

# Chemical, Electrochemical, and Structural Aspects of the Ruthenium Complexes $\text{Ru}(\eta\text{-arene})\text{Cl}_2(\text{P})$ (Where Arene = Benzene, [2.2]Paracyclophane and $\text{P}$ = Triphenylphosphine, *rac*-[2.2]Paracyclophanylphosphine)

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Reaction of diphenyl[2.2]paracyclophanylphosphine, *rac*- $\text{PPh}_2(\text{C}_{16}\text{H}_{15})$  (**1**), with  $[\text{Ru}(\eta\text{-arene})\text{Cl}_2]_2$  (where arene =  $\text{C}_6\text{H}_6$ , [2.2]paracyclophane ( $\text{C}_{16}\text{H}_{16}$ )) in a 2:1 ratio affords the half-sandwich complexes  $\text{Ru}(\eta\text{-arene})\text{Cl}_2\{\text{PPh}_2(\text{C}_{16}\text{H}_{15})\}$  (arene =  $\text{C}_6\text{H}_6$  (**2**),  $\text{C}_{16}\text{H}_{16}$  (**3**)) in high yield. In solution, the structures of **2** and **3** have been probed and assigned using 2D NMR spectroscopy and the structure of the [2.2]paracyclophane derivative, **3**, has been established in the solid-state by single-crystal X-ray diffraction. Cyclic voltammetry and steady-state voltammetry of **2** in 0.25 M  $[\text{nBu}_4\text{N}][\text{PF}_6]/\text{CH}_2\text{Cl}_2$  shows that the complex undergoes a chemically reversible, one-electron oxidation and an irreversible, two-electron reduction. The voltammetry of the related complex  $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}_2(\text{PPh}_3)]$  (**4**), recorded under analogous conditions, is similar both in terms of the processes displayed and the potentials at which they occur.

## Introduction

Phosphines are important ligands in transition-metal-catalyzed reactions and the electronic and steric effects of the phosphine have a pronounced influence on the organic transformation that take place at the transition-metal center.<sup>1</sup> The search for new phosphine ligands that will enhance the rate, yield, or specificity of organic transformations remains an active field of research. A large number of new phosphine ligands are reported each year, but very few prove to be superior to those currently available for use in catalysis. A relatively recent example of a new bis-phosphine ligand that has showed catalytic activity superior to that of other available phosphines is 4,12-bis(diphenylphosphino)[2.2]paracyclophane,  $(\text{PPh}_2)_2(\text{C}_{16}\text{H}_{14})$  or [2.2]PhanePhos,<sup>2</sup> in which the high activity and enantioselectivities obtained

using [2.2]PhanePhos have been ascribed to steric effects emanating from the  $C_2$ -symmetric chiral environment imposed by the [2.2]paracyclophane backbone.

In our studies we selected [2.2]paracyclophane as a substituent group in mono-phosphines, anticipating that it would provide electronic effects that are conducive to catalysis. We noticed that when [2.2]cyclophanes are  $\eta^6$ -coordinated to metal centers, the redox potentials of both oxidation<sup>3</sup> and reduction<sup>4</sup> become more facile as the extent of inter-ring overlap, and hence  $\pi$ - $\pi$  overlap, increases. In [2.2]orthocyclophane there is no  $\pi$ - $\pi$  overlap, in [2.2]metacyclophane there is partial  $\pi$ - $\pi$  overlap, and in [2.2]paracyclophane there is considerable  $\pi$ - $\pi$  overlap. Since many catalytic cycles involve both oxidative-addition and reductive-elimination steps, we postulated that the presence of [2.2]paracyclophane may make these steps more facile and therefore enhance catalytic activity. With this in mind we prepared several paracyclophanylphosphines, including *rac*-diphenyl[2.2]paracyclophanylphosphine, *rac*- $\text{PPh}_2(\text{C}_{16}\text{H}_{15})$ . Monosubstituted [2.2]paracyclophane derivatives are inherently chiral, but since chiral mono-phosphines offer no advantages over bis-phosphines, resolution of *rac*- $\text{PPh}_2(\text{C}_{16}\text{H}_{15})$  into optically pure isomers was not attempted.

Initial studies were concerned with the structural characterization of some palladium<sup>5</sup> and platinum<sup>6</sup> derivatives of the new phosphine. In this paper we

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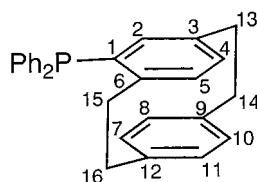
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Table 1. <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR Data for **2** and **3** Recorded in CDCl<sub>3</sub><sup>a</sup>

	<b>2</b>		<b>3</b>
	5.03 (s, 6H)	$\eta$ -C <sub>6</sub> H <sub>6</sub> ( <b>2</b> ) or $\eta$ -C <sub>16</sub> H <sub>16</sub> ( <b>3</b> ) 88.36 (d, $J_{P-C}$ 3.6, 6C)	6.60 (m, 4H) 4.45 (d, 5.6, 2H) 4.24 (d, 5.6, 2H) 2.92 (m, 4H) 2.09 (m, 2H) 2.13 (m, 2H) 132.7 (s, 4C) 84.10 (s, 2C) 87.10 (s, 2C) 31.26 (s, 2C) 33.17 (s, 2C) 139.40 (s, 2C) 122.56 (s, 2C)
		Ph Groups	
	8.37 (m, 4H) 7.99 (m, 4H) 7.46 (m, 2H)	135.99 (s, 4C) 130.98 (s, 4C) 128.39 (s, 2C) 137.19 (d, $J_{P-C}$ 40, 2C)	7.83, 8.18 (br, 4H) 7.41, 7.34 (m, 4H) 7.36, 7.41 (m, 2H) -, 135.6 (s, 2C) 128.1, 127.9 (s, 1C) 130.2, 129.9 (s, 1C) 137.7 (d, $J_{P-C}$ 40, 2C) 130.68 (d, $J_{P-C}$ 40, 2C)
		[2.2]Paracyclophanyl Group	
1		127.5 (d, $J_{P-C}$ 40, 1C)	126.95 (d, $J_{P-C}$ 44, 1C)
2	8.42 (m, 1H)	143.24 (s, 1C)	144.28 (s, 1C)
3		145.61 (s, 1C)	139.77 (s, 1C)
4	6.61 (m, 1H)	137.07 (s, 1C)	136.4 (s, 1C)
5	6.46 (dd, 8, $J_{P-H}$ 3, 1H)	135.90 (s, 1C)	135.3 (s, 1C)
6		140.43 (s, 1C)	139.8 (d, $J_{P-C}$ 14, 1C)
7	5.10 (d, 6.4, 1H)	132.43 (s, 1C)	131.3 (s, 1C)
8	6.25 (d, 7.6, 1H)	133.02 (s, 1C)	132.77 (s, 1C)
9		139.63 (s, 1C)	138.26 (s, 1C)
10	6.60 (m, 1H)	131.70 (s, 1C)	132.7 (s, 1C)
11	6.51 (d, 7, 1H)	136.08 (s, 1C)	132.77 (s, 1C)
12		138.55 (s, 1C)	139.39 (s, 1C)
13 (a)	3.10 (m, 1H)	35.17 (s, 1C)	34.90 (s, 1C)
13 (b)	3.27 (m, 1H)		3.28 (m, 1H)
14 (a)	3.26 (m, 1H)	35.23 (s, 1C)	34.90 (s, 1C)
14 (b)	2.98 (m, 1H)		2.95 (m, 1H)
15 (a)	3.18 (m, 1H)	35.76 (s, 1C)	35.36 (s, 1C)
15 (b)	2.89 (ddd, 4.6, 11.9, 15, 1H)		2.88 (m, 1H)
16 (a)	2.00 (br, t, 11.9, 1H)	34.97 (s, 1C)	1.74 (br, 1H)
16 (b)	2.60 (ddd, 3.4, 11.4, 13.4, 1H)		2.51 (m, 1H)

<sup>a</sup> Atom labels are as shown; the CH<sub>2</sub> protons labeled "a" correspond to those on the same side of cyclophane as the P atom, and those labeled "b" are on the opposite side. Resonances are given in units of ppm and *J* values in Hz.

report more fully on this ligand, describing the synthesis and chemical, electrochemical, and structural characterization of ruthenium(II)-*rac*-PPh<sub>2</sub>(C<sub>16</sub>H<sub>15</sub>) derivatives.

### Results and Discussion

Ru( $\eta$ -C<sub>6</sub>H<sub>6</sub>)Cl<sub>2</sub>{PPh<sub>2</sub>(C<sub>16</sub>H<sub>15</sub>)} (**2**) and Ru( $\eta$ -C<sub>16</sub>H<sub>16</sub>)Cl<sub>2</sub>{PPh<sub>2</sub>(C<sub>16</sub>H<sub>15</sub>)} (**3**) were prepared according to a high-yielding method originally described by Zelonka for related species.<sup>7</sup> Two molecular equivalents of *rac*-diphenyl[2.2]paracyclophanylphosphine (**1**) was stirred with the appropriate dimer, [Ru( $\eta$ -C<sub>6</sub>H<sub>6</sub>)Cl<sub>2</sub>]<sub>2</sub> or [Ru( $\eta$ -C<sub>16</sub>H<sub>16</sub>)Cl<sub>2</sub>]<sub>2</sub>, in CHCl<sub>3</sub> to afford **2** and **3**, respectively. The FAB mass spectra of **2** and **3** recorded in positive mode show strong peaks corresponding to the parent ion, and the [M - Cl]<sup>+</sup> ion along with additional

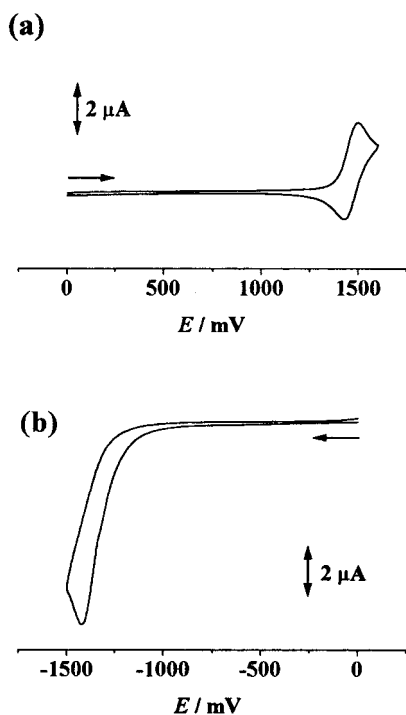
fragment ions (see Experimental Section). The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **2** and **3** are very simple, with a singlet resonance observed at  $\delta$  19.53 for **2** and  $\delta$  32.41 for **3**. In contrast, corresponding <sup>1</sup>H NMR spectra are quite complicated with signals ranging from  $\delta$  2.00 to 8.42 for **2** and from  $\delta$  1.74 to 8.08 for **3**. Full assignments of the <sup>1</sup>H and <sup>13</sup>C NMR spectra are listed in Table 1.

**Electrochemical Investigations.** The redox behavior of **2** and the triphenylphosphine analogue [Ru( $\eta$ -C<sub>6</sub>H<sub>6</sub>)Cl<sub>2</sub>(PPh<sub>3</sub>)] (**4**) have been investigated using cyclic voltammetry and steady-state voltammetry. The cyclic voltammogram of **2**, recorded in 0.25 M [<sup>n</sup>Bu<sub>4</sub>N][PF<sub>6</sub>]/dichloromethane, is shown in Figure 1. A scan from 0 to +1.5 V at 100 mV s<sup>-1</sup> reveals a chemically reversible process at  $E_{1/2} = +1.40$  V, with  $\Delta E_p = 70$  mV. This process corresponds to a one-electron oxidation, as judged by steady-state voltammetry of a solution containing equimolar amounts of **2** and a complex known to undergo a chemically reversible one-electron process. The oxidation of **2**, and related [Ru( $\eta$ -C<sub>6</sub>H<sub>6</sub>)Cl<sub>2</sub>(PR<sub>3</sub>)] compounds, can be considered as a metal-based Ru<sup>II/III</sup>

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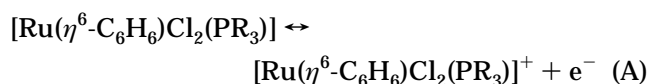
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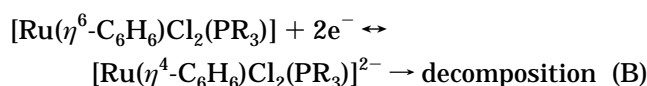


**Figure 1.** Cyclic voltammetry of  $[\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\{\text{PPh}_2(\text{C}_{16}\text{H}_{15})\}]$  (**2**) in 0.25 M  $[\text{nBu}_4\text{N}][\text{PF}_6]/\text{CH}_2\text{Cl}_2$  at 290 K (scan rate  $100 \text{ mV s}^{-1}$ ): (a) scan from 0 to +1.5 V; (b) scan from 0 to -1.5 V.

process, as shown in eq A. Although chemically revers-



ible on the cyclic voltammetric time scale (scan rate  $10 \text{ mV s}^{-1}$ ), the oxidation of **2** is irreversible on the bulk electrochemical time scale. When the oxidation of **2** was performed in an optically transparent thin-layer electrolysis cell, the changes in the electronic spectrum were monitored as the electrolysis progressed. The UV/vis spectrum of **2** in  $\text{CH}_2\text{Cl}_2$  contains a band at  $\sim 27\,100 \text{ cm}^{-1}$ . Upon oxidation spectral changes occurred without retention of isosbestic points, and rereduction failed to regenerate the starting spectrum. An irreversible reduction wave is detected at  $E_{p,c} = -1.48 \text{ V}$  in the cyclic voltammogram of **2** upon scanning from 0 to -1.5 V at  $100 \text{ mV s}^{-1}$ . The wave remains irreversible at fast scan rates (up to  $5 \text{ V s}^{-1}$ ) and at low temperature (220 K) and overall involves two electrons, as shown by steady-state voltammetry at a microdisk electrode, where the limiting current for the reduction is approximately twice that for the  $\text{2}^{0/+}$  oxidation wave. This irreversible two-electron wave is thought to correspond to a metal-based process, as shown in eq B. Studies of bis-arene systems,



e.g.  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)_2]^{2+}$ , have suggested that two-electron reduction results in a  $\eta^6$  to  $\eta^4$  transformation of the coordinated arene.<sup>8</sup>

(8) Finke, R. G.; Voegeli, R. H.; Laganis, E. D.; Boekelheide, V. *Organometallics* **1983**, *2*, 347.

**Table 2. Electrochemical Data for 2 and 4<sup>a</sup>**

complex	$E_{1/2}/\text{V}^b$	$\Delta E_p/\text{mV}^b$	$I_{p,c}/I_{p,a}^c$
$[\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\{\text{PPh}_2(\text{C}_{16}\text{H}_{15})\}]$ ( <b>2</b> )	+1.40	70 (rev)	1.0
	-1.48	irrev	
$[\text{Ru}(\text{PPh}_3)\text{Cl}_2(\eta\text{-C}_6\text{H}_6)]$ ( <b>4</b> )	+1.36	110 (rev)	1.0
	-1.47	irrev	

<sup>a</sup> Measured in  $0.25 \text{ mol dm}^{-3} [\text{nBu}_4\text{N}][\text{PF}_6]/\text{CH}_2\text{Cl}_2$ , vs Ag/AgCl, against which  $\text{Fc}^{0/+}$  is measured at +0.55 V. Abbreviations: rev = reversible, irrev = irreversible. <sup>b</sup>  $E_{1/2} = (E_{p,a} + E_{p,c})/2$ ,  $\Delta E_p = E_{p,a} - E_{p,c}$ . <sup>c</sup>  $I_{p,c}/I_{p,a}$  evaluated by the method given in: Shain, R. S. *Anal. Chem.* **1966**, *38*, 1406.

The redox behavior of **4** is very similar to that of compound **2**, and the results from voltammetric measurements are summarized in Table 2. Both complexes display a quasi-reversible one-electron oxidation and an irreversible two-electron reduction. The small difference in  $E_{1/2}$  potentials (error  $\pm 0.01 \text{ V}$ ) for the oxidation processes of **2** and **4** suggests that the cyclophane substituent on the phosphine does not influence the net electron donor ability of  $\text{PPh}_2(\text{C}_{16}\text{H}_{15})$  (**1**) to any significant extent, such that the electronic parameter  $\chi_1$ ,<sup>9</sup> for  $\text{C}_{16}\text{H}_{15}$  is in effect similar to that for  $\text{C}_6\text{H}_5$ . Since the difference in the basicity of **1** and  $\text{PPh}_3$  is negligible, it is possible that the former phosphine may be suited to catalytic processes which are initiated by dissociation of the phosphine. For example, alkyl-alkyl coupling in *cis*-(alkyl)<sub>2</sub> $\text{Pd}^{\text{II}}(\text{PR}_3)_2$  complexes is inhibited by excess phosphine and it is therefore considered to be initiated by the rate-determining dissociation of the phosphine ligand, producing a three-coordinate intermediate.<sup>10</sup>

**Solid-State Structure of 3.** The structures of some square-planar palladium and platinum complexes carrying the diphenyl[2.2]paracyclophanylphosphine ligand have been previously established, and in each case some unusual features have been observed.<sup>5,6</sup> Single crystals of **3** suitable for the X-ray diffraction analysis were grown from a solution of  $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$  (1:1) by slow evaporation. The asymmetric unit of **3** contains two molecules (**a** and **b**), which differ in the enantiomer of the coordinated phosphine; the structure of **3a** is shown in Figure 2. The structures of the triphenylphosphine analogues of **2** and **3** have been reported previously,<sup>11</sup> and the gross molecular structures of the three compounds are not dissimilar. The structures of **3a** and **3b** are unique in that one [2.2]paracyclophane  $\pi$ -bonds to the ruthenium atom, while the other is  $\sigma$ -bonded to the phosphine atom and therefore interacts indirectly with the ruthenium atom. This allows comparisons to be made between the two [2.2]paracyclophane entities within the same molecule. The inter-centroid distance between the two rings in the  $\pi$ -bonded ligand is 2.914 Å in **3a** and 2.900 Å in **3b**, which is close to that observed in  $\text{Ru}(\eta\text{-C}_{16}\text{H}_{16})\text{Cl}_2(\text{PPh}_3)$  (2.97 Å). The magnitude of the gap between the two decks in [2.2]paracyclophane has been discussed before, following the structural characterization of [2.2]paracyclophane and the first  $\pi$ -complex,  $\text{Cr}(\text{CO})_3(\eta\text{-C}_{16}\text{H}_{16})$ .<sup>12</sup> Coordination

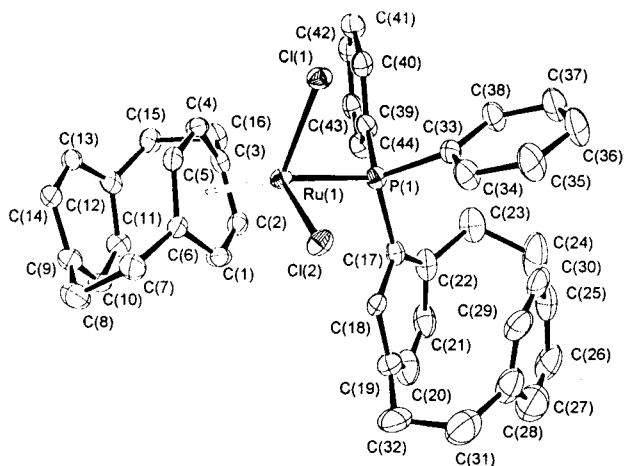
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**Figure 2.** Molecular structure of **3a**. Bond lengths (Å): Ru(1)–P(1) = 2.339(2), Ru(1)–Cl(1) = 2.423(2), Ru(1)–Cl(2) = 2.429(2), Ru(1)–C(1) = 2.157(9), Ru(1)–C(2) = 2.147(8), Ru(1)–C(3) = 2.326(8), Ru(1)–C(4) = 2.197(8), Ru(1)–C(5) = 2.281(8), Ru(1)–C(6) = 2.392(8), P(1)–C(33) = 1.845(9), P(1)–C(39) = 1.823(8), P(1)–C(17) = 1.836(9), C(1)–C(2) = 1.394(12), C(1)–C(6) = 1.431(12), C(2)–C(3) = 1.417(12), C(3)–C(4) = 1.404(12), C(4)–C(5) = 1.411(12), C(5)–C(6) = 1.384(11), C(6)–C(7) = 1.487(12), C(7)–C(8) = 1.584(13), C(8)–C(9) = 1.530(14), C(3)–C(16) = 1.493(12), C(16)–C(15) = 1.579(12), C(15)–C(12) = 1.518(13), C(9)–C(10) = 1.399(13), C(9)–C(14) = 1.380(12), C(10)–C(11) = 1.374(13), C(11)–C(12) = 1.403(12), C(12)–C(13) = 1.381(13), C(13)–C(14) = 1.364(13), C(17)–C(18) = 1.401(12), C(17)–C(22) = 1.404(13), C(18)–C(19) = 1.391(13), C(19)–C(20) = 1.396(16), C(20)–C(21) = 1.336(17), C(21)–C(22) = 1.394(15), C(19)–C(32) = 1.507(16), C(32)–C(31) = 1.587(19), C(31)–C(28) = 1.477(19), C(22)–C(23) = 1.535(14), C(23)–C(24) = 1.585(17), C(24)–C(25) = 1.509(19), C(25)–C(26) = 1.375(19), C(25)–C(30) = 1.395(17), C(26)–C(27) = 1.37(2), C(27)–C(28) = 1.38(2), C(28)–C(29) = 1.326(18), C(29)–C(30) = 1.400(17).

of [2.2]paracyclophane to an electron-withdrawing fragment such as Cr(CO)<sub>3</sub> results in the removal of some  $\pi$ -electron density between the aromatic decks, which allows the rings to move closer together, changing from 3.09 to 3.02 Å. The larger change observed in Ru( $\eta$ -C<sub>16</sub>H<sub>16</sub>)Cl<sub>2</sub>(PPh<sub>3</sub>) (**3a** and **3b**) reflects the greater electron-withdrawing effect of the ruthenium(II) ion versus the chromium(0) atom. The distances between the rings in the [2.2]paracyclophanyl groups of the phosphine ligands are 2.988 and 3.006 Å, also suggesting that the  $\pi$ -electron density between the aromatic rings has decreased. This could also arise from the distortion caused to the [2.2]paracyclophanyl group, where the carbon atom bonds to the phosphorus. This carbon atom causes the aryl ring to adopt more of a butterfly shape, although the torsion angle across the nonbridgehead atoms is only ca. 1.8°. The remaining intramolecular structural features are unremarkable, and the key bonding parameters are listed in the figure caption.

**Comparison of the Catalytic Activity of 2 and 4 in the Hydrogenation of Styrene.** Ruthenium(II)–arene compounds of formula [Ru( $\eta$ <sup>6</sup>-arene)Cl<sub>2</sub>(PR<sub>3</sub>)] have been shown to catalyze the hydrogenation of styrene and phenylacetylene.<sup>13</sup> The catalytic activity of compounds **2** and **4** was compared under similar condi-

tions to those described previously using styrene as the substrate. Compound **4**, with the *rac*-diphenyl[2.2]-paracyclophane ligand, was ca. 50% more active than **2**. However, it is worth noting that in both cases the catalyst had decomposed during the hydrogenation reaction and that the catalytic turnover is very low (see Experimental Section).

While these catalysis results are not very impressive, we have found that *rac*-diphenyl[2.2]paracyclophane is an extremely useful ligand in palladium-catalyzed Heck reactions and our results from these studies will be reported in due course.

## Experimental Section

All reactions were conducted under an atmosphere of nitrogen using dried and degassed solvents, although the products were air stable. The compounds [Ru( $\eta$ -C<sub>6</sub>H<sub>6</sub>)Cl<sub>2</sub>]<sub>2</sub>,<sup>7</sup> [Ru( $\eta$ -C<sub>16</sub>H<sub>16</sub>)Cl<sub>2</sub>]<sub>2</sub>,<sup>14</sup> Ru( $\eta$ -C<sub>6</sub>H<sub>6</sub>)Cl<sub>2</sub>(PPh<sub>3</sub>) (**4**),<sup>11</sup> and *rac*-PPh<sub>2</sub>(C<sub>16</sub>H<sub>15</sub>) (**1**)<sup>5a</sup> were prepared by literature methods. Mass spectra were obtained using positive fast atom bombardment on a Micromass Autospec instrument. NMR spectra were recorded on a Bruker DRX-400 spectrometer with <sup>1</sup>H at 400.13 MHz, <sup>31</sup>P at 161.98 MHz, and <sup>13</sup>C at 100.1 MHz. <sup>1</sup>H NMR chemical shifts are reported in ppm relative to residual <sup>1</sup>H signals in the deuterated solvents (CDCl<sub>3</sub>,  $\delta$  7.29), <sup>31</sup>P{<sup>1</sup>H} NMR spectra are reported in ppm downfield from an external 85% solution of phosphoric acid. Standard gradient-assisted heteronuclear multiple quantum correlation (HMQC), correlation spectroscopy (COSY), and nuclear Overhauser effect spectroscopy (NOESY) pulse sequences were used to obtain two-dimensional heteronuclear correlation spectra.<sup>15</sup>

**Synthesis of Ru( $\eta$ -C<sub>6</sub>H<sub>6</sub>)Cl<sub>2</sub>{PPh<sub>2</sub>(C<sub>16</sub>H<sub>15</sub>)} (**2**).** To [Ru( $\eta$ -C<sub>6</sub>H<sub>6</sub>)Cl<sub>2</sub>]<sub>2</sub> (250 mg, 0.5 mmol) in CHCl<sub>3</sub> (15 mL) was added *rac*-PPh<sub>2</sub>(C<sub>16</sub>H<sub>15</sub>) (392 mg, 1 mmol) and the reaction mixture stirred under reflux for 2 h. The solution was cooled, and the solvent was evaporated in vacuo to give a red-brown solid (0.43 g, 76%). The solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O (1:1) to give red crystals which were characterized as **2** by spectroscopy.

Spectroscopic data for **2**: FAB-MS *m/z* 642 [M]<sup>+</sup>, 607 [M – Cl]<sup>+</sup>, 491 [M – 2Cl – C<sub>6</sub>H<sub>6</sub>]<sup>+</sup>; <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) 19.53 (s) ppm; see Table 1 for other NMR data. Anal. Found (calcd): C, 56.33 (56.25); H, 3.85 (4.10).

**Synthesis of Ru( $\eta$ -C<sub>16</sub>H<sub>16</sub>)Cl<sub>2</sub>{PPh<sub>2</sub>(C<sub>16</sub>H<sub>15</sub>)} (**3**).** To [Ru( $\eta$ -C<sub>16</sub>H<sub>16</sub>)Cl<sub>2</sub>]<sub>2</sub> (95 mg, 0.125 mmol) in CHCl<sub>3</sub> (30 mL) was added *rac*-PPh<sub>2</sub>(C<sub>16</sub>H<sub>15</sub>) (0.098 mg, 0.25 mmol) and the reaction mixture stirred under reflux for 2 h. The solution was cooled, and the solvent was evaporated in vacuo to give a red-brown solid (0.142 g, 74%). The solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O (1:1) to give red crystals which were characterized as **3** by spectroscopy.

Spectroscopic data for **3**: FAB-MS *m/z* 772 [M]<sup>+</sup>, 737 [M – Cl]<sup>+</sup>, 701 [M – 2Cl]<sup>+</sup>; <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) 32.41 (s) ppm; see Table 1 for other NMR data. Anal. Found (calcd): C, 68.51 (68.39); H, 5.25 (5.35).

**Crystal Structure Determination for 3.** Crystals were mounted on a thin glass fiber using silicon grease and cooled on the diffractometer to 100 K using an Oxford Cryostream low-temperature attachment. A total of 90 oscillation frames each of width 2° in  $\phi$  and with 30 s exposure time were recorded using a Nonius Kappa CCD diffractometer, with a detector to crystal distance of 25 mm. Crystals were indexed from the first 10 frames using the DENZO-SMN package,<sup>16</sup>

(14) Elsegood, M. R. J.; Tocher, D. A. *J. Organomet. Chem.* **1988**, 356, C29.

(15) Zhu, J.-M.; Smith, I. C. P. *Concepts Magn. Reson.* **1995**, 7, 281 and references therein.

(16) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: New York, 1996. Vol. 276.

(13) Moldes, I.; de la Encarnación, E.; Ros, J.; Alvarez-Larena, Á.; Piniella, J. F. *J. Organomet. Chem.* **1998**, 566, 165.

and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO-SMN, Scalepack)<sup>16</sup> resulted in unique data sets corrected for Lorentz and polarization effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. The space group was identified as tetragonal  $I1/a$  from systematically absent data and confirmed by successful refinement. The structures were solved using the direct-methods option of SHELXS-97<sup>17</sup> and developed via alternating least-squares cycles and difference Fourier synthesis (SHELXL-97)<sup>17</sup> with the aid of the program RES2INS.<sup>18</sup> All non-hydrogen atoms were modeled anisotropically, while hydrogen atoms are assigned an isotropic thermal parameter 1.2 times that of the parent atom and allowed to ride. The molecule of diethyl ether solvent was refined poorly (possibly as a consequence of partial efflorescence), and DFIX restraints were applied to the bond lengths. Hydrogen atoms were not included in the model for this solvent molecule. All calculations were carried out with either a Silicon Graphics Indy workstation or an IBM-compatible PC.

**Electrochemistry of 2 and 4.** Cyclic and steady-state voltammetry was carried out with a Cypress Systems (Model CS-2000) computerized electroanalytical system, in conjunction with a nitrogen-purged one-compartment cell which supported a platinum-disk working electrode (diameter 1.0 mm or 7  $\mu\text{m}$ ), a platinum-coil counter electrode, and a Ag/AgCl reference electrode, for which the ferrocenium/ferrocene couple ( $\text{Fc}^{+/0}$ ) was measured at +0.55 V. Freshly distilled  $\text{CH}_2\text{Cl}_2$  was used

(17) Sheldrick, G. M. SHELX-97; University of Göttingen, Göttingen, Germany, 1997.

(18) Barbour, L. J. RES2INS; University of Missouri, Columbia, MO, 1995–1998.

throughout with  $[\text{tBu}_4\text{N}][\text{PF}_6]$  electrolyte previously dried at 373 K under vacuum.

**Hydrogenation of Styrene.** Hydrogenations were carried using a Parr stainless steel autoclave (300 mL) fitted with either a glass or a PTFE liner. The catalyst (0.03 mmol) was added together with  $\text{CH}_2\text{Cl}_2$  (40 mL) and styrene (2.08 g). The autoclave was then sealed and purged with hydrogen gas (99.9995% purity) and the reaction pressure set to 30 atm at room temperature. The autoclave was then sealed, heated to 60 °C, and stirred for 18 h. After reaction the contents were then analyzed by  $^1\text{H}$  NMR spectroscopy and GC. The conversion using **2** was 71% and using **4** was 54%.

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**Supporting Information Available:** Tables giving crystallographic data for **2a**. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data (excluding structure factors) for **3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-168655. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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