ELSEVIER

Journal of Organometallic Chemistry 567 (1998) 57–63

Journal of Organometallic Chemistry

Activation and regioselective *ortho*-functionalization of phenols promoted by 'Cp*Ir' fragment: synthesis, structures and applications to organic synthesis. Cp* = C_5Me_5

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Received 15 September 1997; received in revised form 11 December 1997; accepted 23 December 1997

Abstract

Several stable oxo-dienyl–iridium complexes of the type [Cp*Ir(oxo-η^5-dienyl)][BF_4] (**2b**–**6**) have been prepared in high to quantitative yields. Treatment of these oxo-dienyl compounds with NaOMe affords the corresponding novel neutral dienone complexes of the type [Cp*Ir(oxo-η^4-dienone)] (**7**–**11**, **17**). Subsequent mild oxidation of the novel dienone–iridium complexes by I_2 produces the related functionalized free phenols along with the starting organometallic material recycled in the form [Cp*Ir(μ-I)I]$_2$. Extension of this chemistry to other type of nucleophiles such as phosphines, allows the isolation of a stable iridium η^4-phenol tautomer complex [Cp*Ir(η^4-exo-2-(PMe_3)–C_6H_5O)]$^+$. The latter was identified by X-ray diffraction and represents the key intermediate for the nucleophilic phenol functionalization reaction and the first molecular structure of a monocyclic phenol tautomer complex. Finally the use of the Cp*Ir system in organic synthesis is presented and discussed.

Keywords: Phenol; Dienone; Oxo-dienyl; Nucleophilic *ortho*-functionalization; Iridium

1. Introduction

The coordination of arenes to transition metal fragment modifies dramatically the chemistry of the π-hydrocarbon ligands and activates the complexed arenes toward nucleophilic substitution and addition reactions [1]. In 1959, Nicholls and Whiting reported the substitution of chlorine in (η^6-C_6H_5Cl)$Cr(Co)_3$ by methoxide to give (η^6-C_6H_5OMe)$Cr(CO)_3$ [2]. Subsequently, [(arene)$Cr(CO)_3$] complexes were extensively investigated and their use in organic synthesis was demonstrated [3]. Later on several new arene–metal complexes useful for organic syntheses were reported. For instance the arene in [(arene)$Mn(CO)_3$]$^+$ is known to be more electrophilic [4] than in [(arene)$Cr(CO)_3$] and similarly the [(dienyl)$Fe(CO)_3$]$^+$ complexes showed enhanced reactivity relative to the classical chromium arene complexes by displaying reactivity with a much wider range of nucleophiles [5]. This in fact is no doubt related to the positive charge in these Mn- and Fe-complexes [6].

All these examples have shown their importance in organic synthesis but none of these were used to promote phenol functionalization. Although the coordination chemistry of phenol is well established, there is still no organometallic procedure that allows the functionalization of such type of molecules via nucleophilic addition reactions. This may be attributed to the difficulty of obtaining stable complexes of π-coordination phenols by transition metal carbonyl complexes.

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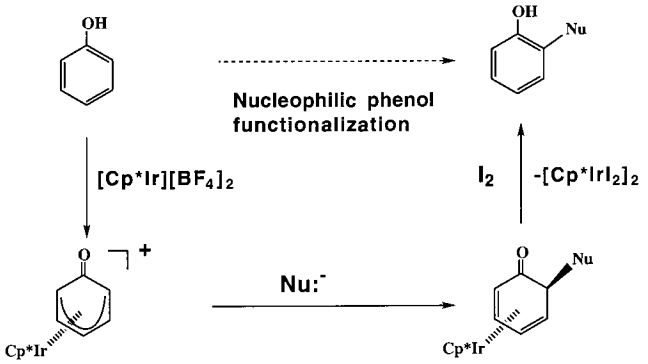
0022-328X/98/$19.00
PII S0022-328X(98)00668-8



Scheme 1. Nucleophilic phenol functionalization.

In this paper we report an efficient, regio- and stereoselective organometallic method to nucleophilic phenol functionalization promoted by the Cp*Ir fragment. Scheme 1 shows the general procedure [7] which involves nucleophilic addition at the *ortho*-position of the cationic oxo-η^5-dienyl–iridium complex and gives the corresponding neutral dienone compound. Subsequent mild oxidation by I_2 affords the functionalized free phenol along with the starting organometallic material recycled in the form $[Cp^*Ir(\mu\text{-}I)I]_2$.

2. Results and discussion

2.1. Syntheses, NMR and structural aspects of the oxo-η^5-dienyl–iridium complexes

Maitlis and coworkers reported in 1977 the synthesis of the first phenoxo-complexes of the type $[Cp^*M(\eta^5\text{-}C_6H_5O)][PF_6]$ (M = Rh, Ir) [8]. These compounds were isolated but only partially characterized. We have found that treatment of $[Cp^*M(S)_3][BF_4]_2$ (**1a**,**b**) (S = acetone, M = Rh, Ir) with the phenol arene in CH_2Cl_2, followed by treatment with NEt_3, affords the rhodium and iridium phenoxo-complexes $[Cp^*M(\eta^5\text{-}C_6H_5O)][BF_4]$ (**2a**,**b**) in 85 and 88% yields, respectively [9]. These compounds were isolated and completely identified. Our method, has been shown to be efficient and practical, and allowed us to prepare in high yields

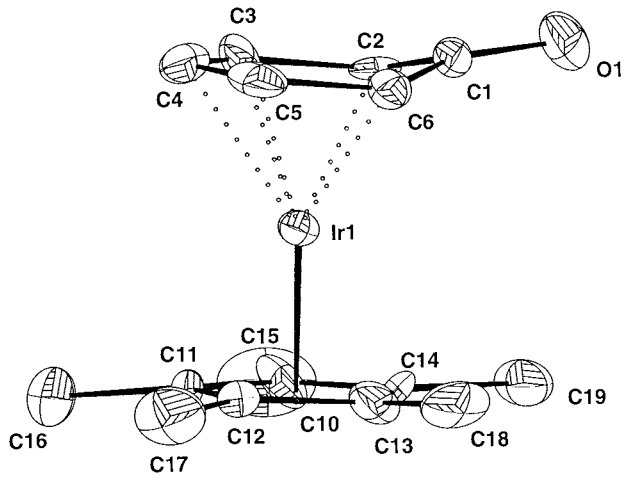
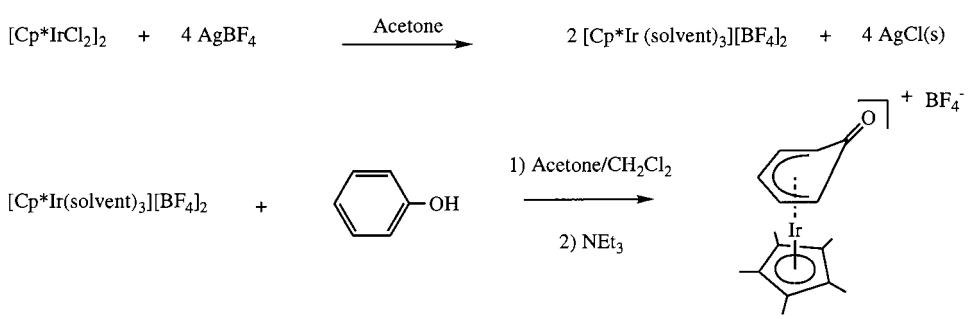


Fig. 1. Molecular structure of $[Cp^*Ir(\eta^5\text{-}C_6H_5O)]^+$ with atom numbering system. Selected bond distances (Å) and angles (°): Ir–C(1) 2.50(2), Ir–C(2) 2.21(2), Ir–C(3) 2.21(2), Ir–C(4) 2.21(2), Ir–C(5) 2.21(2), Ir–C(6) 2.24(2), O(1)–C(1) 1.23(2).

a family of $[Cp^*Ir(oxo\text{-}\eta^5\text{-}dienyl)][BF_4]$ complexes of the following phenols: 3,5 dimethyl phenol (**3**); 3,4 dimethyl phenol (**4**); tetralol (**5**); and β-estradiol (**6a**,**b**; two diastereomers depending on which face the metal fragment is coordinated) [7] (Scheme 2). It should be mentioned that our method avoids the use of aqueous medium as reported previously, which in some cases provokes the hydrolysis of the counter ions [10].

Generally in these complexes the cyclic π-hydrocarbon is coordinated to the metal center by only five carbons while the C=O unit is bent away from the metal. Several X-ray molecular structures of Rh [9] Fe [11] and Ru [12] complexes were reported by us and others. In this paper we include the molecular structure of the novel complex $[Cp^*Ir(\eta^5\text{-}C_6H_5O)][I]$ (**2c**), which represents the simplest molecular model of such oxo-dienyl complexes and confirms the previous observations. Crystals of **2c** were obtained by slow crystallization from CH_3CN/Et_2O solution. Compound **2c** crystallizes in the triclinic space group $P\bar{1}$; there are two independent molecules in the unit cell, Fig. 1 represents a view of cation $[Cp^*Ir(\eta^5\text{-}C_6H_5O)]^+$ with atom numbering system. The structure shows that the 'Cp*Ir' unit is



Scheme 2.

coordinated to only five carbons of the phenyl ring. The distances from the metal to the centers of the π-bonded carbons are 1.73 Å for the phenoxide ligand and 1.80 Å for the η^5-C_5Me_5 ligand, while the bond distance dIr–C_1 is 2.50 Å. Loss of aromaticity in the bonded phenoxo unit is manifested by the irregularity of the arene C–C bond lengths. Another important feature of this structure is described by the distance $d_{C1-O1} = 1.23$ Å, typical of a C=O function. This bond distance is shorter than that reported for the analogous rhodium, ruthenium and iron derivatives [Cp*Rh(η^5-PhO)][BF_4], [Cp*Ru(η^5-PhO)·2PhOH] and [Cp*Fe(η^5-PhO)] with $d_{C-O} = 1.25$, 1.28 and 1.25 Å, respectively [9,11,12]. The dihedral angle θ between the plane C2–C1–C6 and the rest of the ring in **2c** is 21°; this angle θ is greater than that reported for the iron ($\theta = 1.55°$), ruthenium ($\theta =$ 4°) and rhodium ($\theta = 14°$) complexes. In conclusion, we note that the η^5-phenoxide moiety coordinated to the iridium center in **2c** (transition metal of third row) adopts a specific geometry relative to the other metal series (Fe, Ru and Rh) where the ketonic character of the carbonyl group C=O is more pronounced.

Extensive ^{1}H-NMR analysis of these oxo-dienyl complexes show that dienyl protons appear in the range of 5.50–6.75 ppm while the pentamethylcyclopentadienyl CH_3 protons resonate as a singlet in the range 2.0–2.3 ppm. The ^{13}C-NMR of such complexes display a characteristic feature for the non-coordinated C=O function, which appear in the range 150–165 ppm. The preparation of such oxo-dienyl complexes is easy, as is their spectroscopic characterization, but their reactivity with nucleophiles remains unknown. However, we note that recently Chung et al. have reported the synthesis of [$Mn(CO)_3(C_6H_5O)$] which undergoes sequential nucleophilic and electrophilic addition to give the related [$Mn(CO)_3$(η^5-dienyl)] complexes [13]. Oxidative demetallation of these complexes affords substituted alkoxybenzenes.

2.2. Reaction with NaOMe and formation of η^4-2,4-dienone–iridium complexes

The oxo-dienyl–iridium complexes [Cp*Ir(oxo-η^5-dienyl)] [BF_4] (**2b**–**4**) react smoothly at room temperature with freshly prepared NaOMe solution in MeOH to afford the corresponding neutral [Cp*Ir(η^4-dienone)] (**7**–**9**) complexes in high to quantitative yields. In these compounds the methoxide nucleophile adds regio-selectively at the *ortho*-position (Scheme 3).

Interestingly in the oxo-dienyl complex (**4**), the η^5-phenoxide unit is unsymmetrically substituted and displays two distinct *ortho*-positions. We have found that only the less hindered C_6-position is attacked and affords one dienone–iridium complex.

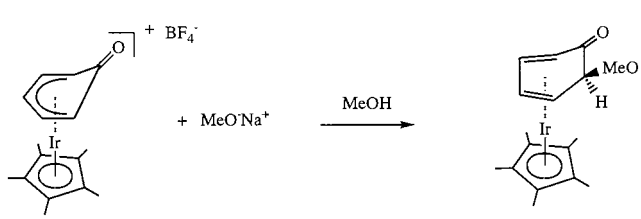
Extension of this chemistry to other sensitive polycyclic phenol ligands such as tetralol and β-estradiol has been performed with success. It is noteworthy that coordination of the A-ring of β-estradiol by metallocarbonyl fragments often gives unstable complexes. This inconvenience has hampered the functionalization of such β-estradiol by using metallacarbonyl fragments despite the fact that $Cr(CO)_3$ is a very useful synthon for organic synthesis. The ability of the Cp*Ir fragment to complex such sensitive ligands (where the oxo-η^5-dienyl moiety is obtained by subsequent *O*-deprotonation of the coordinated tetralol and β-estradiol), represents an advantage for this chemistry. Thus, the [Cp*Ir(oxo-η^5-dienyl)][BF_4] complexes (**5**, **6**) respectively react with NaOMe in methanol at -40°C to give, respectively, the related dienone–iridium complexes [Cp*Ir{η^4-dienone (OMe)}] (**10**, **11**) in 95 and 91% yields, respectively, with nucleophilic attack occurring exclusively at the ortho-position relative to the C=O function.

These dienone–iridium complexes react with an excess of iodine to produce the related free functionalized phenols along with the starting material recycled in the form of [Cp*Ir(μ-I)I]$_2$. These phenols were obtained in good to high yield. We note that the expensive hormone 2-methoxy-estradiol (**16**) was obtained in 60% overall yield starting from β-estradiol. The present synthesis is more efficient than the classical organic procedure which requires five steps starting from β-estradiol and produces **16** with an overall yield of 5% [14]. Our method is a unique addition to the steroid literature and should increase availability of rare steroids and other oxygenated compounds of use to chemists and biochemists who are interested in this area. Table 1 displays the starting phenol molecules and the final products as well as the related oxodienyl– and dienone–iridium complexes.

The key reaction of the previous chemical transformation is the formation of an η^4-dienone complex in which the MeO^- is now attached at C-2 (Scheme 3). Attempts to obtain an X-ray structure of these methoxylated-dienone derivatives have been unsuccessful. As a model system to the previous reaction we used PMe_3 as the nucleophile and were able to isolate and characterize by X-ray structure the η^4-dienone complex.

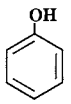
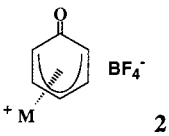
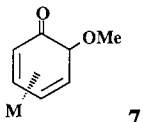
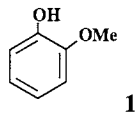
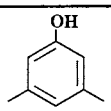
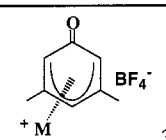
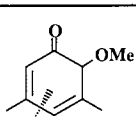
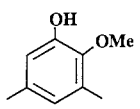
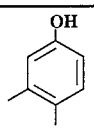
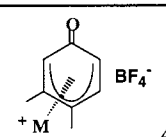
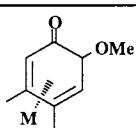
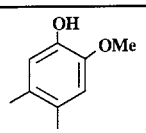
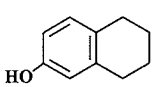
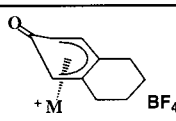
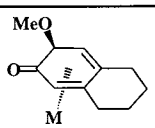
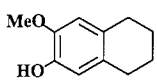
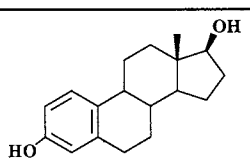
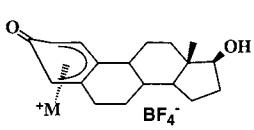
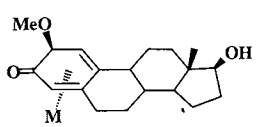
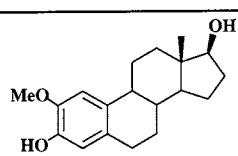
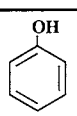
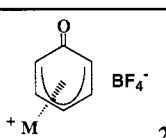
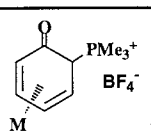
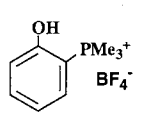
2.3. Reaction with PMe_3 and isolation of the first monocyclic X-ray molecular structure of a stable η^4-dienone–iridium complex

Treatment of a slurry of [Cp*Ir(n^5-C_6H_5O][BF_4] (**2b**)



Scheme 3.

Table 1
Reactants and products of reactions

Starting materials	oxo-η^5-cyclohexadienyl Ir derivatives	η^4-cyclohexadienone-Ir derivatives	I_2 Oxidation / Products	Ref
	 **2b**	 **7**	 **12**	[7]
	 **3**	 **8**	 **13**	[7]
	 **4**	 **9**	 **14**	[7]
	 **5**	 **10**	 **15**	[7]
	 **6**	 **11**	 **16**	[7]
	 **2b**	 **17**	 **18**	This work

M = "Cp*Ir"

in CH_2Cl_2 with an excess of trimethyl phosphine PMe_3 at room temperature gave a yellow solution rapidly. Reaction workup and analysis of the product by NMR spectroscopy showed the formation of only one compound of the type $[Cp^*Ir(\eta^4\text{-exo-2-}(PMe_3)\text{-}C_6H_5O)][BF_4]$ (**17**) where the PMe_3 has been introduced at C-2; this was umambigously confirmed by an X-ray study.

Crystals of **17** were obtained by the slow diffusion method from acetone/Et_2O. The compound crystallizes in the triclinic unit cell, space group $P\bar{1}$. Fig. 2 shows the structure of $[Cp^*Ir(\eta^4\text{-exo-2-}(PMe_3)\text{–}C_6H_5O)]^+$ with atom-numbering system. The structure reveals that the PMe_3 ligand is indeed attached at C-2 with exo-stereochemistry relative to the organometallic moiety 'Cp*Ir'. The distances from the metal to the centers of the π-bonded carbons are 1.68 Å for the dienone and 1.82 Å for the η^5-C_5Me_5 ligand. Further the 'Cp*Ir' moiety is coordinated to only four carbons of the dienone unit. Loss of aromaticity is manifested by the irregularity of the C–C bond distances; the length of the uncoordinated bond C1–C2 = 1.50(1) Å, while the C–O bond distance is 1.22(1) Å, which is characteristic of a C=O double bond of a ketonic function. The uncoordinated part of the dienone is bent in a distorted fashion, this is due to the presence of a linked C1(sp^2)–C2(sp^3) carbons. The dihedral angle 'hinge' across C3–C6 is 36.5°.

At this stage a brief comment on this η^4-phenol tautomer is required. Although cyclohexadienone complexes such as Fe(CO)3(η^4-2,4-cyclohexadien-1-one) are well established [15], no X-ray structure for monocyclic η^4-phenol tautomer compounds has been reported. However, we note the presence of few dienone complexes of molybdenum and chromium were reported where the dienone unit is a part of a complex polycyclic system [16].

When a MeOH solution of **17** was exposed to iodine and the mixture was stirred for 15 min a dark brown precipitate was obtained. Reaction work-up of the supernatant phase and analysis by NMR spectroscopy suggested the formation of the phosphinated phenol salt $[(C_6H_4OH)\text{–}PMe_3][BF_4]$ (**18**) isolated in 52% yield.

The formation of this phosphinated phenol salt is no doubt a result of enone–phenol tautomerization, similar to that observed for the methoxylation reactions.

In conclusion we have reported the nucleophilic *ortho*-functionalization of phenols and polycyclic phenols promoted by the Cp*Ir fragment. We hope that we have demonstrated to the reader that the chemistry exhibited by the Cp*Ir system has many and interesting applications in organic syntheses. Among the examples shown in this paper is the synthesis of 2-methoxy estradiol. We also draw the attention of the reader to the fact that the functionalized organic molecules are obtained along with the starting material recycled in the form $[Cp^*Ir(\mu\text{-}I)I]_2$, this at least would compensate the inconvenience of using a fairly expensive transition metal in organic syntheses. Further the isolation of the key intermediate η^4-dienone complex $[Cp^*Ir(\eta^4\text{-exo-2-}(PMe_3)\text{–}C_6H_5O)][BF_4]$ (**17**) is significant, since it represents the first example of the proposed ultimate intermediate for the nucleophilic phenol functionalization promoted by the Cp^*Ir^{2+} moiety, which to our knowledge represents the only available organometallic procedure in the literature. However, we note that Harman et al. have recently reported on the electrophilic phenol functionalization promoted by the $Os(NH_3)_5^{2+}$ moiety [17].

We recently found that the oxo-dienyl–iridium complexes react with other types of nucleophiles such as hydrides, carbon nucleophiles and thiophenols. These novel reactions as well as the potential use of the 'Cp*Ir' system to prepare *ortho*-functionalized phosphinated phenols including a detailed mechanistic study will be the subject of future reports.

3. Experimental section

3.1. General procedures

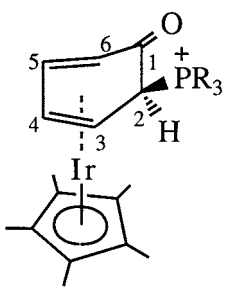
All manipulations were carried out under argon atmosphere using Schlenk techniques. Solvents were purified and dried prior to use by conventional distillation techniques. MeOH was distilled over traces of Na and used freshly in preparation of NaOMe solutions. All reagents obtained from commercial sources were used without further purification. NMR spectra were recorded on Bruker AM 250 and 200 MHz instruments. Chemical shifts are reported in parts per million referenced, to residual solvent proton resonance for ^1H, ^{13}C, and to H_3PO_4 in acetone d_6 for ^{31}P. Infrared spectra were obtained on a Bruker IR 45 spectrometer from samples prepared on KBr disks. Elemental analysis were performed by the Microanalytical Laboratory of the University of Paris VI.

The syntheses of compounds (**2b**–**16**) was already reported in the literature [7].

3.2. Synthesis of $[Cp^*Ir(\eta^5\text{-}C_6H_5O)][I]$ (2c)

This complex was prepared quantitatively from $[Cp^*Ir(\eta^5\text{-}C_6H_5O)][BF_4]$ (**2b**) and NaI through anion exchange or indirectly during oxidation of η^4-dienone complexes $[Cp^*Ir(\eta^4\text{-exo-2-(Nu)-}C_6H_5O)][BF_4]$ (Nu = -SPh, $N(CH_2)_5$) by iodine [18]. Unlike **2b**, the compound $[Cp^*Ir(\eta^5\text{-}C_6H_5O)][I]$ (**2c**) crystallizes easily and afford suitable crystals for an X-ray structure determination; this is probably related to the presence of the iodide atom as a counter anion.

^{1}H-NMR (CD_3CN, 250 MHz): 0 6.48 (t, 1H, J_{H-H} = 5 Hz, H_{para}), 6.36 (t, 2H, J_{H-H} = 5 Hz, H_{meta}). 5.59 (d, 2H, J_{H-H} = 5 Hz, H_{ortho}), 2.20 (s, 15H, Me–Cp). ^{13}C-NMR (CD_3CN, 62.9 MHz): δ 163.7 (C=O), 100.1 (s, η^5-Cp*), 95.9 (s, C_{meta}), 84.5 (s, C_{ortho}), 81.4 (s, C_{para}), 10.2 (s, Me–Cp). IR (KBr, cm^{-1}): 1650 ($\nu_{C=O}$).



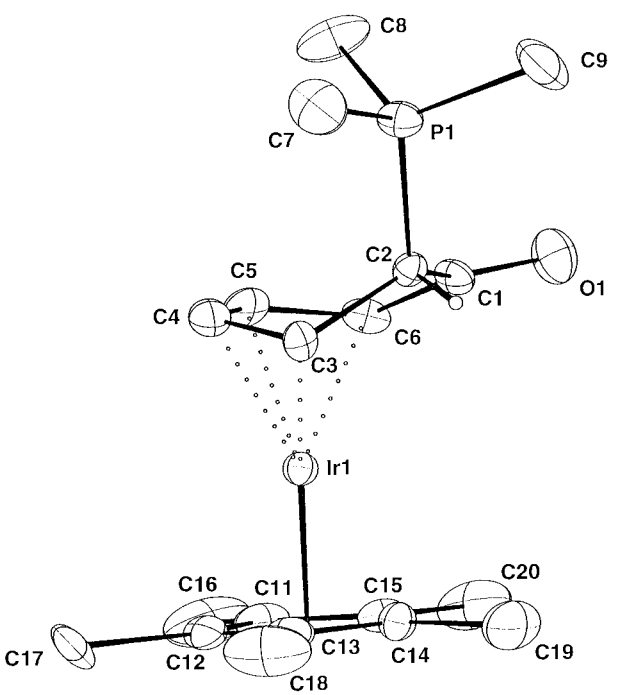


Fig. 2. Molecular structure of $[Cp^*Ir(\eta^4\text{-exo-2-}(PMe_3)\text{–}C_6H_5O)]^+$ with atom numbering system. Selected bond distances (Å) and angles (°): Ir–C(3) 2.14(1), Ir–C(4) 2.14(1), Ir–C(5) 2.11(1), Ir–C(6) 2.14(1), C(1)–C(2) 1.50(1), O(1)–C(1) 1.22(1).

3.3. Synthesis of [Cp*Ir(η^4-exo-2-(PMe_3)–C_6H_5O)][BF_4] (**17**)

PMe_3 (200 μl, 1.93 mmol) was added to a solution of [Cp*Ir(η^5-C_6H_5O)][BF_4] (**2b**) (135 mg, 0.26 mmol) in 20 ml of CH_2Cl_2. The resulting yellow solution was stirred for 12 h. Then, the reaction mixture was reduced under vacuum and subsequent addition of Et_2O (40 ml) afforded a pale yellow precipitate. Yield 86% (133 mg). ^{1}H-NMR (CD_3CN, 250 MHz): δ 5.37 (t, 1H, J_{H-H} = 4.5 Hz, H_5), 5.04 (t, 1H, J_{H-H} = 4.5 Hz, H_4), 3.66 (dd, 1H, J_{P-H} = 14.3 Hz, J_{H-H} = 4.5 Hz, H_2), 3.59 (d, 1H, J_{H-H} = 4.5 Hz, H_6), 2.99 (t, 1H, J_{H-H} = 4.5 Hz, H_3), 2.03 (s, 15H, Me–Cp), 1.60 (d, 9H, J_{P-H} = 14.0 Hz, Me–P). ^{13}C-NMR (CD_3CN, 62.9 MHz): δ 181.7 (d, J_{P-C} = 9.1 Hz, C═O), 92.0 (s, η^5-Cp*), 72.2 (s, C_5), 67.4 (d, J_{P-C} = 4.4 Hz, C_4), 59.0 (d, J_{P-C} = 3.8 Hz, C_6), 40.1 (d, J_{P-C} = 34.4 Hz, C_2), 27.6 (d, J_{P-C} = 6.6 Hz, C_3), 10.2 (s, Me–Cp), 7.5 (d, J_{P-C} = 51.3 Hz, CH_3–P). ^{31}P-NMR (acetone d_6, 101.2 MHz): δ 34.3. IR (KBr, cm^{-1}): 1628.9 ($\nu_{C=O}$)' 1055.7 (ν_{B-F}). Anal. Calc. for $C_{19}H_{29}BF_4IrOP$: C, 39.11; H, 5.01. Found: C, 38.96; H, 5.00.

3.4. Synthesis of [(C_6H_5OH)–PMe_3][BF_4] (**18**)

A solution of [Cp*Ir(η^4-exo-2-(PMe_3)–C_6H_5O)][BF_4] (**17**) (230 mg, 0.39 mmol) in MeOH (5 ml) was treated with a solution of I_2 (100 mg, 0.39 mmol) in MeOH (10 ml) at −80°C. A brown precipitate was obtained, then filtered and washed with MeOH (2 × 5 ml). The product was identified as the organometallic compound [Cp*IrI_2]$_2$. Yield 82% (226 mg). The supernatant phase was evaporated to dryness. The expected organic compound **18** was crystallized from acetone/ether. Yield 52% (51 mg).^{1}H-NMR (acetone d_6, 250 MHz): δ 10.67 (s, 1H, OH), 7.70–7.60 (m, 2H, ArH), 7.28 (m, 1H, ArH), 7.14 (t, 1H, J_{H-H} = 7.5 Hz, ArH), 2.35 (d, 9H, J_{P-H} = 14.8 Hz, CH_3). ^{13}C (acetone d_6, 62.9 MHz): δ 161.3 (d, J_{P-C} = 2.3 Hz, C–O), 137.2 (d, J_{P-C} = 1.9 Hz, Ar), 133.2 (d, J_{P-C} = 8.2 Hz, Ar), 121.4 (d, J_{P-C} = 12.3 Hz, Ar), 117.3 (d, J_{P-C} = 6.7 Hz, Ar), 107.7 (d, J_{P-C} = 89.6 Hz, Ar), 9.5 (d, J_{P-C} = 57.6 Hz, Me–P). IR (KBr, cm^{-1}): 3422.5 (ν_{O-H}), 1055.7 (ν_{B-F}). ^{31}P-NMR (acetone d_6, 101.2 MHz): δ 21.7. Anal. Calc. for $C_9H_{14}BF_4OP$: C, 42.23; H, 5.51. Found: C, 42.25; H, 5.90.

3.5. X-ray crystallography of [Cp*Ir(η^5-C_6H_5O)][I] (**2c**) and [Cp*Ir(η^4-exo-2-(PMe_3)–C_6H_5O)][BF_4] (**17**)

Suitable crystals of **2c** and **17** were obtained by recrystallization from acetonitrile/Et_2O and acetone/Et_2O solutions, respectively. The selected crystal of complex **2c** or **17** was glued on the top of a glass stick. Accurate cell dimensions and orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collection. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS [19]. Scattering factors and corrections for anomalous dispersion were taken from Ref. [20]. The structure of **2c** was solved by standard Patterson and Fourier techniques and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were not introduced. The structure of complex **17** was also solved by standard Patterson and Fourier techniques and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms; however, the hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter.

Acknowledgements

We would like to thank PhosPhoenix for a loan of $IrCl_3 \cdot x H_2O$. The CNRS is gratefully acknowledged for supporting this work.

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