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Dihydroperimidine-Derived PNP Pincer Complexes as Intermediates en Route to N-Heterocyclic Carbene Pincer Complexes

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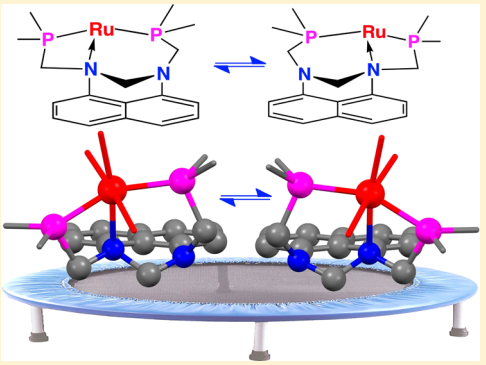
Supporting Information

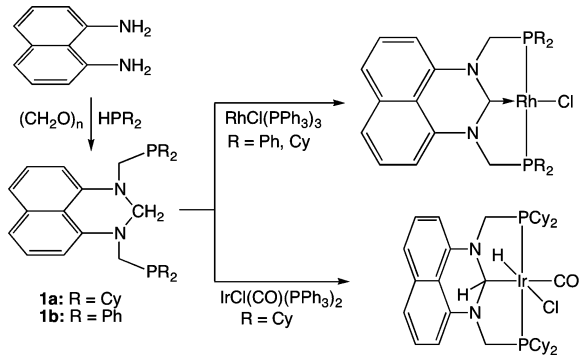
ABSTRACT: The reaction of *N,N′*-bis(dicyclohexylphosphinomethyl)-dihydroperimidine ($H_2C(NCH_2PCy_2)_2C_{10}H_6$-1,8, **1a**) with $[RuCl_2(PPh_3)_3]$ in THF affords the perimidinylidene-based N-heterocyclic carbene (*per*-NHC) pincer complex $[RuCl_2(OC_4H_8)\{{=}C(NCH_2PCy_2)_2C_{10}H_6\}]$ (**2**) via chelate-assisted double C−H activation. In contrast, the reactions of the tetraphenyl analogue $H_2C(NCH_2PPh_2)_2C_{10}H_6$ (**1b**) with $[RuCl_2(PPh_3)_3]$ and of **1a** with $[RuCl(R)(CO)(PPh_3)_2]$ (R = Ph, CH=CHPh) do not result in C−H activation but rather give the asymmetric, PNP-coordinated complexes $[RuCl_2(PPh_3)\{\kappa^3P,N,P'\text{-}CH_2(NCH_2PPh_2)_2C_{10}H_6\}]$ (**3**) and $[RuCl(R)(CO)\{\kappa^3P,N,P'\text{-}CH_2(NCH_2PCy_2)_2C_{10}H_6\}]$ (R = Ph (**4**), CH=CHPh (**5**)), respectively, in which the ruthenium migrates rapidly between nitrogen donors. This provides insight into the mechanistic pathway by which the proligands **1** undergo *per*-NHC formation, as demonstrated by the thermal conversion of **4** to $[RuHCl(CO)\{{=}C(NCH_2PCy_2)_2C_{10}H_6\}]$ (**6**) and benzene.



The chemistries of pincer and N-heterocyclic carbene (NHC) ligands have proven to be particularly fertile avenues in contemporary organometallic research. The high stability and modular variability offered by pincer systems has led to applications in an extensive range of fields,[1] while strongly electron donating NHC ligands have found major utility as supporting ligands in catalytic systems.[2] The combination of NHCs within pincer frameworks has attracted an increasing level of interest, with a particular emphasis on their catalytic potential.[3] While the most commonly used NHC scaffolds remain those based on five-membered heterocyclic rings (imidazolinylidenes, dihydroimidazolinylidenes, etc.), a handful of groups have described perimidinylidene-based NHC ligands (*per*-NHC) with a six-membered N-heterocyclic ring,[4] for which some experimental data have indicated enhanced σ-basicity.[4b,c,e] Furthermore, studies have already demonstrated the catalytic potential of *per*-NHC complexes,[4d,f] including an example in which *per*-NHC groups are incorporated as the axial donors in a meridional pincer framework.[4f]

Recently, we described the first examples of pincer ligands featuring a central equatorial *per*-NHC group, coordinated to rhodium(I) and iridium(III) centers,[5] via remarkably facile double geminal C−H bond activation of the methylene group of readily accessible neutral 2,3-dihydroperimidine precursors $H_2C(NCH_2PR_2)_2C_{10}H_6$-1,8 (R = Cy (**1a**), Ph (**1b**)) (Scheme 1), providing rare examples of such atom-efficient instances of NHC ligand installation.[6] The intimate mechanism by which these *per*-NHC complexes form remains speculative, though the σ-2-perimidinyl complex $[IrHCl(CO)\{CH(NCH_2PR_2)_2C_{10}H_6\}]$, arising from the reaction of **1a** with $[IrCl(CO)(PPh_3)_2]$ (Scheme 1) via a *single* C−H activation, could be subsequently converted to the corresponding NHC complex via hydride abstraction.

Scheme 1. Reaction of Dihydroperimidine-Based Proligands 1 with $[RhCl(PPh_3)_3]$ and $[IrCl(CO)(PPh_3)_2]$



Herein, we describe reactions of these proligands **1** to give PNP-coordinated complexes of ruthenium(II), in which C−H activation has not occurred, providing insight into the C−H activation process.

Reactions between the proligands **1a,b** and $[RuCl_2(PPh_3)_3]$ in THF gave markedly different results (Scheme 2). In the former case, double dehydrogenation of the central methylene group was observed to give the *per*-NHC complex $[RuCl_2(OC_4H_8)\{\kappa^3P,C,P'{=}C(NCH_2PCy_2)_2C_{10}H_6\}]$ (**2**),[8] in a manner similar to the reaction with $[RhCl(PPh_3)_3]$, though the formation of **2** was much less rapid (48 h; cf. 10 min for the

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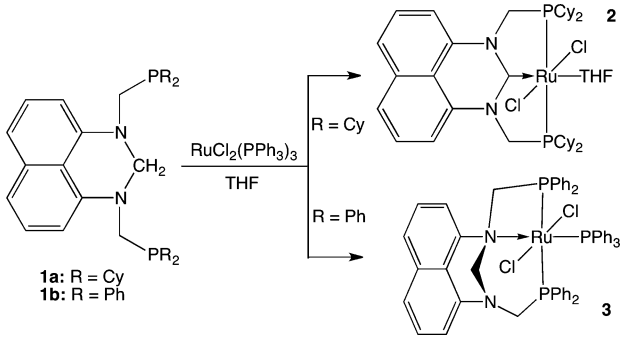
Scheme 2. Reactions of Dihydroperimidine-Based Proligands with $[RuCl_2(PPh_3)_3]$



formation of $[RhCl\{{=}C(NCH_2PCy_2)_2C_{10}H_6\}]$).[7] However, the analogous reaction with **1b** instead yielded the asymmetric PNP pincer complex $[RuCl_2(PPh_3)\{\kappa^3P,N,P'\text{-}CH_2(NCH_2PPh_2)_2C_{10}H_6\}]$ (**3**), in which one amine group is coordinated to the metal center and no C−H activation has occurred. When a solution of **3** was heated to 80 °C in an attempt to promote C−H activation, a discouragingly complex mixture of ^{31}P-containing compounds was obtained, as observed by NMR spectroscopy.[9,10]

The reduced reactivity of the central methylene group toward d^6 ruthenium(II) centers, relative to those in the d^8 rhodium(I) and iridium(I) systems,[5] is presumably due to the less electron rich metal center. The notable difference in reactivity of these two ruthenium systems may also be attributed to electronic factors, the increased σ-basicity of the PCy_2 groups facilitating C−H oxidative addition to form **2**, though we note that the increased steric bulk of the phosphine substituents in **1a** might play a role akin to a Thorpe−Ingold "*gem*-dialkyl" effect.[11]

The $^{31}P\{^1H\}$ NMR spectrum of **2** displayed a singlet peak at 34.6 ppm, while the ^1H NMR spectrum showed a resonance at δ_H 4.24 consistent with the chemically equivalent PCH_2 protons and no additional CH_2 proton resonances apart from those in the cyclohexyl region, consistent with the formulation of **2** as an NHC complex of C_{2v} symmetry. Though a carbene carbon resonance was not observed in the 1D $^{13}C\{^1H\}$ NMR spectrum, it could be detected indirectly at δ_C 224.7 in a $^1H^{13}C$ HMBC experiment through correlation with the PCH_2 proton resonance. The characterization of **2** included a crystal structure determination,[8] the results of which are summarized in Figure 1. This includes a space-filling representation, the steric congestion of which accounts for the preferential coordination of THF over the liberated PPh_3. The Ru1−C1 bond length of 1.943(2) Å lies within the range observed for copious structural data of NHC complexes of ruthenium(II),[12] while the P1−Ru1−P2 bond angle (164.68(2)°) deviates considerably from linearity due to constraints imposed by the rigid pincer system, as was also observed for the four-coordinate rhodium complexes $[RhCl\{{=}C(NCH_2PR_2)_2C_{10}H_6\}]$.[5] The dihydroperimidinylidene ring system exhibits a twist angle of 29.4° relative to the C1−P1−P2−O1 coordination plane around ruthenium. However, the ^1H NMR spectrum of **2** suggests that the Λ- and Δ-twist forms interconvert rapidly in solution at ambient temperature, given that a single, slightly broadened PCH_2 resonance was observed. Such broadening has been noted in previously reported examples of P(NHC)P complexes.[13] As a consequence, the anticipated J_{PH} virtual triplet coupling was not resolved.

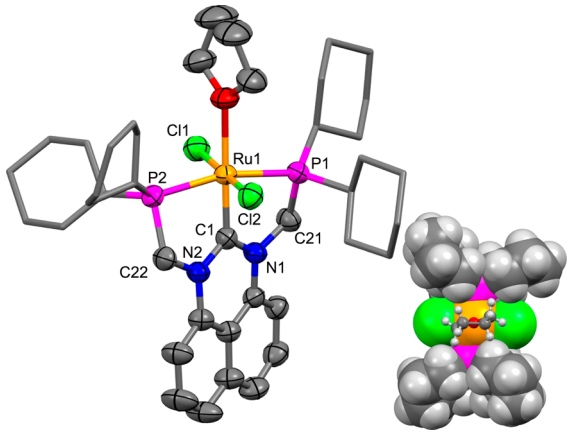


Figure 1. Molecular structure of **2** (hydrogen atoms omitted, cyclohexyl groups simplified, 70% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Ru1−C1 = 1.943(2), Ru1−P1 = 2.3233(5), Ru1−P2 = 2.3162(5), N1−C1 = 1.378(2), N2−C1 = 1.380(2), P1−Ru1−P2 = 164.68(2), P1−Ru1−C1 = 82.52(6). The inset depicts a space-filling representation with the THF ligand simplified.

The $^{31}P\{^1H\}$ NMR spectrum of complex **3** shows one broad peak at δ_P −16.9 ($CDCl_3$) for the two pincer ligand phosphine groups, indicating that the ruthenium atom hops between the two amine donors of the perimidine-based ligand and that this exchange is reasonably rapid in solution at room temperature. At lower temperatures this broad peak separates into two doublets of doublets at δ_P −9.0 and −26.0 (toluene-d_8, −75 °C). These resonances are coupled trans to each other with a characteristically large $^2J_{PP}$ value of 293 Hz, and coupled cis to the PPh_3 resonance with $^2J_{PP}$ = 28 Hz. At higher temperatures a broad doublet is discernible, though the sample decomposes before this becomes well resolved (Figure S5, Supporting Information). The exchange is more rapid with respect to the ^1H NMR time scale, and reasonably sharp coalesced peaks were observed at room temperature. Again, lower temperatures retard the exchange sufficiently so that separate PCH_2 resonances can be seen for both methylene groups, though these did not become clearly resolved within the temperature range used (≥−90 °C). The room-temperature ^1H NMR spectrum of **3** in $CDCl_3$ showed two doublet resonances for the NCH_2N protons at 4.16 and 4.18 ppm ($^2J_{HH}$ = 5 Hz) and two doublet resonances for the PCH_2 protons at 4.83 and 5.48 ppm ($^2J_{HH}$ = 14 Hz). Again, J_{PH} coupling was obscured by signal broadness associated with the dynamic process. The COSY spectrum of **3** showed that the PCH_2 resonances are geminally coupled to one another and suggested the same for the NCH_2N protons (though it is less clear in this case, as the resonances are very close), indicating diastereotopic protons on each of these methylene groups (see the Supporting Information). The reaction of **1b** with $[RuCl_2(PPh_3)_3]$ has very recently been reported to yield a five-coordinate ruthenium(II) complex, without an amine−metal interaction, which shares *some* data with complex **3**.[10] However, the present formulation of **3** is consistent with the NMR data and was also confirmed by an X-ray crystallographic study (Figure 2).[8]

The crystal structure of **3** clearly shows the coordination of the amine to the ruthenium center, which, in combination with the constraints of the pincer ligand, results in significantly distorted geometries around Ru1 and N1. In particular, the P1−Ru−P2 (155.23(3)°) and P1−Ru−N1 (68.13(6)°) angles

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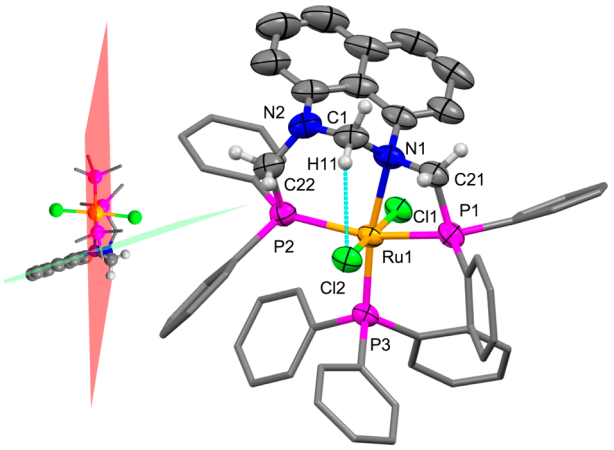


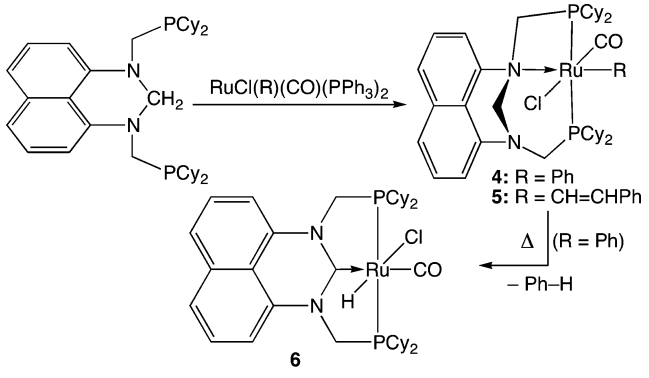
Figure 2. Molecular structure of **3** in a crystal of **3**·CH_2Cl_2 (aryl hydrogen atoms omitted, phenyl groups simplified, 70% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Ru1−N1 = 2.368(2), Ru1−P1 = 2.3689(8), Ru1−P2 = 2.4100(8), N1−C1 = 1.496(4), N2−C1 = 1.427(4), H11···Cl2 = 2.609, P1−Ru1−P2 = 155.23(3), P1−Ru1−N1 = 68.13(6), C2−N1−Ru1 = 115.1(2), C21−N1−Ru1 = 96.0(2). The inset indicates the mutual disposition (71.2°) of naphthalenediamine (green) and P1−P2−P3−N1 (salmon) mean planes.

are significantly contracted from 180 and 90°, respectively, while the C21−N1−Ru (96.0(2)°) and C2−N1−Ru (115.1(2)°) angles deviate considerably from the ideal tetrahedral angle of 109.5°. The naphthalenediamine moiety is almost orthogonal (71.2°) to the N1−P1−P2−P3 mean plane, manifested in the diastereopicity of methylene protons observed in the ^{1}H NMR spectra, with one proton directed toward Cl2 suggesting weak hydrogen bonding (H11···Cl2 = 2.609 Å).

Following the reaction of **1a** to form **2**, the same proligand was treated with [RuCl(R)(CO)(PPh_3)$_2$] (R = Ph, CH=CHPh) with the expectation that elimination of benzene or styrene might facilitate the formation of an NHC complex. The room-temperature reaction, however, yielded the PNP pincer complexes [RuCl(R)(CO){κ^3-*P*,*N*,*P*′-$CH_2(NCH_2PCy_2)_2C_{10}H_6$}] (R = Ph (**4**), CH=CHPh (**5**); Scheme 3), by analogy with the formation of **3**.

Presumably the presence of the π-acidic CO group decreases the electron density at the metal sufficiently to retard C−H oxidative addition. The reactions to form **4** and **5** took place

Scheme 3. Reactions of a Dihydroperimidine-Based Proligand with [RuCl(R)(CO)(PPh_3)$_2$] To Give PNP Complexes



within 2 h at room temperature, as indicated by ^{31}P{^{1}H} NMR singlet resonances at δ_P 16.7 and 16.6, respectively. The formation of PNP complexes was suggested in both cases by the presence of two doublet resonances in the ^{1}H NMR spectra corresponding to NCH_2N protons (**4**, δ_H 4.01 and 5.91, $^2J_{HH}$ = 11 Hz; **5**, δ_H 4.08 and 5.77, $^2J_{HH}$ = 10 Hz), in addition to those corresponding to the PCH_2 groups (**4**, δ_H 4.57 and 4.67, $^2J_{HH}$ = 14 Hz; **5**, δ_H 4.48 and 4.64, $^2J_{HH}$ = 15 Hz). In these cases, the NCH_2N resonances are reasonably far apart, and hence the COSY spectrum of **4** clearly shows that they are mutually coupled. The sharpness of the ^{31}P{^{1}H} NMR signals suggests amine-donor exchange that is more rapid on the ^{31}P NMR time scale for **4** and **5** than for complex **3**. The structures of **4** and **5** were both confirmed crystallographically.[9] The molecular structures (Figure 3 and Figure S5 (Supporting Information))

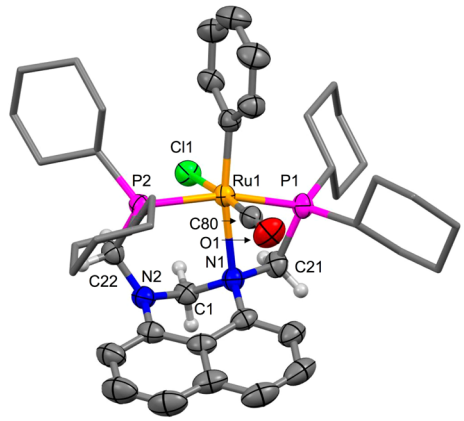


Figure 3. Molecular structure of **4** (aryl and cyclohexyl hydrogen atoms omitted, 70% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Ru1−N1 = 2.419(2), Ru1−P1 = 2.3538(6), Ru1−P2 = 2.3552(6), N1−C1 = 1.501(3), N2−C1 = 1.434(3), P1−Ru1−P2 = 163.28(2), P1−Ru1−N1 = 68.39(5), C2−N1−Ru1 = 93.6(1), C21−N1−Ru1 = 116.7(1).

show distorted geometries similar to that of **3**, though the P1−Ru1−P2 bond angles (**4**, 163.28(2)°, **5**, 163.47(3)°) are significantly less contracted than that of **3** (155.23(3)°), which is presumably a result of steric interactions between the PCy_2 substituents in the latter.

The four-coordinate nitrogen atom in all three complexes is a chiral center. Exchange between the amine donor groups reverses the chirality: i.e., the compounds are racemic both in solution and as crystals in the centrosymmetric space groups $P\bar{1}$ (**3**, **5**) and $P2_1/n$ (**4**). As noted for **3** above, one proton (H11) of the N_2CH_2 methylene unit approaches the chloride ligand to within distances consistent with incipient CH···Cl hydrogen bonding for both **4** (2.524 Å) and **5** (2.556 Å), adding a further stabilizing interaction.[14]

Formation of an NHC product from **4** via double C−H activation could be promoted by heating in toluene under reflux over 4 days to form the dehydroperimidinylidene complex [RuHCl(CO){κ^3*P*,*C*,*P*′=$C(NCH_2PCy_2)_2C_{10}H_6$}] (**6**) with elimination of benzene (Scheme 3). This complex proved to be not very soluble in toluene, precipitating out of solution as the reaction progressed. Several minor unidentified side products were evident in the ^{31}P NMR spectra; however, these conveniently remained dissolved in the toluene solvent. Among the NMR data that characterize **6** (Supporting Information), the triplet hydride resonance at δ_H −16.45

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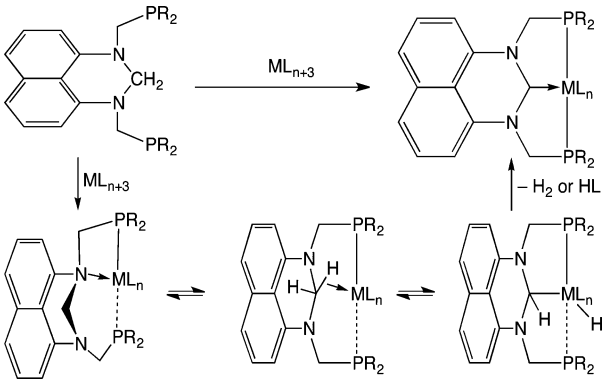
($^2J_{PH}$ = 19 Hz) and the carbene resonance, also a triplet, at δ_C 225.9 ($^2J_{PC}$ = 8 Hz) attest to the α-Ru−H elimination sequence.

From these results, we may begin to discern a pattern in which reactions of **1** with metal centers will form NHC complexes if the system is sufficiently electron rich or else result in a PNP or σ-perimidinyl complex (Scheme 4). We may

Scheme 4. Mechanistic Conjecture for the Formation of *per*-NHC Pincer Complexes via C−H Activation



therefore surmise that the proligands initially bind via the phosphine group(s), encouraging one of the amine centers to interact with the metal, as in complexes **3**−**5**. The proximity of the central methylene group to the metal center might promote interaction with one of the C−H bonds, resulting in oxidative addition to give a σ-perimidinyl hydrido complex such as [IrHCl(CO){CH(NCH$_2$PR$_2$)$_2$C$_{10}$H$_6$}]. Subsequent loss of dihydrogen could then proceed via an addition/elimination or σ-metathesis pathway depending on the nature of the metal and coligands. Alternatively, a HL group, where L^- is a nonhydride ligand, may be expelled.

It should be noted that this mechanistic conjecture is based on isolable ground state geometries, and double C−H activation may conceivably precede the coordination of the second phosphine arm or require its dissociation.

In conclusion, while double dehydrogenation of proligand **1a** was observed on reaction with [RuCl$_2$(PPh$_3$)$_3$] to give the *per*-NHC complex **2**, the analogous reaction of the less electron donating proligand **1b**, as well as reactions of **1a** with less electron rich starting materials, gave the asymmetric PNP coordinated complexes **3**−**5**, in which no C−H activation had occurred. These observations have provided further insight into the likely mechanistic pathway by which proligands **1** form *per*-NHC complexes.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, and CIF files giving crystallographic data for **2** (CCDC 983020), **3** (CCDC 983019), **4** (CCDC 983021), and **5** (CCDC 983022), 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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(7) The formation of **2** was accompanied by a significant proportion of organometallic side products. NMR data[8] also suggested the formation of a side product in which PPh$_3$ replaces the THF ligand. This was difficult to separate from complex **2**, and analytically pure samples of **2** could only be obtained by small-scale crystallization.

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

(9) The reaction of **1b** with [RuCl$_2$(PPh$_3$)$_3$] has very recently been reported to provide a symmetric five-coordinate complex devoid of direct N−Ru coordination, *some* NMR data for which correspond to those for **3**.[10] The complex was also shown to catalyze the transfer hydrogenation of acetophenone but under conditions which our ^{31}P{^{1}H} NMR data indicate it is unstable.

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