ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

*Mendeleev Commun.*, 2012, **22**, 192–193

Mendeleev Communications

# Reactions of the (cyclooctadiene)iridium complex CpIr(cod) with halogens

**Dmitry A. Loginov, Andrey M. Miloserdov, Zoya A. Starikova, Pavel V. Petrovskii and Alexander R. Kudinov***

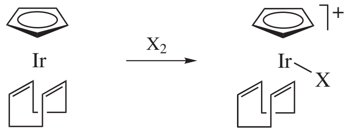
*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5085; e-mail: arkudinov@ineos.ac.ru*

DOI: 10.1016/j.mencom.2012.06.006

**The reactions of CpIr(cod) with halogens afford the cations [CpIr(cod)X]$^+$ (X = Cl, Br, I); the structures of [CpIr(cod)Br]PF$_6$ and [CpIr(cod)I][CpIrI$_3$] were confirmed by X-ray diffraction.**

The reactions of the (cyclooctadiene)rhodium complexes LRh(cod) (L = Cp, η$^5$-indenyl, η$^6$-boratabenzene or η-1-Bu$^t$NH-1,7,9-C$_3$B$_8$H$_{10}$) with halogens are used for the preparation of [LRhX$_2$]$_2$ halides (X = Cl, Br or I), which are synthetically useful.[1] Analogous iridium complexes [CpIrX$_2$]$_2$ were prepared from CpIr(C$_2$H$_4$)$_2$, CpIr(cyclohexadiene) and CpIr(cyclooctatetraene).[2] However, CpIr(cod) reacts with halogens in a different manner; *e.g.*, the reaction with I$_2$ was reported to give the product C$_{13}$H$_{17}$I$_2$Ir according to elemental analysis.[2(*a*)] In this work, we studied the reactions of CpIr(cod) with halogens and established the structures of the products by X-ray diffraction.

We found that the reactions of CpIr(cod)[†,3] with chlorine and bromine afford the cationic complexes [CpIr(cod)X]X [X = Cl ([**1a**]Cl) or Br ([**1b**]Br)][‡] as a result of oxidative addition (Scheme 1).[§] An analogous reaction with I$_2$ gives [CpIr(cod)I]I$_3$ ([**1c**]I$_3$).[¶] Similar transformations are well known for ruthenocenes and osmocenes.[4]



**1a** X = Cl
**1b** X = Br
**1c** X = I

**Scheme 1**

Salts [**1a**]Cl, [**1b**]Br and [**1c**]I$_3$ are stable in air. They are poorly soluble in water and common organic solvents. Interestingly, the stirring of [**1b**]Br in CH$_2$Cl$_2$ yields the salt [**1b**][CpIrBr$_3$][††] as a result of nucleophilic replacement of cyclooctadiene by the bromide anion. The treatment of [**1a**]Cl, [**1b**]Br and [**1c**]I$_3$ with either KPF$_6$, TlPF$_6$ or NaBPh$_4$ gives salts [**1a**]PF$_6$,[‡] [**1b**]PF$_6$[‡] and [**1c**]BPh$_4$,[¶] which are readily soluble in CH$_2$Cl$_2$ and acetone. In the $^1$H NMR spectra of cations [**1a–c**]$^+$, there are two signals of olefinic cyclooctadiene protons, strongly downfield shifted (by ~1.6 and 3.2 ppm) relative to CpIr(cod).[3(*b*),5] The signals of Cp protons are also downfield shifted (by ~1.3 ppm) in accordance with the positive charge of these complexes.

The structures of [**1b**]PF$_6$ and [**1c**][CpIrI$_3$] were confirmed by X-ray diffraction (Figures 1, 2).[‡‡] The structures of cations [**1b**]$^+$ and [**1c**]$^+$ are close to those of the well-known ruthenium neutral complexes CpRu(cod)X (X = Cl, Br, I).[6] In particular, the metal-to-ring Ir···Cp distances in [**1b**]$^+$ (1.857 Å) and [**1c**]$^+$ (1.861 Å) are almost the same as the Ru···Cp distance in CpRu(cod)I

---

[†] The complex CpIr(cod) was prepared by a known procedure[3] with the use of CpTl instead of CpNa or CpK. A mixture of [(cod)IrCl]$_2$ (515 mg, 1.53 mmol) and CpTl (500 mg, 1.86 mmol) in THF (2 ml) was stirred for 2 h. The solvent was removed *in vacuo*. The residue was extracted by diethyl ether and filtered through a layer of Al$_2$O$_3$ (5–7 cm). After evaporation *in vacuo*, the complex CpIr(cod) was prepared as white crystalline solid. Yield, 457 mg (82%). For spectral data, see ref. 3(*b*).

[‡] Cl$_2$ (gas) was passed through a reaction mixture for 15 min or Br$_2$ (25 mg, 0.16 mmol) was added to a solution of CpIr(cod) (50 mg, 0.14 mmol) in diethyl ether (1 ml), and the reaction mixture was stirred for ~0.5 h. The yellow precipitate formed was centrifuged and washed with diethyl ether. Yield, 60 or 72 mg for [**1a**]Cl or [**1b**]Br, respectively. Anion exchange was carried out by two methods.

*Method A*. [**1a**]Cl or [**1b**]Br was added to a saturated solution of KPF$_6$ in water and stirred for 24 h. The precipitate was washed with water, dried *in vacuo* and repricipitated from acetone by diethyl ether. Complexes [**1a**]PF$_6$ and [**1b**]PF$_6$ were obtained as yellow solids.

[**1a**]PF$_6$: yield, 30 mg (39%). $^1$H NMR (acetone-*d*$_6$) $\delta$: 7.15 (m, 2H, cod), 6.61 (s, 5H, Cp), 5.28 (m, 2H, cod), 2.64 (m, 8H, cod). Found (%): C, 28.86; H, 3.11. Calc. for C$_{13}$H$_{17}$ClF$_6$IrP (%): C, 28.60; H, 3.14.

[**1b**]PF$_6$: yield, 57 mg (68%). $^1$H NMR (acetone-*d*$_6$) $\delta$: 7.01 (m, 2H, cod), 6.65 (s, 5H, Cp), 5.38 (m, 2H, cod), 2.81 (m, 4H, cod), 2.63 (m, 4H, cod). Found (%): C, 26.24; H, 2.86. Calc. for C$_{13}$H$_{17}$BrF$_6$IrP (%): C, 26.45; H, 2.90.

*Method B*. A mixture of [**1a**]Cl or [**1b**]Br and TlPF$_6$ (47 mg, 0.13 mmol) was stirred in CH$_2$Cl$_2$ (2 ml) for three days. The solvent was removed *in vacuo*, and the residue was extracted by acetone. An excess of Et$_2$O was added to precipitate [**1a**]PF$_6$ (27 mg, 36%) or [**1b**]PF$_6$ (67 mg, 84%).

[§] Anions are omitted from the reaction schemes for clarity.

[¶] A solution of I$_2$ (70 mg, 0.28 mmol) in diethyl ether (3 ml) was added to CpIr(cod) (50 mg, 0.14 mmol) in the same solvent (1 ml), and the reaction mixture was stirred for ~0.5 h. The brown precipitate formed was centrifuged and washed with diethyl ether. Yield, 113 mg of [**1c**]I$_3$. Found (%): C, 19.54; H, 1.94; I, 58.1. Calc. for C$_{13}$H$_{17}$I$_4$Ir (%): C, 17.88; H, 1.96; I, 58.1.

[**1c**]I$_3$ was dissolved in DMSO (0.2 ml) and added to a saturated solution of NaBPh$_4$ in water. The precipitate was washed with water, dried *in vacuo* and repricipitated from acetone by Et$_2$O. Yeld, 93 mg (84%) of [**1c**]BPh$_4$ as a brown solid. $^1$H NMR (acetone-*d*$_6$) $\delta$: 7.36 (m, 8H, BPh$_4$), 6.93 (m, 8H, BPh$_4$), 6.78 (m, 4H, BPh$_4$), 6.64 (m, 2H, cod), 6.60 (s, 5H, Cp), 5.41 (m, 2H, cod), 2.98 (m, 4H, cod), 2.62 (m, 4H, cod). Found (%): C, 54.84; H, 4.68. Calc. for C$_{37}$H$_{37}$BIIr (%): C, 54.75; H, 4.60.

[††] The crude product of [**1b**]Br obtained from 50 mg of CpIr(cod) was stirred in CH$_2$Cl$_2$ (2 ml) for three days. The colour of the reaction mixture changed from yellow to orange. The precipitate was centrifuged and washed with acetone and Et$_2$O. Yield, 63 mg (90%) of [**1b**][CpIrBr$_3$]·CH$_2$Cl$_2$ as an orange solid. $^1$H NMR (DMSO-*d*$_6$) $\delta$: 6.74 (m, 2H, cod), 6.49 (s, 5H, Cp), 6.00 (s, 5H, Cp), 5.62 (s, 2H, CH$_2$Cl$_2$), 5.20 (m, 2H, cod), 2.65 (m, 4H, cod), 2.37 (m, 4H, cod). Found (%): C, 22.01; H, 2.29. Calc. for C$_{18}$H$_{22}$Br$_4$Ir$_2$·CH$_2$Cl$_2$ (%): C, 22.21; H, 2.35.

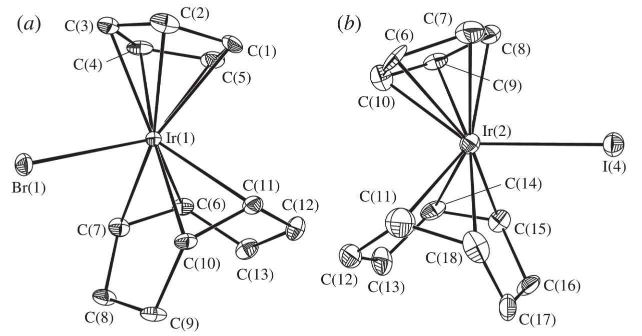


**Figure 1** (*a*) Structure of cation $[\mathbf{1b}]^+$. Ellipsoids are drawn at a 50% probability level. Selected bond lengths (Å): Ir(1)–C(1) 2.226(4), Ir(1)–C(2) 2.207(4), Ir(1)–C(3) 2.224(4), Ir(1)–C(4) 2.227(4), Ir(1)–C(5) 2.207(4), Ir(1)–C(6) 2.256(4), Ir(1)–C(7) 2.243(4), Ir(1)–C(10) 2.255(4), Ir(1)–C(11) 2.262(4), Ir(1)–Br(1) 2.5388(4), C(6)–C(7) 1.390(5), C(10)–C(11) 1.390(5). (*b*) Structure of cation $[\mathbf{1c}]^+$. Ellipsoids are drawn at a 30% probability level. Selected bond lengths (Å): Ir(2)–C(6) 2.261(16), Ir(2)–C(7) 2.197(18), Ir(2)–C(8) 2.226(17), Ir(2)–C(9) 2.226(15), Ir(2)–C(10) 2.180(17), Ir(2)–C(11) 2.26(2), Ir(2)–C(14) 2.211(16), Ir(2)–C(15) 2.251(16), Ir(2)–C(18) 2.274(18), Ir(2)–I(4) 2.7203(12), C(11)–C(18) 1.42(3), C(14)–C(15) 1.39(2). Hydrogen atoms are omitted for clarity.

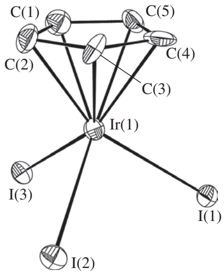


**Figure 2** Structure of anion $[\mathrm{CpIrI_3}]^-$. Ellipsoids are drawn at a 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ir(1)–C(1) 2.136(18), Ir(1)–C(2) 2.163(16), Ir(1)–C(3) 2.160(17), Ir(1)–C(4) 2.163(17), Ir(1)–C(5) 2.183(15), Ir(1)–I(1) 2.7089(13), Ir(1)–I(2) 2.7069(12), Ir(1)–I(3) 2.6931(12).

(1.857 Å). At the same time, these distances are shorter than that in the neutral iridium complexes $(\eta\text{-C}_5\text{H}_4\text{R})\text{Ir(cod)}$ (R = $\text{Pr}^\text{i}$, 1.901 Å; R = CH=CHMe, av. 1.899 Å),[7] suggesting stronger bonding of Cp ligand with $\text{Ir}^\text{III}$ than with $\text{Ir}^\text{I}$. In contrast, longer Ir–$\text{C}_\text{cod}$ bond lengths in $[\mathbf{1b}]^+$ (2.243–2.261 Å, av. 2.254 Å) and $[\mathbf{1c}]^+$ (2.211–2.274 Å, av. 2.248 Å) than in $(\eta\text{-C}_5\text{H}_4\text{R})\text{Ir(cod)}$ (av. 2.120 Å)[7] suggest weaker Ir–cod bonding in the halide complexes. Moreover, the Ir–$\text{C}_\text{cod}$ bonds in $[\mathbf{1b}]^+$ and $[\mathbf{1c}]^+$ are also longer than that in the complexes (cod)Ir(L)Cl (L are phosphine or carbene ligands; ~2.10–2.20 Å).[8] The anion $[\mathrm{CpIrI_3}]^-$ has a half-sandwich structure. The Ir–I bonds in this anion (2.693–2.709 Å, av. 2.703 Å) are shorter than that in cation $[\mathbf{1c}]^+$ (2.720 Å). Only one example of related iridium anions, $[\mathrm{Cp^*IrCl_3}]^-$, has been structurally characterized previously.[9]

Interestingly, the cyclooctadiene ligand in cations $[\mathbf{1a–c}]^+$ is substitutionally labile, making them synthetically useful. In particular, it is easily replaced by DMSO;[§§] the rate of replacement increases in the order **1c** < **1b** < **1a**.

Thus, in contrast to rhodium, the reaction of CpIr(cod) with halogens stops at the stage of the formation of the cationic complexes $[\mathrm{CpIr(cod)X}]^+$, apparently, due to stronger Ir–cod bonding. Similar complexes can be intermediates in the case of rhodium.

## References

1 (*a*) R. Poli, *Chem. Rev.*, 1991, **91**, 509; (*b*) U. Gradler, A. S. Weller, A. J. Welch and D. Reed, *J. Chem. Soc., Dalton Trans.*, 1996, 335; (*c*) D. A. Loginov, M. M. Vinogradov, Z. A. Starikova, P. V. Petrovskii and A. R. Kudinov, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 1871 (*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 1949); (*d*) D. A. Loginov, M. M. Vinogradov, Z. A. Starikova, E. A. Petrovskaya, P. Zanello, F. Laschi, F. Rossi, A. Cinquantini and A. R. Kudinov, *J. Organomet. Chem.*, 2007, **692**, 5777; (*e*) D. A. Loginov, A. V. Vologzhanina, Z. A. Starikova, P. V. Petrovskii, M. M. Vinogradov and A. R. Kudinov, *Izv. Akad. Nauk, Ser. Khim.*, 2008, 1623 (*Russ. Chem. Bull., Int. Ed.*, 2008, **57**, 1653); (*f*) D. A. Loginov, Z. A. Starikova, P. V. Petrovskii and A. R. Kudinov, *Izv. Akad. Nauk, Ser. Khim.*, 2010, 639 (*Russ. Chem. Bull., Int. Ed.*, 2010, **59**, 654); (*g*) D. A. Loginov, Z. A. Starikova, P. V. Petrovskii, J. Holub and A. R. Kudinov, *Inorg. Chem. Commun.*, 2011, **14**, 313.

2 (*a*) H. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 582; (*b*) A. A. Bezrukova, V. S. Khandkarova, V. G. Andrianov, Yu. T. Struchkov and A. Z. Rubezhov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2071 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1922); (*c*) D. M. Heinekey, J. M. Millar, T. F. Koetzle, N. G. Payne and K. W. Zilm, *J. Am. Chem. Soc.*, 1990, **112**, 909; (*d*) A. R. Kudinov, D. A. Loginov, Z. A. Starikova and P. V. Petrovskii, *J. Organomet. Chem.*, 2002, **649**, 136; (*e*) J. D. Blakemore, N. D. Schley, D. Balcells, J. F. Hull, G. W. Olack, C. D. Incarvito, O. Eisenstein, G. W. Brudvig and R. H. Crabtree, *J. Am. Chem. Soc.*, 2010, **132**, 16017.

3 (*a*) G. Pannetier, D. Tabrizi and R. Bonnaire, *J. Less-Common Met.*, 1971, **24**, 470; (*b*) J. R. Sowa Jr. and R. J. Angelici, *J. Am. Chem. Soc.*, 1991, **113**, 2537.

4 (*a*) Y. S. Sohn, A. W. Schlueter, D. H. Hendrickson and H. B. Gray, *Inorg. Chem.*, 1974, **13**, 301; (*b*) T. P. Smith, K. S. Kwan, H. Taube, A. Bino and S. Cohen, *Inorg. Chem.*, 1984, **23**, 1943; (*c*) M. O. Albers, D. C. Liles, D. J. Robinson, A. Shaver, E. Singleton and M. B. Wiege, *Organometallics*, 1986, **5**, 2321.

5 S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1965, 4997.

6 M. O. Albers, D. J. Robinson, A. Shaver and E. Singleton, *Organometallics*, 1986, **5**, 2199.

7 (*a*) J. Müller, R. Stock and J. Pickardt, *Z. Naturforsch., B: Chem. Sci.*, 1981, **36**, 1219; (*b*) C. Herrmann, G. Kehr, R. Fröhlich and G. Erker, *Eur. J. Inorg. Chem.*, 2008, 2273.

8 (*a*) M. Brym and C. Jones, *Transition Met. Chem.*, 2003, **28**, 595; (*b*) W. A. Herrmann, D. Baskakov, E. Herdtweck, S. D. Hoffmann, T. Bunlaksananusorn, F. Rampf and L. Rodefeld, *Organometallics*, 2006, **25**, 2449; (*c*) A. G. Tennyson, E. L. Rosen, M. S. Collins, V. M. Lynch and C. W. Bielawski, *Inorg. Chem.*, 2009, **48**, 6924; (*d*) J.-F. Sun, F. Chen, B. A. Dougan, H.-J. Xu, Y. Cheng, Y.-Z. Li, X.-T. Chen and Z.-L. Xue, *J. Organomet. Chem.*, 2009, 694, 2096; (*e*) C. D. Varnado Jr, V. M. Lynch and C. W. Bielawski, *J. Chem. Soc., Dalton Trans.*, 2009, 7253.

9 (*a*) D. F. Kennedy, B. A. Messerle and M. K. Smith, *Eur. J. Inorg. Chem.*, 2007, 80; (*b*) C. Pettinari, R. Pettinari, F. Marchetti, A. Macchioni, D. Zuccaccia, B. W. Skelton and A. H. White, *Inorg. Chem.*, 2007, **46**, 896; (*c*) M. R. Grochowski, W. W. Brennessel and W. D. Jones, *Organometallics*, 2009, **28**, 2661.

*Received: 21st March 2012; Com. 12/3899*

---

[‡‡] Crystals of $[\mathbf{1b}]\mathrm{PF_6}$ were grown by slow diffusion in two-layer system, $\mathrm{Et_2O}$ and a solution of the complex in acetone. Crystals of $[\mathbf{1c}][\mathrm{CpIrI_3}]$ were obtained by the crystallization of $[\mathbf{1c}]\mathrm{I_3}$ from $\mathrm{CH_2Cl_2}$–light petroleum.

*Crystal data for* $[\mathbf{1b}]\mathrm{PF_6}$: $\mathrm{C_{13}H_{17}BrF_6IrP}$, triclinic, space group $P\bar{1}$, $a$ = 6.7230(3), $b$ = 9.9983(5) and $c$ = 11.2982(5) Å, $\alpha$ = 97.5670(10)°, $\beta$ = 90.5520(10)°, $\gamma$ = 96.0720(10)°, $V$ = 748.40(6) Å$^3$, $Z$ = 2, $d_\text{calc}$ = = 2.620 g cm$^{-3}$, $\mu$ = 11.753 mm$^{-1}$, crystal size 0.35×0.23×0.20 mm, $F(000)$ = = 552, $T_\text{min}/T_\text{max}$ = 0.049509/0.097634, $R_1$ = 0.0251 [from 3398 unique reflections with $I > 2\sigma(I)$] and $wR_2$ = 0.0647 (from all 3572 unique reflections).

*Crystal data for* $[\mathbf{1c}][\mathrm{CpIrI_3}]$: $\mathrm{C_{18}H_{22}I_4Ir_2}$, orthorhombic, space group *Pbca*, $a$ = 16.273(2), $b$ = 16.325(2) and $c$ = 6.461(2) Å, $V$ = 4372.9(10) Å$^3$, $Z$ = 8, $d_\text{calc}$ = 3.434 g cm$^{-3}$, $\mu$ = 17.808 mm$^{-1}$, crystal size 0.30×0.21×0.10 mm, $F(000)$ = 3968, $T_\text{min}/T_\text{max}$ = 0.022322/0.058229, $R_1$ = 0.0451 [from 3037 unique reflections with $I > 2\sigma(I)$] and $wR_2$ = 0.1135 (from all 4715 unique reflections).

There are highly positive residual densities of 2.16 e Å$^{-3}$ (for $[\mathbf{1b}]\mathrm{PF_6}$) and 2.47 e Å$^{-3}$ (for $[\mathbf{1c}][\mathrm{CpIrI_3}]$) near the Ir(1) center (distances of 0.88 and 0.84 Å, respectively) due to considerable absorption effects, which could not be corrected.

CCDC 871722 and 871723 contain 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, 2012.

[§§] Complexes $[\mathbf{1a}]\mathrm{PF_6}$ (8 mg), $[\mathbf{1b}]\mathrm{PF_6}$ (9 mg) and $[\mathbf{1c}]\mathrm{BPh_4}$ (12 mg) were dissolved in DMSO-$d_6$ (0.5 ml) in an NMR tube. The $^1$H NMR measurements showed that the signals of free cyclooctadiene appear within 10 min. After 20 h, the degree of conversion was almost 100% for $[\mathbf{1a}]\mathrm{PF_6}$, 90% for $[\mathbf{1b}]\mathrm{PF_6}$ and 50% for $[\mathbf{1c}]\mathrm{BPh_4}$.