# **Geometrically Distorted and Redox-Active Organometallic Iridium Complexes Containing Biphenyl-2,2'-diyl**

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C-C bond cleavage of biphenylene by an Ir(I) complex via an oxidation addition generates the biph (=biphenyl-2,2'-diyl) ligand. The resulting compound is treated with PPh<sub>3</sub> to give  $[Ir(PPh_3)_2(biph)Cl]$ , having a 16 e five-coordinate structure lying between Y and T geometries, being closer to a Y, which is rationalized on theoretical grounds. The complex  $[Ir(PMe_3)_3-$ (biph)Cl] can be oxidized quasi-reversibly to an Ir(IV) species. Oxidation with NOBF<sub>4</sub> gives the unusual Ir(IV) boryl compound [Ir(PMe<sub>3</sub>)<sub>3</sub>(biphBF)Cl]<sup>+</sup>, which has been isolated and structurally characterized. Extended Hückel (EHT) calculations suggest that the easy oxidation of the  $\{Ir(biph)\}\$  system is associated with the presence of a high-lying Ir  $d_{vz}$  orbital. The {Ir(biph)} fragment is remarkably stable; only  $Br_2$  is able to cleave the Ir-C bonds.

#### Introduction

Organotransition-metal chemistry has been developed largely with cyclopentadienyl or carbonyl groups as stabilizing C-based ligands.<sup>1</sup> Especially for the late transition metals, most of these compounds are diamagnetic, having 16 or 18 valence electrons. Apart from formally giving up two electrons in processes such as oxidative addition, most of them are redox-inactive. Studies on redox-active compounds in general have shown that odd-electron species often have interesting properties, including high reactivity.<sup>2</sup> Complexes of 2,2'bipyridyl (bpy) are often redox-active,<sup>3</sup> but very little redox chemistry of the C analogue, biphenyl-2,2'-diyl, or biph, has been reported, although the ligand itself has been known for many years.<sup>4-6</sup> One of the purposes of this work is to exploit the facile C-C bond opening of biphenylene (1) to give the biphenyl-2,2'-diyl (biph) ligand (2; eq 1). The insertion of transition metals into a carbon-carbon bond through oxidative addition is known for many types of hydrocarbons, especially strained-ring compounds<sup>7</sup> and compounds which become



aromatic on C-C cleavage,<sup>8</sup> where the reaction can even occur with unstrained C-C bonds.9

Most catalytically active organometallic complexes contain low-oxidation-state metals or metal ions which are not strongly oxidizing.<sup>10</sup> Although certain oxidation catalysts do require high-oxidation-state transition metals,<sup>11</sup> they are rarely organometallic compounds. In order to explore new organometallic chemistry in such high oxidation states, we needed a ligand that is stable and can survive severe conditions, including thermolysis in air. Bpy has been widely used in coordination chemistry<sup>3a,b</sup> because of its stability and tendency to stabilize different oxidation states of metal compounds.

In this work, we use an Ir(I) complex to cleave the strained four-membered ring of biphenylene to generate new biph complexes. The resulting  $16 e d^6 Ir^{III}L_5$  system allows us to compare the geometric preference for a Y versus a T structure. We find that biph, like bpy, also promotes redox chemistry. Electrochemical studies

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showed that some of the Ir(III) complexes can be oxidized quasi-reversibly to Ir(IV) species, one of which can also be isolated. The EPR spectroscopic data confirmed that the oxidation is metal-centered. We also interpreted the easy oxidation of {Ir(biph)} complexes using extended Hückel (EHT) studies. Part of this work has appeared as a communication.<sup>8c</sup>

## **Results and Discussion**

Heats of combustion<sup>12</sup> and quantum-chemical calculations<sup>13</sup> show that biphenylene has a relatively low resonance energy of about 15 kcal/mol. X-ray diffraction studies<sup>14</sup> suggest that the central ring of biphenylene has little delocalization. The distances of the C-C bonds joining the two phenylene groups are 1.52 Å, close to a C-C single bond, while the other two bond-lengths in the central four-membered ring are 1.46 Å. The strain energy of the four-membered ring is high, about 63 kcal/mol.<sup>15</sup> This facilitates making a metallacycle from biphenylene by breaking one of the two C-C bonds linking the two phenyl groups.

**Preparation and Structure of**  $[Ir^{III}(PPh_3)_2(biph)$ -Cl] (4). Biphenylene (1) reacts with  $[Ir(COD)Cl]_2$  at 90 °C over 2 h in CH<sub>2</sub>Cl<sub>2</sub> (sealed tube) to give [Ir(COD)-(biph)Cl]<sub>2</sub> (3; 89%, eq 2) as a yellow powder by a known



type<sup>5</sup> of C-C cleavage reaction. The reaction is probably driven by the large ring strain. No reaction was observed under milder thermal conditions, however: for example, reflux in CH<sub>2</sub>Cl<sub>2</sub> for 2 days. **3** does not dissolve in any organic solvent, and we are therefore unable to recrystallize it or to obtain any spectroscopic data to confirm the ring-opened structure. Replacement of COD by PPh<sub>3</sub> can be achieved by reaction at room temperature for 5 h in CH<sub>2</sub>Cl<sub>2</sub> to give [Ir(PPh<sub>3</sub>)<sub>2</sub>(biph)-Cl] (**4**; eq 3). This complex was isolated in high yield



(90%) as air-stable red crystals. <sup>1</sup>H and <sup>31</sup>P NMR data show that 4 has only two bound PPh<sub>3</sub> groups, suggesting that 4 has a five-coordinate (16-electron) geometry. The sixth site in 4 cannot be saturated by addition of PPh<sub>3</sub>,

Table 1. X-ray Crystallographic Data for [Ir(PPh<sub>1</sub>)<sub>2</sub>(biph)Cl] (4)

•		1 ( )
formula		C <sub>48</sub> H <sub>38</sub> ClP <sub>2</sub> Ir
space group		$P2_1/c$ (No. 14)
a, Å		23.259(2)
b, Å		18.955(2)
c, Å		19.096(2)
$\beta$ , deg		114.143(9)
$V, Å^3$		7682(3)
mol wt		904.45
$\rho_{calcd}$ , g/cm <sup>3</sup>		1.564
Z		8
T, °C		23
scan type		$\omega - 2\theta$
max $2\theta$ , deg		50.0
no. of data used		8026
no. of params refined	1	937
esd of unit wt		1.39
radiation		Mo Ka ( $\lambda = 0.710~69$ Å)
convergence, largest	shift/error	0.20
R		0.035 <sup>a</sup>
Rw		0.039

<sup>a</sup> Function minimized:  $R = \sum ||F_0| - |F_c||/|F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ , where  $w = 4F_o^2 / \sigma^2 (F_o)^2$ .

Table 2. Selected Bond Distances (Å) and Angles (deg) for 4

Bond Distances				
Ir-Cl	2.380(3)	Ir-C(12)	2.00(1)	
Ir - P(1)	2.345(3)	C(1) - C(6)	1.43(1)	
Ir - P(2)	2.342(3)	C(6) - C(7)	1.44(1)	
Ir-C(1)	2.00(1)	C(7) - C(12)	1.40(1)	
Bond Angles				
Cl-Ir-P(1)	92.92(9)	P(1) - Ir - C(1)	89.6(3)	
Cl-Ir-P(2)	90.40(9)	P(1) - Ir - C(12)	87.7(3)	
Cl-Ir-C(1)	131.1(3)	P(2) - Ir - C(1)	92.4(3)	
Cl-Ir-C(12)	151.4(3)	P(2) - Ir - C(12)	86.8(3)	
P(1) - Ir - P(2)	173.5(1)	C(1)-Ir- $C(12)$	77.4(4)	

regardless of the amount added (1-20 equiv/Ir). This may reflect the steric bulk of the PPh<sub>3</sub> ligand. The ringopened structure of **4** was further characterized by X-ray crystallographic studies (Figure 1).

X-ray Crystallographic and Geometric Studies on 4. X-ray-quality single crystals of 4 were obtained by slowly evaporating a  $CH_2Cl_2$  solution. The resulting crystallographic data (Table 1) were solved, and an ORTEP diagram of the structure is shown in Figure 1. Selected bond distances and angles are listed in Table 2. As shown in Figure 1, 4 has an electron- and liganddeficient five-coordinate geometry.

The bond angles Cl-Ir-C(1) (131.1°), Cl-Ir-C(12) (151.4°), and C(1)-Ir-C(12) (77.4°) differ from each other and from the value of 120° characteristic of a five-coordinate TBP structure.

Several d<sup>6</sup> Ir<sup>III</sup>(PR<sub>3</sub>)<sub>2</sub>ZZ'X systems similar to ours have been studied by EHT and ab initio calculations.<sup>17</sup> It has been shown that the TBP structure is unfavorable for a diamagnetic d<sup>6</sup> configuration because the e' set is only partially filled. A geometrical distortion of the three equatorial ligands (ZZ'X) leading to the stabilization of one of the two e' orbitals and thus to an opening of the HOMO-LUMO gap has been found to be favorable. The equatorial ligand arrangements for each case are as follows:

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Figure 1. ORTEP drawing of [Ir(PPh<sub>3</sub>)<sub>2</sub>(biph)Cl] (4) with the (biph)IrCl fragment in the insert. Hydrogen atoms are omitted for clarity.



The two axial ligands, not shown, lie above and below the plane of the page. The Z, Z', and X ligands take up a Y or T shape. For equatorial ligands that are pure  $\sigma$ donors the T shape is preferred and the ligand (Z for instance) with the highest  $\sigma$ -donating ability occupies the site which is at the foot of the T (a structure called  $T_Z$ ). In contrast, if X is a  $\pi$  donor and if the Z and Z' ligands do not themselves carry any  $\pi$  orbitals, a Y structure with the X ligand at the foot of the Y  $(Y_X)$ becomes more stable. In this structure, a  $\pi$  bond between one of the lone pair of the  $\pi$ -donor ligand X and the metal empty orbital can be established and leads to electron transfer from X to the electron-deficient complex. This metal-X  $\pi$  bond is the factor responsible for the stability of the Y<sub>X</sub> structure. The stabilization is however small in magnitude, especially for weak  $\pi$ -donor ligands such as Cl, and it has been shown that the Y structure lies in a shallow valley.<sup>17</sup> This valley connects the  $Y_X$  minimum to a structure of  $T_{Z(Z')}$  type with Z (or Z') at the foot of the T. In  $T_Z$  the  $\pi$  bond between X and the metal cannot be established since all symmetry-adapted d (xy, xz, yz) orbitals are filled. The small energy difference between  $Y_X$  and  $T_Z$  comes from the competition between the  $\pi$  effect, which leads to a preference for  $Y_X$ , and the  $\sigma$ -donating effect of Z, which leads to a preference for T<sub>Z</sub>. This last T structure has not been found as a minimum on the potential energy surface (PES), but the presence of constraints such as steric factors in the system have been shown to displace the absolute minimum from a pure Y<sub>X</sub> structure (with a  $C_{2v}$  symmetry when Z = Z') to a situation intermediate between Y<sub>X</sub> and T<sub>Z</sub>.<sup>17c</sup> Any other constraint, such as a rigid bite angle within the equatorial ligands, would necessarily produce a similar displacement of the minimum away from the  $C_{2v}$  structure if the angle between the two constrained ligands does not correspond to the angle calculated for the optimal structure.

In the previous ab initio calculations on the model complex  $[Ir(PH_3)_2ClMe_2]$  it was found that the  $Y_{Cl}$  type structure was the most stable.<sup>17</sup> The calculated C-Ir-C angle is 81.9°, close to that in complex 4. EHT calculations were performed on the model complex Ir(biph)Cl- $(PH_3)_2$ <sup>18</sup> Because the C-Ir-C angle (77.4°) in Ir(biph) does not correspond to the optimal C-Ir-C angle for two monodentate Ir-C bonds, the  $C_{2v}$   $Y_{Cl}$  structure is not calculated to be the minimum. A slightly distorted form in which the Cl group lies off the  $C_2$  axis is preferred. The structure is thus an intermediate between the  $Y_{Cl}$  and  $T_C$  forms, where  $T_C$  describes a geometry in which one of the carbons of the biph ring is at the foot of the T structure. The angle between the  $C_2$  axis and the Ir-Cl bond was calculated to be 23°, which is in fair agreement with the experimental value (10.3°). If the Cl is replaced by a pure  $\sigma$  donor, such as H, the resulting calculated structure lies much closer to a T. A similar distortion has been discussed for a Rh(III) metallacyclic complex.<sup>19</sup> As a result of the existence of the Ir–Cl  $\pi$  bond in a structure of Y type (or very close to it), the Ir-Cl bond length (2.38 Å) is shorter than the sum of the covalent radii of the Ir and Cl atoms (2.45 Å).

**Preparation of [Ir<sup>III</sup>(PMe<sub>3</sub>)<sub>3</sub>(biph)Cl] (5).** Treatment of **3** with PMe<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature under nitrogen affords [Ir(PMe<sub>3</sub>)<sub>3</sub>(biph)Cl] (**5**) as an airstable white powder (eq 4). The biph group is therefore stable to reductive elimination under these conditions. The coordination site of the Cl group in **5**, determined by <sup>31</sup>P NMR ( $\delta$  -42.29, d, 2P; -54.70, t, 1P), is axial, not equatorial, as in the case of [Ir(PPh<sub>3</sub>)<sub>2</sub>(biph)Cl] (**4**).

<sup>(18)</sup> Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. J. Am. Chem. Soc. **1978**, 100, 3686. Atomic parameters for Ir are taken from ref 17.

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This may be a result of the lower steric bulk of  $PMe_3$ versus  $PPh_3$  and perhaps the larger trans effect of  $PR_3$ versus  $Cl.^{20}$ 

**Reactivity of {Ir(biph)} Complexes**. If biph is to be a useful ligand, it should be stable under a variety of conditions. We find that the  $\{Ir(biph)\}\$  group of **3** can persist unchanged on treatment with CO, PhCCPh,  $PR_3$ , or NaBH<sub>4</sub>. The reaction of **3** with CO gives the unstable compound [Ir(CO)<sub>3</sub>(biph)Cl] (6), but the CO insertion product fluorenone is not formed, even on heating (CH<sub>2</sub>Cl<sub>2</sub>, 90 °C). The IR spectroscopic data ( $\nu$ -(CO) 2155, 2116, and 2092  $cm^{-1}$ ) suggest that 6 has a meridional structure. The instability of this complex is consistent with the unusually high-energy CO absorptions in the IR which occur at a frequency close to that of free CO (2143  $\rm cm^{-1}$ ), indicating that metal to CO back-bonding is weak. 4 does not react with  $H_2$  or PPh<sub>3</sub> but reacts rapidly with CO at room temperature to form  $[Ir(PPh_3)_2(biph)(CO)Cl]$  (7;  $\nu(CO)$  2001 cm<sup>-1</sup>). Other small donor molecules such as NH<sub>3</sub> can also react with 4 in a similar way.

As shown in Scheme 1, 6 and NaBH<sub>4</sub> (CH<sub>2</sub>Cl<sub>2</sub>-EtOH,

Scheme 1. Reactivities of {Ir(biph)} Complexes



90 °C, 5 h) give [Ir(PMe<sub>3</sub>)<sub>3</sub>(biph)H] (8; 68%). The hydride in  $\mathbf{8}$  is cis to both biph Ir-C bonds, as shown by <sup>1</sup>H NMR (Ir-H, -11.05 ppm, J(H,P trans) = 133 Hz, J(H,P cis) = 22.7 Hz). Reductive elimination with the cis hydride is not observed under our conditions. The reaction of **3** with 2,2',2''-terpyridine (terpy) did not cleave the Ir-C bond of the metallacycle but gave the new complex [Ir(terpy)(biph)Cl] (9). 9 has an unusually well-resolved <sup>1</sup>H NMR, showing the aromatic protons at chemical shifts ranging from 5.6 to 8.8 ppm. Treatment of 9 with AgBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> under a CO atmosphere gives [Ir(terpy)(biph)CO] (9a) with  $\nu$ (CO) 2059 cm<sup>-1</sup>. Of all the reagents we have used, only Br<sub>2</sub> cleaves the Ir-C bond of the {Ir(biph)} group. In the best-studied case,  $[Ir(COD)(biph)(O_2CCF_3)]$ , formed from 3 and AgO<sub>2</sub>CCF<sub>3</sub>, reacts with Br2 to give 2,2'-dibromobiphenyl (50%) and 2-bromobiphenyl (49%) (eq 5).



Electrochemical Studies. The quasi-reversible electrochemical reduction of [Pt(biph)(bpy)] has been briefly reported,<sup>5</sup> but in this case it is unclear which of the two ligands, bpy or biph, promotes the observed redox activity. In many of our {Ir(biph)} complexes we find that biph alone can promote electrochemical oxidation to give stable odd-electron Ir(IV) complexes. For example, the CV of 5 in CH<sub>2</sub>Cl<sub>2</sub> showed a quasireversible ( $\Delta E = 108 \text{ mV}$ ) diffusion-controlled oxidation wave at E = 836 mV vs SCE (Figure 2a). Multiple-cycle experiments show that no new species are formed having CV waves in the region of 0.0-1.0 V. The number of electrons transferred, determined by exhausive electrolysis, was  $1.0 \pm 0.1$  e. The resulting Ir(IV) species, which can also be generated by bulk electrolysis (eq 6), has been detected by its EPR ( $g_x = 2.37, g_y =$ 



2.28,  $g_z = 1.84$ ; Figure 3). The reversibility of the CV suggests that this Ir(IV) cation is best formulated as  $[Ir^{IV}(PMe_3)_3(biph)Cl]^+(5^+)$ . Isolation and crystallization of  $5^+$  was unsuccessful, probably as a result of decomposition.

The 16 e complex [Ir(PPh<sub>3</sub>)<sub>2</sub>(biph)Cl] (4) also showed quasi-reversible one-electron oxidation in  $CH_2Cl_2$  at room temperature, but the oxidation wave shifts to 950 mV vs SCE, a potential more positive than in 5 (Figure 2b). This shift indicates that the 16 e Ir(III) system is more electron-deficient than 5. The resulting Ir(IV)product was not stable enough for detection by EPR in this case. The CV of [Ir(PPh<sub>3</sub>)<sub>2</sub>(biph)(CO)Cl] (7) in CH<sub>2</sub>- $Cl_2$  showed an even more positive oxidation wave at 1120 mV vs SCE, reflecting the strong back-donation from Ir to CO which makes the Ir even more electrondeficient. The complex [Ir(terpy)(biph)Cl] (9), formed in the reaction of **3** with terpy in methanol, shows only an irreversible oxidation wave at 930 mV but a nearly reversible reduction wave at -1.47 V vs SCE ( $\Delta E = 77.2$ mV).

The EHT calculations suggest<sup>21</sup> that the easy oxidation of the biph system is due to the presence of a highenergy HOMO. The highest filled  $\pi$  level of biph combines in an antibonding way with the filled Ir *yz* orbital, which results in a high-lying HOMO with large metal character (Figure 4). Good overlap and a good energy match between the metal d and  $\pi$  ligand orbitals are responsible for the strong destabilization of the HOMO.

In the case of complex 5, the axial Cl group can also interact with the Ir yz orbital. One of the lone pairs of Cl further destabilizes the yz orbital by mixing into this

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Figure 2. Comparative cyclic voltammetry of  $1.0 \times 10^{-3}$  mol/L [Ir(PPh<sub>3</sub>)<sub>2</sub>(biph)Cl] (4) and  $3.0 \times 10^{-4}$  mol/L [Ir-(PMe<sub>3</sub>)<sub>3</sub>(biph)Cl] (5).



Figure 3. X-Band EPR spectrum of [Ir(PMe<sub>3</sub>)<sub>3</sub>(biph)Cl]<sup>+</sup> (6<sup>+</sup>) at 7 K.

molecular orbital in an antibonding fashion. This suggests why 5 can be oxidized more easily than compound 4 and permits the occurrence of an Ir(IV) structure.





**Figure 4.** Orbital interaction in [Ir(PMe<sub>3</sub>)<sub>3</sub>(biph)Cl] (6) derived from EHT studies.

Synthesis, Characterization, and Crystal Structure of [Ir<sup>IV</sup>(PMe<sub>3</sub>)<sub>3</sub>(biphBF)Cl] (10<sup>+</sup>). In aiming for oxidation catalysts involving air, we wondered whether it would be possible to make a stable {Ir<sup>IV</sup>(biph)} system. Complex 5<sup>+</sup> formed by bulk electrolysis of 5 could not be obtained in crystalline form. A rapid reaction occurred, however, when 5 was treated with NOBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> to give a dark greenish solution, which gave a dark brown solid on isolation. This new complex gives EPR signals ( $g_{xy} = 2.15$  and  $g_z = 1.96$ ; Figure 5) different from those for 5<sup>+</sup>. Stable crystals of the product [Ir(PMe<sub>3</sub>)<sub>3</sub>Cl(biphBF)][BPh<sub>4</sub>] (10[BPh<sub>4</sub>]) are formed in 46% yield after isolation with NaBPh<sub>4</sub> (eq 7). NaBPh<sub>4</sub>



provides the essential large counterion needed to obtain crystals. The X-ray crystal structure (Figure 6) shows it to be an Ir(IV) organometallic boryl compound with a BF unit inserted into one of the Ir-C bonds. Organometallic Ir(IV) complexes are not common,<sup>22</sup> and no Ir(IV) boryl compounds have been reported.<sup>23</sup> This insertion may take place via electrophilic attack of BF<sub>3</sub>, which could come from either NOBF<sub>4</sub> or BF<sub>4</sub><sup>-</sup>, on the Ir-Ar bond. High-resolution mass spectroscopy confirms the formulation, both from the mass of the molecular ion peak of **10**<sup>+</sup> (638.1344 amu, observed; 638,1347 amu, calculated) and from its characteristic seven-line isotope pattern (computer simulation), which cannot be accommodated by any other group than BF.







**Figure 6.** ORTEP drawing of  $[Ir(PMe_3)_3Cl(biphBF)]^+$ (10<sup>+</sup>). Hydrogen atoms are omitted for clarity.

A single crystal of  $10[BPh_4]$  was obtained from slow diffusion of diethyl ether into a solution of  $10[BPh_4]$  in CH<sub>2</sub>Cl<sub>2</sub>. The resulting data (Table 3) were solved by using Patterson methods to give the ORTEP diagram shown in Figure 6. The BPh<sub>4</sub><sup>-</sup> counterion is not shown for clarity. Selected bond distances and angles are listed in Table 4.

The electron density map showed a very unusual structure with a BF group in the six-membered metallacyclic ring. As expected, the structure shows a coplanar arrangement of the boryl group (F, B, Ir, and C atoms). The  $C_6H_4B-F$  fragment shows unusually

Table 3. X-ray Crystallographic Data for [Ir(PMe<sub>3</sub>)<sub>3</sub>(biphBF)Cl]<sup>+</sup> (10<sup>+</sup>)

_		
	formula	$C_{45}H_{55}B_2FP_3ClIr$
	fw	957.14
	cryst habit	dark brown cut plate
	space group	$P2_1/n$ (No. 14)
	a, Å	9.689(2)
	b, Å	35.555(6)
	<i>c</i> , Å	12.576(2)
	$\beta$ , deg	94.44(1)
	V, Å <sup>3</sup>	4320(2)
	Z	4
	$Q_{\text{calcd}}, \text{g/cm}^3$	1.472
	F(000)	1932
	$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	32.85
	radiation	Mo Ka ( $\lambda = 0.710 \ 69 \ \text{\AA}$ )
	T, °C	23
	scan type	$2\theta/\omega$
	$\max 2\theta$ , deg	49.9
	no. of unique rflns	7841
	cor	Lorentz-polarization
		(transmissn factor
		0.71 - 1.29; -28% decline)
	no. of observns	4459
	R	$0.051^{a}$
	$R_{ m w}$	0.061

<sup>a</sup> Function minimized  $\sum w(|F_0| - F_c|)^2$ , where least-squares weights  $w = 4F_o^2/\sigma^2(F_o)^2$ .

Table 4.	Selected Bond Distances (Å) a	and Angles		
(deg)				

for 10 <sup>+</sup>					
Bond Distances					
Ir-Cl	2.504(4)	F(1) - B(1)	1.09(1)		
Ir - P(1)	2.333(4)	C(8) - B(1)	1.47(2)		
Ir - P(2)	2.348(3)	C(1) - C(6)	1.42(2)		
Ir-P(3)	2.432(3)	C(6) - C(7)	1.48(2)		
Ir-C(1)	2.07(1)	C(7) - C(8)	1.39(2)		
Ir-B(1)	2.00(1)				
Bond Angles					
Cl-Ir-P(1)	176.5(1)	P(2)-Ir-P(3)	<b>92.3</b> (1)		
Cl-Ir-P(2)	78.9(1)	P(2) - Ir - B(1)	165.5(4)		
Cl-Ir-P(3)	87.6(1)	P(2)-Ir-C(1)	88.5(3)		
Cl-Ir-C(1)	88.7(4)	P(3)-Ir-C(1)	176.0(4)		
Cl-Ir-B(1)	87.3(4)	P(3) - Ir - B(1)	91.5(4)		
P(1) - Ir - P(2)	102.6(1)	C(1) - Ir - B(1)	86.7(5)		
P(1) - Ir - P(3)	95.5(1)	Ir - B(1) - F(1)	118(1)		
P(1) - Ir - C(1)	<b>88.2</b> (4)	Ir - B(1) - C(8)	114(1)		
P(1) - Ir - B(1)	90.9(5)	F(1)-B(1)-C(8)	127(2)		

large anisotropic thermal ellipsoids, probably due to conformational flexibility of the metallacycle. This leads to an artificially short B-F distance of 1.09 Å (the sum of covalent radii of B and F is 1.26 Å), which should not be regarded as well determined. No disorder model we tried was satisfactory.

The structure of  $10^+$  is essentially octahedral, with the Cl and one of the PMe<sub>3</sub> groups axial. The Ir-Cl bond, which is now cis to the biphBF group, shows a lengthened distance (2.504 Å) as a result of the trans effect of the PMe<sub>3</sub> group. The observed Ir-P(3) bond distance (2.43 Å) is unusual, being longer than that of the other Ir-P bonds (2.33-2.35 Å), suggesting that an aryl group may have a stronger trans effect than a boryl group.

**Catalytic Activity**. Unlike complexes of most other unsaturated metallacycles,<sup>22,23</sup> our biph complexes can survive reaction conditions commonly used in catalytic chemistry, showing the stability of the {Ir(biph)} group. As we have published elsewhere,<sup>24</sup> **4** and **5** are active

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catalysts for the unusual head-to-head dimerization of terminal alkynes.

Conclusion. We have synthesized and characterized a series of new iridium complexes which are obtained from a C-C bond cleavage of biphenylene. Rather than having a pure T or Y structure, the d<sup>6</sup> five-coordinate species [Ir(PPh<sub>3</sub>)<sub>2</sub>(biph)Cl] has a intermediate structure. EHT calculations suggest that this is caused by the angular constraint within the rigid biph group. The complex [Ir(PMe<sub>3</sub>)<sub>3</sub>(biph)Cl] has a quasi-reversible CV with an oxidation wave at 836 mV vs SCE and can be oxidized to an Ir(IV) species by bulk electrolysis. The unusual Ir(IV) boryl complex [Ir(PMe<sub>3</sub>)<sub>3</sub>(biphBF)Cl] was produced when [Ir(PMe<sub>3</sub>)<sub>3</sub>(biph)Cl] was treated with NOBF<sub>4</sub>. The insertion of the BF group probably occurs via an electrophilic attack of BF3 on an Ir-C bond of the metallacycle. Calculations suggest that the easy oxidation of a Ir(biph) system is a result of the metalcentered HOMO of the molecule being high-lying as a consequence of the repulsive interaction between an occupied  $\pi$  orbital of biph and an occupied Ir vz orbital. This permits the existence of an Ir(IV) form. The biph system seems suitable for use as a stabilizing ligand in organometallic chemistry, where it can promote redox and catalytic activities in its metal complexes.

#### **Experimental Section**

General Considerations. All manipulations were carried out under a nitrogen atmosphere. Solvents such as dichloromethane, diethyl ether, and toluene were distilled from calcium hydride or sodium benzophenone ketyl. All the reagents were used as received without further purification.

**Spectroscopy.** Samples for EPR studies were prepared by taking a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex (10) or from the bulk electrolysis experiment (5<sup>+</sup>) under an Ar atmosphere and freezing to -77 °C. In order to form a good glass, an equal volume of toluene was added. Continuous-wave X-band ( $\nu = 9.0519$  GHz) EPR investigations were carried out at 7 K (5<sup>+</sup>) and 5 K (10) on a home-built X-band instrument with an Oxford ESR-900 cryostat.<sup>25</sup>

Infrared spectra were recorded as  $CH_2Cl_2$  solutions in a KBr liquid cell on a Nicolet 5-SX FTIR spectrometer. <sup>1</sup>H and <sup>31</sup>P NMR measurements were obtained on a Bruker WM-250 or WM-500 spectometer.

**Electrochemistry**. Cyclic voltammetry on 4 and 5 was carried out in  $CH_2Cl_2$  solution under  $N_2$  using a PAR273 electrochemical setup with 0.1 M TBAP as supporting electrolyte. Three electrodes were used: a saturated calomel reference electrode (SCE), a 3.0 mm polished glassy-carbon working electrode, and a Pt-wire counter electrode. The solution volume was 5 mL, and the scan rate was 100 mV/s.

Chloro(biphenyl-2,2'-diyl)(1,5-cyclooctadiene)iridium-(III) (3). A red solution of  $[Ir(COD)Cl]_2$  (0.441 g, 1.31 mmol) in 1.5 mL of anhydrous  $CH_2Cl_2$  was treated with 0.200 g (1.31 mmol) of biphenylene under nitrogen and heated for 2 h at 90 °C in a screw-cap vial. The red solution gave a bright yellow precipitate, which was filtered and washed with cooled  $CH_2$ - $Cl_2$ . Yield: 0.571 g, 89%. Anal. Calcd (found) for  $IrC_{20}H_{20}$ -Cl: C, 49.23 (49.41); H, 4.13 (4.22).

Chloro(biphenyl-2,2'-diyl)bis(triphenylphosphine)iridium(III) (4). This red-orange complex was prepared by reacting 0.500 g (1.02 mmol) of 3 and 0.54 g (2.05 mmol) of triphenylphosphine in 15 mL of  $CH_2Cl_2$  at room temperature for 5 h under N<sub>2</sub>. The majority of the  $CH_2Cl_2$  was removed under reduced pressure, diethyl ether was added, and 4 crystallized at 0 °C. Yield: 0.834 g, 90%. Anal. Calcd (found) for  $IrC_{48}H_{38}ClP_2$ : C, 63,74 (63.55); H, 4.24 (4.18). <sup>1</sup>H NMR (CH<sub>2</sub>Cl<sub>2</sub>, 500 Hz): 7.33 (dd, Ph), 7.25 (br s, Ph and biph), 7.17 (t, Ph), 6.47 (t, 2 H, biph), 6.28 (dt, 1.5 and 7.5 Hz, 2 H, biph), 6.25 ppm (dd, 1.5 and 7.5 Hz, 2 H, biph). <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>, 500 Hz): 21.77 ppm (s, 2 P, PPh<sub>3</sub>).

Chloro(biphenyl-2,2'-diyl)tris(trimethylphosphine)iridium(III) (5). A yellow suspension of 0.500 g (1.02 mmol) of 3 in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> turned buff upon adding 0.234 g (3.06 mmol) of trimethylphosphine. After it was stirred for 2 h at room temperature under N<sub>2</sub>, the solution became colorless. The solvent was removed under reduced pressure, and the residue was washed with hexane and filtered on a glass frit. Yield: 0.492, 78%. Anal. Calcd (found): C, 41.48 (41.53); H, 5.80 (5.56). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 Hz): -42.29 (d, 22.2 Hz, 2 P, eq PMe<sub>3</sub>), -54.70 ppm (t, 1 P, ax PMe<sub>3</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 Hz): 8.19 (t, 6.0 Hz, 1 H, biph), 7.41 (d, 6.1 Hz, 2 H, biph), 7.26 (d, 7.5 Hz, 1 H, biph), 6.99 (t, 7.2 Hz, 1 H, biph), 6.92 (d, 7.4 Hz, 1 H, biph), 6.88 (d, 7.4 Hz, 1 H, biph), 6.71 (t, 7.4 Hz, 1 H, biph), 1.74 (d, 7.3 Hz, 9 H, ax PMe<sub>3</sub>), 0.94 ppm (dd, 3.7 Hz, 18 H, eq PMe<sub>3</sub>).

**Observation of Chloro(biphenyl-2,2'-diyl)tricarbonyliridium(III) (6).** CO (20 mL/min) was bubbled through a yellow suspension of **3** (0.500 g, 1.02 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The yellow solid, **3**, slowly disappeared over 15 min to give a yellow solution. The solvent then was removed under reduced pressure to produce a yellow residue of the product. This material was unstable and gave a brown species rapidly. IR: 2155.4, 2116.2, 2092.9 cm<sup>-1</sup>.

Chloro(biphenyl-2,2'-diyl)(terpyridine)iridium(III) (9). A mixture of 0.500 g (1.02 mmol) of 3 and 0.239 (1.02 mmol) of terpy in 20 mL of methanol was stirred at room temperature for 3 days. The resulting greenish precipitate was filtered, washed with hexane, and purified by recrystallization from DMF. Yield: 0.505 g, 80.4%. Anal. Calcd (found): C, 52.89 (52.44); H, 3.12 (3.42); N, 6.86 (6.65). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 250 Hz): 8.79 (d, 2 H, terpy), 8.57 (d, 2 H, terpy), 8.45 (dd, 1 H, biph), 8.33 (t, 1 H, terpy), 7.96 (t, 2 H, terpy), 7.84 (d, 2 H, terpy), 7.51 (dd, 1 H, biph), 7.37 (t, 2 H, terpy), 7.28 (d 1 H, biph), 7.02 (d, 1 H, biph), 7.00 (d, 1 H, biph), 6.52 (t, 1 H, biph), 6.20 (t, 1 H, biph), 5.58 ppm (d, 1 H, biph).

Chloro(2-(fluoroboryl)biphenyl- $C^2$ ,B)tris(trimethylphosphine)iridium(IV) (10<sup>+</sup>). To a red-orange solution of 5 (0.200 g, 0.33 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added NOBF<sub>4</sub> (0.0384 g, 0.33 mmol). An immediate color change to greenish black was observed. The mixture was stirred for an additional 20 min at room temperature. The solvent was then removed under reduced pressure and NaBPh<sub>4</sub> (0.15 g) was added. The complex was purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane. Yield: 0.097 g, 46%. Exact mass: calcd (found) for 10<sup>+</sup> 638.1344 (638.1347) amu. X-Band EPR (5 K):  $g_{xy} = 2.15, g_z$ = 1.96.

X-ray Crystallographic Analysis of 4. Crystals of 4 grew as irregularly shaped, flat plates of orange crystals from CH<sub>2</sub>-Cl<sub>2</sub>/hexane. A crystal of approximate dimensions  $0.85 \times 0.50$ imes 0.18 mm was mounted in a random orientation on a glass fiber. Diffraction measurements were made on a four-circle Enraf-Nonius CAD4 fully automated diffractometer, equipped with a graphite monochromator (Mo K $\alpha$  radiation,  $\lambda = 0.710$  69 Å). The cell constants and an orientation matrix for data collection were obtained from least-squares refinement using setting angles of 25 carefully centered reflections. A total of 13 948 unique reflections were collected with  $2\theta \leq 50^\circ$ ; of those, 8026 with  $I \geq 3\sigma(I)$  were adjudged observed. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient for Mo K $\alpha$  is 36.48 cm<sup>-1</sup>. Owing to the irregular shape of the crystal, the DIFABS program was used to correct for absorption. The structure was solved using SHELXS86. There are two independent but essentially identical C<sub>48</sub>H<sub>38</sub>ClP<sub>2</sub>Ir molecules in the unit cell. All hydrogen positions were calculated and assigned isotropic thermal parameters which were 20% greater than the equivalent value of the atom to which they were bound. The standard deviation

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of an observation of unit weight was 1.39. The weighting scheme was based on counting statistics and included a factor (p = 0.03) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.16 and  $-1.20 \text{ e/Å}^3$ .

X-ray Crystallographic Analysis of 10. Single crystals of 10 were obtained by slow diffusion of diethyl ether into a solution of 10 in CH<sub>2</sub>Cl<sub>2</sub>. A dark brown cut plate crystal of 10having the approximate dimensions  $0.10 \times 0.35 \times 0.35$  mm was mounted on a glass fiber. X-ray crystallographic measurements were made on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Ka radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angle of 25 carefully centered reflections in the range 19.00 < $2\theta < 32.00^{\circ}$ . Moving-crystal-moving-counter background measurements were made by scanning an additional 25% above and below the scan range. Of the 8198 reflections collected, 7841 were unique ( $R_{int} = 0.021$ ). The intensities of two representative reflections measured every 60 min decreased by 28%. A linear correction factor was applied to the data to account for this. The linear absorption coefficient for Mo K $\alpha$  is 32.9 cm<sup>-1</sup>. The data were corrected for Lorentz and

polarization effects. The structure was solved by the Paterson method. The standard deviation of an observation of unit weight was 2.26. The weighting scheme was based on counting statistics and included a factor (p = 0.03) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.04 (located 1.2 Å from the Cl atom) and  $-0.91 \text{ e/Å}^3$ .

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Supplementary Material Available: Full tables of data collection parameters, atom coordinates, bond distances and angles, and anisotropic thermal parameters for  $[Ir(PPh_3)_2-(biph)Cl]$  (4) and  $[Ir(PMe_3)_3(biphBF)Cl][BPh_4]$  (10), figures giving additional views of 4 and 10, and text giving full experimental details for determination of the structures of 4 and 10 (35 pages). Ordering information is given on any current masthead page.

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