Communications

Allylations

DOI: 10.1002/anie.200600447

High-Yield Ruthenium-Catalyzed Friedel–Crafts-Type Allylation Reactions Using Dicationic Ru^{IV} Catalysts**

Ignacio Fernández, René Hermatschweiler, Frank Breher, Paul S. Pregosin,* Luis F. Veiros, and Maria José Calhorda

The organometallic catalytic chemistry of ruthenium continues to expand with applications in organic synthesis involving

[*] Dr. I. Fernández, R. Hermatschweiler, Prof. Dr. P. S. Pregosin Laboratory of Inorganic Chemistry ETHZ Hönggerberg, 8093 Zürich (Switzerland) Fax: (+41) 446-331-071 E-mail: pregosin@inorg.chem.ethz.ch Prof. Dr. F. Breher Institut für Anorganische Chemie Universität Karlsruhe Engesserstrasse 15, 76131 Karlsruhe (Germany) Prof. Dr. L. F. Veiros Centro de Química Estrutural Complexo I Instituto Superior Técnico Av. Rovisco Pais 1, 1049-001 Lisbon (Portugal) Prof. Dr. M. J. Calhorda Departamento de Química e Bioquímica Faculdade de Ciências Universidade de Lisboa, 1749-016 Lisbon (Portugal) [**] P.S.P. thanks the Swiss National Science Foundation, the Bundesamt für Bildung und Wissenschaft, and the ETHZ for financial

support. I.F. thanks the Junta de Andalucía for a research contract. We also thank Johnson Matthey for the loan of precious metals.

under http://www.angewandte.org or from the author.



hydroamination,^[1] isomerization,^[2-4] kinetic resolution,^[5] hydrogenation,^[6] metathesis,^[7] a variety of multiple C–C bond-formation reactions,^[8] and allylic alkylation.^[9,10]

With respect to allylation chemistry, several Cp*Ru precursors (Cp* = C₅Me₅) have been suggested as catalysts. These include the tris(acetonitrile) complex [Ru(Cp*)-(CH₃CN)₃]PF₆ (1) from Trost et al.,^[9] complexes containing bidentate nitrogen ligands,^[10] and the Ru^{IV} carbonate complex **2** reported by us.^[11] The latter complex^[11b] was shown to be an interesting alternative to **1** in the allylic alkylation of



phenylallyl-*tert*-butyl carbonate with sodium dimethyl malonate. Complex **2** can also be used successfully in allylic amination^[12a] and phenolation^[12b] reactions.

If **2** were to decompose to afford CO_2 and *t*-butoxide, the Ru^{IV} solvate complexes, for example **3** and **4**, would be



formed. Consequently, we prepared these dicationic complexes and show herein that **3**, in contrast to **2**, represents a novel catalyst for Friedel–Crafts-type allylation and catalyzes unexpected C–C couplings. Specifically, different arene compounds can be selectively allylated under relatively mild conditions in very good yield without the use of Lewis acidic main-group compounds or other additives.

Complexes **3** and **4** were prepared from our previously reported Ru^{IV} chlorido complex [Ru(Cp*)Cl(CH₃CN)(η^3 -PhCHCHCH₂)]PF₆ [**5**, see Eq. (1)]^[11a] by treatment with AgPF₆ in the appropriate solvent.^[13a] Table 1 shows the



Angew. Chem. Int. Ed. 2006, 45, 6386–6391

Table 1: Selected ruthenium-catalyzed carbon–carbon bond formations in acetonitrile at 353 K using the catalyst precursor **4** with the branched allyl carbonate substrate **6**^[a]



[a] Conditions: 0.07 mmol of allyl substrate **6**, 0.21 mmol of the corresponding arene derivative, 0.002 mmol of catalyst (3 mol%), in 0.5 mL of acetonitrile. [b] The o/m/p ratios were determined by ¹H NMR spectroscopy. [c] 30 equivalents.

Friedel–Crafts-type products from the reaction of the branched phenylallyl carbonate $PhCH(OCO_2tBu)CHCH_2$ (6) with a variety of electron-rich aromatic substrates at 353 K with 4 as the catalyst (which in acetonitrile solution reverts to 3).

In all the examples shown, the conversion to product is high, and ¹H NMR spectroscopic data show only linear and no branched isomer. For a few of the arene compounds *only one isomer* is observed in very high yield (Table 1, entries 2, 5, and 6); however, for several of the arene compounds, one does find a mixture of *ortho*, *meta*, and *para* isomers. For the phenol compounds,^[13b] the reaction is quite rapid, and in some cases complete conversion is observed in less than 10 minutes.

Communications

With chlorobenzene, however, there is no allylation after about 24 hours. We were also able to show that the solvent can have a significant influence on the reaction. With dimethylformamide (DMF) as the solvent and precursor **4**, the reaction of a naphthol substrate affords both C–C (36%) and C–O (64%) coupling products.

To further test the generality of the catalyst precursors for Friedel–Crafts reactions, we used **3** to catalyze the reaction of 6-bromo-2-naphthol with several differently substituted carbonates [Eq. (2)]. For all of the reactions leading to **7**, the



conversion is 100%, and the yield of product is greater than 80%. The reactions leading to 7b-7d were complete within less than 10 minutes, whereas 100% conversion to 7a required about two hours.

The Friedel–Crafts reaction has a long history.^[14] Recently, it has been shown that a number of late-transition-metal complexes^[15,16] are capable of condensing arene compounds with a suitable electrophile (for example, hexanoic acid anhydride^[15]), and this area has recently been reviewed.^[17] We are aware of several reports in which Ru compounds have been employed.^[15,18] Two of these studies^[18] use a dinuclear Ru^{III} species at about 413 K (fairly harsh conditions), and the yields are often only moderate. Fürstner and co-workers have employed RuCl₃ in the acylation of hexanoic acid anhydride with anisole; however, this catalyst seems to be relatively slow. Our catalyst represents a significant improvement relative to these Ru sources in that we use less catalyst and have faster reactions under milder conditions.

It is important to note that the related catalyst $2^{[11b,12b]}$ forms only C–O and no C–C bonds with phenol and the same branched allyl substrate [Eq. (3)], so that by a slight modification of the catalyst, one can completely redirect the nature of the organic product formed. Given this useful flexibility, we considered it appropriate to study aspects of these ruthenium catalysts.



The molecular structures of the two dications of **3** and $4^{[13]}$ are shown in Figures 1 and 2. A selection of bond angles and bond lengths are given in the captions of the figures. Both



Figure 1. Structure of the dication [Ru(Cp*)(η³-CH₂CHCHPh)-(MeCN)₂]²⁺ in **3.** Thermal ellipsoids are drawn at 30% probability; PF₆ anions are omitted for clarity. Bond lengths [pm] and angles [°]: Ru1-N1 207.8(3), Ru1-N2 208.1(3), Ru1-C1 218.0(3), Ru1-C2 218.9(3), Ru1-C3 238.2(3), Ru1-Ct1 185.9(3), Ru1-C10 219.1(3), Ru1-C20 220.6(3), Ru-C30 221.4(3), Ru1-C40 225.7(3), Ru1-C50 223.9(3), N1-C100 112.3(4), N2-C200 112.4(4); C1-C2-C3 119.4(3), N1-Ru1-N2 82.6(1); ϕ =70.3°; Ct1 = centroid of the Cp* ligand; ϕ is the intersection of the planes described by C1, C2, C3 and the five atoms of the Cp* ring.

complexes show the Ru atom complexed by the Cp* ligand, the phenylallyl ligand, and two solvent molecules. As expected, the dmf ligands are complexed through the amide oxygen atoms. The most interesting features in these dications involve the various Ru–C(allyl) bond lengths. Specifically, the Ru–C3 bonds (238.2(3) (3) and 232.3(4) pm (4)) are relatively long with the former separation exceptionally large. We have observed this type of long Ru–C(allyl) bond in both the Ru^{IV} chlorido complex **5** (Ru–C3 235.1(2) pm)^[11a] and Ru^{IV} carbonate complex **2** (Ru–C3 230.3(5) pm).^[11b] However, for the acetonitrile complex **3**, this bond is the longest of the set.

We have previously suggested that this long bond arises from relatively weak π back-bonding.^[11a] The observed ¹³C NMR chemical shift of C3 in **3** (δ = 103.3 ppm) appears at higher frequency than that in the monocation **5** (δ = 91.0 ppm) and is thus consistent with this suggestion.



Figure 2. Structure of the dication [Ru(Cp*)(η³-CH₂CHCHPh)(dmf)₂]²⁺ in **4**. Thermal ellipsoids are drawn at 30% probability; PF₆ anions are omitted for clarity. Bond lengths [pm] and angles [°]: Ru1-O1 211.0(3), Ru1-O2 212.6(3), Ru1-C1 218.4(4), Ru1-C2 215.5(4), Ru1-C3 232.3(4), Ru1-Ct1 186.0(4), Ru1-C10 220.1(4), Ru1-C20 216.3(4), Ru-C30 222.9(4), Ru1-C40 228.1(4), Ru1-C50 223.6(4), O1-C100 123.7(5), O2-C200 125.8(5), N1-C100 133.2(6), N2-C200 129.6(6); C1-C2-C3 117.0(4), O1-Ru1-O2 79.7(1); φ=68.2°; Ct1 = centroid of the Cp* ligand; φ is the intersection of the planes described by C1, C2, C3 and the five atoms of the Cp* ring.

To understand the chemistry of these salts a bit further, we performed DFT calculations^[19] for the three model cations $[\operatorname{Ru}(\operatorname{Cp})(\operatorname{CH}_3\operatorname{CN})_2(\eta^3-\operatorname{Ph}\operatorname{CH}\operatorname{CH}\operatorname{CH}_2)]^{2+}, \ [\operatorname{Ru}(\operatorname{Cp})(\operatorname{dmf})_2(\eta^3-\operatorname{Ch}\operatorname{Ch}_2)]^{2+}, \ [\operatorname{Ru}(\operatorname{Cp})(\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}\operatorname{Ch}\operatorname{Ch}_2)]^{2+}, \ [\operatorname{Ru}(\operatorname{Cp})(\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}\operatorname{Ch}\operatorname{Ch}_2)]^{2+}, \ [\operatorname{Ru}(\operatorname{Cp})(\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}\operatorname{Ch}\operatorname{Ch}_2)]^{2+}, \ [\operatorname{Ru}(\operatorname{Cp})(\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}\operatorname{Ch}\operatorname{Ch}_2)]^{2+}, \ [\operatorname{Ru}(\operatorname{Cp})(\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}\operatorname{Ch}\operatorname{Ch}_2)]^{2+}, \ [\operatorname{Ru}(\operatorname{Cp})(\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}\operatorname{Ch}\operatorname{Ch}_2)]^{2+}, \ [\operatorname{Ru}(\operatorname{Cp})(\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}_3\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}_3\operatorname{Ch}_3\operatorname{Ch}_3\operatorname{Ch}_3\operatorname{Ch}_3\operatorname{Ch})_2(\eta^3-\operatorname{Ch}_3\operatorname{Ch$ PhCHCHCH₂)]²⁺, and [Ru(Cp)(CH₃OCO₂)(η^3 -PhCHCH- CH_2]⁺ (Cp = C₅H₅). The results reveal that the Ru–C bond lengths for the substituted, terminal allyl carbon atom decrease as follows: 264 pm for the acetonitrile complex, 252 pm for the dmf complex, and 233 pm for the carbonate species. The remaining Ru-C(allyl) bond lengths are all in the range 210-222 pm. Although the separations of 264 pm and 252 pm are longer than the X-ray values, they are qualitatively consistent with the solid-state structures. Furthermore, natural population analysis (NPA) reveals the negative charges on the three terminal phenylallyl carbon atoms to be -0.05, -0.08, and -0.15, respectively, that is, the acetonitrile dication has the least amount of negative charge on this carbon atom. A possible reason can be deduced from the three molecular orbitals in Figure 3a, which represent the bonding metal-allyl π interactions. While the dmf and carbonate donors contribute to the orbital of the π interaction, this is not the case for the acetonitrile donors. This observation suggests an electron flow from the oxygen donors to the allyl ligand in the carbonate and dmf complexes, thus rationalizing the charges on the allyl carbon atoms.

The LUMO of the acetonitrile complex shows a greater participation of the substituted carbon atom (Figure 3b). If our reaction were orbital-controlled, one would expect attack at the *substituted*, terminal carbon and not, as found, at the allylic CH₂ carbon atom. Interestingly, there is less positive charge on the Ru atom in the acetonitrile complex (+0.34)than for the dmf (+0.49) and carbonate complexes (+0.51). This difference is consistent with the better donor ability of



Figure 3. a) Bonding Ru allyl π orbitals. Left: HOMO-4 of [Ru(Cp)-(CH₃CN)₂(η^3 -PhCHCHCH₂)]²⁺, with no contribution from the acetonitrile orbitals; middle: HOMO-5 of [Ru(Cp)(dmf)₂(η^3 -PhCHCHCH₂)]²⁺; right: HOMO-4 of [Ru(Cp)(CH₃OCO₂)(η^3 -PhCHCHCH₂)]⁺. b) LUMO of [Ru(Cp)(CH₃CN)₂(η^3 -PhCHCHCH₂)]²⁺, with a large contribution from the Ph–C allyl carbon atom.

the acetonitrile ligand than either of the oxygen ligands. Although the dicationic acetonitrile complex is substantially different from the other two cations, it is not clear from the X-ray and DFT data why the *linear* allyl product (namely, Ph-CH=CH-CH₂-Ar) is formed preferentially. Indeed, relative to palladium, ruthenium catalysts in allylation chemistry are interesting because they can favor the formation of the branched products.^[9,10]

A partial answer to this question is given by diffusion data from pulsed-gradient spin echo (PGSE) NMR measurements for complexes **3** and **5** (Table 2). This diffusion method-

Table 2: D and $r_{\rm H}$ values for the ruthenium complexes in acetonitrile at 299 K.^[a]



[a] All at 2 mm. [b] \pm 2%, \times 10¹⁰ m² s⁻¹. [c] η (CH₃CN, 299 K) = 0.3377 × 10⁻³ kg s⁻¹ m⁻¹.

13.72

24.76

40.34

¹H (cation)

¹⁹F (anion)

¹H (free CH₃CN)

ology^[20] allows one to estimate molecular volumes and ion pairing in solution. From the measured diffusion coefficient values *D* for the cation of **5**, we estimate the hydrodynamic radius $r_{\rm H}$ (using the Stokes–Einstein equation) to be about 4.7 Å, in good agreement with estimates of the size of this cation (4.5 Å) from our crystallographic data.^[21] For the

5

4.7

2.6

1.6

Communications

cation of **3**, we obtain a much larger $r_{\rm H}$ value of about 5.4 Å, which can be the result of ion pairing.^[20] However, the diffusion data from the PF₆ anions of **3** suggest that this is not the case. The $r_{\rm H}$ values for the PF₆ anions of both **3** and **5** (2.6–2.8 Å) are typical of what one finds in a polar solvent such as methanol. We suggest that the larger $r_{\rm H}$ value of 5.4 Å for the cation of **3** arises as a result of some charge-induced aggregation.^[20d,e] The presence of an aggregate may make it more difficult to attack the substituted allylic carbon, so that we tentatively attribute the observed regioselectivity to steric effects as a result of aggregation.^[22]

Perhaps there is a transition state in which the O (or S) donor approaches the Ph–C(allyl) position, but is hindered so that the C–C coupling is favored. To test this aggregation assumption we have carried out a catalytic reaction at tenfold dilution using 6-bromo-2-naphthol as the substrate. Indeed, whereas we had previously found no C–O product, we found 13% C–O bond formation in the diluted reaction mixture.

In conclusion, we have found that a new dicationic Ru^{IV} salt is a very efficient and mild catalyst for the Friedel–Crafts-type allylation of various electron-rich arene substrates. This C–C coupling reaction is in contrast to the selective C–O bond-forming reactions observed with related catalysts.

Received: February 2, 2006 Revised: May 22, 2006 Published online: August 23, 2006

Keywords: allylations · density functional calculations · NMR spectroscopy · ruthenium · structure elucidation

- [1] J. Takaya, J. F. Hartwig, J. Am. Chem. Soc. 2005, 127, 5756.
- B. M. Trost, M. T. Rudd, J. Am. Chem. Soc. 2005, 127, 4763;
 B. M. Trost, M. U. Frederiksen, M. T. Rudd, Angew. Chem. 2005, 117, 6788; Angew. Chem. Int. Ed. 2005, 44, 6630.
- [3] M. Ito, S. Itahara, T. Ikariya, J. Am. Chem. Soc. 2005, 127, 6172.
- [4] R. C. van der Drift, M. Gagliardo, H. Kooijman, A. L. Spek, E. Bouwman, E. Drent, J. Organomet. Chem. 2005, 690, 1044.
- [5] S. Hashiguchi, A. Fujii, K. J. Haack, K. Matsumura, T. Ikariya, R. Noyori, *Angew. Chem.* **1997**, *109*, 300; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 288.
- [6] a) T. Ohkuma, H. Ooka, T. Ikariya, R. Noyori, J. Am. Chem. Soc.
 1995, 117, 10417; b) T. Ohkuma, H. Ooka, M. Yamakawa, T. Ikariya, R. Noyori, J. Org. Chem. 1996, 61, 4872; c) K. J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, Angew. Chem.
 1997, 109, 297; Angew. Chem. Int. Ed. Engl. 1997, 36, 285.
- [7] R. H. Grubbs, *Tetrahedron* 2004, 60, 7117; A. Hejl, O. A. Scherman, R. H. Grubbs, *Macromolecules* 2005, 38, 7214.
- [8] a) P. H. Dixneuf, C. Bruneau in Organic Synthesis via Organometallics OSM 5 (Eds.: D. Helmchen, J. Dibo, J. Flubacher, B. Wiese), Friedr. Vieweg, Braunschwewig, 1997, p. 1; b) S. Derien, P. H. Dixneuf, J. Organomet. Chem. 2004, 689, 1382; c) E. Bustelo, P. H. Dixneuf, Adv. Synth. Catal. 2005, 347, 393; T. Murahashi, Ruthenium in Organic Synthesis, Wiley-VCH, Weinheim, 2004.
- [9] a) B. M. Trost, P. L. Fraisse, Z. T. Ball, Angew. Chem. 2002, 114, 1101; Angew. Chem. Int. Ed. 2002, 41, 1059; b) B. M. Trost, M. L. Crawley, Chem. Rev. 2003, 103, 2921.
- [10] a) M. D. Mbaye, B. Demerseman, J. L. Renaud, L. Toupet, C. Bruneau, *Angew. Chem.* 2003, *115*, 5220; *Angew. Chem. Int. Ed.* 2003, *42*, 5066; b) J. L. Renaud, C. Bruneau, B. Demerseman,

Synlett 2003, 408; c) M. D. Mbaye, J. L. Renaud, B. Demerseman, C. Bruneau, *Chem. Commun.* 2004, 1870; d) M. D. Mbaye,
B. Demerseman, J. L. Renaud, L. Toupet, C. Bruneau, *Adv. Synth. Catal.* 2004, 346, 835; e) N. Gurbuz, I. Ozdemir, B. Cetinkaya, J. L. Renaud, B. Demerseman, C. Bruneau, *Tetrahedron Lett.* 2006, 47, 535.

- [11] a) R. Hermatschweiler, I. Fernandez, P. S. Pregosin, E. J. Watson, A. Albinati, S. Rizzato, L. F. Veiros, M. J. Calhorda, *Organometallics* 2005, 24, 1809; b) R. Hermatschweiler, I. Fernandez, F. Breher, P. S. Pregosin, L. F. Veiros, M. J. Calhorda, *Angew. Chem.* 2005, 117, 4471; *Angew. Chem. Int. Ed.* 2005, 44, 4397.
- [12] a) I. Fernandez, R. Hermatschweiler, P. S. Pregosin, A. Albinati, S. Rizzato, *Organometallics* **2006**, *25*, 323; b) R. Hermatschweiler, I. Fernandez, P. S. Pregosin, F. Breher, *Organometallics* **2006**, *25*, 1440.
- [13] a) Synthesis of 3: AgPF₆ (48 mg, 0.174 mmol) was added to solution of $[Ru(Cp^*)Cl(CH_3CN)(\eta^3-PhCHCHCH_2)]PF_6$ (100 mg, 0.174 mmol) in a mixture of toluene and acetonitrile (2 mL:2 mL). The reaction mixture was stirred for 16 h after which time the solution was filtered and then slowly concentrated under vacuum. The resulting crude solid was washed with diethyl ether to afford an oil, which was dissolved in dichloromethane, filtered, and dried under vacuum to afford a brownyellow solid. This solid was dissolved in dichloromethane, filtered, and dried under vacuum. This sequence was repeated one more time. Yield: 78% (98 mg). An acetone solution of this solid was layered with n-pentane and stored at 5°C to afford airsensitive crystals of 3, which were suitable for X-ray diffraction. ¹H NMR ([D₆]acetone, 298 K, 400.13 MHz): $\delta = 1.96$ (s, 15 H), 2.37 (s, 3 H), 2.68 (s, 3 H), 3.41 (d, 1 H, J = 10.4 Hz), 4.87 (d, 1 H, J = 6.4 Hz), 5.31 (d, 1H, J = 12.0 Hz), 6.59 (ddd, 1H, J = 12.0, 10.4, 6.4 Hz), 7.58 (m, 2H, J=7.6, 7.2 Hz), 7.74 (m, 2H, J=7.6, 1.4 Hz), 7.90 ppm (m, 2H, J = 7.2 Hz); ¹³C NMR: $\delta = 3.7$ (CH₃), 4.0 (CH₃), 9.2 (CH₃), 66.3 (H₂C_{allvl}), 108.8 (C), 94.1 (HC_{allvl}), 103.3 (HCallyl), 129.1 (Cnitrile), 129.2 (Cnitrile), 129.9 (HCAr), 131.1 (HCAr), 132.6 (HCAr), 133.6 ppm (C_{ipso}). Elemental analysis (%) calcd for $C_{23}H_{30}F_{12}N_2P_2Ru$: C 38.08, H 4.17, N 3.86; found: C 38.46, H 4.38, N 3.20; ESI-MS: *m*/*z*: 436.1 [*M*⁺], 354.1 $[M^+-2$ CH₃CN], 237.0 $[M^+-2$ CH₃CN-PhCHCHCH₂). Synthesis of 4: AgPF₆ (48 mg, 0.174 mmol) was added to a solution $[Ru(Cp^*)Cl(CH_3CN)(\eta^3-PhCHCHCH_2)]PF_6$ of (100 mg, 0.174 mmol) in DMF (2 mL). The reaction mixture was stirred for 16 h after which time the solution was filtered and then slowly concentrated under vacuum. The resulting crude mixture was washed with diethyl ether. The resulting red oil was dissolved in dichloromethane, filtered, and dried under vacuum to afford a red-purple solid. This solid was dissolved in dichloromethane, filtered, and dried under vacuum. This sequence was repeated one more time. Yield: 84% (115 mg). A dichloromethane solution of this solid was then layered with *n*-pentane and stored at -30 °C to afford red air-sensitive crystals of 4, which were suitable for X-ray diffraction. ¹H NMR $([D_6]acetone, 298 \text{ K}, 400.13 \text{ MHz}): \delta = 1.76 (s, 15 \text{ H}), 2.60 (d, 3 \text{ H})$ J = 1.0 Hz), 3.05 (s, 3 H), 3.13 (d, 3 H, J = 1.0 Hz), 3.28 (s, 3 H), 3.64 (dd, 1 H, J = 10.0, 0.9 Hz), 4.70 (dd, 1 H, J = 6.5, 0.9 Hz), 5.49 (d, 1 H, J = 11.0 Hz), 6.48 (ddd, 1 H, J = 11.0, 10.0, 6.5 Hz), 7.12 (s, 1H), 7.50 (m, 2H, J = 7.8, 7.5 Hz), 7.72 (m, 1H, J = 7.8, 1.5 Hz), 7.75 (m, 2H, J=7.5 Hz), 7.95 ppm (s, 1H); ¹³C NMR: $\delta = 8.9$ (CH₃), 33.2 (CH₃), 33.8 (CH₃), 39.2 (CH₃), 39.4 (CH₃), 66.0 (H₂C_{allyl}), 107.9 (C), 96.9 (HC_{allyl}), 98.4 (HC_{allyl}), 129.9 (HCAr), 131.5 (HCAr), 131.6 (HCAr), 134.0 (C_{ipso}), 166.5 (C_{dmf}), ESI-MS: 167.8 ppm $(C_{dmf});$ m/z: 459.1 $[M^+]$ -Me₂NCHO+MeOH), 427.1 $[M^+-Me_2NCHO],$ 354.1 $[M^+-2Me_2NCHO]$. Catalysis: In a typical experiment, the Ru catalyst precursor 3 or 4 (0.002 mmol, 3 mol%) was added to a mixture consisting of acetonitrile (0.5 mL) and the allylic

carbonate substrate (0.07 mmol) in an oven-dried 5-mm NMR tube. The arene derivative (0.21 mmol) was added, and the mixture was monitored by ¹H NMR spectroscopy at 353 K. Crystal structure of 3: Yellow crystals of $[Ru(Cp^*)(\eta^3 -$ CH2CHCHPh)(MeCN)2](PF6)2·acetone were obtained from an acetone solution of 3 which was layered with n-hexane; $C_{26}H_{36}F_{12}N_2OP_2Ru$, triclinic, space group $P\bar{1}$; a = 9.535(1), b =11.750(1), c = 15.879(1) Å, a = 109.395(1), $\beta = 96.719(1)$, $\gamma =$ 100.965(1)°, V = 1615.8(2) Å³, Z = 2, $\rho_{calcd} = 1.611$ Mg m⁻³, crystal dimensions 0.48×0.27×0.23 mm, Bruker SMART Apex diffractometer with CCD detector, $Mo_{K\alpha}$ radiation $(0.71073 \text{ Å}), 200 \text{ K}, 2\Theta_{\text{max}} = 56.68^{\circ}, 16798 \text{ reflections}, 7984$ independent ($R_{int} = 0.0217$), empirical absorption correction SADABS (ver. 2.03), direct methods, refinement against full matrix (versus F^2) with SHELXTL (ver. 6.12) and SHELXL-97, 406 parameters, R1 = 0.0504 and wR2 (all data) = 0.1363, max./ min. residual electron density 1.106/-0.464 e Å⁻³. All nonhydrogen atoms were refined anisotropically; the contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Crystal structure of 4: of $[Ru(Cp^*)(\eta^3-CH_2CHCHPh)(dmf)_2]$ -Red crystals (PF₆)₂·CH₂Cl₂·alkane were obtained from a methylene chloride layered solution, which was with *n*-hexane; $C_{28}H_{40}Cl_2F_{12}N_2O_2P_2Ru$, orthorhombic, space group *Pccn*; *a* = 21.369(1), b = 22.712(1), c = 15.580(1) Å, V = 7561.4(6) Å³, Z =8, $\rho_{\text{calcd}} = 1.579 \text{ Mg m}^{-3}$, crystal dimensions $0.44 \times 0.42 \times 0.32 \text{ mm}$, Bruker CCD1k diffractometer, $Mo_{K\alpha}$ radiation (0.71073 Å), 200 K, $2\theta_{\text{max}} = 52.74^{\circ}$, 58019 reflections, 7735 independent $(R_{int} = 0.0272)$, empirical absorption correction SADABS (ver. 2.03), direct methods, refinement against full matrix (versus F^2) with SHELXTL (ver. 6.12) and SHELXL-97, 515 parameters, R1 = 0.0457 and wR2 (all data) = 0.1558, max./min. residual electron density 1.193/-0.568 eÅ⁻³. All non-hydrogen atoms were refined anisotropically; the contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. One CH₂Cl₂ molecule could be refined. Presumably owing to solvent loss or incomplete incorporation, additional crystal solvent molecule(s) could only be refined by positioning two carbon atoms ($\times 0.5 C_4$), one of which had to be split over two positions and refined using the ISOR restraint. One of the PF₆⁻ anions was disordered. Each of the fluorine atoms was split over two positions, which were refined against each other (FVAR = 0.53). CCDC- 295048 and 295049 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif. b) A reviewer has correctly suggested that the Friedel-Crafts chemistry might arise from a rearrangement of the branched organic product PhCH(OPh)CHCH₂ formed from the nucleophilic attack of phenol on the Ru^{IV} allyl complex. To test this we allowed this product, PhCH-(OPh)CHCH₂, to react with catalyst 3 under our standard conditions (CH₃CN at 353 K). After 12 h, that is, more than one order of magnitude longer than necessary for 100% conversion, we did find about 60% of the Friedel-Crafts product. However, this reaction is much too slow to be relevant.

- [14] G. Olah, J. Org. Chem. 2001, 66, 5943.
- [15] A. Fürstner, D. Voigtlander, W. Schrader, D. Giebel, M. T. Reetz, Org. Lett. 2001, 3, 417.
- [16] a) I. Shimizu, T. Sakamoto, S. Kawaragi, Y. Maruyama, A. Yamamoto, *Chem. Lett.* **1997**, 137; b) A. V. Malkov, S. L. Davis, I. R. Baxendale, W. L. Mitchell, P. Kocovsky, *J. Org. Chem.* **1999**, 64, 2751, and references therein; c) J. Choudhury, S. Podder, S. Roy, *J. Am. Chem. Soc.* **2005**, *127*, 6162.
- [17] M. Bandini, A. Melloni, A. Umani-Ronchi, Angew. Chem. 2004, 116, 560; Angew. Chem. Int. Ed. 2004, 43, 550.

- [18] a) Y. Nishibayashi, M. Yamanashi, Y. Takagi, M. Hidai, *Chem. Commun.* **1997**, 859; b) G. Onodera, H. Imajima, M. Yamanashi, Y. Nishibayashi, M. Hidai, S. Uemura, *Organometallics* **2004**, 23, 5841, and references therein.
- [19] DFT calculations were performed with the Gaussian 98 software package using the mPW1PW91 hybrid functional. The basis set that was used included a standard SDD which was augmented with an *f*-polarization function for Ru and 4-31G(d) for the other atoms. The atomic charges resulted from a natural population analysis (NPA). Computational details and the corresponding list of references are given as Supporting Information.
- [20] a) M. Valentini, H. Rüegger, P. S. Pregosin, *Helv. Chim. Acta* 2001, 84, 2833; b) P. S. Pregosin, E. Martinez-Viviente, P. G. A. Kumar, *Dalton Trans.* 2003, 4007; c) P. S. Pregosin, P. G. A. Kumar, I. Fernandez, *Chem. Rev.* 2005, 105, 2977; d) F. Q. Song, S. J. Lancaster, R. D. Cannon, M. Schormann, S. M. Humphrey, C. Zuccaccia, A. Macchioni, M. Bochmann, *Organometallics* 2005, 24, 1315; e) D. Zuccaccia, E. Clot, A. Macchioni, *New J. Chem.* 2005, 29, 430.
- [21] The radii from the X-ray data for the cations in 3, 4, and 5 are 4.6, 4.8, and 4.5 Å, respectively.
- [22] In a typical catalytic experiment the concentration of the catalyst precursor is 4.2 mM. The PGSE diffusion studies were performed at 2 mM, so that, in the catalytic solution, even more aggregation is expected.