Organometallics **2000,** *19,* 1365−1372 1365

Synthesis of Dinuclear Rhodium Complexes with 1,3-Butadiyndiyl Bridges. Coupling of the C_4 and the Two C_2 Units of a $C_2RhC_4RhC_2$ Chain[†,1]

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Compounds *trans*-$[RhF(=C=CHR)(PiPr_3)_2]$ (**2**−**4**), of which **2** (R = H) was prepared for the first time from $[Rh\{\eta^2\text{-}O_2S(O)CF_3\}(PiPr_3)_2]$, C_2H_2, and KF, reacted with $Ph_3SnC\equiv C-C\equiv CSnPh_3$ to give the dinuclear C_4-bridged rhodium(I) complexes *trans,trans*-$[\{Rh(=C=CHR)(PiPr_3)_2\}_2(\mu\text{-}C\equiv C-C\equiv C)]$ (**5**−**7**) in 78−88% isolated yield. On a similar route, by using *trans*-$[RhF(CX)(PiPr_3)_2]$ (**8**, CX = $CNC_6H_3Me_2$-2,6; **9**, CX = CO) and $Ph_3SnC\equiv C-C\equiv CSnPh_3$ in the molar ratio of 2:1 as the starting materials, the diisocyanidedirhodium and dicarbonyldirhodium derivatives *trans,trans*-$[\{Rh(CX)(PiPr_3)_2\}_2(\mu\text{-}C\equiv C-C\equiv C)]$ (**12**, **13**) were obtained. The reactions of **8** and **9** with *equimolar* amounts of $Ph_3SnC\equiv C-C\equiv CSnPh_3$ gave the mononuclear complexes *trans*-$[Rh(C\equiv C-C\equiv CSnPh_3)(CX)(PiPr_3)_2]$ (**10**, **11**), which on further treatment with **8** or **9** afforded the dinuclear compounds **12** and **13**, respectively. The $C-SnPh_3$ bond of **10** could be cleaved both by Al_2O_3/H_2O and *trans*-$[RhF(=C=CHPh)(PiPr_3)_2]$ (**3**) to give the butadiynyl compound *trans*-$[Rh(C\equiv C-C\equiv CH)(CNC_6H_3Me_2\text{-}2,6)(PiPr_3)_2]$ (**14**) and the unsymmetrical dirhodium complex *trans,trans*-$[\{Rh(=C=CHPh)(PiPr_3)_2\}\{Rh(CNC_6H_3Me_2\text{-}2,6)(PiPr_3)_2\}(\mu\text{-}C\equiv C-C\equiv C)]$ (**15**). Moreover, treatment of **5** and **6** with $CNC_6H_3Me_2$-2,6 or CO led to a 2-fold migratory insertion reaction to yield the novel dinuclear compounds *trans,trans*-$[\{Rh(CX)(PiPr_3)_2\}_2\{\mu\text{-}C(=CHR)C\equiv C-C\equiv C-C(=CHR)\}]$ (**16**−**18**), which contain a highly unsaturated eight-membered C_8 chain as a bridge. The molecular structure of **17** (CX = CO; R = Ph) was determined by X-ray crystallography.

Introduction

Following the pioneering work by Sonogashira and Hagihara,[2] and the more recent studies by Gladysz and co-workers,[3] the chemistry of di- and oligonuclear transition metal complexes in which two neighboring metal centers are connected by a “naked” C_n chain has received a great deal of attention.[4] Apart from the possibility that these compounds could reveal NLO properties,[5] it appears challenging to bind the two terminal carbon atoms of a C_n^{2-} dianion to two redox-active metal centers and thus to generate the precursor of a molecular wire.[6]

Our own interest in this field dates back to the observation that hydroxorhodium(I) compounds with $[Rh(PiPr_3)_2]$ as a building block react smoothly with silylated alkynes such as $PhC\equiv CSiMe_3$ and $Me_3SiC\equiv C-C\equiv CSiMe_3$ to afford mono- and dinuclear rhodium(I) complexes with a $Rh-C\equiv CPh$ or $Rh-C\equiv C-C\equiv C-Rh$ bond.[7] Recently, this methodology has also been applied

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[†] Dedicated to Professor Henri Brunner on the occasion of his 65th birthday.

[1] Vinylidene Transition-Metal Complexes. 52. Part 51: Werner, H.; Ilg, K.; Weberndörfer, B. *Organometallics* **2000**, *19*, in press.

[2] (a) Sonogashira, K.; Fujikura, Y.; Yatake, T.; Toyoshima, N.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *145*, 101−108. (b) Sonogashira, K.; Kataoka, S.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *160*, 319−327. (c) Sonogashira, K.; Ohga, K.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1980**, *188*, 237−243. (d) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1981**, *41*, 149−179.

[3] (a) Peters, T. B.; Bohling, J. C.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1999**, *18*, 3261−3263. (b) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775−788, and references therein.

[4] (a) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem.* **1993**, *105*, 969−996; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923−950. (b) Lang, H. *Angew. Chem.* **1994**, *106*, 569−572; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547−550. (c) Le Narvour, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129−7138. (d) Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477−479. (e) Akita, M.; Chung, M.-C.; Sakurai, A.; Terada, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4882−4888. (f) Sakurai, A.; Akita, M.; Moro-oka, Y. *Organometallics* **1999**, *18*, 3241−3244. (g) Bruce, M. I.; Ke, M.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **1998**, *17*, 3539−3549. (h) Bruce, M. I.; Kelly, B. D.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, 847−852. (i) ALQaisi, S.; Galat, K. J.; Chai, M.; Ray, D. G.; Rinaldi, P. L.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1998**, *120*, 12149−12150.

[5] (a) Marder, S. R., Sohn, J. E., Stucky, G. D., Eds. *Materials for Nonlinear Optics: Chemical Perspectives*; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991. (b) Bruce, D. W., O'Hare, D., Eds. *Inorganic Materials*; Wiley: Chichester, U.K., 1992. (c) Long, N. J. *Angew. Chem.* **1995**, *107*, 37−56; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21−40. (d) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G. *Adv. Organomet. Chem.* **1998**, *42*, 291−362. (e) McDonagh, A. M.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Houbrechts, S.; Wada, T.; Sasabe, H.; Persoons, A. *J. Am. Chem. Soc.* **1999**, *121*, 1405−1406. (f) Younus, M.; Köhler, A.; Cron, S.; Chawdhury, N.; Al-Mandhary, M. R. A.; Khan, M. S.; Lewis, J.; Long, N. J.; Friend, R. H.; Raithby, P. R. *Angew. Chem.* **1998**, *110*, 3180−3183; *Angew. Chem., Int. Ed.* **1998**, *37*, 3036−3039. (g) Kingsborough, R. P.; Swager, T. M. *Prog. Inorg. Chem.* **1999**, *48*, 123−231.

[6] (a) Yam, V. W.-W.; Lau, V. C.-Y.; Cheung, K.-K. *Organometallics* **1996**, *15*, 1740−1744. (b) Colbert, M. C. B.; Lewis, J.; Long, N. J.; Raithby, P. R.; Younus, M.; White, A. J. P.; Williams, D. J.; Payne, N. N.; Yellowlees, L.; Beljonne, D.; Chawdhury, N.; Friend, R. H. *Organometallics* **1998**, *17*, 3034−3045. (c) Guillemot, M.; Toupet, L.; Lapinte, C. *Organometallics* **1998**, *17*, 1928−1930. (d) Zhu, Y.; Clot, O.; Wolf, M.; Yap, G. P. A. *J. Am. Chem. Soc.* **1998**, *120*, 1812−1821.

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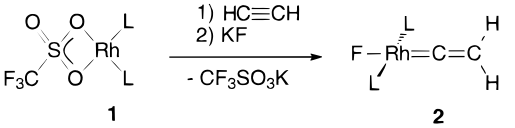
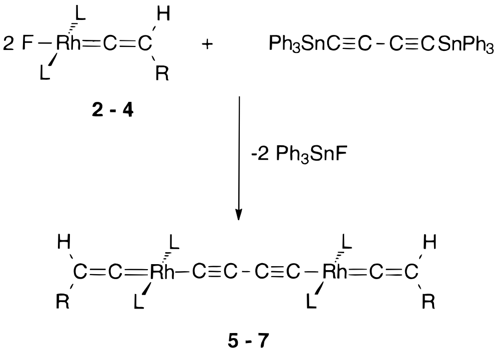
Scheme 1[a]



[a] L = P*i*Pr$_3$.

Scheme 2[a]



	R
2, **5**	H
3, **6**	Ph
4, **7**	*t*Bu

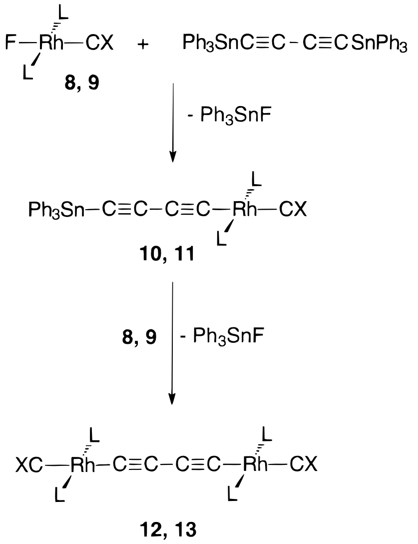
[a] L = P*i*Pr$_3$.

to starting materials with vinylidenes and allenylidenes as ligands, thus allowing the preparation of compounds with a linear $C_2RhC_4RhC_2$ and $C_3RhC_4RhC_3$ chain.[8,9] Since the chemistry of these compounds was almost unexplored, we started two years ago to investigate the reactivity of RhC_4Rh derivatives toward Lewis acids and Lewis bases. In this paper we describe the preparation of a series of symmetrical and unsymmetrical rhodium(I) complexes containing a C_4 bridge and report in particular about a CO- or CNR-initiated intramolecular C−C coupling reaction leading to products with an eight-membered C═C−C≡C−C≡C−C═C moiety as a bridge. Some preliminary results of these studies have already been communicated.[10]

Results and Discussion

Synthesis of Dinuclear Rhodium Complexes with a 1,3-Butadiyndiyl Bridge. The preparative route that we used to obtain the fluoro(vinylidene)rhodium(I) complexes *trans*-[RhF(═C═CHR)(P*i*Pr$_3$)$_2$] (**3**, R = Ph; **4**, R = *t*Bu)[11] could also be applied for the synthesis of the parent compound **2** with R = H (see Scheme 1). The reaction of the starting material **1** with acetylene probably results in the formation of a triflato(vinylidene)metal intermediate, which is converted in situ into complex **2** by treatment with potassium fluoride. The spectroscopic data of **2** (a red-purple crystalline solid), in particular the couplings observed in the ^{31}P and ^{19}F NMR spectra, clearly indicate a trans disposition of the two phosphine ligands.

Scheme 3[a]



	CX
8, **10**, **12**	CN-$C_6H_3Me_2$-2,6
9, **11**, **13**	CO

[a] L = P*i*Pr$_3$.

Treatment of the fluoro(vinylidene) complexes **2**−**4** with $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ affords in each case a green solution together with a white, nearly insoluble solid, which was separated by filtration and identified by comparison of the IR and NMR spectra as Ph_3SnF.[12] From the green solutions, after evaporation of the solvent, the dinuclear complexes **5**−**7** were isolated in 78−88% yield (Scheme 2). The phenylvinylidene derivative **6** was already known and had been prepared in our laboratory from *trans*-[Rh(OH)(═C═CHPh)(P*i*Pr$_3$)$_2$] and $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$.[7] The new route is more favorable insofar as workup of the reaction mixture obtained from the hydroxorhodium compound and $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ is more tedious since it needed low-temperature column chromatography in order to separate the soluble byproduct Ph_3SnOH from complex **6**. The most typical spectroscopic features of the new dinuclear complexes **5** and **7** are the ^{13}C NMR resonances for the α- and β-carbon atoms of the Rh═C═C unit, which are observed as doublets of triplets at δ 307.5 and 92.7 (for **5**) or 307.0 and 121.5 (for **7**), respectively. The signals for the carbon atoms of the C_4 chain appear in both spectra in the range δ 122.2−127.4. It should be noted that the starting material **3** does not react with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ even after stirring the reaction mixture for 24 h at room temperature.

The fluoro(isocyanide) and fluoro(carbonyl) complexes **8** and **9** behave similarly to the fluoro(vinylidene) derivatives **2**−**4** and give upon treatment with $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ in benzene at 60 °C the dinuclear compounds **12** and **13** in moderate to good yields (Scheme 3). Since the rate of the reaction of **8** and **9** with $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ is lower than that of the related complexes **2**−**4** with the distannylated butadiyne, it is

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(7) Gevert, O.; Wolf, J.; Werner, H. *Organometallics* **1996**, *15*, 2806−2809.

(8) Gil-Rubio, J.; Laubender, M.; Werner, H. *Organometallics* **1998**, *17*, 1202−1207.

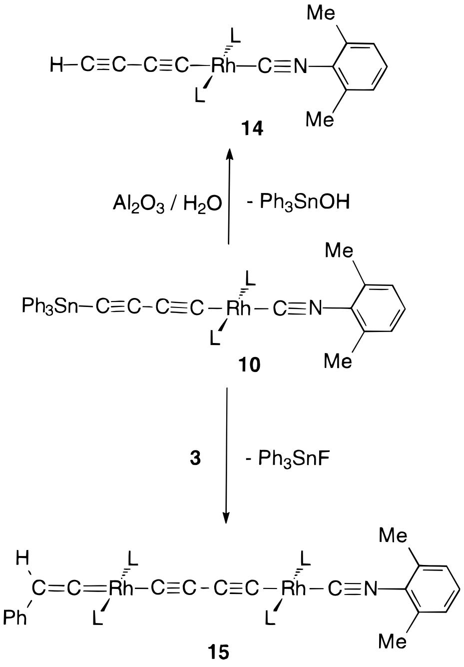
(9) Gil-Rubio, J.; Weberndörfer, B.; Werner, H. *Angew. Chem.* **2000**, *112*, 814−818; *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 786−789.

(10) Gil-Rubio, J.; Callejas-Gaspar, B.; Laubender, M.; Werner, H. 37th IUPAC Congress/27th GDCh General Meeting, Berlin, 1999.

(11) Gil-Rubio, J.; Weberndörfer, B.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1999**, 1437−1444.

(12) Kriegsmann, H.; Geissler, H. *Z. Anorg. Allg. Chem.* **1963**, *323*, 170−189.

Scheme 4[a]



[a] L = P*i*Pr$_3$.

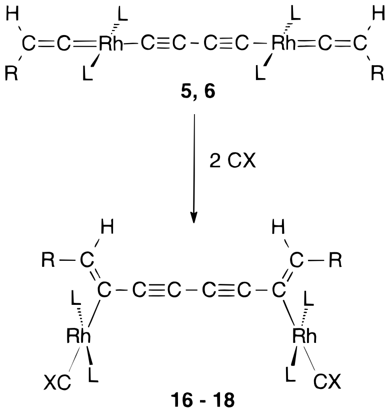
possible to observe the initial formation of the mono-rhodium species **10** and **11**. They both react slowly with a second equivalent of the corresponding fluoro complex **8** or **9** to give the dirhodium complexes **12** and **13**, respectively.

The observed generation of the intermediates **10** and **11** prompted us to study the reactions of **8** and **9** with equimolar amounts of $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ under milder conditions. We found that if a 1:1 mixture of the starting materials in benzene was stirred at room temperature for 18 h, the mononuclear compounds **10** and **11** were formed as the major products together with small amounts (ca. 10%) of the dinuclear complexes **12** and **13**. In the case of **10** we succeeded in isolating an analytically pure sample in 43% yield by extraction of the crude product with acetone followed by crystallization. Attempts to isolate **10** from the reaction mixture in better yields by using column chromatography led to the formation of compound **14** via hydrolysis of the Sn−C bond (Scheme 4). We were not able to obtain complex **11** free of traces of **13** by recrystallization or chromatography.

The most notable spectroscopic features of **10** and **14** are the ^{13}C NMR signals of the carbon atoms of the C_4 chain, which were assigned according to the different values of the Rh−C coupling constants. Both the resonances for the α- and β-carbon atoms appear as doublets of triplets with J(RhC) = 42.3 and 12.4 Hz (for **10**) and 42.7 and 10.2 Hz (for **14**), respectively. While for **10** the signal of the γ-carbon atom is a doublet of triplets (with J(RhC) = 1.4 Hz), it is a singlet for **14**. For both compounds, the resonance of the δ-C atom reveals no coupling with rhodium. In the case of **14**, the correct assignment of this signal could be made by means of a ^{1}H−^{13}C COSY experiment.

The carbon−tin bond of the Rh−C_4−$SnPh_3$ chain in **10** could be cleaved not only by Al_2O_3/H_2O but also upon treatment of **10** with the fluororhodium(I) complex **3** in pentane. After separation of the byproduct Ph_3SnF, the dinuclear compound **15** (see Scheme 4) containing a different ligand sphere at both ends of the Rh−C_4−Rh chain was isolated as a green-yellow solid in 93% yield. The ^{31}P NMR spectrum of **15** displays two doublets with chemical shifts and Rh−P coupling constants that are similar to those of both the alkynyl(vinylidene) complexes **5**−**7** and the alkynyl(isocyanide) compounds **10**, **12**, and **14**. Regarding the ^{13}C NMR signals of the atoms of the C_4 chain in **15**, the two doublets with J(RhC) = 10.1 and 12.2 Hz are assigned to the two central carbons and a doublet of triplets with J(RhC) = 36.6 and J(PC) = 20.3 Hz to one of the carbons bonded to rhodium. The second Rh−*C* resonance is probably obscured by the signal of the solvent.

Scheme 5[a]



	R	CX
16	H	CO
17	Ph	CO
18	Ph	CN-$C_6H_3Me_2$-2,6

[a] L = P*i*Pr$_3$.

A comparison of the spectroscopic data of the unsymmetrical compound **15** with those of the symmetrical counterpart **6** was interesting insofar as it could give a hint how strong the mutual electronic interaction between both metal centers through the C_4 chain is. Since the dinuclear bis(vinylidene) complexes **5**−**7** are green and the bis(isocyanide) complex **12** is yellow, it is not surprising that compound **15** is green-yellow. However, the absorption maxima of **15** arising from the vinylidene−metal chromophore (λ_{max} = 638 and 439 nm, in hexane) are red-shifted compared to the corresponding maxima of **6** (λ_{max} = 621 and 429 nm, in hexane). Moreover, in the ^{13}C NMR spectrum of **15** the signal of the α-carbon atom of the Rh=C=C fragment appears at δ 294.4, while that of **6** is observed at δ 310.0. These differences are probably due to the better donor ability of the isocyanide compared with the vinylidene ligand, indicating that there is a push−pull interaction between the $Rh(CNR)L_2$ and the $Rh(=C=CHPh)L_2$ units.[13]

CO- and CNR-Initiated C−C Coupling Reactions. The recent observation that the mononuclear alkynyl complexes *trans*-[Rh(C≡CR)(=C=CR′R″)(P*i*Pr$_3$)$_2$] react with CO to give the butenynyl compounds *trans*-[Rh{C(C≡CR)=CR′R″}(CO)(P*i*Pr$_3$)$_2$] by migratory inser-

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[13] Mayr, A.; Yu, M. P. Y.; Yam, V. W.-W. *J. Am. Chem. Soc.* **1999**, *121*, 1760−1761.

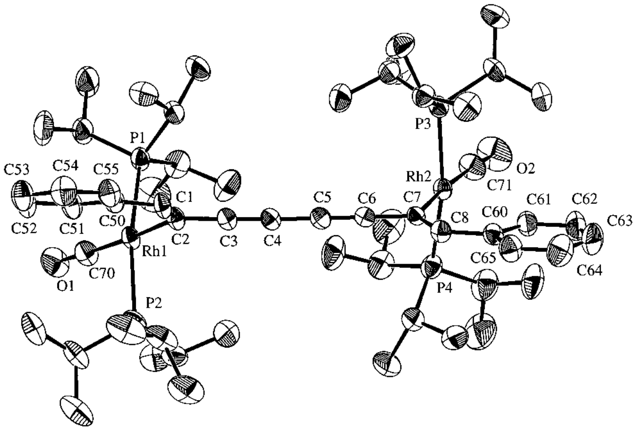

Figure 1. Molecular structure (ORTEP plot) of compound **17**.

Table 1. Selected Bond Distances and Angles with Esd's for Compound 17

Bond Distances (Å)			
Rh1−C2	2.103(6)	C2−C3	1.420(7)
Rh1−C70	1.829(6)	C3−C4	1.214(7)
Rh2−C7	2.103(5)	C4−C5	1.370(7)
Rh2−C71	1.845(6)	C5−C6	1.218(7)
Rh1−P1	2.343(1)	C6−C7	1.409(7)
Rh1−P2	2.340(2)	C7−C8	1.346(7)
Rh2−P3	2.334(2)	C8−C60	1.458(7)
Rh2−P4	2.334(2)	C70−O1	1.162(7)
C1−C50	1.453(8)	C71−O2	1.143(7)
C1−C2	1.345(8)		

Bond Angles (deg)			
C70−Rh1−C2	173.7(3)	C2−C1−C50	130.0(6)
C70−Rh1−P2	89.7(2)	C1−C2−C3	113.9(5)
C2−Rh1−P2	91.0(1)	C1−C2−Rh1	128.6(4)
C70−Rh1−P1	89.3(2)	C3−C2−Rh1	117.5(5)
C2−Rh1−P1	91.4(1)	C4−C3−C2	178.1(6)
P2−Rh1−P1	167.02(6)	C6−C5−C4	176.7(6)
C71−Rh2−C7	174.2(2)	C5−C6−C7	176.0(6)
C71−Rh2−P3	89.4(2)	C8−C7−C6	117.9(5)
C7−Rh2−P3	91.5(2)	C8−C7−Rh2	129.0(4)
C71−Rh2−P4	89.5(2)	C6−C7−Rh2	113.1(4)
C7−Rh2−P4	90.8(2)	C7−C8−C60	129.9(5)
P3−Rh2−P4	167.94(5)		

tion of the vinylidene ligand into the Rh−C σ-bond,[14] prompted us to study also the analogous reactions of the dinuclear complexes *trans,trans*-[{Rh(═C═CHR)-$(PiPr_3)_2\}_2(\mu$-C≡C−C≡C)] with carbon monoxide. The hope was that a 2-fold migratory insertion would occur. Passing a slow stream of CO through a solution (or suspension) of **5** or **6** in pentane or hexane at low temperature led indeed to a smooth conversion of the starting materials to the dicarbonyldirhodium complexes **16** and **17**, which were isolated as yellow solids in, respectively, 74% and 82% yields. The structural proposal for **16** and **17** (Scheme 5) is supported by the analytical and spectroscopic data as well as by an X-ray diffraction analysis of **17**. The molecular diagram (see Figure 1) confirms the formation of an unsaturated C_8 chain generated by C−C coupling of the C_4 bridge and the two vinylidene ligands. Although the central C_6 unit is nearly linear (see Table 1), the C_8 chain is not planar, the dihedral angle between the planes defined by the carbon atoms [C60−65, C6−8] and [C50−55, C1−3] being 27.0(2)°. The distances Rh1−C2 and Rh2−C7 (2.103(6) and 2.103(5) Å) and the linearity of the C≡C−C≡C chain suggest that there is no significant interaction between the π-electrons of the C≡C bonds and the metal centers. Other noteworthy features are the planarity of both C═CHPh fragments and the cis disposition of the phenyl group and the metal−ligand unit at the C═C bonds. We assume that this configuration is also preserved in solution since an NOE experiment revealed a small but significant enhancement of the signal of the phenyl proton in ortho position upon irradiation of the resonances of the methyl protons of the triisopropylphosphine ligands.

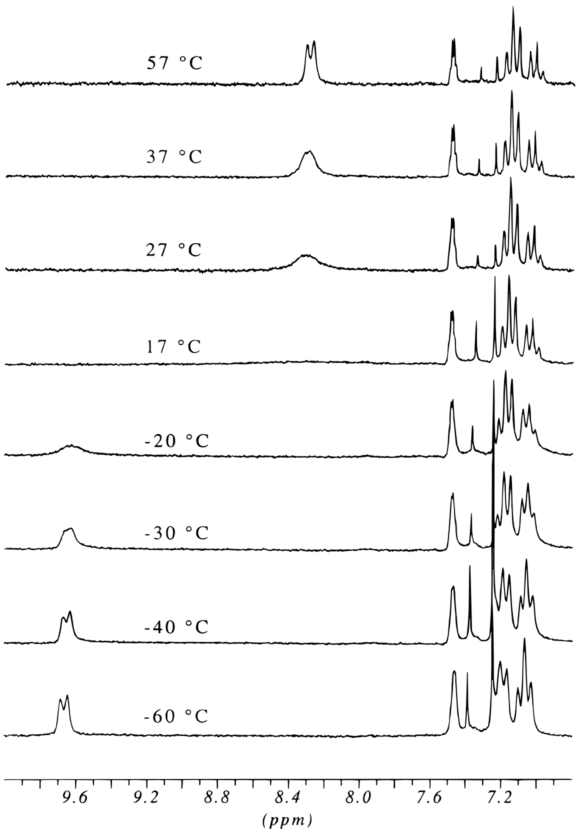

Figure 2. Variable-temperature ^1H NMR spectra (low-field region) of compound **17** in $CDCl_3$. The singlets at δ 7.34 and 7.24 correspond to C_6H_6 and $CHCl_3$, respectively.

On the basis of the result that the distances between one of the ortho hydrogen atoms of the phenyl groups and the metal centers are quite short (Rh1−H51 2.50(1) and Rh2−H61 2.48(1) Å), we also took an agostic interaction into consideration. To prove this hypothesis, the ^1H and ^{13}C NMR spectra of compound **17** were measured at various temperatures. We found that the ^1H NMR spectrum displayed at −60 °C two different signals at δ 9.7 and 7.1 for the phenyl protons in ortho position (see Figure 2), indicating that the rotation of the phenyl groups around the C−C bond is slow on the NMR time scale. These signals coalesce at about 17 °C to give a single resonance at δ 8.3. No coupling was observed between the ortho hydrogens and the ^{103}Rh or ^{31}P nuclei. In the ^{13}C NMR spectrum of **17** also two signals appear for the carbon atoms in ortho position of the phenyl rings at −60 °C but only one resonance at room temperature. Since work by Brookhart and Green has shown that the size of $^1J(CH)$ is indicative of the

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[14] (a) Schäfer, M.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem.* **1993**, *105*, 1377−1379; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1315−1318. (b) Werner, H.; Wiedemann, R.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1997**, *3*, 127−137.

presence of an agostic bond,[15] we determined this coupling constant from the low-temperature ^{13}C NMR spectrum. We found for both signals of the respective ortho carbon atoms $^{1}J(^{13}C^{1}H)$ values of 155.5 and 159.1 Hz, which are nearly the same. Therefore, we conclude that the Rh···H−C interaction is not significant and the barrier to rotation of the phenyl groups not due to an agostic interaction but probably to steric repulsion between the phenyl protons in ortho position and the isopropyl units.

Finally, we note that 2,6-dimethylphenylisocyanide behaves analogously to CO and reacts with **6** to give the dinuclear complex **18**. The spectroscopic data of **18** are quite similar to those of **17** and also indicate a slow rotation of the phenyl group around the C−C bond on the NMR time scale. This finding (illustrated by the temperature dependence of the signals of the ortho C−H protons) together with a ^{1}H NOE experiment suggests that not only in **17** but also in **18** the two C═C bonds possess a *Z* configuration.

Conclusions

The work presented in this paper has shown that by using the bisstannylated butadiyne $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ as the substrate, symmetrical as well as unsymmetrical dinuclear rhodium(I) complexes containing a "naked" C_4 bridge can be prepared. Although a wealth of compounds of the general composition $[ML_n]{-}C_4{-}[ML_n]$ is known,[2−4,7−9] only a few examples with a *different* coordination sphere at the metal centers on both sites of the C_4 chain have been described.[16] The reactivity of the bis(vinylidene)dirhodium complexes **5** and **6** obtained by the SnC_4Sn methodology is highlighted by the observation that in the presence of CO and the isocyanide $CNC_6H_3Me_2$-2,6 these compounds undergo a 2-fold migratory insertion reaction to yield the unusual dinuclear complexes **16**−**18**, which contain a highly unsaturated eight-membered C_8 chain as a bridge. We note that quite recently a related reaction of the dinuclear ruthenium compound $[\{RuCl(CO)(NH_3)(PPh_3)_2\}_2(\mu\text{-}CH{=}CH{-}CH{=}CH)]$ has been observed.[17] This species reacts with CN*t*Bu to afford the dicationic complex $[\{Ru(CNtBu)_3(PPh_3)_2\}\{\mu\text{-}C(O){-}CH{=}CH{-}CH{=}CH{-}C(O)\}]^{2+}$ via the intramolecular insertion of both CO ligands into the C_4H_4 bridge.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by known procedures and distilled before use. The starting materials **1**,[18] **3**, **4**, **8**, **9**,[11] and $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$[19] were prepared as described in the literature. NMR spectra were recorded at room temperature (if not otherwise indicated) on Bruker AC 200 and Bruker AMX 400 instruments [abbreviation: v = virtual coupling; $N = {}^{3}J(PH) + {}^{5}J(PH)$ or ${}^{1}J(PC) + {}^{3}J(PC)$]. IR spectra were measured on a Bruker IFS 25 spectrometer. Decomposition temperatures were determined by DTA.

Preparation of *trans*-[RhF(═C═CH₂)(P*i*Pr₃)₂] (2). A Schlenk flask containing a solution of compound **1** (217 mg, 0.38 mmol) in acetone (15 mL) was connected to a gastight syringe, which was equipped with a glass stopcock and filled with acetylene (0.4 mmol). The flask was partially evacuated by an oil pump and cooled to liquid nitrogen temperature. The stopcock was then opened, and the acetylene was introduced into the flask. The mixture was slowly warmed to room temperature with continuous stirring and stirred at 20 °C for 2.5 h. During this time the color changed initially from red-orange to yellow-orange and then slowly to red. After KF (232 mg, 4.0 mmol) was added to the solution, the resulting suspension was stirred for 30 min and then the solvent removed in vacuo. The residue was extracted twice with 20 mL portions of pentane. The combined extracts were filtered, concentrated to ca. 3 mL, and stored for 2 days at −25 °C. Red-purple crystals precipitated, which were washed three times with 2 mL portions of pentane (−78 °C) and dried: yield 147 mg (83%); mp 71 °C dec; IR (Nujol) ν(C═C) 1638, 1628, ν(Rh−F) 458 cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz) δ 2.60 (m, 6H, PC*H*CH₃), 1.33 (dvt, N = 13.5 Hz, J(HH) = 6.6 Hz, 36H, PCHC*H*₃), 0.06 (m, 2H, Rh═C═CH₂); $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100.6 MHz) δ 297.3 (m, Rh═C), 88.5 (m, CH₂), 22.7 (vt, N = 18.5 Hz, P*C*HCH₃), 20.1 (s, PCH*C*H₃); ^{19}F NMR (C_6D_6, 188.3 MHz) δ −219.3 (dt, J(RhF) = 14.5 Hz, J(PF) = 18.2 Hz); $^{31}P\{^{1}H\}$ NMR (C_6D_6, 81.0 MHz) δ 45.4 (dd, J(RhP) = 145.0 Hz, J(PF) = 18.2 Hz). Anal. Calcd for $C_{20}H_{44}FP_2Rh$: C, 51.28; H, 9.47. Found: C, 51.00; H, 9.33.

Preparation of *trans,trans*-[{Rh(═C═CH₂)(P*i*Pr₃)₂}₂(*μ*-C≡C−C≡C)] (5). A solution of **2** (219 mg, 0.47 mmol) in hexane (20 mL) was treated with $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ (175 mg, 0.23 mmol) at −78 °C. Under continuous stirring, the mixture was slowly warmed to room temperature and stirred at 20 °C for 75 min. A change of color from red-violet to green occurred. The solution was filtered, the filtrate was evaporated to dryness in vacuo, and the residue was extracted 6 times with 10 mL portions of hexane. The combined extracts were concentrated to ca. 3 mL in vacuo, and the concentrated solution was stored for 24 h at −25 °C. A green solid precipitated, which was washed twice with 2 mL portions of pentane (−40 °C) and dried: yield 187 mg (84%); mp 59 °C dec; IR (Nujol) ν(C═C) 1617 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 2.80 (m, 12H, PC*H*CH₃), 1.39 (dvt, N = 13.2 Hz, J(HH) = 6.2 Hz, 72H, PCHC*H*₃), −0.01 (t, J(PH) = 3.4 Hz, 4H, Rh═C═CH₂); $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100.6 MHz) δ 307.5 (dt, J(RhC) = 47.9 Hz, J(PC) = 15.8 Hz, Rh═C), 125.0 (d, J(RhC) = 8.7 Hz, Rh−C≡*C*), 122.2 (dt, J(RhC) = 38.1 Hz, J(PC) = 19.3 Hz, Rh-*C*≡C), 92.7 (dt, J(RhC) = 14.2 Hz, J(PC) = 5.4 Hz, CH₂), 25.2 (vt, N = 20.7 Hz, P*C*HCH₃), 20.6 (s, PCH*C*H₃); $^{31}P\{^{1}H\}$ NMR (C_6D_6, 162.0 MHz) δ 47.2 (d, J(RhP) = 137.3 Hz). Anal. Calcd for $C_{44}H_{88}P_4Rh_2$: C, 55.81; H, 9.37. Found: C, 55.52; H, 9.06.

Preparation of *trans,trans*-[{Rh(═C═CHPh)(P*i*Pr₃)₂}₂-(*μ*-C≡C−C≡C)] (6). A solution of **3** (247 mg, 0.45 mmol) in pentane (20 mL) was treated with $Ph_3Sn{\equiv}CC{\equiv}CSnPh_3$ (170 mg, 0.23 mmol) at −78 °C. Under continuous stirring, the mixture was slowly warmed to room temperature and stirred at 20 °C for 50 min. The green suspension was filtered, the filtrate was evaporated to dryness in vacuo, and the residue extracted 3 times with 20 mL portions of pentane. The combined extracts were concentrated to ca. 4 mL in vacuo, and the concentrated solution was stored for 2 days at −65 °C. A green crystalline solid precipitated and was washed two times with 2 mL portions of pentane (−78 °C) and dried: yield 195 mg (78%). The ^{1}H, ^{31}P NMR and IR data of the compound were identical to those reported for **6** in the literature.[7]

Preparation of *trans,trans*-[{Rh(═C═CH*t*Bu)(P*i*Pr₃)₂}₂-(*μ*-C≡C−C≡C)] (7). A solution of **4** (168 mg, 0.32 mmol) in

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(15) Brookhart, M.; Green, M. L. H.; Wong., L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1−124.

(16) Coat, F.; Guillevic, M.-A.; Toupet, L.; Paul, F.; Lapinte, C. *Organometallics* **1997**, *16*, 5988−5998.

(17) Xia, H. P.; Yeung, R. C. Y.; Jia, G. *Organometallics* **1998**, *17*, 4762−4768.

(18) Werner, H.; Bosch, M.; Schneider, M. E.; Hahn, C.; Kukla, F.; Manger, M.; Windmüller, B.; Weberndörfer B.; Laubender, M. *J. Chem. Soc., Dalton Trans.* **1998**, 3549−3558.

(19) Bréfort, J. L.; Corriu, J. P.; Gerbier, Ph.; Guérin, C.; Henner, B. J. L.; Jean, A.; Kuhlmann, Th.; Garnier, F.; Yassar, A. *Organometallics* **1992**, *11*, 2500−2506.

pentane (15 mL) was treated with $Ph_3SnC\equiv CC\equiv CSnPh_3$ (119 mg, 0.16 mmol) at −78 °C. Under continuous stirring, the mixture was slowly warmed to room temperature and stirred at 20 °C for 2 h. The green suspension was filtered and the filtrate worked up as described for **6**: green crystalline solid; yield 149 mg (88%); mp 52 °C dec; IR (Nujol) ν(C=C) 1664, 1636, 1630 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 2.85 (m, 12H, PC*H*CH$_3$), 1.42 (dvt, *N* = 13.2 Hz, *J*(HH) = 6.2 Hz, 72H, PCHC*H*$_3$), 1.06 (s, 18H, *t*Bu), 0.05 (t, *J*(PH) = 3.7 Hz, 2H, Rh=C=CH); ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz) δ 307.0 (dt, *J*(RhC) = 48.8 Hz, *J*(PC) = 15.8 Hz, Rh=C), 127.4 (d, *J*(RhC) = 8.1 Hz, Rh−C≡*C*), 122.7 (dt, *J*(RhC) = 37.6 Hz, *J*(PC) = 19.3 Hz, Rh-*C*≡C), 121.5 (dt, *J*(RhC) = 12.2 Hz, *J*(PC) = 5.6 Hz, Rh=C=*C*H), 32.4 (s, *C*CH$_3$), 25.4 (vt, *N* = 20.3 Hz, P*C*HCH$_3$), 25.2 (s, C*C*H$_3$), 20.7 (s, PCH*C*H$_3$); ^{31}P{^{1}H} NMR (C_6D_6, 162.0 MHz) δ 46.1 (d, *J*(RhP) = 137.3 Hz). Anal. Calcd for $C_{52}H_{104}P_4Rh_2$: C, 58.97; H, 9.90. Found: C, 58.68; H, 9.59.

Preparation of *trans*-[Rh(CNC$_6$H$_3$Me$_2$-2,6)(P*i*Pr$_3$)$_2$(C≡C−C≡CSnPh$_3$)] (10). A solution of **8** (472 mg, 0.82 mmol) in benzene (30 mL) was added dropwise under continuous stirring to a solution of $Ph_3SnC\equiv CC\equiv CSnPh_3$ (616 mg, 0.82 mmol) in benzene (10 mL) at room temperature. After the addition was completed (ca. 1 h), the mixture was stirred at 20 °C for 18 h. A change of color from yellow to yellow-brown occurred. The ^{31}P NMR spectrum of the resulting solution showed only two doublets corresponding to compounds **10** and **12** in the ratio of ca. 10:1. The suspension was filtered, the filtrate was evaporated to dryness in vacuo, and the residue was extracted 3 times with 10 mL portions of acetone. The remaining yellow solid was identified by NMR spectroscopy as **12** contaminated with small amounts of **10**. The combined acetone extracts were filtered, and the filtrate was concentrated in vacuo until a yellow crystalline solid started to precipitate. After the solution was stored at −25 °C for 6 days, a yellow-brownish crystalline solid was obtained, which was washed three times with 5 mL portions of pentane (−20 °C) and dried: yield 334 mg (43%); mp 106 °C dec; IR (Nujol) ν(C≡C and C≡N) 2136, 2054, 2012, 1988 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 7.72, 7.65, 7.57 (all m, 6H, *ortho*-H of C_6H_5 plus ^{117}Sn and ^{119}Sn satellites), 7.10 (m, 9H, *meta*- and *para*-H of C_6H_5), 6.73 (m, 3H, C$_6$*H*$_3$Me$_2$), 2.49 (m, 6H, PC*H*CH$_3$), 2.28 (s, 6H, C$_6$H$_3$*Me*$_2$), 1.35 (dvt, *N* = 13.6 Hz, *J*(HH) = 6.8 Hz, 36H, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz) δ 169.5 (dt, *J*(RhC) = 55.3 Hz, *J*(PC) = 15.3 Hz, Rh−CN), 138.5 (s plus two satellite d, *J*(^{117}SnC) and *J*(^{119}SnC) = 616.7 and 588.5 Hz, *ipso*-C of C_6H_5), 137.3 (s and one satellite d, *J*(^{117}SnC) = *J*(^{119}SnC) = 42.3 Hz, *meta*-C of C_6H_5), 133.5, 130.2 (both s, *ortho*- and *ipso*-C of $C_6H_3Me_2$), 129.2 (s and one satellite d, *J*(^{117}SnC) = *J*(^{119}SnC) = 12.1 Hz, *para*-C of C_6H_5), 128.8 (s and two satellite d, *J*(^{117}SnC) and *J*(^{119}SnC) = 59.4 and 56.3 Hz, *ortho*-C of C_6H_5), 128.2, 126.5 (s, *meta*- and *para*-C of $C_6H_3Me_2$), 126.1 (dt, *J*(RhC) = 42.3 Hz, *J*(PC) = 19.3 Hz, Rh-*C*≡C), 102.4 (dt, *J*(RhC) = 12.4 Hz, *J*(PC) = 2.9 Hz, Rh−C≡*C*), 101.1 (dt, *J*(RhC) = 1.4 Hz, *J*(PC) = 2.9 Hz, Rh−C≡C-*C*≡C), 71.4 (t, *J*(PC) = 2.2 Hz, Rh−C≡C−C≡*C*, the ^{117}Sn and ^{119}Sn satellites for the two last signals were not observed), 26.3 (vt, *N* = 19.9 Hz, P*C*HCH$_3$), 20.7 (s, PCH*C*H$_3$), 19.9 (s, C$_6$H$_3$*Me*$_2$); ^{31}P{^{1}H} NMR (C_6D_6, 162.0 MHz) δ 52.0 (d, *J*(RhP) = 132.0 Hz). Anal. Calcd for $C_{49}H_{66}NP_2RhSn$: C, 61.78; H, 6.98; N, 1.48. Found: C, 61.48; H, 6.90; N, 1.44.

Preparation of *trans,trans*-[{Rh(CNC$_6$H$_3$Me$_2$-2,6)(P*i*Pr$_3$)$_2$}$_2$(*μ*-C≡C−C≡C)] (12). A solution of **8** (247 mg, 0.43 mmol) in benzene (7 mL) was treated with $Ph_3SnC\equiv CC\equiv CSnPh_3$ (161 mg, 0.22 mmol) at room temperature, and the reaction mixture was then stirred at 60 °C for 14 h. After the brown suspension was cooled to room temperature, it was filtered and the filtrate was evaporated to dryness in vacuo. Addition of acetone (2 mL) led to the precipitation of a yellow solid, which was separated from the solution, washed 6 times with 2 mL portions of acetone and twice with 2 mL portions of pentane, and dried: yield 95 mg (38%); mp 95 °C dec; IR (Nujol) ν(C≡N and C≡C) 2031, 2005, 1965 cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz) δ 6.99 (s, 6H, C$_6$*H*$_3$Me$_2$), 2.50 (m, 12H, PC*H*CH$_3$), 2.33 (s, 12H, C$_6$H$_3$*Me*$_2$), 1.33 (dvt, *N* = 13.3 Hz, *J*(HH) = 6.4 Hz, 72H, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz) δ 133.8, 128.6, 127.8, 125.5 (all s, C_6H_3), 26.2 (vt, *N* = 19.1 Hz, P*C*HCH$_3$), 20.6 (s, PCH*C*H$_3$), 19.0 (s, C$_6$H$_3$*Me*$_2$), owing to the low solubility of **12**, the signals of the Rh−CN and C≡C carbon atoms could not be observed; ^{31}P{^{1}H} NMR (C_6D_6, 162.0 MHz) δ 51.5 (d, *J*(RhP) = 135.7 Hz). Anal. Calcd for $C_{58}H_{102}N_2P_4Rh_2$: C, 60.20; H, 8.88; N, 2.43. Found: C, 59.71; H, 8.41; N, 2.51.

Preparation of *trans,trans*-[{Rh(CO)(P*i*Pr$_3$)$_2$}$_2$(*μ*-C≡C−C≡C)] (13). A solution of **9** (65 mg, 0.14 mmol) in benzene (5 mL) was treated with $Ph_3SnC\equiv CC\equiv CSnPh_3$ (52 mg, 0.07 mmol) at room temperature. After the mixture was stirred for 15 h, its composition was examined by ^{31}P NMR spectroscopy. Three doublets were observed in the ratio of ca. 1:1:1 corresponding to compounds **9**, **13**, and, probably, **11**. The reaction mixture was then stirred at 55 °C for 8.5 h, the solution was filtered, and the filtrate was evaporated to dryness in vacuo. The resulting yellow solid was washed twice with 2 mL portions of acetone and dried: yield 55 mg (83%). The ^{1}H, ^{31}P NMR and IR data of the compound were identical to those reported for **13** in the literature.[7]

When the reaction was carried out at room temperature using equimolar amounts of **9** and $Ph_3SnC\equiv CC\equiv CSnPh_3$, a mixture of **11** and **13** in the ratio of 8:1 together with unreacted alkyne was obtained. Attempts to isolate a pure sample of compound **11** by recrystallization failed. Spectroscopic data for **11**: ^{1}H NMR (C_6D_6, 200 MHz) δ 7.8−7.4 (m, 6H, *ortho*-H of C_6H_5 plus ^{117}Sn and ^{119}Sn satellites), 7.10 (m, 9H, *meta*- and *para*-H of C_6H_5), 2.43 (m, 6H, PC*H*CH$_3$), 1.26 (dvt, *N* = 13.9 Hz, *J*(HH) = 7.1 Hz, 36H, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (C_6D_6, 81.0 MHz) δ 54.1 (d, *J*(RhP) = 125.6 Hz).

Preparation of *trans*-[Rh(CNC$_6$H$_3$Me$_2$-2,6)(P*i*Pr$_3$)$_2$(C≡C−C≡CH)] (14). A solution of **10** was prepared from **8** (80 mg, 0.14 mmol) and $Ph_3SnC\equiv CC\equiv CSnPh_3$ (104 mg, 0.14 mmol) in benzene (5 mL) at room temperature. After the reaction was finished, the solution was concentrated to ca. 2 mL in vacuo and pentane (6 mL) was added. The resulting suspension was chromatographed on Al_2O_3 (neutral, activity grade V, column diameter 2 cm, column length 10 cm). With pentane/benzene (10:1) a yellow fraction was eluted, which was evaporated in vacuo to give a yellow oil. Recrystallization from pentane at −60 °C afforded a yellow microcrystalline solid: yield 60 mg (72%); mp 130 °C dec; IR (Nujol) ν(C−H) 3287, ν(C≡C and C≡N) 2118, 2054, 2005, 1971 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 6.72 (m, 3H, C$_6$*H*$_3$Me$_2$), 2.47 (m, 6H, PC*H*CH$_3$), 2.27 (s, 6H, C$_6$H$_3$*Me*$_2$), 1.76 (t, *J*(PH) = 1.2 Hz, 1H, C$_4$H), 1.33 (dvt, *N* = 13.6 Hz, *J*(HH) = 7.2 Hz, 36H, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz) δ 169.7 (dt, *J*(RhC) = 55.3 Hz, *J*(PC) = 15.1 Hz, Rh−CN), 133.5, 130.3, 128.1, 126.4 (all s, C_6H_3), 122.8 (dt, *J*(RhC) = 42.7 Hz, *J*(PC) = 21.4 Hz, Rh−*C*≡C), 100.9 (dt, *J*(RhC) = 10.2 Hz, *J*(PC) = 3.0 Hz, Rh−C≡*C*), 73.4 (s, Rh−C≡C-*C*≡C), 59.6 (s, Rh−C≡C−C≡*C*), 26.2 (vt, *N* = 20.3 Hz, P*C*HCH$_3$), 20.6 (s, PCH*C*H$_3$), 18.9 (s, C$_6$H$_3$*Me*$_2$); ^{31}P{^{1}H} NMR (C_6D_6, 162.0 MHz) δ 52.0 (d, *J*(RhP) = 132.0 Hz). Anal. Calcd for $C_{31}H_{52}NP_2Rh$: C, 61.68; H, 8.68; N, 2.33. Found: C, 61.61; H, 8.55; N, 2.27.

Preparation of *trans,trans*-[{Rh(CNC$_6$H$_3$Me$_2$-2,6)(P*i*Pr$_3$)$_2$}(*μ*-C≡C−C≡C){Rh(=C=CHPh)(P*i*Pr$_3$)$_2$}] (15). A solution of **3** (95 mg, 0.18 mmol) in pentane (5 mL) was added to a suspension of **10** (170 mg, 0.18 mmol) in pentane (15 mL) at −78 °C. Under continuous stirring, the mixture was slowly warmed to room temperature and stirred at 20 °C for 2 h. The resulting green suspension was filtered, the solvent was removed from the filtrate, and the residue was extracted 3 times with 8 mL portions of pentane. The combined extracts were evaporated to dryness in vacuo, and the remaining green-yellow solid was washed 3 times with 4 mL portions of pentane (0 °C) and dried. The pentane washings were concentrated to ca. 5 mL in vacuo, and after the concentrated solution was stored at −60 °C for 11 days, a second fraction of the green-yellow solid was obtained: overall yield 187 mg (93%); mp 82 °C dec; IR (Nujol) ν(C≡C and C≡N) 2030, 2004, ν(C═C) 1631, 1611 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 7.27 (d, *J*(HH) = 7.3 Hz, 2H, *ortho*-H of C_6H_5), 7.10 (t, *J*(HH) = 7.8 Hz, 2H, *meta*-H of C_6H_5), 6.86 (t, *J*(HH) = 7.4 Hz, 1H, *para*-H of C_6H_5), 6.74 (s, 3H, C$_6$*H*$_3$Me$_2$), 2.75, 2.52 (both m, 6H, PC*H*CH$_3$), 2.33 (s, 6H, C$_6$H$_3$*Me*$_2$), 1.54 (t, *J*(PH) = 3.5 Hz, 1H, Rh═C═CH), 1.42 (dvt, *N* = 13.5 Hz, *J*(HH) = 7.3 Hz, 36H, PCHC*H*$_3$), 1.41 (dvt, *N* = 13.5 Hz, *J*(HH) = 6.7 Hz, 36H, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz) δ 294.4 (dt, *J*(RhC) = 48.8 Hz, *J*(PC) = 16.3 Hz, Rh═*C*═C), 171.0 (dt, *J*(RhC) = 57.0 Hz, *J*(PC) = 14.7 Hz, Rh−CN), 131.4 (d, *J*(RhC) = 10.1 Hz, Rh−C≡*C*), 133.4, 130.9, 128.5, 128.1, 126.7, 126.2, 125.6, 124.4 (all s, C_6H_3 and C_6H_5), 116.1 (dt, *J*(RhC) = 12.2 Hz, *J*(PC) = 6.1 Hz, Rh═C═*C*), 110.0 (dt, *J*(RhC) = 36.6 Hz, *J*(PC) = 20.3 Hz, Rh−*C*≡C), 107.5 (d, *J*(RhC) = 12.2 Hz, Rh−C≡*C*), 26.3, 25.7 (both vt, *N* = 20.3 Hz, P*C*HCH$_3$), 20.8, 20.7 (both s, PCH*C*H$_3$), 19.0 (s, C$_6$H$_3$*Me*$_2$), one of the Rh−*C*≡C signals obscured by the signal of the solvent; ^{31}P{^{1}H} NMR (C_6D_6, 162.0 MHz) δ 52.6 (d, *J*(RhP) = 135.7 Hz, [Rh(CNC$_6$H$_3$Me$_2$-2,6)(P*i*Pr$_3$)$_2$]), 47.6 (d, *J*(RhP) = 137.4 Hz, [Rh(═C═CHPh)(P*i*Pr$_3$)$_2$]). Anal. Calcd for $C_{57}H_{99}NP_4Rh_2$: C, 60.68; H, 8.85; N, 1.25. Found: C, 60.67; H, 9.06; N, 1.23.

Preparation of *trans,trans*-[{Rh(CO)(P*i*Pr$_3$)$_2$}$_2${*μ*-*C*(═CH$_2$)−C≡C−C≡C−*C*(═CH$_2$)}] (16). A slow stream of CO was passed through a suspension of **5** (109 mg, 0.23 mmol) in pentane (12 mL) for 1 min at −78 °C. The mixture was stirred at −78 °C for 15 min, then slowly warmed to room temperature and stirred for 45 min at 20 °C. A very small amount of a brown precipitate was formed, which was separated by filtration. The yellow solution was concentrated to ca. 1 mL in vacuo. A water bath (30−40 °C) was used during the evaporation to avoid a fast precipitation of a fine powder. The concentrated solution was slowly cooled to −25 °C and stored at this temperature for 48 h. Yellow crystals precipitated and were washed 3 times with 1 mL portions of pentane (−60 °C) and dried: yield 86 mg (74%); mp 58 °C dec; IR (Nujol) ν(C≡C) 2134, 2067, ν(CO) 1939, 1927 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 6.72 (m, 2H, CH$_2$); 5.61 (m, 2H, CH$_2$), 2.54 (m, 12H, PC*H*CH$_3$), 1.47 (dvt, *N* = 13.2 Hz, *J*(HH) = 6.2 Hz, 36H, PCHC*H*$_3$), 1.43 (dvt, *N* = 13.5 Hz, *J*(HH) = 6.5 Hz, 36H, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz) δ 196.7 (dt, *J*(RhC) = 56.9 Hz, *J*(PC) = 14.7 Hz, CO), 160.3 (dt, *J*(RhC) = 25.4 Hz, *J*(PC) = 14.4 Hz, Rh−*C*═C), 130.5 (t, *J*(PC) = 4.6 Hz, Rh−C═*C*), 93.0, 84.3 (both s, C≡C), 22.9 (vt, *N* = 19.3 Hz, P*C*HCH$_3$), 20.7, 20.4 (both s, PCH*C*H$_3$); ^{31}P{^{1}H} NMR (C_6D_6, 162.0 MHz) δ 46.3 (d, *J*(RhP) = 140.7 Hz). Anal. Calcd for $C_{46}H_{88}O_2P_4Rh_2$: C, 55.09; H, 8.84. Found: C, 54.96; H, 8.74.

Preparation of *trans,trans*-[{Rh(CO)(P*i*Pr$_3$)$_2$}$_2${*μ*-*C*(═CHPh)−C≡C−C≡C−*C*(═CHPh)}] (17). A slow stream of CO was passed through a solution of **6** (131 mg, 0.12 mmol) in hexane (30 mL) at 0 °C until the color had changed from green to yellow (ca. 30 s). The solution was warmed to room temperature and stirred for 30 min at 20 °C. It was then concentrated to ca. 4 mL in vacuo, and the concentrated solution was stored at 0 °C for 2 h. A yellow solid precipitated, which was washed with hexane (2 mL, 0 °C) and dried: yield 118 mg (82%); mp 88 °C dec; IR (Nujol) ν(C≡C) 2064, ν(CO) 1941 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz, −60 °C) δ 9.67 (d, *J*(HH) = 8.0 Hz, 2H, *ortho*-H of C_6H_5), 7.46 (br s, 2H, Rh−C═CH), 7.20 (t, *J*(HH) = 7.3 Hz, 4H, *meta*-H of C_6H_5), 7.10−7.03 (m, 4H, *para*- and *ortho*-H of C_6H_5), 2.31 (m, 12H, PC*H*CH$_3$), 1.25, 1.03 (both br m, 72H, PCHC*H*$_3$); ^{1}H NMR (CDCl$_3$, 200 MHz, 17 °C) δ 8.7−7.9 (br m, 4H, *ortho*-H of C_6H_5), 7.48 (dt, *J*(RhH) = 1.8 Hz, *J*(PH) = 2.0 Hz, 2H, Rh−C═CH), 7.16 (t, *J*(HH) = 7.7 Hz, 4H, *meta*-H of C_6H_5), 7.03 (t, *J*(HH) = 6.9 Hz, 2H, *para*-H of C_6H_5), 2.36 (m, 12H, PC*H*CH$_3$), 1.30 (dvt, *N* = 13.9 Hz, *J*(HH) = 6.6 Hz, 36H, PCHC*H*$_3$), 1.09 (dvt, *N* = 13.2 Hz, *J*(HH) = 6.2 Hz, 36H, PCHC*H*$_3$); ^{1}H NMR (CDCl$_3$, 200 MHz, 57 °C) δ 8.29 (d, *J*(HH) = 7.3 Hz, 4H, *ortho*-H of C_6H_5), 7.48 (dt, *J*(RhH) = *J*(PH) = 2.2 Hz, 2H, Rh−C═CH), 7.15 (t, *J*(HH) = 7.3 Hz, 4H, *meta*-H of C_6H_5), 7.01 (t, *J*(HH) = 7.1 Hz, 2H, *para*-H of C_6H_5), 2.39 (m, 12H, PC*H*CH$_3$), 1.33 (dvt, *N* = 13.9 Hz, *J*(HH) = 6.9 Hz, 36H, PCHC*H*$_3$), 1.16 (dvt, *N* = 13.2 Hz, *J*(HH) = 6.2 Hz, 36H, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (*d*$_8$-THF, 100.6 MHz) δ 196.2 (dt, *J*(RhC) = 56.3 Hz, *J*(PC) = 16.1 Hz, CO), 160.7 (dt, *J*(RhC) = 27.2 Hz, *J*(PC) = 14.1 Hz, Rh−*C*═C), 147.1 (t, *J*(PC) = 4.0 Hz, Rh−C═*C*), 144.1, 129.2, 128.0, 126.0 (all s, C_6H_5), 95.9, 86.5 (both s, C≡C), 27.0 (vt, *N* = 20.3 Hz, P*C*HCH$_3$), 21.3, 20.2 (both s, PCH*C*H$_3$); ^{31}P{^{1}H} NMR (*d*$_8$-THF, 162.0 MHz) δ 42.9 (d, *J*(RhP) = 138.7 Hz). Anal. Calcd for $C_{58}H_{96}O_2P_4Rh_2$: C, 60.31; H, 8.38. Found: C, 59.98; H, 8.07.

Preparation of *trans,trans*-[{Rh(CNC$_6$H$_3$Me$_2$-2,6)(P*i*Pr$_3$)$_2$}$_2${*μ*^{2}-*C*(═CHPh)−C≡C−C≡C−*C*(═CHPh)}] (18). A solution of **6** (161 mg, 0.15 mmol) in pentane (12 mL) was treated with 2,6-dimethylphenylisocyanide (43 mg, 0.33 mmol) and stirred at room temperature for 40 min. A yellow-orange suspension was formed, from which a microcrystalline solid slowly precipitated. After the suspension was stored for 1 h, the mother liquor was separated, and the yellow-orange solid was washed 3 times with 3 mL portions of pentane and dried: yield 156 mg (78%); mp 79 °C dec; IR (Nujol) ν(C≡C and C≡N) 2025, 1999 cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, − 60 °C) δ 10.62 (d, *J*(HH) = 7.3 Hz, 2H, *ortho*-H of C_6H_5), 7.36 (br s, 2H, Rh−C═CH), 7.27−7.04 (br m, 14H, C_6H_3 plus *ortho*-, *meta*-, and *para*-H of C_6H_5), 2.41 (br s, 12H, C$_6$H$_3$*Me*$_2$), 2.23 (br m, 12H, PC*H*CH$_3$), 1.28, 1.03 (both br m, 72H, PCHC*H*$_3$); ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, 20 °C) δ 7.49 (dt, *J*(PH) = *J*(RhH) = 2.2 Hz, 2H, Rh−C═CH), 7.21 (t, *J*(HH) = 7.9 Hz, 4H, *meta*-H of C_6H_5), 7.05 (m, 8H, C_6H_3 plus *para*-H of C_6H_5), 2.48 (s, 12H, C$_6$H$_3$*Me*$_2$), 2.35 (m, 12H, PC*H*CH$_3$), 1.36 (dvt, *N* = 13.5 Hz, *J*(HH) = 6.6 Hz, 36H, PCHC*H*$_3$), 1.15 (dvt, *N* = 12.8 Hz, *J*(HH) = 6.2 Hz, 36H, PCHC*H*$_3$), signal for *ortho*-H of C_6H_5 extremely broad and thus not exactly located; ^{1}H NMR (C_6D_6, 400 MHz, 60 °C) δ 8.93 (br d, 4H, *ortho*-H of C_6H_5), 7.99 (dt, *J*(RhH) = 1.8 Hz, *J*(PH) = 2.2 Hz, 2H, Rh−C═CH), 7.32 (t, *J*(HH) = 7.9 Hz, 4H, *meta*-H of C_6H_5), 7.11 (t, *J*(HH) = 7.0 Hz, 2H, *para*-H of C_6H_5), 6.81 (m, 6H, C$_6$*H*$_3$Me$_2$), 2.49 (s, 12H, C$_6$H$_3$*Me*$_2$), 2.45 (m, 12H, PC*H*CH$_3$), 1.46 (dvt, *N* = 13.2 Hz, *J*(HH) = 6.2 Hz, 36H, PCHC*H*$_3$), 1.23 (dvt, *N* = 12.8 Hz, *J*(HH) = 5.8 Hz, 36H, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.6 MHz, 25 °C) δ 169.7 (dt, *J*(RhC) = 57.3 Hz, *J*(PC) = 16.1 Hz, Rh−CN), 165.4 (dt, *J*(RhC) = 26.2 Hz, *J*(PC) = 13.6 Hz, Rh-*C*═C), 145.8 (dt, *J*(RhC) = 2.1 Hz, *J*(PC) = 3.8 Hz, Rh−C═*C*), 144.7 (d, *J*(RhC) = 2.0 Hz, *ipso*-C of C_6H_5), 134.2, 130.7, 129.1, 128.3, 127.3, 126.3, 124.7 (all s, C_6H_3 and C_6H_5), 97.8, 85.1 (both s, C≡C), 26.6 (vt, *N* = 18.2 Hz, P*C*HCH$_3$), 21.1, 20.3 (both s, PCH*C*H$_3$), 19.3 (s, C$_6$H$_3$*Me*$_2$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 162.0 MHz, 25 °C) δ 42.6 (d, *J*(RhP) = 145.8 Hz). Anal. Calcd for $C_{74}H_{114}N_2P_4Rh_2$: C, 65.28; H, 8.44; N, 2.07. Found: C, 64.93; H, 8.40; N, 1.97.

X-ray Structural Determination of Compound 17. Single crystals were grown at room temperature from a concentrated solution of **17** in CH$_2$Cl$_2$, which was covered with pentane. Crystal data (from 25 reflections, 10° < θ <15°): triclinic, space group $P\bar{1}$ (No. 2), a = 11.220(1) Å, b = 16.165(2) Å, c = 19.560(2) Å, α = 101.383(7)°, β = 102.456(8)°, γ = 91.781(9)°, V = 3385.9(6) Å^3, Z = 2, d_{calcd} = 1.300 g cm^{-3}, μ(Mo Kα) = 0.771 mm^{-1}, crystal size 0.40 × 0.25 × 0.15 mm. Solution details: Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 16.4), T = 293(2) K, ω/θ scan, maximum 2θ = 48°, 7975 reflections scanned, 7490 independent reflections, 6337 reflections regarded as observed ($I > 2\sigma(I)$), 7490 reflections used for refinement; intensity data corrected for Lorentz and polarization effects, empirical absorption correction (ψ-scan method, minimum transmission 91.91%) applied; structure solved by direct methods (SHELXS-86); atomic coordinates and anisotropic displacement parameters refined by full matrix least squares against F_o^2 (SHELXL-93); R1 = 0.0417, wR2 = 0.1091; reflection/parameter ratio 11.00; residual electron density +0.883/−0.784 e Å^{-3}.

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Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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