*Organometallics* **1994,** *13,* 1089–1097

# Reactions of Alkynylsilanes with $[RhCl(P\textit{i}Pr_3)_2]$: The Synthesis of Four-Coordinate (Alkyne)-, Alkynyl-, and Vinylidenerhodium(I) and Five- and Six-Coordinate Alkynylhydridorhodium(III) Complexes from $RC{\equiv}CSiMe_3$, $Me_3SiC{\equiv}CSiMe_3$, and $HC{\equiv}CSiMe_3$[1]

Helmut Werner,* Matthias Baum, Dirk Schneider, and Bettina Windmüller

*Institut für Anorganische Chemie der Universität, Am Hubland, D-97074 Würzburg, Germany*

*Received October 7, 1993*[⊗]

Treatment of $[RhCl(P\textit{i}Pr_3)_2]$ (**1**) with the alkynylsilanes $RC{\equiv}CSiMe_3$ leads to the formation of the alkyne complexes *trans*-$[RhCl(RC{\equiv}CSiMe_3)(P\textit{i}Pr_3)_2]$ (R = Me (**2**), Ph (**3**), $CO_2Et$ (**4**), $CO_2SiMe_3$ (**5**), $CH_2OH$ (**6**), $C(O)CHPh_2$ (**7**)) or the corresponding vinylidenerhodium(I) derivatives *trans*-$[RhCl({=}C{=}C(SiMe_3)R)(P\textit{i}Pr_3)_2]$ (R = $SiMe_3$ (**8**), *n*Pr (**9**), *n*Bu (**10**), *t*Bu (**11**)). Compounds **2**–**5** rearrange either thermally or photochemically to give the isomeric rhodium vinylidenes **12**–**15**. Whereas the reaction of **1** with $HMe_2SiC{\equiv}CSiMe_2H$ affords the dinuclear hydrido(silyl)rhodium(III) complex $[\{RhHCl(P\textit{i}Pr_3)_2\}_2(\mu\text{-}Me_2SiC{\equiv}CSiMe_2)]$ (**16**), the five-coordinate alkynylhydrido compound $[RhH(C{\equiv}CSiMe_3)Cl(P\textit{i}Pr_3)_2]$ (**18**) is obtained from **1** and $HC{\equiv}CSiMe_3$. **18** rearranges smoothly to yield *trans*-$[RhCl({=}C{=}CHSiMe_3)(P\textit{i}Pr_3)_2]$ (**19**), and it reacts with pyridine to give $[RhH(C{\equiv}CSiMe_3)Cl(py)(P\textit{i}Pr_3)_2]$ (**20**). Treatment of **20** with $Na[N(SiMe_3)_2]$ as a strong base affords the square-planar alkynyl derivative *trans*-$[Rh(C{\equiv}CSiMe_3)(py)(P\textit{i}Pr_3)_2]$ (**21**). The corresponding ethene complex *trans*-$[Rh(C{\equiv}CSiMe_3)(C_2H_4)(P\textit{i}Pr_3)_2]$ (**22**) is similarly obtained from **18** and $Na[N(SiMe_3)_2]$ under a $C_2H_4$ atmosphere. The $Rh{-}C_2H_4$ bond in **22** is rather labile and therefore displacement reactions with alkynes occur readily. With $HC{\equiv}CSiMe_3$, the bis(alkynyl)hydridorhodium(III) compounds $[RhH(C{\equiv}CSiMe_3)_2(P\textit{i}Pr_3)_2]$ (**23**) and $[RhH(C{\equiv}CSiMe_3)_2(py)(P\textit{i}Pr_3)_2]$ (**24**) and with $RC{\equiv}CSiMe_3$ the alkyne(alkynyl)rhodium(I) derivatives *trans*-$[Rh(C{\equiv}CSiMe_3)(RC{\equiv}CSiMe_3)(P\textit{i}Pr_3)_2]$ (R = $CO_2Et$ (**25**), $CO_2SiMe_3$ (**26**)) are obtained. The X-ray crystal structure of **24** (orthorhombic, space group $Pna2_1$ (No. 33) with $a = 19.109(7)$ Å, $b = 17.397(4)$ Å, $c = 12.329(3)$ Å, and $Z = 4$) reveals a *trans* disposition of the two alkynyl, the two phosphine, and the hydride and the pyridine units. The synthesis of some cyclopentadienylrhodium complexes containing alkynylsilane ligands will also be described.

## Introduction

Whereas numerous examples illustrating the transition-metal initiated rearrangement of terminal alkynes $HC{\equiv}CR'$ to the corresponding vinylidenes have been described in the literature,[2] almost nothing is known about the conversion of internal alkynes $RC{\equiv}CR'$ to the vinylidene isomers. The explanation for this is that the R—C bond in the disubstituted alkyne $RC{\equiv}CR'$ is stronger than the H—C bond in $HC{\equiv}CR'$ and that a 1,2-alkyl or -aryl shift to form the vinylidene species $:C{=}CRR'$ is equally hindered for kinetic reasons.

The difficulty to transform an alkyne $RC{\equiv}CR'$ into the isomeric vinylidene $:C{=}CRR'$ may be overcome, however, if R is a silyl instead of an alkyl or aryl group. A 1,2-silyl shift is well-known for substituted cyclopentadienes $C_5H_n(SiMe_3)_{6-n}$[3] and has recently also been observed by Vahrenkamp et al. for a cluster-bound acetylene derivative.[4] We report here that $HC{\equiv}CSiMe_3$ as well as various substituted silylalkynes $RC{\equiv}CSiMe_3$ react with the 14-electron compound $[RhCl(P\textit{i}Pr_3)_2]$ to give initially the expected square-planar (alkyne)rhodium(I) complexes *trans*-$[RhCl(RC{\equiv}CSiMe_3)(P\textit{i}Pr_3)_2]$ which rearrange either thermally or photochemically to form the vinylidenerhodium isomers. The preparation of (silylalkynyl)rhodium derivatives will also be described. Some preliminary results of this work have already been communicated.[5]

## Results and Discussion

**(Alkyne)- and Vinylidenerhodium Complexes from $Me_3SiC{\equiv}CSiMe_3$ and $RC{\equiv}CSiMe_3$.** The highly reactive bis(triisopropylphosphine)rhodium(I) complex **1**,[6] which is a dimer in the solid state[7] but a monomer in solution, reacts with the alkynyltrimethylsilanes $RC{\equiv}CSiMe_3$ (R = Me, Ph, $CO_2Et$, $CO_2SiMe_3$, $CH_2OH$, $C(O)CHPh_2$) in pentane to give the square-planar alkynerhodium(I) derivatives **2**–**7** in good, sometimes almost quantitative, yields. Compounds **2**–**7** (Scheme 1) are

---

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1994.

[1] Vinylidene Transition-Metal Complexes. 27. For part 26, see: Nürnberg, O.; Werner, H. *J. Organomet. Chem.* **1993,** *460,* 163–175.

[2] Reviews: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983,** *22,* 59–128. (b) Bruce, M. I. *Chem. Rev.* **1991,** *91,* 197–257. (c) Antonova, A. B.; Johansson, A. A. *Usp. Khim.* **1989,** *58,* 1197–1230. (d) Werner, H. *Angew. Chem.* **1990,** *102,* 1109–1121; *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 1077–1089.

[3] (a) Fritz, H. P.; Kreiter, C. G. *J. Organomet. Chem.* **1965,** *4,* 313–319. (b) Ustynyuk, Yu. A.; Kisin, A. V.; Pribytkova, I. M.; Zenkin, A. A.; Antonova, N. D. *J. Organomet. Chem.* **1972,** *42,* 47–63. (c) Abel, E. W.; Dunster, M. O.; Waters, A. *J. Organomet. Chem.* **1973,** *49,* 287–321.

[4] Bantel, H.; Powell, A. K.; Vahrenkamp, H. *Chem. Ber.* **1990,** *123,* 661–665.

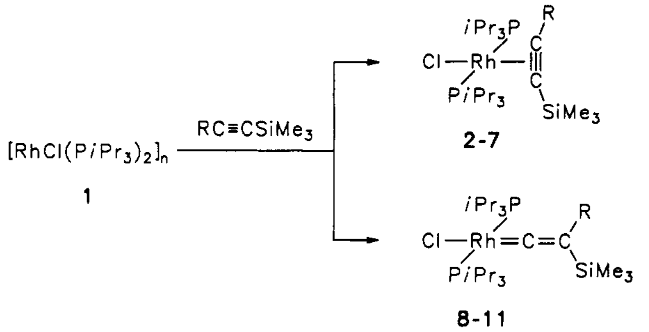
[5] Schneider, D.; Werner, H. *Angew. Chem.* **1991,** *103,* 710–712; *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 700–702.

[6] (a) Preparation in situ: Busetto, C.; D'Alfonso, A.; Maspero, F.; Perego, G.; Zazetta, A. *J. Chem. Soc., Dalton Trans.* **1977,** 1828–1834. (b) Isolation: Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985,** *287,* 395–407.

[7] Haas, J. Dissertation, Universität Kaiserslautern, 1990. We thank Professor P. Binger for this information.

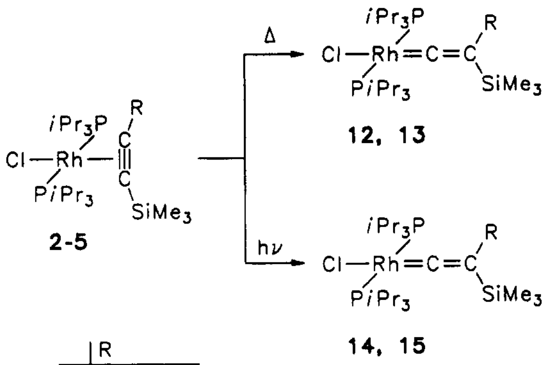
0276-7333/94/2313-1089$04.50/0

**Scheme 1**



| | R | | R | | R |
|---|---|---|---|---|---|
| 2 | Me | 5 | $CO_2SiMe_3$ | 8 | $SiMe_3$ |
| 3 | Ph | 6 | $CH_2OH$ | 9 | *n*Pr |
| 4 | $CO_2Et$ | 7 | C(O)$CHPh_2$ | 10 | *n*Bu |
| | | | | 11 | *t*Bu |

**Scheme 2**



| | R |
|---|---|
| 12 | Me |
| 13 | Ph |
| 14 | $CO_2Et$ |
| 15 | $CO_2SiMe_3$ |

yellow or orange-yellow air-sensitive solids which dissolve in all common organic solvents and are stable under argon at room temperature. For the preparation of 2–7 it is important to use isolated and not in situ generated samples of the starting material 1 because free triisopropylphosphine, even if present in only small excess, may cause problems during the purification procedure and, in the case of R = $CO_2Et$ and $CO_2SiMe_3$, it also reacts with the alkyne.

Treatment of compound 1 with an equimolar amount of $Me_3SiC\equiv CSiMe_3$ at room temperature does not lead to any reaction at all. If, however, a larger excess of $Me_3SiC\equiv CSiMe_3$ is added to a pentane solution of 1 at −20 °C, a quick color change from violet to orange-red is observed. After a few minutes, the solution turns violet again. Upon workup and recrystallization at −78 °C dark-violet, air- and moisture-sensitive crystals with an analytical composition corresponding to 8 are isolated. According to the IR and NMR spectroscopic data, there is no doubt that 8 is a vinylidene- and not an (alkyne)rhodium complex. The most typical spectroscopic features are the low-field signals in the $^{13}C$ NMR spectrum at $\delta$ = 272.0 and 89.7, which by comparison are assigned to the $\alpha$-C and $\beta$-C vinylidene carbon atoms,[8] the sharp doublet in the $^{31}P$ NMR with a Rh—P coupling constant which is substantially larger than in the case of 2–7, and the absence of a C≡C stretching frequency between 1750 and 1850 cm$^{-1}$ in the IR spectrum. With regard to the mechanism of the reaction of 1 with $Me_3SiC\equiv CSiMe_3$, we assume that in the first step the expected alkyne complex *trans*-$[RhCl(Me_3SiC\equiv CSiMe_3)(PiPr_3)_2]$ is formed. This is supported by the observation that if after the addition of the alkyne the solution is worked up immediately at −78 °C, an orange instead of a dark-violet solid can be isolated. Its IR spectrum, which shows a relatively strong band at 1832 cm$^{-1}$, indicates the presence of a coordinated alkyne. The orange intermediate is extremely labile and, even in the solid state, rearranges to give the vinylidene isomer 8.

The reactions of 1 with $RC\equiv CSiMe_3$, where R is *n*Pr, *n*Bu, and *t*Bu, follow a course similar to that of 1 with $Me_3SiC\equiv CSiMe_3$ (Scheme 1). As in the generation of 8, the IR spectra indicate that primarily an alkyne complex is formed but again the rearrangement to the isomeric vinylidenes 9–11 occurs readily and does not allow the complete characterization of the (alkyne)rhodium intermediate.

The alkyne complexes 2 and 3, which are stable not only in the solid state but also in pentane solution at room temperature, upon warming to 35 °C (for 2) or 60 °C (for 3) react to give the vinylidenerhodium derivatives 12 and 13 (Scheme 2). In contrast, the conversion of 4 and 5 to the corresponding compounds 14 and 15 proceeds photochemically; the yields are 55–60%. The reason for the different behaviors of 2 and 3 on the one hand and of 4 and 5 on the other is not yet clear. This is noteworthy insofar as the positions of the charge-transfer (CT) and $\pi$–$\pi^*$ bands in the UV spectra of compounds 4 and 10 (see Experimental Section) are almost the same. It should be mentioned, however, that Antonova et al. in their pioneering work on the synthesis of vinylidenemanganese complexes have already found that the formation of $[C_5H_5Mn(=C=CHR)(CO)_2]$ from $[C_5H_5Mn(CO)_3]$ and 1-alkynes takes place only under UV irradiation but not under thermal conditions.[9]

Attempts to observe a stepwise reaction sequence from 2–5 first to give a five-coordinate alkynyl(silyl)rhodium(III) compound $[RhCl(C\equiv CR)(SiMe_3)(PiPr_3)_2]$ and then the corresponding vinylidene complex 12–15 failed. Even in presence of pyridine, the proposed intermediate cannot be trapped as an octahedral 1:1 adduct. In this context it is interesting to note that Lewis et al. recently reported on the reaction of $[Rh(PMe_3)_4]Cl$ with $PhC\equiv CSnMe_3$ which, if 2 equiv of the alkyne are used, does not lead to a vinylidenerhodium(I) but to the six-coordinate bis(alkynyl)stannylrhodium(III) derivative $[Rh(C\equiv CPh)_2(SnMe_3)(PMe_3)_3]$.[10]

The properties of the violet solids 9–15 are similar to those of 8 and of the previously described compounds *trans*-$[RhCl(=C=CHR)(PiPr_3)_2]$ (R = H, Me, *t*Bu,

---

(8) (a) Werner, H.; Garcia-Alonso, F. J.; Otto, H.; Wolf, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1988**, *43*, 722–726. (b) Werner, H.; Brekau, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1989**, *44*, 1438–1446.

(9) (a) Nesmeyanov, A. N.; Aleksandrov, G. G.; Antonova, A. B.; Anisimov, K. N.; Kolobova, N. E.; Struchkov, Yu. T. *J. Organomet. Chem.* **1976**, *110*, C36–C38. (b) Antonova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Lokshin, B. V.; Obezyuk, N. S. *J. Organomet. Chem.* **1977**, *137*, 55–67.

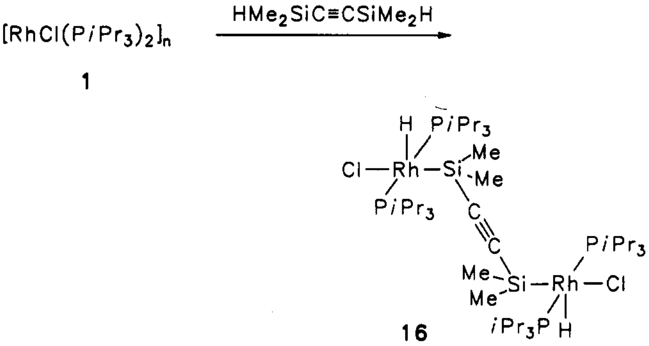
(10) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187–188.

(11) (a) Rappert, T.; Nürnberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992**, *11*, 4156–4164. (b) Werner, H.; Rappert, T. *Chem. Ber.* **1993**, *126*, 669–678.

(12) Werner, H.; Schneider, D.; Schulz, M. *J. Organomet. Chem.* **1993**, *451*, 175–182.

(13) Haszeldine, R. N.; Parish, R. V.; Parry, D. J. *J. Chem. Soc. A* **1969**, 683–690.

**Scheme 3**



$CH{=}CH_2$, Ph, $CO_2Me$).[8,11] A characteristic difference between the Rh=C=CHR and the $Rh{=}C{=}C(SiMe_3)R$ complexes is, however, the presence of two sets of signals for the protons and the carbon atoms of the phosphine $CH_3$ groups in the $^1H$ and the $^{13}C$ NMR spectra of **9**–**15** even at room temperature, which indicates a hindered rotation of the vinylidene ligand around the Rh=C bond. We suppose that this is due to the steric repulsion between the two substituents on the $\beta$-C atom of the vinylidene unit and the bulky triisopropylphosphine ligands. If one of the vinylidene substituents is hydrogen, a comparable restriction of the rotation at room temperature cannot be detected.[8,11]

The C—Si bond in **8**–**15** can easily be cleaved by proton sources. After chromatography of solutions of the silylvinylidene complexes on $Al_2O_3$ (activity grade III) in hexane or benzene, not the original reaction products but the desilylated derivatives *trans*-[RhCl(=C=CHR)-$(PiPr_3)_2$][8,11] are eluted. Treatment of **13** or **14** with $[nBu_4N]F$ also leads to cleavage of the C—Si bond and formation of the square-planar alkynylrhodium(I) anions *trans*-$[RhCl(C{\equiv}CR)(PiPr_3)_2]^-$.[12] The anionic complex with R = $CO_2Et$ is equally accessible on reaction of **4** with $[nBu_4N]F$ which illustrates that the C—Si bond is prone to hydrolysis both in silylalkyne and silylvinylidene ligands.

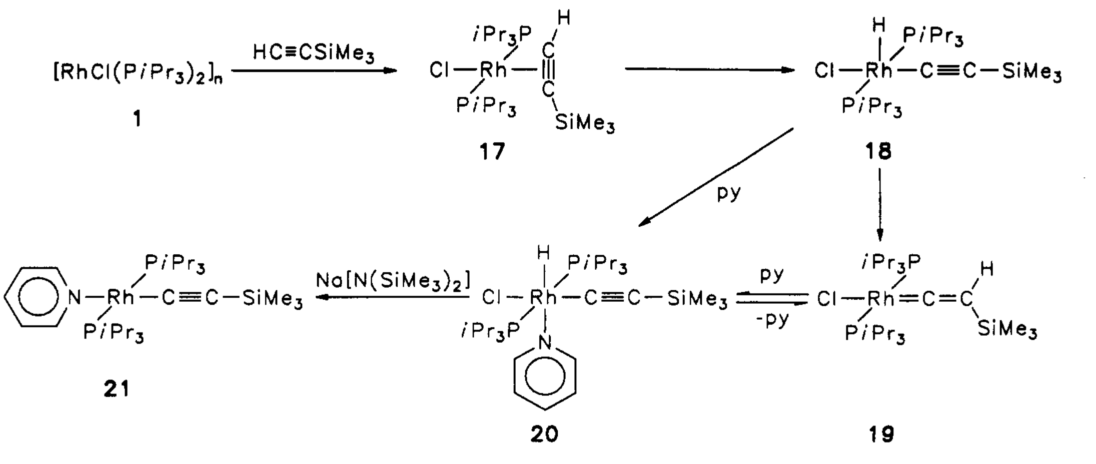
**Reaction of 1 with $HMe_2SiC{\equiv}CSiMe_2H$.** The behavior of the $SiMe_2H$-substituted alkyne $HMe_2SiC{\equiv}CSiMe_2H$ toward **1** is completely different from that of the $SiMe_3$ analogue $Me_3SiC{\equiv}CSiMe_3$. Although it reacts with **1** under the same conditions as used for the synthesis of **8**, the product is not the mononuclear vinylidene complex *trans*-$[RhCl({=}C{=}C(SiMe_2H)_2)(PiPr_3)_2]$ but the dinuclear hydrido(silyl) compound **16** (Scheme 3). The oxidative addition of the Si—H bond to the metal center is obviously preferred over $\pi$-coordination supposed to be the primary step in the reaction of **1** with $Me_3SiC{\equiv}CSiMe_3$. We note that mononuclear rhodium complexes of composition $[RhH(SiR_3)X(PPh_3)_2]$ (X = Cl, Br; R = Cl, OEt, Me, Et, Ph) are known,[13] but for R = alkyl they are unstable in solution.

The structural proposal for compound **16** depicted in Scheme 3 not only is substantiated by elemental analysis but also is in full agreement with the spectroscopic data. Both the observation of only one doublet in the $^{31}P$ NMR and that of two doublets of virtual triplets for the $PCHCH_3$ protons in the $^1H$ NMR spectrum are consistent with the *trans* disposition of the two phosphine ligands. Furthermore, the cleavage of the Si—H bonds in the reacting molecule $HMe_2SiC{\equiv}CSiMe_2H$ and the formation of two equivalent Rh—H and Rh—Si linkages in the product is supported by the appearance of one hydride resonance in the $^1H$ NMR at $\delta = -16.34$ and one signal at $\delta = 14.53$ in the $^{29}Si$ NMR spectrum. In either case, a relatively strong coupling to $^{103}Rh$ and $^{31}P$ is observed. It should be mentioned that the ratio of **1**:$HMe_2SiC{\equiv}CSiMe_2H$ has no influence on the constitution of the reaction product; even if a large excess of the alkyne is used, the formation of a mononuclear complex $[RhH(SiMe_2C{\equiv}CSiMe_2H)Cl(PiPr_3)_2]$ could not be detected.

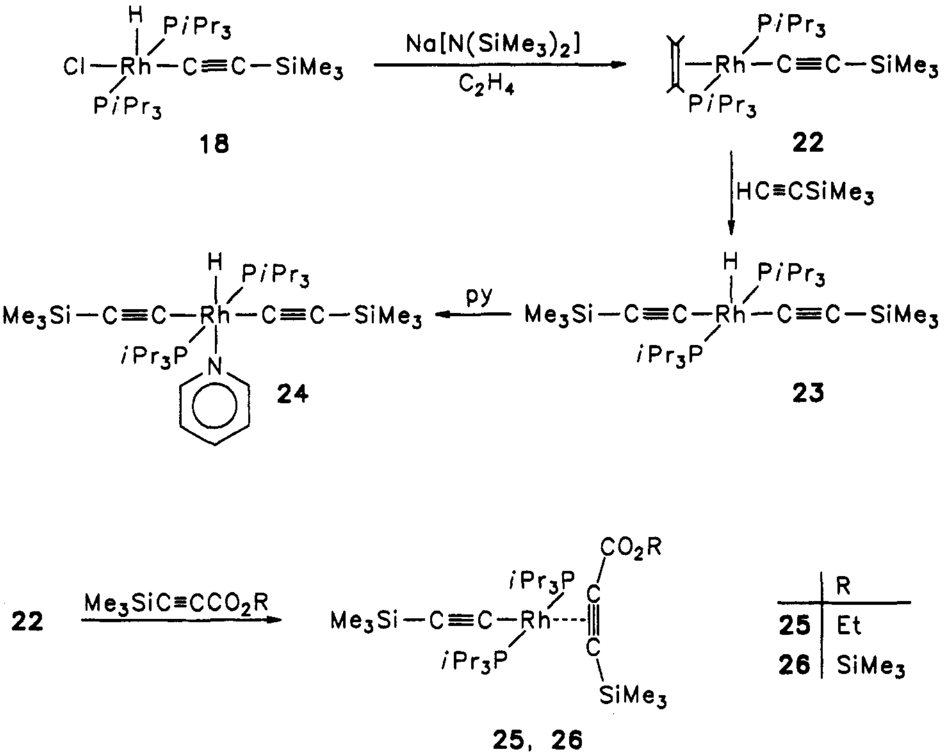
**Alkynyl and Vinylidene Complexes from $HC{\equiv}CSiMe_3$.** Like $HC{\equiv}CtBu$, the homologous terminal alkyne $HC{\equiv}CSiMe_3$ reacts with **1** even at low temperatures not to give an (alkyne)rhodium(I) but an alkynylhydridorhodium(III) derivative. For the isolation of pure samples of the orange-yellow crystalline compound **18** (Scheme 4) it is absolutely necessary to work up the reaction mixture at −30 °C and to use rigorous anhydrous conditions; otherwise the known unsubstituted vinylidene complex *trans*-$[RhCl({=}C{=}CH_2)(PiPr_3)_2]$[8a] is obtained. Similar observations have also been made in related iridium chemistry.[14] As far as the mechanism of the reaction of **1** with $HC{\equiv}CSiMe_3$ is concerned, there is some spectroscopic evidence for the formation of *trans*-$[RhCl(HC{\equiv}CSiMe_3)(PiPr_3)_2]$ (**17**) as the primary intermediate. The $^{31}P$ NMR spectrum, if measured immediately after the addition of the alkyne to a benzene-$d_6$ solution of the starting material, shows besides the doublet of **18** at $\delta$ = 49.29 and the less intensive signal of **19** at $\delta$ = 42.30 a third doublet at $\delta$ = 34.07 [$J$(RhP) = 107.0 Hz], which by comparison could be assigned to **17**. In the $^{31}P$ NMR spectrum of the similar alkyne complex **4**, a corresponding signal at $\delta$ = 34.01 [d, $J$(RhP) = 114.3 Hz] is observed.

Compound **18**, which has been fully characterized by analytical and spectroscopic data, reacts either in solution

**Scheme 4**



**Scheme 5**



(hexane, 40 °C) or in the solid state to yield the vinylidene derivative **19**. As DTA measurements reveal an exothermic peak at 46 °C, we assume that this indicates the rearrangement of the alkynylhydrido complex to the vinylidene isomer. Both compounds **18** and **19** react with pyridine at low temperatures almost quantitatively to give the 1:1 adduct **20** which in solution in contrast to other complexes of this type is rather labile and (e.g. in benzene) re-forms the vinylidene complex **19**. In the presence of excess pyridine, compound **20** reacts with $Na[N(SiMe_3)_2]$ by elimination of HCl to yield the square-planar alkynylrhodium(I) derivative **21**. We note that, in the context of our previous studies on the mechanism of the reaction of $[RhH(C{\equiv}CR)Cl(py)(PiPr_3)_2]$ (R = Me, Ph) with $NaC_5H_5$ to give $[C_5H_5Rh({=}C{=}CHR)(PiPr_3)]$, we have found that also in this case the primary step consists of the formation of *trans*-$[Rh(C{\equiv}CR)(py)(PiPr_3)_2]$ which further reacts with $C_5H_6$ to give the half-sandwich type products.[15]

As our attempts to replace the pyridine ligand in **21** by $C_2H_4$ failed, the synthesis of the alkynyl(olefin)rhodium(I) complex **22** was performed on a different route. Treatment of compound **18** with $Na[N(SiMe_3)_2]$ under an ethene atmosphere leads, presumably via the coordinatively unsaturated intermediate $[Rh(C{\equiv}CSiMe_3)(PiPr_3)_2]$, to the ethene complex **22** which is isolated as an orange air-sensitive solid. Like in the related acetylide derivative *trans*-$[Rh(C{\equiv}CH)(C_2H_4)(PiPr_3)_2]$,[16] the $C_2H_4$—Rh bond in **22** is rather labile and thus the olefin can be easily displaced. The reaction of **22** with $HC{\equiv}CSiMe_3$ gives nearly quantitatively the five-coordinate bis(alkynyl)hydridorhodium(III) compound **23** (Scheme 5) for which a square-pyramidal configuration is assumed in analogy to the crystallographically characterized complex $[RhH(C{\equiv}CCiPr_2OH)_2(PiPr_3)_2]$.[17] The most typical feature of this type of hydridorhodium(III) species is the position of the Rh—H resonance in the $^1H$ NMR spectrum which appears at significantly higher fields (for **23** at $\delta = -29.58$) than in the case of the corresponding six-coordinate derivatives. The open coordination site in **23** is readily occupied by Lewis bases and thus, on treatment of **23** with pyridine, the octahedral rhodium(III) compound **24** is formed. It can also be prepared from the alkynyl(pyridine) complex **21** and an equimolar amount of $HC{\equiv}CSiMe_3$; for both reactions the yield is 85%. Compound **24** is a white crystalline solid which is less air-sensitive than the corresponding counterpart **23**.

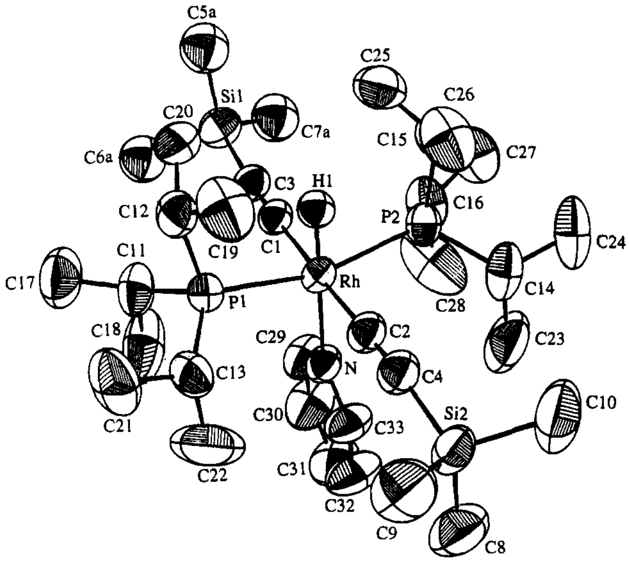


**Figure 1.** Molecular structure (perspective view) and labeling scheme of **24**. Hydrogen atoms are omitted for clarity.

The result of the X-ray structure analysis of **24** is shown in Figure 1, and the most relevant bond distances and

---

[14] (a) Höhn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852–854. (b) Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255–272.

[15] Werner, H.; Wolf, J.; Garcia-Alonso, F. J.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1987**, *336*, 397–411.

[16] Schäfer, M.; Wolf, J.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1991**, 1341–1343.

[17] Wiedemann, R. Diploma Thesis, Universität Würzburg, 1992.

**Table 1. Selected Bond Distances and Angles with Esd's for Compound 24**

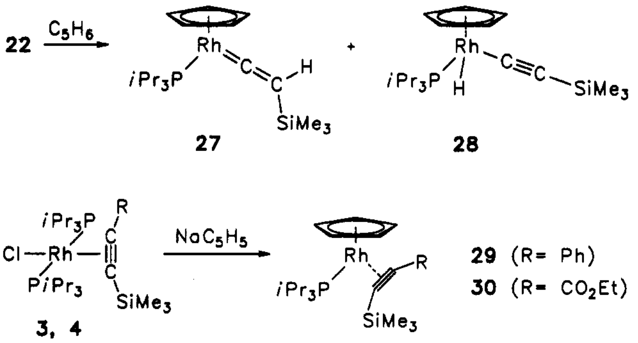
| Distances (Å) | | | |
|---|---|---|---|
| Rh–P1 | 2.352(2) | C1–C3 | 1.207(9) |
| Rh–P2 | 2.353(2) | C2–C4 | 1.219(9) |
| Rh–C1 | 2.032(6) | C3–Si1 | 1.797(7) |
| Rh–C2 | 2.020(6) | C4–Si2 | 1.801(7) |
| Rh–N | 2.275(5) | (Rh–H1 | 1.5421(4)) |
| **Bond Angles (deg)** | | | |
| P1–Rh–P2 | 161.02(6) | P2–Rh–C2 | 90.7(2) |
| C1–Rh–C2 | 176.5(2) | N–Rh–C1 | 92.5(2) |
| P1–Rh–N | 100.3(1) | N–Rh–C2 | 90.9(2) |
| P2–Rh–N | 98.6(1) | C1–C3–Si1 | 171.5(6) |
| P1–Rh–C1 | 89.4(2) | C2–C4–Si2 | 167.5(6) |
| P1–Rh–C2 | 90.4(2) | Rh–C1–C3 | 177.0(5) |
| P2–Rh–C1 | 88.4(2) | Rh–C2–C4 | 176.8(6) |

angles are outlined in Table 1. Although the position of the hydride ligand was calculated (see the hatched circle), on the basis of the positions of the Rh-bound atoms C1, C2, P1, P2, and N and the bond angles, there is no doubt that the metal center is octahedrally coordinated. Whereas the C1—Rh—C2 axis is almost linear, the P1—Rh—P2 axis is slightly bent. The bending is in the direction of the smallest ligand (hydride), a situation which is also found in other six-coordinate hydridobis(triisopropylphosphine)-metal complexes.[11a,18] The Rh—C1—C3 and Rh—C2—C4 units are nearly linear with Rh—C1 (Rh—C2) and C1—C3 (C2—C4) distances typical for Rh—C(sp) single and C≡C triple bonds. Similar bond lengths and angles have been found in the dinuclear compound [{RhH(C≡CSiMe$_3$)$_2$(dmpe)}$_2$($\mu$-dmpe)] (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) which was prepared by Marder et al. from [RhCH$_3$(dmpe)$_2$] and excess HC≡CSiMe$_3$.[19]

The olefin ligand of **22** is not only displaced by HC≡CSiMe$_3$ but also by other silylalkynes. The reactions of **22** with Me$_3$SiC≡CCO$_2$Et and Me$_3$SiC≡CCO$_2$SiMe$_3$ proceed smoothly at room temperature to give the square-planar (alkyne)alkynylrhodium(I) derivatives **25** and **26** (Scheme 5) in 60–70% yields. Both complexes are air- and moisture-sensitive but otherwise quite inert and do not rearrange on either heating or UV irradiation to give the alkynyl(vinylidene)rhodium isomers *trans*-[Rh(C≡CSiMe$_3$)(=C=(SiMe$_3$)CO$_2$R)(P*i*Pr$_3$)$_2$] (R = Et, SiMe$_3$). The behavior of the analogous chloro and alkynyl compounds, **4**, **5** and **25**, **26**, in this respect is distinctly different and possibly reflects the stronger $\sigma$-donor character of the alkynyl compared with that of the chloro ligand.

**Cyclopentadienylrhodium Complexes Containing Silylalkyne, -alkynyl, and -vinylidene Ligands.** Since the previously prepared square-planar alkynyl compounds *trans*-[Rh(C≡CR)(py)(P*i*Pr$_3$)$_2$] (R = Me, Ph) react with cyclopentadiene to yield the half-sandwich type vinylidene derivatives [C$_5$H$_5$Rh(=C=CHR)(P*i*Pr$_3$)],[15] we expected a similar course for the reaction of **22** with C$_5$H$_6$. However, in this case a mixture of two isomeric products **27** and **28** (Scheme 6) is formed which, despite several attempts, could not be completely separated by fractional crystallization or chromatographic techniques. Therefore, both compounds have been identified by spectroscopic means. The $^{13}$C NMR spectrum of the vinylidenerhodium(I) isomer **27** which is the major component shows the typical low-field resonance for the $\alpha$-carbon atom of the vinylidene unit at $\delta$ = 304.71, while the $^1$H NMR spectrum of the alkynylhydridorhodium(III) isomer **28** reveals the expected high-field signal of the Rh—H proton at $\delta$ = −13.09. Attempts to convert **28** to the vinylidene complex **27** failed.

**Scheme 6**



A clean reaction occurs between the four-coordinate alkyne compounds **3** and **4** and NaC$_5$H$_5$. Besides P*i*Pr$_3$ (which is removed by addition of methyl iodide) the cyclopentadienyl complexes **29** and **30** are obtained and isolated as red oils. They are remarkably stable both in substance and in solution and, like **25** and **26**, do not rearrange to give the vinylidene isomers [C$_5$H$_5$Rh(=C=C(SiMe$_3$)R)(P*i*Pr$_3$)]. From the spectroscopic data we conclude that in **29** and **30** the alkyne behaves as a two-electron donor ligand which corresponds to the bonding of phenylacetylene and diphenylacetylene in the related half-sandwiches [C$_5$H$_5$Rh(RC≡CPh)(P*i*Pr$_3$)] (R = H, Ph).[20] Although rhodium compounds of the general type [C$_5$H$_5$Rh(RC≡CR′)(P*i*Pr$_3$)] have been recently used not only by us[20,21] but also by others[22] for synthetic purposes, to the best of our knowledge the complexes **29** and **30** are the first representatives having a silylalkyne linked to the C$_5$H$_5$Rh(P*i*Pr$_3$) fragment.

## Conclusion

The present investigation has confirmed that not only 1-alkynes HC≡CR but also the trimethylsilyl derivatives RC≡CSiMe$_3$ can be transformed in the coordination sphere of rhodium into the isomeric disubstituted vinylidenes :C=C(SiMe$_3$)R. Although no mechanistic details of the rearrangement are known, we assume that the 1,2-SiMe$_3$ shift, which depending on the group R occurs thermally or photochemically, proceeds in a concerted way via an initial slippage of the alkyne to a $\eta^1$ geometry. On the basis of MO calculations, such a reaction pathway has also been considered as energetically preferred for the 1,2-shift in the 18-electron system [C$_5$H$_5$Mn(CO)$_2$(HC≡CR)].[23]

Recent studies in our laboratory as well as in the Sakurai group have shown that the use of silylalkynes as starting materials for the preparation of vinylidene complexes is not restricted to rhodium. Photolysis of *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] (**31**) and RC≡CSiMe$_3$ (R = Ph, CO$_2$Et) directly leads to the formation of *trans*-[IrCl(=C=C(SiMe$_3$)R)(P*i*Pr$_3$)$_2$] whereas the thermal reaction of **31** with Me$_3$SiC≡CC≡CSiMe$_3$ goes stepwise via the alkyne compound *trans*-[IrCl($\eta^2$-Me$_3$SiC≡CC≡CSiMe$_3$)(P*i*Pr$_3$)$_2$] to give the vinylidene isomer *trans*-[IrCl(=C=C(SiMe$_3$)-

---

[18] (a) Schulz, M.; Werner, H. *Organometallics* **1992**, *11*, 2790–2795. (b) Tena, M. A.; Nürnberg, O.; Werner, H. *Chem. Ber.* **1993**, *126*, 1597–1602. (c) Papenfuhs, B.; Mahr, N.; Werner, H. *Organometallics* **1993**, *12*, 4244–4246.

[19] Chow, P.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1545–1547.

[20] Werner, H.; Wolf, J.; Schubert, U.; Ackermann, K. *J. Organomet. Chem.* **1986**, *317*, 327–356.

[21] Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164–1169.

[22] (a) Binger, P.; Haas, J.; Herrmann, A. T.; Langhauser, F.; Krüger, C. *Angew. Chem.* **1991**, *103*, 316–318; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 310–312. (b) Tjaden, E. B.; Stryker, J. M. *Organometallics* **1992**, *11*, 16–18.

[23] Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461–1506.

$\mathrm{C{\equiv}CSiMe_3)(P}i\mathrm{Pr_3)_2]}$.[24] The corresponding rhodium complex *trans*-$[\mathrm{RhCl({=}C{=}C(SiMe_3)C{\equiv}CSiMe_3)(P}i\mathrm{Pr_3)_2]}$ has been prepared photochemically.[25] The advantage of photochemical activation for the isomerization process is also convincingly illustrated in the synthesis of the cyclopentadienylmanganese derivatives $[\mathrm{C_5H_5Mn(CO)_2({=}C{=}C(SiMe_2R)_2)}]$ which are obtained both from cyclic and acyclic acetylenes substituted by two silyl groups on each end of the molecule.[26] Although the yields in these reactions are not overwhelming, it nevertheless should be emphasized that the ease of the 1,2-$\mathrm{SiMe_3}$ shift during the formation of the silylvinylidene complexes is particularly noteworthy because for free silylalkynes such a process only occurs under severe reaction conditions.[27]

## Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk tube techniques. The starting materials $[\mathrm{RhCl(P}i\mathrm{Pr_3)_2]_n}$ (1),[6b] $\mathrm{Me_3SiC{\equiv}C}t\mathrm{Bu}$,[28] $\mathrm{Me_3SiC{\equiv}CC(O)CHPh_2}$,[29] and $\mathrm{HMe_2SiC{\equiv}CSiMe_2H}$[30] were prepared as described in the literature. The other alkynes were commercial products from Aldrich and Fluka. NMR spectra were recorded on JEOL FX 90 Q and Bruker AC 200 instruments, IR spectra on a Perkin-Elmer 1420 infrared spectrometer, and UV spectra on a Hewlett Packard 8452 A spectrometer. Melting points were measured by DTA.

**General Procedure for the Preparation of the Alkyne Complexes *trans*-$[\mathrm{RhCl(RC{\equiv}CSiMe_3)(P}i\mathrm{Pr_3)_2]}$ (2–7).** A solution of 1 (397 mg, 0.87 mmol for $n = 1$) in 30 mL of pentane was treated at −20 °C with an equimolar amount of the alkyne $\mathrm{RC{\equiv}CSiMe_3}$ (R = Me, Ph, $\mathrm{CO_2Et}$, $\mathrm{CH_2OH}$, $\mathrm{C(O)CHPh_2}$). For R = $\mathrm{CO_2SiMe_3}$, a 0.1 M solution of the alkyne in pentane was added dropwise to the violet solution of 1 until a color change to yellow-orange had occurred. After the reaction mixture was warmed to room temperature, it was stirred for 30 min, and then the solvent was removed. The oily residue was dissolved in 2–3 mL of hexane, and the solution was stored at −78 °C. Yellow or orange-yellow air-sensitive solids precipitated which were separated from the mother liquor, washed with 3 mL of pentane (−30 °C), and dried in vacuo. [If instead of a solid, an oily precipitate was formed, it was dissolved in 3–5 mL of ether and then 20 mL of nitromethane was added. The ether was slowly evaporated in vacuo (ca. 50 Torr) until the formation of a crystalline solid was observed. It was filtered off, repeatedly washed with nitromethane, and dried in vacuo.]

2: yield 263 mg (53%). Anal. Calcd for $\mathrm{C_{24}H_{54}ClP_2RhSi}$: C, 50.48; H, 9.53. Found: C, 50.40; H, 9.72. IR (hexane): $\nu(\mathrm{C{\equiv}C})$ 1848 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta$ 2.33 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 2.31 (d, $J$(RhH) = 0.5 Hz, 3H, $\mathrm{{\equiv}CC}H_3$), 1.35 (dvt, $N$ = 13.5, $J$(HH) = 6.9 Hz, 18H, $\mathrm{PCHC}H_3$), 1.19 (dvt, $N$ = 12.9, $J$(HH) = 6.2 Hz, 18H, $\mathrm{PCHC}H_3$), 0.24 (s, 9H, $\mathrm{SiC}H_3$). $^{13}$C NMR ($\mathrm{C_6D_6}$, 50.3 MHz): $\delta$ 112.97 (d, $J$(RhC) = 16.7 Hz, one C of $\mathrm{C{\equiv}C}$), 62.06 (d, $J$(RhC) = 14.3 Hz, one C of $\mathrm{C{\equiv}C}$), 23.03 (vt, $N$ = 15.8 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 21.01, 19.80 (both s, $\mathrm{PCH}C\mathrm{H_3}$), 15.99 (s, $\mathrm{{\equiv}C}C\mathrm{H_3}$), 1.80 (s, $\mathrm{Si}C\mathrm{H_3}$). $^{31}$P NMR ($\mathrm{C_6D_6}$, 36.2 MHz): $\delta$ 32.78 (d, $J$(RhP) = 118.7 Hz).

3: yield 314 mg (57%); mp 86 °C dec. Anal. Calcd for $\mathrm{C_{29}H_{56}ClP_2RhSi}$: C, 55.01; H, 8.92. Found: C, 55.09; H, 9.15. IR (hexane): $\nu(\mathrm{C{\equiv}C})$ 1805 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta$ 7.05 (m, 5H, $\mathrm{C_6H_5}$), 2.33 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.32 (dvt, $N$ = 13.6, $J$(HH) = 7.0 Hz, 18H, $\mathrm{PCHC}H_3$), 1.02 (dvt, $N$ = 13.0, $J$(HH) = 6.1 Hz, 18H, $\mathrm{PCHC}H_3$), 0.33 (s, 9H, $\mathrm{SiC}H_3$). $^{13}$C NMR ($\mathrm{C_6D_6}$, 50.3 MHz): $\delta$ 132.22, 131.05, 130.51 (all s, $C_6\mathrm{H_5}$), 117.00 (dt, $J$(RhC) = 18.3, $J$(PC) = 3.2 Hz, one C of $\mathrm{C{\equiv}C}$), 77.92 (d, $J$(RhC) = 14.4 Hz, one C of $\mathrm{C{\equiv}C}$), 22.45 (vt, $N$ = 16.8 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 21.17, 19.49 (both s, $\mathrm{PCH}C\mathrm{H_3}$), 1.64 (s, $\mathrm{Si}C\mathrm{H_3}$). $^{31}$P NMR ($\mathrm{C_6D_5CD_3}$, 36.2 MHz, −40 °C): $\delta$ 31.20 (d, $J$(RhP) = 115.8 Hz). UV (hexane): λ(CT) 386, λ($\pi$–$\pi^*$) 254, 248, 220 nm.

4: yield 460 mg (84%); mp 69 °C dec. Anal. Calcd for $\mathrm{C_{26}H_{56}ClO_2P_2RhSi}$: C, 49.64; H, 8.97. Found: C, 49.54; H, 9.28. IR (hexane): $\nu(\mathrm{C{\equiv}C})$ 1805, $\nu(\mathrm{C{=}O})$ 1695, 1685 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\nu$ 4.09 (q, $J$(HH) = 7.1 Hz, 2H, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.33 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.31 (dvt, $N$ = 13.6, $J$(HH) = 7.0 Hz, 18H, $\mathrm{PCHC}H_3$), 1.19 (dvt, $N$ = 13.1, $J$(HH) = 6.3 Hz, 18H, $\mathrm{PCHC}H_3$), 1.07 (t, $J$(HH) = 7.1 Hz, 3H, $\mathrm{OCH_2C}H_3$), 0.35 (s, 9H, $\mathrm{SiC}H_3$). $^{13}$C NMR ($\mathrm{C_6D_6}$, 50.3 MHz): $\delta$ 155.35 (s, $C\mathrm{O_2Et}$), 106.61 (dt, $J$(RhC) = 20.2, $J$(PC) = 3.6 Hz, one C of $\mathrm{C{\equiv}C}$), 100.82 (d, $J$(RhC) = 14.6 Hz, one C of $\mathrm{C{\equiv}C}$), 60.40 (s, $\mathrm{O}C\mathrm{H_2CH_3}$), 22.79 (vt, $N$ = 17.5 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 20.75, 19.41 (both s, $\mathrm{PCH}C\mathrm{H_3}$), 14.27 (s, $\mathrm{OCH_2}C\mathrm{H_3}$), 0.75 (s, $\mathrm{Si}C\mathrm{H_3}$). $^{31}$P NMR ($\mathrm{C_6D_6}$, 36.2 MHz): $\delta$ 34.01 (d, $J$(RhP) = 114.3 Hz). UV (hexane): λ(CT) 390, λ(n–$\pi^*$) 336, λ($\pi$–$\pi^*$) 256, 250, 216 nm.

5: yield 521 mg (89%); mp 74 °C dec. Anal. Calcd for $\mathrm{C_{27}H_{60}ClO_2P_2RhSi_2}$: C, 48.17; H, 8.98. Found: C, 47.93; H, 9.13. IR (hexane): $\nu(\mathrm{C{\equiv}C})$ 1805, $\nu(\mathrm{C{=}O})$ 1675, 1663 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta$ 2.33 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.33 (dvt, $N$ = 13.6, $J$(HH) = 7.0 Hz, 18H, $\mathrm{PCHC}H_3$), 1.20 (dvt, $N$ = 13.1, $J$(HH) = 6.3 Hz, 18H, $\mathrm{PCHC}H_3$), 0.34, 0.33 (both s, 18H, $\mathrm{SiC}H_3$). $^{29}$Si NMR ($\mathrm{C_6D_6}$, 17.8 MHz): $\delta$ 22.59 (s, $\mathrm{CO_2}Si\mathrm{CH_3}$), −13.17 (s, $\mathrm{{\equiv}C}Si\mathrm{Me_3}$). $^{31}$P NMR ($\mathrm{C_6D_6}$, 36.2 MHz): $\delta$ 33.97 (d, $J$(RhP) = 114.3 Hz).

6: yield 465 mg (91%); mp 80 °C dec. Anal. Calcd for $\mathrm{C_{24}H_{54}ClOP_2RhSi}$: C, 49.10; H, 9.27. Found: C, 49.22; H, 9.73. IR (hexane): $\nu$(OH) 3595, $\nu(\mathrm{C{\equiv}C})$ 1834 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta$ 4.66 (s, 2H, $\mathrm{C}H_2\mathrm{OH}$), 2.80 (s, br, 1H, $\mathrm{O}H$), 2.30 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.31 (dvt, $N$ = 13.5, $J$(HH) = 6.9 Hz, 18H, $\mathrm{PCHC}H_3$), 1.16 (dvt, $N$ = 12.9, $J$(HH) = 6.3 Hz, 18H, $\mathrm{PCHC}H_3$), 0.22 (s, 9H, $\mathrm{SiC}H_3$). $^{13}$C NMR ($\mathrm{C_6D_5CD_3}$, 22.5 MHz, −20 °C): $\delta$ 116.97 (dt, $J$(RhC) = 18.3, $J$(PC) = 3.4 Hz, one C of $\mathrm{C{\equiv}C}$), 66.52 (dt, $J$(RhC) = 14.0 Hz, $J$(PC) = 1.1 Hz, one C of $\mathrm{C{\equiv}C}$), 56.81 (s, $C\mathrm{H_2OH}$), 22.74 (vt, $N$ = 17.8 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 21.02, 19.54 (both s, $\mathrm{PCH}C\mathrm{H_3}$), 1.94 (s, $\mathrm{Si}C\mathrm{H_3}$). $^{29}$Si NMR ($\mathrm{C_6D_5CD_3}$, 17.8 MHz, −20 °C): $\delta$ −15.15 (t, $J$(PSi) = 1.5 Hz). $^{31}$P NMR ($\mathrm{C_6D_5CD_3}$, 36.2 MHz, −20 °C): $\delta$ 31.75 (d, $J$(RhP) = 117.2 Hz).

7: yield 400 mg (61%); mp 99 °C dec. Anal. Calcd for $\mathrm{C_{37}H_{62}ClOP_2RhSi}$: C, 59.16; H, 8.32. Found: C, 58.93; H, 8.22. IR (KBr): $\nu(\mathrm{C{\equiv}C})$ 1750 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 90 MHz): $\delta$ 7.37 (m, 5H, $\mathrm{C_6}H_5$), 5.77 (s, 1H, $\mathrm{C}H\mathrm{Ph_2}$), 2.26 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.20 (dvt, $N$ = 13.4, $J$(HH) = 7.2 Hz, 18H, $\mathrm{PCHC}H_3$), 1.14 (dvt, $N$ = 13.4, $J$(HH) = 7.2 Hz, 18H, $\mathrm{PCHC}H_3$), 0.50 (s, 9H, $\mathrm{SiC}H_3$). $^{31}$P NMR ($\mathrm{C_6D_6}$, 36.2 MHz): $\delta$ 33.83 (d, $J$(RhP) = 115.7 Hz).

**Preparation of *trans*-$[\mathrm{RhCl({=}C{=}C(SiMe_3)R)(P}i\mathrm{Pr_3)_2]}$ (8–10).** A solution of 1 (287 mg, 0.63 mmol for $n = 1$) in 25 mL of pentane was treated at −20 °C with an excess (ca. 1 mL) of the alkyne. A spontaneous color change from violet to orange-red occurred, but after the solution was stirred for 10 min at room temperature, it became violet again. The solvent was removed, the oily residue was dissolved in 2–3 mL of hexane, and the solution was stored at −78 °C. Violet crystals precipitated which were separated from the mother liquor, washed with pentane (−30 °C), and dried in vacuo. If an oil instead of a crystalline solid precipitated, the second workup procedure described for 2–7 was applied.

8: yield 214 mg (54%); mp 72 °C dec. Anal. Calcd for $\mathrm{C_{26}H_{60}ClP_2RhSi_2}$: C, 49.63; H, 9.61. Found: C, 49.53; H, 9.89. IR (hexane): $\nu(\mathrm{C{=}C})$ 1624 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta$ 2.71 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.34 (dvt, $N$ = 13.4, $J$(HH) = 7.0 Hz, 36H, $\mathrm{PCHC}H_3$), 0.24 (s, 18H, $\mathrm{SiC}H_3$). $^{13}$C NMR ($\mathrm{C_6D_6}$, 50.3 MHz): $\delta$ 272.00 (dt, $J$(RhC) = 58.9, $J$(PC) = 13.7 Hz, $\mathrm{Rh{=}}C\mathrm{{=}C}$), 89.71 (dt, $J$(RhC) = 14.7, $J$(PC) = 4.2 Hz, $\mathrm{Rh{=}C{=}}C$), 24.59 (vt, $N$ = 19.0 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 20.82 (s, $\mathrm{PCH}C\mathrm{H_3}$), 2.87 (s, $\mathrm{Si}C\mathrm{H_3}$; from satellites $J$(SiC) = 52.6 Hz). $^{29}$Si NMR ($\mathrm{C_6D_6}$, 17.8 MHz): $\delta$ −14.49 (t, $J$(PSi) = 2.2 Hz). $^{31}$P NMR ($\mathrm{C_6D_6}$, 36.2 MHz): $\delta$ 41.10 (d, $J$(RhP) = 140.7 Hz).

---

(24) Lass, R. Dissertation, Universität Würzburg, in preparation.

(25) Rappert, T.; Nürnberg, O.; Werner, H.; *Organometallics* **1993**, *12*, 1359–1364.

(26) Sakurai, H.; Fujii, T.; Sakamoto, K. *Chem. Lett.* **1992**, 339–342.

(27) (a) Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1979**, *62*, 852–865. (b) Barton, T. J.; Groh, B. L. *Organometallics* **1985**, *4*, 575–580.

(28) Zweifel, G.; Lewis, W. *J. Org. Chem.* **1978**, *43*, 2739–2744.

(29) Stang, P. J.; Fisk, T. E.; *Synthesis* **1979**, 438–440.

(30) Seyferth, D.; White, D. L. *J. Organomet. Chem.* **1971**, *32*, 317–322.

**9**: yield 193 mg (51%); mp 90 °C dec. Anal. Calcd for $C_{26}H_{58}ClP_2RhSi$: C, 52.12; H, 9.76. Found: C, 51.92; H, 9.92. IR (hexane): *ν*(C=C) 1631 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 200 MHz): *δ* 2.76 (m, 6H, PC*H*CH$_3$), 2.33 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 1.35 (dvt, *N* = 13.4, *J*(HH) = 6.9 Hz, 36H, PCHC*H*$_3$), 0.95, 0.83 (both m, 5H, CH$_2$C*H*$_2$C*H*$_3$), 0.20 (s, 9H, SiC*H*$_3$). $^{13}$C NMR ($C_6D_6$, 50.3 MHz): *δ* 281.35 (dt, *J*(RhC) = 59.0, *J*(PC) = 15.3 Hz, Rh=*C*=C), 99.22 (dt, *J*(RhC) = 16.3 Hz, *J*(PC) = 4.6 Hz, Rh=C=*C*), 25.27 (s, *C*H$_2$CH$_2$CH$_3$), 24.03 (vt, *N* = 18.9 Hz, P*C*HCH$_3$), 21.92 (s, CH$_2$*C*H$_2$CH$_3$), 20.54 (s, PCH*C*H$_3$), 14.89 (s, CH$_2$CH$_2$*C*H$_3$), 0.74 (s, Si*C*H$_3$). $^{29}$Si NMR ($C_6D_6$, 17.8 MHz): *δ* −14.87 (t, *J*(PSi) = 1.8 Hz). $^{31}$P NMR ($C_6D_6$, 36.2 MHz): *δ* 40.96 (d, *J*(RhP) = 137.8 Hz).

**10**: yield 243 mg (63%); mp 82 °C dec. Anal. Calcd for $C_{27}H_{60}ClP_2RhSi$: C, 52.89; H, 9.86. Found: C, 53.12; H, 10.12. IR (hexane): *ν*(C=C) 1639 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 200 MHz): *δ* 2.75 (m, 6H, PC*H*CH$_3$), 2.36 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.35 (dvt, *N* = 14.1, *J*(HH) = 7.1 Hz, 18H, PCHC*H*$_3$), 1.34 (dvt, *N* = 13.6, *J*(HH) = 6.7 Hz, 18H, PCHC*H*$_3$), 0.87 (m, 3H, (CH$_2$)$_3$C*H*$_3$), 0.21 (s, 9H, SiC*H*$_3$); signals of the CH$_2$C*H*$_2$C*H*$_2$CH$_3$ protons partially covered by P*i*Pr$_3$ proton signals. $^{13}$C NMR ($C_6D_6$, 50.3 MHz): *δ* 281.39 (dt, *J*(RhC) = 60.0, *J*(PC) = 15.3 Hz, Rh=*C*=C), 99.16 (dt, *J*(RhC) = 14.2 Hz, *J*(PC) = 4.6 Hz, Rh=C=*C*), 34.21 (s, *C*H$_2$CH$_2$CH$_2$CH$_3$), 24.09 (vt, *N* = 19.3 Hz, P*C*HCH$_3$), 23.69 (s, CH$_2$*C*H$_2$CH$_2$CH$_3$), 20.59 (s, PCH*C*H$_3$), 19.37 (s, CH$_2$CH$_2$*C*H$_2$CH$_3$), 14.07 (s, (CH$_2$)$_3$CH$_3$), 0.80 (s, SiCH$_3$). $^{29}$Si NMR ($C_6D_6$, 17.8 MHz): *δ* −14.91 (t, *J*(PSi) = 1.8 Hz). $^{31}$P NMR ($C_6D_6$, 36.2 MHz): *δ* 40.88 (d, *J*(RhP) = 137.8 Hz). UV (hexane): λ(CT) 414, λ(π–π*) 304, 298, 246, 226 nm.

**Preparation of *trans*-[RhCl(=C=C(SiMe$_3$)*t*Bu)(P*i*Pr$_3$)$_2$] (11).** A solution of **1** (161 mg, 0.35 mmol for *n* = 1) in 20 mL of pentane was treated dropwise with *t*BuC≡CSiMe$_3$ (710 μL, 3.5 mmol) and stirred for 2 h at 40 °C. The workup procedure was the same as that described for **8–10**. Dark-violet crystals were obtained; yield 127 mg (59%); mp 41 °C dec. Anal. Calcd for $C_{27}H_{60}ClP_2RhSi$: C, 52.89; H, 9.86. Found: C, 52.39; H, 9.96. IR (KBr): *ν*(C=C) 1610 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 90 MHz): *δ* 2.83 (m, 6H, PC*H*CH$_3$), 1.39 (dvt, *N* = 13.4, *J*(HH) = 7.1 Hz, 18H, PCHC*H*$_3$), 1.35 (dvt, *N* = 12.8, *J*(HH) = 7.1 Hz, 18H, PCHC*H*$_3$), 1.16 (s, 9H, CC*H*$_3$), 0.42 (s, 9H, SiC*H*$_3$). $^{13}$C NMR ($C_6D_6$, 100.6 MHz): *δ* 291.69 (dt, *J*(RhC) = 57.2, *J*(PC) = 15.8 Hz, Rh=*C*=C), 117.08 (dt, *J*(RhC) = 16.4 Hz, *J*(PC) = 5.9 Hz, Rh=C=*C*), 33.78 (s, *C*CH$_3$), 28.30 (s, C*C*H$_3$), 23.63 (vt, *N* = 19.2 Hz, P*C*HCH$_3$), 20.48, 20.37 (both s, PCH*C*H$_3$), 1.18 (s, Si*C*H$_3$). $^{31}$P NMR ($C_6D_6$, 36.2 MHz): *δ* 39.21 (d, *J*(RhP) = 139.2 Hz).

**Preparation of *trans*-[RhCl(=C=C(SiMe$_3$)Me)(*i*P*i*Pr$_3$)$_2$] (12).** A solution of **2** (171 mg, 0.30 mmol) in 20 mL of pentane was stirred for 6 h at 35 °C. After cooling to room temperature, the solution was evacuated to ca. 3 mL in vacuo and then stored at −78 °C. Dark-violet, moderately air-stable crystals were obtained which were washed with pentane (−30 °C) and dried in vacuo; yield 91 mg (53%); mp 83 °C dec. Anal. Calcd for $C_{24}H_{54}ClP_2RhSi$: C, 50.48; H, 9.53. Found: C, 49.95; H, 9.25. IR (hexane): *ν*(C=C) 1647 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 200 MHz): *δ* 2.72 (m, 6H, PC*H*CH$_3$), 1.74 (t, *J*(PH) = 1.9 Hz, 3H, =CC*H*$_3$), 1.33 (dvt, *N* = 13.4, *J*(HH) = 7.0 Hz, 18H, PCHC*H*$_3$), 1.32 (dvt, *N* = 13.3, *J*(HH) = 6.9 Hz, 18H, PCHC*H*$_3$), 0.10 (s, 9H, SiC*H*$_3$). $^{13}$C NMR ($C_6D_6$, 50.3 MHz): *δ* 280.25 (dt, *J*(RhC) = 57.8, *J*(PC) = 15.3 Hz, Rh=*C*=C), 92.91 (dt, *J*(RhC) = 15.3 Hz, *J*(PC) = 4.9 Hz, Rh=C=*C*), 23.95 (vt, *N* = 19.0 Hz, P*C*HCH$_3$), 20.56 (s, PCH*C*H$_3$), 1.37 (s, =C*C*H$_3$), −0.91 (s, Si*C*H$_3$). $^{31}$P NMR ($C_6D_6$, 36.2 MHz): *δ* 41.44 (d, *J*(RhP) = 136.3 Hz).

**Preparation of *trans*-[RhCl(=C=C(SiMe$_3$)Ph)(P*i*Pr$_3$)$_2$] (13).** A solution of **3** (190 mg, 0.30 mmol) in 20 mL of hexane was stirred for 25 h at 60 °C and was then worked up as described for **12**. Dark-violet crystals were obtained; yield 127 mg (67%); mp 97 °C dec. Anal. Calcd for $C_{29}H_{56}ClP_2RhSi$: C, 55.01; H, 8.92. Found: C, 54.96; H, 8.79. IR (hexane): *ν*(C=C) 1642 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 200 MHz): *δ* 7.64 (m, 2H, C$_6$*H*$_5$), 7.04 (m, 3H, C$_6$*H*$_5$), 2.69 (m, 6H, PC*H*CH$_3$), 1.35 (dvt, *N* = 14.0, *J*(HH) = 7.1 Hz, 18H, PCHC*H*$_3$), 1.27 (dvt, *N* = 13.6, *J*(HH) = 7.0 Hz, 18H, PCHC*H*$_3$), 0.37 (s, 9H, SiC*H*$_3$). $^{13}$C NMR ($C_6D_6$, 22.5 MHz): *δ* 286.68 (dt, *J*(RhC) = 60.7, *J*(PC) = 14.7 Hz, Rh=*C*=C), 128.42, 127.58, 125.65, 124.93 (all s, *C*$_6$H$_5$), 106.44 (dt, *J*(RhC) = 14.5 Hz, *J*(PC) = 4.9 Hz, Rh=C=*C*), 24.80 (vt, *N* = 19.6 Hz, P*C*HCH$_3$), 20.85, 20.50 (both s, PCH*C*H$_3$), 1.13 (s, Si*C*H$_3$). $^{29}$Si NMR ($C_6D_6$, 17.8 MHz): *δ* −15.86 (t, *J*(PSi) = 1.8 Hz). $^{31}$P NMR ($C_6D_6$, 36.2 MHz): *δ* 41.62 (d, *J*(RhP) = 136.3 Hz).

**Preparation of *trans*-[RhCl(=C=C(SiMe$_3$)CO$_2$Et)(P*i*Pr$_3$)$_2$] (14).** A solution of **4** (264 mg, 0.42 mmol) in 30 mL of benzene was irradiated for 4 h at room temperature with a 500-W UV lamp (Osram HBO). A color change from orange-yellow to red-violet occurred. The solvent was removed, and the residue was dissolved in 2–3 mL of hexane. After the solution was stored at −78 °C, violet crystals precipitated which were separated from the mother liquor, washed with pentane (−30 °C), and dried in vacuo; yield 143 mg (54%); mp 116 °C dec. Anal. Calcd for $C_{26}H_{56}ClO_2P_2RhSi$: C, 49.64; H, 8.97. Found: C, 49.61; H, 9.19. IR (hexane): *ν*(C=O) 1675, *ν*(C=C) 1585 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 200 MHz): *δ* 4.03 (q, *J*(HH) = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 2.69 (m, 6H, PC*H*CH$_3$), 1.32 (dvt, *N* = 13.7, *J*(HH) = 7.1 Hz, 36H, PCHC*H*$_3$), 1.03 (t, *J*(HH) = 7.1 Hz, 3H, OCH$_2$C*H*$_3$), 0.39 (s, 9H, SiC*H*$_3$). $^{13}$C NMR ($C_6D_6$, 50.3 MHz): *δ* 284.13 (dt, *J*(RhC) = 63.1, *J*(PC) = 13.1 Hz, Rh=*C*=C), 159.40 (s, *C*O$_2$Et), 105.71 (dt, *J*(RhC) = 15.3 Hz, *J*(PC) = 4.4 Hz, Rh=C=*C*), 59.85 (s, O*C*H$_2$CH$_3$), 24.66 (vt, *N* = 19.9 Hz, P*C*HCH$_3$), 20.55, 20.35 (both s, PCH*C*H$_3$), 14.47 (s, OCH$_2$*C*H$_3$), 0.19 (s, Si*C*H$_3$). $^{31}$P NMR ($C_6D_6$, 36.2 MHz): *δ* 43.08 (d, *J*(RhP) = 136.3 Hz). UV (hexane): λ(CT) 414, λ(π–π*) 250, 226 nm.

**Preparation of *trans*-[RhCl(=C=C(SiMe$_3$)CO$_2$SiMe$_3$)(P*i*Pr$_3$)$_2$] (15).** This compound was prepared analogously as described for **14**, using **5** (283 mg, 0.42 mmol) as starting material. Violet crystals were obtained; yield 167 mg (59%); mp 107 °C dec. Anal. Calcd for $C_{27}H_{60}ClO_2P_2RhSi_2$: C, 48.17; H, 8.98. Found: C, 47.87; H, 9.12. IR (THF): *ν*(C=O) 1675, *ν*(C=C) 1580 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 200 MHz): *δ* 2.68 (m, 6H, PC*H*CH$_3$), 1.33 (dvt, *N* = 13.9, *J*(HH) = 7.1 Hz, 18H, PCHC*H*$_3$), 1.32 (dvt, *N* = 13.5, *J*(HH) = 7.1 Hz, 18H, PCHC*H*$_3$), 0.35, 0.31 (s, 18H, SiC*H*$_3$). $^{13}$C NMR ($C_6D_6$, 50.3 MHz): *δ* 284.82 (dt, *J*(RhC) = 62.1, *J*(PC) = 13.8 Hz, Rh=*C*=C), 159.62 (s, *C*O$_2$SiMe$_3$), 104.70 (dt, *J*(RhC) = 15.3 Hz, *J*(PC) = 4.4 Hz, Rh=C=*C*) 24.73 (vt, *N* = 21.1 Hz, P*C*HCH$_3$), 20.66, 20.32 (both s, PCH*C*H$_3$), 0.06, 0.03 (both s, Si*C*H$_3$). $^{29}$Si NMR ($C_6D_6$, 17.8 MHz): *δ* 20.74 (s, O*Si*Me$_3$), −11.32 (t, *J*(PSi) = 1.5 Hz, =C*Si*Me$_3$). $^{31}$P NMR ($C_6D_6$, 36.2 MHz): *δ* 43.52 (d, *J*(RhP) = 136.3 Hz).

**Preparation of [Rh$_2$H$_2$Cl$_2$(P*i*Pr$_3$)$_4$(μ-Me$_2$SiC≡CSiMe$_2$)] (16).** A solution of **1** (268 mg, 0.58 mmol for *n* = 1) in 20 mL of pentane was treated at 0 °C with HMe$_2$SiC≡CSiMe$_2$H (120 mg, 0.84 mmol) and, after warming to room temperature, stirred for 30 min. A light-yellow solid precipitated which was filtered off, repeatedly washed with pentane until the filtrate became colorless, and dried in vacuo; yield 277 mg (90%); mp 102 °C dec. Anal. Calcd for $C_{42}H_{98}Cl_2P_4Rh_2Si_2$: C, 47.59; H, 9.32. Found: C, 47.73; H, 9.61. IR (KBr): *ν*(RhH) 2108 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 200 MHz): *δ* 2.71 (m, 12H, PC*H*CH$_3$), 1.35 (dvt, *N* = 13.9, *J*(HH) = 7.0 Hz, 36H, PCHC*H*$_3$), 1.25 (dvt, *N* = 13.5, *J*(HH) = 6.6 Hz, 36H, PCHC*H*$_3$), 0.93 (s, 12H, SiC*H*$_3$), −16.34 (dt, *J*(RhH) = 21.5, *J*(PH) = 13.1 Hz, 2H, Rh*H*). $^{29}$Si NMR ($CD_2Cl_2$, 17.8 MHz, −35 °C): *δ* 14.52 (dt, *J*(RhSi) = 36.4, *J*(PSi) = 9.7 Hz). $^{31}$P NMR ($CD_2Cl_2$, 36.2 MHz, −35 °C): *δ* 44.74 (d, *J*(RhP) = 115.7 Hz; dd in off-resonance).

**Preparation of [RhH(C≡CSiMe$_3$)Cl(P*i*Pr$_3$)$_2$] (18).** A solution of **1** (122 mg, 0.27 mmol for *n* = 1) in 10 mL of pentane was treated at −30 °C dropwise with HC≡CSiMe$_3$ (38 μL, 0.27 mmol). A spontaneous color change from violet to orange occurred. The solvent was quickly removed (at −30 °C), the residue was dissolved in 2 mL of ether, and 8 mL of nitromethane was added. The further workup procedure was the same as that described for **2–7**. Orange-yellow, air-sensitive crystals were obtained; yield 115 mg (78%); mp 46 °C (rearrangement to **19**). Anal. Calcd for $C_{23}H_{52}ClP_2RhSi$: C, 49.59; H, 9.41. Found: C, 49.34; H, 9.44. IR ($CHCl_3$): *ν*(RhH) 2220, (C≡C) 2035 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 90 MHz): *δ* 2.84 (m, 6H, PC*H*CH$_3$), 1.34 (dvt, *N* = 13.6, *J*(HH) = 7.1 Hz, 18H, PCHC*H*$_3$), 1.26 (dvt, *N* = 13.6, *J*(HH) = 7.1 Hz, 18H, PCHC*H*$_3$), 0.08 (s, 9H, SiC*H*$_3$), −27.44 (dt, *J*(RhH) = 43.0, *J*(PH) = 24.4 Hz, 1H, Rh*H*). $^{31}$P NMR ($CDCl_3$, 36.2 MHz, −50 °C): *δ* 49.29 (d, *J*(RhP) = 99.6 Hz).

**Preparation of *trans*-[RhCl(=C=CHSiMe$_3$)(P*i*Pr$_3$)$_2$] (19).** (a) A solution of 18 (30 mg, 0.05 mmol) in 5 mL of hexane was stirred at 40 °C for 2 h. A color change from orange-yellow to red-violet occurred. The solution was concentrated to ca. 0.5 mL in vacuo and then stored at −78 °C for 12 h. A violet crystalline solid precipitated which was separated from the mother liquor, washed with 1 mL of pentane (−30 °C) and dried in vacuo; yield 25 mg (83%). (b) A solution of 1 (64 mg, 0.14 mmol for $n$ = 1) in 8 mL of hexane was treated at room temperature with $\mathrm{HC{\equiv}CSiMe_3}$ (20 $\mu$L, 0.14 mmol) and then stirred at 40 °C for 2 h. The workup procedure was the same as for (a); yield 61 mg (79%); mp 93 °C. Anal. Calcd for $\mathrm{C_{23}H_{52}ClP_2RhSi}$: C, 49.59; H, 9.41. Found: C, 49.82; H, 9.60. IR (KBr): $\nu$(C=C) 1625 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 90 MHz): $\delta$ 2.93 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.46 (dvt, $N$ = 13.4, $J$(HH) = 7.3 Hz, 36H, $\mathrm{PCHC}H_3$), 0.21 (s, 9H, $\mathrm{SiC}H_3$), −0.39 (dt, $J$(RhH) = 1.8, $J$(PH) = 2.9 Hz, 1H, $=\!\mathrm{C}H\mathrm{SiMe_3}$). $^{13}$C NMR ($\mathrm{C_6D_6}$, 22.5 MHz): $\delta$ 281.78 (dt, $J$(RhC) = 57.6, $J$(PC) = 15.6 Hz, $\mathrm{Rh{=}}C\mathrm{{=}C}$), 88.76 (dt, $J$(RhC) = 16.6 Hz, $J$(PC) = 4.9 Hz, $\mathrm{Rh{=}C{=}}C$), 23.73 (vt, $N$ = 19.6 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 20.44 (s, $\mathrm{PCH}C\mathrm{H_3}$), 0.99 (s, $\mathrm{Si}C\mathrm{H_3}$). $^{31}$P NMR ($\mathrm{C_6D_6}$, 36.2 MHz): $\delta$ 42.30 (d, $J$(RhP) = 137.7 Hz).

**Preparation of [RhH(C≡CSiMe$_3$)Cl(py)(P*i*Pr$_3$)$_2$] (20).** (a) A solution of 18 (65 mg, 0.12 mmol) in 10 mL of pentane was treated at room temperature with excess pyridine (0.1 mL). Almost immediately a white solid precipitated which after 10 min was filtered off, repeatedly washed with pentane (−30 °C), and dried in vacuo; yield 69 mg (92%). (b) A solution of **19** (53 mg, 0.10 mmol) in 10 mL of pentane was treated at room temperature with excess pyridine (0.1 mL) and stirred for 2 h. A white precipitate was formed which was isolated as described above; yield 54 mg (90%). (c) A solution of 1 (50 mg, 0.11 mmol for $n$ = 1) in 7 mL of pentane was treated with $\mathrm{HC{\equiv}CSiMe_3}$ (16 $\mu$L, 0.11 mmol) and pyridine (0.1 mL) and stirred for 2 h at room temperature. The reaction mixture was worked up as described above; yield 55 mg (79%); mp 78 °C dec. Anal. Calcd for $\mathrm{C_{28}H_{57}ClNP_2RhSi}$: C, 52.87; H, 9.03; N, 2.20. Found: C, 52.61; H, 9.04; N, 2.15. IR (KBr): $\nu$(RhH) 2180, (C≡C) 2030 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta$ 7.05 (m, 5H, $\mathrm{NC_5}H_5$), 2.60 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.39 (dvt, $N$ = 13.2, $J$(HH) = 7.3 Hz, 18H, $\mathrm{PCHC}H_3$), 1.36 (dvt, $N$ = 13.1, $J$(HH) = 7.2 Hz, 18H, $\mathrm{PCHC}H_3$), 0.47 (s, 9H, $\mathrm{SiC}H_3$), −17.01 (dt, $J$(RhH) = 13.9, $J$(PH) = 13.9 Hz, 1H, $\mathrm{Rh}H$). $^{31}$P NMR ($\mathrm{C_6D_6}$, 36.2 MHz): $\delta$ 37.51 (d, $J$(RhP) = 101.8 Hz).

**Preparation of *trans*-[Rh(C≡CSiMe$_3$)(py)(P*i*Pr$_3$)$_2$] (21).** A solution of **20** (343 mg, 0.54 mmol) in 20 mL of freshly distilled THF was treated at 0 °C first with pyridine (1 mL) and then with a solution of $\mathrm{Na[N(SiMe_3)_2]}$ (99 mg, 0.54 mmol) in 5 mL of THF. After the reaction mixture was stirred for 2 min, the solvent was removed, and the orange-red residue was extracted three times with 5 mL of hexane (−30 °C). The combined extracts were concentrated in vacuo until a precipitate appeared, and then stored at −78 °C. Yellow air-sensitive crystals were formed which were separated from the mother liquor, washed with pentane (−78 °C), and dried in vacuo; yield 277 mg (85%); mp 74 °C dec. IR ($\mathrm{CHCl_3}$): $\nu$(C≡C) 2010 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta$ 6.60, 6.21 (both m, 5H, $\mathrm{NC_5}H_5$), 2.30 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.37 (dvt, $N$ = 12.6, $J$(HH) = 7.0 Hz, 36H, $\mathrm{PCHC}H_3$), 0.38 (s, 9H, $\mathrm{SiC}H_3$). $^{31}$P NMR ($\mathrm{C_6D_6}$, 36.2 MHz): $\delta$ 40.10 (d, $J$(RhP) = 152.4 Hz).

**Preparation of *trans*-[Rh(C≡CSiMe$_3$)(C$_2$H$_4$)(P*i*Pr$_3$)$_2$] (22).** A solution of 18 (302 mg, 0.54 mmol) in 25 mL of pentane was treated at −78 °C under an ethene atmosphere with $\mathrm{Na[N(SiMe_3)_2]}$ (120 mg, 0.65 mmol). By warming to room temperature, the solution was stirred for 15 min, and then the solvent was removed. The residue was extracted three times with 5 mL of pentane (−30 °C), the combined extracts were concentrated in vacuo to ca. 2 mL, and the concentrate was stored at −78 °C. Orange, moderately air-sensitive crystals precipitated which were separated out, washed with 1 mL of pentane (−78 °C), and dried in vacuo; yield 208 mg (70%). (b) A solution of 1 (281 mg, 0.61 mmol for $n$ = 1) in 10 mL of ether was treated at room temperature with $\mathrm{HC{\equiv}CSiMe_3}$ (108 $\mu$L, 0.76 mmol). The solvent was removed, and the oily residue was dissolved in 25 mL of pentane. The further reaction with $\mathrm{Na[N(SiMe_3)_2]}$ and ethene was performed as described for (a); yield 228 mg (68%); mp 65 °C dec. Anal. Calcd for $\mathrm{C_{25}H_{55}P_2RhSi}$: C, 54.73; H, 10.10. Found: C, 54.76; H, 10.43. IR (hexane): $\nu$(C≡C) 1996 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta$ 3.19 (dt, $J$(RhH) = 1.6, $J$(PH) = 3.3 Hz, 4H, $\mathrm{C_2}H_4$), 2.43 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.30 (dvt, $N$ = 13.0, $J$(HH) = 6.9 Hz, 36H, $\mathrm{PCHC}H_3$), 0.27 (s, 9H, $\mathrm{SiC}H_3$). $^{13}$C NMR ($\mathrm{C_6D_6}$, 100.6 MHz): $\delta$ 150.61 (dt, $J$(RhC) = 45.7, $J$(PC) = 20.1 Hz, $\mathrm{Rh{-}}C\mathrm{{\equiv}C}$), 125.81 (d, $J$(RhC) = 12.3, $\mathrm{Rh{-}C{\equiv}}C$), 55.56 (d, $J$(RhC) = 9.6 Hz, $\mathrm{C_2H_4}$), 23.32 (vt, $N$ = 17.3 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 20.66 (s, $\mathrm{PCH}C\mathrm{H_3}$), 1.05 (s, $\mathrm{Si}C\mathrm{H_3}$). $^{31}$P NMR ($\mathrm{C_6D_6}$, 81.0 MHz): $\delta$ 39.38 (d, $J$(RhP) = 129.4 Hz).

**Preparation of [RhH(C≡CSiMe$_3$)$_2$(P*i*Pr$_3$)$_2$] (23).** A solution of 22 (100 mg, 0.18 mmol) in 10 mL of pentane was treated at −78 °C dropwise with $\mathrm{HC{\equiv}CSiMe_3}$ (25 $\mu$L, 0.18 mmol) and was then slowly warmed to room temperature. After a change of color from orange-red to yellow had occurred, the solution was concentrated to ca. 2 mL in vacuo and then stored at −78 °C. A yellow air-sensitive solid precipitated which was filtered off, repeatedly washed with pentane (−30 °C), and dried in vacuo; yield 102 mg (91%); mp 67 °C dec. Anal. Calcd for $\mathrm{C_{28}H_{61}P_2RhSi_2}$: C, 54.35; H, 9.94. Found: C, 54.67; H, 10.36. IR (KBr): $\nu$(C≡C) 2000 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta$ 2.88 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.28 (dvt, $N$ = 13.7, $J$(HH) = 6.9 Hz, 36H, $\mathrm{PCHC}H_3$), 0.24 (s, 18H, $\mathrm{SiC}H_3$), −29.58 (dt, $J$(RhH) = 50.8, $J$(PH) = 11.9 Hz, 1H, $\mathrm{Rh}H$). $^{13}$C NMR ($\mathrm{C_6D_6}$, 50.3 MHz): $\delta$ 146.65 (dt, $J$(RhC) = 34.8, $J$(PC) = 15.1 Hz, $\mathrm{Rh{-}}C\mathrm{{\equiv}C}$), 123.12 (d, $J$(RhC) = 7.2, $\mathrm{Rh{-}C{\equiv}}C$), 24.78 (vt, $N$ = 22.9 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 20.25 (s, $\mathrm{PCH}C\mathrm{H_3}$), 1.35 (s, $\mathrm{Si}C\mathrm{H_3}$). $^{31}$P NMR ($\mathrm{C_6D_6}$, 81.0 MHz): $\delta$ 53.36 (d, $J$(RhP) = 99.5 Hz; dd in off-resonance).

**Preparation of [RhH(C≡CSiMe$_3$)$_2$(py)(P*i*Pr$_3$)$_2$] (24).** (a) A solution of **23** (50 mg, 0.08 mmol) in 5 mL of pentane was treated at room temperature with excess pyridine (0.1 mL). After the reaction mixture was stirred for 30 min, a white solid precipitated which was worked up as described for **23**; yield 49 mg (86%). (b) A solution of **21** (97 mg, 0.16 mmol) in 5 mL of pentane was treated at room temperature dropwise with $\mathrm{HC{\equiv}CSiMe_3}$ (23 $\mu$L, 0.16 mmol). A white solid was formed which was isolated as described above; yield 95 mg (85%); mp 80 °C dec. Anal. Calcd for $\mathrm{C_{33}H_{66}NP_2RhSi_2}$: C, 56.79; H, 9.53; N, 2.01. Found: C, 56.74; H, 9.66; N, 2.27. IR (KBr): $\nu$(C≡C) 2002 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta$ 6.75 (m, 5H, $\mathrm{NC_5}H_5$), 2.96 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.24 (dvt, $N$ = 13.1, $J$(HH) = 6.9 Hz, 36H, $\mathrm{PCHC}H_3$), 0.33 (s, 18H, $\mathrm{SiC}H_3$), −18.00 (dt, $J$(RhH) = 16.7, $J$(PH) = 14.5 Hz, 1H, $\mathrm{Rh}H$). $^{13}$C NMR ($\mathrm{C_6D_6}$, 50.3 MHz): $\delta$ 155.18, 136.06, 123.35 (all s, $\mathrm{N}C_5\mathrm{H_5}$) 149.85 (dt, $J$(RhC) = 33.7, $J$(PC) = 15.0 Hz, $\mathrm{Rh{-}}C\mathrm{{\equiv}C}$), 113.99 (d, $J$(RhC) = 5.9 Hz, $\mathrm{Rh{-}C{\equiv}}C$), 25.45 (vt, $N$ = 22.0 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 19.80 (s, $\mathrm{PCH}C\mathrm{H_3}$), 1.69 (s, $\mathrm{Si}C\mathrm{H_3}$). $^{31}$P NMR ($\mathrm{C_6D_6}$, 81.0 MHz): $\delta$ 42.26 (d, $J$(RhP) = 98.1 Hz; dd in off-resonance).

**Preparation of *trans*-[Rh(C≡CSiMe$_3$)(Me$_3$SiC≡CCO$_2$Et)(P*i*Pr$_3$)$_2$] (25).** A solution of **22** (140 mg, 0.26 mmol) in 5 mL of toluene was treated at −78 °C with $\mathrm{Me_3SiC{\equiv}CCO_2Et}$ (55 $\mu$L, 0.29 mmol) and was then slowly warmed to room temperature. After the reaction mixture was stirred for 4 h, the solvent was removed, the oily residue was dissolved in 5 mL of hexane, and the solution was chromatographed on $\mathrm{Al_2O_3}$ (neutral, activity grade V, height of column 1 cm). With hexane, an orange-red fraction was eluted which was concentrated to ca. 2 mL in vacuo and then stored at −78 °C. Red air-sensitive crystals precipitated which were filtered off, washed with small quantities of pentane (−30 °C) and dried in vacuo; yield 100 mg (57%); mp 46 °C dec. Anal. Calcd for $\mathrm{C_{31}H_{65}O_2P_2RhSi_2}$: C, 53.89; H, 9.48. Found: C, 53.16; H, 9.03. IR (KBr): $\nu$(C≡C) 1998, 1835, $\nu$(C=O) 1685 cm$^{-1}$. $^1$H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta$ 4.01 (q, $J$(HH) = 7.1 Hz, 2H, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.42 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.31 (dvt, $N$ = 14.0, $J$(HH) = 6.8 Hz, 18H, $\mathrm{PCHC}H_3$), 1.23 (dvt, $N$ = 14.1, $J$(HH) = 7.0 Hz, 18H, $\mathrm{PCHC}H_3$), 1.00 (t, $J$(HH) = 7.1 Hz, 3H, $\mathrm{OCH_2C}H_3$), 0.29, 0.20 (both s, 18H, $\mathrm{SiC}H_3$). $^{31}$P NMR ($\mathrm{C_6D_6}$, 81.0 MHz): $\delta$ 40.43 (d, $J$(RhP) = 123.5 Hz).

**Preparation of *trans*-[Rh(C≡CSiMe$_3$)(Me$_3$SiC≡CCO$_2$SiMe$_3$)(P*i*Pr$_3$)$_2$] (26).** A solution of **22** (135 mg, 0.25 mmoL) in 10 mL of hexane was treated at −78 °C with $\mathrm{Me_3SiC{\equiv}CCO_2}$-

SiMe$_3$ (70 $\mu$L, 0.30 mmol), and was then slowly warmed to room temperature. After the reaction mixture was stirred for 1 h, the solvent was removed, the oily residue was dissolved in 3 mL of pentane, and the solution was stored at −78 °C. Orange-red air-sensitive crystals precipitated which were filtered off, washed with small quantities of pentane (−30 °C), and dried in vacuo; yield 124 mg (69%); mp 51 °C dec. Anal. Calcd for $C_{32}H_{69}O_2P_2RhSi_3$: C, 52.29; H, 9.46. Found: C, 52.38; H, 10.28. IR (KBr): $\nu(C\equiv C)$ 1987, 1820, $\nu(C{=}O)$ 1665 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 200 MHz): $\delta$ 2.46 (m, 6H, PC*H*CH$_3$), 1.36 (dvt, *N* = 13.9, *J*(HH) = 7.0 Hz, 18H, PCHC*H*$_3$), 1.26 (dvt, *N* = 13.4, *J*(HH) = 6.8 Hz, 18H, PCHC*H*$_3$), 0.33, 0.32, 0.26 (all s, 27H, SiC*H*$_3$). $^{31}$P NMR ($C_6D_6$, 81.0 MHz): $\delta$ 40.58 (d, *J*(RhP) = 123.5 Hz).

**Reaction of 22 with $C_5H_6$.** A solution of **22** (180 mg, 0.33 mmol) in 10 mL of pentane was treated at −50 °C with an excess of freshly distilled cyclopentadiene (0.1 mL) and, under warming to room temperature, stirred for 15 min. The volatile substances were removed in vacuo, and the oily residue was dissolved in 5 mL of pentane. After the solution was treated with $CH_3I$ (0.1 mL), it was stirred for 20 min, and then the white precipitate of [PMe*i*Pr$_3$]I was filtered off. The yellow filtrate was concentrated to ca. 1 mL, and the solution was chromatographed on $Al_2O_3$ (neutral, activity grade V, height of column 2 cm) with hexane. Two yellow fractions were eluted of which the first contained a 9:1 mixture of [$C_5H_5Rh({=}C{=}CHSiMe_3)$(P*i*Pr$_3$)] (**27**) and the isomer [$C_5H_5RhH(C\equiv CSiMe_3)$(P*i*Pr$_3$)] (**28**). The second fraction consisted of a 1:1 mixture of **27** and **28**. Because further attempts to separate the two components remained unsuccessful and led to increasing decomposition of the products, compounds **27** and **28** were characterized by spectroscopic measurements.

**27**: IR (hexane): $\nu(C{=}C)$ 1625 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 400 MHz): $\delta$ 5.22 (s, 5H, C$_5$*H*$_5$), 2.56 (dd, *J*(RhH) = 2.4 Hz, *J*(PH) = 4.0 Hz, 1H, =C*H*SiMe$_3$), 2.06 (m, 3H, PC*H*CH$_3$), 1.07 (dd, *J*(PH) = 13.7, *J*(HH) = 7.1 Hz, 18H, PCHC*H*$_3$), 0.23 (s, 9H, SiC*H*$_3$). $^{13}$C NMR ($C_6D_6$, 100.6 MHz): $\delta$ 304.71 (dd, *J*(RhC) = 65.5, *J*(PC) = 24.9 Hz, Rh=*C*=C), 95.84 (dd, *J*(RhC) = 15.2, *J*(PC) = 2.6 Hz, Rh=C=*C*), 86.04 (s, *C*$_5$H$_5$), 26.59 (d, J(PC) = 12.5 Hz, P*C*HCH$_3$), 20.02 (s, PCH*C*H$_3$), 0.98 (s, Si*C*H$_3$). $^{31}$P NMR ($C_6D_6$, 162 MHz): $\delta$ 74.86 (d, *J*(RhP) = 211.9 Hz).

**28**: IR (hexane): $\nu$(RhH) 2120, $\nu(C\equiv C)$ 2030 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 400 MHz): $\delta$ 5.13 (s, 5H, C$_5$*H*$_5$), 1.68 (m, 3H, PC*H*CH$_3$), 1.03 (dd, *J*(PH) = 14.2, *J*(HH) = 7.0 Hz, 18H, PCHC*H*$_3$), 0.29 (s, 9H, SiC*H*$_3$), −13.09 (dd, *J*(RhH) = 24.0, *J*(PH) = 32.0 Hz, 1H, Rh*H*). $^{31}$P NMR ($C_6D_6$, 162 MHz): $\delta$ 85.19 (d, *J*(RhP) = 142.8 Hz).

**Preparation of [$C_5H_5Rh(PhC\equiv CSiMe_3)$(P*i*Pr$_3$)] (29).** (a) A solid sample of **3** (92 mg, 0.15 mmol) was treated at room temperature with a solution of $NaC_5H_5$ (150 mg, 1.70 mmol) in 10 mL of THF, and the mixture was stirred for 1 h. A color change from yellow to red-brown occurred. The solvent was removed, and the residue was extracted three times with 3 mL of hexane (−30 °C). To remove free P*i*Pr$_3$, the combined extracts were treated with $CH_3I$ (1 mL, 1.61 mmol) and stirred for 30 min at room temperature. The white precipitate was filtered off, and the filtrate was brought to dryness in vacuo. A red, moderately air-stable oil was obtained; yield 50 mg (69%). (b) A solution of **1** (105 mg, 0.23 mmol for *n* = 1) in 10 mL of pentane was treated at 0 °C dropwise with $PhC\equiv CSiMe_3$ (47 $\mu$L, 1.82 mmol) and stirred until a color change from red-violet to yellow had occurred. The solvent was removed in vacuo, and the residue was treated with a solution of $NaC_5H_5$ (160 mg, 1.82 mmol) in 10 mL of freshly distilled THF. The reaction mixture was stirred for 1 h at room temperature and worked up as described for (a); yield 70 mg (61%). Anal. Calcd for $C_{25}H_{40}PRhSi$: C, 59.75; H, 8.02. Found: C, 59.97; H, 8.26. IR (hexane): $\nu(C\equiv C)$ 1795 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 90 MHz): $\delta$ 7.5 (m, 5H, C$_6$*H*$_5$), 5.28 (dd, *J*(RhH) = 0.6, *J*(PH) = 1.3 Hz, 5H, C$_5$*H*$_5$), 1.58 (m, 3H, PC*H*CH$_3$), 1.00 (dd, *J*(PH) = 13.4, *J*(HH) = 7.0 Hz, 9H, PCHC*H*$_3$), 0.86 (dd, *J*(PH) = 13.4, *J*(HH) = 7.0 Hz, 9H, PCHC*H*$_3$), 0.41 (s, 9H, SiC*H*$_3$). $^{13}$C NMR ($C_6D_6$, 22.5 MHz): $\delta$ 133.79, 131.38, 127.51, 125.76 (all s, *C*$_6$H$_5$), 117.36 (dd, *J*(RhC) = 14.6, *J*(PC) = 4.4 Hz, one C of $C\equiv C$), 84.72 (dd, *J*(RhC) = 2.9 Hz, *J*(PC) = 2.9 Hz, *C*$_5$H$_5$), 25.21 (dd, J(RhC) = 1.4, J(PC) = 20.5 Hz, P*C*HCH$_3$), 19.47 (s, PCH*C*H$_3$), 0.97 (s, Si*C*H$_3$); signal of second C of $C\equiv C$ not exactly located. $^{31}$P NMR ($C_6D_6$, 36.2 MHz): $\delta$ 72.6 (d, *J*(RhP) = 196.3 Hz).

**Preparation of [$C_5H_5Rh(Me_3SiC\equiv CCO_2Et)$(P*i*Pr$_3$)] (30).** Analogously as described for **29**, using **4** (115 mg, 0.18 mmol) (route a) or **1** (150 mg, 0.35 mmol for *n* = 1) (route b) as starting materials. A red oil was obtained; yield 66 mg (72%) (route a) or 108 mg (63%) (route b). Anal. Calcd for $C_{22}H_{40}O_2PRhSi$: C, 53.00; H, 8.09. Found: C, 52.82; H, 7.93. IR (hexane): $\nu(C\equiv C)$ 1780, $\nu(C{=}O)$ 1680 cm$^{-1}$. $^1$H NMR ($C_6D_6$, 90 MHz): $\delta$ 5.18 (d, *J*(RhH) = 0.6, *J*(PH) = 1.4 Hz, 5H, C$_5$*H*$_5$), 4.16, 4.13 (both q, *J*(HH) = 7.2 Hz, 2H, OC*H*$_2$CH$_3$), 1.65 (m, 3H, PC*H*CH$_3$), 1.07 (t, *J*(HH) = 7.2 Hz, 3H, OCH$_2$C*H*$_3$), 1.02 (dd, *J*(PH) = 13.1, *J*(HH) = 7.1 Hz, 9H, PCHC*H*$_3$), 0.93 (dd, *J*(PH) = 13.1, *J*(HH) = 7.1 Hz, 9H, PCHC*H*$_3$), 0.39 (s, 9H, SiC*H*$_3$). $^{13}$C NMR ($C_6D_6$, 50.3 MHz): $\delta$ 164.12 (s, *C*O$_2$Et), 107.78 (dd, *J*(RhC) = 19.9, *J*(PC) = 6.5 Hz, one C of $C\equiv C$), 105.27 (dd, *J*(RhC) = 17.3, *J*(PC) = 4.5 Hz, one C of $C\equiv C$), 85.37 (dd, *J*(RhC) = 3.5, *J*(PC) = 3.5 Hz, *C*$_5$H$_5$), 60.15 (s, O*C*H$_2$CH$_3$), 25.36 (d, J(PC) = 20.1 Hz, P*C*HCH$_3$), 19.66, 19.32 (both s, PCH*C*H$_3$), 14.60 (s, OCH$_2$*C*H$_3$), 0.79 (s, Si*C*H$_3$). $^{31}$P NMR ($C_6D_6$, 36.2 MHz): $\delta$ 72.7 (d, *J*(RhP) = 205.1 Hz).

**X-ray Structural Analysis of 24.** Single crystals were grown from pentane/toluene. Crystal data (from 23 reflections, 10° < $\theta$ < 14°): orthorhombic, space group $Pna2_1$ (No. 33), $a$ = 19.109(7) Å, $b$ = 17.397(4) Å, $c$ = 12.329(3) Å, $V$ = 4098(2) Å$^3$, $Z$ = 4, $D_{\text{calcd}}$ = 1.13 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 5.6 cm$^{-1}$, crystal size 0.25 × 0.40 × 0.45 mm; Enraf-Nonius CAD4 diffractometer, Mo K$\alpha$ radiation (0.709 30 Å), graphite monochromator, zirkon filter (factor 16.4), $T$ = 293 K, $\omega/2\theta$-scan, maximum $2\theta$ = 54°, 4954 independent reflections measured, 3668 regarded as being observed [$F_o > 3\sigma(F_o)$]. Intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction ($\psi$-scan method) was applied. The minimum transmission was 94.12%. The structure was solved by the Patterson method (SHELXS-86). Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (349 parameters, unit weights, Enraf-Nonius SDP).[31] The position of the metal-bound hydrogen was calculated with the program HYDEX[32] but not refined, and positions of the other hydrogen atoms were calculated according to the ideal geometry (distance C–H 0.95 Å) and used only in structure factor calculations. The methyl groups of the Si(1)Me$_3$ unit showed a 1:1 disorder; both positions were refined independently with isotropic temperature factors. $R$ = 0.032, $R_w$ = 0.036; reflex/parameter ratio 10.5; residual electron density +0.746/−0.229 e Å$^{-3}$.

**Acknowledgment.** We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. We also gratefully acknowledge support by Mrs. A. Burger, Mrs. R. Schedl, and C. P. Kneis (elemental analysis and DTA), Mrs. M. L. Schäfer (NMR measurements), and Degussa AG (chemicals).

**Supplementary Material Available:** Tables of bond lengths and angles and positional and thermal parameters and a Schakal drawing for 24 (8 pages). Ordering information is given on any current masthead page.

OM930695V

---

(31) Frenz, B. A. The Enraf-Nonius CAD4 SDP—a real system for concurrent X-ray data collection and structure determination. In *Computing in Crystallography*; Delft University Press: Delft, Holland, 1978; pp 64–71.

(32) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509–2516.