# Double Nucleophilic Addition of Carbon Donors to [(benzene)(arene)Ru]$^{2+}$ Cations

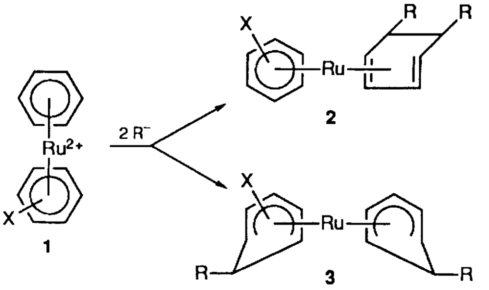
**Catherine Camaioni Neto and Dwight A. Sweigart***
*Department of Chemistry, Brown University, Providence, RI 02912, USA*

The nucleophiles MeLi and PhLi add cleanly to both rings in [($\eta^6$-$C_6H_6$)($\eta^6$-arene)Ru]$^{2+}$ (arene = $C_6H_6$, $C_6H_3Me_3$, $C_6H_3Pr^i_3$, $C_6Me_6$) to yield bis($\eta^5$-cyclohexadienyl) complexes; [($\eta^4$-cyclohexadiene)(arene)Ru] complexes are not formed.

The electrophilic activation of arenes by coordination to transition metals, followed by the addition of carbon-donor nucleophiles, is a viable synthetic route to arene functionalization. The arene rings in [(arene)$_2$Fe]$^{2+}$ are extremely electrophilic, but nucleophilic additions with carbon donors[1–3] are often plagued by electron transfer reactions. Furthermore, the Fischer–Hafner synthesis of [(arene)$_2$Fe]$^{2+}$, while convenient, can easily lead to isomerization of the arenes to be coordinated.[2] The ruthenium analogues, [(arene)(arene′)Ru]$^{2+}$, are attractive alternatives because they are easily synthesized in high yield under mild conditions[4,5] and, unlike the case with iron, are readily available as mixed complexes having arene ≠ arene′. Replacing iron with ruthenium also eliminates interfering single electron transfer reactions when carbon donor nucleophiles are added (*vide infra*). The ruthenium complexes are expected[6] to be *ca.* 30 times less reactive than the iron counterparts, but, nevertheless, should be electrophilic enough for synthetic utility.

The addition of two nucleophiles to a coordinated arene generates a difunctionalized cyclohexadiene. With [(arene)$_2$Fe]$^{2+}$ systems this double addition, with hydride as the first nucleophile and a carbanion as the second, is claimed[2] to produce [(diene)(arene)Fe] products; the use of a carbanion as the first nucleophile leads only to electron transfer and decomposition. Other work[1,7] shows that in some instances two carbanions may be added to [(arene)$_2$Fe]$^{2+}$, but to yield [(cyclohexadienyl)$_2$Fe] products. With [($C_6H_6$)$_2$Ru]$^{2+}$ it is known[8] that PhLi reacts to give [($\eta^5$-$C_6H_6Ph$)$_2$Ru] while hydride donors attack this dication to afford mixtures of [($C_6H_7$)$_2$Ru] and the diene complex, [($\eta^4$-$C_6H_8$)($C_6H_6$)Ru]. More recently, $NaBH_4$ addition to [($C_6H_6$)(arene)Ru]$^{2+}$ was shown[9] to produce a mixture of diene products with the predominant complex arising from double addition to the less hindered (benzene) ring, *i.e.*, [($C_6H_8$)(arene)Ru]. Other work[10] shows that hydride (Red-Al) addition to preformed [(cyclohexadienyl)(arene)Ru]$^+$ cations occurs at the arene to yield [(dienyl)(dienyl′)Ru] products.

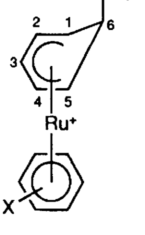
In this paper we present preliminary results of a study of carbon donor addition to [(benzene)(arene)Ru]$^{2+}$ cations, where the arene ligand ranges from $C_6H_6$ to $C_6Me_6$. It was hoped that in cases involving double nucleophilic addition, steric bulk present on the arene could be used to direct both additions to the benzene ring to yield the more desirable [(diene)(arene)Ru] product, *i.e.*, **2** rather than **3**. It may be noted that this strategy is not readily available with the iron analogues due to the difficulty of synthesizing and purifying [(benzene)(arene)Fe]$^{2+}$ (arene ≠ benzene).



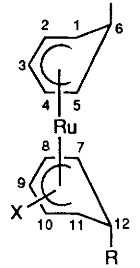
[($C_6H_6$)(arene)Ru]($PF_6$)$_2$ **1** salts were synthesized by a published procedure.[5] The arenes in **1** included $C_6H_6$ **1a**, $C_6Me_6$ **1b** 1,3,5-$C_6H_3Me_3$ **1c** and 1,3,5-$C_6H_3Pr^i_3$ **1d**; all but [($C_6H_6$)($C_6H_3Pr^i_3$)Ru]($PF_6$)$_2$ **1d** have been characterized previously.[4,5] Complex **1d** was obtained in 70% isolated yield and readily characterized by $^1H$ NMR ($CD_3COCD_3$, 250 MHz); δ 7.29 (s, $C_6H_6$), 7.23 (s, $C_6H_3Pr^i_3$), 3.27 (q, $J$ = 7 Hz, $CHMe_2$), 1.46 (d, $J$ = 7 Hz, Me). The addition of excess Na[CH($CO_2Me$)$_2$] to **1a–c** in tetrahydrofuran (THF) at room temperature resulted in [($C_6H_6CH(CO_2Me_2)_2$)(arene)Ru]$^+$ cations **4** with no evidence for addition to the non-benzene arene ring or for double addition products; apparently $CH(CO_2Me)_2^-$ is too weak a nucleophile to effect a second addition. The complexes **4a**, **4b** and **4c** were obtained in isolated yields of 35, 73 and 50%, respectively, and characterized by $^1H$ NMR.†

Dropwise addition at room temperature of LiMe (in diethyl ether) to a slurry of **1a–d** in THF or addition of LiPh to **1c** in THF led to rapid formation of complexes **3**, which were extracted into diethyl ether and isolated as air-sensitive yellow oils in yields ranging from 52 to 95%. $^1H$ NMR spectra were in complete accord with structure **3**; detectable quantities of the diene complex **2** were not found. There was no evidence for products of electron transfer.

From the results presented herein, we conclude that double nucleophilic addition to **1** is possible with strong carbon donors. Even when one of the arene rings in **1** is sterically congested **1b–d** a single addition occurs at each ring to give bis(cyclohexadienyl) complexes (‘pseudoruthenocenes’). This is in accordance with the rules of Davies *et al.*[11] suggesting that the reactions of LiR and [($C_6H_6R$)(arene)Ru]$^+$ are charge-controlled. In contrast, it has been claimed that similar



**4**



**3**

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† *$^1H$ NMR data* (250 MHz) for: **4a** ($CD_3CN$) δ 6.37 (t, H-3), 6.21 ($C_6H_6$), 5.08 (t, H-2,4), 3.90 (t, H-1,5), 3.62 (s, $CO_2Me$), 3.2 (m, H-6), 2.65 (d, CH); **4b** ($CD_3COCD_3$) δ 6.18 (t, H-3), 4.91 (H-2,4), 3.62 (s, $CO_2Me$), 3.34 (t, H-1,5), 3.09 (m, H-6), 2.62 (d, CH), 2.47 (s, $C_6Me_6$); **4c** ($CD_3CN$) δ 6.12 (m, H-3), 6.09 (s, $C_6H_3Me_3$), 5.04, (m, H-2,4), 3.62 (s, $CO_2Me$), 3.46 (m, H-1,5), 3.2 (m, H-6), 2.63 (d, CH), 2.17 (s, $C_6H_3Me_3$).

reactions with the iron analogues are orbital-controlled and often give diene products;[2] apparently, however, this is not always the case.[1,7] It may be possible to force double addition to the benzene in **1** by using an arene with more severe steric congestion, *e.g.*, $C_6Et_6$. Even if this proves not to be feasible, arene monofunctionalization will have been achieved if the ring(s) in **3** can be oxidatively cleaved. Since complexes **3** are electron-rich, removal of the *endo* H-6 or H-12 with trityl cation (*via* an electron transfer mechanism[2]) suggests a route to difunctionalized arenes. It is apparent, therefore, that $[(\text{arene})(\text{arene}')\text{Ru}]^{2+}$ complexes hold significant promise for synthetically useful transformations.

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