sionless parameters such as $\lambda = k(RT/Fv)$, the sensitivity of determinations of k values is reflected by the changes of voltammograms in Figure 5 when the scan rate is modified.

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Synthesis, Reactivity, and Structure of Four-Coordinate (Vinylvinylidene)- and Five- and Six-Coordinate Enynyl(hydrido)rhodium Complexes with $[\mathrm{RhCl(P^iPr_3)_2}]$ as a Molecular Unit[†,1]

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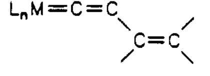
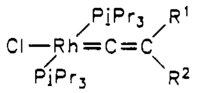
The reaction of $[\mathrm{RhCl(C_8H_{14})_2}]_2$ (**4**) with $\mathrm{P^iPr_3}$ and enynes $\mathrm{HC{\equiv}CC(R){=}CH(R')}$ [R = R' = H; R = CH$_3$, R' = H; R = H, R' = OCH$_3$] leads to the formation of either (enyne)- or enynyl(hydrido)rhodium complexes (**5a,b**, **6c**) as the first isolable products. At 25–45 °C in toluene, *trans*-$[\mathrm{RhCl(HC{\equiv}CC(R){=}CH_2)(P^iPr_3)_2}]$ (**5a,b**) and $[\mathrm{RhH\{C{\equiv}CCH{=}CH(OCH_3)\}Cl(P^iPr_3)_2}]$ (**6c**) smoothly rearrange to give the isomeric (vinylvinylidene)rhodium derivatives *trans*-$[\mathrm{RhCl\{{=}C{=}CHC(R){=}CH(R')\}(P^iPr_3)_2}]$ (**7a–c**) in nearly quantitative yield. The parent complex **7a** (R = R' = H) has also been prepared from **4**, $\mathrm{P^iPr_3}$, and the alkynol $\mathrm{HC{\equiv}CCH(CH_3)OH}$ via the substituted rhodium vinylidene complex *trans*-$[\mathrm{RhCl\{{=}C{=}CHCH(CH_3)OH\}(P^iPr_3)_2}]$ (**9**), which undergoes elimination of water on treatment with acidic $\mathrm{Al_2O_3}$ or traces of HX. Both **5a,b** and **6c** as well as the vinylvinylidene complexes **7a–c** react with pyridine at room temperature to give the octahedral rhodium(III) compounds $[\mathrm{RhH\{C{\equiv}CC(R){=}CH(R')\}Cl(py)(P^iPr_3)_2}]$ (**11a–c**). In contrast, the reaction of **7b** with CO affords, instead of $[\mathrm{RhH\{C{\equiv}CC(CH_3){=}CH_2\}Cl(CO)(P^iPr_3)_2}]$, the four-coordinate carbonyl complex *trans*-$[\mathrm{RhCl(CO)(P^iPr_3)_2}]$ (**13**) and free enyne $\mathrm{HC{\equiv}CC(CH_3){=}CH_2}$. Protonation of **7b** with $\mathrm{HBF_4}$ gives the cationic carbyne rhodium derivative *trans*-$[\mathrm{RhCl\{{\equiv}CCH{=}C(CH_3)_2\}(P^iPr_3)_2]BF_4}$ (**14**), which on treatment with NaH re-forms the vinylvinylidene compound **7b**. The molecular structures of **7b** and **11b** have been determined. Crystallographic data are as follows: **7b**, monoclinic space group $P2_1/c$ (No. 14) with a = 8.117 (3) Å, b = 38.946 (9) Å, c = 17.597 (6) Å, β = 93.99 (1)°, V = 5590 Å^3, and Z = 8; **11b**, triclinic space group $P\bar{1}$ (No. 2) with a = 9.3103 (5) Å, b = 11.7936 (8) Å, c = 15.322 (2) Å, α = 93.246 (7)°, β = 92.832 (6)°, γ = 108.981 (5)°, V = 1584 Å^3, and Z = 2.

Introduction

Transition-metal complexes containing vinylvinylidenes as ligands belong to a type of compound in which a conjugated and a cumulated double-bond system is combined in the same molecule. Complexes of the general composition **1** have previously been obtained from a labile precursor such as $[\mathrm{Cr(CO)_5(OEt_2)}]$ and an activated alkyne, e.g., $\mathrm{HC{\equiv}CCO_2Me}$,[2] or by formal insertion of $\mathrm{C_2(CO_2Me)_2}$ into the C_α–C_β bond of a vinylidene–metal unit.[3] Vinylacetylene, $\mathrm{HC{\equiv}CCH{=}CH_2}$, or derivatives thereof have as far as we know not been used as starting materials for compounds of type **1**, which could be due first to the sophisticated methods of synthesis and second to the sensitivity toward polymerization of these substances. Recently, Devanne and Dixneuf used vinylacetylenes in the presence of ROH to prepare (alkenylcarbene)ruthenium complexes and concluded that the substituted carbene moieties were formed via nucleophilic attack of the alcohol on vinylvinylidene ligands.[4]



1



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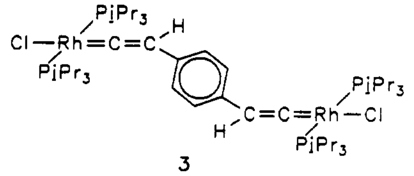
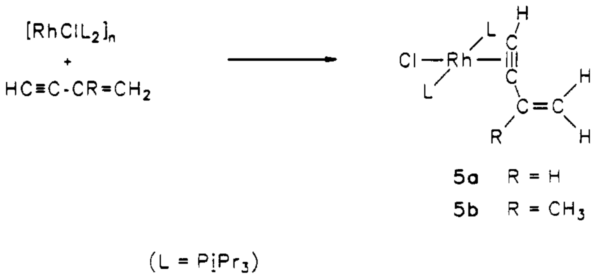


3

Scheme I



[†] Dedicated to Professor Lord Lewis on the occasion of his 65th birthday.

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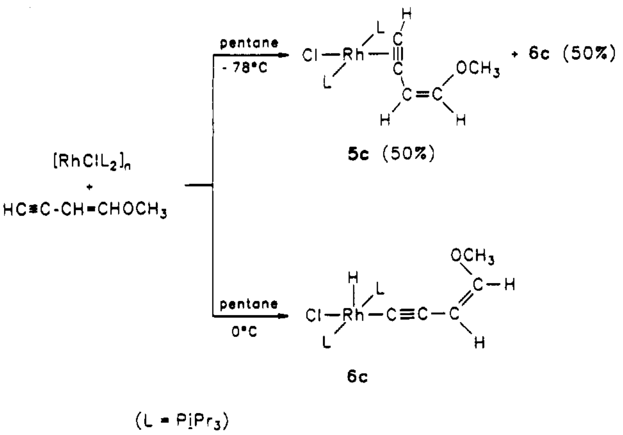
In continuation of our work on square-planar, mono- and dinuclear vinylidenerhodium compounds of type **2**[5,6] and **3**,[7] we became interested to learn whether type **2** complexes with a vinyl substituent R^2 can be obtained from unsaturated alkynes $HC{\equiv}CCR{=}CH_2$. As an alternative to enynes, 1-alkyn-3-ols were tested as starting materials because it was recently reported by Selegue et al. that 1-ethynylcyclopentanol and 1-ethynylcyclohexanol react with $[C_5H_5Ru(PMe_3)_2Cl]$ in the presence of NH_4PF_6 to give cationic (vinylvinylidene)ruthenium derivatives.[8] Some preliminary results of our investigations were described in a recent account.[9]

Results

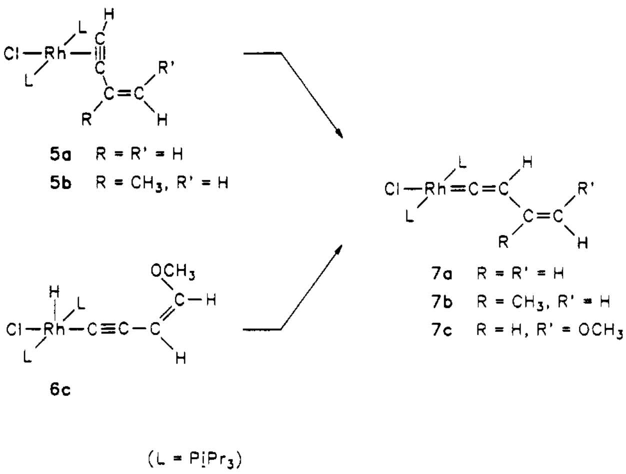
(Vinylvinylidene)rhodium Complexes from Enynes. The highly reactive bis(triisopropylphosphine)rhodium compound $[RhCl(P^iPr_3)_2]_n$,[10] which is prepared from $[RhCl(C_8H_{14})_2]_2$ (**4**) and excess P^iPr_3, reacts with equimolar amounts of vinylacetylene and the related methyl derivative $HC{\equiv}CC(CH_3){=}CH_2$ in pentane at low temperatures to give the enyne complexes **5a**,**b** in good to excellent yields (Scheme I). In order to isolate pure samples it is important to work up the reaction mixture almost immediately because otherwise partial isomerization of **5a** and **5b** to the (vinylvinylidene)rhodium complexes **7a** and **7b** occurs. The yellow microcrystalline solids for which correct elemental analyses have been obtained are only slightly air-sensitive and easily soluble in most organic solvents. They are, however, thermally rather labile, and at least complex **5a** containing the unsubstituted enyne as ligand rearranges *even in the solid state* to give isomer **7a**. The conversion is accompanied by a color change from yellow to dark green and completed at room temperature in 3 days or at 60 °C in approximately 2 h. We note that quite recently Bianchini et al. observed an alkynyl–hydride to vinylidene rearrangement at a cobalt center also *in the solid state* at relatively low temperatures, the driving force being again the formation of a cumulated M=C=C bond system.[12]

The structure proposed in Scheme I for **5a**,**b** is clearly supported by the spectroscopic data. In the IR, the C≡C stretching frequency is found at 1808 (**5a**) and 1807 (**5b**) cm^{-1} and thus shifted by ca. 300 cm^{-1} to lower frequencies compared with the free alkynes. The ^1H NMR spectrum of **5b** at −60 °C (a temperature where only slow isomerization occurs) shows a doublet of virtual triplets for the CH_3 protons of the P^iPr_3 groups, which is consistent with a trans position of the two phosphine ligands.[13] Furthermore, two singlets for the nonequivalent CH_2 protons, one singlet for the methyl substituent, and one doublet for the CH proton of the enyne unit are observed.

Scheme II



Scheme III



Treatment of **4** with (*Z*)-1-methoxybut-1-ene-3-yne (i.e., a δ-functionalized enyne) in pentane at 0 °C does not lead to an alkyne but to an alkynyl–hydrido complex **6c**. Only if the reaction is carried out at −78 °C, besides **6c** also the isomeric compound **5c** is formed (Scheme II). Characteristic features for **5c** are the absorption at 1805 cm^{-1} in the IR (see the data for **5a**,**b**) and the doublet at $\delta = 33.2$ in the ^{31}P NMR spectrum that is in the same region in which also the signals of **5a**,**b** appear.

The isolation and the molecular structure of the five-coordinate rhodium(III) complex **6c** deserves further comments. Previous work from our laboratory has shown that in contrast to iridium, where for R = Me, Ph, and CO_2Me *all three isomers* of composition *trans*-$[IrCl(HC{\equiv}CR)(P^iPr_3)_2]$, $[IrH(C{\equiv}CR)Cl(P^iPr_3)_2]$, and *trans*-$[IrCl({=}C{=}CHR)(P^iPr_3)_2]$ have been prepared,[5a,14] in the case of rhodium the rearrangement of the (1-alkyne)- to the vinylidenemetal derivative usually is very facile and only for bulky substituents R such as ^tBu[5c] or $SiMe_3$[15] can the third isomer $[RhH(C{\equiv}CR)Cl(P^iPr_3)_2]$ be isolated. Therefore, it is indeed remarkable that the reaction of $[RhCl(P^iPr_3)_2]$ with $HC{\equiv}CCH{=}CH(OMe)$ stops at the

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stage of the alkynyl–hydrido complex and does not proceed (in pentane at room temperature it takes more than 1 day) to give the vinylidenerhodium isomer. Compound **6c** is characterized (besides elemental analysis) by an intense IR band at 2090 cm^{-1} for the C≡C stretch, a signal in the high-field region of the ^{1}H NMR spectrum at $\delta = -28.3$ (doublet of triplets due to RhH and PH coupling) for the hydride, and a single resonance (doublet) in the ^{31}P NMR spectrum at $\delta = 49.2$ for the two equivalent phosphine groups. Although it cannot be decided from the spectroscopic data whether **6c** possesses a trigonal-bipyramidal (tbp) or a square-pyramidal (sqp) configuration, owing to recent findings[16] and to the result of the X-ray structural analysis of **11b** (see below), we assume that the sqp coordination is preferred.

Both the alkyne and the alkynyl–hydrido compounds, **5a,b** and **6c**, rearrange quite smoothly in toluene to form the vinylidenerhodium complexes **7a–c** in nearly quantitative yield (Scheme III). Whereas the isomerization from **5a** to **7a** is finished at room temperature after 10 min, solutions of **5b** and **6c** have to be warmed to 45 °C for 2 h to complete the reaction. A one-pot synthesis of **7a–c**, using $[RhCl(C_8H_{14})_2]_2$ (**4**), P^iPr_3, and the enyne as starting materials, has also been achieved. The rhodium vinylvinylidenes **7a–c** are deeply colored solids which for a short time can be handled in air and which, with the exception of pentane and hexane, are easily soluble in all common organic solvents. It is particularly worth mentioning that even on prolonged heating to 65 °C, no conversion of the vinylidenes **7a,b** to the corresponding allenylidene complexes *trans*-$[RhCl\{=C=C=C(Me)R\}(P^iPr_3)_2]$ (R = H, Me) occurs. For [Ru] = $[(arene)RuCl(PR_3)]^+$ and $[RuCl(dppm)_2]^+$, such a rearrangement from [Ru]=C=CH-C(Me)=CH$_2$ to [Ru]=C=C=CMe$_2$ has recently been observed.[4]

As far as the spectroscopic data of **7a–c** are concerned, the most significant features are the low-field signals in the ^{13}C NMR spectra at δ = 295–300 and 102–114, which by comparison are assigned to the α-C and β-C vinylidene carbon atoms.[17] The ^{31}P NMR spectra reveal, like for the alkyne complexes **5a,b**, only one resonance and thus leave no doubt that the phosphine ligands are in the trans position. Regarding the conformation of the vinylidenerhodium compounds, we assume that, in contrast to the allene-type geometry found for **7b** (and other metal vinylidenes[5a,14a,17]) *in the solid state*, the molecules possess a nonrigid structure *in solution* and that a low barrier of rotation around the Rh–C bond exists. Theoretical work by Fenske[18] and Hoffmann[19] is in full agreement with this.

We finally note that the UV spectra of **7a–c** (with maxima at 440 and 582 nm for **7a,b** and at 436 and 583 nm, respectively, for **7c**) are nearly identical to the spectrum of the phenylvinylidene derivative *trans*-$[RhCl(=C=CHPh)(P^iPr_3)_2]$ with λ(max) = 442 and 580 nm (in CH$_2$Cl$_2$). The absorptions are assigned to MLCT transitions and appear at wavelengths similar to those of (carbene)metal complexes.[20]

Molecular Structure of 7b. A single-crystal X-ray diffraction investigation of the vinylvinylidene compound confirms the structural proposal shown in Scheme III. The SCHAKAL drawing reveals (Figure 1) that the coordination geometry about the rhodium(I) center is square-planar. There are two crystallographically independent molecules in the unit cell for which the bond distances and bond angles are nearly the same (Table I).

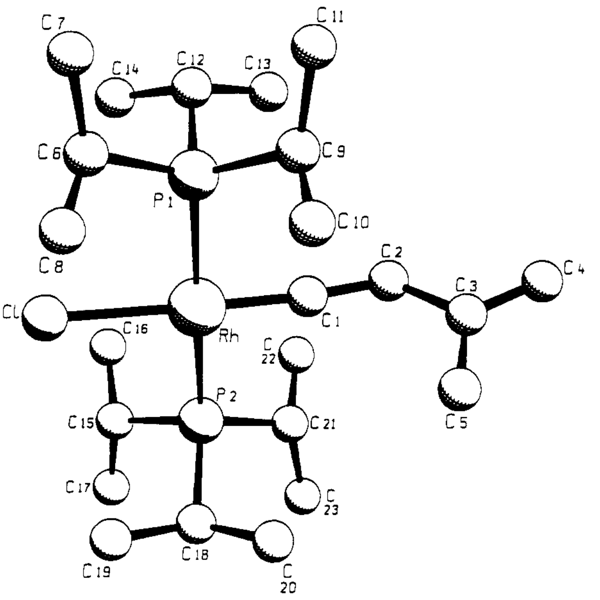

Figure 1. Molecular structure (SCHAKAL drawing) and labeling scheme for complex **7b**.

Table I. Selected Bond Distances and Angles with Esd's for 7b[a]

	Bond Distances (Å)		
Rh–Cl	2.367 (3)	Rh*–Cl*	2.366 (3)
Rh–P1	2.358 (3)	Rh*–P1*	2.365 (3)
Rh–P2	2.349 (3)	Rh*–P2*	2.359 (3)
Rh–C1	1.78 (1)	Rh*–C1*	1.80 (1)
C1–C2	1.33 (2)	C1*–C2*	1.31 (2)
C2–C3	1.46 (2)	C2*–C3*	1.47 (2)
C3–C4	1.33 (2)	C3*–C4*	1.38 (2)
C3–C5	1.46 (2)	C3*–C4*	1.43 (3)
	Bond Angles (deg)		
Cl–Rh–P1	90.7 (1)	Cl*–Rh*–P1*	88.9 (1)
Cl–Rh–P2	90.1 (1)	Cl*–Rh*–P2*	91.3 (1)
Cl–Rh–C1	177.6 (4)	Cl*–Rh*–C1*	177.8 (4)
P1–Rh–P2	175.6 (2)	P1*–Rh*–P2*	178.1 (1)
P2–Rh–C1	90.6 (3)	P2*–Rh*–C1*	89.9 (3)
Rh–C1–C2	174 (1)	Rh*–C1*–C2*	171 (1)
C1–C2–C3	128 (1)	C1*–C2*–C3*	126 (1)
C2–C3–C4	119 (1)	C2*–C3*–C4*	118 (2)
C2–C3–C5	118 (1)	C2*–C3*–C5*	123 (1)
C4–C3–C5	122 (1)	C4*–C3*–C5*	119 (2)

[a] Atoms marked with an asterisk are those of the second independent molecule in the unit cell.

The most notable feature of the structural parameters is the short Rh–C1 distance of 1.78 Å (1.80 Å) which is comparable to that found in *trans*-$[RhCl(=C=CHMe)(P^iPr_3)_2]$[5a,b] but much shorter than in (carbene)rhodium complexes.[21] The Rh–C1–C2 unit is almost linear with the vinyl substituent at C2 lying essentially in a plane which is perpendicular to the plane of the Cl, Rh, P1, P2, and C1 atoms. The C1–C2 and C3–C4 bond lengths differ only slightly and are in the expected range for conjugated C$_4$ hydrocarbon systems. Similar C–C distances and C–C–C angles have also been found in other cyclic and noncyclic (vinylvinylidene)tungsten,[3] -ruthenium,[8] -osmium,[22]

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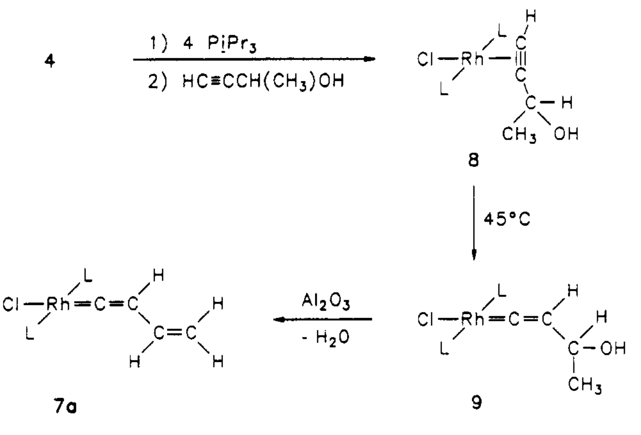
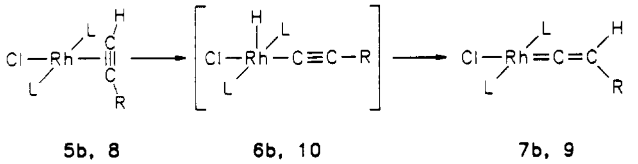
Scheme IV



(L = P^{i}Pr$_3$)

Scheme V



	R
5b, 6b, 7b	C(CH$_3$)=CH$_2$
8, 9, 10	CH(CH$_3$)OH

(L = P^{i}Pr$_3$)

and -rhenium[23] derivatives. The Rh–Cl and Rh–P distances in **7b** are as expected and need no further comment.

(Alkyne)- and (Vinylvinylidene)rhodium Complexes from But-1-yn-3-ol. Following earlier work by Selegue et al.,[8] we decided to test the alkynol HC≡CCH(Me)OH as an alternative starting material for the preparation of the parent (vinylvinylidene)rhodium compound **7a**. The synthesis which proceeds in three steps is outlined in Scheme IV. In the first step, on treatment of the in-situ generated bis(phosphine) complex [RhCl(P^{i}Pr$_3$)$_2$] with an equimolar amount of but-1-yn-3-ol the alkynol rhodium derivative **8** is formed; after removal of the solvent and excess phosphine it is isolated in 64% yield. The yellow, moderately air-stable solid has to be stored at low temperatures because otherwise at least partial isomerization to the vinylidene complex **9** occurs.

In toluene solution at 45 °C, the rearrangement of 8 to **9** is completed in 2 h. The reaction is accompanied by a characteristic color change from yellow to deep green and affords the product in nearly quantitative yield. Compound **9** is stable both in the solid state and in solution, which is worth mentioning insofar as according to recent studies[4,8] it could be concluded that species of the general composition [L$_n$M(=C=CHCH(R)OH]$^{n+}$ (n = 0, 1) would smoothly eliminate water to give either (vinylvinylidene)- or allenylidenemetal complexes. As far as we know, there are only some γ-hydroxy-substituted vinylidenemanganese compounds [C$_5$H$_5$Mn(=C=CHCR(R′)OH)(CO)$_2$] described in the literature[24,25] which are stable and do not react spontaneously to form metal vinylvinylidenes or allenylidenes, respectively.

The final step in Scheme IV, namely the conversion of **9** to **7a**, is easily performed. If a solution of **9** in toluene is passed through a column, usually used for chromatography and filled with acidic Al$_2$O$_3$ of activity grade I, a green fraction is obtained, which owing to the ^{1}H and ^{13}C NMR spectra is not **9** but **7a**. The isolated yield is 93%. The abstraction of water from **9** can also be achieved by using trace amounts of HCl or CF$_3$CO$_2$H, which indicates that the reaction is probably initiated by proton attack on the OH group.

Both complexes, **8** and **9**, were characterized by elemental analyses and IR as well as ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data. The NMR spectra deserve comment insofar as they are more complicated than those of the related (enyne)rhodium compounds **5a,b** because of the chirality of the –CH(Me)OH substituent. Owing to this feature, the ^{31}P NMR spectrum of **8** shows a multiplet of four symmetrically arranged signals centered at δ = 29.64, which represent the four intense lines in the AB-subspectrum of an ABX-spin system. Furthermore, the ^{1}H NMR spectrum of **8** reveals four instead of two signals, differing only slightly in the chemical shift, for the CH$_3$ protons of the ^{i}Pr groups. In contrast to this, the ^{31}P NMR spectrum of the corresponding vinylidene complex **9** displays only one doublet, which is probably due to the fact that the rapid rotation of the vinylidene ligand around the Rh–C bond renders the two phosphorus nuclei equivalent on the NMR time scale. However, as a consequence of the chiral center in the vinylidene ligand, the resonances of the diastereotopic CH$_3$ groups are found at different chemical shifts, and in the ^{1}H NMR spectrum, the signals of these groups therefore appear as two doublets of virtual triplets. That there is only one signal in the ^{13}C NMR spectrum of **9** for the methyl carbons of the phosphine ligands is probably due to the fact that the small difference in the chemical shift for the expected two resonances could not be resolved by the spectrometer used.

Alkynyl–Hydrido Complexes from Rhodium Alkynes and Rhodium Vinylidenes. While the formation of the alkynyl–hydrido compound **6c** from [RhCl(P^{i}Pr$_3$)$_2$] and HC≡CCH=CH(OMe) via **5c** can be taken as to support the stepwise mechanism of conversion from Rh(HC≡CR) to RhH(C≡CR) and finally to Rh(=C=CHR),[26] there was no evidence that *under the conditions used for the preparation of the vinylidene complexes* **7a,b** and **9** from the alkyne metal precursors **5a,b** and **8** an analogous intermediate is formed. We therefore decided to follow the course of the reaction at lower temperatures by NMR spectroscopy and, furthermore, to attempt to trap an intermediary species containing a RhH(C≡CR) fragment by addition of pyridine.

For **5b** and **8** as starting materials, ^{1}H and ^{31}P NMR spectroscopic measurements apparently confirm the primary generation of the alkynyl(hydrido)rhodium derivatives **6b** and **10** (Scheme V). In the ^{31}P NMR spectra (in C$_6$D$_6$) the decrease in intensity of the resonance(s) of **5b** and **8** is accompanied by the appearance of a new signal at δ = 48.9 and 49.4, which could be assigned to **6b** and **10**, respectively. At the same time, in the high-field region of the ^{1}H NMR spectrum of **8**/**10** (in C$_6$D$_6$), a doublet of triplets at δ = –28.16 is observed. We failed to isolate pure samples of the alkynyl(hydrido)metal complexes **6b** and

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Scheme VI

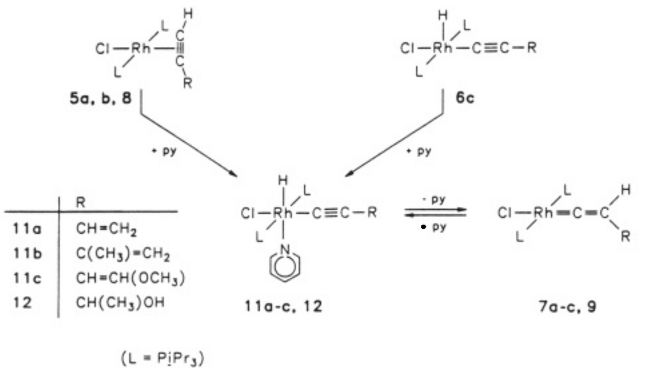


Table II. Selected Bond Distances and Angles with Esd's for 11b

Bond Distances (Å)			
Rh–Cl	2.442 (1)	Rh–N	2.285 (3)
Rh–P1	2.365 (1)	Rh–C1	1.958 (4)
Rh–P2	2.363 (1)	Rh–H	1.56 (4)
C1–C2	1.206 (5)	C3–C4	1.475 (9)
C2–C3	1.432 (6)	C3–C5	1.376 (8)
Bond Angles (deg)			
Cl–Rh–P1	90.55 (4)	Cl–Rh–C1	175.5 (1)
Cl–Rh–P2	89.57 (3)	C1–Rh–H	90 (2)
Cl–Rh–N	90.03 (8)	P1–Rh–P2	163.24 (3)
Cl–Rh–H	85 (2)	C2–C3–C4	116.8 (6)
Rh–C1–C2	177.1 (4)	C2–C3–C5	119.0 (6)
C1–C2–C3	176.1 (5)	C4–C3–C5	124.2 (6)

10 because under the conditions of the spectroscopic measurements further rearrangement of **6b** and **10** to **7b** and **9** also takes place.

The synthesis of the pyridine adducts **11a–c** and **12** (see Scheme VI) is best achieved by treatment of pentane solutions of **5a,b**, **6c**, and **8** with excess pyridine at room temperature. The yield is virtually quantitative. Compounds **11a–c** and **12** are white crystalline solids which for short times can be handled in air. Although we were unable to confirm by NMR spectroscopy the existence of $[RhH(C{\equiv}CCH{=}CH_2)Cl(P^iPr_3)_2]$ (**6a**), we assume that the formation of all the octahedral (pyridine)rhodium complexes **11a–c** and **12** proceeds via the corresponding alkynyl(hydrido)metal intermediate.

In benzene or dichloromethane solutions, compounds **11a–c** and **12** slowly undergo elimination of pyridine and rearrange to the vinylidene complexes **7a–c** and **9**. For other derivatives of the general type $[RhH(C{\equiv}CR)Cl(py)(P^iPr_3)_2]$, a similar behavior has been observed.[5,27] The surprising fact is, however, that the rearrangement is completely reversible, which means that on addition of excess pyridine to solutions of **7a–c** and **9** the octahedral alkynyl–hydrido–pyridine derivatives **11a–c** and **12** are re-formed. An analogous reaction with CO does not occur. Passing a slow stream of carbon monoxide through a benzene solution of **7b** leads to the formation of the enyne $HC{\equiv}CCMe{=}CH_2$ and the square-planar carbonyl complex *trans*-$[RhCl(CO)(P^iPr_3)_2]$ (**13**), which has previously been prepared from $[RhCl(P^iPr_3)_2]$ and CO.[10a]

Molecular Structure of 11b. As the NMR data of **11a–c** and **12** could only confirm that the phosphine ligands are in a trans position but not whether the pyridine or the chloride is trans to the alkynyl unit, a single-crystal X-ray analysis of **11b** was performed. The structure of the molecule is shown in Figure 2 whereas the most relevant bond distances and angles are outlined in Table II. The position of the hydride ligand was determined by a Fourier analysis and refined by fixed thermal parameters.

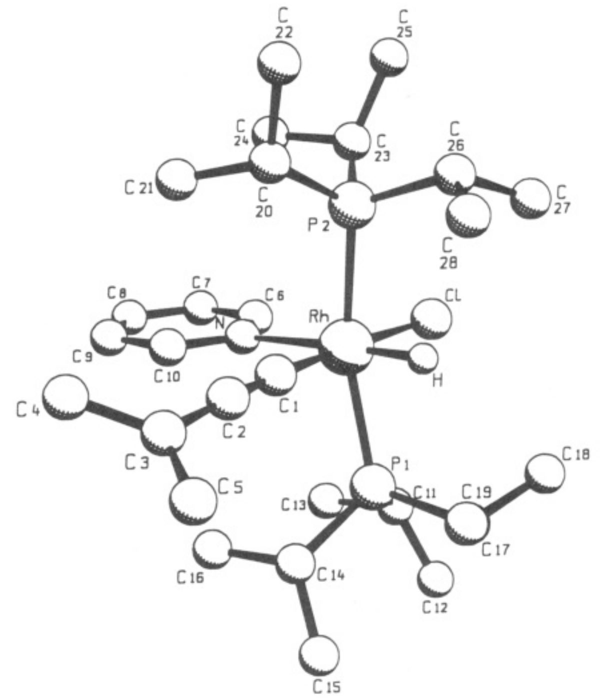
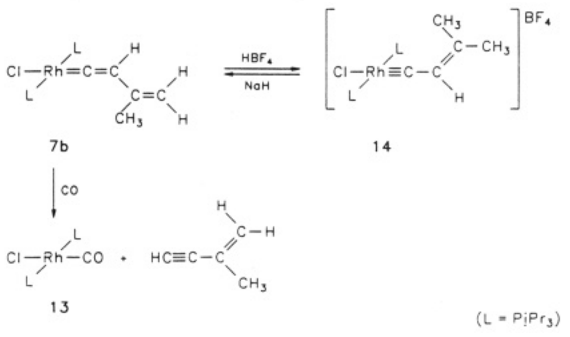


Figure 2. Molecular structure (SCHAKAL drawing) and labeling scheme for complex **11b**.

Scheme VII



The structure of the alkynyl–hydrido complex **11b** is best described as a distorted octahedron with the two phosphines, the alkynyl and the chloride, and the pyridine and the hydride ligand trans to each other. The Rh–H bond length of 1.56 (4) Å is almost identical to that in the cationic derivative *cis*-$[RhH(C{\equiv}CCH_2CH_2OH)(PMe_3)_4]^+$[28] but significantly longer than in the chelate compound $[RhH(C{\equiv}CH)(NP_3)]^+$ ($NP_3 = N(CH_2CH_2PPh_2)_3$).[29] The Rh–C1–C2–C3 unit is nearly linear with a C1–C2 distance (1.20 Å) corresponding to that of a C≡C triple bond.

Preparation of the (Carbyne)rhodium Complex 14. In order to learn whether (vinylvinylidene)rhodium compounds can be transformed like the vinylideneiridium derivatives *trans*-$[IrCl({=}C{=}CHR)(P^iPr_3)_2]$[30] into cationic carbyne complexes, the reaction of **7b** with acids has been investigated.

If an ethereal solution of HBF_4 is added dropwise to a solution of **7b** in OEt_2, a violet solid precipitates, which analyzes as a 1:1 adduct of the two substrates. The solid

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is insoluble in ether, benzene, or other hydrocarbons but dissolves easily in CH_2Cl_2, acetone, or nitromethane. As, even at low temperatures, these solutions decompose quite rapidly, no reliable ^{13}C NMR data for the new compound could be obtained. The ^1H NMR spectrum, in CD_2Cl_2 at −60 °C, reveals besides the signals for the phosphines one singlet for the $-CH=$ and two singlets for the $=C(CH_3)_2$ protons but no resonance for a metal-bound hydrogen in the high-field region. We therefore assume that the protonation of **7b** leads to the formation of a cationic carbyne (**14**; see Scheme VII) and not of an isomeric vinylidene(hydrido)rhodium complex. In the iridium case, an equilibrium between the cations $[IrCl(\equiv CCH_2R)(P^iPr_3)_2]^+$ and $[IrH(=C=CHR)Cl(P^iPr_3)_2]^+$ could be detected.[14b,30] We note that the protonation of **7b** is reversible and thus on treatment of **14** with NaH in ether the vinylvinylidene complex is re-formed.

Conclusions

The present work has shown that enynes of composition $HC\equiv CCR=CH_2$ (R = H, Me) react with the coordinatively unsaturated species $[RhCl(P^iPr_3)_2]$ to form the square-planar complexes *trans*-$[RhCl(HC\equiv CCR=CH_2)(P^iPr_3)_2]$ (**5a,b**). Owing to the spectroscopic data there is no doubt that it is the $C\equiv C$ triple and not the $C=C$ double bond of the enyne which is linked to the metal. Compounds **5a,b** smoothly rearrange to give the isomeric rhodium vinylidenes *trans*-$[RhCl(=C=CHCR=CH_2)(P^iPr_3)_2]$ (**7a,b**) that contain, as confirmed by the X-ray structural analysis of **7b**, a chainlike cumulated/conjugated bond system.

The substituents at the $C=C$ bond of the enyne can exert a remarkable influence on the course of the reaction with the standard starting material $[RhCl(P^iPr_3)_2]$. If this is treated with $HC\equiv CCH=CH(OMe)$, the alkynyl–hydrido complex $[RhH(C\equiv CCH=CHOMe)Cl(P^iPr_3)_2]$ (**6c**) instead of the isomeric alkyne derivative is obtained. The conversion of **6c** to the corresponding vinylvinylidene compound *trans*-$[RhCl(=C=CHCH=CHOMe)(P^iPr_3)_2]$ (**7c**) proceeds under the same conditions as used for the synthesis of **7a,b**, which supports the assumption that the formation of four-coordinate metal vinylidenes such as **7a** or **7b** from the alkyne precursors **5a** or **5b** occurs stepwise via alkynyl(hydrido)metal intermediates. In presence of pyridine, these usually labile intermediates can be trapped and the octahedral rhodium(III) compounds **11a–c** isolated in nearly quantitative yield.

The parent (vinylvinylidene)rhodium complex **7a** can also be prepared from the alkynol $HC\equiv CCH(CH_3)OH$ via the vinylidene derivative *trans*-$[RhCl(=C=CHCH(CH_3)OH)(P^iPr_3)_2]$, which undergoes elimination of H_2O on treatment with acidic Al_2O_3 or traces of HX. It should be noted that the water abstraction only gives **7a** and not the isomeric rhodium allenylidene *trans*-$[RhCl(=C=C=CHCH_3)(P^iPr_3)_2]$. Most recently, the synthesis of compounds of general composition *trans*-$[RhCl(=C=C=CRR')(P^iPR_3)_2]$ (R = R′ = Ph; R = Me, R′ = Ph; R = H, R′ = Ph) has been achieved[31] and will be described in the next full paper.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk tube techniques. The starting material $[RhCl(C_8H_{14})_2]_2$ (**4**) was prepared as described in the literature.[32] The alkynes, 2-methylbut-1-en-3-yne, $HC\equiv CC(CH_3)=CH_2$, (*Z*)-1-methoxybut-1-en-3-yne, $HC\equiv CCH=CH(OMe)$, and but-1-yn-3-ol (D/L-mixture), $HC\equiv CCH(CH_3)OH$, were commercial products from Aldrich; (*Z*)-1-methoxybut-1-en-3-yne was purified as described by Corey.[33] But-1-en-3-yne (vinylacetylene) was prepared from 1,4-dichlorobut-2-ene by published procedure[34] and condensed at −78 °C in pentane. NMR spectra were recorded on JEOL FX 90Q and Bruker AC 200 instruments, IR spectra on a Perkin-Elmer 1420 infrared spectrometer, UV spectra on a Hewlett-Packard 8452A diode-array spectrophotometer, and mass spectra on a Varian MAT CH7 instrument. Melting points were measured by DTA.

Preparation of *trans*-$[RhCl(HC\equiv CCH=CH_2)(P^iPr_3)_2]$ (5a). A suspension of **4** (250 mg, 0.35 mmol) in 20 mL of pentane was treated at room temperature with an excess of P^iPr_3 (0.5 mL, 2.5 mmol). After being stirred for 15 min, the solution was filtered, and the filtrate was cooled to −78 °C. To the violet filtrate was added a pentane solution of vinylacetylene dropwise until the yellow-orange color of the solution remained unchanged. The solution was concentrated in vacuo to ca. 3 mL and stored at −78 °C. Yellow, moderately air-stable crystals were formed, which were separated from the mother liquor, washed with pentane (−78 °C), and dried in vacuo: yield 225 mg (63%); mp 78 °C dec. Anal. Calcd for $C_{22}H_{46}ClP_2Rh$: C, 51.72; H, 9.08. Found: C, 51.75; H, 9.13. IR (KBr): $\nu(\equiv CH)$ 3088, $\nu(C\equiv C)$ 1808 cm^{-1}.

Preparation of *trans*-$[RhCl(HC\equiv CC(CH_3)=CH_2)(P^iPr_3)_2]$ (5b). **5b** was prepared analogously as described for **5a**, using 2-methylbut-1-ene-3-yne as the substrate. Yellow, moderately air-stable crystals were isolated: yield 283 mg (77%); mp 80 °C dec. Anal. Calcd for $C_{23}H_{49}ClP_2Rh$: C, 52.52; H, 9.32. Found: C, 52.64; H, 9.44. IR (KBr): $\nu(\equiv CH)$ 3086, $\nu(C\equiv C)$ 1807 cm^{-1}. ^1H NMR (CD_2Cl_2, 90 MHz, −60 °C): δ 6.02 (s, one H of $=CH_2$), 5.32 (s, one H of $=CH_2$), 3.91 (d, $J(RhH)$ = 3.0 Hz, $\equiv CH$), 2.16 (m, $PCHCH_3$), 1.94 (s, $-C(CH_3)=$), 1.16 (dvt, N = 12.6, $J(HH)$ = 6.6 Hz, $PCHCH_3$). ^{31}P NMR (C_6D_6, 36.2 MHz, 25 °C): δ 33.02 (d, $J(RhP)$ = 118.7 Hz, P^iPr_3).

Preparation of $[RhH(C\equiv CCH=CHOMe)Cl(P^iPr_3)_2]$ (6c). A suspension of **4** (216 mg, 0.30 mmol) in 20 mL of pentane was treated at room temperature with an excess of P^iPr_3 (0.5 mL, 2.5 mmol). After being stirred for 15 min, the solution was filtered and cooled to 0 °C, and (*Z*)-1-methoxybut-1-ene-3-yne was added dropwise to the filtrate until the color of the solution remained unchanged. The solution was brought to dryness in vacuo, and the residue was recrystallized from pentane (25 to −78 °C) to give orange air-sensitive crystals: yield 231 mg (71%); mp 54 °C dec. Anal. Calcd for $C_{23}H_{49}ClOP_2Rh$: C, 50.97; H, 9.11. Found: C, 51.14; H, 9.65. IR (KBr): $\nu(C\equiv C)$ 2090, $\nu(C=C)$ 1617 cm^{-1}. ^1H NMR (CD_2Cl_2, 90 MHz, −30 °C): δ 5.90 (d, $J(HH)$ = 5.7 Hz, $=CHOCH_3$), 4.47 (dt, $J(PH)$ = 2.6, $J(HH)$ = 5.7 Hz, $CH=CHOCH_3$), 3.58 (s, OCH_3), 2.88 (m, $PCHCH_3$), 1.27 (dvt, N = 13.7, $J(HH)$ = 6.8 Hz, $PCHCH_3$), −28.27 (dt, $J(RhH)$ = 43.9, $J(PH)$ = 11.7 Hz, RhH). ^{31}P NMR (C_6D_6, 36.2 MHz, 25 °C): δ 49.21 (d, $J(RhP)$ = 98.2 Hz, P^iPr_3).

If the reaction was carried out at −78 °C and the solution worked up immediately after the addition of the enyne was finished, a yellow solid was isolated, which owing to the spectroscopic data consisted of a 1:1 mixture of **6c** and the isomer *trans*-$[RhCl(HC\equiv CCH=CHOMe)(P^iPr_3)_2]$ (**5c**). Data for **5c**: IR (KBr) $\nu(C\equiv C)$ 1805 cm^{-1}; ^{31}P NMR (C_6D_6, 36.2 MHz, 25 °C) δ 32.33 (d, $J(RhP)$ = 118.7 Hz, P^iPr_3).

Preparation of *trans*-$[RhCl(=C=CHCH=CH_2)(P^iPr_3)_2]$ (7a). An immediate color change from orange-yellow to dark green occurred if a sample of **5a** (67 mg, 0.13 mmol) was dissolved in 10 mL of toluene. After being stirred for 10 min, the solvent was removed in vacuo and the residue was recrystallized from pentane (25 to −78 °C) to give dark green air-stable crystals: yield 54 mg (81%); mp 87 °C dec. Anal. Calcd for $C_{22}H_{46}ClP_2Rh$: C, 51.72; H, 9.08. Found: C, 51.62; H, 9.38. MS (70 eV): m/z 511 (M^+). IR (C_6H_6): $\nu(C=C)$ 1629 cm^{-1}. UV (CH_2Cl_2): λ(max) 582 and 440 nm. ^1H NMR (C_6D_6, 90 MHz): δ 6.65 (ddd, $J(H^2H^4)$ = 17.0, $J(H^1H^2) = J(H^2H^3)$ = 10.3 Hz, H^2), 4.70 (dd, $J(H^2H^4)$ = 17.0, $J(H^3H^4)$ = 1.5 Hz, H^4), 4.22 (dd, $J(H^2H^3)$ = 10.3, $J(H^3H^4)$ = 1.5 Hz, H^3), 2.75 (m, $PCHCH_3$), 1.28 (dvt, N = 13.5, $J(HH)$ = 7.3 Hz,

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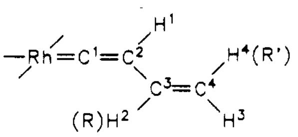

Figure 3. Assignment of protons H^1–H^4 and of carbon atoms C^1–C^4 of the vinylvinylidene ligands in **7a–c**.

PCHCH_3), signal of H^1 obscured by the signal of the PCHCH_3 protons. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 295.93 (dt, *J*(RhC) = 58.5, *J*(PC) = 17.3 Hz, C^1), 118.09 (s, C^3), 111.00 (dt, *J*(RhC) = 17.3, *J*(PC) = 6.3 Hz, C^2), 106.07 (s, C^4), 23.22 (vt, *N* = 19.8 Hz, P*C*HCH$_3$), 19.89 (s, PCHCH_3); for assignment of protons H^1–H^4 and of carbon atoms C^1–C^4, see Figure 3. ^{31}P NMR (C_6D_6, 36.2 MHz): δ 41.69 (d, *J*(RhP) = 134.8 Hz, P^iPr_3).

Preparation of *trans*-[RhCl(=C=CHC(CH_3)=CH_2)(P^iPr_3)$_2$] (7b). A solution of **5b** (149 mg, 0.28 mmol) in 10 mL of toluene was stirred at 45 °C for 2 h. After it was worked up as described for **7a**, blue green crystals were isolated: yield 139 mg (93%); mp 88 °C dec. Anal. Calcd for $C_{23}H_{48}ClP_2Rh$: C, 52.52; H, 9.32. Found: C, 52.40; H, 9.26. MS (70 eV): *m/z* 525 (M^+). IR (CH_2Cl_2): ν(C=C) 1654, 1622 cm^{-1}. UV (CH_2Cl_2): λ(max) 582 and 440 nm. ^1H NMR (C_6D_6, 200 MHz): δ 4.60 (br, one H of =CH_2), 4.14 (br, one H of =CH_2), 2.73 (m, PC*H*CH$_3$), 1.88 (s, CH_3), 1.31 (dvt, *N* = 13.5, *J*(HH) = 6.3 Hz, PCHCH_3), signal of H^1 obscured by the signal of the PCHCH_3 protons. ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ 295.74 (dt, *J*(RhC) = 59.6, *J*(PC) = 16.6 Hz, C^1), 128.01 (t, *J*(PC) = 2.0 Hz, C^3), 113.88 (dt, *J*(RhC) = 15.6, *J*(PC) = 5.6 Hz, C^2), 105.56 (s, C^4), 23.65 (vt, *N* = 17.6 Hz, P*C*HCH$_3$), 22.74 (s, CH_3), 20.10 (s, PCH*C*H$_3$); for assignment of protons H^1–H^4 and of carbon atoms C^1–C^4, see Figure 3. ^{31}P NMR (C_6D_6, 36.2 MHz): δ 41.50 (d, *J*(RhP) = 136.3 Hz, P^iPr_3).

Preparation of *trans*-[RhCl(=C=CHCH=CHOMe)(P^iPr_3)$_2$] (7c). **7c** was prepared analogously as described for **7b**, using **6c** (81 mg, 0.15 mmol) as starting material. Dark violet crystals were isolated: yield 74 mg (91%); mp 61 °C dec. Anal. Calcd for $C_{23}H_{49}ClOP_2Rh$: C, 50.97; H, 9.11. Found: C, 50.60; H, 8.92. MS (70 eV): *m/z* 542 (M^+). IR (CH_2Cl_2): ν(C=C) 1646, 1614 cm^{-1}. UV (CH_2Cl_2): λ(max) 583 and 436 nm. ^1H NMR (C_6D_6, 90 MHz): δ 5.35 (dd, *J*(H^1H^2) = 10.6, *J*(H^2H^3) = 4.6 Hz, H^2), 4.94 (dd, *J*(H^1H^3) = 1.1, *J*(H^2H^3) = 4.6 Hz, H^3), 3.06 (s, OCH_3), 2.77 (m, PC*H*CH$_3$), 1.99 (m, ddd if ^{31}P decoupled, *J*(H^1H^2) = 10.6, *J*(H^1H^3) = 1.1, *J*(RhH) = 1.1 Hz, H^1), 1.28 (dvt, *N* = 13.6, *J*(HH) = 7.2 Hz, PCHCH_3). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 301.10 (dt, *J*(RhC) = 58.7, *J*(PC) = 17.4 Hz, C^1), 134.47 (s, C^3), 102.04 (dt, *J*(RhC) = 17.4, *J*(PC) = 6.5 Hz, C^2), 85.92 (s, C^4), 59.45 (s, OCH_3), 23.07 (vt, *N* = 18.6 Hz, P*C*HCH$_3$), 19.91 (s, PCH*C*H$_3$); for assignment of protons H^1–H^4 and of carbon atoms C^1–C^4, see Figure 3. ^{31}P NMR (C_6D_6, 36.2 MHz): δ 41.46 (d, *J*(RhP) = 136.3 Hz, P^iPr_3).

One-Pot Synthesis of 7a–c. A suspension of **4** (150 mg, 0.21 mmol) in 10 mL of pentane was treated at room temperature with P^iPr_3 (0.2 mL, 1.0 mmol). After being stirred for 15 min, a solution of the corresponding alkyne in pentane was added until the color of the reaction mixture remained unchanged. The solvent was removed in vacuo, the solid residue was dissolved in ca. 5 mL of toluene, and the solution was stirred at 45 °C for 2 h. After being cooled to room temperature, the solution was chromatographed on Al_2O_3 (neutral, activity grade V). With hexane, a dark green or violet fraction was eluted, which was brought to dryness in vacuo. The residue was recrystallized from pentane (25 to −78 °C) to give **7a–c** in 65–75% yield.

Preparation of *trans*-[RhCl(HC≡CCH(CH_3)OH)(P^iPr_3)$_2$] (8). A suspension of **4** (178 mg, 0.25 mmol) in 20 mL of pentane was treated at room temperature with an excess of P^iPr_3 (0.5 mL, 2.5 mmol). After being stirred for 15 min, the solution was filtered, and but-1-yne-3-ol was added dropwise to the filtrate until the color of the solution remained unchanged. The solvent was removed, and the residue was extracted with pentane. The extract was concentrated in vacuo until a precipitate occurred and then stored at −78 °C. Yellow, moderately air-stable crystals were formed: yield 170 mg (64%); mp 60 °C dec. Anal. Calcd for $C_{22}H_{49}ClOP_2Rh$: C, 49.86; H, 9.13. Found: C, 49.97; H, 9.10. IR (KBr): ν(OH) 3450, ν(≡CH) 3103, ν(C≡C) 1850 cm^{-1}. ^1H NMR (C_6D_6, 90 MHz): δ 4.70 (dq, *J*(HH) = 6.3 and 2.4 Hz, C*H*(CH_3)OH), 3.21 (dd, *J*(RhH) = 2.4, *J*(HH) = 2.4 Hz, ≡CH), 2.28 (m, PC*H*CH$_3$), 1.54 (d, *J*(HH) = 6.3 Hz, CH(CH_3)OH), 1.29, 1.26, 1.25 and 1.19 (all dvt, *N* = 13.8, *J*(HH) = 7.3 Hz, PCHCH_3), signal of OH not observed. ^{31}P NMR (C_6D_6, 36.2 MHz): four signals centered at 31.24 ppm (ABX-spin system: A,B = P; X = Rh; *J*(AX) + *J*(BX) = 231.5 Hz).

Table III. Crystallographic Data for 7b and 11b

	7b	11b
formula	$C_{23}H_{48}ClP_2Rh$	$C_{28}H_{53}ClNP_2Rh$
fw	525.95	605.05
cryst size, mm	0.4 × 0.2 × 0.2	0.4 × 0.4 × 0.3
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
cell dimens determn	23 reflns, 12 < θ < 14°	23 reflns, 11 < θ < 13°
a, Å	8.177 (3)	9.3103 (5)
b, Å	38.946 (9)	11.7936 (8)
c, Å	17.597 (6)	15.322 (2)
α, deg		93.246 (7)
β, deg	93.99 (1)	92.832 (6)
γ, deg		108.981 (5)
V, Å^3	5590	1584.3
Z	8	2
d_{calcd}, g·cm^{-3}	1.617	1.27
diffractometer	Enraf Nonius CAD 4	
radiatn (graphite monochrom)	Mo Kα (0.709 30 Å)	
temp, °C	20 ± 1	
μ, cm^{-1}	10.6	7.3
scan method	ω/2θ	ω/2θ
2θ(max), deg	42	44
tot. no. of rflns scanned	6635	4169
no. of unique rflns	6108	3992
no. of obsd rflns	3357 ($F_o > 3\sigma(F_o)$)	3530 ($I_o > 3\sigma(I_o)$)
no. of params refined	487	298
R	0.039	0.027
R_w	0.046	0.030
rfln/param ratio	6.89	11.8
resid electron density, e Å^{-3}	+0.29/−0.30	+0.31/−0.47

Preparation of *trans*-[RhCl(=C=CHCH(CH_3)OH)(P^iPr_3)$_2$] (9). A solution of **8** (121 mg, 0.17 mmol) in 10 mL of toluene was stirred at 45 °C for 2 h. After the solvent was removed in vacuo, the residue was recrystallized from pentane (25 to −78 °C) to give green crystals: yield 114 mg (94%); mp 61 °C. Anal. Calcd for $C_{22}H_{49}ClOP_2Rh$: C, 49.86; H, 9.13. Found: C, 49.52; H, 9.36. IR (KBr): ν(OH) 3450, ν(C=C) 1650 cm^{-1}. ^1H NMR (C_6D_6, 90 MHz): δ 4.83 (dq, *J*(HH) = 9.4 and 6.2 Hz, C*H*(CH_3)OH), 2.82 (m, PC*H*CH$_3$), 1.30 and 1.29 (both dvt, *N* = 13.3, *J*(HH) = 7.1 Hz, PCHCH_3), 1.11 (d, *J*(HH) = 6.2 Hz, CH(CH_3)OH), 0.52 (ddt, *J*(RhH) = 0.9, *J*(PH) = 4.0, *J*(HH) = 9.4 Hz, =CH–), signal of OH not observed. ^{13}C NMR (C_6D_6, 22.5 MHz): δ 288.72 (dt, *J*(RhC) = 58.1, *J*(PC) = 16.2 Hz, =C=), 111.80 (dt, *J*(RhC) = 15.4, *J*(PC) = 6.0 Hz, =CH–), 55.52 (s, *C*H(CH_3)OH), 26.42 (s, CH(*C*H$_3$)OH), 23.35 (vt, *N* = 19.7 Hz, P*C*HCH$_3$), 20.24 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 41.40 (d, *J*(RhP) = 134.8 Hz, P^iPr_3).

Preparation of 7a from 9. A solution of **9** (89 mg, 0.13 mmol) in 3 mL of toluene was passed through a column with Al_2O_3 (acidic, activity grade I). With hexane/toluene (5:1) a green fraction was eluted, which was worked up as described above. Yield of **7a**:82 mg (93%).

Preparation of [RhH(C≡CCH=CH_2)Cl(py)(P^iPr_3)$_2$] (11a). A solution of **5a** (102 mg, 0.20 mmol) in 10 mL of pentane was treated with pyridine (0.2 mL, 2.44 mmol) and stirred for 30 min at room temperature. The solution became colorless, and some white crystals precipitated. After the mixture was stored at −78 °C, the precipitate was filtered off, repeatedly washed with pentane (−20 °C), and dried in vacuo: yield 108 mg (92%); mp 88 °C dec. Anal. Calcd for $C_{27}H_{51}ClNP_2Rh$: C, 54.96; H, 8.71; N, 2.37. Found: C, 55.31; H, 9.19; N, 2.66. IR (KBr): ν(RhH) 2176, ν(C≡C) 2092 cm^{-1}. ^1H NMR (CD_2Cl_2, 90 MHz, −60 °C): δ −17.56 (dt, *J*(RhH) = 13.7, *J*(PH) = 13.7 Hz, RhH), other signals not clearly detected due to limited solubility at low temperature. ^{31}P NMR (C_6D_6, 36.2 MHz, 25 °C): δ 37.36 (d, *J*(RhP) = 98.2 Hz, P^iPr_3).

Preparation of [RhH(C≡CC(CH_3)=CH_2)Cl(py)(P^iPr_3)$_2$] (11b). **11b** was prepared analogously as described for **11a**, using **5b** (105 mg, 0.20 mmol) as starting material. White crystals were obtained: yield 117 mg (97%); mp 87 °C dec. Anal. Calcd for $C_{28}H_{54}ClNP_2Rh$: C, 55.58; H, 9.00; N, 2.31. Found: C, 55.59; H,

Table IV. Positional Parameters and Their Estimated Standard Deviations for 7b

atom	*x*	*y*	*z*	*B*,[a] Å^2
Rh*	0.3670 (1)	0.30950 (2)	0.72509 (4)	3.66 (2)
Rh	0.3526 (1)	0.41631 (2)	0.24311 (4)	3.56 (2)
Cl*	0.3707 (5)	0.26102 (8)	0.6442 (2)	7.7 (1)
Cl	0.3663 (5)	0.37402 (8)	0.3400 (2)	7.43 (9)
P1*	0.2332 (3)	0.34079 (8)	0.6237 (2)	3.96 (6)
P1	0.2316 (3)	0.37653 (7)	0.1551 (1)	3.50 (6)
P2*	0.4917 (3)	0.27794 (7)	0.8279 (2)	3.78 (6)
P2	0.4926 (4)	0.45517 (7)	0.3265 (2)	3.85 (6)
C1*	0.356 (1)	0.3464 (3)	0.7857 (6)	5.0 (3)
C1	0.349 (1)	0.4472 (3)	0.1683 (6)	4.8 (3)
C2*	0.323 (2)	0.3722 (3)	0.8301 (6)	6.5 (3)
C2	0.356 (2)	0.4681 (3)	0.1091 (6)	5.8 (3)
C3*	0.422 (2)	0.4034 (3)	0.8416 (7)	8.1 (4)
C3	0.243 (2)	0.4954 (3)	0.0839 (7)	6.2 (3)
C4*	0.353 (3)	0.4315 (4)	0.8757 (9)	13.8 (7)
C4	0.257 (3)	0.5103 (4)	0.0164 (9)	11.9 (6)
C5*	0.586 (3)	0.4061 (4)	0.820 (1)	12.7 (6)
C5	0.117 (2)	0.5056 (4)	0.1343 (9)	9.0 (5)
C6*	0.381 (1)	0.3592 (3)	0.5607 (6)	4.7 (3)
C6	0.129 (1)	0.3399 (3)	0.1987 (6)	4.0 (2)
C7*	0.497 (2)	0.3840 (3)	0.6032 (8)	7.0 (4)
C7	0.066 (1)	0.3112 (3)	0.1460 (7)	6.3 (3)
C8*	0.481 (2)	0.3318 (4)	0.5239 (7)	7.0 (4)
C8	−0.002 (2)	0.3508 (3)	0.2506 (8)	6.8 (3)
C9*	0.119 (1)	0.3787 (3)	0.6544 (6)	5.5 (3)
C9	0.091 (1)	0.3964 (3)	0.0800 (6)	4.6 (3)
C10*	0.060 (2)	0.4048 (3)	0.5934 (8)	7.0 (4)
C10	−0.052 (2)	0.4134 (4)	0.1147 (8)	8.5 (4)
C11*	−0.021 (2)	0.3682 (4)	0.7036 (8)	8.3 (4)
C11	0.037 (2)	0.3737 (4)	0.0113 (7)	8.1 (4)
C12*	0.100 (1)	0.3138 (3)	0.5574 (7)	5.9 (3)
C12	0.391 (1)	0.3553 (3)	0.1024 (6)	4.5 (3)
C13*	0.019 (2)	0.3323 (4)	0.4878 (8)	8.7 (4)
C13	0.488 (2)	0.3817 (4)	0.0567 (7)	7.1 (4)
C14*	−0.029 (2)	0.2943 (4)	0.5999 (9)	8.5 (4)
C14	0.512 (2)	0.3361 (4)	0.1566 (8)	6.8 (4)
C15*	0.621 (1)	0.3042 (3)	0.8962 (6)	5.3 (3)
C15	0.645 (1)	0.4330 (3)	0.3934 (6)	5.1 (3)
C16*	0.767 (2)	0.3184 (4)	0.8584 (9)	9.1 (4)
C16	0.768 (2)	0.4118 (3)	0.3524 (8)	7.7 (3)
C17*	0.677 (2)	0.2859 (4)	0.9717 (8)	8.6 (4)
C17	0.734 (2)	0.4559 (4)	0.4547 (7)	7.7 (4)
C18*	0.611 (1)	0.2401 (3)	0.7968 (6)	5.1 (3)
C18	0.358 (1)	0.4774 (3)	0.3905 (6)	5.6 (3)
C19*	0.743 (2)	0.2502 (4)	0.7449 (8)	7.7 (4)
C19	0.275 (2)	0.4517 (4)	0.4420 (7)	8.2 (4)
C20*	0.671 (2)	0.2149 (4)	0.8584 (8)	9.1 (4)
C20	0.228 (2)	0.4989 (4)	0.3447 (8)	8.0 (4)
C21*	0.339 (1)	0.2583 (3)	0.8864 (6)	4.6 (3)
C21	0.592 (1)	0.4906 (3)	0.2776 (6)	4.8 (3)
C22*	0.229 (2)	0.2332 (4)	0.8406 (8)	7.7 (4)
C22	0.725 (2)	0.4779 (4)	0.2285 (8)	7.1 (4)
C23*	0.236 (2)	0.2857 (3)	0.9232 (8)	6.8 (3)
C23	0.657 (2)	0.5215 (4)	0.3276 (8)	8.9 (4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

8.81; N, 2.80. IR (KBr): ν(RhH) 2182, ν(C≡C) 2101 cm^{-1}. ^{1}H NMR (C_6D_6, 90 MHz): δ 9.96 and 6.76 (both m, C_5H_5N), 5.15 (dq, *J*(HH) = 2.9 and 1.0 Hz, H^1), 4.96 (dq, *J*(HH) = 2.9 and 1.5 Hz, H^2), 2.92 (m, PC*H*CH$_3$), 1.99 (dd, *J*(HH) = 1.5 and 1.0 Hz, –C(C*H*$_3$)), 1.21 and 1.18 (both dvt, *N* = 14.7, *J*(HH) = 7.3 Hz, PCHC*H*$_3$), –17.62 (dt, *J*(RhH) = 14.2, *J*(PH) = 14.2 Hz, RhH); for assignment of protons H^1 and H^2, see Figure 4. ^{31}P NMR (C_6D_6, 36.2 MHz): δ 37.30 (d, *J*(RhP) = 98.2 Hz, P^{i}Pr$_3$).

Preparation of [RhH(C≡CCH═CHOMe)Cl(py)(P^{i}Pr$_3$)$_2$] (11c). **11c** was prepared analogously as described for **11a**, using **6c** (108 mg, 0.20 mmol) as starting material. White crystals were obtained: yield 118 mg (95%); mp 89 °C dec. Anal. Calcd for $C_{28}H_{54}ClNOP_2Rh$: C, 54.15; H, 8.76; N, 2.26. Found: C, 53.80; H, 9.11; N, 2.07. IR (KBr): ν(RhH) 2182, ν(C≡C) 2095 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 90 MHz, –30 °C): δ 9.70 and 7.20 (both m, C_5H_5N), 5.87 (d, *J*(HH) = 5.7 Hz, H^2), 4.49 (dt, *J*(PH) = 2.6, *J*(HH) = 5.7 Hz, H^1), 3.57 (s, OCH$_3$), 2.80 (m, PC*H*CH$_3$), 1.07 and 1.06 (both dvt, *N* = 12.7, *J*(HH) = 6.8 Hz, PCHC*H*$_3$), –17.72 (dt, *J*(RhH) = 14.0, *J*(PH) = 14.0 Hz, RhH); for assignment of protons H^1 and H^2, see Figure 4. ^{31}P NMR (C_6D_6, 36.2 MHz, 25 °C): δ 37.47 (d, *J*(RhP) = 98.7 Hz, P^{i}Pr$_3$).

11b 11c

Figure 4. Assignment of protons H^1 and H^2 of the vinylalkynyl ligands in **11b,c**.

Table V. Positional Parameters and Their Estimated Standard Deviations for 11b

atom	*x*	*y*	*z*	*B*[a] Å^2
Rh	0.38089 (3)	0.80312 (3)	0.72465 (2)	2.454 (6)
Cl	0.5504 (1)	0.82976 (9)	0.60529 (6)	3.55 (2)
P1	0.3310 (1)	0.59283 (8)	0.70988 (7)	3.06 (2)
P2	0.4883 (1)	1.01045 (8)	0.76837 (6)	2.81 (2)
N	0.1905 (3)	0.8165 (3)	0.6301 (2)	2.82 (7)
C1	0.2571 (4)	0.7785 (3)	0.8259 (3)	3.18 (9)
C2	0.1794 (5)	0.7579 (4)	0.8876 (3)	4.1 (1)
C3	0.0791 (6)	0.7279 (5)	0.9569 (3)	6.3 (1)
C4	−0.0447 (7)	0.7803 (7)	0.9577 (4)	10.4 (2)
C5	0.103 (1)	0.6538 (6)	1.0180 (4)	10.1 (2)
C6	0.2124 (5)	0.8398 (4)	0.5465 (3)	4.1 (1)
C7	0.1029 (5)	0.8557 (4)	0.4895 (3)	5.2 (1)
C8	−0.0370 (5)	0.8473 (4)	0.5195 (3)	5.0 (1)
C9	−0.0630 (5)	0.8226 (4)	0.6040 (3)	4.5 (1)
C10	0.0537 (4)	0.8078 (3)	0.6581 (3)	3.54 (9)
C11	0.3431 (5)	0.5341 (4)	0.5960 (3)	4.4 (1)
C12	0.3681 (6)	0.4132 (4)	0.5848 (3)	5.9 (1)
C13	0.2115 (7)	0.5347 (5)	0.5340 (3)	7.9 (2)
C14	0.1533 (5)	0.4971 (4)	0.7547 (3)	4.1 (1)
C15	0.1336 (6)	0.3637 (4)	0.7582 (4)	6.1 (1)
C16	0.0091 (6)	0.5115 (5)	0.7139 (5)	7.7 (2)
C17	0.4782 (5)	0.5496 (4)	0.7733 (3)	4.5 (1)
C18	0.6385 (5)	0.6095 (4)	0.7424 (4)	5.7 (1)
C19	0.4754 (6)	0.5756 (5)	0.8731 (3)	6.4 (1)
C20	0.3836 (4)	1.0709 (3)	0.8492 (3)	3.45 (9)
C21	0.2185 (5)	1.0547 (4)	0.8196 (3)	4.9 (1)
C22	0.4632 (6)	1.1999 (4)	0.8884 (4)	6.0 (1)
C23	0.5294 (5)	1.1091 (3)	0.6754 (3)	4.1 (1)
C24	0.3851 (6)	1.1279 (4)	0.6356 (3)	5.7 (1)
C25	0.6545 (6)	1.2320 (4)	0.6931 (4)	6.3 (1)
C26	0.6764 (5)	1.0451 (4)	0.8293 (3)	4.0 (1)
C27	0.7923 (5)	1.0089 (4)	0.7758 (3)	5.0 (1)
C28	0.6638 (5)	0.9866 (5)	0.9168 (3)	5.7 (1)
H	0.508 (5)	0.789 (4)	0.789 (3)	4.0[b]

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [b] The position of the hydride ligand was refined with a fixed temperature factor.

Preparation of 11a–c from 7a–c. A solution of 0.20 mmol of **7a–c** in 10 mL of pentane was treated with pyridine (0.2 mL, 2.44 mmol) and stirred for 15 h at room temperature. The solution was concentrated in vacuo until a precipitate was observed. The isolation of the product occurred as described for **11a**, yield 95%.

Preparation of [RhH(C≡CCH(CH$_3$)OH)Cl(py)(P^{i}Pr$_3$)$_2$] (12). A solution of **8** (106 mg, 0.20 mmol) in 10 mL of pentane was treated with pyridine (0.2 mL, 2.44 mmol) and stirred for 30 min at room temperature. The solution was worked up as described for **11a**. White crystals were isolated: yield 93 mg (88%), mp 74 °C dec. Anal. Calcd for $C_{27}H_{54}ClNOP_2Rh$: C, 53.24; H, 8.94; N, 2.30. Found: C, 52.96; H, 8.66; N, 2.60. IR (KBr): ν(OH) 3450, ν(RhH) 2184, ν(C≡C) 2103 cm^{-1}. ^{1}H NMR (C_6D_6, 90 MHz): δ 9.61 and 6.79 (both m, C_5H_5N), 4.74 (q, *J*(HH) = 6.3 Hz, C*H*(CH$_3$)OH), 2.92 (m, PC*H*CH$_3$), 1.51 (d, *J*(HH) = 6.3 Hz, CH(C*H*$_3$)OH), 1.32, 1.31, 1.20 and 1.16 (all dvt, *N* = 13.9, *J*(HH) = 7.3 Hz, PCHC*H*$_3$), –17.55 (dt, *J*(RhH) = 13.7, *J*(PH) = 13.7 Hz, RhH), signal of OH not observed. ^{31}P NMR (C_6D_6, 36.2 MHz): δ 37.47 (d, *J*(RhP) = 98.2 Hz, P^{i}Pr$_3$).

Reaction of 7b with CO. A slow stream of carbon monoxide was bubbled for ca. 1 min through a solution of **7b** (71 mg, 0.14 mmol) in 0.5 mL of C_6D_6. The solution turned yellow, and the carbonyl complex **13** as well as the unsaturated alkyne HC≡C-C(CH_3)=CH_2 could be detected by IR and ^{1}H NMR spectroscopy.

Preparation of *trans*-[RhCl(=CCH=CMe$_2$)(P^{i}Pr$_3$)$_2$]BF$_4$ (14). A solution of **7b** (97 mg, 0.19 mmol) in 10 mL of diethyl ether was treated at room temperature dropwise with 1 mL of a 0.2 M solution of HBF_4 in OEt_2. A violet solid precipitated, which was filtered off, repeatedly washed with ether, and dried in vacuo: yield 107 mg (95%); dec at 76 °C. Anal. Calcd for $C_{23}H_{49}BClF_4P_2Rh$: C, 45.01; H, 8.21. Found: C, 44.73; H, 8.40. ^{1}H NMR (CD_2Cl_2, 90 MHz, −60 °C): δ 3.93 (s, −C*H*=), 2.78 (m, PC*H*CH$_3$), 2.45 and 2.08 (both s, =C(CH$_3$)$_2$), 1.36 (dvt, N = 14.6, J(HH) = 7.3 Hz, PCHC*H*$_3$).

Reaction of 14 with NaH. A suspension of 14 (71 mg, 0.12 mmol) in 10 mL of ether was treated at room temperature with NaH (20 mg, 0.85 mmol). After being stirred for 10 min, a blue-green solution was obtained, which was filtered and concentrated in vacuo. The residue was washed with pentane (−30 °C) and shown by ^{1}H NMR spectroscopy to be **7b**, yield 50 mg (82%).

X-ray Structural Analysis of 7b. Single crystals were grown from pentane at 25 °C. Crystal data collection parameters are summarized in Table III. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied; the minimal transmission was 96.05%. The structure was solved by direct methods (SHELXS-86). There are two crystallographically independent molecules in the unit cell. Atomic coordinates (see Table IV) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares. The positions of all hydrogen atoms were calculated according to ideal geometry (distance C–H = 0.95 Å) and were refined by the riding method. For other details, see Table III.

X-ray Structural Analysis of 11b. Single crystals were grown from benzene/pentane with excess pyridine in 8 h at 25 °C. Crystal data collection parameters are summarized in Table III. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied; the minimal transmission was 95.9%. The structure was solved by direct methods (SHELXS-86). Atomic coordinates (see Table V) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares. The positions of all hydrogen atoms except the metal-bound hydride were calculated according to ideal geometry (distance C–H = 0.95 Å) and were used for structure-factor calculations in the last full-matrix least-squares refinement. For other details, see Table III.

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Supplementary Material Available: SCHAKAL drawings of complexes **7b** and **11b**, showing the atom-numbering schemes, and tables of bond distances, bond angles, positional parameters, and general anisotropic displacement parameter expressions (23 pages). Ordering information is given on any current masthead page.

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Models for Chemisorption: Fluxional Cyanide Adducts of Trinuclear Platinum and Palladium Clusters

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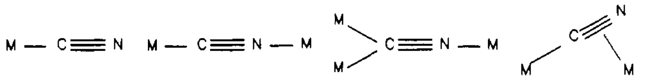
Reaction of the clusters $[M_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$; **1a**, M = Pt; **1b**, M = Pd) with cyanide gave the adducts $[M_3(CN)(\mu_3\text{-CO})(\mu\text{-dppm})_3]^+$ (**2a**, M = Pt; **2b**, M = Pd) in which the carbonyl is asymmetrically bridging and the cyanide is terminal. Solvated crystals of complex **2a**[PF$_6$] have been characterized by X-ray diffraction [crystal data for **2a**[PF$_6$]·Me$_2$CO·H$_2$O: $P\bar{1}$, a = 11.3731 (6) Å, b = 15.4180 (15), c = 24.0242 (29) Å, α = 79.839 (9)°, β = 82.117 (7)°, γ = 81.422 (6)°, V = 4073.5 (7) Å^3, Z = 2, R = 0.047, R_w = 0.066]. Complexes **2** are fluxional in solution, with cyanide migrating rapidly around the M_3 triangle even at −90 °C. Thus, they provide good models for the structure and mobility of terminal cyanide on a metal surface. However, the binding mode of cyanide to the metal triangle appears to be different from that of CN on a Pd(111) or Pt(111) surface.

The binding of cyanide to metal surfaces has been of much recent interest, but the precise mode of attachment has been difficult to determine.[1] Because many ligands bind in similar ways to clusters and surfaces, a study of cyanide binding in clusters might aid assignments. Although cyanide is known to bond in transition metal complexes in the forms A–D (of which A and B are most common), there are remarkably few cyanide cluster complexes and, to our knowledge, no coordinatively unsaturated clusters to act as models for chemisorbed cyanide.[2,3]



A B C D

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