Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2011, **21**, 82–83
Mendeleev Communications

Convenient synthesis of the ruthenium complexes CpRu(diene)X (X = Cl, Br, I) by naphthalene substitution in $[CpRu(C_{10}H_8)]^+$

Dmitry S. Perekalin, Eduard E. Karslyan, Alexandra O. Borissova 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.2011.03.007

The replacement of naphthalene ligand in the ruthenium complex $[CpRu(C_{10}H_8)]^+$ by halide anions in the presence of 1,5-cyclooctadiene (cod) or norbornadiene (nbd) gives important synthetic precursors CpRu(cod)X and CpRu(nbd)X (X = Cl, Br, I) in 60–90% yield; the structure of CpRu(nbd)Br was determined by X-ray diffraction.

Cyclopentadienyl ruthenium complexes $(C_5R_5)Ru(diene)X$ attract a considerable attention due to their wide application in organometallic synthesis and catalysis.[1] For example, compound CpRu(cod)Cl **1a** was recently used for the preparation of ruthenium bioconjugates with neuropeptide enkephalin[2] and as a catalyst of Alder–ene reaction in total synthesis of natural products.[3]

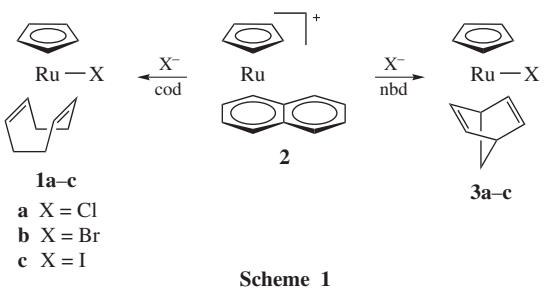
Pentamethylsubstituted compounds Cp*Ru(diene)X are easily accessible *via* reactions of universal precursor $[Cp^*RuCl]_4$ with dienes.[4] Unfortunately, the unsubstituted congeners CpRu(diene)X are much less available. In particular, the chloride **1a** was synthesized by the complicated four-step procedures (1)[5] or (2).[6]

$$RuCl_3 \cdot 3H_2O \rightarrow [(cod)RuCl_2]_x \rightarrow [(cod)RuH(NH_2NMe_2)_3]^+ \rightarrow CpRu(cod)H \rightarrow \mathbf{1a} \quad (1)$$

$$RuCl_3 \cdot 3H_2O \rightarrow CpRu(PPh_3)_2Cl \rightarrow CpRu(allyl)Cl_2 \rightarrow CpRu(allyl)(Me)Cl \rightarrow \mathbf{1a} \quad (2)$$

One of the effective methods for the synthesis of organometallic compounds is replacement of the naphthalene ligand. It was successfully employed for the preparation of chromium,[7] manganese,[8] iron,[9] cobalt,[10] ruthenium,[11] rhodium,[12] and iridium[13] complexes. Recently, Kündig and Monnier reported a simple synthesis of the ruthenium naphthalene complex $[CpRu(C_{10}H_8)]^+$ **2**.[14] Hintermann *et al.*[15] have further reported that **2** reacts with 2-electron ligands giving half-sandwich cations $[CpRuL_3]^+$. We have shown that **2** also reacts with arenes giving $[CpRu(arene)]^+$ complexes.[16] This method can be applied for labeling of aromatic amino acids and small peptides under near-physiological conditions.[17] The reaction of **2** with cyclopentadienes affords substituted ruthenocenes.[18] Herein we report the convenient synthesis of CpRu(cod)X and CpRu(nbd)X complexes *via* naphthalene substitution in **2**.

The reaction of **2** (as BF_4^- or PF_6^-[†] salt) with $[Bu_4N]Cl$ and 1,5-cyclooctadiene in CH_2Cl_2 gives complex **1a** in *ca.* 90% yield (Scheme 1).[‡] The bromide and iodide congeners **1b**,**c** were prepared in a similar way. Analogous reaction of **2** with $[Bu_4N]X$ and norbornadiene yields complexes CpRu(nbd)X **3a–c**.[§] For a large-scale synthesis of the chlorides **1a** and **3a** it is more economical to use dry LiCl in THF as a chloride source.



Scheme 1

Compounds **1a–c** and **3a–c** were characterized by ^1H NMR spectroscopy, as well as by elemental analysis for the previously

† Complex [**2**][PF_6] is commercially available from Aldrich (product no. 685054).

‡ A solution of [**2**][BF_4] (19 mg, 0.05 mmol),[14] 1,5-cyclooctadiene (0.03 ml, 0.25 mmol, 5-fold excess), and $[Bu_4N]X$ (0.05 mmol) in 5 ml of CH_2Cl_2 was stirred under argon overnight. The flask was opened to air and the solvent was removed *in vacuo*. The residue was extracted with Et_2O (5×10 ml) and the extract was evaporated. The resulting solid was washed with hexane and dried *in vacuo* to give pure products. Compounds **1a–c** are stable in air in the solid state but decompose in solution within 1 day.

1a: yellow, 14 mg (90%). ^1H NMR ($CDCl_3$) δ: 2.05 (m, 6H, CH_2), 2.60 (m, 2H, CH_2), 4.39 (m, 2H, CH), 4.95 (s, 5H, Cp), 5.29 (m, 2H, CH); *cf.* ref. 5.

1b: yellow-orange, 16 mg (92%). ^1H NMR ($CDCl_3$) δ: 2.08 (m, 6H, CH_2), 2.67 (m, 2H, CH_2), 4.46 (m, 2H, CH), 4.98 (s, 5H, Cp), 5.18 (m, 2H, CH); *cf.* ref. 5.

1c: orange-brown, 14 mg (70%). ^1H NMR ($CDCl_3$) δ: 2.12 (m, 6H, CH_2), 2.77 (m, 2H, CH_2), 4.49 (m, 2H, CH), 4.98 (m, 2H, CH), 5.06 (s, 5H, Cp); *cf.* ref. 5.

Alternatively, the suspension of [**2**][BF_4] (152 mg, 0.4 mmol), dry LiCl (350 mg, 8 mmol), and 1,5-cyclooctadiene (0.25 ml, 2 mmol, 5-fold excess) in 5 ml of THF was stirred under argon overnight. The flask was opened to air and the solvent was removed *in vacuo*. The residue was extracted with CH_2Cl_2 (3×10 ml) and the extract was evaporated. The resulting solid was washed with hexane and dried to give pure **1a** (107 mg, 86% yield).

§ A solution of [**2**][BF_4] (38 mg, 0.1 mmol), norbornadiene (0.1 ml, 1.0 mmol, 10-fold excess), and $[Bu_4N]X$ (0.1 mmol) in 5 ml of CH_2Cl_2 was stirred under argon atmosphere overnight. The flask was opened to air and the solvent was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2–light petroleum (1:1) mixture, eluted through Al_2O_3 column (10 cm) and evaporated. The resulting solid was washed with hexane and dried to give pure products. Compounds **3a**,**b** are air-stable both in solid and solution at least for several days. The iodide **3c** is less stable and notably decomposes in solution within 1 day.

3a: yellow, 23 mg (78%). ^1H NMR ($CDCl_3$) δ: 1.31 (m, 2H, CH_2), 3.62 (m, 1H, CH_{bridge}), 3.72 (m, 1H, CH_{bridge}), 4.50 (m, 2H, CH), 4.74 (m, 2H, CH), 4.92 (s, 5H, Cp); *cf.* ref. 5.

3b: yellow-orange, 30 mg (88%). ^1H NMR ($CDCl_3$) δ: 1.24 (m, 2H, CH_2), 3.61 (m, 1H, CH_{bridge}), 3.66 (m, 1H, CH_{bridge}), 4.55 (m, 1H, CH), 4.63 (m, 1H, CH), 4.95 (s, 5H, Cp); *cf.* ref. 6.

3c: orange-brown, 22 mg (58%). ^1H NMR ($CDCl_3$) δ: 1.15 (m, 2H, CH_2), 3.54 (m, 1H, CH_{bridge}), 3.57 (m, 1H, CH_{bridge}), 4.42 (m, 2H, CH), 4.57 (m, 2H, CH), 5.02 (s, 5H, Cp). Found (%): C, 37.21; H, 3.18. Calc. for $C_{12}H_{13}IRu$ (%): C, 37.42; H, 3.40.

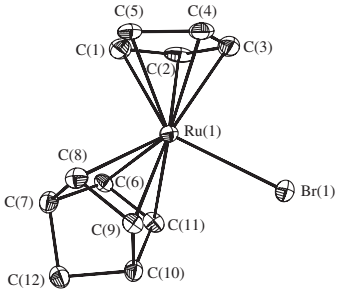


Figure 1 The molecular structure of **3b** with ellipsoids at 50% probability level. All hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ru(1)–C(1) 2.180(5), Ru(1)–C(2) 2.233(5), Ru(1)–C(3) 2.235(5), Ru(1)–C(4) 2.239(5), Ru(1)–C(5) 2.224(5), Ru(1)–C(6) 2.204(5), Ru(1)–C(8) 2.208(5), Ru(1)–C(9) 2.224(5), Ru(1)–C(11) 2.215(4), Ru(1)–Br(1) 2.5927(15).

unknown complex **3c**. Interestingly, ^{1}H NMR signal of Cp ligand in **1** and **3** shifts upfield in the sequence Cl > Br > I, while the signals of the diene ligands shift downfield in the same sequence.

The structure of bromide **3b** was established by X-ray diffraction (Figure 1).¶ The Ru···Cp distance in **3b** (1.865 Å) is longer than that in $CpRu(PPh_3)_2Br$ (1.848 Å),[19] but shorter than in $CpRu(CO)_2Br$ (1.877 Å).[20] This indicates that the norbornadiene ligand is stronger donor than CO but weaker than PPh_3.[21] The double bonds of the norbornadiene moiety in **3b** (av. 1.396 Å) are significantly elongated as compared to the free ligand (av. 1.337 Å)[22] due to coordination with the metal atom.

In summary, we have developed the convenient method for the preparation of CpRu(diene)X complexes which hopefully will promote their wider application.

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

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2011.03.007.

References

1 (*a*) M. O. Albers, D. J. Robinson and E. Singleton, *Coord. Chem. Rev.*, 1987, **79**, 1; (*b*) M. E. Cucullu, L. Luo, S. P. Nolan, P. J. Fagan, N. L. Jones and J. C. Calabrese, *Organometallics*, 1995, **14**, 289; (*c*) B. M. Trost, D. Toste and A. B. Pinkerton, *Chem. Rev.*, 2001, **101**, 2067; (*d*) Y. Yamamoto, T. Arakawa, R. Ogawa and K. Itoh, *J. Am. Chem. Soc.*, 2003, **125**, 12143; (*e*) S. Derien and P. H. Dixneuf, *J. Organomet. Chem*., 2004, **689**, 1382; (*f*) B. M. Trost, M. U. Frederiksen and M. T. Rudd, *Angew. Chem. Int. Ed*., 2005, **44**, 6630; (*g*) D. B. Grotjahn, V. Miranda-Soto, E. J. Kragulj, D. A. Lev, G. Erdogan, X. Zeng and A. L. Cooksy, *J. Am. Chem. Soc.*, 2008, **130**, 20; (*h*) M. Basato, C. Tubaro, A. Biffis, M. Bonato, G. Buscemi, F. Lighezzolo, P. Lunardi, C. Vianini, F. Benetollo and A. Del Zotto, *Chem. Eur. J.*, 2009, **15**, 1516; (*i*) Y. Yamamoto, K. Yamashita and Y. Harada, *Chem. Asian J*., 2010, **5**, 946.

2 J. Zagermanna, M. C. Kuchtaa, K. Merza and N. Metzler-Nolte, *J. Organomet. Chem*., 2009, **694**, 862.

3 C. L. Morris, Y. Hu, G. D. Head, L. J. Brown, W. G. Whittingham and R. C. D. Brown, *J. Org. Chem.*, 2009, **74**, 981.

4 (*a*) P. J. Fagan, M. D. Ward and J. C. Calabrese, *J. Am. Chem. Soc.*, 1989, **111**, 1698; (*b*) P. J. Fagan, W. S. Mahoney, J. C. Calabrese and I. D. Williams, *Organometallics*, 1990, **9**, 1843; (*c*) B. Dutta, E. Solari, S. Gauthier, R. Scopelliti and K. Severin, *Organometallics*, 2007, **26**, 4791.

5 (*a*) M. O. Albers, D. J. Robinson, A. Shaver and E. Singleton, *Organometallics*, 1986, **5**, 2199; (*b*) M. O. Albers, D. J. Robinson and E. Singleton, *J. Organomet. Chem*., 1986, **311**, 207.

6 H. Nagashima, K. Yamaguchi, K. Mukai and K. Itoh, *J. Organomet. Chem*., 1985, **291**, C20.

7 (*a*) M. Cais, D. Fraenkel and K. Weidenbaum, *Coord. Chem. Rev.*, 1975, **16**, 27; (*b*) S. B. Nagelberg, C. E. Reinhold, B. R. Willeford, M. P. Bigwood, K. C. Molloy and J. J. Zuckerman, *Organometallics*, 1982, **1**, 851; (*c*) E. P. Kündig, C. Perret, S. Spichiger and G. Bernardinelli, *J. Organomet. Chem*., 1985, **286**, 183; (*d*) K. Schulkopf, J. J. Stezowski and F. Effenberger, *Organometallics*, 1985, **4**, 922; (*e*) B. F. Bush, V. M. Lynch and J. J. Lagowski, *Organometallics*, 1987, **6**, 1267.

8 (*a*) S. H. Sun, L. K. Yeung, D. A. Sweigart, T. Y. Lee, S. S. Lee, Y. K. Chung, S. R. Switzer and R. D. Pike, *Organometallics*, 1995, **14**, 2613; (*b*) M. Oh, J. A. Reingold, G. B. Carpenter and D. A. Sweigart, *Coord. Chem. Rev*., 2004, **248**, 561.

9 E. P. Kündig, P. Jeger and G. Bernardinelli, *Inorg. Chim. Acta*, 2004, **357**, 1909.

10 E. V. Mutseneck, D. A. Loginov, A. A. Pronin, P. V. Petrovskii and A. R. Kudinov, *Izv. Akad. Nauk, Ser. Khim*., 2007, 1861 (*Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 1927).

11 (*a*) G. Vitulli, P. Pertici and P. Salvadori, *J. Chem. Soc., Dalton Trans.*, 1984, 2255; (*b*) A. R. Kudinov, V. S. Kaganovich and M. I. Rybinskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2636 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 2418); (*c*) M. A. Bennett, H. Neumann, M. Thomas, X. Wang, P. Pertici, P. Salvadori and G. Vitulli, *Organometallics*, 1991, **10**, 3237; (*d*) M. A. Bennett, Z. Lu, X. Wang, M. Bown and D. C. R. Hockless, *J. Am. Chem. Soc.*, 1998, **120**, 10409; (*e*) G. Bodes, F. W. Heinemann, G. Marconi, S. Neumann and U. Zenneck, *J. Organomet. Chem*., 2002, **641**, 90; (*f*) T. Shibasaki, N. Komine, M. Hirano and S. Komiya, *J. Organomet. Chem*., 2007, **692**, 2385.

12 M. Valderrama and R. Ganz, *Transition Met. Chem*., 1983, **8**, 160.

13 V. S. Kaganovich, A. R. Kudinov and M. I. Rybinskaya, *Metalloorg. Khim*., 1988, 294 (*Organomet. Chem. USSR*, 1988, **1**, 162).

14 (*a*) E. P. Kündig and F. R. Monnier, *Adv. Synth. Catal*., 2004, **346**, 901; (*b*) A. Mercier, W. Ch. Yeo, J. Chou, P. D. Chaudhuri, G. Bernardinelli and E. P. Kündig, *Chem. Commun*., 2009, 5227.

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

16 (*a*) E. E. Karslyan, A. I. Konovalov, D. S. Perekalin, P. V. Petrovskii and A. R. Kudinov, *Izv. Akad. Nauk, Ser. Khim*., 2008, 2158 (*Russ. Chem. Bull., Int. Ed.*, 2008, **57**, 2201); (*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).

17 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.

18 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).

19 M. I. Bruce, P. J. Low, B. W. Skelton, E. R. T. Tiekink, A. Werth and A. H. White, *Aust. J. Chem.*, 1995, **48**, 1887.

20 H. Adams, N. A. Bailey and C. White, *Inorg. Chem.*, 1983, **22**, 1155.

21 D. G. Gusev, *Organometallics*, 2009, **28**, 763.

22 J. Benet-Buchholz, T. Haumann and R. Boese, *Chem. Commun.*, 1998, 2003.

¶ For details of X-ray diffraction data collection (R = 0.0322, P–421c, Z = 8), see Online Supplementary Materials.

CCDC 800299 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.

Received: 19th November 2010; Com. 10/3631