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Preparation of some dinuclear rhodium complexes with the orthometallated ligand [2,6-$(PPh_2CH_2)_2C_6H_3$]$^-$ and their catalytic activity for polymerization of phenylacetylene

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Abstract

Reaction of 1,3-$(PPh_2CH_2)_2C_6H_4$ (PCHP) with $[RhCl(COD)]_2$ in isopropanol produced a mixture of dinuclear complexes $[RhCl(COD)]_2(\mu_2$-PCHP), $RhH(PCP)(\mu$-$Cl)_2Rh(COD)$, and $[RhHCl(PCP)]_2(\mu_2$-PCHP). Reaction of $RhH(PCP)(\mu$-$Cl)_2Rh(COD)$ with CCl_4 produced $RhCl(PCP)(\mu$-$Cl)_2Rh(COD)$. The solid-state structure of the latter complex has been characterized by X-ray diffraction. With the exception of $[RhHCl(PCP)]_2(\mu_2$-PCHP), all the dinuclear complexes in THF are catalytically active for the polymerization of phenylacetylene. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium; Phosphine; Orthometallation; Polymerization acetylene

1. Introduction

The formation and properties of transition-metal complexes with [2,6-$(PR_2CH_2)_2C_6H_3$]$^-$ and related orthometallated tridentate ligands have attracted considerable attention. Transition-metal complexes with these ligands have been reported for rhodium [1–15], iridium [1,8,9,15–17], ruthenium [18], palladium [1,7,10,12,19–26], platinum [1,19–21,23–25,27], and nickel [1,12,28]. These complexes are usually prepared from the reactions of 1,3-$(PR_2CH_2)_2C_6H_4$ or 1-R′-2,6-$(PR_2CH_2)_2C_6H_3$ (R′ = alkyl, alkoxyl) with low-valent metal complexes. Most often, mononuclear complexes were obtained from these reactions. We have recently prepared interesting dinuclear complexes containing 2,6-$(PPh_2CH_2)_2C_6H_3$ (PCP) from the reactions of $[RhCl(COD)]_2$ with 1,3-$(PPh_2CH_2)_2C_6H_4$ (PCHP). Some of the dinuclear complexes were found to be catalytically active for polymerization of PhC≡CH.

2. Results and discussion

2.1. Preparation of dinuclear complexes

Reaction of ligand **1** with $[RhCl(COD)]_2$ (**2**) in isopropanol produced a mixture of dinuclear complexes $[RhCl(COD)]_2(\mu_2$-PCHP) (**3**), $RhH(PCP)(\mu$-$Cl)_2Rh$-(COD) (**4**), and $[RhHCl(PCP)]_2(\mu_2$-PCHP) (**5**), the amounts of which depend on the reaction conditions (see Scheme 1). Reaction of ligand **1** with one equivalent of $[RhCl(COD)]_2$ in isopropanol led to a mixture of complexes **3** and **4** in a ratio of ca. 1.4:1 along with a very minor amount of complex **5**. Reaction of ligand **1** with 0.55 equivalents of $[RhCl(COD)]_2$ led to a mixture of complexes **4** and **5** in a ratio of ca. 1:1 along with a very minor amount of complex **3**. There is no evidence for the production of the coordinatively unsaturated complex RhHCl(PCP). Interestingly, the related complex RhHCl[2,6-$((t$-$Bu)_2PCH_2)_2C_6H_3$] has been prepared from the reaction of 1,3-$((t$-$Bu)_2PCH_2)_2C_6H_4$ with $RhCl_3\cdot H_2O$ [1] or from the reaction of 1-OMe-2,6-$((t$-$Bu)_2PCH_2)_2C_6H_3$ with $[RhCl(COE)_2]_2$ [10]. The origin of the failure to obtain RhHCl(PCP) in our case could be the less steric bulkiness of the PCP ligand and the Lewis-acidity character of the

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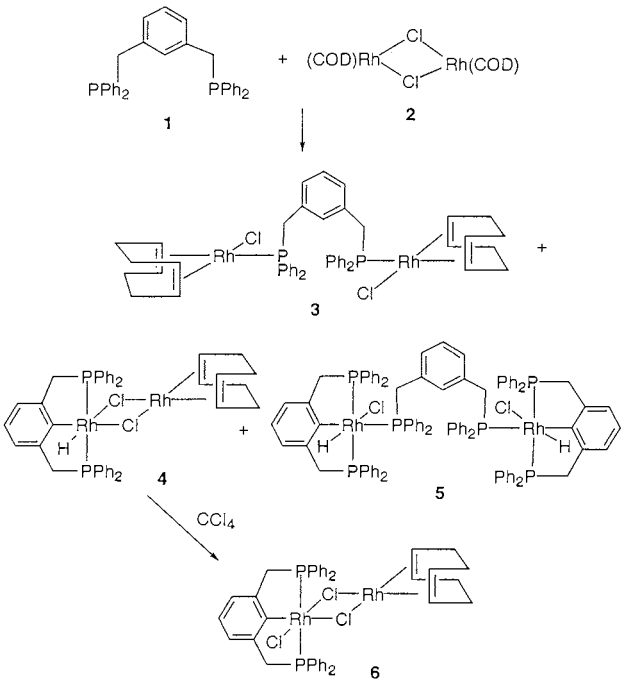


Scheme 1.

rhodium center. In this regard, it is noted that the six-coordinated complex $RhHCl(PPh_3)(PCP)$ has been prepared from the reaction of ligand **1** with $[RhCl(COE)_2]_2$ in the presence of PPh_3 [4].

Complexes **3**–**5** can be readily purified by recrystallization and column chromatography. The presence of the COD ligand in complex **3** is supported by the ^{1}H- and ^{13}C-NMR spectra. In the ^{1}H-NMR spectrum, the signals of the CH_2 protons of the COD ligand were observed in the region 1.84–2.47 ppm and those of the olefinic protons were observed at ca. 2.9 and 5.6 ppm. The ^{1}H-NMR data for the COD ligand are very similar to those of related complexes $RhCl(COD)(PR_3)$ [29]. In the ^{13}C-NMR spectrum, the signals due to the CH_2 groups of the COD ligand were observed at 28.6 and 32.6 ppm, and those assignable to the olefinic carbons of the COD ligand were observed at 70.3 and 104.1 ppm. Consistent with the structure, the ^{31}P-NMR spectrum showed the PPh_2 signal at 26.3 ppm as a doublet.

The NMR and mass spectroscopic data support the structure of **4**. The FAB mass spectrum showed the expected molecular ion peak at 859. The CH_2 signals of the COD ligand were observed in the regions of 1.35–1.50 ppm and 2.10–2.30 ppm and the olefinic signals at 3.38 and 3.80 ppm in the ^{1}H-NMR spectrum. In the ^{13}C-NMR spectrum, the COD signals were observed at 30.3 ppm for CH_2 and at 77.4 and 77.9 ppm for the olefinic carbons. The ^{1}H-NMR spectrum showed a hydride signal at -18.20 ppm as a doublet of triplet. The structural assignment is further supported by its reaction with CCl_4 to give the analogous complex $RhCl(PCP)(\mu\text{-}Cl)_2Rh(COD)$ (**6**). The solid-state structure of compound **6** has been confirmed by an X-ray diffraction study (see below). The reported complex closely related to **6** is $RhCl(NCN)(\mu\text{-}Cl)_2Rh(COD)$ ($NCN = 2,6\text{-}(NMe_2CH_2)_2C_6H_3$) [30].

The structure of complex **5** can be readily assigned based on the ^{31}P- and ^{1}H-NMR spectroscopic data. In particular, the ^{31}P-NMR spectrum showed a doublet of doublet signal for the PCP ligand at 47.4 ppm and a doublet of triplet signal for the bridging diphosphine ligand at 18.8 ppm. The ^{1}H-NMR spectrum showed a hydride signal at -17.20 (dq, $J(Rh–H) = 24$ Hz, $J(PH) = 15$ Hz), indicating that the hydride is *cis* to the three phosphorus atoms and that the bridging ligand is *trans* to the orthometallated carbon.

2.2. Description of the structure of $RhCl(PCP)(\mu\text{-}Cl)_2Rh(COD)$ (6)

The molecular structure of $RhCl(PCP)(\mu\text{-}Cl)_2Rh(COD)$ in solid state is shown in Fig. 1. The crystallographic details are given in Table 1 and selected bond distances and angles in Table 2. The complex contains a four-coordinated and a six-coordinated rhodium center bridged by two chlorides.

The geometry around Rh(1) can be described as a distorted octahedron. The distortion can be attributed to the special geometry of the PCP ligand. The P(1)–Rh(1)–C(1) (82.39(1)°), P(2)–Rh(1)–C(1) (83.0(3)°) and P(1)–Rh(1)–P(2) (165.2(1)°) angles are close to those observed in rhodium complexes containing similar ligands, for example, $RhCl(CH_3)((P(t\text{-}Bu)_2CH_2)_2\text{-}C_6H\text{-}3,5\text{-}Me_2)$ [9], *trans*-$RhCl_2(EtOH)((PCy_2CH_2)_2\text{-}C_6H_3)$ [5], *trans*-$RhCl_2(MeOH)((PCy_2CH_2)_2C_6H_3)$ [5], *trans*-$RhCl_2(H_2O)((PCy_2CH_2)_2C_6H_3)$ [5], and RhCl-

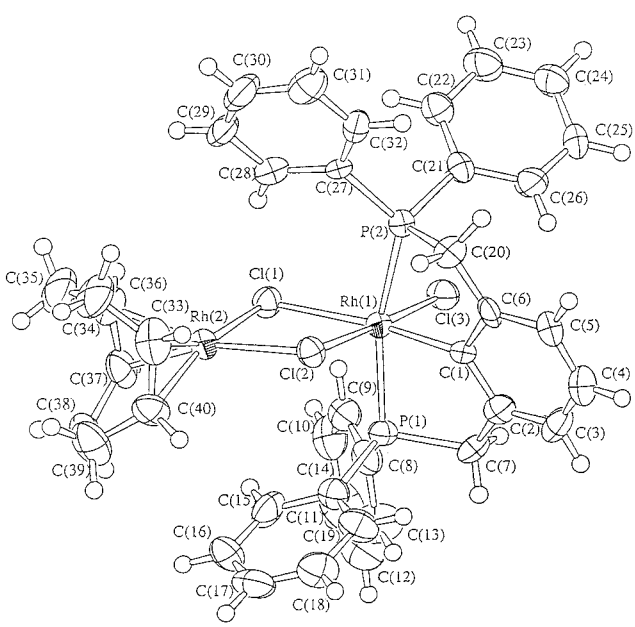


Fig. 1. The molecular structures of $RhCl(PCP)(\mu\text{-}Cl)_2Rh(COD)\cdot CH_2Cl_2$. The solvent molecule is omitted for clarity.

Table 1
Crystallographic details for $RhCl(PCP)(\mu\text{-}Cl)_2Rh(COD)\cdot CH_2Cl_2$

Formula	$C_{41}H_{41}Cl_5P_2Rh_2$
Formula weight	978.80
Color and habit	Red, block
Crystal system	Triclinic
Lattice type	Primitive
Space group	$P\bar{1}$ (no. 2)
a (Å)	11.891(1)
b (Å)	12.950(1)
c (Å)	14.405(1)
α (°)	72.83(2)
β (°)	69.72(2)
γ (°)	85.60(2)
V (Å^3)	1987.2(5)
Z	2
$D_{calc.}$ (g cm^{-3})	1.636
$F(000)$	984
Radiation (Å)	Mo–K_α ($\lambda = 0.71073$)
Scan range (°)	65–63
Exposure (min)	5
$2\theta_{max}$ (°)	51.0
No. of reflections measured	17942
No. of unique reflections measured	6814 ($R_{int} = 0.044$)
Anomalous dispersion	All non-hydrogen atoms
No. of observed reflections	4746 [$I > 3.00\sigma(I)$]
No. of variables refined	452
Reflection/parameter ratio	10.50
Residuals: R; R_w	0.069; 0.131
Goodness-of-fit indicator	3.03
Maximum shift/error in final cycle	0.10
Maximum peak in final difference map (e Å^{-3})	1.54
Minimum peak in final difference map (e Å^{-3})	−1.14

$(CH_3)(PEt_3)((PMe_2CH_2)_2C_6H\text{-}3,5\text{-}Me_2)$ [6]. The Rh(1)–Cl(3) bond distance at 2.344(3) Å is comparable to those [5] observed in *trans*-$RhCl_2(EtOH)((PCy_2CH_2)_2C_6H_3)$ (2.354(3), 2.376(3) Å), *trans*-$RhCl_2(MeOH)((PCy_2CH_2)_2C_6H_3)$ (2.342(3), 2.347(3) Å), and *trans*-$RhCl_2(H_2O)((PCy_2CH_2)_2C_6H_3)$ (2.345(2), 2.371(2) Å). The two bridging chlorides are bonded to Rh(1) unsymmetrically with Rh(1)–Cl(1) = 2.555(3) Å and Rh(1)–Cl(2) = 2.377(3) Å. The longer Rh(1)–Cl(1) bond is undoubtedly caused by the stronger *trans* influence of the orthometallated aryl ligand. For comparison, the Rh–Cl bonds *trans* to orthometallated aryl ligands in $RhCl(CH_3)((P(t\text{-}Bu)_2CH_2)_2C_6H\text{-}3,5\text{-}Me_2)$ [9] and $RhCl(CH_3)((2\text{-}P(t\text{-}Bu)_2CH_2)\text{-}6\text{-}(Et_2NCH_2)C_6H\text{-}3,5\text{-}Me_2)$ [31] were observed at 2.470(4) and 2.4576 (10) Å, respectively.

The overall geometry around Rh(2) is very similar to that of $[Rh(COD)]_2(\mu\text{-}Cl)_2$ except that the Cl(1)–Rh(2)–Cl(2) angle (87.3(1)°) is slightly larger than that in $[Rh(COD)]_2(\mu\text{-}Cl)_2$ (85°) [32]. The C–C and C=C distances in the COD ligand and Rh(2)–ligand bond distances are normal compared to those in related Rh(COD) complexes such as $[Rh(COD)]_2(\mu\text{-}Cl)_2$ [32], $[RuRhHCl(COD)(dppm)_2]BF_4$ [33], and $Cp_2TiRh(COD)(\mu\text{-}CH_2)(\mu\text{-}Cl)$ [34].

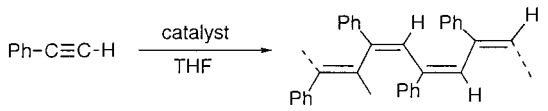
2.3. Reactions with PhC≡CH

During the process of studying the reactivity of complexes **3**–**6** toward terminal acetylenes, it was found that **3**, **4**, and **6** are all catalytically active for polymerization of phenylacetylene (Eq. (1)). As indicated by the ^{1}H- and the ^{13}C-NMR spectra, the poly(phenylacetylene) formed from these reactions has a *cis–transoidal* structure [35,36]. Unfortunately, we have not been able to detect the intermediates for the polymerization reactions. The in situ ^{31}P- and ^{1}H-NMR measurements for the reactions using **3** and **6** as the catalytic precursors in CD_2Cl_2 indicate that poly(phenylacetylene) was formed within minutes, and that the only rhodium-containing species detectable by the ^{1}H- and ^{31}P-NMR are complexes **3** and **6**. When complex **4** was used as the catalytic precursor, a complicated uncharacteristic mixture of rhodium species, which do not contain the Rh–H functional group, were produced along with the

Table 2
Selected bond lengths (Å) and angles (°) for $RhCl(PCP)(\mu\text{-}Cl)_2Rh(COD)\cdot CH_2Cl_2$

Bond lengths			
Rh(1)–Cl(1)	2.555(3)	Rh(1)–Cl(2)	2.377(3)
Rh(1)–Cl(3)	2.344(3)	Rh(1)–P(1)	2.312(3)
Rh(1)–P(2)	2.336(3)	Rh(1)–C(1)	2.03(1)
Rh(2)–Cl(1)	2.412(4)	Rh(2)–Cl(2)	2.404(3)
Rh(2)–C(33)	2.11(2)	Rh(2)–C(36)	2.14(2)
Rh(2)–C(37)	2.11(1)	Rh(2)–C(40)	2.15(1)
C(33)–C(34)	1.49(2)	C(33)–C(40)	1.47(2)
C(34)–C(35)	1.58(3)	C(35)–C(36)	1.53(3)
C(36)–C(37)	1.40(2)	C(37)–C(38)	1.52(2)
C(38)–C(39)	1.49(2)	C(39)–C(40)	1.49(2)
Bond angles			
C(1)–Rh(1)–P(1)	82.39(1)	C(1)–Rh(1)–P(2)	83.0(3)
C(1)–Rh(1)–Cl(1)	173.5(3)	C(1)–Rh(1)–Cl(2)	90.6(4)
C(1)–Rh(1)–Cl(3)	91.6(4)	P(1)–Rh(1)–P(2)	165.2(1)
P(1)–Rh(1)–Cl(1)	93.5(1)	P(1)–Rh(1)–Cl(2)	94.3(1)
P(1)–Rh(1)–Cl(3)	87.3(1)	P(2)–Rh(1)–Cl(1)	101.2(1)
P(2)–Rh(1)–Cl(2)	87.4(1)	P(2)–Rh(1)–Cl(3)	91.7(1)
Cl(1)–Rh(1)–Cl(2)	84.7(1)	Cl(1)–Rh(1)–Cl(3)	93.2(1)
Cl(2)–Rh(1)–Cl(3)	177.5(1)	Cl(1)–Rh(2)–Cl(2)	87.3(1)
Cl(1)–Rh(2)–C(33)	157.3(5)	Cl(1)–Rh(2)–C(36)	93.2(5)
Cl(1)–Rh(2)–C(37)	90.4(5)	Cl(1)–Rh(2)–C(40)	162.3(4)
Cl(2)–Rh(2)–C(33)	89.9(5)	Cl(2)–Rh(2)–C(36)	161.2(5)
Cl(2)–Rh(2)–C(37)	160.4(5)	Cl(2)–Rh(2)–C(40)	4.5(4)
C(33)–Rh(2)–C(36)	82.4(7)	C(33)–Rh(2)–C(37)	99.4(7)
C(33)–Rh(2)–C(40)	40.4(7)	C(36)–Rh(2)–C(37)	38.4(6)
C(36)–Rh(2)–C(40)	90.6(6)	C(37)–Rh(2)–C(40)	81.9(6)
Rh(1)–Cl(1)–Rh(2)	91.2(1)	Rh(1)–Cl(2)–Rh(2)	96.0(1)
C(34)–C(33)–C(40)	123(1)	C(33)–C(40)–C(39)	125(1)
C(35)–C(36)–C(37)	125(1)	C(36)–C(37)–C(38)	123(1)

polymers as indicated by the ^{31}P- and ^{1}H-NMR spectroscopy.



catalyst = $RhX(PCP)(\mu\text{-}Cl)_2Rh(COD)$, X = H, Cl

[$RhCl(COD)]_2(\mu$-PCHP) (1)

It is possible that the active center for the polymerization reaction is the Rh(COD) moiety. In fact, several Rh(diene) complexes have been reported to be active catalysts for polymerization of terminal aromatic acetylenes, for example, $[RhCl(diene)]_2$ (diene = COD, NBD) [36–38], $[Rh(SR)(COD)]_2$ (R = Ph [39], C_6F_5[39,40]), $[Rh(diene)(N–N)]^+$ (diene = NBD, COD; N–N = bidentate nitrogen donor ligands) [36], $Rh(SC_6F_5)(PPh_3)(COD)$ [39], RhCl(L)(COD) (L = neutral nitrogen donors) [36], $Rh(COD)BPh_4/HSiR_3$ [41], $Rh(NBD)(B(C_6H_4\text{-}4\text{-}R)_4)$ (R = H, $C(CH_3)_3$) [42], TpRh(COD) [43], and $Rh(C{\equiv}CPh)(NBD)(PPh_3)_2$ [44]. Like our systems, many of these Rh(diene) complexes promote the formation of predominantly *cis–transoidal* poly(phenylacetylene).

In contrast to complexes **3**, **4** and **6**, which effect polymerization of phenylacetylene, no reaction was observed when complex **5** was treated with phenylacetylene. The lack of catalytic activity of complex **5** for polymerization of phenylacetylene is consistent with the assumption that the active center for polymerization of phenylacetylene is the Rh(COD) moiety. The lack of reactivity of complex **5** toward phenylacetylene is probably not surprising, as it is coordinatively saturated.

Although complexes **3**, **4**, and **6** are active for polymerization of phenylacetylene, these complexes failed to effect polymerization of alkyl terminal acetylenes such as *t*-BuC≡H and 1-octyne. Others also noted that aliphatic terminal acetylenes could not be polymerized with Rh(diene) complexes [39,40]. The reason why our complexes are inactive for polymerization of alkyl terminal acetylenes is not clear, but it could be due to the poorer coordination ability of alkyl terminal acetylenes compared with phenylacetylene.

Table 3
$^{31}P\{^{1}H\}$-NMR data for the new dinuclear complexes [a]

Complex	δ(PCP) (^{1}J(Rh–P)) (Hz)	δ(PCHP) (^{1}J(Rh–P)) (Hz)	^{2}J(PP) (Hz)
3		26.3 (152.3)	
4	44.8 (116.9)		
5	47.4 (111.2)	18.8 (82.8)	24.5
6	33.5 (98.0)		

[a] The spectra were obtained in CD_2Cl_2 on a Bruker NMR spectrometer operating at 121.5 MHz. Chemical shifts are in ppm with respect to 85% H_3PO_4 (δ 0.0).

In summary, we have prepared several interesting dinuclear complexes with PCP or PCHP ligands. Binuclear complexes with Rh(COD) moiety were found to be catalytically active for polymerization of phenylacetylene to give stereo regular *cis*-transoidal poly(phenylacetylene).

3. Experimental

Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ, USA). ^{1}H-, $^{13}C\{^{1}H\}$- and $^{31}P\{^{1}H\}$-NMR spectra were collected on a Bruker ARX-300 spectrometer (300 MHz). ^{1}H- and $^{13}C\{^{1}H\}$-NMR chemical shifts are relative to TMS, and $^{31}P\{^{1}H\}$-NMR chemical shifts relative to 85% H_3PO_4. The $^{31}P\{^{1}H\}$-NMR data are collected in Table 3. Molecular weights of polymers were measured on a Shimadzu LC-4A GPC spectrometer using THF as the eluent. All manipulations were carried out at room temperature under nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium–benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane, $CHCl_3$). The compounds $[RhCl(COD)]_2$ [45], and 1,3-$(PPh_2CH_2)_2C_6H_4$ (PCHP) [19] were prepared according to literature methods. All other reagents were used as purchased from Aldrich or Strem, USA.

3.1. Preparation of $[RhCl(COD)]_2(\mu_2$-PCHP) (**3**) and $RhH(PCP)(\mu\text{-}Cl)_2Rh(COD)$ (**4**)

A mixture of 1,3-$(PPh_2CH_2)_2C_6H_4$ (2.37 g, 5.0 mmol) and $[RhCl(COD)]_2$ (2.71 g, 5.5 mmol) in 150 ml of degassed isopropanol was refluxed for 24 h to give a brown precipitate. The solid was recrystallized with a mixed solvent of CH_2Cl_2 (50 ml) and ether (150 ml). The soluble portion was treated with hexane (200 ml) to give a yellow–brownish precipitate, which was collected by filtration, washed with hexane and dried to give 2.4 g of complex **3** (yield, 43%). The CH_2Cl_2–ether-insoluble portion was redissolved in CH_2Cl_2 and the resulting solution was passed through a silica gel column. The CH_2Cl_2 of the eluent was removed under vacuum to give a yellow solid of complex **4** (1.53 g, 32% yield). Characterization data for **3**: ^{1}H-NMR (CD_2Cl_2, 300.13 MHz): δ 1.84–2.47 (m, 16 H, CH_2 (COD)), 2.96–2.80 (m, 4 H, CH= (COD)), 3.99 (d, J(PH) = 11.6 Hz, 4 H, CH_2 (PCHP)), 5.55 (br, 4 H, CH= (COD)), 7.33–8.10 (m, 24 H, Ph). ^{13}C-NMR (CD_2Cl_2, 75.5 MHz): δ 28.6 (s, CH_2 (COD)), 32.6 (s, CH_2 (COD)), 34.2 (d, J(PC) = 22.6 Hz, CH_2 (PCHP)), 70.3 (d, J(Rh–C) = 13.8 Hz, CH= (COD)), 104.1 (dd, J(P–C) = 7.1, J(Rh–C) = 12.3 Hz, CH= (COD)), 127.7–135.4 (m, aromatic signals).

Anal. Calc. for $C_{48}H_{52}Cl_2P_2Rh$: C, 59.58; H, 5.42; Cl, 7.34. Found: C, 59.73; H, 5.22; Cl, 7.19%. Characterization data for **4**: ^{1}H-NMR (CD_2Cl_2, 300.13 MHz): δ −18.20 (dt, J(Rh–H) = 30.0, J(PH) = 12.0 Hz, 1 H, Rh–H), 1.35–1.50 (m, 4 H, CH_2 (COD)), 2.10–2.30 (m, 4 H, CH_2 (COD)), 3.38 (br, 2 H, CH= (COD)), 3.63 (dt, J(HH) = 16.0, J(PH) = 4.7 Hz, 2 H, CH_2 (PCP)), 3.80 (br, 2 H, CH= (COD)), 4.13 (dt, J(HH) = 16.0, J(PH) = 3.9 Hz, 2 H, CH_2 (PCP)), 6.82–8.09 (m, aromatic signals). ^{13}C-NMR (CD_2Cl_2, 75.5 MHz): δ 30.3 (s, CH_2 (COD)), 40.9 (t, J(PC) = 15.2 Hz, CH_2 (PCP)), 77.4 (d, J(Rh–C) = 14.1 Hz, CH= (COD)), 77.9 (d, J(Rh–C) = 14.2 Hz, CH= (COD)), 167.7 (dd, J(Rh–C) = 25.1, J(P–C) = 125.6 Hz, *ipso*-PCP), 122.4–145.4 (m, aromatic signals). Anal. Calc. for: $C_{40}H_{40}Cl_2P_2Rh_2$: C, 55.90; H, 4.69; Cl, 8.25. Found: C, 56.06; H, 4.55; Cl, 8.41%.

3.2. Preparation of RhH(PCP)(μ-Cl)$_2$Rh(COD) (**4**) and [RhHCl(PCP)]$_2$(μ-PCHP) (**5**)

A mixture of 1,3-(PPh_2CH_2)$_2C_6H_4$ (1.04 g, 2.2 mmol) and [RhCl(COD)]$_2$ (0.49 g, 1.0 mmol) in 60 ml of degassed isopropanol was refluxed for 24 h to give a brown precipitate. The solid was redissolved in CH_2Cl_2 and the resulting solution was loaded on a silica gel column. Complex **4** was obtained (0.36 g, 42% yield) with CH_2Cl_2 as the eluent. Complex **5** was obtained (0.78 g, 46% yield) with acetone as the eluent. Characterization data for **5**: ^{1}H-NMR (CD_2Cl_2, 300.13 MHz): δ −17.20 (dq, J(Rh–H) = 24 Hz, J(PH) = 15 Hz, 1 H, Rh–H), 2.55 (d, J(PH) = 3.8 Hz, 4 H, CH_2 (μ-PCHP)), 3.81 (dt, J(HH) = 11.0, J(PH) = 4.4 Hz, 4 H, CH_2 (PCP)), 4.47 (dbr, J(HH) = 11.0 Hz, 4 H, CH_2 (μ-PCHP)), 4.90 (br, 1 H, 2-C_6H_4 (μ-PCHP)), 5.53 (d, J(HH) = 5.9 Hz, 2 H, 4,6-C_6H_4 (μ-PCHP)), 5.95 (t, J(HH) = 5.9 Hz, 1 H, 5-C_6H_4 (μ-PCHP)), 6.75–7.74 (m, other aromatic signals). ^{13}C-NMR (CD_2Cl_2, 75.5 MHz): δ 30.9 (d, J(PC) = 11.5 Hz, CH_2 (PCHP)), 47.0 (m, CH_2P), 166.6 (dd, J(P–C) = 100.4, J(Rh–C) = 25.1 Hz, *ipso*-PCP), 121.6–144.8 (m, other aromatic signals). Anal. Calc. for: $C_{96}H_{84}Cl_2P_6Rh_2$: C, 67.82; H, 4.98; Cl, 4.17. Found: C, 67.60; H, 5.23; Cl, 4.57%.

3.3. Preparation of RhCl(PCP)(μ-Cl)$_2$Rh(COD) (**6**)

A sample of RhH(PCP)(μ-Cl)$_2$Rh(COD) (0.50 g, 0.58 mmol) in a mixed solvent of $CHCl_3$ (30 ml) and CCl_4 (20 ml) was stirred at room temperature for 3 days. The solvents were then removed under vacuum. The resulting residue was redissolved in a minimum amount of CH_2Cl_2 and the solution was passed through a silica gel column with C_6H_6 as the eluent. Removal of the solvent produced 0.44 g of complex **6** (yield, 85%). ^{1}H-NMR (CD_2Cl_2, 300.13 MHz): δ 1.28–1.57 (m, 4 H, CH_2 (COD)), 2.02–2.36 (m, 4 H, CH_2 (COD)), 3.03 (m, 2 H, CH= (COD)), 4.06 (m, 4 H, CH_2 (PCP)), 4.15 (m, 2 H, CH= (COD)), 6.99–8.18 (m, aromatic signals). ^{13}C-NMR (CD_2Cl_2, 75.5 MHz): δ 30.0 (s, CH_2 (COD)), 30.4 (s, CH_2 (COD)), 37.3 (t, J(PC) = 15.2 Hz, CH_2 (PCP)), 77.7 (d, J(Rh–C) = 13.7 Hz, CH= (COD)), 77.9 (d, J(Rh–C) = 14.0 Hz, CH= (COD)), 123.4–145.5 (m, aromatic signals). Anal Calc. for $C_{40}H_{39}Cl_3P_2Rh_2$: C, 53.75; H, 4.40; Cl, 11.90. Found: C, 54.00; H, 4.68; Cl, 11.70%.

3.4. Polymerization of phenylacetylene

In a typical reaction, a mixture of phenylacetylene (7.0 ml, 64 mmol) and 0.015 mmol of the Rh catalyst in THF (20 ml) was stirred at room temperature for 5 h. Then 60 ml of MeOH was added to the THF solution to give a yellow precipitate. The solid was collected by filtration, washed with MeOH and hexane and dried under vacuum. A second batch of polymer could be obtained when the volume of the filtrate was reduced. The molecular weight of the polymers is around 50 000 as determined by GPC. In the case of RhCl(PCP)(μ-Cl)$_2$Rh(COD), addition of acetonitrile to the reaction mixture accelerated the polymerization rate significantly. ^{1}H-NMR ($CDCl_3$, 300.13 MHz): δ 5.91 (br s, 1 H, =CH), 6.70 (br, 2 H, *o*-Ph), 7.00 (br, 3 H, m, *p*-Ph). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 126.6 (s, *p*-Ph), 127.4 (s, *o*- or *m*-Ph), 127.7 (s, *o*- or *m*-Ph), 131.7 (s, =CH), 139.2 (s, *ipso*-Ph), 142.8 (s, =CPh). The NMR data match those reported in the literature [35,36].

3.5. Crystallographic analysis for RhCl(PCP)(μ-Cl)$_2$Rh(COD)·CH_2Cl_2

Suitable crystals for X-ray diffraction study were grown by slow diffusion of ether to a saturated solution of RhCl(PCP)(μ-Cl)$_2$Rh(COD) in CH_2Cl_2. One molecule of CH_2Cl_2 was co-crystallized with the rhodium compound. A red block crystal of RhCl(PCP)-(μ-Cl)$_2$Rh(COD)·CH_2Cl_2, having approximate dimensions of $0.18 \times 0.28 \times 0.28$ mm^3, was mounted in a glass capillary and used for X-ray structure determination. Intensity data were collected at ambient temperature on a MAR research image plate scanner, using Mo–K_α radiation ($\lambda = 0.71073$ Å) with a graphite-crystal monochromator in the incident beam. 65–3° frames with an exposure time of 5 min per frame were used. The diffraction intensities were corrected for Lorentz and polarization effects. An approximation to absorption corrections by inter-image scaling was also applied. A total of 6814 reflections are unique and 4746 of these are considered, observed with $I > 3\sigma(I)$. The structure was solved by direct methods (SIR 88) [46] and expanded using difference Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically [47]. Hydrogen

atoms were generated in their idealized positions (C–H, 0.95 Å) and were included but not refined. Full-matrix least-squares refinement on F converged with $R = 0.069$ and $R_w = 0.131$. The relative high residual of R factor is due to poor crystal quality (solvent loss rapidly in the monitoring process).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 133677. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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