Regioselective Phosphine Addition to $[(\eta^5\text{-}C_5Me_5)Ir(\eta^5\text{-oxocyclohexadienyl})]^+$ and X-ray Structure of the Stable Phenol Tautomer Complex $[(\eta^5\text{-}C_5Me_5)Ir(\eta^4\text{-}exo\text{-}2\text{-}(PMe_3)C_6H_5O)]^+$: A Key Intermediate for the Nucleophilic Phenol Functionalization Reaction

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Received November 11, 1997

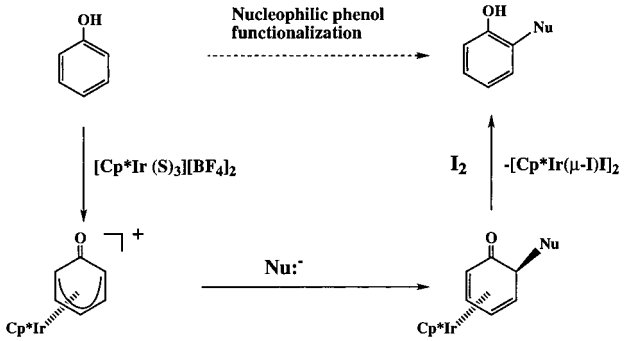
Treatment of $[(\eta^5\text{-}C_5Me_5)Ir(\eta^5\text{-}C_6H_5O)][BF_4]$ (**1**) with an excess of trialkylphosphine (PR_3 = PMe_3, PEt_3, and PMe_2Ph) affords the η^4-phenol tautomers $[(\eta^5\text{-}C_5Me_5)Ir(\eta^4\text{-}exo\text{-}2\text{-}(PR_3)C_6H_5O)][BF_4]$ (**2**−**4**) in which the phosphine nucleophile adds regioselectively at C-2. The X-ray molecular structure of such a phenol tautomer complex $[(\eta^5\text{-}C_5Me_5)Ir$ $(\eta^4\text{-}exo\text{-}2\text{-}(PMe_3)C_6H_5O)][BF_4]$ (**2**) is reported. Complex **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.599(1)$ Å, $b = 9.0173(9)$ Å, $c = 14.448(3)$ Å, $\alpha = 95.90(1)°$, $\beta = 99.47(1)°$, $\gamma = 99.20(1)°$, and $Z = 2$. Oxidation of these η^4-dienone complexes **2**−**4** by iodine affords the related phosphine salts $[(C_6H_4OH)\text{-}PR_3][BF_4]$ (**5**−**7**), and the starting iridium complex is recycled in the form of $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}I)I]_2{\cdot}I_2$ (**8**) as confirmed by an X-ray analysis carried out on compounds **5** and **8**. Complex **5** crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.593(6)$ Å, $b = 19.922(4)$ Å, $c = 11.909(3)$ Å, $\beta = 106.83(4)°$, and $Z = 8$. The structure of **8** can be viewed as an infinite chain of dimeric iridium $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}I)I]_2$ bridged by I_2 units. Complex **8** crystallizes in the monoclinic space group $P2_1/c$ with $a = 15.533(3)$ Å, $b = 8.374(1)$ Å, $c = 23.541(4)$ Å, $\beta = 100.89(4)°$, and $Z = 4$.

Introduction

Coordinated arenes such as in complexes of the type $[M(CO)_3\text{-}(\eta^6\text{-arene})]^{n+}$ (M = Cr, $n = 0$; M = Mn, $n = +1$) are activated toward nucleophilic attack, and the utility of these complexes in organic synthesis has been widely demonstrated;[1a] however there is still no organometallic procedure that allows *functionalization of phenols via nucleophilic reactions*.

Nucleophilic additions to η^5-dienyl complexes have been well investigated and generally afford the related η^4-diene compounds.[1b,c] However the chemistry of η^5-oxo-dienyl complexes remains unknown. Such complexes could be used as precursors to promote *nucleophilic phenol functionalization*. We recently reported a novel system for regioselective ortho-functionalization of phenols promoted by the "$(\eta^5\text{-}C_5Me_5)Ir$" fragment and using NaOMe as the attacking nucleophile (Scheme 1).[2] Our method has been shown also to be efficient for ortho-functionalization of complex organic molecules such as tetralols and steroids.[3]

Scheme 1. Ir-Mediated Nucleophilic Phenol Functionalization



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. Subsequent oxidation of these η^4-dienone complexes by iodine provides the functionalized phenols. Interestingly the C=O function of the η^5-oxo-dienyl complexes is not attacked by MeO^-. Attempts to obtain an X-ray structure of these key intermediates, i.e., the methoxylated (η^4-dienone)-iridium complexes 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.

In this paper we report regiospecific phosphines addition to the η^5-oxo-dienyl iridium complex $[(\eta^5\text{-}C_5Me_5)Ir(\eta^5\text{-}C_6H_5O)]$-

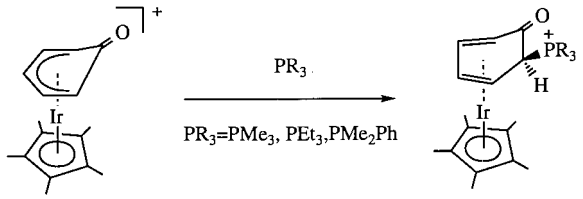
(1) (a) Davies, S. G. *Organotransition Metal Chemistry Applications to organic synthesis*; Pergamon: Press: Oxford, U.K., 1982; Chapter 4, p 116. (b) Pearson, A. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, p 637. (c) Hegedus, L. S. *Transition Metals In The Synthesis Of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994; Chapter 7, p 229.

(2) Le Bras, J.; Amouri, H., Vaissermann, J. *Organometallics* **1996**, *15*, 5706.

(3) Le Bras, J.; Rager, M. N.; Besace, Y.; Vaissermann, J.; Amouri, H. *Organometallics* **1997**, *16*, 1765.

S0020-1669(97)01427-4 CCC: $15.00
Published on Web 09/12/1998

Scheme 2. Synthesis of η^4-Phenol Tautomer Complexes $[(\eta^5\text{-}C_5Me_5)Ir(\eta^4\text{-}exo\text{-}2\text{-}(PR_3)C_6H_5O)][BF_4]$ (**2**-**4**)



$[BF_4]$ (**1**)[4] yielding the corresponding stable η^4-phenol tautomer iridium complexes $[(\eta^5\text{-}C_5Me_5)Ir(\eta^4\text{-}exo\text{-}2\text{-}(PR_3)C_6H_5O)][BF_4]$ (**2**−**4**). Furthermore the X-ray molecular structure of $[(\eta^5\text{-}C_5Me_5)Ir(\eta^4\text{-}exo\text{-}2\text{-}(PMe_3)\text{-}C_6H_5O)]^+$ was determined. To our knowledge this is the first X-ray structure reported in the literature of a stable η^4-phenol tautomer coordinated to an iridium center.[5] This η^4-phenol tautomer complex represents the key intermediate for the nucleophilic phenol functionalization reaction since it can be easily oxidized to give in reasonable yield the related free ortho-phosphinated phenol salt $[(C_6H_4\text{-}OH)PMe_3][BF_4]$ (**5**). This salt was identified unambiguously by X-ray analysis (vide infra). The other η^4-dienone complexes **3** and **4** are oxidized in a similar way to give the functionalized phenols **6** and **7**.

Results and Discussion

Treatment of a slurry of $[(\eta^5\text{-}C_5Me_5)Ir(\eta^5\text{-}C_6H_5O)][BF_4]$ (**1**) in CH_2Cl_2 with an excess of trialkylphosphines PR_3 (PR_3 = PMe_3, PEt_3, PMe_2Ph) at room temperature gave rapidly a yellow solution. Reaction workup and analysis of the product by NMR spectroscopy showed the formation of only one compound of the type $[(\eta^5\text{-}C_5Me_5)Ir(\eta^4\text{-}exo\text{-}2\text{-}(PR_3)C_6H_5O)][BF_4]$ (**2**−**4**), where the PR_3 has been introduced at C-2 (Scheme 2); further, an X-ray study of complex **2** confirmed the site of PR_3 introduction at C-2. Complexes **3** and **4** could not be prepared free of the starting material **1** and were not isolated as pure microcrystalline solids.

The ^1H NMR spectra of these phosphine adducts show the expected five multiplets in the area 3−6 ppm indicating an ortho attack has occurred;[2,3] further, an additional coupling $^2J_{P-H}$ = 13−15 Hz was found for the protons on the ortho carbon bearing the phosphine ligand. To ascertain without ambiguity the structures of these new phosphine adducts **2**−**4** and to determine the stereochemistry of the nucleophilic attack, an X-ray analysis was carried out on $[(\eta^5\text{-}C_5Me_5)Ir(\eta^4\text{-}exo\text{-}2\text{-}(PMe_3)C_6H_5O)][BF_4]$ (**2**). Crystals of **2** were obtained by the slow diffusion method from acetone/Et_2O. The compound crystallizes in the triclinic unit cell, space group $P\bar{1}$. Figure 1 shows the structure of $[(\eta^5\text{-}C_5Me_5)Ir(\eta^4\text{-}exo\text{-}2\text{-}(PMe_3)C_6H_5O)]^+$ with the atom-numbering system; crystallographic data collection parameters and selected bond lengths and angles are listed in Tables 1 and 2.

The structure reveals that the PMe_3 ligand is indeed attached at C-2, with exo-stereochemistry relative to the organometallic moiety "$(\eta^5\text{-}C_5Me_5)Ir$". The distances from the metal to the centers of the π-bonded carbons are 1.68 Å for the arene and 1.82 Å for the $\eta^5\text{-}C_5Me_5$ ligand. Further, the "$(\eta^5\text{-}C_5Me_5)Ir$" moiety is coordinated to only four carbons of the ring. Loss of aromaticity is manifested by the irregularity of the C−C bond distances; the length of the uncoordinated bond C(1)−C(2) = 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 arene is bent in a distorted fashion relative to other η^4-complexes. This is due to the presence of a linked C(1)(sp^2)−C(2)(sp^3) carbons. The dihedral angle "hinge" is 36.5° and slightly less than those reported for the η^4-arene complexes of Rh,[6] Ru,[7] Fe,[8] Ta,[9]and Mn,[10] which lie in the range of 37−44°. At this stage a brief comment on this η^4-phenol tautomer is required. Although cyclohexadienone complexes such as $Fe(CO)_3(\eta^4\text{-}2\text{-}4\text{-cyclohexadien-1-one})$ are well established,[11,12] no X-ray structure for a monocyclic η^4-dienone compound has been reported.[5] On the other hand, it should be borne in mind that the free dienone ligands are unstable and have been generated by vacuum pyrolysis and are partially characterized.[13]

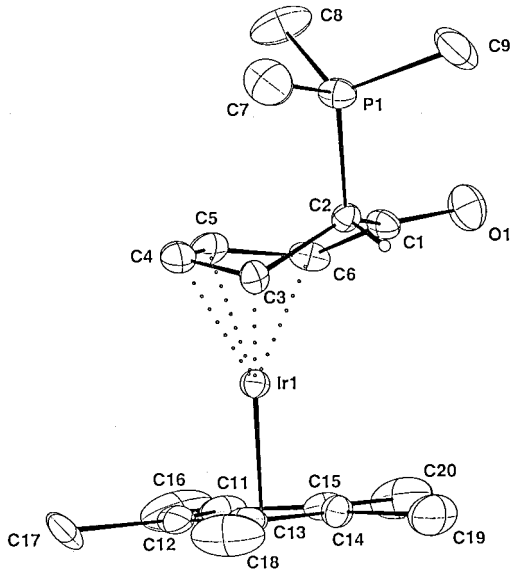


Figure 1. Molecular structure of $[(\eta^5\text{-}C_5Me_5)Ir(\eta^4\text{-}exo\text{-}2\text{-}(PMe_3)\text{-}C_6H_5O)]^+$ with atom numbering system.

When a MeOH solution of **2** was exposed to iodine and the mixture was stirred for 15 min, a dark brown precipitate was

(4) Le Bras, J.; Amouri, H.; Besace, Y.; Vaissermann, J.; Jaouen, G. *Bull. Soc. Chim. Fr.* **1995**, *132*, 1073.

(5) X-ray structures of η^4-dienone complexes are rare in the literature. See: Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P.; Mitchell, J.; Clardy, J. *Organometallics* **1994**, *13*, 102. Pavkovic, S. F.; Zaluzec, E. J. *Acta Crystallogr.* **1989**, *C45*, 18. However, in these two examples the η^4-dienone is a part of a complex organic molecule and therefore cannot be compared to this work, where an X-ray structure of a monocyclic η^4-phenol tautomer $[(\eta^5\text{-}C_5Me_5)Ir$ $(\eta^4\text{-}exo\text{-}2\text{-}(PMe_3)C_6H_5O)]^+$ is presented.

(6) Bowyer, W. J.; Merkert, J. W.; Geiger, W. E. *Organometallics* **1989**, *8*, 191.

(7) Zol'nikova, G. P.; Peregudov, A. S.; Oprunenko, Y. F.; Babakhina, G. M.; Kritskaya, I. I.; Kravtsov, D. N. *Metallorg. Khim.* **1988**, *1*, 79. Batsanov, A. S.; Struchkov, Y. T.; Zol'nikova, G. P.; Kritskaya, I. I.; Kravtsov, D. N. *Metallorg. Khim.* **1988**, *1*, 326. Hull, J. W., Jr.; Gladfelter, W. L. *Organometallics* **1984**, *3*, 605. Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, S. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611. Band, A.; Bottril, M.; Green, M.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, 2372. Huttner, G.; Lange, S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 2049. Barlex, D. M.; Evans, J. A.; Kemmitt, R. D. W.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1971**, 331. Huttner, G.; Lange, S.; Fisher, E. O. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 556. Churchill, M. R.; Mason R. *Proc. R. Soc. London, Ser. A* **1966**, *292*, 61.

(8) Schäufele, H.; Hu, D.; Pritzkow, H.; Zenneck, U. *Organometallics* **1989**, *8*, 396. Herbstein, F. H.; Reisner, M. G. *J. Chem. Soc., Chem. Commun.* **1972**, 1077.

(9) Lucherini, A.; Porri, L. *J. Organomet. Chem.* **1978**, *155*, C45.

(10) Thompson, R. L.; Lee, S.; Rheingold, A. L.; Cooper, N. J. *Organometallics* **1991**, *10*, 1657.

(11) Birch, A. J.; Chamberlain, K. B. *Org. Synth.* **1977**, *57*, 107.

(12) Oshima, N.; Suzuki, H.; Moro-Oka, Y. *Inorg. Chem.* **1986**, *25*, 3407.

(13) Lasne, M. C.; Ripoll, J. L. *Tetrahedron. Lett.* **1980**, *21*, 463.

Table 1. Crystal Data and Structure Refinement

compd	**2**	**5**	**8**
empirical formula	$[C_{19}H_{29}OPIr][BF_4]$	$[C_9H_{13}OP][BF_4]$	$[C_{20}H_{30}I_6Ir_2]$
fw	583.4	255.98	1416.3
cryst system	$P\bar{1}$	$P2_1/c$	$P2_1/c$
b, Å	9.0173(9)	19.922(4)	8.374(1)
c, Å	14.448(3)	11.909(3)	23.541(4)
α, deg	95.90(1)	90	90
β, deg	99.47(1)	106.83(4)	100.89(1)
γ, deg	99.20(1)	90	90
V, Å^3	1081.1(3)	2405(2)	3006.6(9)
Z	2	8	4
ρ(calcd), g/cm^3	1.79	1,41	3.13
μ(Mo Kα), cm^{-1}	62.6	2.48	149.2
cryst size, mm	0.12 × 0.18 × 0.30	0.20 × 0.20 × 0.70	0.16 × 0.32 × 0.40
T, °C	20	20	20
λ(Mo Kα), Å	0.710 69	0.710 69	0.710 69
R^a	0.0443	0.0541	0.0363
$R_w{}^b$	0.0519	0.0538	0.0441

^{a} $R = \sum||F_o| - |F_c||/\sum |F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2**

Bond Lengths			
Ir(1)−C(3)	2.14(1)	Ir(1)−C(4)	2.14(1)
Ir(1)−C(5)	2.11(1)	Ir(1)−C(6)	2.14(1)
C(1)−O(1)	1.22(1)	C(2)−P(1)	1.82(1)
C(1)−C(2)	1.50(1)	C(2)−C(3)	1.51(1)
C(3)−C(4)	1.43(2)	C(4)−C(5)	1.40(1)
C(5)−C(6)	1.41(1)	C(1)−C(6)	1.46(2)
Bond Angles			
C(3)−Ir(1)-C(4)	39.0 (4)	C(3)−Ir(1)-C(5)	68.0(4)
C(3)−Ir(1)−C(6)	75.0(4)	C(1)−C(2)-C(3)	109.4(1)
C(2)−C(1)−C(6)	112.5(9)	C(2)−C(3)-C(4)	117.1(9)
C(2)−C(1)−O(1)	123.5(10)	P(1)−C(2)-C(3)	116.3(7)

Table 3. Selected Bond Distances (Å) and Angles (deg) for **5**

Bond Lengths			
C(12)−O(1)	1.350(8)	C(11)−P(1)	1.782(6)
C(11)−C(12)	1.391(8)	C(12)−C(13)	1.378(9)
C(13)−C(14)	1.38(1)	C(14)−C(15)	1.37(1)
C(15)−C(16)	1.37(1)	C(11)−C(16)	1.388(9)
Bond Angles			
C(12)−C(11)−C(16)	118.5(7)	C(11)−C(12)-C(13)	120.3(6)
C(11)−C(12)−O(1)	115.9(6)	P(1)−C(11)-C(16)	121.4(5)

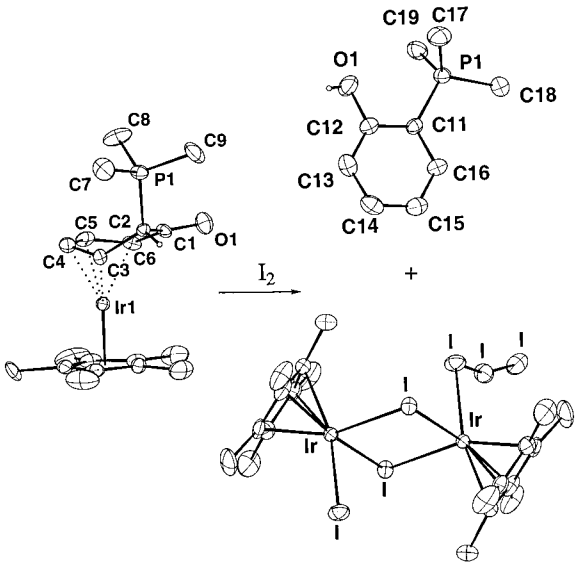
obtained. Reaction workup of the supernatant phase and analysis by NMR spectroscopy suggested the formation of the phosphinated phenol salt $[(C_6H_4OH)PMe_3][BF_4]$ (**5**) isolated in 52% yield. White crystals of **5** were subjected to an X-ray structural determination. Crystal data and selected bond distances and angles are given in Tables 1 and 3. The structure of $[(C_6H_4OH)PMe_3]^+$ (Scheme 3) confirms the aromaticity of the arene ring, where the C−C bond distances of the arene ring are very similar with C−C$_{av}$ = 1.379 Å. The C−O bond distance is 1.350(8) Å, which is characteristic of a C−O simple bond of a phenolic function, while the C−P bond distance is 1.782(6) Å.

The phosphine−iridium complexes **3** and **4** similarly provided after iodine oxidation the free 2-phosphinated phenol salts **6** and **7**. The formation of these phosphinated phenol salts is no doubt a result of enone−phenol tautomerization; such results were also observed for the methoxylation reactions.[4,5]

The dark brown precipitate was identified by ^{1}H NMR spectroscopy and X-ray analysis as $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}I)I]_2{\cdot}I_2$ (**8**)[14]

(14) The X-ray structure of $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}I)I]_2{\cdot}I_2$ was already reported by Maitlis et al.; this polyiodo compound was obtained by a completely different synthetic procedure. See: Millan, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1982**, 73.

Scheme 3. Oxidation Step of Ir-Mediated Nucleophilic Phenol Functionalization Reaction Illustrated by Three X-ray Structures of Reactant **2** and Products **5** and **8**



and isolated in 82% yield; the structure of **8** can be viewed as an infinite chain of dimeric iridium $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}I)I]_2$ bridged by I_2 units. (Figure 2). Therefore our organometallic starting material can be recovered in the form of $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}I)I]_2{\cdot}I_2$ (**8**). Scheme 3 shows the X-ray structures of the reactant and products of the oxidation step of our method for *ortho-functionalization* of phenols. In this step, complex **2** reacts with an excess of iodine and provides the related phosphinated phenol **5** and the polyiodo compound $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}I)I]_2{\cdot}I_2$ (**8**). When complex **8** was left under vacuum, the associated iodine molecule was removed to give the free iridium dimer $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}I)I]_2$. Overall this is a rare example of a recyclable transition metal directed to organic synthesis.

Concluding Remarks

In conclusion we have reported the ortho-functionalization of phenol by trialkylphosphine nucleophiles. The isolation of the key intermediate $[(\eta^5\text{-}C_5Me_5)Ir(\eta^4\text{-}exo\text{-}2\text{-}(PMe_3)C_6H_5O)][BF_4]$ (**2**) is significant, since it represents the first example of the final intermediate for the functionalization of phenols via nucleophilic additions promoted by an "$(\eta^5\text{-}C_5Me_5)Ir^{2+}$" moiety. The potential use of this method to prepare ortho-functionalized

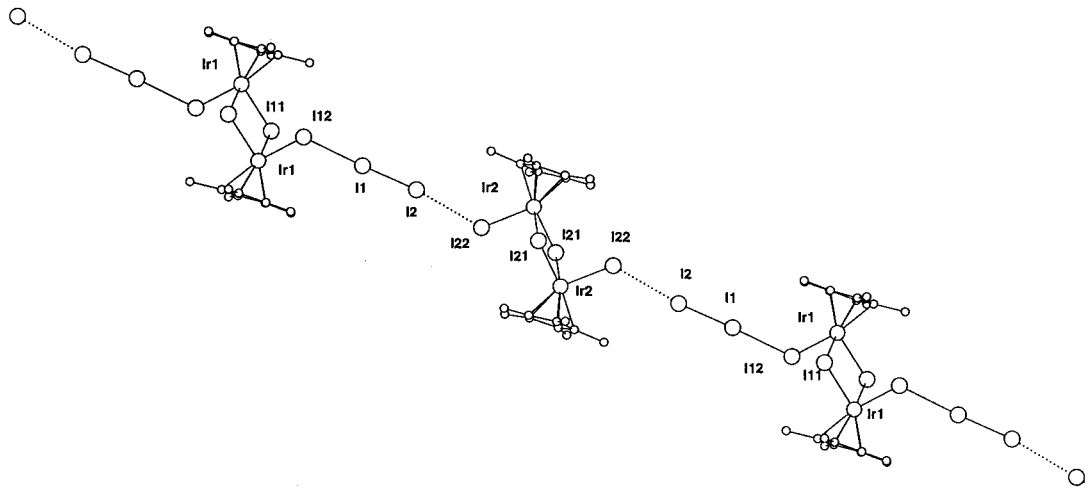


Figure 2. Molecular structure of [(η^5-C_5Me_5)Ir(μ-I)I]$_2$·I_2 (**8**) with I_2 bridging between dimers of iridium [(η^5-C_5Me_5)Ir(μ-I)I]$_2$ in an infinite chain.

phosphinated phenols as well as a detailed mechanistic study will be the subject of a future paper.

Experimental Section

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 ^{1}H and ^{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.

Synthesis of [(η^5-C_5Me_5)Ir (η^4-*exo*-2-(PMe_3)C_6H_5O)][BF_4] (2). A 200 μL amount of PMe_3 (1.93 mmol) was added to a solution of [(η^5-C_5Me_5)Ir(η^5-C_6H_5O)][BF_4] (**1**) (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-H_5-C_5Me_5), 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. Calcd for $C_{19}H_{29}BF_4IrOP$: C, 39.11; H, 5.01. Found: C, 38.96; H, 5.00.

Synthesis of [(η^5-C_5Me_5)Ir (η^4-*exo*-2-(PEt_3)C_6H_5O)][BF_4] (3). A 200 μL amount of PEt_3 (1.35 mmol) was added to a solution of [(η^5-C_5Me_5)Ir(η^5-C_6H_5O)][BF_4] (**1**) (147 mg, 0.29 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 mixture of **3** and **1** in a ratio of 8:2. Spectroscopic data for **3** are as follows. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ 5.38 (t, 1H, J_{H-H} = 4.4 Hz, H_5), 5.12 (t, 1H, J_{H-H} = 4.4 Hz, H_4), 3.80 (dd, 1H, J_{P-H} = 13.5 Hz, J_{H-H} = 4.4 Hz, H_2), 3.68 (d, 1H, J_{H-H} = 4.4 Hz, H_6), 2.99 (t, 1H, J_{H-H} = 4.4 Hz, H_3), 2.20−2.05 (m, 6H, CH_2−P), 2.04 (s, 15H, Me−Cp), 1.40−1.10 (m, 9H, CH_3). ^{13}C NMR (CD_2Cl_2, 62.9 MHz): δ 187.0 (d, J_{P-C} = 9.2 Hz, C═O), 91.3 (s, η^5-H_5−C_5Me_5), 70.1 (s, C_5), 66.9 (d, J_{P-C} = 4.3 Hz, C_4), 59.8 (d, J_{P-C} = 3.9 Hz, C_6), 36.3 (d, J_{P-C} = 31.4 Hz, C_2), 26.8 (d, J_{P-C} = 6.6 Hz, C_3), 19.2 (d, J_{P-C} = 56.0 Hz, CH_2−P), 9.7 (s, Me−Cp), 5.5 (d, J_{P-C} = 4.1 Hz, CH_3−). ^{31}P NMR (acetone-d_6, 101.2 MHz): δ 42.1.

Synthesis of [(η^5-C_5Me_5)Ir (η^4-*exo*-2-(PMe_2Ph)C_6H_5O)][BF_4] (4). A 200 μL amount of PMe_2Ph (1.40 mmol) was added to a solution of [(η^5-C_5Me_5)Ir(η^5-C_6H_5O)][BF_4] (**1**) (130 mg, 0.25 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 mixture of **4** and **1** in a ratio of 9:1. Spectroscopic data for **4** are as follows ^{1}H NMR (CD_2Cl_2, 250 MHz): δ 7.80−7.30 (m, 5H, Ph), 5.00 (t, 1H, J_{H-H} = 4.7 Hz, H_5), 4.86 (t, 1H, J_{H-H} = 4.7 Hz, H_4), 3.92 (dd, 1H, J_{P-H} = 13.7 Hz, J_{H-H} = 4.7 Hz, H_2), 3.51 (d, 1H, J_{H-H} = 4.7 Hz, H_6), 2.97 (t, 1H, J_{H-H} = 4.7 Hz, H_3), 2.07 (d, 6H, J_{P-H} = 13.7 Hz, CH_3−P), 2.00 (s, 15H, Me−Cp). ^{13}C NMR (CD_2Cl_2, 62.9 MHz): δ 185.1 (d, J_{P-C} = 10.4 Hz, C═O), 134.0−127.0 (m, Ph−P), 91.1 (s, η^5-H_5-C_5Me_5), 70.7 (s, C_5), 65.8 (d, J_{P-C} = 4.8 Hz, C_4), 58.1 (d, J_{P-C} = 3.9 Hz, C_6), 40.8 (d, J_{P-C} = 29.4 Hz, C_2), 26.4 (d, J_{P-C} = 6.9 Hz, C_3), 9.7 (s, Me-Cp), 8.1−5.5 (d, J_{P-C} = 51.2 Hz, CH_3−P). ^{31}P NMR (acetone-d_6, 101.2 MHz): δ 56.7.

Synthesis of [(C_6H_5OH)PMe_3][BF_4] (5). A solution of [(η^5-C_5Me_5)-Ir (η^4-*exo*-2-(PMe_3)C_6H_5O)][BF_4] (**2**) (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 and then filtered and washed with MeOH (2 × 5 mL). The product was identified as the organometallic compound [(η^5-C_5Me_5)Ir(μ-I)I]$_2$·I_2. Yield: 82% (226 mg). The supernatant phase was evaporated to dryness. The expected organic compound **5** 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. Calcd for $C_9H_{14}BF_4OP$: C, 42.23; H, 5.51. Found: C, 42.25; H, 5.90.

Synthesis of [(C_6H_5OH)PEt_3][BF_4] (6). The mixture of **3** and **1** (8:2) (174 mg) was treated with a solution of I_2 (283 mg, 1.11 mmol) in MeOH (5 mL) at −80 °C. A brown precipitate was obtained and then filtered and washed with MeOH (2 × 5 mL). The product was identified as the organometallic compound [(η^5-C_5Me_5)Ir(μ-I)I]$_2$·I_2. Yield: 72% (117 mg). The supernatant phase was evaporated to dryness. Addition of CH_2Cl_2 (10 mL) afforded a precipitate identified as the unreacted material **1** (30 mg). The solution was evaporated to dryness. The residue was dried under vacuum and heated (60 °C) for a short period (10 h). The expected organic compound **6** was obtained pure as indicated by spectroscopic analysis. Yield: 38% (26 mg) relative to complex **3**. Spectroscopic data for **6** are as follows. ^{1}H NMR (acetone-d_6, 250 MHz): δ 10.61 (s, 1H, OH), 7.50−7.40 (m, 2H, ArH), 7.20−7.10 (m, 2H, ArH), 2.75−2.60 (m, 6H, CH_2−P), 1.30−1.10 (m, 9H, CH_3). ^{13}C (acetone-d_6, 62.9 MHz): δ 155.9 (s, C−O), 136.6 (d, J_{P-C} = 6.0 Hz, Ar), 133.6 (d, J_{P-C} = 7.3 Hz, Ar), 119.7 (m,

Ar), 101.0 (d, J_{P-C} = 85.9 Hz, Ar), 12.3 (d, J_{P-C} = 52.5 Hz, CH_2−P), 6.1 (d, J_{P-C} = 4.9 Hz, Me). ^{31}P NMR (acetone-d_6, 101.2 MHz): δ 35.1.

Synthesis of [(C_6H_5OH)PMe_2Ph][BF_4] (7). The mixture of **4** and **1** (9:1) (158 mg) was treated with a solution of I_2 (317 mg, 1.25 mmol) in MeOH (5 mL) at −80 °C. A brown precipitate was obtained and then filtered and washed with MeOH (2 × 5 mL). The product was identified as the organometallic compound [(η^5-C_5Me_5)Ir(μ-I)I]$_2$·I_2. Yield: 78% (124 mg). The supernatant phase was evaporated to dryness. Addition of CH_2Cl_2 (10 mL) afforded a precipitate identified as the unreacted material **1** (15 mg). The solution was evaporated to dryness. The residue was dried under vacuum and heated (60 °C) for a short period (10 h). The expected organic compound **7** was obtained pure as indicated by spectroscopic analysis. Yield: 47% (34 mg) relative to complex **4**. Spectroscopic data for **7** are as follows. ^{1}H NMR (acetone-d_6, 250 MHz): δ 10.57 (s, 1H, OH), 8.20−7.50 (m, 8H, Ar H), 7.17 (m, 1H, Ar H), 2.70 (d, 6H, J_{P-H} = 14.5 Hz, CH_3). ^{13}C (acetone-d_6, 62.9 MHz): δ 162.3 (s, C−O), 138.0 (s, Ar), 135.2 (s, Ar), 134.3 (d, J_{P-C} = 8.7 Hz, Ar), 132.8 (d, J_{P-C} = 10.7 Hz, Ar), 130.1 (d, J_{P-C} = 94.3 Hz, Ar), 130.8 (d, J_{P-C} = 12.8 Hz, Ar), 121.7 (d, J_{P-C} = 12.7 Hz, Ar), 118.1 (d, J_{P-C} = 6.8 Hz, Ar), 106.9 (d, J_{P-C} = 90.7 Hz, Ar), 9.4 (d, J_{P-C} = 58.4 Hz, Me). ^{31}P NMR (acetone-d_6, 101.2 MHz): δ 27.3.

X-ray Crystallography of [(η^5-C_5Me_5)Ir (η^4-*exo*-2-(PMe_3)C_6H_5O)]-[BF_4] (2), [(C_6H_5OH)PMe_3][BF_4] (5) and [(η^5-C_5Me_5)Ir(μ-I)I]$_2$·I_2 (8). Suitable crystals of **2** and **5** were obtained respectively by recrystallization from acetone/Et_2O solution, while complex **8** was obtained from cooling a saturated hexane solution. The selected crystal of **2**, **5**, or **8** 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 on a Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation. No significant variations were observed in the intensities of two checked reflections during data collection. An empirical absorption correction (DIFABS)[15] was applied for complex **2** and provided the best structural resolution with T_{min} = 0.92 and T_{max} = 1. As for complexes **5** and **8** absorption corrections were applied empirically using the ψ-scan method with T_{min} = 0.82 and T_{max} = 1 for complex **5** and T_{min} = 0.87 and T_{max} = 1) for complex **8**. Complete crystallographic data and collection parameters for **2**, **5**, and **8** are listed (Table 1). The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[16] Scattering factors and corrections for anomalous dispersion were taken from ref 17. The structures of compounds **2** and **8** were 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 introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter. The structure of complex **5** was solved by direct methods (SHELXS).[18] Refinements were carried out by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were located on a difference Fourier map, and their coordinates were refined with an overall isotropic thermal parameter.

Acknowledgment. The CNRS is gratefully acknowledged for supporting this work.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of complexes **2**, **5,** and **8** are available on the Internet only. Access information is given on any current masthead page.

IC971427I

(15) Walker, N.; Stuart, D. *Acta Cystallogr*. **1983**, *A39*, 159.
(16) Watkin, D. J.; Carruthers, J. R.; Betteridge P. W. *Crystals User Guide*; Chemical Crystallography Laboratory: University of Oxford: Oxford, U. K., 1988.
(17) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(18) Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Solution*; University of Gottingen: Gottingen, Germany, 1986.