# **ORGANOMETALLICS**

# Synthesis and Structures of NCN Pincer-Type Ruthenium and Iridium Complexes Bearing Protic Pyrazole Arms

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**S** Supporting Information

**ABSTRACT:** The reaction of the 1,3-bis(pyrazol-3-yl)benzenes **1** with  $[RuCl(OAc)(PPh_3)_3]$  resulted in selective C-H cleavage at the 2-position of **1** to give the protic NCN pincer-type ruthenium(II) complexes  $[RuCl(R-NCN-LH_2)-(PPh_3)_2]$  (**2**; R-NCN-LH<sub>2</sub> = 4-R-2,6-bis(5-tert-butyl-1H-pyrazol-3-yl)phenyl). Similar cyclometalation with iridium trichloride followed by addition of triphenylphosphine led to the formation of the iridium(III) analogue  $[IrCl(Bu^t-NCN-LH_2)(PPh_3)]Cl$  (**5**). Treatment of the ruthenium complexes **2** with carbon monoxide afforded the carbonyl complexes  $[Ru(CO)(R-NCN-LH_2)(PPh_3)_2]Cl$  (**4**). On the other hand, the pyridine analogue of **1**, 2,6-bis(5-tert-butyl-1H-pyrazol-3yl)pyridine (NNN-LH<sub>2</sub>), reacted with iridium trichloride to



yield the protic NNN pincer-type complex  $[IrCl_3(NNN-LH_3)]$  (7). The stronger  $\sigma$  donation of the NCN pincer-type ligand in comparison with the analogous NNN ligand was suggested by the CO stretching frequencies of the ruthenium carbonyl complexes 4 as well as the M–Cl distances. The catalytic activity of the ruthenium complexes 2a,b toward transfer hydrogenation of a ketone was also evaluated.

# INTRODUCTION

The pincer-type complexes have emerged over the past decades as versatile scaffolds for chemical transformations and materials science.<sup>1</sup> The tunable nature of the steric and electronic parameters for these purposes is one of the distinctive traits of the pincer-type ligands. Protic pyrazole is an attractive pendant group in the pincer-type ligand to modulate the coordination sphere through hydrogen bonding and proton transfer.<sup>2,3</sup> During our extensive study on metal–ligand cooperation in the coordination chemistry of the protic N-heterocycles,<sup>4,5</sup> we have recently been interested in the NNN pincer-type 2,6bis(pyrazol-3-yl)pyridine (NNN-LH<sub>2</sub>; Chart 1) complexes furnished with two protic pyrazole arms<sup>6–12</sup> and investigated their proton-donating ability and metal–ligand cooperation. Particularly remarkable is the disproportionation of hydrazine





into dinitrogen and ammonia catalyzed by a protic pincer-type iron complex, wherein electron transfer between the complex and the substrate molecule is associated with the proton transfer.<sup>7</sup> To promote electron transfer from the metal to the substrate, we embarked on a study of the synthesis of the corresponding NCN pincer-type complexes bearing a central aryl group instead of pyridine, in which the electron density of the metal center would be increased by the strong electron donation of this monoanionic group. Unlike the NNN pincertype analogues, however, this class of complexes has been unexplored so far, possibly due to apparent synthetic incompatibility between the Brønsted basic central carbon atoms and protic arms. In this paper, we describe the efficient synthesis of NCN pincer-type complexes of ruthenium and iridium through cyclometalation of an appropriately designed protic pyrazole. Comparison with related NNN complexes is also described.

#### RESULTS AND DISCUSSION

Synthesis of NCN Pincer-Type Ruthenium Complexes. The protic nature of the desired pyrazole ligand prevents us using some of the typical synthetic protocols for the carboncentered pincer-type complexes such as transmetalation and

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C–H metalation with main-group metals.<sup>1</sup> We thus adapted cyclometalation<sup>13</sup> of the 1,3-bis(pyrazol-3-yl)benzene derivatives 1, which were synthesized according to Scheme  $1.^{14}$ 



<sup>*a*</sup>For 1b, see ref 14.

Heating of 1 with the acetato complex  $[RuCl(OAc)(PPh_3)_3]$  in toluene led to selective C-H cleavage at the 2-position of the central benzene ring to afford the protic pincer-type ruthenium-(II) complexes  $[RuCl(R-NCN-LH_2)(PPh_3)_2]$  (2) in moderate isolated yields (Scheme 2). The reaction of 1 with





 $[RuCl_2(PPh_3)_3]$  under acetate-free conditions was not effective for the formation of **2**. While cyclometalation of arenes furnished with two Schiff-base pendants at the meta positions has been extensively studied,<sup>15</sup> application to the synthesis of protic pincer-type complexes remains rare.<sup>16</sup>

The <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra of **2** are congruent with a  $C_{2\nu}$ -symmetric structure. In the <sup>1</sup>H NMR spectra, the NH resonance appears at  $\delta$  9.53, comparable with that of the NNN analogue [RuCl(NNN-LH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]Cl (3;  $\delta$  10.53).<sup>8</sup> The Xray analysis confirmed that cyclometalation of 1 gave the desired pincer-type framework of 2 (Figure 1). Selected bond distances and angles are given in Table 1. The structures of 2a,b are essentially identical except for the backbone substituent of the pincer ligand. The two phosphine ligands lie in mutually trans positions. One of the two NH groups makes a close contact with the chlorido ligand in a neighboring molecule (H1…Cl1\*, 2.60–2.75 Å) to form a hydrogen-bonded dimeric structure, as in the related NNN pincer-type complex 3. The Ru–Cl distances of 2a (2.5867(13) Å) and 2b (2.600 Å, mean of the two crystallographically independent molecules) are notably longer than those of the NNN pincer-type bis-(pyrazole) complex 3 (2.4438(6) Å) and the deprotonated derivative [RuCl(NNN-LH)(PPh<sub>3</sub>)<sub>2</sub>] (2.498(2) Å),<sup>8</sup> indicating the stronger  $\sigma$  donation of the NCN pincer-type ligand. The N-N-C angles around the uncoordinated nitrogen atoms



**Figure 1.** Crystal structures of (a)  $2a \cdot 0.5$  (hexane) and (b)  $2b \cdot 0.5$ THF. The CH hydrogen atoms, the minor components of the disordered *tert*-butyl groups, and the solvating molecule are omitted for clarity. Asterisks denote atoms generated by a symmetry operation (1 - x, -y, 1 - z). Ellipsoids are drawn at the 30% probability level.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) in 2a,b and 4a  $\,$ 

		2				
	2a	molecule A	molecule B	4a		
Ru1-X <sup>a</sup>	2.5867(13)	2.604(2)	2.595(2)	1.947(3)		
Ru1-C4	1.985(5)	1.964(6)	1.993(6)	2.038(3)		
Ru1-P1	2.3661(13)	2.390(2)	2.377(2)	2.3834(10)		
Ru1-P2	2.3574(13)	2.383(2)	2.372(2)	2.3985(10)		
Ru1-N2	2.117(4)	2.104(4)	2.126(4)	2.101(3)		
Ru1–N4	2.080(4)	2.106(4)	2.116(4)	2.105(3)		
N…Cl <sup>b</sup>	3.528(4)	3.645(6)	3.678(6)	3.227(2)		
H…Cl <sup>b</sup>	2.60	2.73	2.75	2.32		
N2-N1-C1	110.9(4)	111.8(5)	111.4(5)	111.7(3)		
N4-N3-C12	112.7(5)	111.5(5)	112.5(5)	110.9(3)		
<sup>a</sup> X = Cl1 (2a,b), C25 (4a). <sup>b</sup> N1-H1Cl1* for 2a,b, N3-H2Cl1						
for 4a.	. ,					

 $(110.9(4)-112.7(5)^\circ)$  fall in the range of typical protic pyrazole ligands.  $^2$ 

**Derivatization to Carbonyl Complexes.** To further gauge the electron-donating ability of the NCN pincer-type ligands, we next introduced a carbonyl ligand to the chlorido complexes 2. When a solution of 2 was stirred under carbon monoxide at room temperature, the cationic carbonyl complexes  $[Ru(CO)(R-NCN-LH_2)(PPh_3)_2]Cl$  (4) were obtained, as shown in Scheme 2. The facile substitution of the chlorido ligand substantiates the strong trans effect of the

monoanionic NCN ligand. In fact, the corresponding reaction of the NNN pincer-type complex **3** requires addition of a Lewis acid and heating at 100 °C.<sup>5</sup> The electron donation of the NCN ligand in the cationic complexes **4** was also inferred by the CO stretching bands at 1960 (**4a**) and 1963 cm<sup>-1</sup> (**4b**), which are much lower than that of the NNN pincer-type dicationic complex [Ru(CO)(NNN-LH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>](BAr<sup>F</sup><sub>4</sub>)<sub>2</sub> (1989 cm<sup>-1</sup>; Ar<sup>F</sup> = C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>-3,5) and comparable with the wavenumber of the uncharged bis(pyrazolato) complex [Ru(CO)(NNN-L)(PPh<sub>3</sub>)<sub>2</sub>] (1958 cm<sup>-1</sup>).<sup>5</sup>

The crystal structure of the  $Bu^t$ -NCN complex 4a is depicted in Figure 2. The two NH groups are engaged in hydrogen



Figure 2. Crystal structure of 4a·2EtOH. The CH hydrogen atoms, the minor components of the disordered *tert*-butyl groups, and one of the solvating ethanol molecules are omitted for clarity. Ellipsoids are drawn at the 30% probability level.

bonding with the chloride counteranion and one of the two solvating ethanol molecules, suggesting the Brønsted acidic nature. The carbonyl ligand lies in the pincer plane. The Ru1–C4 bond trans to the carbonyl ligand elongated (2.038(3) Å) relative to the chloride complex **2a** (1.985(5) Å).

**Synthesis of NCN Pincer-Type Iridium Complexes.** The synthesis of cyclometalated octahedral iridium(III) complexes has been studied extensively to develop the organic light-emitting devices.<sup>17</sup> One of the standard and reliable methods therein involves thermal reactions of iridium trichloride and the ligand precursor in alcohols at high temperatures.<sup>17,18</sup> We applied this protocol to the 1,3-bis(pyrazol-3-yl)arenes 1, as illustrated in Scheme 3. Although the <sup>1</sup>H NMR spectrum of the

# Scheme 3



product from **1a** was rather complicated, the ESI-MS spectrum exhibited peaks assignable to the cations  $[IrCl(Bu<sup>t</sup>-NCN-LH_2)]^+$  and  $[Ir_2Cl_3(Bu<sup>t</sup>-NCN-LH_2)_2]^+$ . We thus considered that chlorido-bridged oligomer(s)  $[IrCl_2(Bu<sup>t</sup>-NCN-LH_2)]_n$ would be formed in this stage.<sup>19–21</sup> As expected, addition of an excess of triphenylphosphine to the product led to the clean formation of the mononuclear phosphine complex [IrCl(Bu<sup>t</sup>- $NCN-LH_2)(PPh_3)_2]Cl(5)$  in moderate isolated yield. It should be noted that similar treatment of the proligand **1b** without the *tert*-butyl group on the central benzene ring afforded a complicated mixture. Unlike the reactions of the ruthenium complex, this bulky substituent may be crucial in suppressing C–H cleavage at the undesired 4- and 6-positions.<sup>19,22</sup>

The NCN pincer-type iridium(III) complex **5** was characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra, which are in full agreement with the  $C_{2\nu}$ -symmetric structure shown in Scheme 3. The mononuclear structure has been established by an X-ray analysis of the tetraphenylborate salt **6**, which was obtained by anion exchange of **5** (Figure 3 and Table 2). The



**Figure 3.** Structure of the cationic part of  $6\cdot 2\text{Et}_2\text{O}$ . The CH hydrogen atoms and the minor components of the disordered *tert*-butyl groups are omitted for clarity. Asterisks denote atoms generated by a symmetry operation (2 - x, -y, -z). Ellipsoids are drawn at the 30% probability level.

structure of the cationic part of **6** is quite similar to the isoelectronic NNN pincer-type ruthenium complex **3** with a hydrogen-bonded dimeric structure. The Ir-C(central) distance of 1.976(4) Å is comparable with those in the related aprotic complexes bearing pyrazol-1-yl<sup>23</sup> or N-heterocylic

Table 2. Selected Interatomic Lengths (Å) and Angles (deg) in 6 and 7

	6	7
Ir1-Cl1	2.5320(10)	2.366(2)
Ir1-X <sup>a</sup>	1.976(4)	1.980(5)
Ir1–Y1 <sup>b</sup>	2.3672(10)	2.357(2)
Ir1-Y2 <sup>b</sup>	2.3751(11)	2.364(3)
Ir1–N2	2.079(3)	2.050(4)
Ir1–N4	2.083(3)	2.058(4)
N1…Cl1*	3.659(3)	
H1…Cl1*	2.73	
N2-N1-C1	111.5(3)	110.5(5)
N4 $-$ N3 $-$ Z <sup><math>c</math></sup>	112.0(4)	110.6(5)

 ${}^{a}X = C4$  (6), N5 (7).  ${}^{b}[Y1, Y2] = [P1, P2]$  (6), [Cl2, Cl3] (7).  ${}^{c}Z = C12$  (6), C11 (7).

carbene<sup>21,24</sup> pendants in the benzene-centered pincer ligand (1.94(1)-1.987(9) Å).

Synthesis of NNN Pincer-Type Iridium Complexes. The isolation and structural characterization of the protic NCN pincer-type iridium complexes **5** and **6** prompted us to synthesize the corresponding NNN pincer-type complex for comparison. The protic NNN-LH<sub>2</sub> ligand, like the aprotic terpyridine,<sup>25</sup> reacted with iridium trichloride to yield the iridium(III) complex [IrCl<sub>3</sub>(NNN-LH<sub>2</sub>)] (7), which represents the first example of an iridium complex bearing both NNN-LH<sub>2</sub> and labile monodentate coligands (Scheme 4). As related

#### Scheme 4



compounds, a rhodium analogue of 7,  $[RhCl_3(NNN-LH_2)]$ ,<sup>11</sup> as well as an iridium complex bearing a doubly deprotonated NNN-L derivative and a tridentate chelate ligand<sup>26</sup> has been reported quite recently.

Figure 4 depicts the crystal structure of 7. The short contacts between the uncoordinated nitrogen atom and the oxygen



**Figure 4.** Crystal structure of 7·2DMF. The hydrogen atoms except for the NH and formyl hydrogens are omitted for clarity. Ellipsoids are drawn at the 30% probability level.

atom in the solvating dimethylformamide molecules (2.691(7)) and 2.696(7) Å) indicate the presence of the NH protons and the hydrogen bonds (H···O 1.79 and 1.77 Å). The Ir-Cl(equatorial) distance of 2.3659(16) Å is much shorter than that in the NCN pincer-type complex **6** (2.5320(10) Å), in line with the weaker trans influence of the NNN ligand.

Catalytic Hydrogenation of a Ketone with Protic Pincer-Type Ruthenium Complexes. Pincer-type ruthenium complexes bearing the protic NNN-LH<sub>2</sub> and its derivative are known to catalyze transfer hydrogenation of ketones with 2propanol.<sup>12</sup> To assess the impact of the central aryl group in the NCN-LH<sub>2</sub> pincer ligand on the catalysis, we compared the catalytic performance of the NCN pincer-type complexes 2 and the NNN analogue. The reactions were carried out at 50 °C for 15 h in 2-propanol containing 2 mol % of the catalyst and a base (Table 3). All of the protic pincer-type complexes we

Table 3. Transfer Hydrogenation of Acetophenone
Catalyzed by Protic Pincer-Type Ruthenium Complexes

0	ŅН	Ru cat KOBu <sup>t</sup> (1.3 equiv	/Ru) Ol	OH O	
Ph	$\prec$	Pr <sup>i</sup> OH, 50 °C	Ph	、 <sup>*</sup>	
S/C = 50		15 h			
entry		catalyst		yield, % <sup>b</sup>	
1	2a			81	
2	2b			49	
3	[R	uCl(NNN-LH)(PPh	$_{3})_{2}]$	81	
<sup><i>a</i></sup> Conditions: analyses.	[acetophe	mone] = $0.1$ M.	<sup>b</sup> Determined	by <sup>1</sup> H NMR	

examined promoted the reduction of acetophenone to give 1phenylethanol. The catalytic activity of the Bu<sup>t</sup>-NCN pincertype complex **2a** was found to be higher than that of **2b** without an alkyl substituent on the center of the pincer ligand (entries 1 and 2). It is to be noted that the reaction yield with **2a** remains comparable with those with the NNN pincer-type complex [RuCl(NNN-LH)(PPh<sub>3</sub>)<sub>2</sub>] (entry 3), which shows that the central donor of the protic pincer ligand on the transfer hydrogenation catalysis was not prominent.

#### CONCLUSION

We have synthesized protic NCN pincer-type complexes of ruthenium and iridium complexes through cyclometalation of 1,3-bis(pyrazol-3-yl)benzenes in an efficient manner. For the synthesis of the iridium complex, a bulky group at the 5position of the benzene ring was required to disfavor the C-H metalation at the undesired 4- and 6-positions. Comparison of the CO stretching frequencies of the carbonyl complexes 4 and the NNN analogues demonstrated the strong  $\sigma$ -donating ability of the NCN pincer-type ligand endowed by the monoanionic central aryl group. The M-Cl distances are also diagnostic of the  $\sigma$  donation of the pincer-type ligands. On the other hand, the NH groups in the pendant pyrazole maintain the Brønsted acidity, as indicated by the hydrogen bonds observed in the crystal structures. Although the effect of the increased  $\sigma$ donation of the NCN ligand to the catalysis is currently not evident, these insights will be beneficial for future development of the catalytic application of the protic pincer-type complexes.

# EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under an atmosphere of argon using standard Schlenk techniques unless otherwise specified. Solvents were dried by refluxing over sodium benzophenone ketyl (THF, toluene, diethyl ether, 1,4-dioxane, npentane, and *n*-hexane),  $P_2O_5$  (dichloromethane), and Mg(OMe)<sub>2</sub> (methanol) and distilled before use. DMF and ethanol (dehydrated) were purchased from Kanto Chemical and used as received. 2-Methoxyethanol was degassed by argon bubbling before use. Dichloromethane- $d_2$  and methanol- $d_4$  were dried over P<sub>2</sub>O<sub>5</sub> and CaH<sub>2</sub>, respectively, and subjected to trap-to-trap distillation and three subsequent freeze-pump-thaw cycles. Dimethyl sulfoxide- $d_6$  was degassed by three freeze-pump-thaw cycles and dried over MS4A. Compound 1b was prepared according to the literature procedure.<sup>1</sup> Other reagents were used as received. <sup>1</sup>H (399.78 MHz), <sup>13</sup>C{<sup>1</sup>H} (100.53  $\breve{M}Hz)\text{, and }^{31}P\{^{1}H\}$  (161.83 MHz) NMR spectra were obtained on a JEOL JNM-ECX-400 spectrometer. <sup>1</sup>H NMR shifts are relative to the signal of the residual CHCl<sub>3</sub> ( $\delta$  7.26), CHDCl<sub>2</sub> ( $\delta$  5.32), and DMSO- $d_6$  ( $\delta_H$  2.50), while  ${}^{13}C{}^{1}H$  and  ${}^{31}P{}^{1}H$  NMR shifts are referenced to CDCl<sub>3</sub> ( $\delta$  77.0) or CD<sub>2</sub>Cl<sub>2</sub> ( $\delta$  53.5) and phosphoric acid  $(\delta 0.0)$ , respectively. Infrared spectra were recorded on a JASCO FT/

IR-6100 spectrometer. ESI-MS spectra were obtained on a JEOL JMS-T100LC spectrometer with a positive ionization mode. Elemental analyses were performed on a PerkinElmer 2400II CHN analyzer.

**Synthesis of Diethyl 5-***tert***-Butylisophthalate (8).** The title compound was prepared according to a procedure modified from that described in the literature.<sup>27</sup> A mixture of 5-*tert*-butylisophthalic acid (10.3 g, 46.5 mmol) and concentrated  $H_2SO_4$  (2 mL) in ethanol (100 mL) was allowed to reflux for 6 h. Evaporation of the solvent under reduced pressure, the remaining materials were dissolved in dichloromethane (60 mL), and neutralized by saturated sodium bicarbonate solution. The organic layer was separated, washed with water (50 mL) and brine (50 mL), and dried over  $Na_2SO_4$ . Removal of the filtrate afforded 8 as a white solid (11.0 g, 39.5 mmol, 85%), which was used for the subsequent reaction without further purification.

Synthesis of 5-tert-Butyl-1,3-bis(5-tert-butylpyrazol-3-yl)benzene (1a). To a suspension of NaH (60 wt % in mineral oil, 1.89 g, 47.3 mmol) in THF (20 mL) was added 3,3-dimethyl-2butanone (5.50 mL, 44.5 mmol). The mixture was stirred for 20 min at room temperature and then heated to reflux. To the boiling mixture was added 8 (5.62 g, 20.2 mmol) in THF (20 mL) over the course of 25 min, and the mixture was allowed to reflux for an additional 30 min. After cooling, the mixture was treated with a 1 M HCl solution until pH 7 and extracted with diethyl ether (15 mL  $\times$  4). The combined organic layer was washed with brine (30 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent under reduced pressure afforded 5-tertbutyl-1,3-bis(1,3-dioxo-4,4-dimethylpentyl)benzene as a yellow oil (8.41 g). To a boiling solution of the crude diketone in ethanol (70 mL) in an open flask was added hydrazine monohydrate (6.3 mL, 130 mmol) over the course of 10 min. The mixture was allowed to reflux for an additional 4 h. After removal of the solvent in vacuo, the residue was dissolved in chloroform (60 mL), washed with brine  $(30 \text{ mL} \times 3)$ , and dried over Na2SO4. After evaporation of the solvent under reduced pressure, the resultant yellow solid was dissolved in warm dichloromethane (100 mL). Keeping the solution at  $-30\ ^\circ C$  yielded 1a as a white powder (0.934 g, 2.47 mmol, 12% over two steps).  $^{1}H$ NMR (CDCl<sub>3</sub>):  $\delta$  1.39 (s, 18H, Bu<sup>t</sup>), 1.40 (s, 9H, Bu<sup>t</sup>), 6.45 (s, 2H, pyrazole CH), 7.74 (br s, 2H, 4- and 6-CH), 7.87 (br s, 1H, 2-CH), 9.96 (br s, 2H, NH).  $^{13}C{^1H}$  NMR (CDCl<sub>3</sub>, 323 K):  $\delta$  30.4  $(pyrazole-C(CH_3)_3), 31.3 (phenyl-C(CH_3)_3), 34.8 (phenyl-C(CH_3)_3),$ 99.2 (pyrazole 4-CH), 120.8 (2-CH), 122.4 (4- and 6-CH), 132.9, 150.1, 152.0, 156.7. The tert-butyl quaternary carbon signal on the pyrazole arm is overlapped with the signal at  $\delta$  31.3, which was confirmed by HMQC and HMBC experiments. Anal. Calcd for C24H34N4: C, 76.15; H, 9.05; N, 14.80. Found: C, 76.01; H, 9.23; N, 14.85.

Synthesis of [RuCl(Bu<sup>t</sup>-NCN-LH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]·(toluene) (2a·(tol**uene)).** A mixture of  $[RuCl(OAc)(PPh_3)_3]$  (199.0 mg, 0.203 mmol)<sup>2</sup> and 1a (78.4 mg, 0.207 mol) in toluene (10 mL) was stirred for 15 h at 100 °C. The mixture was filtered, and the filtrate was evaporated to dryness. The residue was washed with diethyl ether  $(10 \text{ mL} \times 3)$  and dried in vacuo. The remaining solid was extracted with toluene (10 mL). Slow addition of hexane (40 mL) to the extract afforded 2a-(toluene) as yellowish green crystals (69.9 mg, 0.0618 mmol, 31%). The presence of the solvated toluene was confirmed by <sup>1</sup>H and  ${}^{13}C{\hat{H}}$  NMR.  ${}^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.11 (s, 18H, Bu<sup>t</sup>), 1.41 (s, 9H, Bu<sup>t</sup>), 6.00 (d, 2H,  ${}^{4}J_{HH}$  = 2.2 Hz, pyrazole CH), 6.97 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 7.02-7.20 (m, 30H, PPh<sub>3</sub>), 9.53 (br s, 2H, NH). <sup>13</sup>C{<sup>1</sup>H} NMR  $(CD_2Cl_2)$ :  $\delta$  30.0, 31.0, 32.3, 34.4, 96.4, 116.4, 127.0 (t,  $J_{CP}$  = 3.8 Hz,  $PPh_3$ ), 128.2 ( $PPh_3$ ), 133.7 (t,  $J_{CP} = 5.3$  Hz,  $PPh_3$ ), 134.9 (t,  $J_{CP} = 17.8$ Hz, PPh<sub>3</sub>), 140.8, 154.0, 161.4, 198.5 (br, RuC). The two carbon signals on the phenyl ligand are overlapped at 116.4 ppm, which was confirmed by HMQC and HMBC experiments.  ${}^{31}P{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  33.9 (s, PPh<sub>3</sub>). Anal. Calcd for C<sub>67</sub>H<sub>71</sub>ClN<sub>4</sub>P<sub>2</sub>Ru: C, 71.16; H, 6.33; N, 4.95. Found: C, 70.86; H, 6.60; N, 4.96. Single crystals suitable for X-ray analysis were obtained by recrystallization from THF-hexane.

Synthesis of [RuCl(H-NCN-LH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (2b). This compound was synthesized from 1b by a procedure similar to that used for 2a. Yield: 34%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.10 (s, 18H, Bu<sup>t</sup>), 5.96 (d, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 2H, pyrazole CH), 6.69 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 1H, *p*-C<sub>6</sub>H), 6.82 (d,

 ${}^{3}J_{\text{HH}} = 7.3 \text{ Hz}, 2H, m-C_{6}\text{H}), 7.06-7.18 \text{ (m, 30H, PPh_3)}, 9.53 \text{ (br s, 2H, NH)}. {}^{13}\text{C}{}^{1}\text{H} \text{ NMR (CD}_{2}\text{Cl}_{2}): \delta 30.0 (C(CH_{3})_{3}), 31.0 (C(CH_{3})_{3}), 96.6 (pyrazole 4-CH), 117.0, 118.8, 127.1 (t, <math>J_{\text{CP}} = 3.8 \text{ Hz}, \text{PPh}_{3}), 128.3 (PPh_{3}), 133.7 (t, <math>J_{\text{CP}} = 5.3 \text{ Hz}, \text{PPh}_{3}), 134.7 (t, <math>J_{\text{CP}} = 17.8 \text{ Hz}, \text{PPh}_{3}), 138.8, 154.1, 161.1, 203.6 (t, <math>J_{\text{CP}} = 8.2 \text{ Hz}, \text{RuC}).$  ${}^{31}\text{P}{}^{1}\text{H} \text{ NMR (CD}_{2}\text{Cl}_{2}): \delta 34.0 (s, \text{PPh}_{3}). \text{ Anal. Calcd for C}_{56}\text{H}_{55}\text{ClN}_{4}\text{P}_{2}\text{Ru}: C, 68.46; \text{H}, 5.64; \text{N}, 5.70. \text{ Found: C, 68.85; H, 5.76; N, 5.61. Single crystals suitable for X-ray analysis were obtained by recrystallization from THF-hexane.}$ 

Synthesis of [Ru(Bu<sup>t</sup>-NCN-LH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>(CO)]Cl (4a). To a solution of 2a (toluene) (117.4 mg, 0.1038 mmol) in toluene (8 mL) was introduced CO (1 atm) by freeze-pump-thaw cycles (three times). The mixture was stirred for 14 h at room temperature. The cream yellow precipitate that formed was filtered off and dried in vacuo. Subsequent recrystallization from dichloromethane-hexane (3 mL/18 mL) afforded 4a as cream yellow crystals (73.4 mg, 0.0688 mmol, 66%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.21 (s, 18H, Bu<sup>t</sup>), 1.42 (s, 9H, Bu<sup>t</sup>), 5.67 (d,  ${}^{4}J_{HH}$  = 1.8 Hz, 2H, pyrazole CH), 6.91 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 7.03–7.24 (m, 30H, PPh<sub>3</sub>), 11.99 (br s, 2H, NH).  ${}^{13}C{}^{1H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 29.9 (pyrazole-C(CH<sub>3</sub>)<sub>3</sub>), 32.1 (phenyl-C(CH<sub>3</sub>)<sub>3</sub>), 31.4 (pyrazole-C(CH<sub>3</sub>)<sub>3</sub>), 34.7 (phenyl-C(CH<sub>3</sub>)<sub>3</sub>), 97.2 (pyrazole CH), 118.0 (phenyl CH), 128.0 (t,  $J_{CP}$  = 4.8 Hz, PPh<sub>3</sub>), 129.2 (PPh<sub>3</sub>), 131.9 (t,  $J_{CP} = 21.6$  Hz, PPh<sub>3</sub>), 133.7 (t,  $J_{CP} = 5.3$  Hz, PPh<sub>3</sub>), 138.2, 146.9, 158.2, 161.7, 192.8 (t,  ${}^{2}J_{CP}$  = 11.1 Hz, RuC), 201.8 (t,  ${}^{2}J_{CP}$  = 12.0 Hz, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  37.3 (s, PPh<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu}_{max}$  $(cm^{-1})$  1960 (C=O). Anal. Calcd for  $C_{61}H_{63}ClN_4OP_2Ru$ : C, 68.69; H, 5.95; N, 5.25. Found: C, 68.34; H, 6.13; N, 5.26. Single crystals suitable for X-ray analysis were obtained by recrystallization from ethanol-pentane.

**Synthesis of [Ru(H-NCN-LH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>(CO)]Cl (4b·H<sub>2</sub>O).** This compound was synthesized from 2b by a procedure similar to that used for 4a. Recrystallization from wet dichlomethane-methanol-diethyl ether afforded 4b·H<sub>2</sub>O in 51% yield. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.18 (s, 18H, Bu<sup>1</sup>), 5.65 (s, 2H, pyrazole CH), 6.81 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz, 2H, *m*·C<sub>6</sub>H), 6.98 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, *p*-C<sub>6</sub>H), 7.02-7.24 (m, 30H, PPh<sub>3</sub>), 11.69 (br s, 2H, NH). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>-CD<sub>3</sub>OD = 1:1 v/v): δ 29.8 (C(CH<sub>3</sub>)<sub>3</sub>), 31.3 (C(CH<sub>3</sub>)<sub>3</sub>), 98.3 (pyrazole CH), 121.2, 123.8, 127.9 (t, *J*<sub>CP</sub> = 3.8 Hz, PPh<sub>3</sub>), 129.7 (PPh<sub>3</sub>), 131.6 (t, *J*<sub>CP</sub> = 21.6 Hz, PPh<sub>3</sub>), 133.7 (t, *J*<sub>CP</sub> = 5.3 Hz, PPh<sub>3</sub>), 139.6, 158.4, 161.9, 195.4 (t, <sup>2</sup>*J*<sub>CP</sub> = 11.1 Hz, RuC), 202.4 (t, <sup>2</sup>*J*<sub>CP</sub> = 11.5 Hz, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 37.2 (s, PPh<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu}_{max}$  (cm<sup>-1</sup>) 1963 (C≡O). Anal. Calcd for C<sub>57</sub>H<sub>57</sub>ClN<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Ru: C, 66.56; H, 5.59; N, 5.45. Found: C, 66.82 H, 5.89; N, 5.55.

Synthesis of [IrCl(Bu<sup>t</sup>-NCN-LH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]Cl (5). A mixture of IrCl<sub>3</sub>·xH<sub>2</sub>O (Ir; 52.12%, 179.5 mg, 0.487 mmol) and 1a (187.4 mg, 0.495 mmol) in degassed 2-methoxyethanol (20 mL) was allowed to reflux for 6 h. After evaporation of the solvent under reduced pressure, triphenylphosphine (1.029 g, 3.92 mmol) and 1,4-dioxane (20 mL) were added to the remaining solid, and the reaction mixture was allowed to reflux for 13 h. After removal of the solvent in vacuo, subsequent recrystallization from dichloromethane-diethyl ether (30 mL/50 mL) afforded 5 as pale yellow crystals (305.9 mg, 0.2625 mmol, 54%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.20 (s, 18H, Bu<sup>t</sup>), 1.44 (s, 9H, Bu<sup>t</sup>), 5.79 (d,  ${}^{4}J_{HH}$  = 2.2 Hz, 2H, pyrazole CH), 6.91 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 7.16–7.28 (m, 30H, PPh<sub>3</sub>), 12.14 (br s, 2H, NH).  $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$  NMR  $(CD_2Cl_2)$ :  $\delta$  29.8, 31.7, 32.0, 34.8, 98.2, 118.9, 128.2 (t,  $J_{CP}$  = 4.8 Hz, PPh<sub>3</sub>), 128.3 (t, *J*<sub>CP</sub> = 26.8 Hz, PPh<sub>3</sub>), 129.9 (PPh<sub>3</sub>), 134.2 (t, *J*<sub>CP</sub> = 5.3 Hz, PPh<sub>3</sub>), 134.7, 146.8, 156.6 (t,  ${}^{2}J_{CP}$  = 5.8 Hz, IrC), 157.9, 161.1.  $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –10.0 (s, PPh<sub>3</sub>). Anal. Calcd for C60H63Cl2N4P2Ir: C, 61.84; H, 5.45; N, 4.81. Found: C, 61.85; H, 5.54; N, 4.73. Single crystals of the tetraphenylborate salt 6 for X-ray analysis were obtained by anion exchange of 5 with excess NaBPh4 and recrystallization from dichloromethane-diethyl ether. Data for 6 are as follows. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.12 (s, 18H, Bu<sup>t</sup>), 1.38 (s, 9H, Bu<sup>t</sup>), 6.16 (d,  ${}^{4}J_{HH}$  = 2.1 Hz, 2H, pyrazole CH), 6.85–6.89, 7.00–7.37 (m, 50H, PPh3 and BPh4), 6.98 (s, 2H, m-CH), 9.54 (br s, 2H, NH). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –13.3 (s, PPh<sub>3</sub>).

Synthesis of  $[IrCl_3(NNN-LH_2)]$ ·2DMF (7·2DMF). To a boiling solution of  $IrCl_3$ · $xH_2O$  (Ir 52.12%, 218.3 mg, 0.592 mmol) in ethanol

(25 mL) was added dropwise a solution of 2,6-bis(5-tert-butyl-1H-pyrazol-3-yl)pyridine (193.4 mg, 0.598 mmol)<sup>8</sup> in ethanol (45 mL), and the mixture was allowed to reflux for 3 h in the dark. After the solution was cooled to room temperature, the reaction mixture was filtered. After evaporation of the filtrate in vacuo, the residue was recrystallized from DMF-diethyl ether (25 mL/150 mL). The orange microcrystalline solid that formed was filtered off, washed with diethyl ether (10 mL × 2) and hexane (10 mL), and dried in vacuo (274.7 mg, 0.358 mmol, 60%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  1.43 (s, 18H, Bu<sup>t</sup>), 7.14 (d, <sup>4</sup>J<sub>HH</sub> = 1.9 Hz, 2H, pyrazole CH), 7.97–8.11 (m, 3H, pyridine CH), 14.33 (d, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, 2H, NH). Anal. Calcd for C<sub>25</sub>H<sub>39</sub>Cl<sub>3</sub>N<sub>7</sub>O<sub>2</sub>Ir: C, 39.09; H, 5.12; N, 12.76. Found: C, 38.64; H, 5.28; N, 12.54.

**Catalytic Transfer Hydrogenation of Acetophenone.** A solution of potassium *tert*-butoxide (0.5 M, 1.3 equiv/Ru) in THF was added to a mixture of ruthenium complex (2 mol %) and acetophenone in 2-propanol ([acetophenone] = 0.1 M). The mixture was stirred for 15 h at 50 °C. The yield of 1-phenylethanol was determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Crystallography. Single crystals suitable for X-ray analyses were mounted on a fiber loop. Diffraction experiments were performed on a Rigaku Saturn CCD area detector with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$ = 0.71070 Å). Intensity data were corrected for Lorentz-polarization effects and for absorption. Details of crystal and data collection parameters are shown in the Supporting Information. Structure solution and refinements were carried out by using the CrystalStructure program package.<sup>29</sup> The heavy-atom positions were determined by a direct methods program (SIR92<sup>30</sup>), and the remaining non-hydrogen atoms were found by subsequent Fourier syntheses. The non-hydrogen atoms other than those mentioned below were refined anisotropically by full-matrix least-squares techniques based on  $F^2$ . Some tert-butyl groups in 2a 0.5(hexane), 2b.0.5THF, 4a.2EtOH, and 6.2Et<sub>2</sub>O were placed at two disordered positions and isotropically refined; for 2a.0.5(hexane) and 4a.2EtOH, the isotropic thermal parameters were fixed and the structures were refined with restraint geometries. The solvating hexane in 2a-0.5(hexane), THF in 2b.0.5THF, and one of the two diethyl ether molecules in  $6.2Et_2O$  were partially disordered and the non-hydrogen atoms therein were included in the refinements with fixed isotropic thermal parameters and restraint geometries. The hydrogen atoms in these disordered moieties were not included in the refinements. The OH hydrogen atoms in the solvated ethanol molecules in 4a·2EtOH were found in the difference Fourier map and refined with a riding model. The rest of the hydrogen atoms were placed at calculated positions and included in the refinements with a riding model.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00065.

<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra (PDF) Crystallographic data (CIF)

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# Notes

The authors declare no competing financial interest.

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