Breaking an electronically preferred symmetry by steric effects in a series of [Ir(biph)X(QR_3)$_2$] compounds (X = Cl or I, Q = P or As)

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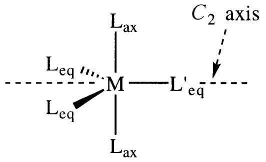
A hybrid quantum mechanical/molecular mechanics IMOMM (B3LYP : MM3) method has been applied to a series of five-coordinate 16-electron d^6 ML_5 Ir^{III} compounds having a relatively flat potential for a distortion from Y to T geometry and for which crystal structures have been obtained. In this series of type [Ir(biph)X(QPh_3)$_2$] (biph = biphenyl-2.2′-diyl; Q = P, X = Cl, **2a**; Q = As, X = Cl, **2b**; Q = P, X = I, **2c**), the halide is found to lie in the (biph)Ir plane but off the C_2 axis of the {Ir(biph)Q_2} fragment by a variable angular distortion ϕ. While $\phi = 0$ is preferred electronically for [Ir(C_4H_4)Cl(PH_3)$_2$], the steric bulk of the real systems **2a**–**2c** leads to ϕ taking experimental values of 8.2–17.2°. The observed deviation of the halide from the C_2 axis is shown by IMOMM to be the result of a direct interaction of the phenyl substituents of the axial ligands with the equatorial ligands and not to an electronic effect. The crystal structures for **2b** and **2c** have been determined.

Quantum chemical calculations have attained an impressive level of reliability in recent years and quantitative studies are possible even on reasonably large molecules. To save computational time, it is nevertheless still usually necessary to simplify the ligand set by replacing PR_3 by PH_3, for example. This means that when there is a significant deviation between the quantum chemical and experimental results on a given system, one cannot immediately tell whether the deviation is due to the steric effects of the real PR_3 ligand or to some nonsteric electronic effect that has not been well represented in the calculations.

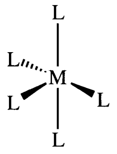
Hybrid quantum mechanics–molecular mechanics (QM/MM) methods have recently become available that can help resolve such ambiguities. In these, the core of the molecule, consisting of the metal and the immediate ligand sphere, is represented by quantum chemical methods, and the exterior part, comprising the substituents on the ligands, is represented by molecular mechanics. In this way a large molecule can be treated realistically without requiring prohibitive amounts of computer time. Here, we report application of a combined (QM/MM) hybrid method IMOMM (B3LYP : MM3) to the title complexes. This particular hybrid method[1] has already proved successful in computing steric effects in several transition-metal complexes.[2]

Following the original experimental discovery,[3a] various theoretical studies have clearly established that five-coordinate d^6 16-electron complexes with one equatorial π-donor ligand (labeled L'_{eq} in diagram **1a**), show a preference for a Y structure, **1a**, This resembles a trigonal bipyramidal structure but has one small angle (<90°) between two equatorial ligands.[3b–d] In such a Y structure, the $M-L'_{eq}$ bond defines the mirror plane which necessarily bisects the angle between the two identical equatorial ligands. A T structure **1b** is not very different in energy, however, and in certain cases can be the ground state. This structure is octahedral with one missing vertex and the π-donor ligand is located in the basal site.



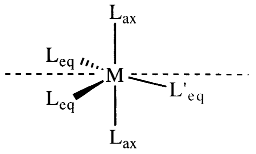
1 a

Y-type



1 b

T-type



1 c

Y/T-type

Two experimental examples, discovered almost simultaneously in the groups of Crabtree and of Caulton,[4–8] showed that in certain circumstances it is possible to break the symmetry in what would otherwise be a pure Y-type molecule. In spite of having two identical ligands in the equatorial plane these compounds adopt structure **1c** intermediate between Y and T geometries, denoted Y/T. For [$IrH_2Cl(P\{Bu^t\}_2Ph)_2$] (**1d**) the Y/T structure is found in the solid state by neutron diffraction[4] and is maintained in solution as shown by ^1H NMR studies at low temperature.[5] IMOMM (B3LYP : MM3) calculations revealed that the observed deviation from Y geometry is a result of steric interactions between the phosphine substituents and the equatorial ligands.[6] The potential energy surface linking Y and T geometries is known to be flat[3d] and it is no doubt this factor that permits the existence of structures with a geometry intermediate between the two pure forms.

This paper probes the generality of these distortions and reports a series of 16-electron Ir^{III} complexes where the IrH_2

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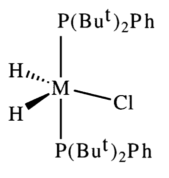
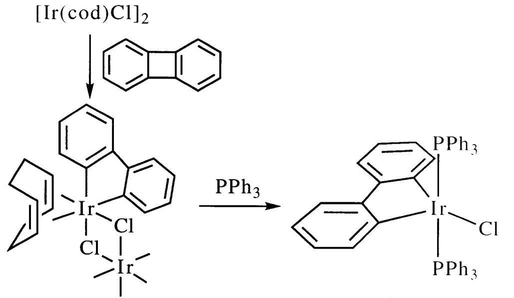


1 d

group of the above system is replaced by an iridium diaryl. This new system shows the same types of distortions and provides a good quantitative test of the hybrid methods mentioned above. The new series of complexes has the advantage that only non-hydride ligands are present, permitting definitive structural study without recourse to neutron diffraction.

Results and Discussion

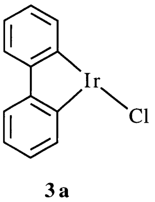
We showed[7] in 1993 that biphenylene undergoes a C—C bond activation reaction with $[Ir(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) to give a biphenyl-1,2-diyl (= biph) complex, $[Ir(cod)(biph)Cl]_2$, where the biph ligand is the organometallic analogue of 2,2′-bipyridine [eqn. (1)]. The complex was found to react readily [eqn. (1)] with PPh_3 to give a 16-electron five-coordinate Ir^{III} species, $[Ir(biph)Cl(PPh_3)_2]$ (**2a**) which was structurally characterized. Five-coordinate Ir^{III} species like **2** are expected to have a pure Y structure owing to the presence of only one equatorial π-donor ligand, a halide.



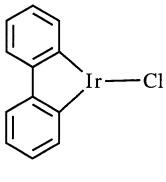
(1)

2 a
Y/T geometry

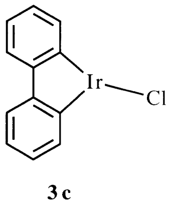
At the time of its discovery, it was surprising to find that in **2a** the experimental structure was neither Y nor T but intermediate between the two situations, as shown in diagram **3c**. This was initially thought to be an electronic effect but work to be described below now makes clear that we are seeing a steric effect. As a test, we wanted to compare a series of complexes of type **2** to see if the deviation from the ideal Y geometry changes with the steric effects of the ligands.



3 a
pure T



3 b
pure Y



3 c
experimental
Y/T structure

Synthesis and structural study

In the present work, we have synthesized and structurally characterized two related species of type **2** with ligands of slightly different steric size: $[Ir(biph)Cl(AsPh_3)_2]$ (**2b**) and $[Ir(biph)I(PPh_3)_2]$ (**2c**). These have now been prepared in good yield as air-stable orange (**2b**) or red (**2c**) crystals by the standard routes shown in eqns. 2 and 3.

$$[Ir(cod)Cl(biph)]_2 \xrightarrow{AsPh_3} [Ir(biph)Cl(AsPh_3)_2] \quad (2)$$

$$[Ir(biph)Cl(PPh_3)_2] \xrightarrow[\text{acetone}]{LiI} [Ir(biph)I(PPh_3)_2] \quad (3)$$

The five-coordinate, 16-electron species **2a**–**2c** are not readily converted to the corresponding six-coordinate species $[Ir(biph)X(QPh_3)_3]$. In more recent work[9] we find that the reaction of $[Ir(biph)Cl(cod)]$ with $SbPh_3$ gives a six-coordinate product, $[Ir(biph)Cl(SbPh_3)_3]$, presumably because $SbPh_3$ is a slightly less sterically bulky ligand largely as a result of its longer Ir—Sb bond. The sterically unencumbered PMe_3 also gives a six-coordinate $[Ir(biph)Cl(PMe_3)_3]$.[9] This suggests that the formation of the five-coordinate compounds **2a**–**2c** is at least in part the result of steric effects, although the presence of the high *trans*-influence biph ligand no doubt also encourages five-coordination.

Crystals suitable for crystallographic study were grown from CH_2Cl_2 solution by slow evaporation. The crystallographic work (Table 1) gave the distance and angular data of Table 2. The corresponding ORTEP diagrams are shown in Fig. 1 and 2. The crystal of compound **2b** contained two independent molecules having very similar but not identical metric parameters.

Both **2b** and **2c** have similar structures to that of $[Ir(biph)Cl(PPh_3)_2]$ (**2a**) which was determined previously.[8] In all cases, the $(biph)IrQ_2$ fragment has near C_{2v} symmetry but the halide, while remaining in the equatorial biph plane (the sum of the three equatorial L—Ir—L angles is 359.87–360°), lies significantly off the C_2 axis so that one biph carbon, denoted C_{trans}, becomes more *trans* than *cis*, and the other, denoted C_{cis}, becomes more *cis* than *trans* to the halide group. Fig. 3 illustrates the situation by showing the equatorial ligands. All the molecules of type **2** studied to date therefore have essentially the same geometry, lying between the ideal Y and T forms, but they show different deviations from pure Y geometry. We have used the angles ω_1, ω_2 and ϕ shown in Fig. 3 as a measure of this deviation in the following discussion. The fact that C_{cis}, C_{trans}, Ir and X are always in the same plane allows the value of ϕ to be derived from ω_1 and ω_2 by eqn. 4.

$$\phi - |\tfrac{1}{2}(\omega_1 + \omega_2) - \omega_1| \quad (4)$$

A pure Y geometry should correspond to a ϕ value of zero and a pure T geometry should lead to a ϕ value close to 45°. The values found in the present work lie between 8.2 and 17.2° and therefore indicate a geometry closer to Y than T.

Table 1 X-Ray crystallographic data for **2b** and **2c**[a]

Compound	**2b**	**2c**
Formula	$C_{48}H_{38}As_2ClIr$	$C_{48}H_{38}P_2IIr$
Space group	$P2_1/c$	$P2_1/n$
a/Å	23.5757(3)	14.5086(2)
b/Å	19.10520(10)	10.92350(8)
c/Å	19.1809(2)	25.52790(10)
β/°	113.2260(10)	103.6310(10)
V/Å^3	7939.30(19)	3931.83(6)
MW	992.27	995.82
ρ(calc)/g cm^{-3}	1.660	1.682
Z	8	4
θ Range/°	1.42–28.17	1.48–28.26
No. of data used	14939	6706
No. of parameters refined	937	467
$R[I > 2\sigma(I)]$[b]	3.28%	3.15%
$R_w[I > 2\sigma(I)]$[b]	8.22%	7.87%

[a] Details in common: $T = 173(2)$ K, scan type ω–2θ, $\lambda = 0.71069$ Å, largest shift/error = 0.2, empirical DIFABS absorption correction. [b] Function minimized: $R = \Sigma\|F_o| - |F_c\|/|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o)^2$.

Table 2 Selected bond distances (Å) and angles (°) for **2b** and **2c**; X = halide, Q = P or As

	2b (1st molecule)[a]	**2b** (2nd molecule)[a]	**2c**
Ir—X	2.3950(10)	2.3967(10)	2.7197(3)
Ir—Q(1)	2.4359(4)	2.4350(4)	2.3374(12)
Ir—Q(2)	2.4362(4)	2.4332(4)	2.3509(12)
Ir—C_{trans}[b]	2.041(4)	2.050(4)	2.051(4)
Ir—C_{cis}[b]	2.035(4)	2.034(4)	2.024(5)
X—Ir—Q(1)	92.99(3)	88.83(3)	91.92(3)
X—Ir—Q(2)	90.37(3)	93.35(3)	91.77(3)
X—Ir—C_{trans}	149.27(12)	151.21(12)	158.1(2)
X—Ir—C_{cis}	132.93(13)	130.96(14)	123.75(14)
Q(1)—Ir—Q(2)	173.28(2)	174.04(2)	172.62(5)
C_{cis}—Ir—C_{trans}	77.8(2)	77.7(2)	78.1(2)
ϕ	8.2(4)	10.1(4)	17.2(4)

[a] The crystal of **2b** contained two independent molecules; the atom numbering of the first has been given unmodified [*e.g.* C(1)] and the second in primes [*e.g.* C(1′)]. [b] The carbon atoms of the biph bound directly to Ir are labeled as being *cis* or *trans* with reference to the halide because of the slightly different numbering system in the two compounds. C_{cis} is C(1) in the first molecule of **2b**, C(12′) in the second molecule of **2b** and C(7) in **2c**; similarly, C_{trans} is C(12) in the first molecule of **2b**, C(1′) in the second molecule of **2b** and C(1) in **2c**.

We find that both the ligand conformations and the ϕ values in the two molecules of **2b** are essentially the same, suggesting that packing forces have only a minor role in determining the distortion. This is a rare case in which an organometallic molecule with a relatively flat bending potential (see below) has been studied in two independent forms. The low influence of packing forces on the distortion suggested by the present work may not be general, however, because ionic solids in particular might be expected to have a much higher effective internal pressure and could therefore show a greater structural variability depending on the details of the packing.

Theoretical study

Previously reported calculations[8] at the extended Hückel theory level seemed to indicate an electronic origin for the deviation, ϕ. The structure of the simplified system [Ir(C_4H_4)Cl(PH_3)$_2$] was thus optimized at the B3LYP level. The results show that the geometry of the complex is close to that of the full biph system with the exception of the presence of a C_2 symmetry which is present in the calculated structure and lacking in the experimental system. The computed geometry had C_2 symmetry despite the fact that the geometry optimization was carried out with no symmetry restrictions and

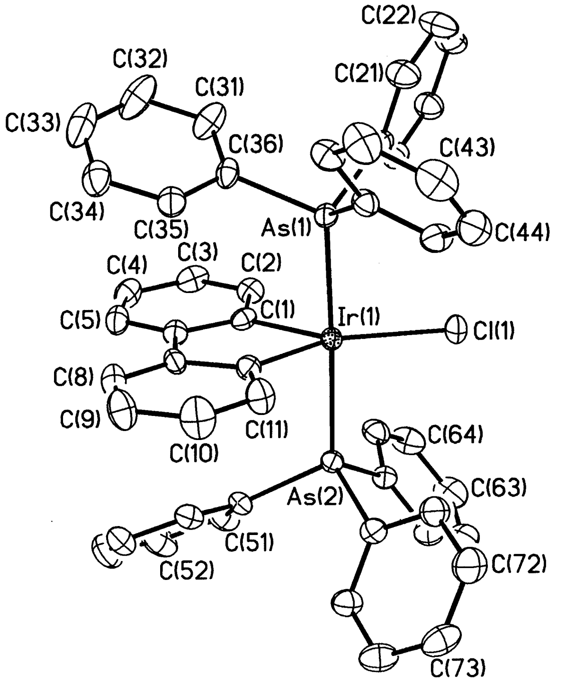


Fig. 1 ORTEP diagram of **2b**. Only one of the two independent but chemically equivalent molecules is shown. The other has essentially the same conformation. The thermal ellipsoids are plotted at 50% probability and the hydrogen atoms are omitted for clarity

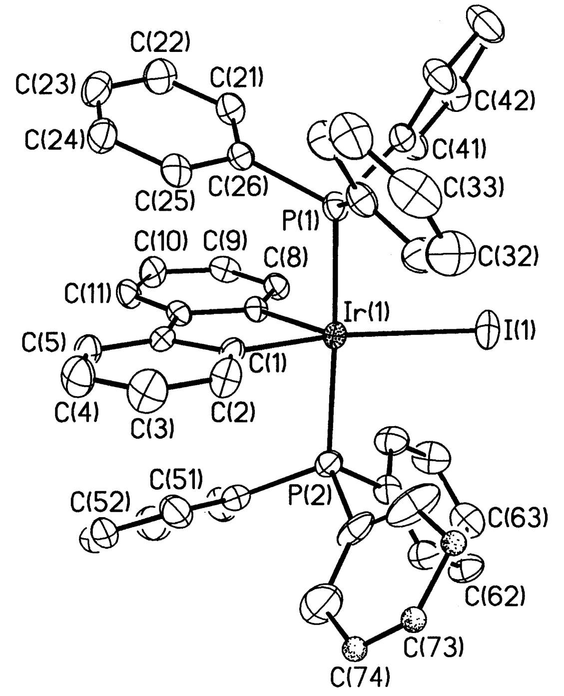


Fig. 2 ORTEP diagram of **2c**. Carbons C(72)–C(74) are disordered over two positions and were refined isotropically. Thermal ellipsoids are plotted at 50% probability and the hydrogen atoms are omitted for clarity

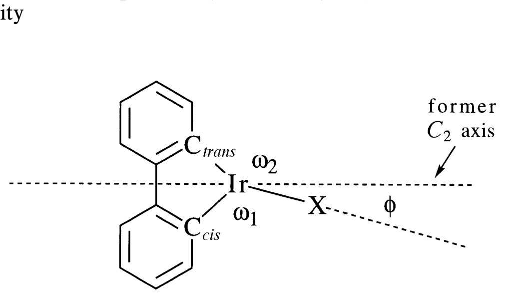


Fig. 3 Ligands in the equatorial plane of complex **2**, showing the deviation of the halide from the ideal C_2 axis (dotted) of a pure Y structure. QR_3 ligands are located above and below the equatorial plane. Angle ϕ is the deviation of the X group from the C_2 axis, ω_1 is the C_{cis}—Ir—X angle and ω_2 is the C_{trans}—Ir—X angle. X always lies in the C_{cis}, C_{trans}, Ir plane

started from a non-symmetrical structure. The Ir—C distances are reasonably well represented (calcd., 2.06 Å; exptl. average, 2.00 Å), the alternating long and short distances within the metallacycle are also well reproduced (calcd., 1.355, 1.459 Å; exptl. 1.415, 1.440 Å). The significant difference between theory and experiment for the C=C of the metallacycle is clearly due to it being part of a phenyl ring in the biph complex, in which case the double bond is delocalized. The calculated Ir—Cl distance of 2.449 Å is reasonably close to the experimental value of 2.380 Å as is also the case for the Ir—P distances (calcd., 2.331 Å; exptl., 2.345 Å). As in the experimental system, the metallacycle is planar. A pure Y structure for [Ir(C_4H_4)Cl(PH_3)$_2$] agrees with the expectations based on the presence of one equatorial π donor (Cl).[3] Our previous proposal[8] that the geometrical constraint of the biph ligand helps cause the distortion has therefore been discarded.

Having established that **2** has an electronic preference for a Y structure with $\phi = 0°$, the observed deviation in **2a**–**2c** seemed likely to be a steric effect. This makes the series of compounds of type **2** suitable for study by the hybrid combined IMOMM (B3LYP:MM3) method. Examination of the experimental structures of **2a**–**2c** showed that in each case the same ligand conformation is adopted. This conformation was therefore taken as the departure point for the IMOMM study so as to minimize the potential problem of falling into a series of local minima of no relevance to the experimental solid-state conformation. The minimization was carried out with the object of seeing how well the φ value that emerged in each case matched the experimental value and if the trend of the values matched the experimental trend.

The IMOMM calculations on [Ir(biph)X(QR_3)$_2$] always reproduce the experimental conformation, indicating that this is a local minimum for the isolated complex and that the crystal packing is not a determining factor. The calculations also show a displacement of the halide from its electronically preferred position on the C_2 axis in a direction which allows the Ir—X bond to stay coplanar with the metallacycle. However, as in the case of the IMOMM calculation on [IrH_2ClL_2], the geometrical results are not quantitatively satisfactory if the radius of Cl is maintained at its standard value contained in the MM3 program because this is the value appropriate for organic chlorides. With the standard radius, [Ir(biph)Cl(PPh_3)$_2$] shows only a slight distortion away from C_{2v} symmetry ($\phi = 1.4°$). If the Cl radius is increased to account for its ionic nature using the procedure described in a previous paper,[6] the optimized structure now comes remarkably close to the experimental one (calc. $\phi = 11.4$; exptl., 10.15°). For all Q and X studied, the displacement, as measured by ω_1, ω_2 and φ, is given in Table 3. The same distorted geometry was obtained from calculations starting both from the experimental non-symmetrical arrangement and starting from a symmetrical C_{2v} arrangement. The latter arrangement was tested specifically in the case of [Ir(biph)Cl(PPh_3)$_3$] to ensure that no other local minimum is present. In spite of the potential energy surface for the displacement of the Cl from the axis being very flat, good agreement with experiment was obtained.

On going from PH_3 to PPh_3 (X = Cl), all the calculated metal–ligand distances increase slightly, probably as a consequence of the increased steric bulk around the metal. The C—C bond of the metallacyclopentadiene is not changed on moving from the IrC_4H_4 to the Ir(biph) model since the adjacent phenyl rings of biph are represented only at the MM3 level and therefore delocalization of the electrons of the C=C bond is not possible.

The calculated value of φ increases on going from Cl to I (L = PPh_3) as is also the case for the experimental results (calc., 14.6; exptl., 17.2°). The increased distortion is clearly associated with a bigger steric interaction with the larger halide. Changing Q from P to As (X = Cl) diminishes the experimental distortion by only one degree [$\phi = 9.15°$(av.)]; the calculations show no change (calc., 11.3°). The longer Ir—Q distance presumably causes the ligand cone angle to decrease.

The calculations thus closely mimic the experimental system, even though the substituents on QR_3 are represented in a purely MM (steric) manner; this suggests that the interactions between the substituents and the other ligands are essentially controlled by steric factors. Previous work in this area[2b,9] has shown that steric effects in organometallic compounds tend to be dispersed over numerous centers and no particular atom or group can be considered as the dominant contributor. Compound **2** has even more atoms than the complexes studied previously and so the possibilities for dispersal of steric effects are even greater. For this reason, we did not conduct any analysis to attempt to estimate the relative size of the interatomic repulsions. It is also very satisfying that the IMOMM hybrid method is able to reproduce subtle structural changes from Y to T even on a potential energy surface known from *ab initio* calculations to be very flat.[3b–d]

Experimental

Syntheses

General procedures and materials. All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures. All the reagents were used as received without further purification. [Ir(cod)Cl(biph)]$_2$ and [Ir(biph)Cl(PPh_3)$_2$] were prepared by literature methods.[7]

^1H and ^{31}P NMR spectra were recorded on a GE Omega 300 spectrometer. Elemental microanalyses were performed by Robertson Microlit Laboratories.

Chloro(biphenyl-2,2′-diyl)bis(triphenylarsine)iridium(III) (2b). A suspension of [Ir(cod)Cl(biph)]$_2$ (0.20 g, 0.21 mmol) and triphenylarsine (0.28 g, 0.92 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 5 h under N_2. The resulting red-orange product was filtered off, washed with Et_2O (2 × 10 mL), and dried *in vacuo*. Yield: 0.28 g (0.28 mmol, 67%). ^1H NMR (CD_2Cl_2, 298 K): δ 7.49 (2H, d,

Table 3 Results of the IMOMM and (B3LYP : MM3) calculation on [Ir(biph)XL_2]

			Calc.			Exptl.		
Compound	L	X	ω_1	ω_2	φ	ω_1	ω_2	φ
2a[a]	PPh_3	Cl	130.6	153.4	11.4	131.3	151.4	10.15
2b	$AsPh_3$	Cl	130.7	153.3	11.3	132.93	149.27	8.2
2b′[b]	$AsPh_3$	Cl	130.7	153.3	11.3	130.96	151.21	10.1
2c	PPh_3	I	128.0	155.3	14.6	123.75	158.1	17.2
2d[c]	PH_3	Cl	142	142	0	—	—	—

Angles in degrees. $\omega_1 = C_{cis}$—Ir—X; $\omega_2 = C_{trans}$—Ir—X; $\phi = |\frac{1}{2}(\omega_1 + \omega_2) - \omega_1|$. [a] With the standard MM3 value of the Cl radius (adapted for organic chlorides) ω_1 and ω_2 are 140.4 and 143.2° ($\phi = 1.4°$). [b] Data for the second molecule in unit cell. [c] Theoretical value only; compound not synthesized.

$J = 7.2$ Hz), 7.2–7.4 (36H, br, Ph), 6.47 (2H, t, $J = 7.2$ Hz, biph), 6.33 (2H, t, $J = 7.2$ Hz, biph), 6.31 (2H, d, $J = 7.2$ Hz, biph). Anal. Calcd. (found) for $C_{48}H_{38}As_2ClIr$: C, 58.10 (57.88); H, 3.86 (4.00%).

Iodo(biphenyl - 2,2′ - diyl) bis (triphenylphosphine) iridium (III) (2c). A mixture of [Ir(biph)Cl(PPh_3)$_2$] (0.10 g, 0.11 mmol) and LiI (0.14 g, 1.0 mmol) in acetone (20 mL) was stirred at ambient temperature for 12 h, during which time the color changed from red-orange to red. The solvent was removed under reduced pressure, and CH_2Cl_2 (20 mL) was added to dissolve the red precipitate. The solution was filtered through Clite, the filtrate was reduced to 5 mL *in vacuo*, followed by addition of Et_2O (15 mL) to precipitate a red product, which was filtered off, washed with Et_2O (2 × 10 mL), and dried *in vacuo*. Yield: 78 mg (0.078 mmol, 71%). ^1H NMR (CD_2Cl_2, 298 K): δ 7.2–7.4 (38H, br, Ph and biph), 6.46 (2H, t, $J = 7.3$ Hz, biph), 6.34 (2H, dt, $J = 1.1$, 7.3 Hz, biph), 6.21 (2H, dd, $J = 1.1$, 7.3 Hz, biph). Anal. Calcd. (found) for $C_{48}H_{38}P_2IIr$: C, 57.90 (58.08); H, 3.84 (3.80%).

Crystallographic structural determination

Crystal, data collection and refinement parameters are given in Table 1. Data was collected on a Siemens P4/CCD diffractometer. The systematic absences in the diffraction data are uniquely consistent with the space groups reported. The structures were solved by direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. An empirical absorption correction was applied, based on a Fourier series in the polar angles of the incident and diffracted beam paths and was used to model an absorption surface for the difference between the observed and calculated structure factors.[10] The asymmetric unit of **2b** consists of two independent molecules. Three carbon atoms of both of the biph rings of **2c**, equally disordered over two positions, were refined isotropically, and the corresponding hydrogen atoms were ignored owing to this disorder. All other non-hydrogen atoms were refined with anisotropic displacement coefficients and all other hydrogen atoms were treated as idealized contributions. Five of the remaining peaks in the final difference map of **2b** (1.06 to 1.54 e Å^{-3}) were in chemically unreasonable positions 1.18–1.44 Å from the Ir and were considered as noise.

All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library.[11]

CCDC reference number 440/062.

Computational details

Pure quantum mechanical calculations on the model systems [Ir(C_4H_4)X(QH_3)$_2$] were carried out with Gaussian 94.[12] Pseudo potentials were used for representing the 60-electron core of Ir,[13] the 10-electron core of P and Cl, the 18-electron core of As and the 26-electron core of I.[13b]

The associated double-ζ basis set with a LANL2DZ contraction[12] was used for the Ir, P, As, Cl and I atoms. A polarization d shell was added for the P,[14] Cl,[14] I[15] and As[15] atoms. The C and H atoms had a valence double-ζ basis set.[16] Full geometry optimizations were carried out at the B3LYP level. [17]

IMOMM calculations were performed on [Ir(biph)X(QPh_3)$_2$] (X = Cl, I; Q = P, As) with a program built from modified versions of two standard programs: Gaussian 92/DFT[18] for the quantum mechanics (QM) part and MM3 (92) for the molecular mechanics[19a] (MM) part. The QM part was always carried out for [Ir(C_4H_4)X(QH_3)$_2$] at the computational level described in the previous paragraph. For the MM part, the MM3(92) force field was used.[19b] Van der Waals parameters for the iridium atom were taken from the UFF force field.[20] Parameters for bending contributions involving As—C—C bond angles and torsional contributions involving As-C-C-R dihedral angles were taken from the values assigned to P-C-C and P-C-C-R. Torsional contributions involving dihedral angles with the metal atom in terminal position were set at zero. The values of the radii of Cl and I in the MM3 program were modified to take into account their greater negative charge when bonded to a transition-metal center according to the procedure described previously:[6] radii for Cl and I were 2.47 Å and 2.71 Å, respectively. All geometrical parameters were optimized without symmetry restrictions except for the bond distance between the QM and MM regions of the molecules. These were frozen at 1.420 (P–H). 1.532 (As–H), 1.101 Å (C–H) in the QM part; and 1.828, 1.943 (As–C), and 1.434 Å (C–C) in the MM part. The starting point of all geometry optimizations was the crystal structure coordinates for the iridium complexes.

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