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Vinylidene transition-metal complexes

XXV *. Novel square-planar alkynylrhodium anions *trans*-$[RhCl(C{\equiv}CR)(P^iPr_3)_2]^-$ as precursors for alkyne, vinylidene and allene rhodium complexes **

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Abstract

The tetrabutylammonium salts of the novel square-planar alkynylrhodium anions *trans*-$[RhCl(C{\equiv}CR)(P^iPr_3)_2]^-$ (R = CO_2Et, **4**; C_6H_5, **6**) have been prepared by $SiMe_3$ abstraction either from the neutral alkyne or vinylidene complexes, *trans*-$[RhCl(RC{\equiv}CSiMe_3)(P^iPr_3)_2]$ (R = CO_2Et, **2**) or *trans*-$[RhCl(=C=C(SiMe_3)R)(P^iPr_3)_2]$ (R = CO_2Et, **3**; C_6H_5, **5**) upon treatment with $[^nBu_4N]F$. Compound **4** reacts with weak acids (H_2O, CH_3OH, CH_3NO_2) to give the vinylidene compound *trans*-$[RhCl(=C=CHCO_2Et)(P^iPr_3)_2]$ (**7**), which is also obtained by the thermal rearrangement of the isomeric alkyne derivative *trans*-$[RhCl(HC{\equiv}CCO_2Et)(P^iPr_3)_2]$ (**9**). The reaction of **4** with methyl iodide unexpectedly gives the allene rhodium complex *trans*-$[RhCl(\eta^2\text{-}CH_2{=}C{=}CHCO_2Et)(P^iPr_3)_2]$ (**10**), whereas treatment of **6** with CH_3I gives the alkyne compound *trans*-$[RhCl(CH_3C{\equiv}CC_6H_5)(P^iPr_3)_2]$ (**11**). The crystal structure of **10** has been determined.

1. Introduction

There have been numerous reports of the rearrangement of terminal alkynes to the corresponding vinylidenes in the coordination sphere of a transition-metal centre [2], but almost nothing is known about the conversion of a disubstituted alkyne $RC{\equiv}CR'$ into the isomeric vinylidene. Recently, we have shown [3] that silylalkynes such as $RC{\equiv}CSiMe_3$ (R = CH_3, C_6H_5, $SiMe_3$, CO_2Et, CO_2SiMe_3) react with $[RhCl(P^iPr_3)_2]_n$ (**1**) [4,5] to give the four-coordinate alkyne rhodium(I) compounds *trans*-$[RhCl(RC{\equiv}CSiMe_3)(P^iPr_3)_2]$, which rearrange thermally or photochemically to form the vinylidene rhodium isomers *trans*-$[RhCl(=C=C(SiMe_3)R)(P^iPr_3)_2]$. If instead of silylalkynes the analogous stannyl derivatives $RC{\equiv}CSnPh_3$ are used, the conversion occurs even more readily and thus the corresponding stannylvinylidene rhodium complexes *trans*-$[RhCl(=C=C(SnPh_3)R)(P^iPr_3)_2]$ are obtained in almost quantitative yield [6].

In continuation of these studies, we now report that both the Me_3Si-substituted alkyne and vinylidene rhodium complexes are useful starting materials for the synthesis of the previously unknown alkynylrhodium(I) anions *trans*-$[RhCl(C{\equiv}CR)(P^iPr_3)_2]^-$, which in spite of the pronounced reactivity of **1** towards various Lewis bases [4,7] are not accessible from **1** and $LiC{\equiv}CR$.

2. Preparation of $[^nBu_4N][RhCl(C{\equiv}CR)(P^iPr_3)_2]$ (R = CO_2Et, C_6H_5)

During our attempts to prepare and characterize the complexes *trans*-$[RhCl(RC{\equiv}CSiMe_3)(P^iPr_3)_2]$ and *trans*-$[RhCl(=C=C(SiMe_3)R)(P^iPr_3)_2]$ we observed previously that these compounds are highly sensitive towards water and react quite smoothly to form the desilylated derivatives *trans*-$[RhCl(RC{\equiv}CH)(P^iPr_3)_2]$ and *trans*-$[RhCl(=C=CHR)(P^iPr_3)_2]$, respectively [8]. As the driving force for this process is obviously the formation of a Si–O bond, we considered it probable that

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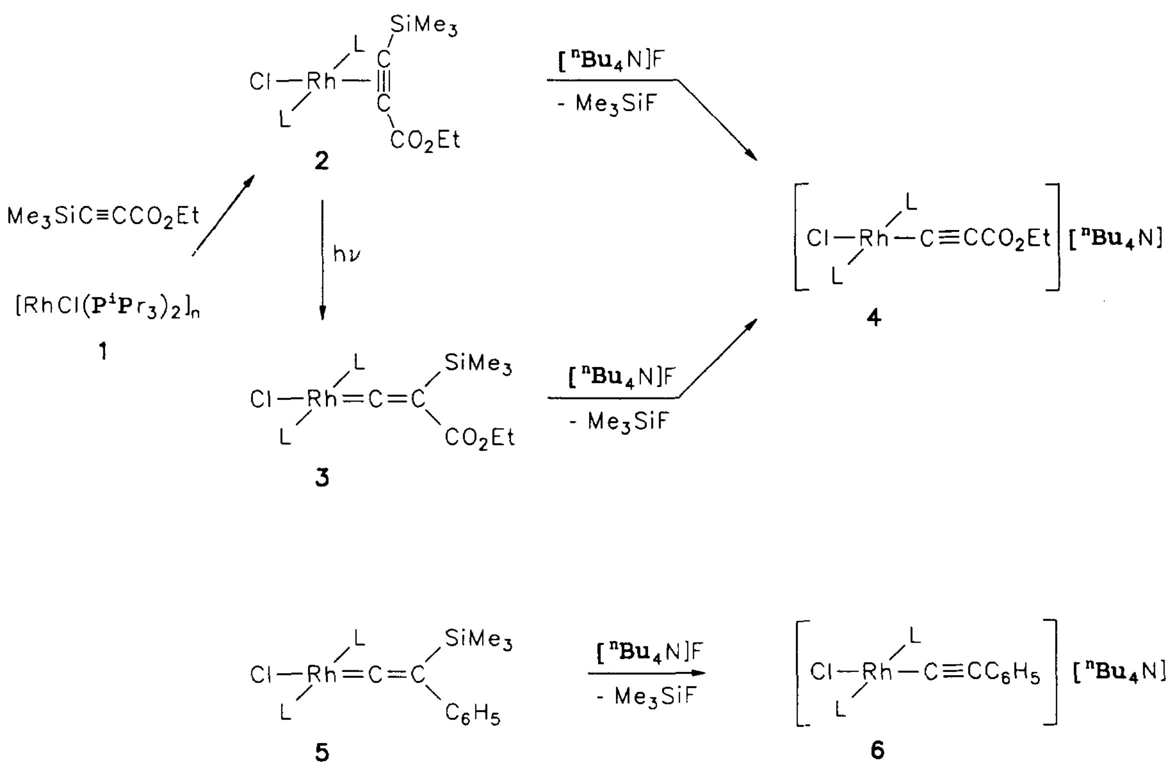
fluorides would behave analogously and so react with *trans*-[RhCl(RC≡CSiMe$_3$)(P^{i}Pr$_3$)$_2$] or *trans*-[RhCl(=C=C(SiMe$_3$)R)(P^{i}Pr$_3$)$_2$] to give the anionic complexes *trans*-[RhCl(C≡CR)(P^{i}Pr$_3$)$_2$]$^-$ and Me$_3$SiF.

Treatment of **2** or **3** (see Scheme 1) with [^{n}Bu$_4$N]F in THF, even at −78°C, results in an almost immediate change of colour from violet to yellow. After warming to room temperature and addition of pentane, a light yellow solid separates; this solid is extremely air- and moisture-sensitive and analyzes as [^{n}Bu$_4$N][RhCl(C≡CCO$_2$Et)(P^{i}Pr$_3$)$_2$] (**4**). If a slight excess of **2** or **3** is used (to avoid the problem of separating [^{n}Bu$_4$N]F and **4**), the yield is almost quantitative. The salt-like character of complex **4** is shown by conductivity data in THF, which are consistent with the presence of a 1:1 electrolyte. The most characteristic features of the spectroscopic data are the C≡C stretching frequency at 2010 cm^{-1} in the IR and the low-field signal of the metal-bonded carbon atom at δ 156.42 in the ^{13}C NMR spectrum, the latter showing strong Rh–C and P–C coupling. As far as the mechanism of the reaction of **2** with [^{n}Bu$_4$N]F is concerned, we assume that in the first step, after cleavage of the C–Si bond, a π-coordinated alkynyl rhodium compound is generated and then undergoes a π/σ rearrangement to form the final product. A similar π-alkynyl intermediate was postulated by Berke to explain the formation of the allenylidene complexes [C$_5$H$_5$Mn(CO)$_2$(=C=C=CR$_2$)] from [C$_5$H$_5$Mn(CO)$_2$(HC≡CCO$_2$Me)] and LiR [9].

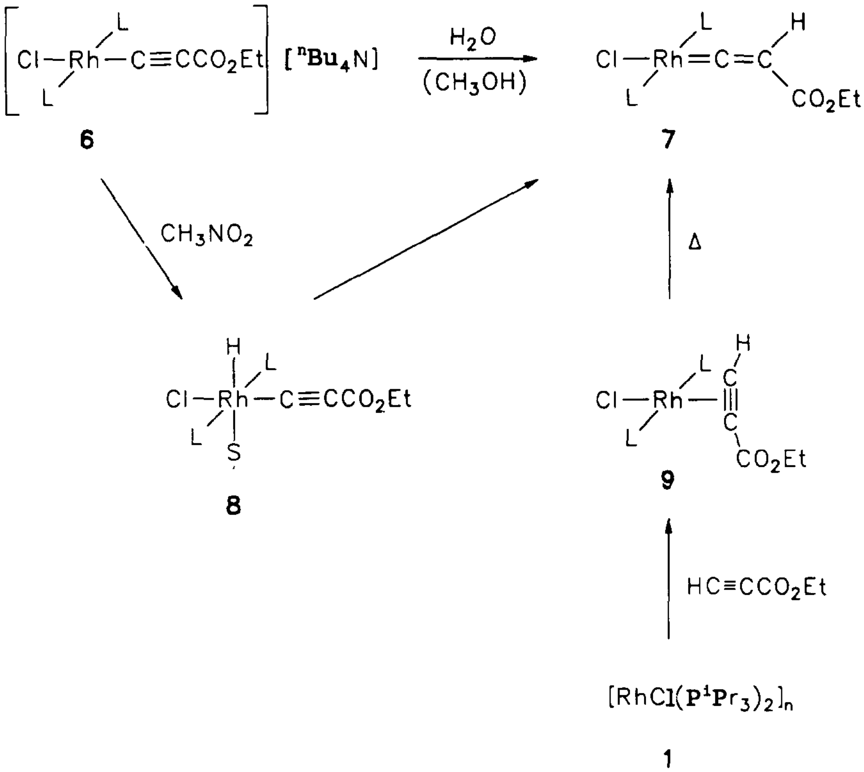
Under the conditions used for the synthesis of **4**, the phenyl-substituted vinylidene complex **5** also reacts with [^{n}Bu$_4$N]F to give **6** (Scheme 1). The yield is virtually quantitative. The *trans* arrangement of the phosphine ligands (as in **4**) is evident from ^{1}H and ^{13}C NMR spectra which, like those of *trans*-[RhCl(CO)(P^{i}Pr$_3$)$_2$] and *trans*-[RhCl(RC≡CR)(P^{i}Pr$_3$)$_2$] [4,10], display a doublet-of-virtual-triplets for the PCHCH_3 protons and a virtual triplet for the PCHCH$_3$ carbon atoms. The low-field shift of the α-carbon signal of the alkynyl ligand in the ^{13}C NMR spectrum of **6** is not as large as for **4**, and this can be attributed to the smaller −M effect of the phenyl compared with that of the CO$_2$Et group.

3. Reactions of the alkynyl complexes 4 and 6 with acids and methyl iodide

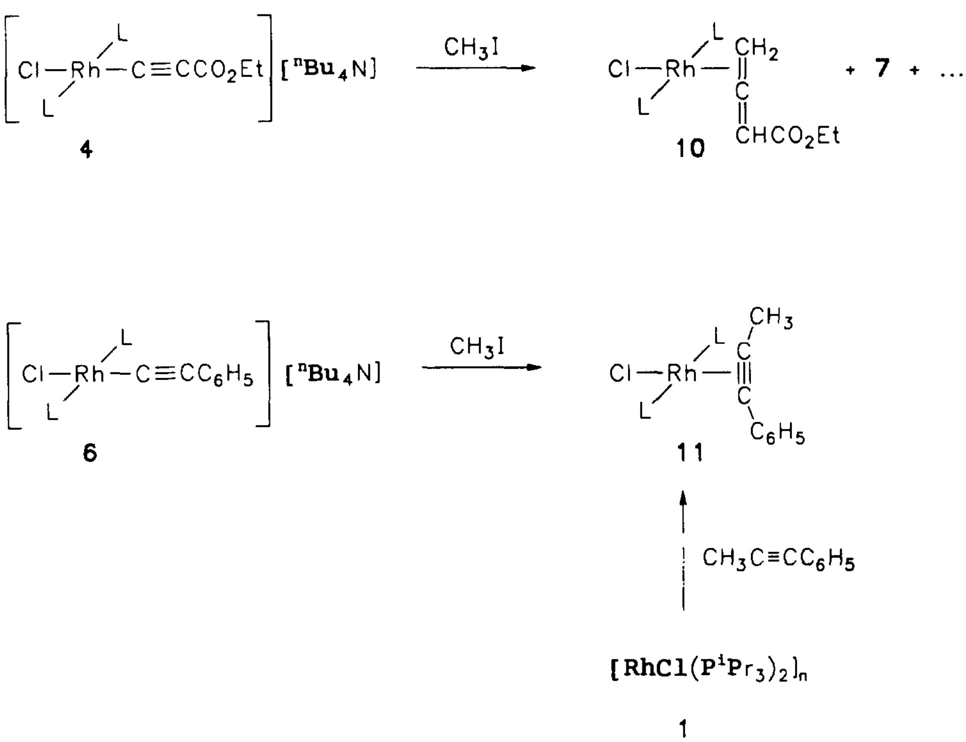
In view of the fact that the alkynyl compounds [RhCl(C≡CR)(P^{i}Pr$_3$)$_2$]$^-$ are obtained by Me$_3$Si-abstraction either from **2** or from **3** and **5**, the question



Scheme 1. L = P^{i}Pr$_3$.



Scheme 2. L = P^iPr_3; S = CH_3NO_2.



Scheme 3. L = P^iPr_3.

arises whether protonation or alkylation of these anions gives the corresponding alkyne or the isomeric vinylidene rhodium derivatives. There is ample evidence in the literature for the attack of an electrophile at the β-carbon atom of a M–C≡CR unit, which is one of the main preparative routes to vinylidene metal complexes [2].

Treatment of **4** with water or methanol in THF at −20°C results in an immediate change of colour from yellow to dark brown, and chromatographic work-up gives the vinylidene rhodium compound **7** in 80–85% yield. If the reaction is carried out with nitromethane (a weaker acid than H_2O or CH_3OH), only a slight change of colour occurs, and an intermediate **8** can be detected. The IR spectrum of **8** shows two bands, at $\nu = 2230$ and $2105\ cm^{-1}$, which are assigned to a Rh–H and a C≡C stretching frequency, respectively, confirming the formation of an alkynyl(hydrido)rhodium derivative. If CD_3NO_2 is used instead of CH_3NO_2, only the band at $2105\ cm^{-1}$ is observed in the IR spectrum of the intermediate. The conclusion is that the proton preferentially attacks the metal and not the alkynyl ligand of **4** and that the vinylidene complex **7** is formed via a RhH(C≡CR) intermediate. Compound **7** can also be prepared by thermal rearrangement of the alkyne rhodium isomer **9** that is obtained from **1** and $HC{\equiv}CCO_2Et$ (see Scheme 2).

The reactions of **4** and **6** with methyl iodide take a different course and surprisingly do not give the expected complexes *trans*-$[RhCl(=C=C(CH_3)R)(P^iPr_3)_2]$ ($R = CO_2Et$, C_6H_5). If a THF-solution of **4** is treated with CH_3I at −78°C and then slowly warmed to room temperature, the ^{31}P NMR spectrum shows that a mixture of products is present. Removal of the solvent followed by column chromatography gives two fractions, the first of which contains compound **7** and the second the substituted allene rhodium complex **10** (Scheme 3). The ^1H and ^{13}C NMR data for **10** reveal that it is the $C{=}CH_2$ and not the $C{=}CHCO_2Et$ double bond of the allene unit which is coordinated to the metal. To account for the relatively low yield of **7** (8%) and **10** (22%), we assume that the electrophile CH_3I attacks both the metal and the alkynyl ligand and that the formation of the substituted allene occurs via β-H elimination of a zwitterionic $Rh{-}C(CH_3){=}CCO_2Et$ intermediate. (It is noteworthy that treatment of *trans*-$[RhCl(C_2H_4)(As^iPr_3)_2]$ with excess propyne also gives an allene rhodium compound *trans*-$[RhCl(\eta^2\text{-}CH_2{=}C{=}CH_2)(As^iPr_3)_2]$ instead of the expected vinylidene complex *trans*-$[RhCl(=C=CHCH_3)(As^iPr_3)_2]$ [11].) With respect to the different courses taken by the reaction of **4** with H_2O on one hand and that with CH_3I on the other, we note that the "hard" proton and "soft" methyl iodide can behave either similarly [12] or differently [13] in electrophilic addition reactions with organometallic substrates.

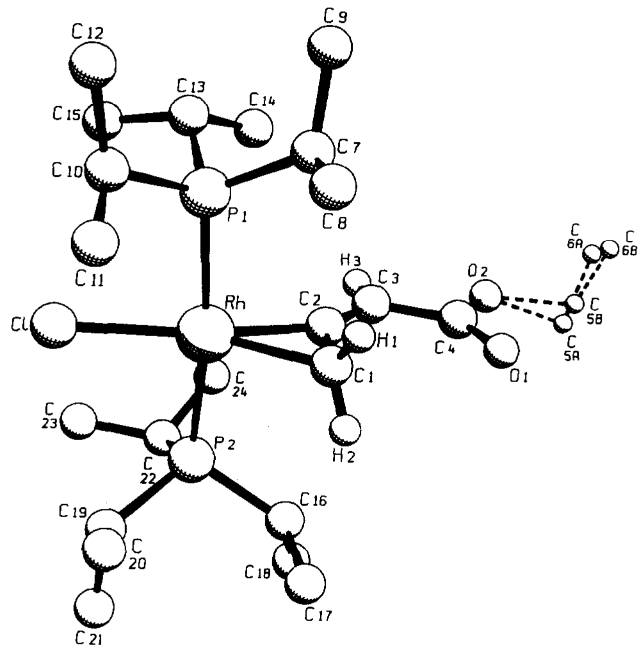


Fig. 1. Molecular structure (SCHAKAL plot) of complex **10**.

Treatment of **6** with methyl iodide under the same conditions employed for the reaction of **4** with CH_3I gives the alkyne complex **11** almost quantitatively. The composition and structure of **11** have been established not only by elemental analysis, IR and NMR spectroscopic data, but also by independent synthesis from **1** and $CH_3C{\equiv}CC_6H_5$. Compound **11** forms orange crystals that are only moderately air-sensitive, and resemble in most of their properties the analogous alkyne rhodium complexes *trans*-$[RhCl(RC{\equiv}CR)(P^iPr_3)_2]$ ($R = CH_3$, C_6H_5, $SiMe_3$) [3,10].

4. Molecular structure of complex 10

A single-crystal X-ray diffraction study of complex **10** has confirmed the structure suggested in Scheme 3. The SCHAKAL plot of the structure (Fig. 1) reveals that the rhodium is coordinated in a somewhat distorted square-planar fashion, with the two phosphine ligands in a *trans* disposition. The bending of the allene (angle C1–C2–C3 141.8(5)°; see Table 1) is very similar to that in *trans*-$[RhCl(\eta^2\text{-}CH_2{=}C{=}CH_2)(As^iPr_3)_2]$ (146(1)°) [11] and $[Pt(\eta^2\text{-}CH_2{=}C{=}CH_2)(PPh_3)_2]$ (142(3)°) [14], and more pronounced than that in *trans*-$[RhI(\eta^2\text{-}CH_2{=}C{=}CH_2)(PPh_3)_2]$ (158(4)°) [15]. The carbon atoms C1–C4 are located in one plane, which is perpendicular to the plane of the Rh, Cl, P1 and P2 atoms. The dihedral angle is 90.8(2)°. The degree of elongation of

TABLE 1. Selected intramolecular bond distances (Å) and bond angles (°) in complex **10**, with e.s.d.s

Rh–Cl	2.372(1)
Rh–P1	2.367(1)
Rh–P2	2.370(1)
Rh–C1	2.120(5)
Rh–C2	1.991(5)
C1–C2	1.390(7)
C2–C3	1.338(7)
C3–C4	1.460(7)
Cl–Rh–P1	87.51(5)
Cl–Rh–P2	86.40(5)
Cl–Rh–C1	157.6(2)
Cl–Rh–C2	163.0(1)
P1–Rh–P2	173.24(4)
P1–Rh–C1	93.5(2)
P1–Rh–C2	93.3(1)
P2–Rh–C1	93.2(2)
P2–Rh–C2	91.6(1)
Rh–C2–C3	142.8(4)
C1–C2–C3	141.8(5)
C2–C3–C4	119.9(5)

the coordinated C=C bond (1.390(7) *versus* 1.338(7) Å) is nearly the same as that in *trans*-[RhCl(η^2-CH_2=C=CH_2)($As^iPr_3)_2$] [11] and other allene transition-metal complexes [16,17]. The Rh–C bond lengths in **10** differ by 0.13 Å, which is in the range expected for four-coordinate allene rhodium(I) derivatives [11,15].

5. Experimental section

All reactions were carried out under argon and in carefully dried solvents. The starting materials $[RhCl(P^iPr_3)_2]_n$ (**1**) [4b], *trans*-[RhCl(Me_3SiC≡CCO_2Et)($P^iPr_3)_2$] (**2**) and *trans*-[RhCl(=C=C($SiMe_3$)R)($P^iPr_3)_2$] (**3**, **5**) [3,8] were prepared by known methods. IR, Perkin-Elmer 457; NMR, Jeol FX 90 Q, Bruker FT WH 90, Bruker AC 200. Equivalent conductivity was measured in THF. Melting points were determined by DTA.

5.1. *Preparation of [$^nBu_4N$][RhCl(C≡CCO_2Et)($P^iPr_3)_2$] (4)*

(a) A solution of 95 mg (0.15 mmol) of **2** in 12 ml of freshly distilled THF was treated dropwise at −78°C with 130 μl (0.14 mmol) of a 1.1 M solution of [$^nBu_4N$]F in THF. The solution was warmed slowly to room temperature then stirred for 15 min and concentrated to *ca.* 1 ml *in vacuo*. Addition of 15 ml of pentane produced a lemon-yellow precipitate, which was separated, repeatedly washed with pentane, and dried *in vacuo*. Yield: 103 mg (89%).

(b) A solution of 230 mg (0.37 mmol) of **3** in 15 ml of freshly distilled THF was treated dropwise at −78°C with 0.31 ml (0.34 mmol) of a 1.1 M solution of [$^nBu_4N$]F in THF. The mixture was allowed to warm to room temperature, then worked-up as described for (a). Yield 252 mg (93%); dec. temp. 85°C; Λ 68 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 57.05; H, 10.20; N, 1.59. $C_{39}H_{83}ClNO_2P_2Rh$ calcd.: C, 58.67; H, 10.48; N, 1.75%. IR (THF): ν(C≡C) 2010, ν(C=O) 1645 cm^{-1}. ^1H NMR (200 MHz, [d_8]THF): δ 4.01 (q, J(HH) = 7.1 Hz, OCH_2); 3.58 (m, NCH_2); 2.87 (m, $PCHCH_3$); 1.87 (m, NCH_2CH_2); 1.50 (dvt, N = 12.2, J(HH) = 6.1 Hz, $PCHCH_3$); 1.13 (t, J(HH) = 7.1 Hz, $N(CH_2)_3CH_3$); signals of OCH_2CH_3 protons and of protons of one CH_2 group covered by $PCHCH_3$ signal. ^{13}C NMR (50.3 MHz, [d_8]THF): δ 156.42 (dt, J(RhC) = 57.0, J(PC) = 19.8 Hz, RhC≡C); 153.03 (s, CO_2Et); 101.70 (d, J(RhC) = 18.0 Hz, RhC≡C); 59.40 (s, NCH_2); 59.19 (s, OCH_2); 24.95 (s, NCH_2CH_2); 24.08 (vt, N = 14.7 Hz, $PCHCH_3$); 21.14 (s, $PCHCH_3$); 20.96 (s, $N(CH_2)_2CH_2$) 15.61 (s, OCH_2CH_3) 14.16 (s, N $(CH_2)_3CH_3$).

5.2. *Preparation of [$^nBu_4N$][RhCl(C≡CC_6H_5)($P^iPr_3)_2$] (6)*

A solution of 150 mg (0.24 mmol) of **5** in 14 ml of freshly distilled THF was treated dropwise at −78°C with 0.20 ml (0.22 mmol) of a 1.1 M solution of [$^nBu_4N$]F in THF. Work-up as for **4** gave the orange-yellow, very air-sensitive product. Yield 173 mg (99%); dec. temp. 74°C; Λ 71 cm^2 Ω^{-1} mol^{-1}. IR (THF): ν(C≡C) 2030 cm^{-1}. ^1H NMR (200 MHz, [d_8]THF): δ 6.70 (m, C_6H_5); 3.41 (m, NCH_2); 2.76 (m, $PCHCH_3$); 1.71 (m, NCH_2CH_2); 1.40 (dvt, N = 12.6, J(HH) = 6.2 Hz, $PCCHH_3$); 0.99 (t, J(HH) = 7.1 Hz, $N(CH_2)_3CH_3$); signal of protons of one CH_2 group covered by $PCHCH_3$ signal. ^{13}C NMR (50.3 MHz, [d_8]THF): δ 137.94 (dt, J(RhC) = 55.1, J(PC) = 21.3 Hz, RhC≡C); 135.23 (s, *ipso*-carbon of C_6H_5); 130.05, 127.78, 119.25 (all s, *ortho*-, *meta*- and *para*-carbons of C_6H_5); 109.53 (dt, J(RhC) = 17.1, J(PC) = 3.1 Hz), RhC≡C; 59.40 (s, NCH_2); 24.92 (s, NCH_2CH_2); 24.18 (vt, N = 14.0 Hz, $PCHCH_3$); 21.23 (s, $PCHCH_3$); 20.66 (s, $N(CH_2)_2$-CH_2); 14.14 (s, $N(CH_2)_3CH_3$).

5.3. *Preparation of trans-[RhCl(=C=$CHCO_2Et$)($P^iPr_3)_2$] (7)*

A solution of 142 mg (0.18 mmol) of **4** in 10 ml of freshly distilled THF was treated dropwise at −20°C with 0.3 ml of water or methanol. The mixture was allowed to warm to room temperature, the solvent removed, and the dark residue dissolved in 3 ml of hexane. Chromatography on Al_2O_3 (neutral, activity grade IV, height of column 10 cm) with hexane as eluent gave an almost black fraction, from which dark green crystals were isolated. Yield 80–85 mg (80–85%);

m.p. (dec) 131°C. Anal. Found: C, 49.43; H, 8.69. $C_{23}H_{48}ClO_2P_2Rh$ calcd.: C, 49.60; H, 8.69%. IR (CH_2Cl_2): ν(C=O) 1684, ν(C=C) 1603 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 4.06 (q, J(HH) = 7.1 Hz, OCH_2); 2.79 (m, PC*H*CH_3); 1.40 (d, J(RhH) = 0.9 Hz, =C*H*CO_2Et); 1.27 (dvt, N = 13.9, J(HH) = 7.1 Hz, PCHC*H*$_3$); 1.02 (t, J(HH) = 7.1 Hz, OCH_2C*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): 284.31 (dt, J(RhC) = 62.1, J(PC) = 14.2 Hz, Rh=*C*=C); 158.00 (s, *C*O_2Et); 105.64 (dt, J(RhC) = 16.0, J(PC) = 5.3 Hz, Rh=C=*C*); 59.55 (s, O*C*H_2); 23.83 (vt, N = 20.7 Hz, P*C*HCH_3); 20.13 (s, PCH*C*H_3); 14.52 (s, OCH_2*C*H_3). ^{31}P NMR (36.2 MHz, C_6D_6): δ 43.63 (d, J(RhP) = 131.9 Hz).

5.4. Preparation of trans-[RhCl(HC≡CCO$_2$Et)(P^{i}Pr$_3$)$_2$] (9)

A solution of 169 mg (0.37 mmol, for n = 1) of **1** in 15 ml of pentane was treated dropwise at −20°C with 40 μl (0.40 mmol) of HC≡CCO$_2$Et. The mixture was allowed to warm to room temperature, then stirred for 15 min, and the solvent then removed. The residue was extracted three times with 8 ml of pentane, and the combined extracts were concentrated *in vacuo* to *ca.* 3 ml and kept at −78°C. Yellow, moderately air-stable crystals separated and were filtered off, washed with small quantities of pentane (0°C), and dried *in vacuo*. (If after cooling to −78°C an oil separates, the product should be purified by column chromatography on Al_2O_3 (neutral, activity grade V) with hexane as eluent.) Yield 121 mg (64%); m.p. (dec) 86°C. Anal. Found: C, 49.65; H, 8.94. $C_{23}H_{48}ClO_2P_2Rh$ calcd.: C, 49.60; H, 8.69%. IR (KBr): ν(≡CH) 2952, ν(C≡C) 1792, ν(C=O) 1688 and 1670 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 4.91 (d, J(RhH) = 2.4 Hz, ≡CH); 4.10 (q, J(HH) = 7.1 Hz, OCH_2); 2.33 (m, PC*H*CH_3); 1.25 and 1.22 (both dvt, N = 13.1, J(HH) = 6.9 Hz, PCHC*H*$_3$); 1.06 (t, J(HH) = 7.1 Hz, OCH_2C*H*$_3$). ^{31}P NMR (36.2 MHz, C_6D_6): δ 34.80 (d, J(RhP) = 112.7 Hz).

5.5. Preparation of 7 from 9

A solution of 123 mg (0.22 mmol) of **9** in 10 ml of benzene was stirred for 3 h at 50°C then allowed to cool to room temperature. The solvent was removed and the oily residue worked-up as described for the preparation of **7**. Yield 100 mg (81%).

5.6. Preparation of trans-[RhCl(η^2-CH$_2$=C=CHCO$_2$Et)(P^{i}Pr$_3$)$_2$] (10)

A solution of 281 mg (0.35 mmol) of **4** in 15 ml of freshly distilled THF was treated dropwise at −78°C with a solution of 31 μl (0.50 mmol) of CH_3I in pentane. The mixture was allowed to warm to room temperature, the solvent removed, the residue extracted three times with 5 ml of hexane/ether (5:1). The combined extracts were evaporated to dryness *in vacuo*, the residue was dissolved in 1 ml of hexane and the solution chromatographed on Al_2O_3 (neutral, activity grade III, height of column 8 cm). With hexane as eluent, a dark-green fraction was eluted first, and yielded the vinylidene complex **7**; yield 16 mg (8%). The second yellow fraction was concentrated to *ca.* 1 ml and then stored at −78°C. Light-yellow crystals separated and were filtered off, washed with small quantities of pentane (0°C), and dried *in vacuo*. Yield 44 mg (22%), m.p. (dec) 132°C. Anal. Found: C, 50.80; H, 8.94. $C_{24}H_{50}ClO_2P_2Rh$ calcd.: C, 50.49; H, 8.83%. IR (hexane): ν(C=C) 1717, ν(C=O) 1670 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 6.44 (dtt, J(RhH) = 1.4, J(PH) = 1.4, J(HH) = 2.7 Hz, =C*H*CO_2Et); 4.18 (q, J(HH) = 7.1 Hz, OCH_2); 2.76 (ddt, J(RhH) = 2.7, J(PH) = 6.5, J(HH) = 2.7 Hz, =CH_2); 2.28 (m, PC*H*CH_3); 1.20 and 1.16 (both dvt, N = 13.2, J(HH) = 7.0 Hz, PCHC*H*$_3$); 1.08 (t, J(HH) = 7.1 Hz, OCH_2C*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 194.34 (dt, J(RhC) = 21.8, J(PC) = 5.2 Hz, =C=); 162.46 (s, *C*O_2Et); 106.26 (d, J(RhC) = 1.5 Hz, =*C*HCO_2Et); 59.53 (s, O*C*H_2CH_3); 23.56 (vt, N = 19.2 Hz, P*C*HCH_3); 20.36 (s, PCH*C*H_3); 14.71 (s, OCH_2*C*H_3); 13.92 (d, J(RhC) = 12.7 Hz, =CH_2). ^{31}P NMR (36.2 MHz, C_6D_6): δ 33.42 (d, J(RhP) = 115.8 Hz).

5.7. Preparation of trans-[RhCl(CH$_3$C≡CC$_6$H$_5$)(P^{i}Pr$_3$)$_2$] (11)

(a) A solution of 187 mg (0.23 mmol) of **6** in 12 ml of freshly distilled THF was treated dropwise at −78°C with a solution of 18 μl (0.30 mmol) of CH_3I in pentane. The mixture was allowed to warm to room temperature, the solvent removed, and the residue extracted three times with 5 ml of pentane. The combined extracts were concentrated *in vacuo* until precipitation occurred. The solution was kept at −78°C for 12 h and the orange crystals were then filtered off, washed with small amounts of pentane (0°C), and dried *in vacuo*. Yield 119 mg (90%).

(b) A solution of 155 mg (0.34 mmol, for n = 1) of **1** in 15 ml of pentane was treated dropwise at −20°C with 42 μl (0.34 mmol) of CH_3C≡CC_6H_5. The solution was allowed to warm to room temperature, then worked-up as described under (a). Yield 131 mg (67%), m.p. (dec) 122°C. Anal. Found: C, 56.50; H, 9.03. $C_{27}H_{50}ClP_2Rh$ calcd.: C, 56.40; H, 8.76%. IR (KBr): ν(C≡C) 1898 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.84 (m, 2H of C_6H_5); 7.19 (m, 3H of C_6H_5); 2.34 (d, J(RhH) = 1.3 Hz, ≡CCH_3); 2.23 (m, PC*H*CH_3); 1.28 and 1.17 (both dvt, N = 13.2, J(HH) = 6.8 Hz, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 130.91 (s, *ipso*-carbon of C_6H_5); 130.59, 127.91 and 125.73 (all s, *ortho*-, *meta*- and *para*-carbons of C_6H_5): 80.56 (dt,

J(RhC) = 14.4, J(PC) = 3.1 Hz, one carbon of C≡C); 69.00 (d, J(RhC) = 16.6 Hz, one carbon of C≡C); 23.93 (vt, N = 17.1 Hz, P*C*HCH$_3$); 20.91 and 20.20 (both s, PCH*C*H$_3$); 13.42 (s, ≡*C*CH$_3$). ^{31}P NMR (36.2 MHz, C_6D_6): δ 33.18 (d, J(RhP) = 118.7 Hz).

5.8. *Crystal structure analysis of* 10

Single crystals were grown from hexane at room temperature. Crystal data (from 25 reflections, $12° < \theta < 14°$): triclinic space group $P\bar{1}$ (No. 2), $a = 9.670(4)$ Å, $b = 9.840(4)$ Å, $c = 15.624(6)$ Å, $\alpha = 99.53(2)°$, $\beta = 97.72(2)°$, $\gamma = 98.30(2)°$, $V = 1431.6$ Å^3, $Z = 2$, $d_{calcd.} = 1.32$ g cm^{-3}, μ(Mo Kα) = 8.1 cm^{-1}. Crystal size 0.2 × 0.3 × 0.35 mm. Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 16.55), T = 293 K, $\omega/2\theta$ scan, max. $2\theta = 44°$; 3511 independent reflections were measured, 2755 were regarded as being observed ($I > 3\sigma(I)$); intensity data were corrected for Lorentz and polarization effects, empirical absorption correction (Ψ-scan method) was applied, minimum transmission was 94.2%. The structure was solved by the Patterson method (SHELXS-86); atomic coordinates (Table 2) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (298 parameters, unit weights, Enraf-Nonius SDP) [18]. The positions of the hydrogen atoms of the allene ligand were taken from a difference Fourier synthesis and refined with fixed temperature factors. The other hydrogen atoms were placed at calculated positions and refined by the riding method. The ethyl group of the CO_2Et unit showed a 1:1 disorder; both positions were refined independently with anisotropic temperature factors. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56778, the names of the authors, and the journal citation.

TABLE 2. Positional parameters for complex **10**, with e.s.d.s [a]

Atom	x	y	z	B (Å^2)
Rh	0.0095(1)	0.1291(1)	0.2831(1)	3.000(8)
Cl	−0.1448(1)	0.2920(1)	0.3120(1)	5.18(4)
P1	0.1901(1)	0.3224(1)	0.28972(9)	3.23(3)
P2	−0.1906(1)	−0.0472(1)	0.27168(9)	3.19(3)
O1	0.2854(5)	−0.2185(4)	0.1932(3)	6.3(1)
O2	0.2228(5)	−0.2295(5)	0.0501(3)	7.4(1)
C1	0.1551(5)	−0.0056(5)	0.3112(4)	3.9(1)
C2	0.1149(5)	−0.0068(5)	0.2223(4)	3.6(1)
C3	0.1332(6)	−0.0684(6)	0.1426(4)	4.1(1)
C4	0.2219(6)	−0.1766(6)	0.1344(4)	4.5(1)
C5	0.271(1)	−0.371(1)	0.0195(9)	5.6(3)
C5*	0.330(1)	−0.329(1)	0.0455(9)	6.8(3)
C6*	0.405(1)	−0.324(2)	−0.019(1)	7.5(5)
C6	0.362(1)	−0.330(2)	−0.038(1)	8.7(4)
C7	0.3747(5)	0.2879(6)	0.3024(4)	4.5(1)
C8	0.4334(6)	0.2791(7)	0.3964(5)	6.3(2)
C9	0.4826(6)	0.3873(7)	0.2677(5)	7.5(2)
C10	0.1802(5)	0.4719(5)	0.3754(4)	3.8(1)
C11	0.1749(7)	0.4340(7)	0.4659(4)	5.4(2)
C12	0.2873(7)	0.6069(6)	0.3816(4)	5.3(2)
C13	0.1727(6)	0.3936(6)	0.1867(4)	4.4(1)
C14	0.1742(9)	0.2803(7)	0.1079(4)	7.6(2)
C15	0.0413(7)	0.4615(7)	0.1722(4)	6.4(2)
C16	−0.1543(6)	−0.2298(6)	0.2654(4)	4.6(1)
C17	−0.1117(7)	−0.2654(6)	0.3550(4)	6.0(2)
C18	−0.2669(7)	−0.3479(6)	0.2103(5)	7.4(2)
C19	−0.2947(5)	−0.0092(6)	0.3611(3)	3.8(1)
C20	−0.2048(7)	0.0322(7)	0.4524(4)	5.5(2)
C21	−0.4258(6)	−0.1175(7)	0.3610(4)	5.6(2)
C22	−0.3191(6)	−0.0601(6)	0.1694(4)	4.1(1)
C23	−0.4135(7)	0.0510(6)	0.1727(4)	6.1(2)
C24	−0.2409(7)	−0.0620(8)	0.0918(4)	6.7(2)
H1	0.255(7)	0.036(6)	0.345(4)	5.2
H2	0.120(7)	−0.087(6)	0.338(4)	5.2
H3	0.088(7)	−0.064(7)	0.081(4)	5.3

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

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