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Bis(pyridylimino)isoindolato−Iridium Complexes as Epoxidation Catalysts for Alkenes

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Summary: The reaction of the sodium salts of ligands **1a**,**b** (**1a** = *1,3-bis(2-(5-(3,5-xylyl)pyridyl)imino)-5,6-dimethylisoindole,* **1b** = *1,3-bis(2-(4-tert-butylpyridyl)imino)-5,6-dimethylisoindole) with* $[Ir(\mu\text{-}Cl)(COD)]_2$ *(COD = cyclooctadiene) and* $[Ir(\mu\text{-}Cl)(C_2H_4)_2]_2$ *afforded the corresponding isoindolato complexes* $[\{BPI(\mathbf{1a,b})\}Ir^I(COD)]$ (**2a**,**b**) *and* $[\{BPI(\mathbf{1a,b})\}Ir^I(C_2H_4)_2]$ (**3a**,**b**)*, respectively. The catalytic activity of the complexes* **2a**,**b** *was tested in the epoxidation of a wide range of non-electron-rich olefins, using PPO (PPO = 3-phenyl-2-(phenylsulfonyl)-1,2-oxaziridine) as oxidizing agent, giving the corresponding epoxides in moderate to high yields.*

Whereas the applications of rhodium in molecular catalysis are now innumerable,[1] the development of catalytic processes involving its heavier congener iridium has progressed more slowly.[2] The latter has been extensively employed in the quest for reactive and structural models of intermediates in the mechanistic cycles of 4d platinum metals and, in particular, rhodium.[3] However, iridium complexes have proved to be active and selective catalysts in the production of both bulk chemicals, such as the carbonylation of methanol,[4] as well as fine chemicals, as exemplified by an ever-growing number of enantioselective hydrogenations of C=C and C=X bonds in prochiral substrates.[5] The recent development of efficient Ir-catalyzed allylic substitutions,[6] C−C and C−X couplings,[7] cycloadditions,[8] and hydrosilylations[9] as well as alkane dehydrogenations[10] indicate the rapid expansion of this field. In contrast, very little is known about iridium in oxidation catalysis. The use of iridium complexes as epoxidation catalysts has been barely developed,[11] probably due to the low activity in this kind of catalysis as reported in some early papers.[12]

The choice of the appropriate ancillary ligands is particularly crucial in the development of oxidation catalysts, since they have to withstand the reactivity of the oxidants employed. Monoanionic meridionally coordinating tridentate ("pincer") ligand systems have proved to give rise to molecular catalysts

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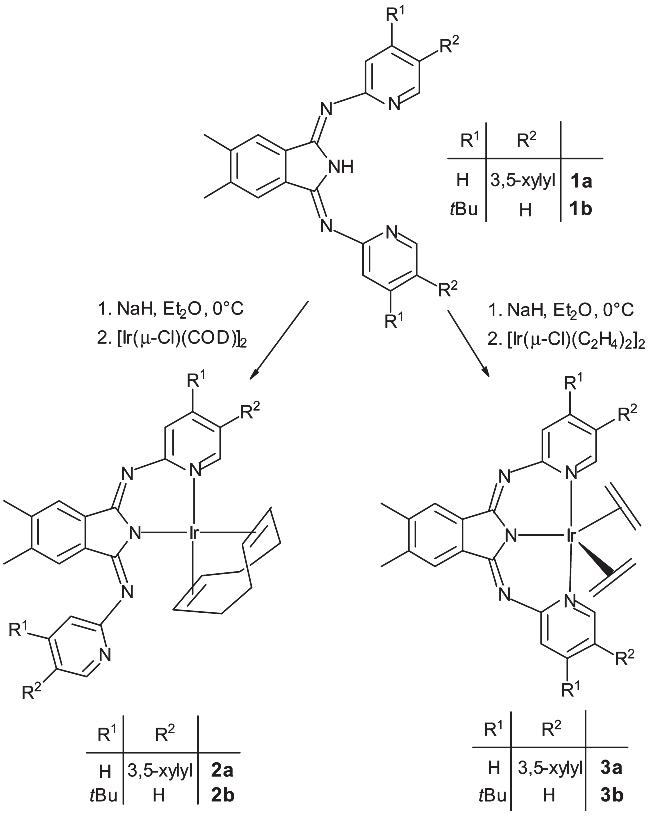
Scheme 1. Synthesis of the Iridium(I) Complexes 2a,b and 3a,b



of great stability.[13] In particular, the readily accessible modular bis(pyridylimino)isoindolato (BPI) derivatives[14] have been employed in oxidation catalysis with cobalt and iron.[15] In this paper, we report the preparation of (BPI)Ir^{I}(COD) complexes and the exploration of their catalytic activity in epoxidations of substituted alkenes using PPO (PPO = 3-phenyl-2-(phenylsulfonyl)-1,2-oxaziridine) as oxidizing agent[16] is discussed.

The iridium complexes **2a**,**b** and **3a**,**b** were prepared by reaction of the in situ generated sodium salts of **1a**,**b** and subsequent addition of $[Ir(\mu\text{-}Cl)(COD)]_2$ or $[Ir(\mu\text{-}Cl)(C_2H_4)_2]_2$ to the resulting suspension. After the reaction mixtures were stirred at ambient temperature for 4 h, the corresponding complexes [{BPI(**1a**,**b**)}Ir^{I}(COD)] (**2a**,**b**) and [{BPI(**1a**,**b**)}Ir^{I}-$(C_2H_4)_2$] (**3a**,**b**) were isolated in good yields (Scheme 1).

The formulation of complexes **2a**,**b** as [{BPI(**1a**,**b**)}Ir^{I}-(COD)] as well as of the corresponding ethylene compounds **3a**,**b** was established by elemental analyses and their mass spectra (FAB+), which were dominated by the respective molecular ion and the complex fragment $\{(BPI)Ir\}^+$. However, the ^{1}H and ^{13}C NMR spectra of the four Ir complexes indicated a significant difference of the structures on going from COD to the bis-ethylene derivatives. Whereas the latter displays resonance patterns consistent with 5-fold coordination at the metal center and overall molecular C_{2v} symmetry, the structures of the COD complexes **2a**,**b** were found to be less symmetrical. The ^{1}H NMR spectra of **2a**,**b** exhibit different sets of signals for the pyridyl and isoindolate protons and two singlets, at 1.34 and 1.28 ppm for **2b**, assigned to two nonequivalent *tert*-butyl groups. This indicates that the deprotonated isoindoles **1a**,**b** coordinate the iridium atom in a κ^2 fashion to form **2a**,**b** and thus the C=N double bond of the uncoordinated pyridine arm is isomerized to an *E* conformation. The resulting perpendicular orientation of the pyridine ring with respect to one of the protons of the isoindole backbone has a large influence on its chemical shift (observed at 6.09 ppm for **2a** and 5.84 ppm for **2b**), since it is located above the anisotropic cone of the pyridine ring. The olefinic protons of the cyclooctadiene ligand resonate at 5.64 and 3.66 ppm for **2a** and at 5.66 and 3.60 ppm for **2b** as broad singlets, which is also consistent with the nonsymmetric structure of the complex.[17] The ^{13}C NMR spectra of **2a**,**b** are in agreement with the nonsymmetric geometry of the complex. The COD ligand gives rise to five ^{13}C NMR signals, unambiguously assigned on the basis of a ^{1}H$-$^{13}C HSQC experiment. Two singlets appear at 67.2 and 63.0 ppm for **2a** and at 67.9 and 62.9 ppm for **2b**, representing the olefinic carbons coordinated to the iridium center, and at 31.7 and 30.6 ppm for **2a** and at 32.0 and 30.4 ppm for **2b**, the methylene ^{13}C nuclei.

A single-crystal X-ray study of complex **2b** confirmed the general structural assignment based on the spectroscopic data and established a slightly distorted square planar structure with the BPI ligand coordinated to the iridium atom by N1 and N3 in a κ^2 fashion (Figure 1).[18] The amido-like N(3)$-$Ir bond length is shorter than the interatomic distance associated with the coordinated pyridyl arm N(1)$-$Ir (by ~0.05 Å) as usually observed in BPI metal complexes.[19] The arrangement of the dangling, uncoordinated pyridyl unit is characterized by the torsion angle C(18)$-$N(4)$-$C(1)$-$N(1) of $-164.3(3)°$. This orientation explains the shift to higher field of the proton of the isoindole group at C(5) observed in the ^{1}H NMR spectrum as discussed above. The distances

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(18) Crystal data and data collection and structure refinement details for complex **2b**: $C_{36}H_{44}IrN_5$, monoclinic, space group $P2_1/c$, a = 13.165(7) Å, b = 10.728(5) Å, c = 22.186(10) Å, β = 101.711(6)°, V = 3068(3) Å^3, Z = 4, μ = 4.386 mm^{-1}, F_{000} = 1488. T = 100(2) K, θ range 2.1$-$31.5°, index ranges h, k, l (indep set) -19 to $+18$, 0$-$15, 0$-$32, 77 512 reflections measured, 10 141 independent reflection (R_{int} = 0.0687), 7698 observed reflections ($I > 2\sigma(I)$), final R indices ($F_o > 4\sigma(F_o)$) $R(F)$ = 0.0292, $R_w(F^2)$ = 0.0515, GOF = 1.017, intensity data collection Bruker AXS Smart 1000 CCD diffractometer, Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å, Lorentz, polarization, and numerical absorption correction,[18b] structure solution by direct methods,[18c,d] refinement by full-matrix least-squares methods based on F^2,[18d,e] all non-hydrogen atoms anisotropic, hydrogen atoms at calculated positions (refined riding), except those of the cod methyne groups (refined with d(CH) restrained equal). (b) Sheldrick, G. M. *SADABS*; Bruker AXS, **2004$-$2008**. (c) Sheldrick, G. M. *SHELXS-97*; University of Göttingen, Göttingen, Germany, 1997. (d) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112. (e) Sheldrick, G. M. *SHELXL-97*; University of Göttingen, Göttingen, Germany, 1997.

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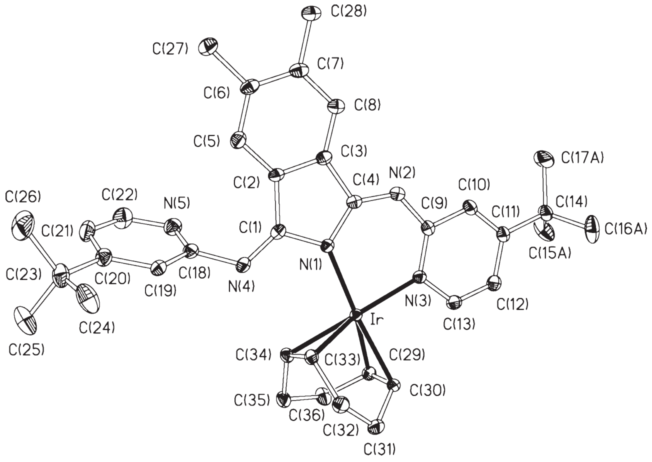
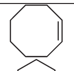
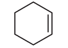
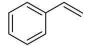
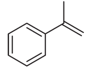
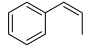
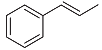
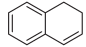
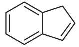
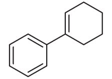
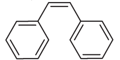
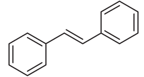
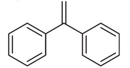
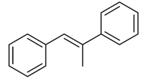
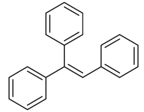
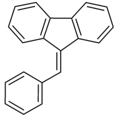
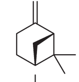
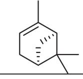


Figure 1. Molecular structure of **2b**. Selected bond lengths (Å) and angles (deg): Ir–N(1) = 2.087(2), N(2)–C(4) = 1.291(4), Ir–C(33) = 2.122(3), N(2)–C(9) = 1.362(4), Ir–C(29) = 2.124(3), N(3)–C(9) = 1.361(4), Ir–N(3) = 2.134(3), N(3)–C(13) = 1.363(4), Ir–C(30) = 2.125(3), N(4)–C(1) = 1.274(4), Ir–C(34) = 2.143(3), N(4)–C(18) = 1.404(4), N(1)–C(4) = 1.380(4), N(5)–C(18) = 1.332(4), N(1)–C(1) = 1.418(4), N(5)–C(22) = 1.342(4); N(1)–Ir–C(33) = 92.0(1), N(3)–Ir–C(29) = 91.5(1), Ir–N(1)–C(1) = 131.1(2), N(1)–Ir–C(34) = 95.6(1), N(3)–Ir–C(30) = 91.6(1), Ir–N(1)–C(4) = 121.6(2), N(1)–Ir–N(3) = 88.82(9), Ir–N(3)–C(13) = 119.8(2), C(33)–Ir–C(30) = 80.5(1), N(1)–C(1)–N(4) = 122.3(3), N(1)–C(4)–N(2) = 132.0(3), C(29)–Ir–C(34) = 79.5(1), C(1)–N(4)–C(18) = 121.7(3), C(4)–N(2)–C(9) = 126.8(3).

between the iridium atom and the olefinic carbons are similar to the values found in the literature.[20]

The robust nature of the BPI ligands, which contain three hard nitrogen donors, makes them of interest for oxidation catalysis. In general, complexes **2a**,**b** and **3a**,**b** behaved in a very similar way in these studies. However, due to the greater thermal stability of the precatalysts **2a**,**b**, only these compounds were studied systematically. In an initial screening of the appropriate oxygenation reagents and reaction conditions, *cis*-cyclooctene was chosen as the test substrate. Hydrogen peroxide, iodosobenzene, and PPO (PPO = 3-phenyl-2-(phenylsulfonyl)-1,2-oxaziridine) were tested as oxygen transfer agents in the presence of the iridium complexes in reaction mixtures using dichloromethane, chloroform, benzene, thf, acetone, and acetonitrile as solvents. All our attempts using hydrogen peroxide as oxidant led to a rapid deactivation of the catalyst, due to the oxidative degradation of the Ir complex. While iodosobenzene gave rise to moderate activity in the epoxidation of the test substrate (49% conversion after 48 h with a catalyst/substrate/oxidant ratio of 1/10/40), PPO proved to be the epoxidizing agent of choice, probably due to its greater solubility in most organic solvents favoring the transfer of oxygen. Initial studies (see the Supporting Information) established the optimized catalyst/substrate/oxidant ratio of 1/100/150 used in all subsequent catalytic tests, which were carried out for a wide range of non-electron-rich olefins. Blank reactions showed that no significant amount of epoxide was formed in the absence of catalyst, corroborating results previously described in the literature.[21] Results obtained for the different substrates, which were converted to their corresponding epoxides, are given in Table 1.

Table 1. Epoxidation Catalysis of Complexes 2a,b[d]

Entry	Substrate	Time, h [b]	Conversion,% [a] (d.e.) Cat. 2a	Cat. 2b	Isolated Yield (%) [c]
1		48	71	80	70
2		48	51	48	32
3		48	60	62	49
4		48	55	53	50
5		48	94	95	93
6		48	95(17)	91(10)	56
7		24	96(99)	98(99)	96
8		14	94	98	95
9		48	71(47)	70(47)	24
10		7	97	97	95
11		48	98(8)	99(0)	42
12		24	99(99)	99(99)	91
13		24	99	99	69
14		48	99	99	69
15		22	88	90	65
16		24	75	77	75
17		48	94(85)	93(97)	72
18		48	94(64)	99(70)	78

[a] Conversion into the corresponding epoxides; determined by ^{1}H NMR integral analysis. In brackets diastereomeric excess determined by ^{1}H NMR integral analysis. [b] After the time indicated no further conversion was observed. [c] The isolated yields were determined using complex **2b** as catalyst and the experimental conditions described above. [d] Experimental conditions for all experiments: 1 equiv of catalyst, 100 equiv of substrate, 150 equiv of PPO in dichloromethane; concentration of the catalyst in the reaction mixture 15 mM.

As displayed in entries 1–10, olefins with different substitutional patterns were epoxidized, giving moderate to high yields. As indicated above, 3-phenyl-2-(phenylsulfonyl)-1,2-oxaziridine is a good epoxidizing agent by itself for very electron rich alkenes such as 2,3-dimethyl-2-butene but is much less reactive toward less electron rich olefins. For example, *trans*-stilbene was epoxidized in high yield in the presence 1 mol % of **2a**,**b** as catalyst within 24 h (entry 12), while *cis*-stilbene required 48 h (entry 11). In this case, virtually no formation of *trans*-stilbene oxide was obtained (compared to 36% of trans epoxide formation observed

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(21) Yuan, L. C.; Bruice, T. C. *J. Chem. Soc., Chem. Commun.* **1985**, 868.

previously when the reaction was performed at 60 °C without catalyst).[22] The comparison of entries 14 and 15 shows a clear effect of the catalytic activity of the iridium complexes: in entry 14 the conversion of *trans*-α-methylstilbene in the epoxide is 99% (within 48 h) for complexes **2a**,**b**; however, with triphenylethylene as substrate 88% (**2a**) or 90% (**2b**) was observed within 22 h (entry 15). In this case the less nucleophilic olefin (entry 15) is epoxidized more rapidly than the more electron rich substrate (entry 14), which is contrary to the observed noncatalyzed behavior.

Bicyclic monoterpenes were also tested as substrates (entries 17 and 18) for the epoxidation, giving good conversion with high diastereomeric excesses in both cases. Whereas *β*-pinene was epoxidized in 94% yield and 85% de using **2a** as catalyst (and in 93% yield and 97% de using **2b** as catalyst), the epoxidation of α-pinene led to a conversion of 94% with 64% de using **2a** as catalyst (and 99% (70% de) for **2b**). The observation that the two catalysts have relatively similar activities indicates that a difference in the substitution patterns of the ancillary BPI ligands does not significantly affect the catalyst performance. The activities of complexes **2a**,**b** in the epoxidation of alkenes with PPO are significantly higher than those reported using this oxidant and manganese porphyrin complexes as catalyst,[23] while being comparable with the results obtained for other oxidants and metal catalysts.

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Supporting Information Available: Text, figures, and a table giving synthesis and characterization data of all new compounds and CIF files giving crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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