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Novel Carbonyliridium and -rhodium Complexes Containing 2,6-Bis[(4′*S*)-4′-isopropyloxazolin-2′-yl]pyridine (*i*Pr-pybox) and 2,6-Bis[(4′*R*)-4′-phenyloxazolin-2′-yl]pyridine (Ph-pybox) Ligands

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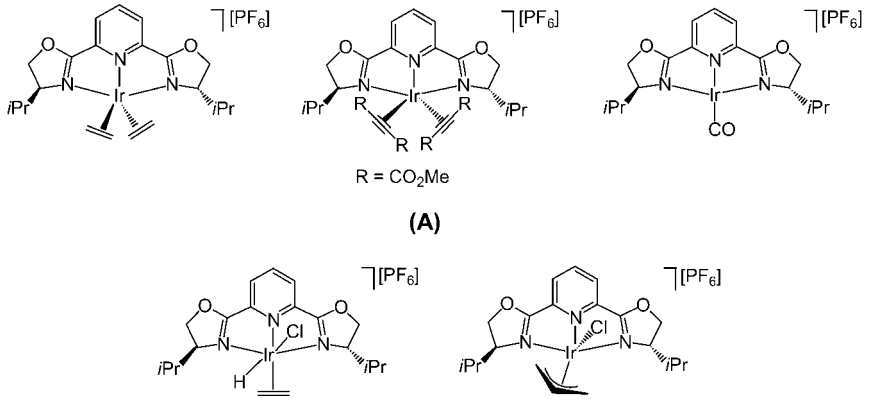
The iridium(I) complexes [Ir(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF_6] [R-pybox = (*S*,*S*)-*i*Pr-pybox (**1**), (*R*,*R*)-Ph-pybox (**2**)] have been prepared by reaction of their precursor complexes [Ir(η^2-C_2H_4)$_2$(κ^3-*N*,*N*,*N*-R-pybox)][PF_6] (R = *i*Pr or Ph) with carbon monoxide. The analogous carbonylrhodium(I) complexes [Rh(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF_6] [R-pybox = (*S*,*S*)-*i*Pr-pybox (**3**), (*R*,*R*)-Ph-pybox (**4**)] have been synthesised by reaction of [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$, carbon monoxide, R-pybox and $NaPF_6$. Complexes **1**–**4** undergo oxidative addition reactions with iodine and CH_3I leading, with high stereoselectivity, to the complexes [MI(X)(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF_6] [M = Ir, R = *i*Pr, X = I (**5**); M = Rh, R = *i*Pr, X = I (**6**); M = Rh, R = Ph, X = I (**7**); M = Ir, R = *i*Pr, X = CH_3 (**8**); M = Ir, R = Ph, X = CH_3 (**9**); M = Rh, R = *i*Pr, X = CH_3 (**10**); M = Rh, R = Ph, X = CH_3 (**11**)]. The treatment of complexes **1** and **2** with HCl, allyl chloride or acyl chloride results, in most cases, in the stereoselective formation of the iridium(III) complexes [IrHCl(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF_6] [R = *i*Pr (**12**), Ph (**13**)], [IrCl(η^1-$CH_2CH{=}CH_2$)(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF_6] [R = *i*Pr (**14**), Ph (**15**)] or [IrCl{η^1-C(O)CH_3}(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF_6] [R = *i*Pr (**16**), Ph (**17**)], respectively. The structures of derivatives **10** and **15** have been determined by single-crystal X-ray diffraction analysis. The catalytic activity of monocarbonylrhodium(I) and -iridium(I) complexes **1** and **3** in the hydrosilylation and dehydrosilylation of acetophenone with diphenylsilane has also been examined.

Introduction

In the last few years the enantiopure, tridentate nitrogen ligands R-pybox [R-pybox = 2,6-bis(4′-R-oxazolin-2′-yl)-pyridine; R = *i*Pr, Ph, *t*Bu, etc.] have been shown to be efficient chiral ancillary ligands in transition-metal-catalysed asymmetric synthesis. A recent and specific survey discusses the state-of-the-art of this field.[1]



Despite the importance of iridium complexes in catalytic processes, as far as we know only a few examples of asymmetric catalysis using [IrCl(cod)]$_2$/pybox mixtures as the catalyst have been described. Thus, a reductive aldol reaction catalysed by [IrCl(cod)]$_2$/indane-pybox[2] and a regio- and enantioselective allylic substitution catalysed by mix-

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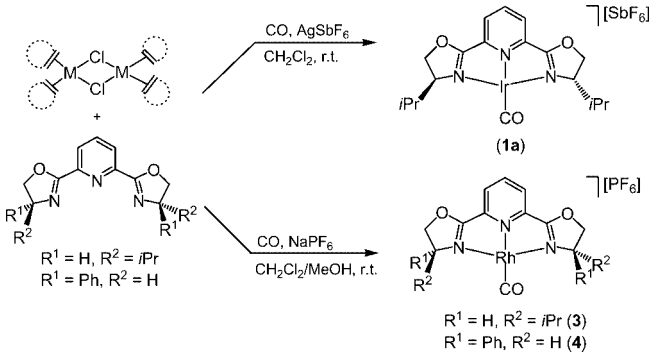
tures of $[IrCl(cod)]_2$/phenyl-pybox and nitrogen nucleophiles such as oximes, amines and hydroxylamines, have been reported recently.[3,4] Moreover, we have just described the preparation of the first (pybox)iridium complexes,[5] namely diolefin-, dialkyne- and monocarbonyliridium(I) complexes (**A**) as well as hydrido(olefin)- and η^3-allyliridium(III) derivatives (**B**). In light of these recent results, we decided it would be interesting to explore the synthesis of (pybox)-iridium complexes in order to understand their properties and eventually apply them in asymmetric catalysis. Therefore, we report here the synthesis of novel carbonyliridium(I) and -iridium(III) complexes containing the enantiopure (*S*,*S*)-*i*Pr-pybox and (*R*,*R*)-Ph-pybox ligands. This paper also deals with the synthesis of the analogous carbonylrhodium complexes, a type of systems that are scarcely found in the literature.[6] Moreover, the monocarbonyl(*i*Pr-pybox)rhodium(I) and -iridium(I) complexes have been tested as catalysts in the asymmetric hydrosilylation of acetophenone with diphenylsilane.

stirring a mixture of $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$ (1 equiv.), R-pybox (2 equiv.) and $NaPF_6$ (3 equiv.) in dichloromethane/methanol (4:1) under CO at room temperature for 1 h. The monocarbonyl complexes $[Rh(CO)(\kappa^3\text{-}N,N,N\text{-R-pybox})][PF_6]$ were isolated as air-stable solids in high yields [R = *i*Pr (**3**), 91%; R = Ph (**4**), 84%; Scheme 2]. The preparation of complexes **1** and **3** has been reported previously.[5,6]



Scheme 2.

Results and Discussion

Synthesis of the Complexes $[M(CO)(\kappa^3\text{-}N,N,N\text{-R-pybox})][PF_6]$ [M = Ir, R = *i*Pr (1), Ph (2); M = Rh, R = *i*Pr (3), Ph (4)]

The reaction of complexes $[Ir(\eta^2\text{-}C_2H_4)_2(\kappa^3\text{-}N,N,N\text{-R-pybox})][PF_6]$ (R = *i*Pr[5] or Ph) with carbon monoxide (1 atm) in dichloromethane at room temperature results in the replacement of two ethylene molecules and the formation of the complexes $[Ir(CO)(\kappa^3\text{-}N,N,N\text{-R-pybox})][PF_6]$ [R = *i*Pr (**1**), Ph (**2**)], which were isolated as air-stable solids in excellent yields (96% and 94%, respectively; Scheme 1). Complexes **1** and **2** can be obtained in higher purity if a flow of nitrogen is slowly bubbled through the dichloromethane solution during the reaction over 50 min and before work-up. The IR spectra in the ν(CO) region show, along the reaction course, the initial formation of a non-isolated dicarbonyl complex intermediate [ν(CO) = 2088, 2021 cm^{-1}], which leads to the 16-electron monocarbonyl complexes when the reaction mixture is worked up [ν(CO) = 1989 (**1**), 1996 (**2**) cm^{-1}].

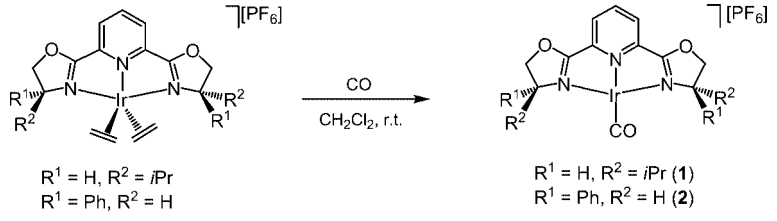
Complex **1** was also isolated as the hexafluoroantimonate derivative $[Ir(CO)\{\kappa^3\text{-}N,N,N\text{-}(S,S)\text{-}i\text{Pr-pybox}\}][SbF_6]$ (**1a**) after treatment of $[Ir(\mu\text{-}Cl)(\eta^2\text{-}C_8H_{14})_2]_2$ (C_8H_{14} = cyclooctene) with *i*Pr-pybox (2 equiv.), CO (1 atm) and $AgSbF_6$ (4 equiv.) in CH_2Cl_2 at room temperature. Similarly, the analogous rhodium complexes were prepared by

The analytical and spectroscopic data [IR and ^1H, $^{13}C\{^1H\}$ NMR] for complexes **1**–**4** support the proposed formulations (see Experimental Section for details). In particular: (a) the NMR spectroscopic data are consistent with the C_2-symmetric structure of the compounds, (b) a low-field singlet or doublet signal in the $^{13}C\{^1H\}$ NMR spectra [δ = 182.3 (**1**), 173.8 (**2**), 191.7 (d, $J_{C,Rh}$ = 76.3 Hz; **3**), 189.9 (d, $J_{C,Rh}$ = 76.3 Hz; **4**) ppm] confirms the presence of the carbonyl group, (c) the IR spectra of CH_2Cl_2 solutions show a strong ν(CO) absorption band in the ranges of 1996–1989 cm^{-1} (for **1** and **2**) and 2014–2001 cm^{-1} (for **3** and **4**).

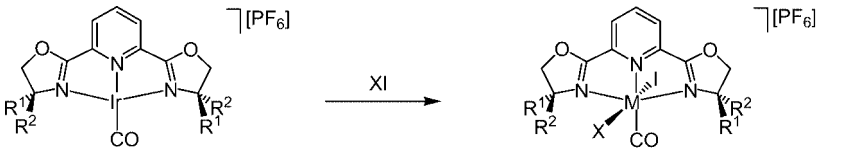
Since oxidative addition is one of the most typical reactions of square-planar iridium(I) and rhodium(I) complexes, a comparative study of such a process for the cationic monocarbonyliridium(I) and -rhodium(I) complexes **1**–**4** was performed.

Synthesis of the Complexes $[MI_2(CO)(\kappa^3\text{-}N,N,N\text{-R-pybox})][PF_6]$ [M = Ir, R = *i*Pr (5); M = Rh, R = *i*Pr (6), Ph (7)]

The reaction of equimolar amounts of $[M(CO)(\kappa^3\text{-}N,N,N\text{-R-pybox})][PF_6]$ (M = Ir, R = *i*Pr; M = Rh, R = *i*Pr, Ph) and iodine in dichloromethane at room temperature



Scheme 1.



1–4

R^1 = H, R^2 = *i*Pr, X = I, M = Ir (**5**), Rh (**6**)
R^1 = Ph, R^2 = H, X = I, M = Rh (**7**)
R^1 = H, R^2 = *i*Pr, X = CH_3, M = Ir (**8**), Rh (**10**)
R^1 = Ph, R^2 = H, X = CH_3, M = Ir (**9**), Rh (**11**)

Scheme 3.

gives stereoselectively the complexes $[IrI_2(CO)\{\kappa^3\text{-}N,N,N\text{-}(S,S)\text{-}i\text{Pr-pybox}\}][PF_6]$ (**5**) and $[RhI_2(CO)(\kappa^3\text{-}N,N,N\text{-R-pybox})][PF_6]$ [R = *i*Pr (**6**),[6] Ph (**7**)] by oxidative addition (Scheme 3). Complexes **5**–**7** were isolated as air-stable, garnet (**5**) or orange-brown (**6**, **7**) solids in high yields (83–89%) and were characterised by elemental analyses and NMR spectroscopy (see Experimental Section for details). In particular, it must be noted that: (a) CH_2Cl_2 solutions of complexes **5**–**7** show the ν(CO) absorption as a strong band in the range of 2125–2092 cm^{-1}, which is at higher energy than that found for the rhodium(I) and iridium(I) precursors **1**–**4** (2014–1989 cm^{-1}), in accordance with the higher effective oxidation state of the metal atom in complexes **5**–**7**; (b) the NMR spectroscopic data for **5**–**7** are consistent with the presence of the C_2 symmetry axis shown by the precursor complexes, thus indicating that the iodine atoms are in a *trans* arrangement;[7] (c) a low-field signal in the $^{13}C\{^1H\}$ NMR spectra due to the carbonyl group is observed as a singlet at δ = 157.8 ppm for **5** or as a doublet at δ = 177.9–177.2 ppm ($J_{C,Rh}$ = 55.1–53.4 Hz) for **6** and **7**.

Synthesis of the Complexes $[MI(CH_3)(CO)(\kappa^3\text{-}N,N,N\text{-R-pybox})][PF_6]$ [M = Ir, R = *i*Pr (8), Ph (9); M = Rh, R = *i*Pr (10), Ph (11)]

The room-temperature reaction of complexes **1** and **2** with methyl iodide (1:10 molar ratio) in dichloromethane leads to the formation of the complexes $[IrI(CH_3)(CO)(\kappa^3\text{-}N,N,N\text{-R-pybox})][PF_6]$ [R = *i*Pr (**8**), Ph (**9**); Scheme 3]. However, the synthesis of analogous rhodium complexes $[RhI(CH_3)(CO)(\kappa^3\text{-}N,N,N\text{-R-pybox})][PF_6]$ [R = *i*Pr (**10**),[6] Ph (**11**)] requires the rhodium complexes **3** and **4** to be heated at 30 °C in neat CH_3I. Complexes **8**–**11** were isolated from the reaction mixture as yellow solids in high yields [up to 90% (**8**, **9**) and 70–80% (**10**, **11**)] and were characterised by elemental analyses and NMR spectroscopy (see Experimental Section for details). In particular: (a) the presence of the methyl group is confirmed in the ^1H NMR spectra by a singlet or doublet ($^2J_{H,Rh}$ = 1.5–1.7 Hz) in the range of δ = 1.40–0.73 ppm; (b) this methyl carbon atom resonates in the $^{13}C\{^1H\}$ NMR spectra at high field as a singlet or doublet [δ = –9.5 (**8**), –10.9 (**9**), 10.3 ($J_{C,Rh}$ = 18.3 Hz; **10**), 9.3 ($J_{C,Rh}$ = 17.2 Hz; **11**) ppm], while the carbonyl carbon atom appears at low field as either a singlet or a doublet at δ = 166.8–165.1 and 185.5–184.0 ppm ($J_{C,Rh}$ = 60.4–59.8 Hz) for the iridium and rhodium complexes, respectively.

Even though the synthesis of complexes **9**–**11** is completely stereoselective, the reaction of complex **1** with CH_3I gives rise to the complex **8** along with a minor amount of another diastereoisomer (*de* = 80%) according to the ^1H NMR spectrum of the crude reaction mixture. Since the NMR and IR spectroscopic data of complexes **9**–**11** did not allow us to unambiguously determine their stereochemistry, an X-ray crystal structure analysis was performed for complex **10**, which shows the expected octahedral coordination of the rhodium atom as well as a *trans* orientation for the methyl and iodo ligands. Selected bond lengths and angles are collected in Figure 1 (see also ref.[6] for further structural data). We assume that complexes **8** (major isomer), **9** and **11** have the same stereochemistry.

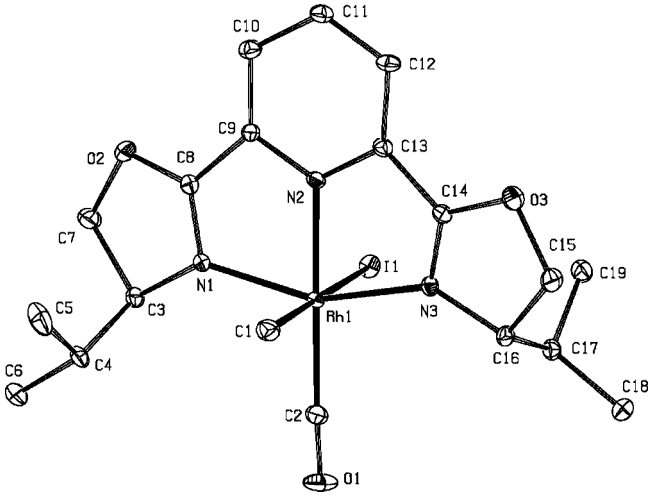


Figure 1. ORTEP-type view of the molecular structure of the cation of $[RhI(CH_3)(CO)\{\kappa^3\text{-}N,N,N\text{-}(S,S)\text{-}i\text{Pr-pybox}\}][PF_6]$ (**10**) drawn at the 10% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh–N(1) 2.059(5), Rh–N(2) 1.994(5), Rh–N(3) 2.056(5), Rh–C(1) 2.120(8), Rh–C(2) 1.900(7), Rh–I 2.7759(14), C(2)–O(1) 1.113(10); N(3)–Rh–N(1) 156.5(2).

As we have described above, monocarbonylrhodium(I) and -iridium(I) complexes **1**–**4** undergo oxidative addition reaction with iodine and CH_3I. However, monocarbonyliridium(I) complexes **1** and **2** also react under mild reaction conditions with HCl and allyl and acyl chloride to give the

iridium(III) complexes **12**–**17**, whereas the rhodium complexes **3** and **4** remain unchanged under similar or stronger conditions (CH_2Cl_2 or refluxing MeOH). This behaviour is in accordance with the well-known higher stability of iridium(III) complexes in comparison with that of rhodium(III) complexes.[8]

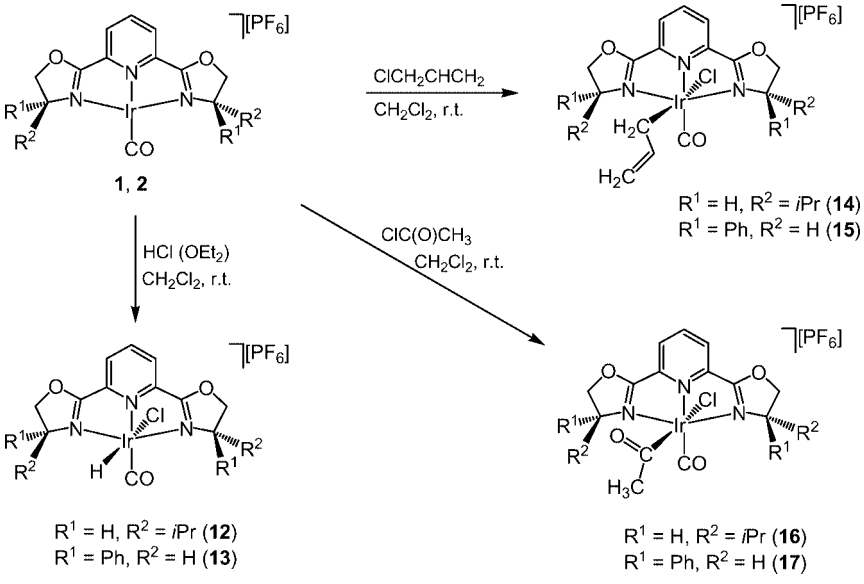
Synthesis of the Complexes [IrHCl(CO)(κ³-*N*,*N*,*N*-R-pybox)][PF_6] [R = *i*Pr (12), Ph (13)]

We are particularly interested in the synthesis of hydrido complexes as they are extensively found as intermediates in both stoichiometric and catalytic processes. The treatment of a solution of complexes **1** and **2** in dichloromethane with a solution of HCl in diethyl ether at room temperature gives stereoselectively the complexes [IrClH(CO){κ³-*N*,*N*,*N*-(*S*,*S*)-R-pybox}][PF_6] [R = *i*Pr (**12**), Ph (**13**)], which were isolated as air-stable, yellow solids (92–94% yield; Scheme 4). Complexes **12** and **13** were characterised by elemental analysis and NMR spectroscopy (see Experimental Section for details). The most significant features of the spectroscopic data are: (a) the characteristic ν(Ir–H) and ν(CO) IR absorptions at 2180–2164 and 2083–2075 cm^{-1}, respectively, (b) the high-field singlet for the hydrido ligand in the ^1H NMR spectra at δ = –19.25 (**12**) and –19.73 (**13**) ppm, and (c) the low-field singlet for the carbonyl carbon atom in the $^{13}C\{^1H\}$ NMR spectra at δ = 165.6 (**12**) and 163.0 (**13**) ppm. The NMR and IR spectroscopic data are consistent with three possible stereoisomers. Unfortunately, all attempts to crystallise complexes **12** or **13** from a number of solvents were unsuccessful, therefore an X-ray analysis could not be performed. We assume that the hydrido and chloro ligands are *trans* to each other, in a similar stereochemical environment to that found for complexes **10** and **15** (see below), whose structures were determined by X-ray diffraction analysis.

Synthesis of the Complexes [IrCl(η¹-$CH_2CH{=}CH_2$)(CO)(κ³-*N*,*N*,*N*-R-pybox)][PF_6] [R = *i*Pr (14), Ph (15)] and [IrCl{η¹-$C(O)CH_3$}(CO)(κ³-*N*,*N*,*N*-R-pybox)][PF_6] [R = *i*Pr (16), Ph (17)]

The oxidative addition of allyl chloride and acyl chloride to complexes **1** and **2** was also performed. Thus, the reaction of **1** and **2** with allyl chloride (3 equiv.) and acyl chloride (1 equiv.) in dichloromethane at room temperature produces the allyl- and acyliridium(III) complexes **14**/**15** and **16**/**17**, respectively (Scheme 4). These complexes were isolated as air-stable, yellow solids in 85–91% yield. Their analytic and spectroscopic data (IR and ^1H, $^{13}C\{^1H\}$ NMR) support the proposed formulations (see Experimental Section for details). In particular, the following can be pointed out: (a) the IR spectra of **16** and **17** show the expected ν(COMe) absorptions of the acyl group at 1677–1669 cm^{-1}, (b) the ^1H and ^{13}C NMR resonances of the allyl group in complexes **14** and **15** are in accordance with the σ-coordination mode [$^{13}C\{^1H\}$ NMR spectra show the expected resonances in the ranges δ = 5.9–5.7 (s) and 112.9–112.1 (s) ppm for the C_α and C_γ nuclei, respectively, of the η¹-allyl group], (c) the low-field singlet signals for the carbonyl carbon nuclei of the acyl and carbonyl ligands in the $^{13}C\{^1H\}$ NMR spectra appear in the range δ = 196.9–196.0 and 165.9–164.1 ppm, respectively.

The stereochemistry of complex **15** was confirmed by a single-crystal X-ray analysis. An ORTEP view of the molecular structure is shown in Figure 2. Selected bond lengths and angles are collected in Table 1.The structure exhibits a distorted octahedral geometry around the iridium atom which is bonded to the three nitrogen atoms of the Ph-pybox ligand, a chlorine atom, a carbon monoxide molecule and an η¹-allyl group (Figure 2). The chlorine atom and the allyl group are located in a *trans* disposition. The Ir–N(1) [2.032(8) Å], Ir–N(2) [2.014(8) Å] and Ir–N(3) [2.024(10) Å] distances as well as the N–Ir–N [77.0(3)°, 78.6(4)° and



Scheme 4.

155.6(4)°] bond angles fall in the range observed for the related complexes [Ir(η^2-C_2H_4)$_2$\{κ^3-*N*,*N*,*N*-(*S*,*S*)-*i*Pr-pybox\}][PF_6][5] and [IrCl(η^3-C_3H_5)\{κ^3-*N*,*N*,*N*-(*S*,*S*)-*i*Pr-pybox\}][PF_6].[5] The Ir–allyl distances [Ir–C(1) = 2.118(11), C(1)–C(2) = 1.427(13) and C(2)–C(3) = 1.223(17) Å] are slightly shorter than those found for other σ-allyliridium(III) complexes such as [Ir(η^1-$CH_2CH{=}CH_2$)$_3$(PP_2)] [PP_2 = $PhP(CH_2CH_2PPh_2)_2$; Ir–C(1) = 2.208(4)–2.186(4), C(1)–C(2) = 1.488(6)–1.463(6) and C(2)–C(3) = 1.319(6)–1.253(9) Å].[9] Finally, the C–O bond length of the CO ligand in complex **15** [1.117(13) Å] is comparable to that found in the case of the carbonylrhodium complex **10** [C(2)–O(1) = 1.113(10) Å]. In conclusion, both complexes **10** and **15** present the same stereochemistry, with the CO ligand *trans* to the pyridine nitrogen atom of the pybox ligand (see Figures 1 and 2).

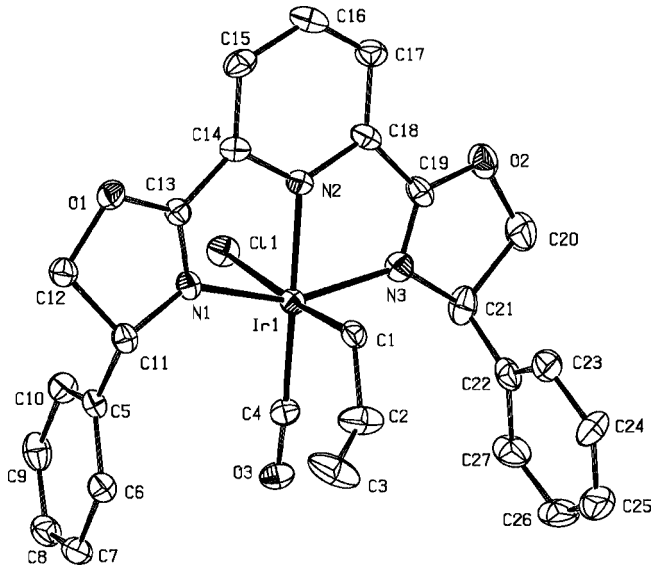


Figure 2. ORTEP-type view of the molecular structure of the cation of [IrCl(η^1-$CH_2CH{=}CH_2$)(CO)\{κ^3-*N*,*N*,*N*-(*S*,*S*)-*i*Pr-pybox\}][PF_6] (**15**) drawn at the 10% probability level. Hydrogen atoms have been omitted for clarity.

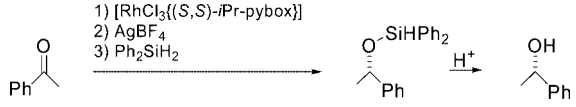
Table 1. Selected bond lengths [Å] and angles [°] for complex **15**.

Ir–Cl	2.470(3)
Ir–N(1)	2.032(8)
Ir–N(2)	2.014(8)
Ir–N(3)	2.024(10)
Ir–C(1)	2.118(11)
Ir–C(4)	1.882(11)
C(1)–C(2)	1.427(13)
C(2)–C(3)	1.223(17)
C(4)–O(3)	1.117(13)
N(1)–Ir–N(3)	155.6(4)
N(1)–Ir–N(2)	77.0(3)
N(2)–Ir–N(3)	78.6(4)
N(1)–Ir–C(4)	103.1(4)
N(3)–Ir–C(4)	101.3(5)
N(2)–Ir–C(4)	178.7(4)
N(1)–Ir–C(1)	87.9(4)
N(3)–Ir–C(1)	92.0(4)
N(2)–Ir–C(1)	89.1(4)
Ir–C(1)–C(2)	116.2(8)
C(1)–C(2)–C(3)	138(2)
C(4)–Ir–C(1)	92.2(4)
Cl–Ir–C(1)	175.2(3)
N(1)–Ir–Cl	91.6(2)
N(2)–Ir–Cl	86.2(3)
N(3)–Ir–Cl	86.6(3)
O(3)–C(4)–Ir(1)	174.6(10)

We have recently reported the synthesis of the complex [IrCl(η^3-C_3H_5)\{κ^3-*N*,*N*,*N*-(*S*,*S*)-*i*Pr-pybox\}][PF_6][5] by treatment of the complex [Ir(η^2-C_2H_4)$_2$\{κ^3-*N*,*N*,*N*-(*S*,*S*)-*i*Pr-pybox\}][PF_6] with allyl chloride in acetone at room temperature. The reaction presumably involves the formation of an intermediate monoolefiniridium(III) complex with the allyl group having a monodentate coordination. However, complexes **14** and **15** are stable in the sense that they do not evolve into the corresponding η^3-allyl complexes [IrCl(η^3-C_3H_5)(κ^3-*N*,*N*,*N*-*R*-pybox)][PF_6] (R = *i*Pr, Ph) by loss of carbon monoxide.

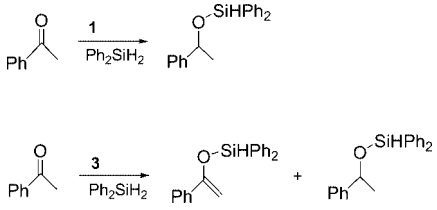
Hydrosilylation of Acetophenone

The rhodium(III) complexes [$RhCl_3$(R-pybox)] (R = *i*Pr, *s*Bu, *t*Bu, etc.) were first used as catalyst precursors by Nishiyama and co-workers in the enantioselective synthesis of secondary alcohols by the asymmetric reduction of ketones with diphenylsilane.[10] (Scheme 5). They assumed the formation of a rhodium(I) complex as the active species in situ by reduction of the precatalyst in the presence of $AgBF_4$ and diphenylsilane.



Scheme 5.

We became interested to know the behaviour of the cationic carbonyliridium(I) and -rhodium(I) complexes reported here since neither the previous reduction of the precatalyst nor the use of $AgBF_4$ as additive would be necessary. Therefore, the catalytic activity of the complexes [M(CO)\{κ^3-*N*,*N*,*N*-(*S*,*S*)-*i*Pr-pybox\}][PF_6] [M = Ir (**1**), Rh (**3**)] in the hydrosilylation/reduction of acetophenone was investigated (Scheme 6 and Table 2).



Scheme 6.

[Ir(CO)\{κ^3-*N*,*N*,*N*-(*S*,*S*)-*i*Pr-pybox\}][PF_6] (**1**) was found to be catalytically active, with complete conversion of the ketone into the corresponding silyl ether at room temperature after 72 h of reaction (Table 2, entry 1). However, the desilylation of the product led to racemic 1-phenylethanol, which means that the reduction takes place without asym-

Table 2. Hydrosilylation of acetophenone catalysed by complexes **1** and **3**.[a]

Entry	Catalyst	*i*Pr-pybox	*T* [°C]	*t* [h]	Conversion [%][b]	Silyl ether [%][b]	Silyl enol ether [%][b]
1	**1**	–	18	72	99	99	–
2	**3**	4 equiv.	0	4	100	16	84
3	**3**	–	0	3	100	30	70
4	**3**	4 equiv.	18	1	100	9	91
5	**3**	–	18	0.5	100	10	90

[a] The reactions were carried out under conditions similar to those reported in the literature.[11] Details of the procedure are given in the Experimental Section. [b] The values in the last three columns were calculated by integration of signals in the ^{1}H NMR spectra.

metric induction. At first sight, this fact can be understood if the *i*Pr-pybox ligand decoordinates before the active species is formed, otherwise some degree of induction should have been observed. This result contrasts with those obtained with the rhodium(I) complex [Rh(CO){κ^3-*N*,*N*,*N*-(*S*,*S*)-*i*Pr-pybox}][PF_6] (**3**; Table 2, entries 2–5), since variable mixtures of the expected diphenylsilyl ether (as racemate) and diphenylsilylenol ether are obtained when the reaction is run either at 0 °C or at room temperature (Scheme 6). The latter product results from the reductive O–Si coupling between diphenylsilane and the enol tautomer of the ketone. In all cases the conversion is quantitative and the diphenylsilyl enol ether is the major reaction product. We also found that the best selectivity in favour of the silyl enol ether is achieved at room temperature (Table 2, Entries 4 and 5 vs. 2 and 3) and that no excess of ligand is required at that temperature (Entries 4 and 5). A dehydrogenative silylation of ketones with a bifunctional organosilane catalysed by a mixture of the chiral or achiral complexes derived from [$RhCl_3$(pybox)] and AgOTf was reported in 1993 by Nishiyama.[11] Representative examples of the transition-metal-catalysed dehydrogenative silylation of ketones with hydrosilanes have been reported.[12]

In conclusion, acetophenone is easily and quantitatively transformed into its corresponding diphenylsilyl enol ether, at room temperature, with very high selectivity (9:1) in the presence of 1.0 mol% of [Rh(CO){κ^3-*N*,*N*,*N*-(*S*,*S*)-*i*Pr-pybox}][PF_6]. Silyl enol ethers are reagents of enormous interest in organic synthesis that take part in numerous organic transformations.[13]

Conclusions

In summary, the synthesis of monocarbonyl derivatives [M(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF_6] (M = Rh, Ir) containing the enantiopure (*S*,*S*)-*i*Pr-pybox and (*R*,*R*)-Ph-pybox ligands has been reported. This paper also deals with the synthesis of new organometallic iridium(III) and rhodium(III) complexes by stereoselective oxidative addition reactions. The catalytic activity of the complexes [M(CO){κ^3-*N*,*N*,*N*-(*S*,*S*)-*i*Pr-pybox}][PF_6] (M = Rh, Ir) in the hydrosilylation of acetophenone has been examined. In particular, the complex [Rh(CO){κ^3-*N*,*N*,*N*-(*S*,*S*)-*i*Pr-pybox}][PF_6] has been demonstrated to be a very efficient catalyst for the dehydro-*O*-silylation of acetophenone to give the silyl enol ether PhC(OSiHPh_2)=CH_2 as the major product.

Experimental Section

General: All reactions were performed under dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The complexes [Ir(η^2-C_2H_4)$_2${κ^3-*N*,*N*,*N*-(*S*,*S*)-*i*Pr-pybox}][PF_6], [Ir(μ-Cl)(η^2-C_8H_{14})$_2$]$_2$ (C_8H_{14} = cyclooctene) and [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ were prepared according to previously reported methods.[5,14] Infrared spectra were recorded with a Perkin–Elmer FT 1720-X or Paragon 1000 spectrometer. The conductivities were measured at room temperature, for approx. 5×10^{-4} M acetone solutions, with a Jenway PCM3 conductimeter. The C, H and N analyses were carried out with a Perkin–Elmer 240-B microanalyzer. Mass spectra (FAB) were determined with a VG-Autospec mass spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. NMR spectra were recorded with a Bruker AC300 (DPX-300 or AV-300) instrument at 300 MHz (^{1}H) or 75.4 MHz (^{13}C) or a Bruker AMX-400 instrument at 400 MHz (^{1}H) or 100.6 MHz (^{13}C), using $SiMe_4$ as standard. DEPT experiments were carried out for most of the complexes.

Synthesis of [Ir(η^2-C_2H_4)$_2${κ^3-*N*,*N*,*N*-(*R*,*R*)-Ph-pybox}][PF_6]: A flow of ethylene was slowly bubbled at room temperature into a suspension of [Ir(μ-Cl)(coe)$_2$]$_2$ (0.448 g, 0.5 mmol) in 5 mL of methanol. After the solution colour became yellow, Ph-pybox (0.369 g, 1 mmol) was added and the mixture stirred at –40 °C for 40 min. $NaPF_6$ (0.248 g, 1.45 mmol) was added to the resulting red solution and the mixture stirred at –40 °C for 45 min. Diethyl ether was then added (ca. 100 mL) and the resulting red solid was washed with cold diethyl ether (3 × 5 mL) and then vacuum-dried (89% yield). Yield: 89% (0.064 g). Colour: red. $C_{27}H_{27}F_6IrN_3O_2P$ (762.70): calcd. C 42.52, H 3.57, N 5.51; found C 41.32, H 3.40, N 5.34. FAB-MS: *m*/*z* = 590 [$M^+ - C_2H_4$], 562 [$M^+ - 2\ C_2H_4$]. IR (KBr): $\tilde{\nu}$ = 840 (PF_6^-) cm^{-1}. Conductivity (acetone, 20 °C): 129 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 8.17 (s, 3 H, C_5H_3N), 7.40, 7.09 (2 × m, 10 H, CH*Ph*), 5.23 (m, 2 H, OCH_2 or C*H*Ph), 4.81 (m, 2 H, OCH_2 or C*H*Ph), 4.47 (m, 2 H, OCH_2 or C*H*Ph), 2.33 (br., 4 H, C_2H_4), 1.97 (br., 4 H, C_2H_4) ppm. ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 20 °C): δ = 170.09 (s, OCN), 145.66 (s, $C^{2,6}$ C_5H_3N), 136.60 (s, C^4H C_5H_3N), 130.31, 129.66, 128.30, 126.52 (s, $C^{3,5}$H C_5H_3N and Ph), 79.27 (s, OCH_2), 66.99 (s, *C*HPh), 32.97 (s, C_2H_4) ppm.

Synthesis of Complexes [Ir(CO)(κ^3-*N*,*N*,*N*-R-pybox)][X] [X = PF_6, R = *i*Pr (1), Ph (2); X = SbF_6, R = *i*Pr (1a)]. Method A: A solution of [Ir(η^2-C_2H_4)$_2$(κ^3-*N*,*N*,*N*-R-pybox)][PF_6] (R = *i*Pr or Ph) (0.1 mmol) in dichloromethane (10 mL) was stirred at room temperature under CO for 5 min. The resulting solution was then concentrated to about 3 mL and the residue diluted with 30 mL of diethyl ether to yield a dark solid, which was washed with diethyl ether (3 × 5 mL) and vacuum-dried. Complexes **1** and **2** were obtained in higher purity if a flow of nitrogen was slowly bubbled into the dichloromethane solution over 50 min and the mixture worked up as above. **Method B:** A solution of [Ir(μ-Cl)(η^2-C_8H_{14})$_2$]$_2$ (0.036 g, 0.04 mmol) in dichloromethane (10 mL) was stirred at room temperature under CO for 5 min. *i*Pr-pybox (0.024 g, 0.08 mmol) and $AgSbF_6$ (0.052 g, 0.15 mmol) were then added and the mixture was stirred in the dark for 4 h. The suspen-

sion was filtered through kieselguhr and the resulting solution was then concentrated to about 3 mL. Addition of hexane (30 mL) yielded a dark solid, which was washed with hexane (3 × 5 mL) and vacuum-dried. **1:** Yield: 96% (0.064 g). Colour: dark green. $C_{18}H_{23}F_6IrN_3O_3P$ (666.58): calcd. C 32.43, H 3.48, N 6.30; found C 31.85, H 3.13, N 5.81. IR (KBr): $\tilde{\nu}$ = 1968 (CO), 840 (PF_6^-) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1989 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 123 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.36 [t, $J_{H,H}$ = 8.0 Hz, 1 H, H^4 C_5H_3N), 8.17 (d, $J_{H,H}$ = 8.0 Hz, 2 H, H^{3,5} C_5H_3N), 5.16 (m, 4 H, OCH_2), 4.48 (m, 2 H, C*H*iPr), 2.22 (m, 2 H, C*H*Me$_2$), 1.06 (d, $J_{H,H}$ = 7.1 Hz, 6 H, CH*Me*$_2$), 0.98 (d, $J_{H,H}$ = 6.8 Hz, 6 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, [D$_6$]acetone, 20 °C): δ = 182.3 (s, CO), 172.0 (s, OCN), 149.0 (s, C^{4}H C^{2,6} C_5H_3N), 125.4 (s, C^{3,5}H C_5H_3N), 74.5 (s, OCH_2), 71.7 (s, *C*HiPr), 31.1 (s, *C*HMe$_2$), 18.3 (s, CH*Me*$_2$), 14.5 (s, CH*Me*$_2$) ppm. **2:** Yield: 94% (0.069 g). Colour: garnet. $C_{24}H_{19}F_6IrN_3O_3P$ (734.62): calcd. C 39.24, H 2.61, N 5.72; found C 38.57, H 2.45, N 5.34. IR (KBr): $\tilde{\nu}$ = 1978 (CO), 842 (PF_6^-) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1996 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 117 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.41 (m, 1 H, H^4 C_5H_3N), 8.28 (d, $J_{H,H}$ = 8.5 Hz, 2 H, H^{3,5} C_5H_3N), 7.43 (m, 10 H, CH*Ph*), 5.63 (m, 2 H, OCH_2), 5.48 (m, 2 H, OCH_2), 5.04 (m, 2 H, C*H*Ph) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, [D$_6$]acetone, 20 °C) δ = 173.8 (s, CO), 166.1 (s, OCN), 143.5 (s, C^{2,6} C_5H_3N), 140.0 (s, C^{4}H C_5H_3N), 132.0 (s, *ipso*-Ph), 123.6, 123.4, 122.7 (s, Ph), 118.9 (s, C^{3,5}H C_5H_3N), 74.7 (s, OCH_2), 65.0 (s, *C*HPh) ppm. **1a:** Colour: very dark green. $C_{18}H_{23}F_6IrN_3O_3Sb$ (757.36): calcd. C 28.55, H 3.06, N 5.55; found C 29.06, H 3.06, N 5.20. IR (KBr): $\tilde{\nu}$ = 1973 (CO), 659 (SbF_6^-) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1989 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 130 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.36 (t, $J_{H,H}$ = 8.0 Hz, 1 H, H^4 C_5H_3N), 8.16 (d, $J_{H,H}$ = 8.0 Hz, 2 H, H^{3,5} C_5H_3N), 5.16 (m, 4 H, OCH_2), 4.47 (m, 2 H, C*H*iPr), 2.24 (m, 2 H, C*H*Me$_2$), 1.07 (d, $J_{H,H}$ = 7.2 Hz, 6 H, CH*Me*$_2$), 0.99 (d, $J_{H,H}$ = 6.9 Hz, 6 H, CH*Me*$_2$) ppm.

Synthesis of Complexes [Rh(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF$_6$] [R = *i*Pr (3), Ph (4)]: A solution of the corresponding pybox ligand (1.028 mmol), [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ (0.200 g, 0.514 mmol) and $NaPF_6$ (0.259 g, 1.542 mmol) in dichloromethane (20 mL)/methanol (5 mL) was stirred at room temperature under CO for 1 h. The solvent was then removed under reduced pressure and the solid residue was extracted with dichloromethane and filtered. The resulting solution was then concentrated to about 3 mL and 30 mL of diethyl ether added to yield a solid, which was washed with diethyl ether (2 × 30 mL) and vacuum-dried. **3:** Yield: 91% (0.542 g). Colour: garnet $C_{18}H_{23}F_6N_3O_3PRh$ (577.26): calcd. C 37.45, H 4.01, N 7.28; found C 37.81, H 3.96, N 7.02. FAB-MS: *m*/*z* = 432 [M$^+$], 404 [M$^+$ – CO]. IR (KBr): $\tilde{\nu}$ = 1981 (CO), 840 (PF_6^-) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 2001 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 118 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.50 (t, $J_{H,H}$ = 8.2 Hz, 1 H, H^4 C_5H_3N), 8.16 (d, $J_{H,H}$ = 8.2 Hz, 2 H, H^{3,5} C_5H_3N), 5.14–4.99 (m, 4 H, OCH_2), 4.36 (m, 2 H, C*H*iPr), 2.16 (m, 2 H, C*H*Me$_2$), 1.05 (d, $J_{H,H}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 0.98 (d, $J_{H,H}$ = 6.8 Hz, 6 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, [D$_6$]acetone, 20 °C): δ = 191.7 (d, $J_{C,Rh}$ = 76.3 Hz, CO), 168.1 (s, OCN), 146.3 (s, C^{4}H C_5H_3N), 144.5 (s, C^{2,6} C_5H_3N), 125.9 (s, C^{3,5}H C_5H_3N), 73.7 and 70.1 (s, OCH_2 and *C*HiPr), 30.9 (s, *C*HMe$_2$), 18.1 (s, CH*Me*$_2$) 14.5 (s, CH*Me*$_2$) ppm. **4:** Yield: 84% (0.557 g). Colour: green. $C_{24}H_{19}F_6N_3O_3PRh$ (645.30): calcd. C 44.67, H 2.96, N 6.51; found C 43.74, H 2.60, N 6.10. FAB-MS: *m*/*z* = 500 [M$^+$], 472 [M$^+$ – CO]. IR (KBr): $\tilde{\nu}$ = 1997 (CO), 840 (PF_6^-) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 2014 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 130 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.52 (t, $J_{H,H}$ = 8.0 Hz, 1 H, H^4 C_5H_3N), 8.23 (d, $J_{H,H}$ = 8.0 Hz, 2 H, H^{3,5} C_5H_3N), 7.43 (m, 10 H, Ph), 5.47 (m, 4 H, OCH_2), 4.93 (pt, $J_{H,H}$ = 8.6 Hz, 2 H, C*H*Ph) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, [D$_6$]acetone, 20 °C): δ = 189.9 (d, $J_{C,Rh}$ = 76.3 Hz, CO), 168.8 (s, OCN), 147.2 and 144.4 (s, Ph and C^{2,6} C_5H_3N), 139.0 (s, C^{4}H C_5H_3N), 129.8, 129.7, 128.9, 126.2 (s, Ph and C^{3,5}H C_5H_3N), 80.6 (s, OCH_2), 69.9 (s, *C*HPh) ppm.

Synthesis of Complex *trans*-[IrI$_2$(CO){κ^3-*N*,*N*,*N*-(*S*,*S*)-*i*Pr-pybox}][PF$_6$] (5): I_2 (0.076 g, 0.30 mmol) was added to a solution of complex **1** (0.100 g, 0.15 mmol) in 10 mL of dichloromethane. Upon addition of iodine, the black solution turned red. The solution was stirred at room temperature for 5 min. The volume was then reduced to about 3 mL and 30 mL of diethyl ether was added to yield an orange solid, which was washed with diethyl ether (2 × 20 mL) and dried under reduced pressure. Yield: 85% (0.125 g). Colour: garnet. $C_{18}H_{23}F_6I_2IrN_3O_3P$ (920.39): calcd. C 23.49, H 2.52, N 4.57; found C 24.28, H 2.68, N 4.51. IR (KBr): $\tilde{\nu}$ = 2102 (CO), 845 (PF_6^-) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 2092 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 128 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.90 (m, 1 H, H^4 C_5H_3N), 8.74 (d, $J_{H,H}$ = 8.0 Hz, 2 H, H^{3,5} C_5H_3N), 5.37 (m, 4 H, OCH_2), 4.64 (m, 2 H, C*H*iPr), 2.28 (m, 2 H, C*H*Me$_2$), 1.17 (d, $J_{H,H}$ = 7.0 Hz, 6 H, CH*Me*$_2$), 1.13 (d, $J_{H,H}$ = 6.6 Hz, 6 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, [D$_6$]acetone, 20 °C): δ = 170.9 (s, OCN), 157.8 (s, CO), 145.9 (s, C^{4}H C_5H_3N), 143.9 (s, C^{2,6} C_5H_3N), 130.8 (s, C^{3,5}H C_5H_3N), 75.3 (s, OCH_2), 71.3 (s, *C*HiPr), 30.4 (s, *C*HMe$_2$), 18.5 (s, CH*Me*$_2$), 15.8 (s, CH*Me*$_2$) ppm.

Synthesis of Complexes *trans*-[RhI$_2$(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF$_6$] [R = *i*Pr (6), Ph (7)]: I_2 (0.044 g, 0.173 mmol) was added to a solution of complex **3** or **4** (0.173 mmol) in 10 mL of dichloromethane or THF. The green solution turned orange. After 5 min, the volume was reduced to about 2 mL and 30 mL of diethyl ether added, yielding an orange-brown solid which was washed with diethyl ether (2 × 20 mL) and vacuum-dried. **6:** Yield: 89% (0.129 g). Colour: orange-brown. $C_{18}H_{23}F_6I_2N_3O_3PRh$ (831.07): calcd. C 26.01, H 2.79, N 5.06; found C 25.58, H 2.86, N 5.34. IR (KBr): $\tilde{\nu}$ = 2110 (CO), 840 (PF_6^-) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 2112 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 122 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 8.73 (t, $J_{H,H}$ = 8.1 Hz, 1 H, H^4 C_5H_3N), 8.41 (d, $J_{H,H}$ = 8.1 Hz, 2 H, H^{3,5} C_5H_3N), 5.12–4.97 (m, 4 H, OCH_2), 4.39 (m, 2 H, C*H*iPr), 2.17 (m, 2 H, C*H*Me$_2$), 1.08 (d, $J_{H,H}$ = 6.5 Hz, 6 H, CH*Me*$_2$), 1.06 (d, $J_{H,H}$ = 6.2 Hz, 6 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 20 °C): δ = 177.9 (d, $J_{C,Rh}$ = 53.4 Hz, CO), 167.4 (s, OCN), 145.1 and 144.6 (2 × s, C^{4}H and C^{2,6} C_5H_3N), 130.1 (s, C^{3,5}H C_5H_3N), 74.5 and 71.0 (s, OCH_2 and *C*HiPr), 30.2 (s, *C*HMe$_2$), 15.9 (s, CH*Me*$_2$), 14.3 (s, CH*Me*$_2$) ppm. **7:** Yield: 83% (0.129 g). Colour: orange-brown. $C_{24}H_{19}F_6I_2N_3O_3PRh$ (899.10): calcd. C 32.06, H 2.13, N 4.67; found C 32.83, H 2.33, N 4.10. IR (KBr): $\tilde{\nu}$ = 2125 (CO), 840 (PF_6^-) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 2125 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 127 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.52 (t, $J_{H,H}$ = 7.8 Hz, 1 H, H^4 C_5H_3N), 8.23 (d, $J_{H,H}$ = 7.8 Hz, 2 H, H^{3,5} C_5H_3N), 7.43 (m, 10 H, Ph), 5.47 (m, 4 H, OCH_2), 5.30 (m, 2 H, C*H*Ph) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, [D$_6$]acetone, 20 °C): δ = 177.2 (d, $J_{C,Rh}$ = 55.1 Hz, CO), 168.3 (s, OCN), 146.0 and 145.7 (2 × s, C^{2,6}H C_5H_3N), 134.4 (s, C^{4}H C_5H_3N), 131.1–128.8 (Ph and C^{3,5}H C_5H_3N), 80.7 (s, OCH_2), 70.9 (s, *C*HPh) ppm.

Synthesis of Complexes [Ir(CH$_3$)I(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF$_6$] [R = *i*Pr (8), Ph (9)]: Iodomethane (0.093 mL, 1.5 mmol) was added to a solution of complex **1** or **2** (0.15 mmol) in 10 mL of dichloromethane. The solution was stirred at room temperature. The re-

sulting orange solution was then concentrated to about 3 mL and 30 mL of a mixture of diethyl ether and hexane (1:1) was added to yield a yellow solid, which was washed with diethyl ether (3 × 5 mL) and dried under reduced pressure. **8:** Reaction time: 1 h. Yield: 93% (0.113 g). Colour: yellow. FAB-MS: *m*/*z* = 664 [M^+]. IR (KBr): $\tilde{\nu}$ = 2076 (CO), 840 (PF_6^-) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 2069 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 125 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.79 (t, $J_{H,H}$ = 8.1 Hz, 1 H, H^4 C_5H_3N), 8.56 (m, 2 H, $H^{3,5}$ C_5H_3N), 5.35 (m, 4 H, OCH_2), 4.66 (m, 2 H, C*H*i*Pr*), 2.27 (m, 2 H, C*H*Me$_2$), 1.13 (m, 9 H, CH*Me*$_2$), 1.11 (s, 3 H, IrMe), 1.02 (d, $J_{H,H}$ = 6.7 Hz, 3 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, [D$_6$]acetone, 20 °C, major isomer): δ = 170.8 (s, OCN), 170.3 (s, OCN), 166.8 (s, CO), 145.0 (s, C^4H C_5H_3N), 144.8 (s, $C^{2,6}$ C_5H_3N), 144.0 (s, $C^{2,6}$ C_5H_3N), 130.0 (s, $C^{3,5}H$ C_5H_3N), 129.8 (s, $C^{3,5}H$ C_5H_3N), 75.2 (s, *C*H*i*Pr), 75.1 (s, *C*H*i*Pr), 71.9 (s, OCH_2), 71.1 (s, OCH_2), 30.7 (s, *C*HMe$_2$), 30.4 (s, *C*HMe$_2$), 19.2 (s, CH*Me*$_2$), 19.0 (s, CH*Me*$_2$), 16.4 (s, CH*Me*$_2$), 15.5 (s, CH*Me*$_2$), –9.5 (s, IrMe) ppm. **9:** Reaction time: 20 min. Yield: 94% (0.123 g). Colour: yellow. $C_{25}H_{22}F_6IIrN_3O_3P$ (876.56): calcd. C 34.26, H 2.53, N 4.79; found C 34.54, H 2.51, N 4.72. IR (KBr): $\tilde{\nu}$ = 2067 (CO), 842 (PF_6^-) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 2075 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 119 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.84 (m, 1 H, H^4 C_5H_3N), 8.65 (m, 2 H, $H^{3,5}$ C_5H_3N), 7.70–7.30 (2 × m, 10 H, CH*Ph*), 5.80 (m, 2 H, OCH_2), 5.62 (m, 2 H, OCH_2), 5.31 (m, 2 H, C*H*Ph), 0.73 (s, 3 H, IrMe) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, [D$_6$]acetone, 20 °C): δ = 170.5 (s, OCN), 170.3 (s, OCN), 165.1 (s, CO), 144.7 (s, C^4H C_5H_3N), 135.8 (s, $C^{2,6}$ C_5H_3N), 135.0 (s, $C^{2,6}$ C_5H_3N), 131.1, 130.7, 130.3, 129.7, 129.7 (s, $C^{3,5}H$ C_5H_3N, Ph), 80.5 (s, OCH_2), 80.3 (s, OCH_2), 71.0 (s, *C*HPh), 70.7 (s, *C*HPh), –10.9 (s, IrMe) ppm.

Synthesis of Complexes [Rh(CH$_3$)I(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF$_6$] [R = *i*Pr (10), Ph (11)]: A suspension of [Rh(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF_6] (0.346 mmol) in CH_3I (5 mL) was stirred at 30 °C for 5 min. The excess of reagent was then removed under reduced pressure and the resulting solid residue was dissolved in dichloromethane (5 mL) and subjected to silica gel column chromatography. Elution with a dichloromethane/methanol mixture gave a yellow band from which complexes **10** and **11** were isolated as yellow solids after solvent removal. **10:** Eluted with dichloromethane/methanol (10:1). Yield: 80% (0.201 g). Colour: yellow. $C_{19}H_{26}F_6IN_3O_3PRh$ (719.20): calcd. C 31.73, H 3.64, N 5.84; found C 31.72, H 3.14, N 6.52. IR (KBr): $\tilde{\nu}$ = 2096 (CO), 843 (PF_6^-) cm^{-1}. Conductivity (acetone, 20 °C): 110 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 8.58 (t, $J_{H,H}$ = 8.0 Hz, 1 H, H^4 C_5H_3N), 8.25 (m, 2 H, $H^{3,5}$ C_5H_3N), 5.12–4.87 (m, 4 H, OCH_2), 4.57 (m, 1 H, C*H*i*Pr*), 4.28 (m, 1 H, C*H*i*Pr*), 2.23 (m, 1 H, C*H*Me$_2$), 2.10 (m, 1 H, C*H*Me$_2$), 1.40 (d, $^2J_{H,Rh}$ = 1.5 Hz, 3 H, RhMe), 1.05–0.93 (m, 12 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, [D$_6$]acetone, 20 °C): δ = 185.5 (d, $J_{C,Rh}$ = 59.8 Hz, CO), 167.6 (s, OCN), 167.3 (s, OCN), 145.1, 144.4 and 144.3 (s, C^4H and $C^{2,6}$ C_5H_3N), 129.8 (s, $C^{3,5}H$ C_5H_3N), 129.6 (s, $C^{3,5}H$ C_5H_3N), 74.8, 74.7, 70.9 and 70.3 (s, OCH_2 and *C*H*i*Pr), 19.2 (s, CH*Me*$_2$), 19.0 (s, CH*Me*$_2$), 16.2 (s, CH*Me*$_2$), 15.4 (s, CH*Me*$_2$), 10.3 (d, $J_{C,Rh}$ = 18.3 Hz, RhMe) ppm. **11:** Eluted with dichloromethane/methanol (50:1). Yield: 74% (0.202 g). Colour: yellow. $C_{25}H_{22}F_6IN_3O_3PRh$ (787.23): calcd. C 38.14, H 2.82, N 5.34; found C 38.99, H 2.61, N 5.46. IR (KBr): $\tilde{\nu}$ = 2099 (CO), 842 (PF_6^-) cm^{-1}. Conductivity (acetone, 20 °C): 128 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.90 (t, $J_{H,H}$ = 8.0 Hz, 1 H, H^4 C_5H_3N), 8.66 (m, 2 H, $H^{3,5}$ C_5H_3N), 7.53 (m, 10 H, Ph), 5.65 (m, 4 H, OCH_2), 5.19 (m, 2 H, C*H*Ph), 1.18 (d, $^2J_{H,Rh}$ = 1.7 Hz, 3 H, RhMe) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, [D$_6$]acetone, 20 °C): δ = 184.0 (d, $J_{C,Rh}$ = 60.4 Hz, CO), 167.7 (s, OCN), 167.3 (s, OCN), 145.6, 145.1 and 144.5 (s, Ph and $C^{2,6}$ C_5H_3N), 136.2 and 135.4 (s, Ph and C^4H C_5H_3N), 131.1–129.7 (Ph and $C^{3,5}H$ C_5H_3N), 80.6 (s, OCH_2), 80.6 (s, OCH_2), 70.3 (s, *C*HPh), 69.9 (s, *C*HPh), 9.3 (d, $J_{C,Rh}$ = 17.2 Hz, RhMe) ppm.

Synthesis of Complexes [IrClH(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF$_6$] [R = *i*Pr (12), Ph (13)]: A solution of HCl in diethyl ether (1 M, 0.1 mL, 0.1 mmol) was added to a solution of complex **1** or **2** (0.1 mmol) in 10 mL of dichloromethane at room temperature and the reaction mixture was stirred. A diethyl ether/hexane (1:1) mixture was added and the resulting yellow solid washed with the same mixture (2 × 5 mL) and then vacuum-dried. **12:** Reaction time: 50 min. Yield: 92% (0.071 g). Colour: yellow. FAB-MS: *m*/*z* = 558 [M^+], 530 [M^+ – CO]. IR (KBr): $\tilde{\nu}$ = 2180 (Ir–H), 2063 (CO), 842 (PF_6^-) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 2075 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 124 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.82 (t, $J_{H,H}$ = 8.0 Hz, 1 H, H^4 C_5H_3N), 8.54 (d, $J_{H,H}$ = 8.0 Hz, 2 H, $H^{3,5}$ C_5H_3N), 5.34 (m, 4 H, OCH_2), 4.63 (m, 2 H, C*H*i*Pr*), 2.26 (m, 2 H, C*H*Me$_2$), 1.12 (d, $J_{H,H}$ = 6.8 Hz, 9 H, CH*Me*$_2$), 0.96 (d, $J_{H,H}$ = 6.8 Hz, 3 H, CH*Me*$_2$), –19.25 (s, 1 H, IrH) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, [D$_6$]acetone, 20 °C): δ = 171.8 (s, OCN), 171.1 (s, OCN), 165.6 (s, CO), 145.6 (s, C^4H C_5H_3N), 145.1 (s, $C^{2,6}$ C_5H_3N), 129.3 (s, $C^{3,5}H$ C_5H_3N), 75.1 (s, OCH_2), 74.7 (s, OCH_2), 72.4 (s, *C*H*i*Pr), 70.2 (s, *C*H*i*Pr), 31.2 (s, *C*HMe$_2$), 30.7 (s, *C*HMe$_2$), 18.7 (s, CH*Me*$_2$), 18.3 (s, CH*Me*$_2$), 15.8 (s, CH*Me*$_2$), 14.3 (s, CH*Me*$_2$) ppm. **13:** Reaction time: 5 min. Yield: 94% (0.073 g). Colour: yellow. $C_{24}H_{20}ClF_6IrN_3O_3P$ (771.30): calcd. C 37.38, H 2.61, N 5.45; found C 36.70, H 2.60, N 5.11. IR (KBr): $\tilde{\nu}$ = 2164 (Ir–H), 2074 (CO), 843 (PF_6^-) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 2083 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 123 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.84 (m, 1 H, H^4 C_5H_3N), 8.61 (m, 2 H, $H^{3,5}$ C_5H_3N), 7.63–7.45 (m, 10 H, Ph), 5.80, 5.56, 5.20 (m, 6 H, OCH_2, C*H*Ph), –19.73 (s, 1 H, IrH) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, [D$_6$]acetone, 20 °C): δ = 171.5 (s, OCN), 171.1 (s, OCN), 163.0 (s, CO), 146.0 (s, $C^{2,6}$ C_5H_3N), 145.6 (s, $C^{2,6}$ C_5H_3N), 145.2 (s, C^4H C_5H_3N), 136.6 (s, *ipso*-Ph), 135.4 (s, *ipso*-Ph), 130.4, 130.2, 130.1, 129.4, 129.3, 128.9, 128.9 (s, $C^{3,5}H$ C_5H_3N, Ph), 80.7 (s, OCH_2), 74.7 (s, OCH_2), 71.9 (s, *C*HPh), 70.1 (s, *C*HPh) ppm.

Synthesis of Complexes [IrCl(η^1-$CH_2CH{=}CH_2$)(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF$_6$] [R = *i*Pr (14), Ph (15)]: Allyl chloride (0.025 mL, 0.30 mmol) was added to a solution of complex **1** or **2** (0.1 mmol) in 10 mL of dichloromethane. The solution was stirred at room temperature. The resulting yellow solution was then concentrated to about 3 mL and 30 mL of a mixture of diethyl ether and hexane (1:3) was added to yield a yellow solid, which was washed with the same solvent mixture (3 × 5 mL) and dried under reduced pressure. **14:** Reaction time: 1 h. Yield: 85% (0.063 g). Colour: yellow. $C_{21}H_{28}ClF_6IrN_3O_3P$ (743.11): calcd. C 33.94, H 3.80, N 5.65; found C 34.05, H 3.99, N 5.77. IR (KBr): $\tilde{\nu}$ = 2079 (CO), 846 (PF_6^-) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 2070 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 126 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.78 (t, $J_{H,H}$ = 8.0 Hz, 1 H, H^4 C_5H_3N), 8.53 (d, $J_{H,H}$ = 8.0 Hz, 1 H, $H^{3,5}$ C_5H_3N), 8.52 (d, $J_{H,H}$ = 8.0 Hz, 1 H, $H^{3,5}$ C_5H_3N), 5.84 (m, 1 H, *H*C=CH_2), 5.32 (m, 4 H, OCH_2), 4.87 (m, 1 H, HC=C*H*$_2$), 4.81 (m, 1 H, HC=C*H*$_2$), 4.64 (m, 1 H, C*H*i*Pr*), 4.56 (m, 1 H, C*H*i*Pr*), 3.18 (m, 1 H, $IrCH_2$), 2.34 (m, 1 H, $IrCH_2$), 2.28 (m, 2 H, C*H*Me$_2$), 1.16 (d, $J_{H,H}$ = 7.0 Hz, 3 H, CH*Me*$_2$), 1.11 (d, $J_{H,H}$ = 7.0 Hz, 3 H, CH*Me*$_2$), 1.09 (d, $J_{H,H}$ = 6.7 Hz, 3 H, CH*Me*$_2$), 1.07 (d, $J_{H,H}$ = 6.7 Hz, 3 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, [D$_6$]acetone, 20 °C): δ = 171.7 (s, OCN), 171.0 (s, OCN), 165.9 (s, CO), 145.7 (s, C^4H C_5H_3N or H*C*=CH_2 allyl), 145.0 (s, $C^{2,6}$ C_5H_3N), 144.3 (s, $C^{2,6}$ C_5H_3N), 142.9 (s, C^4H C_5H_3N or H*C*=CH_2 allyl), 129.8 (s, $C^{3,5}H$ C_5H_3N), 112.9 (s, HC=*C*H_2 allyl), 75.8 (s, OCH_2), 75.1 (s, OCH_2), 71.7 (s, *C*H*i*Pr), 71.0 (s,

*C*H*i*Pr), 31.2 (s, *C*HMe$_2$), 30.4 (s, *C*HMe$_2$), 19.3 (s, CH*Me*$_2$), 18.6 (s, CH*Me*$_2$), 15.8 (s, CH*Me*$_2$), 15.6 (s, CH*Me*$_2$), 5.9 (s, IrCH$_2$) ppm. **15:** Reaction time: 15 min. Yield: 89% (0.072 g). Colour: yellow. $C_{27}H_{24}ClF_6IrN_3O_3P$ (811.14): calcd. C 39.98, H 2.98, N 5.18; found C 39.22, H 3.16, N 5.12. FAB-MS: *m*/*z* = 666 [M$^+$]. IR (KBr): $\tilde{\nu}$ = 2069 (CO), 842 (PF$_6^-$) cm^{-1}. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2077 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 127 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.85 (t, $J_{H,H}$ = 8.0 Hz, 1 H, H^4 C$_5$H$_3$N), 8.64 (d, $J_{H,H}$ = 8.0 Hz, 2 H, H^{3,5} C$_5$H$_3$N), 7.70–7.40 (4m, 10 H, Ph), 5.83 (m, 2 H, OCH$_2$, C*H*Ph), 5.65 (m, 1 H, C*H*Ph), 5.40 (m, 3 H, OCH$_2$, *H*C=CH$_2$ allyl), 5.19 (m, 1 H, OCH$_2$), 4.64 (m, 2 H, HC=C*H*$_2$ allyl), 2.57 (m, 1 H, IrCH$_2$), 2.10 (m, 1 H, IrCH$_2$) ppm. ^{13}C{^{1}H} NMR (75.48 MHz, [D$_6$]acetone, 20 °C): δ = 171.6 (s, OCN), 171.1 (s, OCN), 164.1 (s, CO), 145.7 (s, C^{4}H C$_5$H$_3$N or H*C*=CH$_2$ allyl), 145.4 (s, C^{2,6} C$_5$H$_3$N), 145.3 (s, C^{2,6} C$_5$H$_3$N), 143.6 (s, C^{4}H C$_5$H$_3$N or H*C*=CH$_2$ allyl), 135.9 (s, *ipso*-Ph), 135.4 (s, *ipso*-Ph), 131.1, 130.6, 130.4, 130.2, 129.8, 129.7 (s, Ph, C^{3,5}H C$_5$H$_3$N), 112.1 (s, HC=*C*H$_2$ allyl), 81.0 (s, OCH$_2$), 80.8 (s, OCH$_2$), 70.8 (s, *C*HPh), 70.2 (s, *C*HPh), 5.8 (s, IrCH$_2$) ppm.

Synthesis of Complexes [IrCl{η^1-C(O)CH$_3$}(CO)(κ^3-*N*,*N*,*N*-R-pybox)][PF$_6$] [R = *i*Pr (16), Ph (17)]: Acetyl chloride (0.007 mL, 0.1 mmol) was added to a solution of complex **1** or **2** (0.1 mmol) in 10 mL of dichloromethane. The solution was stirred at room temperature. The resulting yellow solution was then concentrated to about 3 mL and 30 mL of diethyl ether was added to yield a yellow solid, which was washed with diethyl ether (3 × 5 mL) and dried under reduced pressure. **16:** Reaction time: 40 min. Yield: 86% (0.065 g). Colour: yellow. FAB-MS: *m*/*z* = 600 [M$^+$]. IR (KBr): $\tilde{\nu}$ = 2086 (CO), 1677 (COMe), 842 (PF$_6^-$) cm^{-1}. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2079 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 120 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.89 (t, $J_{H,H}$ = 8.0 Hz, 1 H, H^4 C$_5$H$_3$N), 8.63 (d, $J_{H,H}$ = 8.1 Hz, 1 H, H^{3,5} C$_5$H$_3$N), 8.54 (d, $J_{H,H}$ = 8.1 Hz, 1 H, H^{3,5} C$_5$H$_3$N), 5.35 (m, 4 H, OCH$_2$), 4.90 (m, 1 H, C*H*i*P*r), 4.56 (m, 1 H, C*H*i*P*r), 2.62 (s, 3 H, COMe), 2.41 (m, 1 H, C*H*Me$_2$), 2.23 (m, 1 H, C*H*Me$_2$), 1.13 (m, 9 H, CH*Me*$_2$), 0.88 (d, $J_{H,H}$ = 6.8 Hz, 3 H, CH*Me*$_2$) ppm. ^{13}C{^{1}H} NMR (75.48 MHz, [D$_6$]acetone, 20 °C, major isomer): δ = 196.9 (s, *C*OMe), 172.1 (s, OCN), 171.9 (s, OCN), 164.9 (s, CO), 146.3 (s, C^{4}H C$_5$H$_3$N), 144.8 (s, C^{2,6} C$_5$H$_3$N), 144.4 (s, C^{2,6} C$_5$H$_3$N), 130.2 (s, C^{3,5}H C$_5$H$_3$N), 129.5 (s, C^{3,5}H C$_5$H$_3$N), 75.4 (s, OCH$_2$), 75.1 (s, OCH$_2$), 71.6 (s, *C*H*i*Pr), 71.1 (s, *C*H*i*Pr), 46.2 (s, CO*Me*), 31.3 (s, *C*HMe$_2$), 30.4 (s, *C*HMe$_2$), 19.1 (s, CH*Me*$_2$), 18.8 (s, CH*Me*$_2$), 15.6 (s, CH*Me*$_2$), 14.6 (s, CH*Me*$_2$) ppm. **17:** Reaction time: 10 min. Yield: 91% (0.074 g). Colour: yellow. $C_{26}H_{22}ClF_6IrN_3O_4P$ (813.12): calcd. C 38.41, H 2.73, N 5.17; found C 37.97, H 2.60, N 4.98. IR (KBr): $\tilde{\nu}$ = 2080 (CO), 1669 (COMe), 844 (PF$_6^-$) cm^{-1}. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2087 (CO) cm^{-1}. Conductivity (acetone, 20 °C): 123 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, [D$_6$]acetone, 20 °C): δ = 8.93 (t, $J_{H,H}$ = 8.0 Hz, 1 H, H^4 C$_5$H$_3$N), 8.71 (d, $J_{H,H}$ = 8.0 Hz, 1 H, H^{3,5} C$_5$H$_3$N), 8.62 (d, $J_{H,H}$ = 8.0 Hz, 1 H, H^{3,5} C$_5$H$_3$N), 7.80–7.40 (m, 10 H, CH*Ph*), 5.85 (3 H), 5,53 (1 H), 5.42 (1 H), 5.21 (1 H) (4 × m, OCH$_2$, C*H*Ph), 1.92 (s, 3 H, COMe) ppm. ^{13}C{^{1}H} NMR (75.48 MHz, [D$_6$]acetone, 20 °C): δ = 195.9 (s, *C*OMe), 172.3 (s, OCN), 171.4 (s, OCN), 163.3 (s, CO), 146.1 (s, C^{4}H C$_5$H$_3$N), 145.2 (s, C^{2,6} C$_5$H$_3$N), 145.1 (s, C^{2,6} C$_5$H$_3$N), 135.6 (s, *ipso*-Ph), 135.1 (s, *ipso*-Ph), 131.0, 130.7, 130.6, 130.2, 130.2, 130.1, 129.7, 129.4 (s, C^{3,5}H C$_5$H$_3$N, Ph), 81.0 (s, OCH$_2$), 80.7 (s, OCH$_2$), 71.0 (s, *C*HPh), 70.4 (s, *C*HPh), 46.1 (s, CO*Me*) ppm.

General Procedure for Catalytic Reactions: A 10-mL flask was charged with the complex catalyst (0.04 mmol, 1.0 mol%), *i*Pr-pybox (when applicable; 0.16 mmol, 4.0 mol%) and acetophenone (4.00 mmol) under dry nitrogen. After cooling to –10 °C, Ph_2SiH_2 (6.4 mmol) was added dropwise. The reaction mixture was warmed to the reaction temperature and stirred until completion of the reaction. The disappearance of acetophenone was monitored by TLC. Before the aqueous workup, an aliquot was taken and examined by ^{1}H NMR spectroscopy. The workup of the reaction mixture was carried out as described by Nishiyama.[10] The enantiomeric excess was determined, after hydrolysis, by GC analysis with a Supelco β-DEX 120 chiral capillary column.

X-ray Structure Determination of 15: Single crystals suitable for an X-ray study were obtained by slow diffusion of diethyl ether into a solution of complex **15** in dichloromethane. An orange, prismatic single crystal (0.50 × 0.25 × 0.17 mm), orthorhombic, space group $P2_12_12_1$ (determined from systematic absences) was used. Diffraction data were recorded at 293(2) K with a Nonius Kappa CCD single-crystal diffractometer, using Cu-K_α radiation (λ = 1.5418 Å). The crystal–detector distance was fixed at 29 mm, and a total of 2432 frames were collected using the oscillation method, with 2° oscillation and a 60 s exposure time per frame. The data-collection strategy was calculated with the program Collect.[15] Data reduction and cell refinement were performed using the programs HKL Denzo and Scalepack.[16] Unit-cell dimensions were determined from 7669 reflections. Unit-cell parameters: a = 13.0003(8), b = 13.4939(9), c = 17.8850(8) Å, V = 3137.5(3) Å^3, Z = 4, $D_{calcd.}$ = 1.717 g cm^{-3}. Absorption coefficient: μ = 10.121 mm^{-1}. A total of 50428 reflections were collected, with 5662 independent reflections (R_{int} = 0.087). Data completeness was 98.7%. The software package WINGX was used for space-group determination, structure solution and refinement.[17] The structure was solved by Patterson interpretation and phase expansion using DIRDIF.[18] An empirical absorption correction was applied using XABS2.[19] (Ratio of minimum to maximum apparent transmission: 0.164460.) Isotropic least-squares refinement on F^2 was carried out using SHELXL-97.[20] During the final stages of the refinements, all positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. The H atoms were placed geometrically and their coordinates were refined riding on their parent atoms. The final cycle of full-matrix least-squares refinement based on 5662 reflections and 379 parameters converged to a final value of R_1 [$F^2 > 2\sigma(F^2)$] = 0.0607, wR_2 [$F^2 > 2\sigma(F^2)$] = 0.1580, R_1 (F^2) = 0.0656, wR_2 (F^2) = 0.1631. The absolute structure parameter was found to be 0.053(19). The function minimised was $[(\Sigma wF_o^2 - F_c^2)/\Sigma w(F_o^2)]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.1216P)^2]$ with $\sigma(F_o^2)$ from counting statistics and $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[21] Final difference electron density maps showed no features outside the range +1.135 to –0.764 e Å^{-3}. Geometrical calculations were made with PARST.[22] The crystallographic plots were made with PLATON.[23] CCDC-278506 (**15**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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