We have reported earlier\(^1\) a series of examples of vinyl ethers and related electron-rich olefins which are isomerized, upon coordination to the fragment RuHCl(PiPr\(_3\))\(_2\), to heteroatom-substituted carbenes complexed to this metal. Both experiment and DFT computations revealed that the RuHCl(PiPr\(_3\))\(_2\) 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\(^2\) (R\(_2\)PCH\(_2\)SiMe\(_2\))\(_2\)N\(^-\) have already been incorporated\(^3\) in the complex (PNP\(^n\))Re(H)\(_4\), which can be transformed to lower oxidation states by hydrogen transfer to olefins. We now report how (PNP\(^n\))Re(H)\(_4\) converts cyclohexene into coordinated cyclohexylidene and that this carbene is \(\beta\)-agostic\(^4\) to the metal in (PNP\(^n\))Re(H)\(_4\)=C(CH\(_2\))\(_2\)).

\((\text{PNP}^n)\text{Re(H)\(_4\)} + 2\text{C(CH\(_2\))\(_2\)} \rightleftharpoons (\text{PNP}^n)\text{ReH(C(CH\(_2\))\(_2\)))}

\[ R = \text{Cy, 1a; } R = \text{Pr, 1b}\]

\[ R = \text{Pr, 1b, 2b.}\]

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 \(22^\circ\text{C}\), and selective decoupling of the alkyl hydrogens results in a triplet (J\(_{\text{CH}} = 12\text{Hz}\)) \(^{13}\)P NMR signal. The congestion in the aliphatic region of the \(1^\text{H}\) NMR spectra of 2 does not allow assignment of the individual methylene resonances of the cyclohexylidene fragment, but \(13^\text{C}\) 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\(_2\) carbons resonate in the \(25\,\rightarrow\,30\) ppm range, typical for carbons of a cyclohexyl ring. We assign these carbons as \(1\)- and \(3\)-CH\(_2\). The two remaining CH\(_2\) \(^{13}\)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 undecoupled \(^{13}\)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\(^3\))C\(\rightarrow\)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.\(^5\) Assuming a \(\geq 127\) Hz J\(_{\text{CH}}\) coupling constant for the nonagostic H, the J\(_{\text{CH}}\) to the agostic hydrogen is estimated to at ca. \(\geq 107\) Hz. This value is comparable to other examples of weak agostic CH’s.\(^6\) Although the illustrated structure of 2 is chiral (eq 1), the \(^{13}\)P, \(^1\)H, and \(^{13}\)C NMR spectra reveal mirror symmetry; thus, the agostic interaction must be fluxional and involve alternately one of the two hydrogens on one CH\(_2\) group to generate a time-averaged mirror plane of symmetry containing N, Re, and the carbene C. The PNP\(^n\) signals in \(^1\)H and \(^{13}\)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 Re\(^n\)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).\(^6\) The angles Re\(\rightarrow\)(carbene)\(\rightarrow\)C\(_\alpha\) are 100.4(3)\(^\circ\) and 147.2(3)\(^\circ\), thus being distinctly nonequivalent. The Re\(\rightarrow\)C\(_\beta\) distance is 2.635(4) Å. The agostic interaction is established without perceptible distortion of the C\(_\beta\)-C\(_\alpha\)-C\(_\beta\) angle (112.4(3)\(^\circ\)) while the other five angles within the C\(_6\) ring range from 111.0(3)\(^\circ\) to 112.0(4)\(^\circ\) and the carbene carbon is coplanar with its three attached groups.

![Figure 1. ORTEP drawing of (PNP\(^n\))Re(H)\(_2\)(C\(_6\)H\(_6\)) showing selected atom labeling and hydrogen atoms in idealized positions, to see that the agostic hydrogen on C\(_3\) is equatorial in a chair ring conformation. The two hydride ligands are expected to be located in the N\(\rightarrow\)Re\(\rightarrow\)C\(_3\) plane and projecting toward the reader. Only one C of each Cy ring on P is illustrated. Selected structural parameters: Re\(\rightarrow\)P1, 2.4091(9) Å; Re\(\rightarrow\)P2, 2.3715(10) Å; P1\(\rightarrow\)Re\(\rightarrow\)P2, 161.30(4)\(^\circ\); N\(\rightarrow\)Re\(\rightarrow\)C\(_3\), 136.90(15)\(^\circ\); P1\(\rightarrow\)Re\(\rightarrow\)C\(_3\), 103.13(11)\(^\circ\); P2\(\rightarrow\)Re\(\rightarrow\)C\(_3\), 95.10(12)\(^\circ\); P1\(\rightarrow\)Re\(\rightarrow\)N, 79.88(9)\(^\circ\); P2\(\rightarrow\)Re\(\rightarrow\)N, 83.98(9)\(^\circ\).](image-url)
Å, is comparable to those in the Schrock alkylidene of Re.⁷ The Re–N distance, 2.182(3) Å, is longer compared to that in 1a (2.063(2) Å),³ 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 Ï-donation, given the strong manifestation of the latter in 1.¹ It is possible that the strong trans influence of the hydride discourages the amido ligand from taking a position exactly trans to the Re.–C bond.¹⁰ ²H is much longer (2.026 Å) than in 1,² indicating that in 2a the C–H bond is in the same plane as the p-orbital at the carbene carbon, consistent with the lower JCH observed by NMR for 2. The conformation of the C6 ring obtained by calculation reproduces the experimental determination well; thus, one can expect that the Re(I)-C bond has a large barrier and (b) there is no back-donation into the Ï# orbital of C36–H.

Previously reported⁵ cycloalkene to cycloalkylidene rearrangements are effected by d2 Nb and W, while the cyclohexene Ï-cyclohexylidene rearrangement reported here is effected by a d4 fragment, (PNP)ReH2. While the DFT finding (Scheme 1) that 2H is essentially thermoneutral with 4H contradicts the experimental observation of only 2, the PNPk ligand in 2a–b is much more sterically demanding than PNPk 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-2H) 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 2H, 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 Ï-interaction in this geometry.

In summary, we present here an example of a Ï-agonal carbene ligand, obtained by transformation of a cyclic olefin on a Re center.¹⁰ It seems likely that this structural motif will be found again for unsaturated dialkylcarbene complexes, particularly of 5d (vs 4d) metals. There is a precedent⁴ for a Ï-agonal carbene in the cation Tp(OC)2W=C(CH3)Ph3⁺; there, the same bonding 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 Ï-agonal carbones is of relevance to olefin metathesis and C–H activation and most directly to H migration from a metal to the Ï-carbon of an n1-vinyl ligand (5) or a metallacyclop propane (6).¹¹

Acknowledgment. This work was supported by the National Science Foundation.

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.

References


JA035165X