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Experimental and computational studies of two new mono- and dinuclear iridium complexes containing a Buchwald biphenyl phosphine ligand

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Abstract

The reaction of $[(\eta^{4}-1,5-C_{8}H_{12})_{2}Ir_{2}(\mu-Cl)_{2}]$ with 2-di-*t*-butylphosphino-2'-methylbiphenyl (*t*-Bu₂Pbiph^{Me}) in the presence of AgBF₄ afforded the dichlorido-bridged Ir–Ag complex $[(\eta^{4}-1,5-C_{8}H_{12})Ir(\mu-Cl)_{2}Ag(t-Bu_{2}Pbiph^{Me})]$ (1) which was fully characterized by a single crystal X-ray diffraction study. Sequential treatment of the diiridium precursor first with the silver salt and then with the phosphine ligand of 2 forms a strained four-membered iridaheterocycle through orthometalation rather than a sterically congested six-membered chelate structure through C–H activation on the remote phenyl ring. The phosphonium salt [*t*-Bu₂P(H)biph^{Me}]BF₄ was isolated as a by-product of the preparations of 1 and 2; its crystal structure was determined.

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1. Introduction

In previous work, we described some P_2/N_2 -coordinated *cis*-dihydridoiridium(III) compounds [IrH₂(PPh₃)₂(1, 2-diamine)]BF₄ containing the enantiomerically pure *N*,*N* chelates (1*R*,2*R*)-1,2-diaminocyclohexane and (*R*)-2,2'-diamino-1,1'-binaphthyl in addition to two achiral triphenyl-phosphine ligands [1]. They were made by substituting the chelating diamines for the loosely bound solvate ligands of [IrH₂(OCMe₂)₂(PPh₃)₂]BF₄, which in turn was obtained by the hydrogenation of $[(\eta^4-1,5-C_8H_{12})Ir(PPh_3)_2]BF_4$ in acetone [2]. If activated by strong base in methanol, the chiral chelate complexes [IrH₂(PPh₃)₂(1,2-diamine)]BF₄ acted as enantioselective catalysts for the hydrogenation of aceto-phenone to (*S*)-1-phenylethanol, but only with poor selec-

tivity (e.e._{max}: 24%) [1]. Looking for iridium catalysts with possibly improved properties, we therefore set out to synthesize *cis*-dihydrides [IrH₂(P^{*}R₃)₂(H₂N∩^{*}NH₂)]BF₄ bearing one chiral diamine along with two chiral monodentate phosphorus ligands as represented by, e.g., the sterically demanding atropisomeric Buchwald biphenyl phosphines R₂Pbiph (R = *t*-Bu, *cyclo*-C₆H₁₁) [3].

We expected that such compounds might result as enriched diastereomers from reactions between enantiopure 1,2-diamines and the racemates of weakly solvated dihydridobis(biphenyl phosphine) complexes [IrH₂(solv)₂-{(*R*,*S*)-R₂Pbiph}₂]BF₄ or their direct precursors [(η^{4} -1, 5-C₈H₁₂)Ir{(*R*,*S*)-R₂Pbiph}₂]BF₄. In a first effort we therefore addressed the preparation of a (cyclooctadiene)iridium(I) complex with additional Buchwald ligands through the Ag⁺-assisted bridge-opening reaction of [(η^{4} -1,5-C₈H₁₂)₂Ir₂(μ -Cl)₂] with 2-di-*t*-butylphosphino-2'-methylbiphenyl (referred to as "*t*-Bu₂Pbiph^{Me}" in the following) as an exemplary biphenyl phosphine. This approach did

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not afford the hoped-for target compound but rather launched quite an unexpected coordination chemistry of the *t*-Bu₂Pbiph^{Me} ligand toward Ir^{I} and Ag^{I} , which is the subject of the following.

2. Experimental

2.1. General remarks

All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents prior to use. – NMR: Bruker DPX 300 (300.1 MHz for ¹H, 75.5 MHz for ¹³C, and 121.5 MHz for ³¹P) at 20 ± 2 °C with SiMe₄ (or the solvent) as internal or H₃PO₄ as external standards (downfield positive). – Racemic 2-di-*t*-butylphosphino-2'-methylbiphenyl and silver tetrafluoridoborate were used as purchased from Strem. [(η^4 -1,5-C₈H₁₂)₂Ir₂(μ -Cl)₂] was prepared as reported in the literature [4].

2.2. Di- μ -chlorido[(η^4 -1,5-cyclooctadiene)iridium(I)][(2di-t-butylphosphino-2'-methylbiphenyl)silver(I)], [{(η^4 -1, 5-C₈H₁₂)Ir}(μ -Cl)₂{Ag(2-t-Bu₂PC₆H₄C₆H₄Me-2')}] (1)

Solid silver tetrafluoridoborate (62 mg, 0.32 mmol) was added to a mixture of 108 mg (0.16 mmol) of $[(\eta^4-1,5 C_8H_{12}$, $Ir_2(\mu-Cl)_2$ and 200 mg (0.64 mmol) of t-Bu₂Pbiph^{Me} in 20 mL of acetone. The yellow solution was stirred for 24 h at ambient conditions, which caused the product to precipitate as yellow microcrystals which were collected by filtration, washed with diethyl ether $(3 \times 2 \text{ mL})$, and dried under vacuum; yield 74 mg (58%). ¹H NMR (CDCl₃): $\delta = 1.34$, 1.39 (both d, ³J(P,H) = 5.1 and 4.2 Hz, 9H each, both t-butyl CH₃), 2.08 (s, 3H, biphenyl CH₃), 2.23 (m, 8H, diene CH₂), 3.56, 4.00 (both m, 2H each, both diene CH), 7.05-7.92 (m, 8H, biphenyl H). ¹³C{¹H} NMR (CDCl₃): $\delta = 20.92$ (s, biphenyl CH₃), 31.12, 31.55 (both d, ${}^{2}J(P,C) = 10.6$ Hz each, both *t*-butyl CH₃), 31.77, 32.24 (both s, both diene CH₂), 35.53, 35.91 (both dd, ${}^{1}J(P,C) = 9.8$ Hz each, ${}^{2}J({}^{107/109}Ag,C) = 4.5$ Hz each, both t-butyl C_{auart}), 56.74, 61.76 (both s, both diene CH), 126.77 (s), 127.23 (unresolved dd), 128.29, 128.59 (both unresolved d), 129.64, 130.90, 132.54 (all s), 132.69, 134.47 (both d, J(P,C) = 6.5 and 8.0 Hz), 135.33 (s), 140.29 (d, J(P,C) = 8.7 Hz), 149.80 (dd, J(P,C) = 18.9 Hz, $J(^{107/109}\text{Ag,C})$ unresolved): all biphenyl C. $^{31}P{^1H}$ NMR (CDCl₃): $\delta = 43.04$ (pair of d, $J(^{107}Ag,P) = 619$, $J(^{109}\text{Ag,P}) = 715 \text{ Hz})$. Anal. Calc. for $C_{29}H_{41}\text{AgCl}_2\text{IrP}$ (791.56): C, 44.00; H, 5.22. Found: C, 42.92; H, 5.25%. Concentration of the mother liquor induced the crystallization of the phosphonium salt $[t-Bu_2P(H)biph^{Me}]BF_4$ (3) which was formed as a by-product of the above preparation. ¹H NMR (CD₂Cl₂): $\delta = 1.45$, 1.62 (both d, ${}^{3}J(P,H) = 15.0 \text{ Hz}$ each, 9 H each, both *t*-butyl CH₃), 2.14 (s, 3 H, aryl CH₃), 5.84 (d, ${}^{1}J(P,H) = 459.6$ Hz, 1 H, PH), 7.10–8.00 (m, 8 H, aryl H). ${}^{31}P{}^{1}H{}$ NMR (CD₂Cl₂): $\delta = 33.22$ (s).

2.3. $(2\text{-Di-t-butylphosphino-2'-methylbiphenyl-3-yl})(\eta^{4}-1, 5\text{-cyclooctadiene})iridium(I), [(\eta^{4}-1, 5\text{-}C_{8}H_{12})Ir(2\text{-}t\text{-}Bu_{2}-PC_{6}H_{3}C_{6}H_{4}Me\text{-}2'\text{-}\kappa C^{6}, \kappa P)]$ (2)

A solution of 242 mg (0.36 mmol) of $[(\eta^4-1,5 C_8H_{12}$ [2] $Ir_2(\mu$ -Cl)₂ and 140 mg (0.72 mmol) of AgBF₄ in 10 mL of acetone was stirred overnight at room temperature. Precipitated silver chloride was removed by filtration and the filtrate was treated with 225 mg (0.72 mmol) of t-Bu₂Pbiph^{Me} dissolved in 10 mL of acetone. The mixture slowly changed color from orange to dark red and deposited a fine precipitate. Evaporation to dryness followed by trituration of the residue with 20 mL of diethyl ether left some $[t-Bu_2P(H)biph^{Me}]BF_4$ which was filtered off. Concentration of the filtrate gave 275 mg (63%) of 2 as a red solid. ¹H NMR (CDCl₃): $\delta = 1.18$, 1.41 (both d, 3 J(P,H) = 13.7 Hz each, 9 H each, both *t*-butyl CH₃), 1.76-2.52 (m, 8H, diene CH₂), 2.28 (s, 3H, biphenyl CH₃), 4.55, 4.63, 4.71, 4.90 (all m, 1H, each, all diene CH), 6.97–7.50 (m, 7H, biphenyl H). ${}^{13}C{}^{1}H{}$ NMR (C_6D_6) : $\delta = 19.36$ (s, biphenyl CH₃), 29.42, 30.52 (both d, $^{2}J(P,C) = 6.1 \text{ Hz}$ each, both *t*-butyl CH₃), 28.33, 30.90, 32.69 (all s, 1 + 2 + 1C, all diene CH₂), 34.76, 34.98 (both d, ${}^{1}J(P,C) = 10.5$ and 9.1 Hz, both *t*-butyl C_{quart}), 68.21, 69.69 (both d, ${}^{2}J(P,C) = 12.1$ Hz each, both diene CH trans P), 69.06, 70.31 (both s, both diene CH cis P), 123.26 (s), 125.93 (d, J(P,C) = 4.5 Hz), 127.59 (d, J(P,C) = 7.5 Hz), 128.34, 128.55, 128.84, 128.92, 135.53 (all s), 141.88 (d, J(P,C) = 2.3 Hz, 143.13 (s), 151.78 (d, J(P,C) = 33.2 Hz), 160.46 (d, J(P,C) = 9.8 Hz) all biphenyl C. ${}^{31}P{}^{1}H{}$ NMR (C₆D₆): $\delta = 10.67$ (s). Anal. Calc. for C₂₉H₄₀IrP (611.82): C, 56.93; H, 6.59. Found: C, 57.02; H, 6.70%.

2.4. X-ray structure determinations

The specimen used for the structure determination of 1 was picked from a sample of the complex that was re-crystallized from CHCl₃. Single crystals of the phosphonium salt 3 grew from the acetone mother liquor of the preparation of compound 1. Diffraction measurements were made with a Bruker-Nonius Kappa CCD instrument at -173 °C (complex 1) and with an Enraf-Nonius CAD-4 MACH 3 diffractometer at -140 °C (phosphonium salt 3) using Mo K α radiation; data of 3 were uncorrected for absorption, those of **1** were corrected for absorption by an appropriate semi-empirical procedure [5] ($T_{\min} = 0.599$, $T_{\max} = 0.760$). The structures were solved by direct methods and subsequently refined by full-matrix least-squares procedures on F^2 with allowance for anisotropic thermal motion of all non-hydrogen atoms employing both the SHELXTL NT 6.12 [6] and the WINGX [7a] packages with some of the relevant programs (sadabs [5], sir-97 [8], shelxl-97 [9], ortep-3 [7b]) implemented therein. Structure 1 was refined in space group $P2_1$ allowing for racemic twinning with a twin component ratio close to 1:1. Hence, a structure refinement at higher symmetry (space group $P2_1/m$ with the molecule on a crystallographic mirror plane containing the metal

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and phosphorus atoms as well as the phenylene ring and the ipso- and para-C atoms of the tolyl group) was also tested but lead to heavily disordered *t*-butyl carbon atoms with non-positive-definite displacement parameters and ultimately gave significantly higher residuals ($wR_2 =$ 0.0697, $R_1 = 0.0335$) than in $P2_1$ (vide infra). In structure 3, the split occupancies for the disordered tolyl carbon atoms of the biphenyl residue refined to 0.61 for C15a-C21a and 0.39 for C15b-C21b, respectively. The tetrafluoridoborate anion showed threefold disorder about the B1-F1 bond, which was modelled by assigning site occupation factors of 0.50, 0.30, and 0.20 to atoms F2a-F4a, F2b-F4b, and F2c–F4c, respectively. Compound 1 $(0.10 \times$ 0.05×0.05 mm): C₂₉H₄₁AgCl₂IrP (791.56); monoclinic, $P2_1$, a = 9.736(2), b = 12.659(3), c = 11.816(2) Å, $\beta =$ 95.22(3)°, $V = 1450.3(5) \text{ Å}^3$, Z = 2, $d_{\text{calc}} = 1.813 \text{ g cm}^{-3}$, μ (Mo K_a) = 5.514 mm⁻¹; 3.46° $\leq \theta \leq 28.52^{\circ}$, 31100 reflections collected $(-13 \le h \le +13, -16 \le k \le +16, -15 \le k \le +16)$ $l \leq +15$), 7323 unique ($R_{int} = 0.0412$); $wR_2 = 0.0472$ for all data and 307 parameters, $R_1 = 0.0274$ for 6415 intensi-ties $I > 2\sigma(I)$. Compound **3** (0.48 × 0.38 × 0.20 mm): $C_{21}H_{30}P$, BF₄ (400.23); monoclinic, $P2_1/n$, a = 10.133(3), $b = 18.102(4), c = 11.427(2) \text{ Å}, V = 2095.8(9) \text{ Å}^3, Z = 4,$ $d_{\text{calc}} = 1.268 \text{ g cm}^{-3}, \quad \mu(\text{Mo} \quad \text{K}_{\alpha}) = 0.168 \text{ mm}^{-1}; \quad 2.11$ $^{\circ} \leq \theta \leq 22.50^{\circ}$, 2928 reflections collected ($-10 \leq h \leq 0$, $-19 \leq k \leq 0, -12 \leq l \leq +12), 2748$ unique ($R_{int} = 0.043$); $wR_2 = 0.2482$ for all data and 335 parameters, $R_1 = 0.086$ for 1652 intensities $I > 2\sigma(I)$.

2.5. Computational details

All structures were fully optimized using the B3LYP hybrid density functional [10–12] and the LANL2DZ basis set augmented with polarization functions (further denoted as LANL2DZp) [13–16]. All structures were characterized as minima by the computation of vibrational frequencies. The influence of the bulk solvent was probed by single point calculations employing the IPCM formalism [17] with water as solvent, i.e., B3LYP(IPCM)/LANL2DZp//B3LYP/LANL2DZp. The GAUSSIAN 03 suite of programs was used [18]. Additional structure optimizations were carried out with JAGUAR 6.5 [19] applying LMP2/LACVP* [14,20,21]. The pure density functional BP86 [22] together with the LACVP* basis set [14,21] was applied for structure calculations in the gas phase [23] and the water model [24] as implemented in JAGUAR 6.5.

3. Results and discussion

3.1. $[(\eta^4 - 1, 5 - C_8 H_{12}) Ir(\mu - Cl)_2 Ag(t - Bu_2 P biph^{Me})]$ (1)

The most direct route to cationic cyclooctadiene complexes of iridium(I) with two additional monophosphines or one chelating diphosphine such as $[(\eta^{4}-1,5-C_{8}H_{12})Ir(PPh_{3})_{2}]^{+}$ [2d,2e], $[(\eta^{4}-1,5-C_{8}H_{12})Ir\{(R)-binap\}]^{+}$ [1], and the like involves the reaction of $[(\eta^{4}-1,5-C_{8}H_{12})_{2}Ir_{2}(\mu-Cl)_{2}]$ with stoichiometric quantities of the





Coordination of the *t*-Bu₂Pbiph^{Me} ligand to the silver rather than the iridium center of **1** became evident from the ³¹P{¹H} NMR spectrum displaying a pair of doublets due to the coupling of the ³¹P nucleus with the two silver isotopes ¹⁰⁷Ag and ¹⁰⁹Ag. The coupling constants ¹ $J(^{107}Ag, ^{31}P) = 619$ Hz and ¹ $J(^{109}Ag, ^{31}P) = 715$ Hz are close to those previously measured for the tetranuclear compound [{(*p*-cumene)Ru(μ -Cl)₂Ag(μ -*t*-Bu₂PCH₂CH₂-PPh₂)}₂][PF₆]₂ (643 and 743 Hz), where the silver ion is also triply coordinated by two bridging chlorido ligands and one terminal *t*-Bu₂P donor function [25].

Compound 1 was fully characterized by single crystal Xray crystallography. The specimen studied belonged to the monoclinic space group $P2_1$ and turned out to be a racemic twin with a twin component ratio close to 1:1. A perspective view of the molecular model resulting from the refinement is given in Fig. 1.

Although there exist some heterobimetallics in which iridium(I) is linked by halide bridges to a different transition metal [26], the $Ir^{I}(\mu$ -Cl)₂Ag^{I} complex presented in this work is the only example so far for which structural data

¹ The stoichiometry $[(\eta^{4}-1,5-C_8H_{12})_2Ir_2(\mu-Cl)_2]/AgBF_4/t-Bu_2P-biph^{Me} = 1:2:4$ used in the preparation of **1** was originally chosen in view of the attempted synthesis of $[(\eta^{4}-1,5-C_8H_{12})Ir(t-Bu_2Pbiph^{Me})_2]BF_4$ as a target complex. As one of the referees raised the question whether this molar ratio is really needed, the reaction was repeated using the 1:1:1 limiting stoichiometry of the reactants; specifically: 323 mg of $[(\eta^{4}-1,5-C_8H_{12})_2Ir_2(\mu-Cl)_2]$, 93 mg of AgBF₄, and 150 mg of *t*-Bu₂Pbiph^{Me} (0.48 mmol each) in 20 mL of acetone. Work-up gave a reddish orange semisolid shown to be a mixture of **1** (³¹P NMR) and unreacted $[(\eta^{4}-1,5-C_8H_{12})_2Ir_2(\mu-Cl)_2]$ (¹H NMR). Formation of the phosphonium salt [*t*-Bu₂P(H)biph^{Me}]BF₄ as an accompanying product was also observed, implying that for the consumption of the starting homodimer an excess of the highly basic phosphine is indeed required because part of it is lost by protonation.



Fig. 1. A perspective view of the molecule $[(\eta^{4}-1,5-C_8H_{12})Ir(\mu-Cl)_2Ag(t-Bu_2Pbiph^{Me})]$ (1); hydrogen atoms are omitted for clarity; selected bond lengths (Å) and angles (°): Ir1–Cl1, 2.385(2); Ir1–Cl2, 2.375(3); Ag1–Cl1, 2.554(2); Ag1–Cl2, 2.598(3); Ag1–P1, 2.366(1). Cl1–Ir1–Cl2, 89.33(4); Cl1–Ag1–Cl2, 80.97(4); Cl1–Ag1–P1, 137.43(11), Cl2–Ag1–P1, 136.62(11); Ir1–Cl1–Ag1, 92.51(8); Ir1–Cl2–Ag1, 91.66(10).

are available [27,28]. Its structure can be described most simply as having an $(\eta^4-1,5-C_8H_{12})$ IrCl₂ building block to which one Ag(*t*-Bu₂Pbiph^{Me}) group is attached in a slightly asymmetric fashion. The three-coordinate geometry around the silver center is strongly distorted in that the Cl-Ag-Cl angle of 80.97(4)° and the two Cl-Ag-P angles [136.6(1)° and 137.4(1)°] deviate significantly from the ideal value of 120° expected for trigonal planar coordination. The Ag–P^tBu₂ bond length of 1, 2.366(1) Å, is similar to the Ag–P^tBu₂ distance of 2.359(2) Å measured for the ruthenium-silver complex [{(p-cumene)Ru(μ - $Cl_{2}Ag(\mu - t - Bu_{2}PCH_{2}CH_{2}PPh_{2})$ [PF₆]₂ [25]. While the latter possesses one short [2.472(2) Å] and one long [2.726(2) Å] Ag-Cl bond, the distances between the silver ion and the bridging chlorides of 1 [2.554(2) and 2.598(2) Å] show only little divergence. The two Ir-Cl bonds are also comparable in length, 2.375(3) and 2.385(2) Å, and only slightly shorter than those of $[(\eta^4 1,5-C_8H_{12}$ $2Ir_2(\mu-Cl)_2$, 2.399(5) and 2.400(5) Å [29]. Although the $Ir(\mu-Cl)_2Ag$ unit is folded with an angle between the normals to the two MCl₂ planes of 24.4°, this deviation from planarity is much less than that in the bent structure of the starting homodimer, where the dihedral angle between the two IrCl₂ planes is 86° [29]. The l.s.q planes spanned by the tolyl and the phenylene ring of the biphenyl group are almost orthogonal to each other, the value of the associated dihedral angle being 89.2°. Such substantial rotation of the two aromatic systems with respect to each other could facilitate π -bonding between the terminal ring and the d¹⁰ metal center Ag^I similar to that observed for a number of structurally characterized complexes where bulky t-Bu₂Pbiaryl or Cy₂Pbiaryl ligands are linked to d¹⁰-Pd⁰ [30–32]. These palladium compounds typically feature η^1 - and/or η^2 -contacts of 2.298–2.676 Å between the central metal and, respectively, the ipso- and ortho-carbon atoms of the remote ring. The corresponding distances between the Ag^I ion and the aromatic system

roofing the $Ir^{I}(\mu-Cl)_{2}Ag^{I}$ bridge of 1 range from 2.921(7) to 3.188(7) Å, which suggests that there are no obvious d^{10} -metal–arene interactions in the compound studied in this work.

The phosphonium tetrafluoridoborate $[t-Bu_2P(H)biph-$ ^{Me}] BF_4 (3) which crystallized as an accompanying product from the mother liquors of 1 was identified by its ¹H and ³¹P NMR data (see Section 2) and a complete X-ray structure analysis. The structure determination revealed the presence of $P-H\cdots F$ hydrogen-bonded ion pairs consisting of threefold rotationally disordered BF_4^{-} anions and [t- $Bu_2P(H)biph^{Me}$ cations having twofold disordered tolyl groups in their biphenyl residues (Fig. 2). P–C bond lengths and C-P-C angles compare favorably to those previously measured for the phosphonium ions of the compound [t- $Bu_2P(H)Ph_{3}[Zr_6Cl_{18}H_5]$ [33]. This includes the *t*-Bu-P-Bu-t angles which in both cations are expanded to 117.4° due to steric hindrance between the two bulky substituents. In the biphenyl unit, the disordered tolyl rings are rotated with respect to the phenylene group by 72.4° and 76.2° .

3.2. $[(\eta^4 - 1, 5 - C_8 H_{12}) Ir(2 - t - Bu_2 P C_6 H_3 C_6 H_4 M e^{-2' - \kappa} C^6, \kappa P)]$ (2)

If the diiridium complex $[(\eta^{4}-1,5-C_8H_{12})_2Ir_2(\mu-Cl)_2]$ was combined first with 2 equiv. of AgBF₄ and then with 4 equiv. of the *t*-Bu₂Pbiph^{Me} ligand, a red product was obtained which elemental analysis and spectroscopic data confirmed to be cyclometalated $[(\eta^{4}-1,5-C_8H_{12})Ir(t-Bu_2P-biph^{Me}-H^+)]$ (2); Scheme 2. Again, the phosphonium salt $[t-Bu_2P(H)biph^{Me}]BF_4$ (3) was observed as an accompanying product of the reaction.



Fig. 2. A perspective view of the $[t-Bu_2P(H)biph^{Me}]BF_4$ ion pair (3) showing the threefold rotational disorder of the BF_4^- ion about the B1–F1 bond and the twofold disorder of the terminal ring of the biphenyl residue; carbon-bonded hydrogen atoms are omitted for clarity; selected bond lengths (Å) and angles (°): P1–C1, 1.831(8); P1–C5, 1.856(9); P1–C9, 1.791(8). C1–P1–C5, 117.4(4); C1–P1–C9, 109.3(4); C5–P1–C9, 112.7(4). Hydrogen bonding interaction as D–H, H···A, D···A, D–H···A (Å, °): P–H···F2a, 1.00, 2.49, 3.37(1), 145.5.



The presence of a direct metal-to-aryl linkage in 2, which could not be obtained as single crystals, was evidenced from the ${}^{13}C{}^{1}H{}$ spectrum, where the ${}^{13}C$ resonance of the metal-bound carbon atom displays the significant downfield shift ($\delta = 160.46$, d, J(P,C) = 9.8 Hz) known to be diagnostic of phenyl carbon coordination to a transition metal [34]. It is well established that gem-di-tertbutyl groups on phosphorus ligands assist the formation of four- to six-membered metalacycles by enthalpy, entropy, and conformational effects which are similar to those of the gem-dialkyl or "Thorpe-Ingold" effect on ring closure reactions in organic chemistry [35]. In principle, the sterically promoted internal metalation of the Ir-coordinated t-Bu₂Pbiph^{Me} ligand could involve orthometalation of the phenylene ring forming a strained four-membered ring as indicated in Scheme 2 and known from [{Pd(2-t-Bu₂PC₆H₃C₆H₄Me-2'- κC^6 , κP }₂(μ -Cl)₂] [32b]; alternatively, the activation of a C-H bond on the remote tolyl group could give an unstrained six-membered metalacycle, which one might anticipate to be more stable (see Scheme 3) and, hence, has been proposed for the palladacyclic structure of $[Pd(2-t-Bu_2PC_6H_4C_6H_4-\kappa C^{6'},\kappa P)(O_2CMe)]$ [36]. Cyclometalated phosphines featuring four-membered rings show unusual highfield ³¹P resonances compared to their non-cyclometalated counterparts, whereas P donors incorporated in six-membered chelate rings give rise to slightly downfield-shifted ³¹P NMR signals [37]. The ³¹P nucleus of 2 resonates at $\delta = 10.7$, which is 10.4 ppm upfield from the chemical shift of the free ligand $(\delta = 21.1)$ albeit 23.8 ppm downfield from the ³¹P singlet of the structurally established four-membered ring complex $[{Pd(2-t-Bu_2PC_6H_3C_6H_4Me-2'-\kappa C^6,\kappa P)}_2(\mu-Cl)_2] (\delta = -13.1)$ [32b]. Relating the 31 P chemical shift observed for 2 to that of complex 1 ($\delta = 43.0$), where the phosphine is coordinated to a silver atom, an upfield shift of 32.3 ppm is revealed. This comes close to the differences in the shift values of the structurally related phosphine t-Bu₂PPh in



4-membered iridacycle **2-4***r 6-membered iridacycle* **2-6***r*

the Ir^{III} complex [IrH(*t*-Bu₂PC₆H₄- $\kappa C^2, \kappa P$)(*t*-Bu₂PPh)] [B{3,5- (F₃C)₂C₆H₃}], $\delta = 39.7$ and 6.2 [38], pointing to a ³¹P upfield shift of 33.5 ppm upon the incorporation of the di-*t*-butylphosphino group into a four-membered orthometalated iridaheterocycle. Unfortunately, no coordination compounds of iridium are known which bear a cyclometalated *t*-Bu₂Pbiph^{Me} ligand together with a noncyclometalated one and thus could serve to make more than a rough estimate of the changes in its shift values Δ_{coord} and Δ_{ring} upon coordination and formation of a four-membered (or six-membered) iridacyclic chelate complex. To solve these ambiguities, quantum chemical studies aiming at the computation of the relative stabilities of the two isomers **2-4r** and **2-6r** depicted in Scheme 3 were carried out.

3.3. DFT studies

Independent of the quantum chemical method employed, the four-membered ring system 2-4r is seen to be favored over **2-6r** under all conditions studied. Thus, B3LYP/LANL2DZp and BP86/LACVP* revealed 2-4r to be, respectively, 15.2 and 15.0 kcal/mol more stable than the six-membered P,C chelate **2-6r**. A somewhat smaller energy gap of 11.7 kcal/mol between the two isomers was calculated applying LMP2/LACVP*. The influence of solvent effects was investigated by means of IPCM single point calculations [B3LYP(IPCM)/LANL2DZp//B3LYP/ LANL2DZp] which still showed 2-4r to be preferred by 9.5 kcal/mol. Similar to the values obtained with B3LYP/ LANL2DZp and BP86/LACVP* in the gas phase, BP86/ LACVP* optimization of the two structures within the SCRF water model implemented in JAGUAR 6.5 led to an energy difference of 15.6 kcal/mol in favor of the fourmembered metalaheterocycle without resulting in significant structural changes.

Comparison of the structural parameters calculated for the two isomers revealed virtually identical bond lengths and angles (in particular, Ir–P, Ir–C, and P–C_{aryl} distances

Table 1			
Calculated	bond lengths (Å) an	d angles (°) for 2	2-4r and 2-6r

e	· /	e			
Method ^a	Ir–P	Ir–C	P-Caryl	C–Ir–P	Ir–P–C
Isomer 2-4r					
B3LYP/LANL2DZp	2.41	2.06	1.87	67.8	83.6
BP86/LACVP*	2.39	2.06	1.86	68.0	84.4
LMP2//LACVP*	2.39	2.08	1.86	67.3	84.5
"Water"	2.40	2.06	1.87	68.2	83.9
Isomer 2-6r					
B3LYP/LANL2DZp	2.45	2.09	1.89	82.4	99.8
BP86/LACVP*	2.43	2.08	1.88	82.6	101.2
LMP2//LACVP*	2.54	2.11	1.88	82.5	99.3
"Water"	2.43	2.08	1.88	82.7	100.9

^a B3LYP/LANL2DZp: B3LYP/LANL2DZp + ZPE(B3LYP/LANL2-DZp); BP86/LACVP*: BP86/LACVP* + ZPE(B3LYP/LANL2DZp); LMP2/LACVP*: LMP2/LACVP* + ZPE(B3LYP/LANL2DZp); "Water": BP86(water)/LACVP* + ZPE(B3LYP/LANL2DZp).



Fig. 3. Calculated (B3LYP/LANL2DZp) structures of 2-4r and 2-6r; hydrogen atoms are omitted for clarity.

as well as C-Ir-P and Ir-P-C angles) irrespective of the method used – except for 2-6r, where the LMP2/LACVP* results indicate elongated Ir-P and Ir-C bonds (Table 1). Both the Ir-P and the Ir-C distances obtained for the energetically preferred structure 2-4r (average values, 2.39 and 2.06 Å) are in good agreement with those previously measured by X-ray crystallography for a family of orthometalated iridium(I) complexes $[L_2Ir{R_2PC_6H_4-\kappa C^2,\kappa P} (R_2PPh)$] (L = C₂H₄, CO; R = Ph, *i*-Pr), where d(Ir-P) =2.370–2.400 Å and d(Ir-C) = 2.070-2.141 Å [39]. The very same applies for the Ir-P-C valence angles varying between 83.7° and 85.7° in the latter compounds and averaging out at 84.1° for 2-4r. As no C-Ir-P data are available for the structurally established four-membered iridaheterocycles $[L_2Ir{R_2PC_6H_4-\kappa C^2,\kappa P}(R_2PPh)]$ [27,39], we note that the average value of 67.8° calculated for $[(\eta^4-1,5 C_8H_{12}$ Ir(2-*t*-Bu₂PC₆H₃C₆H₄Me-2- κ C⁶, κ P)] compares favorably with the acute C-Pd-P and C-Pt-P angles of the orthometalated Pd^{II} and Pt^{II} complexes [{Pd(2-t-Bu₂PC₆H₃C₆H₄Me-2'- κC^6 , κP }₂(μ -Cl)₂] [32b] and trans- $[Pt(ONO_2)(t-Bu_2PC_6H_4-\kappa C^2,\kappa P)(t-Bu_2PPh)]$ [40], which were measured as 68.7° and 69.7°, respectively.

The reason for the preferred formation of the structure with the four-membered chelate ring becomes obvious from Fig. 3, where rotation of the remote tolyl group about the aryl-aryl linkage of **2-4r** is not constrained by the formation of an iridium-carbon bond. As a result, the tolyl ring lies almost perpendicular to the phenylene plane, which avoids steric overcrowding through collision with the *tert*-butyl groups. In the less favored six-membered ring isomer **2-6r**, on the other hand, coordination of the tolyl residue to the metal prevents the two aromatic rings from rotating about their connecting C–C single bond, such that they are now inclined to each other at an angle of only 50.3°. As a consequence, the phenylene *ortho* C–H bond is forced to adopt an orientation which results in destabilizing steric clash with the *tert*-butyl substituents, the shortest repulsive C–H···H–C contact being 1.88 Å.

4. Concluding remarks

An investigation of the reaction of the Buchwald phosphine t-Bu₂Pbiph^{Me} with $[(\eta^4-1,5-C_8H_{12})_2Ir_2(\mu-Cl)_2]$ has shown that, in the presence of Ag^+ ions, the phosphine coordinates to silver producing heterobimetallic [$(\eta^4-1,5 C_8H_{12}$]Ir(μ -Cl)₂Ag(*t*-Bu₂Pbiph^{Me})]. Precipitation of the bridging chlorido ligands prior to the addition of the phosphine results in the chelation of the remaining (η^4 -1,5- C_8H_{12})Ir⁺ complex fragment through Ir–P coordination and C-H metalation. Detailed DFT calculations indicate that the phosphine ligand of the cyclometalated product $[(\eta^4-1,5-C_8H_{12})Ir(t-Bu_2Pbiph^{Me}-H^+)]$ forms a sterically uncongested albeit strained four-membered iridaheterocycle through orthometalation, i.e., $[(\eta^4-1,5-C_8H_{12})Ir(2-t Bu_2PC_6H_3C_6H_4Me-2'-\kappa C^6,\kappa P$], rather than an unstrained but sterically encumbered six-membered chelate structure through C-H activation on the remote phenyl ring.

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Appendix A. Supplementary material

CCDC 657023 and 657024 contain the supplementary crystallographic data for **1** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.11.006.

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