Catalytic Allylic Alkylation and Allylic Phenolation Reactions with Ruthenium Complexes. Solid-State Structures of a Model Catalytic DMF Intermediate, [Ru(Cp*)(Cl)(η^3-C_3H_5)(DMF)](PF_6), and a New Tetranuclear Salt, [Ru(Cp){Ru(Cp)(η^6-*p*-$CH_3C_6H_4CN$)}$_3$](PF_6)$_4$

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Results from Ru-catalyzed (i) allylic alkylation reactions for linear and branched para-substituted aryl carbonates, *p*-$R^1C_6H_4CH{=}CHCH_2OCO_2Bu^t$ and *p*-$R^1C_6H_4CH(OCO_2Bu^t)$-$CH{=}CH_2$, with dimethyl malonate and (ii) allylic phenolation reactions using $C_6H_5CH(OCO_2Bu^t)CH{=}CH_2$ and phenol compounds are presented. The possible role of the π-arene complexes [Ru(Cp*)(η^6-*p*-$XC_6H_4CH{=}CHCH_2OCO_2Bu^t$)]-$PF_6$ is discussed. Solid-state structures for [Ru(Cp*)(Cl)(η^3-C_3H_5)(DMF)](PF_6) (**12**) and a new tetranuclear salt, [Ru(Cp){Ru(Cp)(η^6-*p*-$CH_3C_6H_4CN$)}$_3$](PF_6)$_4$, based on toluinitrile, are presented. Analysis of the solid-state data for the model salt **12** provides a partial understanding with respect to how several factors, e.g., the choice of solvent and the nature of the reagents themselves, might affect the regioselectivity of these reactions.

Introduction

The allylic alkylation reaction can be catalyzed by an increasing number of transition-metal complexes and represents a facile method of forming new C−C bonds.[1] The literature suggests that the most commonly used catalyst for this reaction still involves palladium.[2−7] However, interest in the applications of Ru(II) complexes is on the rise, on the basis of the observed regioselectivity[3] for unsymmetrical allyl substrates. Specifically, for the allyl substrate $PhCH{=}CHCH_2X$, the preferred site of attack is at the phenyl-substituted allyl carbon, thus affording a branched, rather than a linear, product.

Trost et al.[8] have reported that [Ru(Cp* or Cp)($CH_3CN)_3$](PF_6) (**1a**,**b**) are excellent catalysts for this reaction and, specifically, that with the Cp* complex, **1a**, reaction of the allyl substrate $PhCH{=}CHCH_2X$ (X = carbonate leaving group (**2a**), chloride (**2b**)) with a malonate anion nucleophile, Nu^-, occurs preferentially at the more substituted position (see eq 1).

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

Moreover, Trost and co-workers have employed this catalyst in a variety of useful C−C bond making reactions.[9]

Parallel to these studies, a number of research groups have employed structurally modified Ru(II) cationic complexes as allylic alkylation catalysts with excellent results. Bruneau and co-workers[10−12] have reported the use of a variety of chelating nitrogen complexes, including oxazoline derivatives, for this

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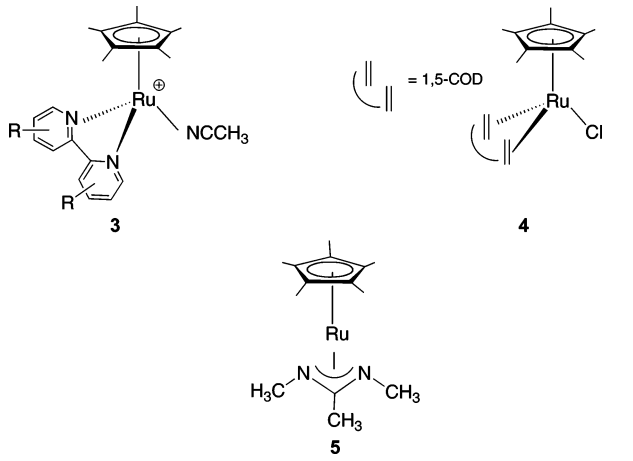
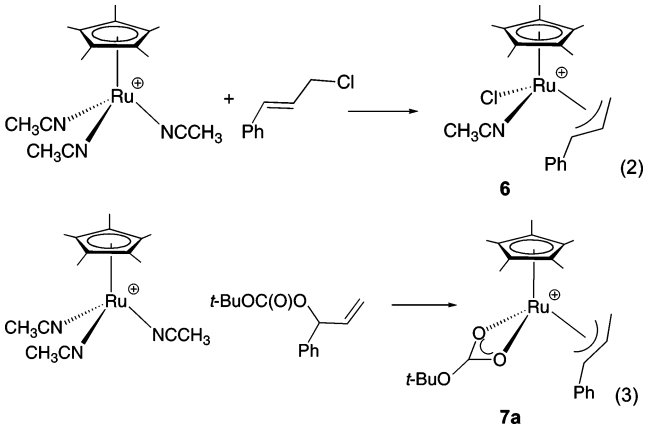
reaction, e.g. **3**, whereas Kondo and co-workers[13] have had success with 1,5-COD and amidinate complexes such as **4** and **5**, respectively.



We have recently reported that the source of the observed branched-to-linear regioselectivity has an electronic origin.[14,15] These conclusions were based on a series of X-ray and ^{13}C NMR measurements, together with DFT calculations on the isolated Ru(IV) allyl salts [Ru(Cp*)Cl(CH_3CN)(η^3-PhCHCHCH$_2$)](PF_6) (**6**) and the novel Ru(IV) carbonate-containing cation [Ru(Cp*)-{OC(OBu^t)O}(η^3-PhCHCHCH$_2$)](PF_6) (**7a**). The salts **6** and **7a** were prepared by oxidative addition reactions involving allyl precursors (as was the Cp analogue **7b**[16]) (see eqs 2 and 3).



In an extension of our allylic alkylation study, we tested **7a** in allylic amination chemistry.[16] Interestingly, using anilines as nucleophile, we observed the best branched-to-linear (b/l) ratios (usually > 90:10).[16] For some aliphatic amines, e.g., *tert*-butylamine, a disappointing b/l ratio of 60:40 was found. We report here allylic alkylation studies in which we consider the relative reaction rates for several linear and branched para-substituted aryl carbonates, *p*-R^{1}C$_6$H$_4$CH=CHCH$_2$OCO$_2$Bu^t and *p*-R^{1}C$_6$H$_4$CH(OCO$_2$Bu^t)-CH=CH$_2$, respectively, and extend the chemistry of catalyst **7a** to O−C bond making with phenols as nucleophiles. We also discuss possible roles for the cationic arene complexes [Ru(Cp*)(η^6-*p*-R^{1}C$_6$H$_4$CH=CHCH$_2$OCO$_2$Bu^t)]

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Table 1. Allylic Alkylation Data for Various Allyl Carbonates using [Ru(Cp)(CH_3CN)$_3$](PF_6)[a]

	R^1	*t*, min[b]	b/l	conversn, %
	tert-Butyl Linear Carbonate			
1	H[c]	30	33/67	97
2	*p*-Me$_2$N	17	85/15	95
3	*p*-MeO	45	55/45	93
4	*p*-Cl	5	30/70	94
5	*p*-NO$_2$	3	22/78	95
	Ethyl Linear Carbonate			
6	H	23	40/60	98
	tert-Butyl Branched Carbonate			
7	H	25	50 /50	96
8	*p*-MeO	17	71/29	97
9	*p*-NO$_2$	11	35/65	96
	Ethyl Branched Carbonate			
10	H	15	63/37	96

[a] Conditions: 0.21 mmol of the carbonate substrate **2a**, 0.65 mmol of dimethyl malonate, 0.65 mmol of NaH, 0.019 mmol of the catalyst [RuCp(CH_3CN)$_3$](PF_6) (**1b**; 9 mol %), 1.5 mL of DMF, room temperature. [b] The time for the conversion and the branched/linear ratio were determined by ^1H NMR. [c] With 3% catalyst the reaction requires 120 min for complete conversion.

Table 2. Allylic Alkylation Data for Various Allyl Carbonates using [Ru(Cp*)(CH_3CN)$_3$](PF_6)[a]

Catalysis at Room Temperature				
	R^1	*t*, min	b/l	conversn, %
	Cinnamyl Chloride			
1		3	90/10	98
	tert-Butyl Linear Carbonate			
2	H	40	90/10	98
3	*p*-Me$_2$N	40	99/1	94
4	*p*-MeO	30	95/5	97
5	*p*-Cl	15	90/10	96
6	*p*-NO$_2$	10	67/33	98
	Ethyl Linear Carbonate			
7		8	94/6	98
	tert-Butyl Branched Carbonate			
8	H	25	90 /10	96
9	*p*-MeO	5	97/3	96
10	*p*-NO$_2$	3	96/4	90
	Ethyl Branched Carbonate			
11		2	94/6	97

Catalysis at −40 °C			
	substrate	b/l	conversn, %
12	cinnamyl chloride	110/1	98
13	*tert*-Bu-lin. carbonate	98/2	90
14	*tert*-Bu-br carbonate	98/2	97

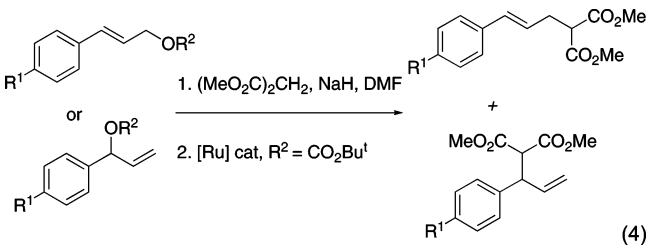
[a] Conditions: 0.21 mmol of the carbonate substrate **2a**,**b**, 0.65 mmol of dimethyl malonate, 0.65 mmol of NaH, 0.006 mmol of the catalyst [RuCp*(CH_3CN)$_3$](PF_6) (**1a**; 3 mol %), 1.5 mL of DMF. The time of conversion and the branched/linear ratio were determined by ^1H NMR.

PF_6 in the catalysis and probe the generality of the observed regioselectivity, as a function of substrate. We believe these studies to be relevant, as there is little known with respect to understanding how the various factors, e.g., type of carbonate, substituents on the aryl, etc., affect the reaction. It is always possible that a chosen model allyl is not representative of the majority of allyl substrates.

Results and Discussion

Alkylation Reactions. Tables 1 and 2 give results using several linear and branched aryl-substituted carbonates, with various R^1 substituents, using [Ru(Cp* or Cp)(CH_3CN)$_3$](PF_6),

1a and **1b** for the classical allylic alkylation reaction with dimethyl malonate (see eq 4).



Using a linear *tert*-butyl carbonate substrate with the Cp catalyst (Table 1, entries 1−5) results in slightly faster reactions when the aryl ring is substituted with an electron-withdrawing group; however, the product b/l ratio is much worse. For the branched *tert*-butyl carbonate substrates (Table 1, entries 7−9) there is not much difference in the rate of the reaction and once again the electron-withdrawing groups afford poor b/l ratios. The use of an ethyl (instead of a *tert*-butyl) carbonate as leaving group offers little advantage. For this set of reactions, we conclude that the substrate does play a role in deciding both the reaction rate and the b/l ratio.

The results from an analogous set of experiments employing $[Ru(Cp^*)(CH_3CN)_3](PF_6)$, but using less catalyst, 3 mol % instead of 9 mol %, are given in Table 2. These results are somewhat different: (a) the ethyl carbonates (entries 7 and 11)

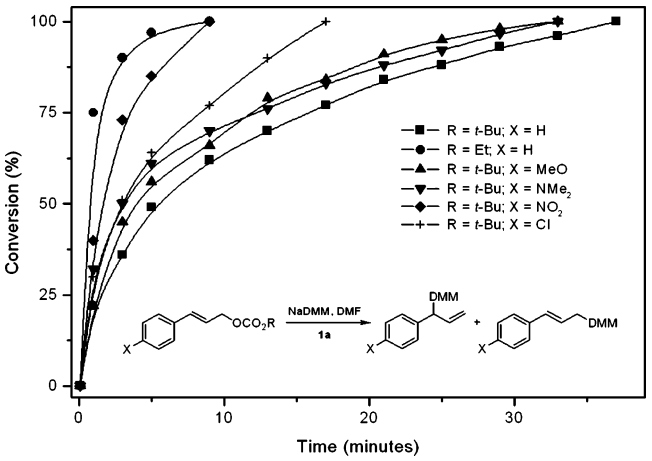


Figure 1. Conversion of the linear carbonate substrate to the organic product vs time using the Ru−Cp* catalyst (3 mol % catalyst).

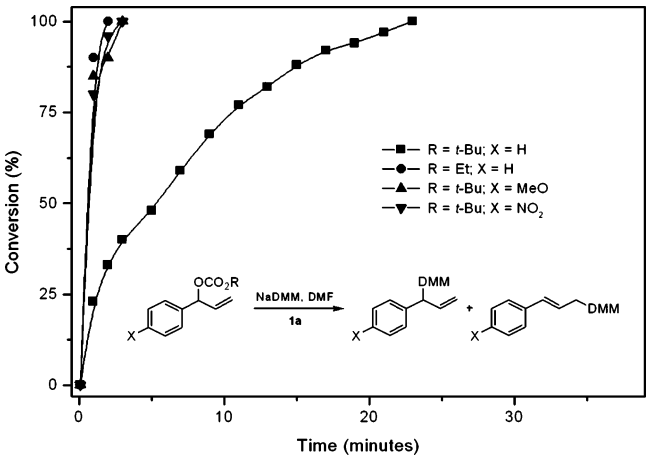


Figure 2. Conversion to product vs time for the Cp* catalyst with branched substrate (3 mol % catalyst).

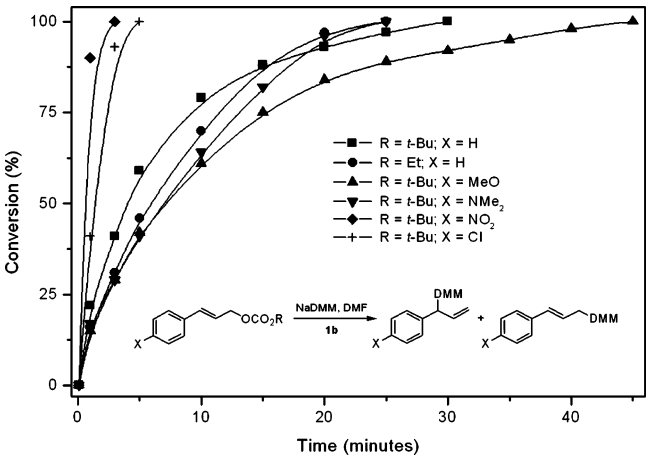
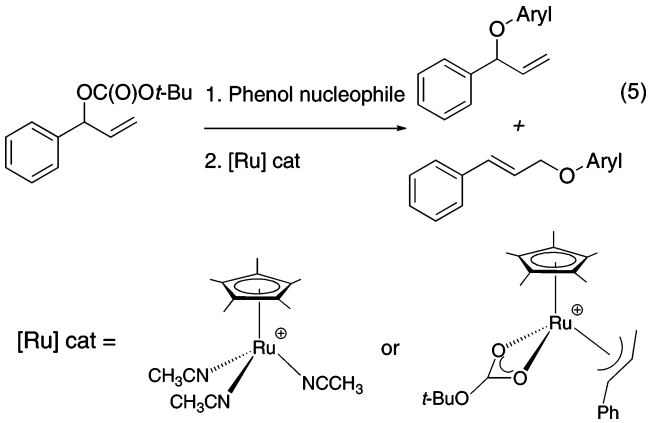


Figure 3. Conversion to product vs time for the Cp catalyst with linear substrate (9 mol % catalyst).

are quite fast, (b) the branched carbonates react more quickly than the analogous linear carbonate, (c) almost all of the b/l ratios are good to excellent, (d) the electron-withdrawing substituents tend to give somewhat faster reactions, and (e) for the linear carbonates, the electron donors afford the best b/l ratios. As reported by Trost, entries 12−14 show that excellent b/l ratios can be obtained by running the alkylation at relatively low temperature using the Cp* catalyst. Figures 1−4 show qualitative plots for the conversion of substrate vs time for the Cp and Cp* sets using linear and branched carbonate substrates. We conclude that **1a** is an excellent catalyst (much better than **1b**) and that the best b/l ratios are obtained at low temperature or with aryl ring donors such as NMe_2.

Phenolation Reactions using the Ru(IV) Catalyst 7a in CH_3CN Solution. Our results for the allylic alkylation[14,15] and amination[16] reactions using our Ru(IV) carbonate catalyst **7a** prompted us to extend our study to allyl ether formation using phenol compounds (see eq 5). The results, for seven different



phenol compounds, are given in Tables 3 and 4. We also include two results using **1a**.

From the data in Table 3, it is clear that both of the catalysts, **1a** and **7a**, afford excellent b/l ratios. The reactions are not quite as rapid as the analogous alkylation but nevertheless proceed to completion at ambient temperature in hours, rather than minutes. It is not necessary to add a base, as the decomposition of the carbonate leaving group provides an alkoxide. The sterically hindered *o*-phenols are somewhat slower than the para-substituted nucleophiles. Bruneau and co-workers[17,18] have also obtained excellent b/l ratios using a $Ru^{IV}(Cp^*)Br$ complex.

On the other hand, using the aliphatic alcohols menthol and 2-butanol *affords very slow reactions which do not readily go*

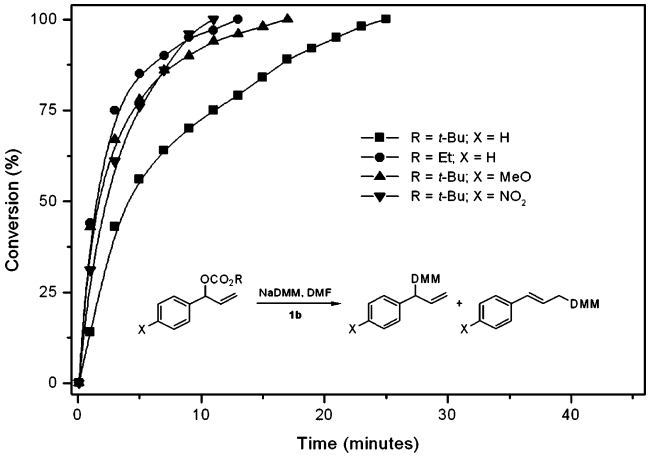


Figure 4. Conversion to product vs time for the Cp catalyst with branched substrate (9 mol % catalyst).

Table 3. Selected Ruthenium-Catalyzed Allylic Etherification Reactions using the Ru(IV) Carbonate Catalyst 7a and a Branched Carbonate Substrate, $C_6H_5CH(OCO_2Bu^t)CH{=}CH_2$[a]

	[Ru]	reagent	*t*	conversn, %	b/l[b]
1	**7a**	C_6H_5OH	124 min	100	99/1
2	**1a**	C_6H_5OH	50 min	100	99/1[d]
3	**7a**	*p*-F-C_6H_4OH	96 min	100	99/1
4	**7a**	*p*-MeO-C_6H_4OH	106 min	100	99/1
5	**7a**	*p*-Me-C_6H_4OH	155 min	100	99/1
6	**7a**	3,5-Me_2-C_6H_3OH	88 min	100	>99[c]
7	**7a**	2,6-Me_2-C_6H_3OH	244 min	100	94/6
8	**7a**	2,6-Bu^t_2-C_6H_3OH	830 min	100	86/14
9	**7a**	(−)-menthol	72 h	14	0/100
10	**7a**	(*S*)-2-butanol	72 h	16	0/100
11	**1a**	(*S*)-2-butanol	72 h	14	0/100

[a] Conditions: 0.07 mmol of the branched carbonate substrate, 0.21 mmol of the corresponding phenol derivative, 0.002 mmol of catalyst (3 mol %), 0.5 mL of acetonitrile, room temperature. [b] The branched/linear ratio was determined by ^{1}H NMR spectroscopy. [c] We do not find any of the linear isomer. [d] 2% of isomerized linear carbonate was also observed.

Table 4. Solvent Dependence of the Ruthenium-Catalyzed Allylic Phenolation Reaction using Catalyst 7a[a]

	base	nucleophile	solvent	*t*	conversn, %	b/l[b]
			Room Temperature			
1		C_6H_5OH	acetone	*d*		
2	K_2CO_3	C_6H_5OH	acetone	48 h	52	60/40
3[c]		C_6H_5OH	acetone	*d*		
4[c]	K_2CO_3	C_6H_5OH	acetone	48 h	49	81/19
5	K_2CO_3	C_6H_5OH	acetone/H_2O (4/1)	48 h	14	80/20
6		C_6H_5OH	DMF	*d*		
7	K_2CO_3	C_6H_5OH	DMF	48 h	49	60/40
8	K_2CO_3	C_6H_5OH	DMF/H_2O (4/1)	48 h	42	57/43
9		C_6H_5OH	THF	*d*		
10	K_2CO_3	C_6H_5OH	THF	*d*		
			333 K			
11	K_2CO_3	C_6H_5OH	acetone	ca. 8 h	100	56:44
12	K_2CO_3	C_6H_5OH	DMF	6.5 h	100	54:46

[a] Conditions: 0.07 mmol of the branched carbonate substrate $C_6H_5CH(OCO_2Bu)CH{=}CH_2$, 0.21 mmol of phenol, 0.002 mmol of catalyst (3 mol %), 0.5 mL of solvent. [b] The branched/linear ratio was determined by ^{1}H NMR spectroscopy. [c] The substrate was $PhCH{=}CHCH_2Cl$ (**2b**). [d] No conversion after 24 h.

to completion (even in the presence of K_2CO_3) and give exclusively linear product.

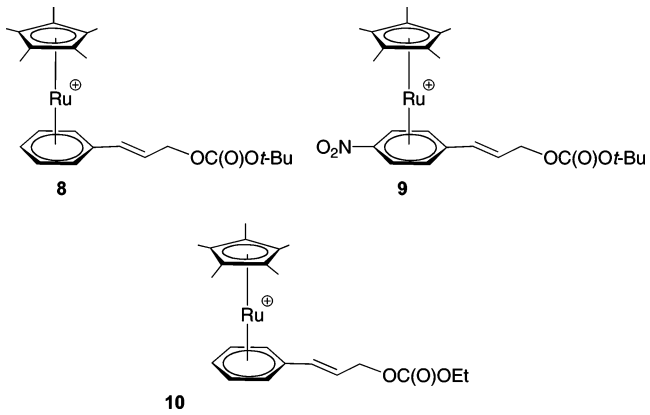
Changing the solvent in this phenolation reaction afforded much poorer results (see Table 4). Addition of base does help the reaction to some extent, as does increasing the temperature; however, clearly acetonitrile is the favored solvent.

Table 5. Allylic Alkylation Catalysis with Cp* Arene Cationic Complexes[a]

	cat.	substrate	*t*, min	b/l	conversn, %
1	**8**	*t*-Bu carbonate	600	90/10	70
2	**9**	*p*-NO_2 *t*-Bu carbonate	280	67/33	97
3	**10**	Et carbonate	250	94/6	97

[a] Conditions: 0.07 mmol of carbonate, 0.217 mmol of dimethyl malonate, 0.213 mmol of NaH, 0.002 mmol of catalyst (3% mol), 0.5 mL of DMF-d_7. The time elapsed for conversion and the branched/linear ratio were determined by ^{1}H NMR.

Arene Complexes. The data in Table 1, our observation that phenols are rather different substrates than, for example, 2-butanol, and the fact that one finds much more rapid reactions for the branched isomers $C_6H_5CH(OCO_2Bu^t)CH{=}CH_2$ relative to $C_6H_5CH{=}CHCH_2OCO_2Bu^t$ [15] prompted us to synthesize (see Experimental Section) and test several linear arene complexes for catalytic activity in the allylic alkylation. We have already shown that the branched isomers, as substrates, give rapid oxidative addition relative to the linear isomers.[14−16] Table 5 shows some results for the three independently prepared cationic complexes **8**−**10** as PF_6 salts. Once again the allylic alkylation



reaction chosen uses diethyl malonate as nucleophile and DMF as the solvent. In each case the substrate corresponded to the complexed arene: e.g., *p*-$NO_2C_6H_4CH{=}CHCH_2OCO_2Bu^t$ was the substrate in the reaction using **9**. In all three cases *the organic product is formed*, albeit relatively slowly.[19a] The ethyl carbonate **10** was the fastest of the three (by a factor of ca. 2−3 relative to **8**).

This result prompted us to determine the composition of the mixture resulting from dissolving the pure cationic arene complexes **8**, **10**, and **11** (the MeO group is a useful NMR probe) as PF_6 salts in DMF-d_7 solution. The ^{1}H NMR spectra reveal two species in all three cases. The major product is the unreacted cationic complex, and the minor component is assigned to the Ru(IV) allyl complex which is the product of the oxidative addition.[20] We assume that the Ru(IV) allyl complex is present as a carbonate complex.[19b] The observed ratios are 91:9, 77:23, and 93:7 for **8**, **10**, and **11**, respectively. It is noteworthy that the ethyl carbonate **10** affords 2−3 times

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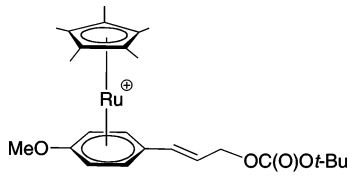
(18) Mbaye, M. D.; Renaud, J. L.; Demerseman, B.; Bruneau, C. *Chem. Commun.* **2004**, 1870−1871.

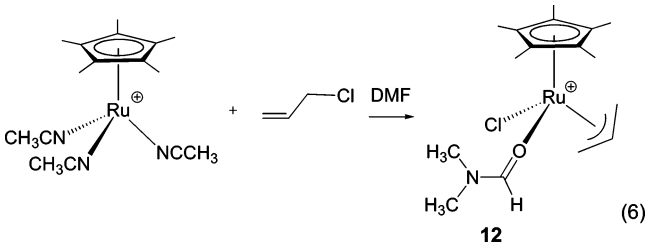
(19) (a) The cationic anisidine complex Ru(Cp*)(η^6-*p*-$CH_3OC_6H_4NH_2$) was inactive in the allylic amination reaction.[16] (b) We cannot exclude DMF as a possible alternative ligand. (c) In solution the two terminal ^{13}C allyl chemical shifts are almost identical.



11

the amount of Ru(IV) allyl complex relative to **8** and, interestingly, is also 2−3 times faster than **8** (see Table 5). We cannot say whether the arene dissociates before the oxidative addition, although this seems likely, but it is useful to know that, whatever the mechanism, formation of the linear arene cation can still lead to a catalytically active species. Consequently, we cannot dismiss the possibility that an η^6-arene complex might be involved in the catalytic cycle, perhaps if only to slow the reaction of the linear substrate.

Ru(IV) Structure 12. Since the catalytic alkylation reactions were carried out in DMF solution, and as the solvent seems to play a role (see Table 4), we have prepared a Ru(IV) allyl DMF complex, [Ru(Cp*)Cl(η^3-CH_2−CH−CH_2)(DMF)](PF_6) (**12**). as shown in eq 6. The model complex **12** would be somewhat



(6)

12

related to entry 1 in Table 2, where we use PhCH═$CHCH_2Cl$ as the substrate in DMF solution.

Crystals of **12** suitable for an X-ray diffraction study were obtained from dichloromethane−ether solution. Figure 5 shows a view of the cation, and selected bond distances and bond angles for this species are given in the caption to the figure.

The immediate coordination sphere of the ruthenium cation contains an oxygen-bound DMF molecule, a chloride donor, the η^3-CH_2CHCH_2 allyl ligand, and the π-bound Cp*. The allyl ligand adopts an endo configuration with respect to the Cp*, as found previously.[17,21,22] While the Ru−Cl separation of 240.1(3) pm and the Ru−O bond length of 212.8(6) pm are as expected, the three Ru−C(allyl) separations, Ru(1)−C(1) = 215.0(9) pm, Ru(1)−C(2) = 212(1) pm, and Ru(1)−C(3) = 222(1) pm, are worthy of note. Chart 1 shows a few comparison data. For the amidate complex of Kondo et al.,[22] one expects and finds ca. two equivalent Ru−C(terminal) bond lengths. For the asymmetric allyl of Gemel et al.,[21] the two terminal Ru−C distances are different, with the longest being found for the CH_2-Br-substituted allyl carbon: i.e., one expects a substituent effect. Interestingly, both the nitrile and DMF cationic complexes show very different Ru−C(terminal) separations, with those pseudo-trans to the halogens being the longest. Indeed, the terminal allyl carbon bond lengths can vary from ca. 215 to 228 pm purely as a function of the two remaining ligands. This suggests that, for a halogen-containing allyl substrate, which will afford

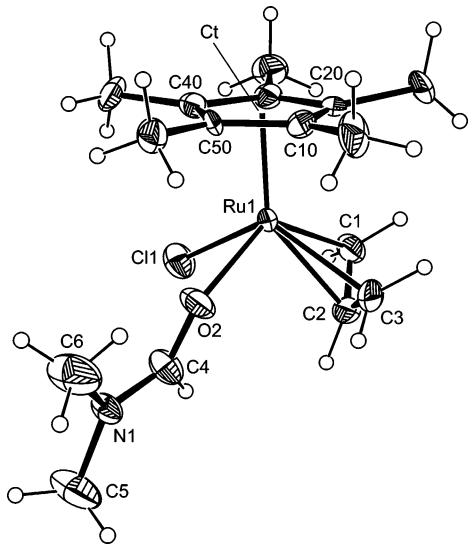
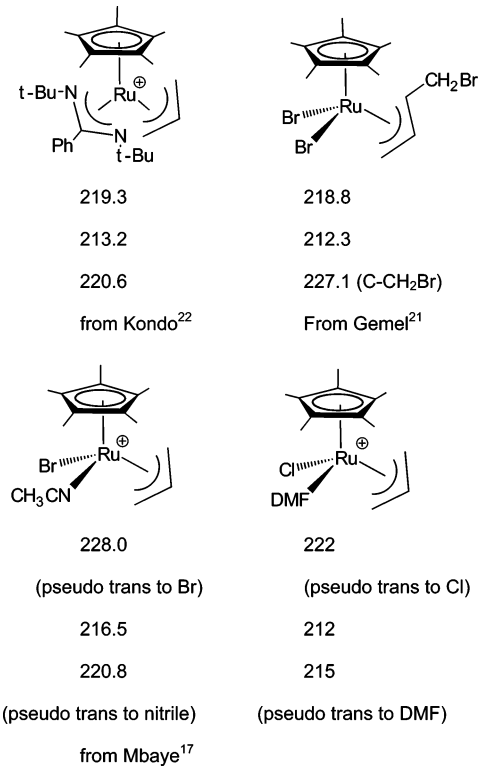


Figure 5. Structure of the cation [Ru(Cp*)Cl(η^3-CH_2CHCH_2)(DMF)]$^+$ in **12**. Thermal ellipsoids are drawn at the 30% probability level; the PF_6 anion is omitted for clarity. Bond lengths (pm) and angles (deg): Ru1−Cl1 = 240.1(3), Ru1−C1 = 215.0(9), Ru1−C2 = 212(1), Ru1−C3 = 222(1), Ru1−O2 = 212.8(6), Ru1−Ct = 187.6(9), Ru1−C10 = 226.3(9), Ru1−C20 = 218.3(8), Ru−C30 = 217.4(8), Ru1−C40 = 225.5(9), Ru1−C50 = 228.6(9), O1−C4 = 117(1), N1−C4 = 130(1), N1−C5 = 143(1), N1−C6 = 147(2); C1−C2−C3 = 117(1), O2−Ru1−Cl1 = 83.5(2), O2−C4−N1 = 129(1), C4−N1−C6 = 117.2(9), C5−N1−C6 = 116.8(9); ϕ = 73.0°. Ct denotes the centroid of the Cp* ligand; ϕ is the intersection of the planes described by C1, C2, and C3 and the atoms of the five-membered Cp* ring.

Chart 1. Comparison of Allyl Bond Length Data (pm) for Ru(IV) Allyl Cp* Cationic and Neutral Complexes[a]



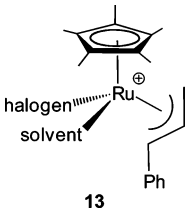
[a] The second distance in all of the examples arises from the central allyl carbon.

(20) Using the linear substrate *p*-$Me_2NC_6H_4CH$═$CH-CH_2CO_3Bu^t$, in DMF solution, together with the Ru(Cp)$(CH_3CN)_3$ cation, we find mostly the η^6 complex but no clear amount of the Ru(IV) allyl complex. However, with the *isolated* Ru(Cp*)(η^6-$Me_2NC_6H_4CH$═$CHCH_2CO_3Bu^t$) cation in DMF solution we estimate that about 90% η^6-arene complex exists together with ca. 10% Ru(IV) allyl complex.

(21) Gemel, C.; Kalt, D.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 427−433.

(22) Kondo, H.; Yamaguchi, Y.; Nagashima, H. *Chem. Commun.* **2000**, 1075−1076.

a presumed catalytic intermediate such as **13**, there may be at



13

least *two* additional important contributors to the distortion of the allyl ligand (apart from the structure of the allyl ligand itself): (i) the strength of the solvent as ligand (which may partially explain the observed solvent effects) and (ii) the relative positions of the halogen and the solvent with respect to the substituted terminal allyl carbon, i.e., the effect of geometric isomers. Extending this line of thought, if one of the reagents in an allylic amination reaction,[16] e.g. morpholine or triethylamine, is a stronger ligand than the solvent, then the exact electronic and steric nature of this donor could drastically change the bonding of the allyl and thus the observed regioselectivity. It is worth emphasizing that the errors associated with the two terminal allyl separations in the structure of **12**, Ru(1)−C(1) = 215.0(9) pm and Ru(1)−C(3) = 222(1) pm, are relatively large. Indeed, taking $\pm 3\sigma$ as the uncertainty in these bond lengths would lead to two values which might not be significantly different.[19c] Nevertheless, these (and the literature) data point to a parameter which might well prove important for the actual structures that arise during the catalysis.

A Novel Tetranuclear Complex, 14. We were curious as to the possibility of exchanging the acetonitrile, in **1a**, for another nitrile. Initial attempts using Bu^{t}CN suggest that this reaction proceeds, but not completely. An analogous nitrile exchange reaction using *p*-$CH_3C_6H_4CN$ gave, once again, a mixture of salts. However, in this case, recrystallization of the crude product from acetone/pentane solution gave a small quantity of crystals suitable for X-ray analysis. Surprisingly, this aryl nitrile leads to the formation of a novel tetranuclear species, [Ru(Cp){Ru(Cp)(η^6-*p*-$CH_3C_6H_4CN$)$_3$}$_3$](PF$_6$)$_4$ (**14**). This small aggregate contains three Ru(Cp)(η^6-*p*-$CH_3C_6H_4CN$) units which contain the nitrile as an η^6 π-bonded ligand to the Ru(Cp) fragment and then each of these functions as a σ-donor, via the nitrile lone pair, to the fourth Ru(Cp) moiety: i.e., both the electrons of the aromatic system and those from the nitrile lone pair are involved in bonding.

A view of the tetracation is given in Figure 6. Selected bond distances (pm) and bond angles (deg) are given in the caption to the figure. The Cp ring at Ru2 is disordered (see Experimental Section); nevertheless, the structure is clear. Although the tetracationic complex itself is somewhat novel, the individual bond lengths and bond angles fall within the known literature range. Specifically, the nitrile bond length, N1−C16 = 112.1(8) pm, is consistent with a triple bond and the various Ru−C separations are what one expects for Ru−Cp and Ru−arene complexes, respectively. The N−Ru−N angle about Ru2 is ca. 88°. We cannot provide an exact yield for this material; however, we estimate it to be on the order of ca. 20% on the basis of the ^{1}H NMR data from the crude product.

Comments and Conclusions. For the alkylation reaction, both the observed reaction rate and the regioselectivity were found to be a function of the carbonate substrate and the solvent, suggesting that this is not as simple a transformation as might be thought. There are indications that η^6-arene complexes form and possibly their relative stability will strongly affect the reaction rates. In any case, the X-ray data for **12** indicate that

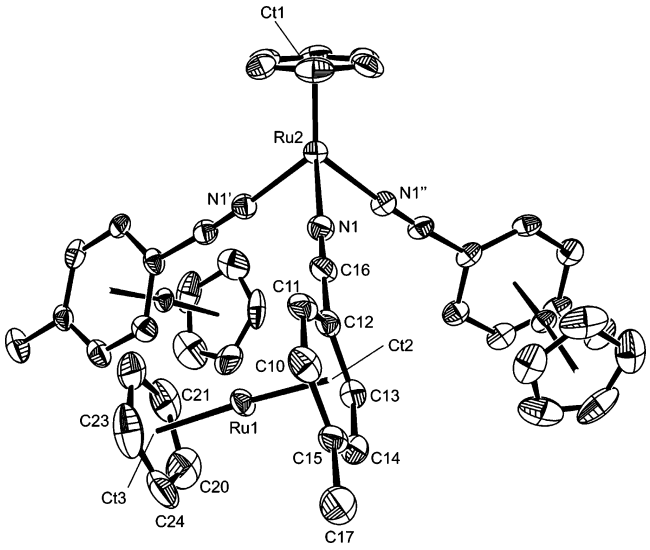
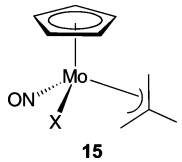


Figure 6. Structure of the tetracation [Ru(Cp){Ru(Cp)(η^6-*p*-$CH_3C_6H_4CN$)$_3$}$_3$]$^{4+}$ in **14**. Thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms and the PF_6 anions are omitted for clarity. The Cp ring of the central ruthenium unit (Ru2) is disordered over six sites (occupation factor of 0.833 33 for each position). Bond lengths (pm) and angles (deg): Ru1−C10 = 220.4(7), Ru1−C11 = 216.9(6), Ru1−C12 = 216.6(6), Ru1−C13 = 218.9(7), Ru1−C14 = 218.9(7), Ru1−C15 = 225.9(6), Ru1−Ct2 = 168.7(7), Ru1−C20 = 213.1(8), Ru1−C21 = 214.0(7), Ru1−C22 = 216.0(8), Ru1−C23 = 214.6(9), Ru1−C24 = 213.5(8), Ru1−Ct3 = 180.5(8), Ru2−N1 = 205.5(5), N1−C16 = 112.1(8); N1−Ru2−N1′ = 88.3(2), Ru2−N1−C16 = 176.7(5); ϕ = 71.3°. Ct is the centroid of the Cp* ligand; ϕ is the intersection of the planes described by the carbon atoms of the Cp ring at Ru2 and the atoms of the six-membered arene ring attached to Ru1. Equivalent atoms are generated by $-x + y + 1$, $-x + 1$, z and $-y + 1$, $x - y$, z.

there may be marked electronic effects on the bonding of the allyl ligand, due to the two remaining ligands in the Ru(IV) coordination sphere (see **13**).

Faller,[23] in his discussion of the selective reactivity of aldehydes with the isoelectronic Mo(II) allyl complexes **15**, notes that "The selectivity of the molybdenum system arises from the electronic asymmetry caused by the difference in the back-bonding between the nitrosyl and halide ligands...".



15

Admittedly, the difference between NO and X (a halogen) is more marked in **15** than the difference between the two ligands in our cations; nevertheless, the two different donors will also create an electronic asymmetry at ruthenium, as suggested by the X-ray data in Scheme 1, so that the principle is the same.

It would seem that for each reaction, be it an alkylation with dimethyl malonate, an amination using an aniline,[16] or a phenolation with a substituted phenol, one can find conditions to afford excellent b/l ratios; however, aliphatic nitrogen[16] and oxygen donors seem much more problematic. DMF as solvent is not always the best for every reaction, and one cannot be exactly certain as to where, and to what extent, the carbonate

(23) Faller, J. W.; Nguyen, J.; Ellis, T.; Mazzieri, M. R. *Organometallics* **1993**, *12*, 1434−1438.

ligands play a role. Clearly, although we now have reasonable protocols, which afford good b/l ratios for the organic products for several of these Ru-catalyzed reactions, the approach remains empirical.

Experimental Section

General Considerations. All reactions and manipulations were performed under a N_2 atmosphere using standard Schlenk techniques. Solvents were dried and distilled under 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.

All the phenol derivatives used for the catalytic runs were obtained from Merck, Sigma-Aldrich, or Fluka and were of reagent grade. Complexes **1a**,[24] **1b**,[25] **8**,[16] and **11**[16] have been synthesized as described in the literature.

X-ray Crystallographic Investigations and Crystal Data. Air-stable, orange crystals of **12** suitable for X-ray diffraction were obtained by layering diethyl ether in a CH_2Cl_2 solution of the isolated complex. Air-stable, brown crystals of **14** suitable for X-ray diffraction were obtained by layering pentane in an acetone solution of the crude isolated complex. To avoid quality degradation, the single crystals were mounted in perfluoropolyalkyl ether oil on top of a glass fiber and then brought into the cold nitrogen stream of a low-temperature device so that the oil solidified. Data collection for the X-ray structure determinations was performed on a Bruker SMART Apex diffractometer system with a CCD detector by using graphite-monochromated Mo Kα (0.710 73 Å) radiation and a low-temperature device. An empirical absorption correction using SADABS (version 2.03) was applied to all structures. All calculations were performed by using SHELXTL (version 6.12) and SHELXL-97. The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against F^2). All non-hydrogen atoms were refined anisotropically; carbon atom C23 in **14** was refined using the ISOR restraint. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Upon convergence, the final Fourier difference map of the X-ray structures of showed no significant peaks. However, for **12** some residual electron density was located close to the heavy atom ruthenium (~0.9 Å) even when an absorption correction was applied. The Cp ring of the central ruthenium unit in **14** is disordered. The midpoint of the disordered Cp is located on a 3-fold axis. To account for the Cp ring disorder over six sites, the positions of the carbon and hydrogen atoms were refined using an occupation factor of 0.833 33 for each position.

Relevant data concerning crystallographic data, data collection, and refinement details are summarized in Table 6. Crystallographic data (excluding structure factors) for the structures reported in this paper have also been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 294949 and 294950. 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).

Catalytic Experiments: Alkylation with 1a,b. (a) Schlenk-Scale Reactions. Dimethyl malonate (76 μL, 0.65 mmol) and NaH (26 mg, 0.64 mmol, of a 60% dispersion in mineral oil) were stirred in DMF (1.5 mL) for 30 min at ambient temperature, after which time the carbonate (0.21 mmol) and the catalyst (0.02 mmol, 3 mol %) were added. The resulting solution was stirred (see Table 2 for reaction times) and then diluted with ca. 10 mL of ether and water. After three extractions with ether, the combined organic extracts were washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by chromatography on silica (hexane/ethyl acetate 6/1). The branched/linear ratio was determined by ^{1}H NMR.

Table 6. Crystal Data and Data Collection and Structure Refinement Details for 12 and 14

	12	**14**
empirical formula	$C_{16}H_{27}ClF_6NOPRu$	$C_{44}H_{41}F_{24}N_3P_4Ru_4$
M_r	530.88	1595.96
cryst syst	orthorhombic	trigonal
space group[a]	$P2_12_12_1$ (No. 19)	$R3c$ (No. 161)
a, pm	855.9(1)	1754.8(1)
b, pm	1444.0(2)	
c, pm	1692.8(2)	3020.3(2)
V, 10^6 pm^3	2092.1(4)	8054.2(6)
μ, mm^{-1}	1.011	1.343
D_{calcd}, g cm^{-3}	1.685	1.974
cryst dimens, mm	0.76 × 0.06 × 0.03	0.02 × 0.01 × 0.01
Z	4	6
T, K	200	200
$2\theta_{max}$, deg	52.74	56.54
no. of rflns measd	18 630	17 798
no. of unique rflns	4263 (R_{int} = 0.0805)	4187 (R_{int} = 0.0756)
no. of params/ restraints	250/0	241/7
R1 ($I \geq 2\sigma(I)$)	0.0740	0.0458
wR2 (all data)	0.1415	0.0939
max/min resid elec dens, e 10^{-6} pm^{-3}	1.338/−1.143	0.994/−0.435

[a] Hahn, T. *International Tables for Crystallography*, 5th ed.; Kluwer Academic: Dordrecht, The Netherlands, 2002; Vol. A.

(b) NMR-Scale Reactions. In a typical experiment, 0.002 mmol (3 mol %) of the Ru catalyst **1a** was added after 30 min to a mixture consisting of acetonitrile (0.5 mL), allylic carbonate substrate (0.07 mmol), dimethyl malonate (0.07 mmol), and pure NaH (0.07 mmol), all in an oven-dried 5 mm NMR tube. The mixture was monitored by ^{1}H NMR spectroscopy at room temperature.

[RuCp*{η^6-(*p*-$NO_2C_6H_4CH$=$CHOCO_2Bu^t$)}]PF_6 (9). [RuCp*-$(CH_3CN)_3$]PF_6 (50 mg, 0.099 mmol) was added to a stirred solution of 3-(*p*-nitrophenyl)-prop-2-enyl *tert*-butyl carbonate (83 mg, 0.297 mmol, 3 equiv) in 2 mL of acetone and the red-brown solution 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_2O. Yield: 50 mg (94%). ^{1}H NMR (CD_2Cl_2, 299 K): δ 6.85 (d, 2 Ar H, ^3J 6.7 Hz), 6.66 (dt, 1H, ^3J = 16.0, ^3J = 5.0 Hz, 1H), 6.32 (dt, 1H, ^3J = 16.0, ^4J = 1.8 Hz), 6.29 (d, 2 Ar H, ^3J = 6.7 Hz), 4.84 (dd, 2H, ^3J = 5.0, ^4J = 1.8 Hz), 1.87 (s, 15H, Cp*), 1.53 (s, 9H, CH_3). ^{13}C NMR (CD_2Cl_2, 299 K): δ 153.4 (CO), 135.4 (=CH), 123.2 (=CH), 110.3 (CAr), 100.9 (C_{ipso}), 95.2 (Cp*), 85.6 (2 CAr), 83.6 (2 CAr), 8.28 (C), 65.7 (CH_2), 27.7 (CH_3), 9.6 (CH_3, Cp*). Anal. Calcd for $C_{24}H_{32}O_5$-$NRuPF_6$: C, 43.64; H, 4.88; N, 2.12; Found: C, 43.50; H, 4.99; N, 2.74. MS (ESI): *m/z* 516.2 (M^+), 458.2 ($M^+ - {}^t$Bu), 416.2 ($M^+ - CO_2{}^t$Bu), 400.2 ($M^+ - OCO_2{}^t$Bu), 315.3 ($M^+ - C_3H_4CO_2{}^t$Bu $- NO_2$).

[RuCp*{η^6-(PhCH=$CHOCO_2$Et)}]PF_6 (10). [Cp*Ru(CH_3-$CN)_3$]PF_6 (100 mg, 0.198 mmol) was added to a stirred solution of 3-phenyl-prop-2-enyl ethyl carbonate (123 mg, 0.595 mmol, 3 equiv) in 2 mL of acetone and the brown solution 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_2O. Yield: 109 mg (94%). ^{1}H NMR (CD_2Cl_2, 298 K): δ 6.46 (dt, 1H, ^3J = 16.0, ^3J = 5.2 Hz), 6.25 (dt, 1H, ^3J = 16.0, ^4J = 1.6 Hz), 5.84 (m, 4 ArH), 5.80 (m, 1 ArH), 4.84 (dd, 2H, ^3J = 5.2, ^4J = 1.6 Hz), 4.25 (q, 2H, ^3J = 7.2 Hz), 1.92 (s, 15H, Cp*), 1.36 (t, 3H, ^3J = 7.2 Hz). ^{13}C NMR (DMF-d_7, 299 K): δ 155.2 (CO), 131.5 (=CH), 126.4 (=CH), 97.4 (C_{ipso}), 87.5 (CAr), 87.3

(24) Fagan, P. J.; Mahomey, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843−1852. Schrenk, J. L.; McNair, A. M.; McCormick, F. B.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 3501−3504.

(25) Trost, B. M.; Older, C. M. *Organometallics* **2002**, *21*, 2544−2546.

(Cp^*), 85.1 (CAr), 64.9 (CH_2), 66.8 (OCH_2), 14.5 (CH_3), 10.6 (CH_3, Cp^*). Anal. Calcd for $C_{22}H_{29}O_3RuPF_6$: C, 44.98; H, 4.98; Found: C C, 44.36; H, 5.26. MS (ESI): *m*/*z* 443.1 (M^+), 401.2 ($M^+ - OEt$), 355.3 ($M^+ - OCO_2Et$), 315.2 ($M^+ - C_3H_4OCO_2Et$).

[Ru(Cp*)Cl(η^3-C_3H_5)(Me_2NCHO)]PF_6 (12). Allyl chloride (9.7 μL, 0.119 mmol) was added to a solution of [RuCp*($NCCH_3$)$_3$]-PF_6 (60 mg, 0.119 mmol) in dimethylformamide (2 mL). The reaction mixture was stirred for 16 h, after which time the solution was slowly concentrated under vacuum. The resulting crude product was washed with diethyl ether, affording 57 mg of a brownish solid (90%). Crystals suitable for diffraction were obtained by layering with diethyl ether a dichloromethane solution of the isolated solid and storing at −5 °C for 24 h. ^{1}H NMR (CD_2Cl_2, 298 K, 400.13 MHz): δ 5.16 (dt, 1H, ^3J = 10.2, ^3J = 6.1 Hz), 4.44 (dd, 1H, ^3J = 6.2, ^4J = 2.9 Hz), 3.74 (dd, 1H, ^3J = 6.1, ^4J = 2.9 Hz), 3.12 (d, 1H, ^3J = 10.2 Hz), 3.09 (3H), 2.94 (3H), 2.70 (d, 1H, ^3J = 10.1 Hz). ^{13}C NMR (CD_2Cl_2, 298 K, 400.13 MHz): δ 167.2 (CO), 107.5 (C), 99.8 (HC_{allyl}), 70.3 (H_2C_{allyl}), 70.3 (H_2C_{allyl}), 39.5 (CH_3), 33.9 (CH_3), 9.7 (CH_3). ^{13}C NMR (DMF-d_7, 298 K; allyl moiety): 99.6 (HC_{allyl}), 70.0 (H_2C_{allyl}), 69.7 (H_2C_{allyl}). Anal. Calcd for $C_{16}H_{27}$-ClF_6NOPRu: C 36.20, H 5.13, N 2.64; Found: C 35.93, H 5.08, N 3.53. ESI MS: *m*/*z* 386.1 (M^+), 345.2 ($M^+ - C_3H_5$), 313.2 ($M^+ - Me_2NCHO$).

Phenolation: NMR Scale. In a typical experiment, a 0.07 mmol sample of the allylic carbonate substrate was added to a mixture consisting of acetonitrile (0.5 mL) and the Ru catalyst **1a** or **7a** (0.002 mmol, 3% mol) in an oven-dried 5 mm NMR tube. The phenol 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.

Reaction of [Ru(Cp)(CH_3CN)$_3$]PF_6 with *p*-Toluinitrile. [Ru-(Cp)(CH_3CN)$_3$]PF_6 (30.5 mg, 0.070 mmol) and toluinitrile (48.5 mg, 0.414 mmol) were stirred in 1.5 mL of acetone for 30 min at room temperature. Concnetration of the solvent in vacuo followed by addition of diethyl ether afforded a brown solid. Washing with ether and drying gave 40 mg of crude product. Layering pentane over an acetone solution of the solid afforded brown needles of **14**. In a second experiment [RuCp(CH_3CN)$_3$]PF_6 (30.4 mg, 0.070 mmol) and toluinitrile (49.2 mg, 0.420 mmol) in acetone (1.5 mL) were stirred for 30 min with mild heating (310 K). Workup as described above gave 64 mg of crude product. NMR analysis of both samples revealed these to be (a) qualitatively the same and (b) a mixture of three to four components. Only a few crystals of the tetracationic salt **14** were collected.

Acknowledgment. The support and sponsorship provided by COST Action D24 "Sustainable Chemical Processes: Stereoselective Transition Metal-Catalyzed Reactions" are kindly acknowledged. Further, P.S.P. thanks the Swiss National Science Foundation and the ETHZ for financial support. I.F. thanks the Junta de Andalucia for a research contract. We also thank Johnson Matthey for the loan of precious metals. We especially thank Ms. Claudia Müller for the synthesis of the Ru tetranuclear species **14**.

Supporting Information Available: CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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