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Vinylidene transition-metal complexes

I. Novel rhodium(I) and rhodium(III) complexes containing alkynes, alkynyls, and vinylidenes as ligands. Crystal structure of $[C_5H_5Rh(=C=CHPh)(PPr^i_3)$

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Abstract

The syntheses of the novel cyclopentadienylphosphinevinylidenerhodium complexes $C_5H_5Rh(=C=CHR)(PPr^i_3)$ (R = Ph, Me, H) and, for R = Ph, of the isomeric alkynyl hydrido compound $C_5H_5RhH(C_2Ph)(PPr^i_3)$ are reported. The square-planar complexes *trans*-$[RhCl(RC_2H)(PPr^i_3)_2]$ (IIa, IIb), which in solution are in equilibrium with the five-coordinated species $RhHCl(C_2R)(PPr^i_3)_2$ (Va, Vb), react with pyridine to give the octahedral compounds $RhHCl(C_2R)(PPr^i_3)_2(py)$ (VIa, VIb). Treatment of VIa, VIb with NaC_5H_5 gives the vinylidene complexes IVa, IVb in good yield. $C_5H_5Rh(=C=CH_2)(PPr^i_3)$ (IVc) is directly obtained from *trans*-$[RhCl(C_2H_2)(PPr^i_3)_2]$ (IIc) and NaC_5H_5. Mechanistic studies confirm that the reaction of VIa, VIb with the cyclopentadienide anion primarily gives, by elimination of HCl, the rhodium(I) compounds *trans*-$[Rh(C_2R)(py)(PPr^i_3)_2]$ (VIIIa, VIIIb), which react with cyclopentadiene, possibly via *trans*-$[Rh(C_2R)(\eta^2\text{-}C_5H_6)(PPr^i_3)_2]$ (X) as an intermediate, to give $C_5H_5Rh(=C=CHR)(PPr^i_3)$ (IVa, IVb). Treatment of VIIIa with cyclopentadiene in presence of water gives the complex $C_5H_5RhH(C_2Ph)(PPr^i_3)$, which isomerizes only slowly to form IVa and, therefore, is not an intermediate in the reaction of VIIIa and C_5H_6 to give IVa. The crystal structure of IVa has been determined. The RhCC arrangement is almost linear. The RhC

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distance is significantly shorter than in carbenerhodium complexes, which, in agreement with ^{13}C NMR data and MO calculations, indicates a high degree of multiple bonding.

Introduction

One of the major advantages of organo-transition metal chemistry is that transition metals can bind organic molecules which are unstable in the free state. A striking example are unsaturated carbenes or vinylidenes $:C{=}CHR$ which if not coordinated to a transition metal are extremely labile and rearrange almost immediately by a 1,2-H-shift to form the corresponding alkynes $HC{\equiv}CR$ [1]. Several theoretical studies [2–4] have led to the conclusion that the energy barrier for the isomerization of the vinylidenes to the alkynes is very low, being only about 4 kJ/mol for the parent derivative $:C{=}CH_2$ [4].

Although the first vinylidene transition metal complex $[Fe(CO)_4]_2(\mu\text{-}C{=}CPh_2)$ was reported as long ago as 1966 [5], the real development in this area started much more recently. A comprehensive picture of the knowledge in the field was given in 1983 by Bruce and Swincer [6], who pointed out that although several vinylidene-metal complexes had been prepared from acetylenes, possibly via acetylene metal intermediates, the mechanism of formation of these complexes was not well understood.

Our interest in this part of organometallic chemistry originated from our work on metal bases [7], particularly on those having the general formula C_5H_5MLL' (M = Co, Rh, Ir). After the synthesis of the first representatives, with $L = PR_3$ and $L' = C_2R_2$ (e.g., $C_5H_5Co(C_2Ph_2)(PMe_3)$ [8] and $C_5H_5Rh(C_2Ph_2)(PPr^i_3)$ [9]), we wished to find out whether the most simple alkyne, C_2H_2, could also be coordinated in the same fashion, and reached the surprising conclusion that it could not. We describe here how acetylene and other alkynes $RC{\equiv}CH$ behave if coordinated to rhodium, and how they are transformed to the isomeric vinylidenes. A preliminary report appeared earlier [10].

Preparation of the complexes $C_5H_5Rh({=}C{=}CHR)(PPr^i_3)$

The rhodium(I) compound *trans*-$[RhCl(PhC_2H)(PPr^i_3)_2]$ (IIa), which is formed on addition of phenylacetylene to the 14-electron species $[RhCl(PPr^i_3)_2]$ (I) [9], reacts with NaC_5H_5 in THF or benzene to give a mixture of $C_5H_5Rh(PhC_2H)(PPr^i_3)$ (IIIa) and $C_5H_5Rh({=}C{=}CHPh)(PPr^i_3)$ (IVa). The relative amount of the two isomeric products mainly depends on the reaction conditions. In benzene, the yield of the vinylidene complex IVa (for ^1H and ^{13}C NMR data see Table 1 and 2) is better than in THF, and it is even higher if the solution of IIa is not treated immediately with NaC_5H_5 but only after some time. In contrast, if the solid starting material IIa is added to an excess of the cyclopentadienide in THF, only the alkynerhodium compound IIIa [9] is obtained.

The propyne complex *trans*-$[RhCl(MeC_2H)(PPr^i_3)_2]$ (IIb) behaves somewhat similarly as IIa toward NaC_5H_5. In THF, a mixture of the alkyne and the vinylidene compound, IIIb and IVb, is again formed (Scheme 1), whereas in benzene only the vinylidenerhodium isomer IVb is produced. With IIb as the starting material it has not been possible to find appropriate conditions under which only IIIb is formed.

The acetylene derivative *trans*-[RhCl(C_2H_2)(PPr$^i_3$)$_2$] (IIc) [9] reacts with NaC_5H_5 in THF to give the unsubstituted vinylidene complex IVc (Scheme 1) in ca. 30% yield. There is no indication that under these conditions the alkyne isomer C_5H_5Rh(HC≡CH)(PPr$^i_3$) is also formed. If the reaction of IIc with NaC_5H_5 is carried out in benzene, a mixture of products is obtained, with the bis(phosphine)rhodium complex C_5H_5Rh(PPr$^i_3$)$_2$ [11] as the major component.

The methods described above for the preparation of the new compounds IVa–IVc have two definite disadvantages, in that they either lead to two products which owing to their similar properties are not easy to separate, or they give the desired complex in unsatisfactory yield, and so we attempted to develop a more efficient route to IVa–IVc. Furthermore, we were also interested in studying the mechanism of formation of the vinylidene complexes because we were keen to answer the question how the unsaturated carbenes are formed from the coordinated alkynes. In most of the previous work it was assumed that the rearrangement occurs via alkynylhydrido compounds as intermediates, although all attempts to isolate these species were unsuccessful [6].

In an initial experiment we proved that under the conditions used for the synthesis of IVa from IIa the alkyne complex IIIa does not rearrange to give the vinylidene isomer. Such stability is not observed for the square-planar starting material IIa; when this compound is dissolved in THF or benzene, it slowly reacts at room temperature to form an equilibrium mixture of IIa and the alkynylhydrido complex RhHCl(C_2Ph)(PPr$^i_3$)$_2$ (Va). The most characteristic feature in the NMR spectrum of the new isomer is a high-field signal at δ −27.70 ppm, which, owing to Rh–H and P–H coupling, appears as a doublet of triplets. In agreement with the proposed structure (discussed below) the IR spectrum of Va shows two relatively strong bands at 2180 and 2100 cm^{-1} that correspond to Rh–H and C≡C stretching frequencies.

Despite various attempts (by changing the solvent and the temperature) we failed to shift the equilibrium between IIa and Va completely to the side of the alkynylhydrido compound, and thus could isolate Va only in very low yield. As the solid compound is also extremely air-sensitive, it was characterized only by spectroscopic means, not by elemental analysis. In addition to the hydride signal at high field and the two multiplets for the C_6H_5 and the phosphine PCH protons, the ^{1}H NMR spectrum shows a doublet of virtual triplets which confirms the equivalence of the two PPr$^i_3$ ligands. We therefore assume that the alkynylhydrido complex Va has either structure **A**, **B** or **C**, and for steric reasons the first of these seems to be favored. Very recently, an X-ray structural analysis confirmed that the related five-coordinated iridium compound IrHCl(C_6H_5)(PPr$^i_3$)$_2$ formed by addition of benzene to [IrCl(PPr$^i_3$)$_2$] has a trigonal bipyramidal configuration [12].

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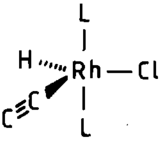
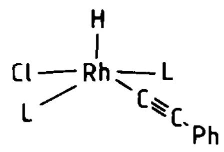


(A)



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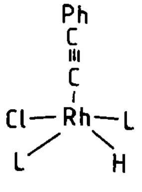
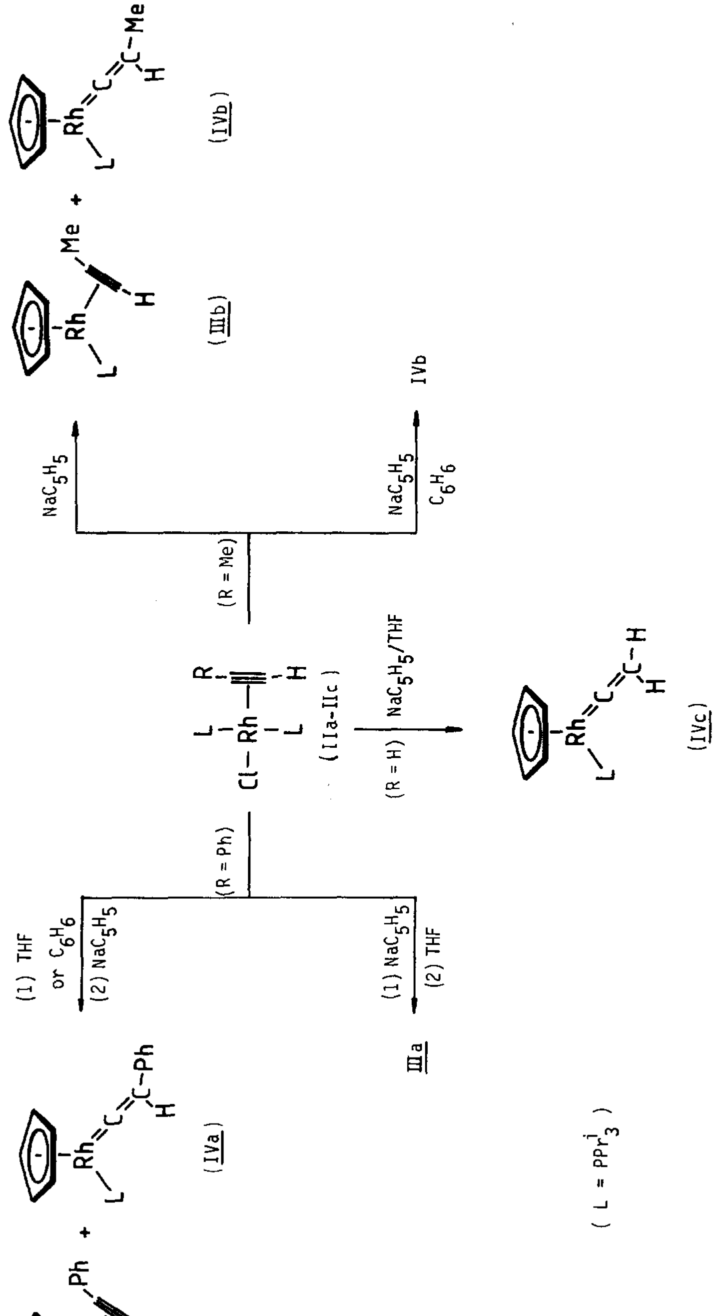


(C)


(IIIa)
(IVa)
(IIIb)
(IVb)
(IVc)
(IIa-IIc)
(R = Ph)
(R = Me)
(R = H)
(1) THF or C6H6
(2) NaC5H5
(1) NaC5H5
(2) THF
IIIa
NaC5H5
NaC5H5 C6H6
IVb
NaC5H5/THF
(L = PPr$^i_3$)

Scheme 1

Table 1

^{1}H NMR data of complexes IVa–IVc (100 MHz; 25 °C, in C_6D_6; δ in ppm, TMS int.; J in Hz)

Complex	$\delta(C_5H_5)$ [a]	δ(C=C*H*R) [a]	J(PH)	J(RhH)	J(HH)	δ(C=CH*R*)	δ(PCH)	δ(PCHC*H*$_3$)	J(PH)	J(HH)
IVa	5.23(m)	4.42(dd)	4.6	1.6		7.20(m)	1.97(m)	1.00(dd)	14.0	7.0
IVb	5.22(m)	3.16(ddq)	4.5	2.0	7.4	1.81(dd) [b]	2.06(m)	1.10(dd)	13.6	7.2
IVc	5.47(m)	2.95(dd) [2H]	4.6	1.5			2.30(m)	1.34(dd)	13.4	7.6

[a] The multiplet pattern of the ring proton signal together with the evident broadening of the signal of the vinylidene proton(s) indicate that the ring protons couple not only with the ^{31}P and ^{103}Rh nuclei but also with the vinylidene proton(s). [b] J(PH) 2.1 Hz; J(HH) 7.4 Hz.

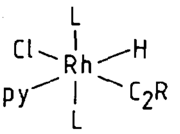
Table 2

^{13}C NMR data of complexes IVa–IVc (IVc: 400 MHz, IVa, IVb: 90 MHz; 25 °C, in C_6D_6; δ in ppm, TMS int.; J in Hz)

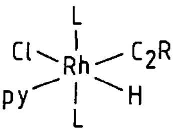
Complex	$\delta(C_5H_5)$	δ(*C*=CHR)	J(RhC)	J(PC)	δ(C=*C*HR)	J(RhC)	J(PC)	δ(C=CH*R*)	δ(P*C*H)	J(PC)	δ(PCH*C*H$_3$)
IVa	85.94(dd) [a]	316.99(dd)	67.7	27.7	116.31(dd)	14.4	4.4	124.42(s) 125.06(s) 128.40(s) 132.39(d) [c]	26.64(dd) [b]	23.3	19.85(s)
IVb	85.40(dd) [a]	311.60(dd)	65.5	27.7	103.59(dd)	15.4	4.4	5.27(d) [c]	26.28(d)	22.2	19.85(s)
IVc	85.93(s)	311.41(dd)	66.1	27.6	94.14(dd)	17.0	3.7		24.43(d)	22.9	19.87(s)

[a] J(RhC) and J(PC) 2.2 Hz. [b] J(RhC) 2.2 Hz. [c] J(RhC) 3.3 Hz.

The fact, mentioned above, that Va reacts at room temperature in THF with NaC_5H_5 to produce IVa in almost quantitative yield strongly supports the proposal that Va is an intermediate in the formation of IVa from IIa. The vinylidene complex IVa is also obtained on addition of NaC_5H_5 to the octahedral compound $RhHCl(C_2Ph)(PPr^i_3)_2(py)$ (VIa), which is easily formed from Va and pyridine (Scheme 2). If IIb is used as the starting material, the corresponding propynyl derivative $RhHCl(C_2Me)(PPr^i_3)_2(py)$ (VIb) is obtained. Although we were unable to prove by ^1H NMR spectroscopy that the five-coordinated intermediate $RhHCl(C_2Me)(PPr^i_3)_2$ is formed from IIb, we assume that there is an equilibrium between these two isomers which is completely shifted to the side of the hydridopropynyl complex by treatment with pyridine. Both VIa and VIb are white, very air-sensitive solids, which have been characterized by elemental analysis and by IR and ^1H NMR spectroscopic data. In the light of the structure proposed for Va, we assume that the ligand arrangement in VIa and VIb corresponds to either **D** or **E**, with the chloride or the pyridine *cis* to the hydride. The NMR spectra leave no doubt that the phosphine ligands are *trans* to each other not only in Va (and probably in Vb) but also in VIa and VIb.

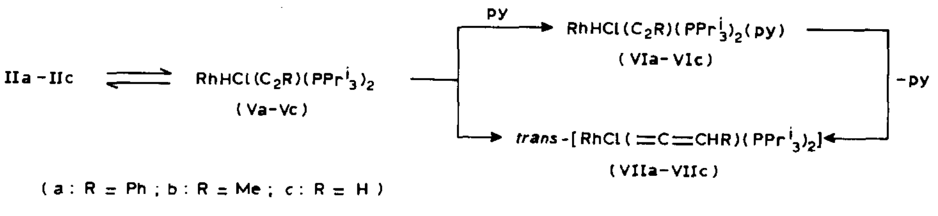


(**D**)



(**E**)

In solution, the octahedral alkynylhydrido complexes VIa and VIb are stable only below −10 °C. Above this temperature they undergo elimination of pyridine and slowly rearrange to the square-planar compounds *trans*-$[RhCl(=C=CHR)(PPr^i_3)_2]$ (VIIa–VIIc) [13]. These are also formed from the isomeric alkyne complexes IIa, IIb if these are warmed in hexane solution to ca. 50 °C [13]. The acetylene derivative IIc behaves similarly, although we found no evidence for the five-coordinated intermediate $RhHCl(C_2H)(PPr^i_3)_2$ (Vc) and also failed to prepare the corresponding pyridine adduct $RhHCl(C_2H)(PPr^i_3)_2(py)$ (VIc). It should be mentioned that the square-planar vinylidene complexes VIIa–VIIc are not useful starting materials for the synthesis of the half-sandwich type compounds IVa–IVc, which are either not obtained from VIIa–VIIc and NaC_5H_5 at all (R = H) or are formed only in unsatisfactory yields (R = Me, Ph).



Scheme 2. Vb, Vc and VIc not isolated.

Mechanistic studies

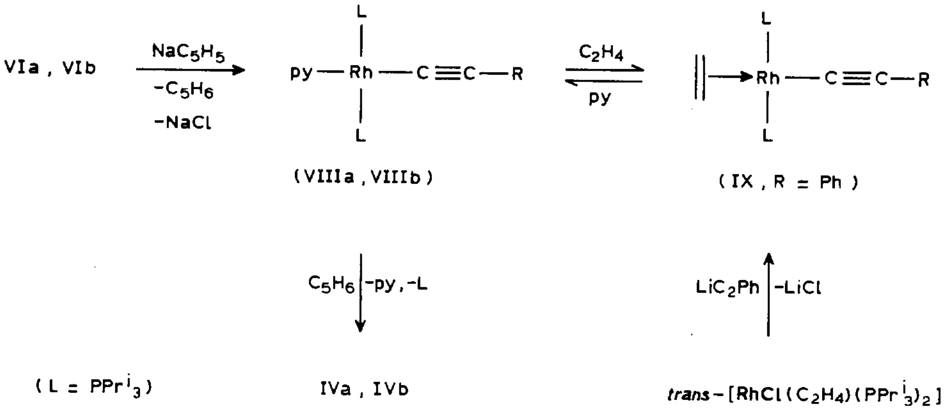
The pyridine adducts VIa and VIb react with NaC_5H_5 in THF to form the vinylidene complexes IVa and IVb in good yields. As it has generally been assumed [6] that the transformation of a coordinated alkyne into a coordinated vinylidene must proceed via an alkynylhydridometal intermediate, we originally expected that during the reaction of VIa and VIb with NaC_5H_5 an intermediate of composition $C_5H_5RhH(C_2R)(PPr^i_3)$ would be formed. It could be generated from VIa, VIb on primary substitution of chloride by cyclopentadienide followed by subsequent displacement of the pyridine and one phosphine ligand to achieve an η^5-coordination of the five-membered ring.

This simplified mechanistic picture, however, turned out to be wrong. By monitoring the reaction of VIa or VIb with NaC_5H_5 in an IR cell, we observed that even after only ca. 2 min the starting materials had completely disappeared, whereas during this time only traces of IVa or IVb were formed. When the mixture thus formed was worked up at 0 ° C, a yellow air-sensitive solid was isolated. Elemental analyses confirmed that the products obtained from VIa, VIb and NaC_5H_5, which are easily soluble even in unpolar solvents, are the square-planar alkynyl pyridine complexes *trans*-$[Rh(C_2R)(py)(PPr^i_3)_2[$ (VIIIa, VIIIb). They are analogues of the well-known alkynyl carbonyl compounds *trans*-$[Rh(C_2R)(CO)(PPh_3)_2]$ [14–16] that have been prepared from *trans*-$[RhCl(CO)(PPh_3)_2]$ and 1-alkynes, sometimes in presence of a strong base [16].

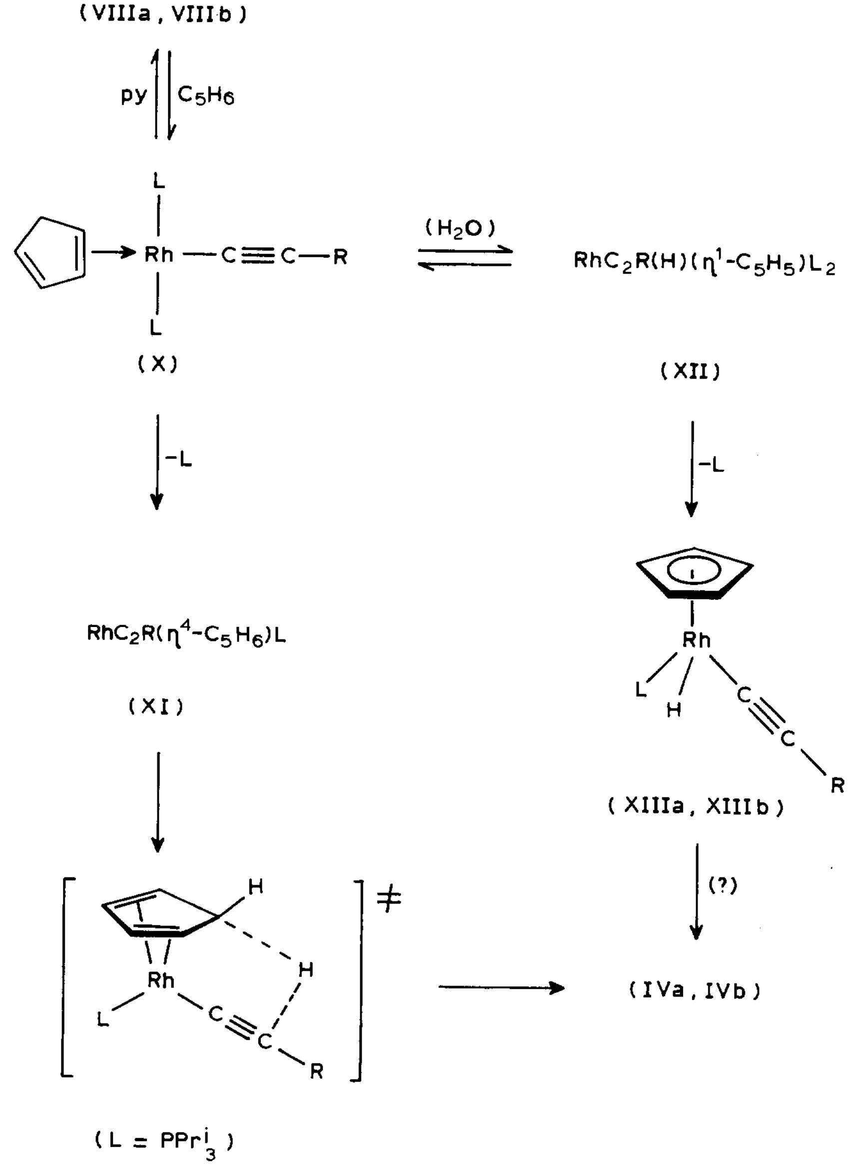
The finding that VIIIa, VIIIb are formed from VIa, VIb and NaC_5H_5 (see Scheme 3) proves that the cyclopentadienide does not behave as a nucleophile but as a Brønsted base. By elimination of H^+ (and Cl^-) cyclopentadiene is formed, and if the reaction is not stopped after a few minutes this reacts smoothly with VIIIa, VIIIb to displace the pyridine and give the corresponding vinylidene complex.

The lability of the Rh–pyridine bond in VIIIa is also evident in the reaction with ethylene, which in benzene at room temperature gives an equilibrium mixture of VIIIa and the corresponding ethylene complex *trans*-$[RhC_2Ph(C_2H_4)(PPr^i_3)_2]$ (IX). The amount of VIIIa and IX strongly depends on the ethylene concentration; at 1 atm the ratio is ca. 1/2, whereas at 2–3 atm of ethylene there is almost quantitative formation of IX. The ethylene complex is also produced, although in low yield, from *trans*-$[RhCl(C_2H_4)(PPr^i_3)_2]$ and lithium phenylacetylide, and because it is stable only in an C_2H_4 atmosphere has been characterized only by ^1H NMR data. On reaction of IX with pyridine, compound VIIIa is reformed.

The reaction of VIIIa and VIIIb with cyclopentadiene can lead not only to IVa and IVb, but in the presence of water can also give the alkynylhydridorhodium compounds $C_5H_5RhH(C_2R)(PPr^i_3)$ (XIIIa, XIIIb). These isomerize only slowly to IVa, IVb and so are probably not intermediates on the route from VIIIa, VIIIb to the η^5-cyclopentadienylvinylidene complexes IVa, IVb. With regard to the reaction mechanism outlined in Scheme 4, we assume that the postulated intermediate X that is obtained from VIII and cyclopentadiene, reacts either by loss of one phosphine ligand to form XI or, in the presence of water, rearranges to give XII and finally XIII. The alkynylhydrido compounds XIIIa, XIIIb are possibly not transformed directly into the isomeric vinylidene complexes IVa, IVb, since MO calculations by Silvestre and Hoffmann [17] indicate that such a 1,3 hydrogen shift should be a high energy pathway. Alternatively, it seems conceivable that XIII slowly rearranges to



Scheme 3



Scheme 4

form the intermediate XI, which then reacts by transfer of the *endo*-H atom of the CH_2 group to the β-carbon atom of the alkynyl ligand, to give IV.

Molecular structure of $C_5H_5Rh(=C=CHPh)(PPr^i_3)$ (IVa)

The results of the X-ray diffraction study of the phenylvinylidene complex IVa are summarized in Table 3 and 4, and Fig. 1. The asymmetric unit contains two independent molecules, which mainly differ with respect to the RhC and CC bond lengths of the vinylidenerhodium moiety. The RhC distances are significantly shorter than in carbenerhodium complexes (193.0(11) to 200.6(15) pm [18–20]), thus indicating, in agreement with the ^{13}C NMR data of IVa (Table 2) and with MO calculations [21], a high degree of multiple bonding. The RhCC arrangement is almost linear; the RhCC angles in the two independent molecules are 173.0(13) and 174.5(15)°.

The dihedral angles between the plane containing C(10), C(11) and C(12) and the planes through P(1), Rh(1) and C(10), and P(1), Rh(1) and M (which is the midpoint of the cyclopentadienyl ring coordinated to Rh(1)) are 81.1 and 80.6°. The corresponding values for the dihedral angles between C(50),C(51),C(52) and P(2),Rh(2),C(50), and between C(50),C(51),C(52) and P(2),Rh(2),M′ (which is the midpoint of the cyclopentadienyl ring coordinated to Rh(2)) are 84.2 and 83.9°, respectively. Taken the α-carbon atom of the vinylidene ligand as the centre, the two sides of the molecule are nearly perpendicular to each other and, therefore, complex IVa (as well as IVb) should be chiral. The ^1H and ^{13}C NMR spectra, however, provide no evidence for this because in a chiral compound of general composition $C_5H_5(PPr^i_3)Rh{=}C{=}CHR$ the CH_3 protons of the triisopropylphosphine ligand are diastereotopic and thus should give rise to two different NMR signals. At room temperature, these have not been observed. The conclusion is that under these conditions IVa and IVb possess a non-rigid structure in solution and therefore

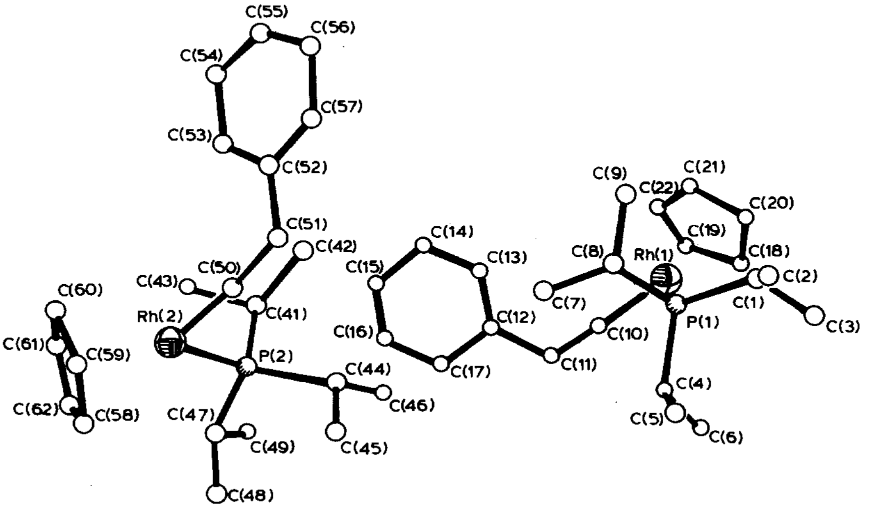


Fig. 1. Molecular structure of IVa (the asymmetric unit contains two independent molecules).

Table 3

Positional parameters and their estimated standard deviations for non-hydrogen atoms in IVa

	x	*y*	*z*
Rh(1)	0.4355(1)	0.1425(1)	0.1733(3)
Rh(2)	−0.0557(1)	−0.1109(1)	−0.0004(3)
P(2)	0.9788(3)	0.3351(3)	0.1062(3)
P(1)	0.4974(2)	0.0975(4)	0.0530(4)
C(1)	0.4220(9)	0.0624(10)	−0.0268(11)
C(2)	0.4508(11)	0.0551(11)	−0.1195(12)
C(3)	0.3805(10)	−0.0140(10)	0.0030(15)
C(4)	0.6122(11)	−0.0163(12)	−0.0118(15)
C(5)	0.5760(11)	0.0177(11)	0.0703(12)
C(6)	0.5475(11)	−0.0489(11)	0.1296(12)
C(7)	0.7287(12)	0.2035(12)	0.0406(14)
C(8)	0.5524(10)	0.1776(10)	−0.0076(14)
C(9)	0.4946(11)	0.2421(15)	−0.0288(17)
C(10)	0.5328(9)	0.1444(10)	0.2289(11)
C(11)	0.5991(9)	0.1515(10)	0.2724(11)
C(12)	0.6421(9)	0.2286(9)	0.2842(11)
C(13)	0.6152(10)	0.3028(9)	0.2545(11)
C(14)	0.6550(11)	0.3749(11)	0.2680(13)
C(15)	0.7249(11)	0.3734(12)	0.3134(13)
C(16)	0.7520(11)	0.3055(11)	0.3469(13)
C(17)	0.7146(10)	0.2326(10)	0.3360(12)
C(18)	0.3102(8)	0.1085(10)	0.2241(11)
C(19)	0.3417(11)	0.1748(11)	0.2716(15)
C(20)	0.3033(11)	0.1487(11)	0.1376(13)
C(21)	0.3310(10)	0.2278(11)	0.1545(13)
C(22)	0.3537(10)	0.2361(13)	0.2354(14)
C(41)	0.9143(13)	0.4079(12)	0.1644(16)
C(42)	0.8382(14)	0.4267(15)	0.1079(18)
C(43)	0.9618(14)	0.4808(14)	0.1963(18)
C(44)	0.9098(11)	0.2556(13)	0.0706(14)
C(45)	0.9538(13)	0.1898(12)	0.0175(16)
C(46)	0.8532(12)	0.2171(13)	0.1350(15)
C(47)	1.0450(11)	0.2959(12)	0.1964(14)
C(48)	1.0923(12)	0.2223(11)	0.1707(18)
C(49)	1.0002(14)	0.2860(14)	0.2828(15)
C(54)	0.8380(13)	0.6243(13)	−0.0970(16)
C(50)	0.9704(9)	0.3954(9)	−0.0658(10)
C(52)	0.8646(9)	0.4843(9)	−0.1332(10)
C(57)	0.8041(11)	0.4890(12)	−0.1974(14)
C(51)	0.9067(9)	0.4075(10)	−0.1247(11)
C(56)	0.7610(12)	0.5623(11)	−0.2103(14)
C(55)	0.7799(13)	0.6226(15)	−0.1605(18)
C(53)	0.8818(12)	0.5470(12)	−0.0830(15)
C(59)	1.1658(11)	0.4033(11)	−0.0835(14)
C(58)	1.1920(9)	0.3518(9)	−0.0140(11)
C(60)	1.1468(10)	0.4818(11)	−0.0398(12)
C(61)	1.1613(12)	0.4662(12)	0.0493(14)
C(62)	1.1865(12)	0.3952(12)	0.0603(15)

Table 4

Selected interatomic distances (pm) and angles (°) in IVa (see Fig. 1)

Rh(1)–P(1)	226.3(6)	Rh(2)–P(2)	227.7(6)	Rh(1)–C(10)–C(11)	174.5(15)
Rh(1)–C(10)	182.6(16)	Rh(2)–C(50)	174.3(15)	Rh(2)–C(50)–C(51)	173.0(13)
C(10)–C(11)	129.5(23)	C(50)–C(51)	141.1(22)	C(10)–C(11)–C(12)	123.6(15)
C(11)–C(12)	147.0(22)	C(51)–C(52)	145.4(22)	C(50)–C(51)–C(52)	122.7(14)
Rh(1)–C(18)	228.7(15)	Rh(2)–C(58)	234.4(15)	P(1)–Rh(1)–C(10)	90.1(5)
Rh(1)–C(19)	224.6(17)	Rh(2)–C(59)	224.5(19)	P(2)–Rh(2)–C(50)	90.0(5)
Rh(1)–C(20)	225.7(18)	Rh(2)–C(60)	223.4(18)	Rh(1)–P(1)–C(1)	110.9(5)
Rh(1)–C(21)	225.0(17)	Rh(2)–C(61)	229.5(19)	Rh(1)–P(1)–C(5)	115.2(6)
Rh(1)–C(22)	227.2(20)	Rh(2)–C(62)	236.2(20)	Rh(1)–P(1)–C(8)	114.0(6)

behave similarly to various other vinylidene transition-metal complexes [6]. In the crystalline state of IVa, the allene-type geometry is obviously frozen out. It is interesting to note that very recently Consiglio and Morandini reported that the vinylidene iron and ruthenium cations $[C_5H_5M(=C=CHR)(L-L)]^+$ where L–L is a diphosphine ligand also show a non-rigid behavior and that the preferred conformation is the one in which the plane of the C=CHR moiety is perpendicular to the plane containing the vinylidene α-carbon atom, the metal and the centroid of the cyclopentadienyl ring [22].

Experimental

All reactions were carried out under argon and in carefully dried solvents. The starting materials $[(C_8H_{14})_2RhCl]_2$ [23] and IIa, IIc [9] were prepared by published methods.

Preparation of trans-[RhCl(MeC$_2$H)(PPr$^i_3$)$_2$] (IIb)

A suspension of 500 mg (0.70 mmol) $[(C_8H_{14})_2RhCl]_2$ in 50 ml of pentane was treated with 1.0 ml (5.0 mmol) PPr^i_3, and was stirred at room temperature for 15 min. The reaction mixture was filtered, the filtrate was cooled to 0 °C, and during ca. 10 s propyne was bubbled through the solution. The solvent was distilled off, and the oily residue was dried for 2 h in vacuo. After recrystallization at −78 °C from pentane, yellow air-sensitive crystals were obtained. Yield 350 mg (50%); m.p. 80 °C (dec). IR (KBr): $\nu(C\equiv C)$ 1880 cm^{-1}. ^1H NMR (C_6D_6): δ 2.95(dq), *J*(HH) = *J*(RhH) = 2.4 Hz, ≡CH; 2.50(m), PCH; 2.17(dd), *J*(HH) 2.4 Hz, *J*(RhH) 1.4 Hz, $\equiv CCH_3$; 1.49(dvt), *J*(HH) 6.1 Hz, *N* 12.2 Hz, $PCHC\mathit{H}_3$. Found: C, 50.79; H, 9.29; Rh, 20.67. $C_{21}H_{46}ClP_2Rh$ calcd.: C, 50.56; H, 9.29; Rh, 20.63%.

Preparation of C$_5$H$_5$Rh(MeC$_2$H)(PPr$^i_3$) (IIIb)

A solution of 1.0 g (11.35 mmol) NaC_5H_5 in 10 ml of THF was warmed to 60 °C and during 15 min treated dropwise with a solution of 200 mg (0.40 mmol) IIb in 5 ml of THF. The reaction mixture was cooled to room temperature and then stirred for 1 h. The solvent was removed in vacuo, and the residue was extracted with pentane. The pentane solution was filtered and the filtrate concentrated in vacuo. After the remaining dark oily residue was kept for several hours at 10^{-3} mmHg, it was dissolved in ca. 2 ml of hexane, and the solution was chromatographed at

$-40\,°C$ on Al_2O_3 (neutral, activity grade V) with hexane. The first yellow band was evaporated to dryness to give a yellow, very air-sensitive oil corresponding to IIIb; yield 21 mg (14%). The second orange band contained (according to the ^1H NMR spectrum) the vinylidene compex IVb. IIIb: IR (hexane): $\nu(C{\equiv}C)$ 1800 cm^{-1}. ^1H NMR (C_6H_6): δ 5.31(dd), $J(PH)$ 1.4 Hz, $J(RhH)$ 0.7 Hz, C_5H_5; 4.36(dq), $J(HH) = J(RhH) = 2.4$ Hz, $\equiv CH$; 2.41(dd), $J(HH)$ 2.4 Hz, $J(RhH)$ 1.2 Hz, $\equiv CCH_3$; 1.70(m), PCH; 1.10(dd), $J(HH)$ 7.0 Hz, $J(PH)$ 13.6 Hz, and 1.06(dd), $J(HH)$ 7.0 Hz, $J(PH)$ 13.6 Hz, $PCHCH_3$.

Preparation of $C_5H_5Rh(=C=CHPh)(PPr^i_3)$ (IVa)

A solution of 369 mg (0.58 mmol) VIa and 120 mg (1.36 mmol) NaC_5H_5 in 15 ml of THF was stirred for 2 h at room temperature. The solvent was removed in vacuo, and the residue was extracted with pentane. The pentane solution was filtered, and to remove the free phosphine was treated with 1 ml (1.61 mmol) of methyl iodide. After 10 min, the phosphonium salt was filtered off, and the filtrate was evaporated to dryness. The residue was dissolved in ca. 2 ml of hexane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V). After removal of the solvent, the residue was recrystallized at $-78\,°C$ from THF/pentane (1/10) to give orange-red, only moderately air-sensitive crystals. Yield 170 mg (68%); m.p. 95 °C (dec). MS (70 eV): m/z (%) 430 (11; M^+), 328 (100; $M^+ - C_2HPh$), 168 (28; $C_5H_5Rh^+$), 102 (14; C_2HPh^+). Found: C, 61.30; H, 7.60; Rh, 24.19. $C_{22}H_{32}PRh$ calcd.: C, 61.40; H, 7.49; Rh, 23.91%.

Preparation of $C_5H_5Rh(=C=CHMe)(PPr^i_3)$ (IVb)

(a) A solution of 235 mg (0.47 mmol) IIb in 10 ml of benzene was treated with 100 mg (1.13 mmol) NaC_5H_5 and stirred for 2 h at room temperature. The reaction mixture was worked up as described for IVa. After column chromatography an orange air-sensitive oil was obtained. Yield 112 mg (65%).

(b) A solution of 280 mg (0.48 mmol) VIb and 100 mg (1.13 mmol) NaC_5H_5 in 10 ml of THF was stirred for 2 h at room temperature. The reaction mixture was worked up as described for IVa. Yield 128 mg (72%). Found: C, 55.04; H, 8.01; Rh, 27.90. $C_{17}H_{30}PRh$ calcd.: C, 55.44; H, 8.21; Rh, 27.94%.

Preparation of $C_5H_5Rh(=C=CH_2)(PPr^i_3)$ (IVc)

A solution of 638 mg (1.32 mmol) IIc in 20 ml of THF was treated with 220 mg (2.50 mmol) NaC_5H_5 and stirred for 1 h at room temperature. The reaction mixture was worked up as described for IVa. After column chromatography an orange oil was obtained which was dissolved in 3 ml of pentane. The pentane solution was cooled to $-78\,°C$ to give orange, very air-sensitive crystals which slowly decompose at 0 °C even under argon. Yield 144 mg (31%); m.p. 66 °C (dec). MS (70 eV); m/z (%) 354 (51; M^+), 328 (91; $M^+ - C_2H_2$), 168 (70; $C_5H_5Rh^+$). Found: C, 54.11; H, 8.00; Rh, 29.61. $C_{16}H_{28}PRh$ calcd.: C, 54.24; H, 7.97; Rh, 29.05%.

Preparation of $RhHCl(C_2Ph)(PPr^i_3)_2$ (Va)

A solution of 350 mg (0.62 mmol) IIa in 10 ml of THF was stirred at 40 °C for 45 min. The solvent was removed in vacuo, and the dark residue was repeatedly washed with cold ether (0 °C) until a white extremely air-sensitive solid separated. The solid was filtered off and dried in vacuo. Yield 12 mg (3%). IR (C_6H_6): $\nu(RhH)$ 2180,

ν(C≡C) 2105 cm^{-1}. ^{1}H NMR (toluene-d_8): 8.00(m) and 7.08(m), C_6H_5; 2.80(m), PCH; 1.35(dvt), J(HH) 6.6 Hz, N 13.2 Hz, PCHCH_3; −27.70(dt), J(PH) 12.7 Hz, J(RhH) 42.0 Hz, RhH.

Preparation of the complexes RhHCl(C_2R)(PPr^i_3)$_2$(py) (VIa, VIb)

A solution of 0.30 mmol IIa, IIb in 20 ml of ether was treated with 48 μl (0.60 mmol) pyridine and stirred for 40 min (IIa) or 20 min (IIb) at 35 °C. After the solution was concentrated to ca. 5 ml in vacuo, 20 ml of pentane was added. The solution was cooled to −78 °C until white air-sensitive crystals separated. These were filtered off, repeatedly washed with cold pentane (0 °C), and dried in vacuo. Yield 72% (VIa) and 77% (VIb).

VIa: M.p. 106 °C (dec.). IR (KBr): ν(RhH) 2180, ν(C≡C) 2100 cm^{-1}. ^{1}H NMR (toluene-d_8 at 8 °C): δ 6.98(m), C_5H_5N and C_6H_5; 2.92(m), PCH; 1.19(dvt) and 1.15(dvt), J(HH) 6.7 Hz, N 13.4 Hz, PCHCH_3; −17.30(dt), J(PH) = J(RhH) = 14.0 Hz, RhH. ^{31}P NMR (C_6D_6): δ 36.09(d), J(RhP) 96.8 Hz. Found: C, 58.13; H, 8.65; N, 2.07; Rh, 16.34. $C_{31}H_{53}ClNP_2Rh$ calcd.: C, 58.17; H, 8.35; N, 2.19; Rh, 16.08%.

VIb: M.p. 87 °C (dec). IR (KBr): ν(RhH) 2180, ν(C≡C) 2120 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.24(m), C_5H_5N; 2.76(m), PCH; 1.88(s), C_2Me; 1.15(dvt) and 1.06 (dvt), J(HH) 7.0 Hz, N 14.0 Hz, PCHCH_3; −17.95 (dt), J(PH) = J(RhH) = 14.0 Hz, RhH. ^{31}P NMR (C_6D_6): δ 35.62(d) J(RhP) 98.3 Hz. Found: C, 53.96; H, 8.77; N, 2.22; Rh, 18.00. $C_{26}H_{51}ClNP_2Rh$ calcd.: C, 54.03; H, 8.89; N, 2.42; Rh, 17.80%).

Preparation of the complexes trans-[Rh(C_2R)(py)(PPr^i_3)$_2$] (VIIIa, VIIIb)

A solution of 0.35 mmol VIa, VIb and 100 mg (1.13 mmol) NaC_5H_5 in 5 ml of THF was stirred for 5 min at 0 °C. The solvent was removed in vacuo, and the residue was extracted with toluene (VIa) or pentane (VIb), respectively. The toluene solution was concentrated in vacuo until the first crystals appeared and then treated with 5 ml of pentane; the pentane extract was also concentrated in vacuo to ca. 5 ml. Both solutions were cooled to −78 °C until yellow (VIIIa) or orange (VIIIb) air-sensitive crystals separated. These were filtered off, repeatedly washed with cold pentane (0 °C), and dried in vacuo. Yield 58% (VIIIa) and 61% (VIIIb).

VIIIa: M.p. 89 °C (dec). IR (hexane): ν(C≡C) 2055 cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.85(m) and 8.82(m), C_5H_5N and C_6H_5; 2.23(m), PCH; 1.35(dvt), J(HH) 6.0 Hz, N 12.0 Hz, PCHCH_3. Found: C, 61.88; H, 8.67; N, 2.12; Rh, 17.00. $C_{31}H_{52}NP_2Rh$ calcd.: C, 61.68; H, 8.68; N, 2.32; Rh, 17.05%.

VIIIb: M.p. 83 °C (dec). IR (hexane): ν(C≡C) 2110 cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.54(m) and 8.82(m), C_5H_5N; 2.25(m), PCH; 2.17(dt), J(PH) 2.4 Hz, J(RhH) 0.7 Hz, ≡CCH_3; 1.38(dvt), J(HH) 7.0 Hz, N 14.0 Hz, PCHCH_3. Found: C, 57.49; H, 9.31; N, 2.33; Rh, 18.80. $C_{26}H_{50}NP_2Rh$ calcd.: C, 57.67; H, 9.31; N, 2.59; Rh, 19.00%.

Reaction of VIIIa, VIIIb with cyclopentadiene

A solution of 0.12 mmol VIIIa, VIIIb in 2 ml of benzene was treated with 35 μl (0.42 mmol) carefully dried C_5H_6 and stirred for 3 min at room temperature. The ^{1}H NMR spectrum of the solution showed that only IVa, IVb was formed. Yield virtually quantitative.

Preparation of *trans*-[Rh(C_2Ph)(C_2H_4)(PPr^i_3)$_2$] (IX)

Ethylene was bubbled through a solution of 85 mg (0.14 mmol) VIIIa in 5 ml of benzene. After ca. 5 min an equilibrium between VIIIa and IX was achieved which could not be shifted by further stirring under an C_2H_4 atmosphere. The ratio of VIIIa and IX at 25 °C was approximately 1/2. The ethylene complex IX was characterized by IR and ^1H NMR spectroscopic data. IR (C_6H_6): $\nu(C{\equiv}C)$ 2060 cm^{-1}. ^1H NMR (C_6D_6): δ 7.13(m), C_6H_5; 3.17(dt), $J(PH)$ 3.6 Hz, $J(RhH)$ 1.6 Hz, C_2H_4; 2.34(m), PCH; 1.27(dvt), $J(HH)$ 6.4 Hz, N 12.8 Hz, PCHCH_3.

Preparation of $C_5H_5RhH(C_2Ph)(PPr^i_3)$ (XIIIa)

A solution of 200 mg (0.33 mmol) VIIIa in 5 ml of benzene was first treated with 0.5 ml (2.7 mmol) water and then with 85 μl (1.02 mmol) cyclopentadiene, and was stirred for 30 min at room temperature. After the solvent was removed in vacuo, the residue was recrystallized at −78 °C from pentane to give yellow crystals. Yield 60 mg (42%); m.p. 45 °C (dec.). IR (KBr): $\nu(RhH)$ 2090, $\nu(C{\equiv}C)$ 2050 cm^{-1}. ^1H NMR (C_6D_6): 7.33(m), C_6H_5; 5.23(m), C_5H_5; 2.00(m), PCH; 1.09 (dd), $J(HH)$ 6.8 Hz, $J(PH)$ 14.6 Hz and 1.04 (dd), $J(HH)$ 7.2 Hz, $J(PH)$ 13.8 Hz, PCHCH_3; −13.07 (dd), $J(PH)$ 32.0 Hz, $J(RhH)$ 22.0 Hz, RhH. Found: C, 61.93; H, 7.55; mol. weight 430. $C_{22}H_{32}PRh$ calcd.: C, 61.40; H, 7.49; mol. weight 430.4.

The compound $C_5H_5RhH(C_2Me)(PPr^i_3)$ (XIIIb) was similarly prepared but always obtained as a mixture with the isomer IVb. XIIIb is characterized by a high-field signal in the ^1H NMR spectrum (C_6D_6) at δ −14.13(dd), $J(PH)$ 32.0 Hz, $J(RhH)$ 22.0 Hz.

X-Ray structural analysis of IVa

Dark-red crystals from pentane. Crystal dimensions: 0.3 × 0.4 × 0.2 mm. Unit cell data: orthorhombic, space group $Pbc2_1$ (non-standard setting of $Pca2_1$ No. 29), $Z = 8$; a 1652.4(4), b 1654.3(3), c 1559.9(5) pm, V 4263.8 × 10^6 pm^3; $d_{rö}$ 1.69 g cm^{-3}; 2θ limits 3–60 ° (Mo-K_α, λ 71.069 pm, graphite monochromator); 2264 independent reflections with $I_0 > 3.0\sigma(I_0)$, Patterson (Rh) and difference Fourier syntheses, anisotropic refinement only for Rh and P; $R_{iso} = 0.045$, $R_{aniso} = 0.042$. The absolute configuration was not determined.

Further details of the crystal structure investigation can be obtained on request from the Fachinformationszentrum Energie Physik Mathematik D-7514 Eggenstein-Leopoldshafen by quoting the number CSD 50344, the names of the authors, and full citation of the journal.

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