Synthesis and Molecular Structures of a Rhoda-lactone and its Alkylation Product; Insertion of a Pendant Alkyne into a Rhodium–Hydrogen Bond

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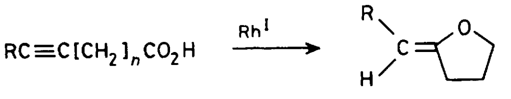
Reaction of $[(PMe_3)_3RhCl]$ with pent-4-ynoic acid yields the novel exocyclic methylene-substituted rhoda-lactone $[(PMe_3)_3Cl\overline{Rh{-}C(=CH_2)CH_2CH_2C(=O)O}]$, which reacts with $Me_3O^+BF_4^-$ to give $[(PMe_3)_3Cl\overline{\overset{+}{Rh}{-}C(=CH_2)CH_2CH_2C(OMe)=O}]BF_4$; both complexes have been structurally characterized.

Intramolecular insertion of a pendant carbon–carbon multiple bond into a metal hydride has been proposed as an important step in several catalytic reactions including the Rh^I-catalysed cyclization of a pent-4-enal to cyclopentanone.[1] Related insertions of 'pendant' alkenes appear to be involved in the asymmetric hydrogenation of prochiral alkenes containing co-ordinating functional groups, wherein hydrido-alkyl complexes have been observed by low temperature n.m.r. spectroscopy.[2] However, few such insertion products have been isolated.

During our investigations of the rhodium-catalysed cyclization of alkynoic acids to alkylidene lactones[3] [reaction (1)] we have investigated the stoicheiometric reaction of pent-4-ynoic acid (**1a**) with the basic 16-electron complex $(PMe_3)_3RhCl$ (**2**).[4] Addition of a slight excess of (**1a**) to (**2**) in tetrahydrofuran (THF) yields the exocyclic methylene-substituted rhoda-lactone[5] complex (**3**), which has been characterized by i.r. and ^1H, $^{13}C\{^1H\}$, ^{13}C, and $^{31}P\{^1H\}$ n.m.r. spectroscopy‡ and by single crystal *X*-ray diffraction.§ The complex (**3**) is precipitated from the reaction solution as a white powder in *ca.* 70% yield. We believe that (**3**) is formed *via* initial activation of the carboxylate O–H group giving a Rh^{III} hydrido-carboxylate species. This proposal is supported by our isolation and structural characterization of an analogous Ir^{III} hydrido-carboxylate complex.[3b] The Rh^{III} complex then undergoes insertion of the pendant alkyne moiety into the Rh–H bond, a process which proceeds in a regiospecific manner forming the six-membered chelate ring with an exocyclic methylene group (Scheme 1). The CO stretching absorption at 1608 cm^{-1} in the i.r. spectrum (Nujol) indicates a chelated monodentate carboxylate group, and a band at 1584 cm^{-1} is assigned to $C=CH_2$ stretching. The $^{13}C\{^1H\}$ n.m.r. spectrum (CD_2Cl_2) shows a singlet at δ 177.08 for the CO_2 group, a doublet of quartets at δ 161.45 ($J_{Rh\text{-}C}$ 29, $^2J_{P\text{-}C}$ 8 Hz) for Rh–C_α, and an apparent doublet of triplets at δ 116.18 (*J* 3 and 9 Hz) for the $=CH_2$ group [$J_{C\text{-}H(a)} = J_{C\text{-}H(b)} = 152$ Hz]. The structure (Figure 1) was confirmed by *X*-ray diffraction.



(1)

(**1**)**a**; $n = 2$, R = H
b; $n = 2$, R = Me
c; $n = 2$, R = Ph
d; $n = 3$, R = H

(**4a**–**d**)

Attempts to confirm the presumed *cis*-stereochemistry of the alkyne insertion reaction (see later) have thus far proved unsuccessful. Thus, reaction of pent-4-ynoic [^{2}H]acid with (**2**) yields (**3**) in which the deuterium atom is equally distributed between the two exocyclic methylene positions. We have found that certain Rh^I complexes are active catalysts for the rapid exchange of acetylenic hydrogen with carboxy protons, a process which scrambles the two hydrogen sites in question prior to alkyne insertion.[6] In addition, reactions of the analogues (**1b** and **c**) with (**2**) give white precipitates which have thus far eluded complete characterization owing to their unusually limited solubility in aprotic solvents. For the phenyl compound, the CO stretching absorption at 1586 cm^{-1} is indicative of a rhoda-lactone structure.

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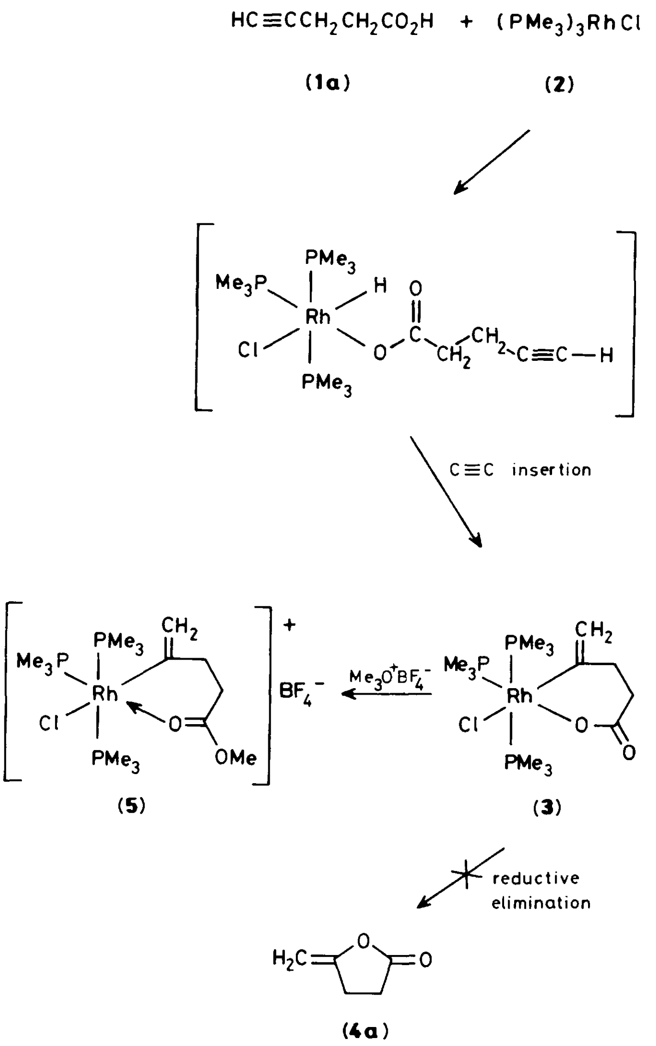
‡ *Spectroscopic data* for (**3**): i.r. (KBr) ν_{max} 1608(s) and 1584m, sh cm^{-1}; $^{31}P\{^1H\}$ n.m.r. (121.69 MHz; CD_2Cl_2) δ 5.48 (dt, $J_{Rh\text{-}P}$ 133, $^2J_{P\text{-}P}$ 36 Hz) and −4.45 (dd, $J_{Rh\text{-}P}$ 93, $^2J_{P\text{-}P}$ 36 Hz); $^{13}C\{^1H\}$ n.m.r. (79.59 MHz; CD_2Cl_2) δ 177.08 (s, $-CO_2-$), 161.45 (dq, $J_{Rh\text{-}C}$ 29, $^2J_{P\text{-}C}$ 8 Hz, Rh–C_α), 116.18 (dt, $^2J_{P\text{-}C}$ 3, $J_{Rh\text{-}C \text{ or } P\text{-}C}$ 9 Hz, $=CH_2$), 43.19 (s, CH_2), 38.42 (s, CH_2), 19.05 (d, $J_{P\text{-}C}$ 35 Hz, 1 PMe_3), and 14.26 (t, $J_{P\text{-}C}$ 16 Hz, 2 PMe_3); ^{13}C n.m.r. (as above) δ 116.18 (t, $J_{C\text{-}H}$ 152 Hz), 43.19 (t, $J_{C\text{-}H}$ 125 Hz), and 38.42 (t, $J_{C\text{-}H}$ 127 Hz); ^1H n.m.r. (360 MHz; CD_2Cl_2) δ 5.28 (br. d, *J* 7.0 Hz, 1H, vinyl), 4.37 (m, 1H, vinyl), 2.15—2.10 (m, 2H, CH_2CH_2), 2.07—2.04 (m, 2H, CH_2CH_2), 1.57 (d, $^2J_{P\text{-}H}$ 9.8 Hz, 9H, PMe_3), and 1.42 (t, *J* 3.5 Hz, 18H, 2 PMe_3).

For (**5**): i.r. (KBr) ν_{max} 1664 s and 1585 m cm^{-1}; $^{31}P\{^1H\}$ n.m.r. (121.69 MHz; CD_2Cl_2) δ 18.14 (dt, $J_{Rh\text{-}P}$ 147, $^2J_{P\text{-}P}$ 35 Hz) and −6.54 (dd, $J_{Rh\text{-}P}$ 95, $^2J_{P\text{-}P}$ 35 Hz); $^{13}C\{^1H\}$ n.m.r. (75.59 MHz; CD_2Cl_2) δ 182.32 (br. d, *J* 2 Hz, $-CO_2-$), 156.61 (dq, $J_{Rh\text{-}C}$ 28, $^2J_{P\text{-}C}$ 8 Hz, Rh–C_α), 120.87 (m, $=CH_2$), 55.34 (s, OCH_3), 39.51 (s, CH_2), 34.52 (s, CH_2), 19.33 (d, $J_{P\text{-}C}$ 39 Hz, 1 PMe_3), and 14.37 (t, $J_{P\text{-}C}$ 16 Hz, 2 PMe_3); ^1H n.m.r. (360 MHz; CD_2Cl_2) δ 5.56 (br. d, *J* 6.6 Hz, 1H, vinyl), 4.66 (br. d, *J* 3.4 Hz, 1H, vinyl), 3.94 (s, 1H, OCH_3), 2.58—2.55 (m, 2H, CH_2), 2.31—2.28 (m, 2H, CH_2), 1.75 (d, $^2J_{P\text{-}H}$ 10.6 Hz, 9H, PMe_3), and 1.52 (t, $J_{P\text{-}H}$ 3.5 Hz, 18H, 2 PMe_3).

§ *Crystal data* for (**3**)·CH_2Cl_2: $RhCl_3P_3O_2C_{15}H_{35}$, monoclinic, $P2_1/n$ (No. 14), $a = 13.696(8)$, $b = 14.996(5)$, $c = 11.807(9)$ Å, $\beta = 99.99(6)°$, $T = -67$ °C, $U = 2388$ Å^3, $Z = 4$, μ(Mo) = 12.48 cm^{-1}; Enraf-Nonius CAD4, Mo-K_α radiation; 5997 data collected using ω scan method, $4.0° \leqslant 2\theta \leqslant 55.0°$; 3776 unique reflections, corrected for absorption (DIFABS), with $I \geqslant 3.0\sigma(I)$ used in solution and refinement; solution by direct methods (MULTAN), refinement by full-matrix least-squares technique, weights $\propto[\sigma^2(I) + 0.0009I^2]^{-\frac{1}{2}}$, 218 parameters, all non-H atoms anisotropic, H atoms fixed, $R = 0.036$, $R_w = 0.038$.

For (**5**): $RhClP_3F_4O_2BC_{15}H_{36}$ orthorhombic, $P2_12_12_1$ (No. 19), $a = 13.117(2)$, $b = 17.935(2)$, $c = 10.220(1)$ Å, $T = 0$ °C, $U = 2404.3$ Å^3, $Z = 4$, μ(Mo) = 10.46 cm^{-1}; Syntex R3, Mo-K_α radiation; 3177 data collected using ω scan method, $4.6° \leqslant 2\theta \leqslant 55.0°$, 2797 unique reflections, corrected for absorption (DIFABS), with $I \geqslant 3.0\ \sigma(I)$ used in solution and refinement; solution by direct methods (MULTAN), refinement by full-matrix least-squares technique, weights $\propto[\sigma^2(I) + 0.0009I^2]^{-\frac{1}{2}}$, 244 parameters, all non-H atoms anisotropic, H atoms fixed, $R = 0.025$, $R_w = 0.028$.

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 1

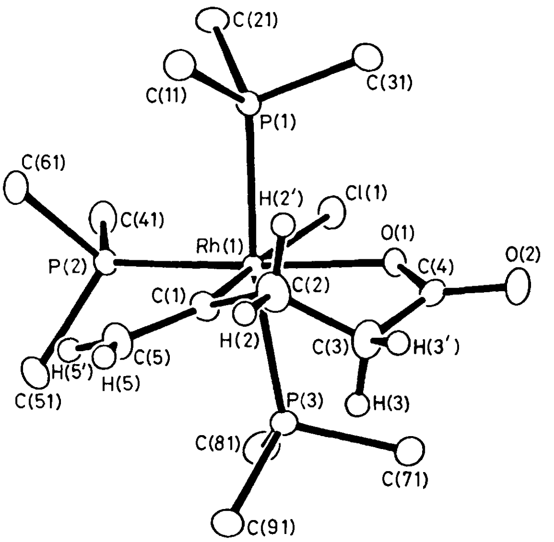


Figure 1. ORTEP drawing of a molecule of (**3**). Selected bond distances (Å) and angles (°): Rh(1)–P(1) 2.350(1); Rh(1)–P(2) 2.270(2); Rh(1)–P(3) 2.348(1); Rh(1)–O(1) 2.108(3); Rh(1)–C(1) 2.043(4); O(1)–C(4) 1.278(5); O(2)–C(4) 1.237(5); C(1)–C(2) 1.513(6); C(1)–C(5) 1.312(6); O(1)–Rh(1)–C(1) 91.2(1); Rh(1)–O(1)–C(4) 132.6(3); Rh(1)–C(1)–C(2) 114.8(3); Rh(1)–C(1)–C(5) 130.0(3).

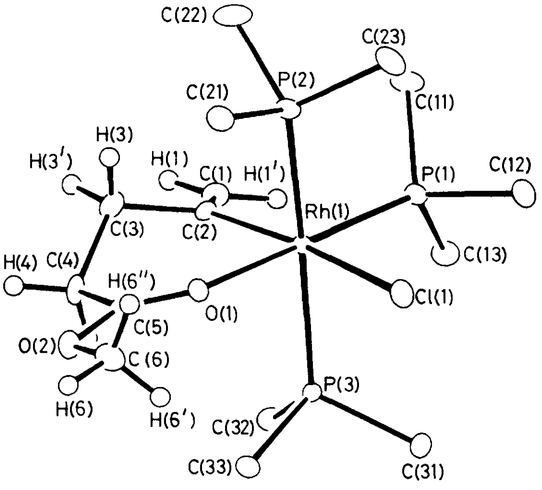


Figure 2. ORTEP drawing of a molecule of (**5**). Selected bond distances (Å) and angles (°): Rh(1)–P(1) 2.260(1); Rh(1)–P(2) 2.359(1); Rh(1)–P(3) 2.370(1); Rh(1)–O(1) 2.171(3); Rh(1)–C(2) 2.053(4); O(1)–C(5) 1.220(5); O(2)–C(5) 1.328(5); O(2)–C(6) 1.459(5); C(1)–C(2) 1.318(6) C(2)–C(3) 1.514(6); Rh(1)–C(2)–C(1) 128.8(3); Rh(1)–C(2)–C(3) 114.3(3); Rh(1)–O(1)–C(5) 128.2(3); O(1)–C(5)–C(4) 125.1(4).

The complex (**3**) is extremely stable (*e.g.* solutions prepared in air show no evidence of decomposition) and all attempts to induce reductive elimination of the C–O bond to yield (**4a**) have failed. This observation and the fact that lactones arise exclusively from *trans*-addition of O–H to C=C in our catalytic systems[3a] lead us to believe that species such as (**3**) are not directly involved in the catalytic cycle[3b] for reaction (1). Although examples of mononuclear σ-alkenyl complexes arising from net *trans* insertion of activated alkynes into M–H bonds exist,[7] in general, the alkyne insertion reaction is believed[8] to occur in a *cis*-fashion analogous to that found for alkene insertions.

The complex (**3**) reacts cleanly with $Me_3O^+BF_4^-$ *via* alkylation at the carbonyl oxygen yielding the cationic complex (**5**) in high yield.† The CO stretching band at 1664 cm^{-1} (KBr) is shifted to higher frequency than in (**3**), compatible with a co-ordinated ester function,[9] whereas the $C{=}CH_2$ stretching band (1585 cm^{-1}) is unchanged. The $^{13}C\{^1H\}$ n.m.r. spectrum (CD_2Cl_2) shows a broad doublet at δ 182.32 (J 2 Hz) for the carbonyl group, a doublet of quartets at δ 156.61 (J_{Rh-C} 28, $^2J_{P-C}$ 8 Hz) for Rh–C_α, and a multiplet at δ 120.87 for the $=CH_2$ group. A singlet at δ 55.34 is assigned to OMe. The molecular structure‡ of (**5**) is shown in Figure 2.

The structures of (**3**) and (**5**) allow direct comparison of co-ordinated carboxylate and ester functions. The Rh–O(1) bond in (**3**) [2.108(3) Å] is significantly shorter than Rh–O(1) in (**5**) [2.171(3) Å], whereas C(4)–O(1) in (**3**) [1.278(5) Å] is longer than C(5)–O(1) in (**5**) [1.220(5) Å]; the C(4)–O(2) double bond in (**3**) [1.237(5) Å] is much shorter than the C(5)–O(2) single bond in (**5**) [1.328(5) Å]. These differences are consistent with the valence bond representations in Scheme 1. The Rh–C_α distances [Rh–C(1) in (**3**) is 2.043(4) Å and Rh–C(2) in (**5**) is 2.053(4) Å] are quite similar. As expected, the longer Rh–O bond in (**5**) *vs.* (**3**) allows for displacement of the co-ordinated ester function by nucleophiles such as PMe_3, as indicated by *in situ* ^1H and ^{31}P n.m.r. spectroscopy.

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