Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2013, **23**, 133–134
Mendeleev Communications

Synthesis and reactivity of the cyclohexadienyl ruthenium complex $[(\eta^5\text{-}C_6H_7)Ru(MeCN)_3]^+$ with labile acetonitrile ligands

Evgeniya A. Trifonova, Natalia L. Loskutova, Dmitry S. Perekalin, Yulia V. Nelyubina and Alexander R. Kudinov*

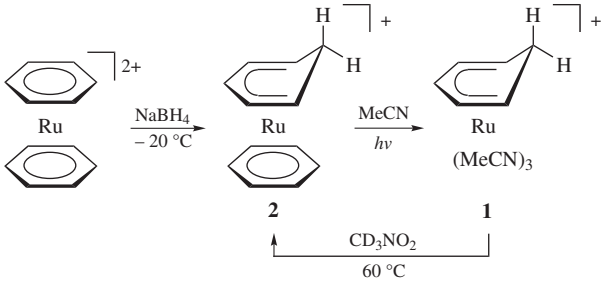
A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5085; e-mail: arkudinov@ineos.ac.ru

DOI: 10.1016/j.mencom.2013.05.003

The UV irradiation of $[(\eta^5\text{-}C_6H_7)Ru(C_6H_6)]^+$ in MeCN gives the title complex, in which acetonitrile ligands are readily replaced by cyclopentadienide and tricarbollide anions; the structure of the tricarbollide derivative 1-$(\eta^5\text{-}C_6H_7)$-12-Bu^{t}NH-1,2,4,12-$RuC_3B_8H_{10}$ was established by X-ray diffraction analysis.

Due to facile replacement of labile acetonitrile ligands, the cyclopentadienyl ruthenium complexes $[(C_5R_5)Ru(MeCN)_3]^+$ are widely used in organometallic synthesis[1] and catalysis.[2,3] However, little is known about analogous cyclohexadienyl complexes $[(\eta^5\text{-}C_6R_7)Ru(MeCN)_3]^+$. Only the 6,6-dimethyl-substituted derivative $[(\eta^5\text{-}C_6H_5Me_2)Ru(MeCN)_3]^+$ was briefly described previously.[4] Here we report the synthesis of parent complex $[(\eta^5\text{-}C_6H_7)Ru(MeCN)_3]^+$ **1** and its reactions with cyclopentadienide and tricarbollide anions.

The reduction of bis(benzene)ruthenium dication $[Ru(C_6H_6)_2]^{2+}$ by $NaBH_4$ at –20 °C gives cyclohexadienyl complex $[(\eta^5\text{-}C_6H_7)\text{-}Ru(C_6H_6)]^+$ **2** in 65% yield (Scheme 1).† Further ultraviolet irradiation of **2** in MeCN results in the replacement of a benzene ligand to afford acetonitrile complex **1** in ~75% yield. A similar procedure was used previously to obtain the cyclopentadienyl congeners $[(C_5R_5)Ru(MeCN)_3]^+$ (R = H, Me).[5] Complex **1** is air-sensitive, and it decomposes within several days in air even in a solid state. Under an argon atmosphere, **1** is stable as a solid,



Scheme 1

but it decomposes in a nitromethane solution giving starting benzene complex **2**. This process is slow at room temperature (10% conversion in four days) and fast at 60 °C (100% in 4 h). In overall, **1** is less thermally stable than $[(C_5R_5)Ru(MeCN)_3]^+$ and $[(\eta^5\text{-}C_6H_5Me_2)Ru(MeCN)_3]^+$ (both can be heated at 100 °C)[4,5] but more stable than its iron analogue $[(\eta^5\text{-}C_6H_7)Fe(MeCN)_3]^+$ (which decomposes at 20 °C).[6]

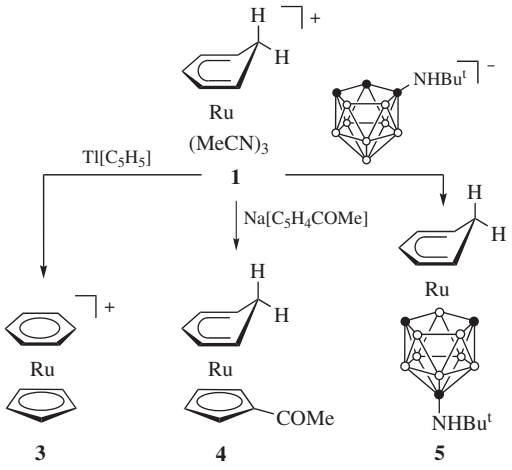
To explore the synthetic utility of cation **1**, we studied its reactions with anionic ligands. Unexpectedly, the reaction with $Tl[C_5H_5]$ gives benzene complex $[(C_6H_6)Ru(C_5H_5)]^+$ **3** (54%) as a result of formal hydride abstraction from the expected product $(\eta^5\text{-}C_6H_7)Ru(C_5H_5)$ (Scheme 2).‡ On the other hand, the less

† [**1**]PF_6: Under an argon atmosphere, a solution of [**2**]PF_6 (1 g, 2.48 mmol) in 200 ml of MeCN was irradiated for 4 h using an immersed 250 W UV lamp with a quartz jacket and water cooling. The solution was constantly bubbled with argon to maintain inert conditions. After irradiation, the solvent was evaporated *in vacuo*, and the solid residue was washed with Et_2O and dried to produce 836 mg (75%) of yellow air-sensitive powder of [**1**]PF_6. ^{1}H NMR (CD_3CN) δ: 5.76 (t, 1H, C_6H_7, *J* 5 Hz), 4.37 (t, 2H, C_6H_7, *J* 5 Hz), 2.44 (m, 1H, C_6H_7), 2.33 (t, 2H, C_6H_7, *J* 5 Hz), 1.94 (s, 9H, MeCN), 1.57 (d, 1H, C_6H_7, *J* 13 Hz). ^{1}H NMR (CD_3NO_2) δ: 6.02 (br. s, 1H, C_6H_7), 4.61 (br. s, 2H, C_6H_7), 2.79 (br. s, 1H, C_6H_7), 2.66 (br. s, 2H, C_6H_7), 2.59 (s, 9H, MeCN), 1.81 (d, 1H, C_6H_7, *J* 10 Hz). ^{13}C NMR (CD_3NO_2) δ: 90.45, 69.65, 32.01, 22.84 (C_6H_7), 2.14 (MeCN). HRMS (ESI), *m/z*: 263.0130 (M – MeCN – PF_6) with the expected isotopic distribution; calc. for $[C_{10}H_{13}N_2Ru]^+$, *m/z*: 263.0119.

[**2**]PF_6: Under an argon atmosphere, a suspension of $[Ru(C_6H_6)_2](BF_4)_2$ (1.508 g, 3.50 mmol) and $NaBH_4$ (133 mg, 3.50 mmol) in THF (15 ml) was stirred at about –20 °C for 2 h. The mixture was then warmed to room temperature and opened to air. HBF_4 (0.2 ml, 48% aqueous solution) was added, and the mixture was stirred for 5 min. The solvent was evaporated *in vacuo*, and the solid residue was extracted with CH_2Cl_2. The extract was evaporated, and the product was reprecipitated from CH_2Cl_2 by Et_2O to give 784 mg (65%) of faint yellow air-stable crystals of [**2**]BF_4. The salt [**2**]PF_6 was quantitatively precipitated from an aqueous solution of [**2**]BF_4 by the addition of KPF_6. ^{1}H NMR (acetone-d_6) δ: 6.60 (t, 1H, C_6H_7, *J* 6 Hz), 6.42 (s, 6H, C_6H_6), 5.26 (t, 2H, C_6H_7, *J* 6 Hz), 3.78 (t, 2H, C_6H_7, *J* 6 Hz), 2.72 (m, 1H, C_6H_7), 2.33 (d, 1H, C_6H_7, *J* 13 Hz). Found (%): C, 38.02; H, 3.27. Calc. for $C_{12}H_{13}F_6PRu\cdot(Me)_2CO$ (%): C, 37.51; H, 3.73. This compound was prepared earlier by a different method.[9] For similar reduction procedures, see also ref. 10.

‡ [**3**]PF_6: Under an argon atmosphere, a suspension of [**1**]PF_6 (45 mg, 0.1 mmol) and $Tl[C_5H_5]$ (41 mg, 0.15 mmol) in THF (2 ml) was stirred overnight. The mixture was opened to air, the solvent was evaporated *in vacuo*, and the residue was extracted with Et_2O. This extract did not contain any noticeable amount of the expected $(\eta^5\text{-}C_6H_7)Ru(C_5H_5)$. The remaining solid was dissolved in acetone/CH_2Cl_2 (1 : 1) and filtered through a short (3 cm) alumina column. The solution was evaporated *in vacuo*, and the residue was reprecipitated from CH_2Cl_2 by Et_2O to give 21 mg (54%) of white air-stable crystals of [**3**]PF_6. ^{1}H NMR (acetone-d_6) δ: 6.33 (s, 6H, C_6H_6), 5.53 (s, 5H, Cp), *cf.* ref. 5.

4: Under an argon atmosphere, a solution of [**1**]PF_6 (59 mg, 0.13 mmol) and $Na[C_5H_4COMe]\cdot THF$ (34 mg, 0.17 mmol) in THF (2 ml) was stirred overnight. The mixture was opened to air, and the solvent was evaporated *in vacuo*. The residue was extracted with Et_2O/CH_2Cl_2 (2 : 1) and filtered through a short (3 cm) alumina column. The solution was evaporated *in vacuo*, and the solid was crystallized from pentane at –78 °C to form 25 mg (67%) of almost colourless air-stable crystals of **4**. ^{1}H NMR (acetone-d_6) δ: 5.87 (t, 1H, C_6H_7, *J* 6 Hz), 5.31 (t, 2H, C_5H_4COMe, *J* 4 Hz), 4.87 (t, 2H, C_5H_4COMe, *J* 4 Hz), 4.52 (t, 2H, C_6H_7, *J* 6 Hz), 2.61 (t, 2H, C_6H_7, *J* 6 Hz), 2.46 (m, 1H, C_6H_7), 2.34 (s, 3H, Me), 2.10 (d, 1H, C_6H_7, *J* 6 Hz). Found (%): C, 54.47; H, 4.99. Calc. for $C_{13}H_{14}ORu$ (%): C, 54.34; H, 4.91.



Scheme 2

reactive acetyl-substituted cyclopentadienide $Na[C_5H_4COMe]$ converts **1** into cyclohexadienyl complex $(\eta^5\text{-}C_6H_7)Ru(C_5H_4COMe)$ **4** (67%) without further hydride abstraction. Similar reaction with the tricarbollide anion $[7\text{-}Bu^tNH\text{-}7,8,9\text{-}C_3B_8H_{10}]^-$ (which is isolobal to cyclopentadienides) affords 12-vertex *closo*-ruthenacarborane $1\text{-}(\eta^5\text{-}C_6H_7)\text{-}12\text{-}Bu^tNH\text{-}1,2,4,12\text{-}RuC_3B_8H_{10}$ **5** in 85% yield. Note that the coordination of a ruthenium atom with the tricarbollide anion is accompanied by a typical room-temperature polyhedral rearrangement.[7]

The air-sensitive complex $[\mathbf{1}]PF_6$ was characterized by ^1H and ^{13}C NMR spectra and a high-resolution mass spectrum. Compounds **4** and **5** were characterized by ^1H NMR spectroscopy and elemental analysis. The structure of **5** was established by X-ray diffraction analysis (Figure 1).[§] The ruthenacarborane framework of **5** is generally similar to that of its cyclopentadienyl analogue $1\text{-}C_5Me_5\text{-}12\text{-}Bu^tNH\text{-}1,2,4,12\text{-}RuC_3B_8H_{10}$ with $Ru\cdots C_2B_3$(plane) distances of 1.61 and 1.58 Å, respectively.[8] However, compound **5** exhibits a significant *trans*-influence of the carborane and cyclohexadienyl ligands. In particular, the Ru(1)–C(5M) bond (2.177 Å) is noticeably shorter than the formally equivalent Ru(1)–C(1M) bond (2.230 Å) due to the *trans*-influence of the C(4) cage carbon atom. Accordingly, the Ru(1)–C(4) bond (2.239 Å) is noticeably longer than the formally equivalent Ru(1)–C(2) bond (2.179 Å). However, the symmetrical structure of **5** is observed in solution according to ^1H and ^{11}B NMR spectra.

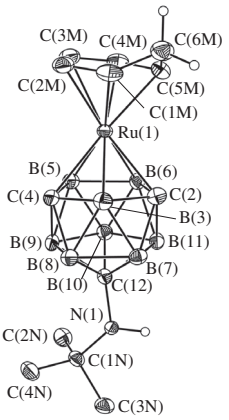


Figure 1 Molecular structure of compound **5** with ellipsoids at a 50% probability level. The disordered part of the molecule and all hydrogen atoms except those of CH_2 and NH groups are omitted for clarity. Selected interatomic distances (Å): Ru(1)–C(2) 2.179(3), Ru(1)–B(3) 2.174(4), Ru(1)–C(4) 2.238(3), Ru(1)–B(5) 2.182(3), Ru(1)–B(6) 2.156(3), Ru(1)–C(1M) 2.230(3), Ru(1)–C(2M) 2.189(3), Ru(1)–C(3M) 2.210(3), Ru(1)–C(4M) 2.178(3), Ru(1)–C(5M) 2.177(3).

Thus, we synthesized cyclohexadienyl ruthenium complex **1** with labile acetonitrile ligands and demonstrated its application as a synthon of the $[Ru(\eta^5\text{-}C_6H_7)]^+$ fragment.

We are grateful to A. Naumova and A. Mikhailov for their assistance. This work was supported in part by the Ministry of Education and Science of the Russian Federation (grant no. 8435).

References

1 (*a*) E. Becker, V. Stingl, K. Mereiter and K. Kirchner, *Organometallics*, 2006, **25**, 4166; (*b*) A. L. Osipov, D. V. Gutsulyak, L. G. Kuzmina, J. A. K. Howard, D. A. Lemenovskii, G. Süss-Fink and G. I. Nikonov, *J. Organomet. Chem.*, 2007, **692**, 5081; (*c*) P. C. Kunz, I. Thiel, A. L. Noffke, G. J. Reiß, F. Mohr and B. Spingler, *J. Organomet. Chem.*, 2012, **697**, 33; (*d*) J. Dubarle-Offner, M. R. Axet, L. M. Chamoreau, H. Amouri and A. L. Cooksy, *Organometallics*, 2012, **31**, 4429; (*e*) Z. Sahli, N. Derrien, S. Pascal, B. Demerseman, T. Roisnel, F. Barrière, M. Achard and C. Bruneau, *Dalton Trans.*, 2011, **40**, 5625.

2 (*a*) L. Hintermann, T. T. Dang, A. Labonne, T. Kribber, L. Xiao and P. Naumov, *Chem. Eur. J.*, 2009, **15**, 7167; (*b*) M. Zhang, H.-F. Jiang, H. Neumann, M. Beller and P. H. Dixneuf, *Angew. Chem. Int. Ed.*, 2009, **48**, 1681; (*c*) M. Austeri, D. Rix, W. Zeghida and J. Lacour, *Org. Lett.*, 2011, **13**, 1394; (*d*) S. Murugesan, F. Jiang, M. Achard, C. Bruneau and S. Dérien, *Chem. Commun.*, 2012, **48**, 6589.

3 (*a*) *Ruthenium Catalysts and Fine Chemistry*, eds. C. Bruneau and P. H. Dixneuf, in *Top. Organomet. Chem.*, Springer, Berlin, 2004, vol. 11; (*b*) B. M. Trost, M. U. Frederiksen and M. T. Rudd, *Angew. Chem. Int. Ed.*, 2005, **44**, 6630.

4 P. T. Dimauro and P. T. Wolczanski, *Polyhedron*, 1995, **14**, 149.

5 (*a*) T. P. Gill and K. R. Mann, *Organometallics*, 1982, **1**, 485; (*b*) J. L. Schrenk, A. M. McNair, F. B. McCormick and K. R. Mann, *Inorg. Chem.*, 1986, **25**, 3501.

6 P. Zanello, R. H. Herber, A. R. Kudinov, M. Corsini, F. Fabrizi de Biani, I. Nowik, D. A. Loginov, M. M. Vinogradov, L. S. Shul'pina, I. A. Ivanov and A. V. Vologzhanina, *J. Organomet. Chem.*, 2009, **694**, 1161.

7 (*a*) B. Štíbr, *J. Organomet. Chem.*, 2005, **690**, 2694; (*b*) D. S. Perekalin, K. A. Lyssenko, P. V. Petrovskii, J. Holub, B. Štíbr and A. R. Kudinov, *J. Organomet. Chem.*, 2005, **690**, 2775; (*c*) D. S. Perekalin, E. A. Trifonova, I. V. Glukhov, J. Holub and A. R. Kudinov, *Czech. Coll. Chem. Commun.*, 2010, **75**, 1139.

8 J. Holub, B. Grüner, D. S. Perekalin, D. G. Golovanov, K. A. Lyssenko, P. V. Petrovskii, A. R. Kudinov and B. Štíbr, *Inorg. Chem.*, 2005, **44**, 1655.

9 N. Oshima, H. Suzuki and Y. Moro-oka, *Inorg. Chem.*, 1986, **25**, 3407.

10 (*a*) M. I. Rybinskaya, V. S. Kaganovich and A. R. Kudinov, *J. Organomet. Chem.*, 1982, **235**, 215; (*b*) S. L. Grundy, A. J. Smith, H. Adams and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1984, 1747.

11 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.

Received: 1st March 2013; Com. 13/4078

5: Under an argon atmosphere, a solution of $[\mathbf{1}]PF_6$ (112 mg, 0.25 mmol) and $Tl[7\text{-}Bu^tNH\text{-}7,8,9\text{-}C_3B_8H_{10}]$ (135 mg, 0.38 mmol) in THF (5 ml) was stirred overnight. The mixture was opened to air, and the solvent was evaporated *in vacuo*; the residue was extracted with Et_2O. This solution was slowly evaporated in a flow of argon to give 82 mg (85%) of light yellow air-stable crystals of **5**. ^1H NMR ($CDCl_3$) δ: 5.97 (t, 1H, C_6H_7, J 5 Hz), 4.74 (dd, 2H, C_6H_7, J 7 and 5 Hz), 3.07 (t, 2H, C_6H_7, J 7 Hz), 2.81 (m, 2H, C_6H_7), 2.47 (s, 1H, NH), 2.00 (br. s, 2H, CH), 1.31 (s, 9H, Bu^t). ^{11}B NMR ($CDCl_3$) δ: –9.6 (2B), –14.2 (1B), –16.0 (2B), –20.2 (1B), –24.1 (2B). Found (%): C, 43.22; H, 7.47; B, 20.55. Calc. for $C_{13}B_8H_{27}NRu\cdot 0.5Et_2O$ (%): C, 42.69; H, 7.64; B, 20.50.

§ *Crystalographic data for* **5**. Crystals of **5** ($C_{13}H_{27}B_8NRu$, M = 384.91) are monoclinic, space group $P2_1/n$, at 100 K: a = 9.1474(4), b = 16.8022(7) and c = 11.9053(5) Å, β = 108.9590(10)°, V = 1730.54(13) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.477 g cm^{-3}, μ(MoKα) = 8.97 cm^{-1}, F(000) = 784. Intensities of 20 851 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, $2\theta < 58°$], and 4597 independent reflections (R_{int} = 0.0232) were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The refinement converged to wR_2 = 0.1317 and GOF = 1.047 for all the independent reflections [R_1 = 0.0384 was calculated against F for 4284 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.[11]

CCDC 924089 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, 2013.