ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

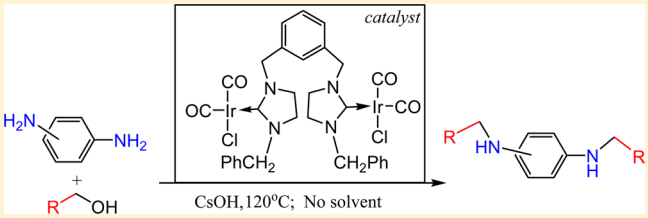
N,N′-Dialkylation Catalyzed by Bimetallic Iridium Complexes Containing a Saturated Bis-N-Heterocyclic Carbene (NHC) Ligand

Hsin-Ya Kuo, Yi-Hong Liu, Shie-Ming Peng, and Shiuh-Tzung Liu*

Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

Supporting Information

ABSTRACT: Reaction of the bis-aminophosphinimine [*m*-$C_6H_4(HNCH_2CH_2N{=}PPh_3)$] with $W(CO)_6$ afforded [*m*-$C_6H_4\{(CNCH_2CH_2NH)W(CO)_5\}_2$] (**2**), which underwent N-alkylation with benzyl bromide to yield [*m*-$C_6H_4\{(CNCH_2CH_2NCH_2Ph)W(CO)_5\}_2$] (**3**). A carbene transfer reaction from W(0) to Ir(I) proceeded smoothly via the reaction of **3** with $[Ir(COD)Cl]_2$ under mild conditions to give the diiridium(I) carbene complex [*m*-$C_6H_4\{(CNCH_2CH_2NH)Ir(CO)_2Cl\}_2$] (**4**). Ligand substitution of **4** with an excess of PPh_3 produced the phosphine complex **5**. All complexes have been characterized by spectroscopic and elemental analyses. Complexes **2** and **5** were further confirmed by X-ray diffraction studies. Complex **4** is an efficient catalyst for the reductive N,N′-dialkylation of phenylenediamines with alcohols. The mechanistic pathway of the catalysis involving the possible synergistic effect between two metal centers is discussed.



INTRODUCTION

Alkylated amines are important chemicals for many uses such as synthetic intermediates, pharmaceuticals, agrochemicals, and bulk chemicals. A variety of synthetic approaches leading to the desired amines are available.[1] However, the selective N-alkylation of amines ought to be the most direct and useful methodology.[1,2] In this context, transition-metal-catalyzed N-alkylation of amines with alcohols by a borrowing-hydrogen strategy affords a concise route for C−N bond formation and has received much attention.[2−11] In this approach, the alcohol is initially oxidized to the corresponding carbonyl compound accompanied by the generation of metal hydride. Subsequently, the carbonyl compound reacts with amines to form imines, which are then reduced to amines by the pregenerated hydrides. Indeed, there are numerous reports concerning the alkylation of monoamine molecules. However, few concern the N,N′-dialkylation of diamino compounds such as benzenediamines.[4a]

In terms of catalysts for the borrowing-hydrogen N-alkylation of amines with alcohols, mononuclear ruthenium and iridium complexes[2−10] and a few other metal ions[4f,8,11] are frequently employed for this purpose. However, the use of bimetallic complexes as precatalysts in this kind of reductive amination has been less frequently reported.[11c] Here we describe the synthesis of diiridium carbene complexes and their uses as catalysts for the N,N′-dialkylation of diamines.

RESULTS AND DISCUSSION

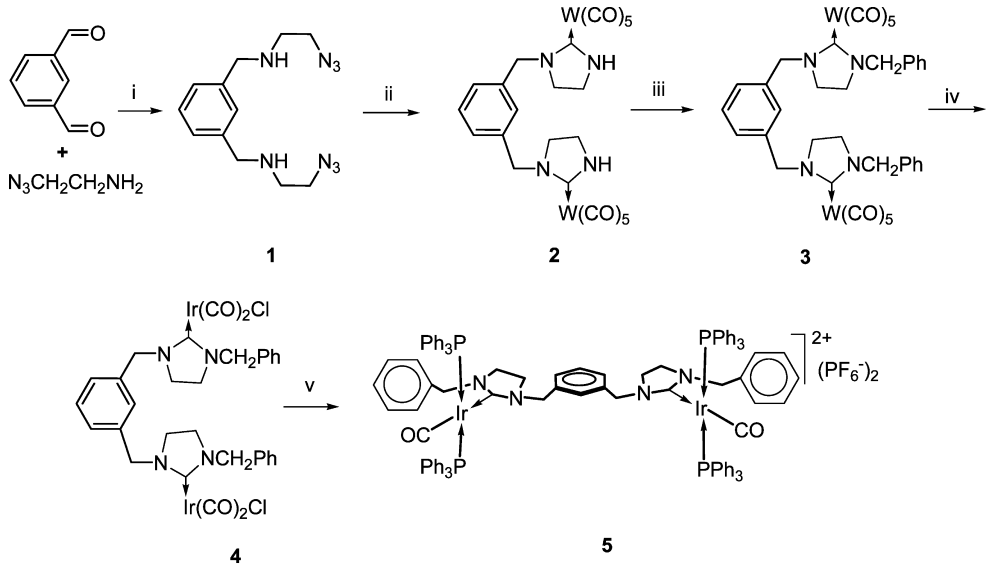
Preparation and Characterization of Bis-NHC-Iridium Complexes. Few bis(NHC) carbene complexes with a phenylene unit as a spacer have been reported,[12] but all have an unsaturated N-heterocyclic carbene moiety. In this work, we developed a synthetic approach to build a bis(saturated NHC) framework via a double cyclization of nucleophilic attacks of iminophosphoranes toward tungsten carbonyls followed by a carbene transfer reaction from tungsten to iridium.[13] Accordingly, the synthetic approach leading to the desired complexes is outlined in Scheme 1. Compound **1** was prepared via the reductive amination of *m*-isophthalaldehyde with $H_2N(CH_2)_2N_3$. Treatment of **1** with triphenylphosphine followed by hexacarbonyltungsten readily gave the desired bis-tungsten carbonyl complex **2**. Deprotonation of **2** by sodium hydride and then alkylation with benzyl bromide yielded **3**. Transfer of carbonyl ligands and carbene from tungsten to iridium proceeded by the reaction of **3** with excess $[Ir(COD)Cl]_2$ at ambient temperature for 72 h. The desired diiridium complex **4** was obtained as a yellow solid in 60% yield. Ligand substitution of **4** with excess triphenylphosphine provided the substitution product **5** in high yield.

It is worth mentioning that we did not observe any formation of mononuclear tungsten bis-carbene complex **6**. Scheme 2 summarizes the reaction pathway of **1** with phosphine and $W(CO)_6$. Reaction of the bis-azido compound **1** with phosphine provides the corresponding iminophosphorane **7**, and one of the imino-phosphorane functionalities undergoes nucleophilic attack on the metal carbonyl accompanied by the elimination of phosphine oxide to form the isocyanide metal complex **8**.[13a] Intramolecular cyclization of **8** followed by proton transfer yields the mono-carbene complex **9** and the other imino-phosphorane functionality proceeds similarly, resulting in the formation of complex **2**. Apparently, the

Received: August 20, 2012
Published: October 8, 2012

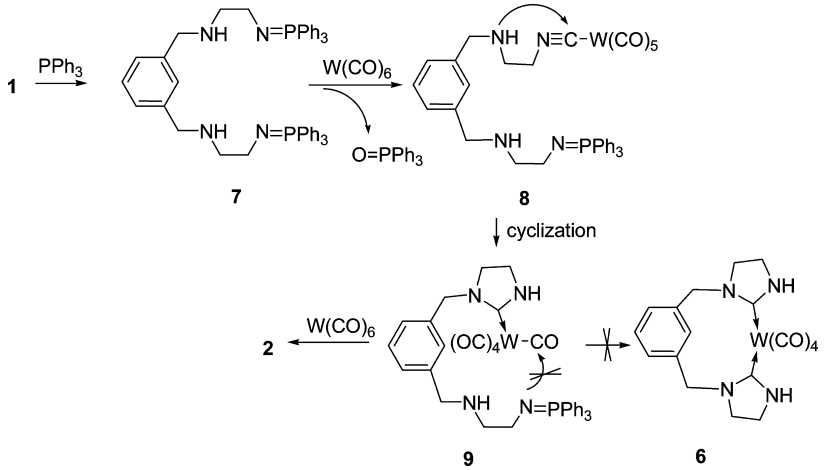
   dx.doi.org/10.1021/om300800c | *Organometallics* 2012, 31, 7248−7255

Scheme 1. Preparation of Bimetallic Iridium Complexes



i. $NaBH_4$, ii. 1) PPh_3, 2) $W(CO)_6$ iii. 1) NaH, 2) $PhCH_2Br$, iv. $[Ir(COD)Cl]_2$, v. excess PPh_3,KPF_6

Scheme 2. Reaction Pathway of 1 with Phosphine Followed by $W(CO)_6$



iminophosphorane moiety in **9** does not undergo the intramolecular nucleophilic attack on the carbonyl ligand in the molecule to yield **6**. Presumably, the strong σ-donating ability of the NHC ligand on the tungsten metal readily causes an increase in the strength of M−C back bonding, which reduces the electrophilic character of that carbon center.[13a]

All tungsten and iridium complexes, which are air-stable, were isolated as solids; complexes **2** and **5** were even obtained in crystalline form. All complexes were characterized by IR, NMR, and elemental analysis, and selected spectral data are collected in Table 1. The presence of two CO bands in the IR spectra of both **2** and **3** are consistent with the existence of a $W(CO)_5$ fragment. Similarly, the IR spectrum of **4** also indicates the presence of a "$Ir(CO)_2$" unit in the molecule. The coordination of the NHC ligands to the metal centers is confirmed by the appearance of a downfield shift in the ^{13}C NMR spectra for the carbenic carbon (Table 1). These shifts are in the range of 198−206 ppm, typical for the coordination of the saturated NHC toward these metal ions.[13c] FAB mass spectra of **2** and **4** show molecular ion peaks at m/z 890.0042 ($[M]^+$: $C_{24}H_{18}O_{10}N_4W_2$) and 991.0980 ($[M + H]^+$: $C_{32}H_{31}O_4N_4Cl_2Ir_2$), respectively, indicating the formation of dimetallic species. For complex **5**, the trans relationship of two phosphine ligands is supported by the ^{13}C NMR spectrum, in which the carbenic and carbonyl carbon signals appear as a triplet splitting and the phosphorus−carbon coupling constants for $J_{P-C(carbene)}$ and $J_{P-C(carbonyl)}$ are 13.2 and 14.7 Hz, respectively. Furthermore, detailed coordination configurations of **2** and **5** were confirmed by X-ray crystal structure analysis.

Table 1. Selected Spectral Data for Carbene Complexes

complex	^{13}C shift,[a] $C_{carbene}$−M	^{13}C shift,[a] $C_{carbonyl}$−M	IR ($\nu_{C=O}$)[b]
2 (M = W)	205.7	201.6 (trans), 198.2 (cis)	2063, 1897
3 (M = W)	208.8	201.5 (trans), 198.4 (cis)	2061, 1898
4 (M = Ir)	198.6	181.9 (trans), 168.5 (cis)	2062, 1977
5 (M = Ir)	203.8 (t, J_{P-C} = 13.2)	183.9 (t, J_{P-C} = 14.7)	1996

[a]In units of ppm with J in Hz; in CD_2Cl_2 except complex **5** in $CDCl_3$. [b]IR in CH_2Cl_2, in units of cm^{-1}.

dx.doi.org/10.1021/om300800c | *Organometallics* 2012, 31, 7248−7255

Crystallography. Figure 1 displays a perspective view of the bis-tungsten carbene complex **2**, whose selected bond distances and angles are reported in Table 2. As expected from the spectral analysis of **2**, both metal centers are in the same coordination mode, surrounded by five carbonyl ligands and by the carbene ligand in an octahedral geometry. All bond distances and bond angles lie within normal ranges. The shorter distances of W(1)−C(1) (1.996(4) Å) and W(1)−C(20) (1.980(3) Å) are due to the trans influence of the NHC donors. The distance between two tungsten centers is 6.953 Å. Both tungsten atoms are arranged in an "anti" conformation.[12a] However, the CH_2 spacer hydrogen atoms showed a single shift, indicating free rotation along these C−C bonds at ambient temperature.

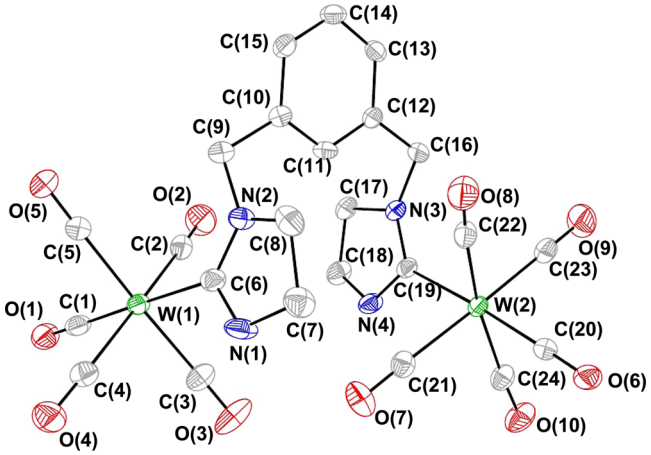


Figure 1. ORTEP plot of **2** (drawn with 30% probability ellipsoids).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 2

W(1)−C(1)	1.996(4)	W(2)−C(20)	1.980(3)
W(1)−C(2)	2.037(4)	W(2)−C(21)	2.044(3)
W(1)−C(3)	2.053(4)	W(2)−C(22)	2.034(4)
W(1)−C(4)	2.046(4)	W(2)−C(23)	2.040(4)
W(1)−C(5)	2.031(4)	W(2)−C(24)	2.043(4)
W(1)−C(6)	2.245(3)	W(2)−C(19)	2.244(3)
C(1)−O(1)	1.151(4)	C(20)−O(6)	1.160(4)
C(6)−W(1)−C(1)	179.1(1)	C(19)−W(2)−C(20)	176.7(1)
C(6)−W(1)−C(2)	95.1(1)	C(19)−W(2)−C(21)	86.6(1)
C(3)−W(1)−C(5)	175.6(1)	C(22)−W(2)−C(24)	170.4(1)

Slow evaporation of a chloroform/hexane solution of **5** yielded bright yellow crystals with the composition **5**·6$CHCl_3$ that were suitable for X-ray analysis. An ORTEP plot of **5** is given in Figure 2. Both iridium centers have square-planar geometry with two phosphine ligands coordinating toward each metal center in a trans fashion. All bond distances and bond angles (Table 3) are in the normal range as compared to those of the related species. The Ir−$C_{carbene}$ bond length (2.060(4) Å) lies in the same range as for other reported Ir-(NHC) complexes.[13c] As expected, the Ir(1)−C(1) distance (1.857(5) Å), trans to the carbene donor, is shorter than those of normal M−$C_{carbonyl}$, again due to the trans influence. The crystal structure of **5** reveals the orientation of both iridium ions in a syn conformation.[12a,f] However, the two metal centers are situated away from the phenylene unit, probably due to steric repulsion. In fact, the Ir(1)···Ir(1A) distance is 11.671 Å, indicating that the two metal centers are far away from each other.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 5

Ir(1)−C(1)	1.857(5)	Ir(1)−P(2)	2.3108(9)
Ir(1)−C(2)	2.060(4)	C(1)−O(1)	1.149(5)
Ir(1)−P(1)	2.3253(9)		
P(1)−Ir(1)−P(2)	174.7(2)	C(2)−Ir(1)−P(1)	90.20(10)
C(1)−Ir(1)−C(2)	178.21(4)	Ir(1)−C(1)−O(1)	177.2(4)
P(1)−Ir(1)−C(1)	89.34(11)		

Catalysis. It is well-documented that iridium complexes are frequently used as precatalysts for N-alkylation of amines with alcohols.[2−10] In addition, the introduction of a NHC ligand to the metal center would enhance its catalytic activity.[14] Thus, with these diiridium carbene complexes in hand, their catalytic activities toward dialkylation of diamines with alcohols were

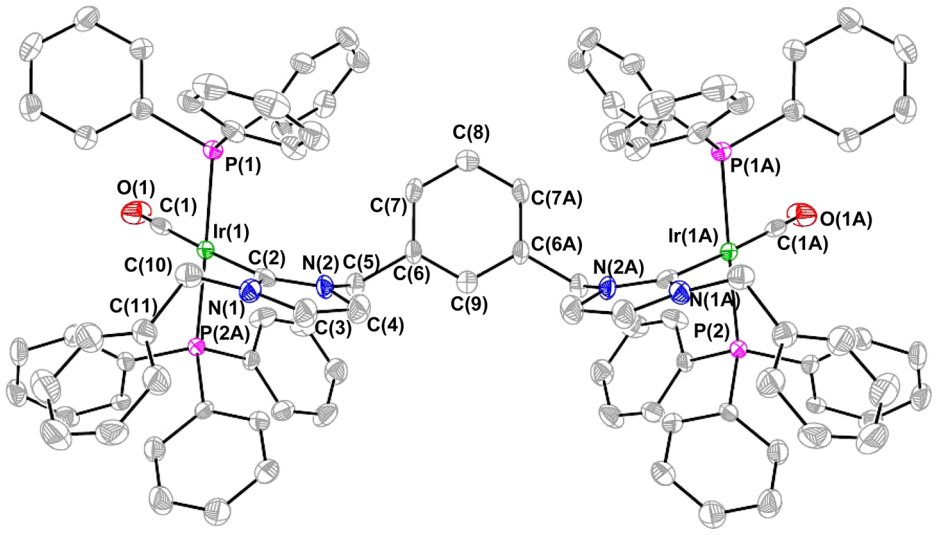
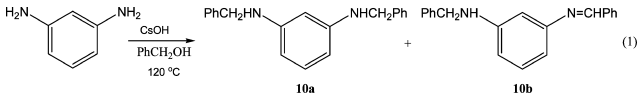


Figure 2. ORTEP plot of the cationic part of **5** (drawn with 30% probability ellipsoids; labels for the phenyl group are omitted for clarity).

dx.doi.org/10.1021/om300800c | *Organometallics* 2012, 31, 7248−7255

investigated. In order to create an environmentally benign process, the catalytic reactions investigated in this work do not use any organic solvent.

To obtain information on the catalytic system, we first examined the amination of *m*-phenylenediamine with benzyl alcohol catalyzed by **4** in the presence of various bases. In a typical experiment, a mixture of *m*-phenylenediamine (0.3 mmol), benzyl alcohol (1.2 mmol), complex **4** (3×10^{-3} mmol), base (0.15 mmol), and molecular sieves (0.3 g) was heated in an oil bath at 120 °C for 24 h. In this reaction, two major products (**10a**,**b**) were found (eq 1). Other partial



(1)

monoamination products were not observed by the NMR spectroscopic determination. The results are summarized in Table 4. It appears that the bases affect the selectivity of

Table 4. N,N′-Dialkylation of *m*-Phenylenediamine with Benzyl Alcohol Catalyzed by 4[a]

				product (%)[c]	
entry	base	temp (°C)	conversn[b] (%)	**10a**	**10b**
1	DBU[d]	120	100	trace	90
2	KOH	120	85	50	30
3	KO^{t}Bu	120	100	56	41
4	LiOH	120	6	4	trace
5	K_2CO_3	120	100	85	trace
6	Cs_2CO_3	120	100	44	32
7	Et_3N	120	55	trace	48
8	CsOH·H_2O	120	100	92	trace
9	CsOH·H_2O	100	87	40	35
10[e]	CsOH·H_2O	120	100	90	trace

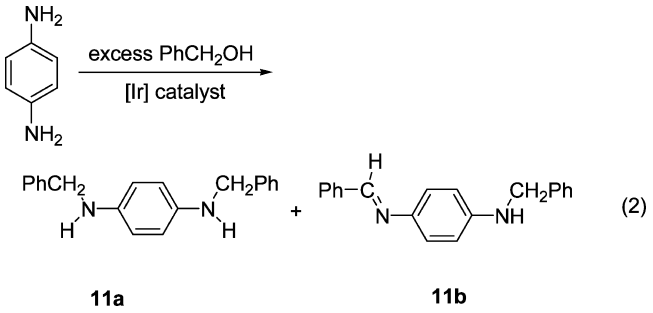
[a]Reaction conditions: *m*-phenylenediamine (0.3 mol), benzyl alcohol (1.2 mmol), complex **4** (3×10^{-3} mmol), base (0.15 mmol), and molecular sieves (0.3 g) for 24 h. [b]Based on the consumption of diamine. [c]NMR yields. [d]DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. [e]*p*-Phenylenediamine (0.5 mol) as the substrate.

product dramatically. A number of bases do catalyze the reactions with excellent conversions but different selectivities. The use of DBU as the base provided the formation of **10b** as the major product. On the other hand, the use of K_2CO_3 or CsOH as the base gave the desired diamine **10a** in excellent yields. Other bases for the reactions show poor results or less selectivity. It is worth mentioning that the reaction proceeded more slowly and less selectively at a lower reaction temperature (Table 4, entry 9). Similarly, the reaction of *p*-phenylenediamine with benzyl alcohol yielded the desired N,N′-dialkylation product in 90% yield under similar reaction conditions with the use of CsOH as the base (Table 4, entry 10).

Encouraged by the promising results, we further looked at extending the above methods to other phenylenediamines and various alcohols (Table 5). A variety of substituted benzyl alcohols were subjected to the N,N′-dialkylation with *m*- or *p*-phenylenediamines (Table 5, entries 1−7). In all cases, we observed the double N-alkylation in good isolated yields, except for *o*-methylbenzyl alcohol (Table 5, entry 3), presumably due to steric reasons. Reactions of simple alkyl alcohols such as ethanol with phenylenediamines under the same catalytic conditions also provided the corresponding N,N′-dialkylating products in very good yields (Table 5, entries 4 and 7). Instead of N-alkylation, reaction of *o*-phenylenediamine with benzyl alcohol gave 2-phenyl-1*H*-benzo[*d*]imidazole as the exclusive product under the catalytic conditions described for other alkylations (Table 5, entry 8). The formation of the cyclized product is due to the intramolecular attack of an amino group at the imine functionality (Scheme 3).

Interestingly, the yield of N,N′-dialkylation of *o*-phenylenediamine with benzyl alcohol increased as the reaction proceeded under an ambient pressure of molecular hydrogen (Table 5, entry 9). Presumably, the hydrogen atmosphere slows down the reductive elimination of hydrides from the metal center, which then facilitates the reduction of imine. Therefore, the intramolecular attack of amine at imine, which leads to the formation of benzo[*d*]imidazole, is suppressed.[15] In the presence of an H_2 atmosphere, the reaction between *o*-phenylenediamine with various alcohols under the standard catalytic conditions provided the N,N′-dialkylation in excellent yields (Table 5, entries 9 and 10).

Next we further ran a series of trial reactions of *p*-phenylenediamine with $PhCH_2OH$ in the presence of various iridium complexes to compare the selectivity of these catalysts (eq 2). Table 6 summarizes the results of amination catalyzed



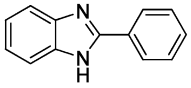
(2)

by various iridium catalysts. On the basis of the 100% conversion and product analysis, all iridium complexes have excellent activity in the oxidation of benzyl alcohol into the benzaldehyde, which subsequently reacts with *p*-phenylenediamine to give the corresponding imine under the catalytic conditions described above. Among these iridium catalysts, complex **4** proves to have the best activity in the reduction of imine to give the desired product **11a**, whereas mononuclear iridium complexes show moderate activity, providing mostly the partial reduction product **11b**. It is noted that the phosphine-substituted complexes, complex **5** and $[Ir(COD)Cl]_2/PPh_3$, gave **11b** as the major product, so was complex **5**.

To further validate the activity of the diiridium system **4**, the product distribution of dialkylation of p-$C_6H_4(NH_2)_2$ with benzyl alcohol catalyzed by complexes **4** and $[Ir(COD)Cl]_2$ was monitored by NMR spectroscopy, and the results are summarized in Figure 3. The direct N,N′-dialkylation catalyzed by diiridium complex **4** proceeded smoothly, particularly with a very low concentration of **11b** during the reaction course, except at the initial stage. Compound **11b** is the partial reduction product, which is the essential intermediate for the final product **11a**. Apparently, **11b** was readily reduced in the bimetallic catalyst system **4**. On the other hand, the catalytic system of $[Ir(COD)Cl]_2$ provided **11b** as the major product accompanied by a minor amount of the desired dialkylation product **11a**. This observation indicates that the diiridium catalytic system **4** is highly efficient and, more importantly, demonstrates enhanced activity in comparison to the

dx.doi.org/10.1021/om300800c | *Organometallics* 2012, 31, 7248−7255

Table 5. *N,N′*-Dialkylation of Phenylenediamines with Various Alcohols[a]

entry	diamine	alcohol	product	yield[b]
1	p-$C_6H_4(NH_2)_2$	$C_6H_4CH_2OH$	p-$C_6H_4(NHCH_2Ph)_2$	78%
2		p-$MeOC_6H_4CH_2OH$	p-$C_6H_4[NHCH_2C_6H_4$-OMe-$p]_2$	86%
3		o-$MeC_6H_4CH_2OH$	p-$C_6H_4[NHCH_2C_6H_4$-CH_3-$o]_2$	37%
4		CH_3CH_2OH	p-$C_6H_4[NHCH_2CH_3]_2$	86%
5	m-$C_6H_4(NH_2)_2$	$C_6H_4CH_2OH$	m-$C_6H_4(NHCH_2Ph)_2$	85%
6		p-$MeOC_6H_4CH_2OH$	m-$C_6H_4[NHCH_2C_6H_4$-OMe-$p]_2$	70%
7		CH_3CH_2OH	m-$C_6H_4[NHCH_2CH_3]_2$	72%
8	o-$C_6H_4(NH_2)_2$	$C_6H_4CH_2OH$		60%
9[c]		$C_6H_4CH_2OH$	o-$C_6H_4(NHCH_2Ph)_2$	90%
10[c]		p-$MeOC_6H_4CH_2OH$	o-$C_6H_4[NHCH_2C_6H_4$-OMe-$p]_2$	90%

[a]Reaction conditions: diamine (0.3 mmol), alcohol (1.2 mmol), complex **4** (3×10^{-3} mmol), $CsOH{\cdot}H_2O$ (0.15 mmol), and molecular sieves (0.3 g) at 120 °C for 24 h. [b]Isolated yields. [c]Under an H_2 atmosphere.

Scheme 3. Pathway for the Formation of 2-Phenyl-1*H*-benzo[*d*]imidazole

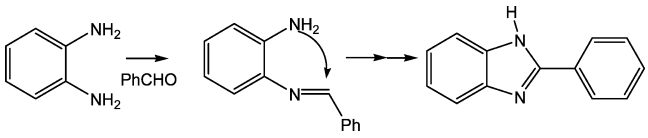


Table 6. Results of Amination Catalyzed by Various Iridium Complexes[a]

			yield (%)[b]	
entry	Ir complex	conversn (%)	**11a**	**11b**
1	complex **4**	100	90	trace
2	complex **5**	100	4	94
3	$[(IBn)Ir(CO)_2Cl]$[c]	100	50	49
4	$[Ir(COD)Cl]_2$	97	23	70
5	$[Ir(COD)Cl]_2/PPh_3$[d]	100	8	90
6	$[Ir(COD)Cl]_2$/TMEDA[e]	99	35	60

[a]Reaction conditions: *p*-phenylenediamine (0.3 mmol), benzyl alcohol (1.2 mmol), complex (3×10^{-3} mmol), $CsOH{\cdot}H_2O$ (0.15 mmol), and molecular sieves (0.3 g) at 120 °C for 24 h. [b]NMR yields. [c]IBn = 1,3-dibenzylimidazolin-2-ylidene. [d]PPh_3 (0.01 mmol). [e]TMEDA = tetramethylethylenediamine (5×10^{-3} mmol).

monoiridium complexes. A possible explanation is that the presence of a second metal in **4** might produce a synergistic or cooperative effect between two metal centers, which is absent in a mononuclear system. In fact, the mass spectrum of the catalytic reaction mixture showed a peak corresponding to the species **I** (ESI-MS $C_{50}H_{51}Ir_2N_6O_3$ m/z found 1167.76 (100%), calcd 1167.28) (Scheme 4). Thus, a plausible catalytic cycle for this dialkylation is proposed in Scheme 4. Basically, the reaction pathway is based on the general reductive amination of amines with alcohols catalyzed by metal ions. Due to the possible synergistic or cooperative effect between two metal centers, the coordination of two nitrogen donors of substrates toward two metal centers is proposed for intermediates in this reaction. Certainly, a kinetic study of the reaction is another alternative for establishing this cooperative effect, which is currently under investigation.

■ SUMMARY

In this work, we have prepared and characterized diiridium NHC complexes. Further utilization of these types of carbene complexes for N,N′-dialkylation of phenylenediamine with alcohols was investigated. It appears that complex **4** is an excellent catalyst for direct N,N′-dialkylation, presumably due to the cooperative effect between the two metal centers in the complex. More studies involving the cooperative effect between metal centers in **4** for other catalyses and theoretical considerations are currently in progress.

■ EXPERIMENTAL SECTION

General Information. All reaction and manipulation steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane was dried over CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used after degassing. Nuclear magnetic resonance spectra were recorded in $CDCl_3$ on a Bruker AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^1H and ^{13}C NMR and relative to 85% H_3PO_4 for ^{31}P NMR. Infrared spectra were measured on a Varian 640-IR spectrometer.

1,3-Bis[(2-azidorthylamino)methyl]benzene (1). A mixture of $H_2NCH_2CH_2N_3$ (2.06 g, 24 mmol) and isophthalaldehyde (0.79 g, 6 mmol) in anhydrous methanol (24 mL) was stirred at ice-cold temperature for 10 min. Then, $NaBH_4$ (1.36 g, 36 mmol) was added slowly under a nitrogen atmosphere. The resulting mixture was stirred at room temperature for 2 h. Water (20 mL) was added slowly to quench the excess hydrides. The reaction mixture was extracted with ethyl acetate (20 mL × 2), and the extracts were dried over $MgSO_4$.

dx.doi.org/10.1021/om300800c | *Organometallics* 2012, 31, 7248−7255

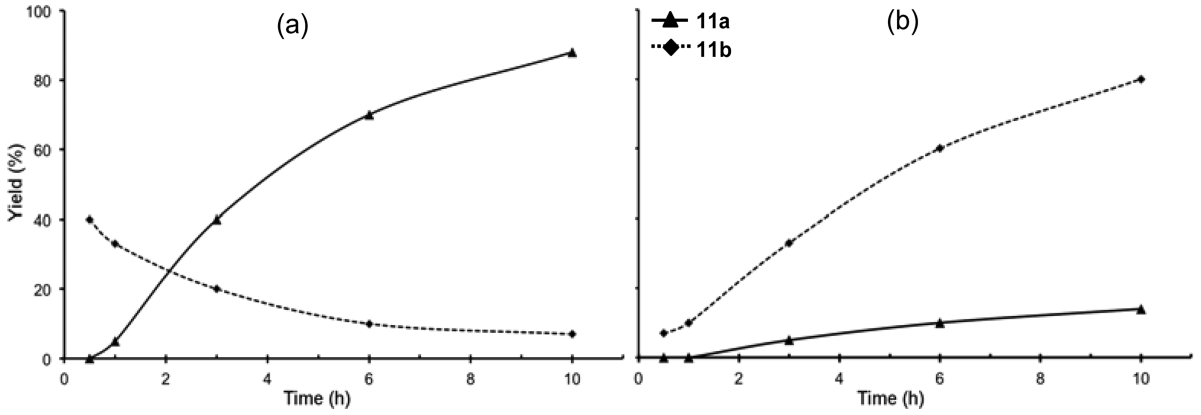
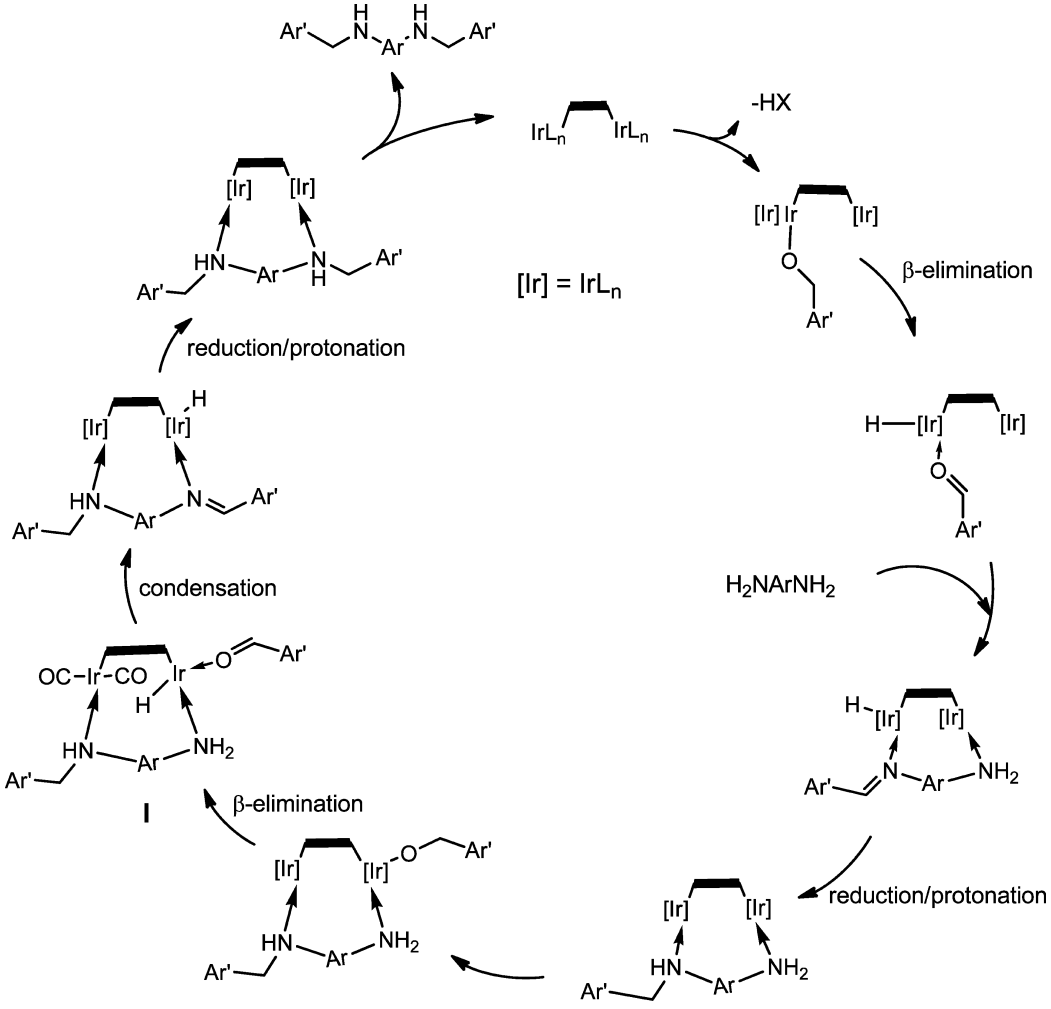


Figure 3. Product distribution during the alkylation of p-$C_6H_4(NH_2)_2$ with $C_6H_5CH_2OH$: (a) complex **4** as catalyst; (b) $[Ir(COD)Cl]_2$ as catalyst. Reaction conditions applied to this study are similar to those described in footnote [a] of Table 6.

Scheme 4. Catalytic Pathway for the Dialkylation



Upon concentration, the desired compound **1** was obtained as a yellow liquid (1.15 g, 70%): IR (CH_2Cl_2) 2099 cm^{-1} ($\nu_{N\equiv N}$); ^1H NMR (400 MHz, d_6-acetone) δ 2.81 (t, J = 5.7 Hz, 4H, CH_2N_3), 3.38 (t, J = 5.7 Hz, 4H, NCH_2), 3.80 (s, 4H, $ArCH_2N$), 7.23−7.25 (br, 3H, ArH), 7.37 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 128.6, 127.7, 126.8, 53.5, 51.4, 47.9; ESI-HRMS for $[M + H]^+$ ($C_{12}H_{19}N_8$) calcd 275.1733, found 275.1723. Anal. Calcd for $C_{12}H_{18}N_8$: C, 52.54; H, 6.61; N, 40.85. Found: C, 52.99; H, 6.81; N, 40.79.

[(1,3-Phenylene)bis(methylene)]bis(4,5-dihydroimidazol-2-ylidene)bis[pentacarbonyltungsten(0)] (2). To a solution of PPh_3 (3.23 g, 11.5 mmol) in anhydrous toluene (100 mL) was added a solution of **1** (1.47 g, 5.3 mmol) in anhydrous toluene (50 mL) by a flux needle under a nitrogen atmosphere. After the mixture was stirred at room temperature for 6 h, a solution of $W(CO)_6$ (9.80 g, 17.5 mmol) in THF (150 mL) was added. The resulting mixture was stirred at room temperature for 72 h. After removal of solvents, the residue was chromatographed on silica gel with CH_2Cl_2/hexane (1/3) as eluent, and a yellow band fraction was collected. Upon concentration, complex **2** was obtained as a yellow solid (4.5 g, 60%), which was recrystallized from CH_2Cl_2/hexane to give a clear yellow crystalline

dx.doi.org/10.1021/om300800c | Organometallics 2012, 31, 7248−7255

Table 7. Crystal Data for 2 and 5·6CHCl$_3$

	2	5
formula	$C_{24}H_{18}N_4O_{10}W_2$	$C_{102}H_{90}F_{12}Ir_2N_4O_2P_6{\cdot}6CHCl_3$
fw	890.12	2918.21
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/m$
a, Å	10.76500(10)	13.6471(2)
b, Å	11.5015(2)	25.3253(3)
c, Å	12.5253(2)	17.3337(2)
α, deg	88.7600(10)	90
β, deg	65.414(2)	99.9070(10)
γ, deg	84.1140(10)	90
V, Å^3; Z	1402.39(4); 2	5901.49(13); 2
d(calcd), Mg/m^3	2.108	1.642
F(000)	836	2892
cryst size, mm^3	0.20 × 0.15 × 0.10	0.20 × 0.15 × 0.10
no. of rflns collected	32 037	36 585
no. of indep rflns	6421 (R_{int} = 0.0386)	36 585 (R_{int} = 0.0000)
θ range, deg	2.87 to 27.50°	4.28 to 27.49°
refinement method	full-matrix least squares on F^2	
goodness of fit on F^2	1.013	0.963
R indices ($I > 2\sigma(I)$)	R1 = 0.0225, wR2 = 0.0528	R1 = 0.0573, wR2 = 0.1342
R indices (all data)	R1 = 0.0279, wR2 = 0.0561	R1 = 0.0995, wR2 = 0.1501

solid: IR (CH_2Cl_2) 2063, 1897 cm^{-1} (ν_{CO}); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.36 (t, J = 10.4 Hz, 4H, NCH_2CH_2N), 3.64 (t, J = 10.4 Hz, 4H, NCH_2CH_2N), 4.89 (s, 4H, ArCH_2N), 5.94 (s, 2H, −NH−), 7.16 (s, 1H, ArH), 7.25 (d, 2H, J = 7.6 Hz, ArH), 7.41 (t, 1H, J = 7.6 Hz, ArH); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 205.7 (W−*C*), 201.6 (*trans*-CO), 198.2 (t, J(^{13}C−^{183}W) = 63 Hz, *cis*-CO), 136.9, 129.4, 127.5, 125.7, 55.8, 47.6, 45.6; FAB-HRMS for [M]$^+$ ($C_{24}H_{18}O_{10}N_4W_2$) calcd 890.0048, found 890.0042. Anal. Calcd for $C_{24}H_{18}N_4O_{10}W_2$: C, 32.38; H, 2.04; N, 6.29. Found: C, 32.70 ; H, 2.24; N, 6.83.

[(1,3-Phenylene)bis(methylene)]bis(1-benzyl-4,5-dihydroimidazol-2-ylidene)bis[pentacarbonyltungsten(0)] (3). Sodium hydride (2.19 g, 60 mmol) in a Schlenk tube was washed with anhydrous hexane (10 mL × 3) under a nitrogen atmosphere. A solution of **3** (4.05 g, 4.5 mmol) in anhydrous THF (70 mL) was added to the tube with stirring. Benzyl bromide (4.44 mL, 36 mmol) was then added to the mixture, and stirring was continued at room temperature for 36 h. Water (10 mL) was slowly added to quench the excess NaH, and the reaction mixture was extracted with ethyl acetate (30 mL × 2). The organic extracts were dried and concentrated. The crude product was washed with hexane to remove the unreacted benzyl bromide. Complex **3** was obtained as a yellow solid (3.9 g, 80%): IR (CH_2Cl_2) 2061, 1898 cm^{-1} (ν_{CO}); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.32 (s, 8H, NCH_2CH_2N), 5.04 (s, 4H, ArCH_2), 5.05 (s, 4H, ArCH_2), 7.26−7.40 (m, 14H, ArH); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 208.8 (W-*C*), 201.5 (*trans*-CO), 198.4 (t, J(^{13}C−^{183}W) = 63 Hz, *cis*-CO), 137.6, 136.5, 129.6, 129.2, 128.3, 127.9, 126.8, 57.5, 48.7; FAB-HRMS for [M]$^+$ ($C_{38}H_{30}O_{10}N_4W_2$) calcd 1070.0994, found 1070.0981. Anal. Calcd for $C_{38}H_{30}N_4O_{10}W_2$: C, 42.64; H, 2.83; N, 5.23. Found: C, 42.80; H, 2.98; N, 5.64.

[(1,3-Phenylene)bis(methylene)]bis(1-benzyl-4,5-dihydroimidazol-2-ylidene)bis[dicarbonyliridium(I) chloride] (4). A mixture of **3** (100 mg, 0.08 mmol) and [Ir(COD)Cl]$_2$ (156 mg, 0.24 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature under a nitrogen atmosphere for 72 h. The reaction mixture was filtered through Celite, and the filtrate was concentrated. The residue was chromatographed on silica gel with acetone/hexane (1/4) as eluent. A yellow band fraction was collected to give complex **4** as a yellow solid (66 mg, 60%): IR (CH_2Cl_2) 2062, 1977 cm^{-1} (ν_{CO}); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.49−3.61 (m, 8H, NCH_2CH_2N), 5.04−5.19 (m, 8H, ArCH_2), 7.37−7.64 (m, 14H, ArH); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 198.6 (Ir-*C*), 181.9 (CO), 168.5 (CO), 136.2, 135.3, 129.1, 128.7, 128.3, 127.8, 127.2, 126,9, 54.4, 54.3, 48.6, 48.5; FAB-HRMS for [M + H]$^+$ ($C_{32}H_{31}O_4N_4Cl_2Ir_2$) calcd 991.0981, found 991.0980. Anal. Calcd for $C_{32}H_{30}O_4N_4Cl_2Ir_2$: C, 38.82; H, 3.05; N, 5.66. Found: C, 38.47; H, 3.39; N, 5.28.

[(1,3-Phenylene)bis(methylene)]bis(1-benzyl-4,5-dihydroimidazol-2-ylidene)bis[*trans*-carbonylbis(triphenylphosphine)-iridium(I)] Bis(hexafluorophosphate) (5). A mixture of **4** (60 mg, 0.06 mmol) and PPh_3 (64.4 mg, 0.24 mmol) in chloroform (20 mL) was stirred for 1 h. Upon removal of solvents, a solution of KPF_6 (25.6 mg, 0.14 mmol) in acetonitrile (20 mL) was added to the residue with stirring at room temperature. The reaction mixture was crystallized from a $CHCl_3$/hexane solution to give a bright yellow crystalline solid (70%): IR (CH_2Cl_2) 1996 cm^{-1} (ν_{CO}); ^{31}P (161.9 MHz, $CDCl_3$) δ 19.2 (s), −144.1 (sept, J_{P-F} = 712.4 Hz); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (t, J = 9.6 Hz, 4H, NCH_2CH_2N), 2.82 (t, J = 9.6 Hz, 4H, NCH_2CH_2N), 3.72 (s, 4H, ArCH_2N), 3.82 (s, 4H, ArCH_2N), 5.80 (d, J = 7.6 Hz, 2H, ArH), 5.99 (s, 1H, ArH), 6.12 (t, J = 7.6 Hz, 2H, ArH), 6.34 (d, J = 7.6 Hz, 4H, ArH), 6.91 (t, J = 7.6 Hz, 4H, ArH), 7.11 (t, J = 7.5 Hz, 2H, ArH), 7.49−7.54 (m, 60H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8 (t, J_{P-C} = 13.2 Hz, Ir-*C*), 183.9 (t, J_{P-C} = 14.7 Hz, *C*O), 134.0, 133.9, 133.1, 132.0, 131.8, 131.5, 130.5, 129.3, 129.2, 129.1, 128.9, 128.7, 128.6, 128.3, 54.8, 54.4, 48.5, 48.2; HRMS-ESI for [M]$^{2+}$ ($C_{102}H_{90}O_2N_4P_4Ir_2$) calcd $m/2$ 956.2631 ($C_{102}H_{90}O_2N_4P_4Ir_2$), found 956.2662.

General Procedure for the Catalytic Dialkylation of Diamines. A mixture of phenylenediamine (0.3 mmol), alcohol (1.2 mmol), iridium complex **4** (3 mg, 1 mol %), CsOH (25.6 mg, 0.15 mmol), and molecular sieves (0.3 g) in a reaction tube was flushed with nitrogen gas. The reaction mixture was heated for 24 h. After the reaction, water and ethyl acetate were added. The organic extract was separated, dried, and concentrated. The desired product was purified by chromatography with CH_2Cl_2/EtOAc 30/1−10/1 as eluent.

Spectral Data of Dialkylation Products. *N,N′-Dibenzyl-p-phenylenediamine.*[16] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.43 (br, 1H, −NH−), 4.25 (s, 4H, −ArCH_2N−), 6.57 (s, 4H, ArH), 7.25−7.28 (m, 2H, ArH), 7.31−7.38 (m, 8H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 139.4, 128.1, 127.2, 126.6, 114.3, 49.6.

N,N′-Bis(p-methoxybenzyl)-p-phenylenediamine.[4a] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 6H, −OCH_3−), 4.17 (s, 4H, −ArCH_2N-), 6.56 (s, 4H, ArH), 6.85 (d, J = 8.8 Hz, 4H, ArH), 7.25 (d, J = 8.8 Hz, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 140.5, 131.6, 128.8, 114.7, 113.8, 55.3, 49.1. ESI-HRMS for [M + H]$^+$: calcd 349.1911 ($C_{22}H_{25}N_2O_2$), found 349.1909.

N,N′-Bis(o-methylbenzyl)-p-phenylenediamine. Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.37 (s, 6H, −CH_3−), 4.21 (s, 4H, −ArCH_2N−), 6.59 (s, 4H, ArH), 7.15−7.19 (m, 6H, ArH), 7.33 (d, J = 6.0 Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 137.1, 135.8, 129.9, 127.9, 126.8, 125.7, 114.2, 47.7, 19.3. ESI-HRMS for [M + H]$^+$: alcd 317.2012 ($C_{22}H_{25}N_2$), found 317.2016.

N,N′-Diethyl-p-phenylenediamine.[17] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, J = 6.8 Hz, 6H, CH_3−), 3.10 (q, J = 6.8 Hz, 4H, −CH_2N−), 6.55 (s, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 114.4, 39.9, 15.5. ESI-HRMS for [M + H]$^+$ calcd 165.1392 ($C_{10}H_{17}N_2$), found 165.1391.

N,N′-Dibenzyl-m-phenylenediamine.[16] ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.26 (s, 4H, −ArCH_2N−), 5.92 (s, 1H, ArH), 6.06 (dd, J = 8.1 Hz, 2.0 Hz, 2H, ArH), 6.97 (t, J = 8.0 Hz, 1H, ArH), 7.24−7.35 (m, 10H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 139.1, 129.6, 128.2, 127.1, 126.7, 102.8, 97.0, 48.5.

N,N′-Bis(p-methoxybenzyl)-m-phenylenediamine.[4a] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 6H, OCH_3), 4.22 (s, 4H, −ArCH_2N−), 5.92 (s, 1H, ArH), 6.07 (dd, J = 8.0 Hz, 2.4 Hz, 2H, ArH), 6.85 (d, J = 8.8 Hz, 4H, ArH), 6.99 (t, J = 8.0 Hz, 1H, ArH), 7.27 (d, J = 8.8 Hz, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 148.8, 131.2, 129.5, 128.4, 113.6, 102.8, 96.9, 55.4, 47.9. ESI-HRMS for [M + H]$^+$: calcd 349.1916 ($C_{22}H_{25}N_2O_2$), found 349.1912.

N,N′-Diethyl-m-phenylenediamine. Purple solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, J = 7.2 Hz, 6H, CH_3−), 3.13 (t, J = 7.2 Hz,

dx.doi.org/10.1021/om300800c | Organometallics 2012, 31, 7248−7255

4H, $-CH_2N-$), 5.88 (s, 1H, Ar*H*), 6.00 (d, J = 7.6 Hz, 2H, Ar*H*), 6.96 (t, J = 7.6 Hz, 1H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 129.7, 102.7, 96.9, 38.6, 15.1. ESI-HRMS for $[M + H]^+$: calcd 165.1392 ($C_{10}H_{17}N_2$), found 165.1390.

2-Phenyl-1H-benzimidazole.[18] ^1H NMR (400 MHz, DMSO-d_6): δ 7.22 (d, J = 6.8 Hz, 2H), 7.57−7.49 (m, 4H), 7.67 (d, J = 6.8 Hz, 1H), 8.19 (d, J = 7.6 Hz, 2H), 12.88 (s, 1H, $-NH-$).

N,N′-Dibenzyl-o-phenylenediamine.[16] ^1H NMR (400 MHz, $CDCl_3$): δ 4.32 (s, 4H, $-ArCH_2N-$), 6.71−6.74 (m, 2H), 6.78−6.81 (m, 2H), 7.26−7.40 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 136.7, 128.2, 127.4, 126.8, 119.1, 111.7, 48.9.

N,N′-Bis(p-methoxybenzyl)-o-phenylenediamine.[4a] Yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 6H, OCH_3), 4.27 (s, 4H, $-ArCH_2N-$), 6.75−6.77 (m, 2H), 6.83−6.85 (m, 2H), 6.92 (d, J = 8.8 Hz, 4H), 7.32 (d, J = 8.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 136.6, 130.9, 128.6, 118.9, 113.6, 111.5, 55.4, 48.4. ESI-HRMS for $[M + H]^+$: calcd 349.1911 ($C_{22}H_{25}N_2O_2$), found 349.1921.

Crystallography. Crystals suitable for X-ray determination were obtained for **2** and **5**·6$CHCl_3$ by recrystallization from dichloromethane/hexane and chloroform, respectively. Cell parameters were determined by a Siemens SMART CCD diffractometer. The structure was solved using the SHELXS-97 program[19] and refined using the SHELXL-97 program[20] by full-matrix least-squares on F^2 values. Crystal data of these complexes are given in Table 7. Other crystallographic data are deposited as Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables and CIF files providing crystallographic data, including atomic positional parameters, bond distances and angles, anisotropic thermal parameters, and calculated hydrogen atom positions, for complexes **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: stliu@ntu.edu.tw.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Council for their financial support (NSC100-2113-M-002-001-MY3). We also thank Miss Yu Chang Chao for her generous support for ESI mass data analysis.

■ REFERENCES

(1) Lawrence, S. A. *Amines: Synthesis Properties and Applications*; Cambridge University Press: Cambridge, U.K., 2004.

(2) (a) Grigg, R.; Mitchell, T. R. B.; Sutthivaiyakit, S.; Tongpenyai, N. *J. Chem. Soc., Chem. Commun.* **1981**, 611. (b) Tsuji, Y.; Huh, K.-T.; Ohsugi, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1365.

(3) Recent reviews: (a) Guillena, G.; Ramón, D. J.; Yus, M. *Chem. Rev.* **2010**, *110*, 1611. (b) Nixon, T. D.; Whittlesey, M. K.; Williams, J. M. J. *Dalton Trans.* **2009**, 753. (c) Suzuki, T. *Chem. Rev.* **2011**, *111*, 1825. (d) Dobereiner, G. E.; Crabtree, R. H. *Chem. Rev.* **2010**, *110*, 681. (e) Bähn, S.; Imm, S.; Neubert, L.; Zhang, M.; Neumann, H.; Beller, M. *ChemCatChem* **2011**, *3*, 1853. (f) Alonso, F.; Riente, P.; Yus, M. *Acc. Chem. Res.* **2011**, *44*, 379.

(4) (a) Michlik, S.; Hille, T.; Kempe, R. *Adv. Synth. Catal.* **2012**, *354*, 847. (b) Michlik, S.; Kempe, R. *Chem. Eur. J.* **2010**, *16*, 13193. (c) Blank, B.; Michlik, S.; Kempe, R. *Chem. Eur. J.* **2009**, *15*, 3790. (d) Blank, B.; Michlik, S.; Kempe, R. *Adv. Synth. Catal.* **2009**, *351*, 2903. (e) Blank, B.; Madalska, M.; Kempe, R. *Adv. Synth. Catal.* **2008**, *350*, 749. (f) Schareina, T.; Hillebrand, G.; Fuhrmann, H.; Kempe, R. *Eur. J. Inorg. Chem.* **2001**, 2421 and references therein.

(5) (a) Bähn, S.; Imm, S.; Mevius, K.; Neubert, L.; Tillack, A.; Williams, J. M. J.; Beller, M. *Chem. Eur. J.* **2010**, *16*, 3590. (b) Imm, S.; Bähn, S.; Neubert, L.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 8126 and references therein.

(6) (a) Kawahara, R.; Fujita, K.-i.; Yamaguchi, R. *Adv. Synth. Catal.* **2011**, *353*, 1161. (b) Kawahara, R.; Fujita, K.-i.; Yamaguchi, R. *J. Am. Chem. Soc.* **2010**, *132*, 15108. (c) Zhu, M. W.; Fujita, K.-i.; Yamaguchi, R *Org. Lett.* **2010**, *12*, 1336 and references therein.

(7) (a) Watson, A. J. A.; Maxwell, A. C.; Williams, J. M. J. *J. Org. Chem.* **2011**, *76*, 2328. (b) Saidi, O.; Blacker, A. J.; Lamb, G. W.; Marsden, S. P.; Taylor, J. E.; Williams, J. M. J. *Org. Process Res. Dev.* **2010**, *14*, 1046. (c) Saidi, O.; Blacker, A. J.; Farah, M. M.; Marsden, S. P.; Williams, J. M. J. *Chem. Commun.* **2010**, *46*, 1541 and references therein.

(8) (a) Martinez-Asencio, A.; Ramón, D. J.; Yus, M. *Tetrahedron* **2011**, *67*, 3140. (b) Martinez-Asencio, A.; Ramón, D. J.; Yus, M. *Tetrahedron Lett.* **2010**, *51*, 325 and references therein.

(9) (a) Feng, C.; Liu, Y.; Peng, S.; Shuai, Q.; Deng, G.; Li, C.-J. *Org. Lett.* **2010**, *12*, 4888. (b) Liu, Y.; Chen, W.; Feng, C.; Deng, G. *Chem. Asian J.* **2011**, *6*, 1142.

(10) (a) Türkmen, H.; Pape, T.; Hahn, F. E.; Cetinkaya, B. *Organometallics* **2008**, *27*, 571. (b) Gnanamgari, D.; Moores, A.; Rajaseelan, E.; Crabtree, R. E. *Organometallics* **2007**, *26*, 1226. (c) Cumpstey, I.; Agrawal, S.; Borbas, K. E.; Martin-Matute, B. *Chem. Commun.* **2011**, *47*, 7827. (d) Lee, C.-C.; Chu, W.-Y.; Liu, Y.-H.; Peng, S.-M.; Liu, S.-T. *Eur. J. Inorg. Chem.* **2011**, 4801 and references therein.

(11) (a) Zhao, Y.; Foo, S. W.; Saito, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 3006. (b) Bertoli, M.; Choualeb, A.; Gusev, D. G.; Lough, A. J.; Major, Q.; Moore, B. *Dalton Trans.* **2011**, *40*, 8941. (c) Zanardi, A.; Mata, J. A.; Peris, E. *Chem. Eur. J.* **2010**, *16*, 10502. (d) Gross, T.; Seayad, A. M.; Ahmad, M.; Beller, M. *Org. Lett.* **2002**, *4*, 2055.

(12) Selected examples: (a) Raynal, M.; Cazin, C. S. J.; Vallée, C.; Olivier-Bourbigou, H.; Braunstein, P. *Dalton Trans.* **2009**, 3824. (b) Baker, M. V.; Brown, D. H.; Haque, R. A.; Skeltona, B. W.; White, A. H. *Dalton Trans.* **2010**, *39*, 70. (c) Baker, M. V.; Brown, D. H.; Haque, R. A.; Simpson, P. V.; Skelton, B. W.; White, A. H.; Williams, C. C. *Organometallics* **2009**, *28*, 3793. (d) Willans, C. E.; Anderson, K. M.; Paterson, M. J.; Junk, P. C.; Barbour, L. J.; Steed, J. W. *Eur. J. Inorg. Chem.* **2009**, 2835. (e) Baker, M. V.; Brown, D. H.; Hesler, V. J.; Skelton, B. W.; White, A. H. *Organometallics* **2007**, *26*, 250. (f) Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S.; Kleinhenz, S.; Eastham, G. *Dalton Trans.* **2000**, 4499.

(13) (a) Liu, C.-Y.; Chen, D.-Y.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **1996**, *15*, 1055. (b) Liu, S.-T.; Hsieh, T.-Y.; Lee, G.-H.; Peng, S.-M. *Organometallics* **1998**, *17*, 993. (c) Chang, Y.-H.; Fu, C.-F.; Liu, Y.-H.; Peng, S.-M.; Chen, J.-T.; Liu, S.-T. *Dalton Trans.* **2009**, 861. (d) Liu, S.-T.; Reddy, K. R. *Chem. Soc. Rev.* **1999**, 315. (e) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122.

(14) (a) Hanasaka, F.; Fujita, K.-i.; Yamaguchi, R. *Organometallics* **2004**, *23*, 1490. (b) Nair, V.; Menon, R. S.; Biju, A. T.; Sinu, C. R.; Paul, R. R.; Jose, A.; Sreekumar, V. *Chem. Soc. Rev.* **2011**, *40*, 5336. (c) Patil, N. T. *Angew. Chem., Int. Ed.* **2011**, *50*, 1759 and references therein.

(15) Lee, C.-C.; Liu, S.-T. *Chem. Commun.* **2011**, *47*, 6981.

(16) Itoh, T.; Nagata, K.; Miyazaki, M.; Ishikawa, H.; Kurihara, A.; Ohsawa, A. *Tetrahedron* **2004**, *60*, 6649.

(17) Doornbos, T.; Zuidema, G.; Strating, J. *Org. Prep. Proced. Int.* **1970**, *2*, 211.

(18) Moorthy, J. N.; Neogi, I. *Tetrahedron Lett.* **2011**, *52*, 3868.

(19) Sheldrick, G. M. SHELXS-97. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, 67.

(20) Sheldrick, G. M. *SHELXL-97*; University of Göttingen, Göttingen, Germany, 1997.