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Phosphaalkene Complexes

CLUSTER ISSUE

# Iridium(I) Complexes Bearing a Noninnocent PNP-Pincer-Type Phosphaalkene Ligand: Catalytic Application in the Base-Free *N*-Alkyl ation of Amines with Alcohols

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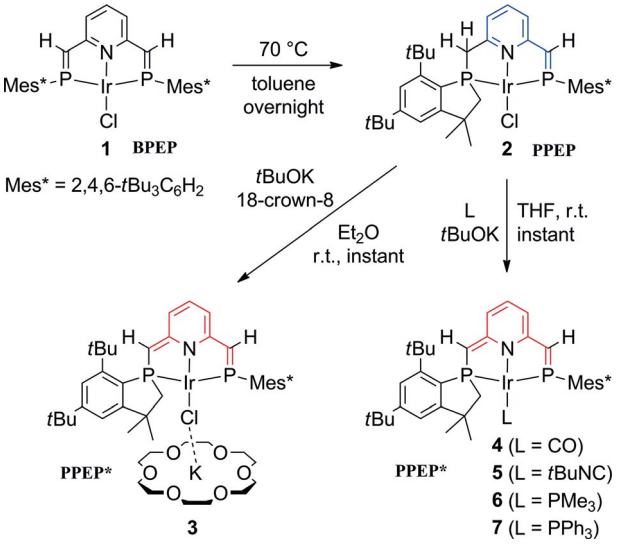
**Abstract:** A series of $Ir^{I}$ complexes [Ir(L)(PPEP*)] [L = $Cl^-$ (**3**), CO (**4**), *t*BuNC (**5**), $PMe_3$ (**6**), $PPh_3$ (**7**)], coordinated with a PNP-pincer-type phosphaalkene ligand bearing a dearomatized pyridine ring (PPEP*), have been prepared and their catalytic properties for the dehydration/condensation of amines with alcohols has been examined. The catalytic reactions successfully proceed under base-free conditions to give *N*-alkylated amines and their dehydrogenation derivatives (imines). The product selectivity is dependent on L coordinated with Ir(PPEP*). Complexes **4** and **5** that contain π-accepting ligands (CO, *t*BuNC) form *N*-alkylated amines as the major products in a closed system using a nitrogen-gas-filled Schlenk tube. In contrast, complex **7** that contain $PPh_3$ as L produces imines as the major products under a nitrogen-gas flow. The reason for the selectivity change depending on L is discussed based on stoichiometric reactions using model compounds of presumed catalytic intermediates.

## Introduction

Since Shvo et al. discovered a cyclopentadienone-ligated ruthenium complex that causes the catalytic reduction of ketones by means of metal–ligand cooperation,[1] various catalytic systems using cooperative ligands have been developed.[2–4] Nowadays, the targeted design of cooperative ligands is recognized as a viable way of finding novel organic transformations as well as highly active catalysts. Pyridine-based pincer ligands have provided particularly great advancements in this area.[4,5] For instance, Milstein et al. developed a series of pyridine-based PNN- and PNP-pincer complexes of $Ru^{II}$.[5] The PNN complex causes catalytic coupling of alcohols with amines to form amides with liberation of $H_2$,[5d] whereas the PNP complex catalyzes the conversion of alcohols and amines into imines along with byproducts $H_2O$ and $H_2$.[5g]

The reaction chemistry of pyridine-based pincer ligands is often discussed with a particular focus on their noninnocent behavior involving the aromatization–dearomatization of the pyridine core, whereby the dearomatized pincer ligands serve as a strong base. However, since metal–ligand cooperation is aided by the Lewis acidity of metals, the electronic conditions of metal centers must be of particular importance as well. Thus, we introduced a phosphaalkene unit, as an extremely strong π acceptor towards transition metals,[6] into a PNP-pincer scaffold.[7] As a result, we generated complex **3** bearing a dearomatized PNP-pincer-type phosphaalkene ligand (PPEP*, Scheme 1), which causes heterolytic cleavage of the N–H bond of ammonia instantly at room temperature. The highly reactive nature of PPEP* complexes towards metal–ligand cooperation was also confirmed for the C–H bond activation of acetonitrile.[8]




Scheme 1. Synthesis of PNP-pincer-type phosphaalkene complexes of $Ir^{I}$.

In this study, as part of our efforts to expand the use of phosphaalkene ligands, we examined the catalytic performance of dearomatized PNP-pincer-type phosphaalkene complexes **3**–**7** in the *N*-alkylation of amines with alcohols. This catalysis has been studied as an environmentally benign process of synthe-

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sizing amines, which produces water as the sole byproduct.[9] Although both heterogeneous and homogeneous catalysts promote the reaction, to date $Ru^{II}$ and $Ir^{III}$ complexes constitute a vast majority of homogeneous catalysts.[9,10] This is probably because the reaction needs a significantly Lewis acidic metal center for the activation of alcohols. Recently, catalytically active $Ir^{I}$ complexes have been developed,[11,12] and Kempe et al. demonstrated synthetic routes to heteroaromatic compounds.[11] However, these catalysts need a strong base to develop catalytic activity. In contrast, PPEP* complexes were found to successfully catalyze the reaction under base-free conditions.

## Results and Discussion

### Synthesis of PNP-Pincer-Type Phosphaalkene Complexes

Scheme 1 illustrates the synthetic routes to **3**–**7**. As we reported before,[7a] complex **2** as a precursor of PPEP* complex **3** is prepared from BPEP complex **1**[12] by C–H addition/cyclization of the 2-phosphaethenyl group with a 2,4,6-tri-*tert*-butylphenyl substituent (Mes*P=CH). Treatment of **2** with *t*BuOK in an ethereal solution causes deprotonation at the benzylic position to afford K[IrCl(PPEP*)] bearing a dearomatized PPEP* ligand, which can be isolated as the crown ether adduct [K(18-crown-8)][IrCl(PPEP*)] (**3**) in high yield. Complexes **4**–**7** that have an additional ligand L were readily formed from isolated **3** by ligand substitution; however, their isolation was troublesome owing to difficulties in removing the [K(18-crown-8)]-Cl generated in the system. Therefore, the synthesis of **4**–**7** on a preparative scale was performed with K[IrCl(PPEP*)] in situ generated from **2**. In this case, the synthesis was accomplished without isolation of **2**, and one-pot synthesis of **4**–**7** from **1** was achieved.

For example, complex **1** was converted to **2** by heating in toluene. The solvent was replaced with THF, and complex **2** was treated with *t*BuOK (1 equiv.) in the presence of *t*BuNC (1 equiv.) at room temperature. The reaction was completed instantly, as confirmed by $^{31}P\{^{1}H\}$ NMR spectroscopy. The desired complex **5** was isolated as dark green crystals in 76 % yield, after removal of KCl by precipitation and filtration using $Et_2O$. Complexes **4**, **6**, and **7** were similarly prepared in 95, 89, and 64 % yields, respectively. The resulting complexes were characterized by NMR spectroscopy and elemental analysis. Although complex **7** did not give a satisfactory elemental analysis, its formation could be confirmed by X-ray diffraction analysis.

Figures 1 and 2 show crystal structures of **5** (L = *t*BuNC) and **7** (L = $PPh_3$), respectively. The single crystal of **5** contains two crystallographically independent molecules in the unit cell, and one of them is depicted for simplicity. The P–Ir–P bond is significantly bent (ca. 160°) and both complexes adopt a square-planar configuration around iridium.[13] Complex **6** (L = $PMe_3$) was identified by X-ray analysis as well, but its structural parameters are not available owing to the disordered arrangement of the PPEP* ligand.

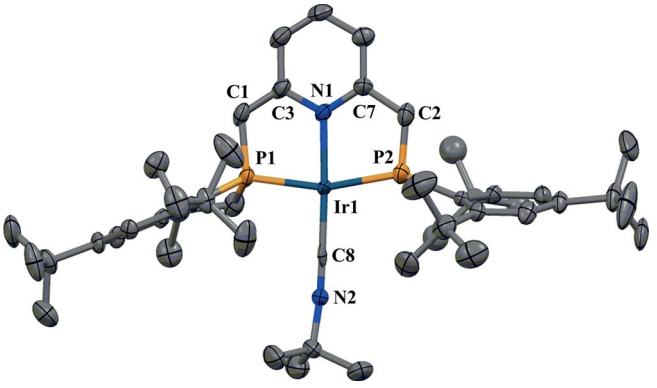



Figure 1. Molecular structure of [Ir(*t*BuNC)(PPEP*)] (**5**) with 50 % probability ellipsoids showing one of the crystallographically independent molecules (**5A**). Hydrogen atoms and disordered carbon atoms (*t*Bu) are omitted for clarity. Selected bond lengths [Å] and angles [°]: [**5A**] Ir1–P1 2.282(3), Ir1–P2 2.238(3), Ir1–N1 2.093(8), Ir1–C8 1.898(11), P1–C1 1.749(11), P2–C2 1.649(12), C1–C3 1.393(16), C2–C7 1.448(14), C8–N2 1.175(14); P1–Ir1–P2 162.37(10), N1–Ir1–C8 176.8(4); [**5B**] Ir2–P3 2.282(3), Ir2–P4 2.231(3), Ir2–N3 2.100(8), Ir2–C56 1.913(12), P3–C49 1.746(12), P4–C50 1.678(10), C49–C51 1.393(18), C50–C55 1.441(14), C56–N4 1.148(14); P3–Ir2–P4 162.39(10), N3–Ir2–C56 177.5(4).

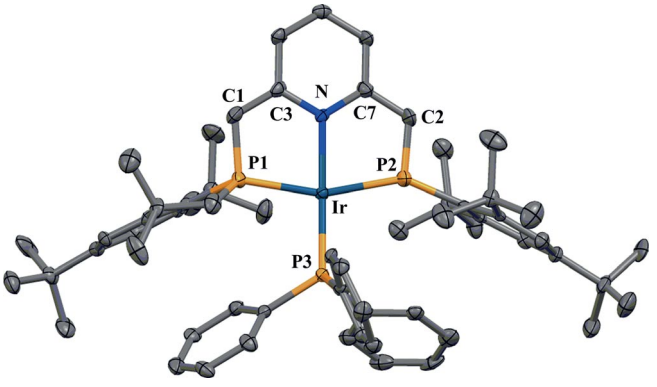



Figure 2. Molecular structure of [Ir($PPh_3$)(PPEP*)] (**7**) with 50 % probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir–P1 2.2994(18), Ir–P2 2.2621(18), Ir–P3 2.2519(16), Ir–N 2.120(5), P1–C1 1.754(7), P2–C2 1.678(7), C1–C3 1.392(10), C2–C7 1.413(10); P1–Ir–P2 160.34(7), N–Ir1–P3 173.57(14).

Table 1 summarizes the X-ray structural parameters and $^{31}P\{^{1}H\}$ NMR spectroscopic data for PPEP* complexes **3**–**7**. The data of **3** and **4** are taken from our previous report,[7a] and the atomic numbering scheme follows that given in Figures 1 and 2. The lengths of the P1–C1 bonds, which are incorporated in the phospholanylmethylidene units, are within the range of 1.744–1.764 Å. These values are between those expected for a P–C single and double bond, which indicates a large contribution of a phosphorus ylide structure,[14] responsible for the strong basicity of dearomatized PNP-pincer ligands.[4] In contrast, the P2–C2 bond lengths for phosphaethenyl units in neutral complexes **4**–**7** are in a typical range of P=C double bonds (1.66–1.68 Å). An exception is found for anionic complex **3**, in which the P2–C2 bond is elongated, whereas the C2–C7 bond is shortened. The π* orbital of PPEP* bears an antibonding and bonding interaction between the P2–C2 and C2–C7 linkage, respectively. Therefore, strong π back donation from the anionic

Table 1. Selected X-ray bond lengths [Å] and angles [°] and $^{31}P\{^1H\}$ NMR spectroscopy data for [Ir(L)(PPEP*)] (**3**–**7**).

| Complex (L) | X-ray structural parameters P1–C1 | C1–C3 | P2–C2 | C2–C7 | Ir–P1 | Ir–P2 | Ir–N | P1–Ir–P2 | $^{31}P\{^1H\}$ NMR data[a] $\delta$(P1) | $\delta$(P2) | $^2J$(P1,P2) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **3** ($Cl^-$) | 1.744(9) | 1.391(13) | 1.701(12) | 1.389(17) | 2.260(2) | 2.206(2) | 2.056(5) | 164.38(9) | 234.6 | 18.9 | 463 |
| **4** (CO) | 1.764(7) | 1.389(9) | 1.674(7) | 1.432(9) | 2.299(2) | 2.2387(19) | 2.067(5) | 162.42(7) | 229.9 | 19.0 | 332 |
| **5** (*t*BuNC) | 1.748(12)[b] | 1.393(17)[b] | 1.664(11)[b] | 1.445(14)[b] | 2.282(3)[a] | 2.307(3)[a] | 2.096(8)[b] | 162.4(1)[b] | 238.2 | 18.9 | 360 |
| **6** ($PMe_3$) | – | – | – | – | – | – | – | – | 233.9 | 18.2 | 357 |
| **7** ($PPh_3$) | 1.754(7) | 1.392(10) | 1.678(7) | 1.413(10) | 2.2994(18) | 2.2621(18) | 2.120(5) | 160.34(7) | 239.4 | 20.4 | 353 |

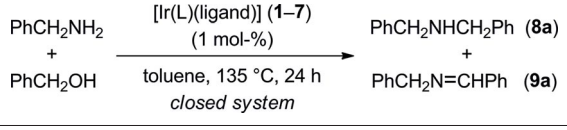
iridium center to the π* orbital results in these bond variations.[7a]

Two $^{31}P\{^1H\}$ NMR spectroscopy signals of the PPEP* ligand appear in typical regions of phosphaalkenes and phosphines, respectively, and the chemical shifts are relatively insensitive to L [$\delta$ = (235 ± 5) and (19 ± 1) ppm]. In contrast, the $^2J$(P1,P2) coupling for **3** (463 Hz) is clearly larger than that for the others [(346 ± 14) Hz]. Although the exact reason for this is unclear, the clearly short Ir–P1 (1.1–1.7 %) and Ir–P2 (1.5–4.4 %) bonds and the wide P1–Ir–P2 angle (1.2–2.5 %) of **3** may be responsible for the large coupling constant.

## Catalytic Properties of PNP-Pincer-Type Phosphaalkene Complexes

Complexes **1**–**7** (1 mol-%) were examined as catalysts for the *N*-alkylation of $PhCH_2NH_2$ (1 mmol) with $PhCH_2OH$ (1 mmol) in toluene (0.3 mL) at 135 °C (oil-bath temperature). The results are listed in Table 2. The monoalkylated amine $PhCH_2NHCH_2Ph$ (**8a**) and its imine derivative $PhCH_2N{=}CHPh$ (**9a**) were formed. The reaction was conducted in a closed system using a nitrogen-gas-filled 10 mL Schlenk tube sealed with a Teflon® screw-cock to facilitate the amine formation involving the hydrogenation of imine (see below).

Table 2. *N*-Alkylation of benzylamine with benzyl alcohol catalyzed by phosphaalkene complexes of $Ir^I$.[a]




| Entry | Complex (ligand, L) | Conversion [%][b,c] | Yield [%][c] **8a** | **9a** |
|---|---|---|---|---|
| 1 | **1** (BPEP, Cl) | 18 | 4 | 13 |
| 2 | **2** (PPEP, Cl) | 21 | 6 | 15 |
| 3 | **3** (PPEP*, $Cl^-$) | 99 | 60 | 36 |
| 4[d] | **4** (PPEP*, CO) | 100 | 92 | 8 |
| 5 | **5** (PPEP*, *t*BuNC) | 100 | 92 | 8 |
| 6 | **6** (PPEP*, $PMe_3$) | 85 | 45 | 39 |
| 7 | **7** (PPEP*, $PPh_3$) | 74 | 13 | 60 |

[a] Reactions were carried out using $PhCH_2NH_2$ (1 mmol), $PhCH_2OH$ (1 mmol), and an $Ir^I$ complex (1 mol-%) in toluene (0.3 mL) at 135 °C (oil-bath temperature) for 24 h, unless otherwise noted. [b] Conversion of $PhCH_2NH_2$. [c] Confirmed by $^1H$ NMR spectroscopy using mesitylene as an internal standard. [d] Reaction was run for 48 h.

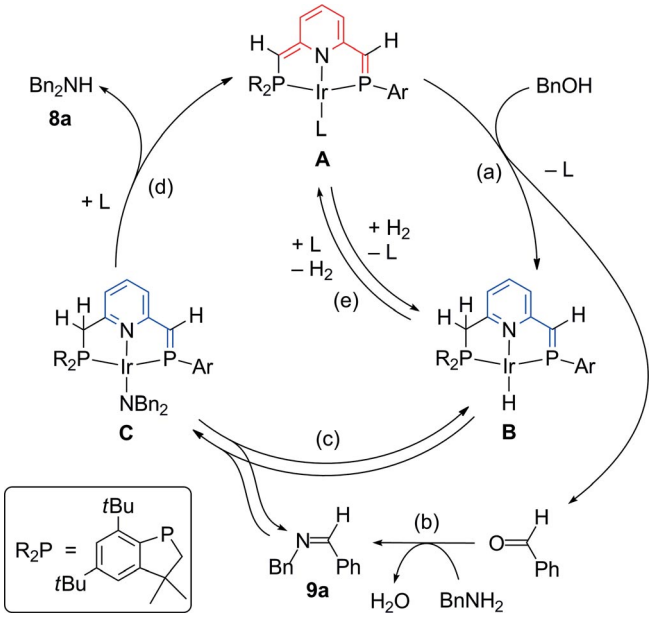
Complex **1** bearing a bis(phosphaethenyl) ligand (BPEP) serves as a good catalyst in the presence of CsOH,[12] but was poorly reactive in the absence of the base (entry 1). The catalytic activity of PPEP complex **2** was also poor, giving **8a** and **9a** in low yields (entry 2). In contrast, the dearomatized complexes [Ir(L)(PPEP*)] (**3**–**7**) successfully catalyzed the reaction under base-free conditions (entries 3–7), and the product selectivity varied significantly with L. Carbonyl complex **4** exhibited a high selectivity for the formation of *N*-alkylated amine by giving a 92 % yield of **8a** in 48 h (entry 4). The catalytic activity was enhanced by isocyanide complex **5**, which afforded the same yield of **8a** in a short time (24 h, entry 5).

Complexes **3**, **6**, and **7**, bearing $Cl^-$, $PMe_3$, and $PPh_3$ ligands as L, respectively, formed a notable amount of imine product **9a** together with **8a**, and $PPh_3$ complex **7** in particular produced **9a** as the major product. As we describe below, the product selectivity for **9a** reached 93 % in an open reaction system under a nitrogen-gas flow.

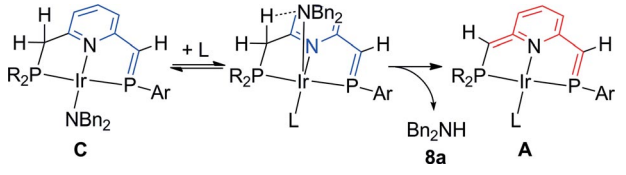
Scheme 2 illustrates a plausible catalytic cycle for the formation of **8a** and **9a** from $PhCH_2NH_2$ ($BnNH_2$) and $PhCH_2OH$ (BnOH). The reaction starts from the dehydrogenation of BnOH by [Ir(L)(PPEP*)] (**A**) to form [Ir(H)(PPEP)] (**B**) and PhCHO (step a). This step is likely to proceed by means of the metal–ligand cooperative activation of BnOH, followed by β-hydrogen elimination from [Ir(OBn)(PPEP)].[15] Then, PhCHO undergoes dehydration/condensation with $BnNH_2$ to form imine **9a** (step b). Insertion of **9a** into the Ir–H bond in **B** forms amido complex **C** (step c). Finally, *N*-alkylated product **8a** is eliminated from **C**, along with **A** (step d).

Since the four-coordinate amido complexes [Ir(NHR)(PPEP)] (R = H, Ph, Bu), corresponding to **C**, have been found to be stable towards amine elimination,[7] step d very probably invokes prior coordination of L to give a five-coordinate intermediate [Ir($NBn_2$)(L)(PPEP)], in which the amido ligand is placed at the apical position close to the benzylic hydrogen, and thereby **8a** is eliminated by means of the reverse process of metal–ligand cooperative activation of amines (Scheme 3). Indeed, treatment of [Ir(NHPh)(PPEP)] (**10**) with CO (1 atm) in [$D_8$]toluene at room temperature led to instant formation of $PhNH_2$ as confirmed by NMR spectroscopy (Scheme 4). We also confirmed that the same complex is fairly stable in the presence of $PPh_3$ (1 equiv.) at room temperature, but eliminates $PhNH_2$ at 60 °C.

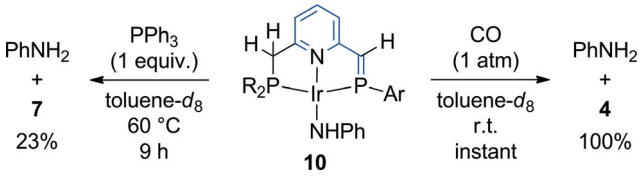
Accordingly, we may consider that the selectivity change depending on L is relevant to the ease of amine elimination from intermediate **C**. π-Accepting ligands greatly facilitate this process, which leads to **8a** in high selectivity. In contrast, **C** is reluctant to eliminate **8a** in the presence of phosphine ligands. In this case, because intermediate **C** as a 16-electron species should be in equilibrium with **9a** and **B**, $H_2$ elimination from **B** makes **9a** the final product.[17]




Scheme 2. Plausible catalytic cycle for the formation of **8a** and **9a**.




Scheme 3. Proposed mechanism for amine elimination from **C**.

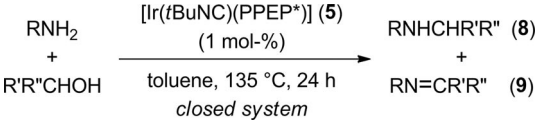



Scheme 4. Elimination of $PhNH_2$ from [Ir(NHPh)(PPEP)] (**10**) in the presence of CO or $PPh_3$.

## Substrate Scope for *N*-Alkylation of Amines

With highly efficient catalyst **5** in hand, a variety of amines were alkylated with alcohols. The results are listed in Table 3. Although the reactivities of *para*-substituted benzylamines (entries 2 and 3) were somewhat lower than that of non-substituted amines (entry 1), the reactions were completed by using a slight excess amount of $PhCH_2OH$ (1.5 equiv.) (entries 4 and 5). In particular, *p*-$ClC_6H_4CH_2NH_2$ was alkylated in 95 % yield (entry 5).

Table 3. *N*-Alkylation of amines with alcohols catalyzed by **5**.[a]




| Entry | Amine | Alcohol | Conv. [%][b,c] | Yield [%][c] 8 | 9 |
|---|---|---|---|---|---|
| 1 | $PhCH_2NH_2$ | $PhCH_2OH$ | 100 | 92 | 8 |
| 2 | *p*-$MeC_6H_4CH_2NH_2$ | $PhCH_2OH$ | 84 | 53 | 21 |
| 3 | *p*-$ClC_6H_4CH_2NH_2$ | $PhCH_2OH$ | 94 | 72 | 21 |
| 4[d] | *p*-$MeC_6H_4CH_2NH_2$ | $PhCH_2OH$ | 100 | 65 | 33 |
| 5[d] | *p*-$ClC_6H_4CH_2NH_2$ | $PhCH_2OH$ | 100 | 95 | 4 |
| 6 | $PhCH_2CH_2NH_2$ | $PhCH_2OH$ | 100 | 95 | 4 |
| 7[d] | $CH_3(CH_2)_7NH_2$ | $PhCH_2OH$ | 100 | 90 | 9 |
| 8[d] | *cyclo*-$C_6H_{11}NH_2$ | $PhCH_2OH$ | 100 | 68 | 32 |
| 9[d] | $PhCH(NH_2)CH_3$ | $PhCH_2OH$ | 100 | 51 | 49 |
| 10[e] | $PhNH_2$ | $PhCH_2OH$ | 93 | 75 | 18 |
| 11 | $PhCH_2NH_2$ | $CH_3(CH_2)_7OH$ | 93 | 86 | 5 |
| 12 | $PhCH_2NH_2$ | *cyclo*-$C_6H_{11}OH$ | 50 | 29 | 21 |
| 13 | $PhCH_2NH_2$ | $PhCH(OH)CH_3$ | 34 | 0 | 29 |

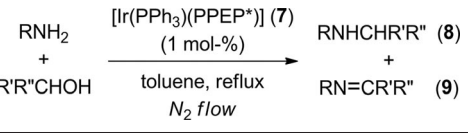
[a] Reactions were carried out using amine (1 mmol), alcohol (1 mmol), and catalyst **5** (1 mol-%) in toluene (0.3 mL) at 135 °C (oil-bath temperature) for 24 h, unless otherwise noted. [b] Conversion of amine. [c] Confirmed by $^1H$ NMR spectroscopy using mesitylene as an internal standard. [d] An excess amount of $PhCH_2OH$ (1.5 mmol) was employed. [e] Reaction was run in neat conditions using an excess amount of $PhCH_2OH$ (3 mmol).

2-Phenylethylamine and octylamine were converted to *N*-benzylated amines in 95 and 90 % yields, respectively (entries 6 and 7). In contrast, reactions of bulky cyclohexylamine and 1-phenylethylamine formed notable amounts of imines (entries 8 and 9), probably due to steric retardation of imine insertion in step c in Scheme 2. Although $PhNH_2$ as an aromatic amine was less reactive than aliphatic amines, the desired product ($PhNHCH_2Ph$) was obtained in 75 % yield under neat conditions (entry 10). Among other alcohols tested for the *N*-alkylation of $PhCH_2NH_2$, *n*-octanol afforded the desired product in 86 % yield (entry 11), whereas bulky alcohols such as cyclohexanol and 1-phenylethyl alcohol were less reactive and selective (entries 12 and 13).

## Dehydrogenative Coupling of Amines with Alcohols

Next, we examined the dehydrogenative coupling of amines with alcohols to give imines (Table 4). Complex **7** was employed as the catalyst based on the results in Table 2. The catalytic reactions were conducted under reflux in a nitrogen-gas flow to remove $H_2$ from the system. Under these conditions, $PhCH_2NH_2$ and $PhCH_2OH$ were converted to $PhCH_2N{=}CHPh$ in 93 % yield, along with byproducts $PhCH_2NHCH_2Ph$ (entry 1). Similarly, three kinds of aliphatic amines ($RNH_2$) were coupled with $PhCH_2OH$ to afford the corresponding imines (RN=CHPh) in 70–93 % yields (entries 2–4). In contrast, the reaction of $PhNH_2$ with $PhCH_2OH$ was less selective. Moreover, attempts at dehydrogenative coupling of $PhCH_2NH_2$ with alcohols other than $PhCH_2OH$ were unsuccessful (entries 6–8). It is reasonable that π-conjugated structures of imines (RN=CHPh) derived from $PhCH_2OH$ provide the thermodynamic stability of the products, which facilitates the dehydrogenative coupling.

Table 4. Dehydrogenative coupling of amines and alcohols catalyzed by **7**.[a]




| Entry | Amine | Alcohol | Conv. [%][b,c] | Yield [%][c] 8 | 9 |
|---|---|---|---|---|---|
| 1 | $PhCH_2NH_2$ | $PhCH_2OH$ | 99 | 6 | 93 |
| 2 | $PhCH_2CH_2NH_2$ | $PhCH_2OH$ | 91 | 7 | 83 |
| 3 | $CH_3(CH_2)_7NH_2$ | $PhCH_2OH$ | 77 | 7 | 70 |
| 4 | *cyclo*-$C_6H_{11}NH_2$ | $PhCH_2OH$ | 99 | 6 | 93 |
| 5 | $PhNH_2$ | $PhCH_2OH$ | 93 | 25 | 65 |
| 6 | $PhCH_2NH_2$ | $CH_3(CH_2)_7OH$ | 97 | 23 | 10 |
| 7 | $PhCH_2NH_2$ | *cyclo*-$C_6H_{11}OH$ | 88 | 67 | 4 |
| 8 | $PhCH_2NH_2$ | $PhCH(OH)CH_3$ | 88[d] | 10 | 36 |

[a] Reactions were carried out using amine (1 mmol), alcohol (1.5 mmol), and catalyst **7** (1 mol-%) in toluene (0.3 mL) at reflux. Reaction time: 24 h (entries 1, 2, 4); 120 h (entries 3, 5–8). [b] Conversion of amine. [c] Confirmed by $^1H$ NMR spectroscopy using mesitylene as an internal standard. [d] Some additional products including PhCOPh were formed.

## Conclusion

We have reported the catalytic application of $Ir^I$ complexes bearing a dearomatized PNP-pincer-type phosphaalkene ligand (PPEP*) to the *N*-alkylation of amines with alcohols. Complexes of formula [Ir(L)(PPEP*)] [L = $Cl^-$ (**3**), CO (**4**), *t*BuNC (**5**), $PMe_3$ (**6**), $PPh_3$ (**7**)] could be prepared in one pot from [IrCl(BPEP)] (**1**) coordinated with bis(phosphaethenyl)pyridine (BPEP). Although catalytic *N*-alkylation often needs the addition of a strong base to the system,[9] complexes **3**–**7** successfully catalyzed the reaction under base-free conditions to afford *N*-alkylated amines and imines in high yields. The product selectivity could be controlled by the choice of auxiliary ligands (L) as well as the reaction conditions. Complexes **4** and **5** bearing π-accepting ligands (CO, *t*BuNC) formed *N*-alkylated amines as the major products, and the selectivity for the formation of $PhCH_2NHCH_2Ph$ (**8a**) from $PhCH_2CH_2$ and $PhCH_2OH$ reached 92 % in a closed reaction system. In contrast, complex **7** bearing $PPh_3$ as L produced imines as the major products, and the product yield of $PhCH_2N{=}CHPh$ (**9a**) reached 93 % under a nitrogen-gas flow. We also demonstrated that the remarkable change in product selectivity depending on L may be rationalized by taking the reactivity difference of presumed intermediate **C** towards amine elimination (step d in Scheme 2) into consideration; namely, this step was dramatically accelerated by CO (Scheme 4).

## Experimental Section

**General Considerations:** All manipulations were carried under a nitrogen atmosphere using standard Schlenk techniques and a glove box. Nitrogen gas was dried by passing it through a $P_2O_5$ column (Merck, SICAPENT). Toluene (Kanto, dehydrated), hexane, and $Et_2O$ (Wako, dehydrated) were used as received. THF was dried with sodium/benzophenone, distilled, and stored over activated MS4A molecular sieves. [IrCl(BPEP)] (**1**),[12] [IrCl(PPEP)] (**2**),[7] [K(18-crown-6)][IrCl(PPEP*)] (**3a**),[7] [Ir(CO)(PPEP*)] (**4**),[7] and [Ir(NHPh)(PPEP)] (**10**)[7] were prepared as previously reported. Other chemicals were purchased from commercial sources and used without purification. NMR spectra were recorded on a Bruker AVANCHE 400 spectrometer ($^1H$ NMR, 400.13 MHz; $^{13}C$ NMR, 100.62 MHz; $^{31}P$ NMR, 161.98 MHz). Chemical shifts are reported in δ referenced to $^1H$ (residual) and $^{13}C$ signals of deuterated solvents as internal standards or to the $^{31}P$ signal of 85 % $H_3PO_4$ as an external standard. Elemental analysis was performed by ICR Analytical Laboratory, Kyoto University.

**Preparation of Complexes 5–7:** Complex **1** (102 mg, 0.12 mmol) was dissolved in toluene (8 mL) and heated at 70 °C overnight. The dark brown solution was concentrated to dryness to form a dark brown solid of **2**, which was dissolved in THF (8 mL) at room temperature. A solution of *t*BuNC in THF (0.6 M, 0.2 mL) and a solution of *t*BuOK (13 mg, 0.12 mmol) in THF (2 mL) were added in sequence. The solution color changed to greenish black. The solution was stirred for 10 min, and volatile substances were evaporated under vacuum. The crude product was dissolved in $Et_2O$ and filtered through a Celite pad to remove the precipitate of KCl. The filtrate was concentrated, layered with hexane, and allowed to stand at –35 °C overnight to give dark green crystals of **5**, which were collected by filtration, washed with hexane three times, and then dried under vacuum (81 mg, 0.088 mmol, 76 %). Complexes **6** and **7** were similarly synthesized in 89 and 64 % yields using $PMe_3$ (1 equiv., 1.0 M toluene solution) and $PPh_3$ instead of *t*BuNC, respectively.

**[Ir(*t*BuNC)(PPEP*)] (5):** $^1H$ NMR ($C_6D_6$, 25 °C): δ = 7.67–7.58 (m, 4 H, PyCH=P + Ar), 7.29 (s, 1 H, Ar), 6.46 (dd, $J_{H,H}$ = 8.7 Hz, $J_{P,H}$ = 6.2 Hz, 1 H, Py), 6.02 (m, 1 H, Py), 5.48 (dd, $J_{H,H}$ = 6.8 Hz, $J_{P,H}$ = 6.8 Hz, 1 H, Py), 4.16 (vt, $J_{app}$ = 4.7 Hz, 1 H, Py=CHP), 2.72 (br. d, $J_{P,H}$ = 14.4 Hz, 1 H, $PCH_2$), 2.08 (s, 9 H, $CH_3$), 1.99 (s, 9 H, $CH_3$), 1.93 (dd, $J_{H,H}$ = 14.4 Hz, $J_{P,H}$ = 7.3 Hz, 1 H, $PCH_2$), 1.87 (s, 9 H, $CH_3$), 1.44 (s, 3 H, $CH_3$), 1.37 (s, 3 H, $CH_3$), 1.28 (s, 9 H, $CH_3$), 1.27 (s, 9 H, $CH_3$), 0.76 (s, 9 H, $CH_3$) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$, 25 °C): δ = 173.5 (d, $J_{P,C}$ = 19 Hz), 162.6 (s), 160.2 (dd, $J_{P,C}$ = 17 and 3 Hz), 159.9 (d, $J_{P,C}$ = 56 Hz, PyCH=P), 157.7 (s), 157.0 (s), 154.8 (d, $J_{P,C}$ = 9 Hz), 153.1 (d, $J_{P,C}$ = 2 Hz), 152.5 (s), 149.0 (t, $J_{P,C}$ = 8 Hz, CN), 133.0 (dd, $J_{P,C}$ = 7 and 4 Hz), 131.8 (dd, $J_{P,C}$ = 45 and 4 Hz), 131.0 (d, $J_{P,C}$ = 12 Hz), 123.6 (d, $J_{P,C}$ = 8 Hz), 122.7 (d, $J_{P,C}$ = 7 Hz), 122.5 (d, $J_{P,C}$ = 7 Hz), 118.8 (d, $J_{P,C}$ = 9 Hz), 118.2 (dd, $J_{P,C}$ = 20 and 15 Hz), 104.9 (d, $J_{P,C}$ = 38 Hz), 79.8 (d, $J_{P,C}$ = 61 Hz, Py=CHP), 55.3 (s), 43.9 (s), 42.9 (d, $J_{P,C}$ = 41 Hz), 39.6 (s), 39.4 (s), 38.6 (s), 35.6 (s), 35.4 (s), 35.3 (s), 34.8 (s), 34.1 (s), 33.5 (s), 32.3 (d, $J_{P,C}$ = 8 Hz), 31.8 (s), 31.7 (s), 31.1 (s) ppm. $^{31}P\{^1H\}$ NMR ($C_6D_6$, 25 °C): δ = 238.2 (d, $J_{P,P}$ = 360 Hz), 18.9 (d, $J_{P,P}$ = 360 Hz) ppm. IR (ATR): $\tilde{\nu}$ = 2063 $cm^{-1}$ ($\nu_{NC}$). $C_{48}H_{71}IrN_2P_2$ (930.27): calcd. C 61.97, H 7.69, N 3.01; found C 61.92, H 7.77, N 2.89.

**[Ir($PMe_3$)(PPEP*)] (6):** $^1H$ NMR ($C_6D_6$, 25 °C): δ = 8.23 (dd, $J_{P,H}$ = 16.2 Hz, $J_{P,H}$ = 4.2 Hz, 1 H, PyCH=P), 7.68 (s, 1 H, Ar), 7.63 (s, 2 H, Ar), 7.29 (s, 1 H, Ar), 6.61 (dd, $J_{H,H}$ = 6.8 Hz, $J_{P,H}$ = 6.8 Hz, 1 H, Py), 6.14 (m, 1 H, Py), 5.82 (dd, $J_{H,H}$ = 6.6 Hz, $J_{P,H}$ = 6.6 Hz, 1 H, Py), 4.16 (vt, $J_{app}$ = 4.6 Hz, 1 H, Py=CHP), 2.57 (br. d, $J_{P,H}$ = 14.1 Hz, 1 H, $PCH_2$), 2.02 (s, 9 H, $CH_3$), 1.92 (s, 9 H, $CH_3$), 1.78 (s, 10 H, $PCH_2$ + $CH_3$), 1.43 (s, 3 H, $CH_3$), 1.34 (s, 3 H, $CH_3$), 1.29 (s, 9 H, $CH_3$), 1.27 (s, 9 H, $CH_3$), 1.06 (d, $J_{P,H}$ = 8.4 Hz, 9 H, $PMe_3$) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$, 25 °C): δ = 173.1 (d, $J_{P,C}$ = 19 Hz), 162.8 (t, $J_{P,C}$ = 4 Hz), 159.6 (dd, $J_{P,C}$ = 15 and 4 Hz), 157.8 (dd, $J_{P,C}$ = 57 and 3 Hz, PyCH=P), 156.1 (s), 156.0 (s), 154.2 (d, $J_{P,C}$ = 9 Hz), 153.1 (d, $J_{P,C}$ = 2 Hz), 152.6 (d, $J_{P,C}$ = 2 Hz), 133.8 (dd, $J_{P,C}$ = 42 and 4 Hz), 133.3 (dd, $J_{P,C}$ = 7 and 4 Hz), 131.8 (d, $J_{P,C}$ = 15 Hz), 124.3 (d, $J_{P,C}$ = 8 Hz), 124.2 (d, $J_{P,C}$ = 7 Hz), 123.5 (d, $J_{P,C}$ = 7 Hz), 119.2 (d, $J_{P,C}$ = 9 Hz), 116.7 (dd, $J_{P,C}$ = 20 and 15 Hz), 103.4 (d, $J_{P,C}$ = 37 Hz), 78.7 (dd, $J_{P,C}$ = 62 and 3 Hz, Py=CHP), 44.2 (t, $J_{P,C}$ = 3 Hz), 42.0 (d, $J_{P,C}$ = 39 Hz), 40.2 (s), 39.7 (s), 38.6 (s), 35.6 (s), 35.5 (s), 35.4 (s), 34.7 (s), 34.5 (s), 34.4 (d, $J_{P,C}$ = 1 Hz), 32.6 (d, $J_{P,C}$ = 9 Hz), 31.9 (s), 31.7 (s), 20.6 (d, $J_{P,C}$ = 35 Hz, $PMe_3$) ppm. $^{31}P\{^1H\}$ NMR ($C_6D_6$, 25 °C): δ = 233.9 (dd, $J_{P,P}$ = 357 and 18 Hz), 18.2 (dd,

$J_{P,P}$ = 357 and 19 Hz), –40.0 (dd, $J_{P,P}$ = 19 and 18 Hz) ppm. $C_{46}H_{71}IrNP_3$ (923.21): calcd. C 59.85, H 7.75, N 1.52; found C 59.67, H 7.80, N 1.46.

**[Ir(PPh$_3$)(PPEP*)] (7):** $^1$H NMR ($C_6D_6$, 25 °C): $\delta$ = 8.16 (vt, $J_{app}$ = 4.6 Hz, 1 H, PyCH=P), 7.63 (m, 1 H, Ar), 7.58 (s, 1 H, Ar), 7.5 (br., 6 H, $PPh_3$), 7.41 (s, 1 H, Ar), 6.82 (s, 1 H + 3 H, Ar + $PPh_3$), 6.61–6.66 (br., m, 6 H + 1 H, $PPh_3$ + Py), 6.16 (m, 1 H, Py), 5.76 (dd, $J_{H,H}$ = 6.4 Hz, $J_{P,H}$ = 6.4 Hz, 1 H, Py), 4.34 (vt, $J_{app}$ = 4.8 Hz, 1 H, Py=CHP), 2.18 (s, 9 H, $CH_3$), 1.58 (s, 9 H, $CH_3$), 1.55 (s, 9 H, $CH_3$), 1.35 (s, 9 H, $CH_3$), 1.30 (s, 9 H, $CH_3$), 1.22 (s, 3 H, $CH_3$), 0.64 (s, 3 H, $CH_3$) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$, 25 °C): $\delta$ = 172.9 (d, $J_{P,C}$ = 17 Hz), 161.7 (d, $J_{P,C}$ = 4 Hz), 159.1–159.5 (m), 155.5 (d, $J_{P,C}$ = 25 Hz), 153.1 (d, $J_{P,C}$ = 9 Hz), 152.1 (d, $J_{P,C}$ = 7 Hz), 136.7 (br), 135.0 (br), 133.0–133.1 (m), 129.6 (d, $J_{P,C}$ = 13 Hz), 129.1 (s), 127.4 (d, $J_{P,C}$ = 9 Hz), 125.1 (d, $J_{P,C}$ = 9 Hz), 124.2 (d, $J_{P,C}$ = 7 Hz), 123.9 (d, $J_{P,C}$ = 7 Hz), 119.0 (d, $J_{P,C}$ = 9 Hz), 117.4 (t, $J_{P,C}$ = 16 Hz), 103.2 (d, $J_{P,C}$ = 37 Hz), 79.1 (d, $J_{P,C}$ = 61 Hz, Py=CH-P), 44.0 (t, $J_{P,C}$ = 3 Hz), 40.4 (d, $J_{P,C}$ = 41 Hz), 40.1 (s), 39.6 (s), 38.9 (s), 35.5 (s), 35.2 (s), 35.1 (s), 35.0 (s), 34.8 (s), 34.5 (s), 31.9 (s), 31.6 (s), 30.9 (d, $J_{C,H}$ = 9 Hz) ppm. $^{31}P\{^1H\}$ NMR ($C_6D_6$, 25 °C): $\delta$ = 239.4 (dd, $J_{P,P}$ = 353 and 19 Hz), 20.4 (t, $J_{P,P}$ = 19 Hz), 16.5 (dd, $J_{P,P}$ = 353 and 21 Hz) ppm. HRMS (ESI): *m/z* calcd. for $C_{61}H_{77}NP_3Ir$ $[M + H]^+$ 1110.4976; found 1110.4974.

**General Procedure for Catalytic *N*-Alkylation of Amines with Alcohols:** A typical procedure (entry 5 in Table 2) was as follows. Benzyl alcohol (103 μL, 1.0 mmol), benzylamine (109 μL, 1.0 mmol), and toluene (0.3 mL) were added to a 10 mL Schlenk tube containing **5** (9.3 mg, 0.010 mmol). The solution was degassed by freeze–pump–thaw cycles, filled with dry nitrogen gas, and stirred for 24 h in an oil bath controlled at 135 °C. The solution was diluted with $CDCl_3$ (0.5 mL) at room temperature, and mesitylene (139 μL, 1.0 mmol) was added as an internal standard. $^1$H NMR spectroscopy analysis of the resulting solution revealed the formation of *N*,*N*-dibenzylamine (0.92 mmol, 92 %) and *N*-benzylidenebenzylamine (0.08 mmol, 8 %). The catalytic reactions given in Tables 2 and 3 were conducted similarly.

**General Procedure for Dehydrogenative Coupling of Amines with Alcohols:** A typical procedure (entry 1 in Table 4) was as follows. Complex **7** (11 mg, 0.010 mmol), benzyl alcohol (103 μL, 1.5 mmol), benzylamine (109 μL, 1.0 mmol), and toluene (0.3 mL) were added to a 10 mL Schlenk tube equipped with a cold finger. The solution was degassed by freeze–pump–thaw cycles, and stirred at reflux for 24 h in a nitrogen gas flow. The solution was diluted with $CDCl_3$ (0.5 mL) at room temperature, and mesitylene (139 μL, 1.0 mmol) was added as an internal standard. $^1$H NMR spectroscopy analysis of the resulting solution revealed the formation of *N*,*N*-dibenzylamine (0.06 mmol, 6 %) and *N*-benzylidene benzylamine (0.93 mmol, 93 %). The catalytic reactions given in Table 4 were conducted similarly.

**Reaction of [Ir(NHPh)(PPEP)] (10) with CO:** Complex **10** (3.2 mg, 3.4 μmol) was dissolved in [$D_8$]toluene (0.5 mL), and charged with CO (1 atm). The color of the solution changed immediately from green to dark violet. The $^1$H and $^{31}P\{^1H\}$ NMR spectra showed quantitative conversion of **10** to **4**, along with the formation of $PhNH_2$.

**Reaction of [Ir(NHPh)(PPEP)] (10) with PPh$_3$:** Complex **10** (3.2 mg, 3.4 μmol) and $PPh_3$ (1.0 mg, 3.8 μmol) were dissolved in [$D_8$]toluene (0.5 mL), and examined by $^1$H and $^{31}P\{^1H\}$ NMR spectroscopy. No notable change was observed at room temperature for 5 h, whereas heating the solution at 60 °C for 9 h lead to the formation of **7** in 23 % yield, along with the formation of $PhNH_2$.

**X-ray Crystal Structure Determination of 5–7:** Single crystals suitable for X-ray diffraction analysis were grown from solutions in $Et_2O$. The intensity data were collected at 103 K on a Rigaku Saturn70 CCD diffractometer with the VariMax Optic, using Mo-$K_\alpha$ radiation ($\lambda$ = 0.71070 Å). The intensity data were corrected for Lorentz and polarization effects and for absorption [numerical (**5**, **7**), multi-scan (**6**)[18]]. The structures were solved by direct methods (SHELXS-97)[19] and refined by least-squares calculations on $F^2$ for all reflections (SHELXL-97)[19] using Yadokari-XG 2009 (Software for Crystal Structure Analyses).[20] Non-hydrogen atoms, except for disordered groups in **5** (*t*Bu), were refined anisotropically. Hydrogen atoms were placed at calculated positions, and included in the final cycles of least-squares calculations without refinement of their parameters. The crystallographic data and the summary of solution and refinement are listed in Table S1 in the Supporting Information.

CCDC-1416896 (for **5**), -1416897 (for **6**), and -1416898 (for **7**) contain 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.

**Supporting Information** (see footnote on the first page of this article): Crystallographic details for **5**–**7** and a crude structure of disordered **6**.

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[1] a) Y. Shvo, D. Czarkie, Y. Rahamim, *J. Am. Chem. Soc.* **1986**, *108*, 7400–7402; b) Y. Blum, D. Czarkie, Y. Rahamim, Y. Shvo, *Organometallics* **1985**, *4*, 1459–1461; c) B. L. Conley, M. K. Pennington-Boggio, E. Boz, T. J. Williams, *Chem. Rev.* **2010**, *110*, 2294–2312.

[2] a) R. Noyori, T. Ohkuma, *Angew. Chem. Int. Ed.* **2001**, *40*, 40–73; *Angew. Chem.* **2001**, *113*, 40; b) J. S. M. Samec, J.-E. Bäckvall, P. G. Andersson, P. Brandt, *Chem. Soc. Rev.* **2006**, *35*, 237–248; c) T. Ikariya, K. Murata, R. Noyori, *Org. Biomol. Chem.* **2006**, *4*, 393–406; d) T. Ikariya, A. J. Blacker, *Acc. Chem. Res.* **2007**, *40*, 1300–1308; e) S. Kuwata, T. Ikariya, *Chem. Eur. J.* **2011**, *17*, 3542–3556; f) T. Ikariya, M. Shibasaki, *Top. Organomet. Chem.* **2011**, *37*, 31–53; g) V. T. Annibale, D. Song, *RSC Adv.* **2013**, *3*, 11432–11449.

[3] a) H. Grützmacher, *Angew. Chem. Int. Ed.* **2008**, *47*, 1814–1818; *Angew. Chem.* **2008**, *120*, 1838; b) J. I. van der Vlugt, J. N. H. Reek, *Angew. Chem. Int. Ed.* **2009**, *48*, 8832–8846; *Angew. Chem.* **2009**, *121*, 8990; c) R. H. Crabtree, *New J. Chem.* **2011**, *35*, 18–23; d) J. I. van der Vlugt, *Eur. J. Inorg. Chem.* **2012**, 363–375; e) S. Schneider, J. Meiners, B. Askevold, *Eur. J. Inorg. Chem.* **2012**, 412–429.

[4] a) C. Gunanathan, D. Milstein, in: *Pincer and Pincer-Type Complexes: Applications in Organic Synthesis and Catalysis* (Eds.: K. J. Szabó, O. F. Wendt), Wiley-VCH, Weinheim, Germany, **2014**, chapter I; b) C. Gunanathan, D. Milstein, *Chem. Rev.* **2014**, *114*, 12024–12087.

[5] a) J. Zhang, M. Gandelman, L. J. W. Shimon, H. Rozenberg, D. Milstein, *Organometallics* **2004**, *23*, 4026–4033; b) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840–10841; c) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2006**, *45*, 1113–1115; *Angew. Chem.* **2006**, *118*, 1131; d) C. Gunanathan, Y. Ben-David, D. Milstein, *Science* **2007**, *317*, 790–792; e) C. Gunanathan, D. Milstein, *Angew. Chem. Int. Ed.* **2008**, *47*, 8661–8664; *Angew. Chem.* **2008**, *120*, 8789; f) C. Gunanathan, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2009**, *131*, 3146–3147; g) B. Gnanaprakasam, J. Zhang, D. Milstein,

*Angew. Chem. Int. Ed.* **2010**, *49*, 1468–1471; *Angew. Chem.* **2010**, *122*, 1510; h) E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon, D. Milstein, *Nat. Chem.* **2011**, *3*, 609–614; i) E. Balaraman, E. Fogler, D. Milstein, *Chem. Commun.* **2012**, *48*, 1111–1113; j) M. Feller, Y. Diskin-Posner, L. J. W. Shimon, E. Ben-Ari, D. Milstein, *Organometallics* **2012**, *31*, 4083–4101; k) C. Gunanathan, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2012**, *134*, 10325–10328; l) A. Anaby, B. Butschke, Y. Ben-David, L. J. W. Shimon, G. Leitus, M. Feller, D. Milstein, *Organometallics* **2014**, *33*, 3716–3726.

[6] a) J. Dugal-Tessier, E. D. Conrad, G. R. Dake, D. P. Gates, in: *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis* (Eds.: P. C. J. Kamer, P. W. N. M. van Leeuwen), Wiley, Chichester, UK, **2012**, chapter 10; b) P. Le Floch, *Coord. Chem. Rev.* **2006**, *250*, 627–681; c) C. Muüller, E. A. Pidko, M. Lutz, A. L. Spek, D. Vogt, *Chem. Eur. J.* **2008**, *14*, 8803–8807.

[7] a) Y.-H. Chang, Y. Nakajima, H. Tanaka, K. Yoshizawa, F. Ozawa, *J. Am. Chem. Soc.* **2013**, *135*, 11791–11794; b) Y.-H. Chang, Y. Nakajima, H. Tanaka, K. Yoshizawa, F. Ozawa, *Organometallics* **2014**, *33*, 715–721.

[8] Y.-H. Chang, K. Takeuchi, M. Wakioka, F. Ozawa, *Organometallics* **2015**, *34*, 1957–1962.

[9] For reviews, see: a) M. H. S. A. Hamid, P. A. Slatford, J. M. J. Williams, *Adv. Synth. Catal.* **2007**, *349*, 1555–1575; b) A. J. A. Watson, J. M. J. Williams, *Science* **2010**, *329*, 635–636; c) G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* **2010**, *110*, 681–703; d) G. Guillena, D. J. Ramón, M. Yus, *Chem. Rev.* **2010**, *110*, 1611–1641; e) R. H. Crabtree, *Organometallics* **2011**, *30*, 17–19; f) S. Bähn, S. Imm, L. Neubert, M. Zhang, H. Neumann, M. Beller, *ChemCatChem* **2011**, *3*, 1853–1864; g) C. Gunanathan, D. Milstein, *Science* **2013**, *341*, 1229712.

[10] For recent examples, see: a) S. Bähn, S. Imm, L. Neubert, M. Zhang, H. Neumann, M. Beller, *Chem. Eur. J.* **2011**, *17*, 4705–4708; b) M. Zhang, S. Imm, S. Bähn, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* **2011**, *50*, 11197–11201; *Angew. Chem.* **2011**, *123*, 11393; c) J. Norinder, A. Börner, *ChemCatChem* **2011**, *3*, 1407–1409; d) F. E. Fernández, M. C. Puerta, P. Valerga, *Organometallics* **2012**, *31*, 6868–6879; e) F. Li, H. Shan, L. Chen, Q. Kang, P. Zou, *Chem. Commun.* **2012**, *48*, 603–605; f) F. Li, Q. Kang, H. Shan, L. Chen, J. Xie, *Eur. J. Org. Chem.* **2012**, 5085–5092; g) A. Bartoszewicz, R. Marcos, S. Sahoo, A. K. Inge, X. Zou, B. Martín-Matute, *Chem. Eur. J.* **2012**, *18*, 14510–14519; h) J.-Q. Li, P. G. Andersson, *Chem. Commun.* **2013**, *49*, 6131–6133; i) R. Ramachandran, G. Prakash, S. Selvamurugan, P. Viswanathamurthi, J. G. Malecki, V. Ramkumar, *Dalton Trans.* **2014**, *43*, 7889–7902; j) A. B. Enyong, B. Moasser, *J. Org. Chem.* **2014**, *79*, 7553–7563; k) Z.-Q. Rong, Y. Zhang, R. H. B. Chua, H.-J. Pan, Y. Zhao, *J. Am. Chem. Soc.* **2015**, *137*, 4944–4947; l) Q. Zou, C. Wang, J. Smith, D. Xue, J. Xiao, *Chem. Eur. J.* **2015**, *21*, 9656–9661; m) A. J. Rawlings, L. J. Diorazio, M. Wills, *Org. Lett.* **2015**, *17*, 1086–1089.

[11] a) B. Blank, M. Madalska, R. Kempe, *Adv. Synth. Catal.* **2008**, *350*, 749–758; b) B. Blank, S. Michlik, R. Kempe, *Adv. Synth. Catal.* **2009**, *351*, 2903–2911; c) B. Blank, S. Michlik, R. Kempe, *Chem. Eur. J.* **2009**, *15*, 3790–3799; d) S. Michlik, R. Kempe, *Chem. Eur. J.* **2010**, *16*, 13193–13198; e) B. Blank, R. Kempe, *J. Am. Chem. Soc.* **2010**, *132*, 924–925; f) S. Michlik, T. Hille, R. Kempe, *Adv. Synth. Catal.* **2012**, *354*, 847–862; g) S. Michlik, R. Kempe, *Nat. Chem.* **2013**, *5*, 140–144; h) S. Michlik, R. Kempe, *Angew. Chem. Int. Ed.* **2013**, *52*, 6326–6329; *Angew. Chem.* **2013**, *125*, 6450; i) D. Forberg, J. Obenauf, M. Friedrich, S.-M. Hühne, W. Mader, G. Motzc, R. Kempe, *Catal. Sci. Technol.* **2014**, *4*, 4188–4192; j) T. Hille, T. Irrgang, R. Kempe, *Chem. Eur. J.* **2014**, *20*, 5569–5572; k) S. Ruch, T. Irrgang, R. Kempe, *Chem. Eur. J.* **2014**, *20*, 13279–13285.

[12] a) Y.-H. Chang, Y. Nakajima, F. Ozawa, *Organometallics* **2013**, *32*, 2210–2215; b) A. Jouaiti, M. Geoffroy, G. Bernardinelli, *Tetrahedron Lett.* **1992**, *33*, 5071–5074.

[13] The sum of the four angles around iridium is 359.8° (**5A**), 360.0° (**5B**), and 359.8° (**7**), respectively.

[14] a) A. Sacco, G. Vasapollo, C. F. Nobile, A. Piergionvanni, M. A. Pellinghelli, M. Lanfranchk, *J. Organomet. Chem.* **1988**, *356*, 397–409; b) H. Qichen, X. Minzhi, Q. Yanlong, X. Weihua, *J. Organomet. Chem.* **1985**, *287*, 419–426.

[15] a) For metal–ligand cooperative activation of alcohols, see ref.[5k] b) We do not exclude the possibility of a bifunctional double hydrogen transfer (BDHT) mechanism.[16]

[16] a) H. Li, X. Wang, F. Huang, G. Lu, J. Jiang, Z.-X. Wang, *Organometallics* **2011**, *30*, 5233–5247; b) H. Li, X. Wang, M. Wen, Z.-X. Wang, *Eur. J. Inorg. Chem.* **2012**, 5011–5020; c) D. Cho, K. C. Ko, J. Y. Lee, *Organometallics* **2013**, *32*, 4571–4576.

[17] The $H_2$ elimination from **B** (step e in Scheme 2) probably proceeds via coordination of L, followed by coupling of an apical hydride with a benzylic proton.[16]

[18] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.

[19] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1997**.

[20] C. Kabuto, S. Akine, E. Kwon, *J. Crystallogr. Soc. Jpn.* **2009**, *51*, 218–224.

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