Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2011, **21**, 163–164
Mendeleev Communications

Arene exchange in the anthracene ruthenium complex $[(C_5Me_4CH_2OMe)Ru(C_{14}H_{10})]^+$

Andrew I. Konovalov, Eduard E. Karslyan, Dmitry S. Perekalin, Yulia V. Nelyubina, Pavel V. Petrovskii and Alexander R. Kudinov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5085; e-mail: arkudinov@ineos.ac.ru

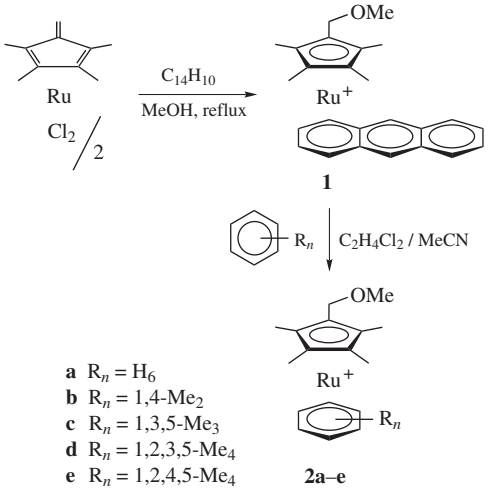
DOI: 10.1016/j.mencom.2011.04.018

Arene exchange in the anthracene ruthenium complex $[(C_5Me_4CH_2OMe)Ru(C_{14}H_{10})]^+$ **1** for alkylbenzenes gives the cations $[(C_5Me_4CH_2OMe)Ru(C_6Me_nH_{6-n})]^+$ in 70–80% yields; the structure of [**1**][PF_6] was established by X-ray diffraction analysis.

The arene ruthenium complexes $[(C_5R_5)Ru(arene)]^+$ attract a considerable attention due to their application in organic synthesis[1] and supramolecular chemistry.[2] Naphthalene and anthracene complexes are particularly interesting because they easily exchange the coordinated polyarene[3] for various ligands providing a general approach to $(C_5R_5)Ru$ complexes. For example, Hintermann *et al.*[4] have recently shown that the replacement of naphthalene in the $[(C_5H_5)Ru(C_{10}H_8)]^+$ cation by 2-electron ligands leads to $[(C_5H_5)RuL_3]^+$ complexes. We have found that $[(C_5H_5)Ru(C_{10}H_8)]^+$ also reacts with cyclopentadienes[5] and arenes[6] giving ruthenocenes and $[(C_5H_5)Ru(arene)]^+$ cations, respectively. Similar reaction with tricarbollide anions affords 11- and 12-vertex ruthenacarboranes.[7]

Recently, Fairchild and Holman have prepared cations $[(C_5Me_4CH_2OR)Ru(arene)]^+$ containing functionalized cyclopentadienyl ligand by reaction of the fulvene complex[8] $[(C_5Me_4CH_2)RuCl_2]_2$ with arenes in the presence of alcohols.[9] Following this method, we synthesized the anthracene complex $[(C_5Me_4CH_2OMe)Ru(C_{14}H_{10})]^+$ **1** by the reaction of $[(C_5Me_4CH_2)RuCl_2]_2$ with anthracene in refluxing MeOH (Scheme 1).†

We found that cation **1** exchanges the anthracene ligand for other arenes. In particular, the reaction of **1** with benzene or its methylated derivatives in refluxing 1,2-dichloroethane gives complexes $[(C_5Me_4CH_2OMe)Ru(arene)]^+$ **2a–e**.‡ The exchange is facilitated by the addition of MeCN (~50 equiv.) presumably due to the formation of reactive intermediates (*e.g.*, $[(C_5Me_4CH_2OMe)Ru(MeCN)_3]^+$).§ Noteworthy, the arene exchange in the related naphthalene complex $[(C_5Me_4CH_2OMe)Ru(C_{10}H_8)]^+$ proceeds much slower; *e.g.*, the reaction with C_6H_6 takes 12 h *vs.* 4 h in the case of the anthracene analogue.



Scheme 1

Cations **1** and **2a–e** were isolated as salts with the PF_6^- anion and characterized by ^{1}H NMR spectroscopy and elemental analysis.

† $[(C_5Me_5)RuCl_2]_2$ (90 mg, 0.15 mmol) was dissolved in CH_2Cl_2 (15 ml) and stirred for 1 h in air resulting in the formation of the fulvene complex $[(C_5Me_4CH_2)RuCl_2]_2$. The solvent was removed *in vacuo*, and the flask was filled with argon. Anthracene (534 mg, 3 mmol) and MeOH (15 ml) were added and the resulting orange suspension was refluxed with stirring for 5 h. The reaction mixture was opened to air and evaporated. The residue was dissolved in H_2O (10 ml), filtered, and KPF_6 (184 mg, 1 mmol) was added to the aqueous solution producing the orange precipitate, which was collected by filtration. The crude product was eluted through a short alumina column (4 cm) with acetone. Reprecipitation from acetone by Et_2O gives [**1**][PF_6] as an orange solid. Yield, 125 mg (71%). ^{1}H NMR (acetone-d_6) δ: 1.61 (s, 6H, Me), 1.62 (s, 6H, Me), 3.26 (s, 3H, OMe), 3.97 (s, 2H, CH_2), 6.44 (m, 2H), 7.23 (m, 2H), 7.57 (m, 2H), 8.03 (m, 2H), 8.53 (s, 2H). Found (%): C, 50.75; H, 4.86. Calc. for $C_{25}H_{27}F_6OPRu$ (%): C, 50.93; H, 4.62.

‡ An orange solution of [**1**][PF_6] (30 mg, 0.05 mmol) and arene (1 mmol) in 1,2-dichloroethane (5 ml) and MeCN (100 μl) was refluxed until it became colorless (the reaction times are given below). The solvent was evaporated *in vacuo*, and the residue was washed with Et_2O (5 ml), dissolved in Me_2CO (1 ml) and eluted through a short alumina column (2 cm). The resulting colorless solution was evaporated, and the solid was reprecipitated from Me_2CO/Et_2O to give white solids [**2a–e**][PF_6].

[**2a**][PF_6]: 4 h, 17 mg (70%). ^{1}H NMR (acetone-d_6) δ: 2.08 (s, 6H, Me), 2.09 (s, 6H, Me), 3.35 (s, 3H, OMe), 4.27 (s, 2H, CH_2), 6.09 (s, 6H, C_6H_6). *Cf.* ref. 9.

[**2b**][PF_6]: 4 h, 21 mg (80%). ^{1}H NMR (acetone-d_6) δ: 2.00 (s, 6H, 2Me), 2.02 (s, 6H, 2Me), 2.27 (s, 6H, $C_6H_4\mathit{Me}_2$), 3.37 (s, 3H, OMe), 4.21 (s, 2H, CH_2), 5.98 (s, 4H, C_6H_4). Found (%): C, 44.12; H, 5.36. Calc. for $C_{19}H_{27}F_6OPRu$ (%): C, 44.10; H, 5.26.

[**2c**][PF_6]: 8 h, 20 mg (76%). ^{1}H NMR (acetone-d_6) δ: 1.96 (s, 6H, 2Me), 1.97 (s, 6H, 2Me), 2.24 (s, 9H, $C_6H_3\mathit{Me}_3$), 3.37 (s, 3H, OMe), 4.17 (s, 2H, CH_2), 5.88 (s, 3H, $C_6\mathit{H}_3Me_3$). Found (%): C, 45.49; H, 5.64. Calc. for $C_{20}H_{29}F_6OPRu$ (%): C, 45.20; H, 5.50.

[**2d**][PF_6]: 18 h, 18 mg (67%). ^{1}H NMR (acetone-d_6) δ: 1.91 (s, 12H, 4Me), 2.14 (s, 3H, $C_6H_2\mathit{Me}_4$), 2.21 (s, 3H, $C_6H_2\mathit{Me}_4$), 2.24 (s, 6H, $C_6H_2\mathit{Me}_4$), 3.36 (s, 3H, OMe), 4.11 (s, 2H, CH_2), 5.88 (s, 2H, $C_6\mathit{H}_2Me_4$). Found (%): C, 46.37; H, 5.80. Calc. for $C_{21}H_{31}F_6OPRu$ (%): C, 46.24; H, 5.73.

[**2e**][PF_6]: 18 h, 19 mg (70%). ^{1}H NMR (acetone-d_6) δ: 1.90 (s, 12H, 4Me), 2.19 (s, 12H, $C_6H_2\mathit{Me}_4$), 3.09 (s, 3H, OMe), 4.12 (s, 2H, CH_2), 5.92 (s, 2H, $C_6\mathit{H}_2Me_4$). Found (%): C, 46.71; H, 5.38. Calc. for $C_{21}H_{31}F_6OPRu$ (%): C, 46.24; H, 5.73.

§ However, even in the presence of MeCN, the reaction of **1** with C_6Me_6 is very slow and is not complete after 24 h of reflux.

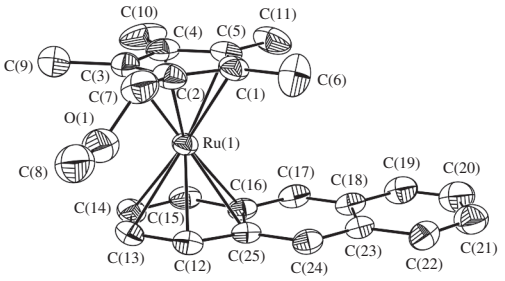


Figure 1 Structure of cation **1** with thermal ellipsoids at a 50% probability level. All hydrogen atoms and the disordered part of the $C_5Me_4CH_2OMe$ ligand are omitted for clarity. Selected interatomic distances (Å): Ru(1)–C(1) 2.167(4), Ru(1)–C(2) 2.163(4), Ru(1)–C(3) 2.153(4), Ru(1)–C(4) 2.178(4), Ru(1)–C(5) 2.173(4), Ru(1)–C(12) 2.207(4), Ru(1)–C(13) 2.217(4), Ru(1)–C(14) 2.223(4), Ru(1)–C(15) 2.210(4), Ru(1)–C(16) 2.283(4), Ru(1)–C(25) 2.289(4).

It is interesting to note that the ^{1}H NMR signals of Me groups in **1** (1.61, 1.62 ppm) are upfield shifted, as compared to those in **2a** (2.08, 2.09 ppm), due to anisotropic shielding caused by the anthracene non-coordinated rings.

The structure of [**1**][PF_6] was established by single-crystal X-ray diffraction (Figure 1).¶ The geometry of cation **1** is generally similar to that of benzene complex **2a**.[9] In particular, the Ru···C_5 distances in **1** (1.795 Å) and **2a** (1.805 Å) are close. The slightly longer Ru···C_6 distance in **1** (1.728 Å), as compared to that in **2a** (1.706 Å), correlates with a weaker binding of the anthracene ligand *vs.* benzene. In accordance with the general tendency for polyarene complexes, the coordinated C_6 ring is folded along the C(12)···C(15) line by 4.4° and the distances from the ruthenium atom to the bridgehead carbons Ru–C(16) and Ru–C(25) (av. 2.286 Å) are longer than other Ru–C(anthracene) bonds (av. 2.214 Å).

In summary, we have synthesized anthracene ruthenium complex **1** containing the functionalized cyclopentadienyl ligand $C_5Me_4CH_2OMe$. The arene exchange in **1** provides the cations [$(C_5Me_4CH_2OMe)Ru(arene)]^+$.

This work was supported by the Russian Foundation for Basic Research (grant no. 11-03-01153-a) and Grant of the President of the Russian Federation for Young Scientists (grant no. MK-684.2011.3).

¶ *Crystallographic data*. Crystals of [**1**][PF_6] ($C_{25}H_{27}F_6OPRu$, M = 589.51) are monoclinic, space group $P2_1/c$, at 100 K: a = 8.3496(4), b = 17.6256(9) and c = 16.4397(8) Å, β = 94.614(1)°, V = 2411.5(2) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.624 g cm^{-3}, μ(MoKα) = 7.79 cm^{-1}, F(000) = 1192. Intensities of 28429 reflections were measured with a Bruker SMART 1000 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, 2θ < 58°] and 6410 independent reflections (R_{int} = 0.0253) were used in a further refinement. Structure was solved by a direct method and refined by the full-matrix least-squares against F^2 in an anisotropic approximation for non-hydrogen atoms. The H(C) atom positions were calculated and refined in an isotropic approximation in a riding model with the U_{iso}(H) parameters equal to 1.2 $U_{eq}(C_i)$, for methyl groups equal to 1.5$U_{eq}(C_{ii})$, where $U(C_i)$ and $U(C_{ii})$ are respectively the equivalent thermal parameters of the carbon atoms to which corresponding H atoms are bonded. The PF_6^- anion and the Cp* moiety are disordered by two positions in a ratio of 50:50; however, we failed to model the disorder of the atoms of the Cp ring due to the proximity of the positions of the two components. For [**1**][PF_6] the refinement converged to wR_2 = 0.1319 and GOF = 1.056 for all independent reflections [R_1 = 0.0476 was calculated against F for 5372 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

CCDC 806129 contains 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. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2011.

References

1 (*a*) A. J. Pearson and D. V. Ciurea, *J. Org. Chem.*, 2008, **73**, 760; (*b*) F. Ch. Pigge, R. Dhanya and E. R. Hoefgen, *Angew. Chem. Int. Ed.*, 2007, **46**, 2887; (*c*) A. Schmid and T. Lindel, *Angew. Chem. Int. Ed.*, 2004, **43**, 1581; (*d*) F. C. Pigge and J. J. Coniglio, *Curr. Org. Chem.*, 2001, **5**, 757 and references therein.

2 (*a*) R. M. Fairchild, A. I. Joseph, K. T. Holman, H. A. Fogarty, T. Brotin, J.-P. Dutasta, C. Boutin, G. Huber and P. Berthault, *J. Am. Chem. Soc.*, 2010, **132**, 15505; (*b*) L. Cuesta, D. Gross, V. M. Lynch, Z. Ou, W. Kajonkijya, K. Ohkubo, S. Fukuzumi, K. M. Kadish and J. L. Sessler, *J. Am. Chem. Soc.*, 2007, **129**, 11696; (*c*) R. M. Fairchild and K. T. Holman, *J. Am. Chem. Soc*., 2005, **127**, 16364.

3 A. M. McNair and K. R. Mann, *Inorg. Chem.*, 1986, **25**, 2519.

4 L. Hintermann, L. Xiao, A. Labonne and U. Englert, *Organometallics*, 2009, **28**, 5739.

5 E. E. Karslyan, A. I. Konovalov, D. S. Perekalin, P. V. Petrovskii and A. R. Kudinov, *Izv. Akad. Nauk, Ser. Khim*., 2008, 1997 (*Russ. Chem. Bull., Int. Ed.*, 2008, **57**, 2032).

6 (*a*) D. S. Perekalin, E. E. Karslyan, P. V. Petrovskii, Y. V. Nelyubina, K. A. Lyssenko, A. S. Kononikhin, E. N. Nikolaev and A. R. Kudinov, *Chem. Eur. J.*, 2010, **16**, 8466; (*b*) E. E. Karslyan, D. S. Perekalin, P. V. Petrovskii, A. O. Borisova and A. R. Kudinov, *Izv. Akad. Nauk, Ser. Khim.*, 2009, 572 (*Russ. Chem. Bull., Int. Ed*., 2009, **58**, 585); (*c*) E. E. Karslyan, D. S. Perekalin, P. V. Petrovskii, K. A. Lyssenko and A. R. Kudinov, *Izv. Akad. Nauk, Ser. Khim*., 2008, 2159 (*Russ. Chem. Bull., Int. Ed*., 2008, **57**, 2201).

7 D. S. Perekalin, E. A. Trifonova, I. V. Glukhov, J. Holub and A. R. Kudinov, *Czech. Coll. Chem. Commun*., 2010, **75**, 1139.

8 (*a*) L. Fan, C. Wei, F. I. Aigbirhio, M. L. Turner, O. V. Gusev, L. N. Morozova, D. R. T. Knowles and P. M. Maitlis, *Organometallics*, 1996, **15**, 98; (*b*) L. Fan, M. L. Turner, M. B. Hursthouse, K. M. A. Malik, O. V. Gusev and P. M. Maitlis, *J. Am. Chem. Soc.*, 1994, **116**, 385.

9 R. M. Fairchild and K. T. Holman, *Organometallics*, 2008, **27**, 1823.

Received: 18th January 2011; Com. 11/3662