Synthesis and Characterization of Chiral Bis(aminato)iridate(I) and Aminato-Bridged Iridium(I) Complexes

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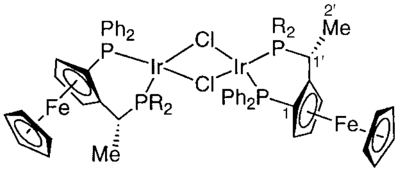
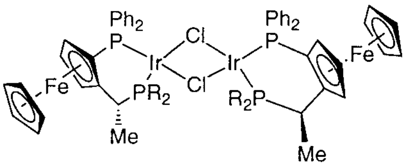
The two dinuclear Ir^I complexes [$Ir_2(\mu\text{-}Cl)_2$ {(*R*)-(*S*)-PPF-PPh_2}$_2$] (**1**; (*R*)-(*S*)-PPF-PPh_2 = (*S*)-1-(diphenylphosphino)-2-[(*R*)-1-(diphenylphosphino)ethyl]ferrocene and [$Ir_2(\mu\text{-}Cl)_2${(*R*)-binap}$_2$] (**3**; (*R*)-binap = (*R*)-[1,1′-binaphthalene]-2,2′-diylbis[diphenylphosphine]) smoothly react with 4 equiv. of the lithium salt of aniline to afford the new bis(anilido)iridate(I) (= bis(benzenaminato)iridate(1-)) complexes Li[Ir(NHPh)$_2${(*R*)-(*S*)-PPF-PPh_2}] (**4**) and Li[Ir(NHPh)$_2${(*R*)-binap}] (**5**), respectively. The anionic complexes **4** and **5** react upon protonolysis to give the dinuclear aminato-bridged derivatives [$Ir_2(\mu\text{-}NHPh)_2${(*R*)-(*S*)-PPF-PPh_2}$_2$] (**6**) and [$Ir_2(\mu\text{-}NHPh)_2${(*R*)-binap}$_2$] (**7**), which were characterized by X-ray crystallography. None of the new complexes **4**–**7** shows catalytic activity in the hydroamination of olefins.

1. Introduction. – Late-transition-metal complexes with aminato ligands evoke growing interest [1]. They are believed to be key intermediates in catalytic imine hydrogenation [2], olefin hydroamination [3], and Pd- [4] and Ni-catalyzed [5] aminations of aryl halides. The generally accepted explanation for the high reactivity of aminato(late transition metal) complexes is the energetic mismatch of the 'soft' metal orbitals and 'hard' orbitals of the aminato ligands [6], although this has lately been somewhat questioned [7]. Of the two or more accessible oxidation states in the organometallic chemistry of late transition metals, almost exclusively the higher oxidation states are preferred in conjunction with aminato (and alkoxo [8]) ligands. This again can be rationalized by the greater 'hardness' of the higher oxidation states and thus by the better match with the 'hard' R_2N ligands. A growing number of aminato (late transition metal) complexes have been structurally characterized [9]. However, corresponding derivatives in low oxidation states are rare [10], and very few have been structurally characterized [11]. Due to our interest in performing enantioselective transformations of organic substrates, in particular those involving C–N bond formation, we were looking for complexes that could act as chiral sources of reactive N-nucleophiles. Thus, our goal was the isolation and characterization of reactive aminatoiridium complexes that could be intermediates or precursors of (*1*) our Ir-catalyzed enantioselective hydroamination [3a], and (*2*) that could function as N-analogs of cuprates. To the best of our knowledge, only one chiral, enantiomerically pure aminato complex has been reported so far [12]. We describe herein the synthesis and structural characterization of novel chiral aminatoiridates and aminato-bridged iridium(I) complexes and the, however unsuccessful, attempts to use them in hydroamination and 1,4-N-additions.

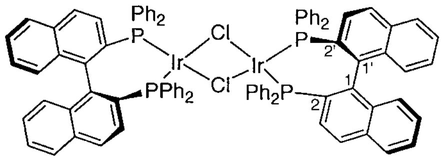
2. Results and Discussion. – 2.1. *Synthesis and Reactivity.* One way to form aminatometal compounds is to oxidatively add an N–H bond to an electron-rich metal center [9g–h] [13]. The new class of dinuclear chloro-bridged diphosphineiridium complexes **1**–**3** [3a][14] are quite active olefin hydroamination catalysts in the presence of co-catalytic amounts of fluoride [3a], are electron-rich, and coordinatively unsaturated. This accounts for their propensity to oxidatively activate N–H, as well as C–H and O–H bonds [15].



trans-**1** R=Ph
trans-**2** R=cyclohexyl



cis-**1** R=Ph
cis-**2** R=cyclohexyl

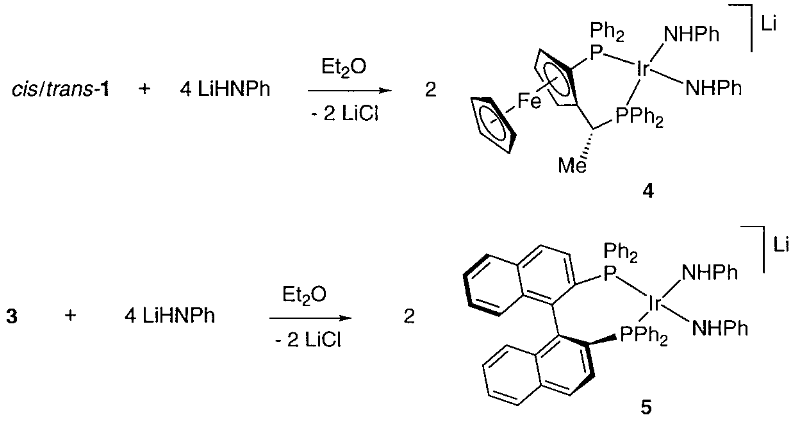


3 ([IrCl{(*S*)-binap}]$_2$)

First attempts to metathetically exchange the chloro bridges of either dinuclear complexes **1** or **3** (chosen as examples for complexes containing C_1- and C_2-symmetric ligands, respectively) with stoichiometric amounts of the lithium salt of aniline (LiNHPh) failed, affording inseparable mixtures of aminato complexes regardless of the reaction conditions (solvent, temperature, and the way of adding LiNHPh). However, when 2 equiv. of LiNHPh in Et_2O were added to an orange Et_2O slurry of the dinuclear Ir complex **1** (*cis*/*trans* mixture), the formation of a dark solution, along with a finely divided precipitate of LiCl, was observed. The ^{31}P-NMR (2 *d* at 4.7 and 41.1 ppm (J(P,P) = 23 Hz)), and the ^{1}H-NMR spectra (NH at 2.55 and 2.72 ppm) of the solution are in agreement with the formulation of compound **4** and with the reaction stoichiometry of *Scheme 1*. Analogously, **3** gave the aminatoiridate complex **5** in excellent yields. The C_2 symmetry of the (*R*)-[1,1′-binaphthalene]-2,2′-diylbis[diphenylphosphine] ((*R*)-binap) ligand of **5** is reflected in its ^{31}P- and ^{1}H-NMR spectra (*s* at 17.1 ppm (P-atoms) and br. *s* at 2.06 ppm (2 NH), resp.).

To the best of our knowledge, **4** and **5** represent the first characterized aminatometallate complexes of late transition metals. Due to their high solubility even in aliphatic solvents such as pentane, we were unable to crystallize these complexes (*vide infra*). The Li cation is probably very effectively complexed by one or more [Ir(aminato)] units. Solvent molecules such as THF and Et_2O cannot be removed completely under vacuum, but no NMR shifts of the solvent molecules due to coordination are observed. However, even the Li$^+$-specific crown ether [12]crown-4 did not separate the ion pairs. Low-temperature 2D-NMR experiments aimed at

Scheme 1

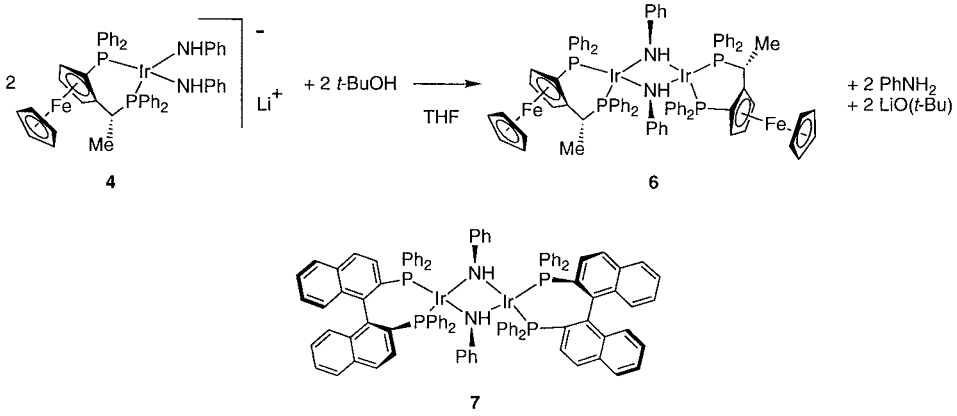


elucidating the structures of **4** and **5**, with emphasis on the location of the Li cation were not conclusive. Complexes **4** and **5** proved to be thermally robust in the solid state. Prolonged heating (373 K for 2.5 d) did not cause any decomposition. These compounds were stable in THF for weeks, whereas in benzene, decomposition took place within days at room temperature.

Complexes **4** and **5** resemble those of the type $[Ir(PP)R_2]Li$, where PP is a bulky diphosphine and R is an aryl or alkyl group [16]. For such complexes, a key stabilizing role was attributed to the Li cation. An analogy of such anionic Ir and Rh compounds to cuprates was suggested. It was, therefore, of interest to probe the reactivity of compounds **4** and **5** towards α,β-unsaturated ketones in view of a potential asymmetric 1,4-N-addition. When **4** was treated with 1 equiv. of cyclopent-2-en-1-one in THF, we observed the immediate formation of a bright yellow precipitate. The ^{1}H-NMR spectrum revealed that all of the cyclopentenone had been consumed, that *ca.* 0.5 equiv. of aniline was formed, and that half of the iridate complex **4** had not reacted. Another equiv. of cyclopentenone drove the reaction to completion. None of the starting material **4** was left in solution, and 1 equiv. of aniline was detected along with unidentified organic products (most probably aldol-condensation products). Furthermore, when **4** was reacted with linear enones such as (*E*)-4-phenylpent-3-en-2-one and (*E*)-1,4-diphenylpent-3-en-2-one, the formation of aniline was observed as well, but no other clean reaction products could be identified. Based on the observed stoichiometry of the former reaction, we formulated the new Ir-containing product as the dinuclear bis(aminato)-bridged complex **6**. Finally, a slight excess of dry *t*-BuOH cleanly protonated the aminato functions of **4** (*Scheme 2*), making it the reagent of choice for the transformation **4** → **6** and allowing for the isolation of the pure material. Compound **6** displayed low solubility in THF but not so in benzene, and the ^{31}P-NMR spectrum was consistent with its structure (2 br. *d* at 0.6 and 24.7 ppm ($J(P,P') = 30$; possible long-range coupling not resolved); the NH protons could not be identified).

Attempts to use **6**, its precursor **4**, and **5** as catalysts for the model addition of aniline to trinorbornene failed. The observation that **4**–**6** did not react with

Scheme 2



trinorbornene even under forcing conditions (100°) is in agreement with the finding that LiNHPh acts as a poison to catalysts **1**–**3** in the addition reaction of aniline to trinorbornene. The reluctance of these (benzeneaminato)iridium derivatives to insert trinorbornene may be explained by their inability to electrophilically activate the olefin. This is in contrast to the corresponding (benzeneaminato)iridium(III) complexes [3a], and to the chloro-bridged Ir^I complexes **1**–**3** [3a]. The aminato-bridged iridium(I) species **6** was also unreactive towards *t*-BuOH and cyclopent-2-en-1-one, whereas reactions occurred with phenol and benzamide leading, however, to intractable mixtures. Finally, LiNHPh did not break the aminato-bridges of **6** in an attempt to form the aminatoiridate complex **4**.

Unfortunately, cyclopent-2-en-1-one did not react in a clean way with **5**, although again free aniline was detected. Protonolysis of **5** with 1 equiv. of *t*-BuOH showed the formation of at least two products after a reaction time of *ca.* 24 h at room temperature, as ascertained by ^{31}P-NMR spectroscopy (2 broad signals at 15.7 and 19.0 ppm and a broad *AB* system at 13.6 and 17.6 ppm (with only J(P,P) = 26.7 Hz resolved)). We speculate that these different species correspond to configurational isomers of **7**, differing in the relative orientation of the *N*-phenyl groups. All attempts to obtain the expected compound **7** in pure form from **5** and *t*-BuOH failed. Thus, this derivative could not be characterized properly. However, in an attempt to grow single crystals of the precursor **5** from a (D_6)benzene/Et_2O solution, we were fortunate enough to obtain few crystals of **7** suitable for an X-ray analysis (*vide infra*). Obviously, the slow and incomplete formation of **7** is due to the instability of **5** in benzene, but could also be due to the presence of adventitious traces of water.

2.2. *Solid-State Structures of* **6** *and* **7**. To unambiguously ascertain the exact structure of complexes **6** and **7**, X-ray diffraction studies were carried out. Single crystals of **6** and **7** were grown from (D_6)benzene/Et_2O and benzene/pentane, respectively. Crystal and data-collection parameters are summarized in *Table 1* and important bond distances and angles in *Table 2*. *Figs. 1* and *2* show ORTEP views of the two dinuclear complexes.

Table 1. *Experimental Data for the X-Ray-Diffraction Study of* **6** *and* **7**

	6 · Pentane	**7** · 2 C_6D_6
Empirical formula	$C_{84}H_{76}Fe_2Ir_2N_2P_4 \cdot C_5H_{12}$	$C_{100}H_{76}Ir_2N_2P_4 \cdot 2C_6D_6$
M_r	1805.74	1982.2
Crystal dimensions/mm	0.20 × 0.20 × 0.10	0.38 × 0.34 × 0.24
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)
Data collection T/K	293	233
a/Å	14.3204(5)	15.8300(10)
b/Å	20.3430(9)	17.0838(11)
c/Å	25.9077(10)	17.9364(11)
β/deg		98.3730(10)
V/Å^3	7547.4(5)	4708.0(5)
Z	4	2
ρ (calc.)/g · cm^{-3}	1.578	1.390
µ/mm^{-1}	0.4024	0.2941
F(000)	3560	1976
Radiation	MoK_α, λ 0.71073 Å	MoK_α, λ 0.71073 Å
2θ range/deg	1.27 – 24.71	1.15 – 27.39
Scan type	ω	ω
Measured reflections	42460	25609
Independent reflections	12876 (R(int) = 0.0822)	15593 (R(int) = 0.0344)
Observed reflections (n)[a])	9818	12728
Abs. correction	empirical (SADABS)	empirical (SADABS)
Quantity minimized	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$
Parameters refined (p)	868	1058
wR_2 ($I > 2.0\sigma(I)$)[b])	0.0837	0.1078
$R1$ ($I > 2.0\sigma(I)$)[c])	0.0439	0.0448
G.o.f. on F^2[d])	1.009	1.015
Data-to-parameters ratio	14.8	14.3

[a]) ($|F_o^2| > 4.0\sigma(|F|^2)$). [b]) $wR_2 = [\sigma(w(F_o^2 - F_c^2)^2]/\sigma[w(F_o^2)^2]^{1/2}$. [c]) $R_1 = \sigma\,||F_o| - |F_c||/\sigma|F_o|$. [d]) G.o.f. = S = $[\sigma(w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

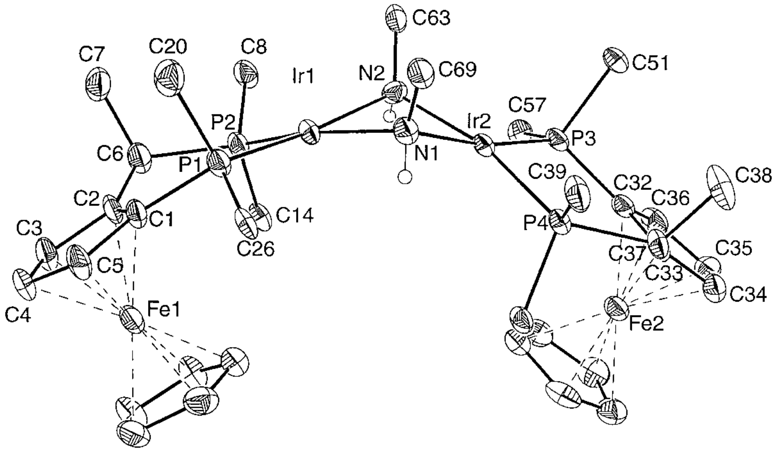


Fig. 1. *ORTEP View of* **6**. Ellipsoids are drawn at the 30% probability level. For clarity, only the C_{ipso} atoms of the Ph groups are shown.

Table 2. *Selected Bond Distances* [Å][a]) *and Angles* [deg][a]) *for* **6** *and* **7**

	6	**7**
Bond distances		
Ir(1)–N(1)	2.173(8)	2.166(7)
Ir(1)–N(2)	2.154(7)	2.128(8)
Ir(1)–P(1)	2.210(3)	2.229(3)
Ir(1)–P(2)	2.206(3)	2.213(3)
Ir(1)–Ir(2)	3.1763(5)	3.0215(5)
Ir(2)–N(1)	2.132(8)	2.168(7)
Ir(2)–N(2)	2.166(7)	2.156(7)
Ir(2)–P(3)	2.192(3)	2.214(2)
Ir(2)–P(4)	2.209(2)	2.198(2)
N(1)–C(69) [N(1)–C(89)][b])	1.397(12)	1.435(12)
N(2)–C(63) [N(2)–C(95)][b])	1.429(12)	1.424(13)
Bond angles		
N(1)–Ir(1)–N(2)	78.1(3)	78.0(3)
N(1)–Ir(1)–P(1)	97.0(2)	94.0(2)
P(1)–Ir(1)–P(2)	93.16(10)	89.08(10)
N(1)–Ir(2)–N(2)	78.7(2)	77.4(3)
C(69)–N(1)–Ir(2)	119.0(6)	117.7(5)
C(69)–N(1)–Ir(1)	124.8(6)	121.7(7)
P(3)–Ir(2)–P(4)	92.46(9)	89.77(9)
N(1)–Ir(2)–P(4)	93.0(2)	174.2(2)
N(1)–Ir(2)–P(3)	170.5(2)	96.0(2)
Ir(1)–N(1)–Ir(2)	95.1(3)	88.4(2)
Ir(1)–N(2)–Ir(2)	94.7(3)	89.7(3)
C(63)–N(2)–Ir(1) [C(95)–N(2)–Ir(1)][b])	119.2(6)	120.6(6)
C(63)–N(2)–Ir(2) [C(95)–N(2)–Ir(2)][b])	122.5(6)	121.5(6)

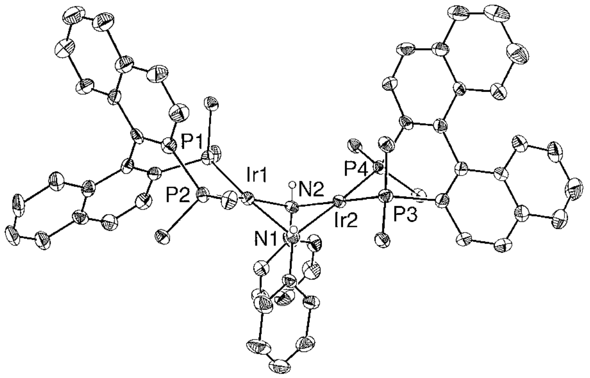


Fig. 2. *ORTEP View of* **7**. Ellipsoids are drawn at the 30% probability level. For clarity, only the C_{ipso} atoms of the Ph groups at the P-atoms are shown.

With respect to the two diphosphine ligand moieties, complex **6** displays a *trans* configuration. The core of the dinuclear complex is butterfly-shaped with an angle of 36.3° between the two different Ir–N–N planes [17]. The square-planar coordination environment of both Ir-atoms is distorted. The angles between the planes defined by the Ir-atoms and the two N-atoms, and Ir- and the two P-atoms are 13.7° for Ir(1) and 11.5° for Ir(2). The aminato ligands occupy bridging positions with the Ph groups oriented on the same convex side of the bent Ir_2N_2 ring. The relative configuration of the aminato fragments may, therefore, be labelled as '*syn-exo*'. The Me groups at the stereogenic C-atoms are placed well above the plane of the substituted cyclopentadienyl (Cp) ring, as shown by the diagnostic torsion angles of 100.2° for C(3)–C(2)–C(6)–C(7) and 91.0° for C(34)–C(33)–C(37)–C(38), indicative of an anomalous ligand conformation. In fact, this is in contrast to most structurally characterized complexes containing phosphino-substituted ferrocenes of the *Josiphos* type, for which the corresponding torsion angles are in the range – 15° to – 20° [18].

An interesting structural feature is the π-stacking of the Ph groups of the aminato ligands and the axial Ph groups at P(2) and P(4). The stacking distances between the C_{ipso} atoms are *ca.* 3.3 Å and are shown in the schematic view along the molecular C_2-axis approximately orthogonal to the N(1)–N(2) and the Ir(1)–Ir(2) vectors, as shown in *Fig. 3*. This π-stacking could be responsible for the high selectivity in the formation of a single isomer (and conformer) during the protonation of **4** in THF.

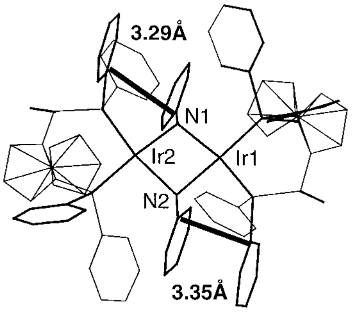


Fig. 3. *Schematic representation of* **6** *projected along the approximate molecular* C_2 *axis showing phenyl-phenyl stacking interactions*

Dinuclear complex **7** also displays a '*syn-exo*'-arrangement of the aminato ligands. Analogously to **6**, the core of the complex is butterfly-shaped, with an angle of 51.6° between the Ir–N–N planes. This value is comparable to that found in the chloro-bridged analogue **3** (54°) [3a]. The Ir(1)–Ir(2) distance of 3.02 Å is shorter than in **3** (3.322 Å) and in **6** (3.18 Å). A significant metal-metal interaction is, however, not to be assumed. The square-planar coordination environment of the Ir-atoms is significantly less distorted than in **3** and **6**. In fact, the interplanar angles between the Ir–N–N and Ir–P–P planes are 3.3° and 4° for the two Ir-atoms Ir(1) and Ir(2), respectively. The dihedral angles between the two pairs of naphthalene planes are 74.1 and 71.5°, respectively. There is no evidence for π-stacking interactions between the axial Ph groups at the phosphine moieties and the Ph groups of the aminato ligands.

3. Conclusion. – We have shown that dinuclear, chloro-bridged diphosphineiridium complexes cleanly react with 4 equiv. of LiNHPh to afford aminatoiridate(I) derivatives that may be isolated as stable Li-salts. This new class of anionic aminato-(late transition metal) complexes are to be considered as 'hard' nucleophiles and were shown to undergo protonolysis by relatively weak acids. This led to the discovery of rare, dinuclear aminato-bridged diphosphineiridium(I) complexes. In contrast to the analogous chloro-bridged dinuclear Ir(I) compounds, these aminato-bridged species displayed much lower reactivity towards N–H and O–H bonds. Furthermore, these complexes were not suitable catalyst precursors for the addition of aniline across the double bond of trinorbornene. This indirectly indicates that the co-catalytic effect of fluoride observed for this reaction in the presence of **1**–**3** is not likely to be explained by fluoride acting as a *Brønsted* base.

We thank *Michael Wörle*, ETH Zürich, for the X-ray crystallographic studies of **6** and **7**. *R.D.* thanks *Novartis Ltd.*, Basel, for financial support.

Experimental Part

General. General experimental considerations have been detailed previously [15].

*Lithium Bis(benzenaminato){(*S*)-1-(diphenylphosphino-κ*P*)-2-[(*R*)-1-(diphenylphosphino-κ*P*)ethyl]ferrocene}iridate(−1)* (Li[Ir(NHPh)$_2${(*R*)-(*S*)-PPF-PPh$_2$}]; **4**). To a bright orange Et$_2$O (8 ml) slurry of [Ir$_2$(*μ*-Cl)$_2${(*R*)-(*S*)-PPF-PPh$_2$}] · 0.2 C$_5$H$_{12}$ (*cis*/*trans*-**1**; 662.8 mg, 0.4055 mmol), a greenish Et$_2$O (8 ml) soln. of LiNHPh (166.6 mg, 1.625 mmol) was added. Stirring at r.t. for 48 h afforded a white fine precipitate and a dark brownish-red supernatant. The precipitate was allowed to settle. The supernatant was then decanted, centrifuged (4000 rpm, 1 h), and again decanted into a *Schlenk* tube, where the volatiles were evaporated and the dark red powder dried *in vacuo:* 762 mg (91%) of **4**. ^{1}H-NMR (250.13 MHz, (D$_8$)THF): 1.17 (*dd*, $J = 7, 6$, 3 H); 2.55 (br. *s*, 1 H); 2.72 (br. *s*, 1 H); 3.39 (*s*, 5 H); 3.60–3.95 (overlapping *m*, 3 H); 4.16 (br. *s*, 1 H); 5.7–7.5 (br. overlapping *m*, 26 H); 8.07 (br. *t*, $J = 8$, 2 H); 8.38 (*m*, 2 H); signals of 1 equiv. of Et$_2$O. ^{31}P{^{1}H}-NMR (101.25 MHz, (D$_8$)THF): 4.66 (*d*, $J = 23.3$); 41.12 (*d*, $J = 23.3$). Anal. calc. for $C_{48}H_{44}FeIrLiN_2P_2 \cdot C_4H_{10}O$: C 60.06, H 5.23, N 2.69; found: C 60.41, H 5.09, N 2.77.

*Lithium Bis(benzenaminato){[1,1′-binaphthalene]-2,2′-diylbis[diphenylphosphine-κ*P*]}iridate(1−)* (Li[Ir(NHPh)$_2${(*R*)-binap}]; **5**). To a bright orange Et$_2$O (4 ml) slurry of [Ir$_2$(*μ*-Cl)$_2${(*R*)-binap}$_2$] (**3**; 370.0 mg, 0.2176 mmol), a greenish Et$_2$O (4 ml) soln. of LiNHPh (89.6 mg, 0.874 mmol) was added. The mixture was treated as described above for **4** affording 390 mg (90%) of **5**. ^{1}H-NMR (250.13 MHz, (D$_8$)THF): 2.06 (br. *s*, 2 H); 5.95 (br. *t*, $J = 7$, 2 H); 6.15–6.55 (*m*, 12 H); 6.72 (br. *t*, $J = 6$, 4 H); 7.07 (br. *t*, $J = 6$, 4 H); 7.05–7.09 (br. *m*, 2 H); 7.25–7.55 (*m*, 10 H); 7.71 (br. *t*, $J = 4$, 4 H); 7.85 (*m*, 4 H); signals of 0.5 equiv. of Et$_2$O. ^{31}P{^{1}H}-NMR (101.25 MHz, (D$_8$)THF): 17.05 (*s*). Anal. calc. for $C_{56}H_{44}IrLiN_2P_2 \cdot 0.5C_4H_{10}O$: C 66.78, H 4.73, N 2.69; found: C 66.92, H 5.01, N 2.92.

*Bis[μ-(benzenaminato)]bis{[(*S*)-1-(diphenylphosphino-κ*P*)-2-[(*R*)-1-(diphenylphosphino-κ*P*)ethyl]ferrocene}iridium(I)* ([Ir$_2$(*μ*-NHPh)$_2${(*R*)-(*S*)-PPF-PPh$_2$}$_2$]; **6**). *t*-BuOH (32 μl, *ca.* 0.34 mmol) was slowly added to a stirred, deep red THF soln. (2 ml) of **4** (306.8 mg, 0.295 mmol). A yellow precipitate formed immediately, and the mixture was stirred for 8 h. The mother liquor was decanted and the solid dissolved in benzene (10 ml), affording a red soln. that was centrifuged at 3000 rpm for 0.3 h. Decantation, concentration to 2 ml, and addition of Et$_2$O (8 ml) caused precipitation of a bright yellow solid. This mixture was stirred overnight and then centrifuged. The mother liquor was decanted and the yellow solid dried *in vacuo*, thereby turning orange (170 mg, 66%). The mother liquor was kept at 250 K for 2 weeks, yielding another crop of crystals (18 mg, 7%). ^{1}H-NMR (250.13 MHz, C$_6$D$_6$): 1.01 (br. *dd*, $J = 7, 6$, 6 H); 3.54–3.72 (br. *m*, 4 H); 3.76–3.99 (*m*, 4 H); 3.87 (*s*, 10 H); 6.46–7.50 (br. *m*, 38 H); 7.76 (br. *t*, $J = 7$, 4 H); 8.45 (br. *t*, $J = 7$, 4 H); 9.31 (br. *t*, $J = 7$, 4 H). ^{31}P{^{1}H}-NMR (101.25 MHz, C$_6$D$_6$): 0.6 (br. *d*, J(P,P) = 30); 24.7 (br. *d*, J(P,P′) = 30). Anal. calc. for $C_{42}H_{38}FeIrNP_2$: C 58.20, H 4.42, N 1.62; found: C 57.80, H 4.10, N 1.73.

X-Ray Crystal-Structure Analysis of **6** *and Bis[μ-(benzenaminato)]bis{(*R*)-[1,1′-binaphthalene]-2,2′-diylbis[diphenylphosphine-κ*P*]}iridium(I)* (**7**). Intensity data were collected at r.t. for **6** and at −40° for **7** on a *Siemens-Platform-CCD* (charge-coupled device) diffractometer. The program SMART (*Siemens Analytical X-Ray Systems Inc.*, Madison, USA) was used for the determination of the unit cells and for data collection. The data reductions were performed using SAINT (*Siemens Analytical X-Ray Systems Inc.*, Madison, USA). An empirical correction of the absorption was performed with SADABS (*G.M. Sheldrick*, University of Göttingen, Germany). The structures were solved and refined with the program SHELXS-96 [19] by direct methods. Least-squares methods with anisotropic displacement parameters for all non-H-atoms were used in the refinement of the complex molecules. However, the displacement parameters of the atoms in the solvent molecules were left isotropic (pentane in the case of **6** and C_6D_6 for **7**). All H-atom positions were placed in calculated positions (riding model) with isotropic parameters, fixed at 1.5 times U(eq) of the C-atom for the Me groups and 1.2 times U(eq) of the C-atom for all the other groups. Crystallographic data (excluding structure factors) for the structures reported in this paper have also been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication no. CCDC 133908 (**6**) and CCDC 133907 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk). Full ORTEP representations of **6** and **7** with complete atom-numbering schemes may be obtained from the authors upon request.

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