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Preliminary communication

Activation of C–H bonds in acetylene and terminal alkynes by rhodium(I) species. Crystal structure of *cis*-(ethynyl)hydride $[(NP_3)Rh(H)(C{\equiv}CH)]BPh_4 \cdot 1.5C_4H_8O$ ($NP_3 = N(CH_2CH_2PPh_2)_3$)

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)

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Abstract

The 16-electron fragment $(NP_3)Rh^+$ inserts in a highly stereospecific manner across C–H bonds from acetylene and 1-alkynes to give the octahedral *cis*-(alkynyl)hydrides $[(NP_3)Rh(H)(C{\equiv}CR)]BPh_4$ (R = H, Ph, COOEt). The structure of the *cis*-(ethynyl)hydride $[(NP_3)Rh(H)(C{\equiv}CH)]BPh_4 \cdot 1.5$ THF has been established by X-ray diffraction. The trigonal bipyramidal rhodium(I) complex $[(NP_3)RhH]$, reacts with terminal alkynes to give H_2 and the neutral σ-acetylides $[(NP_3)Rh(C{\equiv}CR)]$ (R = Ph, COOEt). These undergo metathesis between terminal alkynes and the σ-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 $(NP_3)Rh^+$ which is produced in THF solution by reductive elimination of CH_4 from the unstable *cis*-(methyl)hydride complex cation $[(NP_3)Rh(H)(CH_3)]^+$, where $NP_3 = N(CH_2CH_2PPh_2)_3$ (Scheme 1) [2]. We have found that $(NP_3)Rh^+$ 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 $[(NP_3)Rh(H)(C{\equiv}CR)]^+$ (Scheme 1). These can be isolated as white crystalline tetraphenylborate salts after addition of ethanolic $NaBPh_4$ (R = H, **1**; Ph, **2**; COOEt, **3**) *. All of the compounds appear from their pseudo-octahedral ^{31}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**) (Λ_M 50–54 Ω^{-1} cm^2 mol^{-1} in ca. 10^{-3} *M* nitroethane solutions) or non-electrolytes (**4**, **5**). Selected spectroscopic data for the complexes are given in Table 1.

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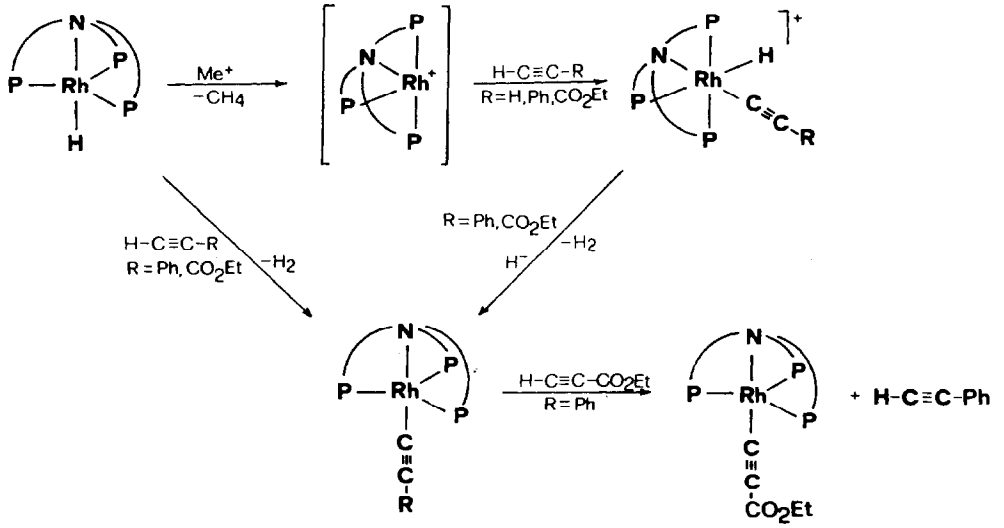


Scheme 1

spectra to behave as AM_2X spin systems characteristic of the $(NP_3)Rh$ fragment arranged in a butterfly shape. The ^1H NMR spectra in the high field region show well resolved doublets of doublets of triplets for the hydride hydrogen atoms. The J(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 $(NP_3)Rh^+$ 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**: $C_{74}H_{76}P_3NBRhO_{1.5}$, $M = 1210.07$, monoclinic, space group $P2_1/n$, a 15.769(3), b 32.458(6), c 13.277(3) Å, β 105.21(2)°, U 6557(1) Å^3, $Z = 4$, D_c 1.22 g cm^{-3}, μ(Mo-K_α) 3.19 cm^{-1}. 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 $2\theta = 50°$ (Mo-K_α radiation, λ 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, $[(NP_3)Rh(H)(C{\equiv}CH)]^+$, is shown in Fig. 1. In keeping with the spectroscopic analysis, the potential threefold symmetry of the $(NP_3)Rh$ fragment is destroyed by the opening of the P(2)–Rh–P(3) angle up to 153.9(1)°. There are hydride and σ-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 $(NP_3)Rh$ fragment has been observed previously; for example in $[(NP_3)Rh(\eta^2\text{-}CS_2)]^+$ [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

Compound	IR (cm^{-1}) [a]	NMR						
		^1H [b]				^{31}P [c]		
		δ	J			δ	J	
1	3275w ν(C–H)	2.31(qu,CH)	HP	2.1	AM_2X	δ(A) 18.51	P_AP_M	19.7
	2015w ν(Rh–H)		HRh	2.1			R_ARh	103.9
	1975m ν(C≡C)	−7.72(ddt,RhH)	HP_{trans}	171.1		δ(M)34.69	P_MRh	86.2
			HP_{cis}	8.9				
			HRh	15.5				
2	2120m ν(C≡C)	−7.61(ddt,RhH)	HP_{trans}	171.1	AM_2X	δ(A) 19.98	P_AP_M	19.7
	2000w ν(Rh–H)	*d*	HP_{cis}	8.9			P_ARh	102.4
			HRh	15.8		δ(M)35.42	P_MRh	85.7
3	2110m ν(C≡C)	4.20(q,OCH_2CH_3)	HH	7.1	AM_2X	δ(A) 20.19	P_AP_M	19.1
	2050w ν(Rh–H)	1.32(t,OCH_2CH_3)					P_ARh	100.9
	1690s ν(C=O)	−7.58(ddt,RhH)	HP_{trans}	169.3		δ(M)36.69	P_MRh	84.0
	1210s ν(COEt)		HP_{cis}	8.4				
			HRh	15.4				
4 [e]	2080m ν(C≡C)	*d*			A_3X	δ(A) 24.68	P_ARh	160.7
5 [e]	2050m ν(C≡C)	4.09(q,OCH_2CH_3)	HH	7.0	A_3X	δ(A) 25.95	P_ARh	157.5
	1660s ν(C=O)	1.28(t,OCH_2CH_3)						
	1195s ν(COEt)							

[a] Samples as Nujol mulls between KBr plates. [b] At 300 MHz at room temperature in CD_3COCD_3 solutions, unless otherwise stated. δ in ppm from external TMS. The resonances due to the hydrogen atoms of the NP_3 ligand and the BPh_4 anion are not reported. Coupling constants in Hz. [c] 32.19 MHz at room temperature in CD_3COCD_3 solutions, unless otherwise stated. δ in ppm from external H_3PO_4 85% with downfield values positive. Coupling constants in Hz. [d] The resonances due to the aromatic protons of the alkyne are masked by the signals of the NP_3 ligand. [e] $CDCl_3$ 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*-$[Rh(PMe_3)_4(H)(C{\equiv}C{-}CH_2CH_2OH]Cl$ [4].

Compounds **2** and **3**, react in THF with hydride sources such as $LiHBEt_3$ or $NaBH_4$ to give H_2 and the trigonal bipyramidal (TBP) acetylides $[(NP_3)Rh(C{\equiv}CR)]$, (R = Ph, **4**; COOEt, **5**) (Yield 75%). The two σ-acetylide complexes and H_2 can be directly obtained by treating the TBP hydride $[(NP_3)RhH]$ (**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, σ-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

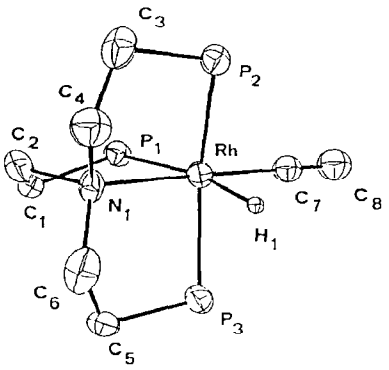
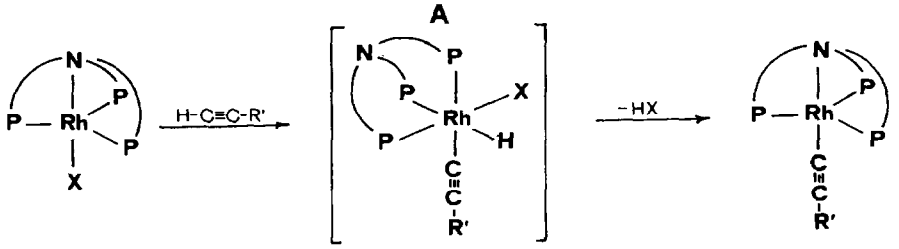


Fig. 1. ORTEP drawing of the cation $[(NP_3)Rh(H)(C{\equiv}CH)]^+$ of **1**. Hydrogen atoms of the ethylenic chains and phenyl rings are omitted for clarity. Some relevant bond distances (Å): Rh–P(1), 2.382(4); Rh–P(2), 2.305(4); Rh–P(3), 2.316(4), Rh–N(1), 2.17(1); Rh–C(7), 1.96(1); Rh–H(1), 1.4(1); C(7)–C(8), 1.20(2). Bond angles (°): 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 σ-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) σ-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≡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 σ-acetylide complex **4** (Scheme 2), from which the less acidic alkyne, namely HC≡CPh, is reductively eliminated. In

keeping with the suggested C–H activation process, disubstituted alkynes such as MeOOCC≡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. Bönnemann 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.