Synthesis of Hydrido-bis(acetylide) Complexes of Rhodium and the Molecular Structures of *mer-trans*-[Rh(PMe$_3$)$_3$(H)(C≡CPh)$_2$] and *mer-trans*-[{Rh(dmpe)(H)(C≡CSiMe$_3$)$_2$}$_2$(μ-dmpe)] (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$)

Pauline Chow, David Zargarian, Nicholas J. Taylor, and Todd B. Marder*

The Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Complexes of the form *mer-trans*-[Rh(PMe$_3$)$_3$(H)(C≡CR)$_2$] and *mer-trans*-[{Rh(dmpe)(H)(C≡CR)$_2$}$_2$(μ-dmpe)] have been prepared by oxidative addition of HC≡CR to [Rh(PMe$_3$)$_4$(C≡CR)] and [Rh(dmpe)$_2$Me] species, respectively; the molecular structures of *mer-trans*-[Rh(PMe$_3$)$_3$(H)(C≡CPh)$_2$] and *mer-trans*-[{Rh(dmpe)(H)(C≡CSiMe$_3$)$_2$}$_2$(μ-dmpe)] (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) have been determined by single crystal *X*-ray diffraction studies.

There is much current interest in the chemistry of hydrido-acetylide complexes of Rh and Ir. We recently reported[1] the synthesis of a series of complexes *cis*-[Rh(PMe$_3$)$_4$(H)-(C≡CR)]Cl (**1**) by oxidative addition of HC≡CR (**2**) to [Rh(PMe$_3$)$_4$]Cl (**3**) in either tetrahydrofuran (THF) suspension or H$_2$O solution. Related *cis*-hydrido-acetylide complexes of Rh and Ir containing two PR$_3$ ligands[2] or the tetradentate ligand[3] NP$_3$ [NP$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$] have also been reported. Werner *et al.*[2] observed the conversion of *cis*-hydrido-acetylides to vinylidene tautomers, and both we[4] and Bianchini *et al.*[3] have examined the deprotonation of cationic Rh^{III} *cis*-hydrido-acetylides to neutral Rh^{I} acetylides. Thus, deprotonation of (**1**) proceeded smoothly in deoxygenated aqueous KOH solutions, yielding trigonal bipyramidal [Rh(PMe$_3$)$_4$(C≡CR)] (**4**) complexes,[4] whereas[3] *cis*-[Rh(NP$_3$)-(H)(C≡CR)]$^+$ (**5**) gave [Rh(NP$_3$)(C≡CR)] (**6**) when treated with LiHBEt$_3$ or NaBH$_4$.

Complexes (**4**) are also formed from the stoicheiometric reaction of [Rh(PMe$_3$)$_4$Me] (**7**) with (**2**), as was reported[5] for the reaction of [Co(PMe$_3$)$_4$Me$_3$] with HC≡CPh, and the analogous complexes [Rh(dmpe)$_2$(C≡CR)] (**8**) [dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) are prepared[4] by stoicheiometric addition of (**2**) to [Rh(dmpe)$_2$Me$_3$] (**9**). The observation that (**6**; R = Ph) reacted with excess HC≡CCO$_2$Et yielding (**6**; R = CO$_2$Et) and HC≡CPh led to a proposal[3] of the intermediacy of an unobserved *fac-cis*-[Rh(NP$_3$)(H)(C≡CR)(C≡CR′)] complex, in which NP$_3$ functions as a tridentate ligand. A brief report in 1968 suggested[6] the formation of *trans-trans*-

cis-$[Rh(PMe_3)_4(H)(C{\equiv}CR)]Cl$
(1)

$HC{\equiv}CR$
(2)

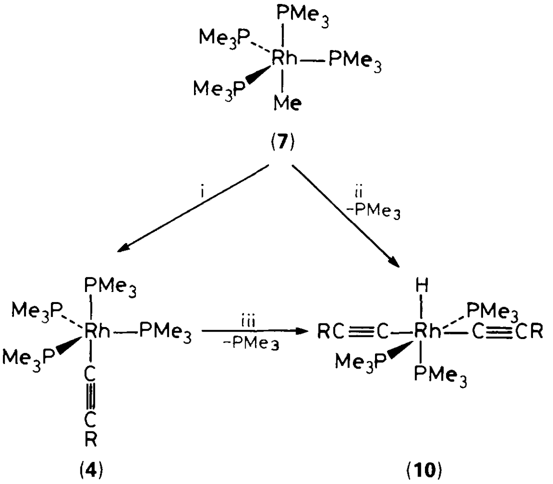
$[Rh(PMe_3)_4]Cl$
(3)

$[Rh(PMe_3)_4(C{\equiv}CR)]$
(4)

$[Rh(NP_3)(H)(C{\equiv}CR)]^+$
(5)

$[Rh(NP_3)(C{\equiv}CR)]$
(6)

a; R = CH_2OMe
b; R = Ph



a; R = CH_2OMe
b; R = Ph

Scheme 1. *Reagents*: i, $HC{\equiv}CR$ (1 equiv.); ii, $HC{\equiv}CR$ (excess); iii, $HC{\equiv}CR$ (1 equiv.).

$[Pt(PPh_3)_2(H)_2(C{\equiv}CC_6H_{10}OH)_2]$ from the reaction of $[Pt(PPh_3)_4]$ with ethyn-1-ylcyclohexanol. We report herein the synthesis and structures of the first fully characterised hydrido-bis(acetylide) complexes.

Upon reaction of our 5-co-ordinate PMe_3 complexes **(4)** with **(2)**, one PMe_3 ligand is lost and the stable complexes *mer-trans*-$[Rh(PMe_3)_3(H)(C{\equiv}CR)_2]$ **(10)**† can be isolated in high yield (Scheme 1). Two such species [R = CH_2OMe, **(10a)**; R = Ph, **(10b)**] have been structurally characterised by single crystal *X*-ray diffraction studies;‡ the latter is illustrated in Figure 1. The symmetric bis(acetylides) **(10)** are also formed when **(7)** is reacted with an excess of **(2)**. Interestingly, when **(9)** is treated with 4 equivs. of $HC{\equiv}CSiMe_3$, 0.5 equivs. of dmpe/Rh are lost and the novel dinuclear complex *mer-trans*-$[\{Rh(dmpe)(H)(C{\equiv}CSiMe_3)_2\}_2(\mu\text{-dmpe})]$ **(11)**† is formed in modest yield in addition to **(8)** (Scheme 2). The molecular structure‡ of **(11)** is illustrated in Figure 2, and the analogy to **(10)** is apparent.

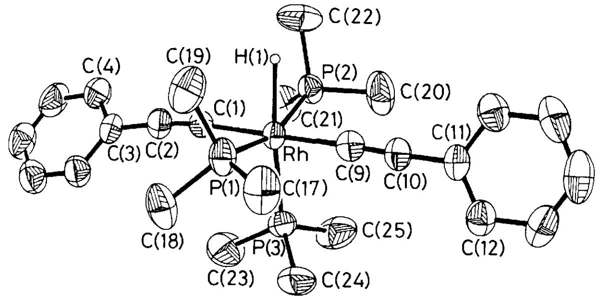


Figure 1. Molecular structure of **(10b)**. Hydrogen atoms, except for Rh–H, have been omitted for clarity. Selected distances (Å) and angles (°): Rh–P(1) 2.297(1), Rh–P(2) 2.298(1), Rh–P(3) 2.348(1), Rh–C(1) 2.019(4), Rh–C(9) 2.031(4), Rh–H(1) 1.90, C(1)–C(2) 1.204(6), C(2)–C(3) 1.439(6), C(9)–C(10) 1.213(6), C(10)–C(11) 1.440(6), P(1)–Rh–P(2) 161.43(3), P(1)–Rh–P(3) 98.26(4), P(1)–Rh–C(1) 85.8(1), P(1)–Rh–C(9) 92.0(1), P(1)–Rh–H(1) 87, P(2)–Rh–P(3) 99.61(4), P(2)–Rh–C(1) 88.3(1), P(2)–Rh–C(9) 92.7(1), P(2)–Rh–H(1) 76, P(3)–Rh–C(1) 93.0(1), P(3)–Rh–C(9) 87.9(1), P(3)–Rh–H(1) 174, C(1)–Rh–C(9) 178.6(2), C(1)–Rh–H(1) 91, C(9)–Rh–H(1) 88; Rh–C(1)–C(2) 173.9(2), C(1)–C(2)–C(3) 172.0(2), Rh–C(9)–C(10) 178.4(2), C(9)–C(10)–C(11) 178.3(3).

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† *Selected spectroscopic data* for **(10a)**: i.r. (hexane) 2105 s ($\nu_{C{\equiv}C}$), 1952 m cm^{-1} ($\nu_{Rh\text{–}H}$); $^{31}P\{^1H\}$ n.m.r. (hexane/C_6D_6, 298 K) δ − 6.34 (dd, $J_{Rh\text{–}P}$ 94, $^2J_{P\text{–}P}$ 26 Hz) and −24.4 p.p.m. (dt, $J_{Rh\text{–}P}$ 76, $^2J_{P\text{–}P}$ 26 Hz); ^1H n.m.r. (C_6D_6, 298 K) δ 4.33 (q, *J* 2.2 Hz, $\equiv C\text{–}CH_2$), 3.38 (s, OMe), 1.41 (vt, $^2J_{P\text{–}H}$ 3.4 Hz, 2 PMe_3), 1.17 (d, $^2J_{P\text{–}H}$ 7.2 Hz, 1 PMe_3), −9.30 (dq, $^2J_{P\mathit{trans}\text{-}H}$ 194.4, $^2J_{P\mathit{cis}\text{-}H}$ = $J_{Rh\text{–}H}$ 17.0 Hz, Rh–H).

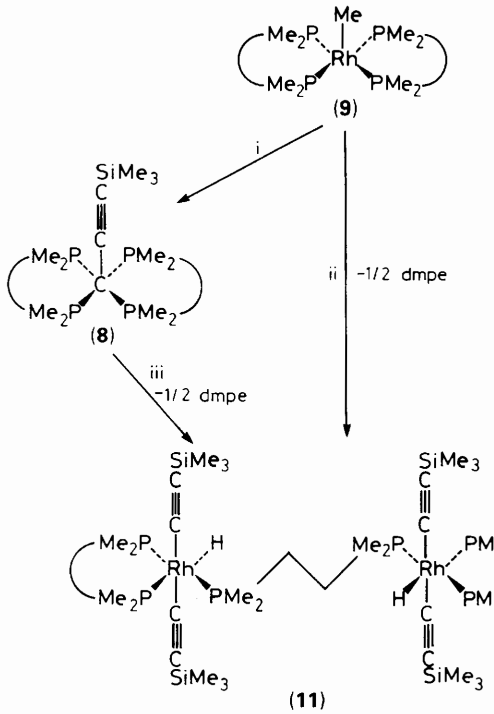
(10b): i.r. (hexane) 2097 s ($\nu_{C{\equiv}C}$), 1959 m ($\nu_{Rh\text{-}H}$), 1596 m cm^{-1} (Ph); $^{31}P\{^1H\}$ n.m.r. (hexane/C_6D_6, 298 K) δ − 6.50 (dd, $J_{Rh\text{–}P}$ 94, $^2J_{P\text{–}P}$ 26 Hz) and −24.4 p.p.m. (dt, $J_{Rh\text{–}P}$ 76, $^2J_{P\text{–}P}$ 26 Hz); ^1H n.m.r. (C_6D_6, 298 K) δ 7.52, 7.16, 7.03 (2 Ph), 1.46 (vt, $^2J_{P\text{–}H}$ 3.1 Hz, 2 PMe_3), 1.21 (d, $^2J_{P\text{–}H}$ 7.4 Hz, 1 PMe_3), −9.13 (dq, $^2J_{P\mathit{trans}\text{-}H}$ 193.4, $^2J_{P\mathit{cis}\text{-}H}$ = $J_{Rh\text{–}H}$ 17.0 Hz, Rh–H).

(11): i.r. (hexane) 2023 s ($\nu_{C{\equiv}C}$), 1913 m cm^{-1} ($\nu_{Rh\text{–}H}$). The $^{31}P\{^1H\}$ n.m.r. spectrum of **(11)** (C_6D_6, 298 K) displays three sets of resonances characteristic of an AA′DD′MM′XX′ 8 spin system. A detailed computer simulation of this complex spin system is in progress, the results of which will be reported in due course. ^1H n.m.r. (C_6D_6, 298 K) δ 1.30, 1.23 (m, dmpe), 0.29 (s, $SiMe_3$), −8.15 (dq, $^2J_{P\mathit{trans}\text{-}H}$ 189.9, $^2J_{P\mathit{cis}\text{-}H}$ = $J_{Rh\text{–}H}$ 16.0 Hz, Rh–H).

‡ *Crystal data* for **(10b)**: $RhP_3C_{25}H_{38}$, *M* = 534.408, monoclinic, space group $P2_1$, *a* = 9.071(1), *b* = 16.319(3), *c* = 9.380(1) Å, β = 97.27(1)°, *U* = 1377.4(3) Å^3, *Z* = 2, D_c = 1.288 g cm^{-3}, *F*(000) = 556, λ = 0.71073 Å, *T* = 294 ± 1 K, μ(Mo-K_α) = 7.86 cm^{-1}. Data were collected on a Syntex $P2_1$ diffractometer using an epoxy-coated crystal of dimensions 0.26 × 0.30 × 0.31 mm by the ω-scan method (2θ ≤ 50°). From 2537 unique measured data, the structure was solved by Patterson and Fourier methods using 2398 reflections with $I \geqslant 3\sigma(I)$. The structure was refined by full-matrix least-squares methods to *R* and R_w values of 0.021 and 0.025 respectively. All hydrogen atoms were located on a difference map and were refined isotropically except H(1), which had to be constrained. Refinement of the alternative enantiomorph resulted in minimal differences. The molecular structure of **(10a)** is similar and will be reported elsewhere.

For **(11)**: $Rh_2P_6Si_4C_{38}H_{86}\cdot C_6H_{14}$, *M* = 1133.285, monoclinic, space group $P2_1/c$, *a* = 10.100(1), *b* = 15.880(2), *c* = 20.831(3) Å, β = 100.75(1)°, *U* = 3282.6(6) Å^3, *Z* = 2, D_c = 1.146 g cm^{-3}, *F*(000) = 1200, λ = 0.71073 Å, *T* = 294 ± 1 K, μ(Mo-K_α) = 7.29 cm^{-1}. Data were collected on a Nicolet R3 diffractometer using an epoxy-coated crystal of dimensions of 0.27 × 0.28 × 0.28 mm by the ω-scan method (2θ ≤ 50°). From 5781 unique measured data, the structure was solved by Patterson and Fourier techniques using 4148 data with $I \geqslant 3\sigma(I)$. The structure was refined by full-matrix least-squares methods to *R* and R_w values of 0.047 and 0.056 respectively. A disordered solvent of crystallization (hexane) was found situated on a centre of inversion (0 1/2 0). Owing to the considerable thermal motion exhibited by the methyl groups, only the position of H(1) could be located with any certainty. This was not, however, included in the refinement.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 2. *Reagents*: i, $HC{\equiv}CSiMe_3$ (1 equiv.); ii, $HC{\equiv}CSiMe_3$ (excess); iii, $HC{\equiv}CSiMe_3$ (1 equiv.).

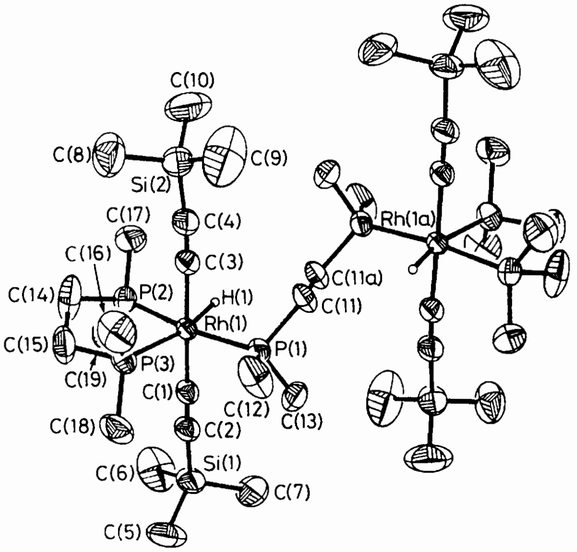


Figure 2. Molecular structure of (**11**). Hydrogen atoms, except for Rh–H, have been omitted for clarity. Selected distances (Å) and angles (°): Rh(1)–P(1) 2.295(1), Rh(1)–P(2) 2.277(2), Rh(1)–P(3) 2.346(2), Rh(1)–C(1) 2.023(6), Rh(1)–C(3) 2.031(6), C(1)–C(2) 1.200(9), C(3)–C(4) 1.203(9), C(2)–Si(1) 1.810(7), C(4)–Si(2) 1.797(7), P(1)–Rh(1)–P(2) 170.9(1), P(1)–Rh(1)–P(3) 103.2(1), P(1)–Rh(1)–C(1) 90.1(2), P(1)–Rh(1)–C(3) 89.2(2), P(2)–Rh(1)–P(3) 85.5(1), P(2)–Rh(1)–C(1) 92.4(2), P(2)–Rh(1)–C(3) 88.2(2), P(3)–Rh(1)–C(1) 91.1(2), P(3)–Rh(1)–C(3) 89.8(2), Rh(1)–C(1)–C(2) 178.1(6), Rh(1)–C(3)–C(4) 176.9(5), C(1)–C(2)–Si(1) 175.3(6), C(3)–C(4)–Si(2) 174.6(6).

The stepwise incorporation of two acetylide moieties in a *trans* disposition is important as it should allow the design of highly conjugated linear complexes incorporating different electronic properties at the two ends, and thus intramolecular charge-transfer transitions. Such complexes are of interest owing to their potential to exhibit large second-order optical non-linearities[7] (χ^2). It should also be noted[7] that non-zero values of χ^3 can be obtained for symmetric systems exhibiting significant π electron delocalisation. Frazier *et al.* have recently reported[8] measurements of χ^3 for the palladium poly-yne $[-Pd(PBu_3)_2C{\equiv}CC_6H_4C{\equiv}C-]_n$ which are encouraging. We have therefore begun[9] a systematic investigation of several aspects of transition metal acetylide chemistry including preparation of symmetric and unsymmetric *trans*-bis(acetylide) complexes bearing strong π-donor and π-acceptor substituents, and related complexes with $C{\equiv}C{-}C{\equiv}CR$ moieties, and measurements of their non-linear optical properties.

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