

Synthesis and characterization of pentadienyl-iridium(III) and -rhodium(III) complexes

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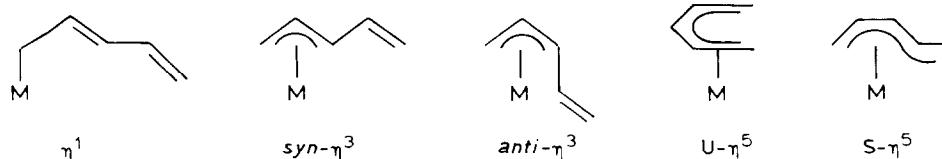
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Abstract

1-Halopenta-2,4-dienes $\text{CH}_2=\text{CHCH}=\text{CHCH}_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) undergo facile oxidative addition with complexes of the type *trans*- $\text{MCl}(\text{CO})(\text{PR}_3)_2$ ($\text{M} = \text{Rh}, \text{PR}_3 = \text{PMe}_2\text{Ph}$; $\text{M} = \text{Ir}, \text{PR}_3 = \text{PMe}_2\text{Ph}, \text{PPh}_3$). The configurations of these adducts were elucidated by combining their far-IR, ^1H and ^{31}P NMR spectra.

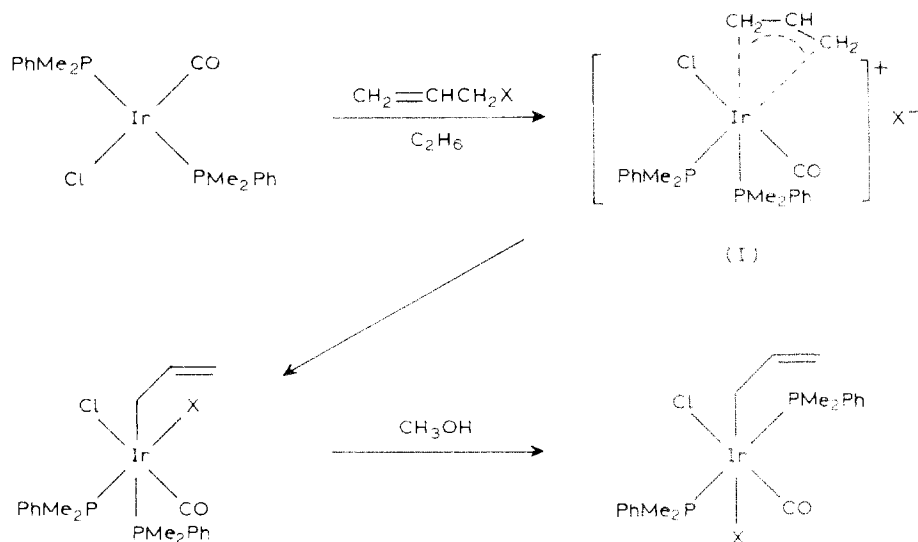
Introduction

The chemistry of transition-metal acyclic pentadienyl complexes has become the subject of some intensive studies in recent years [1,2]. One of the intriguing features of these complexes is the variety of geometries which are possible for the pentadienyl group bound to the metal center:



The presence of appropriate reagents such as the pentadienyltin compound $(\text{C}_5\text{H}_7)\text{Sn}(\text{CH}_3)_3$ [3] and pentadienyl alkaline-metal salts $[2,4-(\text{CH}_3)_2\text{C}_5\text{H}_5]\text{M}$ ($\text{M} = \text{Na}, \text{K}$) [4] has greatly contributed to the synthesis and has prompted the rapid development in this area. In our laboratory [5–9], we have used 1-halopenta-2,4-dienes for preparation of these compounds. The 1-halopenta-2,4-diene seems to be an intriguing reagent because it reacts with metal carbonyl anions to give η^1 -pentadienyl complexes, which can be further converted to *syn*- η^3 and η^5 forms by thermal or photochemical activation [5–9].

Allyl, acyl and alkyl halides are known to undergo oxidative addition with d^8 square planar complexes [10–12]. The stereochemistry of the addition depends largely on the molecule that is added. Methyl and acyl halides add *trans* to



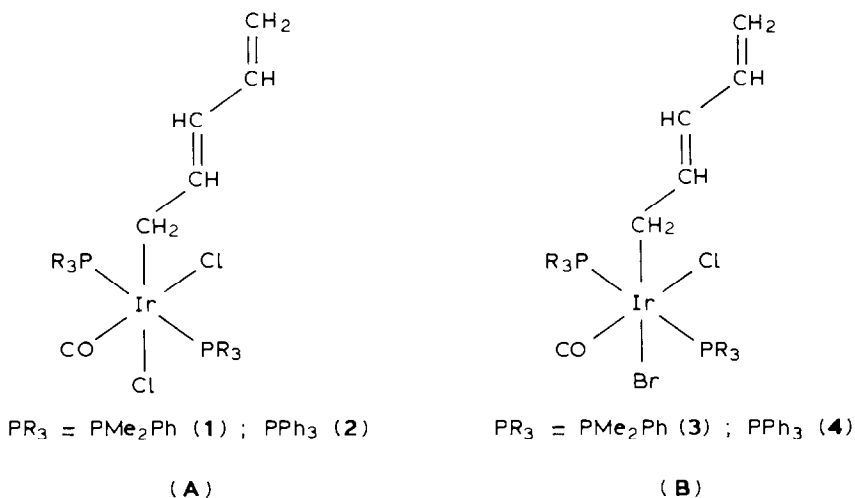
Scheme 1.

$\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2$ in an S_N2 type mechanism [12]. Nevertheless, allyl halides add *cis* to $\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2$ in benzene [10,11], and an S_N2 type mechanism via the transition state (I) as depicted in Scheme 1, is suggested for the reaction. In order to further investigate the behaviour of 1-halopenta-2,4-dienes in their reaction with low-valence metal species, their addition reactions to the square-planar complexes *trans*- $\text{MCl}(\text{CO})(\text{PR}_3)_2$ ($\text{M} = \text{Rh}$, $\text{P} = \text{Me}_2\text{Ph}$; $\text{M} = \text{Ir}$, $\text{P} = \text{PMe}_2\text{Ph}$, PPh_3) were studied.

Results and discussion

The 1-halopenta-2,4-diene $\text{CH}_2=\text{CHCH}=\text{CHCH}_2\text{X}$ ($\text{X} = \text{Cl}$, Br) readily adds to the complexes *trans*- $\text{IrCl}(\text{CO})(\text{PR}_3)_2$ ($\text{PR}_3 = \text{PMe}_2\text{Ph}$, PPh_3) in benzene or chloroform to afford the adducts $\text{IrCl}_2(\text{CO})(\eta^1\text{-C}_5\text{H}_7)(\text{PR}_3)_2$ ($\text{PR}_3 = \text{PMe}_2\text{Ph}$ (**1**); $\text{PR}_3 = \text{PPh}_3$ (**2**)) and $\text{IrClBr}(\text{CO})(\eta^1\text{-C}_5\text{H}_7)(\text{PR}_3)_2$ ($\text{PR}_3 = \text{PMe}_2\text{Ph}$ (**3**); $\text{PR}_3 = \text{PPh}_3$ (**4**)) in good yields (80–92%). In a typical reaction, *trans*- $\text{IrCl}(\text{CO})(\text{PR}_3)_2$ was dissolved in a mixture of 1-halopenta-2,4-diene and benzene at 10°C . The products separated as colorless needles on addition of ether to the solution. Notable here is that the addition of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ to pentadienyl halides is reversible in solution, whereas colorless crystals of the products can be isolated in the presence of pentadienyl halides. Attempts to recrystallize the products, in the absence of pentadienyl halides, however, led to the dissociation of the complex, and the yellow material of $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ ($\text{X} = \text{Cl}$, for pentadienyl chloride; $\text{X} = \text{Cl}$, Br for pentadienyl bromide) gradually reformed after the solution had been allowed to stand for several hours.

All of the elemental analyses are consistent with the proposed formula. Combination of the ^1H , ^{31}P NMR and far-infrared spectra permitted the determination of their structural configurations. Jenkins and Shaw [13] have shown that the metal-chloride stretching frequencies in the far-infrared region of octahedral com-

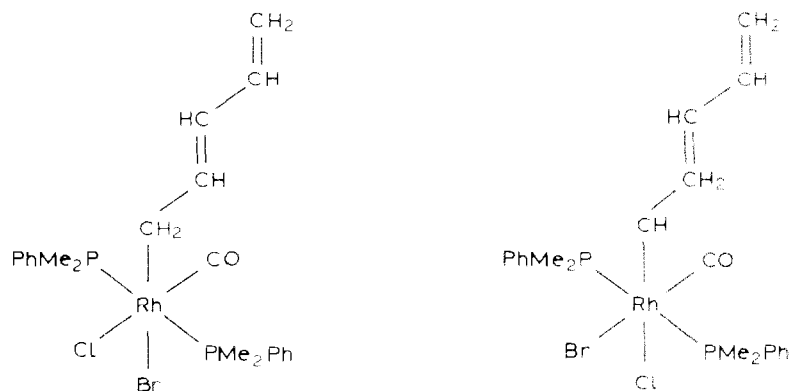


plexes vary as follows; $\nu(\text{Ir}-\text{Cl}, \text{trans to CO}) \sim 300 \text{ cm}^{-1}$, $\nu(\text{Ir}-\text{Cl}, \text{trans to phosphine}) \sim 275 \text{ cm}^{-1}$, $(\text{Ir}-\text{Cl}, \text{trans to alkyl}) \sim 250 \text{ cm}^{-1}$. Configurations **A** and **B** are assigned to **1** and **2**, and to **3** and **4** respectively on the basis of their spectroscopic data. All compounds have η^1 -*trans*-pentadienyl group as shown from their proton NMR resonances. The *trans* configuration is inferred from the coupling constant $J_{23} = 14\text{--}15 \text{ Hz}$. In addition to the $\nu(\text{C}=\text{C})$ bands at $1620\text{--}1610 \text{ cm}^{-1}$, all complexes show $\nu(\text{C}=\text{O})$ absorption bands at $2045\text{--}2030 \text{ cm}^{-1}$ indicative of the presence of Ir^{III} -bound CO groups [10,13]. For complexes **1** and **2**, in the far-infrared region, two $\nu(\text{Ir}-\text{Cl})$ bands at ~ 305 and $\sim 245 \text{ cm}^{-1}$ are observed, which are assignable to the $\text{Ir}-\text{Cl}$ frequency *trans* to carbonyl and pentadienyl groups respectively. The two *trans* phosphines of these two compounds were further confirmed by a single resonance in ^{31}P NMR spectra, indicative of the chemical equivalence of the two phosphines. Similarly, the designation of configuration **B** to **3** and **4** relies largely on the presence of far-infrared $\nu(\text{Ir}-\text{Cl})$ bands at $\sim 305 \text{ cm}^{-1}$ and a single ^{31}P NMR resonance at $\delta 29.6$ and 18.1 , respectively. Moreover, in the proton NMR spectra of **1** and **3**, the resonances of phosphine methyls show two 1/2/1 triplets, which suggest that the phosphines occupy the *trans* positions with no plane of symmetry through the $\text{Ir}-\text{P}$ bonds. The observed $\text{P}-\text{CH}_3$ triplet arises from the strong coupling between the *trans* phosphorus nuclei [14]. The values of $^2J(\text{PH}) + ^4J(\text{PH}) = 8.0 \text{ Hz}$ of phosphine methyls are consistent with the reported values for the isostructural $\text{IrX}_2(\text{CO})(\eta^1\text{-allyl})(\text{PMe}_2\text{Ph})_2$ ($\text{X} = \text{Cl}, \text{Br}$) [10].

Scheme 1 shows the reaction mechanism of allyl halides with $\text{Ir}(\text{CO})\text{Cl}(\text{PMe}_2\text{Ph})_2$. In benzene, the *cis*-addition adduct with *cis* phosphines is formed first, and in methanol it gradually isomerizes to the *trans* product. Although pentadienyl halides are higher homologs of allyl halides, their reactions with $\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2$, all give *trans* addition products in both benzene or chloroform. The vinyl group probably exerts unfavorable steric hinderance, which prevents the formation of transition state I. We believe that the reaction mechanism is analogous to that considered for the addition of CH_3I to $\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2$. In the latter case, the transition state is highly polar $\text{Ir}^+ \cdots \text{CH}_3 \cdots \text{X}^-$, which in benzene gives the ion

pair $[\text{IrCl}(\text{CO})\text{CH}_3(\text{PMe}_2\text{Ph})_2]^+ \text{X}^-$. The ions then combine to give the specifically *trans* product.

In a similar manner, $\text{RhCl}(\text{CO})(\text{PMe}_2\text{Ph})_2$ undergoes smooth oxidative addition with pentadienyl halides in benzene or chloroform. Pale yellow crystals of adducts $\text{RhCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_2(\eta^1\text{-C}_5\text{H}_7)$ (**5**) and $\text{RhClBr}(\text{CO})(\text{PMe}_2\text{Ph})_2(\eta^1\text{-C}_5\text{H}_7)$ (**6**) are obtained in moderate yields, 42–45%. In contrast, the reaction of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ with pentadienyl halides fails to produce the desired adducts. $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ was recovered exclusively after the mixture was stirred for 1 h in both benzene and chloroform. Complex **5** has configuration **A** which was deduced from its IR, ^1H and ^{31}P NMR data. For complex **6** two $\nu(\text{Ir}-\text{Cl})$ bands are observed at 306 and 248 cm^{-1} , and this finding suggests the presence of the two isomers, depicted below. The ^1H and ^{31}P NMR spectra further confirm these structures, which are present in



a molar ratio of about 2/1. In addition to the distinct proton resonances of $\eta^1\text{-trans}$ -pentadienyl ligand, each isomer was characterized by its phosphine methyl proton resonances as two 1/2/1 triplets and phosphorus resonance as a doublet with $J(\text{Rh}-\text{P}) = 45$ Hz. Absolute assignment of NMR data to each isomer is not possible at this stage. These two isomers appear to be in thermal equilibrium since no further changes in relative intensity are observed if the NMR sample is allowed to stand for a few hours.

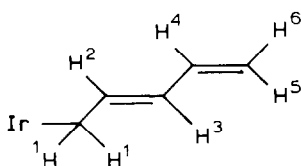
Experimental

All reactions were carried out under dry nitrogen using Schlenk-type glassware. *Trans*-1-chloro and -bromopenta-2,4-diene were synthesized by treatment of penta-1,4-diene-3-ol with the acids, $\text{HCl}_{(\text{aq})}$ and $\text{HBr}_{(\text{aq})}$ at 0°C [15]. Complexes *trans*- $\text{MCl}(\text{CO})(\text{PR}_3)_2$ ($\text{M} = \text{Ir}$, $\text{PR}_3 = \text{PMe}_2\text{Ph}$, PPh_3 ; $\text{M} = \text{Rh}$, $\text{PR}_3 = \text{PMe}_2\text{Ph}$, PPh_3) were prepared according to the methods in the literature [16]. PMe_2Ph , PPh_3 and $\text{MCl}_3 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Rh}$, Ir) were obtained from Strem Chemicals and used without further purifications. NMR spectra were recorded on either a JEOL FX-100 or a Bruker AM-400 spectrometer. The values of ^1H and ^{31}P resonances are relative to Me_4Si and H_3PO_4 respectively. Infrared spectra in the 2300–1400 cm^{-1} region were recorded in Nujol mulls on KBr plates and the far-IR region 400–200 cm^{-1} were recorded in Nujol mulls on polyethylene films, by use of a Perkin-Elmer 580

spectrophotometer. Microanalyses were performed by the Microanalytic Laboratory at National Taiwan University.

Synthesis of $\text{IrCl}_2(\text{CO})(\eta^1\text{-C}_5\text{H}_7)[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2$ (1)

Trans-1-chloropenta-2,4-diene (0.2 ml, 1.76 mmol) was added to a rapidly stirred solution of *trans*- $\text{IrCl}(\text{CO})[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2$ (0.20 g, 0.38 mmol) in 10 ml benzene at 10 °C. Complex **1** separated as colorless needles in good yields (0.212 g, 0.34 mmol) when ether was added to the solution, which was then stored at 0 °C. Similarly, the reaction carried out in chloroform gave **1** of the same configuration. Anal. Found: C, 42.04; H, 4.52; $\text{C}_{22}\text{H}_{29}\text{IrP}_2\text{Cl}_2\text{O}$ calc: C, 41.64; H, 4.61%. IR (Nujol): $\nu(\text{CO})$ 2041vs, $\nu(\text{C}=\text{C})$ 1614w, $\nu(\text{Ir}-\text{Cl})$: 241s, 301s. ^1H NMR (400 MHz, benzene- d_6): δ 1.90 (t, 6H, CH_3), 2.01 (t, 6H, CH'_3), 2.48 (q, 2H, H^1), 4.70 (d, 1H, H^6), 4.95 (d, 1H, H^5), 5.22 (dd, 1H, H^3), 5.40 (dt, 1H, H^2), 6.10 (dt, 1H, H^4), 6.97 and 7.42 (complex m, 10H, Ph), $^2J(\text{P}-\text{CH}_3) + ^4J(\text{P}-\text{CH}_3) = 8.7$ Hz, $^2J(\text{P}-\text{CH}'_3) + ^4J(\text{P}-\text{CH}'_3) = 8.0$ Hz, $J(\text{P}-\text{H}^1) = J_{12} = 6.3$ Hz, $J_{23} = 14.5$ Hz, $J_{34} = J_{46} = 10.2$ Hz, $J_{45} = 16.0$ Hz; ^{31}P NMR (40.3 MHz, benzene- d_6): δ 26.6(s).



Synthesis of $\text{IrCl}_2(\text{CO})(\eta^1\text{-C}_5\text{H}_7)(\text{P}(\text{C}_6\text{H}_5)_3)_2$ (2)

This was prepared similarly using *trans*-1-chloropenta-2,4-diene and $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$. The product was isolated as colorless needles in 88% yield. Anal. Found: C, 56.84; H, 4.01; $\text{C}_{42}\text{H}_{37}\text{IrP}_2\text{Cl}_2\text{O}$ calc: C, 57.14; H, 4.22%. IR (Nujol): $\nu(\text{CO})$, 2040vs; $\nu(\text{C}=\text{C})$, 1612w; $\nu(\text{Ir}-\text{Cl})$, 245s, 305s. ^1H NMR (400 MHz, benzene- d_6): δ 3.27 (q, 2H, H^1), 4.84 (d, 1H, H^6), 4.87 (d, 1H, H^5), 5.10 (dd, 1H, H^3), 5.86 (dt, 1H, H^2), 6.20 (dt, 1H, H^4), 6.89–6.98 and 8.20 (complex m, 30H, Ph), $J(\text{H}^4-\text{P}) = J_{12} = 4.6$ Hz, $J_{23} = 15.4$ Hz, $J_{34} = J_{46} = 9.8$ Hz, $J_{45} = 17.7$ Hz, ^{31}P NMR (benzene- d_6 , 40.3 MHz): δ 14.7(s).

Synthesis of $\text{IrClBr}(\text{CO})(\eta^1\text{-C}_5\text{H}_7)[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2$ (3)

This was prepared similarly using *trans*-1-bromopenta-2,4-diene and $\text{IrCl}(\text{CO})[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2$. The product was isolated as colorless needles in 82% yield. Anal. Found: C, 39.14; H, 4.54; $\text{C}_{22}\text{H}_{29}\text{IrP}_2\text{ClBrO}$ calc: C, 38.91; H, 4.30%, IR (Nujol): $\nu(\text{CO})$, 2035vs, $\nu(\text{C}=\text{C})$, 1615w; $\nu(\text{Ir}-\text{Cl})$, 305s; ^1H NMR (400 MHz, benzene- d_6): δ 1.83 (t, 6H, CH_3), 1.93 (t, 6H, CH'_3), 2.40 (q, 2H, H^1), 4.78 (d, 1H, H^6), 4.92 (d, 1H, H^5), 5.15 (dd, 1H, H^3), 5.46 (dt, 1H, H^2), 6.10 (dt, 1H, H^4), 6.97 and 7.42 (complex m, 10H, Ph), $^2J(\text{PCH}_3) + ^4J(\text{PCH}_3) = 8.2$ Hz, $^2J(\text{PCH}'_3) + ^4J(\text{PCH}'_3) = 8.6$ Hz, $J(\text{P}-\text{H}^1) = J_{12} = 6.0$ Hz, $J_{23} = 14.7$ Hz, $J_{34} = J_{46} = 10.3$ Hz, $J_{45} = 16.1$ Hz; ^{31}P NMR (40.3 MHz, benzene- d_6): δ 29.6 MHz.

Synthesis of $\text{IrClBr}(\text{CO})(\eta^1\text{-C}_5\text{H}_7)[\text{P}(\text{C}_6\text{H}_5)_3]_2$ (4)

This was prepared similarly using *trans*-1-bromopenta-2,4-diene and $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$. The product was isolated as colorless needles in 85% yield. Anal.

Found: C, 54.93; H, 4.43. $C_{42}H_{37}IrClBrP_2O$ calc: C, 54.37; H, 4.02%. IR (Nujol): $\nu(CO)$ 2036vs, $\nu(C=C)$ 1612w, $\nu(Ir-Cl)$ 303s; 1H NMR (400 MHz, benzene- d_6): δ 3.50 (q, 2H, H^1), 4.84 (d, 1H, H^6), 4.87 (d, 1H, H^5), 5.10 (dd, 1H, H^3), 5.86 (dt, 1H, H^2), 6.20 (dt, 1H, H^4), 6.89–6.97 and 8.20 (complex m, 30H, Ph). $J(H^1-P) = J_{12} = 4.8$ Hz, $J_{23} = 15.6$ Hz, $J_{34} = J_{46} = 9.6$ Hz, $J_{45} = 17.8$ Hz, ^{31}P NMR (40.3 MHz, benzene- d_6): δ 18.1(s).

Synthesis of $RhCl_2(CO)(\eta^1-C_5H_7)[P(CH_3)_2C_6H_5]_2$ (5)

This was prepared similarly using *trans*-1-chloro-penta-2,4-diene and $RhCl(CO)[P(CH_3)_2C_6H_5]_2$. The product was isolated as pale yellow prisms in 42% yield. Anal. Found: C, 48.54; H, 5.47. $C_{22}H_{29}RhP_2Cl_2O$ calc: C, 48.46; H, 5.36%. IR (Nujol): $\nu(CO)$, 2035vs; $\nu(C=C)$, 1613w, $\nu(Ir-Cl)$, 247s, 307s; 1H NMR (400 MHz, benzene- d_6): δ 1.90 (t, 6H, CH_3), 2.04 (t, 6H, CH_3), 2.86 (m, 2H, H^1), 4.90 (d, 1H, H^6), 5.10 (d, 1H, H^5), 5.50 (dd, 1H, H^3), 5.60 (dt, 1H, H^2), 6.20 (dt, 1H, H^4), 6.94 and 7.50 (complex m, 10H, Ph), $^2J(PCH_3) + ^4J(PCH_3) = 8.3$ Hz, $^2J(PCH'_3) + ^4J(PCH'_3) = 8.6$ Hz, $J_{23} = 14.9$ Hz, $J_{34} = J_{46} = 10.0$ Hz, $J_{45} = 16.8$ Hz, ^{31}P NMR (40.3 MHz, benzene- d_6): δ -1.1 (d, $J(Rh-P)$ 43.9 Hz).

Synthesis of $RhClBr(CO)(\eta^1-C_5H_7)[P(CH_3)_2C_6H_5]_2$ (6)

This was prepared similarly using *trans*-1-bromo-penta-2,4-diene and $RhCl(CO)[P(CH_3)_2C_6H_5]_2$. The product was isolated as pale yellow prisms in 45% yield. Anal. Found: C, 44.96; H, 5.34. $C_{22}H_{29}RhP_2ClBrO$ calc: C, 44.81; H, 4.96%. IR (Nujol): $\nu(CO)$, 2043 vs; $\nu(C=C)$, 1618w; $\nu(Ir-Cl)$: 245vs, 304vs, 1H NMR (400 MHz, benzene- d_6): major species δ 1.93 (t, 6H, CH_3), 1.99 (t, 6H, CH_3), 2.68 (complex m, 2H, H^1), 4.85 (d, 1H, H^6), 4.94 (d, 1H, H^5), 5.32 (dd, 1H, H^3), 5.49 (dt, 1H, H^2), 6.20 (dt, 1H, H^4), 6.97 and 7.50 (complex m, 10H, Ph), $^2J(PCH_3) + ^4J(PCH_3) = 8.5$ Hz, $^2J(PCH'_3) + ^4J(PCH'_3) = 8.6$ Hz, $J_{23} = 14.7$ Hz, $J_{34} = J_{46} = 10.1$ Hz, $J_{45} = 16.7$ Hz; minor species, 1.82 (t, 6H, CH_3), 1.86 (t, 6H, CH_3), 2.68 (complex m, 2H, H^1), 4.85 (d, 1H, H^6), 4.95 (d, 1H, H^5), 5.37 (dd, 1H, H^3), 5.49 (dt, 1H, H^2), 6.20 (dt, 1H, H^4), 6.97 and 7.50 (complex m, 10H, Ph), $^2J(PCH_3) + ^4J(PCH_3) = 8.4$ Hz, $^2J(PCH'_3) + ^4J(PCH'_3) = 8.8$ Hz, $J_{23} = 14.6$ Hz, $J_{34} = J_{46} = 10.0$ Hz, $J_{45} = 16.6$ Hz, ^{31}P NMR (40.3 MHz, benzene- d_6): major species δ 0.69 (d, $J(Rh-P) = 45.1$ Hz); minor species 4.57 (d, $J(Rh-P) = 45.2$ Hz).

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