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Iodide $[(\eta^5\text{-indenyl})IrI_2]_n$: an effective precursor to (indenyl)iridium sandwich complexes

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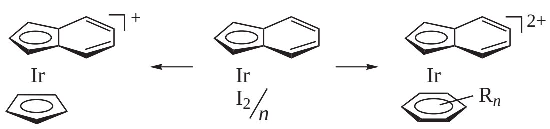
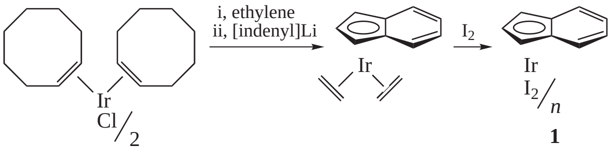
The reactions of $[(\eta^5\text{-indenyl})IrI_2]_n$ with CpTl or arenes in the presence of $AgBF_4$ afford $[(\eta^5\text{-indenyl})IrCp]^+$ or $[(\eta^5\text{-indenyl})Ir(arene)]^{2+}$ cations (arene = benzene, mesitylene, durene or hexamethylbenzene); the structures of $(\eta^5\text{-indenyl})Ir(C_2H_4)_2$ and $[(\eta^5\text{-indenyl})IrCp]PF_6$ were characterized by X-ray diffraction analysis.



In the last decade, the halide cyclopentadienyl rhodium and iridium complexes $[(C_5R_5)MX_2]_2$ proved to be effective catalysts for the C–H activation of aromatic compounds.[1] Moreover, they are widely used as the synthons of $(C_5R_5)M$ fragments in organometallic synthesis.[2] For example, we prepared a number of arene, triple-decker and metallacarborane complexes using the reactions of $[(C_5R_5)M]^{2+}$ cationic species (generated by a reaction of $[(C_5R_5)MX_2]_2$ with silver salts) with arenes, sandwich compounds and carborane ligands.[3] The related indenyl complexes attract considerable attention due to their higher chemical reactivity (indenyl effect). The enhanced reactivity is caused by the easy slippage of an indenyl ligand from η^5 to η^3 coordination mode. Here, we report the synthesis of the iodide $[(\eta^5\text{-indenyl})IrI_2]_n$ and demonstrate its applicability to the preparation of sandwich compounds containing the $(\eta^5\text{-indenyl})Ir$ moiety.

The iodide $[(\eta^5\text{-indenyl})IrI_2]_n$ **1**[†] was synthesized by the Bergman method[4] based on a reaction of iodine with the bis(ethylene) derivative $(\eta^5\text{-indenyl})Ir(C_2H_4)_2$ (Scheme 1). The latter was prepared without purification from the cyclooctene complex $[(C_8H_{14})_2IrCl]_2$,[5,‡] ethylene and indenyllithium.[§] In the ^1H NMR spectrum of **1**, there are only signals from the indenyl system. The polymeric structure was suggested based on the insolubility of **1** in dichloromethane, acetone and acetonitrile and on an analogy with the cyclopentadienyl derivative $[CpIrI_2]_n$. Recently, we have shown that the cyclooctadiene complex CpIr(cod) reacts with halogens giving cationic complexes [CpIr(cod)X]X containing a coordinated cyclooctadiene ligand.[6] However, a similar reaction of $(\eta^5\text{-indenyl})Ir(cod)$ with I_2 leads to an unidentified mixture of products, the formation of which is probably caused by the partial elimination of cyclooctadiene.



Scheme 1

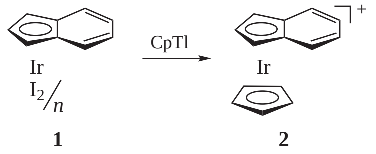
Iodide **1** proved to be an effective synthon of the $(\eta^5\text{-indenyl})Ir$ species. For example, the reaction of **1** with CpTl affords the mixed ligand sandwich cation $[(\eta^5\text{-indenyl})IrCp]^+$ **2**[¶] (Scheme 2).[††]

[†] Ethylene was passed through a solution of $[(C_8H_{14})_2IrCl]_2$ (700 mg, 0.78 mmol) in THF (10 ml) for 20 min. A solution of indenyllithium (0.25 M, 7.6 ml, 1.9 mmol) was added to the dark red reaction mixture with stirring under argon. The resulting greenish solution was kept with stirring for two days. The solvent was removed *in vacuo* and the residue was chromatographed on SiO_2 (20 cm × 1 cm) by elution with light petroleum and then diethyl ether. The light yellow band was collected and evaporated *in vacuo* to give $[(\eta^5\text{-indenyl})Ir(C_2H_4)_2]$ as a pale brown oily solid. A solution of I_2 (400 mg, 1.57 mmol) in Et_2O (8 ml) was added to $[(\eta^5\text{-indenyl})Ir(C_2H_4)_2]$ in the same solvent (4 ml) in air, and the reaction mixture was stirred for 1 h. The dark brown precipitate was centrifuged off, washed three times with Et_2O, one time with CH_2Cl_2 and then was washed with Et_2O until discoloration of the solvent. The residue was dried *in vacuo*. Yield, 400 mg (46%) as a dark purple presumably polymeric substance. ^1H NMR (DMSO-d_6) δ: 7.56–7.60 (m, 4H, indenyl), 6.52 (m, 2H, indenyl), 6.27 (m, 1H, indenyl). Found (%): C, 19.34; H, 1.31. Calc. for $C_9H_7I_2Ir$ (%): C, 19.26; H, 1.26.

[‡] The cyclooctene complex $[(C_8H_{14})_2IrCl]_2$ was prepared by a well-known procedure[5] with the use of K_2IrCl_6 instead of $(NH_4)_3IrCl_6$. A degassed mixture of H_2O (30 ml) and Pr^iOH (10 ml) was stirred while *cis*-cyclooctene (4 ml, 31 mmol) and K_2IrCl_6 (2.2 g, 4.54 mmol) were added under argon. The reaction mixture was refluxed with vigorous stirring for 4 h. The upper water-alcohol layer was decanted and cold EtOH (7 ml) was added to the orange oily residue. The resulting mixture was kept at 0 °C for ~16 h. The precipitate formed was filtered off, washed with cold EtOH and dried *in vacuo*. Yield, 1.31 g (65%) as an orange solid.

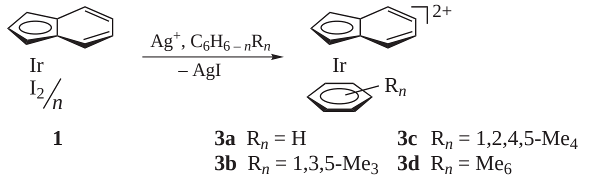
[§] A solution of BuLi (2.5 M, 2.8 ml, 7 mmol) in hexanes was added to a solution of indene (1 g, 8.6 mmol) in THF (25 ml) with stirring under argon. The mixture was stirred for ~1 h. The solution obtained (2.5 M of indenyllithium in hexanes–THF) was used without further isolation.

[¶] Dry MeCN (2 ml) was added to a mixture of **1** (60 mg, 0.107 mmol) and CpTl (38 mg, 0.14 mmol) under argon. The solution was stirred for 3 h and then filtered; the solvent was removed *in vacuo*. The residue was treated with a saturated aqueous solution of KPF_6. The aqueous layer was decanted and the solid residue was twice washed with water. After drying over P_2O_5, product [**2**]PF_6 was obtained as a white solid, yield 35 mg (63%). ^1H NMR (acetone-d_6) δ: 7.66 (m, 2H, indenyl), 7.39 (m, 2H, indenyl), 6.7 (d, 2H, indenyl, J 2.8 Hz), 6.0 (t, 1H, indenyl, J 2.8 Hz), 5.83 (s, 5H, Cp). Found (%): C, 32.37; H, 2.29. Calc. for $C_{14}H_{12}F_6IrP$ (%): C, 32.50; H, 2.34.



Scheme 2

We found that iodide abstraction from **1** by $AgBF_4$ in nitromethane in the presence of benzene and its derivatives resulted in dicationic arene complexes $[(\eta^5\text{-indenyl})Ir(arene)]^{2+}$ **3a–d** (Scheme 3).[‡‡] Note that the intermediate solvates $[(\eta^5\text{-indenyl})Ir(MeNO_2)_3]^{2+}$ are unstable in nitromethane solution. Thus, a control experiment with their preliminary generation and subsequent interaction with benzene did not give target complex **3a**. The thermal instability of the solvate complexes did not allow us to prepare polymethylated complexes **3c**,**d** in analytically pure forms owing to their low formation rates.



Scheme 3

The salts [**2**]PF_6 and [**3a–d**]$(BF_4)_2$ are air-stable solids. Moreover, the benzene derivative [**3a**]$(BF_4)_2$ is stable in dry acetonitrile solution for at least two days, similar to $[CpIr(C_6H_6)](BF_4)_2$.[3(b)] In the ^1H NMR spectrum of [**3a**]$(BF_4)_2$, the signal of the protons of a coordinated benzene ligand is very close ($\Delta\delta = 0.04$ ppm) to that for free benzene. This is a consequence of a high positive charge, whose effect compensates the opposite effect of coordination to the transition metal atom.

The structures of $(\eta^5\text{-indenyl})Ir(C_2H_4)_2$[§§,7] and [**2**]$PF_6$ were determined by X-ray diffraction analysis (Figures 1 and 2).[¶¶] The indenyl ligand in both complexes is η^5-coordinated to the iridium atom with moderate slippage; the hinge angles[†††,8] are 7.7–8.0° and 7.3°, respectively. The slip parameter[‡‡‡] is another characteristic used to describe the slip–fold distortion in the indenyl complexes.[1] Note that this parameter considerably increased on going from cation **2** (0.074 Å) to a bis(ethylene) derivative (0.163 Å). This is in accordance with a general tendency to the more favorable formation of 16VE complexes for Ir^I than for Ir^{III}. For other Ir^I complexes, $(\eta^5\text{-indenyl})Ir(cod)$[9] and $(\eta^5\text{-indenyl})Ir(\eta^4\text{-}HC_4Tol_4Ph)$,[10] the slip parameter also achieves high values (0.149 and 0.155 Å, respectively).

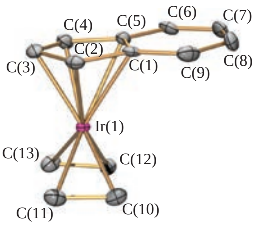


Figure 1 One of the two independent molecules of the complex $(\eta^5\text{-indenyl})Ir(C_2H_4)_2$ with atoms shown as thermal ellipsoids at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ir(1)–C(1) 2.355(5), Ir(1)–C(2) 2.199(5), Ir(1)–C(3) 2.210(5), Ir(1)–C(4) 2.212(6), Ir(1)–C(5) 2.374(5), Ir(1)–C(10) 2.131(6), Ir(1)–C(11) 2.108(6), Ir(1)–C(12) 2.130(6), Ir(1)–C(13) 2.132(6), C(1)–C(2) 1.450(8), C(2)–C(3) 1.431(8), C(3)–C(4) 1.424(8), C(4)–C(5) 1.448(7), C(1)–C(5) 1.438(7), C(10)–C(11) 1.423(9), C(12)–C(13) 1.439(8).

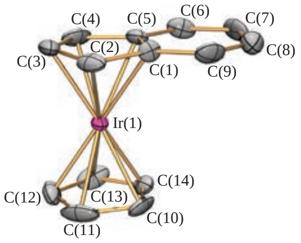


Figure 2 Cation **2** with atoms shown as thermal ellipsoids at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ir(1)–C(1) 2.254(13), Ir(1)–C(2) 2.162(14), Ir(1)–C(3) 2.178(15), Ir(1)–C(4) 2.168(15), Ir(1)–C(5) 2.223(12), Ir(1)–C(10) 2.161(15), Ir(1)–C(11) 2.174(14), Ir(1)–C(12) 2.157(15), Ir(1)–C(13) 2.181(14), Ir(1)–C(14) 2.172(14), C(1)–C(2) 1.445(19), C(2)–C(3) 1.39(3), C(3)–C(4) 1.42(3), C(4)–C(5) 1.46(3), C(1)–C(5) 1.448(19), C(10)–C(11) 1.43(2), C(11)–C(12) 1.41(3), C(12)–C(13) 1.42(2), C(13)–C(14) 1.37(2), C(10)–C(14) 1.41(2).

The C–C bond lengths of coordinated ethylene in $(\eta^5\text{-indenyl})Ir(C_2H_4)_2$ [1.423(9)–1.439(8) Å, av. 1.43 Å] are close to those in cyclopentadienyl analogues $(\eta\text{-}C_5H_4R)Ir(C_2H_4)_2$ (1.40–1.44 Å)[11]

[††] Anions are omitted in the schemes for clarity.

[‡‡] Dry $MeNO_2$ (1 ml) was added to a mixture of **1** (60 mg, 0.107 mmol), $AgBF_4\cdot C_4H_8O_2$ (61 mg, 0.214 mmol) and arene (0.5 ml of benzene or mesitylene; 60 mg, 0.43 mmol of durene; 70 mg, 0.43 mmol of hexamethylbenzene) with stirring under argon. The reaction mixture was kept for 1 h with stirring; then, the solvent was removed *in vacuo* and the oily residue was dissolved in $MeNO_2$ (0.5 ml). After the solution was filtered, the product was reprecipitated from $MeNO_2$ by diethyl ether, centrifuged off and washed with diethyl ether three times.

For [**3a**]$(BF_4)_2$: yield 24 mg (40%) as a golden brown solid. ^1H NMR (CD_3NO_2) δ: 7.92 (m, 2H, indenyl), 7.85 (m, 2H, indenyl), 7.41 (s, 6H, C_6H_6), 7.36 (d, 2H, indenyl, J 2.5 Hz), 6.7 (t, 1H, indenyl, J 2.5 Hz). Found (%): C, 32.04; H, 2.33. Calc. for $C_{15}H_{13}B_2F_8Ir$ (%): C, 32.22; H, 2.34.

For [**3b**]$(BF_4)_2$: yield 47 mg (73%) as an orange solid. ^1H NMR (CD_3NO_2) δ: 8.00 (m, 2H, indenyl), 7.78 (m, 2H, indenyl), 7.16 (d, 2H, indenyl, J 2.9 Hz), 7.12 (s, 3H, $C_6\mathit{H}_3Me_3$), 6.66 (t, 1H, indenyl, J 2.9 Hz), 2.57 (s, 9H, $C_6H_3\mathit{Me}_3$). Found (%): C, 35.97; H, 3.15. Calc. for $C_{18}H_{19}B_2F_8Ir$ (%): C, 35.96; H, 3.19.

For [**3c**]$(BF_4)_2$: yield 14 mg (22%) as a cream solid. ^1H NMR (CD_3NO_2) δ: 8.07 (m, 2H, indenyl), 7.65 (m, 2H, indenyl), 7.30 (s, 2H, $C_6\mathit{H}_2Me_4$), 7.15 (d, 2H, indenyl, J 2.5 Hz), 6.49 (t, 1H, indenyl, J 2.5 Hz), 2.35 (s, 12H, $C_6H_2\mathit{Me}_4$).

For [**3d**]$(BF_4)_2$: yield 4 mg (6%) as a cream solid. ^1H NMR (CD_3NO_2) δ: 8.09 (m, 2H, indenyl), 7.65 (m, 2H, indenyl), 6.91 (d, 2H, indenyl, J 2.5 Hz), 6.47 (t, 1H, indenyl, J 2.5 Hz), 2.46 (s, 18H, C_6Me_6).

[§§] The structure of $(\eta^5\text{-indenyl})Ir(C_2H_4)_2$ was studied earlier by Merola.[7] In this study, a crystal had the same crystallographic parameters. The crystallographic cell contains two independent molecules; data for only one of them will be used in the discussion.

[¶¶] Crystals of $(\eta^5\text{-indenyl})Ir(C_2H_4)_2$ were grown by the slow evaporation of light petroleum solution. Crystals of [**2**]PF_6 were grown up by slow diffusion in two-layer system, diethyl ether and a solution of the complex in acetone.

Crystal data for $(\eta^5\text{-indenyl})Ir(C_2H_4)_2$: $C_{13}H_{15}Ir$, monoclinic, space group $P2_1/c$, a = 7.7314(3), b = 10.7823(4) and c = 25.7026(10) Å, β = 98.4434(8)°, V = 2119.40(14) Å^3, Z = 8, d_{calc} = 2.278 g cm^{-3}, μ = = 12.554 mm^{-1}, F(000) = 1360, R_1 = 0.0352 [from 5586 unique reflections with $I > 2\sigma(I)$] and wR_2 = 0.0888 (from all 6184 unique reflections).

Crystal data for [**2**]PF_6: $C_{14}H_{12}F_6IrP$, monoclinic, space group $P2_1/n$, a = 9.0455(11), b = 13.9932(17) and c = 11.2372(13) Å, β = 92.647(2)°, V = 1420.8(3) Å^3, Z = 4, d_{calc} = 2.419 g cm^{-3}, μ = 9.568 mm^{-1}, F(000) = = 968, R_1 = 0.0648 [from 3478 unique reflections with $I > 2\sigma(I)$] and wR_2 = 0.1841 (from all 4149 unique reflections).

CCDC 1477235 and 1477236 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.

[†††] The hinge angle is defined as an angle between the planes defined by C(2)C(3)C(4) and C(2)C(1)C(5)C(4).

[‡‡‡] The slip parameter is defined as difference between the average distances from the metal to bridgehead carbons and from the metal to adjacent carbon atoms.

and longer than that in free ethylene (1.333 Å).[12] The $\mathrm{Ir}\cdots\mathrm{C_9H_7}$ distance in **2** (1.828 Å) is longer than the $\mathrm{Ir}\cdots\mathrm{C_5Me_5}$ distances in iridocenium cations $[\mathrm{CpIrCp}^*]^+$ (av. 1.798 Å)[13] and $[\mathrm{IrCp}^*_2]^+$ (av. 1.819 Å),[14] suggesting the weaker bonding of iridium with an indenyl ligand than with Cp.

Recently, we have found that the cyclopentadienyl complexes $[\mathrm{CpMI_2}]_2$ (M = Rh, Ir) effectively catalyze the oxidative coupling of benzoic acid with diphenylacetylene to give 1,2,3,4-tetraphenylnaphthalene.[15] Taking into account that indenyl complexes often exhibit higher catalytic activity as compared to that of cyclopentadienyl analogues,[16] we tried to use complex **1** as a catalyst in this reaction. Unfortunately, this complex was found catalytically inactive. For example, the reaction in the presence of 2 mol% of the catalyst afforded 1,2,3,4-tetraphenylnaphthalene in only 12% yield.[§§§] At the same time, the use of an equimolar quantity of **1** increased the yield up to 98%. This behaviour can be explained by the low stability of the (η^5-indenyl)Ir species, which were proposed as catalytic intermediates, under reaction conditions (refluxing in *o*-xylene).

In summary, we have demonstrated that iodide **1** can be used as a synthon of the (indenyl)iridium fragment (η^5-indenyl)Ir for the preparation of its cyclopentadienyl and arene derivatives.

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[§§§] A mixture of benzoic acid, diphenylacetylene, $\mathrm{Ag_2CO_3}$, **1** and *o*-xylene was refluxed with stirring under argon for about 6 h. The solvent was removed *in vacuo* and the residue was chromatographated on $\mathrm{SiO_2}$ (15 cm × 1 cm) by elution with light petroleum first and then diethyl ether. The yellow band was collected and evaporated *in vacuo* to give 1,2,3,4-tetraphenylnaphthalene as a yellow oil.

Catalytic experiment: benzoic acid (31 mg, 0.25 mmol), diphenylacetylene (89 mg, 0.5 mmol), $\mathrm{Ag_2CO_3}$ (138 mg, 0.5 mmol), **1** (2.8 mg, 0.005 mmol) and *o*-xylene (2 ml) were used. Yield, 12 mg (12%). ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 7.63–7.65 (m, 2H), 7.38–7.40 (m, 2H), 7.17–7.32 (m, 10H), 6.82–6.86 (m, 10H) [*cf*. ref. 1(*e*)].

Equimolar experiment: benzoic acid (7.5 mg, 0.06 mmol), diphenylacetylene (21 mg, 0.12 mmol), $\mathrm{Ag_2CO_3}$ (33 mg, 0.12 mmol), **1** (34 mg, 0.06 mmol) and *o*-xylene (1.5 ml) were used. Yield, 26 mg (98%).