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Dihydroperimidine-Derived N-Heterocyclic Pincer Carbene Complexes via Double C−H Activation

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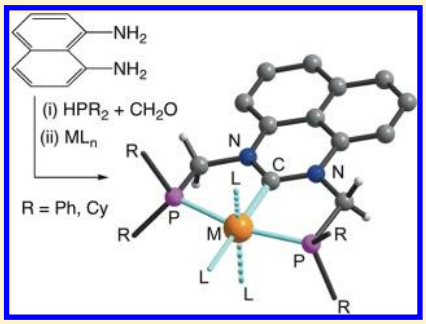
Supporting Information

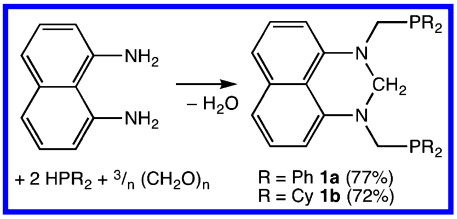
ABSTRACT: The reactions of 1,8-diaminonaphthalene with paraformaldehyde and secondary phosphines (HPR_2, R = Ph, Cy) directly afford *N*,*N*′-bis(phoshinomethyl)-dihydroperimidines $H_2C(NCH_2PR_2)_2C_{10}H_6$ (R = Ph (**1a**), Cy (**1b**)), the methylene group of which undergoes chelate-assisted double C−H activation with $[RhCl(PPh_3)_3]$ to afford dihydroperimidine-derived N-heterocyclic pincer carbene (*per*-NHC) complexes $[RhCl\{{=}C(NCH_2PR_2)_2C_{10}H_6\}]$ (R = Ph (**2a**), Cy (**2b**)). Insight into the mechanism of these C−H activation processes is provided by the reaction of **1b** with $[IrCl(CO)(PPh_3)_2]$ to provide the dihydroperimidinyl-hydrido complex $[IrHCl(CO)\{CH(NCH_2PR_2)_2C_{10}H_6\}]$ (**3b**), which in turn reacts with silver salts Ag[Y] to afford, via hydride abstraction and subsequent C−H activation, the *per*-NHC ligated salts $[IrHCl(CO)\{{=}C(NCH_2PR_2)_2C_{10}H_6\}]$ ([**4b**]Y, Y = PF_6, SbF_6, PO_2F_2).



N-heterocyclic carbene (NHC)[1] and pincer[2] ligands have in recent times provided fertile avenues for the design of numerous effective and robust metal catalysts. The high stability and modular variability offered by pincer systems has led to applications in an extensive range of fields, while strongly electron-donating NHC ligands have become well-established as supporting ligands in catalytic systems, emulating the donor properties of phosphines, but less prone to dissociation. It is therefore unsurprising that the inclusion of NHC donors within pincer systems has attracted an increasing level of interest, with a particular emphasis on their catalytic potential.[3] While the most popular NHC scaffolds remain those based on five-membered heterocyclic rings (imidazolinylidenes, dihydroimidazolinylidenes, etc.), Fehlhammer,[4] Richeson,[5] Özdemir,[6] Herrmann,[7] Dötz,[8] and Mashima[9] have each described dihydroperimidine-based NHC ligands (*per*-NHC) for which both experimental[5−9] and computationally derived data[10] indicate enhanced σ basicity. Though *per*-NHCs have been comparatively little studied, their catalytic potential has already been demonstrated,[6,9] as has their inclusion as *axial* donors within meridional pincer frameworks.[9] However, a pincer system incorporating a *per*-NHC as the central *equatorial* group has not been reported, despite the relaxed geometric constraints that should allow appended axial donors to more readily occupy *trans* sites with reduced metallabicycle strain. Herein we describe the first examples of such ligands, coordinated to rhodium(I) and iridium(III) centers, arising from the double geminal C−H bond activation of the methylene group of readily accessible neutral precursors.

NHC installation usually requires activation of a cationic azolium precursor using either a basic coligand (e.g., OMe, OAc), an external base, or the intermediacy of silver or mercury reagents.[1] Atom-efficient instances of carbene ligand installation via geminal double C−H bond activation have become increasingly frequent[11] but for NHC synthesis remain rare and, to date, have required a hydrogen acceptor.[12] With this in mind, we have devised a remarkably convenient one-pot, solvent-free synthesis of 2,3-dihydriperimidine *per*-NHC-H_2 pincer proligands $H_2C(NCH_2PR_2)_2C_{10}H_6$-1,8 (R = Ph (**1a**), Cy (**1b**)) from 1,8-diaminonaphthalene, paraformaldehyde, and secondary phosphines HPR_2 (Scheme 1). The ligands are obtained analytically pure in high yields after a single recrystallization.

Scheme 1. Synthesis of 2,3-Dihydroperimidine PCP Pincer Proligands



Both proligands were structurally characterized, and the results obtained for **1a** are summarized in Figure 1,[13] which suggest that the molecular geometry appears well disposed to subsequent chelate-assisted C−H activation of the methylenic unit upon reaction with appropriate metal centers. This was indeed found to be the case: both **1a** and **1b** were observed to undergo double dehydrogenation of the central methylene group upon direct reaction with $[RhCl(PPh_3)_3]$ to afford the *per*-NHC pincer complexes $[RhCl\{\kappa^3\text{-}P,C,P'{=}C(NCH_2PR_2)_2C_{10}H_6\}]$ (R = Ph (**2a**), Cy (**2b**); Scheme 2). These reactions proceed at ambient temperature to give the

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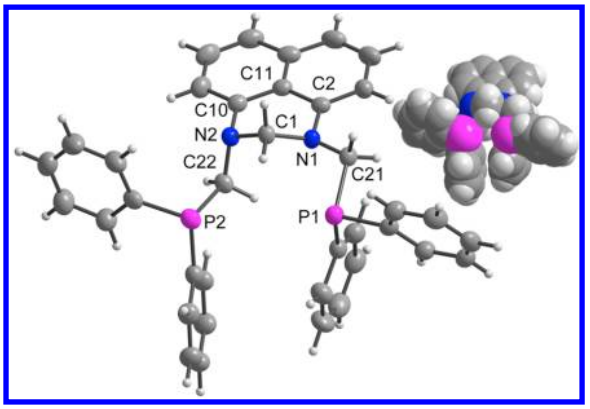
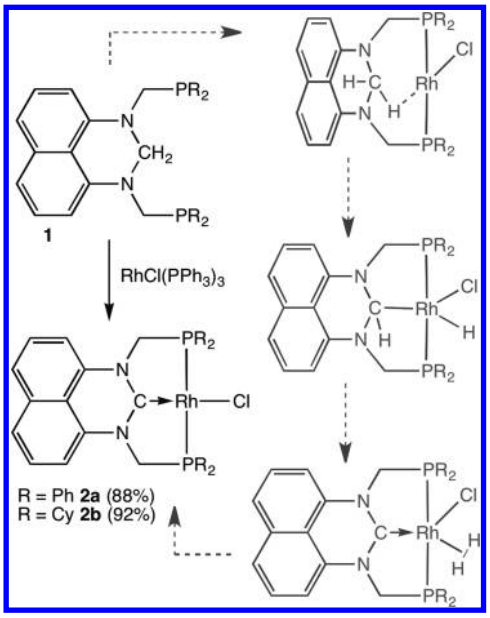


Figure 1. Molecular structure of **1a** (50% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): C1−N1 = 1.469(3), C1−N2 = 1.451(3), C2−N1 = 1.402(3), C10−N2 = 1.433(3); ∑(N1) = 350.1, ∑(N2) = 336.0.

Scheme 2. Synthesis of *per*-NHC Pincer Complexes via Double Geminal C−H Activation with Associated Mechanistic Conjecture (in Gray)



products in high isolated yields (**2a**, 88%; **2b**, 92%). The $^{31}P\{^{1}H\}$ NMR spectra of the reaction mixtures (C_6D_6) showed spectroscopically quantitative conversion to the final products, within 21 h (R = Ph) or 10 min (R = Cy), with the evolution of dihydrogen being confirmed by ^{1}H NMR spectroscopy.

The formulations of **2** are based on spectroscopic data and substantiated by a crystal structure determination of **2a** (Figure 2).[13] Notable among the spectroscopic data for **2b** is the ^{13}C carbene resonance (δ_C 206.7; cf. 200.4 ppm for [RhCl(cod){=C(NMe)$_2$C$_{10}$H$_6$}][7]). The molecular structure of **2a** (Figure 2) reveals a conventional d^8 square-planar geometry about rhodium, for which the primary distortion involves contraction of the P1−Rh1−P2 angle to 165.01(4)° to accommodate the geometric constraints of meridional pincer coordination. The coordination plane about rhodium is slightly rotated (19.8°) relative to that of the dihydriperimidine backbone, while the Rh1−C1 bond length of 1.948(4) Å falls within the range typical of the copious structural data available for NHC complexes of rhodium(1).[14] We may therefore surmise that

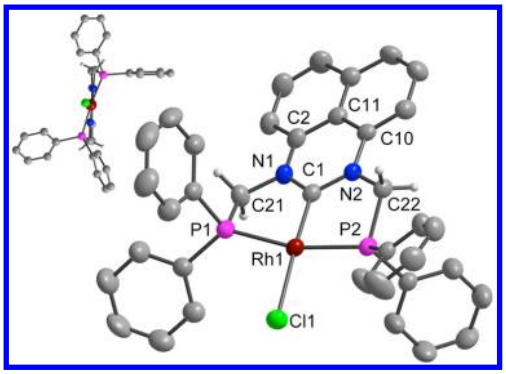


Figure 2. Molecular structure of **2a** (aryl hydrogen atoms omitted, 50% displacement ellipsoids), including a view along the coordination plane. Selected bond lengths (Å) and angles (deg): Rh1−Cl1 = 2.401(1), Rh1−P1 = 2.247(1), Rh1−P2 = 2.2545(1), Rh1−C1 = 1.948(4), N1−C1 = 1.388(4), N2−C1 = 1.372(5); P1−Rh1−P2 = 165.01(4), N1−C1−N2 = 114.3(3), N1−C1−Rh1 = 122.2(3), N2−C1−Rh1 = 123.4(2), ∑(N1) = 359.4, ∑(N2) = 359.6.

rhodium(I) sits comfortably within the *per*-NHC pincer embrace.

The facility of the reactions leading to **2**, without recourse to a sacrificial hydrogen acceptor, may be attributed to chelation assistance. While it might be argued from a Thorpe−Ingold perspective that steric factors play a role in the rapidity of the metallacyclization of **2b** with regard to **2a**, we are inclined to suspect that it is rather the potent σ basicity of the PCy_2 groups that facilitates C−H oxidative addition. A possible mechanism for how this chelate-assisted bond activation might proceed is suggested in Scheme 2,[15] in which a putative σ-2-perimidinyl complex plays a role, arising from the first C−H activation process. Subsequent loss of dihydrogen could then occur either via an oxidative addition/reductive elimination sequence or, perhaps less likely, via a concerted σ-CAM process.[16] It should be noted that, at this stage, we have no evidence that would indicate whether the first C−H activation precedes or follows coordination of the second phosphine donor (vide infra). The inclusion of a π-acidic coligand such as CO might be expected to retard such processes, while replacement of rhodium by iridium would be expected to decelerate the kinetics. Given that σ-2-perimidinyl ligands are as yet without precedent, we therefore investigated the reaction of **1b** with Vaska's complex [IrCl(CO)(PPh$_3$)$_2$] and were indeed able to isolate a model complex in support of the proposed mechanism. A remarkably facile reaction ensues which is complete within 2 h at room temperature to afford the complex [IrHCl(CO){κ^3-*P*,*C*,*P*′-CH(NCH$_2$PR$_2$)$_2$C$_{10}$H$_6$}] (**3b**) in 93% isolated yield. Although **3b** is a complex of iridium(III), infrared data (ν_{IrH}, ν_{CO} 2012, 1940 cm^{-1}) suggest a particularly π-basic metal center.[17] The hydrido ligand gives rise to a triplet resonance in the ^{1}H NMR spectrum (δ_H −17.9, $^{2}J_{PH}$ = 11 Hz). The spectrum also includes a singlet resonance (δ_H 5.75) which correlates with that at δ_C 87.7 ($^{1}H^{13}C$ HSQC), these being attributed to the methine of the perimindinyl heterocycle. The approximate C_s symmetry of **3b** (cf. C_{2v} for **2**) renders the PCH_2 protons diastereotopic, as reflected in the multiplicity of the associated ^{1}H resonances.[13]

The complex **3b** was structurally characterized, thereby confirming the novel coordination mode for σ-perimidinyl ligand.[13] As depicted in Figure 3, 4-coordination at C1 is also accompanied by a pyramidalization of the amino nitrogen centers N1 and N2 (angle sums 342.8, 343.0°). It is interesting to note that the methine- and iridium-bound hydrogen atoms

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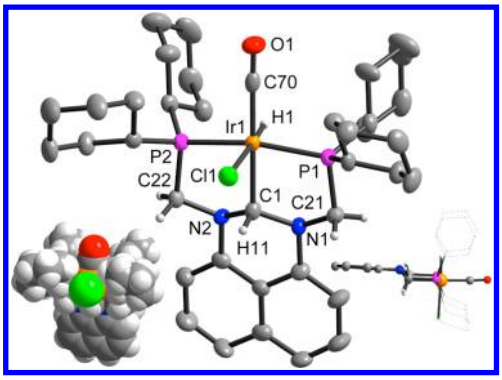
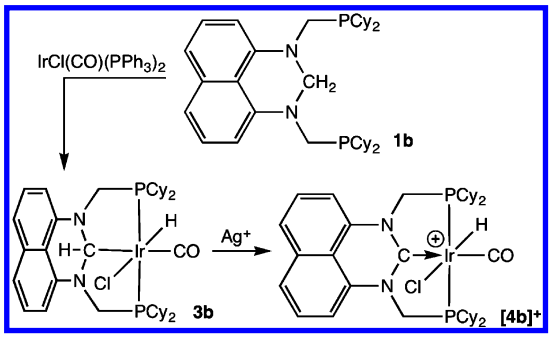


Figure 3. Molecular structure of **3b** (cyclohexyl and naphthyl hydrogen atoms omitted, 50% displacement ellipsoids) including a space-filling representation and a simplified view along the N1−N2 vector. Selected bond lengths (Å) and angles (deg): Ir1−Cl1 = 2.4923(14), Ir1−P1 = 2.2935(15), Ir1−P2 = 2.2998(15), Ir1−C1 = 2.141(5), Ir1−C70 = 1.904(6), Ir1−H1 = 1.539, N1−C1 = 1.493(6), N2−C1 = 1.477(7); P1−Ir1−P2 = 162.76(5), P1−Ir1−C1 = 83.35(14), P2−Ir1−C1 = 82.31(14), Ir1−C1−N1 = 113.2(4), Ir1−C1−N2 = 113.0(3), N1−C1−N2 = 107.5(4), Ir1−C1−H11 = 107.7, ∑(N1) = 342.8, ∑(N2) = 343.0.

adopt an antiperiplanar disposition, from which it might be inferred that the mechanism of metallacyclization is distinct from that leading to **2**: i.e., C−H activation must precede coordination of the second phosphine arm. This geometry also precludes spontaneous σ-metathesis elimination of dihydrogen as well as migratory insertion involving the carbonyl ligand.

The ultimate step en route to *per*-NHC installation requires transfer of the remaining methine proton to the metal center, which is precluded in the case of coordinatively saturated **3b**. In an attempt to provide a suitably receptive vacant coordination site, **3b** was treated with various silver salts (Ag[Y]; Y = PF_6, SbF_6, PO_2F_2) with the expectation that halide abstraction would occur. Surprisingly, these salts resulted in hydride rather than halide abstraction, but nevertheless the desired α-Ir−H elimination could be demonstrated with the formation of the *per*-NHC salts [IrHCl(CO){=C(NCH_2PR_2)$_2C_{10}H_6$}] ([**4b**]Y, Y = PF_6, SbF_6, PO_2F_2; Scheme 3). Most notable among the

Scheme 3. Synthesis of a *per*-NHC Pincer Complex via Stepwise Double Geminal C−H Activation



spectroscopic data for [**4b**]$^+$ is the replacement of the methine resonance for **3b** (δ_C 87.7) with one at δ_C 190.1 in a region typical of NHC complexes of iridium.[1] The cationic nature of the metal center is reflected in an increase in the frequency of the ν_{CO} and ν_{IrH} absorptions[17] to 2067 and 2189 cm^{-1}. Similar values are observed for the cationic NHC complexes [IrHCl(CO)(PPh_3)$_2$(NHC)]$^+$ (NHC = :CNMeCMeCHS,[19] 2050, 2251 cm^{-1}; NHC = :C(NMeCH)$_2$,[20] 2068, 2308 cm^{-1}), though it should be noted that these complexes have the NHC plane orthogonal to the P−P vector.

The salt [**4b**][PO_2F_2] was structurally characterized (Figure 4),[13] thereby confirming the formation of the Ir−NHC linkage

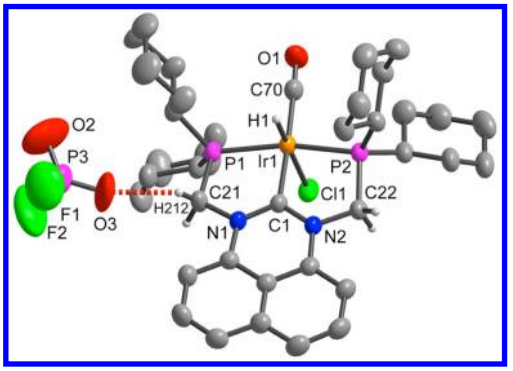


Figure 4. Crystal structure of the salt [**4b**][PO_2F_2] (cyclohexyl and naphthyl hydrogen atoms omitted, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Ir1−Cl1 = 2.4670(12), Ir1−P1 = 2.3107(11), Ir1−P2 = 2.3184(11), Ir1−C1 = 2.078(4), Ir1−H1 = 1.56(5), N1−C1 = 1.356(6) N2−C1 = 1.345(5), O3···H212 = 2.243(6); P1−Ir1−P2 = 165.74(4), Ir1−C1−N1 = 121.0(3), Ir1−C1−N2 = 121.4(3), N1−C1−N2 = 117.6(4), ∑(N1) = 359.9, ∑(N2) = 359.8.

(Ir1−C1 = 2.078(4) Å), which is contracted relative to that in the precursor **3b** (Ir1−C1 = 2.141(5) Å). The difluorophosphate counteranion is weakly associated with the complex cation via hydrogen bonding (O3···H212 = 2.243(6) Å) to one PCH_2 hydrogen, the acidity of which is enhanced by coordination of the phosphine to a cationic iridium(III) center.

Although mechanistically distinct, it should be noted that Hahn has recently demonstrated the synthesis of (κ^2-*P*,*C*) phosphine-NHC chelates, presumably via chelate-assisted C−H activation of phosphinomethylbenzimidazoles.[21] This type of metal-mediated benzimidazole/benzimidazolylidene tautomerism, however, recalls the landmark discovery of a similar (acid-catalyzed) process by Taube some 40 years earlier, in which the formation of [Ru{=C(NH)$_2C_6H_4$}(NH_3)$_5$]$^{2+}$ from benzimidazole and [Ru(OH_2)(NH_3)$_5$]$^{2+}$ proceeds without chelate asistance.[22]

In conclusion, novel N-heterocyclic carbene pincer complexes of rhodium have been generated via chelate-assisted double C−H activation of substituted 2,3-dihydroperimidine proligands. This attractively straightforward method of *per*-NHC installation, the application of which has so far been limited, proved to be exceptionally facile for these proligands, proceeding at ambient temperature without the need for a hydrogen acceptor. Investigations into the broader applicability of this method are underway, though as noted the reaction of **1b** with [IrCl(CO)(PPh_3)$_2$] resulted in only single C−H activation to form an iridium dihydroperimindinyl hydrido complex. However, it was shown that *per*-NHC formation could be induced via hydride abstraction. The ease of preparation of the proligands **1** bodes well for the wider inclusion of highly σ-basic 2,3-dihydroperimidine-based NHC groups within a variety of pincer ligand scaffolds.

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■ ASSOCIATED CONTENT

Supporting Information

CIF files giving crystallographic data for **1a** (CCDC 898434), **2a** (CCDC 898436), **3b** (CCDC 898439), and [**4b**][PO_2F_2] (CCDC 898440) and text giving synthetic procedures and spectroscopic and analytical data for the compounds described. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(13) Characterization data and preparative details are presented in the the Supporting Information.

(14) Cambridge Crystallographic Data Centre, Conquest May 2012 release.

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