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Synthesis, Redox Properties, and Reactivity of a Novel Family of Electron-Rich Vinylidene and Vinylphosphonium Complexes of Rhodium(I)

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The trigonal-bipyramidal Rh(I) vinylidene complexes $[(NP_3)Rh{=}C{=}C(H)(R)]^+$ have been prepared by treatment of the neutral σ-acetylides $[(NP_3)Rh(C{\equiv}CR)]$ with strong protic acids and isolated as BPh_4^- or PF_6^- salts ($NP_3 = N(CH_2CH_2PPh_2)_3$; R = Ph, CO_2Et). Reaction of the vinylidene complexes with nucleophiles such as NEt_3, MeLi, and PhLi leads to deprotonation to restore the parent σ-acetylide compounds. When the vinylidene complexes are treated with $NaBH_4$ or $LiHBEt_3$, the acid–base reaction competes with the nucleophilic addition of H^- to the vinylidene C_α atom to form the alkenyl derivatives $[(E)\text{-}(NP_3)Rh(CH{=}C(H)R)]$. Two-electron oxidation of the vinylidene complexes by controlled-potential electrolysis results in the deprotonation of the vinylidene ligand. In this way, the Rh(III) σ-acetylides $[(NP_3)Rh(C{\equiv}CR)]^{2+}$ are obtained and isolated in the solid state as the ethanol adducts $[(NP_3)Rh(C{\equiv}CR)(C_2H_5OH)](BPh_4)_2$. In contrast, one-electron reduction gives the neutral σ-acetylides and H_2. The vinylidene compounds can also be oxidized by peroxo acids such as *m*-chloroperbenzoic acid. As a result, the deprotonation of the vinylidene ligand occurs and the Rh(III) complexes $[(NP_3)Rh(C{\equiv}CR)(O_2CC_6H_4Cl)]BPh_4$ are formed. When O_2 is bubbled into CH_2Cl_2 solutions of the vinylidene complexes, the Rh(III) hydroxide acetylide compounds $[(NP_3)Rh(OH)(C{\equiv}CR)]BPh_4$ are obtained in ca. 60% yield because of extensive decomposition of the starting compounds. For R = Ph, an appreciable amount of phenol is found. Thermal decomposition of the vinylidene complexes in refluxing THF produces H_2 and the paramagnetic Rh(II) derivatives $[(NP_3)Rh(C{\equiv}CR)]^+$. Unlike the NP_3 σ-acetylides, the PP_3 analogues ($PP_3 = P(CH_2CH_2PPh_2)_3$) react with strong acids in THF or CH_2Cl_2 to form unusual examples of vinylphosphonium compounds of formula $[((Ph_2PCH_2CH_2)_2P(CH_2CH_2PPh_2))Rh(C{=}C(H)C(O)R)]BPh_4$. When the protonation reaction is carried out in benzene, the alternative oxidation of the Rh(I) σ-acetylide to the paramagnetic Rh(II) derivatives $[(PP_3)Rh(C{\equiv}CR)]^+$ occurs. All of the compounds have been characterized by chemical–physical measurements, including IR, ESR, and NMR techniques, and their redox behavior has been studied by electrochemical methods.

Introduction

Transition-metal vinylidene complexes are the object of active investigation, as they show excellent potential for use in several stoichiometric and catalytic reactions.[1-4] The implications for both homogeneous and heterogeneous catalysis are evident as one looks at the types and nature of the hydrocarbyl ligands that can be readily generated from terminal vinylidenes, i.e. alkynyl, vinyl, vinylidene, alkylidene, alkylidine, alkyl, acyl, and carbonyl. The chemistry of metal vinylidene compounds has been extensively reviewed.[1] It is now apparent that these organometallics are endowed with great reactivity toward a plethora of reagents, including nucleophilic and electrophilic addenda,[2,5] unsaturated organic and inorganic molecules,[6] transition-metal fragments,[7] and oxidants and reductants.[8] However, scarce information has been provided so far on the redox properties, the thermal stability, and the reactions with dioxygen of vinylidene compounds.[8,9]

Herein, we present a multiform study on the chemical and electrochemical properties of a new family of terminal vinylidene and vinylphosphonium complexes of rhodium(I) synthesized by electrophilic attack at the β-carbon of the σ-acetylide ligand in $[(NP_3)Rh(\sigma\text{-}C{\equiv}CR)]$ (R = Ph (**1**), CO_2Et (**2**)) and $[(PP_3)Rh(\sigma\text{-}C{\equiv}CR)]$ (R = Ph (**3**), CO_2Et (**4**), CHO (**5**)) respectively ($NP_3 = N(CH_2CH_2PPh_2)_3$; PP_3

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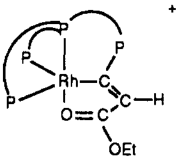
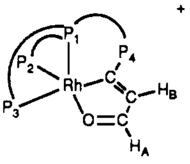
= $P(CH_2CH_2PPh_2)_3$). Particular attention has been devoted to the reactions of the trigonal-bipyramidal vinylidene complexes $[(NP_3)Rh{=}C{=}C(H)(R)]^+$ with oxidizing agents.

A preliminary communication of part of this work has already appeared.[10]

Experimental Section

General Data. All the reactions and manipulations were routinely performed under a nitrogen or argon atmosphere with standard Schlenk tube techniques. The σ-acetylide complexes $[(NP_3)Rh(C{\equiv}CR)]$ (R = Ph (**1**), CO_2Et (**2**)) and $[(PP_3)Rh(C{\equiv}CR)]$ (R = Ph (**3**), CO_2Et (**4**), CHO (**5**)) were prepared as described in ref 11. All the other chemicals were reagent grade and were used as received by commercial suppliers. Tetrahydrofuran, THF, was purified by distillation over $LiAlH_4$ under nitrogen just prior to use. Benzene and *n*-hexane were dried over sodium, dichloromethane and chloroform were dried over P_2O_5, and acetone was dried over K_2CO_3 before being purified by distillation under a nitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. Proton NMR spectra were recorded at 299.945 MHz on a Varian VXR 300 spectrometer. $^{13}C\{^1H\}$ NMR spectra were recorded on the same instrument operating at 75.429 MHz. ^1H and ^{13}C chemical shifts are reported relative to tetramethylsilane as external reference or calibrated against the solvent as the reference signal. $^{31}P\{^1H\}$ NMR spectra were recorded on Varian CFT 20 and Varian VXR 300 spectrometers operating at 32.19 and 121.42 MHz, respectively. Chemical shifts are relative to external 85% H_3PO_4, with downfield values reported as positive. Two-dimensional NMR spectra were recorded by using the Varian program COSY with optimized window functions. Conductivities were measured with a WTW Model LBR/B conductivity bridge. The conductivity data were obtained at sample concentrations of ca. 10^{-3} M in nitromethane solutions. GC analyses were performed on a Shimadzu GC-8A gas chromatograph fitted with a thermal conductivity detector and a 10-ft 100/120 Carbosieve-SII or a 6-ft 0.1% SP-1000 on Carbopack C stainless-steel column (Supelco Inc.). Quantification was achieved with a Shimadzu C-R6A Chromatopac coupled with the chromatograph, operating with an automatic correct area normalization method. The materials and the apparatus used for the electrochemical experiments have been described elsewhere.[12] The potential values are relative to an aqueous calomel electrode (SCE). The temperature was controlled at 20 ± 0.1 °C. Under the present experimental conditions, the ferrocenium/ferrocene couple was located at +0.49 V in CH_2Cl_2. The simulation of the $^{31}P\{^1H\}$ and ^1H NMR spectra was carried out by using an updated version of the LAOCN4 program.[13] The initial choices of shifts and coupling constants were refined by successive iterations, the assignment of the experimental lines being performed automatically. The final parameters gave a fit to the observed line positions better than 0.3 Hz.

Table I. ^1H NMR Data for the Complexes[a]

compd	δ, ppm[b]	assignt	coupling constant, Hz
6	4.93 qd	$C{=}C(H)Ph$	13.8 ($^4J(HP)$) 1.1 ($^3J(HRh)$)
7	4.25 qd	$C{=}C(H)CO_2Et$	12.3 ($^4J(HP)$) 1.6 ($^3J(HRh)$)
	4.07 q 1.08 t	OCH_2CH_3 OCH_2CH_3	7.3 ($J(HH)$)
8	1.77 q	$C{=}C(CH_3)Ph$	1.8 ($^5J(HP)$)
 cation of **9**	6.32 bd 4.36 q 1.28 t	$C{=}CH$ OCH_2CH_3 OCH_2CH_3	22.3 ($^3J(HP)$) 7.1 ($J(HH)$)
 cation of **10**	8.85 m	H_A	7.1 ($^3J(H_AH_B)$) 11.4 ($^4J(H_AP_2)$) 11.3 ($^4J(H_AP_3)$) 4.3 ($^4J(H_AP_1)$) 1.3 ($^4J(H_AP_4)$) 9.5 ($^3J(H_ARh)$)
	c	H_B	
14	4.50 q 1.55 t	OCH_2CH_3 OCH_2CH_3	7.2 ($J(HH)$)
15	*d*	OH	
16	*d*	OH	
	4.31 q 1.29 t	OCH_2CH_3 OCH_2CH_3	7.2 ($J(HH)$)

[a] All ^1H NMR spectra were recorded at 300 MHz in CD_2Cl_2 solutions at ambient temperature (298 K). The resonances due to the hydrogen atoms belonging to the NP_3 and PP_3 ligands are not reported. [b] Key: d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. [c] H_B resonance is obscured by the aromatic protons of the ligands and of the tetraphenylborate anion. [d] Not observed.

Synthesis of the Complexes. The solid compounds were collected on sintered-glass frits and washed, unless otherwise stated, with ethanol and *n*-pentane before being dried under a stream of nitrogen.

Selected NMR spectral data for all of the new complexes are collected in Table I (^1H NMR spectra) and Table II ($^{31}P\{^1H\}$ NMR spectra).

Preparation of $[(NP_3)Rh{=}C{=}C(H)Ph]BPh_4$ (6a). To a stirred suspension of 1 (0.40 g, 0.47 mmol) in THF (35 mL) at 0 °C was added $HOSO_2CF_3$ (45 μL, 0.51 mmol) via syringe. The

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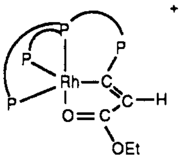
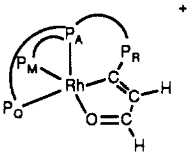
Table II. $^{31}P\{^1H\}$ NMR Data for the Complexes[a]

compd	pattern	δ, ppm	coupling constant, Hz J(PP)	 J(PRh)
6	A_3X	37.86		136.8
7	A_3X	41.11		130.3
8	A_3X	36.45		135.7
	AM_2QX	87.20 (P_A)	7.0 (P_AP_M)	142.9
			3.4 (P_AP_Q)	
		56.49 (P_M)	20.0 (P_MP_Q)	123.3
		11.42 (P_Q)		≅0
cation of **9**				
	AMQRX	104.17 (P_A)	9.9 (P_AP_M)	118.1
			9.8 (P_AP_Q)	
			5.0 (P_AP_R)	
		49.44 (P_M)	22.9 (P_MP_Q)	124.3
			15.9 (P_MP_R)	
		36.03 (P_Q)	≅0 (P_QP_R)	123.1
		18.29 (P_R)		≅0
cation of **10**				
13	AM_2X	35.39 (P_A)	24.0 (P_AP_M)	119.0
		28.58 (P_M)		92.0
14	AM_2X	31.36 (P_A)	22.5 (P_AP_M)	112.8
		28.37 (P_M)		90.3
15	AB_2X	30.06 (P_A)	22.2 (P_AP_M)	107.2
		30.52 (P_B)		94.5
16	AM_2X	29.53 (P_A)	22.0 (P_AP_M)	111.1
		31.80 (P_M)		92.8

[a] $^{31}P\{^1H\}$ NMR spectra were recorded at 121.42 or 32.19 MHz in CD_2Cl_2 at ambient temperature and were referenced to external 85% H_3PO_4 with downfield values assumed as positive.

starting yellow acetylide dissolved to give a burgundy red solution, from which deep red crystals were obtained after addition of $NaBPh_4$ (0.40 g, 1.17 mmol) in ethanol/*n*-hexane (30 mL, 2:1 v/v); yield 70%. $\Lambda_M = 54\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: ν(C═C) 1620, 1640 cm^{-1}; phenyl reinforced vibration 1590 cm^{-1}. Anal. Calcd for $C_{74}H_{68}BNP_3Rh$: C, 75.45; H, 5.82; N, 1.19; Rh, 8.74. Found: C, 75.04; H, 5.93; N, 1.10; Rh, 8.53.

Preparation of $[(NP_3)Rh{=}C{=}C(H)Ph]PF_6$ (6b). The hexafluorophosphate salt of **6a** was prepared as described above by using NH_4PF_6 (0.20 g, 1.23 mmol) instead of $NaBPh_4$; yield 65%. $\Lambda_M = 48\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Calcd for $C_{50}H_{48}F_6NP_4Rh$: C, 59.83; H, 4.82; N, 1.40; Rh, 10.25. Found: C, 59.39; H, 4.72; N, 1.29; Rh, 10.06.

Preparation of $[(NP_3)Rh{=}C{=}C(H)CO_2Et]BPh_4$ (7a). After workup as for **6a**, the reaction of **2** (0.40 g, 0.47 mmol) with triflic acid yielded the vinylidene complex **7a**; yield 80%. $\Lambda_M = 50\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: ν(CO) 1700 cm^{-1}; ν(C═C) 1615 cm^{-1}; ν(C—O—C) 1225 cm^{-1}. Anal. Calcd for $C_{71}H_{68}BNO_2P_3Rh$: C, 72.62; H, 5.84; N, 1.19; Rh, 8.77. Found: C, 72.38; H, 5.91; N, 1.03; Rh, 8.70.

Preparation of $[(NP_3)Rh{=}C{=}C(H)CO_2Et]PF_6$ (7b). This compound was obtained in 70% yield in a manner analogous to that used to prepare **7a**, except for the substitution of NH_4PF_6 (0.20 g, 1.23 mmol) for $NaBPh_4$. $\Lambda_M = 49\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Calcd for $C_{47}H_{48}F_6NO_2P_4Rh$: C, 56.47; H, 4.84; N, 1.40; Rh, 10.29. Found: C, 55.99; H, 4.93; N, 1.23; Rh, 10.11.

Preparation of $[(NP_3)Rh{=}C{=}C(CH_3)Ph]BPh_4$ (8a). A suspension of **1** (0.30 g, 0.35 mmol) in THF (30 mL) was treated with a stoichiometric amount of freshly distilled $MeOSO_2CF_3$ (40 μL, 0.35 mmol). The solution became deep red while the starting complex dissolved. Addition of $NaBPh_4$ (0.40 g, 1.17 mmol) in ethanol/*n*-hexane (30 mL, 2/1 v/v) gave deep red crystals; yield 50%. $\Lambda_M = 53\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: ν(C═C) 1640 cm^{-1}; phenyl reinforced vibration 1590 cm^{-1}. Anal. Calcd for $C_{75}H_{70}BNP_3Rh$: C, 75.57; H, 5.92; N, 1.17; Rh, 8.63. Found: C, 75.32; H, 5.69; N, 1.02; Rh, 8.39.

Preparation of $[(NP_3)Rh{=}C{=}C(CH_3)Ph]PF_6$ (8b). Substitution of NH_4PF_6 (0.20 g, 1.23 mmol) for $NaBPh_4$ in the above synthetic procedure gave **8b** in 55% yield. $\Lambda_M = 45\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Calcd for $C_{51}H_{50}F_6NP_4Rh$: C, 60.20; H, 4.95; N, 1.38; Rh, 10.11. Found: C, 59.94; H, 4.81; N, 1.22; Rh, 9.97.

Preparation of $[(PP_3)Rh(C{=}C(H)CO_2Et)]BPh_4$ (9). To a solution of **4** (0.40 g, 0.46 mmol) in CH_2Cl_2 (30 mL) at 0 °C was added 45 μL (0.51 mmol) of neat $HOSO_2CF_3$. The initial yellow color immediately disappeared to produce a deep violet solution, from which violet microcrystals separated after addition of $NaBPh_4$ (0.40 g, 1.17 mmol) in ethanol (30 mL); yield 45%. $\Lambda_M = 53\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: ν(C═C) 1585 cm^{-1}; ν(CO) 1400 cm^{-1}; ν(C—O—C) 1180 cm^{-1}. Anal. Calcd for $C_{71}H_{68}BO_2P_4Rh$: C, 71.61; H, 5.76; Rh, 8.64. Found: C, 71.46; H, 5.94; Rh, 8.49.

Preparation of $[(PP_3)Rh(C{=}C(H)CHO)]BPh_4$ (10). The vinylphosphonium salt **10** was obtained as deep violet microcrystals in a manner similar to that employed for **9** except for substitution of **5** for **4**; yield 65%. $\Lambda_M = 48\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: ν(C═C) 1535 cm^{-1}; ν(CO) 1410 cm^{-1}. Anal. Calcd for $C_{69}H_{64}BOP_4Rh$: C, 72.26; H, 5.63; Rh, 8.97. Found: C, 72.07; H, 5.54; Rh, 8.82.

Reaction of $[(PP_3)Rh(C{\equiv}CPh)]$ with $HOSO_2CF_3$. (A) THF Solution. Reaction of **3** with triflic acid in THF did not afford after the usual workup (see above) any definite material. Extensive decomposition occurred, and the only isolated products were intractable tan powders. On the other hand, it was possible to characterize by NMR techniques the phosphaalkenyl complex cation $[(PPh_3)Rh(C{=}C(H)Ph)]^+$ directly in THF-d_8 solution. The typical procedure is described below.

THF-d_8 (1.5 mL) was added to solid **3** (30 mg, 34.3 μmol) to give a yellow solution, which was stirred at −28 °C (ice/2-propanol bath) while triflic acid was added (3.0 μL, 34.3 μmol). Immediately, the solution turned green and was placed directly into a NMR tube, which was inserted in the spectrometer precooled at −25 °C. The spectrum was immediately recorded at this temperature. When the temperature was increased above 0 °C, extensive decomposition occurred.

(B) C_6H_6 Solution. Protonation of **3** (0.30 g, 0.34 mmol) in C_6H_6 (40 mL) gave a deep green solution, which after the usual workup produced emerald green microcrystals of $[(PP_3)Rh(C{\equiv}CPh)]BPh_4$, yield 80%.

Reaction of $[(PP_3)Rh(C{\equiv}CR)]$ (R = CO_2Et, CHO) with $HOSO_2CF_3$ in C_6H_6. By workup in benzene as above **4** and **5** yielded the Rh(II) acetylides $[(PP_3)Rh(C{\equiv}CR)]BPh_4$ (R = CO_2Et, CHO) in ca. 60–70% yield.

Reaction of $[(NP_3)Rh{=}C{=}C(H)R]BPh_4$ (R = Ph (6a), CO_2Et (7a)) with NEt_3. Neat triethylamine (0.10 mL, 0.72 mmol) was pipetted into a THF solution (20 mL) of **6a** (0.25 g, 0.21 mmol) to give a light yellow solution, from which **1** precipitated after addition of ethanol (20 mL); yield 95%. The same reaction was accomplished by using THF solutions of MeLi and PhLi.

Analogously, by treatment of **7a** (0.25 g, 0.21 mmol) with NEt_3, MeLi, or PhLi the acetylide **2** formed in ca. 90% yield.

Reaction of $[(NP_3)Rh{=}C{=}C(H)Ph]BPh_4$ with $LiHBEt_3$. The reaction of $LiHBEt_3$ (0.35 mL of a 1.0 M THF solution, 0.35 mmol) with a THF solution (25 mL) of the vinylidene complex **6a** (0.40 g, 0.34 mmol) gave a yellow solution, from which yellow crystals containing the parent acetylide complex **1** and the σ-alkenyl derivative $[(NP_3)Rh(CH{=}C(H)Ph)]$ (**11**) were obtained after addition of ethanol (20 mL);[14] total yield based on **6a** 90%. The two compounds were separated by column chromatography with benzene as eluent; yield 20% of **1** and 80% of **11**.

Reaction of $[(NP_3)Rh{=}C{=}C(H)CO_2Et]BPh_4$ with $LiHBEt_3$. By workup as above the reaction of **7a** (0.40 g, 0.34 mmol) with $LiHBEt_3$ (0.35 mL of a 1.0 M THF solution, 0.35 mmol) yielded a mixture of the acetylide **2** (30%) and of the σ-alkenyl complex $[(NP_3)Rh(CH{=}C(H)CO_2Et)]$ (**12**, 70%);[14] total yield based on **7a** 90%.

Preparation of $[(NP_3)Rh(C{\equiv}CR)(O_2CC_6H_4Cl)]BPh_4$ (R = Ph (13), CO_2Et (14)). Method A. Solid *m*-chloroperbenzoic acid (85%, 0.05 g, 0.25 mmol) was added with vigorous stirring to a CH_2Cl_2 (25 mL) solution of **6a** (0.30 g, 0.25 mmol). The solution immediately turned pale yellow and produced, after addition of $NaBPh_4$ (0.12 g, 0.35 mmol) in ethanol (30 mL), yellow crystals of **13**, yield 60%. $\Lambda_M = 51\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: $\nu(C{\equiv}C)$ 2120 cm^{-1}; $\nu(CO)$ 1610 cm^{-1}; phenyl reinforced vibration 1600 cm^{-1}. Anal. Calcd for $C_{81}H_{71}BClNO_2P_3Rh$: C, 73.01; H, 5.37; N, 1.05; Rh, 7.72. Found: C, 72.87; H, 5.47; N, 0.96; Rh, 7.50.

The same procedure was employed to prepare **14** from **7a**; yield 65%. $\Lambda_M = 54\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: $\nu(C{\equiv}C)$ 2110 cm^{-1}; $\nu(CO)_{COOEt}$ 1680 cm^{-1}; $\nu(CO)_{m\text{-CPBA}}$ 1610 cm^{-1}; $\nu(COEt)$ 1220 cm^{-1}. Anal. Calcd for $C_{78}H_{71}BClNO_4P_3Rh$: C, 70.52; H, 5.39; N, 1.05; Rh, 7.75. Found: C, 70.49; H, 5.31; N, 0.94; Rh, 7.63.

Method B. Compounds **13** and **14** were prepared by using the procedure described above except for substitution of **1** and **2** for **6a** and **7a**, respectively, in 85–90% yield.

Preparation of $[(NP_3)Rh(C{\equiv}CR)(OH)]BPh_4$ (R = Ph (15), CO_2Et (16)). Dioxygen was bubbled into a THF (30 mL) solution of the vinylidene complex **6a** (0.30 g, 0.25 mmol) for 30 min. The solution turned yellow and, after addition of ethanol (30 mL) and slow concentration under nitrogen, yielded pale yellow crystals of **15**, yield 60%. $\Lambda_M = 49\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: $\nu(OH)$ 3490 cm^{-1}; $\nu(C{\equiv}C)$ 2115 cm^{-1}; phenyl reinforced vibration 1595 cm^{-1}. Anal. Calcd for $C_{74}H_{69}BNOP_3Rh$: C, 74.37; H, 5.82; N, 1.17; Rh, 8.61. Found: C, 74.09; H, 5.77; N, 1.02; Rh, 8.48.

The hydroxy carbethoxyacetylide complex **16** was prepared in 70% yield by using **7a** instead of **6a**. $\Lambda_M = 53\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: $\nu(OH)$ 3490 cm^{-1}; $\nu(C{\equiv}C)$ 2105 cm^{-1}; $\nu(CO)$ 1680 cm^{-1}; $\nu(C{-}O{-}C)$ 1210 cm^{-1}. Anal. Calcd for $C_{71}H_{68}BNO_3P_3Rh$: C, 71.66; H, 5.76; N, 1.17; Rh, 8.65. Found: C, 71.44; H, 5.59; N, 1.03; Rh, 8.55.

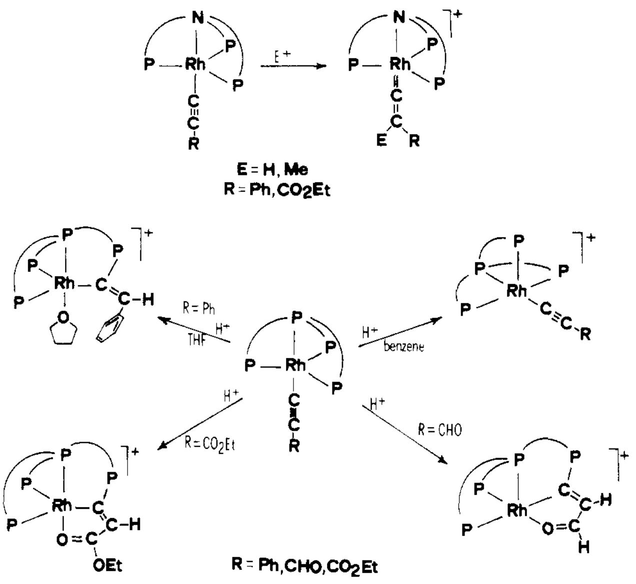
Thermal Decomposition of 6a and 7a. When **6a** or **7a** in THF was heated at reflux temperature, there was an immediate color change from deep red to yellow. Addition of ethanol to the reaction mixture precipitated yellow crystals of $[(NP_3)Rh(C{\equiv}CR)]BPh_4$ (R = Ph (**17**), CO_2Et (**18**)), which were identified by comparison with authentic specimens.[17]

Results and Discussion

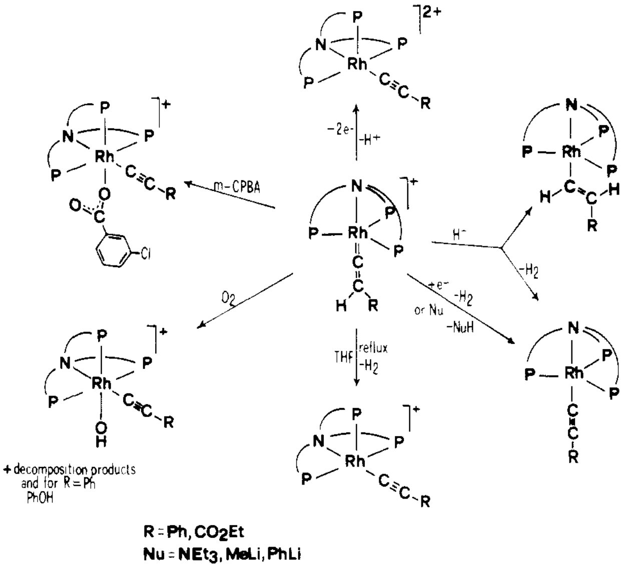
The preparations and the principal reactions of the complexes described in this paper are reported in Schemes I and II.

Protonation and Methylation of the NP_3 σ-Acetylides. Vinylidene Complexes. Treatment of the σ-acetylides **1** and **2** in THF, CH_2Cl_2, or benzene with stoichiometric amounts of $HOSO_2CF_3$ results in a fast color change from yellow to burgundy red. Addition of $NaBPh_4$ or NH_4PF_6 in ethanol to the solutions precipitates red crystals of the vinylidene complexes $[(NP_3)Rh{=}C{=}C(H)R]Y$ (R = Ph, Y = BPh_4 (**6a**); R = Ph, Y = PF_6 (**6b**); R = CO_2Et, Y = BPh_4 (**7a**), R = CO_2Et, Y = PF_6 (**7b**)). Since the counteranion does not influence at all the chemical-physical properties of the complexes, each pair of vinylidenes is considered, from now on, as a unique entity.

Scheme I



Scheme II



Compounds **6** and **7** are moderately air-stable in the solid state but rapidly decompose in solution unless air is excluded. In contrast, they are stable in deoxygenated, ambient-temperature solutions, in which they behave as 1:1 electrolytes. Solvents that may behave as Lewis bases, such as THF, may cause some decomposition of the vinylidene ligands (see below).

The $^{31}P\{^1H\}$ NMR spectra of **6** and **7** consist of doublets (A_3X spin system), indicating the magnetic equivalence of the three phosphorus atoms of NP_3. Such a pattern is typical of trigonal-bipyramidal (TBP) Rh(I) complexes of NP_3 in which the fifth ligand does not destroy the C_{3v} symmetry.[15,16] Given the steric requirements of NP_3, there is little doubt that the $C{=}C{=}(H)R$ ligands are located in

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[14] Authentication of the σ-alkenyl derivatives **11** and **12** was made by comparison with specimens obtained by alkyne insertion into the Rh–H bond in $[(NP_3)RhH]$:[15] Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F. *Organometallics*, in press.

[15] Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411.

[16] (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Chem. Soc., Chem. Commun.* **1987**, 971. (b) Bianchini, C.; Laschi, F.; Ottaviani, F.; Peruzzini, M.; Zanello, P.; Zanobini, F. *Organometallics* **1989**, *8*, 893.

[17] Bianchini, C.; Laschi, F.; Meli, A.; Ottaviani, F.; Peruzzini, M.; Vacca, A.; Zanello, P. *Organometallics*, in press.

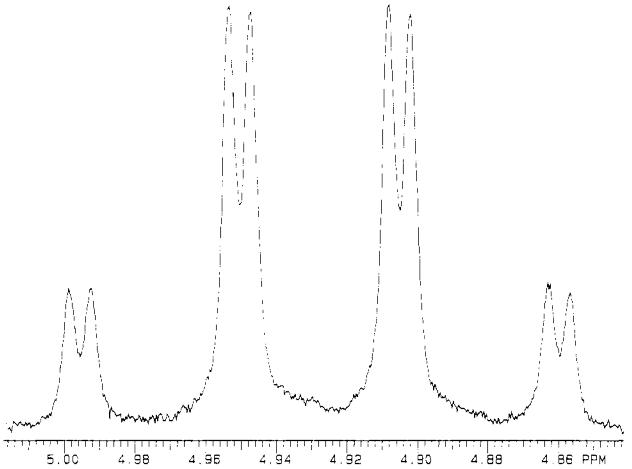


Figure 1. ^1H NMR resonance of the vinylidene hydrogen of 6 (300 MHz, CD_2Cl_2, 298 K, Me_4Si reference).

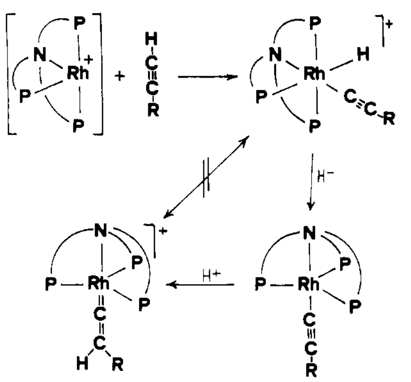
the axial position trans to the bridgehead nitrogen atom. The spectra are temperature-invariant down to −100 °C, thus indicating that, at least in solution, the vinylidene ligands are freely rotating around the C_{3v} axis. This phenomenon is not new for metal vinylidene complexes and is ascribed to a very low energy barrier to rotation.[2b,4a] The infrared spectra of **6** and **7** in solution differ from the solid-state spectra, especially in the ν(C=C) region. In particular, both compounds exhibit a unique band for the vinylidene C=C stretch in CH_2Cl_2 solution (1660 and 1625 cm^{-1} for **6** and **7**, respectively), whereas two bands of variable intensities are found in the solid-state spectrum of **6** (1620 and 1640 cm^{-1}) and a broad absorption at 1615 cm^{-1} is observed for **7**.

The ^1H NMR spectra exhibit quartets of doublets in the proper region of vinylidene hydrogens. The multiplicity of these signals, which originate from coupling of the vinylidene hydrogen to rhodium and to the three phosphorus atoms, is consistent with the equivalence in solution of the three terminal donors of NP_3 (Figure 1 shows the resonance of the vinylidene hydrogen atom in **6a**).

Conclusive evidence that protonation of **1** and **2** has occurred at C_β of the acetylide ligands is provided by the $^{13}C\{^1H\}$ NMR spectra, which exhibit very low field resonances at 316.8 (**6**) and 306.3 ppm (**7**) characteristic of the highly electron deficient α-carbon of the vinylidene ligand.[1a] Each resonance appears as a doublet of quartets, as expected, by coupling of C_α to rhodium and to the three equivalent phosphorus atoms. The J(CP) and J(CRh) values are in line with those reported for a number of rhodium vinylidene complexes containing phosphine coligands (**6**, J(CRh) = 44.2 Hz, J(CP) = 20.0 Hz; **7**, J(CRh) = 47.8 Hz, J(CP) = 16.4 Hz).[3] The presence of as many as 11 phenyl rings in the compounds makes it difficult to detect the resonance of the vinylidene β-carbons, which generally fall in the region of aromatic carbons.[1a]

The methylvinylidene complexes $[(NP_3)Rh{=}C{=}C(CH_3)Ph]Y$ (Y = BPh_4 (**8a**), Y = PF_6 (**8b**)) are prepared in a fashion identical with that used to synthesize the proton analogues **6a** and **6b** except that the acid $HOSO_2CF_3$ is replaced by the ester $MeOSO_2CF_3$. As is specified in the Experimental Section, the ester must be distilled just prior to use in order to prevent the competing formation of **6**. In effect, the reaction of the σ-phenylacetylide **1** with the acid is much faster than that with the ester. Accordingly, even adventitious acidity present in the methylating reagent, due to hydrolysis, may produce appreciable amounts of the proton vinylidene complex.

Scheme III



Compound **8** shares with the proton derivative **6** a large part of the chemical-physical properties. The resonance of the methyl group appears as a quartet at δ 1.77 ppm (^5J(HP) = 1.8 Hz), the coupling to rhodium now being undetectable. The equivalence of the three phosphorus atoms of NP_3 is again evidenced by the $^{31}P\{^1H\}$ NMR spectrum, which consists of a doublet at 36.45 ppm. A low-field $^{13}C\{^1H\}$ NMR multiplet (qd) at 317.4 ppm (J(CRh) = 42.6 Hz, J(CP) = 18.1 Hz) is safely assigned to the vinylidene α-carbon.

There is little doubt that vinylidenes **6**–**8** form via regiospecific addition of H^+ and CH_3^+ at C_β of the acetylide ligands. This result is in perfect accord with theoretical calculations, which indicate the C_β atom of the σ-acetylide ligand as the site where the HOMO is largely localized.[1,4] Since the metal–acetylide bonding in **1**–**5** also contains a significant back-donation contribution,[17] one may reasonably conclude that the transfer of electron density to the σ-acetylide ligand and the nucleophilic character of the β-carbon are related to each other. Interestingly, vinylidenes **6** and **7** are stable with respect to conversion into the hydride acetylide derivatives $[(NP_3)RhH(C{\equiv}CR)]BPh_4$, which, on the other hand, are readily prepared by reaction of the 16-electron fragment $[(L)Rh]^+$ with terminal alkynes (L = NP_3, PP_3).[11,18] In turn, the hydride acetylide complexes are quite stable in solution and in no case undergo a hydrogen shift to form vinylidene derivatives (Scheme III).

Protonation of the PP_3 σ-Acetylides. Vinylphosphonium Complexes. In no case does protonation of the PP_3 acetylides **3**–**5** by strong protic acids such as $HOSO_2CF_3$ or HBF_4 lead to the formation of either vinylidene or cis hydride acetylide complexes.

Treatment of **3**–**5** in benzene with a protic acid results in the one-electron oxidation of the complexes to the corresponding square-pyramidal Rh(II) derivatives $[(PP_3)Rh(C{\equiv}CR)]^+$ (R = Ph, CO_2Et, CHO).[17] In contrast, when the rhodium acetylides **4** and **5** are dissolved in THF or CH_2Cl_2, the reactions give deep violet solutions from which violet microcrystals of the novel vinylphosphonium complexes[2a,b,19,20] $[((Ph_2PCH_2CH_2)_2P(CH_2CH_2PPh_2))Rh(C{=}C(H)C(O)R)]BPh_4$ (R = OEt (**9**), H (**10**)) can be precipitated after addition of solid $NaBPh_4$ and ethanol. Compounds **9** and **10** are air-sensitive both in the solid

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[18] Bianchini, C.; Mealli, C.; Peruzzini, M.; Vizza, F.; Zanobini, F. *J. Organomet. Chem.* **1988**, *346*, C53.

[19] (a) Kobalova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Sizoi, V. F.; Nekrasov, Y. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 2393. (b) Kolobova, N. E.; Skripkin, V. V.; Alexandrov, G. G.; Struchov, Y. T. *J. Organomet. Chem.* **1979**, *169*, 293.

[20] For other examples of these types of compounds see: (a) Davidson, J. L.; Vasapollo, G.; Manolojvic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1982**, 1025. (b) Alt, H. G.; Engelhardt, H. E.; Steinlein, E. *J. Organomet. Chem.* **1988**, *344*, 227. (c) Alt, H. G.; Engelhardt, H. E.; Filippou, A. C. *J. Organomet. Chem.* **1988**, *355*, 139.

state and in solution. They behave as 1:1 electrolytes in deareated nitromethane solution. The structural formulations for these vinylphosphonium complexes, as determined by spectroscopic techniques, are given in Scheme I.

Medium-intensity bands at 1585 (**9**) and 1535 cm^{-1} (**10**) are present in the IR spectra, which are assigned to the ν(C=C) band of a vinyl ligand. Low-energy vibrations, in the proper region of C=O groups engaged in bonding to the metal via the C—C double bond, are also present at 1400 (**9**) and 1410 cm^{-1} (**10**). The ^{31}P{^{1}H} NMR spectrum of **9** exhibits a first-order AM$_2$QX splitting pattern consisting of three well-separated multiplets of intensity ratio 1:2:1. The high-field signal (δ(P$_Q$) = 11.42 ppm), which appears as a triplet of doublets, does not show coupling to the metal center as occurs for uncoordinated arms of PP$_3$. However, the presence of a dangling phosphine arm in **9** is readily ruled out by chemical shift considerations.[15,21] The splitting pattern of this multiplet clearly points to the equivalence of the other two terminal–PPh$_2$ groups (J(P$_M$P$_Q$) = 20 Hz). Each component of the triplet is doubled by coupling of P$_Q$ to P$_A$. The J(P$_Q$P$_A$) value is somewhat small, 3.4 Hz, but is in line with a coupling connection that does not proceed through the metal.[22] In contrast, in the remaining two resonances, a strong coupling to rhodium is evident.[15,23] The most intense signal (2 P), located at 56.49 ppm, consists of a doublet of doublets of doublets originating from coupling to rhodium, to the apical phosphorus P$_A$, and to the phosphonium P$_Q$ atom. Noticeably, the chemical shift of the two equivalent P$_M$ atoms is in the proper range for equatorial phosphorus atoms of Rh(I) TBP complexes with PP$_3$.[15,16] In effect, the formation of the vinylphosphonium complex **9** is not expected to greatly alter the magnetic properties of the two P$_M$ atoms, which continue to be engaged in a highly deshielding five-membered metalla ring. This does not evidently occur for the P$_Q$ atom, which moves from a five-membered metalla ring to a six-membered one. Accordingly, the P$_Q$ resonance is strongly shifted upfield by ca. 45 ppm, in accord with the well-known shielding effect occurring when a phosphorus donor is engaged in a six-membered ring.[24] A similar argument explains the relatively strong low-field shift of the apical phosphorus P$_A$ (δ = 87.20 ppm). The latter resonance appears as a doublet of triplets of doublets arising from coupling to rhodium and to the two equivalent P$_M$ atoms. In turn, each component of the triplets is doubled by the phosphonium P$_Q$ atom. The formation of the phosphonium P$_Q$–C$_\alpha$ bond is responsible for the unusual upfield shift of the P$_A$ resonance as compared to that in canonical rhodium TBP complexes of PP$_3$, in which the bridgehead phosphorus resonates between 136 and 159 ppm.[15,16] This fact may be explained by considering that the bridgehead phosphorus atom in **9** is now involved in a highly shielding six-membered metalla ring.[24]

The ^{1}H NMR spectrum of **9** is fully consistent with the structure shown in Scheme I. In particular, a doublet at 6.32 ppm (1 H) is assigned to the vinyl proton. The coupling constant between this proton and the phosphonium atom is in the proper range for complexes containing the PC=CH unit arranged in a cis geometry (^3J(HP$_C$) = 22.3 Hz).[2b,25] Actually, the geometry of the PP$_3$ tripodal ligand is such that only a cis disposition of the phosphonium P$_C$ atom and of the vinyl proton is allowed.

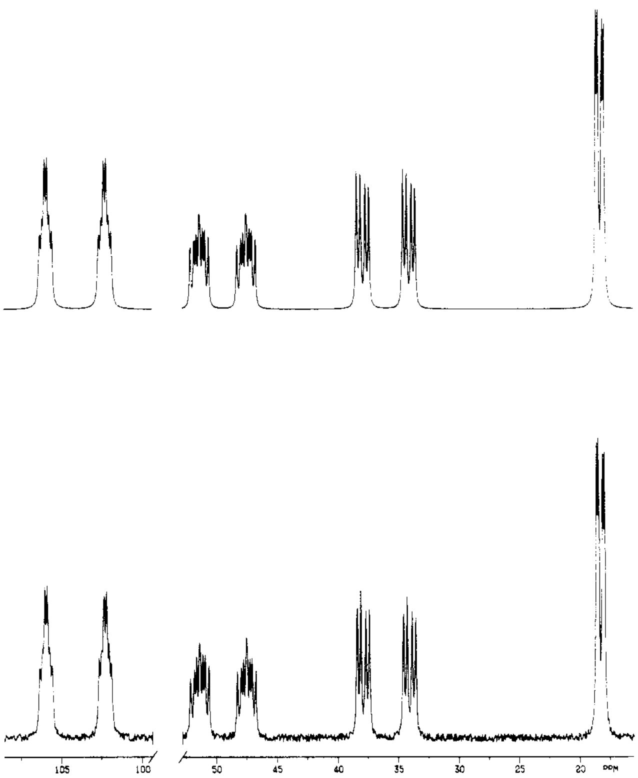

Figure 2. Experimental (lower) and computed (upper) ^{31}P{^{1}H} NMR spectra of **10** (32.19 MHz, CD$_2$Cl$_2$, 298 K, H$_3$PO$_4$ reference).

Figure 2 reports the experimental and computed ^{31}P{^{1}H} NMR spectra of **10**.

Although there is a different spin system (AMQRX instead of AM$_2$QX), the spectrum is closely related to that of **9**. The highest field resonance at 18.29 ppm is not coupled to rhodium and consists of a narrow doublet of doublets. It is assigned to the phosphonium atom P$_R$, which undergoes a high-field shift similar to that observed for the phosphonium atom in **9**. The multiplicity of P$_R$ is due to interaction with the apical phosphorus atom P$_A$ (J(P$_A$P$_R$) = 5.0 Hz) and with only one of the two other terminal PPh$_2$ groups. In actuality, it is not easy to discriminate between the two rhodium-bonded PPh$_2$ groups, i.e. P$_M$ and P$_Q$; however, taking into account that an AMQRX spin system is consistent only with a square-pyramidal geometry around rhodium, we conclude that P$_R$ couples to P$_M$ rather than to P$_Q$ because it is located trans to the vinylphosphonium ligand (J(P$_M$P$_R$) = 15.9 Hz; J(P$_Q$P$_R$) $\simeq$ 0 Hz). The other extreme signal of the spectrum (δ = 104.17 ppm), which appears as a pair of pseudotriplets of doublets, is readily assigned to the bridgehead phosphorus atom P$_A$, which couples to rhodium, to the two terminal P$_M$ and P$_Q$ atoms, and to the phosphonium P$_R$ atom. The pseudotriplet multiplicity of the resonance originates from the quasi-coincidence of the J(P$_A$P$_M$) and J(P$_A$P$_Q$) values (see Table II). The same argument used for the interpretation of the ^{31}P{^{1}H} NMR spectrum of **9** can be used now to assign the two middle-field resonances to the two nonequivalent PPh$_2$ groups bonded to rhodium. The two multiplets differ from each other only in a coupling connection. In particular, while the lower field signal

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(21) Transition-metal complexes containing a tridentate PP$_3$ ligand exhibit resonances at ca. −15 ppm for the free arm. See for example: (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Vizza, F.; Zanobini, F. *Organometallics* **1989**, *8*, 337. (b) Mazanek, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 85.

(22) Hohman, W. H.; Kountz, D. J.; Meek, D. W. *Inorg. Chem.* **1986**, *25*, 616.

(23) Pregosin, P. S.; Kounz, R. W. In *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, 1979.

(24) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(25) Seyferth, D.; Fogel, J. *J. Organomet. Chem.* **1966**, *6*, 205.

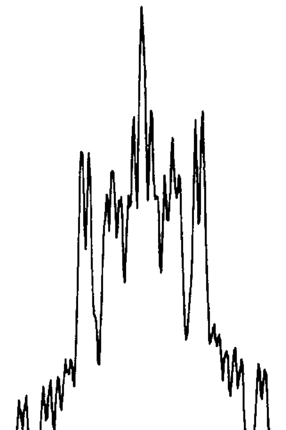


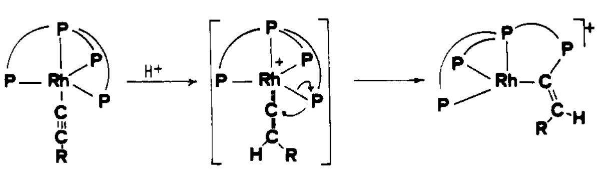
Figure 3. Experimental (upper) and computed (lower) ^1H NMR resonances of the formyl hydrogen of **10** (300 MHz, CD_2Cl_2, 298 K, Me_4Si reference).

appears as a 16-line pattern (as expected for a canonical AMQRX spin system), the higher field resonance is composed of 8 lines. We can therefore conclude that the higher field resonance is due to P_M with $J(P_MP_R)$ = 15.9 Hz, while the other signal, which is not coupled to the phosphonium P_R atom, is assigned to P_Q.

The proton NMR spectrum recorded in CD_2Cl_2 strongly supports the structure of **10** as given in Scheme I. A low-field resonance at 8.85 ppm is readily assignable to a formyl proton (Figure 3). This complex multiplet can be simulated as the A part of an ABMNPQX system, the aldehydic proton being coupled to the vicinal cis vinyl proton ($J(H_AH_B)$ = 7.1 Hz), to the four nonequivalent PP_3 phosphorus atoms ($J(H_AP_A)$ = 4.3 Hz; $J(H_AP_B)$ = 11.3 Hz; $J(H_AP_C)$ = 11.4 Hz; $J(H_AP_D)$ = 1.3 Hz), and to the central rhodium atom ($J(H_ARh)$ = 9.5 Hz). The resonance of the vinyl proton could not be identified, as it falls in the crowded aromatic region of the spectrum between 6.7 and 7.9 ppm. Indeed, a chemical shift correlated 2D NMR (COSY) experiment unequivocally showed that the formyl resonance exhibits only one off-diagonal peak throughout the spectrum; this peak is correlated with a resonance in the region of the phenyl hydrogens.

The presence of $\nu(C{=}O)$ at very low wavenumbers in **9** and **10** has been interpreted in terms of coordination to rhodium of the ester and aldehyde C=O functionalities,

Scheme IV



respectively.[26] This proves to be necessary to electronically and coordinatively saturate the metal center. As a matter of fact, when the phenylacetylide derivative **3** is reacted in THF with triflic or tetrafluoroboric acid, no product can be isolated, although the occurrence of a fast reaction is clearly evidenced by a neat color change from yellow to deep green. Working up the reaction mixture as usual produces only an intractable powder. However, the THF solution remains green for hours, especially at low temperature, suggesting that some interaction with the solvent may contribute to stabilize the protonated metal species. Accordingly, we decided to protonate **3** in THF-d_8 directly in the NMR tube at −25 °C (see Experimental Section). On the basis of the ^1H NMR spectrum, which contains a resonance at 6.6 ppm (J(HP) = 22.0 Hz, 1 H), and of the $^{31}P\{^1H\}$ NMR spectrum, which exhibits an AM_2QX spin system very similar in its main features to that of **9**($\delta(P_A)$ = 106.05 ppm; $\delta(P_M)$ = 39.05 ppm; $\delta(P_Q)$ = 19.28 ppm; $J(P_AP_M)$ = 9.7 Hz; $J(P_AP_Q)$ = 1.2 Hz; $J(P_MP_Q)$ = 12.9 Hz; $J(P_ARh)$ = 131.0 Hz; $J(P_MRh)$ = 122.0 Hz; $J(P_QRh) \simeq 0$ Hz), the metal species in solution is assigned the vinylphosphonium structure $[((Ph_2PCH_2CH_2)_2P(CH_2CH_2PPh_2))Rh(THF)(C{=}C(H)Ph)]^+$.

A reasonable mechanism for the formation of the present family of vinylphosphonium complexes is the one that implies the initial protonation of the acetylide complexes at the C_β atom to give vinylidene complex cations, followed by nucleophilic attack of a terminal phosphorus donor of PP_3 at the electron-deficient vinylidene C_α atom (Scheme IV).

The vinylphosphonium complexes are electronically unsaturated and need to be stabilized by an additional bonding interaction. This can be provided by the vinyl substituent or, when the substituent has a very scarce nucleophilic character, by the solvent. Actually, we have no evidence for the intermediacy of PP_3 vinylidene complexes but the mechanism has some good precedents.[2a,b,19,27]

Provided the mechanism shown in Scheme IV is valid, it remains to be explained why the NP_3 vinylidenes are stable and isolable compounds whereas the PP_3 analogues receive stabilization only through an intramolecular process involving the making and breaking of C–P and Rh–P bonds, respectively. In our opinion, it is not possible to address the question with any certainty at this stage. Most likely, a combination of electronic and steric factors, associated with the presence of a bridgehead phosphorus atom in the place of nitrogen, is responsible for the instability of the PP_3 vinylidene complexes.

Reactivity of the NP_3 Vinylidene Complexes. Reactions with Nucleophiles. The NP_3 vinylidenes **6** and **7** are readily deprotonated by bases such as MeLi, PhLi, and NEt_3 to yield the corresponding acetylides **1** and **2** and

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[26] (a) Bianchini, C.; Laschi, F.; Meli, A.; Peruzzini, M.; Zanello, P.; Frediani, P. *Organometallics* **1988**, *7*, 2575. (b) Kashef, N.; Richards, L. L. *J. Organomet. Chem.* **1989**, *365*, 309.

[27] (a) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Orlandini, A. *J. Organomet. Chem.* **1983**, *246*, C13. (b) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Orlandini, A. *J. Organomet. Chem.* **1984**, *270*, 251. (c) Bianchini, C.; Masi, D.; Mealli, C.; Meli, A.; Sabat, M.; Scapacci, G. *J. Organomet. Chem.* **1984**, *273*, 91.

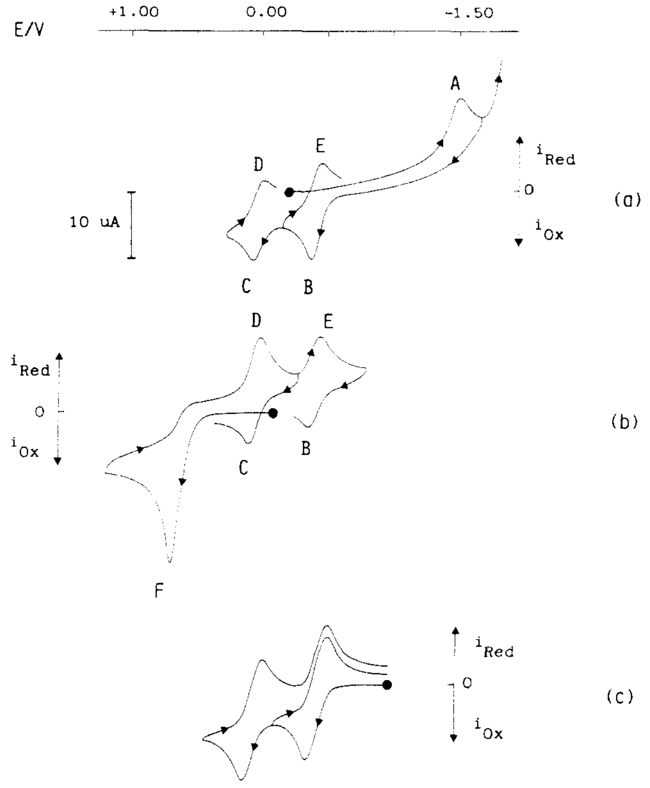

Figure 4. Cyclic voltammograms recorded at a platinum electrode on deareated CH_2Cl_2 solutions containing $[NBu_4]ClO_4$ (0.1 mol dm^{-3}) and (a, b) **6b** (1.28×10^{-3} mol dm^{-3}) or (c) 1 (8.5×10^{-4} mol dm^{-3}). The scan rate was 0.2 V s^{-1}; ● indicates the starting potential.

methane, benzene, and $[NEt_3H]BPh_4$, respectively (Scheme II).

In contrast, **6** and **7** react with $NaBH_4$ or $LiHBEt_3$ to give mixtures of **1** or **2** and of the Rh(I) σ-alkenyl derivatives [(*E*)-$(NP_3)Rh(CH{=}C(H)R)$] (R = Ph (**11**), CO_2Et (**12**)). We have no spectroscopic evidence for the *Z* isomer. The (*E*)-σ-alkenyls were identified by comparison with authentic specimens.[14] The nucleophilic addition of hydride to the vinylidene C_α atom[28] constitutes the predominant reaction path (70–80%), as determined by ^{31}P NMR integration over a number of different preparations.

As may be deduced from the procedure used to synthesize vinylidenes **6** and **7**, these compounds are fairly stable in alcohols with respect to the conversion to alkylidenes.[1a] We ascribe the stability of the present vinylidene derivatives essentially to the large steric crowding around the C_α atom. In effect, C_α, like many other similar atoms in TBP metal complexes of NP_3 or PP_3, is deeply encapsulated into the natural cavity of the tripodal ligand–metal moiety and protected from external attacks by as many as six phenyl rings. It is therefore reasonable to have found that the only nucleophilic attack at C_α is that carried out by the smallest nucleophile, namely the hydride ion.

Redox Properties. The redox pattern of the present vinylidene complexes is exemplified in Figure 4a,b, which shows the cyclic voltammetric responses exhibited by **6b** in CH_2Cl_2. It is evident that the cation $[(NP_3)Rh{=}C{=}C(H)Ph]^+$ undergoes a reduction process at peak A, where upon it generates a species that can be oxidized in two subsequent steps (peaks B and C). Each step shows a directly associated rereduction response (peaks D and E).

Table III. Peak Potential Values[a] (V, vs SCE) for the One-Electron Reduction and Two-Electron Oxidation of the Vinylidene Complexes 6 and 7 in CH_2Cl_2

complex	E_p redn	E_p oxidn
6	−1.54	+0.64
7	−1.44	+0.82

[a] Measured at a scan rate of 0.2 V s^{-1}.

Controlled-potential coulometric tests at −1.6 V indicated that the reduction of **6b** involves the consumption of 1 e/molecule. Analysis[29] of the cathodic response with scan rates varying from 0.02 to 50 V s^{-1} shows that no reoxidation peak directly associated with peak A can be detected even at the highest scan rate. The relevant $i_{p(A)}/v^{1/2}$ ratio remains constant. The peak potential value $E_{p(A)}$ shifts cathodically by 45 mV for a 10-fold increase in v. These data may naively be interpreted in terms of an electrochemically irreversible one-electron charge transfer with a transfer coefficient α equal to 0.66. However, in agreement with Figure 4a, the exhaustive one-electron reduction affords a yellow solution exhibiting in cyclic voltammetry a redox profile fully coincident with that reported in Figure 4c, which refers to the two successive one-electron oxidations of the corresponding Rh(I) σ-acetylide 1.[17] It is therefore apparent that the irreversibility of the reduction step arises from a fast chemical reaction coupled to the one-electron addition (i.e. a chemical irreversibility) rather than from an intrinsically slow heterogeneous charge transfer. In other words, the experimental results are consistent with a cathodically induced β-hydrogen elimination of the vinylidene ligand and the overall reduction reaction

$$[(NP_3)Rh{=}C{=}C(H)Ph]^+ + e^- \rightarrow [(NP_3)Rh(C{\equiv}CPh)] + \tfrac{1}{2}H_2$$

The redox properties of vinylidenes **6** and **7** are further evidenced by their anodic behavior. As reported in Figure 4b, complex **6b** also undergoes an irreversible oxidation process in correspondence with peak F, whereupon it generates a species that is reduced just at the electrode potentials of the two successive one-electron reductions of $[(NP_3)Rh(C{\equiv}CPh)]^{2+}$.[17] Controlled-potential coulometry at +0.8 V showed the oxidation process to involve 2 e/molecule. Furthermore, the addition of ethanol/*n*-heptane to the electrolyzed solution results in the precipitation of the known Rh(III) σ-acetylide $[(NP_3)Rh(C{\equiv}CPh)(C_2H_5OH)](ClO_4)_2$.[17] Accordingly, as a result of the two-electron oxidation, proton elimination occurs to give a Rh(III) σ-acetylide:

$$[(NP_3)Rh{=}C{=}C(H)Ph]^+ \rightarrow [(NP_3)Rh(C{\equiv}CPh)]^{2+} + 2e^- + H^+$$

Anodic processes like that shown in the above reaction, involving enhancement of the acid strength of the β-hydrogen, have been observed for other hydrocarbyl ligands.[8b]

A qualitatively similar trend is displayed by **7**. Table III summarizes the electrode potentials for the conversion of vinylidenes **6** and **7** into the corresponding σ-acetylide of rhodium(I) and rhodium(III).

As far as the vinylphosphonium complexes **9** and **10** are concerned, the redox chemistry is quite different from that of the parent vinylidene compounds. As an example, **9** in CH_2Cl_2 apparently undergoes a one-electron irreversible

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(28) Davison, A. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2455.

(29) Brown, E. R.; Sandifer, J. R. In *Physical Methods of Chemistry: Electrochemical Methods*; Rossiter, B. W., Hamilton, J. F., Eds.; Wiley: New York, 1986; Vol. 2, Chapter 4.

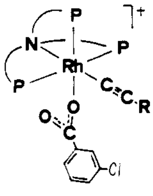
reduction (E_p = −1.70 V) and a two-electron irreversible oxidation (E_p = +0.94 V) as well. However, both processes do not show in the reverse scan any peak system correlating with the generation of the corresponding σ-acetylides, but only minor fragmentation peaks. For this reason, the redox properties of the vinylphosphonium compounds were not studied in detail.

Reactions with Peroxo Acids and Dioxygen. Having discovered that the deprotonation of the vinylidene ligand can be promoted by electrochemical oxidation, we decided to investigate the reactions of **6** and **7** with chemical oxidants such as peroxo acids and dioxygen. In actuality, we were particularly interested in the reactions with dioxygen, as this reagent, at least in one case, proved able to cleave the vinylidene C=C bond to give carbonyl and aldehyde under very mild conditions (CH_2Cl_2, 25 °C).[8a] The reaction illustrated below is of great relevance, as it provides further support for the intermediacy of vinylidene complexes in the metal-promoted oxidation of alkynes:[30]

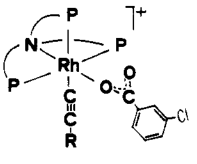
$$[Ru(=C=CHPh)(PPh_3)(\eta^5\text{-}C_5H_5)]^+ + O_2 \rightarrow [Ru(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]^+ + PhCHO$$

Stoichiometric amounts of *m*-chloroperbenzoic acid, *m*-CPBA, readily decolorize red-brown CH_2Cl_2 solutions of **6** and **7** to pale yellow. On addition of $NaBPh_4$ in ethanol, crystals of $[(NP_3)Rh(C\equiv CR)(O_2CC_6H_4Cl)]BPh_4$ separate in ca. 60% yield (R = Ph (**13**), CO_2Et (**14**)). The rather low yield is ascribed to a side reaction occurring at the metal vinylidene moiety that, in the case of **6**, produces phenol (see below).

Compounds **13** and **14** are fairly air-stable both in the solid state and in solution, in which they behave as 1:1 electrolytes. An octahedral (OCT) geometry around the rhodium atom in both compounds can be readily assigned on the basis of the ^{31}P NMR AM_2X spin systems (Table II). The presence of a terminal acetylide ligand bonded to a Rh(III) center can be deduced by $\nu(C\equiv C)$, which is shifted to higher wavenumbers as compared to the parent Rh(I) σ-acetylides (2115 and 2110 cm^{-1} for **13** and **14**, respectively). Strong absorptions in the IR spectra of both compounds at 1610 cm^{-1} are assigned to $\nu(C=O)$ of the η^1-carboxylate ligand. While the geometric requirements of the tripodal ligand permit one to precisely determine the relative positions of the carboxylate and acetylide ligands, i.e. mutually cis, in the absence of an X-ray analysis it is not possible to establish the position of these ligands with respect to the nitrogen or phosphorus donors of NP_3. Therefore, **13** and **14** can be equally formulated either as in A or as in B.



A



B

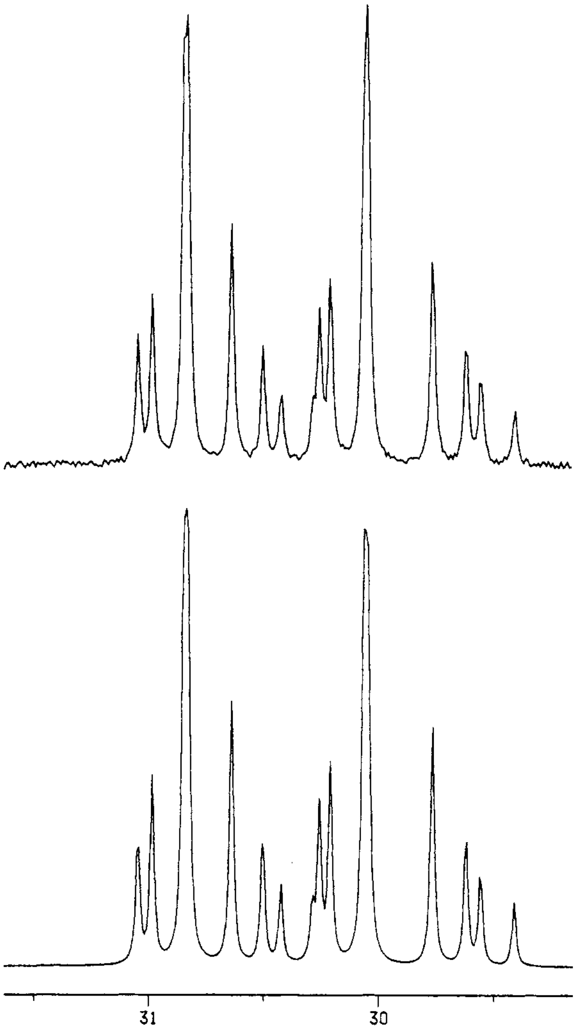


Figure 5. Experimental (upper) and computed (lower) $^{31}P\{^1H\}$ NMR spectra of **15** (CD_2Cl_2, 121.42 MHz, 298 K, H_3PO_4 reference).

From a mechanistic point of view, the reactions leading to **13** and **14** may involve either nucleophilic attack by the vinylidene complexes at the peroxo acid or two-electron transfer followed by coordination of the benzoate ligand to rhodium in the dication $[(NP_3)Rh(C\equiv CR)]^{2+}$. Water has been detected as a byproduct of the reactions by ^1H NMR spectroscopy. Interestingly, **13** and **14** can be prepared in almost quantitative yields also by reacting the Rh(I) acetylides **1** and **2** in CH_2Cl_2 with *m*-CPBA:

$$[(NP_3)Rh(C\equiv CR)] + m\text{-CPBA} \rightarrow [(NP_3)Rh(C\equiv CR)(O_2CC_6H_4Cl)]^+ + OH^-$$

No production of phenol or of other organic products eventually derived from the carbethoxyvinylidene is observed. This is an important point, as it clearly suggests that the vinylidene ligand can directly interact with the peroxo acid.

Bubbling O_2 into CH_2Cl_2 or THF solutions of **6** and **7** results in the slow formation of pale yellow mixtures from which the complexes $[(NP_3)Rh(C\equiv CR)(OH)]BPh_4$ (R = Ph (**15**), CO_2Et (**16**)) precipitate by addition of ethanol in ca. 60% yield. ^{31}P NMR analysis of the filtrates revealed the presence of NP_3 oxides, whereas GC analysis for the reaction of **6** showed an appreciable formation of phenol (ca. 30% based on **6**).

Compounds **15** and **16** are air-stable both in the solid state and in solution, in which they behave as 1:1 electrolytes. The IR spectra of both compounds contain weak bands at 3490 cm^{-1}, which are assigned to $\nu(O\text{–}H)$ of the hydroxide ligand.[31] The C–C stretching of the acetylide ligand falls in the proper region for the Rh(III) σ-acetylide of NP_3 (2115 and 2105 cm^{-1} for **15** and **16**, respectively).

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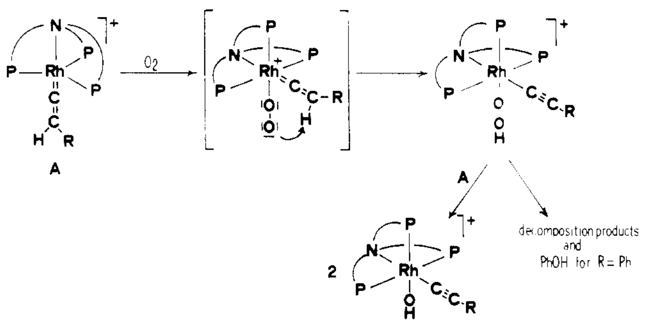
[30] Sullivan, B. P.; Smythe, R. S.; Kober, E. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4701.

[31] (a) Green, L. M.; Meek, D. W. *Organometallics* **1989**, *8*, 659. (b) Atlay, M. T.; Preece, M.; Strukul, K.; James, B. R. *Can. J. Chem.* **1983**, *61*, 1332.

Scheme V



On the basis of ^{31}P NMR spectroscopy, both compounds are assigned OCT structures. However, while **16** exhibits the expected first-order AM_2X pattern, the spectrum of **15** (Figure 5) is perturbed by the second-order effects and can be simulated as the AB_2 portion of an AB_2X system by using the parameters reported in Table II. As previously discussed for **13** and **14**, the coordination positions of the acetylide and hydroxide ligands cannot be precisely determined by spectroscopic methods only.

The two-electron reduction of **15** ($E_p = -1.5$ V) and **16** ($E_p = -1.4$ V) in CH_2Cl_2 via controlled-potential coulometry results in the regeneration of the parent Rh(I) σ-acetylide complexes **1** and **2**, respectively. The diminution of the total number of chemical bonds at the metal by one unit upon addition of two electrons is fairly common in coordination chemistry.[32] Interestingly, but in good accord with the bond strengths, we note that the Rh–O bond is preferentially cleaved over the Rh–C one.

In an attempt of building a possible mechanism for the formation of the hydroxide complexes **15** and **16**, the following experimental pieces of information are noteworthy. (i) From a perusal of the redox potentials, it is evident that, unlike peroxo acids, molecular oxygen is not able to oxidize vinylidenes **6** and **7** under the present conditions. (ii) It is well-known that TBP complexes of Rh(I) such as vinylidenes **6** and **7** can generate an occupied frontier σ orbital that can be attacked by electrophiles, including dioxygen.[33] (iii) The reaction between **6** and O_2 produces an appreciable amount of phenol, the phenyl group of which undoubtedly comes from the C=C(H)Ph moiety. The partial decomposition of the complex framework was observed also for the reaction of **7** with O_2. Except for traces of CO_2, no organic product was recognized in the reaction mixture. (iv) The formation of some phenol was detected also in the reaction mixture between **6** and *m*-CPBA. In contrast, treatment of the Rh(I) σ-acetylide **1** with *m*-CPBA does not produce phenol at all.

In view of all of these results, a reasonable mechanism for the formation of the hydroxo complexes **15** and **16** is the one shown in Scheme V. This involves electrophilic attack by O_2 at the metal, followed by intramolecular β-deprotonation of the vinylidene ligand to give an η^1-hydroperoxide σ-acetylide intermediate. Because of the positive charge, this intermediate may display high electrophilic properties[34] and, therefore, appears appropriate either to attack intramolecularly the nucleophilic β-carbon of the acetylide, producing phenol and, consequently, destroying the complex framework, or to oxidize intermolecularly a second vinylidene complex molecule, forming the hydroxo complexes **15** and **16**.

Notice, however, that one cannot exclude, a priori, that the degradation of the hydroperoxide intermediate to hydroxide may be due to interaction with other eventual nucleophiles such as adventitious water.

Thermal Decomposition. Compounds **6** and **7** are thermally unstable and quickly decompose to the square-pyramidal (SQ) Rh(II) σ-acetylides $[(NP_3)Rh(C{\equiv}CPh)]BPh_4$ (**17**) and $[(NP_3)Rh(C{\equiv}CCO_2Et)]BPh_4$ (**18**) when heated under nitrogen or argon in THF solutions.[17] During the decomposition, dihydrogen is evolved. In contrast, **6** and **7** are stable in refluxing CH_2Cl_2 whereas the methyl derivatives **8** are stable even in refluxing THF. Given the latter experimental evidence and the fact that the redox potential values for the Rh(I)/Rh(II) redox changes of Rh(I) σ-acetylides **1** and **2** in THF at 60 °C are −0.36 and −0.24 V, respectively,[17] one may interpret the decomposition of **6** and **7** also in terms of an acid–base/redox reaction. In fact, it is well-known that transition-metal vinylidene complexes can be in an acid–base equilibrium with the acetylide form and that the equilibrium may be shifted to the acetylide form in a basic solvent such as THF or acetone.[1] If this occurs, the $E^{\circ\prime}$ values in THF for the $[(NP_3)Rh(C{\equiv}CR)]/[(NP_3)Rh(C{\equiv}CR)]^+$ couple are such that the proton itself can act as an effective oxidant toward **1** and **2**. In summary, a reasonable sequence to account for the present Rh(I) vinylidene → Rh(II) acetylide conversion is

$$[(NP_3)Rh{=}C{=}C(H)R]^+ \rightleftarrows [(NP_3)Rh(C{\equiv}CR)] + H^+ \rightleftarrows [(NP_3)Rh(C{\equiv}CR)]^+ + \tfrac{1}{2}H_2$$

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