C–H Rather than O–H Activation: Synthesis and Molecular Structure of a Cationic *cis*-Hydrido-σ-Acetylide Complex of Rhodium

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Terminal alkynes, including those with acidic O–H groups, react with $[Rh(PMe_3)_4]Cl$ in tetrahydrofuran (THF) or in water yielding *cis*-hydrido-σ-acetylide complexes *via* C–H activation; the molecular structure of *cis*-$[Rh(PMe_3)_4(H)(C{\equiv}C{-}CH_2CH_2OH)]Cl$ has been determined by *X*-ray diffraction.

During our studies[1] of the rhodium-catalysed cyclization of alkynoic acids to enol lactones [reaction (1)] we observed another Rh-catalysed process, the exchange of terminal alkyne C–H bonds with RCO_2D deuterons [reaction (2)]. The cationic complex[2] $[Rh(PMe_3)_4]Cl$ (**1**) is a good catalyst for reaction (1), ($R = H$, $n = 2$, in H_2O/Et_2O); the product is efficiently partioned into the Et_2O layer. Although reactions (1) and (2) may proceed simultaneously,† it seems likely that the two mechanisms are distinct. We report here preliminary results of an investigation of the reactivity of terminal alkynes with (**1**) in tetrahydrofuran (THF) and in water.

$[Rh(PMe_3)_4Cl]$
(**1**)

$HC{\equiv}C[CH_2]_2R$
(**2**) **a**; $R = CO_2H$
b; $R = OH$

Reaction of (**1**) with $HC{\equiv}CCH_2CH_2CO_2H$ (**2a**) in THF suspension results in rapid decolourisation of the orange mixture and the formation of a white precipitate (95% yield). The i.r. spectrum (Nujol) of the THF-insoluble product showed bands at 2135w, 1961s, and 1745s cm^{-1} suggesting that it was a hydrido-acetylide complex rather than a hydrido-carboxylate species. That the complex was indeed *cis*-$[Rh(PMe_3)_4(H)(C{\equiv}CCH_2CH_2CO_2H)]^+Cl^-$ (**3a**) was confirmed by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ n.m.r. spectroscopy.‡ Similarly, reaction of (**1**) with $HC{\equiv}CCH_2CH_2OH$ (**2b**) in THF suspension gave *cis*-$[Rh(PMe_3)_4(H)(C{\equiv}CCH_2CH_2OH)]^+Cl^-$ (**3b**) in 98% yield.‡ The reaction is quite general and the complexes (**3c**—**h**) were prepared in high yield by this procedure. In certain cases, neutral *cis*-hydrido-acetylides (**4g** and **h**) were isolated by vacuum removal of solvent from the reaction filtrate. Although six-co-ordinate *cis*-hydrido acetylide complexes of iridium, analogous to (**4**) but containing PPh_3 ligands,[3] and five-co-ordinate complexes[4] such as $[Rh(PPr^i_3)_2Cl(H)(C{\equiv}CR)]$ have been reported, no structural details have appeared. To our knowledge, the only structurally characterized[5] mononuclear complex containing hydride and acetylide ligands is the square-planar Pt^{II} species *trans*-$[Pt(H)\{C{\equiv}C{-}C(OH)MeEt\}(PPh_3)_2]$; we therefore undertook an *X*-ray crystallographic study of one of our

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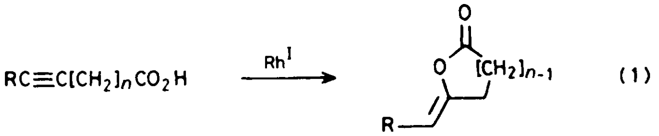
† If $[(cy_2PCH_2CH_2Pcy_2)RhCl]_2$ (cy = cyclohexyl) and $HC{\equiv}CCH_2CH_2CO_2D$ are used in CH_2Cl_2, reaction (2) is significantly faster than reaction (1).

‡ (**3a**): i.r. (Nujol) 1961s, 2135w, and 1745s cm^{-1}; ^1H n.m.r. (CD_2Cl_2) δ 14.3 (br s, CO_2H) and −10.53 (d quint, $^2J_{H\text{-}P(trans)} = 178$, $^2J_{H\text{-}P(cis)} = J_{H\text{-}Rh} = 18$ Hz, Rh-H); $^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2) −12.10 (dt, $J_{Rh\text{-}P} = 87$, $^2J_{P\text{-}P} = 28$ Hz, $2PMe_3$), −18.08 (dq, $J_{Rh\text{-}P} = 91$, $^2J_{P\text{-}P} = 28$ Hz, PMe_3 *trans* to $-C{\equiv}C$), and −28.99 p.p.m. (dq, $J_{Rh\text{-}P} = 77$, $^2J_{P\text{-}P} = 28$ Hz, PMe_3 *trans* to H); $^{13}C\{^1H\}$ n.m.r. (CD_3CN) δ 175.08 (s, CO_2H), 105.11 (d, $J_{C\text{-}P(trans)} = 31$ Hz, $RhC{\equiv}\mathit{C}$) and 87.50 (dm, $J_{C\text{-}P(trans)} = 112$ Hz, $Rh\mathit{C}{\equiv}C$).

(**3b**): i.r. (Nujol) 3246m, 2124w, and 1958m cm^{-1}; ^1H n.m.r. (D_2O) δ −10.61 (d quint, $J_{H\text{-}P(trans)} = 180$, $^2J_{H\text{-}P(cis)} = J_{H\text{-}Rh} = 16$ Hz, Rh–H); $^{31}P\{^1H\}$ n.m.r. (CD_3CN) −11.24 (dt, $J_{Rh\text{-}P} = 87$, $^2J_{P\text{-}P} = 28$ Hz, $2PMe_3$), −17.83 (dq, $J_{Rh\text{-}P} = 90$, $^2J_{P\text{-}P} = 28$ Hz, PMe_3 *trans* to $-C{\equiv}C$), and −28.89 p.p.m. (dq, $J_{Rh\text{-}P} = 76$, $^2J_{P\text{-}P} = 28$ Hz, PMe_3 *trans* to H); $^{13}C\{^1H\}$ n.m.r. (CD_3CN) δ 103.27 (dm, $J_{C\text{-}P(trans)} = 32$ Hz, $RhC{\equiv}\mathit{C}$) and 88.44 (ddtd, $^2J_{C\text{-}P(trans)} = 112$, $J_{C\text{-}Rh} = 35$, $^2J_{C\text{-}P(cis)} = 24$, 14 Hz, $Rh\mathit{C}{\equiv}C$).



$$RC{\equiv}CH + R'CO_2D \underset{}{\overset{Rh^I}{\rightleftharpoons}} RC{\equiv}CD + R'CO_2H \qquad (2)$$

cationic species. The molecular structure§ of (**3b**) (Figure 1) consists of a distorted octahedral arrangement of the four phosphines, the hydride, and the σ-acetylide ligand. The Rh(1)–C(1)–C(2) moiety is virtually linear [178.5(5)°], as is C(1)–C(2)–C(3) [173.4(3)°]. The two mutually *trans* PMe_3 groups are bent slightly over the plane defined by Rh(1), H(1), and C(1), with P(2)–Rh(1)–P(4) = 156.02(3)°. Interestingly, the *trans* influence of the acetylide ligand in (**3b**) is no greater than that of a PMe_3 group; *cf.* Rh(1)–P(3) = 2.3322(7) Å *vs.* Rh(1)–P(2), P(4) = 2.3353(8) Å (avg.). The hydride ligand exerts the strongest *trans* influence: Rh(1)–P(1) = 2.3966(8) Å. This structural *trans* influence order is maintained in solution as evidenced[6] by the values of $J_{Rh\text{-}P}$ which increase in the order P(1) = 76, P(2,4) = 87, P(3) = 90 Hz.

cis-$[Rh(PMe_3)_4(H)(C{\equiv}CR)]^+ Cl^-$
(**3**) **a**; R = $[CH_2]_2CO_2H$
b; R = $[CH_2]_2OH$
c; R = Ph
d; R = CH_2OMe
e; R = $CH_2CH_2O_2CH$
f; R = CMe_3
g; R = $SiMe_3$
h; R = H

mer-$[Rh(PMe_3)_3Cl(H)(C{\equiv}CR)]$
(**4**) **g**; R = $SiMe_3$
h; R = H

The C(1)–C(2) distance of 1.196(4) Å along with $\nu_{C\equiv C}$ of 2123 w cm^{-1} are typical for an alkyne triple bond,[7] indicating a lack of π-back-donation from Rh d orbitals to acetylide π* orbitals. The unambiguous identification of $\nu_{Rh\text{-}H}$ = 1958 m cm^{-1} was made possible by the fact that (**3b**) can be prepared in quantitative yield by reaction of (**1**) with (**2b**) in D_2O solution. The direct oxidative addition product (**3b**) containing Rh–H is formed; subsequent slow exchange of Rh–H for solvent deuterium gives [Rh-^{2}H]-(**3b**)which exhibits a new i.r. band at 1404 cm^{-1} along with a very weak band at 1958 cm^{-1} due to residual [Rh-^{1}H]-(**3b**). This result represents a novel C–H activation process in aqueous solution. It also demonstrates that the oxidative addition reaction does not involve deprotonation of H_2O (or D_2O) by (**1**) followed by deprotonation of alkyne by HO^-.

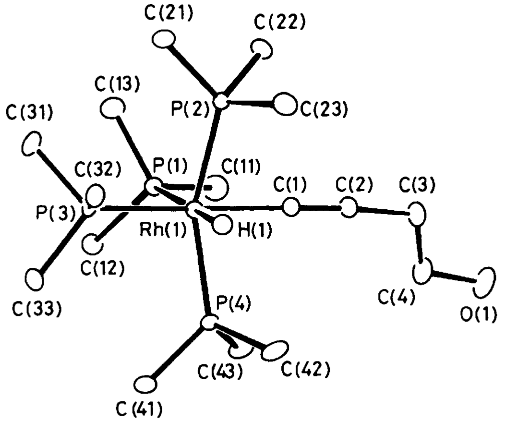


Figure 1. Molecular structure of (**3b**). Hydrogen atoms other than Rh*H* and the Cl^- counterion are omitted for clarity. Selected distances (Å) and angles (°): Rh(1)–P(1) 2.3966(8), Rh(1)–P(2) 2.3345(8), Rh(1)–P(3) 2.3322(7), Rh(1)–P(4) 2.3361(8), Rh(1)–H(1) 1.506(28), Rh(1)–C(1) 2.035(3), C(1)–C(2) 1.196(4); P(4)–Rh(1)–C(1) 80.69(8), P(2)–Rh(1)–C(1) 81.50(8), P(4)–Rh(1)–H(1) 80(1), P(2)–Rh(1)–H(1) 82(1), P(2)–Rh(1)–P(4) 156.02(3), P(3)–Rh(1)–C(1) 172.24(9), P(1)–Rh(1)–H(1) 176(1), Rh(1)–C(1)–C(2) 178.5(5), C(1)–C(2)–C(3) 173.4(3).

We believe that the Rh-catalysed C–H/O–D exchange [reaction (2)] may take place *via* a C–H oxidative addition reaction. Further labelling studies aimed at elucidating the intimate mechanism of alkyne C–H oxidative addition by (**1**) are in progress.

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§ *Crystal data*, collection and refinement for (**3b**): $RhClP_4OC_{16}H_{42}$, *M* = 512.77, monoclinic, space group, $P2_1/c$ (No. 14), *a* = 8.970(2), *b* = 14.603(2), *c* = 19.507(2) Å, β = 102.08(1)°, *T* = −65 °C, *U* = 2498.6 $Å^3$, *Z* = 4, D_c = 1.363 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 10.36 cm^{-1}, λ = 0.71069Å. From 6138 data collected on a CAD4 instrument ($4.7° \leqslant 2\theta \leqslant 55.0°$), 4440 absorption corrected reflections with $I \geqslant 3\sigma(I)$ were considered observed and used in the structure solution (Patterson) and refinement. The Rh-hydrogen atom was refined successfully; other hydrogen atoms were included in fixed positions. Final *R* = 0.027, R_w = 0.032; weights $\propto [\sigma^2(I) + 0.0009I^2]^{-\frac{1}{2}}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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