Synthesis, characterization and catalytic activity of saturated and unsaturated *N*-heterocyclic carbene iridium(I) complexes†

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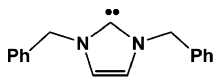
Both saturated and unsaturated *N*-benzyl substituted heterocyclic carbene (NHC) iridum(I) complexes were synthesized. The unsaturated carbene complex [(un-NHC-Bn)Ir(CO)$_2$Cl] in the *cis* form was prepared *via* the carbene transfer from the corresponding silver complex to [Ir(COD)$_2$Cl]$_2$ followed by ligand substitution with CO, whereas the saturated complex was obtained *via* the transfer from (sat-NHC-Bn)W(CO)$_5$. The treatment of phosphines with (NHC)Ir(CO)$_2$Cl complexes yielded the products with the phosphine ligand *trans* to the carbene moiety *via* substitution. X-Ray structural determination shows that distances of Ir–C$_{(carbene)}$ in both (un-NHC-Bn)Ir(CO)(PR$_3$)Cl and (un-NHC-Bn)Ir(CO)(PR$_3$)Cl are essentially the same. Analyses of spectroscopic and crystal structural data of iridium complexes [(NHC)Ir(CO)(PR$_3$)Cl] and Vaska's complex show similar corresponding data in both types of complexes, suggesting that the studied NHC ligands and phosphines have similar bonding with Ir(I) metal center. All iridium complexes studied in this work illustrated their catalytically activity on *N*-alkylation of amine with alcohol *via* hydrogen transfer reduction. It appears no dramatic difference on the catalytic activity among these iridium carbene complexes; but the saturated carbene complex (sat-NHC-Bn)Ir(CO)(PR$_3$)Cl appears to be slightly more active. For example, the reaction of benzyl alcohol with aniline in the presence of catalyst (1 mol%) under basic conditions at 100 °C provided the secondary amine (*N*-benzylaniline) in 96% yield.

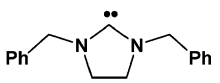
Introduction

Recently, transition metal catalyzed reactions involving the use of *N*-heterocyclic carbenes (NHCs) as ligands have received considerable attention due to their strong σ-donor property.[1] It is believed that the donation property of NHCs, stronger than phosphines, are able to increase the stability of the catalysts or pre-catalysts.[2–6] Through the analysis of υ_{CO} for (NHC)M(CO)$_x$ to estimate the Tolman electronic parameters (TEP) of ligands, *N*-heterocyclic carbenes have been considered to be stronger electron donors than the basic phosphine ligands.[6] Like other ligand systems, the modification of NHCs to fine-tune their coordination ability and catalytic activity has been amply demonstrated.[3] Along this context, the difference between saturated and unsaturated *N*-heterocyclic carbene (NHC) ligands was also one of the features to investigate. Nolan and co-workers reported that 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene, a saturated carbene donor, appeared to be a better donor than its unsaturated analogue in Cp*Ru(NHC)Cl, but showing little difference in the catalytic activity in the olefin metathesis.[4] Few other studies on various metal complexes reveal similar results.[5]

In this work, we report the preparation of both saturated and unsaturated *N*-benzyl substituted heterocyclic carbene (NHC) iridum(I) complexes *via* carbene transfer reactions from different metal complexes and their phosphine substituted species. In particular, we make comparison of donating ability between phosphines and NHCs toward iridium(I) by means of crystallographic and spectroscopic analyses. In addition, the preparation of secondary amines from alcohols and primary amines by using iridium carbene complexes as the catalyst was investigated.



un-NHC-Bn



sat-NHC-Bn

Results and discussion

Iridium carbene complexes

Iridium carbene complexes were prepared *via* the carbene transfer method.[7] The saturated iridium carbene complex was from the reaction of (sat-NHC-Bn)W(CO)$_5$ with [Ir(COD)Cl]$_2$,[7b] whereas the unsaturated complex was from the reaction of the [(un-NHC-Bn)AgI]$_2$ complex with [Ir(COD)Cl]$_2$.

Tungsten carbene, complex **1**, was prepared according to the previously reported procedure, by a deoxygenation reaction of W(CO)$_6$ with NH$_2$(CH$_2$)$_2$N=PPh$_3$ to form the corresponding isocyanide complex, which subsequently underwent intramolecular cyclization to give the un-substituted NHC complex **1**.[7a] Deprotonation of **1** with an excess of NaH followed by treatment of benzyl bromide yielded the desired tungsten carbene complex **2**.[7c] The reaction of **2** with an equal molar amount of [Ir(COD)Cl]$_2$ resulted in the formation of the iridium carbonyl complex **3** (Scheme 1). Apparently, both the carbene and the carbonyl

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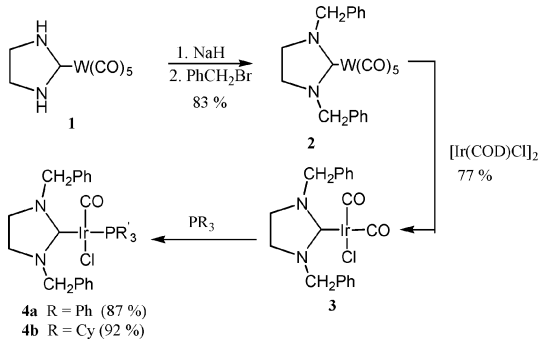
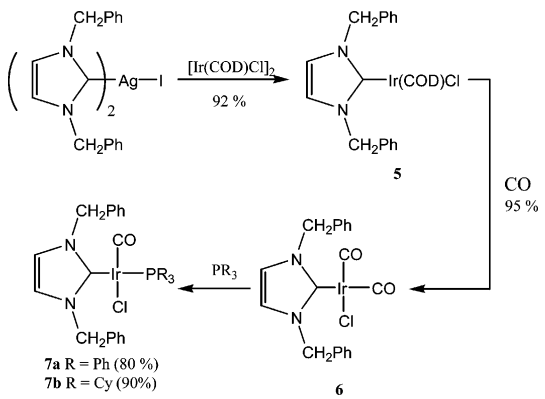
† Electronic supplementary information (ESI) available: ORTEP plot of **7a**. CCDC reference numbers: 698437 **4a** and 698438 **7a**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814234c



Scheme 1

ligands readily transfer from the tungsten metal center to the iridium(I). This carbonyl substitution was expected due to the strong donating of NHC ligand leading the enhancement of back-bonding to the carbonyls, which was also observed in the platinum complexes.[7c] In probing the donating ability of carbene ligands, the corresponding phosphine complexes were prepared for the investigation. Substitution of a carbonyl ligand by phosphine proceeded smoothly to yield the substituted product **4**, which the phosphine was seated *trans* to the carbene moiety. Both triphenylphosphine and tricyclohexylphosphine behave similarly.

For the unsaturated NHC complex, the carbene moiety transfer from silver to iridium was employed to deliver the desired species.[8] Treatment of 1,3-dibenzylimidazolium bromide with Ag_2O in the presence of NaI smoothly afforded silver-(un-NHC-Bn) complexes, which was subsequently reacted with $[Ir(COD)Cl]_2$ to provide **5**. Under an atmospheric pressure of carbon monoxide, the COD was completely replaced by carbonyl ligands to form **6**. The synthetic route for the silver and iridium complexes is illustrated in Scheme 2. The phosphine substituted complexes **7** were obtained similarly as described for **4**.



Scheme 2

The NMR spectroscopic data for the iridium complexes prepared in this work are consistent with their proposed formulations and selected data are summarized in Table 1. The ^{13}C NMR signals of the carbene carbons appear down-field in the range of 174–205 ppm of these iridium complexes, consistent with $C_{(carbene)}$-bound toward metal center. ^{13}C chemical shifts of carbonyls appeared at 181.4 and 168.3 ppm for **3** as well as 181.1 and 167.9 ppm for **6**, respectively. The carbonyl stretching frequencies for both **3** and **6** are essentially identical. Based on the donating ability of carbene is stronger than that of chloride, the down-field ^{13}C chemical shifts of the carbonyl groups of the compounds **3** and **6** are assigned to those *trans* to carbene.[9]

The stereoisomers of phosphine substituted complexes $[(NHC)Ir(CO)Cl(PR_3)]$ were identified by both spectroscopic analyses and X-ray structural determination. The *trans* relationship of phosphine to the carbene ligand is supported by the ^{13}C NMR spectrum, in which the phosphorus–carbon coupling constants for ($J_{P\text{–}C(carbene)}$) and ($J_{P\text{–}C(carbonyl)}$) are around 100 and 10 Hz, respectively. The carbonyl stretching frequencies for **4a** and **7a** are 1944 and 1945 cm^{-1}, respectively, which are essentially identical to the corresponding data for Vaska's complex.[10] These data also verify that the carbonyl ligands are *trans* to the chloride in **4a** and **7a**. The detail coordination configurations of **4a** and **7a** were confirmed by the X-ray crystal structural analysis.

The crystal structures of **4a** and **7a** are isomorphous. Fig. 1 displays the ORTEP plots of **4a**. The structures of both compounds **4a** and **7a** show that the metal is in a square planar geometry and clearly displays the *trans* relationship between carbene and phosphine donors. Selected bond lengths and bond angles are summarized in Table 2 and all are in the normal range as compared to those of the related species. Bond lengths of Ir–$C_{(carbene)}$ [**4a**:1.807(4) and **7a**: 1.813(4) Å, respectively] lie in the same range for other iridium NHC complexes.[6,11] There is no significant difference in both structures in all aspect except the distances of C(3)–C(4) [single *vs.* double bond], thus indicating that the introduction of saturated or unsaturated NHC ligand has little effect on the structural parameters around metal center.

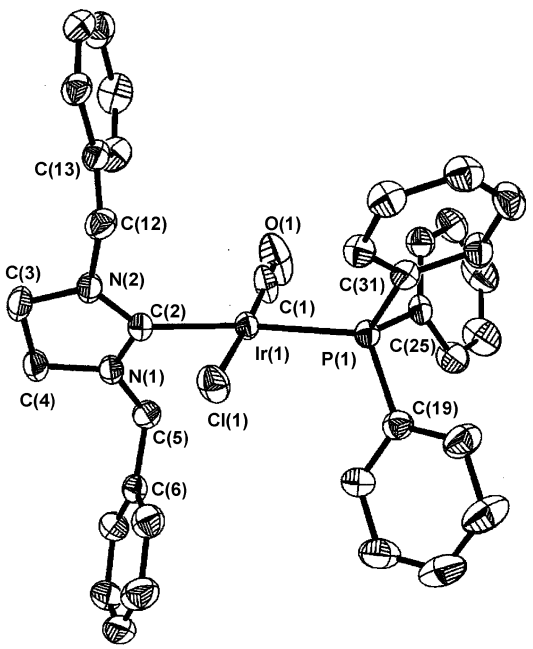


Fig. 1 ORTEP plot of complex **4a** (drawn with 30% probability ellipsoids).

The iridium phosphine carbene complexes and Vaska's complex are compared as illustrated in Tables 1 and 2. ^{31}P NMR shifts for these species do not show any significant difference, neither are the carbonyl stretching frequencies. According to Table 2, there is no substantial difference in either bond distances or bond angles for

Table 1 Selected spectral data for iridium carbene complexes[a]

Complex	^{13}C NMR, $C_{(carbene)}$–Ir	^{13}C NMR, $C_{(carbonyl)}$–Ir	^{31}P NMR[a]	IR ($\upsilon_{C=O}$)[b]
3	198.6	181.4, 168.3	—	2064, 1979 (KBr) 2067, 1983 (CH_2Cl_2)
4a	202.1 ($J_{P-C} = 108.2$)	171.7($J_{P-C} = 9.8$)	24.6	1944 (KBr)
4b	204.9 ($J_{P-C} = 99.4$)	172.0 ($J_{P-C} = 10.6$)	29.5	1932 (KBr)
5	181.0	—	—	—
6	174.2	181.1, 167.9	—	2064, 1978 (KBr) 2065, 1983 (CH_2Cl_2)
7a	177.6 ($J_{P-C} = 116$)	171.3 ($J_{P-C} = 10.4$)	24.7	1945 (KBr)
7b	181.0 ($J_{P-C} = 105.8$)	171.6 ($J_{P-C} = 10.5$)	29.3	1932 (KBr)
[*trans*-(PPh_3)$_2$IrCl(CO)]			23.4	1945 (KBr)[c]
[*trans*-(PCy_3)$_2$IrCl(CO)]			30.5	1931 (KBr); 1922 (CH_2Cl_2)[c]

[a] In $CDCl_3$, ppm, J in Hz. [b] Units are cm^{-1}. [c] Ref. 10*a*.

Table 2 Selected bond distances (Å) and bond angles (°) for **4a**, **7a** and Vaska's complex

Complex	**4a**	**7a**	Vaska's complex[a]
Bond lengths/Å			
Ir(1)–C(1)	1.807(4)	1.813(4)	1.791(13)
Ir(1)–C(2)	2.070(3)	2.069(3)	—
Ir(1)–P(1)	2.3204(8)	2.3075(8)	2.330(1)
Ir(1)–Cl(1)	2.3680(9)	2.3655(8)	2.382(3)
C(1)–O(1)	1.128(5)	1.127(4)	1.161(18)
C(3)–C(4)	1.505(5)	1.338(5)	—
Bond angles/°			
C(1)–Ir(1)–C(2)	92.0(1)	92.3(1)	—
P(1)–Ir(1)–C(2)	175.10(9)	174.77(8)	—
P(1)–Ir(1)–C(1)	91.84(11)	91.78(10)	90.81(40)
C(1)–Ir(1)–Cl(1)	177.6(1)	178.1(1)	178.08(40)

[a] Ref. 10*b*.

4a, **7a** and Vaska's complex, except the bond length corresponding to C(1)–O(1) is slightly shorter than that in the Vaska's complex by about 0.04 Å. From the above observation, we conclude that the donating ability of both NHC ligands are quite similar, and appear to be comparable to phosphine.

By adopting the analysis of Tolman electronic parameter (TEP) for carbene ligands developed by Crabtree and co-workers,[6] TEP values for un-NHC-Bn and sat-NHC-Bn were estimated. Since both complexes **3** and **6** have similar carbonyl stretching frequencies, their TEP values are comparable and are evaluated as 2054 and 2055 cm^{-1}, respectively. These values are very close to that for tricyclohexylphosphine. Such an outcome is in agreement with an earlier conclusion obtained from a qualitative comparison using IR data of (NHC)Ir$(CO)_2$Cl reported by Crabtree.[6] This trend is consistent, with a very limited distinct, to that observed for the related Vaska's complex as discussed in the previous section.

Catalytic *N*-alkylation of amine with alcohol

Few reports have demonstrated that iridium complexes are good catalysts for *N*-alkylation of amine with alcohols.[12] It has also been established that the introduction of a NHC ligand to the metal center would enhance the catalytic activity on the hydrogen transfer reaction.[13] Thus, with the new carbene complexes in hand, their abilities to catalyze *N*-alkylation of amine with alcohol were examined.

In a typical experiment for the reaction, aniline (1 mmol), benzyl alcohol (3 mmol), base and 1 mol% of the iridium catalyst were placed in the flask. An excess amount of alcohol was used for not only as the reactant, but also as the solvent. The mixture was heated to 100 °C for a certain period. The organic product was isolated by extraction and then analyzed by both GC and ^{1}H NMR spectroscopy. The results are summarized in Table 3.

Besides the *N*-benzylaniline, we found the un-reduced imine intermediate presented in each reaction. However, the mono-alkylated product was formed selectively; no formation of di-alkylated *N*,*N*-dibenzylaniline was observed. When the reaction was carried out without a base, *N*-benzylaniline and *N*-benzylideneaniline were formed in low yields (entry 1). The production of amine and imine was considerably accelerated by the addition of base. It was noticed that the amount and nature of base also affected the product distribution. Both KOH and CsOH gave excellent conversions of the reactions, but CsOH provided more *N*-benzylaniline than KOH did. When the reaction was carried out in the presence of 50 mol% CsOH, *N*-benzylaniline was formed in an excellent yield (96%) with **4a** as the catalyst (Table 3, entry 14), which can be considered the best reaction conditions for this particular transformation. It was noticed that the use of organic bases gives poor yields, but the hydroxide salts provide better results. Presumably, the dissolution of hydroxide salts in alcohols generates the corresponding alkoxide, which facilitates the reactions. In these catalytic studies, we found that there is no dramatic difference among iridium complexes prepared in this work (Table 3, entries 9, 10, 15, 16 and 17).

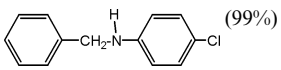
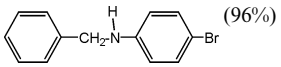
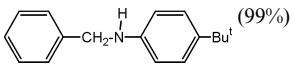
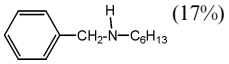
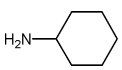
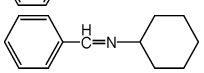
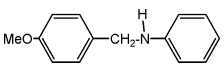
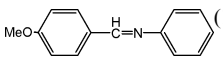
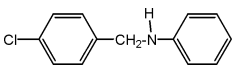
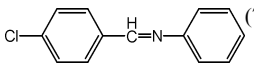
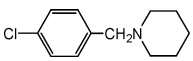
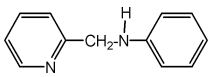
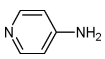
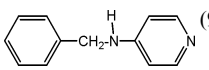
We also explored the *N*-alkylation of other primary amines (Table 4). The reactions of substituted anilines with benzyl alcohol proceeded in excellent yields (Table 4, entries 1–3). In the reaction of hexylamine with benzyl alcohol, a low yield was obtained. However, we found that the amine was completely consumed and converted into other unidentified products. When the reaction of cyclohexylamine with benzyl alcohol proceeded under similar conditions, only the corresponding imine was obtained. The use of a secondary amine or secondary alcohol gave poor yields for the corresponding product. However, the use of pyridinyl derivatives gave satisfactory results in the production of the corresponding amine (entries 11 and 12).

Table 3 Results of *N*-alkylation of aniline with benzyl alcohol[a]

Entry	Catalyst	Base	Amount of base (mol%)	Yield (%)[b]	
				$PhNHCH_2Ph$	PhN=CHPh
1	**4a**	—	—	5	11
2	**4a**	K_2CO_3	15	Trace	29
3	**4a**	NaOEt	15	20	30
4	**4a**	KO^{t}Bu	15	25	39
5	**4a**	Et_3N	15	Trace	20
6	**4a**	DBU	15	5	36
7	**4a**	DMAP	15	0	15
8	**4a**	KOH	15	47	32
9	**3**	KOH	15	24	61
10	**4b**	KOH	15	17	50
11	**4a**	KOH	50	85	7
12	**4a**	KOH	75	68	11
13	**4a**	LiOH	50	37	29
14	**4a**	CsOH	50	96	3
15	**4b**	CsOH	50	82	3
16	**7a**	CsOH	50	81	15
17	**7b**	CsOH	50	89	4
18	**4a**	CsOH	75	73	19

[a] Aniline (1 mmol) and catalysts (1 mol% based on aniline) in benzyl alcohol (3 mmol) at 100 °C for 24 h. [b] Yield based on ^{1}H NMR integration.

Table 4 *N*-alkylation reactions catalysed by the iridium complex **4a**[a]

Entry	Substrates		*t*/h	Product (yield)[b]
1	*p*-$ClC_6H_4NH_2$	$C_6H_5CH_2OH$	20	 (99%)
2	*p*-$BrC_6H_4NH_2$	$C_6H_5CH_2OH$	20	 (96%)
3	*p*-^{t}$BuC_6H_4NH_2$	$C_6H_5CH_2OH$	24	 (99%)
4	$CH_3(CH_2)_5NH_2$	$C_6H_5CH_2OH$	24	 (17%)
5		$C_6H_5CH_2OH$	24	 (62%)
6	$C_6H_5NH_2$	*p*-$MeOC_6H_5CH_2OH$	24	 (72%)  (18%)
7	$C_6H_5NH_2$	*p*-$ClC_6H_5CH_2OH$	24	 (87%)  (7%)
8	$C_6H_5NH_2$	$CH_3(CH_2)_7OH$	24	$C_8H_{17}NHC_6H_5$ (67%)
9	$C_6H_5NH_2$	Cyclohexanol	24	Cyclohexanone (< 5%)
10		$C_6H_5CH_2OH$	24	 (< 8%)
11	$C_6H_5NH_2$		24	 (90%)
12		$C_6H_5CH_2OH$	24	 (99%)

[a] Amine (1 mmol), CsOH (0.5 mmol) and **4a** (1 mol% based on amine) in alcohol (3 mmol) at 100 °C. [b] Isolated yield.

Summary

We have reported the synthesis of both saturated and unsaturated *N*-heterocyclic carbene iridium complexes *via* different carbene transfer methods. In having these complexes, substitution reactions by phosphine ligands were studied. The properties of the obtained complexes [*trans*-(NHC)Ir(PR_3)COCl] are quite similar to those of Vaska's complexes in many aspects,

indicating that both carbene ligands and phosphine have comparable coordinating ability. Iridium complexes prepared in this work showed good catalytic activities on *N*-alkylation of aniline with benzyl alcohol. However, there is no significant difference among these iridium carbene complexes on this catalytic reaction. We are currently performing methods for investigation of the mechanistic pathway for the catalysis, and the selectivity in the processes.

Experimental

General information

All reactions, manipulations and purification steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried over CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used after degassing. Tungsten carbene complex **2**[7a] and 1,3-dibenzylimidazolium bromide[14] were prepared accordingly to the method reported previously.

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ on either a Bruker AM-300 or AVANCE 400 spectrometer. Chemical shifts are given in parts per million (ppm) relative to Me_4Si for ^1H and ^{13}C NMR and relative 85% H_3PO_4 for ^{31}P NMR. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II) as KBr pallets, unless otherwise noted.

Complex [(sat-NHC-Bn)Ir(CO)$_2$Cl] 3. A mixture of **2** (100 mg, 0.174 mmol) and $[Ir(COD)Cl]_2$ (117 mg, 0.174 mmol) in a 50 mL flask capped with a septum was evacuated and flashed with nitrogen three times. CH_2Cl_2 (6 mL) was syringed into the mixture and the resulting solution was stirred at room temperature for 72 h. The reaction mixture was filtered through Celite to remove the tungsten species. The residue was chromatographed on silica with elution of hexane–ethyl acetate (3 : 1) and the yellow band was collected. Upon concentration, the desired product was obtained as a yellow solid (72 mg, 77%). IR (KBr)/cm^{-1}: 2064, 1979 (υ_{CO}). ^1H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.40–7.31 (m, 10H, Ar*H*), 5.17 (d, J = 14.8 Hz, 2H, ArCH_2N), 4.93 (d, J = 14.8 Hz, 2H, ArCH_2N), 3.47 (s, 4H, NCH_2–CH_2N). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 198.6 (Ir=*C*), 181.4, 168.3 (*C*O), 135.0, 128.9, 128.24, 128.23 (phenyl), 54.7 (Ar*C*H$_2$N), 48.3 (N*C*H$_2$–*C*H$_2$N). Anal. calcd for $C_{19}H_{18}ClIrN_2O_2$: C 42.73, H 3.40, N 5.25. Found: C 42.75, H 3.67, N 5.00.

Complex [(sat-NHC-Bn)Ir(CO)(PPh$_3$)Cl] 4a. Triphenyl phosphine (35.4 mg, 0.135 mmol) and **3** (72 mg, 0.135 mmol) in anhydrous CH_2Cl_2 (5 mL) was placed in a flask under nitrogen atmosphere. After stirring at room temperature for 2.5 h, the solvent was removed and the residue was washed with diethyl ether (3 × 2 mL). The phosphine substituted complex was obtained as a yellow solid (90 mg, 87%). IR (KBr)/cm^{-1}: 1944 (υ_{CO}). $^{31}P\{^1H\}$ (161.9 MHz, $CDCl_3$) δ/ppm: 24.6 (s). ^1H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.65–7.63 (m, 6H, Ar*H*), 7.48 (d, J = 7.4 Hz, 4H, Ar*H*), 7.34–7.30 (m, 15 H, Ar*H*), 5.59 (d, J = 14.7 Hz, 2H, ArCH_2N), 5.08 (d, J = 14.7 Hz, 2H, ArCH_2N), 3.47–3.43 (m, 4H, NCH_2–CH_2N). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 202.1 (d, $J_{P\text{-}C}$ = 108.2 Hz, Ir=*C*), 171.7 (*C*O), 136.4, 134.7, 134.6, 133.7, 133.2, 129.8, 128.7, 128.5, 128.0, 127.9, 127.7 (phenyl), 54.9 (Ar*C*H$_2$N), 48.1 (d, $J_{P\text{-}C}$ = 3.8 Hz, N*C*H$_2$–*C*H$_2$N). Anal. calcd for $C_{36}H_{33}ClIrN_2OP$: C 56.28, H 4.33, N 3.65. Found C 55.70, H 4.56, N 3.38.

Complex [(sat-NHC-Bn)Ir(CO)(PCy$_3$)Cl] 4b. This procedure was similar to that for **4a** except for the phosphine ligand. Tricyclohexyl phosphine (37.9 mg, 0.135 mmol) and **3** (72 mg, 0.135 mmol) in anhydrous CH_2Cl_2 (5 mL) was placed in a flask under nitrogen atmosphere. After stirring at room temperature for 2.5 h, the solvent was removed and the residue was washed with diethyl ether (3 × 2 mL). The phosphine substituted complex **4b** was obtained as a yellow solid (98 mg, 92%). IR (KBr)/cm^{-1}: 1932 (υ_{CO}). $^{31}P\{^1H\}$ (161.9 MHz, $CDCl_3$) δ/ppm: 29.5 (s). ^1H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.51 (d, J = 7.4 Hz, 4H, Ar*H*), 7.39–7.26 (m, 6H, Ar*H*), 5.52 (d, J = 14.6 Hz, 2H, ArCH_2N), 5.01 (d, J = 14.6 Hz, 2H, ArCH_2N), 3.43–3.38 (m, 4H, NCH_2–CH_2N), 2.32–1.13 (m, 33H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 204.9 (d, $J_{P\text{-}C}$ = 99.4 Hz, Ir=*C*), 172.0 (d, $J_{P\text{-}C}$ = 10.6 Hz, *C*O), 136.8, 128.6, 128, 127.62, 127.61 (phenyl), 54.5 (Ar*C*H$_2$N), 48.1 (d, $J_{P\text{-}C}$ = 3.5 Hz, N*C*H$_2$–*C*H$_2$N), 33.6 (d, $J_{P\text{-}C}$ = 25.4 Hz, Cy), 30.1 (s, Cy), 27.7 (d, $J_{P\text{-}C}$ = 10.4 Hz, Cy), 26.8 (s, Cy). Anal. calcd for $C_{36}H_{51}ClIrN_2OP$: C 54.98, H 6.54, N 3.56. Found: C 54.71, H 6.61, N 3.23.

Complex [(un-NHC-Bn)AgI]$_2$. To a solution of 1,3-dibenzylimidazolium bromide (2.2 g, 6.59 mmol), silver oxide (0.8 g, 3.30 mmol) and sodium iodide (0.99 g, 6.59 mmol) in CH_2Cl_2 (50 mL) were stirred at room temperature under nitrogen atmosphere for 48 h. Filtration of the reaction mixture through Celite gave a colourless solution. Upon the addition of hexane to the filtrate, the desired silver complex was precipitated and isolated as a white solid (1.8 g, 72%). ^1H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.33–7.23 (m, 20H, Ar*H*), 6.87 (s, 4H, C=C*H*N), 5.30 (s, 8H, ArCH_2N). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 185.0 (Ag=*C*), 136.0, 128.9, 128.3, 128.0 (phenyl), 121.2 (N*C*H=*C*HN), 55.6 (Ar*C*H$_2$N). Anal. calcd for $C_{17}H_{16}AgIN_2$: C 42.27, H 3.34, N 5.80. Found C 42.00, H 3.09, N 5.56.

Complex [(un-NHC-Bn)Ir(COD)Cl] 5. A mixture of silver complex $[(un\text{-}NHC\text{-}Bn)AgI]_2$ (100 mg, 0.128 mmol) and $[IrCl(COD)]_2$ (86 mg, 0.128 mmol) in dichloromethane (6 mL) was stirred at room temperature for 10 h. The resulting solution was filtrated through Celite followed by concentration and chromatographed on silica gel with elution of CH_2Cl_2–hexane to afford yellow crystalline solids upon concentration (69 mg, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.38–7.28 (m, 10H, Ar*H*), 6.65 (s, 2H, C=C*H*N), 5.76 (d, J = 14.8 Hz, 2H, ArCH_2N), 5.60 (d, J = 14.8 Hz, 2H, ArCH_2N), 4.67–4.61 (m, 2H, COD), 2.98–2.94 (m, 2H, COD), 2.18–2.10 (m, 4H, COD), 1.72–1.68 (m, 2H, COD), 1.57–1.51 (m, 2H, COD). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 181.0 (Ir=*C*), 136.3, 128.9, 128.2, 128.1 (phenyl), 120.5 (N*C*H=*C*HN), 85.1 (COD), 54.3 (Ar*C*H$_2$N), 52.0, 33.5, 29.5 (COD). Anal. calcd for $C_{25}H_{28}ClIrN_2$: C 51.40, H 4.83, N 4.80. Found: C 51.17, H 5.15, N 4.49.

Complex [(un-NHC-Bn)Ir(CO)$_2$Cl] 6. A solution of **5** (100 mg, 0.171 mmol) in CH_2Cl_2 (6 mL) was stirred under an atmosphere of carbon monoxide at room temperature overnight. Upon removal of organic molecules, the residue was washed with a small portion of hexane (0.5 mL) to yield **6** as a yellow solid (87 mg, 95%). IR (KBr)/cm^{-1}: 2064, 1978 (υ_{CO}). ^1H NMR (400 MHz, $CDCl_3$)

Table 5 Crystal data for **4a** and **7a**

Complex	**4a**	**7a**
Formula	$C_{36}H_{33}ClIrN_2OP$	$C_{36}H_{31}ClIrN_2OP$
FW	768.26	766.25
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	10.2700(3)	10.1220(5)
b/Å	32.3955(7)	32.2279(14)
c/Å	10.8716(3)	10.7193(6)
α/°	90	90
β/°	117.397(1)	117.211(6)
γ/°	90	90
V/Å^3	3211.3(2)	3109.8(3)
Z	4	4
D_{calcd}/Mg m^{-3}	1.589	1.637
F(0,0,0)	1520	1512
Crystal size/mm	0.25 × 0.20 × 0.15	0.25 × 0.20 × 0.15
Reflections collected	22 873	18 105
Independent reflections	7295 (R_{int} = 0.0436)	6807 (R_{int} = 0.0265)
θ range/°	1.26–27.50	2.59–27.50
Refinement method	Full-matrix least-squares on F^2	
Goodness of fit on F^2	1.006	1.074
R indices [$I > 2\sigma(I)$]	R_1 = 0.0277, wR_2 = 0.0680	R_1 = 0.0266, wR_2 = 0.0470
R indices (all data)	R_1 = 0.0363, wR_2 = 0.0728	R_1 = 0.0373, wR_2 = 0.0485

δ/ppm: 7.38–7.32 (m, 10H, Ar*H*), 6.82 (s, 2H, C=C*H*N), 5.53 (dd, J = 14.8 Hz, 4H, ArCH_2N). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 181.1(Ir–*C*O), 174.2 (Ir–$C_{carbene}$), 167.9 (Ir–*C*O), 135.2, 129.0, 128.6, 128.3 (phenyl), 121.6 (N*C*H=*C*HN), 55.1 (Ar*C*H$_2$N). Anal. calcd for $C_{19}H_{16}ClIrN_2O_2$: C 42.89, H 3.03, N 5.27. Found C 42.57, H 3.35, N 5.65.

Complex [(un-NHC-Bn)Ir(CO)(PPh$_3$)Cl] 7a. The preparation of **7a** is similar to that of **4a**. Yield 80%. IR (KBr)/cm^{-1}: 1945 (υ_{CO}). ^{31}P{^{1}H} (161.9 MHz, $CDCl_3$) δ/ppm: 24.7 (s). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.69–7.65 (m, 6H, phenyl), 7.44–7.42 (m, 4H, phenyl), 7.35–7.31 (m, 15H, phenyl), 6.76 (s, 2H, C=C*H*N), 5.90 (d, J = 14.8 Hz, 2H, ArCH_2N), 5.66 (d, J = 14.8 Hz, 2H, ArCH_2N). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 177.6 (d, J_{P-C} = 116 Hz, Ir=*C*), 171.3 (d, J_{P-C} = 10.4 Hz, *C*O), 136.5, 134.7, 134.6, 133.8, 133.3, 129.8, 128.8, 128.5, 128.1, 128.0, 127.9 (phenyl), 120.6 (d, J_{P-C} = 3.5 Hz, N*C*H=*C*HN), 54.9 (Ar*C*H$_2$N). Anal. calcd for $C_{36}H_{31}ClIrN_2OP$: C 56.43, H 4.08, N 3.66. Found: C 56.52, H 4.24, N 3.45.

Complex [(un-NHC-Bn)Ir(CO)(PCy$_3$)Cl] 7b. The preparation of **7b** is similar to that of **4a**. 90% yield, IR (KBr)/cm^{-1}: 1932 (υ_{CO}). ^{31}P{^{1}H} (161.9 MHz, $CDCl_3$) δ/ppm: 29.3 (s). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.46 (d, J = 7.0 Hz, 4H, phenyl), 7.35–7.28 (m, 6H, phenyl), 6.76 (s, 2H, C=C*H*N), 5.85 (d, J = 14.7 Hz, 2H, ArCH_2N), 5.59 (d, J = 14.7 Hz, 2H, ArCH_2N), 2.34–1.16 (m, 33H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 181.0 (d, J_{P-C} = 105.8 Hz, Ir=*C*), 171.6 (d, J_{P-C} = 10.5 Hz, *C*O), 136.9, 128.7, 128.5, 127.9 (phenyl), 120.3 (d, J_{P-C} = 3.1 Hz, N*C*H=*C*HN), 54.4 (Ar*C*H$_2$N), 33.7 (d, J_{P-C} = 25.7 Hz, Cy), 30.1 (s, Cy), 27.7 (d, J_{P-C} = 10.4 Hz, Cy), 26.8 (s, Cy). Anal. calcd for $C_{36}H_{49}ClIrN_2OP$: C 55.12, H 6.30, N 3.57. Found: C 54.98, H 6.11, N 3.19.

Catalysis general procedure. A mixture of 1 mol% iridium complex was placed in a flask under a nitrogen atmosphere. Then, alcohol (3 mmol), amine (1 mmol) and base were added subsequently to the above iridium complex. The mixture was stirred at room temperature for 10 min, and then heated and kept at 100 °C by an oil bath. The reaction was then monitored by ^{1}H NMR. After completion of the reaction, brine (3 mL) and CH_2Cl_2(5 mL) were added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried over magnesium sulfate, filtered and then concentrated *in vacuo*. The residue was chromatographed on silica gel with the elution of a mixture of hexane and ethyl acetate. Products obtained in this work were characterized by spectral methods particularly with ^{1}H NMR, and the data were consistent with those reported: *N*-(4-chlorophenyl)benzenemethanamine,[15a] *N*-(4-bromophenyl)benzenemethanamine,[15b] *N*-(4-*t*-butylphenyl)-benzenemeth-anamine,[15c] *N*-hexylbenzenemethanamine,[15a] benzylidene-cyclohexylamine,[15d] 4-methoxy-*N*-phenylbenzene-methan-amine,[15a] *N*-[(4-methoxyphenyl)methylene]benzen-amine,[15e] 4-chloro-*N*-phenyl-benzenemethanamine,[15a] *N*-[(4-chloro-phenyl)methylene]benzenamine,[15e] *N*-octylbenzen-amine,[15f] 1-[(4-chlorophenyl)methyl]piperidine,[15g] *N*-phenyl-2-pyrid-inemetha-namine,[15a] *N*-(phenylmethyl)-4-pyridinamine.[15h]

Crystallography. Crystals suitable for X-ray determination were obtained for **4a** and **7a** by recrystallization from dichloromethane/ether at room temperature. Cell parameters were determined using a Siemens SMART CCD diffractometer. The structure was solved using the SHELXS-97 program[16] and refined using the SHELXL-97 program[17] by full-matrix least-squares on F^2 values. The crystal data of these complexes are listed in Table 5. An ORTEP plot of **4a** is drawn with 30% probability ellipsoids and partial labelling for clear view in Fig. 1, whereas an ORTEP plot of **7a** is deposited as ESI.† Other crystallographic data are deposited as ESI.†

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