New rhodacyclopentane with phenylvinylidene substituents, *mer*-[$\overline{\mathrm{Rh}\{\mathrm{CH_2C({=}CHPh)C({=}CHPh)CH}}_2\}\mathrm{Cl(PMe_3)_3}$]. Structure and formation through concerted cycloaddition of phenylallene molecules to [$\mathrm{RhCl(PMe_3)_3}$]

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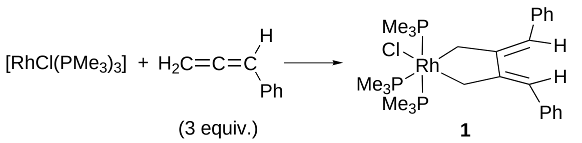
[$\mathrm{RhCl(PMe_3)_3}$] reacts with an excess of phenylallene to give a new rhodacyclopentane, *mer*-[$\mathrm{Rh\{CH_2C({=}CHPh)C({=}CHPh)CH_2\}Cl(PMe_3)_3}$] 1, which is not obtained *via* the reaction of [$\mathrm{RhCl(\eta^2\text{-}CH_2{=}C{=}CHPh)(PMe_3)_3}$] 2 with phenylallene.

Several complexes of Ti, Ta, Co, Ir and Ni have been reported to undergo addition of two alkene molecules to give the corresponding saturated metallacyclopentanes.[1] Similar formation of metallacycles from the 2 : 1 reaction of allene and transition-metal complexes is much less common,[2] while the reaction is involved as a crucial step in cyclooligomerization of allene or substituted allene promoted by metal complexes.[3] Chlororhodium(I) complexes catalyze polymerization[4] or cyclooligomerization[5] of 1,2-dienes depending on the ligands bonded to the Rh center. Formation of a rhodacyclopentane from allene would be intriguing in relation to the the mechanism of the above cyclooligomerization of the 1,2-dienes catalyzed by Rh complexes. Here, we report the addition of phenylallene to [$\mathrm{RhCl(PMe_3)_3}$], to give a novel rhodacyclopentane which is structurally characterized.

[$\mathrm{RhCl(PMe_3)_3}$] reacts with 3 equiv. of phenylallene to give *mer*-[$\mathrm{Rh\{CH_2C({=}CHPh)C({=}CHPh)CH_2\}Cl(PMe_3)_3}$] **1** as shown in eqn. (1).†



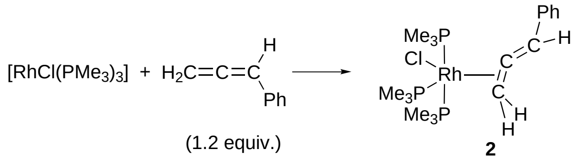
1

(1)

The reaction mixture does not contain any other rhodacyclopentanes that would be formed through addition of phenylallene in a different orientation of the double bonds. Fig. 1 shows the molecular structure of **1** which has an octahedral coordination around the Rh center with three $\mathrm{PMe_3}$ ligands at meridional coordination sites.‡ Three C–C bond distances in the five-membered chelate ring are quite similar, while the Rh–C(1) bond [2.16(1) Å] is longer than the Rh–C(10) bond [2.061(1) Å] owing to a larger *trans* influence of $\mathrm{PMe_3}$ relative to Cl. The C–C bond distances [1.49(2) Å] are significantly longer than the corresponding bond of the platinacyclopentane prepared from dimerization of cycloheptatetraene in the presence of a platinum(0) complex.[2b] Both of the two C=C double bonds in **1** have *Z* structure owing to less steric congestion around the *s-cis* diene moiety than the other possible geometry of the double bonds.

The $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum gives rise to signals due to the $\mathrm{CH_2}$ carbons at δ 22.26 and 13.21. The former peak, with a large *J*(CP) value (77 Hz), is assigned to the carbon bonded *trans* to $\mathrm{PMe_3}$ and the latter to carbon *trans* to Cl. Two ^{1}H NMR signals due to the $\mathrm{CH_2}$ hydrogens are observed at δ 3.02 and 2.11, which are assigned to the $\mathrm{CH_2}$ group *trans* to $\mathrm{PMe_3}$ and *trans* to Cl, respectively, based on the ^{1}H–^{13}C COSY spectrum. The other ^{1}H and ^{13}C NMR signals as well as the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum are in accord with the structure obtained by X-ray crystallography.

Reaction of a reduced amount of phenylallene with [$\mathrm{RhCl(PMe_3)_3}$] has been examined in order to obtain an insight for the pathway of reaction (1). Reaction in a 1.2 : 1 ratio in hexane results in the formation of [$\mathrm{RhCl(\eta^2\text{-}CH_2{=}C{=}CHPh)(PMe_3)_3}$] **2** which is isolated as the hexane insoluble product.§



2

(2)

Fig. 2 shows the molecular structure of **2** which shows a trigonal-bipyramidal coordination around the Rh centre with P(1) and P(3) at the apical positions.‡ Elongation of the π-coordinated C=C double bond [$\mathrm{CH_2{=}C}$ 1.406(9), C=CHPh

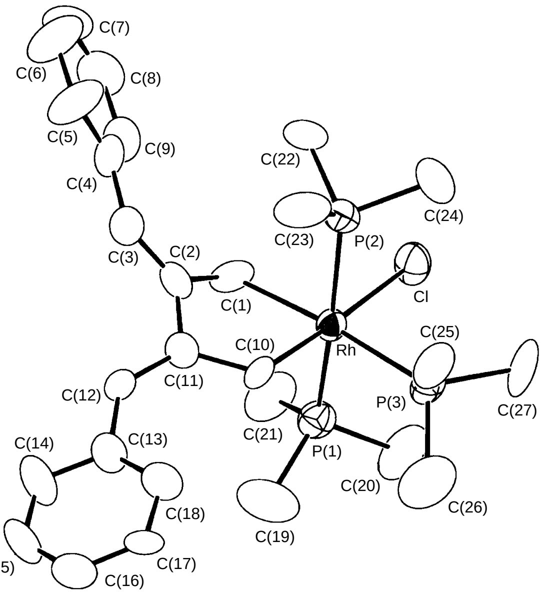


Fig. 1 ORTEP drawing of **1** at 30% probability level. Selected bond distances (Å) and angles (°): Rh–Cl 2.503(3), Rh–P(1) 2.331(5), Rh–P(2) 2.326(4), Rh–P(3) 2.368(3), Rh–C(1) 2.16(1), Rh–C(10) 2.06(1), C(1)–C(2) 1.49(2), C(2)–C(3) 1.38(2), C(2)–C(11) 1.49(2), C(10)–C(11) 1.49(2), C(11)–C(12) 1.35(2); Cl–Rh–P(1) 86.9(1), Cl–Rh–P(2) 85.5(1), Cl–Rh–P(3) 95.8(1), Cl–Rh–C(1) 94.3(4), Cl–Rh–C(10) 176.3(3), P(1)–Rh–P(2) 168.9(1), P(2)–Rh–P(3) 94.6(2), P(1)–Rh–P(3) 94.1(2), P(1)–Rh–C(1) 88.4(4), P(1)–Rh–C(10) 92.7(4), P(2)–Rh–C(1) 84.1(4), P(2)–Rh–C(10) 94.3(4), P(3)–Rh–C(1) 169.6(4), P(3)–Rh–C(10) 87.8(3), C(1)–Rh–C(10) 82.0(5), Rh–C(1)–C(2) 107.6(9), C(1)–C(2)–C(3) 125(1), C(1)–C(2)–C(11) 111(1), C(11)–C(2)–C(3) 122(1), Rh–C(10)–C(11) 112.6(8), C(10)–C(11)–C(12) 128(1), C(2)–C(11)–C(10) 112(1), C(2)–C(11)–C(12) 119(1).

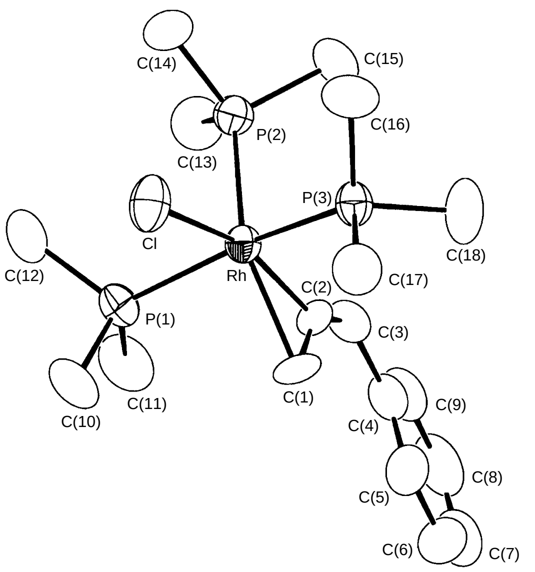
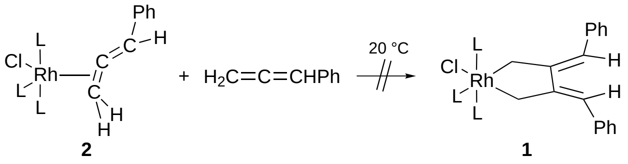


Fig. 2 ORTEP drawing of **2** at 50% probability level. Selected bond distances (Å) and angles (°): Rh–Cl 2.540(2), Rh–P(1) 2.320(2), Rh–P(2) 2.323(2), Rh–P(3) 2.325(2), Rh–C(1) 2.126(7), Rh–C(2) 1.988(6), C(1)–C(2) 1.406(9), C(2)–C(3) 1.353(9); Cl–Rh–P(1) 84.79(7), Cl–Rh–P(2) 97.80(7), Cl–Rh–P(3) 83.36(7), Cl–Rh–C(1) 118.3(2), Cl–Rh–C(2) 158.0(2), C(1)–Rh–C(2) 39.8(3), P(1)–Rh–P(2) 96.74(7), P(2)–Rh–P(3) 96.94(7), P(1)–Rh–P(3) 162.98(7), C(1)–C(2)–C(3) 142.1(7).



Scheme 1

1.353(9) Å] as well as a bend of the cumulated double bonds [C(1)–C(2)–C(3) 142.1(7)°] indicate the presence of significant back-donation from the Rh center to the phenylallene ligand. The ^{1}H NMR spectrum of **2** above 25 °C shows partial liberation of a PMe$_3$ ligand to afford a square-planar rhodium(I) complex [Rh(η^2-CH$_2$=C=CHPh)Cl(PMe$_3$)$_2$] **3** which is isolated from the mixture and characterized by X-ray crystallography.¶

Reaction of **2** and phenylallene in a 1 : 2 molar ratio in toluene for 8 h at 20 °C does not give **1** but causes quantitative recovery of **2** as shown in Scheme 1.

The results are in contrast with previous reports indicating that several transition-metal complexes containing π-coordinated alkenes react further with alkenes to give the corresponding metallacyclopentane.[1d,f,g] The present study has disclosed that the π-coordinated phenylallene complex **2**, with an 18 electron Rh center, is not a precursor of the metallacycle **1** in reaction (1) and that formation of **1** proceeds through direct cycloaddition of two phenylallene molecules to [RhCl(PMe$_3$)$_3$].

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Footnotes

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† To a toluene (8 ml) solution of [RhCl(PMe$_3$)$_3$] (158 mg, 0.43 mmol) was added phenylallene (150 mg, 1.3 mmol) at room temp. The initial pale yellow solution gradually turned pale brown accompanied by deposition of an off-white solid which was collected by filtration after the reaction for 8 h, and dried *in vacuo* to give **1** (203 mg, 79%).

‡ *Crystal data*: for **1**: $C_{27}H_{43}ClP_3Rh$, M_r = 598.92, orthorhombic, space group *Pbca* (no. 61), a = 35.023(6), b = 13.823(3), c = 12.155(2) Å, U = 5884 Å^3, Z = 8, D_c = 1.353 g cm^{-3}, μ(Mo-Kα) = 8.37 cm^{-1} (graphite-monochromated radiation, λ = 0.71069 Å), F(000) = 2496. The data collection was made on a Rigaku AFC5R diffractometer at ambient temperature (293 K) using ω scan mode for Lorentz and polarization effects. An empirical absorption correction (ψ scan) was applied. Of the unique 5877 reflections with $2\theta \leqslant 55°$, 1959 reflections with $I > 3\,\sigma(I)$ were used in the refinement. A total of 289 parameters (non-hydrogen atoms modelled anisotropically) were refined with $w = [\sigma(F_o)]^{-2}$. Hydrogen atoms were placed in idealised geometries and included in the structure calculation without refinement of the parameters. The structure converged to R = 0.054 and R_w = 0.044. For **2**: $C_{18}H_{35}ClP_3Rh$, M_r = 482.75, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 12.926(2), b = 15.979(2), c = 11.307(3) Å, U = 2336 Å^3, Z = 4, D_c = 1.373 g cm^{-3}, μ(Mo-Kα) = 10.36 cm^{-1} (graphite-monochromated radiation, λ = 0.71069 Å), F(000) = 1000. The data collection and absorption correction were carried out similarly to **1**. Of the unique 2528 reflections with $2\theta \leqslant 55°$, 2066 reflections with $I > 3\sigma(I)$ were used in the refinement. A total of 208 parameters were refined with $w = [\sigma(F_o)]^{-2}$ and the structure converged to R = 0.038 and R_w = 0.029. Treatment of hydrogen atoms is similar to **1**. CCDC 182/513.

§ To a hexane (8 ml) dispersion of [RhCl(PMe$_3$)$_3$] (115 mg, 0.31 mmol) was added phenylallene (44 mg, 0.38 mmol) at room temp. Stirring the mixture for 26 h led to separation of a yellow solid which was collected by filtration and dried *in vacuo*. Recrystallization from thf–hexane afforded **2** as yellow crystals (85 mg, 57%).

¶ Dissociation of PMe$_3$ from **2** is not thermodynamically favoured. The equilibrium constant for **2** = **3** + PMe$_3$ is 5.1×10^{-4} l mol^{-1} even at 60 °C and is probably much smaller near 25 °C although precise measurement of the equilibrium constant was not feasible. Crystallographic results of **3** which show a square-planar coordination around the Rh center will be reported separately.

References

1 (*a*) A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White and J. A. Osborn, *J. Am. Chem. Soc.*, 1973, **95**, 597; (*b*) J. X. McDermott, M. E. Wilson and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6529; (*c*) R. H. Grubbs and A. Miyashita, *J. Organomet. Chem.*, 1978, **161**, 371; (*d*) S. J. McLain, C. D. Wood and R. R. Schrock, *J. Am. Chem. Soc.*, 1979, **101**, 4558; (*e*) S. A. Cohen, P. R. Auburn and J. E. Bercaw, *J. Am. Chem. Soc.*, 1983, **105**, 1136; (*f*) P. Binger, T. R. Martin, R. Benn, A. Rufinska and G. Schroth, *Z. Naturforsch. Teil B*, 1984, **39**, 993; (*g*) K. Mashima and H. Takaya, *Organometallics*, 1985, **4**, 1464.

2 (*a*) G. K. Barker, M. Green, J. A. K. Howard, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1978, 1839; (*b*) W. R. Winchester, M. Gawron, G. J. Palenik and W. M. Jones, *Organometallics*, 1985, **4**, 1894.

3 D. J. Pasto, N.-Z. Huang and C. W. Eigenbrot, *J. Am. Chem. Soc.*, 1985, **107**, 3160.

4 S. Otsuka and A. Nakamura, *J. Polym. Sci., Part B: Polym. Lett. Ed.*, 1967, **5**, 973; J. P. Scholten and H. J. van der Ploeg, *J. Polym. Sci., Polym. Chem. Ed.*, 1972, **10**, 3067; J. P. Scholten and H. J. van der Ploeg, *J. Polym. Sci., Polym. Chem. Ed.*, 1973, **11**, 3205; J. Leland, J. Boucher and K. Anderson, *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15**, 2785.

5 F. N. Jones and R. V. Lindsey, *J. Org. Chem.*, 1968, **33**, 3838; S. Otsuka, A. Nakamura and H. Minamida, *Chem. Commun.*, 1969, 191; J. P. Scholten and H. J. van der Ploeg, *Tetrahedron Lett.*, 1972, 1685.

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