## Homogeneous Catalysis

## Hydrogen-Bonding Pincer Complexes with Two Protic N-Heterocyclic Carbenes from Direct Metalation of a 1,8-Bis(imidazol-1-yl)carbazole by Platinum, Palladium, and Nickel

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**Abstract:** Pincer protic N-heterocyclic carbene (PNHC) complexes were synthesized by direct metalation, the formation of a metal carbon bond from an unfunctionalized C–H bond in a single synthetic step. Significantly, direct metalation succeeded even for a first-row metal, nickel. The chloride complexes were isolated and then converted to the acetate, triflate, or in the platinum case, a hydride analogue. Crystal structures and <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR data, as well as IR spectra, document the effects of intramolecular hydrogen bonding and the planar but flexible pincer framework. Anti-Markovnikov addition of O–H bonds to alkynes, including catalyzed alkyne hydration, were demonstrated on the Pt triflate analog.

N-Heterocyclic carbenes (NHC) have become a prolific area of research over the last two decades.<sup>[1]</sup> NHC ligands are usually altered by changing the alkyl or aryl groups on each nitrogen, for either steric or electronic reasons. However, in the much more rare case when there is no R group, the NH moiety introduces a possible reactive site, in a protic NHC (PNHC) complex. Synthesis of PNHC complexes is still a challenge, as was insightfully outlined in informative reviews.<sup>[2]</sup> The main routes to imidazolidene and imidazolylidene PNHC complexes have been: 1) forming the PNHC heterocycle in two or three steps, including isocyanide coordination to metal, followed by addition of an amine;<sup>[3]</sup> 2) using a pre-existing heterocycle with a halide substituent at C-2, performing oxidative addition to a metal, followed by N-protonation;<sup>[4]</sup> and 3) using a pre-existing heterocycle without a substituent at C-2, installing a protecting group, metallating, and then removing the protecting

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group;<sup>[5]</sup> 4) a fourth method that also uses a pre-existing heterocycle without a substituent at C-2, but generates a PNHC in a single synthetic step.<sup>[6]</sup> The clear operational simplicity of (4), which we would like to term "direct metalation" (without implying simplicity of mechanism) motivates us to extend the scope of the method, which, to the best of our knowledge, until the work reported herein, has not been achieved with a first-row transition metal.

Most examples of direct metalation on imidazoles use a second ligand to help direct and anchor the metal.<sup>[6]</sup> We were attracted to pincer systems of type D (Figure 1) because



Figure 1. Known poly(PNHC) complexes A and B, carbazole-based pincer  $\mathsf{C},$  and bis-PNHC pincer complexes  $\mathsf{D}.$ 

of the possibility of two PNHC ligands in close proximity to a bound substrate (L'). Meier et al. used a Rh-PNHC complex to hydrogenate 1-dodecene and an alkene containing an ester, showing approximately threefold faster hydrogenation of the latter. On the basis of hydrogen-bond donation to a urea derivative, the difference in catalysis was suggested to arise from PNHC-substrate interaction.<sup>[7]</sup> We have reported hydrogen transfer and bond activation chemistry on mono-PNHC complexes and their conjugate bases, imidazol-2-yl species.<sup>[8]</sup> Because of the known stability and versatile reactivity of pincers featuring phosphines and normal NHC ligands,<sup>[9]</sup> we thought that **D** would be of great interest, especially if direct metalation made **D** in only one step. Hahn and co-workers made remarkable tetrakis-PNHC complexes of type A, and related Fe species, using multistep method (1) summarized in the first paragraph.<sup>[2b, 3h]</sup> Coordinative saturation in **A** and related spe-

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cies may prevent further chemistry at the metal, although alkylation of the nitrogens was possible. Similarly, although Flowers and Cossairt et al. very recently showed the power of phosphine-facilitated direct metalation to make two PNHCs in one step,<sup>[6g]</sup> their product was coordinatively saturated. Kunz et al. reported intriguing species **B**, made using a three-step protecting-group strategy, but without an indication of its chemistry, other than aqueous acid stability.<sup>[5d]</sup>

For our purpose of wanting to create a stable pincer PNHC framework with one site available for chemistry and catalysis, the Kunz ligand framework of **C1–7** was very attractive, because of indications from X-ray crystal structure of favorable accommodation of a metal in the binding pocket.<sup>[10]</sup> However, the formidable challenge of synthesizing PNHC complexes demands different synthetic routes than normal NHC analogs. We envisioned **1** (Scheme 1) as starting point, with *tert*-butyl sub-



**Scheme 1.** (a) Preparation of bis PNHC complexes. (b) AgOAc, acetone, rt, 12–15 h; (c) NaBH<sub>4</sub>, THF, 70 °C, 20 h; (d) AgOTf, THF, rt, 40 min (**5 a**) or 7.5 h (**5 c**); AgOTf, acetone, rt, 1 h (**5 c**); (e) CO or  $C_2H_4$  (1 atm), [D<sub>6</sub>]benzene; **6 a**-**c** were characterized in situ.

stituents on imidazoles to disfavor metal N coordination. Herein, we report the successful synthesis of Pd and Pt bis(PNHC) complexes, and even Ni analogs, all using direct metalation. Moreover, we show effects of PNHC hydrogen bonding, as well as preliminary studies of reactivity, including *anti*-Markovnikov alkyne functionalization and catalysis of hydration to aldehyde. The air stability of the pincer complexes can be an attractive feature for further applications in catalysis.

The synthesis of **1** in multigram quantities was accomplished in 37% overall yield in three steps from carbazole. The *tert*-butylation method of Hou and co-workers<sup>[11a]</sup> gave 3,6-di-*tert*butyl-carbazole, which was subjected to electrophilic iodination, described by Inoue and Nakada<sup>[11b]</sup> on a similar compound, utilizing PhCH<sub>2</sub>NEt<sub>3</sub><sup>+</sup> ICl<sub>2</sub><sup>-,[11c]</sup> giving 1,8-di-iodo-3,6-di*tert*-butyl-carbazole. Copper-catalyzed coupling described by Kunz,<sup>[10]</sup> but using 4-*tert*-butylimidazole gave **1**.<sup>[11d]</sup>

For the first application of 1, metals of square planar geometry were targeted so that the fourth coordination site would certainly be in close proximity to the NH wingtips. Although to the best of our knowledge, none of the Group 10 metals have successfully engaged in PNHC formation by direct metalation, Pd<sup>II</sup> and Pt<sup>II</sup> were tested first, because of their extensive C-H metalation literature.<sup>[12]</sup> The Pt analogue 2c was formed by using Cl<sub>2</sub>Pt(COD) at 100 °C for six days (Scheme 1). After experimentation, it was found that the best way to make 2b was to use [Pd(OAc)<sub>2</sub>] to enable metalation, followed by treatment with aqueous NaCl. More remarkably, the Ni analogue 2a could be made in similar way, at higher temperature. Carboxylate-assisted C-H bond activation is widespread, in which various proton-shuttling roles are possible.<sup>[13]</sup> To ease the purification of metalation products, the crude samples of 3b and c were converted cleanly to the chloride species 2a and b, which were more readily purified by silica-gel column chromatography.

The chloride complexes **2a–c** were converted to the acetate or triflate analogues by using the respective silver salts (Scheme 1). Bubbling CO through a solution of the triflate complexes **5a–c** in benzene gave **6a–c**. Removal of solvent by oil-pump vacuum from solutions of **6a** and **b** led to CO loss and recovery of **5a** and **b**, suggesting that the M–CO bond is weaker in the Ni and Pd cases, than for Pt. Bubbling ethene through solutions of **5a–c** in benzene gave only Pt analogue **7c** with no reaction in the Ni and Pd cases. The Pt hydride species **4c** could be crystallized, whereas attempts at isolating the Pd and Ni hydrides were unsuccessful.

To give insight into structure and hydrogen bonding, Table 1 compares the coordination sphere of seven PNHC complexes prepared in this study<sup>[14]</sup> to those for **C1–C3**, aprotic analogs of Kunz. With the exception of **6c**, discussed below, the structures of the new PNHC pincers are all close to ideal square planar geometry, with C-M-C and N-M-X angles near 180°. The metal bond lengths in the Pd and Pt species (e.g., **2b** and **c**) are quite similar, as expected for second- and third-row congeners, whereas the first-row Ni complex, **3a**, showed shorter bonds than Pd analogue **3b**.

The role of hydrogen bonding involving the PNHC ligands was determined by using a combination of X-ray crystallography, NMR, and IR spectroscopies (with the latter confirming solid-state studies, see below). Complexes with acetato and triflato ligands (3, 5) exhibit intramolecular hydrogen bonding, whereas intermolecular interaction was seen in 6. The structure of 3b (Figure 2a) clearly shows the acetato ligand and one NH interacting, whereas the structure of 5b (Figure 2b) shows the triflato ligand reaching both NH moieties. In both cases, the planarity of the pincer ligand is essentially maintained, with some flexibility to accommodate the asymmetry introduced by the tetrahedral sulfur of the triflate in 5b. The planarity of the pincer framework can be gauged by noting the dihedral angle between the bond between PNHC carbene C and protic N atoms, and the bond between metal and coordinated atom of X or L, which in the case of **3 b** is 3.2 and 4.7° for the two independent molecules in the unit cell, and in the case of 5b is slightly larger (9.5, 11.1°). Greater distortion and stronger hy-

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Table 1. Key bond lengths [Å] and angles [°] from the crystal structuresof new PNHC complexes and aprotic complexes C1-C3.

Complex	C–M	N-M	X—M	C-M-C	N-M-X			
C1 <sup>1[10a]</sup>	2.060(6),	2.028(4)	1.814 (6)	166.68(19)	161.0(2)			
	2.047(5)							
2b	2.006(4),	1.961(3)	2.3424(12)	175.43(17)	178.09(10)			
	1.998(4)							
C3 <sup>[10b]</sup>	2.037(4),	1.991(3)	2.3477(13)	164.8(2)	160.80(12)			
	2.037(5)							
2 c	2.007(2),	1.9627(19)	2.3451(6)	176.29(9)	179.85(6)			
	2.014(2)							
3 a <sup>[a]</sup>	1.8902(16),	1.8259(13)	1.9067(11)	175.95(7)	174.84(5)			
	1.8920(16)							
3 b <sup>(b)</sup>	2.003(4) <sup>[c]</sup>	1.957(5)	2.035(5)	177.7(2)	180.0 <sup>[c]</sup>			
	2.014(5)	1.947(5)	2.052(6)	177.1(3)	180.0 <sup>[c]</sup>			
4 c	2.007(3),	2.027(2)	1.46(3)	177.07(10)	178.9(12)			
	2.012(3)							
C2 <sup>[10b]</sup>	2.022(6)	2.010(5)	1.590 <sup>[d]</sup>	178.7(4)	180.0			
5 b <sup>(b)</sup>	2.017(6),	1.952(7),	2.111(7),	178.2(3),	172.8(2),			
	2.006(6)	1.954(10)	2.11(3)	179.1(4)	166.0(8)			
	2.007(6) <sup>[e]</sup>		2.097(10) <sup>[e]</sup>		170.0(3) <sup>[e]</sup>			
6c	2.017(3),	1.973(3)	1.864(4)	164.41(13)	167.63(13)			
	2.020(3)							
[a] One HOAc solvate molecule donates a hydrogen bond to the bound OAc; no intramolecular NH–OAc interaction (Figure S31 in the Supporting								

OAc; no intramolecular NH–OAc interaction (Figure S31 in the Supporting Information). [b] Two independent molecules in unit cell, values for each given on separate rows. [c] Crystal structure refinement determined N-M-X angle to be 180° with no uncertainty and C–M distances equal; –OAc atoms are refined at 50% occupancy. [d] From DFT. [e] OTf refined at 50% occupancy.

drogen bonding was seen in the case of  $\mathbf{6c}$  (Figure 2c), because the CO ligand now occupies the site between the two

PNHC pincer arms, and the now-ionized triflate enters into stronger hydrogen bonding, as was evidenced by shorter NH– O contacts (and IR data, see below). The relative orientation of the CO ligand and the two PNHC ligands can be defined by the torsion angles (H)N-C-Pt-C(O) = 34.7 and  $35.4^{\circ}$ ; compare for **C1**, (CH<sub>3</sub>)N-C-Rh-C(O) = 29.6 and  $41.6^{\circ}$ ). The interligand angles across the metal for **6c** (164.4, 167.6°) also reflect distortions, which can be significant for reactivity and catalysis, because they show the ability of the pincer backbone to accommodate changes in the steric and hydrogen bonding demands of the ligand in the site between the two pincer arms.

Solution-phase studies on PNHC hydrogen bonding ability were carried out to verify interactions seen in the solid state. All of the complexes described herein were soluble in [D<sub>6</sub>]benzene. A combination of NMR techniques was used to assign <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR chemical shifts. The NH <sup>1</sup>H NMR shift showed the greatest change (Table S1 in the Supporting Information); after converting the chloride compounds (2a-c) to the acetates (3a-c) the NH peak shifted downfield by 1.56 to 2.71 ppm, evidence of intramolecular hydrogen bonding. To study bonding further, <sup>15</sup>N NMR chemical shifts were examined (Table 2).<sup>[15a]</sup> For the PNHC nitrogen incapable of hydrogen bonding (N2),  $\delta_{\rm N}$  hardly changes for a given metal as the X ligand changed. In contrast,  $\delta_{\rm N}$  for the NH nitrogen (N1) is sensitive to X, in which the downfield shift from X = CI to X = OAcamounts to 2.7 for nickel, 7.6 for palladium, and 10.3 ppm for platinum (N1 entries for 3a-c). A similar progression in downfield shifts relative to X = CI from 6.3 to 14.5 is seen for X = CO(N1 entries for **6a**–**c**). Also notable is the sensitivity of  $\delta_N$  for the carbazolyl nitrogen (N3) to the identity of X, being 17 to



32 ppm upfield for X=OAc and OTf compared with X=Cl, and 17.7 to 31.6 ppm downfield for X=CO. Changing the metal but keeping X constant,  $\delta_N$  for the carbene nitrogens shifts upfield in the order Ni, Pd, Pt,<sup>[15b]</sup> but for N3 the order is Pd, Ni, Pt.

IR spectra obtained in benzene further clarified the hydrogen bonding. The NH peaks for the chloride complexes **2** were relatively sharp between 3360-3380 cm<sup>-1</sup> (Table 3). In contrast,

Figure 2. X-ray diffraction structures: (a) 3 b, showing hydrogen bonding between the acetato ligand and one NH
wingtip; (b) 5 b, showing concurrent interaction of the triflato ligand and two NH wingtips. For the two independ-
ent molecules in the unit cell, H-bond networks exhibited $d(H-O) = 2.087$ to 2.676 Å; (c) <b>6 c</b> , showing bonding be-
tween the free triflate and both NH wingtips. For the two H bonds, $d(H-O) = 1.993(13)$ , $d(N-O) = 2.849(4)$ Å, $\bigstar$ (N-O) = 0.0000000000000000000000000000000000
H-Q) = 167(3)°, and $d$ (H–Q) = 2.055(16), $d$ (N–Q) = 2.873(4) Å, $X$ (N-H-Q) = 159(3)°.

	Table 2. "IN INVIK Chemical shirts [ppm].												
	M=Ni			M=Pd			M=Pt						
atom	2 a	3 a	5 a	бa	2 b	3 b	5 b	6 b	2 c	3 c	4 c	5 c	бc
N1 = NH of	-201.8	-199.1	-204.4	-195.5	-205.9	-198.3	-205.5	-196.8	-210.6	-200.3	-191.9	-207.1	-196.1
PNHC		(2.7)	(-2.6)	(6.3)		(7.6)	(0.4)	(9.1)		(10.3)	(18.7)	(3.5)	(14.5)
N2 = aprotic N	-192.8	-192.8	-191.8	-191.6	-194.5	-195.1	-193.8	-192.9	-197.9	-197.6	-196.2	-196.4	-195.8
of PNHC		(0.0)	(1.0)	(1.2)		(-0.6)	(0.7)	(1.6)		(0.3)	(1.7)	(1.5)	(2.1)
N3 = carbazolyl	-293.5	-310.7	-321.6	n.d.	-277.1	-295.6	-300.3	-259.4	-298.4	-324.6	n.d.	-330.5	-266.8
Ν		(-17.2)	(-28.1)			(-18.5)	(-23.2)	(17.7)		(-26.2)		(-32.1)	(31.6)

[a] Natural abundance material in  $[D_6]$  benzene, using  ${}^{1}H^{-15}N$  gradient heteronuclear multiple bond coherence (gHMBC) NMR technique. Differences between X = Cl in parentheses. n.d. = not detected.

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Table 3. Solution-phase IR data [cm <sup>-1</sup> ]. <sup>[a]</sup>								
Complex	М	X or L	$\tilde{\nu}$ (NH)	$\Delta$ from chloride $^{\rm [b]}$	$\tilde{\nu}(CO)$			
2a	Ni	Cl	3363.3 (s)	-				
3 a <sup>[c]</sup>		OAc	3403.9 (s) 2650 (vb)	40.6 713				
5a		OTf	3331.2 (b)	-32.1	2002.0 (-)			
6 a 2 b <sup>[c]</sup>	Pd	Cl	3190.6 (VD) 3373.7 (s)	-172.2	2092.8 (S)			
3 b <sup>[c]</sup>		OAc	3359.3 (s) 2668 (vb)	-14.4 -706				
5 b 6 b		OTf CO <sup>+</sup> OTf <sup>-</sup>	3320.5 (b) 3249.8 (b)	-53.2 -123.9	2120.6 (s)			
2 c 3 c <sup>[c]</sup>	Pt	Cl OAc	3383.5 (s) 3384.7 (s)	- 1.2				
5c 6c		OTf CO <sup>+</sup> OTf <sup>-</sup>	2690 (Vb) 3338.6 (b) 3206.8 (b)	695 44.9 176.7	2092.1 (s)			
[a] $C_6H_6$ solutions in a $CaF_2$ cell. s=sharp; b=broad; vb=very broad. See the Supporting Information for spectra. [b] Change in absorbance from that of corresponding chloride complex. [c] In [D <sub>6</sub> ]benzene.								

for the acetate complexes **3**, one very broad peak was centered around 2650 cm<sup>-1</sup> along with another sharp peak at similar frequency as in the chloride case. The new very broad peak is assigned to one NH donating a hydrogen bond to the OAc ligand, with the other NH unperturbed. For the bound triflate cases (**5**), a single slightly broadened NH peak is seen, shifted only approximately 30-50 cm<sup>-1</sup> lower, showing H bonding to both of the NHs. In the case when the complexes are ionized (**6**), the NH stretch is approximately 125-175 cm<sup>-1</sup> lower, consistent with triflate more strongly bonding to both NHs, as has been seen in the **6c** crystal structure. Finally, for **6**, the values for  $\hat{\nu}$ (CO) are similar and not that shifted from the value for free CO, consistent with minimal backbonding and observed reversible CO binding.

Preliminary studies of reactivity on **5**c are promising, showing CO or ethylene binding. As for reactivity with alkynes, **5**c was dissolved in a mixture of acetone/water, then 1-hexyne  $(20 \times 5c)$  was added. Heating at 70 °C gave a mixture of hexanal and 2-hexanone in approximately 4 to 1 ratio throughout the reaction.<sup>[16a]</sup> Yields of hexanal were 7, 63, and 79% after 1, 14, and 24 h at which point hexyne was consumed. Moreover, phenylacetylene is hydrated to the aldehyde, without the ketone. Reaction of **5**c with **8** was stoichiometric in CD<sub>2</sub>Cl<sub>2</sub>, giving cyclic carbene complex **8**c (Scheme 2). Dissolving **5**c in [D<sub>6</sub>]acetone and water gave a mixture of two complexes, in which the major one (2.5 to 1 ratio) shows a broad 2H singlet consistent with it being an aqua complex. To further study the



Scheme 2. Alkyne-derived complexes from pincer complex 5 c.

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formation of aldehyde products, <sup>13</sup>C-labeled alkyne **9** was added, leading to a new species identified by 2D NMR as acyl complex **9c** with a broadened resonance with Pt satellites at  $\delta = 251.5$  ppm (Figure S17 in the Supporting Information).<sup>[16b]</sup> Further work will be needed to define the role of the PNHC ligand in these transformations, which as we know for other bifunctional systems could be extraordinarily complex.<sup>[16c]</sup> Nonetheless, formation of **9c**, **8c**, and catalysis of aldehyde formation are all consistent with alkyne-to-vinylidene transformation at the pincer active site.<sup>[17]</sup>

In conclusion, using appropriate ligand design, bis-PNHC pincer complexes have been synthesized with two metalations of C–H bonds occurring in one synthetic step. Significantly, direct metalation succeeded even for the first-row nickel complex. Hydrogen bonding and structural changes of the resulting pincer complexes consistent with ligand flexibility have been characterized by X-ray diffraction, NMR, and IR data, and the species showed promising *anti*-Markovnikov selectivity in O–H additions to alkynes. Extension to other metals, reactivity, and study of the mechanism of metalation is in progress and results will be reported in due course.

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**Keywords:** alkynes · carbenes · homogeneous catalysis · hydrogen bonding

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