

Syntheses, solution and solid state $^{31}\text{P}\{^1\text{H}\}$ NMR studies, of the first symmetrically-bridging μ -perpendicular phosphalkyne dirhodium(I) complexes $[\text{Rh}_2\text{X}_2(\mu\text{-dppm})_2(\mu\text{-RCP})]$ ($\text{R} = \text{}^t\text{Bu}, \text{Ad}; \text{X} = \text{Cl or Br}$)

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Abstract

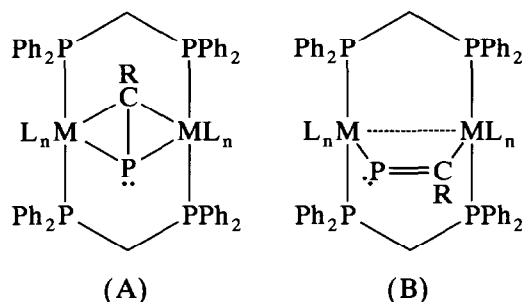
The first examples of symmetrically bridging μ -perpendicular phosphalkyne complexes are reported. Their structures have been established by solution and solid state $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Key words: Phosphorus; Rhodium; Alkyne; Nuclear magnetic resonance

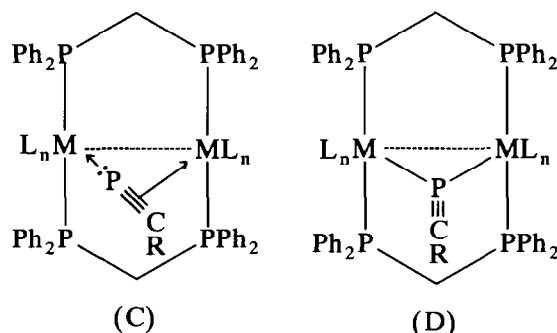
1. Introduction

The chemistry of bimetallic systems bridged by bis(diphenylphosphino)methane (dppm, $\text{Ph}_2\text{PCH}_2\text{-PPh}_2$), including the so-called "A-frame" complexes has developed rapidly in recent years [1,2].

Of particular interest in connection with the work described in this paper is the interaction of these dinuclear A-frame complexes with alkynes, which affords *cis*-dimetallated alkyne complexes, in which the alkyne molecule lies either in a perpendicular bridging mode [3–6] or parallel to the metal–metal axis.



It was of interest to investigate analogous reactions of the A-frame complexes with phosphalkynes in view of their known similar ligating ability to alkynes [7–9]. In addition to the two possible bonding modes, types (A) and (B), for the phosphalkyne complexes discussed earlier, the presence of a lone pair of electrons on phosphorus could conceivably lead to two new coordination modes, *viz.* (C) and (D).



In structures (A) and (B), the lone pair at the phosphorus atom is not involved in bonding to the metals, while in structure (C) one of the metals is bonded to the $\text{RC}\equiv\text{P}$ *via* its lone pair, and the other is π -bonded to the triple bond of the phosphalkyne. Structure (D) must also be considered in view of the observation by Shaw *et al.* [10] of this type of molecular structure in the symmetrically bonded acetylide complex $[\text{MePt}(\mu\text{-}\eta^1\text{-C}\equiv\text{CMe})(\mu\text{-dppm})_2\text{PtMe}][\text{BF}_4]$.

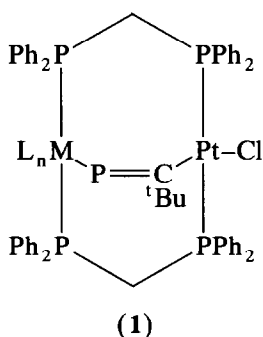
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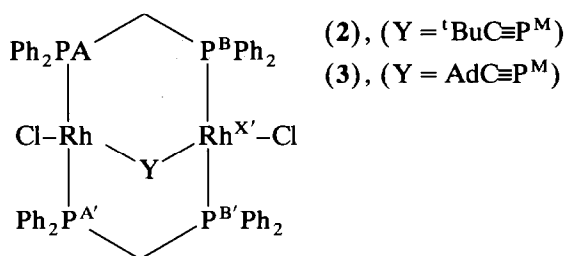
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2. Results and discussion

Previously [11], we showed that treatment of $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$ with ${}^t\text{BuC}\equiv\text{P}$ afforded the μ -parallel ligated phosphalkyne complex $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})(\mu\text{-}{}^t\text{BuCP})]$ (**1**), whose identity was established by ${}^{31}\text{P}$ and ${}^{195}\text{Pt}$ NMR studies. On the other hand, when the mixed metal complex $[\text{PtPdCl}_2(\mu\text{-dppm})_2]$ was used, a novel infinite chain carbene complex $[\text{PdPt}(\mu\text{-Cl})_2(\text{C}(\text{PPh}_2)_2)]_n$, structurally characterised by a single crystal X-ray diffraction study was formed along with $[\text{PdPtCl}_2(\mu\text{-dppm})({}^t\text{BuCP})]$ and $[\text{PtCl}_2(\text{dppm})]$ [12].

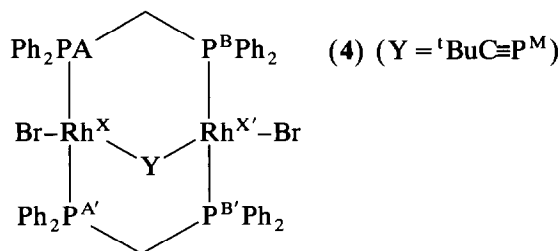


We now find that treatment of a mixture of $[\{\text{Rh}(\mu\text{-Cl})(\eta^4\text{-C}_6\text{H}_{10})_2\}]_2$ and dppm in toluene with $\text{RC}\equiv\text{P}$ ($\text{R} = {}^t\text{Bu}, \text{Ad}$) at room temperature affords high yields of the dark-red complexes $[\text{Rh}_2\text{Cl}_2(\mu\text{-dppm})_2(\text{RCP})]$, **2** ($\text{R} = {}^t\text{Bu}$), **3** ($\text{R} = \text{Ad}$), respectively.



The ${}^1\text{H}$ NMR spectra and the elemental analyses of both products indicate that one mole of $\text{RC}\equiv\text{P}$ ($\text{R} = {}^t\text{Bu}, \text{Ad}$) had been consumed during the reaction.

Treatment of **2** with an excess of LiBr in THF at room temperature readily afforded the dibromo complex $[\text{Rh}_2\text{Br}_2(\mu\text{-dppm})_2({}^t\text{BuCP})]$ (**4**).



The ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectra at 145.8 MHz of complexes **2** and **3** are shown in Figs. 1 and 2 respectively. The

spectra of **2** and **3** exhibit two widely separated (*ca.* 350 ppm) multiplets ($\delta(\text{P}) \sim 236$ ppm and $\delta(\text{P}) \sim -120$ ppm) in the ratio of 1:4. The spectra were also recorded in the range -90°C to 35°C without any observable change.

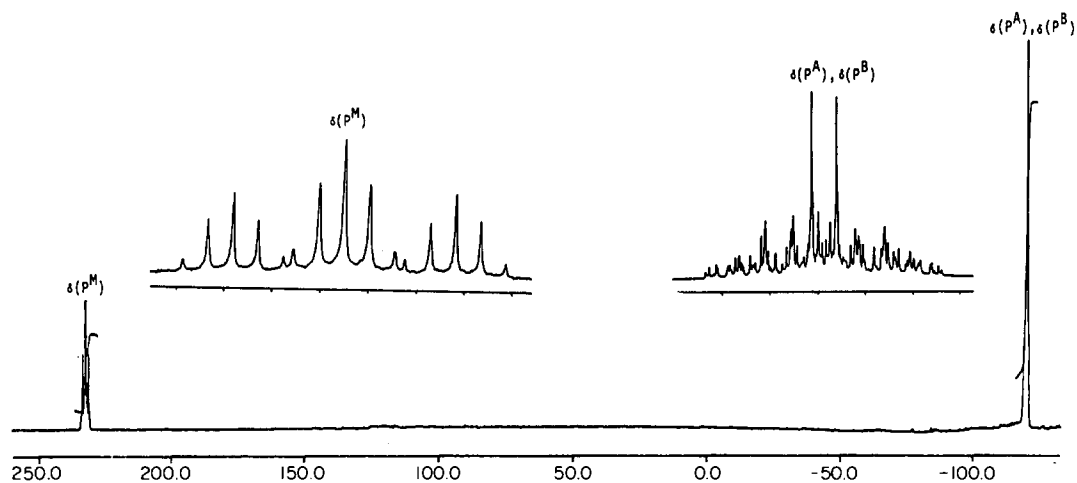
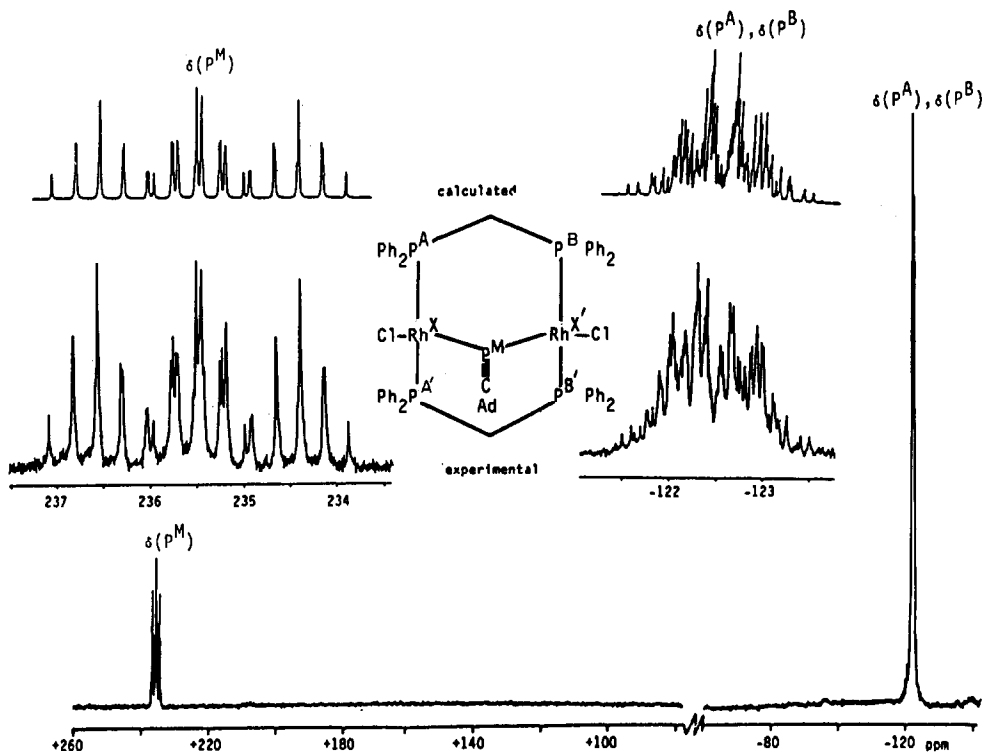
The ${}^{31}\text{P}$ chemical shift data for the μ -dppm ligands in **2**, **3**, and **4** are unremarkable, lying within the range normally observed for a number of related 'A-frame' complexes (*e.g.*, $[\text{Rh}_2({}^t\text{BuNC})_2(\mu\text{-CO})(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ [12] $[\text{Rh}_2(\text{SO}_2)({}^t\text{BuNC})_4(\mu\text{-dppm})_2]^{2+}$ [13], and $[\text{Rh}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ [13,14]. Likewise the ${}^1J(\text{RhP}^{\text{A}})$ and ${}^1J(\text{RhP}^{\text{B}})$ coupling constants to the dppm ligands are within the range normally observed, ${}^1J(\text{RhP}) = 90\text{--}144$ Hz [15].

Closer examination of the ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** reveals that the multiplet at $\delta(\text{P}^{\text{M}}) = 235$ ppm which arises from coordinated ${}^t\text{BuCP}$ is, in fact, a triplet of quintets (${}^1J(\text{RhP}^{\text{M}}) = 166.0$ Hz, ${}^2J(\text{P}^{\text{A}}\text{P}^{\text{M}}) = 36.8$ Hz). A similar pattern of lines in the ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is observed for complex **3**, which exhibits a slightly distorted triplet of quintets (see Table 1). Both ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2** and **3** strongly suggest a symmetrical structure, and have been successfully analysed and simulated as an $[\text{AA}'\text{BB}'\text{MXX}']$ spin system ($\text{A}, \text{A}', \text{B}, \text{B}' = {}^{31}\text{P}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$; $\text{M} = {}^{31}\text{P}(\text{RC}\equiv\text{P}, \text{R} = {}^t\text{Bu}$ or $\text{Ad})$; $\text{X}, \text{X}' = {}^{103}\text{Rh}$). The calculated spin-coupling parameters of **2** and **3** are listed in Table 1, and the observed and calculated spectra for **3** are shown in Fig. 2.

The multiplicity of the ${}^{31}\text{P}\{^1\text{H}\}$ NMR signals for the coordinated ${}^t\text{BuCP}$ in **2** and **3** suggests that the four phosphorus nuclei ($\text{P}^{\text{A}}, \text{P}^{\text{A}'}, \text{P}^{\text{B}}, \text{P}^{\text{B}'}$) of the dppm ligands and the two rhodium ($\text{Rh}^{\text{X}}, \text{Rh}^{\text{X}'}$) atoms are equivalent thus ruling out (C). The large ${}^1J(\text{RhP}^{\text{M}})$ coupling constant is inconsistent with a phosphalkyne π -bonded to the two rhodium atoms, thus ruling out structures (A) and (B).

Similar conclusions come from inspection of the ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4**, although its complexity prevented a full simulation. The solution ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes **2**–**4** are thus consistent *either* with structure (D) *or* alternatively with (C) if there were a 'fluxional' process in which the phosphalkyne undergoes *intramolecular* exchange between the two rhodium centres.

Such dynamic behaviour is well known for several structurally related 'A-frame' alkynyl complexes that have structures of type (C) in the solid state, but are fluxional in solution [2,16,17]. For example, $[\text{Pt}_2(\text{C}\equiv\text{C}({}^t\text{Bu})_3)(\mu\text{-dppm})_2][\text{BF}_4]$, whose structure has been confirmed by a single crystal X-ray diffraction study to be of type (C) in the solid state, exhibits only a singlet resonance in the solution ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectrum even at -60°C , indicating that the molecule is fluxional in

Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Rh}_2\text{Cl}_2(\mu\text{-dppm})_2(\text{tBuCP})]$, **2**, at 145.8 MHz.Fig. 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Rh}_2\text{Cl}_2(\mu\text{-dppm})_2(\text{AdCP})]$, **3**, observed and calculated.TABLE 1. $^{31}\text{P}\{^1\text{H}\}$ NMR data for (**2**), (**3**), and (**4**)

Compound	δ $\text{P}^{\text{A,A'}/\text{B,B}'}$	δ P^{M} ^a	1J RhP^{M} ^b	1J $\text{Rh}^{\text{X}}\text{P}^{\text{M}}$ ^b	1J $\text{Rh}^{\text{X}'}\text{P}^{\text{M}}$ ^b	1J $\text{RhP}^{\text{A,A'}/\text{B,B}'}$ ^b	2J $\text{P}^{\text{A}}\text{P}^{\text{B}} = \text{P}^{\text{A'}}\text{P}^{\text{B}'}$ ^b	2J $\text{P}^{\text{A}}\text{P}^{\text{A'}} = \text{P}^{\text{B}}\text{P}^{\text{B}'}$ ^b	2J $\text{P}^{\text{A,A'}}\text{P}^{\text{M}}$ ^b	2J $\text{P}^{\text{B,B}'}\text{P}^{\text{M}}$ ^b
2	235.7	-121.5	166	—	—	102.8	120.0	35.0	36.8	36.8
3	235.5	-122.5	—	163.0	154.5	92	120.0	30.0	39.4	36.4
4	239.0	-116.9	—	188.7	171.7	—	—	—	42.4	36.4

^a Measured in ppm relative to trimethylphosphite. ^b Measured in Hertz.

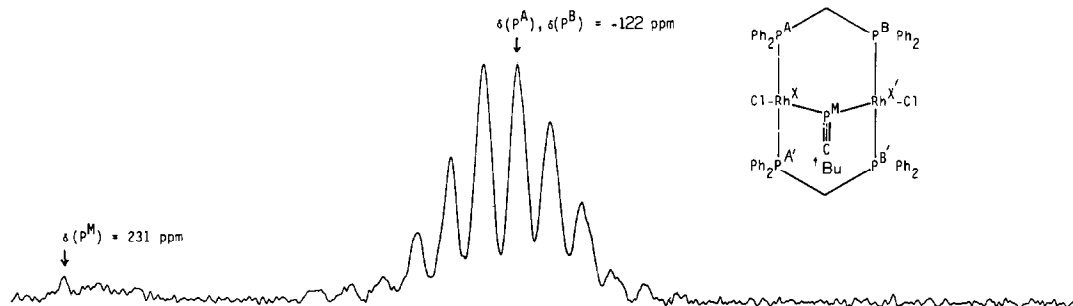
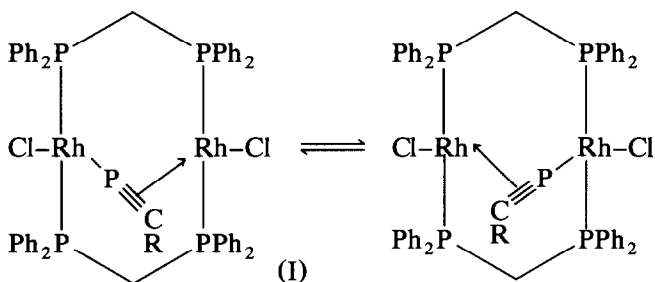


Fig. 3. Solid state $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Rh}_2\text{Cl}_2(\mu\text{-dppm})_2(^t\text{BuCP})]$, **2**.

solution. The σ , π -mode of bonding of the alkynyl ligand rapidly alternates between the two platinum metals *via* a so-called 'windscreen wiper' motion.

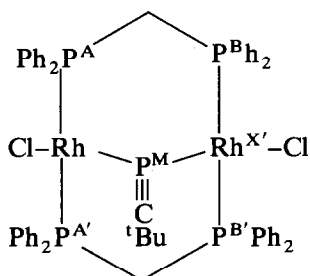
Despite many attempts, it proved impossible to obtain suitable single crystals of the phosphalkyne complexes **2–4**, and in order to distinguish between (I) structure (C) undergoing a dynamic exchange process in solution, and (II) structure (D) involving the symmetric μ - η^1 -bridging phosphalkyne, a solid state $^{31}\text{P}\{^1\text{H}\}$ NMR study of **2** was undertaken.

The solid state spectrum of **2** shown in Fig. 3 reveals the same high degree of symmetry as in solution, the chemical shift data being extremely close in the two phases. This observation strongly suggests that the phosphalkyne in **2** is ligated to the two metal



(R = ^tBu or Ad)

centres in a symmetrical fashion (type (D)) *via* an unprecedented μ - η^1 -perpendicular mode. It seems likely that all three phosphalkyne complexes have the same type of bonding.



Since completion of this work, we have recently observed a related type of ligation in the symmetrically

μ^2 -bridging phosphalkyne diiron complex $[\text{Fe}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-dppm})(\mu^2\text{-}^t\text{BuCP})]$ in which, however, there is also significant interaction of the $\text{C}\equiv\text{P}$ moiety with the two Fe atoms [18], as shown by a single crystal X-ray diffraction study.

3. Experimental details

All manipulations were carried out under dry argon or dinitrogen by standard Schlenk-tube techniques. Solvents were freshly dried and distilled. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded using either a Bruker WP80 (32.4 MHz) or Bruker WM 360 (145.8 MHz) spectrometer for **2** and **3**, or AC 250 (101.3 MHz) for **4**, operating in the FT mode. $^{31}\text{P}\{^1\text{H}\}$ chemical shifts were referenced to trimethylphosphite. $^t\text{BuCP}$ and AdCP were prepared by literature methods [19–21], and $[(\text{Rh}(\mu\text{-Cl})(\eta^4\text{-C}_6\text{H}_{10}))_2]$ by a modification [22] of the method used by Giordano and Crabtree [23]. The $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ used was part of a loan from Messrs. Johnson Matthey.

3.1. Preparation of $[\text{Rh}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-}^t\text{BuCP})]$, **2**

Treatment of a solution of $[(\text{Rh}(\mu\text{-Cl})(\eta^4\text{-C}_6\text{H}_{10}))_2]$ (348 mg, 0.789 mmol) and dppm (606 mg, 1.58 mmol) in toluene (10 ml) with one of $^t\text{BuC}\equiv\text{P}$ (91.6 mg, 0.916 mmol) in toluene (10 ml) afforded a red-brown solution. The mixture was stirred at room temperature for 2 h and the solvent then removed under reduced pressure. The red-brown residue was dissolved in CH_2Cl_2 (5 ml) and eluted through a silica gel column to afford a deep-red eluate. Removal of solvent *in vacuo* gave the red crystalline complex [1,2-dichloro-di $\{\mu$ -bis(diphenylphosphino)-methane-*P,P'*\}- $\{\mu$ -dimethylpropylidyne-phosphine (*P*)\}]dirhodium(I) (Rh^1, Rh^2), **2**, (0.72 g, 80.0%). (Found: C, 54.5; H, 4.7; $\text{C}_{55}\text{H}_{53}\text{P}_5\text{Cl}_2\text{Rh}_2$. Requires: C, 57.7; H, 4.76%)*; ^1H

* The analytical data are representative. It proved impossible to obtain reproducible analyses, although the ^{13}P NMR spectra indicated that there were no phosphorus-containing impurities.

NMR (CD_2Cl_2): δ 3.50, δ 4.90 (m, 4H, CH_2); δ 7.11–7.93 ppm (m, 40H, C_6H_5).

3.2. Preparation of $[\text{Rh}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-AdCP})]$, **3**

In an analogous way, a solution of $[\{\text{Rh}(\mu\text{-Cl})(\eta^4\text{-C}_6\text{H}_{10})\}_2]$ (302 mg, 0.685 mmol) and dppm (505 mg, 1.37 mmol) in toluene (8 ml) was treated with $\text{AdC}\equiv\text{P}$ (142.3 mg, 0.80 mmol) in toluene (8 ml). The red-brown solution was stirred at room temperature for 2 h and solvent was then removed under reduced pressure. The resulting red-brown residue was washed several times with petroleum ether (30–40°C) and dried *in vacuo* to give the deep-red crystalline complex [1,2-dichloro-di $\{\mu$ -bis(diphenylphosphino)methane-*P,P*\} $\{\mu$ -1-adamantylphosphaethyne(*P*)\}]dirhodium(I) (Rh^1 , Rh^2), **3**, (0.70 g, 83.5%). Found: C, 56.2; H, 4.9; $\text{C}_{61}\text{H}_{59}\text{Cl}_2\text{-P}_5\text{Rh}_2$. Requires: C, 59.9, H, 4.9%*. ^1H NMR (CD_2Cl_2): δ 16–1.81 (m, 15H, Ad); δ 3.40, 4.85 (m, 4H, CH_2); δ 7.09–7.94 ppm (m, 40H, C_6H_5).

3.3. Preparation of $[\text{Rh}_2\text{Br}_2(\mu\text{-dppm})_2(\text{tBuCP})]$, **4**

A solution of LiBr (1.2 g, 13.9 mmol) in THF (10 ml) was added during 15 min to a solution of $[\text{Rh}_2\text{Cl}_2(\mu\text{-dppm})_2(\text{tBuCP})]$ (170 mg, 0.15 mmol) in THF (10 ml). The resulting green-brown solution was stirred at room temperature for 4 days, after which the solvent was removed under reduced pressure. The residue was extracted with toluene (10 ml) and the extract filtered, removal of the solvent left a green-brown residue, which was dissolved in CH_2Cl_2 (5 ml) and eluted through a silica gel column. Removal of solvent *in vacuo* gave the green complex [1,2-dibromo-di $\{\mu$ -bis(diphenylphosphine)methane-*P,P*\} $\{\mu$ -dimethylpropylidynephosphine(*P*)\}]dirhodium(I) (Rh^1 , Rh^2), **4**, (120 mg, 65.5%). (Found: C, 48.8; H, 4.0; $\text{C}_{55}\text{H}_{53}\text{P}_5\text{Br}_2\text{Rh}_2$. Requires: C, 53.8; H, 4.3)*; ^1H NMR (CD_2Cl_2): δ 0.93 (s, 9H, tBu); δ 3.45, δ 4.86 (m, 4H, CH_2); δ 6.95–7.773 (m, 40 H, C_6H_5).

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