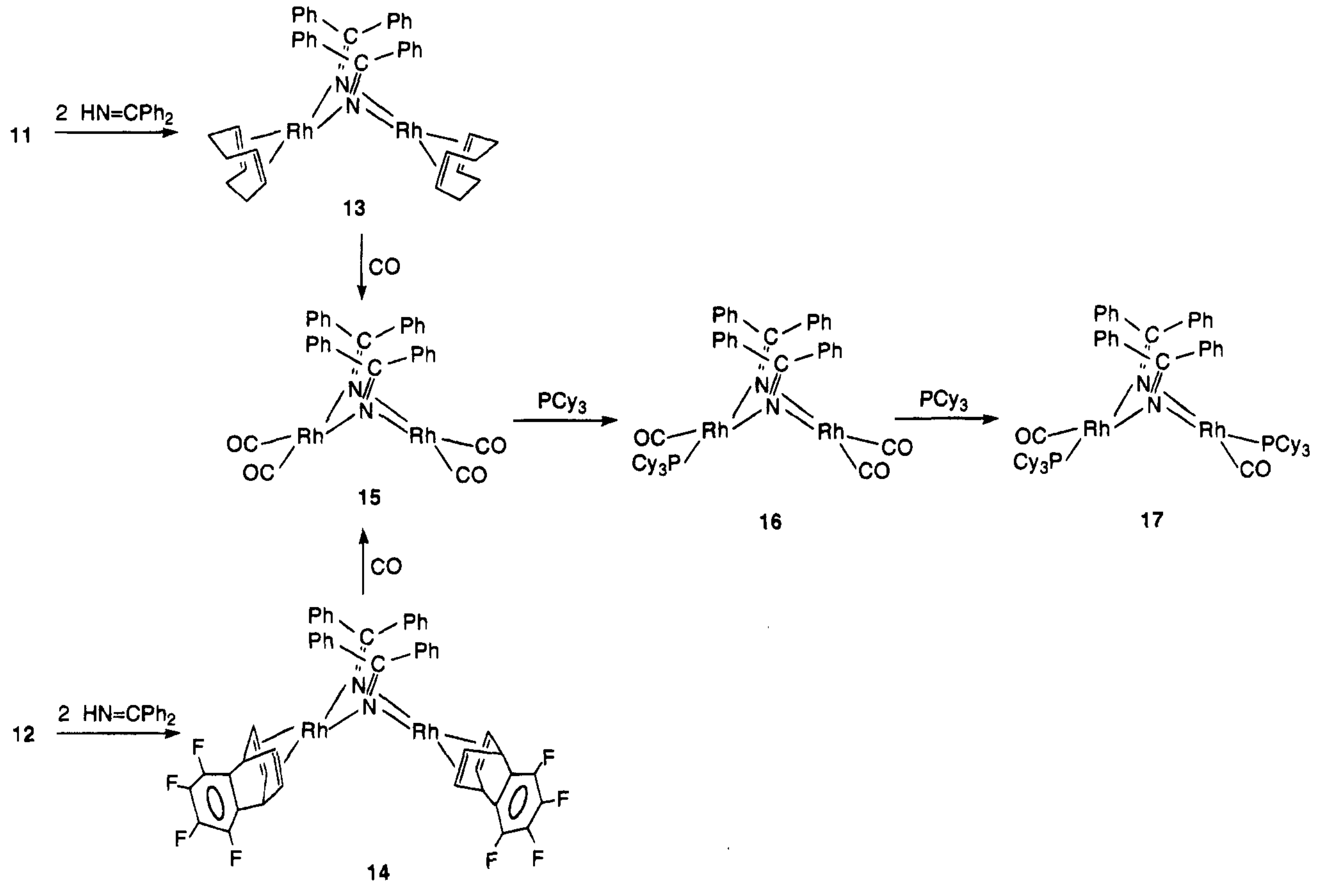
[18] Szajek, L. P.; Shapley, J. R. *Organometallics* **1993**, *12*, 3772.

Scheme 2



good agreement with the structure proposed in Scheme 1. The IR spectrum shows three ν(CO) bands at 2060, 2035, and 1990 cm^{-1}, whereas in the $^{13}C\{^1H\}$ NMR spectrum only a single resonance is observed at 183.35 ppm for the four CO ligands. Similar spectra have been recently reported for the complex $[Ir\{\mu\text{-}NH(p\text{-tolyl})\}(CO)_2]_2$, comparable in structure to **9**.[19]

Complex **9** reacts with tricyclohexylphosphine in a 1:2 molar ratio in hexane to give **10** (Scheme 1), which was isolated as a dark green solid in 63% yield. The IR spectrum of **10** shows a ν(CO) band at 1925 cm^{-1}, suggesting a *trans* disposition. In the $^{13}C\{^1H\}$ NMR spectrum only a single resonance is observed at 185.77 ppm for the two carbonyl groups. This resonance appears as a doublet with a P—C coupling constant of 12.9 Hz.

In addition, it should be mentioned that the ν(C=N) bands of the bridging-azavinylidene ligands of **7**–**10** appear at 1600 (**7**, **9**) and 1605 (**8**, **10**) cm^{-1}, between 20 and 40 cm^{-1} toward lower frequency than the resonance of the azavinylidene compounds **5** and **6**. There is also a marked difference in the chemical shift between *C*=N carbon atom resonances of the bridging-azavinylidene ligands of **7**–**10** and those of the azavinylidene groups of **5** and **6**. Thus, the $^{13}C\{^1H\}$ NMR spectra of **7**–**10** show the *C*=N signals between 169.82 and 176.14 ppm, about 16 ppm toward lower fields than the *C*=N signals observed in the $^{13}C\{^1H\}$ NMR spectra of **5** and **6**. A similar relationship has been found between the corresponding signals of vinylidene and bridging-vinylidene ligands.[1]

Synthesis and Characterization of Azavinylidene-Bridged Rhodium Complexes. Similarly to the reactions of **1** and **3** with benzophenone imine, the dimers $[Rh(\mu\text{-}OMe)(diolefin)]_2$ (diolefin = COD (**11**), TFB (**12**)) react with the stoichiometric amount of imine to afford the azavinylidene-bridged rhodium compounds **13** and **14** (Scheme 2). Complex **13** was isolated as a dark red solid in 80% yield, whereas the derivative **14** was obtained as a dark blue solid in 94% yield.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **13** at room temperature are similar to those shown in Figure 1. The ^1H NMR spectrum shows two olefinic resonances at 4.45 and 3.08 ppm and three aliphatic resonances at 2.71, 1.91, and 1.59 ppm. The $^{13}C\{^1H\}$ NMR spectrum contains in the δ 80–30 ppm region two olefinic resonances at 78.92 and 78.49 ppm and two aliphatic resonances at 31.71 and 31.22 ppm. The signals due to the olefinic carbon atoms of the coordinated 1,5-cyclooctadiene ligands appear as doublets with Rh—C coupling constants of 12.0 and 11.4 Hz, respectively. The ^1H NMR spectrum of **14** is temperature dependent, as is the spectrum of its analogous iridium derivative. At room temperature, it shows two broad signals due to the diolefin at 5.35 and 3.12 ppm. At −60 °C, the spectrum contains two aliphatic resonances at 5.87 and 5.10 ppm and two olefinic resonances at 3.81 and 2.56 ppm.

The ^1H NMR spectrum of **13** at room temperature and the ^1H NMR spectrum of **14** at −60 °C suggest that, in the solid state, these compounds have a bent configuration, as was previously proposed for the analogous iridium derivatives. In order to confirm this, an X-ray diffraction experiment was carried out on a single

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[19] Kolel-Veetil, M. K.; Rheingold, A. L.; Ahmed, K. J. *Organometallics* **1993**, *12*, 3439.

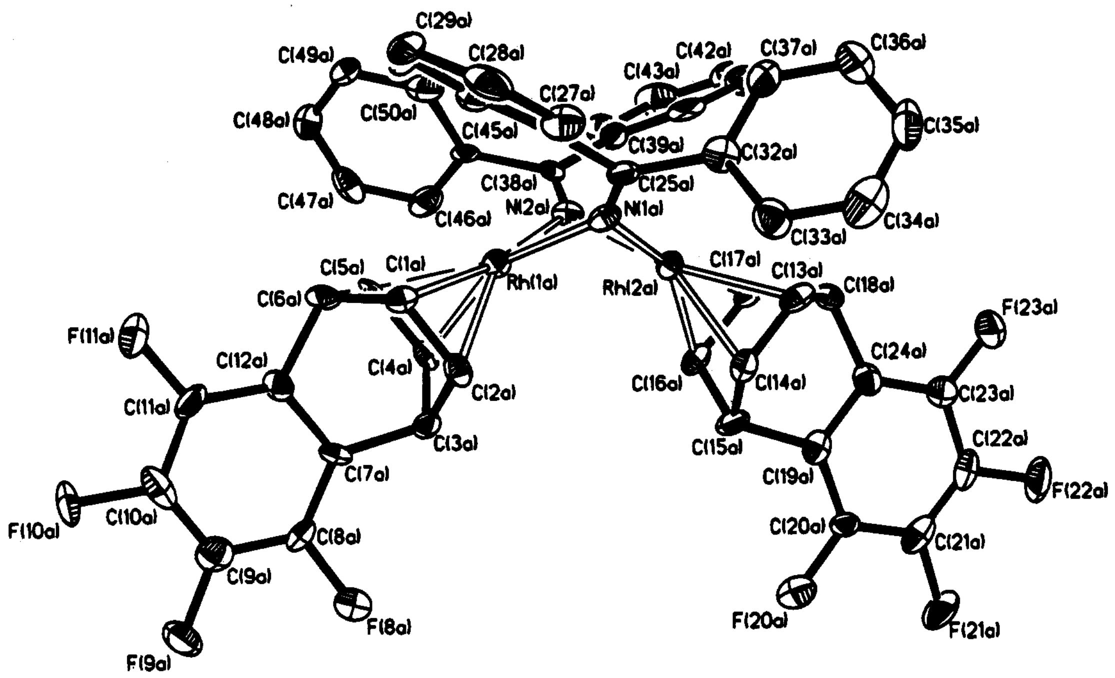

Figure 2. ORTEP diagram of complex **14**. Thermal ellipsoids are shown at the 50% level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex[a] [Rh(μ-N=CPh$_2$)(TFB)]$_2$·0.5C$_6$H$_{14}$ (14)

	a	b		a	b
Rh(1)—Rh(2)	2.827(1)	2.835(1)	C(4)—C(5)	1.370(14)	1.386(14)
Rh(1)—N(1)	2.046(7)	2.052(7)	Rh(2)—N(1)	2.038(7)	2.049(6)
Rh(1)—N(2)	2.054(6)	2.054(7)	Rh(2)—N(2)	2.048(9)	2.046(9)
Rh(1)—C(1)	2.150(8)	2.145(9)	Rh(2)—C(13)	2.142(11)	2.158(11)
Rh(1)—C(2)	2.124(8)	2.122(9)	Rh(2)—C(14)	2.117(11)	2.127(11)
Rh(1)—C(4)	2.129(7)	2.131(7)	Rh(2)—C(16)	2.121(8)	2.144(7)
Rh(1)—C(5)	2.144(9)	2.153(9)	Rh(2)—C(17)	2.154(9)	2.133(9)
N(1)—C(25)	1.282(10)	1.278(9)	C(13)—C(14)	1.368(9)	1.399(10)
N(2)—C(38)	1.264(12)	1.281(13)	C(16)—C(17)	1.393(9)	1.402(11)
C(1)—C(2)	1.403(14)	1.385(14)			
N(1)—Rh(1)—N(2)	76.0(3)	76.2(3)	N(1)—Rh(2)—N(2)	76.3(3)	76.5(3)
N(1)—Rh(1)—M(1)[b]	105.1(3)	106.2(3)	N(1)—Rh(2)—M(3)	107.4(3)	105.3(3)
N(1)—Rh(1)—M(2)	171.9(3)	169.8(3)	N(1)—Rh(2)—M(4)	170.5(3)	173.6(3)
N(2)—Rh(1)—M(1)	170.9(3)	173.4(3)	N(2)—Rh(2)—M(3)	173.2(3)	169.1(3)
N(2)—Rh(1)—M(2)	107.2(3)	106.2(3)	N(2)—Rh(2)—M(4)	105.0(3)	107.2(3)
M(1)—Rh(1)—M(2)	70.5(3)	70.4(3)	M(3)—Rh(2)—M(4)	70.4(3)	70.1(3)
Rh(1)—N(1)—Rh(2)	87.6(3)	87.5(3)	Rh(1)—N(2)—Rh(2)	87.1(3)	87.5(3)
Rh(1)—N(1)—C(25)	136.6(6)	135.5(7)	Rh(1)—N(2)—C(38)	134.6(6)	137.1(7)
Rh(2)—N(1)—C(25)	135.7(6)	137.0(7)	Rh(2)—N(2)—C(38)	138.3(6)	135.3(7)

[a] The two sets of data (a and b) correspond to equivalent parameters in both crystallographically independent molecules. [b] M(1), M(2), M(3), and M(4) represent the midpoints of the C(1)—C(2), C(4)—C(5), C(13)—C(14), and C(16)—C(17) olefin double bonds, respectively.

crystal of **14**. The structure exhibits two chemically equivalent, but crystallographically independent, molecules of the complex in the asymmetric unit. An ORTEP diagram of one of them is shown in Figure 2. The values used in the discussion of the geometry of **14** correspond to the average value of the parameters determined for each of the crystallographically independent molecules. Selected bond distances and angles for both molecules are listed in Table 1.

The coordination around each rhodium atom is almost square planar. The dihedral angle between the two coordination planes, 115.0(1)°, gives a bent configuration to the molecule, as is predicted by the ^{1}H NMR spectrum. This geometry seems to be an intrinsic salient feature for molecules containing the four-membered Rh$_2$L$_2$ core.[20] The intramolecular Rh—Rh distance (2.831 Å) lies in the upper part of the range of distances (2.62–2.84 Å) observed for other rhodium dimers where a single bond is thought to exist.[21] The Rh—N bond lengths (about 2.05 Å) are comparable with those reported for complexes with ligands containing two nitrogen atoms bridging two Rh atoms (pyrazolato,[22]

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imidazolato,[23] biimidazolato,[24] 7-azaindolato,[25] and benzamidinato[26]).

Distances within bridging-azavinylidene ligands are essentially as expected. The nitrogen–carbon distances, N(1)–C(25) = 1.280 Å and N(2)–C(38) = 1.273 Å, are consistent with the formulation of these linkages as N=C.[11-14]

The distances between the rhodium atoms and the midpoint of the carbon–carbon double bonds of the diolefin (about 2.021 Å) compare well with the values previously found for other (tetrafluorobenzobarrelene)-rhodium complexes.[26] Similarly, the olefinic bond distances (about 1.38 Å) are in the range found in transition-metal–olefin complexes, in agreement with the usual Chatt–Dewar metal–olefin bonding scheme.

Complexes **13** and **14** react with carbon monoxide to give the tetracarbonyl derivative **15**, which was isolated as a brown solid in 78% yield. In accordance with the bent geometry of this molecule, the IR spectrum contains three ν(CO) bands at 2075, 2025, and 2005 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectrum, the four carbonyl groups appear as a doublet at 187.90 ppm with a Rh–C coupling constant at 66.2 Hz. The *C*–N carbon atom of the azavinylidene ligand is observed as a singlet at 179.20 ppm.

Treatment of **15** with tricyclohexylphosphine in a 1:1 molar ratio in hexane leads to the formation of an orange solid in 49% yield, which was characterized as the tricarbonyl complex **16** (Scheme 2). The IR spectrum of **16** shows in the terminal carbonyl region three ν(CO) bands at 2045, 1985, and 1950 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectrum the carbonyl ligands give three resonances at 195.32, 191.72, and 189.41 ppm. The first resonance appears as a double doublet with a Rh–C coupling constant of 71.3 Hz and a P–C coupling constant of 19.8 Hz. The second and third resonances are observed as doublets with Rh–C coupling constants of 66.3 and 68.1 Hz, respectively. In addition, two signals due to two chemically inequivalent *C*=N carbon atoms at 175.07 and 173.59 ppm are also observed. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet at 48.2 ppm with a Rh–P coupling constant of 147.4 Hz.

Related tricarbonylrhodium compounds containing carboxylato groups as bridging ligands have recently been prepared in our laboratory. These complexes were synthesized by reaction of the corresponding tetracarbonyl derivatives with tricyclohexylphosphine.[27]

Complex **16** in the presence of a second molecule of tricyclohexylphosphine is converted into the dicarbonyl complex **17**. This compound was obtained as a dark red solid in 72% yield. In agreement with the *trans* structure shown in Scheme 2, the IR spectrum of **17** shows a ν(CO) band at 1925 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectrum, the most distinctive spectroscopic data are a double doublet at 197.90 ppm (J_{Rh-C} = 71.1 Hz and J_{P-C} = 19.7 Hz) due to the carbonyl groups and a singlet at 170.53 ppm assigned to the *C*=N carbon atoms of the bridging-azavinylidene ligands. The $^{31}P\{^1H\}$ NMR spectrum contains a doublet at 50.7 ppm with a Rh–P coupling constant of 150.9 Hz.

Concluding Remarks

This study has shown that reactions of the complexes Ir(OMe)(diolefin)(PR$_3$) with HN=CR$_2$ afford azavinylidene derivatives of the type Ir(=N=CR$_2$)(diolefin)(PR$_3$). The complexes Ir(=N=CPh$_2$)(diolefin)(PCy$_3$) (diolefin = COD, TFB) reported in this paper are the first examples of (azavinylidene)iridium(I) derivatives.

Azavinylidene-bridged iridium and rhodium complexes of the formula [M(μ-N=CPh$_2$)(diolefin)]$_2$ (M = Rh, Ir; diolefin = COD, TFB) can be prepared in high yield by reaction of the corresponding dimers [M(μ-OMe)(diolefin)]$_2$ with benzophenone imine. These azavinylidene-bridged diolefin compounds react with carbon monoxide to give [M(μ-N=CPh$_2$)(CO)$_2$]$_2$ (M = Rh, Ir), which afford [M(μ-N=CPh$_2$)(CO)(PCy$_3$)]$_2$ and Rh$_2$(μ-N=CPh$_2$)$_2$(CO)$_3$(PCy$_3$) in the presence of PCy$_3$. From a structural point of view, it should be mentioned that the M$_2$N$_2$ (M = Rh, Ir) skeleton of these molecules has a bent configuration.

The binuclear compounds mentioned above are the first examples of azavinylidene-bridged complexes of rhodium and iridium.

Experimental Section

General Data. All reactions were carried out with the use of standard Schlenk procedures. Solvents were dried and purified by known procedures and distilled prior to use. Elemental analyses were performed with a Perkin-Elmer 240 microanalyzer. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian UNITY 300 spectrometer. Chemical shifts are expressed in parts per million upfield from Si(CH$_3$)$_4$ (^1H and $^{13}C\{^1H\}$ NMR spectra) of 85% H$_3$PO$_4$ ($^{31}P\{^1H\}$ NMR spectra). Infrared spectra were run on a Perkin-Elmer 783 spectrophotometer, as either solids (Nujol mulls on polyethylene sheets) or solutions (NaCl cell windows). MS data were recorded on a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the standard Cs$^+$ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix. Benzophenone imine (Aldrich) was used as purchased. The starting materials [Ir(μ-OMe)(COD)]$_2$ (**1**),[28] Ir(OMe)(COD)(PCy$_3$) (**2**),[15a] [Ir(μ-OMe)(TFB)]$_2$ (**3**),[29] [Rh(μ-OMe)(COD)]$_2$ (**11**),[28] and [Rh(μ-OMe)(TFB)]$_2$ (**12**)[28] were prepared by published methods.

Preparation of Ir(OMe)(TFB)(PCy$_3$) (4). PCy$_3$ (62.4 mg, 0.22 mmol) was added to a suspension of **3** (100 mg, 0.11 mmol) in 5 mL of methanol and the mixture stirred at room temperature for 30 min. The solution was decanted, and the orange solid was washed with methanol and dried in vacuo; yield 138 mg (85%). Anal. Calcd for C$_{31}$F$_4$H$_{42}$IrOP: C, 51.01; H, 5.80. Found: C, 50.57; H, 6.22. IR (Nujol, cm^{-1}): ν(CO) 1035 (m). ^1H NMR (C$_6$D$_6$, 20 °C): δ 5.29 (br, 2H, –C*H*), 4.12 (s, 3H, O*Me*), 3.59 (br, 2H, =C*H*), 2.00–1.10 (m, 35 H, =C*H*, Cy). $^{31}P\{^1H\}$ NMR: δ 19.2 (s).

Preparation of Ir(=N=CPh$_2$)(COD)(PCy$_3$) (5). A stoichiometric amount of HN=CPh$_2$ (27.5 μL, 0.16 mmol) was added to a suspension of **2** (100 mg, 0.16 mmol) in 10 mL of hexane, and the mixture was stirred at room temperature for 1 h. The resulting orange solution was cooled over 12 h at

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−78 °C, and then an orange solid formed. The solution was decanted, and the solid was washed with hexane and dried in vacuo; yield 42 mg (36%). Anal. Calcd for $C_{39}H_{55}IrNP$: C, 61.55; H, 7.28; N, 1.84. Found: C, 61.53; H, 8.18; N, 1.99. IR (Nujol, cm^{-1}): ν(C=N) 1625 (m). ^{1}H NMR (C_6D_6, 20 °C): δ 7.92−7.12 (m, 10 H, Ph), 4.43 (br, 2H, =C*H*), 2.99 (br, 2H, =C*H*), 2.58 (br, 2H, −C*H*$_2$−), 2.31−2.18 (br, 4H, −C*H*$_2$−), 1.75−0.95 (m, 35 H, −C*H*$_2$−, Cy). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ 156.28 (d, J_{P-C} = 1.8 Hz, *C*=N), 139.86 (d, J_{P-C} = 1.3 Hz, Ph C_{ipso}), 127.90 (s, *Ph*), 127.04 (s, *Ph*), 83.39 (d, J_{P-C} = 12.9 Hz, =CH *trans* to PCy$_3$), 48.41 (s, =CH *trans* to N=CPh$_2$), 35.77 (s, −CH$_2$−), 35.71 (s, −CH$_2$−), 33.70 (d, J_{P-C} = 23 Hz, P−*C*H, PCy$_3$), 30.38 (s, P*Cy*$_3$), 27.99 (d, J_{P-C} = 10.1 Hz, P*Cy*$_3$), 26.87 (s, P*Cy*$_3$). ^{31}P{^{1}H} NMR: δ 12.02 (s). MS (FAB): *m/e* 763 (M$^+$), 580 (M$^+$ − N=CPh$_2$).

Preparation of Ir(=N=CPh$_2$)(TFB)(PCy$_3$) (6). This compound was prepared analogously as described for **5**, by starting from **4** (100 mg, 0.137 mmol) and HN=CPh$_2$ (23 μL, 0.137 mmol). The solution was decanted, and the orange solid was washed with hexane and dried in vacuo; yield 72 mg (60%). Anal. Calcd for $C_{43}F_4H_{49}IrNP$: C, 58.75; H, 5.62; N, 1.59. Found: C, 58.92; H, 5.70; N, 1.48. IR (Nujol, cm^{-1}): ν(C=N) 1640 (m). ^{1}H NMR (C_6D_6, 20 °C): δ 7.93−7.21 (m, 10 H, *Ph*), 5.25 (br, 2H, −C*H*), 3.60 (br, 2H, =C*H*), 1.86−0.98 (m, 35H, =C*H*, *Cy*). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ 157.90 (d, J_{P-C} = 1.4 Hz, *C*=N), 139.18 (d, J_{P-C} = 1.9 Hz, Ph, C_{ipso}), 128.20 (s, *Ph*), 127.86 (s, *Ph*), 127.48 (s, *Ph*), 56.70 (d, J_{P-C} = 11.9 Hz, =CH *trans* to PCy$_3$), 37.98 (s, −CH), 34.39 (d, J_{P-C} = 26.2 Hz, P−*C*H, PCy$_3$), 30.21 (s, P*Cy*$_3$), 27.86 (d, J_{P-C} = 5.9 Hz, P*Cy*$_3$), 26.75 (s, P*Cy*$_3$), 16.15 (s, =CH *trans* to N=CPh$_2$). ^{31}P{^{1}H} NMR: δ 15.84 (s). MS (FAB): *m/e* 881 (M$^+$).

Preparation of [Ir(μ-N=CPh$_2$)(COD)]$_2$ (7). A suspension of **1** (100 mg, 0.15 mmol) in 10 mL of hexane was treated with the stoichiometric amount of HN=CPh$_2$ (51 μL, 0.30 mmol), and the resulting suspension was stirred for 2 h at room temperature. The solution was decanted, and the dark green solid that formed was washed with hexane and dried in vacuo; yield 119 mg (82%). Anal. Calcd for $C_{42}H_{44}Ir_2N_2$: C, 52.48; H, 4.61; N, 2.91. Found: C, 51.89; H, 4.85; N, 3.21. IR (Nujol, cm^{-1}): ν(C=N) 1600 (m). ^{1}H NMR (C_6D_6, 20 °C): δ 7.73−7.15 (m, 20 H, *Ph*), 4.20 (br, 4H, =C*H*), 3.12 (br, 4H, =C*H*), 2.45 (br, 4H, −C*H*$_2$−), 1.95 (br, 4H, −C*H*$_2$−), 1.78 (m, 8H, −C*H*$_2$−). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ 169.82 (s, *C*=N), 144.56 (s, Ph C_{ipso}), 129.11 (s, *Ph*), 128.24 (s, *Ph*), 127.58 (s, *Ph*), 64.25 (s, =CH), 63.54 (s, =CH), 32.76 (s, −CH$_2$−), 32.40 (s, −CH$_2$−). MS (FAB): *m/e* 961 (M$^+$).

Preparation of [Ir(μ-N=CPh$_2$)(TFB)]$_2$ (8). This compound was prepared analogously as described for **7**, by starting from **3** (100 mg, 0.11 mmol) and HN=CPh$_2$ (37 μL, 0.22 mmol). It was isolated as a dark green solid: yield 108 mg (81%). Anal. Calcd for $C_{50}F_4H_{32}Ir_2N_2$: C, 50.16; H, 2.69; N, 2.34. Found: C, 50.52; H, 2.89; N, 1.92. IR (Nujol, cm^{-1}): ν(C=N) 1605 (m). ^{1}H NMR (C_6D_6, 20 °C): δ 7.64−7.05 (m, 20 H, *Ph*), 5.39 (br, 4H, −C*H*), 2.50 (br, 8H, =C*H*). ^{1}H NMR (C_7D_8, −60 °C): δ 7.62−7.05 (m, 20H, *Ph*), 5.74 (br, 2H, −C*H*), 5.14 (br, 2H, −C*H*), 3.05 (br, 4H, =C*H*), 1.90 (br, 4H, =C*H*). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ 173.54 (s, *C*=N), 143.74 (s, Ph C_{ipso}), 128.99 (s, *Ph*), 128.62 (s, *Ph*), 127.83 (s, *Ph*), 40.50 (br, −CH and =CH). MS (FAB): *m/e* 1196 (M$^+$).

Preparation of [Ir(μ-N=CPh$_2$)(CO)$_2$]$_2$ (9). A dichloromethane solution (10 mL) of **7** (80 mg, 0.08 mmol) or **8** (100 mg, 0.08 mmol) was stirred under CO for 15 min and the resulting solution concentrated under reduced pressure to 0.5 mL. Addition of hexane caused the precipitation of a brown solid. The solution was decanted, and the solid was washed with hexane and dried in vacuo: yield 28.5 mg (40%). Anal. Calcd for $C_{30}H_{20}Ir_2N_2O_4$: C, 42.05; H, 2.35; N, 3.27. Found: C, 42.19; H, 2.60; N, 2.69. IR (Nujol, cm^{-1}): ν(CO) 2060 (s), 2035 (s), 1990 (s); ν(C=N) 1600 (m). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2060 (s), 2040 (s), 1990 (s). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ 183.35 (s, *C*O), 176.14 (s, *C*=N), 144.74 (s, Ph C_{ipso}), 129.87 (s, *Ph*), 128.65 (s, *Ph*), 128.11 (s, *Ph*). MS (FAB): *m/e* 856 (M$^+$), 828 (M$^+$ − CO), 800 (M$^+$ − 2 CO), 772 (M$^+$ − 3 CO), 744 (M$^+$ − 4 CO).

Preparation of [Ir(μ-N=CPh$_2$)(CO)(PCy$_3$)]$_2$ (10). A suspension of **9** (100 mg, 0.116 mmol) in 10 mL of hexane was treated with PCy$_3$ (65.4 mg, 0.23 mmol). Immediately the color of the suspension changed from brown to dark green and at the same time evolution of CO was observed. This suspension was stirred for 15 min at room temperature. The solution was decanted, and the dark green solid was washed with hexane and dried in vacuo: yield 100 mg (63%). Anal. Calcd for $C_{64}H_{86}Ir_2N_2O_2P_2$: C, 56.45; H, 6.36; N, 2.06. Found: C, 56.22; H, 6.84; N, 1.80. IR (Nujol, cm^{-1}): ν(CO) 1925 (vs); ν(C=N) 1605 (m). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 1920 (s). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ 185.77 (d, J_{P-C} = 12.9 Hz, *C*O), 173.32 (s, *C*=N), 148.68 (d, J_{P-C} = 2.8 Hz, Ph C_{ipso}), 144.88 (d, J_{P-C} = 7.3 Hz, Ph C_{ipso}), 131.09 (s, *Ph*), 129.54 (s, *Ph*), 128.40 (s, *Ph*), 128.06 (s, *Ph*), 127.34 (s, *Ph*), 127.24 (s, *Ph*), 36.35 (d, J_{P-C} = 29.4 Hz, P−*C*H PCy$_3$), 30.66 (s, P*Cy*$_3$), 30.14 (s, P*Cy*$_3$), 28.14 (d, J_{P-C} = 10.6 Hz, P*Cy*$_3$), 28.08 (d, J_{P-C} = 10.6 Hz, P*Cy*$_3$), 27.19 (s, P*Cy*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ 23.2 (s). MS (FAB): *m/e* 1362 (M$^+$).

Preparation of [Rh(μ-N=CPh$_2$)(COD)]$_2$ (13). This compound was prepared analogously as described for **7**, by starting from **11** (100 mg, 0.205 mmol) and HN=CPh$_2$ (69.3 μL, 0.41 mmol). It was isolated as a dark red solid: yield 129 mg (80%). Anal. Calcd for $C_{42}H_{44}N_2Rh_2$: C, 64.46; H, 5.67; N, 3.58. Found: C, 64.89; H, 5.89; N, 3.49. IR (Nujol, cm^{-1}): ν(C=N) 1605 (m). ^{1}H NMR (C_6D_6, 20 °C): δ 7.67−7.09 (m, 20 H, *Ph*), 4.45 (br, 4H, =C*H*), 3.08 (br, 4H, =C*H*), 2.71 (br, 4H, −C*H*$_2$−), 1.91 (br, 8H, −C*H*$_2$−), 1.59 (br, 4H, −C*H*$_2$−). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ 169.79 (s, *C*=N), 144.40 (s, Ph C_{ipso}), 128.93 (s, *Ph*), 127.52 (s, *Ph*), 78.92 (d, J_{Rh-C} = 12.0 Hz, =CH), 78.94 (d, J_{Rh-C} = 11.4 Hz, =CH), 31.71 (s, −CH$_2$−), 31.22 (s, −CH$_2$−). MS (FAB): *m/e* 602 (M$^+$ − N=CPh$_2$), 573 (M$^+$ − Rh(COD)), 392 (M$^+$/2).

Preparation of [Rh(μ-N=CPh$_2$)(TFB)]$_2$ (14). This compound was prepared analogously as described for **7**, by starting from **12** (100 mg, 0.14 mmol) and Ph$_2$C=NH (47 μL, 0.28 mmol) and stirring the mixture for 12 h. It was isolated as a dark blue solid: yield 133 mg (94%). Anal. Calcd for $C_{50}F_8H_{32}N_2Rh_2$: C, 58.95; H, 3.17; N, 2.75. Found: C, 58.90; H, 3.62; N, 2.51. IR (Nujol, cm^{-1}): ν(C=N) 1620 (m). ^{1}H NMR (C_6D_6, 20 °C): δ 7.60−7.04 (m, 20 H, *Ph*), 5.35 (br, 4H, −C*H*), 3.12 (br, 8H, =C*H*). ^{1}H NMR (C_7D_8, −60 °C): δ 7.60−7.04 (m, 20H, *Ph*), 5.87 (br, 2H, −CH), 5.10 (br, 2H, −CH), 3.81 (br, 4H, =CH), 2.56 (br, 4H, =CH). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ 172.36 (s, *C*=N), 144.20 (s, Ph C_{ipso}), 128.65 (s, *Ph*), 128.11 (s, *Ph*), 127.85 (s, *Ph*), 57.20 (d, J_{Rh-C} = 9.7 Hz, =CH), 40.94 (d, J_{Rh-C} = 3.7 Hz, −CH). MS (FAB): *m/e* 691 (M$^+$ − Rh(COD)), 510 (M$^+$/2).

Preparation of [Rh(μ-N=CPh$_2$)(CO)$_2$]$_2$ (15). This compound was prepared analogously as described for **9**, by starting from **13** (100 mg, 0.13 mmol) or **14** (130 mg, 0.13 mmol). It was isolated as a brown solid: yield 68 mg (78%). Anal. Calcd for $C_{30}H_{20}N_2O_4Rh_2$: C, 53.13; H, 2.97; N, 4.13. Found: C, 53.27; H, 3.14; N, 4.02. IR (Nujol, cm^{-1}): ν(CO) 2080−2000 (vs); ν(C=N) 1610 (m). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2075 (s), 2025 (s), 2005 (s). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ 187.90 (d, J_{Rh-C} = 66.2 Hz, *C*O), 179.20 (s, *C*=N), 145.10 (t, J_{Rh-C} = 1.8 Hz, Ph C_{ipso}), 129.37 (s, *Ph*), 128.49 (s, *Ph*), 128.12 (s, *Ph*). MS (FAB): *m/e* 678 (M$^+$), 622 (M$^+$ − 2CO), 594 (M$^+$ − 3 CO), 566 (M$^+$ − 4 CO), 521 (M$^+$ − Rh(CO)$_2$).

Preparation of Rh$_2$(μ-N=CPh$_2$)$_2$(CO)$_3$(PCy$_3$) (16). This compound was prepared analogously as described for **10**, by starting from **15** (100 mg, 0.147 mmol) and PCy$_3$ (41.3 mg, 0.147 mmol). It was isolated as a deep orange solid: yield 67.2 mg (49%). Anal. Calcd for $C_{47}H_{53}N_2O_3PRh_2$: C, 60.65; H, 5.74; N, 3.01. Found: C, 60.07; H, 6.10; N, 3.07. IR (Nujol, cm^{-1}): ν(CO) 2040 (s), 1975 (vs), 1960 (vs); ν(C=N) 1615 (m). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2045 (s), 1985 (s), 1950 (s). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ 195.32 (dd, J_{Rh-C} = 71.3 Hz, J_{P-C} = 19.8 Hz,

Table 2. Atomic Coordinates[a] (×10⁴; ×10⁵ for Rh Atoms) and Equivalent Isotropic Displacement Coefficients (Å² × 10³; ×10⁴ for Rh Atoms) for Selected Atoms of $[Rh(\mu\text{-}N{=}CPh_2)(TFB)]_2{\cdot}0.5C_6H_{14}$ (14)

atom	*x/a*	*y/b*	*z/c*	U_{eq}[b]
Rh(1a)	24508(4)	30972(4)	27231(4)	189(2)
Rh(2a)	39340(4)	39226(4)	27504(4)	187(2)
N(1a)	2967(4)	4391(4)	2251(4)	20(2)
N(2a)	3727(4)	3065(4)	2248(4)	21(2)
C(1a)	1096(5)	3097(5)	3025(5)	18(2)
C(2a)	1370(5)	3030(5)	3713(5)	21(2)
C(3a)	1396(5)	2071(5)	4313(5)	20(2)
C(4a)	2038(5)	1784(5)	3687(5)	18(2)
C(5a)	1759(5)	1859(5)	3018(5)	22(2)
C(6a)	887(5)	2190(5)	3042(5)	22(2)
C(13a)	4449(5)	4899(6)	3045(5)	24(2)
C(14a)	3777(5)	4377(5)	3710(5)	22(2)
C(15a)	4013(5)	3549(6)	4344(5)	26(2)
C(16a)	4390(5)	3099(5)	3763(5)	21(2)
C(17a)	5088(5)	3622(5)	3097(5)	20(2)
C(18a)	5298(5)	4518(5)	3086(5)	20(2)
C(25a)	2788(5)	5159(5)	1808(5)	21(2)
C(26a)	2070(5)	5276(6)	1420(5)	25(2)
C(32a)	3320(5)	6001(5)	1628(5)	24(2)
C(38a)	4159(5)	2685(5)	1819(5)	20(2)
C(39a)	5101(5)	2873(6)	1453(5)	23(2)
C(45a)	3715(5)	2006(5)	1641(5)	17(2)
Rh(1b)	14189(4)	22342(4)	73152(4)	190(2)
Rh(2b)	22376(4)	7271(4)	73081(4)	190(2)
N(1b)	1009(4)	904(4)	7796(4)	20(2)
N(2b)	2365(4)	1620(4)	7797(4)	21(2)
C(1b)	386(5)	2981(6)	7046(6)	28(2)
C(2b)	792(5)	2787(5)	6372(5)	23(2)
C(3b)	1530(5)	3495(6)	5727(5)	27(2)
C(4b)	2082(5)	3445(5)	6301(5)	23(2)
C(5b)	1665(5)	3634(5)	6975(5)	24(2)
C(6b)	756(5)	3857(6)	6976(6)	26(2)
C(13b)	2166(5)	−356(5)	6949(5)	22(2)
C(14b)	2169(5)	454(5)	6276(5)	23(2)
C(15b)	3069(5)	885(5)	5716(5)	20(2)
C(16b)	3435(5)	994(6)	6361(5)	20(2)
C(17b)	3402(5)	183(6)	7048(5)	27(2)
C(18b)	3059(5)	−614(6)	6979(5)	27(2)
C(25b)	300(5)	414(5)	8227(5)	19(2)
C(26b)	−511(5)	843(6)	8421(5)	25(2)
C(32b)	207(5)	−572(6)	8565(5)	26(2)
C(38b)	2826(5)	1725(5)	8224(5)	23(2)
C(39b)	3481(5)	1128(5)	8467(5)	22(2)
C(45b)	2705(5)	2434(6)	8545(5)	23(2)

[a] Atoms labeled a and b correspond to analogous atoms in the two independent molecules. [b] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

CO), 191.72 (d, J_{Rh-C} = 66.3 Hz, CO), 189.41 (d, J_{Rh-C} = 68.1 Hz, CO), 175.07 (s, *C*=N), 173.59 (s, *C*=N), 149.01 (s, Ph C_{ipso}), 146.52 (s, Ph C_{ipso}), 144.56 (s, Ph C_{ipso}), 143.10 (s, Ph C_{ipso}), 130.11 (s, *Ph*), 129.05 (s, *Ph*), 128.18 (s, *Ph*), 127.86 (s, *Ph*), 127.59 (s, *Ph*), 36.40 (d, J_{P-C} = 21.6 Hz, P—CH PCy₃), 30.61 (s, P*Cy*₃), 30.43 (s, P*Cy*₃), 28.05 (d, J_{P-C} = 10.6 Hz, P*Cy*₃), 26.92 (s, P*Cy*₃). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): *δ* 48.2 (d, J_{Rh-P} = 147.4 Hz). MS (FAB): *m/e* 593 ($M^+ - Rh({=}N{=}CPh_2)(CO)_2$), 521 ($M^+ - Rh({=}N{=}CPh_2)(CO)(PCy_3)$).

Preparation of $[Rh(\mu\text{-}N{=}CPh_2)(CO)(PCy_3)]_2$ (17). A suspension of **16** (100 mg, 0.107 mmol) in 5 mL of hexane was treated with PCy_3 (30.1 mg, 0.107 mmol). Immediately the color of the suspension changed from deep orange to dark red and at the same time evolution of CO was observed. This suspension was stirred for 5 h at room temperature. The solution was decanted, and the dark red solid that formed was washed with hexane and dried in vacuo: yield 91.5 mg (72%). Anal. Calcd for $C_{64}H_{86}N_2O_2P_2Rh_2$: C, 64.97; H, 7.33; N, 2.37. Found: C, 64.27; H, 8.09; N, 2.50. IR (Nujol, cm⁻¹): *ν*(CO) 1935 (vs); *ν*(C=N) 1610 (m). IR (CH_2Cl_2, cm⁻¹): *ν*(CO) 1925 (s). ¹H NMR (C_6D_6, 20 °C): *δ* 7.60–6.90 (m, 20 H, *Ph*), 2.00–0.90 (m, 66H, *Cy*). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): *δ* 197.90 (dd, J_{Rh-C} = 71.1 Hz, J_{P-C} = 19.7 Hz, *CO*), 170.53 (s, *C*=N), 148.87 (s, Ph C_{ipso}), 144.88 (s, Ph C_{ipso}), 131.77 (s, *Ph*), 130.68 (s, *Ph*), 129.64 (s, *Ph*), 128.82 (s, *Ph*), 127.12 (s, *Ph*), 126.41 (s, *Ph*), 35.83–25.29 (m, P*Cy*₃). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): *δ* 50.7 (d, J_{Rh-P} = 150.9 Hz). MS (FAB): *m/e* 1182 (M⁺).

Table 3. Crystal Data and Data Collection and Refinement for $[Rh(\mu\text{-}N{=}CPh_2)(TFB)]_2{\cdot}0.5C_6H_{14}$ (14)

Crystal Data	
formula	$C_{50}H_{32}N_2F_8Rh_2{\cdot}0.5C_6H_{14}$
mol wt	1061.70
color and habit	dark blue, transparent prism
cryst size, mm	0.342 × 0.304 × 0.171
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	16.468(5)
b, Å	16.569(5)
c, Å	18.139(5)
α, deg	66.03(1)
β, deg	74.32(2)
γ, deg	89.71(2)
V, Å³	4323(2)
Z	4
D(calcd), g cm⁻³	1.631
Data Collection and Refinement	
diffractometer	four-circle Siemens-STOE AED
λ(Mo Kα), Å; technique	0.710 73; bisecting geometry
monochromator	graphite oriented
μ, mm⁻¹	0.82
scan type	*ω*/2*θ*
2*θ* range, deg	$3 \le 2\theta \le 45$
temp, K	200
no. of data collected	11 794
no. of unique data	11 323 (R_{int} = 0.040)
no. of params refned	1169
R^a ($F_o \ge 4.0\sigma(F_o)$)	0.0532
wR^b (all data)	0.1366
S^c	0.988

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$, $a = 0.0729$, and $b = 0.00$. [c] $S = [\sum\{w(F_o^2 - F_c^2)^2\}/(n-p)]^{0.5}$, where *n* is the number of data and *p* the number of parameters.

X-ray Structure Analysis of $[Rh(\mu\text{-}N{=}CPh_2)(TFB)]_2{\cdot}0.5C_6H_{14}$ (14). Crystals suitable for an X-ray diffraction experiment were obtained by slow diffusion of hexane into a concentrated solution of **14** in toluene. Selected atomic coordinates and U_{eq} values are listed in Table 2. A summary of crystal data, intensity collection procedures, and refinement data is reported in Table 3. The prismatic crystal studied was glued on a glass fiber and mounted on a Siemens-Stoe AED-2 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 45 reflections in the range $20 \le 2\theta \le 41°$. The 11 794 recorded reflections were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored every 55 min of measuring time; no variation was observed. Reflections were also corrected for absorption by an empirical method.[30]

The structure was solved by Patterson (Rh atoms) and conventional Fourier techniques. The asymmetric unit was formed by two crystallographically independent, but chemically analogous, molecules of $[Rh(\mu\text{-}N{=}CPh_2)(TFB)]_2$. Refinement was carried out by full-matrix least squares with initial isotropic thermal parameters. At this stage, the electronic residuals revealed the presence of a partial disordered solvent molecule (hexane). This static disorder was modeled with two molecules refined with a complementary occupancy factor and with internal C—C bonds and angles restrained to an ideal geometry. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms, except those of the solvent molecule. Hydrogen atoms were calculated (C—H = 0.96 Å) and included in the refinement riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion

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[30] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

for Rh, were taken from ref 31. Final $R(F, F < 4\sigma(F))$ and $wR(F^2$, all reflections) values were 0.0532 and 0.1366. All calculations were performed by use of the SHELXTL-PLUS[32] and SHELXL-93[33] system of computer programs.

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Supplementary Material Available: Tables of all atomic coordinates, anisotropic thermal parameters, experimental details of the X-ray study, bond distances and angles, least-squares planes and deviations therefrom, and interatomic distances (37 pages). Ordering information is given on any current masthead page.

OM940249N

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(31) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(32) Sheldrick, G. M. SHELXTL-PLUS; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

(33) Sheldrick, G. M. SHELXL-93, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1993.