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Versatile reactivity of amines towards the ruthenocenylmethylium cation $[Cp^*Ru(C_5Me_4CH_2)]^+$

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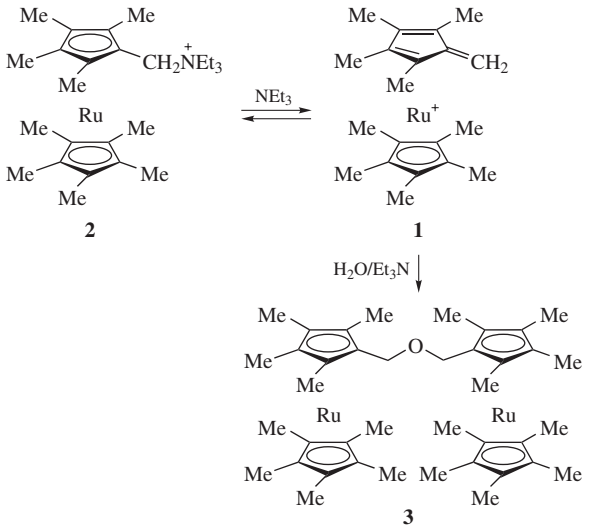
The cationic complex $[Cp^*Ru(C_5Me_4CH_2)]^+$ reacts with Et_3N primarily giving the ammonium salt $[Cp^*Ru(C_5Me_4CH_2NEt_3)]^+$. The prolonged standing of the reaction mixture results in the formation of the ether $Cp^*Ru(C_5Me_4CH_2OCH_2C_5Me_4)RuCp^*$. The reaction of $[Cp^*Ru(C_5Me_4CH_2)]^+$ with $PhNEt_2$ leads to the electrophilic aromatic substitution product $[Cp^*Ru(C_5Me_4CH_2C_6H_4NHEt_2)]^+$.

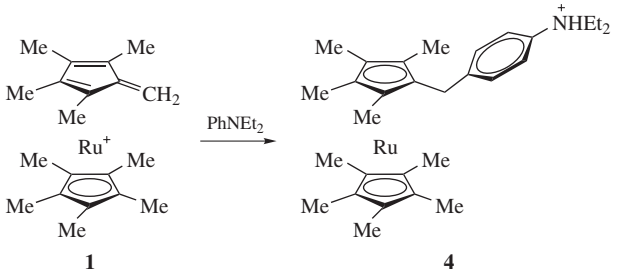
Metallocenyl substituents are known to stabilize carbenium ions.[1,2] For instance, Koelle and Grub[3] prepared the nonamethylruthenocenylmethylium cation $[Cp^*RuC_5Me_4CH_2]^+$ **1** by the reaction between $RuCp^*_2$ and $[CPh_3]^+$. This cation was found to react only with strong nucleophiles (OH^-, OR^-, SR^- and PR_3).[4] The reaction with Pr^i_2NH resulting in the formation of the amino-substituted ruthenocene $Cp^*RuC_5Me_4CH_2NPr^i_2$ was also described.[3]

Here, we found that the reaction of cation **1** with Et_3N immediately gives ammonium salt **2** (identified by ^1H NMR spectra).† However, the standing of this mixture for three days results in the formation of ether **3** bearing two methylruthenocenyl substituents (Scheme 1).‡ This can be explained by the occurrence of two competitive processes: (a) the reversible addition of amine to cation **1** giving **2**[5] and (b) the irreversible hydrolysis of **1** by water traces resulting in **3**. Apparently, the hydrolysis is caused by the formation of the OH^- anion in the presence of basic Et_3N (in the absence of the amine, cation **1** does not react with water).



Scheme 1

Interestingly, the reaction of **1** with the aromatic amine $PhNEt_2$ occurs in a different way affording cationic complex **4** as a result of electrophilic substitution in the *para*-position of the benzene ring (Scheme 2).§



Scheme 2

Apparently, the aromatic ring in $PhNEt_2$ is more nucleophilic toward cation **1** compared with the NEt_2 group. Note that Nesmeyanov *et al.*[6] described a similar reaction for the ferrocenyl analogues $[CpFeCH(R)Ph]^+$ (R = H, Ph).

The ^1H NMR spectra of **2**–**4** exhibit signals due to Me and CH_2 groups and (in the case of **4**) an acidic NH proton (δ 7.61 ppm) and signals corresponding to the *para*-disubstituted benzene ring

† NMR-tube experiment: NEt_3 (0.01 ml, ~7 mg, 0.069 mmol) was added to the solution of $\mathbf{1}PF_6$ (30 mg, 0.059 mmol) in acetone-d_6 (0.5 ml, contains ~5 vol% water). After several minutes, the resonances due to the starting material $\mathbf{1}PF_6$ completely disappeared and a set of new signals related to $\mathbf{2}PF_6$ was observed. ^1H NMR (acetone-d_6) δ: 4.01 (s, 2H, CH_2), 3.44 [q, 6H, $N(CH_2Me)_3$, J ~ 9.0 Hz], 1.67 (overlapping singlets, 6H from C_5Me_4, and 15H from Cp*), 1.59 (s, 6H, C_5Me_4), 1.31 [t, 9H, $N(CH_2Me)_3$, J ~ 9.0 Hz].

‡ The NMR tube from previous experiment was left for three days, after which colorless crystals were formed. The crystals of **3** were separated, washed with 1 ml of hexane and dried *in vacuo*. Yield, 18 mg (82%). ^1H NMR (CD_2Cl_2) δ: 3.90 (s, 4H, CH_2), 2.15 (s, 12H, C_5Me_4), 1.67 (s, 30H, Cp*), 1.66 (s, 12H, C_5Me_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: 84.13 (C_5), 83.45 (C_5), 83.17 (C_5), 82.43 (C_{ipso}-C_5), 29.69 (CH_2), 10.03 (C*Me*, Cp*), 9.58 (C_5Me_4), 9.50 (C_5Me_4). Found (%): C, 63.59; H, 7.98. Calc. for $C_{40}H_{58}ORu_2$ (%): C, 63.46; H, 7.72.

§ $PhNEt_2$ (0.03 ml, ~28 mg, 0.188 mmol) was added to the solution of $\mathbf{1}PF_6$ (89 mg, 0.173 mmol) in acetone (2 ml); then, it was stirred overnight, after which hexane (15 ml) was added. The white precipitate of $\mathbf{4}PF_6$ was separated, washed with diethyl ether (3×5 ml) and dried *in vacuo*. Yield, 0.097 g (83%). ^1H NMR (CD_2Cl_2) δ: 7.61 (s, 1H, NH), 7.41 (d, 2H, *p*-C_6H_4, AA′BB′, J_{AB} ~ 7.5 Hz), 7.33 (d, 2H, AA′BB′, J_{AB} ~ 7.5 Hz), 3.59 [q, 4H, $N(CH_2Me)_2$, J ~ 7.0 Hz], 3.38 (s, 2H, CH_2), 1.70 (s, 15H, Cp*), 1.68 (s, 6H, C_5Me_4), 1.64 (s, 6H, C_5Me_4), 1.17 [t, 6H, $N(CH_2Me)_2$, J ~ 7.0 Hz]. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 144.97, 130.69, 130.26, 121.66, 84.30, 83.85, 83.39, 82.68, 54.65, 31.60, 10.37, 10.31, 10.16, 10.05. Found (%): C, 54.13; H, 7.01. Calc. for $C_{30}H_{43}F_6NPRu$ (%): C, 54.21; H, 6.67.

In a similar experiment, the NMR tube was charged with complex $\mathbf{1}PF_6$ (0.0051 g, 0.01 mmol), acetone-d_6 (0.5 ml) and $PhNEt_2$ (1.7 mg, 0.012 mmol, 14% excess). The disappearance of the resonances for $\mathbf{1}PF_6$ was observed after 8 h.

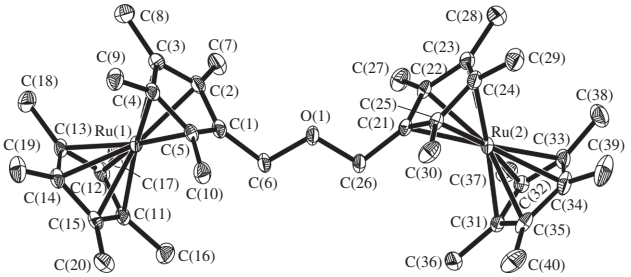


Figure 1 Structure of complex **3**. Ellipsoids are shown at a 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ru(1)–C(1) 2.163(3), Ru(1)–C(2) 2.179(3), Ru(1)–C(3) 2.182(3), Ru(1)–C(4) 2.185(3), Ru(1)–C(5) 2.182(3), Ru(1)–C(11) 2.177(3), Ru(1)–C(12) 2.175(3), Ru(1)–C(13) 2.177(3), Ru(1)–C(14) 2.170(3), Ru(1)–C(15) 2.177(3), Ru(2)–C(21) 2.164(3), Ru–C(22) 2.186(3), Ru(2)–C(23) 2.192(3), Ru(2)–C(24) 2.182(3), Ru(2)–C(25) 2.168(3), Ru(2)–C(31) 2.175(3), Ru(2)–C(32) 2.169(3), Ru(2)–C(33) 2.170(3), Ru(2)–C(34) 2.181(3), Ru(2)–C(35) 2.183(3).

(δ 7.41 and 7.33, AA′BB′ system, J_{AB} ~ 7.5 Hz). These data are consistent with the proposed structures of the products.

The structure of **3** was determined by X-ray diffraction analysis (Figure 1).[¶] The ring ligands are almost parallel (the Cp*/C_5Me_4 dihedral angles of 0.4 and 1.0°). The mutual orientation of Cp* and C_5Me_4 ligands is eclipsed for both Cp*Ru$C_5Me_4CH_2$ moieties. The Ru–C bond lengths in **3** (av. 2.177 Å) are very close to those in $RuCp^*_2$ (2.178 Å). The Ru–C(Cp*) distances (av. 2.175 Å) are shorter than analogous Ru–C(C_5Me_4) distances (av. 2.178 Å).

To explain the experimental facts, we carried out DFT calculations for the reactions of cation **1** and its unsubstituted analogue $[CpRuC_5H_4CH_2]^+$ **1′**[8] with trimethylamine and dimethylaniline (see Online Supplementary Materials) using BPBE and PBE functionals; the following discussion cites energy values obtained with the BPBE functional since it provides a better correlation of the calculated energies with experimental results.[9]

Table 1 summarizes the activation free energies G_a. A comparison of the reactions of cation **1** at the nitrogen atoms of NMe_3 and Me_2NPh shows that dimethylaniline is less reactive; moreover, this reaction is reversible. The formation of a C–C bond is more favorable and irreversible, making electrophilic substitution preferable. The transition states for the formation of C–N and C–C bonds are shown in Figure 2. The same tendency is true for parent cation **1′**; however, the computation suggests its much higher reactivity compared with **1**.

In conclusion, the experiment and computation revealed that aliphatic and aromatic amines display versatile reactivity towards ruthenocenylmethylium cation $[Cp^*Ru(C_5Me_4CH_2)]^+$ **1**. The addition of amines to the carbenium center of cation **1** with the formation of a C–N bond is reversibile. Aliphatic amines promote the hydrolysis of **1** giving organometallic ether **4**. In the case of aromatic amines, the electrophilic substitution at the benzene ring becomes more favorable.

Table 1 Activation free energies G_a (at 298.15 K) for the interaction of cations **1** and **1′** with amines at BPBE/L2.

Reaction	Bond formed	G_a/kcal mol^{-1}
1 + NMe_3	C–N	17.5
1′ + NMe_3	C–N	—[a]
1 + Me_2NPh	C–N	25.6
	C–C	23.9
1′ + Me_2NPh	C–N	9.6
	C–C	9.4

[a] The transition state was not found.

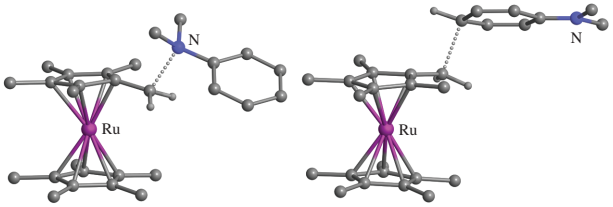


Figure 2 Optimized structures of transition states for the formation of C–N (left) and C–C (right) bonds at BPBE/L2. Most hydrogen atoms are omitted for clarity.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.03.009.

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¶ Crystals of **3** were grown up by the slow evaporation of acetone solution.

Crystallographic data for **3**: $C_{40}H_{58}ORu_2$ (M = 757.00), monoclinic, space group $P2_1/n$, a = 17.754(3), b = 8.6461(12) and c = 23.567(3) Å, β = 91.590(3)°, V = 3616.2(9) Å^3, Z = 4, d_{calc} = 1.390 g cm^{-3}, μ(MoKα) = = 0.864 mm^{-1}, T = 100(2) K, $2\theta_{max}$ = 56°, 12080 reflections measured, R_1 = 0.0385 [10615 reflections with $I > 2\sigma(I)$], wR_2 = 0.1056 (all data), T_{max}/T_{min} = 0.9034/0.7184, GOF = 0.991, max. res. density peaks: 0.61 to –0.69 e Å^{-3}. A crystal of **3** was found to be twinned and refined with HKLF 5 (BASF = 0.254).

X-ray diffraction experiments were carried out with a Bruker SMART APEX2 CCD area detector, using graphite monochromated MoKα radiation (λ = 0.71073 Å) at 100 K.[10] The structures were solved by a direct method and refined by the full-matrix least-squares technique against F^2 in an anisotropic approximation for non-hydrogen atoms. All hydrogen atoms were refined in isotropic approximation in riding model. The absorption correction was applied semi-empirically using the SADABS program. All calculations were performed using SHELXTL 5.1.[11]

CCDC 1009281 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.