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Communications

Conversion of Ethylene to Hydride and Ethylidyne by an Amido Rhenium Polyhydride

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Summary: Reaction of $(PNP^{Cy})ReOCl_2$ *(*$PNP^{Cy} = N(SiMe_2CH_2PCy_2)_2$*) with Mg and* H_2 *yields* $(PNP^{Cy})Re(H)_4$*, whose unsaturation is demonstrated by its ability to add* H_2*. "*$(PNP^{Cy})ReH_6$*" is an equilibrium mixture of a structure where all six H's are on Re and a structure where five H's are on Re and one H is on N.* $(PNP^{Cy})Re(H)_4$ *reacts with* C_2H_4 *within 10 min at 25 °C to give ethane and* $(PNP^{Cy})ReH(\equiv C-CH_3)$*, together with its ethylene adduct.*

Whereas "pure" polyhydride compounds, L_nMH_m (L = Lewis base), are almost invariably saturated and resist becoming unsaturated, the presence of at least one π-donor ligand, $L_nMH_{m-3}X$, even one as weak as chloride, makes such unsaturated species achievable. This is illustrated by $(R_3P)_2MH_5$ versus $(R_3P)_2MH_2Cl$ (M = Rh, Ir), and $(R_3P)_2M'H_6$ versus $(R_3P)_2M'H_3Cl$ (M′ = Ru, Os).[1,2] We desired to extend this class of compounds to include $X = NR_2$ and to do this via the class of ligands developed by Fryzuk: $(R_2PCH_2SiMe_2)_2N^-$ ("PNP^R").[3] We were especially interested in enhancing the π-basicity of the metal to accomplish the isomerization of olefins lacking any π-donor substituents into coordinated carbenes, which was not possible for the fragment $(R_3P)_2RuHCl$.[4] We envisioned doing this by moving from Ru(II) to Re(I),[5] and from Cl to the more π-donating NR_2.

Mg powder under H_2 (1 atm, 25 °C, Et_2O) functions well to remove oxide and chloride from $(PNP^{Cy})ReOCl_2$ (**1**)[6] to give red-purple $(PNP^{Cy})ReH_4$ (**2**) in good yield upon workup (Scheme 1).[7] The hydrides give only one ^1H NMR triplet at −9.24 ppm ($J_{PH} = 22$ Hz) in the −80 to +22 °C temperature range, but a crystal structure determination (Figure 1a)[8] was sufficient to reveal four hydride ligands in an unusual seven-coordinate geometry. The peculiarity of this approximately C_{2v} symmetric structure results from the fact that Ha1 and Ha2 are bent away from being mutually *trans* in order to avoid competition of two strong *trans*-effect ligands and to rehybridize one empty d_π orbital for more effective π bonding with the filled p_π orbital of the amide nitrogen.[2b,9] DFT calculations (see Supporting Information) on a model species, $(H_2PCH_2SiH_2)_2NReH_4$ ($\mathbf{2^H}$), give a tetrahydride ground state structure with the relevant

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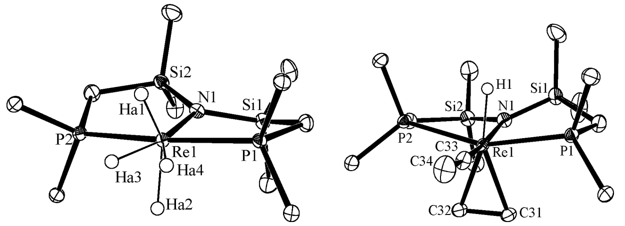
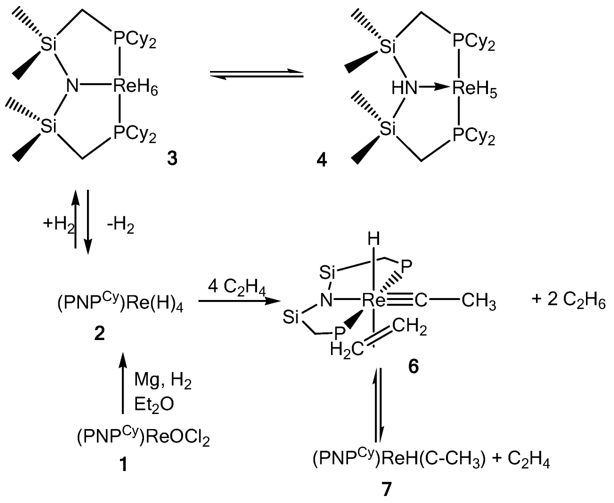


Figure 1. Selected bond distances (Å) and angles (deg). (a) Molecular structure of **2**: Re(1)−P(1), 2.3877(6); Re(1)−P(2), 2.3860(6); Re(1)−N(1), 2.0633(19); N(1)−Re(1)−H(a1), 119.4(11); N(1)−Re(1)−H(a2), 116.8(11); H(a1)−Re(1)−H(a2), 123.7(16). (b) Molecular structure of **6**: Re(1)−P(1), 2.4412(5); Re(1)−P(2), 2.4292(5); Re(1)−N(1), 2.2768(17); Re(1)−C(31), 2.232(2); Re(1)−C(32), 2.242(2); Re(1)−C(33), 1.762(2); C(31)−C(32), 1.422(3); P(1)−Re(1)−P(2), 157.482(18); N(1)−Re(1)−C(33), 173.82(8); Re(1)−C(33)−C(34), 174.03(19). [Hydrogen atoms, except Re−H, and all cyclohexyl CH$_2$ were omitted for clarity.]

Scheme 1

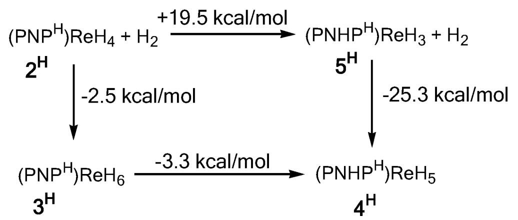


geometrical parameters closely corresponding to those of **2**. No dihydrogen isomer was found as an energy minimum.

(PNP^{Cy})ReH$_4$ is an operationally unsaturated complex and does indeed bind H$_2$ (Scheme 1) to produce a mixture of two tautomers: (PNP^{Cy})ReH$_6$ (**3**) and (PNHP^{Cy})ReH$_5$ (**4**). Under an H$_2$ atmosphere, the hydride signal of **4** (t, $J_{HP} = 17$ Hz) can be observed at ambient temperature by ^{1}H NMR at −6.82 ppm. The peaks corresponding to **2** and **3** are coalesced at ambient temperature and give rise to a very broad upfield hydride resonance and one very broad ^{31}P NMR resonance. At −40 °C and below, the resonances of **2** and **3** decoalesce to give two broad triplets for their corresponding hydrides and two singlets for their corresponding Si−Me groups in ^{1}H NMR, as well as two singlets in the ^{31}P{^{1}H} NMR.

We undertook a DFT computational study of the Re polyhydrides **2^H**−**5^H** (Scheme 2). Tautomerization of **2^H** to **5^H** is found to be highly unfavorable, whereas the tautomers **3^H** and **4^H** are approximately isoenergetic. Both **3^H** and **4^H** are saturated 18e complexes, while **2^H** and **5^H** are unsaturated 16e complexes. However, the Re center in **2^H** is stabilized by π-donation from N; no such option exists for **5^H**. The much shorter Re−N bond in **2^H** (2.062 Å) than in **3^H** (2.209 Å) is consistent with a multiple Re−N bond in **2^H**. In contrast, the lengths of the dative Re←N bonds in **4^H** (2.362 Å) and **5^H** (2.357 Å) are very similar. The addition of H$_2$ to the unambiguously unsaturated **5^H** is favorable by 25.3 kcal/mol, while the addition of H$_2$ to the *operationally* unsaturated **2^H** is favorable only by 2.5 kcal/mol.

Scheme 2



Our computational results are consistent with the experimental observation of species **2**−**4** and not of **5** and with the observation that H$_2$ addition to **2** is reversible and that even in the presence of excess H$_2$ and at −80 °C the conversion of (PNP^{Cy})ReH$_4$ to "(PNP^{Cy})ReH$_6$" isomers is incomplete.[10] (PNP^{Cy})ReH$_4$ (**2**) also slowly exchanges its hydrides and the hydrogens of the cyclohexyl rings with D from C$_6$D$_6$ at 25 °C.[11]

The unsaturated character of (PNP^{Cy})ReH$_4$ allows it to react with ethylene rapidly (10 min) at 25 °C to

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[7] (PNP^{Cy})ReH$_4$ (**2**). A 200 mL flask equipped with a Kontes Teflon stopcock was charged with (PNP^{Cy})ReOCl$_2$ (**1**) (0.730 g, 0.876 mmol), Mg powder (0.20 g, 8.3 mmol), 20 mL of ether, and a stir bar. The suspension was degassed and the flask was refilled with H$_2$ (ca. 1 atm). The contents of the flask were vigorously stirred for 72 h, over which time the color changed from green to red-purple, then the volatiles were removed in vacuo. The residue was triturated with heptane, extracted with pentane, and filtered. The volume of the filtrate was reduced to ca. 5 mL in vacuo, and this solution was kept at −30 °C for 24 h. Red-purple crystalline product was separated by decantation and washed with cold pentane and dried in vacuo. Yield: 0.410 g (63%). The exact time needed for the completion of the reaction depends on the amount and the surface area of Mg used. Utilization of a large excess of Mg is not detrimental, and the remaining Mg can be reused in future preparations of **2**. Mg activated by previous reaction runs generally promotes faster (several hours) conversion to the product. ^{1}H NMR (C$_6$D$_6$): δ 2.23 (br d, 12 Hz, 4 H, Cy), 1.83 (br t, 8 Hz, 4 H, Cy), 1.74 (br m, 12 H, Cy), 1.40−1.60 (br m, 12 H, Cy), 1.06−1.30 (br m, 12 H, Cy), 0.94 (t, 6 Hz, 4 H, PC*H*$_2$Si), 0.40 (s, 12 H, SiC*H*$_3$), −9.24 (t, 22 Hz, Re*H*$_4$). The hydride resonance at −9.24 ppm remains essentially unchanged upon cooling the toluene-d_8 solution of (PNP^{Cy})ReH$_4$ down to −80 °C. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 56.2 (s). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 41.4 (t, 14 Hz, *C*H of PCy), 29.1 (s, *C*H$_2$ of PCy), 28.6 (s, *C*H$_2$ of PCy), 27.4 (t, 5 Hz, *C*H$_2$ of PCy), 27.3 (t, 6 Hz, *C*H$_2$ of PCy), 26.9 (s, *C*H$_2$ of PCy), 10.7 (s, P*C*H$_2$Si), 6.7 (t, 2 Hz, Si*C*H$_3$).

[8] Crystallographic data for **2** (−162 °C): $a = 10.6141(4)$ Å, $b = 11.1066(4)$ Å, $c = 17.6560(7)$ Å; $\alpha = 71.902(1)°$, $\beta = 75.498(1)°$, $\gamma = 78.701(1)°$ with $Z = 2$ in space group $P\bar{1}$. $R(F) = 0.0178$ for 9824 reflections with $I > 2.33\sigma(I)$. Crystallographic data for **6** (−158 °C): $a = 11.2777(3)$ Å, $b = 11.5672(3)$ Å, $c = 15.5630(5)$ Å; $\alpha = 92.868(1)°$, $\beta = 94.163(1)°$, $\gamma = 109.906(1)°$, $Z = 2$ in space group $P\bar{1}$. $R(F) = 0.0153$ for 9898 reflections with $I > 3\sigma(I)$.

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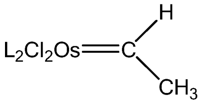
fragment C_2H_4 into hydride and carbyne ligands (Scheme 1). In this reaction, the four original hydride ligands are “abstracted” by two molecules of ethylene, effectively a *four*-electron reduction of Re, which enables reconstruction (and reduction) of ethylene into a hydride and a strongly π-acidic ethylidyne ligand. The ethylidyne moiety is characterized by the downfield ^{13}C NMR resonance of the α-carbon (**6**, 259.5 ppm; **7**, 271.0 ppm).[12]

While ethylene does bind to the hydridocarbyne, its enthalpy of binding is modest (like that of H_2 binding to $(PNP^{Cy})ReH_4$) to the point that it can be removed from the colorless **6** in a vacuum, albeit under drastic conditions (0.1 Torr, >100 °C),[13] to give isolable, operationally unsaturated, deep red $(PNP^{Cy})ReH(CCH_3)$ (**7**). Ethylene in **6** does not undergo free rotation at ambient temperature on the NMR time scale, as evidenced by the observation of two different ^1H NMR resonances for the two diastereotopic pairs of H’s in the C_2H_4 unit and a single ^{13}C NMR signal. Solution NMR evidence is thus consistent with the alignment of the C=C bond along the P−Re−P vector, as found in the solid state (Figure 1b).



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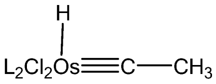

B

These results show that an amide supporting ligand, even one with two (electron-withdrawing) silyl substituents, has sufficient π-donor ability to make thermodynamically accessible either unsaturated polyhydride or carbyne complexes. The mechanism of conversion of ethylene to hydride[14] and ethylidyne may involve either vinyl C−H oxidative addition or hydrogenation to a $ReCH_2CH_3$ intermediate. Because the product is not $Re{=}CHCH_3$, but instead a hydride carbyne, this is similar to an osmium analogue (**B** preferred over **A**), while the latter (an unsaturated carbene complex) is preferred for the 4d analogue Ru.[4,12,15]

This work shows that the (PNP)Re substructure has the versatility to (a) permit ready ligand (e.g., H_2 or olefin) loss and thus access unsaturated rhenium and still retain (b) an ability of Re to bind a new substrate and (c) effect olefin hydrogenation and C/H bond cleavage. These capabilities can be attributed to an amide nitrogen which can either donate or retain a lone electron pair and to a metal that has the ability to span a large range of oxidation states, including +5, and still have sufficient π-basicity to bind an olefin at the d^2 configuration in **2** and **6**.

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Supporting Information Available: Synthetic, spectroscopic and crystallographic, and computational details and the drawings and Cartesian coordinates of DFT geometries. Also two crystallographic files are available free of charge via the Internet at http://pubs.acs.org.

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[12] On the formation of Re carbynes from alkynes[10a] and Os carbynes from alkenes[10b] and alkynes[10c−e] see: (a) Leeaphon, M.; Ondracek, A. L.; Thomas, R. J.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 9715. (b) Spivak, G. J.; Coalter, J. N.; Olivan, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 999. (c) Esteruelas, M. A.; Lahoz, F. J.; Onate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935. (d) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683. (e) Buil, M. L.; Eisenstein, O.; Esteruelas, M. A.; Garcia-Yebra, C.; Gutierrez-Puebla, E.; Olivan, M.; Onate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* **1999**, *18*, 4949.

[13] Only ethylene was detected among trapped volatiles from the thermolysis of **6**.

[14] Conversion of $W{-}CH_2CH_3$ to $W{\equiv}C{-}CH_3$ has been reported: (a) Shih, K.-Y.; Tortland, K.; Seidel, S. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 12103. (b) Dobbs, D. A.; Schrock, R. R.; Davis, W. M. *Inorg. Chim. Acta* **1997**, *263*, 171.

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