Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2024, **34**, 547–549

Mendeleev Communications

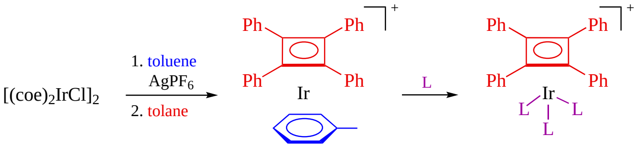
Synthesis, reactivity, and catalytic application of tetraphenylcyclobutadiene iridium complexes

Nikita V. Shvydkiy,* Yulia V. Nelyubina and Dmitry S. Perekalin

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119334 Moscow, Russian Federation. E-mail: shvydkiy@ineos.ac.ru

DOI: 10.1016/j.mencom.2024.06.025

Reaction of $[(coe)_2IrCl]_2$ (coe = cyclooctene) with $AgPF_6$, arene (toluene, *p*-xylene, mesitylene), and diphenylacetylene, followed by counter anion exchange to $BARF^-$, gives cyclobutadiene iridium complexes $[(C_4Ph_4)Ir(arene)]BARF$ in 10–22% yield. Replacement of toluene in $[(C_4Ph_4)Ir(toluene)]BARF$ by various ligands (trimethylphosphite, 1,3,5-triaza-7-phosphaadamantane, *tert*-butyl isonitrile) provides access to the half-sandwich cyclobutadiene iridium complexes $[(C_4Ph_4)Ir(L)_3]BARF$. Complex $[(C_4Ph_4)Ir(toluene)]BARF$ in combination with $[NBnEt_3]Cl$ catalyses the insertion reaction between phenyl diazoacetate and various amines.

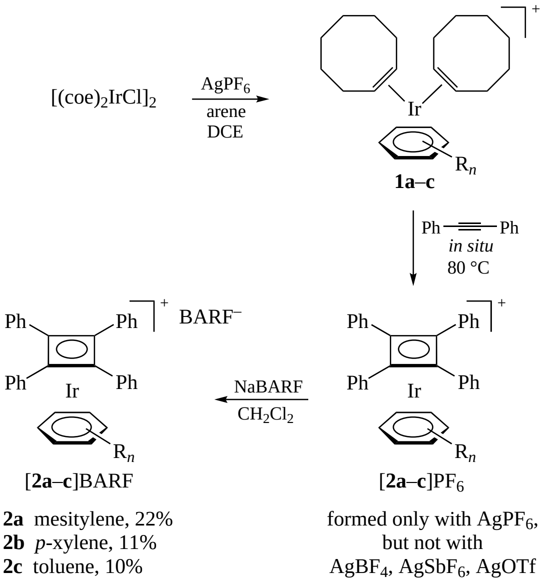


Keywords: cyclobutadiene, diene ligands, homogeneous catalysis, iridium, diazo compounds.

Cyclobutadiene rhodium complexes represent a relatively new type of organometallic catalysts that have demonstrated remarkable activity in several organic transformations.[1] It was assumed that their efficiency is due to the strong bond between the cyclobutadiene ligand and rhodium, which stabilizes the active metal center during a catalytic cycle.[2] At the same time, iridium analogs with a theoretically more robust cyclobutadiene–metal bond have remained essentially unknown since no method for their synthesis has been developed. Herein we report the general procedure for the synthesis of cyclobutadiene iridium complexes with arene ligands, investigation of their chemical properties and catalytic application for transformations of phenyl diazoacetate.

Previously we found that the reaction of $[(coe)_2IrCl]_2$ with diethylacetylene and $AgPF_6$ leads to the iridium complex $[(C_4Et_4)Ir(C_6Et_6)]PF_6$.[3] Until now, this compound has remained the only one fully characterized cyclobutadiene iridium complex and due to the inert sandwich structure with sterically shielding ethyl groups it could not be used for synthesis of other derivatives. In the same work we have tried to synthesize cyclobutadiene iridium complex with a more labile xylene ligand $[(C_4Ph_4)Ir(p\text{-xylene})]PF_6$ (**2b**, Scheme 1). This compound was characterized by ^1H and ^{13}C NMR spectroscopy, but it seemed to be rather unstable and we were unable to obtain correct elemental analysis for it. The analysis of the literature revealed that such behaviour may arise not from the instability of the complex itself, but rather from the hydrolysis of PF_6^- anion under the reaction conditions.[4,5] In order to check this hypothesis we carried out the synthesis of $[(C_4Ph_4)Ir(mesitylene)]PF_6$ and changed the counter ion to BARF (BARF – tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) ([**2a**]BARF, see Scheme 1). In the first step, the starting compound $[(coe)_2IrCl]_2$ reacted with $AgPF_6$ in presence of mesitylene at room temperature to give cationic complex $[(coe)_2Ir(mesitylene)]PF_6$. Then diphenylacetylene was added and the reaction mixture was heated at 80 °C for 18 h. The obtained cyclobutadiene product $[(C_4Ph_4)Ir(mesitylene)]PF_6$ (**2a**) was subjected to counter-ion exchange with NaBARF. We found that the resulting novel complex $[(C_4Ph_4)Ir(mesitylene)]BARF$ is stable in air in the solid state as well as in the acetone solution. Its structure was established by X-ray analysis and the purity was confirmed by elemental analysis (see Online Supplementary Materials).

We then attempted to use silver salts with other counter-anions such as AgOTf and $AgBF_4$, which are less prone to hydrolysis than $AgPF_6$, under the same reaction conditions. Surprisingly, the substitution of coordinated cyclooctene in **1a**

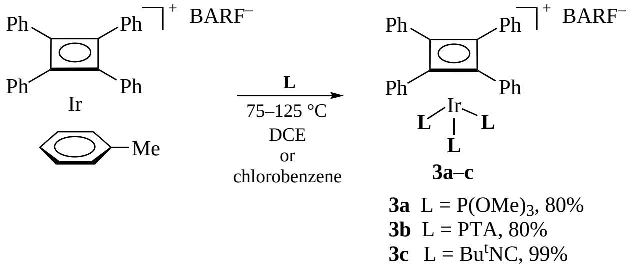


Scheme 1 Synthesis of cyclobutadiene iridium arene complexes.

by alkynes was not observed. The cationic complex $[(coe)_2Ir(mesitylene)]SbF_6$ (**1a**) was isolated in 64% yield in case of $AgSbF_6$. These results indicate that the decomposition of the hexafluorophosphate anion plays a crucial role in the cyclobutadiene complex formation. However, the exact mechanism remains unclear, since the formation of cyclobutadiene complex was not observed upon the addition of KPF_6 (as a source of PF_6 anion) to the reaction of the isolated $[(coe)_2Ir(mesitylene)]SbF_6$ and diphenylacetylene. Presumably, this can be explained by significantly greater stability of potassium hexafluorophosphate toward hydrolysis.[6] Thus, the developed procedure for the synthesis of the cyclobutadiene iridium arene complexes occurs successfully only in the presence of $AgPF_6$ and requires further counter ion exchange to isolate these products in pure form.

The developed method allowed us to synthesize cyclobutadiene iridium complexes with other arenes, namely *p*-xylene and toluene. The yields were moderate (10–20%) and did not depend on the electron donating properties of the arene. The structure of $[(C_4Ph_4)Ir(toluene)]BARF$ was confirmed by X-ray diffraction (Figure 1). The reaction with other alkynes proceeds significantly less selective. In particular, unsymmetrical 1-phenyl-1-propyne gave a mixture of isomeric cyclobutadiene complexes in 1 : 1 ratio. Interestingly, the analogous reaction of $[(C_2H_4)_2Rh(arene)]^+$ with 1-phenyl-1-propyne gives the sole isomer with the sterically unfavourable adjacent position of the phenyl substituents.[7] Lower selectivity in the case of iridium may be attributed to the higher reaction temperature (80 °C *vs*. room temperature). The reactions of $[(coe)_2Ir(mesitylene)]PF_6$ with functionalized internal acetylenes, such as dimethyl acetylenedicarboxylate and 1,4-dimethoxy-2-butyne led to mixtures of unidentified products.

Next we investigated the chemical properties of the synthesized cyclobutadiene iridium complexes. It was found that mesitylene complex [**2a**]BARF is rather inert. For instance, it does not react with trimethylphosphite at 90 °C, and only 50% arene replacement was reached after 24 h at 120 °C. Noteworthy that arene ligand in the cyclobutadiene rhodium complex $[(C_4Et_4)Rh(xylene)]PF_6$ is displaced by $P(OMe)_3$ at room temperature. The reactivity of cyclobutadiene iridium complexes is also significantly different from cyclooctadiene analogs $[(cod)Ir(arene)]^+$, in which the arene ligand is readily displaced at room temperature.[8,9] Toluene in $[(C_4Ph_4)Ir(toluene)]BARF$ ([**2c**]BARF) was expected to be more labile compared to more hindered mesitylene. Indeed, it is completely displaced by trimethylphosphite at 110 °C with the formation of $[(C_4Ph_4)Ir(P(OMe)_3)_3]BARF$ (**3a**) in 80% yield (Scheme 2). Similarly, the reaction with 1,3,5-triaza-7-phosphaadamantane gives **3b** at 125 °C. It should be noted that cyclobutadiene ligand remains intact under those harsh conditions thus demonstrating its good stabilizing properties toward iridium. A more active and less hindered ligand, *tert*-butyl isonitrile, displaces toluene at 75 °C, affording the corresponding complex **3c** in almost quantitative yield. The reaction with Bu^tNC at a higher temperature (90 °C) leads to the partial displacement of the cyclobutadiene ligand according to ^1H NMR. At the same time, carbon monoxide does not react with [**2c**]BARF at 125 °C (1 bar pressure). Acetonitrile was able to replace toluene in **2c** under reflux but we were unable to isolate corresponding product $[(C_4Ph_4)Ir(MeCN)_3]BARF$ in pure form apparently due to its partial decomposition under reaction conditions. Similarly, inseparable mixture of products was formed in case of pyridine.



Scheme 2 Synthesis of half-sandwich cyclobutadiene iridium complexes.

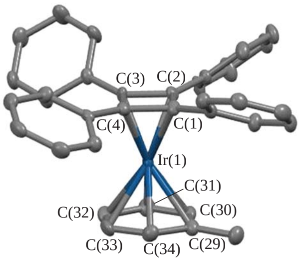


Figure 1 X-ray structure of the cyclobutadiene rhodium complex [**2c**]BARF represented in 50% thermal ellipsoids. Counter ion and hydrogen atoms are omitted for clarity. Selected interatomic distances (in Å): $Ir-C_{4plane}$ 1.851, Ir(1)−C(29) 2.294(5), Ir(1)−C(30) 2.258(6), Ir(1)−C(31) 2.232(6), Ir(1)−C(32) 2.268(6), Ir(1)−C(33) 2.266(5), Ir(1)−C(34) 2.353(4).

The structures of all half-sandwich complexes have been confirmed by X-ray structural analysis (Figure 2 and Online Supplementary Materials).† The distances between C_4-plane and iridium in phosphine complexes (*i.e*. 1.933 Å for **3a** and 1.949 Å for **3b**) are significantly longer than those in arene derivatives

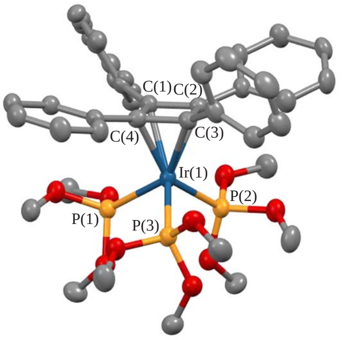


Figure 2 X-ray structure of the cyclobutadiene rhodium complex **3a** represented in 50% thermal ellipsoids. Counter ion and hydrogen atoms are omitted for clarity. Selected distances (in Å): $Ir-C_{4plane}$ 1.933, Ir(1)−P(1) 2.261(1), Ir(1)−P(2) 2.265(2), Ir(1)−P(3) 2.264(1).

---

† *Crystal data for* [**2a**]BARF. $C_{70}H_{45}BCl_3F_{24}Ir$, $F_w = 1651.42$, triclinic, $T = 100$ K, space group $P\bar{1}$, $Z = 2$, $a = 12.9068(2)$, $b = 15.3711(3)$ and $c = 18.7714(4)$ Å, $\alpha = 66.8600(10)$, $\beta = 77.1040(10)$ and $\gamma = 76.6160(10)°$, $V = 3294.88(11)$ Å^3, $D_{calc} = 1.665$ g cm^{-1}.

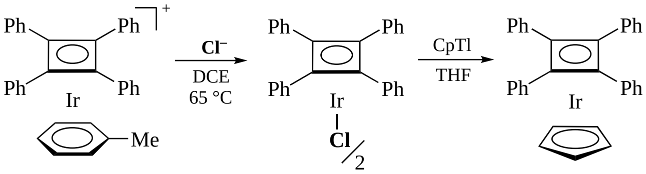
Crystal data for [**2c**]BARF. $C_{67}H_{40}BF_{24}Ir$, $F_w = 1504.00$, triclinic, $T = 100$ K, space group $P\bar{1}$, $Z = 2$, $a = 13.1494(5)$, $b = 13.7078(5)$ and $c = 18.6267(6)$ Å, $\alpha = 109.123(2)$, $\beta = 98.914(2)$ and $\gamma = 101.687(2)°$, $V = 3016.24(19)$ Å^3, $D_{calc} = 1.656$ g cm^{-1}.

Crystal data for **3a**. $C_{69}H_{59}BF_{24}IrO_9P_3$, $F_w = 1784.08$, monoclinic, $T = 100$ K, space group $P2_1/c$, $Z = 4$, $a = 20.9647(10)$, $b = 19.8476(11)$ and $c = 18.9490(11)$ Å, $\alpha = 90$, $\beta = 116.315(3)$ and $\gamma = 90°$, $V = 7067.6(7)$ Å^3, $D_{calc} = 1.677$ g cm^{-1}.

Crystal data for **3b**. $C_{79}H_{70}BCl_2F_{24}IrN_9P_3$, $F_w = 1968.26$, triclinic, $T = 100$ K, space group $P\bar{1}$, $Z = 2$, $a = 14.5303(3)$, $b = 16.1628(3)$ and $c = 19.7165(4)$ Å, $\alpha = 67.5970(10)$, $\beta = 84.4340(10)$ and $\gamma = 80.0490(10)°$, $V = 4214.08(15)$ Å^3, $D_{calc} = 1.551$ g cm^{-1}.

Crystal data for **3c**. $C_{75}H_{59}BF_{24}IrN_3$, $F_w = 1661.26$, triclinic, $T = 100$ K, space group $P\bar{1}$, $Z = 2$, $a = 13.1984(5)$, $b = 14.0409(5)$ and $c = 21.4867(8)$ Å, $\alpha = 76.546(2)$, $\beta = 72.677(2)$ and $\gamma = 75.527(2)°$, $V = 3626.3(2)$ Å^3, $D_{calc} = 1.521$ g cm^{-1}.

CCDC 2343022 ([**2a**]BARF), 2343024 ([**2c**]BARF), 2343026 (**3a**), 2343025 (**3b**) and 2343023 (**3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.



4 **5**, 16%

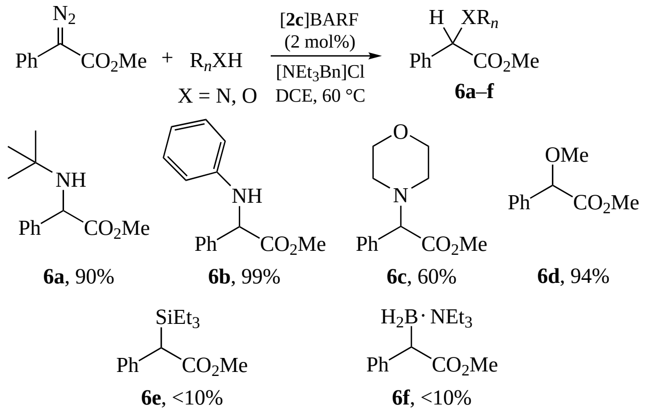
Scheme 3 The reaction of [(C_4Ph_4)Ir(toluene)]BARF with [NEt_3Bn]Cl.

(1.851 Å for [**2a**]BARF), which may be attributed to steric repulsion caused by the phosphine ligands.

We also tried to synthesize the neutral complex [(C_4Ph_4)IrCl]$_x$ by the reaction of [(C_4Ph_4)Ir(toluene)]BARF with the source of chloride anion (Scheme 3). According to ^{1}H NMR spectroscopy, the toluene in [**2c**]BARF is completely displaced after 24 h at 65 °C. However, we could not separate the expected product [(C_4Ph_4)IrCl]$_x$ (**4**) from the by-product [NEt_3Bn]BARF. Addition of CpTl to this mixture led to the formation of sandwich complex [(C_4Ph_4)IrCp], although the yield was low (16%). This suggested that the structure of **4** may be more sophisticated[10,11] than simple dimeric structure of [(cod)IrCl]$_2$.[12]

We have briefly investigated catalytic activity of cyclobutadiene iridium complex [**2c**]BARF in the reaction of phenyl diazoacetate decomposition with subsequent insertion in the insertion reaction of phenyl diazoacetate into X–H bonds (Scheme 4). It was found that reaction of phenyl diazoacetate with *tert*-butylamine proceeds in the presence of by 2 mol% of [(C_4Ph_4)Ir(toluene)]BARF and 4 mol% of [NEt_3Bn]Cl at 60 °C. Only 50% conversion was reached with 1 mol% of the catalyst. Interestingly that cyclobutadiene iridium complex is active at room temperature, but the rate of the reaction was slow (*ca*. 30% conversion after 24 h).

The reaction proceeded well with both aliphatic and aromatic amines (**6a**–**c**). High yield of the product **6d** was also obtained in reaction with methanol. However, insertion into Si–H and B–H bonds gave poor yields (**6e**,**f**). Generally, activity of cyclobutadiene iridium complexes in this process is similar to those of cyclobutadiene rhodium analogs, excepting reactions with triethylsilane and triethylamine-borane.[13] Noteworthy more active iridium catalysts (0.1–1 mol% catalyst loading, active at room temperature) for this kind of transformation have been proposed.[14–16] Lower catalytic activity of cyclobutadiene iridium complexes is in a good agreement with inert properties of this class of organometallic compounds.



Scheme 4 Substrate scope of X–H insertion reactions. Conditions: 0.1 mmol of phenyl diazoacetate, 0.2 mmol of substrate, 2 mol% of [**2c**]BARF, 4 mol% of [NEt_3Bn]Cl, DCE, 60 °C, 24 h.

To conclude, synthetic approach to the cyclobutadiene iridium complexes has been developed, enabling the synthesis of previously unknown sandwich and half-sandwich compounds. The scope and limitations of this approach were explored. Satisfactory results were obtained only with diphenylacetylene and alkyl-substituted arenes, functionalized substrates were not tolerated. Among silver salts only silver hexafluorophosphate promoted the formation of cyclobutadiene products. The cyclobutadiene iridium fragment forms very stable arene complexes, whose chemical properties are strikingly different from those of cyclobutadiene rhodium and cyclooctadiene iridium analogs. Reaction of arene replacement in [(C_4Ph_4)Ir(toluene)]BARF is convenient route for the synthesis of half-sandwich cyclobutadiene iridium complexes. Finally, catalytic activity of these complexes in the insertion of carbenoids into X–H bonds has been demonstrated.

This work was financially supported by the Russian Science Foundation (grant no. 22-73-00149). Access to the electronic resources and databases was provided by INEOS RAS with financial support from the Ministry of Science and Higher Education of the Russian Federation (075-03-2023-642).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.06.025.

References

1 N. V. Shvydkiy, T. N. Petrushina and D. S. Perekalin, *ChemCatChem*, 2021, **13**, 2873 and references therein.
2 T. N. Petrushina, Y. V. Nelyubina, D. S. Perekalin and N. V. Shvydkiy, *New J. Chem.*, 2024, **48**, 3952.
3 N. V. Shvydkiy, E. A. Trifonova, A. M. Shved, Y. V. Nelyubina, D. Chusov, D. S. Perekalin and A. R. Kudinov, *Organometallics*, 2016, **35**, 3025.
4 M. G. Freire, C. M. S. S. Neves, I. M. Marrucho, J. A. P. Coutinho and A. M. Fernandes, *J. Phys. Chem. A*, 2010, **114**, 3744.
5 R. Fernandez-Galan, B. R. Manzano, A. Otero, M. Lanfranchi and M. A. Pellinghelli, *Inorg. Chem.*, 1994, **33**, 2309.
6 M. M. Woyski, W. J. Shenk and E. R. Pellon, *Inorg. Synth.*, 1950, **3**, 111.
7 D. S. Perekalin, N. V. Shvydkiy, Y. V. Nelyubina and A. R. Kudinov, *Chem. – Eur. J.*, 2015, **21**, 16344.
8 A. C. Sievert and E. L. Muetterties, *Inorg. Chem.*, 1981, **20**, 489.
9 N. V. Shvydkiy and D. S. Perekalin, *Coord. Chem. Rev.*, 2020, **411**, 213238.
10 S. Takemoto, H. Ishii, M. Yamaguchi, A. Teramoto, M. Tsujita, D. Ozeki and H. Matsuzaka, *Organometallics*, 2019, **38**, 4298.
11 M. J. McGlinchey, *ChemPlusChem*, 2018, **83**, 480.
12 F. A. Cotton, P. Lahuerta, M. Sanau and W. Schwotzer, *Inorg. Chim. Acta*, 1986, **120**, 153.
13 N. L. Loskutova, N. V. Shvydkiy, Y. V. Nelyubina and D. S. Perekalin, *J. Organomet. Chem.*, 2018, **867**, 86.
14 B. J. Anding and L. K. Woo, *Organometallics*, 2013, **32**, 2599.
15 I. K. Mangion, I. K. Nwamba, M. Shevlin and M. A. Huffman, *Org. Lett.*, 2009, **11**, 3566.
16 J.-C. Wang, Z.-J. Xu, Z. Guo, Q.-H. Deng, C.-Y. Zhou, X.-L. Wan and C.-M. Che, *Chem. Commun.*, 2012, **48**, 4299.

Received: 28th March 2024; Com. 24/7437