Articles

Synthesis, X-ray Studies, and Catalytic Allylic Amination Reactions with Ruthenium(IV) Allyl Carbonate Complexes

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Results from selected ruthenium-catalyzed allylic amination reactions, using a carbonate Ru−Cp* (or Cp) allyl cationic precursor, are reported. With a phenyl-substituted allyl substrate as the starting material, the rates of the amination reactions, as well as the regioselectivity, are shown to depend on the structure of the allyl substrate, the amine nucleophile, and the solvent. Two new Ru−allyl carbonate complexes are reported, as well as the solid-state structure for the new carbonate salt [Ru(Cp)(O_2C{OBu^t})(η^3-$PhCHCHCH_2$)](PF_6). A number of aniline- and substrate-related Cp* and Cp η^6-arene complexes of Ru(II) are described.

Introduction

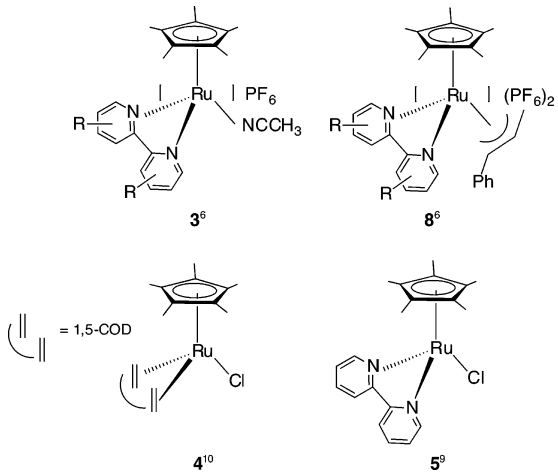
The allylic alkylation reaction can be catalyzed by a number of transition-metal complexes. The most commonly used metal is palladium;[1] however, molybdenum,[2a] iridium,[2b] and ruthenium[3] are all currently in use. The interest in Ru(II) complexes is based on the observed regioselectivity[3] in that, for unsymmetrical allyl substrates, the preferred site of attack leads to a branched, rather than a linear, product.

The most commonly used ruthenium catalyst precursor contains a Cp or Cp* ligand. Trost and co-workers[3] have reported that [Ru(Cp* or Cp)($CH_3CN)_3$](PF_6) (**1a**,**b**, respectively) are excellent catalysts for this reaction and, specifically, that with the Cp* complex, **1a**, reaction of the allyl substrate $PhCH{=}CHCH_2X$ (X = carbonate (**2a**), chloride (**2b**)) with a carbon nucleophile, Nu^-, occurs preferentially at the more substituted position (see eq 1).

$$PhCH{=}CHCH_2X + Nu^- \xrightarrow[\text{DMF or acetone}]{[Ru(Cp^*)(CH_3CN)_3](PF_6)} PhCH(Nu)CH{=}CH_2 + X^- \quad (1)$$

Bruneau[4−7] and co-workers have used chelating nitrogen complexes of Ru(II) for this reaction (e.g. **3**; see Chart 1); however, although their catalysts are selective (and some are enantioselective[7]), they are relatively slow. Several reports[8−10] suggest that Ru(1,5-COD) complexes such as **4**,[10] or even the relatively simple chloro derivative **5**,[9] are also useful catalysts for this allylation chemistry.

Chart 1



3[6] **8**[6] **4**[10] **5**[9]

We have recently reported[11] that the source of the observed high branched-to-linear regioselectivity, for X = Cl, has an

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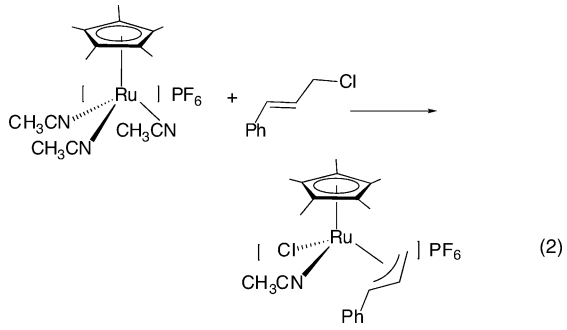
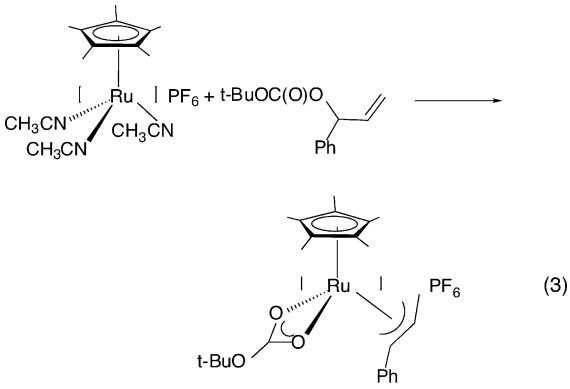
electronic origin[11] on the basis of X-ray and NMR data, together with DFT calculations. These conclusions were based on studies of the Ru(IV) allyl complex [Ru(Cp*)Cl(CH_3CN)(η^3-PhCHCH-CH_2)](PF_6) (**6**), which was prepared via the reaction of the allyl substrate **2b** with **1a** (eq 2). We have also synthesized[12] the



(2)

6

novel Ru(IV) carbonate complex [Ru(Cp*){OC(OBu^t)O}(η^3-PhCHCHCH$_2$)](PF_6) (**7b**) from the branched *tert*-butyl carbonate plus **1a** in DMF at ambient temperature (eq 3). A number of



(3)

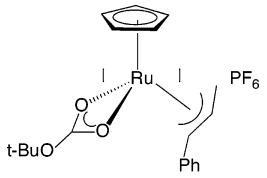
7a

Ru−allyl complexes are known:[4,6,13−18] e.g., **8** in Chart 1.

The solid-state structure[12] of this unexpected carbonate, **7a**, reveals that the *tert*-butyl carbonate ligand is coordinated in a bidentate fashion via two oxygen atoms, with the allyl ligand showing an *endo* configuration such that the phenyl substituent is remote from the bulky Cp* ligand. Obviously, the oxidative addition affords the monocationic carbonate and *not* the bis-(acetonitrile) dicationic complex. It is often thought that the carbonate leaving group rapidly decomposes to alkoxide and CO_2.[3] DFT calculations[11,12] carried out on model complexes revealed that the phenylallyl ligands in these cationic complexes are distorted, such that the bond distance from the metal to the allyl carbon adjacent to the phenyl group is much longer than the corresponding distance to the methylene allyl carbon.

Subsequently, we have used the allyl carbonate complex **7a** as a catalyst[12] for the allylic alkylation reaction using the dimethyl malonate anion as the nucleophile and find relatively rapid formation of the organic products. Specifically, a comparison of the rate of complete conversion to organic products (followed by NMR) for **7a** vs **1a**, using the *branched* carbonate substrate, revealed that complex **7a** was 25 times faster than the tris(nitrile) **1a**. Using the *linear* substrate, catalyst **7a** is only a factor of 2 faster than **1a**.

We report here new synthetic and structural studies on Ru(IV) Cp and Cp* carbonate complexes, e.g. the Cp analogue **7b**, as

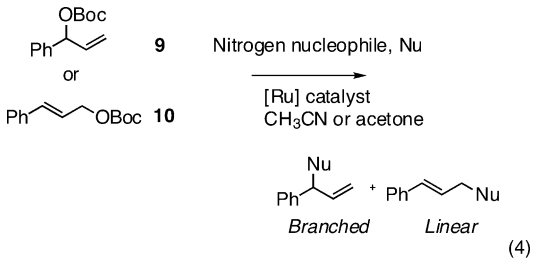


7b

well the results of a series of Ru-catalyzed allylic amination reactions. These new catalytic results suggest an important role for the solvent in the catalysis and raise some questions with respect to the generality of the regioselectivity of ruthenium in this amination reaction. There are not many examples of allylic amination using Ru(II).[4,8,19]

Results and Discussion

Catalytic Allylic Amination. The results from Ru-catalyzed allylic amination reactions (eq 4) using (a) the branched and linear substrates **9** and **10**, respectively, (b) a number of different catalysts, including **1**, and (c) several amine nucleophiles are given in Tables 1−5.



(4)

Several important points are immediately obvious.

1. In acetonitrile solution, both the branched/linear product ratio and the reaction rate depend markedly on the structure of the allyl carbonate, with the branched isomer reacting quickly and the linear analogue slowly or not at all (see Table 1). In some, but not all, cases the branched/linear ratio is good to excellent: e.g., for the aniline nucleophiles. The use of aliphatic amines affords mixed results. The reaction can be either faster or slower than that for aniline, and the branched/linear ratio can be good (morpholine, entry 3, 91:1) or poor (diethylamine, entry 6, 33:67; triethylamine, entry 7, 0:100).

2. The reactions with the CpRu carbonate catalyst **7b** (instead of the Cp* catalyst; see Table 2) were slower but afforded similar (but not identical) branched/linear product ratios. Entries 2−4 are based on 9 mol % instead of 3 mol % catalyst, so that

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Table 1. Selected Cp* Ruthenium Catalyzed Allylic Amination Reactions Using the Cp* Carbonate Complex 7a in Acetonitrile Solution[a]

entry	substrate	amine	*t* (min)	branched/linear[b]
		Branched Carbonate		
1	**9**	*tert*-butylamine	110	60:40[c]
2	**9**	morpholine	27	91:9
3	**9**	morpholine[d]	30	91:9
5	**9**	piperidine	62	83:17
6	**9**	diethylamine	6	33:67
7	**9**	triethylamine	1320	0:100[e]
8	**9**	aniline	16	93:7
9	**9**	4-methoxyaniline	12	95:5
10	**9**	4-fluoroaniline	15	93:7
11	**9**	4-nitroaniline	96	85:15
		Linear Carbonate		
12	**10**	morpholine	1920	68:32
13	**10**	aniline	*f*	*f*

[a] Conditions: 0.07 mmol of the carbonate substrate, 0.21 mmol of amine, 0.002 mmol of catalyst (3 mol %), in 0.5 mL of acetonitrile, room temperature. [b] All reactions led to 100% conversion. The branched/linear ratio was determined by ^{1}H NMR spectroscopy. [c] 6% of isomerized linear carbonate **10** was also detected. [d] 0.08 mmol of amine was employed. [e] We believe this to be a hydroxide salt. [f] No conversion after 24 h.

Table 2. Selected Ruthenium-Catalyzed Allylic Amination Reactions Using the Cp Carbonate Complex 7b in Acetonitrile Solution[a]

entry	substrate	amine	*t* (min)	branched/linear[b]
1	**9**	morpholine	210	89:11
2[c]	**9**	morpholine	70	89:11
3[c]	**9**	aniline	*d*	
4[c]	**9**	4-fluoroaniline	840 (14 h)	86:14

[a] Conditions: 0.07 mmol of the branched carbonate substrate **9**, 0.21 mmol of amine, 0.002 mmol of catalyst (3 mol %), in 0.5 mL of acetonitrile, room temperature. [b] All reactions led to 100% conversion. The branched/linear ratio was determined by ^{1}H NMR spectroscopy. [c] 0.006 mmol of catalyst (9 mol %). [d] No conversion after 36 h.

Table 3. Selected Ruthenium-Catalyzed Allylic Amination Reactions with Morpholine in Acetone[a] with Different Catalysts

entry	substrate	[Ru]	amine	*t* (min)[a]	branched/linear[b]
1	**9**	**7a**	morpholine	1	29:71
2	**10**	**7a**	morpholine	1	11:89
3	**9**	**7b**[c]	morpholine	1	80:20[d]
4	**9**	**1a**	morpholine	1	61:39
5	**9**	**1b**[c]	morpholine	1	82:18

[a] Conditions: 0.07 mmol of the carbonate substrate, 0.21 mmol of amine, 0.002 mmol of catalyst (3 mol %), in 0.5 mL of acetone, room temperature. The entry "1" for time, in the table, indicates only that the reaction was finished by the time the sample could be measured in the NMR spectrometer. [b] All reactions led to 100% conversion. The branched/linear ratio was determined by ^{1}H NMR spectroscopy. [c] 0.006 mmol of catalyst (9 mol %). [d] 2% of isomerized linear carbonate **10** was also detected.

the times shown (for 100% conversion) are much slower than for the data in Table 1. The lack of conversion for aniline will be discussed below.

3. In acetone solution (instead of acetonitrile; see Table 3) with morpholine as the nitrogen nucleophile, the reaction is relatively fast, i.e., ca. 100% conversion in about 1 min; however, the branched/linear ratio is poor. Interestingly, the best branched/linear ratio is found for **1b**, Trost's Cp complex. This complex is reported[3] to give a poorer branched/linear ratio, relative to Cp*, in the alkylation reaction.

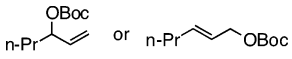
4. With the Trost catalysts **1a** and **1b** (see Table 4), the regioselectivity is as good as or better than that with **7a.** Catalyst

Table 4. Comparison of 1a and 1b in the Ruthenium-Catalyzed Allylic Amination Reactions in Acetonitrile[a]

entry	substrate	[Ru]	amine	*t* (min)	branched/linear[b]
1	**9**	**1a**	morpholine	28	91:9[c]
2	**9**	**1a**	aniline	15	93:7
3	**9**	**1b**[d]	morpholine	65	91:9
4	**9**	**1b**[d]	aniline	*e*	

[a] Conditions: 0.07 mmol of the branched carbonate substrate **9**, 0.21 mmol of amine, 0.002 mmol of catalyst (3 mol %), in 0.5 mL of acetonitrile, room temperature. [b] All reactions led to 100% of conversion. The branched/linear ratio was determined by ^{1}H NMR spectroscopy. [c] 3% of isomerized linear carbonate **10** was also detected. [d] 0.006 mmol of catalyst (9 mol %). [e] No conversion after 24 h.

Table 5. Selected Ruthenium-Catalyzed Allylic Amination Reactions Using a Substrate with an *n*-Propyl (Instead of Phenyl) Side Chain[a]



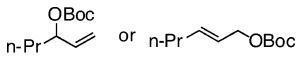
11 **12**

entry	sub-strate	[Ru]	amine	solvent	*t* (min)[20]	branched/linear[b]
1	**11**	**7a**	morpholine	MeCN	360	45:55
2	**11**	**7a**	morpholine	acetone	1	29:71
3	**11**	**7a**	aniline	MeCN	*c*	*c*
4	**12**	**7a**	morpholine	MeCN	1200 (20 h)	21:79
5	**12**	**7a**	morpholine	acetone	1	10:90
5	**12**	**7a**	aniline	MeCN	*c*	*c*

[a] Conditions: 0.07 mmol of the carbonate substrate, 0.21 mmol of amine, 0.002 mmol of catalyst (3 mol %), in 0.5 mL of acetonitrile, room temperature. The entry "1" for time, in the table, indicates only that the reaction was finished by the time the sample could be measured in the NMR spectrometer. [b] All reactions led to 100% of conversion. The branched/linear ratio was determined by ^{1}H NMR spectroscopy. [c] No conversion after 24 h.

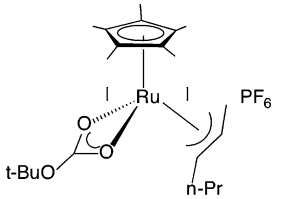
1a is much faster than **1b** (9 mol % was used for **1b** instead of 3 mol % with **1a**).

5. The amination reactions with the two *n*-propyl substrates **11** and **12** (see Table 5), gave poor branched/linear ratios and were very slow in acetonitrile solution. Again, the catalyses were



11 **12**

rapid in acetone. Obviously, the presence of a phenyl group in the substrate plays a role, as does the solvent. However, the substitution of an *n*-propyl group for a phenyl group does not interfere with the oxidative addition reaction. We have been able to prepare the Ru(IV) carbonate analogue of **7a**, complex **13**, in good yield, via reaction with substrate **11** (see Experimental Section).



13

The reaction with triethylamine, the only tertiary amine tried, afforded a surprising result: 100% of the cationic linear

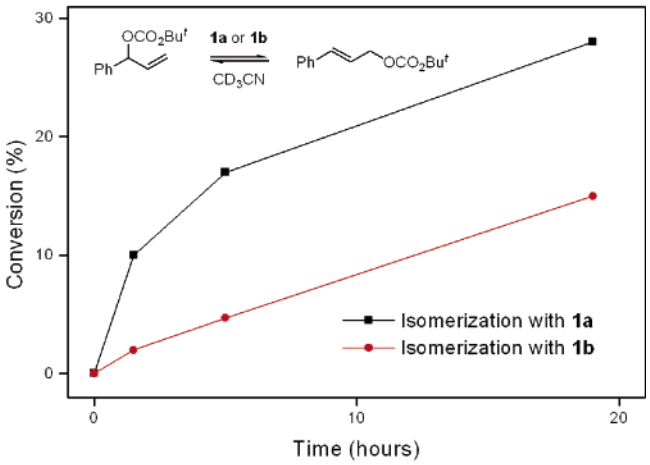
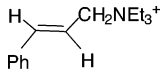


Figure 1. Isomerization of the branched *tert*-butyl carbonate to the linear isomer in CD_3CN using 3 mol % of both [RuCp*$(CH_3CN)_3$](PF_6) (black) and [RuCp$(CH_3CN)_3$](PF_6) (red) (0.0021 mmol). The salt and the branched *tert*-butyl carbonate (0.07 mmol) were dissolved in CD_3CN, and the isomerization was monitored by ^1H NMR spectroscopy.

compound **14**, which was not isolated[20] but readily identified via its ^1H and ^{13}C NMR spectra. Apart from the two olefinic



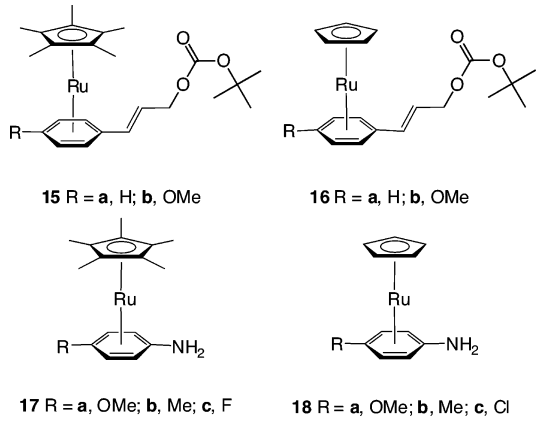
14

resonances (δ 6.31 and 7.00, ^3J(H,H) = 15.7 Hz), and the methylene protons (δ 3.96), the three equivalent ethyl groups are readily visible. We are not certain as to the anion.

The various branched/linear ratios (Table 1) might arise, partially, from isomerization processes. Indeed, one can show that the branched substrate **9** can isomerize to **10** (see Figure 1); however, this seems to be a rather slow reaction when compared to the catalytic amination. An alternate isomerization pathway, suggested by a reviewer, concerns isomerization of the product rather than the starting material. In a second repeat experiment, we have allowed anisidine to react with **9** in the presence of our catalyst **7a** (see Table 1, entry 9). After 14 min we find a ca. 94:6 branched/linear ratio. We then let this reaction mixture stand for 16 h and found the branched/linear ratio to be ca. 88:12. Once again there is slow isomerization. We conclude that our observed branched/linear ratios in Table 1 may indeed be affected by isomerization reactions;[21] however, isomerization is not likely to be important for the fast reactions.

Arene Complexes of Ru(II). Given the differences observed in the rates of the catalytic experiments, especially those found between the branched and linear substrates, **9** and **10** in Table 2, it seemed likely that η^6-arene complexes of Ru(II) might be formed:[22−24] e.g., the cation RuCp*$(\eta^6$-$C_6H_5F)^+$ has been

Chart 2. Monocationic Arene Complexes of Ru(II) as PF_6 Salts



15 R = **a**, H; **b**, OMe **16** R = **a**, H; **b**, OMe

17 R = **a**, OMe; **b**, Me; **c**, F **18** R = **a**, OMe; **b**, Me; **c**, Cl

reported.[23] Indeed, reaction of a small excess of linear substrate **10** with **1a** or **1b** affords the η^6-arene complexes **15** and **16** in good yield (see Chart 2). These complexes show the expected[25,26] low-frequency proton and carbon resonances associated with a complexed aromatic moiety. The anisidine complex **17a** was tried as the catalyst for the reaction of anisidine with the branched carbonate **9**. There is no conversion at all after 16 h.

With no excess of linear substrate, i.e., in the stoichiometric 1:1 reaction, we do *not* find complete formation of the arene complex **15**. Interestingly, the analogous reaction with the branched substrate **9** *immediately* affords the Ru(IV) allyl **7a**, via an oxidative addition reaction, in high yield. We have already shown via DFT calculations[12] that there should be a ca. 3 kcal/mol energy difference between the two arene complexes, with the branched isomer being higher in energy. Moreover, the leaving group is much further away from the ruthenium atom in **15** than it would be in the isomeric arene complex from the branched isomer. Consequently we suggest that the observed differences in rate between these two substrates, in the catalytic amination, are related to the time necessary for the η^6-arene to dissociate, thus allowing the oxidative addition to proceed.

Continuing, given the lack of reactivity of aniline with substrate **10** when **7b** is the catalyst (Table 1) as well as the failure of aniline to react with the *n*-propyl substrates **11** and **12** (see Table 5), we considered the possibility of intermediates such as the η^6-arene complexes **17** and **18**, also shown in Chart 2. In fact, **17a**−**c** are readily obtained via reaction of [RuCp*-$(CH_3CN)_3$](PF_6) and aniline in acetone solution at room temperature. These complexes, as purple powders, can be precipitated from acetone in excellent yield by addition of diethyl ether. The rate of formation of the η^6-anisidine complex, in CD_3CN solution, starting from the Trost complexes **1a**,**b** (see Figure 2), can be monitored using ^1H NMR spectroscopy. Clearly, the Cp* analogue forms the arene complex at a faster rate. We conclude that arene complexes are likely to exist in acetonitrile solution. Indeed, in an in situ experiment using 5 equiv of substrate **10**, 5 equiv of anisidine, and 1 equiv of catalyst **7a**, a small amount of the η^6-aniline derivative can be

(20) In the paper by Matsushima et al. (Matsushima, Y.; Onitsuka, K.; Takahashi, S. *Organometallics* **2004**, *23*, 3763−3765), a Ru(II) compound containing the olefin-complexed cation $Et_3NCH{=}CH_2$ is suggested as "possible". The authors do not give either NMR or solid-state data for this structure.

(21) In a report by Cadierno et al. (Cadierno, V.; Garcia-Garrido, S. E.; Gimeno, J.; Nebra, N. *Chem. Commun.* **2005**, 4086−4088), the authors report oxidative addition of the C−N bond of an allylamine using ruthenium.

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(26) den Reijer, C. J.; Dotta, P.; Pregosin, P. S.; Albinati, A. *Can. J. Chem.* **2001**, *79*, 693−704. den Reijer, C. J.; Drago, D.; Pregosin, P. S. *Organometallics* **2001**, *20*, 2982−2989. Geldbach, T. J.; den Reijer, C. J.; Worle, M.; Pregosin, P. S. *Inorg. Chim. Acta* **2002**, *330*, 155−160.

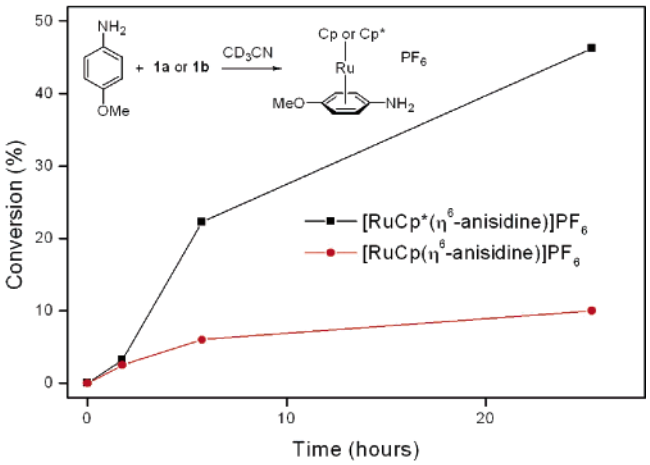


Figure 2. Formation of the η^6-aniline complexes in CD_3CN with $[RuCp^*(CH_3CN)_3](PF_6)$ (black) and $[RuCp(CH_3CN)_3](PF_6)$ (red). The salt, e.g., $[RuCp^*(CH_3CN)_3](PF_6)$ (0.012 mmol), and anisidine (0.012 mmol) were dissolved in CD_3CN, and the η^6-aniline complex formation was monitored by ^1H NMR spectroscopy.

Table 6. ^1H and ^{13}C NMR Data for Cp* η^6-Carbonate Complexes 15a and 15b in DMF-d_7 at 299 K

	Site	^1H	$^nJ_{HH}$	^{13}C
15a				
	1	4.85	5.7, 1.6	66.6
	2	6.71	16.0, 5.7	131.4
	3	6.49	16.0, 1.5	127.4
	4			96.8
	5	6.34	6.0	85.8
	6	6.16	6.0, 5.7	88.2
	7	6.11	5.7, 1.5	88.2
	8			153.7
	9			82.3
	10	1.51		27.5
	11	1.98		10.0
	12			97.4
	Site	^1H	$^nJ_{HH}$	^{13}C
15b				
	1	4.83	5.7, 1.5	66.6
	2	6.67	15.7, 5.7	131.0
	3	6.46	15.7, 1.5	126.8
	4	-		95.2
	5	6.22	6.7	76.5
	6	6.29	6.7	84.7
	7			133.2
	8	3.92		57.2
	9			153.7
	10			82.3
	11	1.51		27.5
	12	1.95		9.9
	13			96.1

observed via ^1H NMR. Presumably, in acetone solution, these η^6-aniline derivatives are much more labile such that more reactive organometallic complexes are formed. Selected NMR data for these arene complexes are given in Tables 6−8.

Solid-State Studies. Reaction of the Cp salt **1b** with the branched allyl precursor **9**, in acetone solution, gave the new carbonate complex **7b** in good yield. The ^{13}C resonances for the allyl ligand, δ 62.3 (=CH_2), 97.6 (=HC), and 99.9 (=HCPh), are consistent with our previous findings.[11,12]

X-ray Study of 7b. The solid-state structure of **7b** was determined by X-ray diffraction methods, and selected bond angles and bond distances are given in Table 9, along with some comparison data for the Cp* cation **7a**. This is only the second reported structure of such an allyl carbonate complex. A view of the cation is given in Figure 3.

The immediate coordination sphere for this coordinatively saturated Ru(IV) cation consists of an Ru atom surrounded by the Cp ligand, the η^3-allyl ligand, and the *tert*-butyl carbonate ligand. The last group is clearly coordinated in a bidentate fashion via the two oxygen atoms. The O−Ru−O bite angle is small, ca. 62°, and the two Ru−O separations, 2.116(2) and

Table 7. ^1H and ^{13}C NMR Data for η^6-Carbonate Complexes 16a and 16b in CD_3CN at 299 K

	Site	^1H	$^nJ_{HH}$	^{13}C
16a				
	1	4.69	5.0, 1.2	66.2
	2	6.51	15.9, 4.9	131.6
	3	6.43	15.9	127.3
	4			99.3
	5	6.33	5.8	84.4
	6	6.17	5.8	85.9
	7	6.10	5.8, 1.1	86.1
	8			153.5
	9			81.2
	10	1.50		27.3
	11	5.31		81.4
	Site	^1H	$^nJ_{HH}$	^{13}C
16b				
	1	4.66	4.3	65.8
	2	6.43	15.9, 4.9	130.7
	3	6.37	15.9	126.4
	4			96.2
	5	6.20	6.9	74.0
	6	6.26	6.9	82.2
	7			134.4
	8	3.76		57.1
	9			153.1
	10			80.2
	11	1.49		26.9
	12	5.29		80.6

Table 8. ^1H and ^{13}C NMR Data for the Cp* Aniline Complexes 17a−c in CD_3CN at 299 K

	Site	^1H	$^3J_{HH}$	^{13}C
17a				
	1			129.0
	2	5.22	6.5	71.7
	3	5.57	6.5	73.9
	4			120.4
	5	4.31		
	6	3.68		56.8
	7	1.91		9.7
	8			94.6
	Site	^1H	$^3J_{HH}$	^{13}C
17b				
	1			95.5
	2	5.56	6.0	86.7
	3	5.36	6.0	73.4
	4			122.0
	5	4.51		
	6	2.18		17.2
	7	1.99		9.5
	8			94.3
	Site	^1H	$^3J_{HH}$ ($^nJ_{FH}$)	^{13}C ($^nJ_{FC}$)
17c				
	1			132.4 (267.3)
	2	5.88	6.5 (3.0)	76.7 (23.1)
	3	5.32	6.5 (1.5)	71.5 (6.7)
	4			122.1
	5	4.53		
	6	1.94		9.6
	7			96.0

Table 9. Bond Lengths (Å) and Angles (deg) for 7b and 7a

7b		7a	
Ru−O(1)	2.116(2)	Ru1−O	2.148(3)
Ru−O(2)	2.124(3)	Ru1−O	2.116(3)
Ru−C(1)	2.190(4)	Ru1−C	2.162(5)
Ru−C(2)	2.150(3)	Ru1−C	2.137(5)
Ru−C(3)	2.294(4)	Ru1−C	2.303(5)
Ru−C(1P)	2.177(4)	Ru−C(10)	2.192(3)
Ru−C(2P)	2.236(4)	Ru−C(20)	2.206(3)
Ru−C(3P)	2.236(4)	Ru−C(30)	2.214(3)
Ru−C(4P)	2.184(4)	Ru−C(40)	2.257(3)
Ru−C(5P)	2.168(4)	Ru−C(50)	2.239(3)
O(1)−Ru−O(2)	62.1(1)		

2.124(3) Å, are not significantly different and correspond to literature expectations.[27] However, the three Ru−C(allyl) distances, Ru−C(1) = 2.190(4) Å, Ru−C(2) = 2.150(3) Å, and Ru−C(3) = 2.294(4) Å, are all different, with the Ru−C(H)Ph separation being much larger than the other two. Similar distortions have been observed previously,[11,12] and the pattern is similar to that found for the Cp* cation (see Table 9).

(27) Kuznetsov, V. F.; Jefferson, G. R.; Yap, G. P. A.; Alper, H. *Organometallics* **2002**, *21*, 4241−4248.

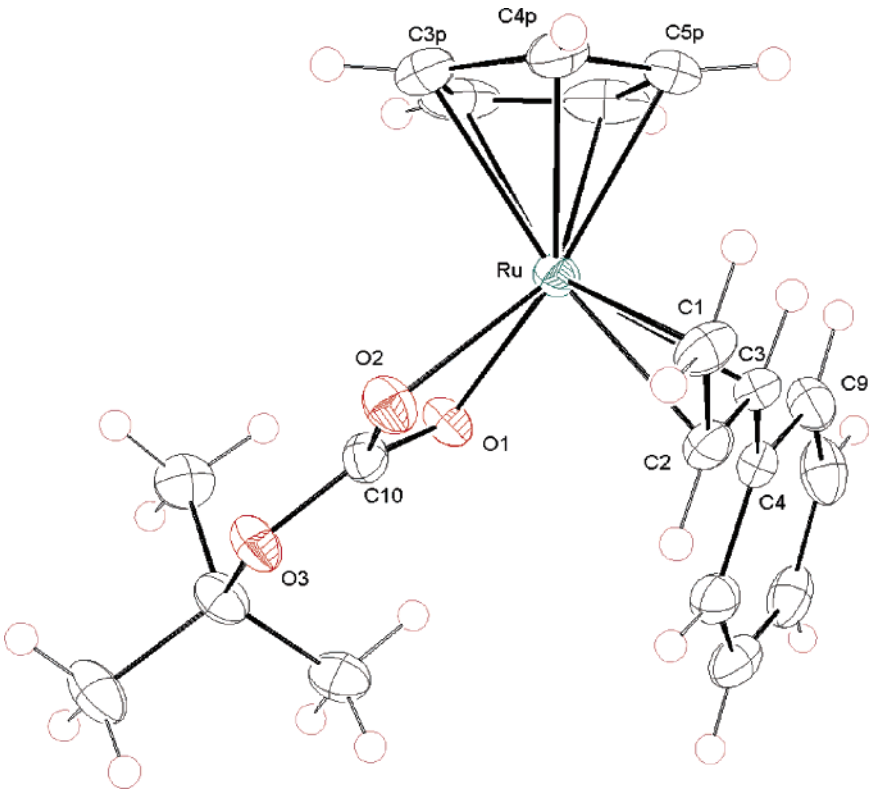
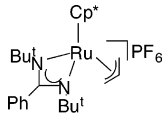


Figure 3. ORTEP view of the Ru(II) cationic complex **7b**. The PF_6 anion is omitted for clarity.

Kondo et al.[18] have reported the structure of **19** and find Ru−C(allyl) separations of 2.193(5) and 2.206(3) Å, for the two terminal carbons, and 2.132(3) Å for the central allyl carbon. Clearly, the Ru−C(3) value of 2.294(4) Å is relatively long.



19

The average Ru−C(Cp) distance in **7b** is 2.212 (4) Å, only marginally different (4σ) from that found in the Cp* cation **7a**, at ca. 2.221 Å.

Conclusions. For our Ru(II) catalysts, it would seem that there are a number of variables which are important with respect to the nature of the amine product formed in our reactions. The allyl substrate, the structure of the nucleophile, and certainly the reaction solvent all play important roles in this allylic amination chemistry. There are indications that the differing observed reaction rates are, partly, related to formation of η^6-arene complexes. Moreover, while it is possible to greatly accelerate these catalytic reactions via the use of acetone as solvent, the desired regioselectivity is lost. Obviously, there are subtle changes in the organometallic chemistry which are not yet understood and these can lead to catalytic results that are not readily explainable. Specifically, from Table 3, one notes that changing from the Cp* catalyst **7a** (entry 1) to the Cp catalyst **7b** (entry 3) results in a substantial change of the preferred regioselectivity. Clearly, further studies in this area will be necessary.

Experimental Section

All reactions and manipulations were performed under a N_2 atmosphere using standard Schlenk techniques. Solvents and amines were dried and distilled by using standard procedures and stored under nitrogen. NMR spectra were recorded with Bruker DPX 300, 400, and 500 MHz spectrometers at room temperature. Chemical shifts are given in ppm and coupling constants (J) in hertz. Elemental analyses and mass spectroscopic studies were performed at the ETHZ.

Crystallography. Air-stable orange crystals of **7b** suitable for X-ray diffraction were obtained by layering pentane in a CH_2Cl_2 solution of the isolated complex. A crystal of **7b** was mounted on a Bruker SMART diffractometer, equipped with a CCD detector, and cooled, using a cold nitrogen stream, to 150(2) K for the data collection. The space group was determined from the systematic absences, while the cell constants were refined at the end of the data collection with the data reduction software SAINT.[28] The experimental conditions for the data collection and crystallographic and other relevant data are given in the Supporting Information. The collected intensities were corrected for Lorentz and polarization factors[28] and empirically for absorption using the SADABS program.[29]

The structure was solved by direct and Fourier methods and refined by full-matrix least squares,[30] minimizing the function $\sum w(F_o^2 - (1/k)F_c^2)^2$ and using anisotropic displacement parameters for all atoms, except the hydrogens and those affected by disorder (see below).

The difference Fourier maps clearly showed severe disorder of the fluorine atoms in the equatorial plane of the PF_6 octahedron, even at low temperature. A model was constructed allowing 12 different positions for the equatorial fluorine atoms. During the refinement the sum of the site occupancy factors was constrained to obtain the correct stoichiometry. This model clearly shows that

(28) BrukerAXS. SAINT Integration Software; Bruker Analytical X-ray Systems, Madison, WI, 1995.
(29) Sheldrick, G. M. SADABS, Program for Absorption Correction; University of Göttingen, Göttingen, Germany, 1996.
(30) Sheldrick, G. M. SHELX-97. Structure Solution and Refinement Package; University of Göttingen, Göttingen, Germany, 1997.

there is an almost continuous scattering density in the equatorial plane and that this anion behaves in a manner resembling a spinning top.

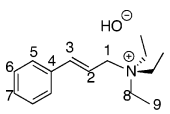
No extinction correction was deemed necessary. Upon convergence the final Fourier difference map showed no significant peaks. The contribution of the hydrogen atoms in their calculated positions was included in the refinement using a riding model ($B(H) = a[B(C_{bonded})]$ (Å^2), where $a = 1.5$ for the hydrogen atoms of the methyl groups and $a = 1.2$ for the others). The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[31] The standard deviations on intensities were calculated in terms of statistics alone. All calculations were carried out by using the PC version of the programs WINGX,[32] SHELX-97,[30] and ORTEP.[33]

Catalytic Experiments. In a typical experiment, a 0.07 mmol sample of allylic carbonate **9** or **10** was added to a mixture consisting of acetonitrile (0.5 mL) and the Ru catalyst (0.002 mmol, 3% mol) in an oven-dried 5 mm NMR tube. The amine derivative (0.21 mmol) was added, and the mixture was monitored by ^{1}H NMR spectroscopy at room temperature. Modifications to these experimental conditions are reported in the tables.

[RuCp(O$_2$C{OBu^t})(η^3-phenylallyl)]PF$_6$ (7b). [RuCp(CH$_3$CN)$_3$]PF$_6$ (100 mg, 0.230 mmol) and branched phenyl *tert*-butyl carbonate (57.0 mg, 0.242 mmol) were stirred in acetone (2 mL) for 15 min at room temperature. The solution volume was reduced under vacuum, and Et$_2$O was added, precipitating an orange-brown powder. The solid was washed with diethyl ether (Et$_2$O) and dried under vacuum to yield 114 mg (91%) of crude product. Crystals suitable for X-ray study were obtained by layering pentane in a CH_2Cl_2 solution of the isolated complex. NMR (Me$_2$CO-d_6, 299 K): ^{1}H, δ 1.46 (9H), 4.80 (1H, $J = 11.0$ Hz), 4.81 (1H, $J = 6.5$ Hz), 5.95 (1H, $J = 11.3$, 6.5 Hz), 6.32 (5H), 6.45 (1H, $J = 11.3$ Hz), 7.43 (2H, $J = 7.7$, 7.3 Hz), 7.62 (1H, $J = 7.7$), 7.77 (2H, $J = 7.3$); ^{13}C, δ 27.9 (CH$_3$), 62.3 (=CH$_2$), 95.8 (C), 97.6 (CH), 99.9 (CH), 129.4 (HCAr), 131.2 (HCAr), 131.3 (HCAr), 134.5 (C$_{ipso}$), 164.1 (CO$_3$). Anal. Calcd for $C_{19}H_{23}O_3F_6PRu$: C, 41.84; H, 4.25; Found: C, 40.80; H, 4.20. ESI MS: *m*/*z* 401.1 (M$^+$), 301.1 (M$^+$ − OC(OBu^t)O + H$_2$O), 283.1 (M$^+$ − OC(OBu^t)O).

[RuCp*(O$_2$C{OBu^t})(η^3-*n*-propylallyl)]PF$_6$ (13). [RuCp*(CH$_3$CN)$_3$]PF$_6$ (50 mg, 0.099 mmol) and branched *n*-propyl *tert*-butyl carbonate (19.8 mg, 0.099 mmol) were stirred in acetone (1.5 mL) for 30 min at room temperature. The solution volume was reduced under vacuum, and Et$_2$O was added, precipitating a yellow-brown powder. The solid was washed with Et$_2$O and dried under vacuum to yield 54.7 mg (95%) of crude product. NMR (DMF-d_7, 299 K): ^{1}H, δ 1.69 (9H), 1.71−2.02 (4H), 1.93 (15H), 3.48 (1H, $J = 10.0$ Hz), 4.26 (1H, $J = 10.0$, 10.0, 3.5 Hz), 4.66 (1H, $J = 6.5$ Hz), 5.54 (1H, $J = 10.0$, 10.0, 6.5 Hz), 7; ^{13}C, δ 8.8 (CH$_3$), 13.93 (CH$_3$), 23.3 (CH$_2$), 28.2 (CH$_3$), 33.6 (CH$_2$), 67.4 (=CH$_2$), 86.2 (C), 92.4 (=CH), 106.1 (=CH), 107.4 (C), 164.5 (CO$_3$). Anal. Calcd for $C_{21}H_{35}O_3F_6PRu$: C, 43.37; H, 6.07. Found: C, 42.63; H, 5.76. ESI MS: *m*/*z* 437.1 (M$^+$), 319.2 (M$^+$ − OC(OBu^t)O).

***N*-Triethyl-3-phenylprop-2-ene Ammonium Salt (14).** NMR



(CD$_3$CN-d_7, 299 K, 400.13 MHz): ^{1}H, δ 1.32 (3H, $J = 7.1$, $^3J_{NH} = 1.7$, H-9), 3.28 (2H, $J = 7.2$ Hz, H-8), 3.96 (2H, $J = 7.6$ Hz, H-1), 6.31 (1H, $J = 15.7$, 7.6 Hz, H-2), 7.00 (1H, $J = 15.7$ Hz, H-3), 7.32−7.43 (3H, H-5, 6), 7.59 (2H, $J = 6.6$, 1.1 Hz, H-5); ^{13}C, δ 7.3 (CH$_3$, C-9), 53.0 (CH$_2$, $^1J_{NC} = 2.9$ Hz, C-8), 59.4 (CH$_2$, $^1J_{NC} = 2.8$ Hz, C-1), 115.4 (HC=, C-2), 142.0 (HC=, C-3), 127.6 (HCAr, C-5), 129.2 (CAr, C-6), 129.1 (CAr, C-7), 153.7 (C$_{ipso}$, C-4). We are assuming hydroxide is the anion, although this has not been proven.

[RuCp*{η^6-(PhCH=CHOCO$_2$Bu^t)}]PF$_6$ (15a). [Cp*Ru(CH$_3$CN)$_3$]PF$_6$ (100 mg, 0.198 mmol) was added to a stirred solution of *tert*-butyl cinnamyl carbonate (140 mg, 0.595 mmol, 3 equiv) in 2 mL of acetone, and the brown solution was stirred at room temperature for 1 h. The solvent was removed under vacuum, and the product was precipitated twice from acetone/pentane and washed with Et$_2$O. Crystallization from acetone/Et$_2$O (diffusion) afforded a yellow-brown crystalline powder. Yield: 115 mg (94%). NMR (DMF-d_7, 299 K): ^{1}H, δ 1.51 (9H), 1.98 (15H), 4.85 (2H, $J = 5.7$, 1.6 Hz), 6.11 (1ArH, $J = 5.7$, 1.5 Hz), 6.16 (1ArH, $J = 6.0$, 5.7 Hz), 6.34 (1ArH, $J = 6.0$ Hz), 6.49 (1H, $J = 16.0$, 1.5 Hz), 6.71 (1H, $J = 16.0$, 5.7 Hz); ^{13}C, δ 10.0 (CH$_3$), 27.5 (CH$_3$), 66.6 (CH$_2$), 82.3 (C), 85.8 (HCAr), 88.2 (HCAr), 88.3 (HCAr), 96.8 (C$_{ipso}$), 97.4 (C), 127.4 (HC=) 131.4 (HC=), 153.7 (CO$_3$). Anal. Calcd for $C_{24}H_{33}O_3RuPF_6$: C, 46.83; H, 5.40. Found: C, 46.75; H, 5.57. MS (ESI): *m*/*z* 471.2 (M$^+$), 401, 371.2 (M$^+$ − OBu^t), 371.2 (M$^+$ − CO$_2$Bu^t), 355.3 (M$^+$ − OCO$_2$Bu^t), 315.3 (M$^+$ − C$_3$H$_4$OCO$_2$Bu^t).

[RuCp*{η^6-(*p*-OMe-C$_6$H$_4$CH=CHOCO$_2$Bu^t)}]PF$_6$ (15b). [Cp*Ru(CH$_3$CN)$_3$]PF$_6$ (100 mg, 0.198 mmol) was added to a stirred solution of *tert*-butyl para-methoxycinnamyl carbonate (157 mg, 0.595 mmol, 3 equiv) in 2 mL of acetone, and the brown solution was stirred at room temperature for 1 h. The solvent was removed under vacuum, and the product was precipitated twice from acetone/pentane and washed with Et$_2$O. Crystallization from acetone/Et$_2$O (diffusion) afforded a yellow-brown crystalline powder. Yield: 122 mg (95%). NMR (DMF-d_7, 299 K): ^{1}H, δ 1.51 (9H), 1.95 (15H), 3.92 (3H), 4.83 (2H, $J = 5.7$, 1.5 Hz), 6.22 (1ArH, $J = 6.7$ Hz), 6.29 (1ArH, $J = 6.7$ Hz), 6.46 (1H, $J = 15.7$, 1.5 Hz), 6.67 (1H, $J = 15.7$, 5.7 Hz); ^{13}C, δ 9.9 (CH$_3$), 27.5 (CH$_3$), 57.2 (OMe), 66.6 (CH$_2$), 76.5 (HCAr), 82.3 (C), 84.7 (HCAr), 95.2 (C$_{ipso}$), 96.1 (C), 126.8 (HC=), 131.0 (HC=), 153.7 (CO$_3$). Anal. Calcd for $C_{25}H_{35}O_4RuPF_6$: C, 46.51; H, 5.46. Found: C, 46.30; H, 5.47. MS (ESI): *m*/*z* 501.2 (M$^+$), 442.2 (M$^+$ − Bu^t), 385.2 (M$^+$ − OCO$_2$Bu^t), 315.3 (M$^+$ − C$_3$H$_4$OCO$_2$Bu^t − MeO).

[RuCp{η^6-(PhCH=CHOCO$_2$Bu^t)}]PF$_6$ (16a). *tert*-Butyl cinnamyl carbonate (135 mg, 0.57 mmol, ca. 5 equiv) was added to a stirred solution of [CpRu(CH$_3$CN)$_3$]PF$_6$ (50 mg, 0.115 mmol) in 2 mL of acetone, and the brown solution was stirred at room temperature for 2 h. The solvent was removed under vacuum, affording a brownish oil, which was precipitated from CH_2Cl_2/hexane at 4 °C and washed with Et$_2$O. Yield: 56 mg (89%). NMR (CD$_3$CN, 299 K): ^{1}H, δ 1.50 (9H), 4.69 (2H, $J = 5.0$, 1.2 Hz), 5.31 (5H, Cp), 6.10 (1ArH, $J = 5.8$, 1.1 Hz), 6.17 (2ArH, $J = 5.8.7$ Hz), 6.33 (2ArH, $J = 5.7$ Hz), 6.43 (1H, $J = 15.9$ Hz), 6.51 (1H, $J = 15.9$, 4.9 Hz); ^{13}C, δ 27.3 (CH$_3$), 66.2 (CH$_2$), 81.2 (C), 81.4 (CH), 84.4 (HCAr), 85.9 (HCAr), 86.1 (HCAr), 99.3 (C$_{ipso}$), 127.3 (HC=), 131.6 (HC=), 153.5 (CO$_3$). Anal. Calcd for $C_{19}H_{23}O_3RuPF_6$: C, 41.84; H, 4.25. Found: C, 41.95; H, 4.23. MS (ESI): *m*/*z* 401.1 (M$^+$), 345.0 (M$^+$ − Bu^t), 301.0 (M$^+$ − CO$_2$Bu^t).

[RuCp{η^6-(*p*-OMe-C$_6$H$_4$CH=CHOCO$_2$Bu^t)}]PF$_6$ (16b). *tert*-Butyl para-methoxycinnamyl carbonate (91 mg, 0.35 mmol, ca. 5 equiv) was added to a stirred solution of [CpRu(CH$_3$CN)$_3$]PF$_6$ (30 mg, 0.069 mmol) in 1.5 mL of acetone, and the brown solution was stirred at room temperature for 2 h. The solvent was removed under vacuum, affording a deep brown oil, which was precipitated twice from CH_2Cl_2/hexane at 4 °C and washed with Et$_2$O. Yield: 35 mg (87%). NMR (CD$_3$CN, 299 K): ^{1}H, δ 1.49 (s, 9H), 3.76 (s, 3H), 4.66 (d, 2H, $J = 4.8$, 0.9 Hz), 5.29 (s, 5H, Cp), 6.20 (2ArH, $J = 6.9$ Hz), 6.26 (2ArH, $J = 6.9$ Hz), 6.37 (1H, $J = 16.1$ Hz), 6.43 (1H, $J = 16.1$, 4.7 Hz); ^{13}C, δ 26.9 (CH$_3$), 57.1 (OCH$_3$), 65.8 (CH$_2$), 74.0 (HCAr), 80.2 (C), 80.6 (CH), 82.2 (HCAr), 96.2 (C$_{ipso}$), 126.4 (HC=), 130.7 (HC=), 134.4 (C$_{ipso}$), 153.1 (CO$_3$). Anal. Calcd

(31) *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic: Dordrecht, The Netherlands. 1992; Vol. C.
(32) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
(33) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

for $C_{20}H_{25}O_4RuPF_6$: C, 41.74; H, 4.38. Found: C, 41.97; H, 4.41. MS (ESI): *m*/*z* 431.0 (M^+), 375.0 ($M^+ - Bu^t$), 331.1 ($M^+ - CO_2Bu^t$).

[RuCp*(η^6-anisidine)]PF_6 (17a). $RuCp^*(CH_3CN)_3]PF_6$ (50 mg, 0.099 mmol) and anisidine (12.2 mg, 0.099 mmol) were stirred in acetone (1.5 mL) for 20 min at room temperature. The solution volume was reduced under vacuum, and Et_2O was added, precipitating a purple powder. The solid was washed with Et_2O and dried under vacuum to yield 46 mg (92%) of crude product. NMR (CD_3CN, 299 K): ^{1}H, δ 1.91 (15H), 3.68 (3H), 4.31 (2H), 5.22 (2H, J = 6.5 Hz), 5.57 (2H, J = 6.5 Hz); ^{13}C, δ 9.7 (CH_3), 56.8 (OCH_3), 71.7 (HCAr), 73.9 (HCAr), 94.6 (C), 120.4 (C_{ipso}), 129.0 (C_{ipso}). Anal. Calcd for $C_{17}H_{24}NOF_6PRu$: C, 40.48; H, 4.80; N, 2.78. Found: C, 41.11; H, 4.88; N, 3.10. ESI MS: *m*/*z* 360.2 (M^+).

[RuCp*(η^6-*p*-toluidine)]PF_6 (17b). $[RuCp^*(CH_3CN)_3]PF_6$ (45 mg, 0.079 mmol) and *p*-toluidine (8.6 mg, 0.08 mmol) were stirred in acetone (1.5 mL) for 40 min at room temperature. The solution volume was reduced under vacuum, and Et_2O was added, precipitating a pale purple powder. The solid was washed with Et_2O and dried under vacuum to yield 38 mg (98%) of crude product. NMR (CD_3CN-d_7, 299 K, 500.23 MHz): ^{1}H, δ 1.99 (15H), 2.18 (3H), 4.51 (2H), 5.36 (2H, J = 6.0 Hz), 5.56 (2H, J = 6.0 Hz); ^{13}C, δ 9.5 (CH_3), 17.2 (CH_3), 73.4 (HCAr), 86.7 (HCAr), 94.3 (C), 95.5 (C_{ipso}), 122.0 (C_{ipso}). Anal. Calcd for $C_{17}H_{24}NF_6PRu$: C, 41.81; H, 4.95; N, 2.87. Found: C, 41.96; H, 5.00; N, 2.96. ESI MS: *m*/*z* 344.2 (M^+).

[RuCp*(η^6-*p*-fluoroaniline)]PF_6 (17c). $[RuCp^*(CH_3CN)_3]PF_6$ (45 mg, 0.079 mmol) and *p*-fluoroaniline (7.7 μl, 0.08 mmol) were stirred in acetone (1.5 mL) for 60 min at room temperature. The solution volume was reduced under vacuum, and Et_2O was added, precipitating a pale purple powder. The solid was washed with Et_2O and dried under vacuum to yield 35 mg (80%) of crude product. NMR (CD_3CN-d_7, 299 K, 500.23 MHz): ^{1}H, δ 1.94 (15H), 4.53 (2H), 5.32 (2H, J = 6.5, J_{FH} 1.5 Hz), 5.88 (2H, J = 6.5, J_{FH} 3.0 Hz); ^{13}C, δ 9.6 (CH_3), 71.5 (HCAr, J_{CF} = 6.7 Hz), 76.7 (HCAr, J_{CF} = 23.1 Hz), 96.0 (C), 122.1 (C_{ipso}), 132.4 (C_{ipso}, J_{CF} = 267.3 Hz). Anal. Calcd for $C_{16}H_{21}NF_7PRu$: C, 39.03; H, 4.30; N, 2.84. Found: C, 39.20; H, 4.30; N, 2.96. ESI MS: *m*/*z* 348.1 (M^+).

[RuCp(η^6-anisidine)]PF_6 (18a). $[RuCp(CH_3CN)_3]PF_6$ (40 mg, 0.092 mmol) and *p*-methoxyaniline (15 mg, 0.122 mmol) were stirred in acetone (1.5 mL) for 30 min at room temperature. The solvent was concentrated under vacuum, and the product was precipitated with Et_2O. The purple solid was washed with Et_2O to yield 33 mg (82%) of product. NMR (CD_3CN, 299 K): ^{1}H, δ 3.66 (s, 3H), 4.49 (s, 2H, NH_2), 5.21 (s, 5H, Cp), 5.71 (2ArH), 5.92 (2ArH); ^{13}C, δ 57.0 (OCH_3), 68.3 (HCAr), 71.9 (HCAr), 79.3 (CH), 122.5 (C_{ipso}), 130.2 (C_{ipso}). Anal. Calcd for $C_{12}H_{14}NOF_6PRu$: C, 33.19; H, 3.25; N, 3.23; Found: C, 34.34; H, 3.40; N, 3.40. ESI MS: *m*/*z* 290.1 (M^+).

[RuCp(η^6-*p*-toluidine)]PF_6 (18b). $[RuCp(CH_3CN)_3]PF_6$ (30 mg, 0.069 mmol) and *p*-toluidine (11 mg, 0.103 mmol) were stirred in acetone (1.5 mL) for 30 min at room temperature. The solvent was concentrated under vacuum, and the product was precipitated with Et_2O. The light purple solid was washed with Et_2O to yield 21 mg (73%) of product. NMR (CD_3CN, 299 K): ^{1}H, δ 2.18 (s, 3H), 4.53 (s, 2H, NH_2), 5.15 (s, 5H, Cp), 5.75 (2ArH), 5.87 (2ArH); ^{13}C, δ 18.9 (CH_3), 70.1 (HCAr), 79.5 (CH), 84.7 (HCAr), 96.6 (C_{ipso}), 124.2 (C_{ipso}). Anal. Calcd for $C_{12}H_{14}NF_6PRu$: C, 34.46; H, 3.37; N, 3.35. Found: C, 35.67; H, 3.78; N, 3.45. ESI MS: *m*/*z* 274.0 (M^+).

[RuCp(η^6-*p*-chloroaniline)]PF_6 (18c). $[RuCp(CH_3CN)_3]PF_6$ (40 mg, 0.092 mmol) and *p*-chloroaniline (46 mg, 0.361 mmol) were stirred in acetone (1.5 mL) for 30 min at room temperature. The solvent was concentrated under vacuum, and the product was precipitated with Et_2O. The purple solid was washed with Et_2O to yield 20 mg (50%) of product. NMR (CD_3CN, 299 K): ^{1}H, δ 4.78 (s, 2H, NH_2), 5.28 (s, 5H, Cp), 5.85 (2ArH), 6.28 (2ArH); ^{13}C, δ 69.7 (HCAr), 81.3 (CH), 85.1 (HCAr), 121.2 (C_{ipso}), 125.4 (C_{ipso}). Anal. Calcd for $C_{11}H_{11}NF_6PClRu$; C, 30.12; H, 3.53; N, 3.19. Found: C, 31.47; H, 2.81; N, 3.47. ESI MS: *m*/*z* 294.0 (M^+).

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Supporting Information Available: A CIF file giving crystallographic data for compound **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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