Stepwise Insertion of Alkylisocyanides into the Metal-Alkyne Bond of Half-Sandwich Type Rhodium Complexes: Synthesis and Structural Characterization of Metallacyclobutenes and Metallacyclopentenes☆

Helmut Werner*, Anja Heinemann, Bettina Windmüller, and Paul Steinert

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

Received April 18, 1996

Key Words: Rhodium complexes / Alkyne complexes / Insertion reactions / Alkyl isocyanides / Metallacycles

The cyclopentadienyl complexes $[C_5H_5Rh(RC{\equiv}CR')(Sb\textit{i}Pr_3)]$ (**5**–**8**), which were prepared from *trans*-$[RhCl(RC{\equiv}CR')(Sb\textit{i}Pr_3)_2]$ (**1**–**4**) and NaC_5H_5 and which contain a labile $Rh-Sb\textit{i}Pr_3$ bond, reacted with CO and CNR″ (R″ = Me, *t*Bu) to give the carbonyl and isocyanide derivatives $[C_5H_5Rh(RC{\equiv}CR')(CO)]$ (**9**–**11**) and $[C_5H_5Rh(RC{\equiv}CR')(CNR'')]$ (**12**–**16**), respectively. On treatment of **12** (R = R′ = Ph; R″ = Me) with $Sb\textit{i}Pr_3$, the metallacyclobutene complex $[C_5H_5Rh\{\kappa^2(C,C)\text{-}C(=NMe)CPh{=}CPh\}(Sb\textit{i}Pr_3)]$ (**17**) was formed; it reacts with excess CNMe or CN*t*Bu to yield the metallacyclopentenes $[C_5H_5Rh\{\kappa^2(C,C)\text{-}C(=NMe)CPh{=}CPhC(=NR)\}(CNR)]$ (**18**, **19**). Similar compounds **20**–**23** containing a five-membered RhC_4 metallacycle were prepared either from $[C_5H_5Rh(RC{\equiv}CR')(Sb\textit{i}Pr_3)]$ (**7**, **8**) or $[C_5H_5Rh(PhC{\equiv}CPh)(CN\textit{t}Bu)]$ (**14**) and excess isocyanide. The crystal and molecular structures of **17** and **18** (R = Me) have been determined.

We had two goals for the work presented in this paper. First, we were interested in whether *trans*-$[RhCl(RC{\equiv}CR')(Sb\textit{i}Pr_3)_2]$ compounds, which we had recently prepared from *trans*-$[RhCl(C_2H_4)(Sb\textit{i}Pr_3)_2]$ and alkynes by ligand exchange[1], would be appropriate starting materials for the synthesis of cyclopentadienyl complexes $[C_5H_5Rh(RC{\equiv}CR')(Sb\textit{i}Pr_3)]$. While compounds $[C_5H_5Rh(RC{\equiv}CR')(PR''_3)]$ containing, e.g., triphenyl- or triisopropyl*phosphane* had already been described[2,3], related derivatives with triaryl- or trialkylstibanes as ligands were unknown.

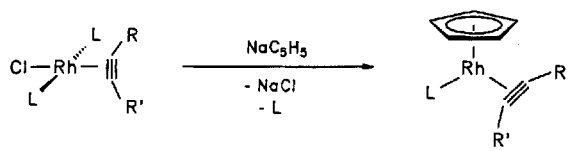
Second, assuming that the half-sandwiches $[C_5H_5Rh(RC{\equiv}CR')(Sb\textit{i}Pr_3)]$ were accessible by this route, we were eager to know whether they would react with CO and isocyanides simply by displacement of the stibane to give $[C_5H_5Rh(RC{\equiv}CR')(CO)]$ and $[C_5H_5Rh(RC{\equiv}CR')(CNR'')]$, respectively, or whether the coupling of CO or CNR″ with the coordinated alkyne would be the preferred reaction pathway. Previously it had been reported by Wakatsuki et al. that on treatment of $[C_5H_5Co(RC{\equiv}CR')(PPh_3)]$ with aryl- or *tert*-butylisocyanides, diiminobutadienecobalt complexes as well as four- and five-membered cobaltacycles are formed, possibly via the non-isolable alkyne-isocyanide compounds $[C_5H_5Co(RC{\equiv}CR')(CNR'')]$ as intermediates[4]. More recently, Hirpo and Curtis observed[5] that the reaction of $[C_5Me_5Ta(PhC{\equiv}CPh)(CH_3)_2]$ with CN*t*Bu and CO gives metallacycles in which, surprisingly, the N*t*Bu group or the oxygen atom is part of the metal-containing five-membered ring system.

Results

Ligand Substitution Reactions

Treating the alkyne complexes **1**–**4** with a fivefold excess of NaC_5H_5 in THF leads to the formation of the half-sandwich compounds **5**–**8** in good to excellent yields (Scheme 1). Whereas the diphenylacetylene derivative **5** has been isolated as red crystals, the analogous compounds **6**–**8** are orange or orange-red oils, which even after storing at −78 °C did not crystallize. Nevertheless, for all the complexes **5**–**8**, correct elemental analyses were obtained. In agreement with the data for the phosphane derivatives $[C_5H_5Rh(RC{\equiv}CR')(P\textit{i}Pr_3)]$[3], the IR spectra of **5**–**8** display an intense C≡C stretching frequency at 1785–1855 cm^{-1}, which is ca. 50 cm^{-1} lower than that for the square planar compounds **1**–**4**[1]. With regard to the NMR data, the most characteristic feature is the appearance of one (**5**)

Scheme 1



1 – 4 **5 – 8**

	R	R'
1, 5	Ph	Ph
2, 6	$SiMe_3$	Ph
3, 7	$SiMe_3$	CO_2Et
4, 8	Me	Ph

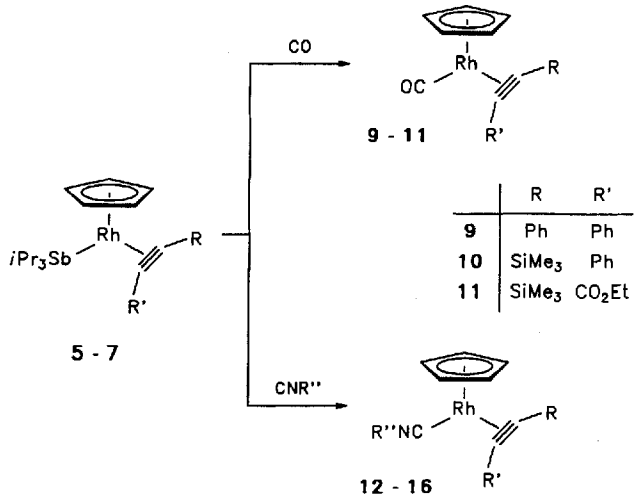
(L = $Sb\textit{i}Pr_3$)

  0009–2940/96/0808–0903 $ 15.00+.25/0

or two doublets (**6**–**8**) in the ^{13}C-NMR spectra for the alkyne carbon atoms between $\delta = 71$ and 112 with a Rh–C coupling of 13–19 Hz.

Like the carbene complex $[C_5H_5Rh(=CPh_2)(SbiPr_3)]$[6], the alkyne compounds **5**–**7** also react quite smoothly with CO in pentane at room temperature by ligand exchange to give the carbonylrhodium derivatives **9**–**11** almost quantitatively. The coordination of a CO ligand is best illustrated by the IR spectra of **9**–**11** in which a strong ν(CO) band at 1985–1995 cm^{-1} is observed. The related isocyanide complexes **12**–**16** (Scheme 2) were prepared by treatment of **5**–**7** with CNMe (−40 to −78 °C) or CN*t*Bu (25 °C) in pentane and – with the exception of **12** – also isolated in excellent yields. The ^{13}C-NMR spectra of **9**–**11** display a characteristic doublet at ca. $\delta = 191$ and those of **13**–**16** one at $\delta = 148$–152. Both show a large Rh–C coupling (82–86 Hz) and are assigned to the *C*O or *C*NR carbon atom, respectively.

Scheme 2



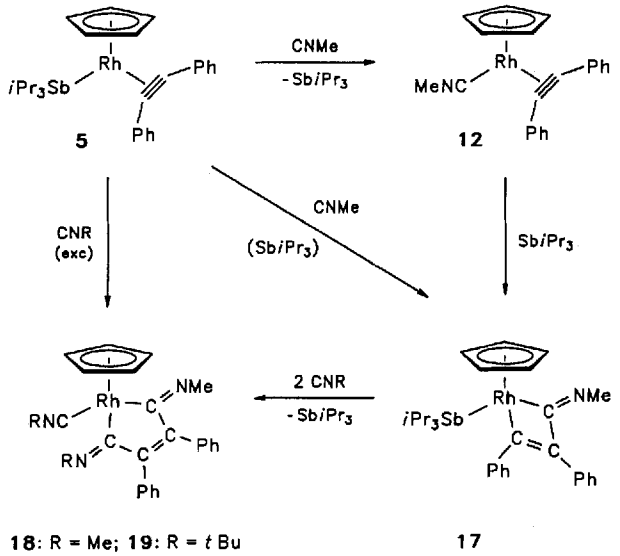
	R	R'
9	Ph	Ph
10	$SiMe_3$	Ph
11	$SiMe_3$	CO_2Et

	12	**13**	**14**	**15**	**16**
R	Ph	$SiMe_3$	Ph	$SiMe_3$	$SiMe_3$
R'	Ph	Ph	Ph	Ph	CO_2Et
R''	Me	Me	*t*Bu	*t*Bu	*t*Bu

Single and Double Isocyanide Insertion Reactions

If the reaction mixture obtained from equimolar amounts of **5** and CNMe in pentane at −78 °C is warmed to room temperature and stirred for 1.5 h, the two components **12** and $SbiPr_3$ react with each other to yield an orange crystalline product, which formally is a 1:1 adduct of the alkyne(isocyanide)rhodium(I) complex and the stibane. The IR spectrum of the new compound **17** does not show a C≡N stretching absorption near 2100 cm^{-1} but displays (in KBr) a sharp band at 1641 cm^{-1}. This observation indicates that the [Rh(PhC≡CPh)(CNMe)] moiety was transformed into a metallacyclobutene ring containing an exocyclic C=N bond. Moreover, since the ^1H-NMR spectrum supports the coordination of a $SbiPr_3$ ligand to the metal centre, the structure shown in Scheme 3 can be assigned to **17**. Although there is precedence for the insertion of isocyanides into metal-alkyne bonds[4,7], we note that in previous investigations it had never been proved whether the coordination of the isocyanide precedes the insertion process. Such an insertion definitely occurs in the formation of **17** from the in situ generated compound **12** and $SbiPr_3$. It should be mentioned that the addition of a twofold excess of the stibane to a solution of **5** and CNMe not only facilitates the formation of **17** but also slightly increases the yield of the metallacyclobutene product.

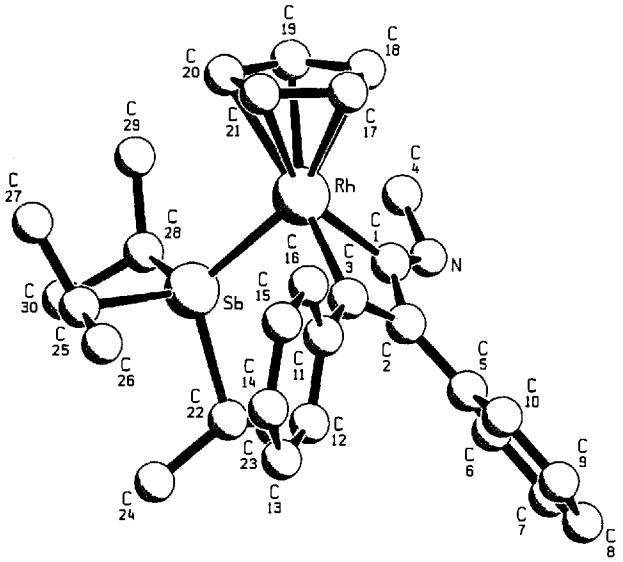
Scheme 3



In order to confirm the cyclic structure proposed for **17**, an X-ray crystal structure investigation was undertaken. As is illustrated in Figure 1, the molecule indeed contains a four-membered RhC_3 ring which is perfectly planar. While one of the bond angles (C1–Rh–C3) of the metallacyclobutene unit is significantly smaller than 90°, the three others are larger and lie between 95.7(2)° and 100.6(2)°. The atoms N, C5 and C11 are almost coplanar with the four-membered ring with a maximum deviation from the ring plane at C5 and C11 of 0.135 Å. The bond length C1–C2 is slightly shorter and the distance C2–C3 slightly longer than in the related cobaltacyclobutenes $[C_5H_5Co\{\kappa^2(C,C)\text{-}C(=NC_6H_4\text{-}4\text{-}Me)CPh=C(CO_2Me)\}(PPh_3)]$ and $[C_5H_5Co\{\kappa^2(C,C)\text{-}C(=NC_6H_4\text{-}4\text{-}Me)C(CO_2Me)=CPh\}(PPh_3)]$[2e]. This finding indicates that the π-electron delocalization in **17** might be more pronounced. Furthermore, not only the metallacyclobutene but also the cyclopentadienyl ring is planar, the dihedral angle between the two planes being 47.8(1)°.

The reaction of **5** with an *excess* of methylisocyanide in pentane at room temperature does not lead to **17** but affords instead the metallacycle **18** in 90% yield. The yellow crystalline compound is only moderately air-sensitive and remarkably thermally stable, decomposing at 186 °C. In contrast to the IR spectrum of **17**, the spectrum of **18** does not only display a C=N stretching frequency at 1595 cm^{-1},

Figure 1. Molecular structure of **17**; selected bond lengths [Å] and angles [°]: Rh–Sb 2.5177(3), Rh–C1 2.067(3), Rh–C2 2.649(3), Rh–C3 2.053(3), Rh–C17 2.235(3), Rh–C18 2.243(3), Rh–C19 2.278(3), Rh–C20 2.286(4), Rh–C21 2.289(3), C1–C2 1.465(4), C2–C3 1.360(4), C1–N 1.260(3), C4–N 1.453(5), C2–C5 1.473(4), C3–C11 1.457(4); Sb–Rh–C1 89.41(7), Sb–Rh–C3 88.85(7), C1–Rh–C3 63.7(1), Rh–C1–C2 95.7(2), Rh–C3–C2 99.2(2), Rh–C1–N 136.6(2), Rh–C3–C11 129.9(2), C1–C2–C3 100.6(2), C1–N–C4 119.8(3), C2–C1–N 127.6(3), C2–C3–C11 130.3(2), C1–C2–C5 127.7(2), C3–C2–C5 131.7(3)

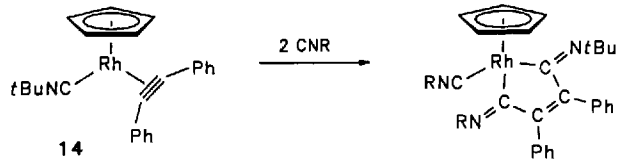


which is assigned to the exocyclic methylimino groups, but it also displays a C≡N absorption at 2189 cm^{-1}; this confirms the presence of a methylisocyanide ligand. In agreement with the structure proposed for **18** (see Scheme 3), the ^{1}H-NMR spectrum shows, in addition to the signals of the C_5H_5 and C_6H_5 protons, two methyl resonances at δ = 3.53 and 1.75 in the ratio of 2:1 which are assigned to the protons of the $=NCH_3$ and $CNCH_3$ groups, respectively.

Complex **18** can not only be prepared from **5** and excess methylisocyanide but also on treatment of **17** with two equiv. of CNMe. In the same way the reaction of **17** with CN*t*Bu yields the metallacycle **19**. Due to the ^{1}H and ^{13}C-NMR spectroscopic data of **19** there is no doubt that one of the *tert*-butylisocyanide molecules is coordinated to the metal while the other has inserted into the Rh–C(Ph) bond to form the five-membered ring. With regard to the mechanism of formation of **18** and **19** from **17** we assume that initially the stibane is displaced by CNR to give a metallacyclobutene derivative containing a metal-bonded isocyanide. This intermediate further reacts by insertion of the CNR ligand into the four-membered ring to yield a coordinatively unsaturated metallacyclopentene, which on addition of a second CNR molecule affords the final product. We note that with cobalt as the metal centre a compound of the composition $[C_5H_5Co\{\kappa^2(C,C)$-$C(=NPh)CPh=CPhC(=NPh)\}]$, formed as an intermediate from $[C_5H_5Co(PhC{\equiv}CPh)(PPh_3)]$ and two equiv. of CNPh, has been isolated and characterized by X-ray structural analysis[4a,c].

The *tert*-butylisocyanide complex **14** reacts with a threefold excess of CNMe or CN*t*Bu to give the metallacyclopentene derivatives **20** and **21** in nearly quantitative yield (Scheme 4). Although we followed the reaction by ^{1}H-NMR spectroscopy, we failed to identify a metallacyclobutene compound, related in structure to **17**, as an intermediate. Nevertheless, the fact that only complex **20** and not the isomeric species $[C_5H_5Rh\{\kappa^2(C,C)$-$C(=NMe)CPh=CPhC(=NMe)\}(CNtBu)]$ is formed from **14** and CNMe, supports the assumption that it is the coordinated isocyanide and not the incoming substrate that is initially inserted into the rhodium-alkyne bond. In agreement with the synthesis of **18** from **5** and excess methylisocyanide (see Scheme 3), the metallacyclopentene complex **21** can similarly be prepared from **5** and CN*t*Bu.

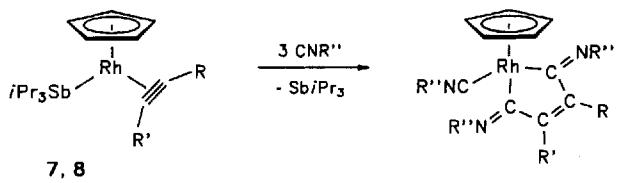
Scheme 4



20: R = Me; **21**: R = *t*Bu

To show that double insertion of either CNMe or CN*t*Bu into the Rh–C bond of a Rh(RC≡CR′) unit is not restricted to R = R′ = Ph, the reactions shown in Scheme 5 have been performed. Under the same conditions as used for the preparation of **18** and **21**, the metallacyclopentenes **22** and **23** were obtained in good to excellent yield. In contrast to **22**, the IR spectrum of **23** (in hexane) displays two bands in the ν(C≡N) region, which is rather surprising with regard to the coordination of only one CN*t*Bu ligand. A similar double splitting, however, has already been observed in the case of *trans*-$[RhCl(CNR)(PR'_3)_2]$[1,8] and $[C_5H_5Rh(C_2H_4)(CNtBu)]$[9] as well as for half-sandwich type arenechromium isocyanide compounds[10].

Scheme 5



	R	R′	R″
22	$SiMe_3$	CO_2Et	Me
23	Me	Ph	*t*Bu

22, 23

The molecular structure of the metallacyclopentene derivative **18**, formed by ring expansion from **17**, is shown in Figure 2. In contrast to the related cobalt complex $[C_5H_5Co\{\kappa^2(C,C)$-$C(=NR)CPh=CPhC(=NR)\}(CNR)]$ (R = 2,6-dimethyl-C_6H_3)[4c], which contains a nearly planar CoC_4 framework (Figure 3), the five-membered RhC_4 ring of **18** is considerably tilted; the rhodium atom lies 0.54(1) Å above the plane of the four carbon atoms. As expected, the three bonds of the C1–C3–C2–C4 unit show a long-

short-long sequence with C–C single and C=C double bond lengths, which are similar to those of the four-membered ring of **17**. The molecule as a whole has a piano stool configuration with C–Rh–C angles of 80.5(2), 85.6(2) and 89.6(2)°, respectively. Both the Rh–C19–N3 and C19–N3–C20 axes are almost linear. The distance Rh–C19 [1.914(7) Å] is relatively short, indicating some back-bonding from the metal to the isocyanide, although the rhodium is in the +3 oxidation state.

Figure 2. Molecular structure of **18**; selected bond lengths [Å] and angles [°]: Rh–C1 2.035(6), Rh–C4 2.022(6), Rh–C19 1.914(7), Rh–C21 2.289(7), Rh–C22 2.199(7), Rh–C23 2.256(6), Rh–C24 2.325(6), Rh–C25 2.345(6), C1–N1 1.256(7), C1–C3 1.494(8), C2–C3 1.344(8), C2–C4 1.481(8), C4–N2 1.267(7), N1–C5 1.453(8), N2–C6 1.455(8), C2–C7 1.487(8), C3–C8 1.478(8), C19–N3 1.149(8), C20–N3 1.430(8); C1–Rh–C4 80.5(2), C1–Rh–C19 85.6(2), C4–Rh–C19 89.6(2), Rh–C1–C3 111.1(4), Rh–C1–N1 129.5(5), Rh–C4–C2 112.0(4), Rh–C4–N2 129.7(5), Rh–C19–N3 174.8(6), C1–N1–C5 122.8(5), C4–N2–C6 121.2(6), C1–C3–C2 115.2(5), C4–C2–C3 115.7(5), C1–C3–C8 120.0(5), C4–C2–C7 120.8(5), C19–N3–C20 175.2(7)

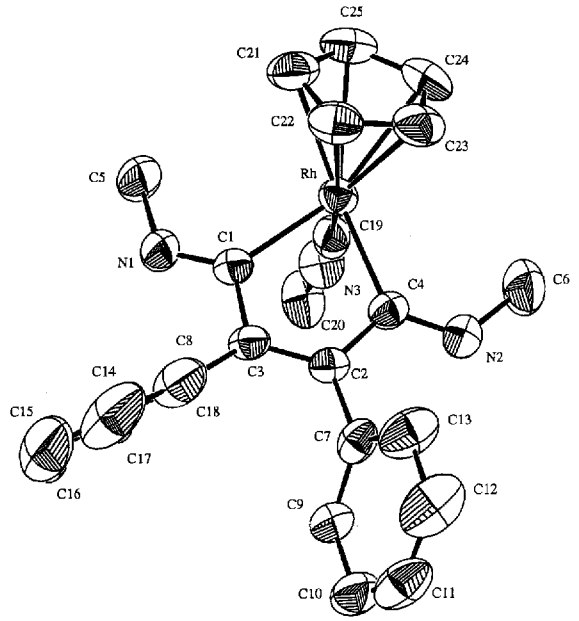
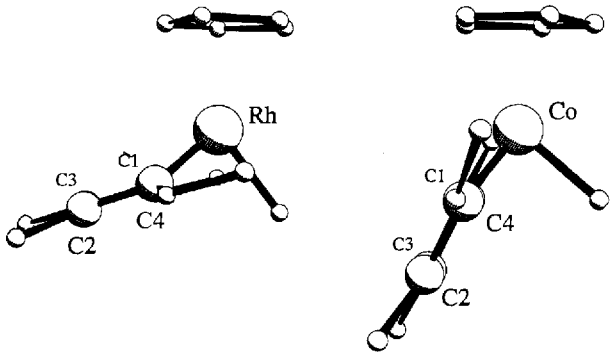


Figure 3. Side view of the molecular structure of **18** and the related cobalt complex $[C_5H_5Co\{\kappa^2(C,C)\text{-}C(=NR)CPh=CPhC(=NR)\}(CNR)]$ (R = 2,6-dimethyl-C_6H_3) (the substituents on the metallacycle and the NR fragments of the isocyanide ligands are omitted for clarity)



Conclusions

The work presented in this paper has confirmed that the double insertion of isocyanides into the rhodium-alkyne bond of half-sandwich type complexes $[C_5H_5Rh(RC{\equiv}CR')(SbiPr_3)]$ occurs stepwise to give metallacyclopentenes via intermediate metallacyclobutenes. The insertion is preceded by the coordination of the isocyanide to rhodium and, therefore, the presence of a weakly bonded ligand such as $SbiPr_3$ in the starting material is necessary. Under the conditions used for the preparation of the metallacyclopentenes **18** and **21**, $PiPr_3$ cannot be displaced by CNMe or CN*t*Bu; therefore the phosphane-substituted compounds $[C_5H_5Rh(RC{\equiv}CR)(PiPr_3)]$ (R = Me, Ph)[3a,b] are completely inert toward CNMe and CN*t*Bu. A remarkable facet of this work regarding the reactivity of alkyne-rhodium complexes **5**–**8** is that isocyanides are much more suitable than CO for insertion reactions, although both types of ligands possess similar donor-acceptor properties and easily displace $SbiPr_3$ in the starting complexes.

This work was supported by the *Deutsche Forschungsgemeinschaft* (SFB 347) and the *Fonds der Chemischen Industrie*. We also thank *Degussa AG* for generous gifts of chemicals, Mrs. *R. Schedl* and Mr. *C. P. Kneis* for elemental analyses and DTA measurements, and Dr. *G. Lange* and Mr. *F. Dadrich* for recording the mass spectra.

Experimental

All operations were carried out under argon with the Schlenk-tube technique. The starting materials **1**–**4** were prepared by published procedures[1]. – IR: Perkin-Elmer 1420. – NMR: Bruker AC 200 and AMX 400. – MS: Varian CH7 MAT and Finnigan 90 MAT (70 eV).

1. *Preparation of* $[C_5H_5Rh(PhC{\equiv}CPh)(SbiPr_3)]$ (**5**): A solution of 118 mg (0.14 mmol) of **1** in 15 ml of THF was treated with 62 mg (0.70 mmol) of NaC_5H_5 and stirred for 1.5 h at room temp. The solvent was removed in vacuo, and the residue was extracted with 15 ml of pentane. The extract was concentrated to ca. 4 ml and the solution was stored at −78°C for 20 h. Red crystals precipitated, which were separated from the mother liquor, repeatedly washed with pentane (−20°C) and dried in vacuo; yield 73 mg (87%), m.p. 90°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1815 cm^{-1} [ν(C≡C)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 8.17 (m, 4H, *ortho*-H of C_6H_5), 7.15 (m, 4H, *meta*-H of C_6H_5), 6.96 (m, 2H, *para*-H of C_6H_5), 5.14 (s, 5H, C_5H_5), 1.41 [sept, 3H, *J*(HH) = 7.3 Hz, SbC*H*CH_3], 0.84 [d, 18H, *J*(HH) = 7.3 Hz, SbCHC*H*$_3$]. – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 134.55 (s, *ipso*-C of C_6H_5), 132.15, 128.0, 125.9 (each s, C_6H_5), 88.2 [d, *J*(RhC) = 17.1 Hz, C≡C], 81.95 [d, *J*(RhC) = 3.7 Hz, C_5H_5], 21.35 (s, SbCH*C*H_3), 17.6 [d, *J*(RhC) = 3.7 Hz, Sb*C*HCH$_3$]. – $C_{28}H_{36}RhSb$ (597.3): calcd. C 56.31, H 6.08; found C 56.37, H 6.05.

2. *Preparation of* $[C_5H_5Rh(PhC{\equiv}CSiMe_3)(SbiPr_3)]$ (**6**): A solution of 162 mg (0.20 mmol) of **2** in 15 ml of THF was treated with 88 mg (1.00 mmol) of NaC_5H_5 and stirred for 30 min at room temp. The solvent was removed in vacuo, and the residue was extracted with 15 ml of pentane. The extract was brought to dryness in vacuo, the oily residue was dissolved in 1 ml of hexane, and the

solution was chromatographed on Al_2O_3 (neutral, activity grade III, height of column 6 cm). With hexane, an orange-red fraction was eluted from which, after removal of the solvent, an orange oil was isolated; yield 95 mg (80%). – IR (hexane): $\tilde{\nu}$ = 1808 cm^{-1} [ν(C≡C)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 8.05 (m, 2H, *ortho*-H of C_6H_5), 7.26 (m, 2H, *meta*-H of C_6H_5), 7.12 (m, 1H, *para*-H of C_6H_5), 5.24 (s, 5H, C_5H_5), 1.76 [sept, 3H, *J*(HH) = 7.3 Hz, SbC*H*CH_3], 1.08 and 1.03 [both d, 18H, *J*(HH) = 7.3 Hz, SbCHC*H*$_3$], 0.45 [s, 9H, $Si(CH_3)_3$]. – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 134.45 (s, *ipso*-C of C_6H_5), 132.6, 127.9, 126.5 (each s, C_6H_5), 111.9 [d, *J*(RhC) = 17.4 Hz, *C*≡C], 81.4 [d, *J*(RhC) = 3.3 Hz, C_5H_5], 77.45 [d, *J*(RhC) = 13.1 Hz, C≡*C*], 21.6, 21.5 (both s, SbCH*C*H_3), 17.6 [d, *J*(RhC) = 2.2 Hz, Sb*C*HCH$_3$], 1.3 [s, $Si(CH_3)_3$]. – ^{29}Si NMR (79.50 MHz, C_6D_6): δ = –13.8 [d, *J*(RhSi) = 2.4 Hz]. – $C_{25}H_{40}RhSbSi$ (593.3): calcd. C 50.61, H 6.80; found C 50.83, H 6.86.

3. *Preparation of [$C_5H_5Rh(Me_3SiC{\equiv}CCO_2Et)(SbiPr_3)$]* (**7**): Compound **7** was prepared analogous to **6** by using 95 mg (0.12 mmol) of **3** and 53 mg (0.60 mmol) of NaC_5H_5 as starting materials; orange-red oil, yield 53 mg (75%). – IR (hexane): $\tilde{\nu}$ = 1786 cm^{-1} [ν(C≡C)], 1687 [ν(C=O)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 5.16 (s, 5H, C_5H_5), 4.19 [dq, 1H, $J(H^aH^{a'})$ = 10.8, $J(H^aH^b)$ = 7.2 Hz, $CO_2CH^aH^{a'}CH_3^b$], 4.14 [dq, 1H, $J(H^aH^{a'})$ = 10.8, $J(H^{a'}H^b)$ = 7.2 Hz, $CO_2CH^aH^{a'}CH_3^b$], 1.76 [sept, 3H, *J*(HH) = 7.3 Hz, SbC*H*CH_3], 1.15, 1.12 [both d, 18H, *J*(HH) = 7.0 Hz, SbCHC*H*$_3$], 1.10 [t, 3H, *J*(HH) = 7.2 Hz, $CO_2CH_2CH_3$], 0.37 [s, 9H, $Si(CH_3)_3$]. – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 164.2 (s, *C*$O_2CH_2CH_3$), 102.0 [d, *J*(RhC) = 19.1 Hz, *C*≡C], 100.5 [d, *J*(RhC) = 12.7 Hz, C≡*C*], 81.6 [d, *J*(RhC) = 3.8 Hz, C_5H_5], 60.15 (s, $CO_2CH_2CH_3$), 21.5, 21.4 (both s, SbCH*C*H_3), 17.7 [d, *J*(RhC) = 2.5 Hz, Sb*C*HCH$_3$], 14.6 (s, $CO_2CH_2CH_3$), 0.4 [s, $Si(CH_3)_3$]. – $C_{22}H_{40}O_2RhSbSi$ (589.3): calcd. C 44.84, H 6.84; found C 44.60, H 6.80.

4. *Preparation of [$C_5H_5Rh(MeC{\equiv}CPh)(SbiPr_3)$]* (**8**): Compound **8** was prepared analogous to **6** by using 130 mg (0.17 mmol) of **4** and 75 mg (0.85 mmol) of NaC_5H_5 as starting materials; orange-red oil, yield 58 mg (63%). – IR (hexane): $\tilde{\nu}$ = 1857 cm^{-1} [ν(C≡C)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 7.77 (m, 2H, *ortho*-H of C_6H_5), 7.20 (m, 2H, *meta*-H of C_6H_5), 7.02 (m, 1H, *para*-H of C_6H_5), 5.20 [d, 5H, *J*(RhH) = 0.6 Hz, C_5H_5], 2.51 [d, 3H, *J*(RhH) = 0.7 Hz, ≡CCH_3], 1.72 [sept, 3H, *J*(HH) = 7.3 Hz, SbC*H*CH_3], 1.08 and 1.05 [both d, 18H, *J*(HH) = 7.3 Hz, SbCHC*H*$_3$]. – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 134.5 (s, *ipso*-C of C_6H_5), 131.6, 127.8, 124.8 (each s, C_6H_5), 83.4 [d, *J*(RhC) = 15.7 Hz, *C*≡C], 81.7 [d, *J*(RhC) = 3.8 Hz, C_5H_5], 71.3 [d, *J*(RhC) = 16.4 Hz, C≡*C*], 21.5, 21.45 (both s, SbCH*C*H_3), 17.7 (s, ≡C*C*H_3), 17.5 [d, *J*(RhC) = 2.9 Hz, Sb*C*HCH$_3$]. – $C_{23}H_{34}RhSb$ (535.18): calcd. C 51.62, H 6.40; found C 51.68, H 6.49.

5. *Preparation of [$C_5H_5Rh(PhC{\equiv}CPh)(CO)$]* (**9**): A slow stream of CO was passed for 2 min through a solution of 89 mg (0.15 mmol) of **5** in 15 ml of pentane. After the solution was stirred for 4 h at room temp., the solvent was removed in vacuo, the residue was dissolved in 2 ml of hexane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 4 cm). With hexane, a brigth-yellow fraction was eluted, which was brought to dryness in vacuo. The residue was dissolved in 3 ml of ether and then stored for 2 d at –78 °C. Yellow crystals were formed, which were separated from the mother-liquor, washed with small quantities of pentane (–20 °C) and dried in vacuo; yield 47 mg (84%), m.p. 110 °C (dec.). – IR (hexane): $\tilde{\nu}$ = 1995 cm^{-1} [ν(CO)], 1860 [ν(C≡C)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 7.94 (m, 4H, *ortho*-H of C_6H_5), 7.20 (m, 4H, *meta*-H of C_6H_5), 7.08 (m, 2H, *para*-H of C_6H_5), 5.09 (s, 5H, C_5H_5). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 190.75 [d, *J*(RhC) = 86.7 Hz, RhCO], 130.45 (s, *ipso*-C of C_6H_5), 132.7, 128.4, 127.65 (each s, C_6H_5), 88.7 [d, *J*(RhC) = 2.9 Hz, C_5H_5], 82.3 [d, *J*(RhC) = 13.6 Hz, C≡C]. – MS; *m/z* (I_r): 374 (6, M^+), 346 (40, M^+ – CO), 178 (72, $C_2Ph_2^+$), 168 (100, $C_5H_5Rh^+$), 103 (15, Rh^+). – $C_{20}H_{15}ORh$ (374.2): calcd. C 64.19, H 4.04; found C 63.78, H 4.30.

6. *Preparation of [$C_5H_5Rh(PhC{\equiv}CSiMe_3)(CO)$]* (**10**): Compound **10** was prepared analogous to **9** by using 147 mg (0.25 mmol) of **6** and 15 ml of pentane; yellow crystalline solid; yield 76 mg (82%), m.p. 97 °C (dec.). – IR (hexane): $\tilde{\nu}$ = 1990 cm^{-1} [ν(CO)], 1870 [ν(C≡C)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 7.90 (m, 2H, *ortho*-H of C_6H_5), 7.21 (m, 2H, *meta*-H of C_6H_5), 7.13 (m, 1H, *para*-H of C_6H_5), 5.15 (s, br, 5H, C_5H_5), 0.37 [s, 9H, $Si(CH_3)_3$]. – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 191.3 [d, *J*(RhC) = 86.7 Hz, RhCO], 133.45, 132.2 (both s, C_6H_5), 130.1 (s, *ipso*-C of C_6H_5), 128.3 (s, C_6H_5), 102.9 [d, *J*(RhC) = 16.6 Hz, *C*≡C], 88.2 [d, *J*(RhC) = 3.5 Hz, C_5H_5], 72.55 [d, *J*(RhC) = 11.7 Hz, C≡*C*], 0.4 [s, $Si(CH_3)_3$]. – ^{29}Si NMR (79.50 MHz, C_6D_6): δ = –11.4 [d, *J*(RhSi) = 1.6 Hz]. – $C_{17}H_{19}ORhSi$ (370.3): calcd. C 55.14, H 5.17; found C 55.20, H 5.19.

7. *Preparation of [$C_5H_5Rh(Me_3SiC{\equiv}CCO_2Et)(CO)$]* (**11**): Compound **11** was prepared analogous to **9**, by using 183 mg (0.31 mmol) of **7** in 15 ml of pentane; orange-yellow oil, yield 94 mg (83%). – IR (hexane): $\tilde{\nu}$ = 1985 cm^{-1} [ν(CO)], 1850 [ν(C≡C)], 1687 [ν(C=O)]. – ^1H NMR (C_6D_6, 400 MHz): δ = 5.07 (s, 5H, C_5H_5), 4.07 [dq, 1H, $J(H^aH^{a'})$ = 10.8, $J(H^aH^b)$ = 7.2 Hz, $CO_2CH^aH^{a'}CH_3^b$], 4.03 [dq, 1H, $J(H^aH^{a'})$ = 10.8, $J(H^{a'}H^b)$ = 7.2 Hz, $CO_2CH^aH^{a'}CH_3^b$], 0.97 [t, 3H, *J*(HH) = 7.2 Hz, $CO_2CH_2CH_3$], 0.39 [s, 9H, $Si(CH_3)_3$]. – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 190.6 [d, *J*(RhC) = 85.5 Hz, RhCO], 161.8 (d, *J*(RhC) = 2.0 Hz, *C*$O_2CH_2CH_3$), 93.4 [d, *J*(RhC) = 18.4 Hz, *C*≡C], 88.5 [d, *J*(RhC) = 3.5 Hz, C_5H_5], 87.8 [d, *J*(RhC) = 11.4 Hz, C≡*C*], 61.45 (s, $CO_2CH_2CH_3$), 14.2 (s, $CO_2CH_2CH_3$), –0.5 [s, $Si(CH_3)_3$]. – ^{29}Si NMR (79.50 MHz, C_6D_6): δ = –11.9 [d, *J*(RhSi) = 1.6 Hz]. – $C_{14}H_{19}O_3RhSi$ (366.3): calcd. C 45.91, H 5.23; found C 45.98, H 5.29.

8. *Preparation of [$C_5H_5Rh(PhC{\equiv}CPh)(CNMe)$]* (**12**): A solution of 134 mg (0.22 mmol) of **5** in 15 ml of pentane was treated at –78 °C with 12 µl (0.22 mmol) of CNMe. The solution was stirred for 30 min and during this time warmed to room temp. A change of color from red to orange-yellow occurred. The solvent was removed in vacuo, the oily residue was dissolved in 2 ml of hexane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With hexane, a red fraction was eluted that contained the remaining starting material **5**. With hexane/benzene (1:1) a yellow fraction was obtained from which after evaporation of the solvent and recrystallization of the oily residue from ether at –78 °C yellow crystals were isolated; yield 47 mg (55%). – IR (KBr): $\tilde{\nu}$ = 2133 cm^{-1} [ν(CN)], 1820 [ν(C≡C)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 8.25 (m, 4H, *ortho*-H of C_6H_5), 7.30 (m, 4H, *meta*-H of C_6H_5), 7.15 (m, 2H, *para*-H of C_6H_5), 5.40 [s, br, 5H, C_5H_5], 1.77 [d, 3H, *J*(RhH) = 0.7 Hz, CNCH_3]. – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 132.9 (s, *ipso*-C of C_6H_5), 132.7, 128.4, 126.7 (each s, C_6H_5), 88.2 [d, *J*(RhC) = 15.6 Hz, C≡C], 86.3 [d, *J*(RhC) = 3.6 Hz, C_5H_5], 28.3 (s, RhCN*C*H_3), signal of Rh*C*NCH_3 not observed. – $C_{21}H_{18}NRh$ (387.3): calcd. C 65.13, H 4.68, N 3.62; found C 65.44, H 4.72, N 3.60.

9. *Preparation of [$C_5H_5Rh(PhC{\equiv}CSiMe_3)(CNMe)$]* (**13**): A solution of 94 mg (0.16 mmol) of **6** in 10 ml of pentane was treated at –40 °C with 21 µl (0.38 mmol) of CNMe. After the solution was warmed to room temp., it was stirred for 1 h, then concentrated to

ca. 3 ml in vacuo, and chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With hexane, a yellow fraction was eluted which was brought to dryness in vacuo. The residue was recrystallized from ether at −78 °C to give yellow crystals; yield 50 mg (82%), m.p. 65 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 2096 cm^{-1} [ν(CN)], 1830 [ν(C≡C)]. − ^1H NMR (C_6D_6, 200 MHz): 8.19 (m, 2H, *ortho*-H of C_6H_5), 7.24 (m, 2H, *meta*-H of C_6H_5), 7.10 (m, 1H, *para*-H of C_6H_5), 5.35 [d, 5H, *J*(RhH) = 0.7 Hz, C_5H_5], 1.95 (s, 3H, $CNCH_3$), 0.50 [s, 9H, $Si(CH_3)_3$]. − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 151.4 [d, *J*(RhC) = 82.7 Hz, Rh*C*NCH$_3$], 132.45 (s, *ipso*-C of C_6H_5), 133.2, 128.15, 127.3 (each s, C_6H_5), 109.6 [d, *J*(RhC) = 17.8 Hz, *C*≡C], 85.8 [d, *J*(RhC) = 3.8 Hz, C_5H_5], 77.4 [d, *J*(RhC) = 11.5 Hz, C≡*C*], 28.35 (s, RhCN*C*H$_3$), 0.7 [s, $Si(CH_3)_3$]. − $C_{18}H_{22}NRhSi$ (383.4): calcd. C 56.37, H 5.78, N 3.65; found C 56.58, H 5.81, N 3.68.

10. *Preparation of [C_5H_5Rh(PhC≡CPh)(CNtBu)]* (**14**): A solution of 107 mg (0.18 mmol) of **5** in 15 ml of pentane was treated with 75 µl (0.60 mmol) of CN*t*Bu and stirred for 2 h at room temp. The solvent was removed in vacuo, the residue was dissolved in 5 ml of hexane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With hexane, an almost colorless fraction containing triisopropylstibane, and with hexane/benzene (1:3), a yellow fraction was eluted. The latter was brought to dryness in vacuo, and the residue was recrystallized from ether at −78 °C to give yellow crystals; yields 69 mg (89%), m.p. 108 °C (dec.). − IR (hexane): $\tilde{\nu}$ = 2110, 2065 cm^{-1} [ν(CN)], 1835 [ν(C≡C)]. − ^1H NMR (C_6D_6, 200 MHz): δ = 8.21 (m, 4H, *ortho*-H of C_6H_5), 7.28 (m, 4H, *meta*-H of C_6H_5), 7.12 (m, 2H, *para*-H of C_6H_5), 5.38 (s, 5H, C_5H_5), 0.67 [s, 9H, $CNC(CH_3)_3$]. − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 151.0 [d, *J*(RhC) = 81.8 Hz, Rh*C*NC(CH$_3$)$_3$], 132.9 (s, *ipso*-C of C_6H_5), 132.4, 128.2, 126.5 (each s, C_6H_5), 88.2 [d, *J*(RhC) = 14.6 Hz, C≡C], 86.4 [d, *J*(RhC) = 2.4 Hz, C_5H_5], 56.3 [s, RhCN*C*(CH$_3$)$_3$], 30.6 [s, RhCNC(*C*H$_3$)$_3$]. − $C_{24}H_{24}NRh$ (429.4): calcd. C 67.84, H 5.93, N 3.26; found C 66.71, H 5.46, N 3.18.

11. *Preparation of [C_5H_5Rh(PhC≡CSiMe$_3$)(CNtBu)]* (**15**): A solution of 116 mg (0.20 mmol) of **6** in 20 ml of pentane was treated with 45 µl (0.40 mmol) of CN*t*Bu and stirred for 3 h at room temp. The solvent was removed in vacuo, the oily residue was dissolved in 2 ml of hexane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 4 cm). With hexane, a yellow fraction was eluted from which after evaporation of the solvent and recrystallisation from pentane at −78 °C, yellow crystals were isolated; yield 73 mg (86%), m.p. 91 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 2100, 2057 cm^{-1} [ν(CN)], 1848 [ν(C≡C)]. − ^1H NMR (C_6D_6, 400 MHz): δ = 8.13 (m, 2H, *ortho*-H of C_6H_5), 7.23 (m, 2H, *meta*-H of C_6H_5), 7.09 (m, 1H, *para*-H of C_6H_5), 5.34 [d, 5H, *J*(RhH) = 0.7 Hz, C_5H_5], 0.79 [s, 9H, $CNC(CH_3)_3$], 0.50 [s, 9H, $Si(CH_3)_3$]. − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 152.7 [d, *J*(RhC) = 82.5 Hz, Rh*C*NC(CH$_3$)$_3$], 133.0 (s, *ortho*-C of C_6H_5), 132.6 (s, *ipso*-C of C_6H_5), 127.9, 127.1 (both s, C_6H_5), 109.6 [d, *J*(RhC) = 17.1 Hz, *C*≡C], 85.9 [d, *J*(RhC) = 4.0 Hz, C_5H_5], 77.7 [d, *J*(RhC) = 12.1 Hz, C≡*C*], 55.9 [s, RhCN*C*(CH$_3$)$_3$], 30.85 [s, RhCNC(*C*H$_3$)$_3$], 0.9 [s, $Si(CH_3)_3$]. − ^{29}Si NMR (79.50 MHz, C_6D_6): δ = −13.1 [d, *J*(RhSi) = 2.4 Hz]. − MS; *m/z* (I_r): 425 (4, M^+), 342 (3, M^+ − CN*t*Bu), 251 (4, M^+ − $PhC_2SiMe_3^+$), 195 (100, $C_5H_5RhCNH^+$), 174 (3, $PhC_2SiMe_3^+$), 168 (7, $C_5H_5Rh^+$). − $C_{21}H_{28}RhNSi$ (425.5): calcd. C 59.29, H 6.63, N 3.29; found C 59.39, H 6.61, N 3.34.

12. *Preparation of [C_5H_5Rh(Me$_3$SiC≡CCO$_2$Et)(CNtBu)]* (**16**): Compound **16** was prepared analogous to **14** by using 84 mg (0.14 mmol) of **7** and 19 µl (0.17 mmol) of CN*t*Bu; orange-yellow oil; yield 44 mg (75%). − IR (hexane): $\tilde{\nu}$ = 2100, 2070 cm^{-1} [ν(CN)], 1823 [ν(C≡C)], 1698 [ν(C=O)]. − ^1H NMR (C_6D_6, 400 MHz): δ = 5.27 (s, 5H, C_5H_5), 4.15 [dq, 1H, *J*($H^aH^{a'}$) = 10.9, *J*(H^aH^b) = 7.2 Hz, $CO_2CH^aH^{a'}CH_3^b$], 4.12 [dq, 1H, *J*($H^aH^{a'}$) = 10.9, *J*($H^{a'}H^b$) = 7.2 Hz, $CO_2CH^aH^{a'}CH_3^b$], 1.03 [t, 3H, *J*(HH) = 7.2 Hz, $CO_2CH_2CH_3$], 0.91 [s, 9H, $CNC(CH_3)_3$], 0.41 [s, 9H, $Si(CH_3)_3$]. − ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 164.1 [d, *J*(RhC) = 1.0 Hz, *C*O$_2$CH$_2$CH$_3$], 148.5 [d, *J*(RhC) = 81.5 Hz, Rh*C*NC(CH$_3$)$_3$], 99.4 [d, *J*(RhC) = 19.2 Hz, *C*≡C], 93.6 [d, *J*(RhC) = 12.07 Hz, C≡*C*], 85.9 [d, *J*(RhC) = 3.5 Hz, C_5H_5], 60.6 (s, $CO_2CH_2CH_3$), 56.2 [s, RhCN*C*(CH$_3$)$_3$], 30.7 [s, RhCNC(*C*H$_3$)$_3$], 14.15 (s, $CO_2CH_2CH_3$), 0.1 [s, $Si(CH_3)_3$]. − $C_{18}H_{28}NO_2RhSi$ (421.4): calcd. C 51.30, H 6.70, N 3.32; found C 51.56, H 6.87, N 3.14.

13. *Preparation of [C_5H_5Rh\{κ^2(C,C)-C(=NMe)CPh=CPh\}(SbiPr$_3$)]* (**17**): (a) A solution of 107 mg (0.18 mmol) of **5** in 20 ml of pentane was treated at −78 °C with 10 µl (0.18 mmol) of CNMe. After warming to room temp., the solution was stirred for 1.5 h, and then the solvent was removed in vacuo. The oily residue was dissolved in 2 ml of hexane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With hexane/benzene (1:4), an orange fraction was eluted; after evaporating of the solvent an oily residue was obtained. It was recrystallized from ether at −78 °C to give orange crystals; yield 78 mg (68%). − (b) A solution of 158 mg (0.26 mmol) of **5** in 20 ml of pentane was treated at −78 °C first with 108 µl (0.52 mmol) of Sb*i*Pr$_3$ and then with 15 µl (0.26 mmol) of CNMe. After the solution was warmed to room temp. and then stirred for 1 h, it was worked up as described for (a); yield 130 mg (78%), m.p. 120 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 1641 cm^{-1} [ν(C=N)]. − ^1H NMR (C_6D_6, 400 MHz): δ = 8.11 (m, 2H, *ortho*-H of C_6H_5), 7.61 (m, 2H, *ortho*-H of C_6H_5), 7.13 (m, 4H, *meta*-H of C_6H_5), 6.92 (m, 2H, *para*-H of C_6H_5), 5.17 (s, 5H, C_5H_5), 3.36 (s, 3H, C=NCH$_3$), 1.92 [sept, 3H, *J*(HH) = 7.4 Hz, SbC*H*CH$_3$], 1.08, 1.05 [both d, 18H, *J*(HH) = 7.4 Hz, SbCHC*H*$_3$]. − ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 151.3 [d, *J*(RhC) = 2.8 Hz, RhC(=NCH$_3$)*C*], 149.8 [d, *J*(RhC) = 20.8 Hz, Rh*C*=NCH$_3$], 147.5 (s, *ipso*-C of C_6H_5), 144.5 [d, *J*(RhC) = 27.7 Hz, Rh*C*(C$_6$H$_5$)], 135.0 [d, *J*(RhC) = 2.8 Hz, *ipso*-C of C_6H_5], 128.8, 128.7, 128.0, 127.9, 126.1, 125.8 (each s, C_6H_5), 85.4 [d, *J*(RhC) = 3.4 Hz, C_5H_5], 47.6 [d, *J*(RhC) = 2.5 Hz, C=N*C*H$_3$], 21.4, 21.3 (both s, SbCH*C*H$_3$), 18.4 [d, *J*(RhC) = 2.3 Hz, Sb*C*HCH$_3$]. − $C_{30}H_{39}NRhSb$ (638.3): calcd. C 56.45, H 6.16, N 2.19; found C 56.69, H 6.08, N 2.09.

14. *Preparation of [C_5H_5Rh\{κ^2(C,C)-C(=NMe)CPh=CPhC(=NMe)\}(CNMe)]* (**18**): (a) A solution of 105 mg (0.18 mmol) of **5** in 20 ml of pentane was treated with 53 µl (0.90 mmol) of CNMe and stirred for 8 h at room temp. A change of color from red to yellow occurred and a light-yellow solid precipitated. The precipitate was separated from the mother liquor, repeatedly washed with pentane (2 ml each), and recrystallized from toluene to give yellow crystals; yield 77 mg (91%). − (b) A solution of 95 mg (0.15 mmol) of **17** in 25 ml of pentane was treated with 34 µl (0.61 mmol) of CNMe, stirred for 7 h at room temp. and worked up as described for (a); yield 65 mg (92%), m.p. 186 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 2189 cm^{-1} [ν(CN)], 1595 [ν(C=N)]. − ^1H NMR (C_6D_6, 200 MHz): δ = 7.52 (m, 4H, *ortho*-H of C_6H_5), 7.10 (m, 4H, *meta*-H of C_6H_5), 6.96 (m, 2H, *para*-H of C_6H_5), 5.27 (s, br, 5H, C_5H_5), 3.53 (s, 6H, C=NCH$_3$), 1.75 [d, 3H, *J*(RhH) = 1.1 Hz, CNCH$_3$]. − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 186.85 [d, *J*(RhC) = 33.1 Hz, *C*=NCH$_3$], 163.0 [d, *J*(RhC) = 3.8 Hz, C=C], 138.9 (s, *ipso*-C of C_6H_5), 131.4, 127.3, 126.5 (each s, C_6H_5), 90.45 [d, *J*(RhC) = 2.5 Hz, C_5H_5], 45.6 (s, C=N*C*H$_3$), 30.2 (s, RhCN*C*H$_3$), signal of Rh*C*NCH$_3$ not observed. − MS; *m/z* (I_r): 469 (2, M^+), 428 (4, M^+ − CNMe), 387 (1, M^+ − 2 CNMe), 346 (1, M^+ − 3 CNMe), 250 (10, $C_5H_5Rh(CNMe)_2^+$), 209 (100,

$C_5H_5RhCNMe^+$), 178 (1, $C_2Ph_2^+$), 168 (12, $C_5H_5Rh^+$), 144 (2, $RhCNMe^+$), 103 (2, Rh^+). – $C_{25}H_{24}N_3Rh$ (469.4): calcd. C 63.97, H 5.15, N 8.95; found C 63.77, H 5.19, N 8.75.

15. *Preparation of [$C_5H_5Rh\{\kappa^2(C,C)$-C(=NMe)CPh=CPhC(=NtBu)}(CNtBu)]* (**19**): A solution of 118 mg (0.18 mmol) of **17** in 20 ml of pentane was treated with 45 µl (0.40 mmol) of CN*t*Bu and stirred for 12 h at room temp. The solvent was removed in vacuo, the residue was dissolved in 5 ml of hexane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With hexane, an almost colorless fraction containing triisopropylstibane, and with ether a yellow fraction was eluted and brought to dryness in vacuo. The residue was dissolved in 4 ml of ether, and after the solution had been stored for 12 h at −78 °C, a yellow microcrystalline solid was obtained; yield 78 mg (78%), m.p. 117 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2135 cm^{-1} [ν(CN)], 1590 [ν(C=N)]. – ^1H NMR (C_6D_6, 400 MHz): δ = 7.37 (m, 4H, *ortho*-H of C_6H_5), 7.07 (m, 4H, *meta*-H of C_6H_5), 6.96 (m, 2H, *para*-H of C_6H_5), 5.32 (s, 5H, C_5H_5), 3.56 (s, 3H, C=NCH$_3$), 1.48 [s, 9H, C=NC(CH$_3$)$_3$], 0.83 [s, 9H, CNC(CH$_3$)$_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 186.65 [d, *J*(RhC) = 33.2 Hz, *C*=NCH$_3$], 171.8 [d, *J*(RhC) = 34.2 Hz, *C*=NC(CH$_3$)$_3$], 166.1 [d, *J*(RhC) = 3.0 Hz, *C*=C], 161.2 [d, *J*(RhC) = 2.0 Hz, C=*C*], 143.1 [d, *J*(RhC) = 79.8 Hz, Rh*C*NC(CH$_3$)$_3$], 139.9, 139.3 (both s, *ipso*-C of C_6H_5), 131.4, 131.2, 127.2, 126.8, 126.2, 126.0 (each s, C_6H_5), 92.0 [d, *J*(RhC) = 2.3 Hz, C_5H_5], 57.1, 56.9 [both s, CN*C*(CH$_3$)$_3$], 48.0 [s, C=N*C*H$_3$], 31.4, 30.0 [both s, CNC(*C*H$_3$)$_3$]. – MS; *m/z* (I_r): 553 (2.5, M^+), 497 (2, $M^+ - C_4H_8$), 470 (1, M^+ – CN*t*Bu), 372 [2, $C_5H_5Rh(C_2Ph_2)(CN)^+$], 346 [1, $C_5H_5Rh(C_2Ph_2)^+$], 292 [4, $C_5H_5Rh(CNMe)(CNtBu)^+$], 236 [100, $C_5H_5Rh(CNMe)(CNH)^+$], 209 (1, $C_5H_5RhCNMe^+$), 195 (3, $C_5H_5RhCNH^+$), 178 (1, $C_2Ph_2^+$), 168 (5, $C_5H_5Rh^+$), 144 (2, $RhCNMe^+$), 103 (1, Rh^+). – $C_{31}H_{36}N_3Rh$ (553.6): calcd. C 67.25, H 6.56, N 7.59; found C 67.22, H 6.58, N 7.62.

16. *Preparation of [$C_5H_5Rh\{\kappa^2(C,C)$-C(=NMe)CPh=CPhC(=NtBu)}(CNMe)]* (**20**): A solution of 127 mg (0.30 mmol) of **14** in 15 ml of pentane was treated with 50 µl (0.90 mmol) of CNMe and stirred for 12 h at room temp. A yellow solid precipitated which was worked up as described for **18**; yield 135 mg (88%), m.p. 162 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2190 cm^{-1} [ν(CN)], 1595 [ν(C=N)]. – ^1H NMR (C_6D_6, 400 MHz): δ = 7.39 (m, 4H, *ortho*-H of C_6H_5), 7.07 (m, 4H, *meta*-H of C_6H_5), 6.96 (m, 2H, *para*-H of C_6H_5), 5.33 (s, br, 5H, C_5H_5), 3.52 (s, 3H, C=NCH$_3$), 1.89 [d, 3H, *J*(RhH) = 0.4 Hz, CNCH$_3$], 1.45 [s, 9H, C=NC(CH$_3$)$_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 186.8 [d, *J*(RhC) = 33.2 Hz, *C*=NCH$_3$], 171.9 [d, *J*(RhC) = 34.2 Hz, *C*=NC(CH$_3$)$_3$], 166.1 [d, *J*(RhC) = 3.0 Hz, *C*=C], 161.3 [d, *J*(RhC) = 2.0 Hz, C=*C*], 144.5 [d, *J*(RhC) = 78.5 Hz, Rh*C*NCH$_3$], 139.8, 139.2 (both s, *ipso*-C of C_6H_5), 131.4, 131.2, 127.2, 126.8, 126.2, 126.1 (each s, C_6H_5), 91.9 [d, *J*(RhC) = 2.2 Hz, C_5H_5], 56.7 [s, C=N*C*(CH$_3$)$_3$], 47.95 (s, C=N*C*H$_3$), 31.35 [s, C=NC(*C*H$_3$)$_3$], 28.35 (s, RhCN*C*H$_3$). – MS; *m/z* (I_r): 511 (2, M^+), 470 (2, M^+ – CNMe), 372 [2, $C_5H_5Rh(C_2Ph_2)(CN)^+$], 346 [2, $C_5H_5Rh(C_2Ph_2)^+$], 292 [4, $C_5H_5Rh(CNMe)(CNtBu)^+$], 236 [100, $C_5H_5Rh(CNMe)(CNH)^+$], 209 (7, $C_5H_5RhCNMe^+$), 195 (3, $C_5H_5RhCNH^+$), 178 (2, $C_2Ph_2^+$), 168 (10, $C_5H_5Rh^+$), 144 (1, $RhCNMe^+$). – $C_{28}H_{30}N_3Rh$ (511.5): calcd. C 65.75, H 5.91, N 8.22; found C 65.73, H 5.92, N 8.20.

17. *Preparation of [$C_5H_5Rh\{\kappa^2(C,C)$-C(=NtBu)CPh=CPhC(=NtBu)}(CNtBu)]* (**21**): (a) A solution of 134 mg (0.22 mmol) of **5** in 20 ml of pentane was treated with 124 µl (1.10 mmol) of CN*t*Bu and stirred for 3 d at room temp. The solvent was removed in vacuo, the residue was dissolved in 5 ml of hexane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 6 cm). With ether an orange-yellow fraction was eluted and brought to dryness in vacuo. After the solution had been stored for 12 h at −78 °C, a yellow microcrystalline solid precipitated that was washed with pentane (−30 °C) and dried in vacuo; yield 109 mg (83%). – (b) A solution of 100 mg (0.23 mmol) of **14** in 20 ml of pentane was treated with 78 µl (0.69 mmol) of CN*t*Bu, stirred for 3 d at room temp., and worked up as described for (a); yield 112 mg (82%), m.p. 63 °C (dec.). – IR (hexane): $\tilde{\nu}$ = 2123 cm^{-1} [ν(CN)], 1607 [ν(C=N)]. – ^1H NMR (C_6D_6, 400 MHz): δ = 7.28 (m, 4H, *ortho*-H of C_6H_5), 7.06 (m, 4H, *meta*-H of C_6H_5), 6.95 (m, 2H, *para*-H of C_6H_5), 5.38 [d, 5H, *J*(RhH) = 0.9 Hz, C_5H_5], 1.49 [s, 18H, C=NC(CH$_3$)$_3$], 0.89 [s, 9H, CNC(CH$_3$)$_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 171.35 [d, *J*(RhC) = 33.2 Hz, *C*=NC(CH$_3$)$_3$], 164.4 [d, *J*(RhC) = 2.0 Hz, C=C], 145.7 [d, *J*(RhC) = 81.5 Hz, Rh*C*NC(CH$_3$)$_3$], 140.35 (s, *ipso*-C of C_6H_5), 131.2, 126.75, 125.8 (each s, C_6H_5), 93.5 [d, *J*(RhC) = 2.6 Hz, C_5H_5], 57.0 [s, RhCN*C*(CH$_3$)$_3$], 56.9 [s, C=N*C*(CH$_3$)$_3$], 31.5 [s, C=NC(*C*H$_3$)$_3$], 30.0 [s, RhCNC(*C*H$_3$)$_3$]. – MS; *m/z* (I_r): 595 (1, M^+], 512 (1, M^+ – CN*t*Bu), 429 (1, M^+ – 2 CN*t*Bu), 372 (1, $C_5H_5Rh(C_2Ph_2)(CN)^+$], 346 [1, $C_5H_5Rh(C_2Ph_2)^+$], 334 [1, $C_5H_5Rh(CNtBu)_2^+$], 278 [2, $C_5H_5Rh(CNtBu)(CNH)^+$], 195 (5, $C_5H_5RhCNH^+$), 178 (100, $C_2Ph_2^+$), 168 (3, $C_5H_5Rh^+$). – $C_{34}H_{42}N_3Rh$ (595.6): calcd. C 68.56, H 7.11, N 7.05; found C 68.66, H 7.10, N 6.99.

18. *Preparation of [$C_5H_5Rh\{\kappa^2(C,C)$-C(=NMe)C(SiMe$_3$)=C(CO$_2$Et)C(=NMe)}(CNMe)]* (**22**): Compound **22** was prepared analogous to **18**, by using 121 mg (0.21 mmol) of **7** and 47 µl (0.84 mmol) of CNMe; yellow crystalline solid; yield 89 mg (92%), m.p. 145 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2173 cm^{-1} [ν(CN)], 1712 [ν(C=O)], 1588 [ν(C=N)]. – ^1H NMR (C_6D_6, 400 MHz): δ = 5.10 (s, br, 5H, C_5H_5), 4.32 [dq, 1H, *J*($H^aH^{a'}$) = 10.9, *J*(H^aH^b) = 7.0 Hz, CO$_2$CH^{a}H$^{a'}$CH$_3^b$], 4.26 [dq, 1H, *J*($H^aH^{a'}$) = 10.9, *J*($H^{a'}H^b$) = 7.0 Hz, CO$_2$CH^{a}H$^{a'}$CH$_3^b$], 3.47, 3.40 (both s, 6H, C=NCH$_3$), 1.64 [d, 3H, *J*(RhH) = 0.6 Hz, CNCH$_3$], 1.09 [t, 3H, *J*(HH) = 7.0 Hz, CO$_2$CH$_2$CH$_3$], 0.59 [s, 9H, Si(CH$_3$)$_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 192.7 [d, *J*(RhC) = 33.2 Hz, *C*=NCH$_3$], 189.9 [d, *J*(RhC) = 34.2 Hz, *C*=NCH$_3$], 170.0 (s, *C*O$_2$CH$_2$CH$_3$), 166.25 [d, *J*(RhC) = 4.0 Hz, *C*=C], 164.7 [d, *J*(RhC) = 3.0 Hz, C=*C*], 140.6 [d, *J*(RhC) = 77.5 Hz, Rh*C*NCH$_3$], 89.95 [d, *J*(RhC) = 2.2 Hz, C_5H_5], 60.5 (s, CO$_2$*C*H$_2$CH$_3$), 48.35, 48.3 (both s, C=N*C*H$_3$), 27.9 (s, RhCN*C*H$_3$), 14.3 (s, CO$_2$CH$_2$*C*H$_3$), 0.7 [s, Si(CH$_3$)$_3$]. – MS; *m/z* (I_r): 461 (1, M^+), 420 (7, M^+ – CNMe), 379 (1, M^+ – 2 CNMe), 250 [15, $C_5H_5Rh(CNMe)_2^+$], 209 (100, $C_5H_5RhCNMe^+$), 168 (12, $C_5H_5Rh^+$), 144 (2, $RhCNMe^+$), 103 (2, Rh^+). – $C_{19}H_{28}N_3O_2RhSi$ (461.4): calcd. C 49.49, H 6.12, N 9.11; found C 49.45, H 6.19, N 9.20.

19. *Preparation of [$C_5H_5Rh\{\kappa^2(C,C)$-C(=NtBu)CMe=CPhC(=NtBu)}(CNtBu)]* (**23**): Compound **23** was prepared analogous to **21**, by using 147 mg (0.27 mmol) of **8** and 152 µl of CN*t*Bu; orange-yellow crystalline solid; yield 96 mg (67%), m.p. 118 °C (dec.). – IR (hexane): $\tilde{\nu}$ = 2120, 2065 cm^{-1} [ν(CN)], 1600 [ν(C=N)]. – ^1H NMR (C_6D_6, 400 MHz): δ = 7.30 (m, 2H, *ortho*-H of C_6H_5), 7.27 (m, 2H, *meta*-H of C_6H_5), 7.16 (m, 1H, *para*-H of C_6H_5), 5.34 (s, 5H, C_5H_5), 2.34 (s, 3H, =CCH$_3$), 1.61 [s, 9H, C=NC(CH$_3$)$_3$], 1.44 [s, 9H, C=NC(CH$_3$)$_3$], 0.86 [s, 9H, RhCNC(CH$_3$)$_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 172.45 [d, *J*(RhC) = 33.7 Hz, *C*=N(CH$_3$)$_3$], 171.2 [d, *J*(RhC) = 32.9 Hz, *C*=N(CH$_3$)$_3$], 163.05 (s, *C*=C), 160.75 (s, C=*C*), 141.6 (s, *ipso*-C of C_6H_5), 133.4, 127.2, 126.1 (each s, C_6H_5), 93.3 [d, *J*(RhC) = 1.9 Hz, C_5H_5], 56.9 [s, RhCN*C*(CH$_3$)$_3$], 56.75, 56.7 [both s, C=N*C*(CH$_3$)$_3$], 31.9, 31.5 [both s, C=NC(*C*H$_3$)$_3$], 30.1 [s, RhCNC(*C*H$_3$)$_3$], 17.25 (s, =C*C*H$_3$), signal of Rh*C*NC(CH$_3$)$_3$ not

observed. – $C_{29}H_{40}N_3Rh$ (533.6): calcd. C 62.28, H 7.56, N 7.88; found C 61.90, H 7.47, N 7.90.

20. *X-ray Structure Determination of Compounds* **17** *and* **18**[11]: Single-crystals of **17** were grown at −78 °C from ether and of **18** at room temp. from toluene. Crystal data collection parameters are summarized in Table 1. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction (Ψ-scan method) was applied, the minimum transmission for **17** was 96.93%, for **18** 92.25%. The structure of **17** was solved by direct methods, the structure of **18** by the Patterson method (SHELXS-86). Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares (unit weights) with the program package SDP (**17**) and SHELXL-93 (**18**). The position of the hydrogen atoms were calculated according to ideal geometry and were refined by the riding method.

Table 1. Crystallographic data for **17** and **18**

	17	**18**
formula	$C_{30}H_{39}NRhSb$	$C_{25}H_{24}N_3Rh$
fw	638.30	469.38
cryst size, mm	0.45 x 0.60 x 0.75	0.18 x 0.18 x 0.38
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	*Pbca* (No. 61)
a, Å	10.915(2)	15.197(4)
b, Å	14.133(2)	15.982(3)
c, Å	18.420(2)	18.141(5)
β, deg	99.516(9)	90
V, Å^3	2802.3(9)	4406(2)
Z	4	8
d_{calcd}, g cm^{-3}	1.51	1.42
diffractometer	Enraf-Nonius CAD 4	Enraf-Nonius CAD 4
radiation (graphite monochromated)	Mo K_α (0.70930 Å)	Mo K_α (0.70930 Å)
temp, K	293	293
μ, cm^{-1}	15.7	7.81
h, k, l	11, 16, ±21	18, 19, 22
scan method	ω/θ	ω/θ
2θ (max), deg	48	52
tot. no. of reflns scanned	4746	4326
no. of unique reflns	4218	4321
no. of observed reflns	3880 ($F_o > 3\sigma(F_o)$)	4313 ($F_o > 2\sigma(F_o)$)
no. of params refined	454	258
R	0.020	0.047
R_w	0.021	0.088
refln/param ratio	8.55	16.71
resid electron density, [e Å^{-3}]	+0.38/-0.46	+0.40/-0.45

[☆] Dedicated to Professor *Gerhard E. Herberich* on the occasion of his 60th birthday.

[1] H. Werner, P. Schwab, A. Heinemann, P. Steinert, *J. Organomet. Chem.* **1995**, *496*, 207–216.

[2] Y. Wakatsuki, H. Yamazaki, H. Iwasaki, *J. Am. Chem. Soc.* **1973**, *95*, 5781–5783.

[3] [3a] H. Werner, J. Wolf, U. Schubert, K. Ackermann, *J. Organomet. Chem.* **1986**, *317*, 327–356. – [3b] J. Wolf, H. Werner, *Organometallics* **1987**, *6*, 1164–1169. – [3c] H. Werner, M. Baum, D. Schneider, B. Windmüller, *Organometallics* **1994**, *13*, 1089–1097.

[4] [4a] H. Yamazaki, K. Aoki, Y. Yamamoto, Y. Wakatsuki, *J. Am. Chem. Soc.* **1975**, *97*, 3546–3548. – [4b] Y. Wakatsuki, S. Miya, S. Ikuta, H. Yamazaki, *Chem. Soc., Chem. Commun.* **1985**, 35–37. – [4c] Y. Wakatsuki, K. Aoki, H. Yamazaki, *J. Chem. Soc., Dalton Trans.* **1986**, 1193–1199. – [4d] Y. Wakatsuki, S. Miya, H. Yamazaki, S. Ikuta, *J. Chem. Soc., Dalton Trans.* **1986**, 1201–1205. – [4e] Y. Wakatsuki, S. Miya, H. Yamazaki, *J. Chem. Soc., Dalton Trans.* **1986**, 1207–1212.

[5] W. Hirpo, M. D. Curtis, *Organometallics* **1994**, *13*, 2706–2712.

[6] [6a] P. Schwab, Dissertation Universität Würzburg, **1994**. – [6b] H. Werner, *J. Organomet. Chem.* **1995**, *500*, 331–336.

[7] [7a] M. A. Bennett, T. Yoshida, *J. Am. Chem. Soc.* **1978**, *100*, 1750–1759. – [7b] T. V. Harris, J. W. Rathke, E. L. Muetterties, *J. Am. Chem. Soc.* **1978**, *100*, 6966–6977. – [7c] J.-M. Basset, M. Green, J. A. K. Howard, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **1980**, 1779–1788.

[8] W. D. Jones, E. T. Hessell, *Organometallics* **1990**, *9*, 718–727.

[9] S. T. Belt, S. B. Duckett, D. M. Haddleton, R. N. Perutz, *Organometallics* **1989**, *8*, 748–759.

[10] G. W. Harris, M. O. Albers, J. C. A. Boeyens, N. J. Coville, *Organometallics* **1983**, *2*, 609–614.

[11] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-59310 (**17**) and -405139 (**18**), the names of the authors, and the journal citation.

[960078]