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Synthesis and Characterization of [(η^6-arene)RuCl$_2$(R$_2$AsCH=CH$_2$)] and Tethered Arsinopropylarene−Ruthenium(II) Complexes

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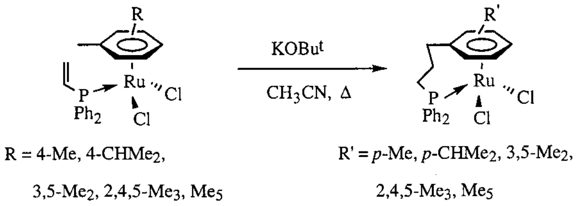
The complexes [(η^6-arene)RuCl$_2$(R$_2$AsCH=CH$_2$)] [arene = MeC$_6$H$_5$, R = Ph (**1a**), R = Cy (**1b**); *p*-MeC$_6$H$_4$Me, R = Ph (**2a**), R = Cy (**2b**); *o*-MeC$_6$H$_4$Me, R = Ph (**3a**), R = Cy (**3b**); 1,3,5-Me$_3$C$_6$H$_3$, R = Ph (**4a**); *p*-MeC$_6$H$_4$CHMe$_2$, R = Ph (**5a**), R = Cy (**5b**); 1,2,4,5-Me$_4$C$_6$H$_2$, R = Ph (**6a**), R = Cy (**6b**); C$_6$Me$_6$, R = Ph (**7a**)] have been synthesized by reacting [(η^6-arene)-RuCl$_2$]$_2$ with the respective vinyl arsine. The compounds [(η^6-MeC$_6$H$_5$)RuCl$_2$(Ph$_2$AsCH=CH$_2$)] (**1a**) and [(η^6-1,3,5-Me$_3$C$_6$H$_3$)RuCl$_2$(Ph$_2$AsCH=CH$_2$)] (**4a**) undergo KOBu^t-promoted intramolecular hydroalkylation in boiling acetonitrile to produce tethered arsinopropylarene−ruthenium(II) complexes **1c** and **4c**, respectively. The complexes have been characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, elemental analyses, cyclic voltammetry, and in several cases by X-ray crystallography.

Introduction

In the past decade the chemistry of [(η^6-arene)RuCl$_2$(PR$_3$)] complexes has attracted a great deal of attention.[1−3] Reports indicate that they are useful precursors for a variety of catalytic and stoichiometric organic transformations.[3] For example, they react with terminal alkynes to form novel vinylidene,[4−7] allenylidene[7,8] and cumulenylidene[7,8] complexes. Although the phosphine complexes [(η^6-arene)RuCl$_2$(PR$_3$)] have been widely investigated, few arsine complexes of this type are available for comparative study.[9−15]

We recently reported the synthesis and characterization of a number of [(η^6-arene)RuCl$_2$(PR$_3$)] complexes containing unsaturated phosphines, such as diphenylvinylphosphine (DPVP), divinylphenylphosphine, allyldiphenylphosphine, and 1-phenyl-3,4-dimethylphosphole.[16] In addition, we have shown that the complexes [(η^6-arene)RuCl$_2$(DPVP)] undergo a novel KOBu^t-promoted hydroalkylation in boiling acetonitrile to produce tethered phosphinopropylarene−ruthenium(II) compounds, as shown in eq 1.[17]



(1)

During the course of this work, a number of reports on tethered arene−ruthenium(II) complexes have appeared. Smith and Wright,[18] Noels and co-workers,[11,19] and Fürstner et al.[20] have synthesized related complexes by thermal displacement of *p*-cymene (1,4-MeC$_6$H$_4$-CHMe$_2$) from the *p*-cymene κ-P-γ-arylpropylphosphine complexes. Therrien et al.[21] had previously employed a

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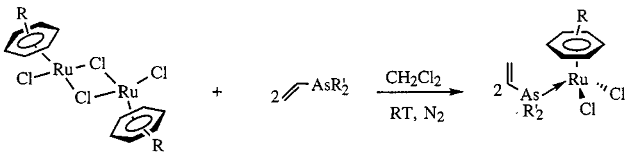
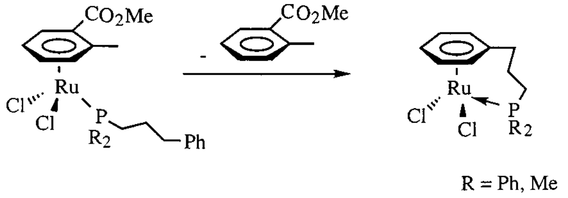
Scheme 1



(**1a-7a, 1b-3b, 5b, 6b**)

more reactive ethyl benzoate complex in a similar synthesis. Bennett et al.[22] have recently used an *o*-toluate precursor to prepare tethered arene–ruthenium(II) complexes, as shown eq 2.



(2)

As a continuation of our work in this area, we now report the synthesis and characterization of a series of complexes of the type $[(\eta^6\text{-arene})RuCl_2(R_2AsCH{=}CH_2)]$, where R = phenyl and cyclohexyl. Hydroalkylation reactions of these arsine complexes have been investigated in order to probe the generality of base-promoted synthesis of tethered arene complexes.

Results and Discussion

Synthesis and Characterization of 1a–7a, 1b–3b, 5b, and 6b. The $[(\eta^6\text{-arene})RuCl_2(R_2AsCH{=}CH_2)]$ complexes [arene = MeC_6H_5, R = Ph (**1a**), R = Cy (**1b**); *p*-MeC_6H_4Me, R = Ph (**2a**), R = Cy (**2b**); *o*-MeC_6H_4Me, R = Ph (**3a**), R = Cy (**3b**); 1,3,5-$Me_3C_6H_3$, R = Ph (**4a**); *p*-$MeC_6H_4CHMe_2$, R = Ph (**5a**), R = Cy (**5b**); 1,2,4,5-$Me_4C_6H_2$, R = Ph (**6a**), R = Cy (**6b**); C_6Me_6, R = Ph (**7a**)] were prepared by reacting the $[(\eta^6\text{-arene})RuCl_2]_2$ complexes with 2.2 equiv of diphenylvinylarsine (DPVAs) or dicyclohexylvinylarsine (DCVAs)] in dichloromethane at ambient temperature (Scheme 1).

After of stirring for 4 h, the solution was layered with *n*-hexane and left overnight to crystallize. The product separated and was isolated by filtration and recrystallized from dichloromethane/*n*-hexane. The products were obtained in almost quantitative yields as orange-red-brown solids. They are air and moisture stable solids that are soluble in halocarbons, methanol, acetone, and acetonitrile. They slowly decompose in solution, however, apparently by dissociation and subsequent polymerization and/or oxidation of the arsine. The DCVAs complexes are less stable in solution than the DPVAs complexes, and complexes **4b** and **7b** could not be isolated in an analytically pure state. Attempts to prepare the more bulky $Bu^t{}_2AsCH{=}CH_2$ derivatives ultimately led to the recovery of the $[(\eta^6\text{-arene})RuCl_2]_2$ starting materials and the arsine oxide.

The compounds were characterized by elemental analyses, melting point determination, ^1H and $^{13}C\{^1H\}$ spectroscopy, and cyclic voltammetry. The ^1H NMR spectra contain in each case three multiplets in the olefinic region. The integrated ratios of these resonances to those of the η^6-arene protons indicated one DPVAs or DCVAs ligand per ruthenium and confirmed that the vinyl group had not undergone hydroalkylation with the η^6-arene ligands. The proton chemical shifts for the DPVAs complexes, except for the protons H_C, are similar to those of the analogous DPVP complexes.[17] The average chemical shift of H_C for the DPVAs complexes occurs about 0.2 ppm downfield of the corresponding average value for the DPVP complexes. The carbon chemical shifts for the two series of complexes are also similar, except for those of the vinyl carbon atoms. The vinyl carbon resonances were conclusively assigned by a combination of APT and HETCOR (Figure 1) spectroscopies. For the DPVP complexes the chemical shift for C_α is greater than that for C_β; for the DPVAs complexes the reverse is true.

Reactions of 1a–7a, 1b–3b, 5b, and 6b with KOBu^t. We have recently shown that the complexes $[(\eta^6\text{-arene})RuCl_2(DPVP)]$ undergo novel base promoted hydroalkylations with $KOBu^t$ in boiling acetonitrile[17] (eq 1). To explore the application of this synthetic methodology further, we have attempted to prepare analogous hydroalkylated compounds from the vinyl arsine complexes. As our first attempt we investigated the reaction of $[(\eta^6\text{-arene})RuCl_2(DPVAs)]$ with $KOBu^t$ in boiling acetonitrile (Scheme 2).

Complexes **1a** and **4a** undergo base-promoted hydroalkylation with 1 equiv of $KOBu^t$ to produce **1c** and **4c**, in 20–25% yields. The conversion was accompanied by a change in the color of the solution from a clear red to a dark red. Excess base caused excessive decomposition. The precursors **2a, 3a**, **5a–7a**, **1b–3b**, **5b**, and **6b** underwent extensive decomposition under the same reaction conditions.

Following workup, both **1c** and **4c** were isolated as air stable microcrystalline red solids by precipitation with *n*-hexane. Their ^1H and $^{13}C\{^1H\}$ NMR spectral data are consistent with the structures proposed. In the ^1H NMR spectra, in both cases the three vinyl resonances and one methyl resonance are replaced by three multiplets in the aliphatic region due to the three sets of methylene protons. In the $^{13}C\{^1H\}$ NMR spectra, the C_α, C_β, and one methyl resonance disappear and are replaced by three new resonances in the aliphatic region. The proton and carbon chemical shifts are similar to those of their phosphine analogues.[17]

X-ray crystallographic analyses confirmed the structures of the precursors **2a, 4a-6a**, **1b**, **3b**, **5b**, and **6b**. The structures of **4a** and **5b** are shown in Figures 2 and 3; the structures of the remaining compounds are given in the Supporting Information. Crystallographic data are summarized in Tables 1 and 3, and selected bond distances and angles are given in Tables 2 and 4. The coordination sphere around the ruthenium center in each case is that of a pseudo-octahedral half-sandwich with the η^6-arene ligand, the vinyl arsine, and the two chlorine atoms occupying the six coordination sites. The average Ru–As bond length observed for the DPVAs complexes **1a**, **2a**, and **4a–6a** [2.4485(2) Å] is slightly shorter than that observed for the complexes **1b**, **3b**, **5b**, and **6b** [2.4707(4) Å], which contain the larger and

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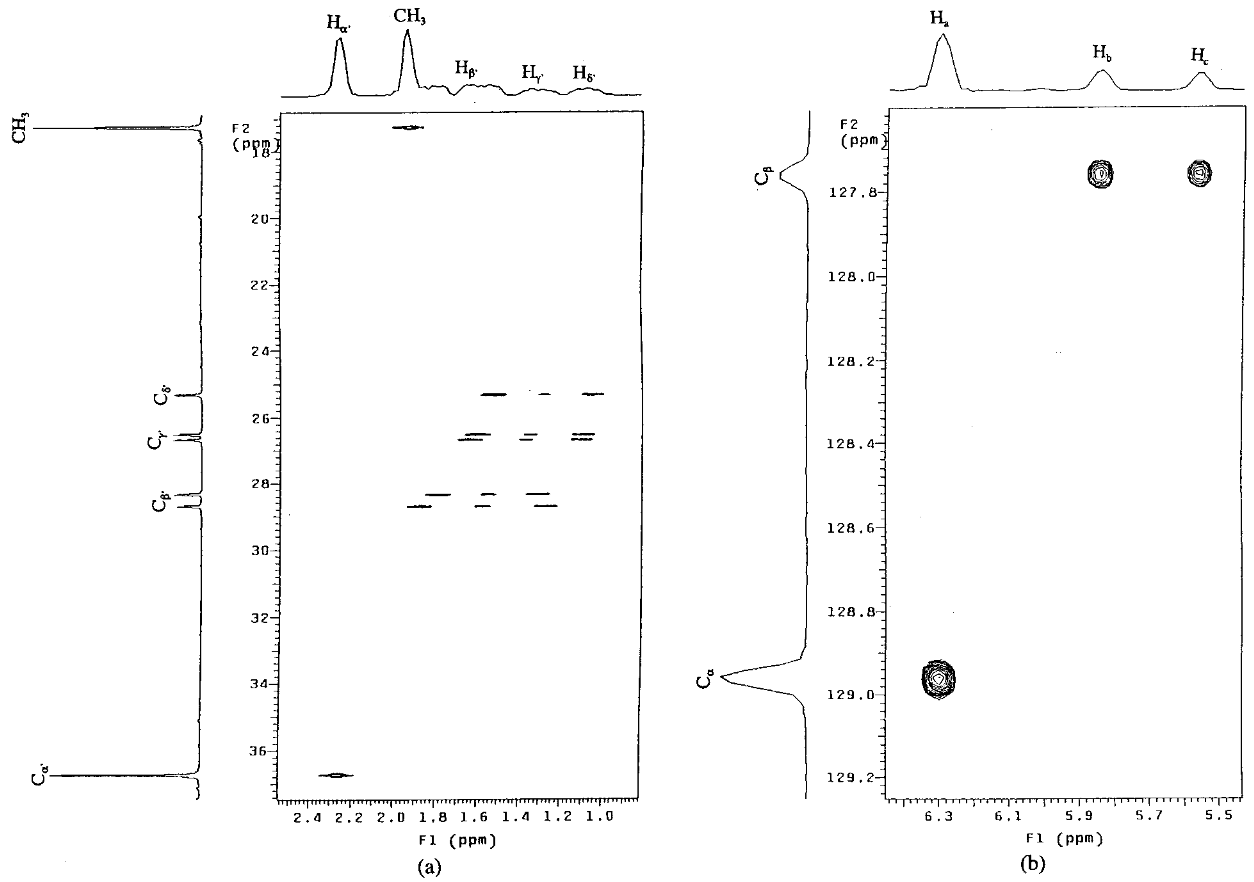
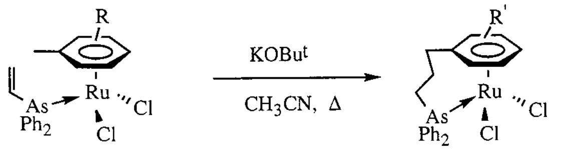


Figure 1. (a) Expansion of the $^{13}C/^{1}H$ HECTOR spectrum of **2b** in the aliphatic region; (b) expansion of the $^{13}C/^{1}H$ HECTOR spectrum of **2b** in the vinyl region.

Scheme 2



1a, 4a **1c, 4c**

more basic DCVAs. The global average Ru–As bond length for these complexes is slightly shorter than the Ru–As bond distance reported[9] for $[(p\text{-Cy})RuCl\{(As,O)\text{-}Ph_2P(O)CH_2CH_2As^tBu_2\}]PF_6$. The Ru–Cl distances in all of the complexes are similar to those observed in the related phosphine complexes.[16,17]

The electrochemistry of the complexes was investigated by cyclic voltammetry (Table 5). The compounds exhibit chemically reversible one-electron oxidations with the Ru(II/III) potentials ranging from 0.48 to 0.76 V for **1a**–**7a**, **1c**, and **4c** and 0.50–0.67 V for **1b**–**3b**, **5b**, and **6b**. Oxidations of the DPVP complexes[17] and the DPVAs complexes occur at essentially the same potentials, indicating that these two ligands have equivalent donor properties toward ruthenium(II). Oxidations of the DCVAs complexes occur about 0.1 V less than for the DPVAs complexes, suggesting that DCVAs is a slightly better donor than either DPVAs or DPVP. As observed for the DPVP complexes and their hydroalkylation products, the oxidations of **1a** and **1c** (0.76/0.77 V) and **4a** and **4c** (0.66/0.65 V) occur at the same potentials within experimental error. For all complexes, the trends in the Ru(II/III) potentials as a function of the arene follow the expected decrease in the donating ability of the arene ligands: the addition of each methyl group to the arene ring lowers the oxidation potential by about 60 mV.

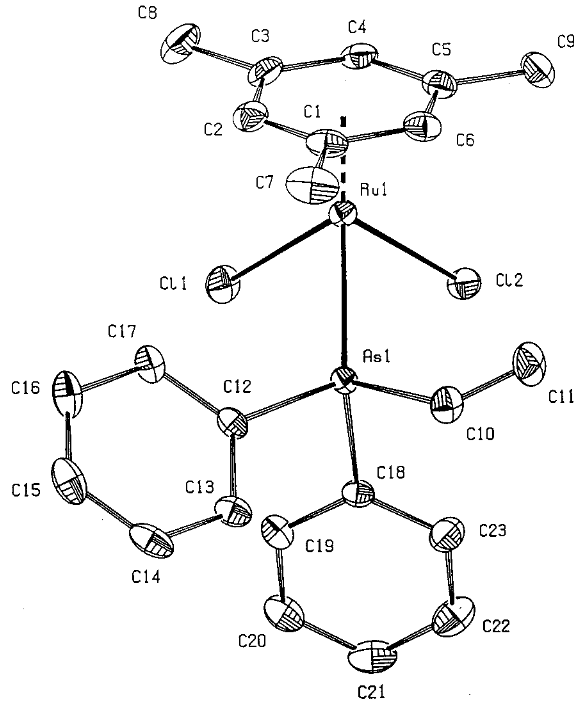


Figure 2. Structural drawing of **4a** showing the atom-numbering scheme (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.

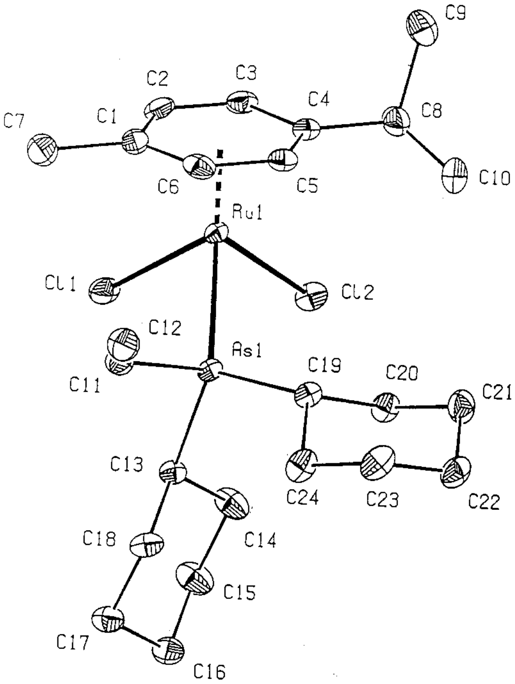


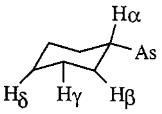
Figure 3. Structural drawing of **5b** showing the atom-numbering scheme (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Conclusion

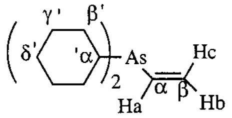
A series of Ru(II) vinylarsine complexes of the type [(η^6-arene)RuCl$_2$(R$_2$AsCH=CH$_2$)] were prepared and the compounds characterized. They are air stable in the solid state but decompose in solution at ambient temperature. The complexes show reversible Ru(II/III) redox couples. The Ru−As distances are sensitive to the substituent (R) on the vinylarsine. **1a** and **4a** underwent intramolecular base-promoted hydroalkylation. The novel products of these reactions contain a tethered arsinopropyl-η^6-arene ligand. The new complexes are stable and are electronically similar to their precursors.

Experimental Section

All chemicals were reagent grade and were used as received or synthesized as described below. Acetonitrile was dried over CaH$_2$ and distilled immediately before use. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl under nitrogen. Acetone was dried over potassium carbonate and distilled from P$_2$O$_5$ under nitrogen. Cyclohexylmagnesium chloride, *tert*-butylmagnesium chloride, and vinylmagnesium chloride were purchased from Aldrich and were used as received. 1,3,5-Trimethylcyclohexa-1,4-diene, 3,6-dimethylcyclohexa-1,4-diene,[23] [(η^6-arene)RuCl$_2$]$_2$,[24] Ph$_2$AsCH=CH$_2$,[25] Cy$_2$AsCH=CH$_2$,[26] and Bu$^t{}_2$AsCl[27] were synthesized by literature procedures. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were obtained using a Mel-Temp apparatus and are uncorrected. NMR spectra were recorded on CDCl$_3$ solutions with a Varian Inova 500-FT NMR spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C for the compounds **1a**−**7a**, **1b**−**3b**, **5b**, and **6b**, and on a Varian Unity plus-500 FT-NMR spectrometer operating at 500 MHz for ^{1}H and 125.7 MHz for ^{13}C for **1c** and **4c**. Proton and carbon chemical shifts are quoted relative to internal Me$_4$Si, with positive values being downfield of the reference. Cyclic voltammograms were recorded at 25 °C in freshly distilled CH$_2$Cl$_2$ solutions containing 0.1 M tetrabutylammonium hexafluorophosphate using a BAS CV50-W voltammetric analyzer. A three-electrode system was used. The working electrode was a glassy carbon disk, the auxiliary electrode was a platinum electrode, and the reference electrode was an aqueous Ag$^+$/AgCl electrode separated from the cell by a Luggin capillary. The Fc/Fc$^+$ couple occurred at 497 mV under the same conditions.[28] Carbon atoms and the attached hydrogen atoms are numbered as shown in **I** and **II** below.



I



II

Synthesis. Preparation of Bu$^t{}_2$AsCH=CH$_2$. Since reaction of Bu$^t{}_2$AsCl with excess vinylmagnesium chloride afforded only a 20% conversion with Bu$^t{}_2$AsCl and Bu$^t{}_2$AsCH=CH$_2$ not being separable by distillation, Bu$^t{}_2$AsCl was converted to Bu$^t{}_2$AsI. A solution of Bu$^t{}_2$AsCl (27.10 g = 120.7 mmol) in acetone (25 mL) was added to a solution of sodium iodide (28.60 g = 190.8 mmol) in acetone (175 mL). A white precipitate formed instantly, and the solution became yellow. The suspension was heated at reflux for 22 h and filtered, and the filtrate was concentrated under vacuum. The residue was extracted with ether (200 mL) and filtered. After removal of the solvent, under reduced pressure, the yellow residue was distilled, affording a pale yellow oil, bp 79 °C/1 mm, yield 82%. Anal. Calcd for C$_8$H$_{18}$AsI: C, 30.40; H, 5.74. Found: C, 30.72; H, 5.79. ^{1}H NMR (300.1 MHz, C$_6$D$_6$, 25 °C): δ 1.21 (s, 18H, CH$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_6$, 25 °C): δ 35.4 (s, C$_q$), 29.6 (s, CH$_3$).

To a solution of 21.50 g (68.03 mmol) of Bu$^t{}_2$AsI in 120 mL of tetrahydrofuran was slowly added 200.0 mL of a 1.6 M tetrahydrofuran solution of vinylmagnesium chloride at ambient temperature under dry nitrogen. The mixture was then heated at reflux for 22 h, cooled to 0 °C, and hydrolyzed with degassed 2 M aqueous NH$_4$Cl solution (50 mL). The organic layer was separated and the aqueous layer extracted with ether (3 × 50 mL). The combined organic fractions were concentrated under vacuum, and the residue was distilled under reduced pressure to afford a pale yellow oil, bp 78 °C/10 mm, yield 41%. Anal. Calcd for C$_{10}$H$_{21}$As: C, 55.56; H, 9.79. Found: C, 54.48; H, 9.47. ^{1}H NMR (300.1 MHz, CD$_2$Cl$_2$, 25 °C): δ 6.51 (dd, $^3J(\mathrm{H_aH_c}) = 18.5$ Hz, $^3J(\mathrm{H_aH_b}) = 11.4$ Hz, 1H, H$_a$), 5.92 (dd, $^3J(\mathrm{H_aH_b}) = 11.4$ Hz, $^2J(\mathrm{H_bH_c}) = 2.7$ Hz, 1H, H$_b$), 5.78 (dd, $^3J(\mathrm{H_aH_c}) = 18.5$ Hz, $^2J(\mathrm{H_bH_c}) = 2.7$ Hz, 1H, H$_c$), 1.13 (s, 18H, CH$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD$_2$Cl$_2$, 25 °C): δ 138.6 (s, C$_\alpha$), 131.4 (s, C$_\beta$), 32.7 (C$_q$), 29.9 (CH$_3$).

Preparations of 1a−7a, 1b−3b, 5b, and 6b. The complexes were synthesized from the appropriate [(η^6-arene)RuCl$_2$]$_2$ as follows. A suspension of 1.0 mmol of the dimer in 40 mL of dichloromethane was treated with 2.2 equiv of diphenylvinylarsine or dicyclohexylvinylarsine via syringe. The mixture was stirred at ambient temperature for 4 h. The volume of the solution was reduced to about 10 mL on a rotary evaporator, and *n*-hexane was added. The products were isolated by filtration, washed with *n*-hexane, and dried under vacuum to give the pure products as microcrystalline orange-red-brown solids. Similar reactions with Bu$^t{}_2$AsCH=CH$_2$ led to inseparable mixtures of [(η^6-arene)RuCl$_2$]$_2$, [(η^6-arene)Ru(Bu$^t{}_2$AsCH=CH$_2$)Cl$_2$], Bu$^t{}_2$As=O(CH=CH$_2$), and polymeric Bu$^t{}_2$AsCH=CH$_2$.

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Table 1. Crystallographic Data and Structure Refinement for 1a, 2a, and 4a−6a

	1a	**2a**	**4a**	**5a**[c]	**6a**
formula	$C_{21}H_{21}AsCl_2Ru$	$C_{22}H_{23}AsCl_2Ru$	$C_{23}H_{25}AsCl_2Ru$	$C_{24}H_{27}AsCl_2Ru$	$C_{24}H_{27}AsCl_2Ru$
M_w	520.29	534.32	608.04	562.38	562.37
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	16.6943(1)	16.9549(2)	8.2468(1)	17.2658(2)	8.8486(1)
b (Å)	7.2377(1)	7.1927(1)	8.6891(2)	7.32020(10)	15.0305(3)
c (Å)	16.9808(3)	17.4522(2)	18.8657(3)	18.9833(2)	17.5860(3)
Z	4	4	2	4	2
α (deg)	90	90	99.543(1)	90	89.384(1)
β (deg)	105.453(1)	100.1886(8)	95.976(1)	105.4484(8)	83.995(1)
γ (deg)	90	90	112.9407(9)	90	77.814(1)
volume (Å^3)	1977.59(1)	2094.76(4)	1206.34(4)	2312.60(5)	2273.52(6)
ρ_{calcd} (Mg/m^3)	1.747	1.694	1.674	1.62	1.643
no. of reflns collcd	46 382	54 987	34 020	53 512	60 968
no. of ind reflns	5765	6180	7036	6744	13 219
R1[a]	0.0330	0.0336	0.0346	0.0338	0.0438
wR2[b]	0.0343	0.0331	0.0464	0.0354	0.0381
GOF	1.756	1.677	1.810	1.0152	1.559

[a] The data were refined by the method of full-matrix least squares on F^2, with the final R indices having $I > 2.00\sigma(I)$, $R1 = \sum||F_o| - |F_c||/\sum F_o$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $I > 3.00\sigma(I)$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 1a, 2a, and 4a−6a

	1a	**2a**	**4a**	**5a**	**6a**
Ru−As	2.4490(3)	2.45389(2)	2.4471(3)	2.4441(1)	2.4486(3)
Ru−Cl(1)	2.4090(5)	2.4183(5)	2.4076(6)	2.4193(5)	2.4121(7)
Ru−Cl(2)	2.4070(5)	2.4080(5)	2.4046(6)	2.4144(5)	2.4067(6)
Ru−(C_1−C_6)[a]	2.195(2)	2.200(2)	2.212(2)	2.207(8)	2.215(3)
As−Ru−Cl(1)	85.26(1)	80.07(1)	82.42(2)	82.583(14)	84.82(2)
As−Ru−Cl(2)	80.21(1)	86.08(1)	81.70(2)	82.148(15)	84.31(2)
Cl(1)−Ru−Cl(2)	88.23(2)	88.05(2)	88.63(2)	88.77(2)	88.03(3)

[a] (C_1−C_6) denotes the average Ru−C distances.

Table 3. Crystallographic Data and Structure Refinement for 1b, 3b, 5b, and 6b

	1b	**3b**[c]	**5b**	**6b**
formula	$C_{21}H_{33}AsCl_2Ru$	$C_{22}H_{35}AsCl_2Ru$	$C_{24}H_{39}AsCl_2Ru$	$C_{24}H_{39}AsCl_2Ru$
M_w	532.39	546.42	574.47	574.47
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/a$	$P2_1/c$
a (Å)	6.8817(2)	6.8884(1)	12.9473(1)	7.5720(1)
b (Å)	12.3822(3)	10.8798(2)	9.9644(1)	17.7649(2)
c (Å)	13.3182(4)	30.8497(6)	19.0128(2)	18.49849(2)
Z	2	4	4	4
α (deg)	84.7614(9)	90	90	90
β (deg)	81.8110(9)	91.6770(6)	90.9678(5)	100.5395(5)
γ (deg)	83.394(1)	90	90	90
volume (Å^3)	1112.58(5)	2311.02(6)	2452.53(4)	2446.35(5)
ρ_{calcd} (mg/m^3)	1.589	1.570	1.556	1.560
no. of reflns collcd	17 968	30 220	56 694	59 722
no. of ind reflns	3925	5198	7152	7164
R1[a]	0.0400	0.0598	0.0435	0.0418
wR2[b]	0.0377	0.1092	0.0449	0.0422
GOF	1.309	2.872	1.727	1.578

[a] The data were refined by the method of full-matrix least squares on F^2, with the final R indices having $I > 2.00\sigma(I)$. $R1 = \sum||F_o| - |F_c||/\sum F_o$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $I > 3.00\sigma(I)$.

1a: mp 200−202 °C (97% yield). ^{1}H NMR (500.0 MHz, CDCl$_3$, 25 °C): δ 7.67 (m, 4H, H$_o$), 7.43 (m, 6H, H$_{m,p}$), 6.84 (dd, ^3J(H$_a$H$_c$) = 18.5 Hz, ^3J(H$_a$H$_b$) = 11.3 Hz, 1H, H$_a$), 6.06 (d, ^3J(H$_a$H$_b$) = 11.3 Hz, 1H, H$_b$), 5.55 (d, ^3J(H$_a$H$_c$) = 18.5 Hz, 1H, H$_c$), 5.42 (apparent t, ^3J(HH) = 5.8 Hz, 2H, H$_m$), 5.26 (d, ^3J(HH) = 5.8 Hz, 1H, H$_p$), 4.98 (apparent t, ^3J(HH) = 5.8 Hz, 1H, H$_o$) 2.16 (s, 3H, CH$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ 133.77 (C$_\beta$), 132.98 (C$_o$), 130.94 (C$_\alpha$), 130.46 (C$_i$), 130.17 (C$_p$), 128.75 (C$_m$), (104.48, 86.10, 85.31, 78.63, (C, arene), 18.05 (CH$_3$, arene). Anal. Calcd for $C_{21}H_{21}AsCl_2Ru$: C, 48.49; H, 4.04; Cl, 13.63. Found: C, 48.46; H, 3.87; Cl, 13.47.

2a: mp >300 °C dec (95% yield). ^{1}H NMR (500.0 MHz, CDCl$_3$, 25 °C): δ 7.70 (m, 4H, H$_o$), 7.44 (m, 6H, H$_{m,p}$), 6.90 (dd, ^3J(H$_a$H$_c$) = 18.5 Hz, ^3J(H$_a$H$_b$) = 11.5 Hz, 1H, H$_a$), 6.04 (d, ^3J(H$_a$H$_b$) = 11.5 Hz, 1H, H$_b$), 5.53 (d, ^3J(H$_a$H$_c$) = 18.5 Hz, 1H, H$_c$), 5.24 (s, 4H, arene) 1.92 (s, 6H, 2CH$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ 133.80 (C$_\beta$), 133.17 (C$_o$), 131.17 (C$_\alpha$), 130.18 (C$_p$), 130.13 (C$_i$), 128.07 (C$_m$), 95.67 (Cq, arene), 86.34 (CH, arene), 17.72 (CH$_3$, arene). Anal. Calcd for $C_{22}H_{23}AsCl_2Ru$: C, 49.47; H, 4.31; Cl, 13.27. Found: C, 49.28; H, 4.32; Cl, 13.19.

3a: mp 282−284 °C (93% yield). ^{1}H NMR (500.0 MHz, CDCl$_3$, 25 °C): δ 7.70 (m, 4H, H$_o$), 7.40 (m, 6H, H$_{m,p}$), 6.84 (dd, ^3J(H$_a$H$_c$) = 18.5 Hz, ^3J(H$_a$H$_b$) = 11.5 Hz, 1H, H$_a$), 6.04 (d, ^3J(H$_a$H$_b$) = 11.5 Hz, 1H, H$_b$), 5.57 (d, ^3J(H$_a$H$_c$) = 18.5 Hz, 1H, H$_c$), 5.11 (m, [AX]$_2$, 2H, arene), 5.07 (m, [AX]$_2$, 2H, arene), 2.02 (s, 6H, 2CH$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ 134.19 (C$_\beta$), 133.07 (C$_o$), 131.48 (C$_\alpha$), 130.37 (C$_p$), 130.07 (C$_i$), 128.67 (C$_m$), 100.82 (Cq, arene), 86.45 (CH, arene), 80.53 (CH, arene), 16.45 (CH$_3$, arene). Anal. Calcd for $C_{22}H_{23}AsCl_2Ru$: C, 49.47; H, 4.31; Cl, 13.27. Found: C, 49.28; H, 4.32; Cl, 13.19.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for 1b, 3b, 5b, and 6b

	1b	**3b**	**5b**	**3b**
Ru−As	2.4630(6))	2.4649(5)	2.4834(3)	2.4713(3)
Ru−Cl(1)	2.429(1)	2.436(2)	2.4242(7)	2.4166(7)
Ru−Cl(2)	2.391(1)	2.392(2)	2.4117(3)	2.4021(7)
Ru−(C$_1$−C$_6$)[a]	2.187(4)	2.200(7)	2.198(3)	2.206(30
As−Ru−Cl(1)	85.84(3)	86.11(5)	84.47(3)	84.92(2)
As−Ru−Cl(2)	86.04(3)	85.65(5)	88.70(2)	82.74(2)
Cl(1)−Ru−Cl(2)	86.06(4)	87.66(8)	87.61(3)	88.09(2)

[a] (C$_1$−C$_6$) denotes the average Ru−C distances.

4a: mp 211−213 °C (90% yield). ^{1}H NMR (500.0 MHz, CDCl$_3$, 25 °C): δ 7.71 (m, 4H, H$_o$), 7.40 (m, 6H, H$_{m,p}$), 6.80 (dd, ^3J(H$_a$H$_c$) = 18.5 Hz, ^3J(H$_a$H$_b$) = 11.5 Hz, 1H, H$_a$), 5.98 (d, ^3J(H$_a$H$_b$) = 11.5 Hz, 1H, H$_b$), 5.47 (d, ^3J(H$_a$H$_c$) = 18.5 Hz, 1H, H$_c$), 4.82 (s, 3H, CH, arene), 1.99 (s, 9H, 3CH$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ 133.41 (C$_o$), 132.66 (C$_\beta$), 132.30 (C$_\alpha$), 129.98 (C$_p$), 129.10 (C$_i$), 128.48 (C$_m$), 101.62 (Cq, arene), 81.72 (CH, arene), 18.63 (CH$_3$). Anal. Calcd for C$_{23}$H$_{25}$AsCl$_2$Ru: C, 50.40; H, 4.56; Cl, 12.94. Found: C, 50.26; H, 4.39; Cl, 12.68.

5a: mp 186−189 °C (95% yield). ^{1}H NMR (500.0 MHz, CDCl$_3$, 25 °C): δ 7.68 (m, 4H, H$_{o,}$), 7.40 (m, 6H, H$_{m,p}$), 6.91 (dd, ^3J(H$_a$H$_c$) = 18.5 Hz, ^3J(H$_a$H$_b$) = 11.4 Hz, 1H, H$_a$), 5.98 (d, ^3J(H$_a$H$_b$) = 11.4 Hz, 1H, H$_b$), 5.43 (d, ^3J(H$_a$H$_c$) = 18.5 Hz, 1H, H$_c$), 5.28, 5.30 (AB, ^3J(HH) = 6.0 Hz, 4H, CH, arene), 2.63 (septet, ^3J(HH) = 6.9 Hz, 1H, CH), 1.91 (s, 3H, CH$_3$), 0.96 (d, ^3J(HH) = 6.9 Hz, 6H, 2CH$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ 133.88 (C$_\beta$), 133.15 (C$_o$), 131.14 (C$_\alpha$) 130.03 (C$_p$), 128.57 (C$_m$) C$_i$ not observed, 106.84, 95.19, 85.62, 83.25 (C, arene), 38.26 (CH, arene), 21.48 (2CH$_3$), 17.69 (CH$_3$). Anal. Calcd for C$_{24}$H$_{27}$AsCl$_2$Ru: C, 51.28; H, 4.80; Cl, 12.61. Found: C, 51.41; H, 4.98; Cl, 12.52.

6a: mp 199−200 °C (85% yield). ^{1}H NMR (500.0 MHz, CDCl$_3$, 25 °C): δ 7.71 (m, 4H, H$_o$), 7.39 (m, 6H, H$_{m,p}$), 6.90 (dd, ^3J(H$_a$H$_c$) = 18.3 Hz, ^3J(H$_a$H$_b$) = 11.3 Hz, 1H, H$_a$), 5.93 (d, ^3J(H$_a$H$_b$) = 11.3 Hz, 1H, H$_b$), 5.46 (d, ^3J(H$_a$H$_c$) = 18.3 Hz, 1H, H$_c$), 4.98 (s, 2H, arene) 1.82 (s, 12H, 4CH$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ 132.74 (C$_o$), 132.42 (C$_\beta$), 131.92 (C$_\alpha$), 129.38 (C$_p$), 128.59 (C$_i$), 127.91 (C$_m$), 94.49 (Cq, arene), 87.49 (CH, arene), 15.64 (CH$_3$). Anal. Calcd for C$_{24}$H$_{27}$AsCl$_2$Ru: C, 51.28; H, 4.80; Cl, 12.61. Found: C, 51.14; H, 4.63; Cl, 12.49.

7a: mp > 200 dec (92% yield). ^{1}H NMR (500.0 MHz, CDCl$_3$, 25 °C): δ 7.73 (m, 4H, H$_o$), 7.41 (m, 6H, H$_{m,p}$), 6.89 (dd, ^3J(H$_a$H$_c$) = 18.5 Hz, ^3J(H$_a$H$_b$) = 11.5 Hz, 1H, H$_a$), 5.92 (d, ^3J(H$_a$H$_b$) = 11.5 Hz, 1H, H$_b$), 5.47 (d, ^3J(H$_a$H$_c$) = 18.5 Hz, 1H, H$_c$), 1.85 (s, 18H, 6CH$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ 134.10 (C$_o$), 133.99 (C$_\alpha$), 132.34 (C$_\beta$), 129.86 (C$_p$), 128.42 (C$_m$), 128.07 (C$_i$), 93.90 (C, arene), 15.49 (CH$_3$, arene). Anal. Calcd for C$_{26}$H$_{31}$AsCl$_2$Ru: C, 52.91; H, 5.25; Cl, 12.01. Found: C, 52.69; H, 5.31; Cl, 11.94.

1b: mp 177−179 °C (95% yield). ^{1}H NMR (500.0 MHz, CDCl$_3$, 25 °C): δ 6.31 (dd, ^3J(H$_a$H$_c$) = 19.0 Hz, ^3J(H$_a$H$_b$) = 12.0 Hz, 1H, H$_a$), 5.87 (d, ^3J(H$_a$H$_b$) = 12.0 Hz, 1H, H$_b$), 5.60 (d, ^3J(H$_a$H$_c$) = 19.0 Hz, 1H, H$_c$), 5.50 (apparent t, ^3J(HH) = 5.0 Hz, 2H, H$_m$), 5.22 (d, ^3J(HH) = 5.0 Hz, 2H H$_o$) 5.16 (t, ^3J(HH) = 5.0 Hz, 1H, H$_p$), 2.31 (t, ^3J(HH) = 12.5 Hz, 2H, H$_{\alpha a}$), 2.09 (s, 3H, CH$_3$), 1.90 (d, ^2J(HH) = 11.5 Hz, 2H, H$_{\beta e}$), 1.82 (d, ^2J(HH) = 12.5 Hz, 2H H$_{\beta e}$), 1.67 (d, ^2J(HH) = 11.5 Hz, 2H, H$_{\gamma\ e}$), 1.62 (d, ^2J(HH) = 11.0 Hz, 2H, H$_{\gamma e}$), 1.54 (d, ^3J(HH) = 9.5 Hz, 2H, H$_\delta$), 1.33 (q ^2J(HH) = ^3J(HH) = 12.5 Hz, 2H, H$_{\beta a}$), 1.30 (q, ^2J(HH) = ^3J(HH) = 12.5 Hz, 2H, H$_{\beta a}$), 1.10 (m, 6H, H$_{\gamma\delta}$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ 129.29 (C$_\alpha$), 128.48 (C$_\beta$), 105.16 (C$_i$, arene), 84.24 (C$_o$, arene), 84.20 (C$_m$, arene), 74.73 (C$_p$, arene), 32.28 (C$_{\alpha'}$), 29.94 (C$_{\beta'}$), 28.83 (C$_{\beta'}$), 26.92 (C$_{\gamma''}$) 26.74 (C$_{\gamma''}$), 25.48 (C$_{\delta'}$), 18.04 (CH$_3$). Anal. Calcd for C$_{22}$H$_{35}$AsCl$_2$Ru: C, 47.40; H, 6.20; Cl, 13.32. Found: C, 47.16; H, 6.27; Cl, 13.09.

Table 5. Ru(II/III) Potentials for 1a−7a, 1b−3b, 5b, 6b, 1c, and 4c

compound	$E_{1/2}$ Ru(II/III) (V)[a]	ΔE_p (mV)	compound	$E_{1/2}$ Ru(II/III) (V)[a]	ΔE_p (mV)
1a	0.76	152	**1b**	0.67	83
2a	0.70	122	**2b**	0.60	145
3a	0.71	272	**3b**	0.60	112
4a	0.66	161	**5b**	0.60	94
5a	0.70	174	**6b**	0.51	133
6a	0.61	150	**1c**	0.77	153
7a	0.48	126	**4c**	0.65	158

[a] Measured at 298 K in CH$_2$Cl$_2$ solutions at a glassy carbon working electrode, 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. All potentials are vs Fc/Fc$^+$. Scan rate 100 mV/s.

2b: mp 219−221 °C (85% yield). ^{1}H NMR (500.0 MHz, CDCl$_3$, 25 °C): δ 6.31 (dd, ^3J(H$_a$H$_c$) = 19.0 Hz, ^3J(H$_a$H$_b$) = 12.0 Hz, 1H, H$_a$), 5.85 (d, ^3J(H$_a$H$_b$) = 12.0 Hz, 1H, H$_b$), 5.57 (d, ^3J(H$_a$H$_c$) = 19.0 Hz, 1H, H$_c$), 5.34 (s, 4H, arene), 2.28 (t, ^3J(HH) = 12.0 Hz, 2H H$_{\alpha a}$) 1.95 (s, 6H, CH$_3$), 1.90 (d, ^2J(HH) = 13.0 Hz, 2H, H$_{\beta e}$), 1.80 (d, ^2J(HH) = 13.0 Hz, 2H, H$_{\beta e}$), 1.65 (d, ^2J(HH) = 13.0 Hz, 2H, H$_{\gamma\ e}$), 1.62 (d, ^2J(HH) = 13.0 Hz, 2H, H$_{\gamma e}$), 1.54 (d, ^3J(HH) = 10.0 Hz, 2H, H$_\delta$), 1.32 (dt, ^2J(HH) = 13.0 Hz, ^3J(HH) = 12.0 Hz, 2H, H$_{\beta a}$), 1.29 (dt, ^2J(HH) = 13.0 Hz, ^3J(HH) = 12.0 Hz, 2H, H$_{\beta a}$), 1.07 (m, 6H, H$_{\gamma\delta}$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ 128.97 (C$_\alpha$), 127.77 (C$_\beta$), 93.42 (Cq, arene), 84.87 (CH, arene), 36.74 (C$_{\alpha'}$), 28.70 (C$_{\beta'}$), 28.34 (C$_{\beta'}$), 26.66 (C$_{\gamma'}$), 26.50 (C$_{\gamma'}$), 25.32 (C$_{\delta'}$), 17.24 (2CH$_3$). Anal. Calcd for C$_{22}$H$_{35}$AsCl$_2$Ru: C, 48.38; H, 6.41; Cl, 12.98. Found: C, 48.12; H, 6.19; Cl, 12.73.

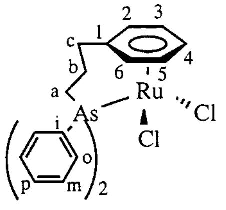
3b: mp 210−200 °C (87% yield). ^{1}H NMR (500.0 MHz, CDCl$_3$, 25 °C): δ 6.38 (dd, ^3J(H$_a$H$_c$) = 19.0 Hz, ^3J(H$_a$H$_b$) = 12.0 Hz, 1H, H$_a$), 5.94 (d, ^3J(H$_a$H$_c$) = 12.0 Hz, 1H, H$_c$), 5.67 (d, ^3J(H$_a$H$_c$) = 19.0 Hz, 1H, H$_b$), 5.27 (m, [AX]$_2$, 2H, arene), 5.16 (m, [AX]$_2$, 2H arene) 2.36 (tt, ^3J(HH) = 12.5, ^3J(HH) = 12.5 Hz, 2H, H$_{\alpha a}$), 2.05 (s, 6H, 2CH$_3$), 1.95 (d, ^2J(HH) = 13.0 Hz, 2H, H$_{\beta e}$), 1.89 (d, ^2J(HH) = 13.0 Hz, 2H H$_{\beta e}$), 1.77 (d, ^2J(HH) = 19.5 Hz, H$_\gamma$), 1.71 (t, ^2J(HH) = ^3J(HH) = 12.5 Hz, 2H, H$_\delta$), 1.61 (d, ^2J(HH) = 11.0 Hz, 2H, H$_\delta$), 1.39 (apparent qd, ^2J(HH) = ^3J(HH) = 12.5 Hz,^3J(HH) = 2.5 Hz, 2H, H$_{\beta a}$), 1.36 (apparent qd, ^2J(HH) = ^3J(HH) = 12.5 Hz,^3J(HH) = 2.5 Hz, 2H, H$_{\beta a}$), 1.15 (m, 6H, 4H$_\gamma$, 2H$_\delta$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ 130.06 (C$_\alpha$), 128.81 (C$_\beta$), 101.29 (C$_i$, arene), 85.23 (CH, arene), 77.40 (CH, arene), 37.47 (C$_{\alpha'}$), 29.32 (C$_{\beta'}$), 29.15 (C$_{\beta'}$), 27.25 (C$_{\gamma''}$), 27.08 (C$_{\gamma''}$), 25.84 (C$_{\delta'}$), 16.26 (2CH$_3$). Anal. Calcd for C$_{22}$H$_{35}$AsCl$_2$Ru: C,48.38; H, 6.41; Cl, 12.98. Found: C, 48.14; H, 6.29; Cl, 12.82.

5b: mp 173−176 °C (88% yield). ^{1}H NMR (500.0 MHz, CDCl$_3$, 25 °C): δ 6.37 (dd, ^3J(H$_a$H$_c$) = 19.0 Hz, ^3J(H$_a$H$_b$) = 12.0 Hz, 1H, H$_a$), 5.95 (d, ^3J(H$_a$H$_b$) = 12.0 Hz, 1H, H$_b$), 5.65 (d, ^3J(H$_a$H$_c$) = 19.0 Hz, 1H, H$_c$), 5.40, 5.38 (AB, ^3J(HH) = 6.0 Hz, 4H, ring), 2.79 (sept, ^3J(HH) = 7.0 Hz, 1H, CH) 2.37 (t, ^3J(HH) = 12.5 Hz, 2H, H$_{\alpha a}$) 2.02 (s, 3H, CH$_3$) 1.95 (d, ^2J(HH) = 12.5 Hz, 2H, H$_{\beta e}$), 1.87 (d, ^2J(HH) = 12.5 Hz, 2H, H$_{\beta e}$), 1.68 (m, 4H, H$_\gamma$), 1.59 (m, 4H, H$_\delta$), 1.43 (apparent quart., ^3J(HH) = 12.5 Hz, 2H, H$_{\beta a}$), 1.36 (aparent q, ^2J(HH) = ^3J(HH) = 12.5 Hz, 2H, H$_{\beta a}$), 1.15 (d, ^3J(HH) = 7.0 Hz, 6H, CH$_3$), 1.14 (m, 6H, H$_{\gamma\delta}$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ 129.53 (C$_\alpha$), 128.14 (C$_\beta$), 105.89 (Cq, arene), 93.69 (Cq, arene), 84.95 (CH, arene), 81.60 (CH, arene), 36.97 (C$_{\alpha'}$), 29.84 (CH), 29.02 (C$_{\beta'}$), 28.54 (C$_{\beta'}$), 27.06 (C$_{\gamma'}$), 26.92 (C$_{\gamma'}$), 25.62 (C$_{\delta'}$), 21.58 (2CH$_3$), 17.66 (CH$_3$). Anal. Calcd for C$_{24}$H$_{39}$AsCl$_2$Ru: C, 50.16; H, 6.79; Cl, 12.35. Found: C, 49.93; H, 6.60; Cl, 12.21.

6b: mp 198−200 °C (93% yield). ^{1}H NMR (500.0 MHz, CDCl$_3$, 25 °C): δ 6.40 (dd, ^3J(H$_a$H$_c$) = 19.0 Hz, ^3J(H$_a$H$_b$) = 12.0 Hz, 1H, H$_a$), 5.95 (d, ^3J(H$_a$H$_b$) = 12.0 Hz, 1H, H$_b$), 5.65 (d, ^3J(H$_a$H$_c$) = 19.0 Hz, 1H, H$_c$), 5.25 (s, 2H, arene H), 2.37 (tt, ^3J(HH) = 12.5 Hz, ^3J(HH) = 3.0 Hz, 2H H$_{\alpha a}$) 1.97 (s, 12H CH$_3$), 1.96 (d, ^2J(HH) = 12.5 Hz, 2H, H$_{\beta e}$), 1.87 (d, ^2J(HH) = 12.5

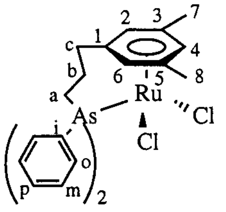
Hz, 2H, $H_{\beta e}$), 1.76 (d, ^2J(HH) = 12.5 Hz, 2H, H_γ), 1.71 (d, ^2J(HH) = 12.0 Hz, 2H, H_γ), 1.64 (d, ^3J(HH) = 10.5 Hz, 2H, H_δ), 1.38 (qd, ^2J(HH) = ^3J(HH) = 12.5 Hz, ^3J(HH) = 3.0 Hz, 2H, $H_{\beta a}$), 1.37 (qd, ^2J(HH) = ^3J(HH) = 12.5 Hz, ^3J(HH) = 3.0 Hz, 2H, $H_{\beta a}$), 1.18 (m, m, 6H, $H_{\gamma\delta}$). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 129.38 (C_α), 128.20 (C_β), 94.56 (Cq, arene), 86.31 (CH, arene), 36.38 ($C_{\alpha'}$), 29.84 (CH), 29.62 ($C_{\beta'}$), 28.96 ($C_{\beta'}$), 27.45 ($C_{\gamma'}$), 27.26 ($C_{\gamma''}$), 26.04 ($C_{\delta'}$), 21.58 ($2CH_3$), 16.46 (CH_3). Anal. Calcd for $C_{24}H_{39}AsCl_2Ru$: C, 50.16; H, 6.79; Cl, 12.35. Found: C, 50.01; H, 6.59; Cl, 12.22.

Preparations of 1c and 4c. The complexes were prepared by the following procedure. A solution of [(η^6-arene)$RuCl_2$(DPVAs)] (0.20 g) in 25 mL of CH_3CN was stirred at room temperature for 15 min under nitrogen. To this solution was added $KOBu^t$ (0.02−0.03 g) and 5 mL of CH_3CN. The clear red solution turned dark red upon addition of the base. The solution was heated at reflux for 48 h. The solvent was removed on a rotary evaporator. The residue was washed with ether to remove some decomposition products. The mixture was then filtered and rotary evaporated to dryness. The residue was dissolved in a small quantity of dichloromethane, the solution was layered with *n*-hexane, and the products were allowed to crystallize in a freezer. The resulting solid was isolated by filtration and dried in vacuo to give the pure products as red powders.



1c

1c: mp 198−200 °C (20% yield). ^1H NMR (500.0 MHz, $CDCl_3$, 25 °C): δ 7.66 (m, 4H, H_o), 7.36 (m, 6H, $H_{m,p}$), 6.29 (t, ^3J(HH) = 5.5 Hz, 1H, H_4), 5.78 (dd, ^3J(HH) = 6.0 Hz, ^3J(HH) = 5.5 Hz, 2H, $H_{2,6}$), 5.22 (d, ^3J(HH) = 6.0 Hz, 2H, $H_{3,5}$), 2.64 (t, ^3J(HH) = 6.0 Hz, 2H, H_c), 2.43 (t, ^3J(HH) = 6.0 Hz, 2H, H_a) 2.27 (m, 2H, H_b). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 133.22 (C_o), 132.89 (C_i), 130.10 (C_p), 128.62 (C_m), 96.67 (C_1), 88.40 (C_4), 87.36 ($C_{2,6}$), 82.27 ($C_{3,5}$), 30.68 (C_c), 29.67 (C_a), 20.82 (C_b). Anal. Calcd for $C_{21}H_{21}AsCl_2Ru$: C, 49.49; H, 4.04; Cl, 13.63. Found: C, 49.23; H, 3.88; Cl, 13.46.



4c

4c: mp 212−214 °C (25% yield). ^1H NMR (500.0 MHz, $CDCl_3$, 25 °C): δ 7.66 (m, 4H, H_o), 7.33 (m, 6H, $H_{m,p}$), 5.71 (s, 1H, H_4), 4.76 (d, ^4J(HH) = 1.5 Hz, 2H, $H_{2,6}$), 2.54 (t, ^3J(HH) = 5.0 Hz, 2H, H_c), 2.33 (t, ^3J(HH) = 5.0 Hz 2H, H_a), 2.28 (s, 6H, $H_{7,8}$), 2.17 (m, 2H, H_b). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 133.81 (C_o), 133.12 (C_i), 129.83 (C_p), 128.38 (C_m), 102.76 (C_1), 94.52 (C_4), 88.90 ($C_{2,6}$), 79.23 ($C_{3,5}$), 30.58 (C_c), 20.99 (C_a), 20.18 (C_b), 18.05 ($C_{7,8}$). Anal. Calcd for $C_{23}H_{25}AsCl_2Ru$: C, 50.40; H, 4.56; Cl, 12.94. Found: C, 50.21; H, 4.43; Cl, 12.60.

X-ray Data Collection and Processing. Crystals of the compounds were obtained from $CHCl_3$/*n*-hexane solvent mixtures mounted on glass fibers and placed on a Nonius Kappa CCD diffractometer. Intensity data were taken in the ω-mode for **1a**, **2a**, and **4a**−**6a**, and ϕ- and ω-mode for **1b**, **3b**, **5b**, and **6b** at 200 K with Mo Kα graphite-monochromated radiation (λ = 0.71073 Å). The data were corrected for Lorentz−polarization effects and absorption by integration using the Gaussian method.[29] Scattering factors and corrections for anomalous dispersion were taken from a standard source.[30] Calculations were performed with the teXsan (MSC 1992−1997) software package version 1.8[31] for **1a**, **2a**, **4a**−**6a**, **1b**, **3b**, **5b**, and **6b** and CRYSTALS Issue 10[32] for **5a** on the Silicon Graphics Power Challenge computer of the Australian National University's super computer facility. The structures were solved by Patterson methods, DIRDIF-92,[33] for **1a**, **2a**, **4a**, **6a**, **1b**, **3b**, **5b**, and **6b** and SIR-92[34] for **5a**. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were included at calculated positions in which the C−H vector was fixed at 0.95 Å but not refined. Compound **4a** crystallized as a chloroform solvate.

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Supporting Information Available: Structural drawings of **1a**, **2a**, **5a**, **6a**, **1b**, **3b**, and **6b**, tables of crystal data and structure refinement, atomic coordinates, isotropic and anisotropic displacement parameters, bond lengths and angles, and hydrogen coordinates for **1a**, **2a**, **4a**−**6a**, **1b**, **3b**, **5b**, and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM011092J

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