ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Synthesis and Crystal Structure of Iridium-1,4-benzoquinone Complexes of Tris(3,5-dimethylpyrazolyl)methane Ligand: Decarbonylation, Protonation, and Substitution Reactions

Martín Hernández-Juárez,[†,‡] Verónica Salazar,[‡] Efrén V. García-Báez,[†] Itzia I. Padilla-Martínez,*[,†] Herbert Höpfl,[§] and Maria de Jesus Rosales-Hoz[⊥]

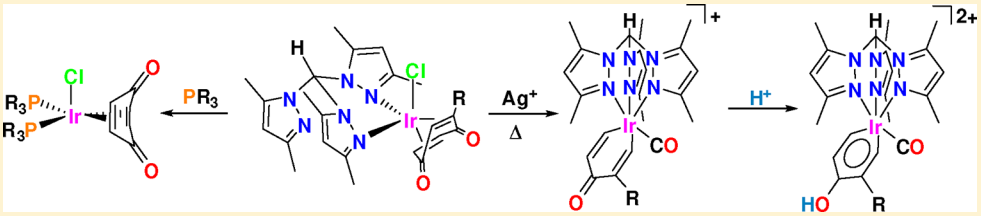
[†]Departamento de Ciencias Básicas, Unidad Profesional Interdisciplinaria de Biotecnología del Instituto Politécnico Nacional, Avenida Acueducto s/n Barrio la Laguna Ticomán, México, D. F. 07340, Mexico

[‡]Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Hidalgo, Carretera Pachuca a Tulancingo Km 4.5, 42184, Mineral de la Reforma, Hidalgo, Mexico

[§]Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, Cuernavaca Morelos 62210, Mexico

[⊥]Departamento de Química, CINVESTAV-IPN, Avenida Instituto Politécnico Nacional 2508, Col. San Pedro Zacatenco, México D. F. 07360, Mexico

Supporting Information



ABSTRACT: Complexes [κ^2-Tpm^{Me2}Ir(2,3,5,6-η-2-R-1,4-benzoquinone)Cl] (R = H, **1a**; Cl, **1b**; Ph, **1c**; ^{t}Bu, **1d**; Tpm^{Me2} = tris(3,5-dimethylpyrazolyl)methane) and [κ^3-Tpm^{Me2}Ir(2,3,5,6-η-1,4-benzoquinone)][BF_4], **2a-BF_4**, have been prepared from the dimeric complex [Ir(μ-Cl)(coe)$_2$]$_2$ and structurally characterized. Compounds **1a−d** were then thermally transformed to the corresponding iridacyclohexa-2,5-dien-4-one complexes [κ^3-Tpm^{Me2}Ir(1,5-η-CH═C(R)C(O)CH═CH−)(CO)][BF_4], **3-BF_4**, and for **1a** the reactivity toward CO, phosphines, and HBF_4−OEt_2 was examined. Compounds **1a**, **1b**, **2a-BF_4**, **3a-BF_4**, **3b-BF_4**, carbonyl complex [κ^3-Tpm^{Me2}Ir(2,3-η-1,4-benzoquinone)(CO)][Ir(CO)$_2$Cl$_2$], **4-[Ir(CO)$_2$Cl$_2$]**, phosphine complexes [(PR_3)$_2$Ir-(2,3,5,6-η-1,4-benzoquinone)Cl] (PR_3 = PPh_3, $PPhMe_2$, PMe_3), **5−7**, and [(μ-$PPh_2CH_2CH_2PPh_2$)Ir(2,3,5,6-η-1,4-benzoquinone)Cl]$_2$, **8**, were characterized by X-ray diffraction analysis. Treatment of **1a** with HBF_4 led, through the intermediacy of [κ^2-Tpm^{Me2}Ir(2-6-η-semiquinone)Cl][BF_4], **9-BF_4**, to the isolation of hydroquinone [κ^2-Tpm^{Me2}Ir(1-6-η-1,4-hydroquinone)Cl][BF_4]$_2$, **10-(BF_4)$_2$**, and treatment of **3-BF_4** with HSO_3CF_3 led to dicationic iridaphenol complexes [κ^3-Tpm^{Me2}Ir(1,5-η-CH═C(R)-C(OH)═CH−CH═)(CO)][SO_3CF_3]$_2$ (R = H, ^{t}Bu), **11-(O_3SCF_3)$_2$**.

INTRODUCTION

1,4-Benzoquinones (BQ) are an important class of compounds that play key roles in chemistry and biology. They are useful synthons in organic synthesis and building blocks for hormones, pigments, and other derivatives.[1,2] Their potential as anticancer drugs and as central components of antibiotics has also been reported.[1]

Quinonoid complexes of transition metals have been known since the late 1950s.[3] However, the organometallic chemistry of hydroquinone−benzoquinone complexes has emerged only in the past 30 years, using soft donors such as phosphines and principally π-acceptors such as carbonyl, allyl, COD, COT, indenyl, cyclopentadienyl, and arene ligands.[4] Hard N-donor ligands containing bipy and imine functions have been used also,[5] but there is only one report on a complex containing simultaneously a benzoquinone and a scorpionate-type ligand,[6] in spite of their wide use in organometallic chemistry as ancillary ligands. Important scorpionate ligands are those derived from 3,5-dimethylpyrazole such as the anionic tris(3,5-dimethylpyrazolyl)borate (Tp^{Me2}) or the neutral analogue tris(3,5-dimethylpyrazolyl)methane (Tpm^{Me2}). Both ligands are versatile hard N-donor ligands that can coordinate in a mono-, bi-, or tridentate fashion to the metal center.[7] Despite the similarity of the two ligands, Tp^{Me2} has widespread use in organometallic and coordination chemistry; in contrast, the Tpm^{Me2} ligand has received comparatively little attention. However, this ligand can act as more than a simple spectator in the course of the chemical reactions experienced by their compounds, because of the possibility of temporary changes in

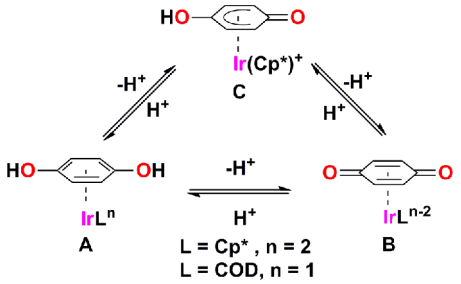
Received: May 21, 2012
Published: July 13, 2012

   dx.doi.org/10.1021/om300439c | *Organometallics* 2012, 31, 5438−5451

denticity and its ambidentate nature after the removal of the $CH(Pz^{Me2})_3$ proton.[8] More recently the syntheses of Co, Pd, and Ir complexes with ditopic ligands that combine quinonoid and bis-pyrazolyl-methane moieties have been reported.[9] These ligands exhibit κ^2- and κ^3-coordination modes or can act like a bridge, leading to heterodinuclear complexes.

Only a few metal complexes have been reported in which quinonoids are coordinated to heavier elements, mainly with Pt.[10] In the particular case of iridium,[5a,11,12] only COD and Cp* have been used as ancillary ligands so far. In both cases the synthesis started from the cationic 1-6-η-hydroquinone complex **A**, which after deprotonation with a strong base gave the corresponding 2,3,5,6-η-quinone complex **B** (Scheme 1). In the case of Cp* as intermediate, the 2-6-η-semiquinone

Scheme 1. Reported Synthesis of 1,4-Benzoquinone Ir Complexes by Deprotonation of the Corresponding Hydroquinone Derivatives[11,12]



complex **C** was observed. Herein, a general synthesis of a series of iridium complexes of the composition [κ^2-Tpm^{Me2}Ir(2,3,5,6-η-2-R-1,4-benzoquinone)Cl] (R = H, **1a**; Cl, **1b**; Ph, **1c**; ^{t}Bu, **1d**) and [κ^3-Tpm^{Me2}Ir(2,3,5,6-η-1,4-benzoquinone)][BF_4], **2a-BF_4**, are reported, starting from the dimeric complex [Ir(μ-Cl)(coe)$_2$]$_2$. After thermal treatment of **1a–d** several novel compounds resulted. Further, substitution reactions of complex **1a** with CO and PR_3 as well as reactions with the mineral acids HBF_4 and HSO_3CF_3 were performed on **1a** and **3-BF_4**, respectively, and are also discussed.

RESULTS AND DISCUSSION

^{1}H and ^{13}C{^{1}H} NMR data corresponding to the BQ ligand in complexes **1a–d**, **2a-BF_4**, **3a–d-BF_4**, **4-[Ir(CO)$_2$Cl$_2$]**, **5–8**, **9-BF_4**, **10-$(BF_4)_2$** and **11a,d-$(O_3SCF_3)_2$** are listed in Table 1. Selected bond distances and angles of **1a**, **2a-BF_4**, **3a-BF_4**, **3b-BF_4**, **4-[Ir(CO)$_2$Cl$_2$]**, **5**, and **8** are given in the corresponding captions of Figures 1, 2, and 4–8. A full list of data is found in the Supporting Information, SI.

Benzoquinone Complexes [κ^2-Tpm^{Me2}Ir(2,3,5,6-η-2-R-1,4-benzoquinone)Cl]. The iridium benzoquinone complex **1a** [κ^2-Tpm^{Me2}Ir(2,3,5,6-η-1,4-benzoquinone)Cl] was easily synthesized as an air-stable solid in 85% yield by reaction of [Ir(μ-Cl)(coe)$_2$]$_2$ with two equivalents of 1,4-benzoquinone and tris(3,5-dimethylpyrazolyl)methane (Tpm^{Me2}), at room temperature (Scheme 2).

The IR spectrum of complex **1a** shows a couple of medium-intensity bands characteristic of C=O vibrations at 1643 and 1563 cm^{-1}. These frequencies are very similar to those observed for uncoordinated 1,4-benzoquinone at 1640 and 1589 cm^{-1}. The ^{1}H and ^{13}C{^{1}H} NMR spectra are in agreement with an η^4:π^2 coordination mode of the BQ ligand to the Ir(I) center: in ^{1}H NMR a singlet at δ 4.55, equivalent to four protons, and in ^{13}C{^{1}H} NMR two signals at δ 64.4 (CH, $^1J_{C-H}$ = 173 Hz) and 169.2 (CO). Comparison with the chemical shifts of the free BQ ligand, δ 6.77, 136.7 (CH, $^1J_{C-H}$ = 169 Hz) and 187.4 (CO), showed that the alkenyl atoms are strongly shielded by the nearby metal center. The symmetry exhibited by the Tpm^{Me2} ligand in complex **1a** is in agreement with C_s point group symmetry: two single signals with 2:1 intensities at δ 6.25 and 5.91 for the pyrazole C*H* protons, four signals at δ 2.65, 2.51, 2.08, and 1.53 (intensities 2:2:1:1) for the Me groups, and a single signal at δ 7.61 corresponding to the methine $CH(Pz^{Me2})_3$ proton. A similar pattern is observed in the ^{13}C{^{1}H} NMR spectrum: four signals at δ 158.4, 150.6, 144.3, and 140.0 (2:2:1:1) for the six quaternary carbons of

Table 1. Selected ^{1}H and ^{13}C NMR Data, δ in ppm and $^1J_{C-H}$ in Hz

compound	H2	H3	H5	H6	C1	C2 ($^1J_{C-H}$)	C3 ($^1J_{C-H}$)	C4	C5 ($^1J_{C-H}$)	C6 ($^1J_{C-H}$)	$CH_{(Pz)3}$
1a	4.55	4.55	4.55	4.55	169.2	64.4 (171)	64.4	169.2	64.4	64.4	7.61
1b		5.05	4.13	4.81	165.4	71.5	53.6	169.5	74.6	76.6	7.62
1c		5.45	3.96	4.85	165.9	71.6	54.0	171.4	70.1	75.0	7.60
1d		5.2	3.10	4.93	163.1	88.7	50.1	172.4	65.1	77.4	7.61
2a-BF_4[a]	5.45	5.45	5.45	5.45	177.5	61.6	61.6	177.5	61.6	61.6	8.15
3a-BF_4	8.73	6.89	6.89	8.73	197.5	135.8	136.7	158.8	136.7	135.8	8.23
3b-BF_4	8.86		7.18	8.67	188.1	127.6	129.8	NO[f]	138.4	134.3	8.24
3c-BF_4	8.78		7.05	8.61	195.9	133.8	140.1	159.2	137.8	132.6	8.22
3d-BF_4	8.42		6.88	8.25	198.1	125.8	144.3	159.6	139.1	129.5	8.23
4-[Ir(CO)$_2$Cl$_2$][a]	4.89	6.56	6.56	4.89	161.2	138.6	28.2		28.2	138.6	8.24
5	4.22	4.22	4.22	4.22	166.4	81.0 (170)	81.0 (170)		81.0 (170)	81 (170)	
6	4.70	4.70	4.70	4.70	162.4	80.8	80.8	162.4	80.8	80.8	
7	4.84	4.84	4.84	4.84	162.3	79.8	79.8	162.3	79.8	79.8	
8	4.88	4.88	4.88	4.88	163.3	80.9	80.9	163.3	80.9	80.9	
9-BF_4[a]	6.1	4.39	4.39	6.1	176.4	61.7 (177)	82.7 (178)	152.4	82.7 (178)	61.7 (177)	8.45
10-$(BF_4)_2$[b]	5.39	5.39	5.39	5.39	152.1	74.6	74.6	152.1	74.6	74.6	8.38
11a-$(O_3SCF_3)_2$[c,d]	11.02	7.79	7.79	11.02	198.7	177.4	132.2 (158)	155.0	132.2 (158)	177.4	8.12
11d-$(O_3SCF_3)_2$[c,e]	11.67		7.79	10.50	198.9	169.3	134.7	156.1	149.8	165.9	8.12

[a]Measured in $(CD_3)_2OD$. [b]Measured in CD_3OD. [c]Measured in CD_2Cl_2. All other compounds were reported in $CDCl_3$. [d] δ OH: 13.65. [e] δ OH: 13.44. [f]NO = not observed.

dx.doi.org/10.1021/om300439c | Organometallics 2012, 31, 5438–5451

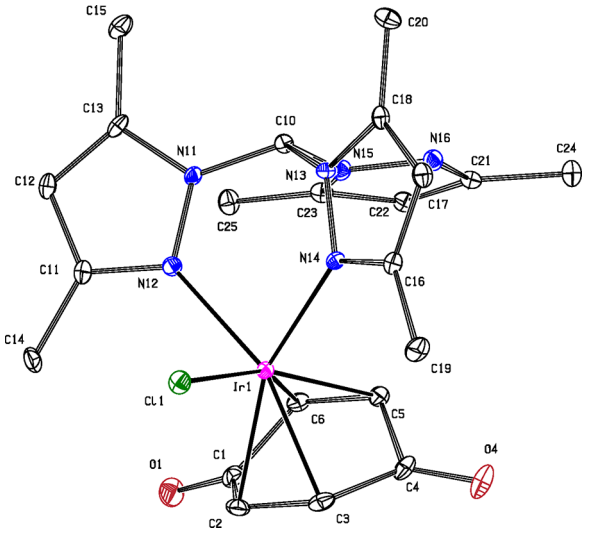


Figure 1. Molecular structure of the neutral iridium complex **1a** (drawn at the 30% probability level). H atoms and water molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−N12 2.151(4), Ir1−N14 2.139(4), Ir1−Cl1 2.364(3), Ir1···Cg(C2,C3) 2.004(4), Ir1···Cg(C5,C6) 2.066(4), C2−C3 1.445(6), C5−C6 1.401(6), C1−O1 1.236(5), C4−O4 1.232(5); N12−Ir1−N14 83.75(12), Cl1−Ir1−N12 86.95(10), N12−Ir1−C2 119.33(14), N14−Ir1−C2 156.83(13), Cl1−Ir1−C2 91.76(11), Cl1−Ir1−C3 92.97(11), Cl1−Ir1−C5 156.25 (11), Cl1−Ir1−C6 154.42(10).

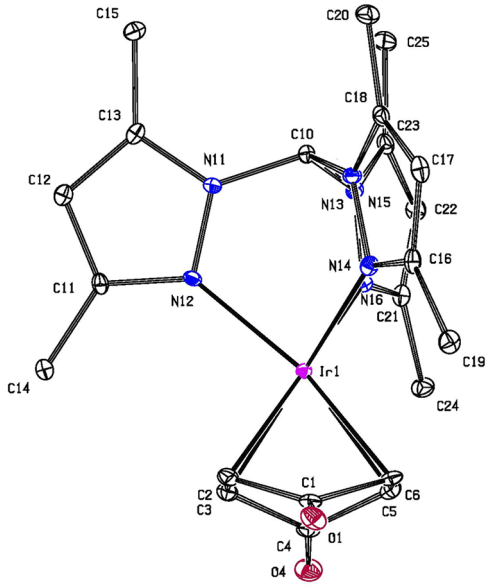


Figure 2. Molecular structure of the cationic complex **2a-BF$_4$** (drawn at the 30% probability level). H atoms, **BF$_4$** anion, and acetone molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−N12 2.116(3), Ir1−N14 2.224(3), Ir1−N16 2.185(3), Ir1···Cg(C2,C3) 2.002(3), Ir1···Cg(C5,C6) 2.083(3), C2−C3 1.443(5), C5−C6 1.405(5), C1−O1 1.226(4), C4−O4 1.225(4); N12−Ir1−N14 86.62(11), N12−Ir1−N16 82.72(10), N12−Ir1−C2 95.88(12), N12−Ir1−C3 95.96(12), N12−Ir1−C5 156.88(12), N12−Ir1−C6 158.37(12), N14−Ir1−C2 117.42(12).

pyrazole, two signals at δ 111.0 and 110.0 (2:1) for the three pyrazole CH, four signals at δ 14.4, 13.5, 11.7, and 10.6 (2:2:1:1) for the six methyl groups, and one signal for the CH(Pz^{Me2})$_3$ carbon atom at δ 74.0. On the basis of the IR and NMR data it was not possible to differentiate between a κ^2- and

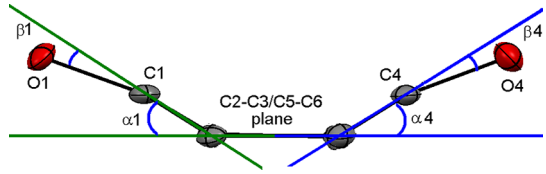


Figure 3. Quantification of the distortion from planarity of metal-coordinated BQ rings: angles α and β.

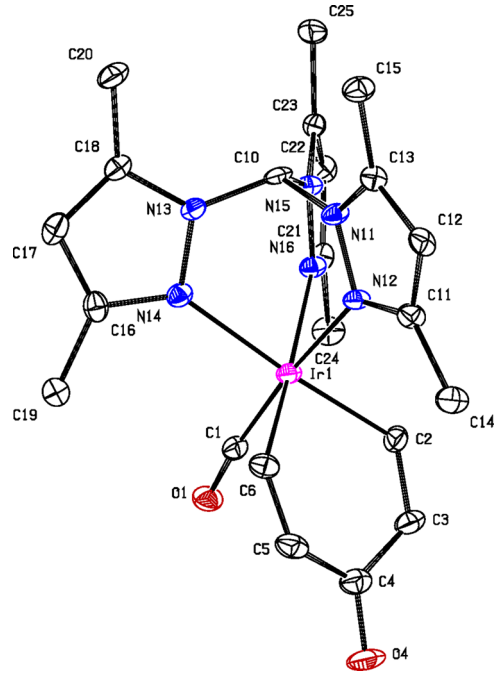


Figure 4. Molecular structure of cationic iridium(III) complex **3a-BF$_4$** (drawn at the 30% probability level). H atoms and BF$_4$ anion omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−N12 2.106(3), Ir1−N14 2.165(4), Ir1−N16 2.149(4), Ir1−C1 1.869(6), Ir1−C2 2.028(5), Ir1−C6 2.037(7), C2−C3 1.334(8), C3−C4 1.468(10), C4−O4 1.234(7), C1−O1 1.119(7); N12−Ir1−N14 85.77(13), N12−Ir−N16 84.07(14), N12−Ir−C2 92.13(17), N12−Ir1−C6 91.74(18), N14−Ir1−C2 175.9(2), N14−Ir1−C6 95.1(2), N16−Ir1−C6 174.54(18), C2−Ir1−C6 88.5(3), C3−C4−C5 118.9(5), Ir1−C1−O1 173.6(5).

κ^3-coordination mode of the Tpm^{Me2} ligand to give either neutral [κ^2-Tpm^{Me2}Ir(2,3,5,6-η-1,4-benzoquinone)Cl] or cationic [κ^3-Tpm^{Me2}Ir(2,3,5,6-η-1,4-benzoquinone)]Cl.

Single-crystal X-ray diffraction analysis confirmed the presence of the chlorine atom in the coordination sphere of the metal and the κ^2-coordination mode of the Tpm^{Me2} ligand (Figure 1). Compound **1a** crystallized in the monoclinic crystal system, space group *C*2/*c*, with one water molecule in the asymmetric unit. The geometry around the Ir(I) center in compound **1a** is distorted trigonal-bipyramidal (tbpy). The Tpm^{Me2} ligand occupies the two equatorial positions with a N12−Ir1−N14 bite angle of 83.75(12)° and a mean Ir−N bond length of 2.145(4) Å. The BQ ligand is coordinated in η^4:π^2 fashion to the Ir(I) center through the C2−C3 and C5−C6 double bonds, the former occupying the remaining equatorial position and the latter the axial position opposed to the chlorine atom, with a mean Cl1−Ir1−C(5−6) angle of 155.3(10)°. The Ir1−C(5,6) are elongated and the C5−C6 bond lengths are shortened, in both cases by approximately 0.05 Å, when compared to the corresponding Ir1−C(2,3) and

dx.doi.org/10.1021/om300439c | *Organometallics* 2012, 31, 5438−5451

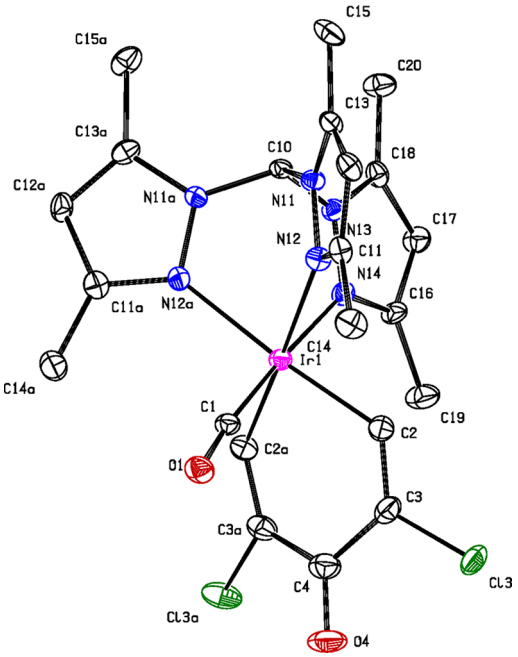


Figure 5. Molecular structure of complex **3b-BF$_4$** (drawn at the 30% probability level). Cl3 and H3 atoms are disordered (occ = 0.5 each). H atoms and BF_4 anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−N12 2.154(6), Ir1−N14 2.106(10), Ir1−C1 1.870(12), Ir1−C2 2.016(8), C2−C3 1.329(12), C3−C4 1.509(11), C4−O4 1.226(14), C3−C13 1.679(9), C1−O1 1.127(12); N12−Ir1−N14 84.3(3), N12−Ir−C2 93.8(3), N14−Ir1−C2 92.2(3), N12−Ir1−C2a 175.7(3), C2−Ir1−C2a 88.8(5), C3−C4−C3a 117.8(10), Ir1−C1−O1 173.2(10).

C2−C3 bond lengths located in the equatorial plane. These geometric features are in agreement with the favorable disposition of the equatorial ligands to a better orbital overlapping with the metal center. Upon coordination, the BQ ligand is bent to a boat-like conformation, according to the Cremer and Pople[12] parameters, Q = 0.451(5) Å, θ = 92.7(6)°, φ = 0.4(6)°, Table 2. The rigid conformation exhibited by the BQ ligand in compound **1a** in the solid state contrasts with the fluxional behavior observed in solution. On the NMR time scale, at room temperature, the BQ ligand is in fast rotation, which would explain the high symmetry observed in solution.

The reaction of $[Ir(\mu\text{-Cl})(coe)_2]_2$ with benzoquinones and Tpm^{Me2} is quite general; thus, the analogous products **1b** and **1c** could be obtained starting from the corresponding 2-Cl and 2-Ph-1,4-benzoquinone in 78% and 93% yield, respectively. The

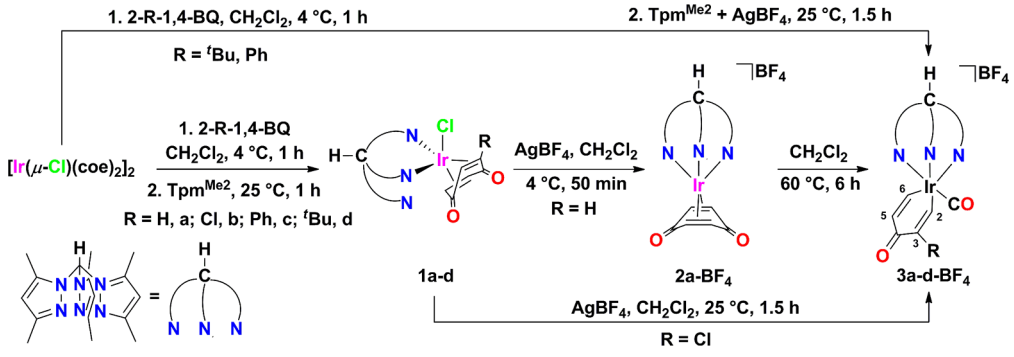
Table 2. Ring Puckering Parameters of the BQ Rings (C1/C2/C3/C4/C5/C6) in Compounds 1a, 1b, 2a-BF$_4$, 4-[Ir(CO)$_2$Cl$_2$] and 5−8; and (Ir/C2/C3/C4/C5/C6) for 3a-BF$_4$, and (Ir/C2/C3/C4/C3a/C2a) for 3b-BF$_4$

	parameter		
compound	Q/Å	θ/deg	φ/deg
1a	0.451(5)	92.7(6)	0.4(6)
1b	0.460(13)	92.7(16)	2.1(17)
2a-BF$_4$	0.529(4)	90.4(4)	−2.4(4)
3a-BF$_4$	0.360(5)	74.0(9)	0.2(10)
3b-BF$_4$	0.418(8)	73.6(13)	360.0(13)
4-[Ir(CO)$_2$Cl$_2$]	0.117(5)	87(2)	3(3)
5	0.437(9)	93.5(12)	180.8(11)
6	0.368(11)	96.1(17)	179.8(16)
7	0.412(11)	90.5(15)	356.7(15)
8	0.466(5)	87.7(6)	180.2(6)

2-substituent in the BQ ligand destroys the symmetry in the ^{1}H and ^{13}C{^{1}H} NMR spectra of the corresponding complexes, and the signals appear at lower frequencies, as a consequence of the metal shielding effect, but exhibit a pattern similar to the corresponding free 2-R-1,4-benzoquinone (R = Cl, **b**; Ph, **c**). With regard to complex **1b**, as an example, the signals at δ 5.05 (d, ^4J = 3.0 Hz), 4.81 (d, ^3J = 9.0 Hz), and 4.13 (dd, $^{4,3}J$ = 3.0, 9.0 Hz) were assigned to protons H-3, H-6, and H-5 of the 2-Cl-BQ ligand. In the ^{13}C{^{1}H} NMR spectrum the corresponding signals appear at δ 53.6, 76.6, and 74.6, respectively, whereas the carbonyl signals appear at δ 169.5 and 165.4. The lack of symmetry is observed also in the signal patterns arising from the ancillary ligand Tpm^{Me2}: one ^{1}H NMR signal at δ 7.62 for $CH(Pz^{Me2})_3$, three signals for pyrazole C*H* in the range δ 6.27−5.90, and six signals for the methyl groups in the range δ 2.62 to 1.50. The ^{13}C{^{1}H} NMR spectrum gave six signals at δ 158.8−150.9 and 145.0−140.2, three signals at δ 111.2−109.9, for the quaternary and CH carbons of the pyrazole rings, one at δ 74.0 for $CH(Pz^{Me2})_3$, and six for the methyl groups in the range δ 14.6 to 10.4 ppm. The molecular structure of **1b** was confirmed by single-crystal X-ray diffraction analysis. Compound **1b** crystallized in the monoclinic crystal system, space group $P2_1/c$, and the geometry is very similar to that observed for compound **1a** (see the SI). The mean Cl1−Ir1−(C5, C6) angle for the higher order axis is 156.4(3)°, the N12−Ir1−N14 bite angle is 85.2(4)°, and the mean Ir−N bond length is 2.12(9) Å.

When the bulky 2-^{t}Bu-1,4-benzoquinone is reacted with the $[Ir(\mu\text{-Cl})(coe)_2]_2$ dimer and Tpm^{Me2} under the already described conditions, a mixture of **1d** and the corresponding

Scheme 2. Synthesis of Complexes 1, 2a-BF$_4$, and 3-BF$_4$



dx.doi.org/10.1021/om300439c | *Organometallics* 2012, 31, 5438−5451

cationic complex **3d-Cl** is obtained in a relation of 1:1. If the reaction is performed at −40 °C, the isolated ratio changes to 1:4. Attempts to isolate **1d** in pure form were unsuccessful, and we observed that solutions of **1d** always progress with an increase of **3d-Cl** (*vide infra*). At this point it is worth noting that the related Ir(I) complexes [Cp*Ir(2,3,5,6-η-BQ)][12] and [CODIr(2,3,5,6-η-BQ)]$^{-}$[11b] were synthesized by deprotonation of the corresponding hydoquinone complexes with a strong base, whereas the synthesis of complexes **1a−d** is achieved by direct coordination of the 2-R-BQ ligand (R = H, Cl, Ph, ^{t}Bu). Besides, upon coordination, the ^{1}H and ^{13}C{^{1}H} NMR chemical shifts of the BQ ligand in **1a−d** are shifted to lower frequencies, whereas the IR frequency of the CO group and $^1J_{C-H}$ remain almost unchanged with regard to free BQ, in agreement with reported data for the analogous neutral [Cp*Ir(2,3,5,6-η-BQ)][12] and anionic [(CO)$_3$Mn(2,3,5,6-η-BQ)]$^{-}$[14] complexes.

Benzoquinone Complex [κ^3-Tpm^{Me2}Ir(2,3,5,6-η-1,4-benzoquinone)][BF$_4$]. Addition of one equivalent of AgBF$_4$ to a CH_2Cl_2 solution of **1a** at 4 °C resulted in the formation of the cationic complex **2a-BF$_4$** in 53% yield (Scheme 2). This Ir(I) complex can also be synthesized starting from [Ir(μ-Cl)(coe)$_2$]$_2$ and BQ, under the simultaneous addition of the Tpm^{Me2} ligand and AgBF$_4$. This procedure does not require the isolation of **1a** and improves the yield to 88%. Compound **2a-BF$_4$** is highly fluxional in solution, and both ^{1}H and ^{13}C{^{1}H} NMR spectra are highly symmetric. The ^{1}H NMR spectrum gave one signal at δ 6.40 for the three pyrazole C*H* hydrogens, two single signals at δ 2.80 and 2.50 for the six methyl groups of the Tpm^{Me2} ligand, and in addition one singlet at δ 8.15 corresponding to the C*H*(Pz^{Me2})$_3$ proton. The corresponding signals in the ^{13}C{^{1}H} NMR spectrum are at δ 112.7 (3CH_{Pz}), 15.4 and 12.4 (6Me$_{Pz}$), and 70.6 (*C*H(Pz^{Me2})$_3$), besides a pair of signals for the six quaternary pyrazole carbon atoms at δ 161.0 and 146.0. The NMR data for the BQ ligand are in agreement with a η^4:π^2-coordination mode to the Ir(I) center: the olefin atoms give rise to signals at δ 5.45 and at 61.6 ($^1J_{C-H}$ = 171 Hz) in the ^{1}H and ^{13}C{^{1}H} NMR, respectively, besides a signal at δ 177.5 for CO-BQ. These data strongly resemble those observed for the highly fluxional complex [κ^3-Tpm^{Me2}Ir-(1,2-η-C_2H_4)$_2$]PF$_6$.[15] The positive charge at the metal center deshields the ^{1}H and ^{13}CO NMR chemical shifts of the coordinated BQ ligand, which in comparison with **1a** appear at higher frequencies, approximately 1 and 8 ppm, respectively, in the cationic complex **2a-BF$_4$**. The deshielding effect is also exerted in the resonance of the C*H*(Pz^{Me2})$_3$ proton of the ancillary ligand by a shift of 0.5 ppm (Table 1).

The structure of **2a-BF$_4$** was unambiguously confirmed by single-crystal X-ray diffraction analysis (Figure 2). This complex crystallized as an acetone solvate in a monoclinic crystal system with space group $P2_1/c$. The ancillary ligand Tpm^{Me2} is coordinated to the metal center in a κ^3 fashion; thus two pyrazole rings are located in equatorial positions with a N12−Ir1−N16 bite angle of 82.72(10)°. The axial positions are occupied by the third pyrazole nitrogen and the C5−C6 double bond, with a mean N12−Ir1−C(5,6) angle of 157.6(12)°. As observed for **1a**,**b**, the Ir−C$_{ax}$(C5,C6) bond is longer than the Ir−C$_{eq}$(C2,C3) bond by 0.07 Å, and the C5−C6 bond is shorter than the C2−C3 bond by 0.04 Å. This structure closely resembles that of [κ^3-TpIr(1,2-η-C_2H_4)$_2$].[16] The replacement of Cl (**1a**) with pyrazole (**2a-BF$_4$**) in the coordination sphere of the Ir(I) center does not significantly change the geometric parameters associated with the ligand Tpm^{Me2}. As mentioned before for **1a**,**b**, the BQ ligand presents a boat conformation, in which the vertices C2−C1−C6 and C3−C4−C5 are pointing away from the metal center but the carbonyl tips are pointing toward the metal. Such a distortion from planarity has been observed previously in duroquinone Rh complexes[17] and quantified by angles α and β (Figure 3), of which the former is the angle formed between the mean planes of the olefin carbon atoms C2/C3/C5/C6 and the CC(O)C segments C6/C1/C2 and C3/C4/C5 and the latter is the angle formed between the CO group and the plane of the three neighboring carbon atoms. Herein, α1 and β1 are reserved for the planes involving segment C2−C1(O1)−C6, while α4 and β4 are used for fragment C3−C4(O4)−C5. The corresponding values are listed in Table 3. This asymmetric representation has to be employed for complexes **1a**, **1b**, and **2a-BF$_4$**, because one vertex is more bent than the other, even when the Ir−C(olefin) distances are similar. The magnitude of the largest bending is sensitive to the coordination mode of the Tpm^{Me2} ligand: α4 has a larger value (α4 = 32.1(2)°) in [κ^3-Tpm^{Me2}Ir(2,3,5,6-η-1,4-benzoquinone)][BF$_4$], **2a-BF$_4$**, than in [κ^2-Tpm^{Me2}Ir-(2,3,5,6-η-1,4-benzoquinone)Cl], **1a**, α4 = 28.7(2)°, or [κ^2-Tpm^{Me2}Ir(2,3,5,6-η-2-Cl-1,4-benzoquinone)Cl], **1b**, α4 = 29.7(5)°. Larger values of α are associated with smaller values of β in compounds **1a** and **1b**, but in compound **2a-BF$_4$** it is the opposite. Nevertheless β values are smaller than α values. A comparison among several known complexes of the general composition [LM-2,3,5,6,-η-BQ] makes clear that the BQ bending can be attributed mainly to steric effects caused by the size of the metal M, the bulkiness of the ligand L (Cp*Ir,[13] α = 15.4 ± 6°; Cp*Rh,[18] α = 12.9 ± 9°; CODRh,[19] α = 8.0 ± 0.1°), or the presence of bulky substituents in the benzoquinone ring ([Cp*Rh-2,3,5,6,-η-di-^{t}Bu-BQ],[17] α = 24.5 ± 2.5°; [κ^3-B(Pz)$_4$Rh-2,3,5,6,-η-duroquinone],[5a] α = 25.3 ± 1.3°). Thus, the bending observed in complexes **1a**, **1b**, and **2a-BF$_4$** is the largest so far reported for Ir(I) complexes, which, however, is not unexpected because of the large cone angle of the Tpm^{Me2} ligand (239°).[20]

Table 3. Angles between the Mean Planes within the BQ Rings of Compounds 1a, 1b, 2a-BF$_4$, 3a-BF$_4$, 3b-BF$_4$, 4-[Ir(CO)$_2$Cl$_2$], and 5−8

	angle between planes[a]			
compound	α1	β1	α4	β4
1a	25.4(2)	10.7(2)	28.7(2)	8.3(2)
1b	25.8(5)	10.2(5)	29.7(5)	8.4(5)
2a-BF$_4$	30.8(1)	8.6(1)	32.1(2)	7.9(2)
3a-BF$_4$	18.7(2)		13.4(3)	0.8(3)
3b-BF$_4$	21.7(1)		14.4(0)	0.6(0)
4-[Ir(CO)$_2$Cl$_2$]	8.2(4)	2.2(3)	7.0(3)	2.6(3)
5	29.6(4)	3.9(4)	23.9(4)	4.6(4)
6	26.0(4)	5.1(4)	18.4(4)	2.9(4)
6A	25.7(5)	6.3(5)	18.1(5)	3.6(5)
7	25.5(4)	5.3(4)	26.5(4)	7.3(4)
8	29.5(2)	3.5(2)	26.3(2)	5.1(2)

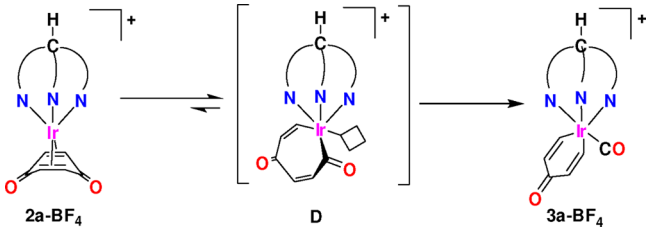
[a] α1: angle between planes C2/C3/C5/C6 and C2/C1/C6 for compounds **1a**, **1b**, **2a-BF$_4$**, and **4−8**, and C2/Ir/C6 for compounds **3a-BF$_4$**, **3b-BF$_4$**; α4: angle between planes C2/C3/C5/C6 and C3/C4/C5 for compounds **1a**, **1b**, **2a-BF$_4$**, **4-[Ir(CO)$_2$Cl$_2$]**, and **5−8**.

Iridacyclohexa-2,5-dien-4-one Complexes [κ^3-Tpm^{Me2}Ir(1,5-η-CH═C(R)C(O)CH═CH−)(CO)][BF$_4$] (R = H, Cl, Ph, ^{t}Bu). When complex **2a-BF$_4$** is refluxed in CH_2Cl_2

dx.doi.org/10.1021/om300439c | *Organometallics* 2012, 31, 5438−5451

for 6 h, Ir(III) complex **3a-BF$_4$** is afforded in 92% yield (Scheme 2). This reaction was monitored by ^{1}H NMR, heating a DMSO-d_6 solution of compound **1a** to 60 °C at regular time intervals. After 4.5 h, compound **1a** has been completely transformed into a mixture of **3a-Cl** and free Tpm^{Me2} in a 4:1 ratio. Under these conditions also some decomposition occurs because of the strongly coordinating solvent. Characteristic IR features for complex **3a-BF$_4$** are stretching bands at 2066 and 1614 cm^{-1}, respectively, for the terminal IrC≡O and RC═O carbonyls, which generate signals at δ 197.5 and 158.8 ppm in the ^{13}C{^{1}H} NMR spectrum. The vinyl hydrogen atoms are observed as a pair of doublets at δ 8.73 and 6.89 ($^3J_{H2-H3}$= 9 Hz), which, on the basis of NOE experiments using the pyrazole methyl groups, have been assigned to the IrC*H* and COC*H* hydrogens, respectively, in the ^{1}H NMR spectrum. The corresponding signals in the ^{13}C{^{1}H} NMR are observed at δ 135.8 (C-2,6, $^1J_{C-H}$ = 159 Hz) and 136.7 (C-3,5, $^1J_{C-H}$ = 153 Hz). For the ancillary ligand Tpm^{Me2}, the typical signal pattern for molecules with C_s symmetry is observed, similar to that described for compound **1a**. This **2a-BF$_4$** → **3a-BF$_4$** transformation probably proceeds through the intermediacy of the corresponding 16-electron complex iridacyclohepta-3,6-diene-2,5-dione, **D**, which might be formed by insertion of the Ir atom into the ═C−CO BQ bond of **2a-BF$_4$** and the subsequent migration of CO to form the 18-electron iridacyclohexa-2,5-dien-4-one complex **3a-BF$_4$** (Scheme 3). This change is in agreement with the tendency of the Tpm^{Me2} ligand to favor d^6 Ir(III) over d^8 Ir(I) systems, enforcing octahedral coordination to the metal center.[21]

Scheme 3. Pathway Proposed for the Transformation of 2a-BF$_4$ to 3a-BF$_4$



The chemical shift of Ir−^{13}CH (δ 135.8) in compound **3a-BF$_4$** is comparable with the value reported for the iridacyclohexa-3,5-dien-2-one isomer (δ 136.7) [(PMe$_3$)$_4$Ir-(1,5-η-C(O)-C(Me)═CH-C(Me)═CH−)][CF$_3$SO$_3$], already known.[22] It is worth highlighting that these complexes were synthesized by treating the iridabenzene complex [(PMe$_3$)$_3$Ir-(1,5-η═CH-C(Me)═CH-C(Me)═CH−)] with N$_2$O, which was obtained after several steps, in contrast to the simplicity of the method reported herein. The structure of **3a-BF$_4$** was unambiguously confirmed by single-crystal X-ray diffraction analysis (Figure 4). Complex **3a-BF$_4$** crystallized in a monoclinic crystal system, space group $P2_1/c$. The ancillary ligand is κ^3-coordinated with almost equal values for the three orthogonal N−Ir−C angles, mean value of 175(1)°, and a mean N−Ir−N bite angle of 85(1)°. The π-acceptor ability of CO forces a strong electron release from N12 toward the metal, and as a consequence, the Ir1−N12 bond is 0.05 Å shorter than the equatorial Ir1−N14 and Ir−N16 bonds. The C2−Ir1−C6 angle is 88.5(3)°, and the Ir1−C2 and Ir1−C6 distances are practically identical, with a mean value of 2.03(1) Å. These geometric data are in agreement with the slightly distorted octahedral geometry around the Ir(III) center. The C2−C3 (1.334(8) Å) and C5−C6 (1.326(8) Å) distances of the alkenyl fragments, the C4−O4 (1.234(7) Å) distance of the carbonyl group, and the C3−C4 (1.468(10) Å) and C4−C5 (1.479(9) Å) distances are very close to the values observed for free BQ with values of 1.333(11), 1.222(13), and 1.478(11) Å, respectively.[23] Thus, **3a-BF$_4$** can be considered as an iridacyclohexa-2,5-dien-4-one complex. In general, the bond lengths and angles found in **3a-BF$_4$** are similar to the cationic iridacyclohexa-3,5-dien-2-one isomer [(PMe$_3$)$_4$Ir(1,5-η-C(O)-C(Me)═CH-C(Me)═CH−)][O$_3$SCF$_3$], which, however, is almost planar.[22]

Addition of AgBF$_4$ to complex **1b** at room temperature gave **3b-BF$_4$** in 87% yield. This transformation was performed also under simultaneous addition of Tpm^{Me2} and AgBF$_4$ starting from [Ir(μ-Cl)(coe)$_2$]$_2$ and 2-Ph and 2-^{t}Bu-1,4-benzoquinone to obtain **3c-BF$_4$** (78%) and **3d-BF$_4$** (81%), respectively (Scheme 2). In neither case were the intermediate compounds analogous to **2a-BF$_4$** observed.

From these results and the fact that compound **1d** is spontaneously transformed into **3d-Cl** (*vide supra*), it becomes clear that the transformation of **1** into **3-BF$_4$** is made faster by the influence of steric effects in the BQ ring. Complex **3b-BF$_4$** crystallized in the orthorhombic crystal system with space group *Pnma*. The molecular structure of this compound is very similar to **3a-BF$_4$**, but H-5 and the chlorine atoms are disordered over two positions (occ = 0.50) (Figure 5). The iridacycles in compounds **3a-BF$_4$** and **3b-BF$_4$** present boat-like conformations[13] (Table 2) similar to those described for complexes **1a**,**b** and **2a-BF$_4$**. The bending of the Ir vertex (angle α1) from the central diolefin plane in complexes **3a-BF$_4$** and **3b-BF$_4$** is larger, 18.7(2)° and 21.7(1)°, than the bending of the CO vertex (angle α4), with values of 13.4(3)° and 14.4(0)°, respectively (Table 3), and the CO tip becomes almost coplanar with the C3/C4/C5 fragment (β values close to zero).

Substitution Reactions of 1a with CO and Phosphines. Cationic compound [κ^3-Tpm^{Me2}Ir(2,3-η-1,4-benzoquinone)(CO)][Ir(CO)$_2$Cl$_2$], **4**-[**Ir(CO)$_2$Cl$_2$**], was isolated from the reaction of compound **1a** with CO (1 atm) in CH$_2$Cl$_2$ solution at room temperature in 71% yield. This reaction was monitored by ^{1}H NMR spectroscopy, using the appropriate pressure tube. After 5 min the solution changed from pale yellow to green-yellow, and the free ligands BQ and Tpm^{Me2} and complexes **1a** and **4**$^+$ were observed in 1:1:1:1 proportion. The reaction proceeds with depletion of **1a** in 50 min; afterward polycarbonylated species appear, which were not further characterized. Compound **4**$^+$ is similar to the complex [κ^3-Tpm^{Me2}Ir(1,2-η-C$_2$H$_4$)(CO)]$^+$ reported as an intermediate in the carbonylation of [κ^3-Tpm^{Me2}Ir(1,2-η-(C$_2$H$_4$)$_2$]$^+$.[15] Characteristic IR features for **4**-[**Ir(CO)$_2$Cl$_2$**] include two IrC≡O stretching bands observed at ν 2042 and 1957 cm^{-1}, corresponding to cationic and iridate fragments, respectively. It is worth mentioning that in the ^{13}C{^{1}H} NMR spectrum only the Ir−CO signal corresponding to the cationic fragment is observed at δ 198.9. According to the symmetry of the molecule, two singlets appear at δ 4.89 and 6.56, in the ^{1}H NMR, and at δ 28.2 and 138.6 in the ^{13}C{^{1}H} NMR spectra, which were assigned to coordinated and free alkenyl CH, respectively. The typical pattern for a C_s-symmetric molecule was observed in both ^{1}H and ^{13}C{^{1}H} NMR for the ancillary ligand Tpm^{Me2}. The molecular structure of compound **4**-[**Ir(CO)$_2$Cl$_2$**] was undoubtedly established by X-ray analysis (Figure 6). This compound crystallized in the monoclinic

dx.doi.org/10.1021/om300439c | *Organometallics* 2012, 31, 5438−5451

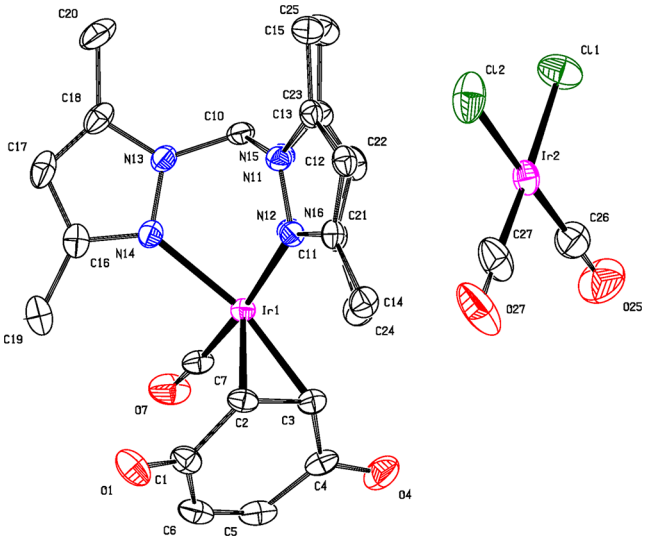


Figure 6. Molecular structure of the cationic complex **4**-$[\mathbf{Ir(CO)_2Cl_2}]$ (drawn at the 30% probability level). H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−N12 2.184(4), Ir1−N14 2.142(3), Ir1−N16 2.147(3), Ir1−C2 2.114(4), Ir1−C3 2.121(4), Ir1−C7 1.843(5), Ir2−C26 1.819(6), Ir2−Cl1 1.224(6), C7−O7 1.141(7), C1−C2 1.476(6), C2−C3 1.470(6), C3−C4 1.485(6), C4−C5 1.472(8), C5−C6 1.331(7), C1−C6 1.475(7), O1−C1 1.224(6), O4−C4 1.229(6), N12−Ir1−N14 82.75(14), N12−Ir1−N16 82.35(13), N12−Ir1−C2 92.32(14), N14−Ir1−C2 116.28(14), N12−Ir1−C3 93.87(15), N14−Ir1−C3 156.73(15), C2−C1−C6 117.1(4), C3−C4−C5 118.4(4), C1−C2−C3 120.2(4), C4−C5−C6 122.7(5), Cl1−Ir2−C26 91.7(2).

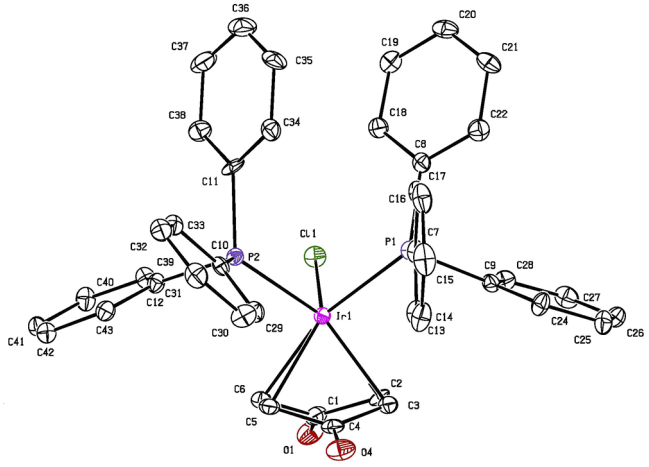


Figure 7. Molecular structure of complex **5** (drawn at the 30% probability level). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−P1 2.346(2), Ir1−P2 2.340(2), Ir1−Cl1 2.456(2), Ir1···Cg(C2,C3) 2.137(12), Ir1···Cg(C5,C6) 2.099(12), C1−O1 1.239, C4−O4 1.252(9), C2−C3 1.413(10), C5−C6 1.407(11); P1−Ir1−P2 96.87(6), Cl1−Ir1−P1 95.28(6), Cl1−Ir1−P2 94.94(6), Cl1−Ir1···Cg(C2,C3) 105.8(2), Cl1−Ir1···Cg(C5,C6) 109.6(2), P1−Ir1···Cg(C2,C3) 94.60(2), P1−Ir1···Cg(C5,C6) 152.79(2), P2−Ir1···Cg(C2,C3) 155.25(2), P2−Ir1···Cg(C5,C6) 91.81(2).

crystal system with space group $P2_1/c$. The Tpm^{Me2} ligand is coordinated in a facial shape with C7O and N12 atoms in the apical positions, N12−Ir1−C7 = 171.79(17)°, and the BQ ligand is positioned in the equatorial plane of a tbpy. As expected, the bond length of the coordinated olefin is longer,

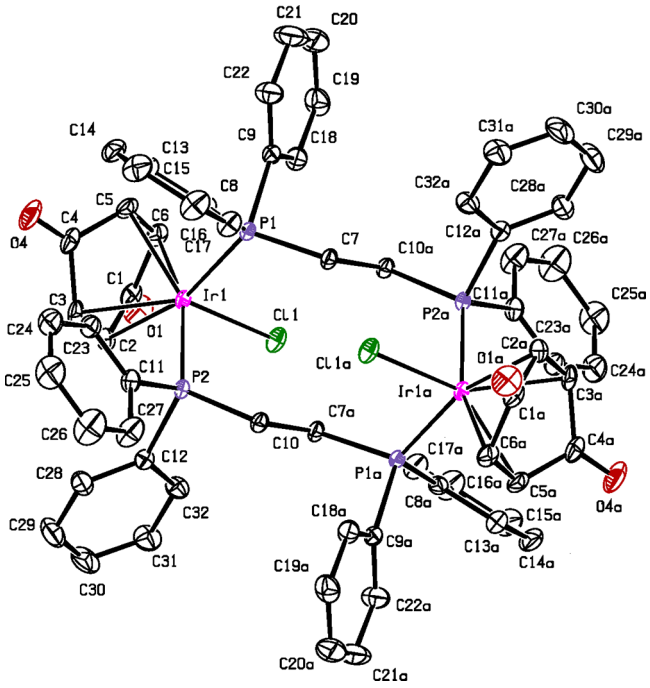


Figure 8. Molecular structure of dimer complex **8** (drawn at the 30% probability level). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−P1 2.328(9), Ir1−P2 2.326(8), Ir1−Cl 2.460(10), Ir1···Cg(C2,C3) 2.085(7), Ir1···Cg(C5,C6) 2.147(7), C1−O1 1.217(6), C4−O4 1.232(6); P1−Ir1−P2 95.41(3), Cl1−Ir1−P1 95.46(3), Cl1−Ir1−P2 96.07(3), Cl1−Ir1···Cg(C2,C3) 112.7(3), Cl1−Ir1···Cg(C5,C6) 102.8(3), C3−C4−C5 109.2(4), C2−C1−C6 107.6(4).

C2−C3 = 1.470(6) Å, than that of the uncoordinated bond, C5−C6 = 1.331(7) Å. The BQ ring is almost planar, as indicated by the ring puckering parameters (Table 2) and the smaller values for angles $\alpha 1$ and $\alpha 4$ (Table 3).

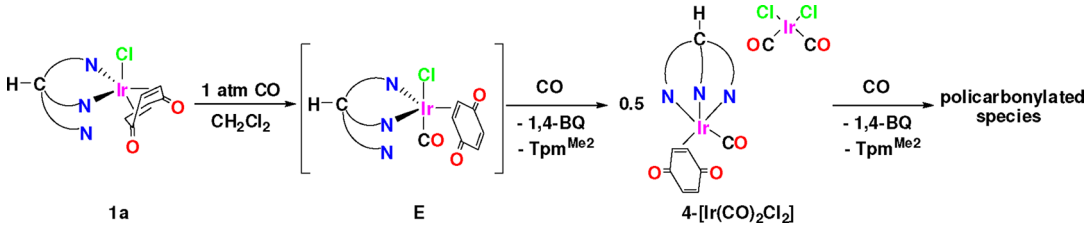
The reaction proceeds through the intermediacy of the neutral species [κ^2-Tpm^{Me2}Ir(2,3-η-1,4-benzoquinone)(CO)-Cl], **E**, which was fortuitously crystallized (see the SI). CO displaces one alkenyl bond, changing the coordination mode of the BQ ligand from η^4:π^2, in **1a**, to η^2:π, in intermediate **E**. In the presence of CO, **E** rapidly disproportionates, with elimination of one molecule of Tpm^{Me2} and BQ ligands, into the more stable cationic Ir(I) complex $\mathbf{4}^+$, generating *in situ* the anion $[\mathbf{Ir(CO)_2Cl_2}]^-$ (Scheme 4). This reaction is probably promoted by the trans effect of the already coordinated CO.

On the other hand, when complex **1a** is reacted with two equivalents of PPh_3 at room temperature, the Tpm^{Me2} ligand is replaced with two PPh_3 moieties to give [$(PPh_3)_2$Ir(2,3,5,6-η-1,4-benzoquinone)Cl], **5**, in 91% yield (Scheme 5). Initially, the reaction was performed using one equivalent of PPh_3, and in this case only a half-equivalent of the metal complex was converted. The fluxional compound **5** is symmetric, and the NMR data are in agreement with a complex having C_s symmetry: in ^{1}H NMR only the signal for the phenyl protons was observed as well as one signal at δ 4.22 for the protons of coordinated BQ; in $^{13}C\{^1H\}$ NMR the CO signal was located at δ 166.4 ($^3J_{C-P}$= 2.2 Hz) and the alkenyl carbons gave signals at δ 81.0 ($^1J_{C-H}$ = 169, $^2J_{C-P}$ = 5.9 Hz). $^{31}P\{^1H\}$ NMR showed a signal at δ −13.6, characteristic for coordinated PPh_3.

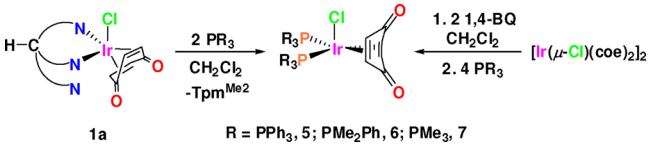
This reaction is quite general, and analogous complexes with PMe_2Ph (δ $^{31}P\{^1H\}$ = −33.1) **6** and PMe_3 (δ $^{31}P\{^1H\}$= −39.4) **7** could be obtained also, in 83% and 31% yield, respectively.

dx.doi.org/10.1021/om300439c | *Organometallics* 2012, 31, 5438−5451

Scheme 4. Proposed Reaction Sequence for the Combination of 1a with CO



Scheme 5. Reactivity of 1a with Phosphines and Synthesis of Complexes 5−7



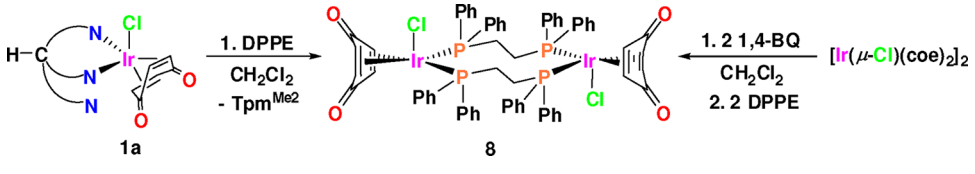
The displacement reaction with PMe_3 leads to a complex mixture of unidentified compounds observed by ^1H NMR; however, no further efforts were undertaken for a more complete analysis and separation. In order to avoid the adventitious reactions observed with PMe_3, we performed the reaction also with the bidentate ligand $Ph_2PCH_2CH_2PPh_2$ (DPPE), but instead the dimeric cyclic compound **8** (δ $^{31}P\{^1H\}$ = 32.8) was obtained in 80% yield (Scheme 6).

Compounds **5**−**8** can be synthesized alternatively with similar yields by addition of two equivalents of BQ to a suspension of $[Ir(\mu\text{-Cl})(coe)_2]_2$ in CH_2Cl_2, followed by addition of four equivalents of PR_3 (two in the case of DPPE). This reaction and that described for **2a** (*vide supra*) probably proceed through the formation of $[Ir(\mu\text{-Cl})(2,3,5,6\text{-}\eta\text{-benzoquinone})]_2$, which is formed by displacement of the coe ligand from the coordination sphere of the Ir(I) center by chelating BQ. Neither this latter method nor the displacement of the Tpm^{Me2} ligand gave better yields of compound **7**. The molecular structures of compounds **5**−**8** were confirmed by single-crystal X-ray diffraction analysis. The X-ray structures of compounds **5** and **8** are show in Figures 7 and 8, respectively, and those corresponding to compounds **6** and **7** are in the SI.

The phosphine complexes **5** and **7** crystallized in the monoclinic crystal system with space group $P2_1/c$, and the crystal structures of compounds **6** (two independent molecules in the asymmetric unit) and **8** belong to the triclinic system, with space group $P\bar{1}$. In all cases the geometry around the Ir(I) center is in agreement with a distorted square-based pyramid (sbpy) with the chlorine atoms in apical position. The τ parameter[24] were calculated to establish the percentage of the sbpy character: **5** (τ = 0.04, 96%), **6** (τ = 0.09, 91%), **6A** (τ = 0.07, 93%), **7** (τ = 0.19, 81%), **8** (τ = 0.11, 89%). The BQ ligand is coordinated to the Ir center in a $\eta^4{:}\pi^2$ fashion, occupying two neighboring positions of the square base, opposite the phosphine ligands. The C_2 axis of the BQ ligand, which passes through both carbonyl groups, is aligned with the vertical axis of the molecule, one of them being almost eclipsed by the Ir−Cl bond. The largest deviation was observed in the PMe_3 derivative **7** (O1−C1−Ir1−Cl1 = −11.0(3)°). The values for the olefin bonds C2−C3 and C5−C6 are almost equal in compounds **5** (PPh_3), **8** ($PPh_2(CH_2)_2Ph_2P$), and **6** ($PPhMe_2$), but for compounds **6A** ($PPhMe_2$) and **7** (PMe_3) a mean difference of 0.06(2) Å was detected. Although the structures of the phosphine derivatives **5**−**8** are rather similar, some structural trends arise because of the stereoelectronic effects inherent to the nature of the phosphine. The triphenylphosphine complex **5** has the largest P1−Ir−P2 angle, 96.87(7)°, and the smallest was measured in the dimethylphenylphosphine complex **6A**, 92.56(10)°. The coordinated BQ adopts a boat-like conformation, in which both carbonyls are displaced out of the diene plane, as suggested by the ring puckering parameters (Table 2). In all cases, one of the two carbonyl vertexes is more deviated from the central diolefin plane than the other, as indicated by the angles formed between the mean planes (Table 3). The magnitudes of the largest α value follow the order PPh_3 (29.6(4)°) ≈ DPPE (29.5(2)° mean value of **6** and **6A**) > $PPhMe_2$ (25.9(4)°) ≈ PMe_3 (26.5(4)°), in agreement with the tendency of the corresponding cone angles.[25] Is worth noting that β values for phosphine complexes are almost half of the values corresponding to Tpm^{Me2} complexes and thus more sensitive to steric crowding.

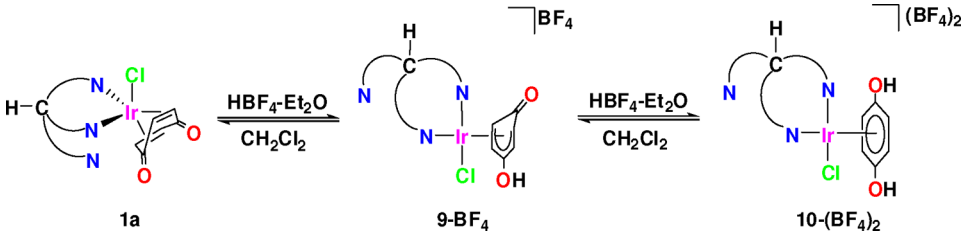
Reactions with Acids. Reaction of **1a** with one equivalent of HBF_4 always led to a mixture of semiquinone **9-BF$_4$** and hydroquinone **10-(BF$_4$)$_2$** (Scheme 7). Other approaches to isolate **9-BF$_4$** were unsuccessful, and in solution an equilibrium mixture of **10-(BF$_4$)$_2$** and **1a** was always established. Thus, the titration of **1a** with aqueous HBF_4 (48 wt %) was monitored by ^1H NMR in $(CD_3)_2CO$ solution. The highest concentration of semiquinone **9-BF$_4$** was achieved after addition of 0.75 molar equivalents of the acid (Figure 9). We then selected these conditions to prepare and characterize this compound by NMR, but using $HBF_4{-}OEt_2$ instead of the aqueous HBF_4 solution to improve the solubility. Protonation of **1a** with 0.8 molar equivalents of $HBF_4{-}OEt_2$ lead to a mixture of semiquinone (SQ) [κ^2-Tpm^{Me2}Ir(2-6-η-semiquinone)Cl][BF_4], **9-BF$_4$**, and unreacted **1a** in 1:3 proportion, respectively. The SQ ring gave a pair of doublets at δ 6.11 and 4.39 with $^3J_{H3-H2}$ = 6 Hz and were assigned to H-3 and H-2, respectively. The corresponding carbon atoms gave signals at δ 82.7 ($^1J_{C-H}$ = 180

Scheme 6. Reaction of 1a with the Bidentate Ligand DPPE Leads to Dimer 8



dx.doi.org/10.1021/om300439c | *Organometallics* 2012, 31, 5438−5451

Scheme 7. Protonation of 1a with HBF_4



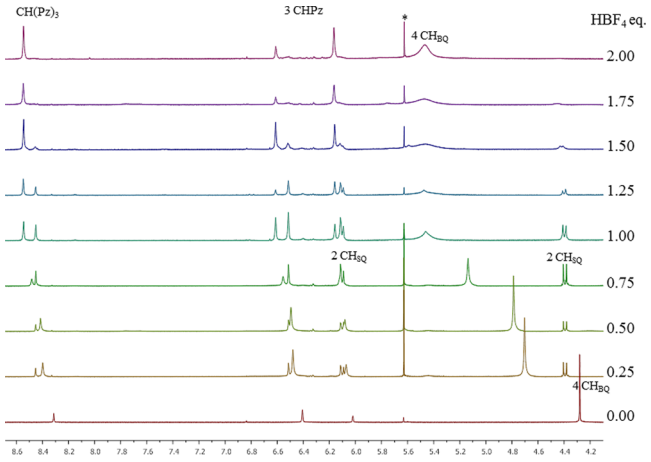
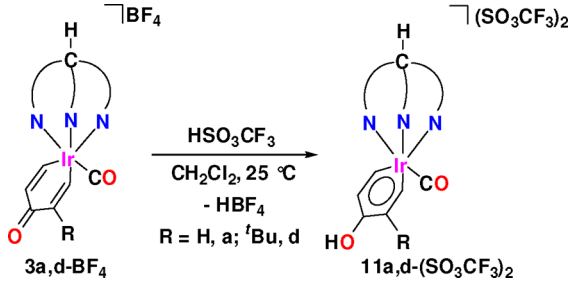


Figure 9. ^1H NMR titration experiments of **1a** with aqueous HBF_4 in $(CD_3)_2CO$.

Hz) and 61.7 ($^1J_{C-H}$ = 178 Hz), respectively, and the signals at δ 176.4 and 152.4 were assigned to the *C*=O and *C*−OH carbon atoms. To completely shift the equilibrium to the dicationic HQ compound **10-$(BF_4)_2$**, addition of two equivalents of HBF_4−OEt_2 to **1a** in CH_2Cl_2 solution was necessary (93% yield). The ^1H and $^{13}C\{^1H\}$ NMR signals corresponding to the coordinated HQ ligand appeared at δ 5.39, 74.6 (CH, $^1J_{C-H}$ = 179 Hz) and 152.1 (*C*−OH), respectively. For both complexes the NMR signals of the ancillary Tpm^{Me2} ligand were consistent with C_s point group symmetry, showing a similar pattern to the one already described for **1a**. The NMR data are in agreement with a localized bonding in the SQ ring of the **9-BF_4** complex, in contrast to the delocalized bonding observed for $[(CO)_3Mn(2\text{-}6\text{-}\eta\text{-SQ})]$ species.[26] This difference could be attributed to the steric effects exerted by both the ancillary ligand Tpm^{Me2} and the BQ ligands carrying a bulky group, as observed in complex $[(CO)_3Mn(2\text{-}6\text{-}\eta\text{-}^t\text{Bu-SQ})]$.[14]

Metallabenzenes have been synthesized from the corresponding metallacyclohexadienes by treatment with acids such as HBF_4, CH_3COOH, or HSO_3CF_3.[27] Thus, the aromatization of the iridacycle **3a-BF_4** to form the corresponding iridabenzene seems to be a feasible reaction. Several preparative efforts were carried out in CH_2Cl_2 solutions, using up to 10 equivalents of HSO_3CF_3, but only unreacted **3a-BF_4** was isolated. The reaction was followed by ^1H NMR in CD_3OD solution, showing that addition of 10 equivalents of the strong acid HSO_3CF_3 leads to a mixture of $\mathbf{3a}^+$ and irida-4-phenol $\mathbf{11}^{2+}$ in 1:4 proportion. Addition of the acid in increments of 10 equivalents up to a total of 80 displaces the equilibrium to a steady state of 1:9 proportion. In spite of the excess of acid used, the transformation was not complete, probably because of the involvement of the polar solvent CD_3OD in the acid−base equilibria. The acid medium modifies the chemical shifts of $\mathbf{3a}^+$ to higher frequencies; nevertheless, the signals for $\mathbf{11}^{2+}$ were clearly different from $\mathbf{3a}^+$. The addition of 10 equivalents of HSO_3CF_3 in THF solution were required to complete the transformation for preparative purposes, and under these conditions the irida-4-phenol **11a-$(SO_3CF_3)_2$** was isolated in 70% yield (Scheme 8).

Scheme 8. Synthesis of the Iridaphenol Complex 11-$(SO_3CF_3)_2$



The spectroscopic data of **11a-$(SO_3CF_3)_2$** is in agreement with the proposed structure: the O−H group gave a broad signal at δ 13.65 (^1H NMR) and a band at ν 3420 cm^{-1} (IR); the IrCH and OCCH ring protons appeared at δ 11.02 and 7.79 as doublets ($^3J_{H2-H3}$ = 9 Hz), respectively, and were assigned by the NOE effect observed when irradiating IrCH protons on the pyrazole methyl groups; the corresponding signals in the $^{13}C\{^1H\}$ NMR appeared at δ 177.4 and 132.2 ($^1J_{C-H}$ = 158 Hz) for the CH functions; at δ 155.0 for *C*−OH; and at δ 198.7 for Ir*C*≡O (ν 2085 cm^{-1} in IR). The coordinated Tpm^{Me2} ligand displayed a signal pattern consistent with C_s symmetry. The spectroscopic data of complex **11a-$(SO_3CF_3)_2$** bear close similarity to those of the irida-2-phenol isomer $[(PMe_3)_3\text{-Ir}(1,5\text{-}\eta\text{-CH=C(Me)-CH=C(Me)-C(OH)−})(O_3SCF_3)]O_3SCF_3$ reported by Bleeke.[22] Transformation of **3a-BF_4** into the irida-4-phenol **11a-$(SO_3CF_3)_2$** is reversible in $(CD_3)_3CO$ solution, and it seems that the weak basic nature of this solvent assists in shifting the equilibrium. Thus, after one week crystals of the starting **3a-SO_3CF_3** complex were isolated from this experiment. This is in contrast to the already reported irida-2-phenol isomers $[(PMe_3)_3\text{-Ir}(1,5\text{-}\eta\text{-CH=C(Me)-CH=C(Me)-C(OH)−})X]\text{-}SO_3CF_3$ (X = $CF_3SO_3^-$ or CF_3COO^-), which are formed by addition of 1.5 equivalents of HSO_3CF_3 or CF_3COOH.[27] The low reactivity of **3a-BF_4** may be due to several factors inherent to the iridacyclohexa-2,5-dien-4-one ring including the furthest position from the metal center of the carbonyl group, the strong distortion from planarity, and the nonalternated disposition of the diolefin bonds, thus limiting π-electron delocalization within the ring. A further contribution might

dx.doi.org/10.1021/om300439c | *Organometallics* 2012, 31, 5438−5451

result from an electronic effect on the metal, provided by the hard Tpm^{Me2} ligand, which does not realize back-bonding.

The aromatization of the bulkier iridacyclohexadien-4-one complex **3d-BF$_4$** was performed with one equivalent of HSO_3CF_3 in CH_2Cl_2 solution to lead to the isolation of [κ^3-Tpm^{Me2}Ir(1,5-η-CH=C(^{t}Bu)-C(OH)=CH−CH=)(CO)]-[O_3SCF_3]$_2$, **11d-(O$_3$SCF$_3$)$_2$**, in 85% yield. In fact two additional equivalents of the acid were just added to guarantee the full exchange of the anion. This result highlights the participation of steric effects in the aromatization of **3-BF$_4$** into **11-(O$_3$SCF$_3$)$_2$**. In contrast to the relatively simple methodology reported herein, iridabenzenes from the closely related ligand Tp^{Me2} have been synthesized[27] by contraction of the iridacycloheptatriene complex [κ^3-Tp^{Me2}Ir(1,6-η-C(R)=C(R)-C(R)=C(R)C(R)=C(R)(H$_2$O)] using ^{t}BuOOH as oxidizing agent[28a] or by expansion of the iridacyclopentadiene complex [(Tp^{Me2})Ir(1,4-η-CH=C(R)C(R)=C(R))(H$_2$O)] (R = CO_2Me) by reaction with propene.[28b] The synthesis and structure of Tp^{Me2}-iridabenzenes have been recently reviewed.[28c]

CONCLUSIONS

The synthesis of a series of complexes of the type [κ^2-Tpm^{Me2}Ir(2,3,5,6-η-2-R-BQ)Cl] (R = H, Cl, Ph, ^{t}Bu) **1a−d** starting from [Ir(μ-Cl)(coe)$_2$]$_2$ and the appropriate 2-R-BQ and Tpm^{Me2} ligands is feasible. The combined steric effects of the R substituent and the Tpm^{Me2} ligand lead to the formation of novel iridaciclohexa-2,5-dien-4-one complexes, **3-BF$_4$**, after activation of the C(sp^2)−C(sp^2)O double bond and decarbonylation of **1a−d**. This unprecedented transformation for coordinated 1,4-BQ is promoted by steric hindrance, characteristic of the κ^3-coordination mode of the ancillary ligand Tpm^{Me2}, and proceeds through the intermediacy of [κ^3-Tpm^{Me2}Ir(2,3,5,6-η-1,4-benzoquinone)][BF$_4$], **2a-BF$_4$**, species.

This contribution expands by twofold the available range of currently known Ir(I) compounds of composition [LIr(2,3,5,6-η-1,4-benzoquinone]^m. The neutral compound **1** is analogous to an anionic COD complex, and the cationic compound **2a-BF$_4$** is analogous to a neutral Cp* complex; thus the range of charged compounds (m = −1, 0, 1) is widened.

Phosphines displace the Tpm^{Me2} ligand in compound **1a** selectively, leading to the formation of Ir(I) complexes **5−8**, whereas the BQ ligand remains in the coordination sphere of the metal. The exchange of the ligand Tpm^{Me2} is accompanied with a change of the coordination geometry at the metal center from accentuated tbpy in **1a** to sbpy in complexes **5−8**. Conversely, CO sequentially displaces the BQ double bonds, giving compound **4-[Ir(CO)$_2$Cl$_2$]** in the first place; however, carbonylation continues, generating polycarbonylated species and making evident the preference of the metal for stronger bonds. Protonation of **1a** with HBF_4 allowed the isolation of the dicationic hydroquinone complex **10-(BF$_4$)$_2$**. The monoprotonated semiquinone complex **9-BF$_4$** is little favored when less than one equivalent of acid is added, and the equilibrium is shifted to unprotonated **1a**. In contrast, more than one equivalent of acid shifts the equilibrium to complex **10-(BF$_4$)$_2$**. Finally, irida-4-phenol complexes [κ^3-Tpm^{Me2}Ir(1,5-η-CH=C(R)-C(OH)=CH−CH=)(CO)][O_3SCF_3]$_2$ (R = H, ^{t}Bu), **11-(O$_3$SCF$_3$)$_2$**, were formed by aromatization, in acid media, of iridacyclohexa-2,5-dien-4-one complexes **3-BF$_4$**, in spite of unfavorable geometric features associated with the coordinated BQ ligand and the hard donor nature of the Tpm^{Me2} ligand.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under a dry, oxygen-free N_2 atmosphere, following conventional Schlenk techniques. Solvent evaporation, filtering, and drying procedures were performed under vacuum. Solvents were dried by standard methods (hexane and dichloromethane with CaH_2 and diethyl ether and THF with Na/benzophenone) and distilled under nitrogen prior to use. [Ir(μ-Cl)(coe)$_2$]$_2$ was obtained by the published procedure,[29] whereas Tpm^{Me2} was synthesized by a modified procedure of the method reported by Elguero.[30,15] All other chemicals, including ammonium hexachloroiridate(IV), 2-Cl-1,4-benzoquinone, 2-Ph-1,4-benzoquinone, 2-^{t}Bu-1,4-benzoquinone, PMe_3, PMe_2Ph, PPh_3, and DPPE, were used as received except for 1,4-benzoquinone, which was sublimed before use. Melting points were measured on an Electrothermal IA9100 apparatus and were uncorrected. IR spectra were recorded neat using a Varian 3100 FT-IR spectrophotometer of the Excalibur Series equipped with an ATR system. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Mercury 300 (^{1}H, 300.08; ^{13}C, 75.46; ^{31}P, 121.47 MHz) instrument in deoxygenated and deuterated solvents. Spectra were referenced to external $SiMe_4$ (δ = 0 ppm) using the residual protio solvent peaks as internal standards (^{1}H NMR) or characteristic resonances of the solvent nuclei (^{13}C NMR). For ^{31}P{^{1}H} NMR spectroscopy, 85% H_3PO_4 was used as the reference. Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropriate. Microanalyses were performed by the Microanalytical Service of the Centro de Investigaciones Químicas de la Universidad Autónoma del Estado de Hidalgo (UAEH) and Micro Analysis Inc. (Wilmington, DE, USA). Due to the strong tendency of these ionic complexes to retain crystallization solvent, the calculated elemental analyses for some of them are reported considering CH_2Cl_2, Et_2O, and adventitious H_2O content.

XRD Experiments. Single-crystal X-ray diffraction data for molecules **1a** and **1b** were collected at 100(2) or 173(2) K for molecules **2a-BF$_4$**, **3a-BF$_4$**, and **3b-BF$_4$**, on Bruker Apex II and Nonius Kappa diffractometers equipped with area detectors using Mo Kα radiation, λ = 0.71073 Å, and at 293(2) K (**5−8** and **E**) on a CrysAlis Pro diffractometer with an area detector and Cu Kα radiation, λ = 1.54178, and **4-[Ir(CO)$_2$Cl$_2$]** with Mo Kα radiation, λ = 0.71073 Å. Summaries of crystal data and collection parameters are listed in Tables 6 and 7 (SI). Either a semiempirical absorption correction was applied using SADABS[31] and the program SAINT,[32] or the CrysAlis Pro program[33] was used for integration of the diffraction profiles. The structures were solved by direct methods using SHELXS97[34] in the WinGX package.[35] The final refinement was performed by full-matrix least-squares methods on F^2 with SHELXTL97.[32] H atoms on C, N, and O were positioned geometrically and treated as riding atoms, with C−H = 0.93−0.98 Å, and with U_{iso}(H) = 1.2 U_{eq}(C, N, O). The program Mercury was used for visualization, molecular graphics, and analysis of crystal structures.[36] Software used to prepare material for publication was PLATON.[37] The molecules in the crystal structure of **3b-BF$_4$** are disordered over two positions at the sites corresponding to Cl and H3 atoms; they were refined with occupancy factors of 0.50 each. In compound **8**, CH_2Cl_2 solvent molecules were disordered over three positions (occ = 0.45, 0.18, and 0.37). Disorder was treated with PART1-3 instructions. Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation of a solution of compound **3a-BF$_4$**, **4-[Ir(CO)$_2$Cl$_2$]**, or **E** in acetone or slow diffusion of Et_2O into saturated CH_2Cl_2 solutions of complexes **1a**, **1b**, **2a-BF$_4$**, **3b-BF$_4$**, and **5−8**.

[κ^2-Tpm^{Me2}Ir(2,3,5,6-η-1,4-benzoquinone)Cl] (1a). In a Schlenk flask equipped with a stir bar and immersed in an ice−water bath was suspended 500 mg (0.558 mmol) of the [Ir(μ-Cl)(coe)$_2$]$_2$ dimer in 15 mL of CH_2Cl_2. Then, 121 mg (1.11 mmol) of 1,4-benzoquinone in 5 mL of CH_2Cl_2 was added, followed, after 1 h, by 333 mg (1.11 mmol) of Tpm^{Me2} ligand in 1 mL of CH_2Cl_2, whereupon the mixture was allowed to react for 1 h at room temperature. The solvent was evaporated, and the resulting solid was washed with Et_2O (3 × 3 mL), filtered, and dried to obtain a pale

dx.doi.org/10.1021/om300439c | Organometallics 2012, 31, 5438−5451

yellow solid in 85% yield (598 mg, 0.943 mmol). Mp = 178 °C. IR ν_{neat} (cm^{-1}): (CO) 1643, 1563.^{1}H NMR ($CDCl_3$): δ 7.61 (s, 1H, $CH_{(Pz)3}$), 6.25, 5.91 (s, 3H, CH_{Pz} (2:1)), 4.55 (s, 4H, CH_{BQ}), 2.65, 2.51, 2.08, 1.53 (s, 18H, $6Me_{Pz}$ (2:2:1:1)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.2 ($2CO_{BQ}$), 158.4, 150.6, 144.3, 140.0 ($6Cq_{Pz}$, 2:1:2:1), 111.0, 110.0 ($3CH_{Pz}$ (1:2)), 74.0 ($CH_{(Pz)3}$), 64.4 ($4CH_{BQ}$), 14.4, 13.5, 11.7, 10.6 (6 Me_{Pz}, 2:2:1:1). Anal. Calcd for $C_{22}H_{26}N_6O_2ClIr$ (634.14 g/mol): C, 41.6; H, 4.1; N, 13.2. Found: C, 41.5; H, 4.2; N, 13.5.

[κ^2-Tpm^{Me2}Ir(2,3,5,6-η-2-Cl-1,4-benzoquinone)Cl] (1b). This compound was prepared following a procedure similar to that described for **1a**, but with 200 mg of $[Ir(\mu\text{-}Cl)(coe)_2]_2$ (0.223 mmol), 7 mL of CH_2Cl_2, 63.6 mg (0.446 mmol) of 2-Cl-1,4-benzoquinone, and 133 mg (0.446 mmol) of Tpm^{Me2}. A dark yellow solid was obtained in 78% yield (232 mg, 0.348 mmol). Decomposition without melting occurred at 166 °C. IR ν_{neat} (cm^{-1}): (CO) 1645, 1563. ^{1}H NMR [$CDCl_3$, J(Hz)]: δ 7.62 (s, 1H, $CH_{(Pz)3}$), 6.27, 6.24, 5.90 (s, 1H each, CH_{Pz}), 5.05 (d, 1H, $^4J_{H3-H5}$ = 3.0, H-3), 4.81 (d, 1H, $^3J_{H6-H5}$ = 9.0, H-6), 4.13 (dd, 1H, $^4J_{H5-H3}$ = 3.0, $^3J_{H5-H6}$ = 9.0, H-5), 2.62, 2.52, 2.51, 2.50, 2.08, 1.50 (s, 3H each, $6Me_{Pz}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.5, 165.4 ($2CO_{BQ}$), 158.8, 158.6, 150.9, 145.0, 144.7, 140.2 ($6Cq_{Pz}$), 111.2, 110.2, 109.9 ($3CH_{Pz}$), 76.6 (C-6), 74.6 (C-5), 74.0 ($CH_{(Pz)3}$), 71.5 (C−Cl), 53.6 (C-3), 14.6, 14.4, 13.7, 11.9, 11.8, 10.4 ($6Me_{Pz}$). Anal. Calcd for $C_{22}H_{25}N_6O_2Cl_2Ir$ (668.58 g/mol): C, 39.5; H, 3.7; N, 12.5. Found: C, 39.2; H, 4.0; N, 12.4.

[κ^2-Tpm^{Me2}Ir(2,3,5,6-η-2-Ph-1,4-benzoquinone)Cl] (1c). This compound was prepared following a procedure similar to that described for **1a**, but with 150 mg of $[Ir(\mu\text{-}Cl)(coe)_2]_2$ (0.167 mmol), 6 mL of CH_2Cl_2, 61.7 mg (0.334 mmol) of 2-Ph-1,4-benzoquinone, and 99.9 mg (0.334 mmol) of Tpm^{Me2}. A dark brown solid in 93% yield (221 mg, 0.311 mmol) was obtained. Decomposition without melting occurred at 136 °C. IR ν_{neat} (cm^{-1}): (CO) 1624, 1563. ^{1}H NMR [$CDCl_3$, J(Hz)]: δ 8.16−8.13 (m, 2H, H_o), 7.60 (s, 1H, $CH_{(Pz)3}$), 7.41−7.29 (m, 3H, $H_{m\text{-}p}$), 6.26, 6.20, 5.95 (s, 3H, H_{Pz} (1:1:1)), 5.45 (d, 1H, $^4J_{H3-H5}$ = 2.4, H-3), 4.85 (d, 1H, $^3J_{H6-H5}$ = 7.5, H-6), 3.96 (dd, 1H, $^3J_{H5-H6}$ = 7.5, $^4J_{H5-H3}$ = 2.4, H-5), 2.67, 2.50, 2.48, 2.46, 2.10, 1.54 (s, 3H each, $6Me_{Pz}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.4, 165.95 ($2CO_{BQ}$), 158.8, 158.4, 150.8, 144.8, 144.5, 140.3 ($6Cq_{pz}$), 134.4 (Cq_{Ph}), 129.1 ($2CH_o$), 128.2 ($2CH_m$), 127.8 (CH_p), 111.3, 110.5, 109.8 ($3CH_{Pz}$), 75.0 (C-6), 74.0 ($CH_{(Pz)3}$), 71.6 (C-Ph), 70.1 (C-5), 54.0 (C-3), 15.1, 14.9, 13.8, 11.9, 11.8, 10.3 ($6Me_{Pz}$). Anal. Calcd for $C_{28}H_{30}N_6O_2ClIr{\cdot}H_2O$ (728.26 g/mol): C, 46.2; H, 4.4; N, 11.5. Found: C, 46.5; H, 4.3; N, 11.2.

[κ^2-Tpm^{Me2}Ir(2,3,5,6-η-2-^{t}Bu-1,4-benzoquinone)Cl] (1d) in a Mixture with 3d-Cl. The reaction was performed as described for **1a**, but with 50 mg of $[Ir(\mu\text{-}Cl)(coe)_2]_2$ (0.056 mmol), 4 mL of CH_2Cl_2, 18.3 mg of 2-^{t}Bu-1,4-benzoquinone immersed in a liquid nitrogen−methanol cooling bath (−40 °C), and 33.3 mg (0.111 mmol) of Tpm^{Me2} during 80 min at −40 °C. After workup, 67 mg of a dark brown solid was obtained as an inseparable mixture of compounds **1d** and **3d-Cl** in a 4:1 ratio, respectively. The mixture melts at 123 °C. Spectroscopic data for **1d**: IR ν_{neat} (cm^{-1}): (CO) 1648, 1564. ^{1}H NMR [$CDCl_3$, J(Hz)]: δ 7.61 (s, 1H, $CH_{(pz)3}$), 6.29, 6.21, 5.95 (s, 1H each, H_{Pz}), 5.21 (d, 1H, $^4J_{H3-H5}$ = 3, H-3), 4.93 (d, 1H, $^3J_{H6-H5}$ = 9, H-6), 3.10 (dd, 1H, $^3J_{H5-H6}$ = 9, $^4J_{H5-H3}$ = 3, H-5), 2.72, 2.63, 2.52, 2.46, 2.04, 1.55 (s, 3H each, $6Me_{Pz}$), 1.45 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 172.4, 163.1 ($2CO_{BQ}$), 158.5, 158.3, 150.2, 144.8, 144.6, 140.1 ($6Cq_{Pz}$), 111.0, 110.9, 109.4 ($3CH_{Pz}$), 88.7 (C-^{t}Bu), 77.4 (C-6), 73.9 ($CH_{(Pz)3}$), 65.1 (C-5), 50.1 (C-3), 36.1 (Cq_{tBu}), 27.4 ($3Me_{tBu}$) 15.7, 14.9, 13.6, 12.0, 11.8, 10.0 ($6Me_{Pz}$).

[κ^3-Tpm^{Me2}Ir(2,3,5,6-η-1,4-benzoquinone)][BF_4] (2a-BF_4). Method A. In a Schlenk flask equipped with a stir bar and immersed in an ice−water bath were placed 150 mg (0.0236 mmol) of compound **1a**, 46 mg (0.0236 mmol) of $AgBF_4$, and 8 mL of CH_2Cl_2. The mixture was allowed to react for 50 min at 4 °C, whereupon the AgCl precipitate was filtered off and washed with CH_2Cl_2 (2 × 3 mL). The CH_2Cl_2 solution was evaporated to dryness to obtain a greenish-yellow solid in 53% yield (87.5 mg, 0.100 mmol). **Method B.** The same procedure as for the synthesis of **1a** was followed, but 217 mg (1.1 mmol) of $AgBF_4$ was added together with the Tpm^{Me2} ligand, to obtain a greenish-yellow solid in 88% yield (673 mg, 0.981 mmol). Decomposition without melting occurred at 111 °C. IR ν_{neat} (cm^{-1}): (CO) 1662, 1569. ^{1}H NMR [$(CD_3)_2CO$]: δ 8.15 (s, 1H, $CH_{(Pz)3}$), 6.40 (s, 3H, H_{Pz}), 5.45 (s, 4H, H_{BQ}), 2.80, 2.50 (s, 9H each, $6Me_{Pz}$). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 177.5 ($2CO_{BQ}$), 161.0, 146.0 ($6Cq_{Pz}$), 112.7 ($3CH_{Pz}$), 70.6 ($CH_{(Pz)3}$), 61.6 ($4CH_{BQ}$), 15.4, 12.4 ($6Me_{Pz}$). Anal. Calcd for $C_{22}H_{26}N_6O_2Ir\ BF_4{\cdot}$(685.50 g/mol): C, 38.5; H, 3.8; N, 12.2. Found: C, 38.7; H, 3.8; N, 12.4.

[κ^3-Tpm^{Me2}Ir(1,5-η-CH═CHC(O)CH═CH−)(CO)][BF_4] (3a-BF_4). In a Schlenk flask equipped with a stir bar were placed 100 mg (0.146 mmol) of compound **1a** and 12 mL of CH_2Cl_2. The yellow solution was stirred at 60 °C for 6 h to give a brown solution. After solvent evaporation, a brown solid was obtained in 92% yield (92 mg, 0.134 mmol). Decomposition without melting occurred at 149 °C. IR ν_{neat} (cm^{-1}): (IrC≡O) 2066, (CO) 1614, (B−F) 1053. ^{1}H NMR [$CDCl_3$, J(Hz)]: δ 8.73 (d, 2H, $^3J_{H2-H3}$ = 9, H-2,6), 8.23 (s, 1H, $CH_{(Pz)3}$), 6.89 (d, 2H, $^3J_{H3-H2}$ = 9, H-3,5), 6.31, 6.10 (s, 3H, H_{Pz} (2:1)), 2.79, 2.76, 2.39, 2.19 (s, 18H, $6Me_{Pz}$ (2:1:2:1)). $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 197.5 (CO-Ir), 158.8 (CO), 158.4, 154.8, 144.4, 136.6 ($6Cq_{Pz}$, 2:1:2:1), 136.7 (2C-3,5), 135.8 (2C-2,6), 110.8, 109.9, ($3CH_{Pz}$, 1:2), 69.8 ($CH_{(Pz)3}$), 14.2, 14.1, 11.2, 11.1, ($6Me_{Pz}$ (2:1:2:1)). Anal. Calcd for $C_{22}H_{26}N_6O_2IrBF_4$ (685.50 g/mol): C, 38.5; H, 3.8; N, 12.2. Found: C, 38.3; H, 3.9; N, 12.3.

[κ^3-Tpm^{Me2}Ir(1,5-η-CH═C(Cl)C(O)CH═CH−)(CO)][BF_4] (3b-BF_4). In a Schlenk flask equipped with a stir bar were placed 200 mg (0.299 mmol) of compound **1b**, 58.2 mg (0.299 mmol) of $AgBF_4$ and 12 mL of CH_2Cl_2, and the reaction mixture was allowed to react at room temperature for 90 min. The AgCl precipitate was removed by filtration and washed with CH_2Cl_2 (2 × 3 mL). The resulting red solution was evaporated to dryness to obtain a dark brown solid in 87% yield (187 mg, 0.260 mmol). Decomposition without melting occurred at 138 °C. IR ν_{neat} (cm^{-1}): (IrC≡O) 2061, (CO) 1624, (B−F) 1053. ^{1}H NMR [$CDCl_3$, J(Hz)]: δ 8.86 (s, 1H, H-2), 8.67 (d, 1H, $^3J_{H6-H5}$ = 9, H-6), 8.24 (s, 1H, $CH_{(Pz)3}$), 7.18 (d, 1H, $^3J_{H5-H6}$ = 9, H-5) 6.33, 6.32, 6.13 (s, 1H each, H_{Pz}), 2.80, 2.79, 2.76, 2.41, 2.40, 2.20 (s, 3H each, $6Me_{Pz}$). $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 188.1 (CO-Ir), not observed (CO), 158.4, 157.9, 155.1, 155.0, 144.9, 144.8, ($6Cq_{Pz}$), 138.4 (C-5), 134.3 (C-6), 129.8 (C−Cl), 127.6 (C-2), 111.0, 110.1, 110.0 ($3CH_{Pz}$), 69.9 ($CH_{(Pz)3}$), 14.4, 14.3, 13.3, 11.5, 11.3, 11.2 ($6Me_{Pz}$). Anal. Calcd for $C_{22}H_{25}N_6O_2ClIrBF_4$ (719.94 g/mol): C, 36.7; H, 3.4; N, 11.6. Found: C, 36.9; H, 3.4; N, 11.3.

[κ^3-Tpm^{Me2}Ir(1,5-η-CH═C(Ph)C(O)CH═CH−)(CO)][BF_4] (3c-BF_4). The same procedure as for the synthesis of **1a** was followed, but 100 mg (0.111 mmol) of $[Ir(\mu\text{-}Cl)(coe)_2]_2$, 14 mL of CH_2Cl_2, and 41.1 mg (0.223 mmol) of 2-Ph-1,4-benzoquinone were used. Then 66.6 mg (0.223 mmol) of Tpm^{Me2} and 43.4 mg (0.223 mmol) of $AgBF_4$ were simultaneously added. After solvent evaporation, the solid was washed with Et_2O (3 × 3 mL) and dried. The remaining solid was dissolved in CH_2Cl_2, and the solution was filtered to separate AgCl and evaporated to obtain a brown solid in 78% yield (132 mg, 0.174 mmol). Decomposition without melting occurred at 134 °C. IR ν_{neat} (cm^{-1}): (IrC≡O) 2057, (CO) 1614, (B−F) 1051. ^{1}H NMR [$CDCl_3$, J(Hz)]: δ 8.78 (s, 1H, H-2), 8.61 (d, 1H, $^3J_{H6-H5}$ = 9, H-6), 8.22 (s, 1H, $CH_{(Pz)3}$), 7.34−7.22 (m, 5H, H_{Ph}), 7.05 (d, 1H, $^3J_{H5-H6}$ = 9, H-5), 6.31, 6.29, 6.10 (s, 1H each, CH_{Pz}), 2.77, 2.76, 2.73, 2.44, 2.40, 2.24 (s, 3H each, $6Me_{Pz}$). $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 195.9 (CO-Ir), 159.2 (CO), 158.2, 154.9, 154.7, 146.8, 144.5, 144.4, ($6Cq_{Pz}$), 140.1(C-Ph), 137.8 (C-5), 133.8 (C-2), 132.6 (C-6), 130.2 (Cq_{Ph}), 128.6, 128.0, 127.2 ($5CH_{Ph}$, 2:2:1), 110.8, 109.9, 109.8 ($3CH_{Pz}$), 69.9 ($CH_{(Pz)3}$), 14.4, 14.2, 13.3, 11.4, 11.2, 11.1 (6 Me_{Pz}). Anal. Calcd for $C_{28}H_{30}N_6O_2IrBF_4$ (761.59 g/mol): C, 44.1; H, 3.9; N, 11.0. Found: C, 44.4; H, 4.0; N, 10.7.

[κ^3-Tpm^{Me2}Ir(1,5-η-CH═C(^{t}Bu)C(O)CH═CH−)(CO)][BF_4] (3d-BF_4). This compound was prepared as described for **3c-BF_4**, but 100 mg (0.111 mmol) of $[Ir(\mu\text{-}Cl)(coe)_2]_2$, 14 mL of CH_2Cl_2, 36.6 mg (0.223 mmol) of 2-^{t}Bu-1,4-benzoquinone, 66.6 mg (0.223 mmol) of Tpm^{Me2}, and 43.4 mg (0.223 mmol) of $AgBF_4$ were used. A brown solid was obtained in 81% yield (134 mg, 0.180 mmol). Decomposition without melting occurred at 134 °C. IR ν_{neat} (cm^{-1}): (IrC≡O) 2052, (CO) 1609, (B−F) 1051. ^{1}H NMR

dx.doi.org/10.1021/om300439c | Organometallics 2012, 31, 5438−5451

[$CDCl_3$, J(Hz)]: δ 8.42 (s, 1H, H-2), 8.25 (d, 1H, $^3J_{H6-H5}$ = 9, H-6), 8.23 (s, 1H, $CH_{(Pz)3}$), 6.88 (d, 1H, $^3J_{H5-H6}$ = 9, H-5), 6.31, 6.29, 6.11 (s, 1H each, H_{Pz}), 2.79, 2.78, 2.76, 2.36, 2.36, 2.19 (s, 3H each, $6Me_{Pz}$), 1.23 (s, 9H, $3Me_{tBu}$). $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 198.1 (CO-Ir), 159.6 (CO), 158.1, 154.8, 154.5, 151.9, 144.4, 144.4 ($6Cq_{Pz}$), 144.3 (C-^{t}Bu), 139.1 (C-5), 129.5 (C-6), 125.8 (C-2), 110.7, 109.8, 109.7 ($3CH_{Pz}$), 69.9 ($CH_{(Pz)3}$), 38.1 (Cq_{tBu}), 30.2 ($3Me_{tBu}$), 14.1, 14.1, 12.9, 11.4, 11.3, 11.2 ($6Me_{Pz}$). Anal. Calcd for $C_{26}H_{34}N_6O_2BF_4Ir$ (741.60 g/mol): C, 42.1; H, 4.6; N, 11.3. Found: C, 42.3; H, 4.9; N, 11.2.

[κ^3-Tpm^{Me2}Ir(2,3-η-1,4-benzoquinone)(CO)][Ir(CO)$_2$Cl$_2$] (4-[Ir(CO)$_2$Cl$_2$]). In a Fisher-Porter glass pressure vessel equipped with a stir bar was placed 150 mg (0.236 mmol) of compound **1a**, and after three cycles of treatment with N_2/vacuum 12 mL of CH_2Cl_2 was added and the reactor was charged with 1 atm of CO. The mixture was allowed to react at room temperature during 50 min; then it was transferred to a Schlenk flask, and half the solvent was evaporated under reduced pressure. Then, 8 mL of Et_2O was added until saturation, and the solution was cooled to 4 °C until precipitation. The ethereal solution was discarded, and the resulting solid was washed twice with 2 mL of Et_2O. The yellow solid was dried under vacuum to give **4** in 71% yield (80 mg, 0.084 mmol). Decomposition without melting occurred at 179 °C. IR ν_{neat} (cm^{-1}): (IrC≡O) 2042, 1957 (C═O) 1648, 1566, (C═C) 1697. ^{1}H NMR [$(CD_3)_2CO$, J(Hz)]: δ 8.24 (s, 1H, $CH_{(Pz)3}$), 6.56 (s, 2H, H-5,6), 6.49, 6.31 (s, 3H,H_{Pz}, 2:1), 4.89 (s, 2H, H-2,3), 2.84, 2.82, 2.53, 2.30 (s, 18H, $6CH_{Pz}$, 2:1:1:2). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 198.9 (Ir-CO), 161.2 (2CO), 158.3, 157.4, 145.8, 145.2 ($6Cq_{Pz}$, 1:2:1:2), 138.6 (C-5,6), 112.8, 109.8 ($3CH_{Pz}$, 1:2), 70.3 ($CH_{(Pz)3}$), 28.2 (C-2,3), 14.1, 13.4, 11.9, 11.2 ($6Me_{Pz}$, 2:1:1:2). Anal. Calcd for $C_{25}H_{26}N_6O_5Cl_2Ir_2$ (985.85 g/mol): C, 31.7; H, 2.8; N, 8.9. Found: C, 32.0; H, 2.8; N, 8.5.

[(PPh$_3$)$_2$Ir(2,3,5,6-η-1,4-benzoquinone)Cl] (5). Method A. In a Schlenk flask equipped with a stir bar were placed 100 mg (0.157 mmol) of compound **1a**, 10 mL of CH_2Cl_2, and 82.7 mg (0.315 mmol) of PPh_3, and the mixture was allowed to react for 2 h at room temperature. Then, the bright yellow solution was evaporated to dryness, and the resulting dark yellow solid was washed with Et_2O (3 × 4 mL) and dried under vacuum to obtain a yellow solid in 91% yield (123 mg, 0.143 mmol). **Method B.** Into a Schlenk flask equipped with a stir bar and immersed in an ice−water bath were placed 100 mg (0.111 mmol) of [Ir(μ-Cl)(coe)$_2$]$_2$, 8 mL of CH_2Cl_2, and 24 mg (0.223 mmol) of 1,4-benzoquinone. The mixture was allowed to react for 1 h, whereupon 117 mg (0.446 mmol) of PPh_3 was added. The reaction mixture was allowed to react for 1.5 h at RT, whereby it turned from dark orange to light orange. The solvent was evaporated, and the resulting solid was washed with Et_2O (3 × 3 mL), filtered, and dried to obtain an orange solid in 87% yield (168 mg, 0.195 mmol). Decomposition without melting occurred at 197 °C. IR ν_{neat} (cm^{-1}): (CO) 1675, 1630, (P−C) 1434, (C═C$_{arom}$) 1482. ^{1}H NMR [$CDCl_3$]: δ 7.36−7.18 (m, 30H, H_{PPh3}), 4.22 (s, 4H, H_{BQ}). $^{13}C\{^1H\}$ NMR [$CDCl_3$, J(Hz)]: δ 166.4 (t, 2CO, $^3J_{C-P}$ = 2.2), 134.3 (t, $12CH_m$, $^3J_{C-P}$ = 4.5), 131.9 (virtual t, $6Cq_{Ph}$, $^1J_{C-P}$ = 28.3), 130.8 ($6CH_p$), 128.2 (t, $12CH_o$, $^2J_{C-P}$ = 5.2), 81.0 (t, $4CH_{BQ}$,$^2J_{C-P}$ = 5.9). $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ −13.6 (PPh_3). Anal. Calcd for $C_{42}H_{34}O_2P_2ClIr\cdot H_2O$ (878.35 g/mol): C, 57.4; H, 4.1. Found: C, 57.1; H, 3.9.

[(PMe$_2$Ph)$_2$Ir(2,3,5,6-η-1,4-benzoquinone)Cl] (6). This compound was prepared as described for **5** (method A), but 45.0 μL (0.315 mmol) of PMe_2Ph was used to obtain a pale orange solid in 83% yield (80.5 mg, 0.131 mmol). Decomposition without melting occurred at 162 °C. IR ν_{neat} (cm^{-1}): (CO) 1644, 1603, (P−C) 1437, 1309, (C═C) 1683. ^{1}H NMR [$CDCl_3$, J(Hz)]: δ 7.47−7.41 (m, 10H, H_{Ph}), 4.70 (s, 4H, H_{BQ}), 1.84, 1.71 (d, 6H each,$^2J_{H-P}$ = 10.8, $P(CH_3)_2$). $^{13}C\{^1H\}$ NMR [$CDCl_3$, J(Hz)]: δ 162.4 (t, 2CO, $^3J_{C-P}$ = 2.5), 131.4 ($2CH_p$), 130.5 (t, $4CH_m$, $^3J_{C-P}$ = 4.6), 129.1 (t, $4CH_o$, $^2J_{C-P}$ = 5.1), 80.8 (t, $4CH_{BQ}$, $^2J_{C-P}$ = 4.8), 15.1 (t, $2CH_3$, $^1J_{C-P}$ = 20), 13.4 (t, $2CH_3$, $^1J_{C-P}$ = 20). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −33.1 (PMe_2Ph). Anal. Calcd for $C_{22}H_{26}O_2P_2ClIr$ (612.06 g/mol): C, 43.2; H, 4.3. Found: C, 43.3; H, 4.2.

[(PMe$_3$)$_2$Ir(2,3,5,6-η-1,4-benzoquinone)Cl] (7). This compound was prepared as described for **5** (method A), but 331.0 μL of a 1.0 M solution of PMe_3 in THF was used (0.311 mmol). The mixture was allowed to react for 1.5 h to obtain a dark yellow solid after solvent evaporation, which was washed with Et_2O (3 × 4 mL) and dried. The resulting solid was redissolved in 4 mL of CH_2Cl_2, and 3 mL of Et_2O was added. The resulting solution was discarded after filtration, and the remaining solid was treated as before. After drying, 24 mg (0.048 mmol) of a yellow solid was obtained in 31% yield. Decomposition without melting occurred at 163 °C. IR ν_{neat} (cm^{-1}): (CO) 1614, 1583, (P−C) 1293, (C═C) 1695. ^{1}H NMR [$CDCl_3$]: δ 4.84 (s, 4H, H_{BQ}), 1.72 (virtual d, 9H, $^2J_{H-P}$ = 9, $P(CH_3)_3$). ^{13}C NMR [$CDCl_3$, J(Hz)]: δ 162.3 (t, 2CO, $^3J_{C-P}$ = 2.6), 78.9 (t, $4CH_{BQ}$, $^2J_{C-P}$ = 3.8), 16.4−15.6 (m, $6CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −39.4 (PMe_3). Anal. Calcd for $C_{12}H_{22}O_2P_2ClIr\cdot 0.25Et_2O$ (508.97 g/mol): C, 30.7; H, 5.3. Found: C, 30.6; H, 5.1.

[(μ-PPh$_2$CH$_2$CH$_2$PPh$_2$)Ir(2,3,5,6-η-1,4-benzoquinone)Cl]$_2$ (8). This compound was prepared as described for **5** (method A), but 60 mg (0.094 mmol) of **1a**, 5 mL of CH_2Cl_2, and a solution of 39.6 mg (0.099 mmol) of 1,2-bis(diphenylphosphino)ethane in 5 mL of CH_2Cl_2 were used. Washing was performed with a 70:30 mixture of hexane−ethyl acetate (4 × 3 mL) followed by Et_2O (2 × 3 mL). After workup an orange solid was obtained in 80% yield (112 mg, 0.076 mmol). Decomposition without melting occurred at 144 °C. IR ν_{neat} (cm^{-1}): (CO) 1638, 1607, (P−C) 1434, 1332, (C═C$_{arom}$) 1483, (C═C) 1723. ^{1}H NMR [$CDCl_3$, J(Hz)]: δ 7.57−7.29 (m, 20H, H_{Ph}), 4.88 (s, 4H, H_{BQ}), 3.08, 2.35 (m, 2H each, $P(CH_2)$). $^{13}C\{^1H\}$ NMR [$CDCl_3$, J(Hz)]: δ 163.3 (t, 2CO, $^3J_{C-P}$ = 2.1), 132.9 (t, $4CH_o$, $^2J_{C-P}$ = 5.5), 132.7 (t, $4CH_m$, $^3J_{C-P}$ = 4.5), 131.9, 131.6 ($2CH_p$), 129.2 (t, $4CH_m$, $^3J_{C-P}$ = 5.4), 128.8 (t, $4CH_o$, $^2J_{C-P}$ = 5.5), 80.9 (t, $4CH_{BQ}$, $^2J_{C-P}$ = 5.4), 27.9 (d, $2CH_2$, $^1J_{C-P}$ = 4.2), 27.4 (d, $2CH_2$, $^1J_{C-P}$ = 4.2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.81 (1,2-bis(diphenylphosphino)ethane). Anal. Calcd for $C_{64}H_{56}O_4P_4Cl_2Ir_2\cdot CH_2Cl_2$ (1553.29 g/mol): C, 50.3; H, 3.8. Found: C, 50.2; H, 3.6.

[κ^2-Tpm^{Me2}Ir(2-6-η-semiquinone)Cl][BF$_4$] (9-BF$_4$) in a Mixture with 1a. In a Schlenk flask equipped with a stir bar and immersed in an ice−water bath was dissolved 100 mg (0.157 mmol) of **1a** in 8 mL of CH_2Cl_2, whereupon 17 μL (0.126 mmol) of HBF_4−OEt_2 was added. Immediately, a pale yellow solid appeared. The mixture was allowed to react for 1 h under vigorous stirring and allowed to reach RT during one more hour. The solvent was evaporated to dryness, and the resulting solid was dissolved in $(CD_3)CO$ to give a mixture of **9-BF$_4$**−**1a** in 1:3 proportion as established from ^{1}H NMR. ^{1}H NMR [$(CD_3)_2CO$]: δ 8.45 (s, 1H, $CH_{(Pz)3}$), 6.52, 6.11 (s, 3H, H_{Pz}, 2:1), 6.11 (d, 2H, $^3J_{H3-H2}$ = 6, H-3), 4.39 (d, 2H, $^3J_{H2-H3}$ = 6, H-2), 2.79, 2.58, 2.10, 1.64 (s, 18H, $6CH_{Pz}$, 2:2:1:1). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 176.4 (CO), 159.5, 150.8, 148.6, 142.6 ($6Cq_{Pz}$, 2:1:2:1), 152.4 (C−OH), 111.5, 110.8 ($3CH_{Pz}$, 1:2), 82.7 (2C-3, $^1J_{C-H}$= 180), 75.6 ($CH_{(Pz)3}$), 61.7 (2C-2, $^1J_{C-H}$ = 178), 14.8, 14.4, 11.7, 11.3 ($6Me_{Pz}$, 2:1:2:1).

[κ^2-Tpm^{Me2}Ir(1-6-η-1,4-hydroquinone)Cl][BF$_4$]$_2$ (10-(BF$_4$)$_2$). In a Schlenk flask immersed in an ice−water bath and equipped with a stir bar were placed 100 mg (0.157 mmol) of compound **1a**, 12 mL of CH_2Cl_2, and 47 μL (0.347 mmol) of a HBF_4−OEt_2 solution. Immediately, a pale yellow solid appeared. The reaction mixture was allowed to react for 1 h at 4 °C and for 1 h at room temperature. The solvent was evaporated, and the remaining solid was washed with Et_2O (3 × 4 mL) and evaporated to dryness. A pale yellow solid was obtained in 93% yield (118 mg, 0.146 mmol). Decomposition without melting occurred at 75 °C. IR ν_{neat} (cm^{-1}): (O−H) 3561, (C−O) 1062, 1032, (C═C) 1676, 1569, (B−F) 1049. ^{1}H NMR [$(CD_3)_2CO$]: δ 8.55 (s, 1H, $CH_{(Pz)3}$), 6.61, 6.19 (s, 3H, H_{Pz}, 2:1), 5.49 (br, 4H, H_{HQ}), 2.82, 2.60, 2.12, 1.67 (s, 18H, $6CH_{Pz}$, 2:2:1:1).^{1}H NMR [CD_3OD]: δ 8.38 (s, 1H, $CH_{(Pz)3}$), 6.53, 6.12 (s, 3H, H_{Pz}, 2:1), 5.39 (s, 4H, H_{HQ}), 2.66, 2.59, 2.15, 1.65 (s, 18H, $6CH_{Pz}$, 2:2:1:1). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 159.6, 151.3, 149.4, 143.1 ($6Cq_{Pz}$, 2:1:2:1), 112.1, 111.4 ($3CH_{Pz}$, 1:2), 75.8 ($CH_{(Pz)3}$), 74.6 (br, $4CH_{HQ}$), not observed (COH), 15.1, 13.3, 11.8, 10.4 ($6Me_{Pz}$, 2:1:2:1). $^{13}C\{^1H\}$ NMR [CD_3OD]: δ 160.2, 152.0, 149.6, 143.3 ($6Cq_{Pz}$, 2:1:2:1), 152.1 (C−OH), 112.4, 111.6 ($3CH_{Pz}$, 1:2), 76.2 ($CH_{(Pz)3}$), 74.6 ($4CH_{HQ}$, $^1J_{C-H}$ = 179), 15.1, 13.3, 11.7, 10.4 ($6Me_{Pz}$, 2:1:2:1). Anal. Calcd for $C_{22}H_{28}N_6O_2F_8B_2ClIr\cdot H_2O$ (827.79 g/mol): C, 31.9; H, 3.7; N, 10.2. Found: C, 31.9; H, 3.4; N, 9.9.

dx.doi.org/10.1021/om300439c | Organometallics 2012, 31, 5438−5451

[κ^3-Tpm^{Me2}Ir(1,5-η-CH=CH-C(OH)=CH−CH=)(CO)]-[O_3SCF_3]$_2$ (11a-(O_3SCF_3)$_2$). In a Schlenk flask equipped with a stir bar was suspended 100 mg (0.145 mmol) of **3a-BF$_4$** in 15 mL of THF. The brown suspension turned to a light brown solution after dropwise addition of 129 μL (1.45 mmol) of HSO_3CF_3 under vigorous stirring, and after 30 min it turned gelatinous. After solvent evaporation, the remaining brown oil was crushed in 15 mL of Et_2O until a yellow solid appeared. The solvent was removed by filtration, and the solid was washed with Et_2O (3 × 2 mL) and dried to obtain a pale yellow solid in 70% yield (94.1 mg, 0.102 mmol). Decomposition without melting occurred at 199 °C. IR ν_{neat} (cm^{-1}): (O−H) 3420, (IrC≡O) 2085, (C=C) 1571, 1470, (C−OH) 1255, (S=O) 1307, 1166. ^{1}H NMR [CD_2Cl_2, J(Hz)]: δ 13.65 (br, 1H, OH), 11.02 (d, 2H, $^3J_{H2-H3}$ = 9, H-2,6), 8.12 (s, 1H, $CH_{(Pz)3}$), 7.79 (d, 2H, $^3J_{H3-H2}$ = 9, H-3,5), 6.38, 6.16 (s, 3H, H_{Pz}, 2:1), 2.76, 2.71, 2.37, 1.85 (s, 18H, 6CH_{Pz}, 2:1:2:1). ^{1}H NMR [CD_3OD, J(Hz)]: δ not observed (OH), 11.52 (br d, 2H, H-2,6), 7.92 (s, 1H, $CH_{(Pz)3}$), 7.68 (d, 2H, $^3J_{H3-H2}$ = 9, H-3,5), 6.16, 5.97 (s, 3H, H_{Pz}, 2:1), 2.49, 2.46, 2.13, 1.54 (s, 18H, 6CH_{Pz}, 2:1:2:1). ^{13}C{^{1}H} NMR [CD_2Cl_2, J(Hz)]: δ 198.7 (Ir-CO), 177.4 (C-2,6), 158.7, 156.5, 145.5, 145.4 (6Cq_{Pz}, 2:1:2:1), 155.0 (C-OH), 132.2 (C-3,5, $^1J_{C-H}$ = 158), 111.1, 110.6 (3CH_{Pz}, 1:2), 70.1 ($CH_{(Pz)3}$), 14.9, 12.2, 11.9, 11.7 (6Me_{Pz}, 2:1:1:2). ^{13}C{^{1}H} NMR [CD_3OD, J(Hz)]: δ 196.9 (Ir-CO), 187.1 (br, C-2,6), 157.5, 155.9, 144.9, 144.7 (6Cq_{Pz}, 2:1:2:1), 153.9 (C-OH), 129.0 (C-3,5, $^1J_{C-H}$ = 158), 109.9, 109.6 (3CH_{Pz}, 1:2), 69.6 ($CH_{(Pz)3}$), 13.5, 10.4, 10.4, 10.2 (6Me_{Pz}, 2:1:1:2). Anal. Calcd for $C_{24}H_{27}N_6O_8F_6S_2Ir\cdot H_2O$ (915.86 g/mol): C, 31.5; H, 3.2; N, 9.2. Found: C, 31.5; H, 3.1; N, 8.9.

[κ^3-Tpm^{Me2}Ir(1,5-η-CH=C(^{t}Bu)-C(OH)=CH-CH=)(CO)]-[O_3SCF_3]$_2$ (11d-(O_3SCF_3)$_2$). In a Schlenk flask equipped with a stir bar were placed 164 mg (0.221 mmol) of **3d-BF$_4$** in 4 mL of CH_2Cl_2. The brown solution turned orange after dropwise addition of 59 μL (0.663 mmol) of HSO_3CF_3 under vigorous stirring, and after 30 min the solvent was evaporated. The remaining brown oil was crushed in 7 mL of Et_2O until an orange solid appeared. The solvent was removed by filtration, and the solid was washed with Et_2O (3 × 2 mL) and dried to obtain a pale orange solid in 85% yield (178.6 mg, 0.187 mmol). Decomposition without melting occurred at 206 °C. IR ν_{neat} (cm^{-1}): (O−H) 3471, (IrC≡O) 2089, (C=C) 1562, 1468, (C−OH) 1257, (S=O) 1311, 1149. ^{1}H NMR [CD_2Cl_2, J(Hz)]: δ 13.44 (br, 1H, OH), 11.67 (s, 1H, H-2), 10.50 (d, 1H, $^3J_{H6-H5}$ = 9, H-6), 8.12 (s, 1H, $CH_{(Pz)3}$), 7.79 (d, 1H, $^3J_{H5-H6}$ = 9, H-5), 6.39, 6.37, 6.17 (s, 1H each, H_{Pz}), 2.76, 2.75, 2.72, 2.35, 2.35, 1.86 (s, 3H each, 6CH_{Pz}), 1.35 (s, 9H, 3Me_{tBu}). ^{13}C{^{1}H} NMR [CD_2Cl_2]: δ 198.9 (Ir-CO), 169.3 (C-2), 165.9 (C-6), 158.4, 156.3, 155.9, 145.3, 145.5, 145.1 (6Cq_{Pz}), 156.1 (C-OH), 149.8 (C-5), 134.7 (C-^{t}Bu), 110.9, 110.4, 110.4 (3CH_{Pz}), 70.1 ($CH_{(Pz)3}$), 39.4 (Cq_{tBu}), 29.9 (3Me_{tBu}), 14.8, 14.7, 11.9, 11.8, 11.6, 11.6 (6Me_{pz}). Anal. Calcd for $C_{28}H_{36}N_6O_8F_6S_2Ir\cdot 0.75CH_2Cl_2$ (1012.89 g/mol): C, 33.5; H, 3.7; N, 8.3. Found: C, 33.8; H, 4.0; N, 8.1.

*Titration of **1a** with Aqueous HBF$_4$ (48 wt %).* Eight independent samples were prepared starting from 10 mg of **1a** in CH_2Cl_2 and adding the acid solution in aliquots of 0.25 molar equivalents in the NMR tubes to complete two molar equivalents in tube No. 8. After solvent evaporation each reaction mixture was washed with Et_2O, to remove the remaining H_2O, and dried. The resulting solid was dissolved in deuterated acetone for ^{1}H NMR.

*Monitoring Reaction of **1a** with CO (1 atm.).* In an NMR tube with a J. Young valve was placed 25 mg (0.039 mmol) of compound **1a**, and after three cycles of alternate N_2/vacuum application, 0.5 mL of CD_2Cl_2 was added and the solution was immersed in a bath with liquid N_2. The tube was charged with 1 atm of CO, and after defrosting the solution to room temperature, ^{1}H NMR spectra were recorded at regular time intervals.

■ ASSOCIATED CONTENT

Supporting Information

CIFs, structure factors, tables of crystallographic data and comparative tables of selected bond lengths and angles of complexes **1a**, **1b**, **2a-BF$_4$**, **3a-BF$_4$**, **3b-BF$_4$**, **4**-[Ir(CO)$_2$Cl$_2$], **5**−**8**, and **E** are available. Ortep drawings of compounds **1b**, **6**, **7**, and **E** are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ipadillamar@ipn.mx.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank CONACYT (grants 33438-E and 83378 (I.I.P.M.), Scholarship 214238 (M.H.J.)) and Secretaría de Posgrado e Investigación del Instituto Politécnico Nacional (SIP-IPN) for financial support.

■ REFERENCES

(1) Patai, S.; Rappoport, Z., Eds. *The Chemistry of the Quinonoid Compounds*; Vol. 2, Pts. 1 and 2; Wiley: New York, 1988; p 1711.
(2) Vigalok, A.; Milstein, D. *Acc. Chem. Res.* **2001**, *34*, 798.
(3) (a) Sternberg, H. W.; Barkby, R.; Wender, J. *J. Am. Chem. Soc.* **1956**, *78*, 3621. (b) Sternberg, H. W.; Markby, R.; Wender, J. *J. Am. Chem. Soc.* **1958**, *80*, 1009.
(4) Reingold, J. A.; Son, S.-U.; Kim, S.-B.; Dullagham, C. A.; Oh, M.; Frake, P. C.; Carpenter, G. B.; Sweigart, D. A. *Dalton Trans.* **2006**, 2585.
(5) (a) Schrauzer, G. N.; Dewhirst, K. C. *J. Am. Chem. Soc.* **1964**, *86*, 3265. (b) Glick, M. D.; Dahl, L. F. *J. Organomet. Chem.* **1965**, *3*, 200. (c) Milani, B.; Anzilutti, A.; Vicentini, L.; Santi, A.; Zangrando, E.; Geremia, S.; Mestroni, G. *Organometallics* **1997**, *16*, 5064. (d) Klein, R. A.; Elsevier, C.; Hartl, J. F. *Organometallics* **1997**, *16*, 1284. (e) Westcott, S. A.; Taylor, N. J.; Marder, T. B. *Can. J. Chem.* **1999**, *77*, 199.
(6) Cocivera, M.; Ferguson, G.; Kaitner, B.; Lalor, F. J.; O'Sullivan, D. J.; Parvez, M.; Ruhl, B. *Organometallics* **1982**, *1*, 1132.
(7) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.
(8) Cushion, M. G.; Meyer, J.; Heath, A.; Schwarz, A. D.; Fernandez, I.; Breher, F.; Mountford, P. *Organometallics* **2010**, *29*, 1174.
(9) (a) Scheuermann, S.; Sarkar, B.; Bolte, M.; Bats, W. J.; Lerner, H.-W.; Wagner, M. *Inorg. Chem.* **2009**, *48*, 9385. (b) Blasberg, F.; Bats, W. J.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Inorg. Chem.* **2010**, *49*, 7435. (c) Blasberg, F.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2012**, *31*, 3213.
(10) (a) Chetcuti, M. J.; Herbert, J. A.; Howard, J. A. K.; Pfeffer, M.; Spencer, J. L.; Stone, F. G.; Woodward, P. J. *Chem. Soc., Dalton Trans.* **1981**, 284. (b) Chetcuti, M. J.; Howard, J. A. K.; Pfeffer, M.; Spencer, J. L.; Stone, F. G. *J. Chem. Soc. Dalton Trans.* **1981**, 276. (c) Klein, R. A.; White, P.; van Belzen, R.; Fraanje, J.; Goubitz, K.; Numan, M.; Schenk, H.; Ernsting, J. M.; Elsevier, C. J. *Eur. J. Inorg. Chem.* **1998**, *319*, 4.
(11) (a) Bodner, G. M.; Englemann, T. R. *J. Organomet. Chem.* **1975**, *88*, 391. (b) Kim, S.-B.; Cai, C.; Faust, M. D.; Trenkle, W. C.; Sweigart, D. A. *J. Organomet. Chem.* **2009**, *694*, 52.
(12) Le-Bras, J.; Amouri, H.; Vaissermann, J. *Organometallics* **1998**, *17*, 1116.
(13) Cremer., D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.
(14) Oh, M.; Reingold, J. A.; Carpenter, G. B.; Sweigart, D. A. *J. Organomet. Chem.* **2003**, *687*, 78.
(15) Padilla-Martínez, I. I.; Poveda, M. L.; Carmona, E.; Monge, M. A.; Ruiz-Valero, C. *Organometallics* **2002**, *21*, 93.
(16) Wiley, J. S.; Oldham, W. J.; Heinekey, D. M. *Organometallics* **2000**, *19*, 1670.
(17) Aleksandrov, G. G.; Struchkov, Y. T. *J. Strtuct. Chem.* **1969**, *10*, 672.
(18) Moussa, J.; Guyard-Duhayon, C.; Herson, P.; Amouri, H. *Organometallics* **2004**, *23*, 6231.

(19) Son, S.-U.; Reingold, J. A.; Kim, S.-B.; Carpenter, G. B.; Sweigart, D. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 7710.
(20) Janiak, C. *Coord. Chem. Rev.* **1997**, *163*, 107.
(21) Slugovc, C.; Padilla-Martínez, I.; Sirol, S.; Carmona, E. *Coord. Chem. Rev.* **2001**, *213*, 129.
(22) Bleeke, J. R.; Behm, R. *J. Am. Chem. Soc.* **1997**, *119*, 8503.
(23) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *International Tables for Crystallography*; Wilson, C. A. J. C., Vol. Ed.; The International Union of Crystallography; Kluwer Academic Publishers: The Netherlands, 1992; p 685.
(24) Holmes, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 3745.
(25) Tolman, C. A. *Chem. Rev.* **1985**, 171.
(26) Oh, M.; Carpenter, G. B.; Sweigart, D. A. *Organometallics* **2002**, *21*, 1290.
(27) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. *J. Am. Chem. Soc.* **1989**, *111*, 4118.
(28) (a) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Santos, L. L.; Álvarez, E.; Salazar, V.; Mereiter, K.; Oñate, E. *Organometallics* **2007**, *26*, 3403. (b) Paneque, M.; Poveda, M. L.; Rendón, N.; Álvarez, E.; Carmona, E. *Eur. J. Inorg. Chem.* **2007**, 2711. (c) Paneque, M.; Poveda, M. L.; Rendón, N., E. *Eur. J. Inorg. Chem.* **2011**, 19.
(29) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 19.
(30) Julia, S.; del Mazo, J.; Ávila, L.; Elguero, J. *Org. Prep. Proc. Int.* **1984**, *16*, 299.
(31) Hoffman, M.; Rychlewska, U.; Warżajtis, B. *CrystEngComm* **2005**, *7*, 260.
(32) *APEX II*, *SAINT*, *SADABS*, and *SHELXTL*; Bruker AXS Inc.: Madison, WI, USA, 2004.
(33) *CrysAlis Pro*; Oxford Diffraction Ltd.: Yarnton, England, 2009.
(34) Sheldrick, G. M. *Acta Crystallogr. Sect. A: Found. Crystallogr.* **2008**, *64*, 112.
(35) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
(36) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Crystallogr.* **2006**, *39*, 453.
(37) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on July 13, 2012, with errors in Scheme 1 and refs 12 and 13 and their associated citations. The corrected version was reposted on July 17, 2012.