Organometallics **1993**, *12*, 1359–1364

Reactions of Diynes with [RhCl(P*i*Pr$_3$)$_2$]: Unsaturated C$_4$ and Partly Unsaturated C$_6$ Chains between Two Rhodium Centers[1]

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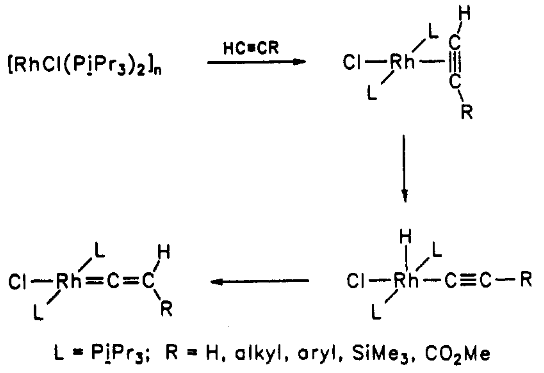
Received November 12, 1992

Treatment of [RhCl(P*i*Pr$_3$)$_2$]$_n$ (**1**) (n = 1 in solution) with HC≡CC≡CH leads to the formation of the diynediyl dihydrido complex [(P*i*Pr$_3$)$_2$Cl(H)Rh(C≡CC≡C)Rh(H)Cl(P*i*Pr$_3$)$_2$] (**2**) in 68% yield. In contrast to this, the corresponding reaction with the bis(trimethylsilyl) derivative Me$_3$SiC≡CC≡CSiMe$_3$ gives the mononuclear compound *trans*-[RhCl(η^2-Me$_3$SiC≡CC≡CSiMe$_3$)(P*i*Pr$_3$)$_2$] (**3**) in which one of the C≡C triple bonds is uncoordinated. Photolysis of **3** in benzene solution affords quantitatively the isomeric vinylidene complex *trans*-[RhCl(=C=C(SiMe$_3$)C≡CSiMe$_3$)(P*i*Pr$_3$)$_2$] (**4**) which on hydrolysis gives *trans*-[RhCl(=C=CHC≡CSiMe$_3$)(P*i*Pr$_3$)$_2$] (**5**). The bis(vinylidene)dirhodium compound *trans*-[(P*i*Pr$_3$)$_2$ClRh(=C=CHCH=C=)RhCl(P*i*Pr$_3$)$_2$] (**6**) is obtained in low yield from **5** and **1** in presence of traces of water and almost quantitatively by the thermal rearrangement of **2**. Both **2** and **6** react with pyridine to give [(P*i*Pr$_3$)$_2$(py)Cl(H)Rh(C≡CC≡C)Rh(H)Cl(py)(P*i*Pr$_3$)$_2$] (**7**). Treatment of **1** with 1,4-dichlorobut-2-yne ClCH$_2$C≡CCH$_2$Cl, which is the starting material for the preparation of buta-1,3-diyne, affords the butatriene rhodium(I) complex *trans*-[RhCl(η^2-ClHC=C=C=CH$_2$)(P*i*Pr$_3$)$_2$] (**8**). From **1** and hexa-1,5-diyne the dinuclear compounds [(P*i*Pr$_3$)$_2$ClRh(HC≡CCH$_2$CH$_2$C≡CH)RhCl(P*i*Pr$_3$)$_2$] (**9**), [(P*i*Pr$_3$)$_2$ClRh(=C=CHCH$_2$CH$_2$CH=C=)RhCl(P*i*Pr$_3$)$_2$] (**10**), and [(P*i*Pr$_3$)$_2$(py)Cl(H)Rh(C≡CCH$_2$CH$_2$C≡C)Rh(H)Cl(py)(P*i*Pr$_3$)$_2$] (**11**) have been prepared. The X-ray crystal structure of **3** has been determined (orthorhombic space group $P2_12_12_1$ (No. 19) with a = 11.19(1) Å, b = 15.89(2) Å, c = 20.75(2) Å, and Z = 4).

Introduction

Recently we reported that the highly reactive bis(triisopropylphosphine)rhodium compound [RhCl(P*i*Pr$_3$)$_2$]$_n$ (**1**), which is prepared from [RhCl(C$_8$H$_{14}$)$_2$]$_2$ and excess P*i*Pr$_3$,[2,3] is an excellent starting material for the synthesis of square-planar vinylidenerhodium(I) complexes of the type *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$].[4] The first step of the reaction shown in Scheme I consists of the coordination of a terminal alkyne to the metal center which is followed by an intramolecular oxidative addition to give an alkynyl(hydrido)rhodium(III) compound. This five-coordinate intermediate frequently reacts very smoothly by hydrogen transfer from the metal to the β-carbon atom of the alkynyl ligand to form the final product. It is interesting to note that the kinetic stability of the alkynyl(hydrido)metal intermediate seems to depend quite critically on the substituent R of the alkynyl unit because if this is C(CH$_3$)$_3$ (*t*Bu) instead of CH$_3$ the reaction to *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$] can be stopped at the RhH(C≡CR) stage.[5]

Scheme I



L = P*i*Pr$_3$; R = H, alkyl, aryl, SiMe$_3$, CO$_2$Me

The aim of the present work was to find out whether buta-1,3-diyne as the most simple and presumably most reactive diyne behaves in a similar way toward **1** as the other 1-alkyne derivatives. Moreover, since both sides of the molecule can interact with the metal center the possibility to isolate a dinuclear rhodium complex with a "naked" C$_4$-bridge was of interest. Since we have found very recently that not only 1-alkynes but also the silylated analogues Me$_3$SiC≡CR (R = Me, *t*Bu, SiMe$_3$, Ph, CO$_2$Me) can be transformed in the coordination sphere of rhodium to the isomeric vinylidenes,[6] we included the corresponding diyne Me$_3$SiC≡CC≡CSiMe$_3$ into these studies. As a third substrate we finally used hexa-1,5-diyne HC≡CCH$_2$CH$_2$C≡CH in order to find out whether this alkyne derivative, in contrast to the highly conjugated

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(1) Vinylidene Transition-Metal Complexes. 24. For part 23, see: Daniel, T.; Mahr, N.; Braun, T.; Werner, H. *Organometallics*, in press.

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

(3) Complex [RhCl(P*i*Pr$_3$)$_2$]$_n$ is a dimer in the solid state but a monomer in solution. (a) X-ray crystal structure: Haas, J. Dissertation, Universität Kaiserslautern, 1990. (b) Molecular weight measurements: Schneider, D. Dissertation, Universität Würzburg, 1992 (see also ref 6).

(4) (a) Garcia Alonso, F. J.; Höhn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem.* 1985, *97*, 401–402; *Angew. Chem., Int. Ed. Engl.* 1985, *24*, 406–407. (b) Werner, H.; Garcia Alonso, F. J.; Otto, H.; Wolf, J. *Z. Naturforsch.* 1988, *43B*, 722–726.

(5) Werner, H.; Brekau, U. *Z. Naturforsch.* 1989, *44B*, 1438–1446.

(6) Schneider, D.; Werner, H. *Angew. Chem.* 1991, *103*, 710–712; *Angew. Chem., Int. Ed. Engl.* 1991, *30*, 700–702.

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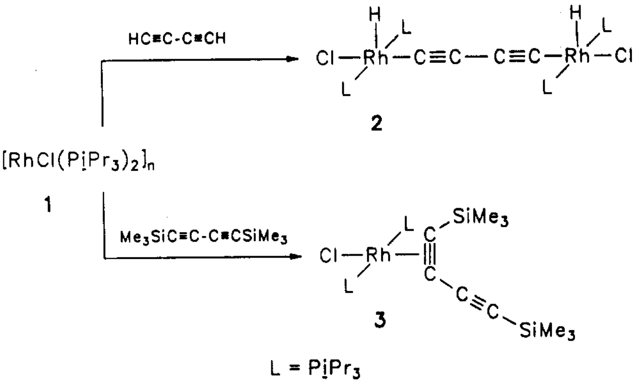
Scheme II



system $HC\equiv CC_6H_4C\equiv CH$,[7] would allow the isolation of a mononuclear complex *trans*-[RhCl($HC\equiv CCH_2CH_2C\equiv CH$)(P*i*Pr$_3$)$_2$]. This could then be used as the starting material for dinuclear heterometallic bis(alkyne) or bis(vinylidene) compounds. Some preliminary results of this work have been briefly mentioned in a recent account.[8]

Results and Discussion

Alkynyl(hydrido) and Alkyne Complexes from $HC\equiv CC\equiv CH$ and $Me_3SiC\equiv CC\equiv CSiMe_3$. Buta-1,3-diyne is a gaseous compound which is not easy to handle due to its high tendency for polymerization and its explosive behavior in the presence of air. It has been prepared from 1.4-dichlorobutyne and a concentrated aqueous solution of KOH and upon distillation was trapped and subsequently stored in pentane at −60 °C.[9] If buta-1,3-diyne in pentane solution is added dropwise to a solution of 1 in pentane at −78 °C, a change of color from deep-violet to orange-red takes place. After partial removal of the solvent in vacuo red crystals precipitate whose analytical data are consistent with a 1:2 adduct of buta-1,3-diyne and [RhCl(P*i*Pr$_3$)$_2$]. The spectroscopic data show, however, that it is not a diyne but the dihydridodiethynediyldirhodium complex 2 (Scheme II) in which the two metal centers are five-coordinate. The clearest evidence for this structural proposal comes from the high-field signal in the ^{1}H NMR spectrum at $\delta = -27.83$ which is split due to Rh–H and P–H coupling into a doublet of triplets, as well as from the $C\equiv C$ stretching frequency in the IR at 2011 cm^{-1} that is substantially higher than expected for an alkyne rhodium(I) complex.[10] The position of the ^{31}P NMR resonance at $\delta = 49.16$ is also in full agreement with the proposed structure. All attempts to isolate a mononuclear compound [RhH($C\equiv CC\equiv CH$)Cl(P*i*Pr$_3$)$_2$] analogous to [RhH($C\equiv C$*t*Bu)Cl(P*i*Pr$_3$)$_2$][5] but with an ethynyl substituent on the β-carbon atom failed. Even if we add a large excess of buta-1,3-diyne to a solution of 1 in pentane, only the dinuclear product 2 can be isolated. We note that quite recently Pörschke et al. described the synthesis of mono- and dinuclear buta-1,3-diyne nickel complexes [{(*i*Pr$_2$PCH$_2$CH$_2$CH$_2$P*i*Pr$_2$)Ni}$_n$($HC\equiv CC\equiv CH$)] (n = 1 and 2) by treatment of [(*i*Pr$_2$PCH$_2$CH$_2$CH$_2$P*i*Pr$_2$)Ni(C$_8$H$_{12}$)] with 0.5 or 1 equiv of the diyne.[11] In this case, obviously the reaction can be stopped after the addition of one $C\equiv C$ triple bond to one nickel center.

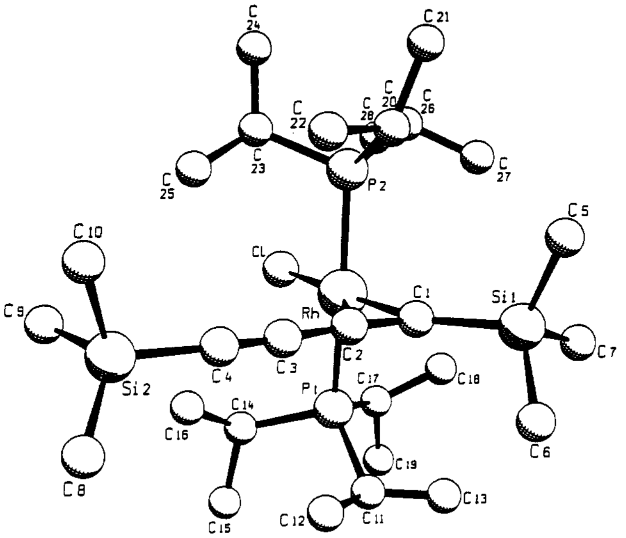


Figure 1. SCHAKAL drawing of complex 3.

In contrast to what we observed with buta-1,3-diyne, the bis(silylated) derivative $Me_3SiC\equiv CC\equiv CSiMe_3$ reacts with 1 in pentane at room temperature to give the mononuclear alkyne complex 3 in 65% yield. The orange-yellow microcrystalline solid is soluble in all common organic solvents, including pentane and hexane, and is only slightly air-sensitive. Most remarkably, even if a solution of 3 in toluene is chromatographed on deactivated Al$_2$O$_3$, no rearrangement or desilylation occurs. The structural proposal shown in Scheme II is mainly supported by the IR spectrum in which besides an absorption at 1820 cm^{-1}, typical for a coordinated alkyne at rhodium(I),[10] another band at 2125 cm^{-1} assigned to $\nu(C\equiv C)$ of a free alkyne moiety is observed. In accordance with this, there are also two signals in the ^{1}H NMR for the two different trimethylsilyl groups and four signals in the ^{13}C NMR due to the carbon atoms of the coordinated and the uncoordinated triple bond.

Although only small single crystals of 3 have been obtained, the crystal structure has been determined. The SCHAKAL drawing in Figure 1 reveals that the rhodium is coordinated in a slightly distorted square-planar fashion with the two phosphine ligands and the chloro and the alkyne ligands in trans position. The Rh–Cl and Rh–C2 bond lengths differ significantly (2.16(1) and 2.03(1) Å), which is in marked contrast to the nickel complex [(*i*Pr$_2$PCH$_2$CH$_2$CH$_2$P*i*Pr$_2$)Ni(η^2-$HC\equiv CC\equiv CH$)][11] and may be explained by the different inductive and mesomeric effects of the silyl and the alkynyl substituents. We note that unequal M–C(alkyne) bond lengths have also been found in the manganese compound [{(C$_5$H$_4$Me)(CO)$_2$Mn}$_2$($MeC\equiv CC\equiv CMe$)] (2.136(4) and 2.109(5) Å).[12]

The C1–C2 bond is elongated by ca. 0.07 Å compared to C3–C4 (see Table I) which is analogous to the situation in the above mentioned nickel complex[11] and indicates

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[7] (a) Werner, H.; Rappert, T.; Wolf, J. *Isr. J. Chem.* **1990**, *30*, 377–384. (b) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188–189.

[8] Werner, H. *Nachr. Chem. Tech. Lab.* **1992**, *40*, 435–444.

[9] Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1988; pp 178–179.

[10] (a) Werner, H.; Wolf, J.; Schubert, U.; Ackermann, K. *J. Organomet. Chem.* **1986**, *317*, 327–356. (b) Werner, H.; Wolf, J.; Garcia Alonso, F. J.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1987**, *336*, 397–411.

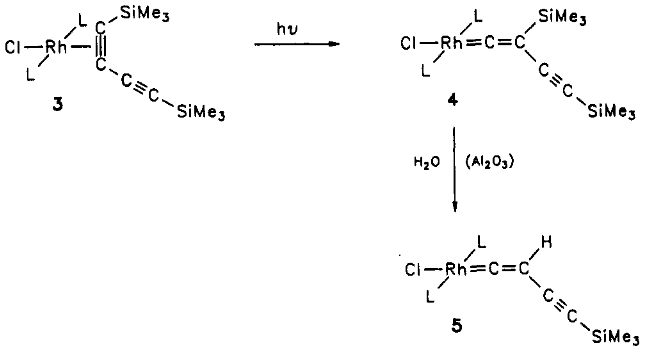
[11] Bonrath, W.; Pörschke, K. R.; Wilke, G.; Angermund, K.; Krüger, C. *Angew. Chem.* **1988**, *100*, 853–855; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 833–835.

[12] Cash, G. G.; Pettersen, R. C. *J. Chem. Soc., Dalton Trans.* **1979**, 1630–1633.

Table I. Selected Bond Distances and Angles with Esd's for Compound 3

		Bond Distances (Å)			
Rh–Cl	2.353 (4)	Rh–C2	2.03 (1)	C1–C2	1.26 (2)
Rh–P1	2.376 (5)	Si1–C1	1.83 (2)	C2–C3	1.38 (2)
Rh–P2	2.353 (5)	Si2–C4	1.83 (2)	C3–C4	1.19 (2)
Rh–C1	2.16 (1)				
		Bond Angles (deg)			
Cl–Rh–P1	83.5 (2)	P1–Rh–C2	95.7 (4)	Rh–C1–Si1	146.4 (8)
Cl–Rh–P2	86.5 (2)	P2–Rh–C1	93.1 (4)	Si1–C1–C2	147 (1)
Cl–Rh–C1	173.8 (5)	P2–Rh–C2	94.5 (4)	Rh–C2–C3	126 (1)
Cl–Rh–C2	151.4 (5)	C1–Rh–C2	34.8 (5)	C1–C2–C3	156 (2)
P1–Rh–P2	169.6 (2)	Rh–C1–C2	66.7 (9)	C2–C3–C4	173 (2)
P1–Rh–C1	96.5 (4)	Rh–C2–C1	79 (1)	Si2–C4–C3	174 (2)

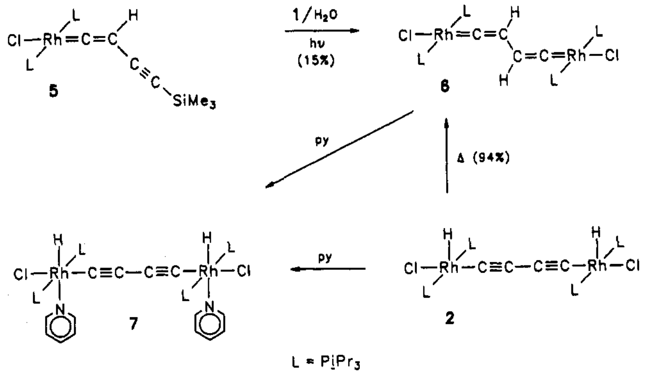
Scheme III



that the coordinated alkyne Me$_3$SiC≡CR, bearing an alkynyl group as a substituent R, is a rather good π-acceptor ligand. The distance C3–C4 is exactly the same as that in free buta-1,3-diyne.[13] The bending of the C1–C2–C3 axes (156(2)°) is smaller than that found in [(*i*Pr$_2$PCH$_2$CH$_2$CH$_2$P*i*Pr$_2$)Ni(η^2-HC≡CC≡CH)] (146.2(6)°)[11] but similar to that in the above-mentioned dinuclear manganese complex (158.5(5)°).[12] The angle Si1–C1–C2 is 147(1)° and thus almost identical to that in [{WCl$_4$(py)}$_2$(PhC≡CC≡CSiMe$_3$)].[14]

Preparation of Mono- and Dinuclear Vinylidenerhodium(I) Complexes. Although complex **3** is quite inert to thermal activation, it smoothly rearranges on irradiation with a 500-W Hg lamp in benzene solution to give the vinylidenerhodium(I) isomer **4** (see Scheme III) in practically quantitative yield. The red-violet solid is modestly air-stable but extremely sensitive to water or other protonating agents. If it is treated with a small amount of H$_2$O in THF or chromatographed on deactivated Al$_2$O$_3$, a complete conversion to **5** takes place. There is a selective cleavage of the =CSiMe$_3$ but not of the ≡CSiMe$_3$ bond to give the β-H vinylidene complex in 98% isolated yield. Both compounds, **4** and **5**, are characterized by elemental analysis and IR as well as ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data. The most typical features besides the low-field resonance in the ^{13}C NMR spectra for the vinylidene α-C atom at δ = 285.00 (for **4**) and 293.26 (for **5**) are the two signals for the SiMe$_3$ protons in the ^{1}H NMR of **4** at δ = 0.22 and 0.14 and for the SiMe$_3$ and the C=CH hydrogens of **5** at δ = 0.12 and 0.86. In agreement with previous observations,[4,5,7] the signal of the vinylidene proton is split into a doublet of triplets due to Rh–H and P–H coupling.

Scheme IV



The attempt to coordinate the free C≡C bond in **5** by a second [RhCl(P*i*Pr$_3$)$_2$] unit has led to an unexpected result. Treatment of a pentane solution of **5** with 1 equiv of **1** gives a mixture of products from which no definite complex could be isolated. If the solid product mixture, however, is dissolved in benzene that contains a small amount of water and irradiated for 2 h, a violet microcrystalline compound precipitates which according to elemental analysis and IR as well as NMR spectroscopic data is the bis(vinylidene)dirhodium complex **6**. The yield is 15%. The same compound is obtained almost quantitatively if a solution of **2** in toluene is stirred for 6 h at 45 °C (Scheme IV). The presence of a Rh=C=CH unit in **6** is substantiated by the appearance of two low-field signals in the ^{13}C NMR spectrum at δ = 294.49 and 84.78 which are assigned to the α-C and β-C carbon atoms of the vinylidene unit. Compound **6** reacts with pyridine to regenerate the "naked" C$_4$ bridge and forms the dinuclear complex **7** in which both metal centers are six coordinate. The same product is obtained in 83% yield upon treatment of **2** with pyridine. The dihydridobis(pyridine)dirhodium compound forms white crystals which are stable under argon in the solid state but rearrange in solution to give **6**. Attempts to abstract not only pyridine but also H$_2$ from **7** with trityl radicals or in the presence of Pd/C to afford a rhodium complex with a Rh=C=C=C=C=Rh linear chain have failed.

Formation of a Butatrienerhodium Complex. Compound **1** not only reacts with buta-1,3-diyne but also with 1,4-dichlorobut-2-yne which is the starting material for the synthesis of the diyne. We discovered this when solutions of HC≡CC≡CH still containing some unreacted ClCH$_2$C≡CCH$_2$Cl were used for the preparation of **2**. The reaction of **1** with pure 1,4-dichlorobut-2-yne in pentane proceeds spontaneously and gives the mononuclear rhodium complex **8** as a yellow slightly air-sensitive solid in 87% yield. Both the elemental analysis and the spectroscopic data of the new compound indicate that the butatriene H$_2$C=C=C=CHCl and not the original alkyne is bound to the metal. Obviously, the three-coordinate rhodium complex **1** (*n* = 1)[3] supports the elimination of HCl from ClCH$_2$C≡CCH$_2$Cl and traps the butatriene in the coordination sphere. If NEt$_3$ is added to the reaction mixture, the ammonium salt [HNEt$_3$]Cl is formed together with **8**; the yield of the rhodium complex remains unchanged.

The ^{1}H NMR spectrum of **8** (see Scheme V) shows two signals at δ = 1.33 and 1.27 for the protons of the diastereotopic CH$_3$ groups of the phosphines and three resonances at δ = 6.76, 5.16, and 5.05 for the unequivalent hydrogens of the chlorobutatriene. In the ^{13}C NMR

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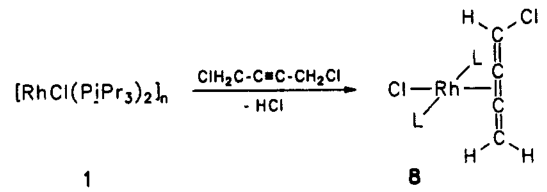
[13] Pauling, L.; Springall, H. D.; Palmer, K. J. *J. Am. Chem. Soc.* **1939**, *61*, 927–937.

[14] Kersting, M.; Dehnicke, K.; Fenske, D. *J. Organomet. Chem.* **1986**, *309*, 125–141.

Scheme V



1 8

L = PiPr3

spectrum four signals for the carbons of the cumulated chain are observed, three of which (at δ = 141.95, 133.94, and 106.12) are split by Rh–C and P–C coupling into doublet of triplets. The singlet at δ = 98.07 originates from the CH_2 carbon of the chain as proved by DEPT measurements. There is a precedent for the proposed structure of **8** insofar as Wilkinson's catalyst $[RhCl(PPh_3)_3]$ reacts with $Ph_2C{=}C{=}C{=}CPh_2$ and related butatrienes to form complexes *trans*-$[RhCl(R_2C{=}C{=}C{=}CR_2)(PPh_3)_2]$ in which the metal is linked to the central C=C bond of the triene.[15] The same is also true for the butatriene chromium and manganese complexes $[(arene)Cr(CO)_2(R_2C{=}C{=}C{=}CR_2)]$ and $[(C_5H_4Me)Mn(CO)_2(R_2C{=}C{=}C{=}CR_2)]$ (R = Me, Ph) which are obtained by formal coupling of two vinylidene units at the metal center.[16] It should be mentioned that complex **8** reacts rapidly with CO in benzene at room temperature to give *trans*-$[RhCl(CO)(PiPr_3)_2]$.[2a] Furthermore, a brownish oily product is formed which presumably is an oligomer or a polymer of the highly unstable chlorobutatriene.

Rhodium Complexes from Hexa-1,5-diyne. The reaction of **1** with $HC{\equiv}CCH_2CH_2C{\equiv}CH$ follows the course which we have already observed with the C_6H_4-bridged diyne $HC{\equiv}CC_6H_4C{\equiv}CH$.[7a] Treatment of **1** with hexa-1,5-diyne in pentane at 0 °C gives the dinuclear diyne complex **9** irrespective of whether the two starting materials are reacted in a 2:1, 1:1, or 1:10 molar ratio. Changing both the solvent and the temperature does not alter the result.

9, which is stable as a solid, slowly rearranges in solution to form the bis(vinylidene)dirhodium isomer **10** in nearly quantitative yield. The reaction is accompanied by a characteristic change of color from yellow to brown and finally to dark blue. Although we have no conclusive evidence we assume that a stepwise conversion from **9** to **10** via an alkynyl(hydrido)rhodium intermediate occurs. The spectroscopic data of **10** are fully consistent with the symmetrical structure shown in Scheme VI and deserve no further comment.

On treatment of **9** with excess pyridine in hexane at 45 °C, the bis(pyridine) complex **11** is quantitatively formed. It is a white crystalline solid which can be handled for a short time in air. The ^1H NMR spectrum of **11** shows one hydride signal at δ = −17.90 and thus supports the structural proposal outlined in Scheme VI. Compound **11** reacts smoothly in benzene solution to give the dinuclear bis(vinylidene) derivative **10** which itself can be used for the preparation of **11**.

Concluding Remarks

The work presented in this paper has shown that two of the most simple diynes, $HC{\equiv}CC{\equiv}CH$ and $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, behave differently if treated with **1**. Whereas buta-1,3-diyne affords the dinuclear dihydrido complex **2** with the buta-1,3-diyndiyl anion twice σ-bonded to two rhodium centers, the bissilylated derivative prefers to yield the mononuclear compound **3** in which only one C≡C triple bond is coordinated to rhodium. A remarkable contrast also exists between $HC{\equiv}CC{\equiv}CH$ and $HC{\equiv}CCH_2CH_2C{\equiv}CH$: in the reaction with **1**, the latter forms the diynedirhodium complex **9** which only after treatment with pyridine gives a diyndiyl dihydrido derivative. All the three diynes afford vinylidene rhodium complexes, from which the mononuclear compound **4**, to the best of our knowledge, is the first representative that contains one silyl and one alkynyl substituent on the vinylidene β-carbon atom.[17] We note that dinuclear nickel, palladium, and platinum complexes with a "naked C_4-bridge" have already been prepared by Hagihara, Sonogashira, et al.[18] and that most recently Dixneuf and coworkers have used derivatives of buta-1,3-diyne to obtain novel metallacumulenes with a $R_2C{=}C{=}C{=}Ru{=}C{=}C{=}CR_2$ unit.[19] We are presently exploring the possibility producing rhodium-containing polymers from $HC{\equiv}CC{\equiv}CH$ and other diynes[8] and will report these results in an upcoming paper.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk tube techniques. The starting material $[RhCl(PiPr_3)_2]_n$ (**1**) was prepared as described in the literature.[2b] Hexa-1,5-diyne was a commercial product from ABCR, and buta-1,3-diyne[9] and bis(trimethylsilyl)buta-1,3-diyne[20] were prepared by published procedures. NMR spectra were recorded at room temperature on JEOL FX 90Q, Bruker AC 200, and Bruker AMX 400 instruments, IR spectra on a Perkin-Elmer 1420 infrared spectrophotometer, and mass spectra on a Varian MAT CH7 instrument. Melting points were measured by DTA.

Preparation of $[(PiPr_3)_2Cl(H)Rh(C{\equiv}CC{\equiv}C)Rh(H)Cl(PiPr_3)_2]$ (2). To a solution of **1** (212 mg, 0.46 mmol for *n* = 1) in 20 mL of pentane was added a pentane solution of buta-1,3-diyne dropwise at −78 °C until the orange-red color of the solution remained unchanged. After being stirred for 15 min, the solution was concentrated in vacuo to ca. 3 mL and stored at −78 °C. Red crystals were formed which were filtered off, repeatedly washed with pentane, and dried in vacuo, yield 151 mg (68%): mp 62 °C dec; IR (KBr) $\nu(C{\equiv}C)$ 2010 cm^{-1}, ν(RhH) not found; ^1H NMR (C_6D_6, 400 MHz) δ 2.85 (m, $PCHCH_3$), 1.32 [dvt, *N* = 13.8 Hz, *J*(HH) = 7.3 Hz, $PCHCH_3$], −27.83 [dt, *J*(RhH) = 42.8 Hz, *J*(PH) = 13.1 Hz, RhH]; ^{31}P NMR (C_6D_6, 36.2 MHz) δ 49.16 [d, *J*(RhP) = 99.6 Hz, $PiPr_3$]. Anal. Calcd for $C_{40}H_{86}Cl_2P_4Rh_2$: C, 49.65; H, 8.96. Found: C, 49.75; H, 9.02.

Preparation of *trans*-$[RhCl(\eta^2-Me_3SiC{\equiv}CC{\equiv}CSiMe_3)(PiPr_3)_2]$ (3). A solution of **1** (246 mg, 0.54 mmol for *n* = 1) in 15 mL of pentane was treated at room temperature with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ (156 mg, 0.80 mmol). After being stirred for 15 min, the solution was concentrated in vacuo to ca. 2 mL and stored at −78 °C. Orange, moderately air-stable crystals were

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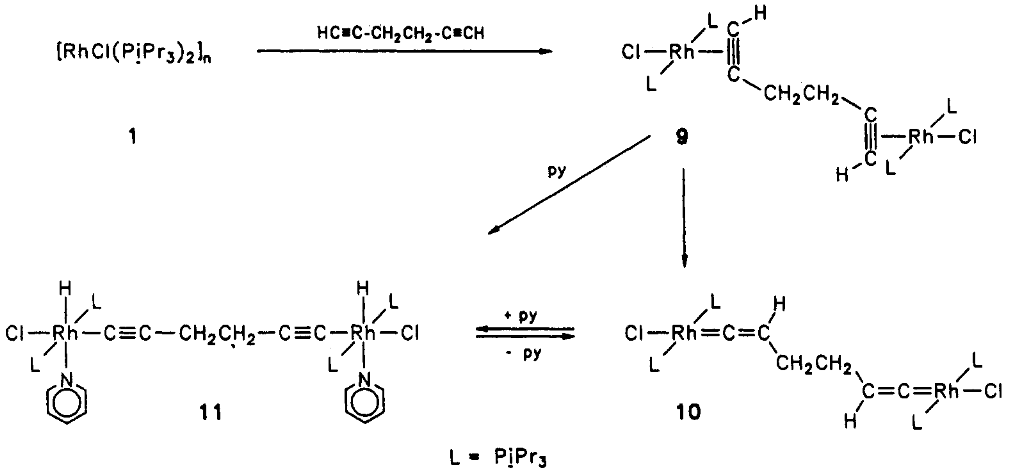
Scheme VI



formed which were separated from the mother liquor, washed with pentane (−78 °C), and dried in vacuo, yield 228 mg (65%): mp 86 °C dec; IR (KBr) $\nu(C{\equiv}C_{free})$ 2125, $\nu(C{\equiv}C_{coord.})$ 1820 cm^{-1}; ^{1}H NMR (C_6D_6, 90 MHz) δ 2.45 (m, PC*H*CH$_3$), 1.39 and 1.34 [both dvt, *N* = 13.4 Hz, *J*(HH) = 7.2 Hz, PCHC*H*$_3$], 0.31 and 0.20 [both s, Si(CH$_3$)$_3$]; ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 101.13 and 95.71 (both s, $C{\equiv}C_{free}$), 88.83 [d, *J*(RhC) = 17.4 Hz, *C*≡C$_{coord.}$], 84.91 [d, *J*(RhC) = 26.2 Hz, C≡*C*$_{coord.}$], 22.74 (vt, *N* = 16.6 Hz, P*C*HCH$_3$), 20.34 and 19.74 (both s, PCH*C*H$_3$), 1.06 and 0.82 [both s, Si(CH$_3$)$_3$]; ^{31}P NMR (C_6D_6, 36.2 MHz) δ 32.70 [d, *J*(RhP) = 115.8 Hz, P*i*Pr$_3$]. Anal. Calcd for $C_{28}H_{60}ClP_2RhSi_2$: C, 51.48; H, 9.26. Found: C, 51.78; H, 9.36.

Preparation of *trans*-[RhCl(=C=C(SiMe$_3$)C≡CSiMe$_3$)(P*i*Pr$_3$)$_2$] (4). A solution of 3 (114 mg, 0.17 mmol) in 10 mL of benzene was irradiated with a 125-W Hg lamp. A change of color from yellow to red-violet occurred within 2 h. The solvent was removed in vacuo, and the residue was recrystallized from pentane (25 to −60 °C) to give red-violet air-stable crystals, yield 107 mg (94%): mp 82 °C dec; IR (KBr) ν(C≡C) 2120, ν(C=C) 1623 cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz) δ 2.74 (m, PC*H*CH$_3$), 1.33 und 1.31 [both dvt, *N* = 13.2 Hz, *J*(HH) = 6.9 Hz, PCHC*H*$_3$], 0.22 and 0.14 [both s, Si(CH$_3$)$_3$]; ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 285.00 [dt, *J*(RhC) = 62.8 Hz, *J*(PC) = 15.4 Hz, =C=], 99.79 and 85.51 (both s, C≡C), 87.67 [dt, *J*(RhC) = 17.4, *J*(PC) = 4.4 Hz, =*C*(SiMe$_3$)−], 24.02 (vt, *N* = 19.8 Hz, P*C*HCH$_3$), 20.53 (s, PCH*C*H$_3$), 0.63 and −0.82 [both s, Si(CH$_3$)$_3$]; ^{31}P NMR (C_6D_6, 36.2 MHz) δ 42.06 [d, *J*(RhP) = 134.8 Hz, P*i*Pr$_3$]. Anal. Calcd for $C_{28}H_{60}ClP_2RhSi_2$: C, 51.48; H, 9.26. Found: C, 51.31; H, 8.89.

Preparation of *trans*-[RhCl(=C=CHC≡CSiMe$_3$)(P*i*Pr$_3$)$_2$] (5). A solution of 4 (110 mg, 0.17 mmol) in 10 mL of THF was treated at room temperature with 0.1 mL (5.56 mmol) of H$_2$O. After the solution was stirred for 2 h, the solvent was removed in vacuo and the residue was recrystallized from pentane (25 to −60 °C) to give red-violet air-stable crystals, yield 97 mg (98%): mp 80 °C dec; IR (KBr) ν(C≡C) 2121, ν(C=C) 1645 cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz) δ 2.71 (m, PC*H*CH$_3$), 1.25 [dvt, *N* = 13.7 Hz, *J*(HH) = 7.0 Hz, PCHC*H*$_3$], 0.86 [dt, *J*(PH) = 3.1 Hz, *J*(RhH) = 0.8 Hz, =C=CH−], 0.12 [s, Si(CH$_3$)$_3$]; ^{13}C NMR (C_6D_6, 50.2 MHz) δ 293.26 [dt, *J*(RhC) = 61.6 Hz, *J*(PC) = 17.4 Hz, =C=], 104.44 and 83.47 (both s, C≡C), 91.31 [dt, *J*(RhC) = 17.4, *J*(PC) = 6.4 Hz, =CH−], 23.48 (vt, *N* = 20.7 Hz, P*C*HCH$_3$), 20.16 (s, PCH*C*H$_3$), 0.43 [s, Si(CH$_3$)$_3$]; ^{31}P NMR (C_6D_6, 36.2 MHz) δ 43.09 [d, *J*(RhP) = 133.3 Hz, P*i*Pr$_3$]. Anal. Calcd for $C_{25}H_{52}ClP_2RhSi$: C, 51.67; H, 9.02. Found: C, 51.85; H, 9.22.

Preparation of *trans*-[(P*i*Pr$_3$)$_2$ClRh(=C=CHCH=C=)RhCl(P*i*Pr$_3$)$_2$] (6). (a) A solution of 5 (93 mg, 0.16 mmol) in 10 mL of pentane was treated with 1 (73 mg, 0.16 mmol for *n* = 1) and stirred for 30 min at room temperature. The solution was brought to dryness in vacuo. The residue, which according to the IR spectrum (ν(C≡C) 1870 cm^{-1}) consists of an alkyne complex, was dissolved in 1 mL of benzene, and the solution was irradiated for 2 h with a 125-W Hg lamp. A violet precipitate was formed, which was filtered off, washed with pentane, and dried in vacuo, yield 23 mg (15%).

(b) A solution of 2 (102 mg, 0.11 mmol) in 30 mL of toluene was stirred at 45 °C for 6 h. The solution became violet, and some violet crystals precipitated. After the mixture was stored at −78 °C, the precipitate was filtered off, repeatedly washed with pentane, and dried in vacuo, yield 95 mg (94%): mp 64 °C dec; IR (KBr) ν(C=C) 1620 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 2.74 (m, PC*H*CH$_3$), 1.29 [dvt, *N* = 13.9 Hz, *J*(HH) = 7.2 Hz, PCHC*H*$_3$], signal of =CH obscured by the signal of the PCHC*H*$_3$ protons; ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 294.49 [dt, *J*(RhC) = 59.9 Hz, *J*(PC) = 15.3 Hz, =C=], 84.78 [dt, *J*(RhC) = 15.8 Hz, *J*(PC) = 5.9 Hz, =CH−], 22.90 (vt, *N* = 20.0 Hz, P*C*HCH$_3$), 19.75 (s, PCH*C*H$_3$); ^{31}P NMR (CDCl$_3$, 36.2 MHz) δ 41.60 [d, *J*(RhP) = 134.8 Hz, P*i*Pr$_3$]. Anal. Calcd for $C_{40}H_{86}Cl_2P_4Rh_2$: C, 49.65; H, 8.96. Found: C, 49.44; H, 8.93.

Preparation of *trans*-[(P*i*Pr$_3$)$_2$(py)Cl(H)Rh(C≡CC≡C)Rh(H)Cl(py)(P*i*Pr$_3$)$_2$] (7). (a) A solution of 6 (120 mg, 0.13 mmol) in 10 mL of pentane was treated with pyridine (1 mL, 12.2 mmol) and stirred for 24 h at room temperature. The solution became colorless, and white crystals precipitated. The precipitate was filtered off, repeatedly washed with pentane, and dried in vacuo, yield 130 mg (89%).

(b) A solution of 2 (121 mg, 0.13 mmol) in 20 mL of pentane was treated with pyridine (0.1 mL, 1.22 mmol) and stirred for 30 min at room temperature. The solution became colorless, and some white crystals precipitated. The precipitate was filtered off, repeatedly washed with pentane, and dried in vacuo, yield 117 mg (83%): mp 70 °C dec; IR (KBr) ν(RhH) 2180, ν(C≡C) 2000 cm^{-1}; ^{1}H-NMR (CD$_2$Cl$_2$, 90 MHz, −30 °C) δ 9.84, 6.57–6.92 (both m, C$_5$H$_5$N), 2.98 (m, PC*H*CH$_3$), 1.29 and 1.25 [both dvt, *N* = 12.7 Hz, *J*(HH) = 7.3 Hz, PCHC*H*$_3$], −18.06 [dt, *J*(RhH) = *J*(PH) = 16.1 Hz, RhH]; ^{13}C NMR (CDCl$_3$, 50.2 MHz) δ 153.33, 136.37 and 123.39 (all s, C$_5$H$_5$N), 110.22 [d, *J*(RhC) = 13.3 Hz, RhC≡*C*], 23.94 (vt, *N* = 21.1 Hz, P*C*HCH$_3$), 19.40 and 19.35 (both s, PCH*C*H$_3$), the signal for Rh*C*≡C was not observed; ^{31}P NMR (C_6D_6, 36.2 MHz) δ 37.47 [d, *J*(RhP) = 98.2 Hz, P*i*Pr$_3$]. Anal. Calcd for $C_{50}H_{96}Cl_2N_2P_4Rh_2$: C, 53.34; H, 8.59; N, 2.49. Found: C, 53.14; H, 8.60; N, 2.23.

Preparation of *trans*-[RhCl(η^2-ClHC=C=C=CH$_2$)(P*i*Pr$_3$)$_2$] (8). An immediate change of color from violet to yellow occurred if a solution of 1 (200 mg, 0.43 mmol for *n* = 1) in 20 mL of pentane was treated at room temperature with ClH$_2$CC≡CCH$_2$Cl (53 mg, 0.43 mmol). After being stirred for 10 min, the solution was concentrated in vacuo to ca. 3 mL and stored at −78 °C. Yellow, moderately air-stable crystals were obtained, yield 204 mg (87%): mp 82 °C dec; MS (70 eV) *m/z* 545 (M$^+$); IR (KBr) ν(C=C=C) 1770 cm^{-1}; ^{1}H NMR (C_6D_6, 90 MHz) δ 6.76 [dd, *J*(HH) = 2.6 Hz, *J*(HH) = 1.2 Hz, =CHCl], 5.16 [dd, *J*(HH) = 3.0 Hz, *J*(HH) = 1.2 Hz, one H of =CH$_2$], 5.05 [dd, *J*(HH) = 3.0 Hz, *J*(HH) = 2.6 Hz, one H of =CH$_2$], 2.42 (m, PC*H*CH$_3$), 1.33 and 1.27 [both dvt, N = 13.5 Hz, J(HH) = 7.2 Hz, PCHCH_3]; ^{13}C NMR (C_6D_6, 50.2 MHz) δ 141.95 [dt, J(RhC) = 18.3 Hz, J(PC) = 4.6 Hz, =C=], 133.94 [dt, J(RhC) = 19.8 Hz, J(PC) = 4.6 Hz, =C=], 106.12 [dt, J(RhC) = 4.6 Hz, J(PC) = 3.1 Hz, =CHCl], 98.07 (s, =CH_2), 24.40 (vt, N = 19.2 Hz, $PCHCH_3$), 20.78 and 20.30 (both s, $PCHCH_3$); ^{31}P NMR (C_6D_6, 36.2 MHz) δ 32.92 [d, J(RhP) = 114.3 Hz, P*i*Pr$_3$]. Anal. Calcd for $C_{22}H_{45}Cl_2P_2Rh$: C, 48.27; H, 8.66. Found: C, 48.26; H, 8.36.

Reaction of *trans*-[RhCl(ClHC=C=C=CH$_2$)(P*i*Pr$_3$)$_2$] (8) with CO. A slow stream of carbon monoxide was passed for ca. 1 min through a solution of 8 in benzene. The solution turned yellow, and the carbonyl complex *trans*-[RhCl(CO)(P*i*Pr$_3$)$_2$] could be detected by IR and ^{31}P and ^{1}H NMR spectroscopy.[2a]

Preparation of *trans*-[(P*i*Pr$_3$)$_2$ClRh(HC≡C(CH$_2$)$_2$C≡CH)-RhCl(P*i*Pr$_3$)$_2$] (9). To a solution of 1 (180 mg, 0.40 mmol for n = 1) in 10 mL of pentane was added the diyne HC≡C-(CH_2)$_2$C≡CH dropwise at 0 °C until the yellow 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 isolated, yield 139 mg (70%): mp 89 °C dec; IR (KBr) ν(C≡C) 1834 cm^{-1}; ^{31}P NMR (C_6D_6, 90 MHz) δ 32.31 [d, J(RhP) = 115.6 Hz, P*i*Pr$_3$]. Anal. Calcd for $C_{42}H_{90}Cl_2P_4Rh_2$: C, 50.66; H, 9.11. Found: C, 50.83; H, 9.36.

Preparation of *trans*-[(P*i*Pr$_3$)$_2$ClRh(=C=CH(CH$_2$)$_2$CH=C=)RhCl(P*i*Pr$_3$)$_2$] (10). A solution of 0.20 mmol of 9 or 11 in 10 mL of toluene was stirred at 45 °C for 2 h. After the solution was cooled to room temperature, it was concentrated in vacuo to ca. 3 mL and stored at −78 °C. Violet, air-stable crystals were formed, yield 187 mg (94%), from 9; 161 mg (81%), from 11: mp 153 °C dec; IR (THF) ν(C=C) 1624 cm^{-1}; ^{1}H NMR (C_6D_6, 90 MHz) δ 2.81 (m, PC*H*CH$_3$), 1.55 (m, CH$_2$), 1.33 [dvt, N = 13.4 Hz, J(HH) = 7.2 Hz, PCHCH_3], signal of =CH— obscured by the signal of the PCHCH_3 protons; ^{13}C NMR (C_6D_6, 50.2 MHz) δ = 289.93 [dt, J(RhC) = 56.5 Hz, J(PC) = 16.9 Hz, =C=], 103.90 [dt, J(RhC) = 15.8 Hz, J(PC) = 6.8 Hz, =CH—], 23.42 (vt, N = 19.9 Hz, $PCHCH_3$), 20.27 (s, $PCHCH_3$), 18.08 (s, CH$_2$); ^{31}P NMR (C_6D_6, 36.2 MHz) δ 42.28 [d, J(RhP) = 136.3 Hz, P*i*Pr$_3$]. Anal. Calcd for $C_{42}H_{90}Cl_2P_4Rh_2$: C, 50.66; H, 9.11. Found: C, 50.78; H, 9.27.

Preparation of [(P*i*Pr$_3$)$_2$(py)Cl(H)Rh(C≡C(CH$_2$)$_2$C≡C)-Rh(H)Cl(py)(P*i*Pr$_3$)$_2$] (11). Prepared as described for 7, using 10 (145 mg, 0.15 mmol) as starting material. White crystals were obtained, yield 161 mg (96%): mp 103 °C dec; IR (KBr) ν(RhH) 2182, ν(C≡C) 2100 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 90 MHz, −30 °C) δ 7.20–9.73 (m, C_5H_5N), 2.79 (m, PC*H*CH$_3$), 2.32 (m, CH$_2$), 1.06 [dvt, N = 13.2 Hz, J(HH) = 6.8 Hz, PCHCH_3], −17.90 [dt, J(PH) = 13.7 Hz, J(RhH) = 13.7 Hz, RhH]. Anal. Calcd for $C_{52}H_{100}Cl_2N_2P_4Rh_2$: C, 54.12; H, 8.73; N, 2.43. Found: C, 54.00; H, 9.01; N, 2.14.

X-ray Structural Analysis of 3. Single crystals were grown from THF at 25 °C. Crystal data (from 23 reflections, 12° < θ < 14°): orthorhombic space group $P2_12_12_1$ (No. 19), a = 11.19(1) Å, b = 15.89(2) Å, c = 20.75(2) Å, V = 3693 Å^3, Z = 4, D_{calcd} = 1.175 g cm^{-3}, μ(Mo Kα) = 6.9 cm^{-1}. Crystal size: 0.25 × 0.25 × 0.30 mm. Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.709 30 Å), graphite monochromator, zirkon filter (factor 16.4), T = 293 K, $\omega/2\theta$-scan, maximum 2θ = 44°, 3359 independent reflections measured, 1425 regarded as being observed [$F_o > 2\sigma(F_o)$]; intensity data corrected for Lorentz and polarization effects, empirical absorption correction (Ψ-scan method) applied, minimum transmission 77.79%; structure solved by Patterson method (SHELXS-86); atomic coordinates and anisotropic thermal parameters refined by full-matrix least-squares (Enraf-Nonius SDP);[21] carbon atoms refined isotropically; positions of the hydrogen atoms calculated according to ideal geometrie and used only in structure factor calculation; in the last cycles of the refinement a weighing scheme has been applied with a weighing factor $w = 1/\sigma^2(F_o)$; R = 0.057, R_w = 0.062; reflex/parameter ratio 8.53; residual electron density +0.791/−0.473 e Å^{-3}.

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

Supplementary Material Available: Tables of bond lengths and angles, positional and thermal parameters, and least-squares planes for 3 (8 pages). Ordering information is given on any current masthead page.

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