Synthesis of Bis(imino)aryl Iridium Pincer Complexes and Demonstration of Catalytic Hydrogen-Transfer Activity

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Monomeric iridium(III) dihalide complexes containing terdentate bis(imino)aryl ligands, synthesized through oxidative addition of 2-bromoisophthalaldimines RNC(Br)NR (R = Ph **1**, Mes **2**, *i*-Pr **3**, Me **4**) to $[IrCl(cod)]_2$ in the presence of NaBr to form $[(RNCNR)IrBr_2 \cdot solvent]$ (R = Ph **5**, Mes **6**, *i*-Pr **7**, Me **8**; solvent = MeCN; R = *i*-Pr **7a**; DMSO), are reported. The development of a synthetic route to the complexes is outlined, and full characterization of each member of the series is discussed. X-ray structures for **3** and **4** confirm the retention of the imino groups upon coordination to the metal center. An investigation into the catalytic activity of $[(PhNCNPh)IrBr_2 \cdot MeCN]$ (**5**) as a hydrogen-transfer reagent through the base-catalyzed transfer hydrogenation of ketones (1,3-diphenyl acetone and acetophenone) to alcohols at room temperature was undertaken. Preliminary results indicate that a catalytic species is generated, leading to reasonable conversions at room temperature.

Introduction

The organometallic chemistry of pincer ligand complexes [(ECE)M] where E = PR_2, SR, NR_2, and M = late transition/platinum group metal (i.e., Ru, Os, Ni, Pd, Pt, Rh, Ir, etc.) (Scheme 1), first described by Moulton and Shaw in 1976[1] for the di-*tert*-butylphosphino derivative, has been the focus of much research in the following 30 years. The diversity of complexes formed and their stability due to the presence of at least one C−M σ-bond supported by two *ortho,ortho*-chelated heteroatom groups has led to their application in a wide range of metal-catalyzed organic reactions[2−4] and, increasingly, in their use in materials science in self-assembled systems and as switches and sensors.[5,6]

The primary approach to the synthesis of the pincer complexes is through coordination of two donor atom groups and cyclometalation of a central $C(sp^2)$−H (Scheme 1: X = H) to a low oxidation state metal, thus forming a terdentate ligand complex. For E = N, amines, benzimidazoles, imidazoles, oxazolines, and pyridines have all been utilized as pincer ligands through this methodology, albeit with fewer examples than the P/S analogues. This is likely due to the lower M−N bond strength (compared to P−M and S−M bonds), inhibiting initial bidentate N,N coordination to the metal precursor.

The formation of non-heterocyclic bis(imino)aryl (alternatively referred to as isophthalaldimine, RNCNR) metal complexes via cyclometalation has received some attention in the literature. Examples reported include Mn(I), R = Cy; Pd(II), R = Cy,[8] R = Et, Bu, Oct, Tol,[9] R = tetrahydrofurfuryl,[10] R = Py;[11] and Pt(II), R = Py,[11] R = *t*-Bu, Cy, Bu, Bn, Ph.[12] Worthy of note is that use of palladium in particular leads to the preferential activation of the 4- and 6-positions of the aryl backbone (Chart 1A, C) as the kinetic product over the required 2-position (Chart 1B) with platinum analogues forming the required pincer complexes albeit in low yields (12−50%).

Scheme 1. General Scheme for the Formation of Pincer Complexes[7]

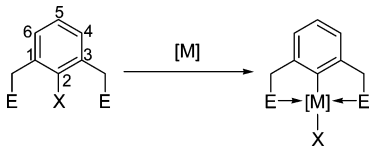
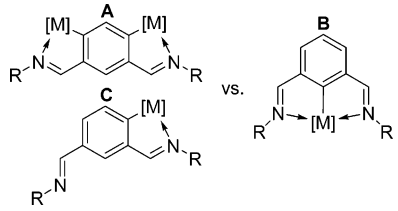


Chart 1. C−H Activation Sites for Non-heterocyclic 1,3-Bis(imino)aryl Ligands



High-yielding syntheses of the desired terdentate non-heterocyclic bis(imino)aryl metal complexes (Chart 1B) have been achieved through either oxidative addition of a $C(sp^2)$−X (X = Br, I) bond across a low oxidation state metal center (M = Pt(II): R = 2,6-diisopropylphenyl, 4-methoxyphenyl,[13] R = 2,6-dimethylphenyl;[14] Rh(III): R = Me, ^{i}Pr, ^{t}Bu[15]) or through dehydrative introduction of the imino groups to *trans*-(4-*tert*-butyl-2,6,diformylphenyl)chlorobis(triphenylphosphine)palladium (R = Cy, Bn, Ph[16]).

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(7) Numbering scheme used for all ligands and pincer complexes in this report.
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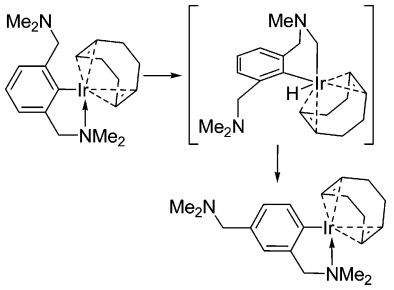
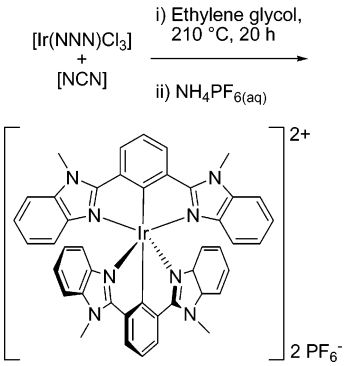
Scheme 2. Isomerization of Bis(dimethylamino)aryl Iridium(I) Complexes



Scheme 3[a]

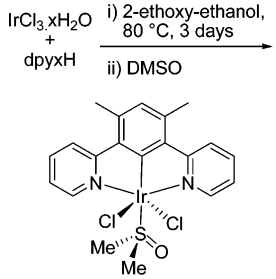


[a] NNN = 2,6-bis(1-methylbenzimidazol-2-yl)pyridine, NCN = 1,3-bis(1-methylbenzimidzol-2-yl)benzene.

To date, however, iridium [NCN] pincer complexes have proved elusive. Bis(amino)aryliridium(I) and -(III) complexes synthesized via the lithiation/ transmetalation route developed by van Koten[5] using $[IrCl(cod)]_2$ produce only the bidentate C,N-coordinated complexes.[17,18] The studies showed that steric hindrance from the diene prevented formation of the pincer complex through an associative substitution involving coordination of the second amine, with the reversible conversion of the 1,2-coordinated species to the 5,6-species proceeding via a hydridic intermediate (Scheme 2).

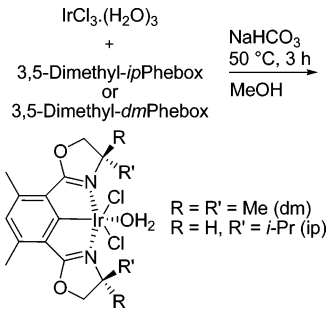
To our knowledge, there are only three groups of bis(N-donor)aryl terdentate iridium pincer complexes in the literature, all of which use heterocyclic N-donor ligands (N-donor = benzimidazolyl,[19] Scheme 3; pyridyl,[20,21] Scheme 4; oxazolinyl,[22] Scheme 5), studied for their photophysical and electrochemical properties (benzimidazolyl, pyridyl) and used in asymmetric catalysis (oxazolinyl). In particular, Williams reported the primary binding mode of 1,3-di(2-pyridyl)benzene (dpyxH) as bidentate, with cyclometalation at the 4- or 6-position occurring. This was overcome only by introducing blocking

Scheme 4[a]



[a] dpyxH = 1,3-di(2-pyridyl)benzene.

Scheme 5[a]



[a] Phebox = bis(oxazolinyl)phenyl.

substituents at these sites to afford the required tridentate pincer ligated complex as a dimeric species (also observed in the formation of the oxazolinyl complexes which did not proceed without the use of blocking substituents).[22] Dissolution in DMSO formed the monomeric complex $[Ir(dpyx)Cl_2(DMSO)]$. However, even this small number of examples is composed solely of N-heterocyclic species, with no simple iridium [NCN] pincer complexes composed of non-heterocyclic imines being reported.

The addition of non-hetorocyclic bis(imines) to the library of iridium(III) pincer complexes could prove significant especially considering the importance of iridium-containing pincer complexes in catalysis.[2−6] Thus far, a lack of reliable routes to these complexes has prevented in-depth studies of these processes. Therefore, we wish to report the first monomeric iridium(III) dihalide complexes containing terdentate bis(imino)-aryl ligands, synthesized through oxidative addition of 2-bromoisophthalaldimines to $[IrCl(cod)]_2$ under reasonably mild conditions.

Results and Discussion

Bis(*N*-phenyl)-2-bromoisophthalaldimine (**1**) and bis(*N*-mesityl)-2-bromoisophthalaldimine (**2**) were prepared in good yields (**1**: 85%; **2**: 87%) by condensation of the appropriate amine with 2-bromoisophthalaldehyde in either toluene or THF as per synthetic routes for R = *i*-Pr (**3**) and *t*-Bu (**4**).[15] **1** and **2** proved to be moderately air- and moisture-stable in the solid state, although partial hydrolysis of **1** to the monoaldimine 2-bromo-3-phenyliminomethyl benzaldehyde **1a** occurs slowly over time in ethanol (Scheme 6) (or more rapidly when passed through a silica column). Evidence for **1a** was obtained by mass spectrometry (EI) and also by ^{1}H NMR spectroscopy, with a d_1-chloroform solution revealing the presence of a mixture of the mono- and bis(imino) species.

Preliminary work on the formation of Rh(III) and Ir(III) pincer compounds with the two new ligands **1** and **2** was carried out using the same conditions and stoichiometries as those of

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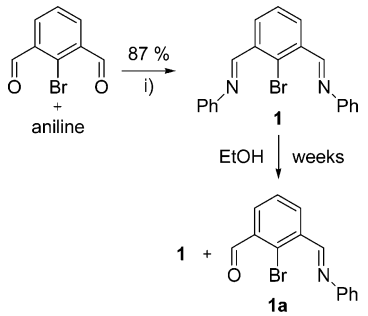
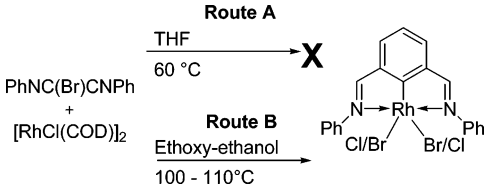
Scheme 6[a]



[a] (i) Toluene or THF, 60 °C, 2−4 h, nitrogen atmosphere.

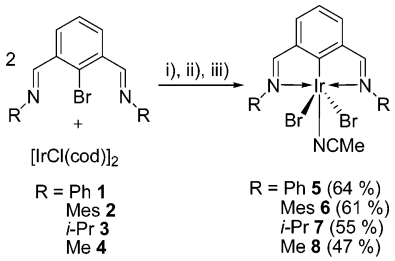
Scheme 7. Synthetic Route to Rhodium(III) [NCN] Complexes



Elsevier et al.[15] to form the bis(imino)aryl rhodium(III) dihalide complexes (i.e., a ligand to metal ratio of 1 to 2). Our first attempt, using the phenyl derivative **1** with $[RhCl(cod)]_2$ as the metal precursor in THF as solvent at reflux, was unsuccessful, with only unreacted starting materials present in the reaction vessel, even after prolonged heating (Scheme 7 , Route A). Therefore, we opted for more forcing conditions, using the higher boiling and more polar solvent 2-ethoxyethanol (Scheme 7, Route B). Heating the reactants to 110 °C overnight, followed by removal of volatiles in vacuo, resulted in a deep red-brown solid. The ^{1}H NMR spectrum of a d_1-chloroform solution of this solid showed a set of three doublets centered at ∼8.3 ppm in a 1:2:1 ratio. These doublets are characteristic of imine protons coupled to ^{103}Rh, indicative of N−M coordination of the ligand, and correlate well with the pattern observed with the Me, Et, and *i*-Pr analogues.[15] The three groups of resonances are a result of halide redistribution, forming three discrete Rh(III) species, which are distinguishable by ^{1}H NMR spectroscopy as discussed by Elsevier (X = X′ = Cl, Br; X = Cl, X′ = Br).[15] The backbone aryl protons also exhibit broadening due to the overlap of the three species, plus significant shifts to lower frequency, again indicative of M−C coordination. Attempts to convert the mixed halide species to the dibromide via addition of excess NaBr in acetone were only partially successful, with ratios of ca. 1:5:11 (by ^{1}H NMR spectroscopy) being the best obtained, and no further purification attempts were made.

The success that the change in solvent brought spurred us on to try the analogous reaction with $[IrCl(cod)]_2$, which could provide access to the Ir(III) [NCN] bisimine complexes. Utilizing the same reaction stoichiometries as depicted in Scheme 7, Route B, an initial yellow precipitate was formed that gradually dissolved to form a deep red solution, from which a small amount of the desired Ir(III) pincer complex was obtained (vida infra). Sampling the reaction mixture at intervals by ^{1}H NMR spectroscopy showed signals (ca. −15 ppm) that indicated multiple species containing M−H interactions were present, although from the number of such signals observed, a range of species were evidently formed and in dynamic equilibrium as their ratios varied with time. Attempts at following the progress of the reaction in situ in a d_1-chloroform solution showed the rapid formation of multiple hydridic resonances plus a range of cyclic alkenyl species derived from

Scheme 8. Synthetic Route to Iridium(III) [NCN] Complexes[a]



R = Ph **1**
Mes **2**
i-Pr **3**
Me **4**

R = Ph **5** (64 %)
Mes **6** (61 %)
i-Pr **7** (55 %)
Me **8** (47 %)

[a] Reaction conditions: (i) >10 equiv of NaBr, ethoxyethanol, 100−110 °C, 15 h, under N_2. (ii) MeCN/H_2O. (iii) Recrystallized from DCM/hexanes, **5** and **6**; DCM/EtOH, **7**; or $CHCl_3$/hexanes, **8**.

cyclooctadiene (free, bound to starting material and other alkenyl resonances). This is suggestive of C−H interactions occurring at either the phenyl groups on the nitrogen or the aryl backbone plus noninnocent interactions of the cyclooctadiene ligand with the metal center.[23] This observation can possibly be explained by the reaction stoichiometries creating one coordinatively saturated iridium complex from the dimer, with the second metal center remaining reactive enough to activate other C−H moieties in the reaction mix. Multiple resonances for the aryl components would further suggest that bidentate coordination of the ligand to the metal center also plays a part. Experimentation with d_3-acetonitrile as the solvent produced similar spectra. However, elucidation of any of the component species was not possible given the complexity of the spectra obtained. Further, whether the hydridic species are intermediaries en route to either the pincer complexes or decomposition products is not entirely clear.

A stoichiometry of one ligand to one metal center, plus the inclusion of excess NaBr (in order to facilitate halide exchange), produced a synthetic route to the desired pincer complex in good yield (64% following recrystallization), with a single halide distribution pattern (X = X′ = Br) seen in the ^{1}H NMR spectra. Removal of volatiles followed by precipitation from MeCN by addition of H_2O afforded a deep red solid that has been characterized as iridium(III) *κN,κC,κN*-bis(phenyl)isophthalaldimin-2-yl dibromide·MeCN (0.5 H_2O), **5** (Scheme 8). A d_1-chloroform solution of the solid was analyzed by ^{1}H NMR spectroscopy, showing the 2-fold symmetry of a tridentate ligand group with a singlet at 8.25 ppm (N=C*H*-C_6H_3), matching the lower frequency resonance of the three imino signals observed prior to halide substitution, a doublet at 7.64 ppm (*m*-C_6H_3) and a triplet at 7.12 ppm (*p*-C_6H_3), shifted to lower frequency with respect to the free ligand. There was no evidence of coordinated MeCN in the ^{1}H NMR spectra, which contrasts with the solid-state findings (vide infra). ^{13}C NMR spectroscopy demonstrated M−C coordination with the disappearance of the C−Br resonance (129.1 ppm) and appearance of an M−C resonance at higher frequency (187.4 ppm). Mass spectrometry revealed that the solvent-free molecule was present in the mass spectrometer as well as a high molecular weight species that had the formula $C_{40}H_{30}N_4Ir_2Br_4$, corresponding to a dimeric species, presumably bridging through two halides. The solid is air- and moisture-stable and is soluble in $CHCl_3$, CH_2Cl_2, MeCN, MeOH, and DMSO and sparingly soluble in toluene and diethyl ether.

Recrystallization from DCM/hexanes formed single crystals that gave elemental analyses indicating the inclusion of H_2O (solvent:complex ratio of 1:2) plus the presence of MeCN

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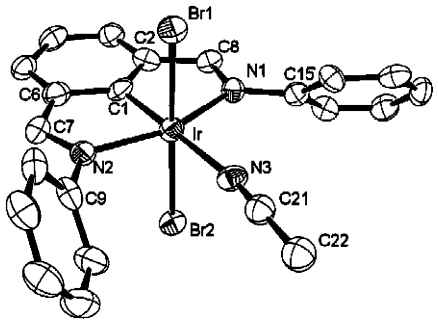


Figure 1. ORTEP[24] representation of iridium(III) $\kappa N,\kappa C,\kappa N$-bis(phenyl)isophthalaldimin-2-yl dibromide·MeCN (0.5 H_2O), **5**. Thermal ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths and Angles for 5

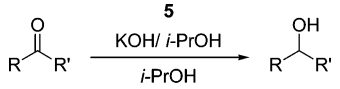
Bond Lengths (Å)			
Ir−C1	1.926(13)	Ir−Br1	2.4867(15)
Ir−N1	2.075(10)	Ir−Br2	2.4898(15)
Ir−N2	2.063(10)	N1−C8	1.282(16)
Ir−N3	2.149(11)	N2−C7	1.306(17)
Angles (deg)			
C1−Ir−N2	79.4(5)	N1−Ir−Br2	89.8(3)
C1−Ir−N1	78.5(5)	N2−Ir−Br1	89.6(3)
C1−Ir−N3	178.3(5)	N2−Ir−Br2	90.3(3)
N1−Ir−N2	157.9(5)	C1−Ir−Br1	89.9(4)
N1−Ir−N3	99.1(4)	C1−Ir−Br2	92.8(4)
N2−Ir−N3	103.0(4)	Br1−Ir−Br2	177.27(5)
N1−Ir−Br1	89.8(3)		

(solvent:complex ratio of 1:1). X-ray crystallographic analysis of suitable crystals showed **5** to be monomeric, forming a distorted octahedron with the two bromine atoms *trans* to each other. An acetonitrile molecule occupies the fourth coordination site in the plane defined by the [NCN] pincer donors and *trans* to the cyclometalated carbon of the backbone aryl group (Figure 1). Selected bond lengths and angles are presented in Table 1. This spacial arrangement is a result of the relative donor strengths and *trans* effects (i.e., MeCN is *trans* to the strongest σ-donor, as it is a better π-acceptor than bromine). The octahedral geometry about the metal is distorted from ideal angles due to the geometric constraints of the isophthalaldime, enforcing an N−Ir−N angle of 157.9(5)°. The N_{imine}−C bond lengths [N2−C18, 1.306(17) Å; N5−C6, 1.282(16) Å] confirm the presence of the imino nitrogen and are comparable to those of the analogous rhodium complexes reported by Elsevier (Rh{Br}$_2$Ir{RNCNR}: R = *i*-Pr, N_{imine}−C = 1.295(2) Å).[15] The Ir−C [1.926(13) Å] and Ir−N [2.063(10) and 2.075(10) Å] bond lengths in **5** are comparable to those in the related pyridyl analogue Ir(dpyx)(DMSO)Cl_2 [Ir−C, 1.976(4) Å; Ir−N, 2.067(3) and 2.087(3) Å].[21]

Replacing the phenyl group with the bulkier mesityl moiety led to similar results, with the synthesis of iridium(III) $\kappa N,\kappa C,\kappa N$-bis(mesityl)isophthalaldimin-2-yl dibromide·MeCN (0.5 H_2O) (**6**) in 61% yield. Unfortunately, the ^{13}C NMR spectrum of **6** in d_1-chloroform, d_3-acetonitrile, or d_4-methanol failed to reveal the M−C resonance (these signals are usually weak as a result of the long relaxation times of metallo-aryl carbon nuclii). Crystals suitable for X-ray crystallography were grown from a DCM/hexanes solution with elemental analyses again indicating the presence of both H_2O and MeCN in the solid.

In order to assess the applicability of this synthetic route to a wider class of bis(imino)aryl ligands, we opted for the alkyl derivatives R = *i*-Pr (**3**) and Me (**4**) to form iridium(III) $\kappa N,\kappa C,\kappa N$-bis(isopropyl)isophthalaldimin-2-yl dibromide·MeCN (0.5 H_2O) (**7**) (55%) and iridium(III) $\kappa N,\kappa C,\kappa N$-bis(methyl)-isophthalaldimin-2-yl dibromide·MeCN (**8**) (47%). The synthesis of **7** proceeds along the familiar route, although producing a lower yield of the expected pincer complex. The ^1H spectroscopic data of a d_1-chloroform solution of the orange crystalline solid isolated from a DCM/MeOH solution revealed the expected symmetrical aryl and imino resonances shifted to lower frequency. A septet at 4.12 ppm (N−C*H*$(CH_3)_2$) and a doublet at 1.53 ppm (N−CH$(CH_3)_2$) indicate free rotation of the isopropyl unit in solution at room temperature.

Scheme 9. Transfer Hydrogenation of Ketones



A significant byproduct, insoluble in chlorinated solvents, methanol, THF, and MeCN, was separated from a DCM solution of the bulk material as a yellow powder. It did prove to be soluble in d_6-DMSO, giving ^1H resonances with similar chemical shifts to those of **7** but with a signal at 3.00 ppm (solvent residue 2.50 ppm) indicative of coordinated DMSO. Two doublets centered at 1.56 and 1.49 ppm for the two methyl groups of the isopropyl unit indicate that the bulk of the DMSO molecule appears to restrict rotation of the isopropyl unit about the C−N bond. However, heating to 50 °C did not lead to coalescence of the two signals. The insoluble species is likely to be dimeric in nature (as per the pyridyl variant reported by Williams et al.);[20] the DMSO is sufficiently strongly coordinating to break up the dimer and occupy the vacant coordination site. The two complexes both crystallize as apparently single crystals (**7** from DCM/MeOH and **7a** from THF/DMSO) but neither gave crystallographic data of sufficient quality to obtain structural characterization. The synthesis of the methyl derivative through the same route as **7** produced a crystalline solid that has been characterized as **8**, via elemental analysis, ^1H and ^{13}C NMR spectroscopy, and high-resolution mass spectrometry; thus this route appears applicable to a wide range of alkyl- and aryl-substituted analogues.

Catalysis. Having established a reliable route to the hitherto elusive Ir NCN bis(imine) pincer family of complexes, their robustness and utility were explored via a preliminary test of catalytic function. A facile and well-studied reaction is the transfer hydrogenation of ketones to alcohols (Scheme 9).[25−27] For this study, the iridium(III) complex **5** was used as the catalyst and KOH as the base, with acetophenone and 1,3-diphenylacetone as the ketones. Results are summarized in Table 2.

The results indicate that complex **3** generates a catalytically active species under the reaction conditions employed, with reasonable conversions at room temperature. Several mechanistic observations can be drawn from these data. The addition of a further 100 equiv of ketone after 2.5 h leads to further conversion (entry iv); thus, the active species is still present under these reaction conditions. This indicates reasonable catalyst stability and the possibility of high turnover numbers. Second, the reaction is base-dependent, in line with the generally accepted mechanism reviewed by Bäckvall[27] with no conversion in the absence of added base, but when the more acidic 1,3-diphenylacetone replaces acetophenone (entries ii, iii, and iv),

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Table 2. Transfer Hydrogenation of Ketones

entry	ketone	B:C:K[a]	time (h)	conversion (%)[b]
i	acetophenone	2:1:200	5	50
ii	1,3-diphenylacetone	2:1:200	24	0
iii	1,3-diphenylacetone	10:1:200	2.5[c] (3.25)	30 (65)
iv	1,3-diphenylacetone	25:1:200	2.5[d] (3.5)	75 (92)

[a] Reaction conditions: temperature = 20−25 °C. Base (B) = *i*-PrOH/KOH, 0.17 M; *i*-PrOH (10 mL); catalyst (C) = **5**; ketone (K) = acetophenone or 1,3-diphenylacetone. [b] Determined by ^{1}H NMR. [c] Addition of further 10 equiv of base. [d] Addition of further 100 equiv of ketone.

the reaction fails unless a higher concentration of base is used (entries iii and iv), presumably to generate sufficient alkoxide to initiate the reaction. These routes, which are nonoptimized, indicate that Ir−NCN pincer complexes are promising candidates for further catalytic studies, especially in the important field of hydrogen-transfer reactions.

Conclusion

We have demonstrated a facile and general synthetic route to bis(imino)aryl iridium(III) pincer complexes through oxidative addition of a range of 2-bromoisophthalaldimines to $[IrCl_2(cod)]_2$. The complexes thus formed are both air- and moisture-stable and represent a new class of iridium pincer complex. An initial foray into the utility of these species demonstrates their ability to form active catalytic species for use in hydrogen-transfer reactions.

Experimental Section

General Considerations. Ligand synthesis was carried out using standard Schlenk techniques under a nitrogen atmosphere with degassed solvents (drying carried out in situ; see relevant data in Experimental Section), and subsequent ligand workup was done under air. The complexes were synthesized using degassed solvents under either argon or nitrogen to prevent any decomposition of reactive intermediates, but all subsequent workup was carried out under air. All reagents were used as received; $[RhCl(cod)]_2$,[28] $[IrCl(cod)]_2$,[29] 2-bromoisophthalaldehyde,[30] and bis(*N*-isopropyl)- and bis(*N*-methyl)-2-bromoisophthalaldimine,[15] **3** and **4**, respectively, were prepared according to literature methods. ^{1}H and ^{13}C NMR spectroscopy was carried out on a Bruker DPX-400 spectrometer with ^{13}C spectra being recorded at 100 MHz unless otherwise stated. Mass spectra were obtained using a Waters LCT Premier XE mass spectrometer, and high-resolution mass spectra were obtained from the EPSRC mass spectrometry service at Swansea. Elemental analyses were carried out by Warwick Analytical Services, the University of Warwick, UK. Infrared spectra were recorded on a JASCO FT/IR-660 Plus instrument. X-ray diffraction data were collected on a Nonius Kappa CCD, solved using the Patterson method and resolved using a least squares model on the SHELX suite of programs.[31]

Bis(*N*-phenyl)-2-bromoisophthalaldimine, 1. Aniline (0.34 mL, 3.76 mmol) and 2-bromoisophthalaldehyde (0.4 g, 1.88 mmol) were added to a two-necked round-bottomed flask containing THF (10 mL) and activated 3 Å molecular sieves and refluxed for 2 h. Upon cooling, the pale brown solution was filtered through a glass sinter, followed by evaporation of the solvent in vacuo to afford a pale brown solid. Recrystallization by slow cooling of a hot methanolic solution afforded 0.584 g (1.61 mmol, 85%) of **1** as a pale brown, crystalline solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.91 (s, 2H, N=C*H*-C_6H_3), 8.26 (d, 2H, $^3J_{HH}$ = 7.7, *m*-C_6H_3), 7.43 (tr, 1H, $^3J_{HH}$ = 7.7, *p*-C_6H_3), 7.39−7.33 (m, 4H, *o*-C_6H_5), 7.22−7.17 (m, 6H, *m,p*-C_6H_5). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 159.1 (N=*C*H−C_6H_3), 151.5 (*i*-C_6H_5), 135.5 (*o*-C_6H_3), 131.8 (*m*-C_6H_3), 129.3 (*m*-C_6H_5), 129.1 (Br-C_6H_3), 127.8 (*p*-C_6H_3), 126.7 (*p*-C_6H_5), 121.2(*o*-C_6H_5). *m/z* (ES+): 363.0 $[^{79}BrM + H]^+$ 98%, 365 $[^{81}BrM + H]^+$ 100%. HRMS (ES+): calcd $[M + H]^+$ $C_{20}H_{16}N_2{}^{79}Br$ 363.0497, found 363.0480. IR (Nujol): ν(C=N) 1613s, 1590s. Melting point: 104−106 °C.

Bis(*N*-mesityl)-2-bromoisophthalaldimine, 2. 2,4,6-Trimethylaniline (0.53 mL, 3.76 mmol) and 2-bromoisophthalaldehyde (0.4 g, 1.88 mmol) were added to a two-necked round-bottomed flask containing toluene (20 mL), activated 3 Å molecular sieves, and a catalytic amount of TsOH (1−2 mg) and refluxed for 1 h. Upon cooling, the bright yellow solution was filtered through a glass sinter and the solvent removed in vacuo. Precipitation from hot methanol afforded 0.849 g (1.90 mmol, 87%) of **2** as a bright yellow, fibrous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 2H, N=C*H*-C_6H_3), 8.31 (d, 2H, $^3J_{HH}$ = 7.6, *m*-C_6H_3), 7.49 (tr, 1H, $^3J_{HH}$ = 7.6, *p*-C_6H_3), 7.05 (s, 4H, *m*-C_6H_2), 2.23 (s, 6H, CH_3), 2.10 (s, 12H, CH_3). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 162.0 (N=*C*H), 148.3 (N-*C*), 135.7 (*C*), 133.6 (*C*), 131.3 (*C*H), 128.9 (*C*H), 128.4 (Br-*C*), 127.9 (*C*H), 127.0 (*C*H), 20.8 (*p*-*C*H_3), 18.4 (*o*-*C*H_3). *m/z* (ES+): 447.0 $[^{79}BrM + H]^+$ 93%, 449.0 $[^{81}BrM + H]^+$ 100%. HRMS (ES+): calcd $[M + H]^+$ $C_{20}H_{16}N_2{}^{79}Br$ 447.1436, found 447.1422. IR ($CHCl_3$): ν(C=N) 1627s. Melting point: 156−158 °C.

Iridium(III) $\kappa N,\kappa C,\kappa N$-Bis(phenyl)isophthalaldimin-2-yl Dibromide·Acetonitrile (0.5 H_2O), 5. A Schlenk was charged with $[IrCl(cod)]_2$ (0.05 g, 0.07 mmol), **1** (0.055 g, 0.15 mmol), and NaBr (0.1 g, 14 molar equiv with respect to Ir) and degassed through three inert gas/vacuum cycles. Degassed 2-ethoxyethanol (10 mL) was then added to the solid reactants, and the mixture was heated to 110 °C for 15 h under an inert gas atmosphere. The resultant deep red solution was then filtered, the solvent evaporated to an external trap, and the red paste redissolved in acetonitrile (5 mL). Water was added (10 mL) and the solution left to stand overnight with precipitation of a deep red solid. Recrystallization from DCM/hexanes formed 0.065 g (0.096 mmol, 64%) of deep red, needle-like crystals of **5** suitable for X-ray crystallography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 2H, N=C*H*-C_6H_3), 7.64 (d, 2H, $^3J_{HH}$ = 7.6, *m*-C_6H_3), 7.59 (m, 4H, *o*-C_6H_5), 7.36−7.26 (m, 6H, *m,p*-C_6H_5), 7.12 (tr, 1H, $^3J_{HH}$ = 7.6, *p*-C_6H_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4 (Ir-*C*), 177.5 (N=*C*H), 151.5 (*C*), 143.3 (*C*), 129.7 (*C*H), 129.3 (*C*H), 128.2 (*C*H), 123.7 (*C*H), 122.4 (*C*H). *m/z* (FAB): 1269.9 $[2M - 2CH_3CN]^+$, 8%; 636.0 $[M - CH_3CN]^+$ 100%; 555.0 $[M - CH_3CN - Br]^+$; 476.1 $[M - CH_3CN - 2Br]^+$. Anal. Calcd for $C_{22}H_{18}N_3IrBr_2$(0.5 H_2O): (%) C, 38.55; H, 2.79; N, 6.13. Found: C, 38.60; H, 2.59; N, 6.02. IR (Nujol): ν(C=N) 1584s, 1506. Melting point: decomposed at ∼290 °C.

Iridium(III) $\kappa N,\kappa C,\kappa N$-Bis(mesityl)isophthalaldimin-2-yl Dibromide·Acetonitrile (0.5 H_2O), 6. Compound **6** was prepared according to the route outlined for **5** using $[IrCl(cod)]_2$ (0.025 g, 0.037 mmol), **2** (0.034 g, 0.074 mmol), and NaBr (0.077 g, 10 molar equiv with respect to Ir). Claret-colored prisms of **6** were collected (0.057 g, 61%) and were suitable for X-ray crystallography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 2H, N=C*H*), 7.51 (d, 2H, $^3J_{HH}$ = 7.6, *m*-C_6H_3), 7.12 (tr, 1H, $^3J_{HH}$ = 7.6, *p*-C_6H_3), 6.83 (s, 4H, *m*-C_6H_2), 2.39 (s, 12H, CH_3), 2.21 (s, 6H, CH_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 180.2 (N=*C*H), 141.8 (N-*C*), 135.7 (*C*), 133.6 (*C*), 131.3 (*C*H), 128.9 (*C*H), 128.4 (Br-*C*), 127.9 (*C*H), 127.0 (*C*H), 20.8 (*p*-*C*H_3), 18.4 (*o*-*C*H_3). HRMS (ES+): calcd $C_{26}H_{27}N_2Br_2$ 718.0176, found 718.0176. Intact molecule with solvent not observed. Anal. Calcd for $C_{28}H_{30}N_3Br_2$ (0.5 H_2O): (%) C, 43.70; H, 4.06; N, 5.46. Found: C, 43.62; H, 3.90; N, 5.19. IR

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(Nujol): 1607w, 1590m, 1572w, 1510s. Melting point: decomposed at 234−240 °C.

Iridium(III) $\kappa N,\kappa C,\kappa N$-Bis(*N*-isopropyl)isophthalaldimin-2-yl Dibromide·MeCN (0.5 H_2O), 7. Compound **7** was prepared according to the route outlined for **5** using $[IrCl(cod)]_2$ (0.033 g, 0.049 mmol), **3** (0.029 g, 0.098 mmol), and NaBr (0.061 g, 10 molar equiv with respect to Ir). Recrystallization from DCM/EtOH afforded **7** as a red, crystalline solid (55%, 0.031 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 2H, N=C*H*), 7.46 (d, 2H, $^3J_{HH}$ = 7.6, *m*-C_6H_3), 6.97 (tr, 1H, $^3J_{HH}$ = 7.6, *p*-C_6H_3), 4.12 (sept, 2H, $^3J_{HH}$ = 6.6, CH_3CHCH_3), 2.59 (br s, H_2O/MeCN), 1.53 (d, 12H, $^3J_{HH}$ = 6.6, CH_3CHCH_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 182.4 (Ir-*C*) 173.2 (N=*C*H), 142.6 (*C*), 127.9 (*C*H), 121.9 (*C*H), 64.2 (CH_3CHCH_3), 23.8 (CH_3CHCH_3). *m/z* (ES+): 566.0 [^{79}BrM − solvent]$^+$ 85%, 568.0 [^{81}BrM − solvent]$^+$ 100%. HRMS (ES+): calcd $C_{14}H_{19}N_2Ir^{79}Br$ 565.9550, found 565.9546. Anal. Calcd for $C_{16}H_{22}N_3IrBr_2$: (%) C, 31.59; H, 3.64; N, 6.91. Found: C, 31.49; H, 3.56; N, 6.53. IR (Nujol): ν(C=N) 1592, 1528. Melting point: >300 °C.

Iridium(III) $\kappa N,\kappa C,\kappa N$-Bis(*N*-isopropyl)isophthalaldimin-2-yl Dibromide DMSO, 7a. Compound **7a** was prepared by addition of DMSO to an orange powder separated from **7** during purification. Recrystallization from DMSO/THF afforded an orange-yellow, crystalline solid that was identified as **7a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 2H, N=C*H*), 7.58 (d, 2H, $^3J_{HH}$ = 7.7, *m*-C_6H_3), 7.16 (tr, 1H, $^3J_{HH}$ = 7.7, *p*-C_6H_3), 4.67 (sept, 2H, $^3J_{HH}$ = 6.5, CH_3CHCH_3), 3.00 (s, 6H, $\{CH_3\}_2SO$), 1.56 (d, 6H, $^3J_{HH}$ = 6.5, CH_3CHCH_3), 1.48 (d, 6H, $^3J_{HH}$ = 6.5, CH_3CHCH_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 174.8 (N=*C*H), 142.4 (*C*), 129.3 (*C*H), 123.3 (*C*H), 61.4 (CH_3CHCH_3), 43.5 ($\{CH_3\}_2SO$), 24.8 (CH_3CHCH_3), 22.8 (CH_3CHCH_3).

Iridium(III) $\kappa N,\kappa C,\kappa N$-Bis(*N*-methyl)isophthalaldimin-2-yl Dibromide·Acetonitrile, 8. Compound **8** was prepared according to the route outlined for **5** using $[Ir(Cl)cod]_2$ (0.128 g, 0.21 mmol), **4** (0.099 g, 0.41 mmol), and NaBr (0.2 g, ∼40 molar equiv with respect to Ir). Recrystallization from $CHCl_3$/hexanes afforded an orange-red, crystalline solid (47%, 0.11 g) that was identified by ^{1}H and ^{13}C NMR spectroscopy as **8**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (s, 2H, N=C*H*), 7.45 (d, 2H, $^3J_{HH}$ = 7.6, *m*-C_6H_3), 6.97 (tr, 1H, $^3J_{HH}$ = 7.6, *p*-C_6H_3), 3.85 (s, 6H, CH_3), 2.56 (br s, H_2O/MeCN). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 176.0 (N=*C*H), 142.3 (*C*), 127.0 (*C*H), 121.6 (*C*H), 49.9 (CH_3). HRMS (ES+): calcd $C_{10}H_{11}N_2{}^{191}Ir^{79}Br_2$ 507.8889, found 507.8893. Anal. Calcd for $C_{12}H_{14}N_3IrBr_2$: (%) C, 26.19; H, 2.20; N, 7.64. Found: C, 26.19; H, 2.49; N, 7.29. IR (Nujol): ν(C=N) 1610, 1590, 1535. Melting point: >300 °C.

Transfer Hydrogenation Reaction Conditions. The catalyst **5** (2 mg, 0.003 mmol) was added to a round-bottomed Schlenk and degassed through three nitrogen/vacuum cycles followed by addition of *i*-PrOH (10 mL). The required amount of base (a 0.178 M solution of KOH in *i*-PrOH) was added via syringe, and the reactants were stirred at room temperature for ∼30 min before addition of the ketone (0.6 mmol). Aliqouts (∼0.5 mL) were removed at intervals, the solvent was removed in vacuo, and ^{1}H NMR spectroscopy in $CDCl_3$ was carried out to ascertain the extent of reaction.

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Supporting Information Available: Crystallographic data for **3** and **4** (CIF) are available free of charge via the Internet at http://pubs.acs.org.

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