

### Preliminary communication

## Activation of C–H bonds in acetylene and terminal alkynes by rhodium(I) species. Crystal structure of *cis*-(ethynyl)hydride $[(\text{NP}_3)\text{Rh}(\text{H})(\text{C}\equiv\text{CH})]\text{BPh}_4 \cdot 1.5\text{C}_4\text{H}_8\text{O}$ ( $\text{NP}_3 = \text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ )

Claudio Bianchini, Carlo Mealli, Maurizio Peruzzini, Francesco Vizza,  
 and Fabrizio Zanobini

*Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, C.N.R.,  
 Via J. Nardi, 39, Firenze 50132 (Italy)*

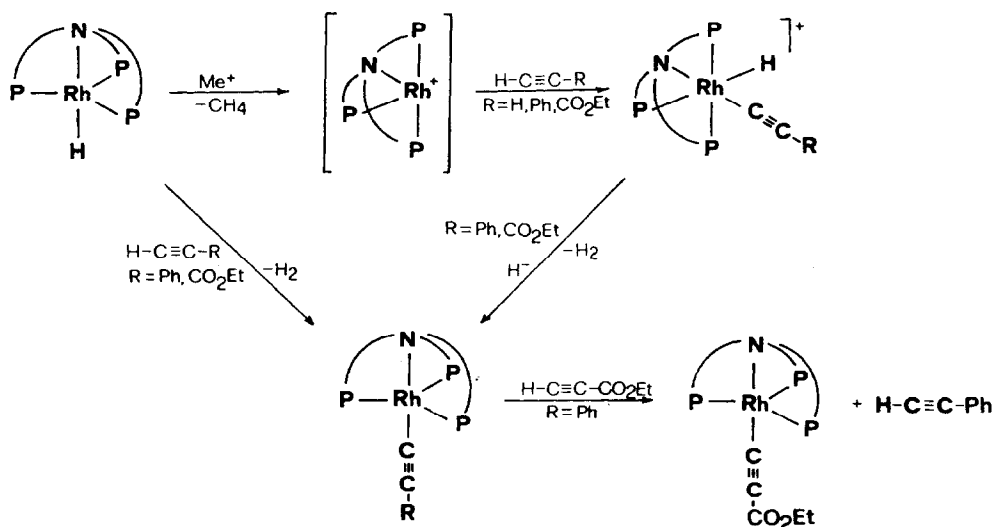
(Received February 15th, 1988)

### Abstract

The 16-electron fragment  $(\text{NP}_3)\text{Rh}^+$  inserts in a highly stereospecific manner across C–H bonds from acetylene and 1-alkynes to give the octahedral *cis*-(alkynyl)hydrides  $[(\text{NP}_3)\text{Rh}(\text{H})(\text{C}\equiv\text{CR})]\text{BPh}_4$  ( $\text{R} = \text{H}, \text{Ph}, \text{COOEt}$ ). The structure of the *cis*-(ethynyl)hydride  $[(\text{NP}_3)\text{Rh}(\text{H})(\text{C}\equiv\text{CH})]\text{BPh}_4 \cdot 1.5 \text{ THF}$  has been established by X-ray diffraction. The trigonal bipyramidal rhodium(I) complex  $[(\text{NP}_3)\text{RhH}]$ , reacts with terminal alkynes to give  $\text{H}_2$  and the neutral  $\sigma$ -acetylides  $[(\text{NP}_3)\text{Rh}(\text{C}\equiv\text{CR})]$  ( $\text{R} = \text{Ph}, \text{COOEt}$ ). These undergo metathesis between terminal alkynes and the  $\sigma$ -acetylide ligand through a mechanism involving consecutive breaking and making of C–H bonds.

An essential requirement for C–H bond cleavage by transition metal systems is creation of an "activation site" by formation of a coordinatively and electronically unsaturated species [1]. In this respect, an excellent candidate should be the 16-electron fragment  $(\text{NP}_3)\text{Rh}^+$  which is produced in THF solution by reductive elimination of  $\text{CH}_4$  from the unstable *cis*-(methyl)hydride complex cation  $[(\text{NP}_3)\text{Rh}(\text{H})(\text{CH}_3)]^+$ , where  $\text{NP}_3 = \text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$  (Scheme 1) [2]. We have found that  $(\text{NP}_3)\text{Rh}^+$  does indeed insert in a highly stereospecific manner into the C–H bonds of ethyne and terminal alkynes to form the stable *cis*-(alkynyl)hydrides  $[(\text{NP}_3)\text{Rh}(\text{H})(\text{C}\equiv\text{CR})]^+$  (Scheme 1). These can be isolated as white crystalline tetraphenylborate salts after addition of ethanolic  $\text{NaBPh}_4$  ( $\text{R} = \text{H}$ , 1;  $\text{Ph}$ , 2;  $\text{COOEt}$ , 3) \*. All of the compounds appear from their pseudo-octahedral  $^{31}\text{P}$  NMR

\* All compounds were isolated as crystalline solids which gave correct elemental analyses. They are air-stable in the solid state and in deoxygenated solutions, in which they behave as 1/1 electrolytes (1, 2, 3) ( $\Lambda_M$  50–54  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in ca.  $10^{-3} \text{ M}$  nitroethane solutions) or non-electrolytes (4, 5). Selected spectroscopic data for the complexes are given in Table 1.



Scheme 1

spectra to behave as  $\text{AM}_2\text{X}$  spin systems characteristic of the  $(\text{NP}_3)\text{Rh}$  fragment arranged in a butterfly shape. The  $^1\text{H}$  NMR spectra in the high field region show well resolved doublets of doublets of triplets for the hydride hydrogen atoms. The  $J(\text{HP})$  values, of 169–171 Hz, unequivocally indicate that the hydride ligand is located *trans* to the equatorial phosphorus atom.

The stereospecific addition of alkynes to the  $(\text{NP}_3)\text{Rh}^+$  fragment has been confirmed by an X-ray diffraction study of **1**, which is the first authenticated *cis*-(ethynyl)hydride complex.

*Crystal data for 1:*  $\text{C}_{74}\text{H}_{76}\text{P}_3\text{NBRhO}_{1.5}$ ,  $M = 1210.07$ , monoclinic, space group  $P2_1/n$ ,  $a$  15.769(3),  $b$  32.458(6),  $c$  13.277(3) Å,  $\beta$  105.21(2)°,  $U$  6557(1) Å<sup>3</sup>,  $Z = 4$ ,  $D_c$  1.22 g cm<sup>-3</sup>,  $\mu(\text{Mo}-K_\alpha)$  3.19 cm<sup>-1</sup>. The structure was solved by Patterson and Fourier techniques and refined to an  $R$  factor of 0.079 ( $R_w = 0.086$ ) using 3735 reflections with  $I > 3\sigma(I)$  recorded on a Philips PW 1100 diffractometer up to  $2\theta = 50^\circ$  (Mo- $K_\alpha$  radiation,  $\lambda$  0.71069 Å). The hydrogen atom bound to rhodium was found from a difference Fourier map, and its positional and isotropic thermal parameters were refined. During the refinement the phenyl rings were treated as rigid groups of  $D_{6h}$  symmetry\*.

The solid state structure of the complex cation,  $[(\text{NP}_3)\text{Rh}(\text{H})(\text{C}\equiv\text{CH})]^+$ , is shown in Fig. 1. In keeping with the spectroscopic analysis, the potential threefold symmetry of the  $(\text{NP}_3)\text{Rh}$  fragment is destroyed by the opening of the P(2)–Rh–P(3) angle up to 153.9(1)°. There are hydride and  $\sigma$ -ethynyl ligands in *cis* positions in the plane defined by the metal and the N(1) and P(1) donors, and so the overall geometry can be described as pseudo-octahedral. The butterfly shape of the  $(\text{NP}_3)\text{Rh}$  fragment has been observed previously; for example in  $[(\text{NP}_3)\text{Rh}(\eta^2\text{-CS}_2)]^+$  [3], in

\* A list of atomic coordinates and a full table of bond angles and distances will be deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (U.K.).

Table 1  
Spectroscopic data for the complexes

Com- pound	IR ( $\text{cm}^{-1}$ ) <sup>a</sup>	NMR			<sup>31</sup> P <sup>c</sup>			
		<sup>1</sup> H <sup>b</sup>			$\delta$	$J$		
		$\delta$	$J$			$\delta$	$J$	
<b>1</b>	3275w $\nu(\text{C-H})$	2.31(qu,CH)	HP	2.1	AM <sub>2</sub> X	$\delta(\text{A})$ 18.51	P <sub>A</sub> P <sub>M</sub>	19.7
	2015w $\nu(\text{Rh-H})$		HRh	2.1			R <sub>A</sub> Rh	103.9
	1975m $\nu(\text{C}\equiv\text{C})$	-7.72(ddt,RhH)	HP <sub>trans</sub>	171.1		$\delta(\text{M})$ 34.69	P <sub>M</sub> Rh	86.2
			HP <sub>cis</sub>	8.9				
<b>2</b>	2120m $\nu(\text{C}\equiv\text{C})$	-7.61(ddt,RhH)	HP <sub>trans</sub>	171.1	AM <sub>2</sub> X	$\delta(\text{A})$ 19.98	P <sub>A</sub> P <sub>M</sub>	19.7
	2000w $\nu(\text{Rh-H})$	<i>d</i>	HP <sub>cis</sub>	8.9			P <sub>A</sub> Rh	102.4
			HRh	15.8		$\delta(\text{M})$ 35.42	P <sub>M</sub> Rh	85.7
<b>3</b>	2110m $\nu(\text{C}\equiv\text{C})$	4.20(q,OCH <sub>2</sub> CH <sub>3</sub> )	HH	7.1	AM <sub>2</sub> X	$\delta(\text{A})$ 20.19	P <sub>A</sub> P <sub>M</sub>	19.1
	2050w $\nu(\text{Rh-H})$	1.32(t,OCH <sub>2</sub> CH <sub>3</sub> )					P <sub>A</sub> Rh	100.9
	1690s $\nu(\text{C=O})$	-7.58(ddt,RhH)	HP <sub>trans</sub>	169.3		$\delta(\text{M})$ 36.69	P <sub>M</sub> Rh	84.0
	1210s $\nu(\text{COEt})$		HP <sub>cis</sub>	8.4				
<b>4</b> <sup>e</sup>	2080m $\nu(\text{C}\equiv\text{C})$	<i>d</i>			A <sub>3</sub> X	$\delta(\text{A})$ 24.68	P <sub>A</sub> Rh	160.7
<b>5</b> <sup>e</sup>	2050m $\nu(\text{C}\equiv\text{C})$	4.09(q,OCH <sub>2</sub> CH <sub>3</sub> )	HH	7.0	A <sub>3</sub> X	$\delta(\text{A})$ 25.95	P <sub>A</sub> Rh	157.5
	1660s $\nu(\text{C=O})$	1.28(t,OCH <sub>2</sub> CH <sub>3</sub> )						
	1195s $\nu(\text{COEt})$							

<sup>a</sup> Samples as Nujol mulls between KBr plates. <sup>b</sup> At 300 MHz at room temperature in CD<sub>3</sub>COCD<sub>3</sub> solutions, unless otherwise stated.  $\delta$  in ppm from external TMS. The resonances due to the hydrogen atoms of the NP<sub>3</sub> ligand and the BPh<sub>4</sub> anion are not reported. Coupling constants in Hz. <sup>c</sup> 32.19 MHz at room temperature in CD<sub>3</sub>COCD<sub>3</sub> solutions, unless otherwise stated.  $\delta$  in ppm from external H<sub>3</sub>PO<sub>4</sub> 85% with downfield values positive. Coupling constants in Hz. <sup>d</sup> The resonances due to the aromatic protons of the alkyne are masked by the signals of the NP<sub>3</sub> ligand. <sup>e</sup> CDCl<sub>3</sub> solution.

which the angle P-Rh-P is opened to 161.9(1)°. The Rh-H bond distance in **1** is slightly shorter than that in *cis*-[Rh(PMe<sub>3</sub>)<sub>4</sub>(H)(C≡C-CH<sub>2</sub>CH<sub>2</sub>OH)]Cl [4].

Compounds **2** and **3**, react in THF with hydride sources such as LiHBet<sub>3</sub> or NaBH<sub>4</sub> to give H<sub>2</sub> and the trigonal bipyramidal (TBP) acetylides [(NP<sub>3</sub>)Rh(C≡CR)], (R = Ph, **4**; COEt, **5**) (Yield 75%). The two  $\sigma$ -acetylide complexes and H<sub>2</sub> can be directly obtained by treating the TBP hydride [(NP<sub>3</sub>)RhH] (**6**) [5], with a twofold proportion of the appropriate terminal alkyne in boiling THF (Yield 90%). In general terminal alkynes react with transition metal hydrides to give alkenyl derivatives through insertion across M-H bonds [6], but in at least two cases,  $\sigma$ -acetylide complexes were obtained, though possible mechanisms were not discussed [7]. In contrast, in the light of our results it is possible to propose that the

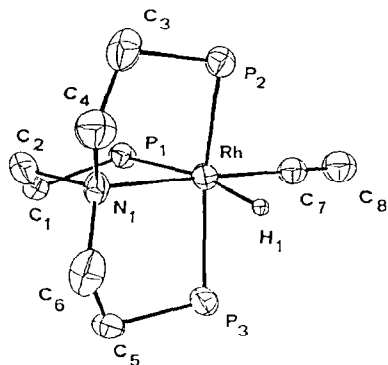
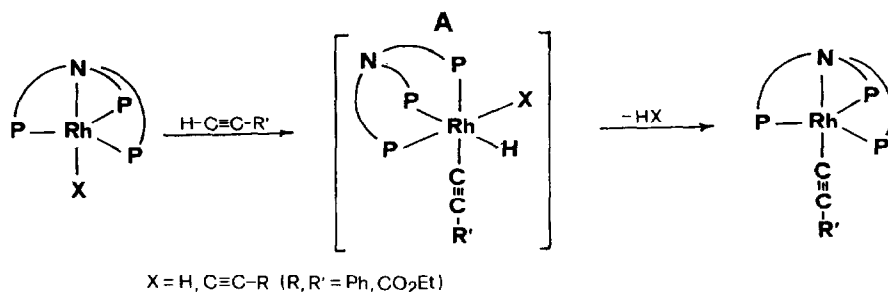


Fig. 1. ORTEP drawing of the cation  $[(NP_3)Rh(H)(C\equiv CH)]^+$  of **1**. Hydrogen atoms of the ethylenic chains and phenyl rings are omitted for clarity. Some relevant bond distances (Å): Rh–P(1), 2.382(4); Rh–P(2), 2.305(4); Rh–P(3), 2.316(4); Rh–N(1), 2.17(1); Rh–C(7), 1.96(1); Rh–H(1), 1.4(1); C(7)–C(8), 1.20(2). Bond angles ( $^\circ$ ): P(1)–Rh–P(2), 102.9(1); P(1)–Rh–P(3), 100.4(1); P(2)–Rh–P(3), 153.9; N(1)–Rh–P(1), 84.2(3); N(1)–Rh–P(2), 86.3(3); N(1)–Rh–P(3), 84.8(7); N(1)–Rh–C(7), 178.2(5); P(1)–Rh–C(7), 96.7(4); P(2)–Rh–C(7), 95.1(4); P(3)–Rh–C(7), 93.5(4); Rh–C(7)–C(8), 177(1).

key-step of the reaction involves insertion of the metal–ligand fragment into the *sp*-C–H bond of the alkyne (Scheme 2), to give, an octahedral intermediate in



Scheme 2

which the two hydrides and the acetylide groups occupy three *facial* sites. The “activation site” in **6** is provided by detachment of the nitrogen donor of  $NP_3$ . As the amine reenters the coordination sphere of the metal, dihydrogen is reductively eliminated and the  $\sigma$ -acetylide complexes formed. We have no evidence for the formation of any intermediate, but there are good precedents for the mechanism [5,8]; for the octahedral iridium trihydride  $[(NP_3)IrH_3]$ , in which the nitrogen donor is uncoordinated, has been synthesized by  $H^-$  addition to the *cis*-dihydride  $[(NP_3)Ir(H_2)]^+$  [5]. Furthermore, the participation of an intermediate of type A has the additional merit of explaining the formation of the rhodium(I)  $\sigma$ -acetylides **4** and **5** by reactions of the rhodium(III) *cis*-(alkynyl)hydrides **2** and **3** with  $H^-$ .

In order to substantiate the oxidative addition/reductive elimination mechanism we treated **4** with a twofold proportion of  $HC\equiv CCOOEt$ , and showed that there was quantitative replacement of the substituent on the alkyne. Such a process, which may be formally regarded as a metathesis between alkynes, probably proceeds via C–H oxidative addition of ethyl propiolate to the  $\sigma$ -acetylide complex **4** (Scheme 2), from which the less acidic alkyne, namely  $HC\equiv CPh$ , is reductively eliminated. In

keeping with the suggested C–H activation process, disubstituted alkynes such as  $\text{MeOOC}\equiv\text{CCOOMe}$  do not displace the acetylide ligand.

The present findings suggest that there may be alternative pathways for important metal-catalyzed processes involving 1-alkynes, such as disproportionation [9] or oligomerization [10]; an initial C–H bond oxidative addition of the alkyne to the metal may represent an alternative to the usual mechanism involving metallacyclic intermediates [11].

## References

- 1 R.A. Periana and R.G. Bergmann, *J. Am. Chem. Soc.*, 108 (1986) 7332; M. Ephritikhine, *Nouv. J. Chem.*, 10 (1986) 9; J. Halpern, *Inorg. Chim. Acta*, 100 (1985) 41; R.H. Crabtree, *Chem. Rev.*, 74 (1986) 245; I.P. Rothwell, *Polyhedron*, 4 (1985) 77; M.L. Deem, *Coord. Chem. Rev.*, 74 (1986) 101.
- 2 C. Bianchini, D. Masi, A. Meli, M. Peruzzini, M. Sabat, and F. Zanobini, *Organometallics*, 5 (1986) 2557; C. Bianchini, A. Meli, M. Peruzzini, A. Vacca, and F. Zanobini, *Organometallics*, 6 (1987) 2453; C. Bianchini, A. Meli, M. Peruzzini, and F. Zanobini, *J. Chem. Soc., Chem. Commun.*, (1987) 971.
- 3 C. Bianchini, D. Masi, C. Mealli, A. Meli and M. Sabat, *Organometallics*, 4 (1985) 1014.
- 4 T.B. Marder, D. Zargarian, J.C. Calabrese, T.H. Herskowitz, and D. Milstein, *J. Chem. Soc., Chem. Commun.*, (1987) 1484.
- 5 C. Bianchini, D. Masi, A. Meli, M. Peruzzini, and F. Zanobini, *J. Am. Chem. Soc.*, submitted for publication.
- 6 H.C. Clark, G. Ferguson, A.B. Goel, E.G. Janzen, H. Ruegger, P.Y. Siew, and C.S. Wang, *J. Am. Chem. Soc.*, 108 (1986) 6961; H. Werner, M.A. Esteruelas, and H. Otto, *Organometallics*, 5 (1986) 2295; G.E. Herberich, and W. Barlage, *ibid.*, 6 (1987) 1924; G.E. Herberich, and W. Barlage, *J. Organomet. Chem.*, 331 (1987) 63.
- 7 M.I. Bruce, R.C.F. Gardner, J.A.K. Howard, F.G.A. Stone, M. Welling, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, (1977) 621; T.G. Appleton, H.C. Clark, and R.J. Puddephat, *Inorg. Chem.*, 11 (1972) 2074.
- 8 C. Bianchini, A. Meli, and G. Scapacci, *Organometallics*, 2 (1983) 1834.
- 9 D.H. Berry and R. Eisenberg, *Organometallics*, 6 (1987) 1796.
- 10 See for example, H. Bönemann and W. Brijoux, *Aspects of Homogeneous Catalysis*, Vol. 5, D. Reidel, Dordrecht, NL, 1984.
- 11 M.A. Bruck, A.S. Copenhaver, and D.E. Wigley, *J. Am. Chem. Soc.*, 109 (1987) 6525 and ref. therein.