Azide Migration and Azide Bridging: Preparation of Metalated Acrylonitriles and of Dinuclear Complexes Containing an Almost Linear Eleven-Membered $C_3RhN_3RhC_3$ Chain

Matthias Laubender and Helmut Werner*[a]

Dedicated to Professor Hans H. Brintzinger on the occasion of his 65th birthday

Abstract: A series of isoelectronic square-planar azido- and isocyanatorhodium(I) complexes of the general composition *trans*-[RhX(=C=C=CRR′)(P*i*Pr$_3$)$_2$] (X = N$_3$: **9**–**12**; X = CNO: **13**–**16**) was prepared from the related chloro derivatives *trans*-[RhCl(=C=C=CRR′)(P*i*Pr$_3$)$_2$] by salt metathesis. A single-crystal X-ray diffraction study of **12** (R = Ph, R′ = *t*Bu) confirmed an almost linear arrangement of the Rh-C-C-C chain, but a significant bending of the Rh-N-N-N unit. In contrast to the isocyanato complexes **13**–**16**, which are quite inert toward carbon monoxide, the azido derivatives **9**, **11**, and **12** react with CO by migratory insertion of the allenylidene ligand into the Rh–N$_3$ bond. While the product obtained from **12** and CO, in which the N$_3$ substituent is linked to the γ-carbon atom of the C$_3$ chain, is exceedingly stable, the corresponding species with R = R′ = aryl are quite labile and rearrange to the metalated acrylonitrile compounds *trans*-[Rh{C(CN)=CRR′}(CO)(P*i*Pr$_3$)$_2$] (**19**, **20**) by elimination of N$_2$. The reactions of **19** and **20** (which was crystallographically characterized) with trifluoracetic acid gave the corresponding acrylonitriles R′RC=CHCN in quantitative yields. Treatment of the mononuclear compounds **9**–**12** with Meerwein's salt [OMe$_3$]BF$_4$ led to the formation of the dinuclear complexes [{(P*i*Pr$_3$)$_2$(R′RC=C=C=)Rh}$_2$(μ-1,3-N$_3$)]BF$_4$ (**21**–**24**) containing an almost linear eleven-membered C$_3$RhN$_3$RhC$_3$ chain. The X-ray crystal structure analysis of **22** (R = Ph, R′ = *o*-Tol) revealed that the conformations of the two halves of the cation are quite different and that the angle between the two metal-centered planes is 56.5(1)°.

Keywords: allenylidene complexes · azido complexes · insertions · isocyanato complexes · N ligands · rhodium

Introduction

In the search of carbon-rich analogues of the easily accessible vinylidenerhodium(I) complexes *trans*-[RhCl(=C=CRR′)(P*i*Pr$_3$)$_2$][1] we recently reported that corresponding allenylidene compounds *trans*-[RhCl(=C=C=CRR′)(P*i*Pr$_3$)$_2$] can be obtained from [RhCl(P*i*Pr$_3$)$_2$]$_2$ and substituted propargylic alcohols or amines HC≡CCR(R′)X (X = OH, NH$_2$), respectively.[2, 3] Since allenylidenes (which were generated in the coordination sphere of a transition metal for the first time by Fischer et al.[4] and Berke[5]) are predicted to be good π-acceptor ligands,[6] it was anticipated that in the square-planar rhodium complexes of the general composition *trans*-[RhCl(=C=C=CRR′)(P*i*Pr$_3$)$_2$] the allenylidene unit, like CO, isocyanides CNR, and vinylidenes C=CRR′, would exert a strong influence on the ligand in the *trans* position. Substitution of the chloride in the above-mentioned compounds should therefore be favored and this had been confirmed with various nucleophiles.[7] One of the most remarkable results of these studies was that the chloride in *trans*-[RhCl(=C=C=CRR′)(P*i*Pr$_3$)$_2$] is not only readily replaced by *soft* but also by *hard* Lewis bases such as OH$^-$, PhO$^-$, or RCO$_2{}^-$, and that the reaction products *trans*-[Rh(OR″)(=C=C=CRR′)(P*i*Pr$_3$)$_2$] (if R″ is phenyl or acetyl) in the presence of CO undergo insertion of the allenylidene ligand into the Rh–O bond.[8] With this methodology, several γ-functionalized alkynyl ligands and alkynes were formed.

This novel reaction pathway prompted us to prepare rhodium complexes of the type *trans*-[Rh(X)(=C=C=CRR′)(P*i*Pr$_3$)$_2$], where X is a N-bonded ligand, to find out whether they behave similarly to the O-bonded counterparts and also react with CO or isocyanides by migratory insertion of the C$_3$RR′ unit into the Rh–N bond. Herein we illustrate that for X = N$_3$ such a reaction takes place indeed and, even more noteworthy, that the migration of the azide is followed by an unprecedented C–N coupling to yield a substituted acrylonitrile ligand. Moreover, we report that treatment of the azido derivatives *trans*-[Rh(N$_3$)(=C=C=CRR′)(P*i*Pr$_3$)$_2$] with Meer-

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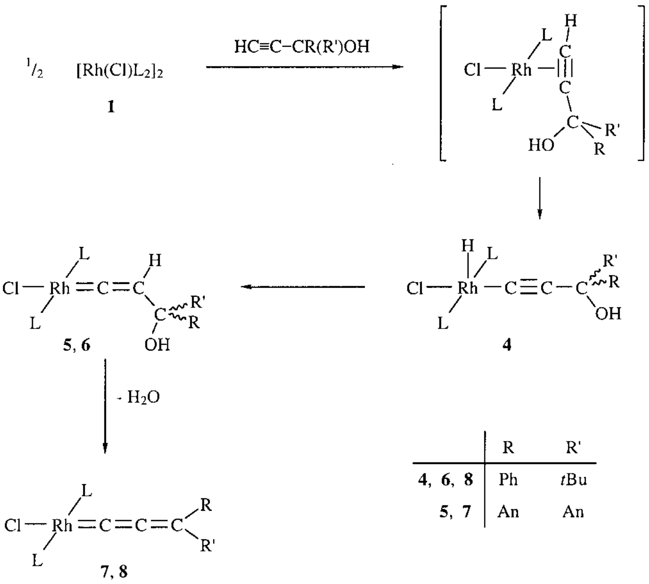
wein's salt $[OMe_3]BF_4$ formally generate a coordinatively unsaturated species $[Rh(C{=}C{=}CRR')(PiPr_3)_2]^+$, which reacts with a second molecule of the starting material to afford a series of dinuclear complexes with an almost linear eleven-membered $C_3RhN_3RhC_3$ chain. Some preliminary results of this work were already communicated.[9]

Results and Discussion

Square-planar allenylidenerhodium(I) complexes with azide and isocyanate as ligands: In addition to the formerly known allenylidene(chloro)rhodium(I) complexes **2** and **3**,[2, 3] the structurally related compounds **7** and **8** were also prepared. The aim was to broaden the scope for the studies concerned to the reactivity of complexes *trans*-$[RhCl({=}C{=}C{=}CRR')(PiPr_3)_2]$ and to introduce instead of an aryl a bulky alkyl group as a substituent at the γ-carbon atom of the allenylidene chain. The procedure to obtain the starting materials **7** and **8** followed the route which we had developed for the analogous compounds **2** and **3**, respectively. Treatment of dimer **1** with the alkynols $HC{\equiv}CCR(R')OH$ in diethyl ether at −60°C leads to the formation of a labile (yellow) intermediate which for R = *t*Bu and R′ = Ph has been spectroscopically characterized as the five-coordinate alkynyl(hydrido)rhodium(III) species **4** (Scheme 1). Typical features of **4** are the hydride signal at $\delta = -28.25$ in the ^1H NMR spectrum and the Rh–H and C≡C stretching frequencies at $\nu = 2191$ and $2087\ cm^{-1}$ in the IR spectrum. Similar data have been obtained for the related stable complex $[RhH(C{\equiv}CtBu)Cl(PiPr_3)_2]$.[10] Although there is no spectroscopic evidence, we assume that the intermediate **4** is formed via the extremely short-lived π-alkyne compound *trans*-$[RhCl\{HC{\equiv}CCPh(tBu)OH\}(PiPr_3)_2]$ which rapidly reacts by intramolecular oxidative addition to the alkynyl(hydrido)rhodium(III) derivative. On warming to room temperature or, preferably, upon addition of NEt_3 the intermediate **4** as well as the noncharacterized counterpart $[RhH\{C{\equiv}CC(p\text{-}C_6H_4OMe)_2OH\}Cl(PiPr_3)_2]$ rearrange to the functionalized vinylidene complexes **5** and **6** which have been isolated as deeply colored, only moderately air-sensitive solids in 85–90% yield.



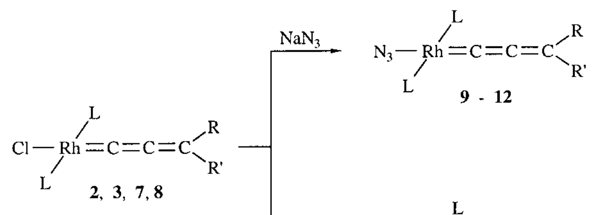
	R	R′
4, 6, 8	Ph	*t*Bu
5, 7	An	An

Scheme 1. L = P*i*Pr$_3$; An = *p*-C_6H_4OMe.

On passing a solution of **5** or **6** in benzene through a column filled with acidic alumina, a quick change of color from dark blue to red or green occurs and, if chromatography is continued, the allenylidene compounds **7** or **8** are eluted. They were isolated in almost quantitative yield. The IR and NMR spectroscopic data of **7** and **8** are similar to those of **2** and **3** and are in agreement with the structural proposal shown in Scheme 1. A noteworthy difference between **2**, **3**, and **7** on one hand and **8** on the other is, that while in the ^{13}C NMR spectra of the bisaryl-substituted allenylidene complexes the signal of the β-carbon atom appears at lower field than that of the α-carbon atom, for compound **8** where one aryl group at γ-C is replaced by a *tert*-butyl group the order in the chemical shift is reversed.

The chlororhodium complexes **2**, **3**, **7** and **8** react not only with KI or KO*t*Bu[8] but also with excess NaN_3 in acetone at room temperature to give the dark red, red-violet or dark green azido derivatives **9**–**12** (Scheme 2) in 87–98% yield of isolated product. The procedure is similar to that for the preparation of the related compounds $[RhN_3(PPh_3)_3]$[11] and

Abstract in German: *Eine Reihe isoelektronischer, quadratisch-planarer Azido- und Isocyanatorhodium(I)-Komplexe der allgemeinen Zusammensetzung trans-*$[RhX({=}C{=}C{=}CRR')(PiPr_3)_2]$ *(X =* N_3*:* ***9**–**12**; X = CNO: **13**–**16**) wurde aus den entsprechenden Chloro-Derivaten trans-*$[RhCl({=}C{=}C{=}CRR')(PiPr_3)_2]$ *durch Salzmetathese hergestellt. Eine Einkristallstrukturanalyse von **12** (R = Ph, R′ = tBu) bestätigte eine fast lineare Anordnung der Rh-C-C-C-Kette, jedoch eine erhebliche Abwinkelung der Rh-N-N-N-Einheit. Im Gegensatz zu den Isocyanatokomplexen **13**–**16**, die völlig inert gegenüber Kohlenmonoxid sind, reagieren die Azido-Derivate **9**, **11** und **12** mit CO unter Einschiebung des Allenylidenliganden in die Rh-*N_3*-Bindung. Während das aus **12** und CO entstehende Produkt, in dem sich der* N_3*-Substituent am γ-Kohlenstoffatom der* C_3*-Kette befindet, ausserordentlich stabil ist, sind die analogen Verbindungen mit R = R′ = Aryl sehr labil und lagern sich unter Abspaltung von* N_2 *in die metallierten Acrylonitril-Derivate trans-*$[Rh\{C(CN){=}CRR'\}(CO)(PiPr_3)_2]$ *(**19**, **20**) um. Die Umsetzungen von **19** und **20** (letztere Verbindung wurde kristallographisch charakterisiert) mit Trifluoressigsäure liefern die entsprechenden Acrylnitrile* $R'RC{=}CHCN$ *in quantitativer Ausbeute. Die Einwirkung von Meerwein's-Salz* $[OMe_3]BF_4$ *auf die einkernigen Verbindungen **9**–**12** führt zur Bildung der zweikernigen Komplexe* $[\{(PiPr_3)_2(R'RC{=}C{=}C{=})Rh\}_2(\mu\text{-}1,3\text{-}N_3)]BF_4$ *(**21**–**24**), in denen eine nahezu lineare elfgliedrige* $C_3RhN_3RhC_3$*-Kette vorliegt. Die Kristallstrukturanalyse von **22** (R = Ph, R′ = o-Tol) zeigt, dass die Konformationen der beiden Hälften des Kations deutlich verschieden sind und der Winkel zwischen den zwei Metall-zentrierten Ebenen 56.5(1)° beträgt.*



	R	R'
2, 9, 13	Ph	Ph
3, 10, 14	Ph	*o*-Tol
7, 11, 15	An	An
8, 12, 16	Ph	*t*Bu

Scheme 2. L = P*i*Pr$_3$.

trans-[RhN$_3$(CO)(PR$_3$)$_2$] (R = Ph, Cy),[12] respectively. The most characteristic features of the spectroscopic data of **9**–**12** are the two low-field ^{13}C NMR resonances (both doublets of triplets) between $\delta = 255$ and 228 for the α- and β-carbon atoms of the Rh=C=C=C chain and the strong IR stretching vibration at 2050–2070 cm^{-1} for the N$_3$ unit. It should be mentioned that although numerous examples for cycloaddition reactions of hydrocarbons containing C=C or C=C=C bonds with azides are known,[13] the formation of by-products of this type from the allenylidene complexes *trans*-[RhCl(=C=C=CRR')(P*i*Pr$_3$)$_2$] and NaN$_3$ has not been observed.

Similarly to **9**–**12**, the isoelectronic isocyanatorhodium compounds **13**–**16** were prepared from **2**, **3**, **7**, and **8**, respectively, and an excess of KOCN in acetone. The deeply colored, almost air-stable crystalline solids were isolated in virtually quantitative yield. The IR spectra of **13**–**16** display two strong absorptions at around 2200–2215 and 1450–1480 cm^{-1} which are assigned to the asymmetrical and symmetrical NCO stretching frequencies. Since it has been established that the symmetrical stretch for O-bonded isocyanates appears below 1200 cm^{-1} and that for N-bonded NCO ligands in the region between 1300 and 1500 cm^{-1},[14] we conclude that in the complexes **13**–**16** a Rh–NCO linkage exists.

The molecular structure of compound 12: To compare the structural data of one of the complexes *trans*-[RhN$_3$(=C=C=CRR')(P*i*Pr$_3$)$_2$] with those of other azidometal derivatives, a single-crystal X-ray structure analysis of **12** was carried out. The structural diagram (Figure 1) reveals that the coordination geometry around the rhodium center is square-planar with the two phosphane ligands in *trans* disposition. The Rh-C1-C2-C3 chain is not exactly linear with a slight bending at the carbon atom C2. In contrast, the Rh-N1-N2-N3 unit is significantly bent, the bond angle Rh-N1-N2 (143.9(5)°) being considerably larger than in the analogous carbonyl complex *trans*-[RhN$_3$(CO)(PPh$_3$)$_2$] (132(1)°).[15] The N–N distances of the almost linear azido ligand (bond angle N1-N2-N3 176.0(6)°) are nearly the same (1.177(6) and 1.161(7) Å), which is in agreement with the IR spectroscopic data of **12**. The bond length Rh–N1 (2.055(5) Å) differs only slightly to that of *trans*-[RhN$_3$(CO)(PPh$_3$)$_2$] (2.08(1) Å),[15] thus confirming the similar π-acceptor capabilities of CO and the allenylidene unit.[6] A special feature of the ligand arrangement around the rhodium center is that the N$_3$ moiety does not lie in the plane of the ligand atoms P1, P2, C1 and N1. The dihedral angle between the two planes [Rh,N1,N2,N3] and [Rh,P1,P2,C1] is 29.5(7)°, which we assume is due to the steric repulsion between the nitrogen atoms N2 and N3 and the six bulky isopropyl groups.

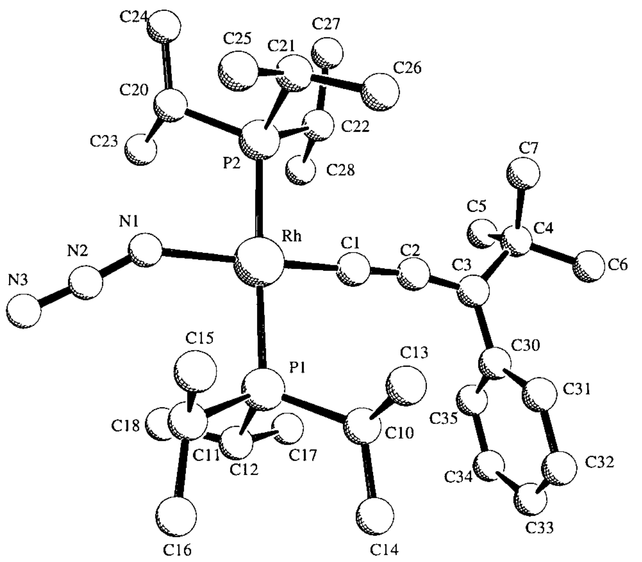
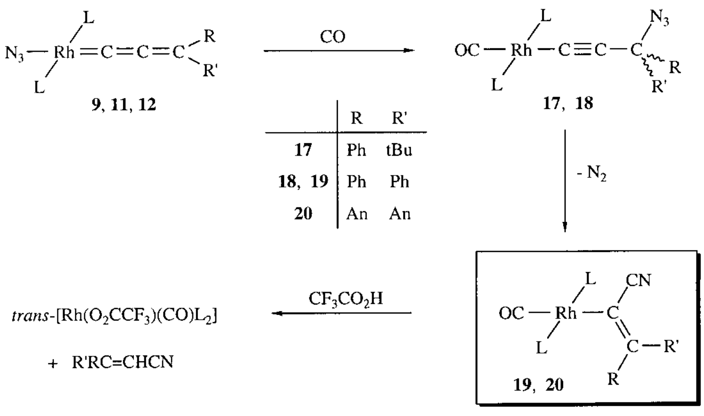


Figure 1. Molecular structure of **12**. Important bond lengths [Å] and angles [°]: Rh–P1 2.348(2), Rh–P2 2.347(1), Rh–C1 1.849(5), Rh–N1 2.055(5), C1–C2 1.27(1), C2–C3 1.35(1), N1–N2 1.18(1), N2–N3 1.16(1); P1-Rh-P2 175.6(1), C1-Rh-N1 175.7(2), C1-Rh-P1 89.4(2), C1-Rh-P2 89.9(2), N1-Rh-P1 93.4(2), N1-Rh-P2 87.5(2), Rh-C1-C2 177.7(5), C1-C2-C3 169.1(6), Rh-N1-N2 143.9(5), N1-N2-N3 176.0(6).

Reactions of the azido complexes 9–12 with CO: Like the phenolato- and acetatorhodium(I) derivatives *trans*-[Rh(OR'')(=C=C=CRR')(P*i*Pr$_3$)$_2$], the azido complexes **9**–**12** are also highly reactive toward carbon monoxide. Passing a slow stream of CO through a solution of **12** in benzene at room temperature for 30 s leads to a change of color from dark green to yellow and, after removal of the solvent and recrystallization of the residue from methanol, to the formation of the yellow microcrystalline solid **17** in 90% yield. The analytical composition of **17** corresponds to that of a 1:1 adduct between **12** and CO. In analogy to the complexes *trans*-[Rh{C≡CCR(R')OPh}(CO)(P*i*Pr$_3$)$_2$],[8, 16] the ^{13}C NMR spectrum of **17** displays two signals (doublets of triplets) at $\delta =$ 121.5 and 112.8 for the carbon atoms of the C–C triple bond, while the IR spectrum exhibits two absorptions at 2099 and 2063 cm^{-1} which are assigned to the N=N=N and C≡C stretching frequencies. From these data we conclude (Scheme 3) that treatment of **12** with CO results in a migration of the N$_3^-$ ligand to the allenylidene unit and that the intact azido group in the product is linked to the γ-carbon atom of the C$_3$ chain.

The reactions of compounds **9** and **11** with CO at low temperatures probably take a similar course. If a solution of **9** in [D$_8$]toluene is treated at −60 °C with CO, the ^{13}C and ^{31}P NMR spectra of the generated species exhibit resonances, the



Scheme 3. L = P*i*Pr$_3$.

chemical shift, the splitting pattern, and the coupling constants of which are consistent with the presence of the functionalized alkynyl complex **18** (Scheme 3). Upon warming to room temperature, this species is rapidly and cleanly converted to compound **19** by elimination of N_2. The IR spectrum of **19** (which like **17** is a yellow, almost air-stable solid) displays only *one* sharp absorption between 2000 and 2200 cm^{-1}, and the ^{13}C NMR spectrum *three* resonances at δ = 160-125, which all show P,C couplings. These data, together with the elemental analysis, indicate that the final product of the reaction of **9** with CO is a carbonyl(vinyl)metal derivative. Compound **11** behaves analogously to **9** and affords upon treatment with CO the rhodium(I) complex **20** in 92% yield. It should be mentioned that under the conditions under which **18** reacts to give **19** and under which **20** is formed, compound **17** is completely inert and does not produce either thermally or photochemically the vinyl complex *trans*-[Rh{C(CN)=C(Ph)*t*Bu}(CO)(P*i*Pr$_3$)$_2$]. Treatment of **19** and **20** with trifluoracetic acid results in the cleavage of the Rh–C σ bond, leading to the formation of the corresponding acrylonitrile derivatives R′RC=CHCN in quantitative yields.

The molecular structure of compound 20: The result of the single-crystal X-ray diffraction study of **20** confirms (Figure 2) that in the course of the reaction of **11** with CO the [Rh(P*i*Pr$_3$)$_2$] moiety is shifted from the α-carbon to the β-carbon atom of the C_3 chain. The four-coordinate metal center possesses a slightly distorted square-planar configuration with Rh–C1, Rh–C3, Rh–P1, and Rh–P2 distances that are quite similar to those of the butadienyl complex *trans*-[Rh{C(CH=CH$_2$)=CHPh}(CO)(P*i*Pr$_3$)$_2$].[17] While the C1-Rh-C3 axis is nearly linear, the P1-Rh-P2 axis is somewhat bent; the bending of 167.10(4)° being more pronounced than in compound **12** (175.6(1)°). The plane including C2, C3, and C4 is almost perpendicular (86.8(1)°) to that formed by Rh, C1, C3, P1, and P2, which probably minimizes the repulsive interactions between the isopropyl groups at phosphorus and the substituents at the C–C double bond. Although the hybridization of the α-carbon atom C3 in **20** and C1 in **12** is different, the Rh–C distances in the two compounds are nearly the same, namely 1.834(5) Å in **20** and 1.849(5) Å in **12**, respectively.

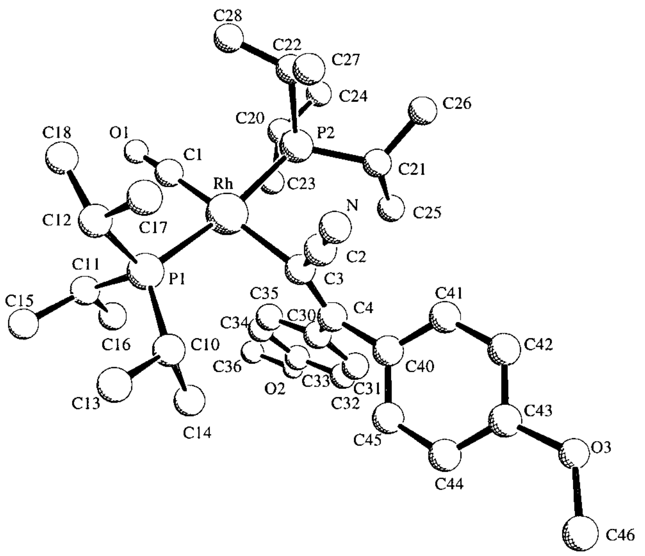
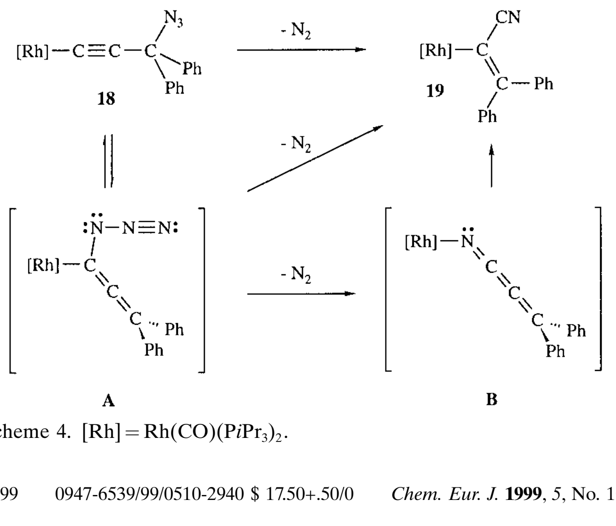


Figure 2. Molecular structure of compound **20**. Important bond lengths [Å] and angles [°]: Rh–P1 2.338(1), Rh–P2 2.340(1) Rh–C1 1.834(5), Rh–C3 2.106(4), C1–O1 1.146(5), C2–C3 1.428(6), C3–C4 1.367(3), C2–N 1.144(5); P1-Rh-P2 167.10(4), C1-Rh-C3 174.6(2), C1-Rh-P1 89.7(2), C1-Rh-P2 88.5(1), C3-Rh-P1 91.9(1), C3-Rh-P2 91.2(1), Rh-C1-O1 175.1(4), Rh-C3-C2 109.8(3), Rh-C3-C4 133.2(3), C3-C2-N 174.9(5), C2-C3-C4 117.0(4).

Mechanistic considerations: In contrast to several azidometal complexes,[18] the allenylidene derivatives **9**–**12** do not react with carbon monoxide to give the corresponding isocyanato compounds **13**–**16**. A reasonable explanation for this result is that the attack of CO at the rhodium center of **9**–**12** is accompanied by a concerted shift of the azido group to the γ-carbon atom of the allenylidene unit along the RhC_3 chain. The isolation of **17** and the spectroscopic characterization of **18** support this proposal. The crucial question is on which pathway the cyano-substituted vinyl complex **19** is formed from **18** and, similarly, the analogous compound **20** from the supposed intermediate *trans*-[Rh{C≡CC(*p*-C$_6$H$_4$OMe)$_2$-N$_3$}(CO)(P*i*Pr$_3$)$_2$]. Two alternatives are conceivable, which for the conversion of **18** to **19** are shown in Scheme 4.

The first possibility is that a migration of the azido moiety from the γ-carbon to the α-carbon atom of the alkynyl ligand takes place to generate the intermediate **A**, which by

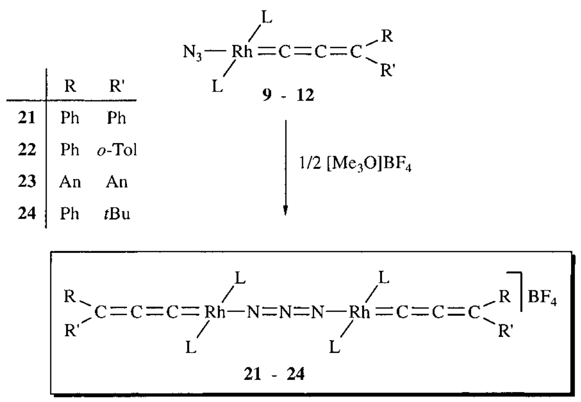


Scheme 4. [Rh] = Rh(CO)(P*i*Pr$_3$)$_2$.

elimination of N_2 and shifting of the metal–ligand fragment from α-C to β-C affords **19**. Precedence for the migration of a substituent from the γ- to the α-carbon of an alkynyl unit stems from recent work by Gimeno et al.,[19] which revealed that the indenyl complex $[(\eta^5\text{-}C_9H_7)Ru\{C{\equiv}CCPh_2(PMe_3)\}(dppm)]PF_6$ ($dppm = CH_2(PPh_2)_2$) is smoothly converted to the corresponding isomer $[(\eta^5\text{-}C_9H_7)Ru\{C(PMe_3){=}C{=}CPh_2\}(dppm)]PF_6$. The alternative is that the intermediate **A**, instead of being directly transformed to **19**, reacts by loss of N_2 to give the iminato derivative **B** which rearranges by a 1.3-shift to yield the product **19**. We note that the conversion of **A** to **B** is reminiscent to the formation of the chromium nitriles $[(CO)_5Cr(NCR)]$ from the azidocarbene complexes $[(CO)_5Cr\{{=}C(N_3)R\}]$, the latter being generated either from $[(CO)_5Cr\{{=}C(R)OC(O)Me\}]$ and HN_3 or from $[(CO)_5Cr({\equiv}CR)]^+$ and N_3^-.[20]

The reason why in contrast to **18** the azido-substituted alkynyl compound **17** is quite inert and does not react to the corresponding vinyl complex *trans*-$[Rh\{C(CN){=}C(Ph)t\text{Bu}\}(CO)(PiPr_3)_2]$ is not clear yet. Since neither the conversion of **A** nor of **B** to **19** should be significantly hindered by the substituents R and R′ at the C_3 chain, we assume that the bulky *t*Bu group in **17** blocks the migration of the N_3 unit from the γ-C to the α-C atom. A similar phenomenon has recently been reported by Banert et al. who found that the [3.3]-sigmatropic rearrangement of propargylazides to allenylazides is facilitated by aryl but not by alkyl groups.[21]

Preparation of azido-bridged dinuclear rhodium(I) complexes: Following the observation that the allenylidene(chloro) compounds **2** and **3** react with methyl iodide by oxidative addition and subsequent C–C coupling to give the butatriene complexes *trans*-$[RhX(H_2C{=}C{=}C{=}CRR')(PiPr_3)_2]$ with X = Cl and I, respectively,[22] we decided to investigate also the behavior of **9**–**12** toward methylating reagents. While we failed by using CH_3I to isolate a pure product, a clean reaction took place between the starting materials and Meerwein's salt $[OMe_3]BF_4$. In analogy to previous work by von Werner and Beck,[23] we found that on treatment of **9**–**12** with 0.5 equivalents of $[OMe_3]BF_4$ in CH_2Cl_2 the dinuclear compounds **21**–**24** are formed (Scheme 5). They were isolated as black-violet solids in 80–90% yield. The elemental analyses confirm the supposed composition, and the conductivity data (in nitromethane) the presence of 1:1 electrolytes. Since the ^{31}P NMR spectra of **21**–**24** display only one resonance (a doublet with a similar Rh,P coupling constant as for the mononuclear complexes **9**–**12**) and the ^{13}C NMR spectra only one set of signals for the pairs of α-, β-, and γ-carbon atoms of the allenylidene ligands, a symmetrical structure of the cationic moiety can be assumed. However, on the basis of the NMR and also of the IR data it can not be decided whether the two fragments $[Rh({=}C{=}C{=}CRR')(PiPr_3)_2]$ are bridged through *one* terminal nitrogen atom (μ-end-on) or through *both* terminal nitrogen atoms (μ-end-to-end) of the N_3 unit. In the IR spectra of **21**–**24**, the asymmetrical N_3 stretching frequency appears at 2140–2144 cm^{-1} and similarly high wave numbers have also been found for the related carbonyl derivatives $[\{(PPh_3)_2(CO)M\}_2(\mu\text{-}N_3)]BF_4$ (M = Rh, Ir).[23] Owing to the ^{15}N NMR spectroscopic data, Beck and co-workers concluded that in these compounds the azido ligand bridges the two metal centers end-on, that is, only through *one* nitrogen atom.[23]



	R	R'
21	Ph	Ph
22	Ph	*o*-Tol
23	An	An
24	Ph	*t*Bu

Scheme 5. L = P*i*Pr$_3$.

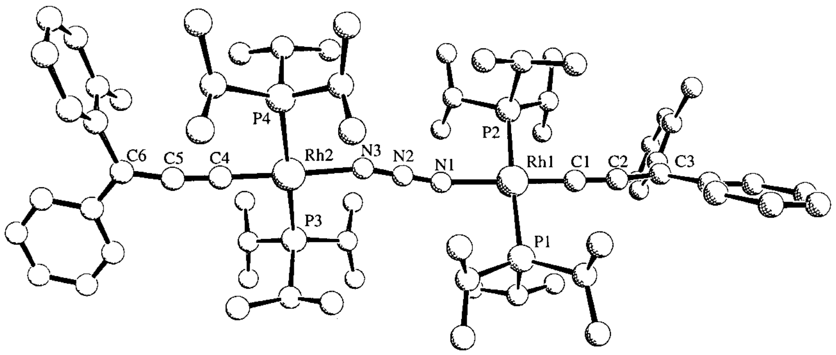


Figure 3. Molecular structure of the cation of compound **22**. Important bond lengths [Å] and angles [°]: Rh1–C1 1.826(3), Rh1–N1 2.061(3), Rh1–P1 2.339(1), Rh1–P2 2.336(1), C1–C2 1.261(4), C2–C3 1.355(4), N1–N2 1.146(3), N2–N3 1.149(3), Rh2–C4 1.841(3), Rh2–N3 2.049(3), Rh2–P3 2.349(1), Rh2–P4 2.352(1), C4–C5 1.261(4), C5–C6 1.349(4); P1-Rh1-P2 177.32(3), C1-Rh1-N1 178.1(1), P1-Rh1-C1 89.0(1), P1-Rh1-N1 91.2(1), P2-Rh1-C1 88.5(1), P2-Rh1-N1 91.3(1), Rh1-C1-C2 178.3(2), C1-C2-C3 172.7(3), Rh1-N1-N2 164.2(3), N1-N2-N3 177.5(3), P3-Rh2-P4 178.11(3), C4-Rh2-N3 177.8(1), P3-Rh2-C4 89.4(1), P3-Rh2-N3 92.0(1), P4-Rh2-C4 89.2(1), P4-Rh2-N3 89.3(1), Rh2-C4-C5 177.8(3), C4-C5-C6 170.5(3), Rh2-N3-N2 164.3(3).

The molecular structure of compound 22: The single-crystal X-ray structure analysis of **22** (Figure 3) reveals that the azido ligand forms an end-to-end bridge and hence builds an almost linear eleven-membered $C_3RhN_3RhN_3$ chain. The coordination geometry around the two rhodium centers is almost perfectly square-planar with bond angles C-Rh-P and N-Rh-P of 90 ± 2°. The Rh-C-C-C units are slightly bent, likewise to the situation in **12** and in the chloro compound **3**.[3] In contrast to the mononuclear azido complex **12**, where the bond angle Rh-N-N is 143.9(5)°, the corresponding bending in the dinuclear derivative is much less pronounced, the bond angles

Rh-N-N being 164.2(3)° and 164.3(3)°, respectively. Since the N_3 bridge is nearly linear (bond angle N1-N2-N3 177.5(3)°), the Rh-N-N-N-Rh fragment is only slightly bent and the deviation from linearity for the $C_3RhN_3RhN_3$ chain is considerably less than for the N_3RhC_3 moiety in compound **12**.

A characteristic structural feature of **22** is shown in Figure 4. A view along the eleven-membered $C_3RhN_3RhN_3$ axis illustrates that the conformations of the two halves are quite different. While the two planes [Rh2,P3,P4,C4,N3] and [C6,C70,C80] are nearly coplanar (the angle between the planes being 13.8(2)°), the dihedral angle between the planes [Rh1,P1,P2,C1,N1] and [C3,C50,C60] amounts to 51.8(2)°. Moreover, the expected perpendicular arrangement of the metal-centered planes [Rh1,P1,P2,C1,N1] and [Rh3,P3,P4,C4,N3] is not observed and the interplanar angle is found to be 56.5(1)°. It should also be mentioned that whereas the distances Rh1–N1 and Rh2–N3 are almost identical to the Rh–N distance in **12**, the bond lengths N1–N2 and N2–N3 in **22** are slightly shorter than in complex **12** which contains a terminal azido ligand.

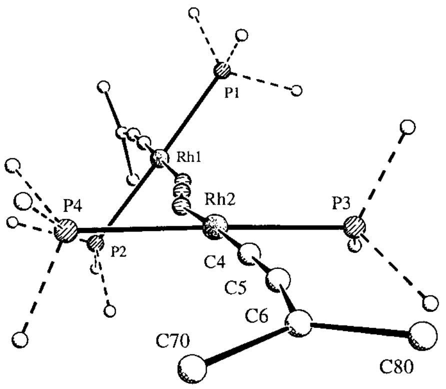


Figure 4. Perspective view of the central core of the cation of **22** to illustrate the conformations around the metal centers.

Conclusion

The present investigations have shown that the allenylidene(azido)rhodium(I) complexes of the general composition *trans*-[RhN_3(=C=C=CRR′)(P*i*$Pr_3)_2$] as well as the isoelectronic isocyanato derivatives *trans*-[Rh(NCO)(=C=C=CRR′)(P*i*$Pr_3)_2$] are readily accessible from the corresponding chlororhodium(I) precursors *trans*-[RhCl(=C=C=CRR′)(P*i*$Pr_3)_2$] by salt metathesis. While the isocyanato compounds are quite inert in the presence of CO, the azido complexes react with carbon monoxide by migratory insertion of the allenylidene ligand into the Rh–N_3 bond. The initially formed product, in which the N_3 substituent is linked to the γ-carbon atom of the C_3 chain, can be isolated for R = Ph and R′ = *t*Bu. If, however, both substituents R and R′ are aryl groups, the corresponding alkynyl complexes *trans*-[Rh{C≡CCR(R′)N_3}(CO)(P*i*$Pr_3)_2$] are highly labile and react to the metalated acrylonitrile derivatives *trans*-[Rh{C(CN)=CRR′}(CO)(P*i*$Pr_3)_2$] by elimination of N_2. To the best of our knowledge, there is no precedence for this type of C–N coupling which is accompanied by a 1.2-shift of the rhodium center from the α- to the β-carbon atom of the formerly alkynyl ligand. The reaction of the cyanovinyl complexes *trans*-[Rh{C(CN)=CRR′}(CO)(P*i*$Pr_3)_2$] with trifluoracetic acid results in the cleavage of the Rh–C σ bond and leads to the formation of the corresponding acrylonitriles R′RC=CHCN in quantitative yields.

The second remarkable feature of this work is the preparation and structural characterization of the azido-bridged dinuclear complexes [{(P*i*$Pr_3)_2$(R′RC=C=C=)Rh}$_2$(μ-1.3-N_3)]BF_4. The X-ray crystal structure analysis of one representative (with R = Ph and R′ = *o*-Tol) revealed that the backbone of the cation consists of an eleven-membered $C_3RhN_3RhC_3$ chain for which an extensive π-electron delocalization can be assumed. We note that recently a series of di- and oligonuclear copper(II) compounds with alternating μ-oxalato-μ-azido chains have been described which due to their magnetic behavior show strong antiferromagnetic coupling in each case.[24] The azido-bridged compounds prepared in this work could be considered as the counterparts of transition-metal complexes with bridging C_4 (and more general C_n) ligands, of which various examples have been reported by Sonogashira et al.,[25] Gladysz et al.,[26] Lapinte et al.,[27] and others including us.[28, 29]

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk tube techniques. The starting materials **1**,[30] **2**,[2] **3**,[3] and the alkynols[31] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments, IR spectra on a Perkin-Elmer 1420 spectrophotometer. Abbreviations used: s, singlet; d, doublet; t, triplet; vt, virtual triplet; m, multiplet; br, broadened signal; $N = {}^3J(P,H) + {}^5J(P,H)$ or ${}^1J(P,C) + {}^3J(P,C)$. Melting points were measured by differential thermal analysis (DTA).

***trans*-[RhH{C≡C–CPh(*t*Bu)OH}Cl(P*i*Pr$_3$)$_2$] (4)**: A solution of **1** (156 mg, 0.17 mmol) in diethyl ether (2 mL) was treated at −60°C with HC≡C–CPh(*t*Bu)OH (65 mg, 0.34 mmol). A change of color from red to yellow occurred. After the solvent was removed in vacuo, the residue was washed twice with cold (−10°C) pentane (2 mL) and dried. Since compound **4** is only stable below −20°C, it was characterized by spectroscopic means. IR (C_6H_6): $\tilde{\nu} = 3547$ [ν(OH)], 2191 [ν(RhH)], 2087 [ν(C≡C)] cm^{-1}; ^1H NMR (200 MHz, $C_6D_5CD_3$, 263 K): $\delta = 7.86$, (m, 2 H, *o*-C_6H_5), 7.25 (m, 3 H, *m*- and *p*-C_6H_5), 2.92 (m, 6 H, PC*H*CH_3), 1.23 [dvt, $N = 16.0$, $J(H,H) = 7.3$ Hz, 36 H, PCHCH_3], −28.25 [dt, $J(Rh,H) = 42.1$, $J(P,H) = 13.1$ Hz, 1 H, RhH]; ^{31}P NMR (81.0 MHz, $C_6D_5CD_3$, 263 K): $\delta = 50.3$ [d, $J(Rh,P) = 99.2$ Hz].

***trans*-[RhCl{=C=CH-C(*p*-C$_6$H$_4$OMe)$_2$OH}(P*i*Pr$_3$)$_2$] (5)**: A solution of **1** (101 mg, 0.11 mmol) in diethyl ether (5 mL) was treated at room temperature with HC≡C–C(*p*-C_6H_4OMe)$_2$OH (59 mg, 0.22 mmol). After a rapid change of color from red to yellow took place, triethylamine (2 mL) was added to the reaction mixture which was then stirred for 10 h at room temperature. During that time a change of color from yellow to blue occurred. The solvent was removed in vacuo and the residue was recrystallized from diethyl ether at −20°C. Dark blue crystals were obtained which were separated from the mother liquor, washed with cold (0°C) diethyl ether (2 × 1 mL) and dried; yield 136 mg (85 %); m.p. 146°C (decomp); IR (C_6H_6): $\tilde{\nu} = 3580$ [ν(OH)], 1646 [ν(C=C)] cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.26$, 6.79 [both d, $J(H,H = 8.8$ Hz, 4 H each, C_6H_4OMe], 3.76 (s, 6 H, OCH_3), 2.72 (m, 6 H, PC*H*CH_3), 2.55 (s, 1 H, OH), 1.25 [dvt, $N = 13.6$, $J(H,H) = 6.8$ Hz, 36 H, PCHCH_3], 1.07 [t, $J(P,H) = 2.8$ Hz, 1 H, =CH]; ^{31}P NMR (162.0 MHz, CD_2Cl_2): $\delta = 41.4$ [d, $J(Rh,P) = 133.3$ Hz]; ^{13}C NMR (100.6 MHz, CD_2Cl_2): $\delta = 287.1$ [dt, *J*(Rh,C) = 61.4, *J*(P,C) = 15.1 Hz, Rh=*C*=C], 158.8 (s, *C*OMe), 141.8 (br s, *i*-C_6H_4), 126.6, 113.5 (both s, =CH of C_6H_4), 117.7 [dt, *J*(Rh,C) = 15.1, *J*(P,C) = 6.0 Hz, Rh=C=*C*], 67.4 [s, *C*($C_6H_4OMe)_2$OH], 55.6 (s, OCH_3), 23.6 (vt, *N* = 20.1 Hz, P*C*HCH_3), 20.1 (s, PCH*C*H_3); $C_{35}H_{58}ClO_3P_2Rh$ (727.2): calcd C 57.81, H 8.04; found C 57.59, H 8.31.

***trans*-[RhCl{=C=CH−CPh(*t*Bu)OH}(P*i*Pr$_3$)$_2$] (6)**: This was prepared as described for **5**, using **1** (119 mg, 0.13 mmol) and HC≡C−CPh(*t*Bu)OH (49 mg, 0.27 mmol) as starting materials. Blue, only moderately air-sensitive crystals; yield 153 mg (91 %); m.p. 135 °C (decomp); IR (C_6H_6): $\tilde{\nu}$ = 3560 [ν(OH)], 1620 [ν(C=C)] cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (m, 5 H, C_6H_5), 2.61 (m, 6 H, PC*H*CH_3), 2.10 (s, 1 H, OH), 1.23 [dvt, *N* = 13.5, *J*(H,H) = 6.6 Hz, 18 H, PCHC*H*$_3$], 1.18 [dvt, *N* = 13.4, *J*(H,H) = 6.7 Hz, 18 H, PCHC*H*$_3$], 0.80 [s, 9 H, C($CH_3)_3$], signal of =C*H*R not observed; ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 36.6 [d, *J*(Rh,P) = 132.8 Hz]; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 288.4 [dt, *J*(Rh,C) = 62.4, *J*(PC) = 15.1 Hz, Rh=*C*=C], 145.7 (s, *i*-C_6H_5), 127.3, 126.6, 126.3 (all s, C_6H_5), 113.4 [dt, *J*(Rh,C) = 15.1, *J*(P,C) = 5.3 Hz, Rh=C=*C*], 65.8 [s, *Ct*Bu(Ph)OH], 39.9 [s, *C*($CH_3)_3$], 25.3 [s, C(*C*$H_3)_3$], 23.4 (vt, *N* = 20.0 Hz, P*C*HCH_3), 19.9 (s, PCH*C*H_3); $C_{31}H_{58}ClOP_2Rh$ (647.1): calcd C 57.54, H 9.03; found C 57.28, H 9.11.

***trans*-[RhCl{=C=C=C(*p*-C_6H_4OMe)$_2$}(P*i*Pr$_3$)$_2$] (7)**: A solution of **5** (87 mg, 0.12 mmol) in benzene (5 mL) was passed through a column of Al_2O_3 (acidic, activity grade I, height of column 5 cm). Almost instantaneously, a change of color from dark-blue to red occurred. After the product was eluted with benzene, the solvent was removed in vacuo and the residue was recrystallized from acetone at −40 °C. Dark red crystals were obtained which were separated, washed with cold (0 °C) diethyl ether (2 × 1 mL) and dried; yield 75 mg (88 %); m.p. 135 °C; IR (C_6H_6): $\tilde{\nu}$ = 1884 [ν(C=C=C)] cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.92, 6.50 [both d, *J*(H,H) = 8.8 Hz, 4 H each, C_6H_4], 3.21 (s, 6 H, OCH_3), 2.95 (m, 6 H, PC*H*CH_3), 1.38 [dvt, *N* = 13.6, *J*(H,H) = 7.2 Hz, 36 H, PCHC*H*$_3$]; ^{31}P NMR (162.0 MHz, C_6D_6): δ = 38.5 [d, *J*(Rh,P) = 132.5 Hz]; ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 232.3 [dt, *J*(R,hC) = 16.1, *J*(PC) = 6.0 Hz, Rh=C=*C*=C], 227.5 [dt, *J*(Rh,C) = 64.4, *J*(P,C) = 18.1 Hz, Rh=*C*=C=C], 159.4 (s, *C*OMe), 146.6 (s, *i*-C_6H_4), 142.0 (s, Rh=C=C=*C*), 126.5, 115.3 (both s, =CH of C_6H_4), 55.8 (s, OCH_3), 24.1 (vt, *N* = 19.3 Hz, P*C*HCH_3), 20.3 (s, PCH*C*H_3); $C_{35}H_{56}ClO_2P_2Rh$ (709.1): calcd C 59.28, H 7.96; found C 59.00, H 8.11.

***trans*-[RhCl{=C=C=C(*t*Bu)Ph}(P*i*Pr$_3$)$_2$] (8)**: This was prepared as described for **7**, using **6** (149 mg, 0.23 mmol) as starting material. Green crystals; yield 135 mg (93 %); m.p. 148 °C (decomp); IR (C_6H_6): $\tilde{\nu}$ = 1875 [ν(C=C=C)] cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (m, 2 H, *o*-C_6H_5), 7.09 (m, 3 H, *m*- and *p*-C_6H_5), 2.63 (m, 6 H, PC*H*CH_3), 1.18 [dvt, *N* = 13.4, *J*(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$], 1.08 [s, 9 H, C($CH_3)_3$]; ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 38.9 [d, *J*(Rh,P) = 131.7 Hz]; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 245.9 [dt, *J*(Rh,C) = 66.5, *J*(P,C) = 17.5 Hz, Rh=*C*=C=C], 232.8 [dt, *J*(Rh,C) = 16.6, *J*(P,C) = 6.4 Hz, Rh=C=*C*=C], 161.4 (br s, Rh=C=C=*C*), 153.9 (br s, *i*-C_6H_5), 126.6, 126.6, 118.9 (all s, C_6H_5), 51.6 [s, *C*($CH_3)_3$], 24.8 [s, C(*C*$H_3)_3$], 23.3 (vt, *N* = 20.0 Hz, P*C*HCH_3), 19.9 (s, PCH*C*H_3); $C_{31}H_{56}ClP_2Rh$ (629.1): calcd C 59.19, H 8.97, Rh 16.36; found C 58.72, H 8.55, Rh 15.75.

***trans*-[RhN_3(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (9)**: A solution of **2** (90 mg, 0.14 mmol) in acetone (15 mL) was treated with NaN_3 (500 mg, 7.7 mmol) and stirred for 3 h at room temperature. A smooth change of color from red to dark red occurred. The solvent was removed in vacuo and the residue was extracted with benzene (10 mL). After removal of the solvent in vacuo the residue was recrystallized from acetone at −78 °C. Dark red crystals were obtained which were separated from the mother liquor, washed with cold (0 °C) diethyl ether (2 × 1 mL) and dried; yield 89 mg (98 %); m.p. 86 °C; IR (C_6H_6): $\tilde{\nu}$ = 2060 [ν(N=N=N)], 1870 [ν(C=C=C)] cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.80 (m, 4 H, *o*-C_6H_5), 7.46 (m, 2 H, *p*-C_6H_5), 6.87 (m, 4 H, *m*-C_6H_5), 2.66 (m, 6 H, PC*H*CH_3), 1.27 [dvt, *N* = 13.6, *J*(H,H) = 7.2 Hz, 36 H, PCHC*H*$_3$]; ^{31}P NMR (162.0 MHz, C_6D_6): δ = 41.1 [d, *J*(Rh,P) = 132.3 Hz]; ^{13}C NMR (100.6 MHz, C_6D_6): δ = 244.6 [dt, *J*(Rh,C) = 15.1, *J*(P,C) = 6.0 Hz, Rh=C=*C*=C], 230.7 [dt, *J*(Rh,C) = 62.4, *J*(P,C) = 17.1 Hz, Rh=*C*=C = C], 154.0 (br s, *i*-C_6H_5), 140.5 (s, Rh=C=C=*C*), 129.9, 127.2, 123.7 (all s, C_6H_5), 24.4 (vt, *N* = 19.3 Hz, P*C*HCH_3), 19.9 (s, PCH*C*H_3); $C_{33}H_{52}N_3P_2Rh$ (665.7): calcd C 60.45, H 7.99, N 6.41, Rh 15.70; found C 60.15, H 7.77, N 6.26, Rh 15.74.

***trans*-[RhN_3{=C=C=C(*o*-Tol)Ph}(P*i*Pr$_3$)$_2$] (10)**: This was prepared as described for **9**, using **3** (83 mg, 0.12 mmol) as starting material. Red crystals; yield 80 mg (97 %); m.p. 140 °C (decomp); IR (C_6H_6): $\tilde{\nu}$ = 2070 [ν(N=N=N)], 1870 [ν(C=C=C)] cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.05 (m, 1 H, *p*-C_6H_5), 7.99 (m, 2 H, *o*-C_6H_5), 7.31 (m, 1 H, *p*-C_6H_4), 7.14 (m, 1 H, *o*-C_6H_4), 7.01 (m, 4 H, *m*-C_6H_5 and *o*-C_6H_4), 2.58 (m, 6 H, PC*H*CH_3), 2.12 (s, 3 H, C_6H_4C*H*$_3$), 1.26 [dvt, *N* = 13.6, *J*(H,H) = 6.8 Hz, 36 H, PCHC*H*$_3$]; ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 41.3 [d, *J*(Rh,P) = 131.4 Hz]; ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 241.7 [dt, *J*(Rh,C) = 15.1, *J*(P,C) = 6.0 Hz, Rh=C=*C*=C], 235.3 [dt, *J*(Rh,C) = 62.4, *J*(P,C) = 17.1 Hz, Rh=*C*=C=C], 152.6 (br s, *i*-C_6H_4), 144.3 (br s, Rh=C=C=*C*), 129.1 (s, *C*Me of *o*-C_6H_4Me), 131.8, 130.6, 127.9, 127.7, 124.8, 124.6, 120.1 (all s, C_6H_4R), 24.5 (vt, *N* = 19.6 Hz, P*C*HCH_3), 19.9 (s, PCH*C*H_3); $C_{34}H_{54}N_3P_2Rh$ (669.68): calcd C 60.98, H 8.13, N 6.27; found C 60.69, H 8.37, N 6.08.

***trans*-[RhN_3{=C=C=C(*p*-C_6H_4OMe)$_2$}(P*i*Pr$_3$)$_2$] (11)**: This was prepared as described for **9**, using **7** (87 mg, 0.12 mmol) as starting material. Red crystals; yield 75 mg (87 %); m.p. 124 °C (decomp); IR (C_6H_6): $\tilde{\nu}$ = 2050 [ν(N=N=N)], 1885 [ν(C=C=C)] cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.93, 6.60 [both d, *J*(H,H) = 8.8 Hz, 4 H each, *p*-C_6H_4], 3.32 (s, 6 H, OCH_3), 2.76 (m, 6 H, PC*H*CH_3), 1.40 [dvt, *N* = 13.6, *J*(H,H) = 7.2 Hz, 36 H, PCHC*H*$_3$]; ^{31}P NMR (162.0 MHz, C_6D_6): δ = 41.9 [d, *J*(Rh,P) = 133.5 Hz]; ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 235.0 [dt, *J*(Rh,C) = 61.4, *J*(P,C) = 17.1 Hz, Rh=*C*=C=C], 228.4 [dt, *J*(Rh,C) = 15.1, *J*(P,C) = 6.0 Hz, Rh=C=*C*=C], 159.6 (s, *C*OMe), 145.8 (br s, *i*-C_6H_4), 142.0 (s, Rh=C=C=*C*), 127.1, 115.2 (both s, =CH of C_6H_4), 55.8 (s, OCH_3), 24.6 (vt, *N* = 19.2 Hz, P*C*HCH_3), 20.0 (s, PCH*C*H_3); $C_{35}H_{56}N_3O_2P_2Rh$ (715.7): calcd C 58.74, H 7.89, N 5.87, Rh 14.38; found C 58.40, H 7.80, N 5.92, Rh 14.35.

***trans*-[RhN_3{=C=C=C(*t*Bu)Ph}(P*i*Pr$_3$)$_2$] (12)**: This was prepared as described for **9**, using **8** (96 mg, 0.15 mmol) as starting material. Dark green crystals; yield 92 mg (96 %); m.p. 97 °C (decomp); IR (C_6H_6): $\tilde{\nu}$ = 2049 [ν(N=N=N)], 1883 [ν(C=C=C)] cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.02 (m, 1 H, *p*-C_6H_5), 7.14 (m, 2 H, *o*-C_6H_5), 7.00 (m, 2 H, *m*-C_6H_5), 2.49 (m, 6 H, PC*H*CH_3), 1.21 [dvt, *N* = 13.6, *J*(H,H) = 6.8 Hz, 36 H, PCHC*H*$_3$], 1.03 [s, 9 H, C($CH_3)_3$]; ^{31}P NMR (162.0 MHz, C_6D_6): δ = 42.6 [d, *J*(Rh,P) = 133.2 Hz]; ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 255.0 [dt, *J*(Rh,C) = 62.4, *J*(P,C) = 17.1 Hz, Rh=*C*=C=C], 230.3 [dt, *J*(Rh,C) = 16.1, *J*(P,C) = 6.0 Hz, Rh=C=*C*=C], 162.0 (br s, *i*-C_6H_5), 153.8 (br s, Rh=C=C=*C*), 127.2, 127.1, 119.9 (all s, C_6H_5), 51.4 [s, *C*($CH_3)_3$], 25.3 [s, C(*C*$H_3)_3$], 24.3 (vt, *N* = 19.5 Hz, P*C*HCH_3), 19.9 (s, PCH*C*H_3); $C_{31}H_{56}N_3P_2Rh$ (635.7): calcd C 58.58, H 8.88, N 6.61, Rh 16.19; found C 58.63, H 9.09, N 6.36, Rh 16.79.

***trans*-[Rh(NCO)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (13)**: This was prepared as described for **9**, using **2** (90 mg, 0.14 mmol) and KOCN (500 mg, 7.2 mmol) as starting materials. Dark red crystals; yield 87 mg (96 %); m.p. 79 °C (decomp); IR (C_6H_6): $\tilde{\nu}$ = 2201 [ν_{as}(NCO)], 1877 [ν(C=C=C)], 1449 [ν_s(NCO)] cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.81 (m, 4 H, *o*-C_6H_5), 7.45 (m, 2 H, *p*-C_6H_5), 6.77 (m, 4 H, *m*-C_6H_5), 2.64 (m, 6 H, PC*H*CH_3), 1.25 [dvt, *N* = 13.6, *J*(H,H) = 7.2 Hz, 36 H, PCHC*H*$_3$]; ^{31}P NMR (162.0 MHz, C_6D_6): δ = 40.6 [d, *J*(Rh,P) = 132.0 Hz]; ^{13}C NMR (100.6 MHz, C_6D_6): δ = 244.6 [dt, *J*(Rh,C) = 15.1, *J*(P,C) = 6.0 Hz, Rh=C=*C*=C], 237.4 [dt, *J*(Rh,C) = 60.4, *J*(P,C) = 16.1 Hz, Rh=*C*=C=C], 153.7 (br s, *i*-C_6H_5), 142.9 (t, *J*(PC) = 2.0 Hz, Rh=C=C=*C*), 142.2 (m, NCO), 130.0, 127.6, 124.0 (all s, C_6H_5), 24.5 (vt, *N* = 19.5 Hz, P*C*HCH_3), 20.1 (s, PCH*C*H_3); $C_{34}H_{52}NOP_2Rh$ (655.7): calcd C 62.29, H 7.99, N 2.14, Rh 15.70; found C 61.99, H 8.13, N 2.22, Rh 16.27.

***trans*-[Rh(NCO){=C=C=C(*o*-Tol)Ph}(P*i*Pr$_3$)$_2$] (14)**: This was prepared as described for **9**, using **3** (86 mg, 0.13 mmol) and KOCN (500 mg, 7.2 mmol) as starting materials. Dark red crystals; yield 83 mg (95 %); m.p. 124 °C (decomp); IR (C_6H_6): $\tilde{\nu}$ = 2212 [ν_{as}(NCO)], 1877 [ν(C=C=C)], 1481 [ν_s(NCO)] cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 8.11 (m, 2 H, *o*-C_6H_4R), 7.75 (m, 1 H, *o*-C_6H_5), 7.06 (m, 2 H, C_6H_4R), 6.73 (m, 4 H, C_6H_4R), 2.60 (m, 6 H, PC*H*CH_3), 1.96 (s, 3 H, C_6H_4C*H*$_3$), 1.23 [dvt, *N* = 13.6, *J*(H,H) = 7.2 Hz, 36 H, PCHC*H*$_3$]; ^{31}P NMR (162.0 MHz, C_6D_6): δ = 40.5 [d, *J*(Rh,P) = 131.7 Hz]; ^{13}C NMR (100.6 MHz, C_6D_6): δ = 245.2 [dt, *J*(Rh,C) = 15.1, *J*(P,C) = 6.0 Hz, Rh=C=*C*=C], 236.3 [dt, *J*(Rh,C) = 59.9, *J*(P,C) = 18.8 Hz, Rh=*C*=C=C], 153.2 (s, *i*-C_6H_5), 144.1 (m, NCO), 143.1 (br s, Rh=C=C=*C*), 131.8, 130.5, 127.6, 127.4, 124.7, 124.4, 119.6 (all s, C_6H_4R), 128.6 (s, *C*Me of C_6H_4R), 24.3 (vt, *N* = 20.4 Hz, P*C*HCH_3), 20.1 (s, PCH*C*H_3), 19.8 (s, C_6H_4*C*H_3); $C_{35}H_{54}NOP_2Rh$ (669.7): calcd C 62.77, H 8.13, N 2.09; found C 62.65, H 7.95, N 2.10.

***trans*-[Rh(NCO){=C=C=C(*p*-C_6H_4OMe)$_2$}(P*i*Pr$_3$)$_2$] (15)**: This was prepared as described for **9**, using **7** (92 mg, 0.13 mmol) and KOCN (500 mg, 7.2 mmol) as starting materials. Dark red crystals; yield 90 mg (97 %); m.p. 155 °C (decomp); IR (C$_6$H$_6$): $\tilde{\nu}$ = 2217 [ν_{as}(NCO)], 1896 [ν(C=C=C)], 1462 [ν_s(NCO)] cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.74, 6.60 [both d, *J*(H,H) = 8.8 Hz, 4H each, C$_6$H$_4$] 3.75 (s, 6H, OCH$_3$), 2.57 (m, 6H, PC*H*CH$_3$), 1.23 [dvt, *N* = 13.2, *J*(H,H) = 6.8 Hz, 36H, PCHC*H*$_3$]; ^{31}P NMR (162.0 MHz, CDCl$_3$): δ = 41.4 [d, *J*(Rh,P) = 133.0 Hz]; ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 237.4 [br d, *J*(Rh,C) = 62.1 Hz, Rh=*C*=C=C], 230.4 [dt, *J*(Rh,C) = 15.1, *J*(P,C) = 6.0 Hz, Rh=C=*C*=C], 159.0 (s, *C*OMe), 145.7 (s, *i*-C$_6$H$_4$), 141.4 (s, Rh=C=C=*C*), 140.5 (br m, NCO), 128.3, 114.8 (both s, =CH of C$_6$H$_4$), 55.4 (s, OCH$_3$), 24.0 (vt, *N* = 19.2 Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$); C$_{36}$H$_{56}$NO$_3$P$_2$Rh (715.7): calcd C 60.42, H 7.89, N 1.96; found C 60.26, H 7.97, N 1.95.

***trans*-[Rh(NCO){=C=C=C(*t*Bu)Ph}(P*i*Pr$_3$)$_2$] (16)**: This was prepared as described for **9**, using **8** (98 mg, 0.16 mmol) and KOCN (500 mg, 7.2 mmol) as starting materials. Dark green crystals; yield 95 mg (96 %); m.p. 116 °C (decomp); IR (C$_6$H$_6$): $\tilde{\nu}$ = 2213 [ν_{as}(NCO)], 1892 [ν(C=C=C)], 1472 [ν_s(NCO)] cm^{-1}; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 7.02 (m, 1H, *p*-C$_6$H$_5$), 6.97 (m, 2H, *o*-C$_6$H$_5$), 6.83 (m, 2H, *m*-C$_6$H$_5$), 2.48 (m, 6H, PC*H*CH$_3$), 1.19 [dvt, *N* = 13.6, *J*(H,H) = 7.2 Hz, 36H, PCHC*H*$_3$], 1.03 [s, 9H, C(CH$_3$)$_3$]; ^{31}P NMR (162.0 MHz, C$_6$D$_6$): δ = 42.1 [d, *J*(Rh,P) = 132.3 Hz]; ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 255.2 [dt, *J*(Rh,C) = 60.4, *J*(P,C) = 17.1 Hz, Rh=*C*=C=C], 233.5 [dt, *J*(Rh,C) = 15.1, *J*(P,C) = 6.0 Hz, Rh=C=*C*=C], 159.9 (br s, Rh=C=C=*C*), 154.1 (br s, *i*-C$_6$H$_5$), 142.8 (m, NCO), 127.0, 126.8, 119.4 (all s, C$_6$H$_5$), 51.3 [s, *C*(CH$_3$)$_3$], 24.9 [s, C(*C*H$_3$)$_3$], 24.0 (vt, *N* = 19.4 Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$); C$_{32}$H$_{56}$NOP$_2$Rh (635.7): calcd C 60.47, H 8.88, N 2.20, Rh 16.18; found C 60.58, H 8.56, N 2.21, Rh 16.67.

***trans*-[Rh{C≡C−CPh(*t*Bu)N$_3$}(CO)(P*i*Pr$_3$)$_2$] (17)**: A slow stream of CO was passed through a solution of **12** (81 mg, 0.13 mmol) in benzene (7 mL) for 30 s at room temperature. A change of color from green to yellow occurred. After the solvent was removed in vacuo, the residue was dissolved in methanol (3 mL) and the solution was stored at −78 °C. A yellow microcrystalline solid precipitated which was separated from the mother liquor, washed with cold (0 °C) methanol (2 × 1 mL) and dried; yield 76 mg (90 %); m.p. 73 °C (decomp); IR (KBr): $\tilde{\nu}$ = 2099 [ν(N=N=N)], 2063 [ν(C≡C)], 1944 [ν(CO)] cm^{-1}; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 7.55 (m, 2H, *o*-C$_6$H$_5$), 7.25 (m, 3H, *m*-, *p*-C$_6$H$_5$), 2.61 (m, 6H, PC*H*CH$_3$), 1.33 [dvt, *N* = 14.0, *J*(H,H) = 6.8 Hz, 18H, PCHC*H*$_3$], 1.30 [dvt, *N* = 14.0, *J*(H,H) = 6.8 Hz, 18H, PCHC*H*$_3$], 0.92 [s, 9H, C(CH$_3$)$_3$]; ^{31}P NMR (162.0 MHz, C$_6$D$_6$): δ = 53.3 [d, *J*(Rh,P) = 125.9 Hz]; ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ = 195.4 (m, RhCO), 141.3 (s, *i*-C$_6$H$_5$), 129.3, 128.4, 127.2 (all s, C$_6$H$_5$), 121.5 [dt, *J*(Rh,C) = 44.3, *J*(P,C) = 19.1 Hz, Rh−*C*≡C], 112.8 [dt, *J*(Rh,C) = 12.1, *J*(P,C) = 2.0 Hz, Rh−C≡*C*], 77.7 (br s, Rh−C≡C−*C*), 40.9 [s, *C*(CH$_3$)$_3$], 28.9 [s, C(*C*H$_3$)$_3$], 26.3 (vt, *N* = 21.2 Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$); C$_{32}$H$_{56}$N$_3$OP$_2$Rh (663.7): calcd C 57.91, H 8.51, N 6.33; found C 57.60, H 8.64, N 6.05.

***trans*-[Rh{C≡C−C(N$_3$)Ph$_2$}(CO)(P*i*Pr$_3$)$_2$] (18)**: In an NMR tube a slow stream of CO was passed through a solution of **9** (62 mg, 0.09 mmol) in [D$_8$]toluene (2 mL) for 30 s at −60 °C. A change of color from red to yellow occurred. The resulting compound was characterized at −60 °C by NMR spectroscopy. ^{1}H NMR (400 MHz, C$_6$D$_5$CD$_3$, 213 K): δ = 7.61 [br d, *J*(H,H) = 7.6 Hz, 4H, *o*-C$_6$H$_5$], 7.04 [br t, *J*(H,H) = 7.6 Hz, 4H, *m*-C$_6$H$_5$], 6.93 [br t, *J*(H,H) = 7.6 Hz, 2H, *p*-C$_6$H$_5$], 2.26 (br s, 6H, PC*H*CH$_3$), 1.14 (br s, 36H, PCHC*H*$_3$); ^{31}P NMR (162.0 MHz, C$_6$D$_5$CD$_3$, 213 K): δ = 52.5 [br d, *J*(Rh,P) = 124.4 Hz]; ^{13}C NMR (100.6 MHz, C$_6$D$_5$CD$_3$, 213 K): δ = 196.3 (br m, Rh-CO), 161.7 (s, *i*-C$_6$H$_5$), 128.1, 127.9, 127.5 (all s, C$_6$H$_5$), 113.2 [br d, *J*(Rh,C) = 12.1 Hz, Rh−C≡*C*], 71.4 (s, Rh−C≡C−*C*), 25.9 (br m, P*C*HCH$_3$), 19.8 (br s, PCH*C*H$_3$), signal of Rh−*C*≡C probably covered by a signal of the solvent.

***trans*-[Rh(CO){C(CN)=CPh$_2$}(P*i*Pr$_3$)$_2$] (19)**: A slow stream of CO was passed through a solution of **9** (98 mg, 0.15 mmol) in toluene (10 mL) for 30 s at −50 °C. A change of color from red to yellow occurred. Upon warming the solution to room temperature, a gas evolution was observed and the color changed from yellow to orange. After the solvent was removed in vacuo, the residue was washed with cold (−10 °C) pentane (2 × 5 mL) and recrystallized from acetone at −40 °C. Yellow crystals were obtained which were separated from the mother liquor, washed with cold (0 °C) diethyl ether (2 × 1 mL) and dried; yield 86 mg (87 %); m.p. 74 °C; IR (C$_6$H$_6$): $\tilde{\nu}$ = 2145 [ν(C≡N)], 1945 [ν(CO)], 1716 [ν(C=C)] cm^{-1}; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 8.63 (br s, 2H, *o*-C$_6$H$_5$), 7.41 (m, 2H, *o*-C$_6$H$_5$), 7.34, 7.16 (both m, 2H each, *m*-C$_6$H$_5$), 7.07 (m, 2H, *p*-C$_6$H$_5$), 2.28 (m, 6H, PC*H*CH$_3$), 1.29 [dvt, *N* = 13.6, *J*(H,H) = 6.8 Hz, 18H, PCHC*H*$_3$], 1.04 [dvt, *N* = 13.2, *J*(H,H) = 6.4 Hz, 18H, PCHC*H*$_3$]; ^{31}P NMR (162.0 MHz, C$_6$D$_6$): δ = 42.7 [d, *J*(Rh,P) = 133.8 Hz]; ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ = 195.3 [dt, *J*(Rh,C) = 56.3, *J*(P,C) = 15.6 Hz, Rh-CO], 160.3 [br t, *J*(P,C) = 4.5 Hz, =*C*Ph$_2$], 145.3, 143.7 (both br s, *i*-C$_6$H$_5$), 143.0 [dt, *J*(Rh,C) = 31.2, *J*(P,C) = 14.6 Hz, Rh−C], 129.8, 129.4, 128.6, 127.7, 127.4, 127.0 (all s, C$_6$H$_5$), 125.2 [t, *J*(P,C) = 2.0 Hz, CN], 26.5 (vt, *N* = 20.4 Hz, P*C*HCH$_3$), 20.6, 19.7 (both s, PCH*C*H$_3$); C$_{34}$H$_{52}$NOP$_2$Rh (655.7): calcd C 62.29, H 7.99, N 2.14; found C 62.12, H 8.15, N 2.07.

***trans*-[Rh(CO){C(CN)=C(*p*-C$_6$H$_4$OMe)$_2$}(P*i*Pr$_3$)$_2$] (20)**: This was prepared as described for **19**, using **11** (115 mg, 0.16 mmol) as starting material. After recrystallization from diethyl ether at −78 °C orange crystals were obtained which were separated from the mother liquor, washed with cold (0 °C) pentane (2 × 1 mL) and dried; yield 106 mg (92 %); m.p. 92 °C (decomp); IR (C$_6$H$_6$): $\tilde{\nu}$ = 2145 [ν(C≡N)], 1947 [ν(CO)] cm^{-1}; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 8.31 (br s, 2H, C$_6$H$_4$), 6.98, 6.88, 6.70 [all d, *J*(H,H) = 8.8 Hz, 2H each, C$_6$H$_4$], 3.77, 3.76 (both s, 3H each, OCH$_3$), 2.38 (m, 6H, PC*H*CH$_3$), 1.36 [dvt, *N* = 14.4, *J*(H,H) = 7.2 Hz, 18H, PCHC*H*$_3$], 1.16 [dvt, *N* = 13.6, *J*(H,H) = 7.2 Hz, 18H, PCHC*H*$_3$]; ^{31}P NMR (162.0 MHz, CDCl$_3$): δ = 42.8 [d, *J*(Rh,P) = 133.3 Hz]; ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 194.4 [dt, *J*(Rh,C) = 57.3, *J*(P,C) = 15.1 Hz, Rh−CO], 160.4 [br t, *J*(P,C) = 5.0 Hz, =*C*(*p*-C$_6$H$_4$OMe)$_2$], 159.2, 158.1 (both s, *C*OMe), 137.2, 136.3 (both s, *i*-C$_6$H$_4$), 136.9 [dt, *J*(Rh,C) = 31.2, *J*(P,C) = 15.1 Hz, Rh−C], 130.7, 129.7, 113.6, 112.2, (all s, C$_6$H$_4$), 126.3 (s, CN), 55.2, 55.1 (both s, OCH$_3$), 26.1 (vt, *N* = 20.3 Hz, P*C*HCH$_3$), 20.5, 19.7 (both s, PCH*C*H$_3$); C$_{34}$H$_{52}$NOP$_2$Rh (655.7): calcd C 60.42, H 7.89, N 1.96; found C 60.13, H 7.77, N 1.97.

[{(P*i*Pr$_3$)$_2$(Ph$_2$C=C=C=)Rh}$_2$(*μ*-1,3-N$_3$)]BF$_4$ (21): A solution of **9** (289 mg, 0.43 mmol) in CH$_2$Cl$_2$ (4 mL) was treated at room temperature with [Me$_3$O]BF$_4$ (32 mg, 0.21 mmol). A change of color from red to violet occurred. The solvent was removed in vacuo and the residue was recrystallized from methanol at −20 °C. Black-violet crystals were obtained which were washed with cold (0 °C) diethyl ether (2 × 1 mL) and dried; yield 251 mg (86 %); m.p. 84 °C; IR (C$_6$H$_6$): $\tilde{\nu}$ = 2143 [ν(N=N=N)], 1909 [ν(C=C=C)] cm^{-1}; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 7.80 (m, 12H, C$_6$H$_5$), 7.21 (m, 8H, C$_6$H$_5$), 2.41 (m, 12H, PC*H*CH$_3$), 1.25 [dvt, *N* = 14.0, *J*(H,H) = 7.2 Hz, 72H, PCHC*H*$_3$]; ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): δ = 43.4 [d, *J*(Rh,P) = 127.3 Hz]; ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 246.0 [dt, *J*(Rh,C) = 64.4, *J*(P,C) = 19.1 Hz, Rh=*C*=C=C], 230.1 [dt, *J*(Rh,C) = 18.1, *J*(P,C) = 6.0 Hz, Rh=C=*C*=C], 151.1 [t, *J*(P,C) = 2.0 Hz, *i*-C$_6$H$_5$], 149.3 [t, *J*(PC) = 2.0 Hz, Rh=C=C=*C*], 129.9, 129.1, 125.6 (all s, C$_6$H$_5$), 24.9 (vt, *N* = 19.3 Hz, P*C*HCH$_3$), 20.0 (s, PCH*C*H$_3$); C$_{66}$H$_{104}$BF$_4$N$_3$P$_4$Rh (1344.0): calcd C 58.93, H 7.74, N 3.13; found C 58.58, H 7.59, N 2.91.

[{(P*i*Pr$_3$)$_2$(Ph(*o*-Tol)C=C=C=)Rh}$_2$(*μ*-1,3-N$_3$)]BF$_4$ (22): This was prepared as described for **21**, using **10** (271 mg, 0.40 mmol) and [Me$_3$O]BF$_4$ (32 mg, 0.21 mmol) as starting materials. Dark violet crystals; yield 232 mg (82 %); m.p. 127 °C (decomp); IR (C$_6$H$_6$): $\tilde{\nu}$ = 2142 [ν(N=N=N)], 1903 [ν(C=C=C)] cm^{-1}; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 8.01 (m, 6H, C$_6$H$_4$R), 7.93 (m, 2H, C$_6$H$_4$R), 7.08 (m, 10H, C$_6$H$_4$R), 2.37 (m, 12H, PC*H*CH$_3$), 2.01 (s, 6H, C$_6$H$_4$C*H*$_3$), 1.19 [dvt, *N* = 14.0, *J*(H,H) = 7.2 Hz, 72H, PCHC*H*$_3$]; ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): δ = 43.2 [d, *J*(Rh,P) = 129.7 Hz]; ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 245.8 [dt, *J*(Rh,C) = 64.4, *J*(P,C) = 18.1 Hz, Rh=*C*=C=C], 229.8 [dt, *J*(Rh,C) = 17.1, *J*(P,C) = 6.0 Hz, Rh=C=*C*=C], 151.7 (br s, Rh=C=C=*C*), 150.8, 150.4 (both br s, *i*-C$_6$H$_4$R), 131.6, 130.9, 129.5, 128.6, 125.7, 125.1, 121.5 (all s, C$_6$H$_4$R), 130.3 (s, *C*Me of C$_6$H$_4$Me), 24.9 (vt, *N* = 20.0 Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$), 17.9 (s, C$_6$H$_4$*C*H$_3$); C$_{68}$H$_{108}$BF$_4$N$_3$P$_4$Rh (1384.1): calcd C 59.01, H 7.87, N 3.03; found C 58.70, H 7.85, N 3.10.

[{(P*i*Pr$_3$)$_2$((*p*-C$_6$H$_4$OMe)$_2$C=C=C=)Rh}$_2$(*μ*-1,3-N$_3$)]BF$_4$ (23): This was prepared as described for **21**, using **11** (312 mg, 0.44 mmol) and [Me$_3$O]BF$_4$ (34 mg, 0.22 mmol) as starting materials. Dark violet crystals; yield 261 mg (81 %); m.p. 114 °C (decomp); IR (C$_6$H$_6$): $\tilde{\nu}$ = 2140 [ν(N=N=N)], 1911 [ν(C=C=C)] cm^{-1}; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 7.75, 6.75 (both d, *J*(H,H) = 8.8 Hz, 8 H each, C$_6$H$_4$), 3.82 (s, 12H, OCH$_3$), 2.38 (m, 12H, PC*H*CH$_3$), 1.24 [dvt, *N* = 13.2, *J*(H,H) = 6.8 Hz, 72H, PCHC*H*$_3$]; ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): δ = 44.1 [d, *J*(Rh,P) = 132.0 Hz]; ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 244.6 [dt, *J*(Rh,C) = 63.4, *J*(P,C) = 20.1 Hz, Rh=*C*=C=C], 214.6 [dt, *J*(Rh,C) = 18.1, *J*(P,C) = 6.0 Hz, Rh=C=*C*=C], 161.0 (s, *C*OMe), 148.4 (s, Rh=C=C=*C*), 143.2 (s, *i*-C$_6$H$_4$), 129.0, 115.2 (both s, =CH of C$_6$H$_4$), 56.0 (s, OCH$_3$), 25.0 (vt, *N* = 19.5 Hz, P*C*HCH$_3$), 20.1 (s, PCH*C*H$_3$); C$_{70}$H$_{112}$BF$_4$N$_3$O$_4$P$_4$Rh (1476.2): calcd C 56.96, H 7.65, N 2.84, Rh 13.94; found C 56.49, H 7.28, N 2.85, Rh 13.98.

[{(P*i*Pr$_3$)$_2$(Ph(*t*Bu)C=C=C=)Rh}$_2$(*μ*-1,3-N$_3$)]BF$_4$ (24): This was prepared as described for **21**, using **12** (295 mg, 0.46 mmol) and [Me$_3$O]BF$_4$ (35 mg, 0.23 mmol) as starting materials. Dark violet crystals; yield 283 mg (88 %); m.p. 66 °C (decomp); IR (C$_6$H$_6$): $\tilde{\nu} = 2144$ [ν(N=N=N)], 1906 [ν(C=C=C)] cm^{-1}; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 7.35$ (m, 2H, C$_6$H$_5$), 7.19, 7.11 (both m, 4 H each, C$_6$H$_5$), 2.26 (m, 12H, PC*H*CH$_3$), 1.15 [dvt, $N = 14.0$, J(H,H) = 6.8 Hz, 72H, PCHC*H*$_3$], 1.15 [s, 18H, C(C*H*$_3$)$_3$]; ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): $\delta = 44.1$ [d, J(Rh,P) = 130.4 Hz]; ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta = 265.3$ [dt, J(Rh,C) = 65.4, J(P,C) = 18.1 Hz, Rh=*C*=C=C], 222.6 [br d, J(Rh,C) = 19.1, Rh=C=*C*=C], 170.7 (s, Rh=C=C=*C*), 152.0 [t, J(P,C) = 2.0 Hz, , *i*-C$_6$H$_5$], 127.9, 127.5, 120.7 (all s, C$_6$H$_5$), 51.3 [s, *C*(CH$_3$)$_3$], 26.0 [s, C(*C*H$_3$)$_3$], 24.7 (vt, $N = 20.1$ Hz, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$); C$_{68}$H$_{108}$BF$_4$N$_3$P$_4$Rh (1384.1): calcd C 56.58, H 8.58, N 3.19; found C 56.32, H 8.40, N 3.23.

X-ray structure determination of compounds 12, 20, and 22:[32] Single crystals of **12** were grown from pentane at −20 °C, those of **20** from diethyl ether at −20 °C, and those of **22** from CH$_2$Cl$_2$/pentane at 0 °C. Crystal data collection parameters for these structures are presented in Table 1. The data were collected on an Enraf-Nonius CAD 4 diffractometer using monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Intensity data were corrected by Lorentz and polarization effects. The structures were solved by direct methods with SHELXS-86.[33] All structures were refined by full-matrix least-squares procedures on F^2, using SHELXL-93.[34] The positions of all hydrogen atoms were calculated according to ideal geometry and were refined by employing the riding method. The asymmetric unit of **22** contains one solvent molecule of CH$_2$Cl$_2$ which was refined anisotropically without any restrictions. For the atoms of the disordered BF$_4$ anion of **22** (except F2) two alternative positions could be refined using restraints on anisotropical displacement parameters, bond lengths, and bond angles (occupation ratio 80:20).

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Table 1. Crystal structure data for **12**, **20**, and **22**.

Compound	**12**	**20**	**22**
formula	C$_{31}$H$_{56}$N$_3$P$_2$Rh	C$_{36}$H$_{56}$NO$_3$P$_2$Rh	C$_{68}$H$_{108}$F$_4$N$_3$P$_4$Rh$_2$
M_r	635.64	715.67	1469.01
T [K]	293(2)	293(2)	173(2)
cryst. size [mm^3]	0.54 × 0.32 × 0.30	0.43 × 0.36 × 0.31	0.6 × 0.3 × 0.3
space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
cell dim. determn.	25 rflns, $10 < \theta < 15$	25 rflns, $10 < \theta < 15$	25 rflns, $10 < \theta < 15$
a [pm]	908.08(6)	1156.0(1)	1185.4(1)
b [pm]	1175.79(6)	1679.0(1)	1872.2(1)
c [pm]	1688.6(2)	1925.3(1)	1915.1(2)
α [°]	98.035(8)	–	117.440(8)
β [°]	90.944(8)	93.48(1))	94.203(9)
γ [°]	102.408(5)	–	89.313(7)
V [nm^3]	1.7415(3)	3.7301(4)	3.7609(7))
Z	2	4	2
ρ_{calcd} [Mg m^{-3}]	1.212	1.274	1.297
μ [mm^{-1}]	0.598	0.571	0.638
F(000)	676	1512	1540
2θ max [°]	46	46	46
no. meas. reflns.	4465	4984	10505
no. unique reflns.	4105	4238	9904
no. reflns. used	4105	4235	9903
refined parameters	374	402	829
$R1$ [$I > 2\sigma(I)$][a]	0.0399	0.0340	0.0278
$wR2$ (all data)[b]	0.1069	0.0792	0.0698
$g1$; $g2$[c]	0.0256; 3.4688	0.0315; 2.5595	0.0323; 3.8185
resid. elec. ρ [10^{-6} e pm^{-3}]	0.753/ − 0.484	0.343/ − 0.223	0.734/ − 0.343

[a] $R1 = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (g1 \times P)^2 + g2 \times P]$; $P = (F_o^2 + 2F_c^2)/3$.

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[32] Crystallographic data (excluding structure factors) for the structures reproted in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 118850 (**12**), 118851 (**20**), and 118852 (**22**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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