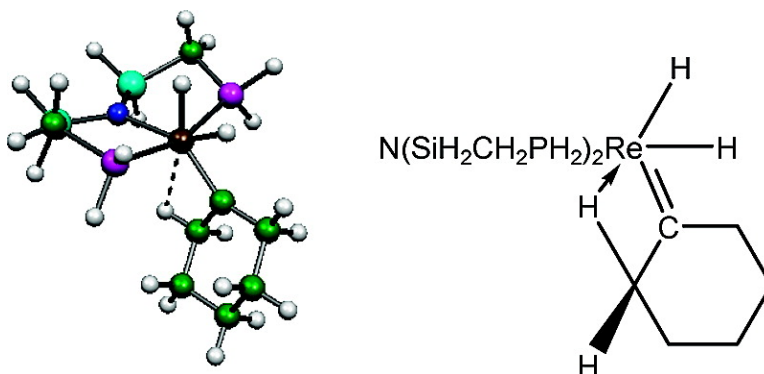


## A $\sigma$ -Basic Rhenium Center that Effects Cyclohexene Isomerization to a $\beta$ -Agostic Carbene Ligand

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## A $\pi$ -Basic Rhenium Center that Effects Cyclohexene Isomerization to a $\beta$ -Agostic Carbene Ligand

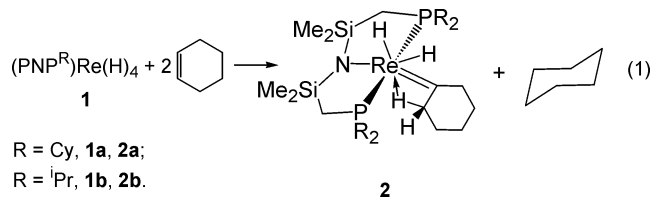
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We have reported earlier<sup>1</sup> a series of examples of vinyl ethers and related electron-rich olefins which are isomerized, upon coordination to the fragment  $\text{RuHCl}(\text{P}^i\text{Pr}_3)_2$ , to heteroatom-substituted carbenes complexed to this metal. Both experiment and DFT computations revealed that the  $\text{RuHCl}(\text{P}^i\text{Pr}_3)_2$  fragment lacks the ability to isomerize an olefin to a non-heteroatom-substituted carbene ligand, an effect we have attributed to insufficient ability of this metal fragment to back-donate to a more  $\pi$ -acidic carbene ligand. To address this limitation, we proposed to use a more  $\pi$ -basic metal, Re, and a more powerful  $\pi$ -donor ligand, amide, to isomerize a coordinated hydrocarbon olefin to a coordinated carbene. The anionic pincer ligands<sup>2</sup> ( $\text{R}_2\text{PCH}_2\text{SiMe}_2\text{N}^-$  (“PNP<sup>R</sup>”)) have already been incorporated<sup>3</sup> in the complex  $(\text{PNP}^{\text{R}})\text{Re}(\text{H})_4$ , which can be transformed to lower oxidation states by hydrogen transfer to olefins. We now report how  $(\text{PNP}^{\text{R}})\text{Re}(\text{H})_4$  converts cyclohexene into coordinated cyclohexylidene and that this carbene is  $\beta$ -agostic<sup>4</sup> to the metal in  $(\text{PNP}^{\text{R}})\text{Re}(\text{H})_2[\text{C}(\text{CH}_2)_5]$ .

$(\text{PNP}^{\text{R}})\text{Re}(\text{H})_4$  (R = Cy, **1a**; R = <sup>i</sup>Pr, **1b**) reacts readily with 2 or more equiv of cyclohexene (22 °C, 1 h) to produce cyclohexane and **2** (eq 1). The reaction with **1b** is essentially quantitative (NMR

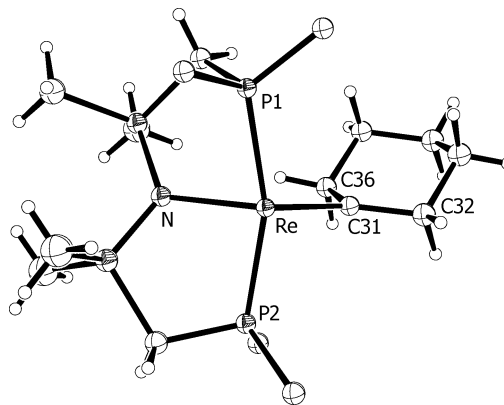


evidence), but the reaction of **1a** with only 2 equiv of cyclohexene produces a significant amount of a byproduct resulting from the cyclometalation of the Cy rings of the PNP ligand. This side reaction is 99% suppressed by using a 15-fold excess of cyclohexene. The complex **2b** could only be obtained as an orange oil, but **2a** could be isolated in high yield as a crystalline solid of analytical purity.

The collective observations on **2a(b)** reveal them to be carbene complexes with a  $\beta$ -agostic hydrogen. The two hydride ligands resonate as two broad peaks at  $-6.4$  ( $-6.7$ ) and  $-9.9$  ( $-10.0$ ) ppm at 22 °C, and selective decoupling of the alkyl hydrogens results in a triplet ( $J_{\text{PH}} = 12$  Hz) <sup>31</sup>P NMR signal. The congestion in the aliphatic region of the <sup>1</sup>H NMR spectra of **2** does not allow assignment of the individual methylene resonances of the cyclohexylidene fragment, but <sup>13</sup>C NMR spectra show separate signals for each of the six carbons of the cyclohexylidene. The  $\alpha$ -C resonates at 262.9 (264.9) ppm, consistent with a multiple rhenium carbon bond. Three of the CH<sub>2</sub> carbons resonate in the 25–30 ppm range, typical for carbons of a cyclohexyl ring. We assign these carbons as  $\gamma$ - and  $\delta$ -CH<sub>2</sub>. The two remaining CH<sub>2</sub> <sup>13</sup>C signals resonate at 57.4 (57.4) and 14.9 (15.6) ppm, respectively. Both of these are outside of the normal cyclohexyl range and we assign them as the two  $\beta$ -carbons. In the uncoupled <sup>13</sup>C NMR spectrum of **2b** both the peak at 57.4 ppm and the peak at 15.6 ppm are triplets; however, the triplet at 57.4 ppm is characterized by a  $J_{\text{CH}}$

= 127 Hz, a typical value for (sp<sup>3</sup>)C–H, while the triplet at 15.6 ppm is characterized by a smaller  $J_{\text{CH}} = 117$  Hz. A diminished  $J_{\text{CH}}$  is one of the indicators of an agostic interaction.<sup>5</sup> Assuming a  $\geq 127$  Hz  $J_{\text{CH}}$  coupling constant for the nonagostic H, the  $J_{\text{CH}}$  to the agostic hydrogen is estimated at ca.  $\leq 107$  Hz. This value is comparable to other examples of weak agostic CH's.<sup>5</sup> Although the illustrated structure of **2** is chiral (eq 1), the <sup>31</sup>P, <sup>1</sup>H, and <sup>13</sup>C NMR spectra reveal mirror symmetry; thus, the agostic interaction must be fluxional and involve alternately one of the two hydrogens on one CH<sub>2</sub> group to generate a time-averaged mirror plane of symmetry containing N, Re, and the carbene C. The PNP<sup>R</sup> signals in <sup>1</sup>H and <sup>13</sup>C NMR spectra all show that there is no time-averaged mirror plane containing N and the two P; therefore, the hydrides do not migrate past the ReP<sub>2</sub>N plane.

Performing the reaction of **1a** with excess cyclohexene in pentane leads to the precipitation of **2a** in the form of single crystals suitable for an X-ray diffraction study, which confirmed the proposed structure of **2a** as a  $\beta$ -agostic cyclohexylidene complex (Figure 1)<sup>6</sup> The angles Re–C(carbene)–C <sub>$\beta$</sub>  are 100.4(3)° and 147.2(3)°, thus being distinctly nonequivalent. The Re–C36 distance is 2.635(4) Å. The agostic interaction is established without perceptible distortion of the C <sub>$\beta$</sub> –C <sub>$\alpha$</sub> –C <sub>$\beta$</sub>  angle (112.4(3)° while the other five angles within the C<sub>6</sub> ring range from 111.0(3)° to 112.0(4)° and the carbene carbon is coplanar with its three attached groups.



**Figure 1.** ORTEP drawing of  $(\text{PNP}^{\text{Cy}})\text{Re}(\text{H})_2(\text{C}_6\text{H}_{10})$  showing selected atom labeling and hydrogen atoms in idealized positions, to see that the agostic hydrogen on C36 is equatorial in a chair ring conformation. The two hydride ligands are expected to be located in the N–Re–C31 plane and projecting toward the reader. Only one C of each Cy ring on P is illustrated. Selected structural parameters: Re–P1, 2.4091(9) Å; Re–P2, 2.3715(10) Å; P1–Re–P2, 161.30(4)°; N–Re–C31, 136.90(15)°; P1–Re–C31, 103.13(11)°; P2–Re–C31, 95.10(12)°; P1–Re–N, 79.88(9)°; P2–Re–N, 83.98(9)°.

In addition, the two C <sub>$\alpha$</sub> –C <sub>$\beta$</sub>  distances are also different to a statistically significant degree (1.500(6) and 1.526(6) Å), with the longer distance to C <sub>$\alpha$</sub>  being the one involved in the agostic interaction. While surprising, this inequality is also present in a DFT optimized geometry (see below). The Re–C <sub>$\alpha$</sub>  distance, 1.889(4)

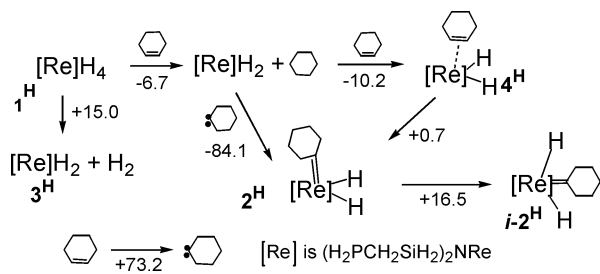
Å, is comparable to those in the Schrock alkylidenes of Re.<sup>7</sup> The Re–N distance, 2.182(3) Å, is longer compared to that in **1a** (2.063(2) Å),<sup>3</sup> indicating that in **2a** the amide N→Re lone pair donation is diminished or absent in favor of an agostic interaction as a means to achieve an 18 valence electron configuration at Re.

It is perhaps surprising that the agostic interaction is preferred to amide  $\pi$ -donation, given the strong manifestation of the latter in **1**.<sup>3</sup> It is possible that the strong trans influence of the hydride discourages the amido ligand from taking a position exactly trans to it, as would be necessary for a competent  $\pi$ -donation from N to Re.

We undertook a DFT computational study of the model compound ((H<sub>2</sub>PCH<sub>2</sub>SiH<sub>2</sub>)<sub>2</sub>N)Re(H)<sub>2</sub>(=C(CH<sub>2</sub>)<sub>5</sub>) (**2<sup>H</sup>**). The optimized structure of **2<sup>H</sup>** reproduces the relevant features of the experimental structure of **2a** very closely (see Supporting Information). This supports the conclusion that the origin of the distortions observed in **2a** is of electronic and not steric nature. The agostic C <sub>$\beta$</sub> –H bond is slightly longer than the other C–H bonds around the C<sub>6</sub> ring, consistent with the lower *J*<sub>CH</sub> observed by NMR for **2**. The conformation of the C<sub>6</sub> ring obtained by calculation reproduces the experimental determination well; thus, one can expect that the positions of the H atoms on the C<sub>6</sub> ring are also accurately predicted by DFT. The calculated dihedral angle H–C36–C31–Re is 2.7°, showing that the C–H bond is in the same plane as the p-orbital at N with which it competes for the coordination site at Re. The complex is formally d<sup>4</sup> at Re (neutral carbene formalism), but the two filled d-orbitals in a pentagonal bipyramidal geometry are orthogonal to the N–Re–C plane. As a consequence, (a) the rotation of the carbene about the Re/C bond has a large barrier and (b) there is no back-donation into the  $\sigma^*$  orbital of C36–H.

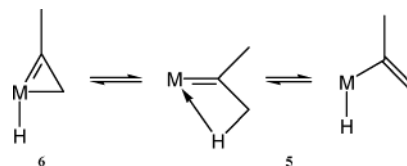
Previously reported<sup>8,9</sup> cycloalkene to cycloalkylidene rearrangements are effected by d<sup>2</sup> Nb and W, while the cyclohexene → cyclohexylidene rearrangement reported here is effected by a d<sup>4</sup> fragment, (PNP)ReH<sub>2</sub>. While the DFT finding (Scheme 1) that **2<sup>H</sup>** is essentially thermoneutral with **4<sup>H</sup>** contradicts the experimental observation of only **2**, the PNP<sup>R</sup> ligand in **2a–b** is much more sterically demanding than PNP<sup>H</sup> used in the DFT calculations. An olefin complex should always be sterically disfavored compared to an isomeric carbene, so that one *should expect* larger ancillary ligands to bolster the preference for the carbene isomer.

**Scheme 1.** DFT Calculated Free Energies (kcal/mol, 298 K) for Key Transformations



We also considered an alternative structure for **2**. An isomer with the cyclohexylidene ligand between the two hydrides and trans to N (*i*-**2<sup>H</sup>**) was found to be considerably higher (16.5 kcal/mol) in energy. No agostic interactions are present in this isomer (consequently the Re–N distance, 2.079 Å, is shorter, the Re–C distance is much longer (2.026 Å) than in **2<sup>H</sup>**, and the cyclohexylidene ligand is not angularly distorted.) The factors that could be responsible for the higher energy of this isomer may include (a) the unfavorable *trans* disposition of the carbene and the amide, (b) steric repulsion between the hydrides and the carbene substituents, (c) inadequate Re–C  $\pi$ -interaction in this geometry.

In summary, we present here an example of a  $\beta$ -agostic carbene ligand, obtained by transformation of a cyclic olefin on a Re center.<sup>10</sup> It seems likely that this structural motif will be found again for unsaturated dialkylcarbene complexes, particularly of 5d (vs 4d) metals. There is a precedent<sup>4</sup> for a  $\beta$ -agostic carbene in the cation Tp(OC)<sub>2</sub>W=[C(CH<sub>3</sub>)Ph]<sup>+</sup>; there, the same bending around the carbene C and the same reduction of the agostic J(C–H) value is observed, all parameters suggesting somewhat stronger agostic donation in that example, despite its being isoelectronic with our Re example. The existence of  $\beta$ -agostic carbenes is of relevance to olefin metathesis and C–H activation and most directly to H migration from a metal to the  $\beta$ -carbon of an  $\eta^1$ -vinyl ligand (**5**) or a metallocyclopropene (**6**).<sup>11</sup>



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**Supporting Information Available:** Full synthetic, spectroscopic, computational and crystallographic details, including a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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