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Fluxionality in [$ReH_5(PPh_3)_2$(pyridine)]

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The new polyhydrides [$ReH_5(PPh_3)_2$(L)] (**1**; L = 4-carbomethoxypyridine (**a**), pyridine (**b**), 4-picoline (**c**), 4-(dimethylamino)pyridine (**d**)), formed by reaction of L with [$ReH_7(PPh_3)_2$], are rigid on the NMR time scale at low temperature. The low-temperature spectrum is assigned by ROESY NMR studies, and turnstile and pseudorotation fluxionality mechanisms are suggested to account for the two successive coalescence events in the VT NMR spectra.

Introduction

The mechanisms of fluxionality for polyhydride complexes of high coordination number (CN > 6) are not well established partly because many of these species are nonrigid at all accessible temperatures, and so NMR studies are unable to provide details of the rearrangements involved.[1] Rigid polyhydrides are also of interest in connection with the problem of quantum exchange coupling, which has so far only been seen in a very small class of complexes, most notably [$CpIrLH_3$]$^+$ and $CpRuLH_3$.[2] On the basis of one current theory of quantum exchange,[3] the phenomenon should be seen when a hydride has inequivalent hydrogens and a sufficiently low barrier to exchange.

In this paper, we show that [$ReH_5(PPh_3)_2$(L)] (**1**; L = 4-carbomethoxypyridine (**a**), pyridine (**b**), 4-picoline (**c**), 4-(dimethylamino)pyridine (**d**)), formed by reaction of L with [$ReH_7(PPh_3)_2$], are rigid on the proton NMR time scale at low temperature but show two coalescence processes on warming. The fluxionality mechanisms we propose involve a turnstile motion of three hydrides for the low-temperature process and a pseudorotation of the coordination dodecahedron for the high-temperature process. Exchange barriers for these two processes were obtained by ^{1}H NMR and shown to depend on the electronic properties of the ligands L. Quantum exchange is not observed in any of these systems; possible reasons are discussed.

Results and Discussion

Synthesis. [$ReH_7(PPh_3)_2$] was previously known to react in refluxing THF with a wide range of ligands, L to give [$ReH_5(PPh_3)_2$(L)] and H_2.[4] We now show that **1a**−**d** can be prepared via a milder route, reaction at 20 °C in benzene for about 20 h (eq 1). The complexes are air-stable solids. Compound **1b** had been prepared by Chatt et al.,[4] but no detailed NMR study was reported.

$$[ReH_7(PPh_3)_2] + L \rightarrow \underset{\mathbf{1}}{[ReH_5(PPh_3)_2(L)]} + H_2 \qquad (1)$$

1: L = 4-carbomethoxypyridine (**a**), pyridine (**b**),
4-picoline (**c**), 4-(dimethylamino)pyridine (**d**)

UV/Visible Spectroscopy. The colors of the complexes vary in a striking way with the electronic properties of L (**1a**, dark-purple; **1b**, bright-yellow; **1c**, yellow; **1d**, pale-yellow; all in powder form). This has been traced to a shift in a prominent band, assigned to metal to ligand charge transfer, from 533 nm for **1a** to 422, 400, and 364 nm for **1b**−**d**.

Variable-Temperature NMR Spectra. Complexes **1a**−**d** were all rigid on the ^{1}H NMR time scale at −90 °C but underwent two coalescence events on warming. This behavior constrasts with that of most polyhydrides, including [$ReH_7(PPh_3)_2$] and [$ReH_5(PPh_3)_3$], both of which are completely nonrigid at all accessible temperatures (>−90 °C). For example, **1b** gave the spectra shown in Figure 1. At −90 °C the spectrum consists of four resonances at −0.91 ppm (t, $^2J_{H,P} = 29$ Hz), −2.62 ppm (AA′XX′, $^2J_{H,P(trans)} + {}^2J_{H,P(cis)} = 26$ Hz), −8.38 ppm (t, $^2J_{H,P} = 23$ Hz), and −9.65 ppm (br s); the

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(3) (a) Clot, E.; Leforestier, C.; Eisenstein, O.; Pélissier, M. *J. Am. Chem. Soc.* **1995**, *117*, 1797. (b) In contrast to this proposal, another current theory[3c] invokes dihydrogen complexes as necessary intermediate states. Since different definitions of the term “dihydrogen complex” seem to have been adopted by the two parties, it is worth pointing out that H_2 complexes can be “stretched” of “unstretched”.[3d] Use of these terms might bring more precision to the discussion. (c) Limbach, H.-H.; Scherer, G.; Maurer, M.; Chaudret, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1369. (d) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.

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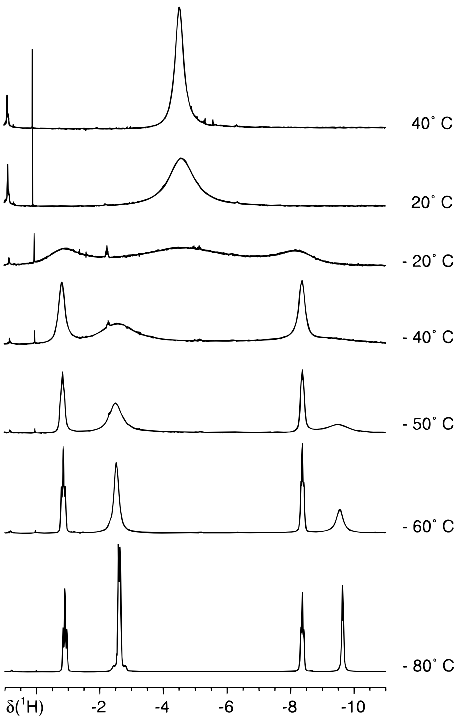


Figure 1. ^{1}H NMR spectra of **1b** at 500 MHz and various temperatures.

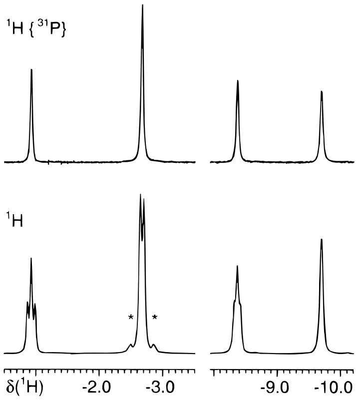


Figure 2. Expansion of the 500 MHz ^{1}H NMR (below) and ^{1}H{^{31}P} NMR (above) spectra for **1b** recorded at −90 °C. The asterisks emphasize the outer lines of the AA′XX′ type multiplet which disappear under ^{31}P decoupling conditions.

intensities correspond respectively to 1, 2, 1, and 1 protons (Figure 2).

When the temperature is raised, the resonances at −2.62 and −9.65 ppm broaden significantly, the latter at twice the rate of the former, however. At −20 to −40 °C, these two resonances coalesce to a single broad signal. At about the same temperature, the resonances at −0.91 and −8.38 ppm also start to broaden. Above 0 °C, all resonances coalesce to give one single broad signal at −4.51 ppm integrating for five protons. The ^{1}H{^{31}P} spectrum (Figure 2) taken at −90 °C shows four *singlet* resonances. Furthermore, unresolved H−Re−H hydride−hydride couplings are evident from ^{1}H{^{31}P} 1D COSY experiments. **1a**, **1c**, and **1d** show similar low-temperature ^{1}H NMR spectra as does **1b**, but with different coalescence temperatures.

A similar result was briefly reported by Ginsberg et al.[5] for $ReH_5(AsPh_2Et)_3$ in the range −135 to +25 °C. At low temperature, the same 1:2:1:1 integral ratio pattern of hydride peaks is seen. In this case, three separate coalescences were noted, but the resonances were not assigned and no mechanism was suggested.

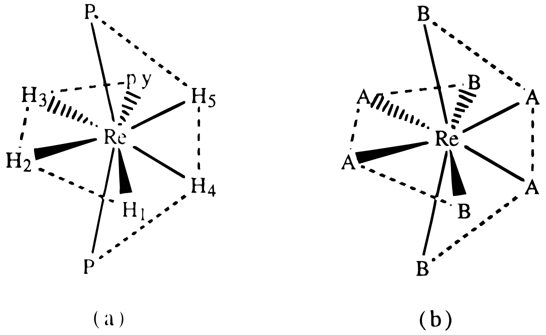
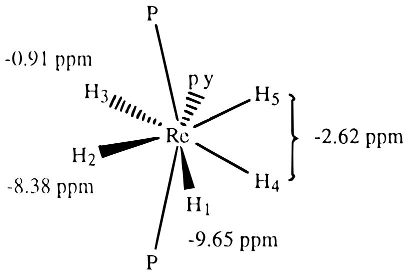


Figure 3. (a) Dodecahedral geometry of **1**. (b) Assignment of A and B sites.

Structure and Hydride Assignment. Eight-coordinate polyhydrides are almost always dodecahedral. Figure 3b shows this geometry and identifies the inequivalent A and B sites. The bulkiest ligands normally occupy the B sites preferentially. The low-temperature spectra of the rigid complexes of type **1** are consistent with a dodecahedral geometry with the non-hydrogen ligands being in the B sites. This is exactly what is expected for an 8-coordinate polyhydride.[1]

The hydride resonances exhibit T_1 values around 300 ms at −90 °C at 300 MHz. Although a minimum T_1 was not achieved at −90 °C, this value is consistent[6] with the classical hydride structure for **1**. $[ReH_5(PPh_3)_3]$ is a classical hydride, and replacing a PPh_3 by a pyridine is not expected to change this. The 1:2:1:1 intensity ratio seen in the low-temperature NMR spectrum for **1b** suggests that the pyridine is located on a plane of symmetry, as shown in the diagram, making two of the hydrides isochronous. Examination of the spectra shown in Figure 1 reveals that, on warming, two of the resonances coalesce before any other process occurs. These two resonances have intensity 2 and intensity 1, so the first can be identified as the pair of equivalent hydrogens, H_4 and H_5 in the diagram.



1 b

One other hydrogen is found to exchange rapidly with this pair, and it seemed most likely that this hydrogen is H_1, which is the closest of the other hydrides to H_4 and H_5. The hydride resonance at −8.38 ppm seemed most likely to be H_2 because the chemical shifts of this resonance and H_1 are most influenced by a change in the N-donor ligand; both H_1 and H_2 are almost *trans* to py. This leaves the −0.91 ppm resonance assigned as H_3.

This tentative assignment is fully supported by 2-dimensional rotating-frame Overhauser spectroscopy (ROESY);[7] see Figure

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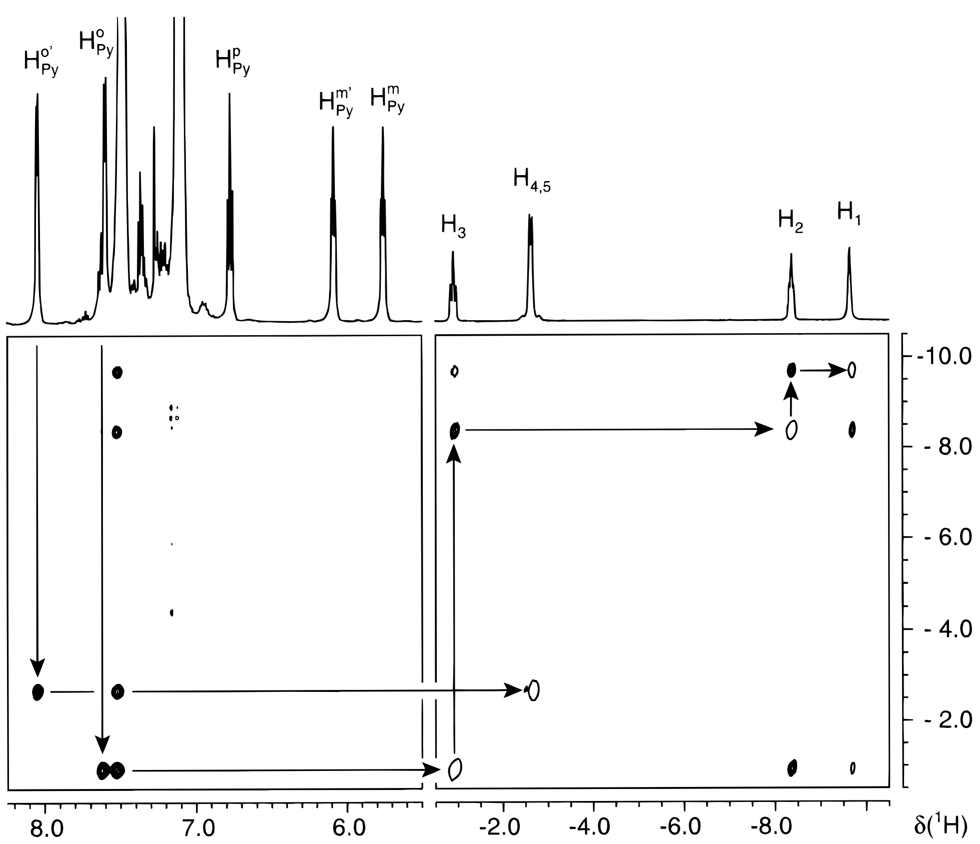


Figure 4. $^1H\{^{31}P\}$ ROESY spectrum of **1b**.

Table 1. Exchange Barriers for High- and Low-Temperature Processes in 1a−c from Initial Line Broadening

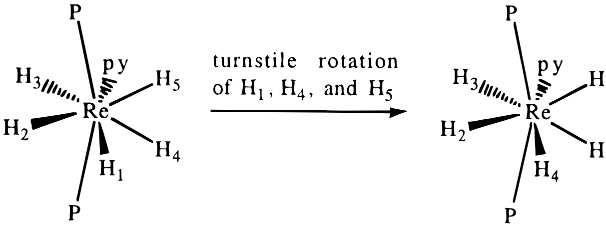
	barrier, $\Delta G^\ddagger$ (kcal/mol)	
compd	low temp	high temp
1a	10.2 ± 0.3	11.2 ± 0.3
1b	8.5 ± 0.3	10.4 ± 0.3
1c	8.4 ± 0.3	10.0 ± 0.3

Table 2. $\Delta G^\ddagger_c$ Values and ^1H NMR Data for the *meta* Protons on Ligand py of 1 at 20 and −90 °C

	1a	1b	1c	1d
δ(*meta*), 20 °C	6.53 (d)	6.10 (t)	5.95 (d)	5.40 (d)
δ(*meta*), −90 °C	6.21 (d)	5.81 (t)	5.64 (d)	5.08 (br s)
	6.58 (d)	6.14 (t)	5.98 (d)	5.41 (br s)
$\Delta G^\ddagger_c$ (kcal/mol)	11.0 ± 0.3	10.4 ± 0.3	10.0 ± 0.3	9.5 ± 0.3
$T_{coalescence}$ (K)	233	219	212	203

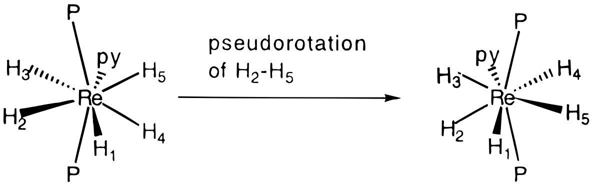
4. As will be discussed later, the *ortho* and *meta* protons of the pyridine ligand in **1b** are nonequivalent at low temperature due to hindered rotation about the rhenium−nitrogen bond. One of these protons, $H_{py}{}^{o'}$, is found to be located close to the previously assigned hydride pair, H_4 and H_5. From the other *ortho* proton, $H_{py}{}^{o}$, an uninterrupted chain of close hydrogen−hydrogen contacts extends to H_3 and H_2 and on to H_1, i.e., along one of the trapezoidal edges of the dodecahedral coordination polyhedron.

Mechanism and Barriers of Fluxionality. The first exchange on warming, involving H_1, H_4, and H_5, could be due to a turnstile rotation of all three H's, although a pairwise exchange process among all three pairs cannot be excluded. Since, in such a turnstile mechanism, H_1 always leaves its site, while H_4 and H_5 have a 50% chance of leaving their (equivalent) sites, the H_1 peak shows twice the broadening of the $H_{4,5}$ peak. The turnstile process, which allows the three hydrides to avoid each other and the other ligands, is illustrated in eq 2. Values for $\Delta G^\ddagger$ were calculated from the ^1H NMR line shape (Table 1). Comparative values for compound **1d** could not be obtained because the two fluxional processes occur at very similar temperatures.



(2)

The high-temperature coalescence causes all the hydrides to exchange. Many processes would have this effect, but a likely one is the pseudorotation of eq 3, which permits all the non-hydrogen ligands to remain in their preferred B sites. Other processes are possible, however. The $\Delta G^\ddagger$ values of this process were also calculated from the line broadening and are reported in Table 1. For **1d**, no static hydride ^1H NMR spectrum can be obtained, and this has prevented us from obtaining an exchange barrier for the higher temperature process.



(3)

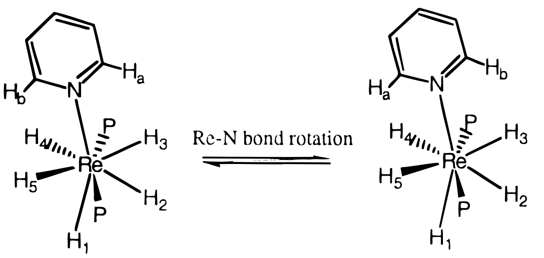
Besides the hydrides, the *ortho* and *meta* pairs of aromatic protons on py decoalesce upon cooling; the *ortho* pairs are obscured by the PPh_3 resonance, an therefore only *meta* proton resonances are reported in Table 2 as well as $\Delta G^\ddagger_{coalescence}$ for

Table 3. Line Widths, UV/Vis λ_{max}, and ΔG_c for the High-Temperature Fluxional Process versus Hammett Substituent Constant σ_{para}

	1a	**1b**	**1c**	**1d**
line width (Hz)[a]	341 ± 13	184 ± 7	124 ± 5	66 ± 3
λ_{max} (nm)[b]	533	422	400	364
ΔG_c (kcal/mol)	11.2 ± 0.3	10.4 ± 0.3	10.0 ± 0.3	9.5 ± 0.3
σ_{para}[c]	0.44	0.0	−0.14	−0.3

[a] Measured in CD_2Cl_2 at 298 K and 300 MHz. [b] Measured in CH_2Cl_2 at 298 K. [c] Advanced Organic Chemistry, 2nd ed.; Carey, F. A., Sundberg, R. J. P., Eds.; Plenum Press: New York, 1984; Part A, p 183.

this dynamic process. Although both Re−N rotation (eq 4) and pseudorotation (eq 5) can lead to the decoalescence observed,



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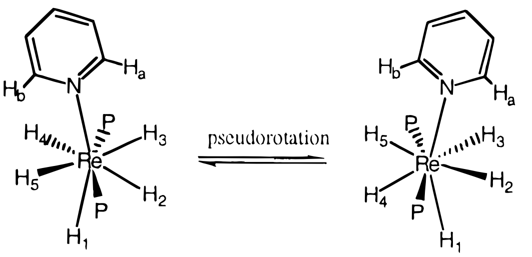

(5)

we prefer pseudorotation because the $\Delta G^{\ddagger}$ values for the pyridine decoalescence (10.4 ± 0.3) and for the high-temperature hydride decoalescence (10.4 ± 0.3) are identical.

Substituent Effect of py on Fluxionality. The different rates of fluxionality of **1a**−**d** in the high-temperature process are shown by the different line widths observed for the hydride resonance at 20 °C. The line widths, UV/vis λ_{max}, and ΔG_c for the high-temperature fluxional process (Table 3) all correlated well with the Hammett substituent constant σ_{para} of the R group on L. The plot shown in Figure 5 clearly shows fluxionality of **1** is dependent on the electronic effect of ligands py. An electron-withdrawing group in L (**1a**) increases both exchange barriers; on the other hand, an electron-donating group on py (**1d**) decreases the barriers.

Quantum Exchange. Quantum exchange coupling was not seen in any of the complexes studied, even though the situation superficially seems favorable. The phenomenon is expected whenever two inequivalent hydrides have a modest exchange barrier. The situation is somewhat delicate in that if the barrier is too low, the hydrides become equivalent in the NMR spectrum and so any quantum exchange cannot be detected; if the barrier is too high, then the quantum exchange becomes too weak to detect by NMR. The lack of quantum exchange in our system could be a result of the fluxional exchange barrier in our system being still too high to permit it. In our earlier work on $ReH_6(PPh_3)_2(SiPh_3)$,[8] where a turnstile exchange mechanism was also proposed, we were unable to observe quantum exchange, even though the hydrides were inequivalent at low temperature; in the hexahydride case, however, the barrier was 10.5 ± 0.5 kcal/mol, rather high relative to the cases where quantum exchange has been seen. In the present case, the barrier is much lower, only 8.5 ± 0.3 kcal/mol for **1b**, and so the absence of quantum exchange is more surprising.

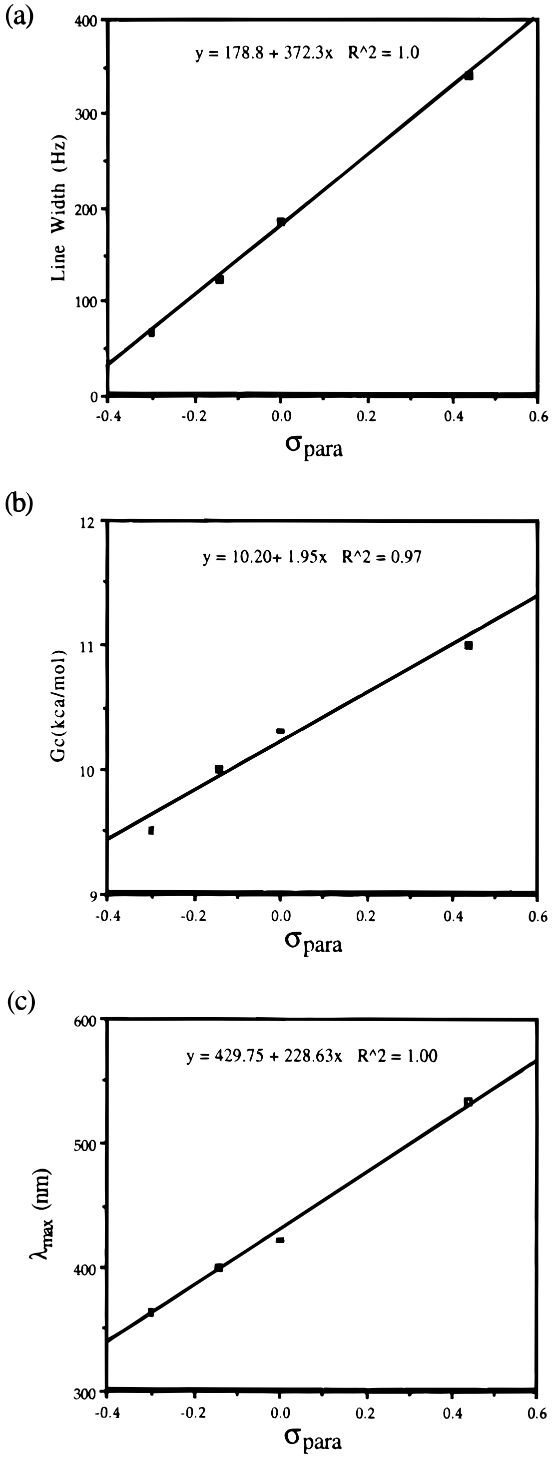

Figure 5. Plots of (a) line widths, (b) coalescence energies, and (c) λ_{max} against σ_{para}.

Conclusion

A series of 8-coordinated metal polyhydrides of type **1** were prepared and shown to be fluxional by NMR. The colors and fluxional barriers depend on the electronic character of the pyridine ligand. Two coalescence events were found. On the basis of the assignment of the low-temperature hydride proton NMR spectrum, made by ROESY studies, we propose turnstile and pseudorotation mechanisms for the two fluxional processes.

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Experimental Section

General Procedures and Material. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures. Isonicotinoyl chloride hydrochloride, pyridine, 4-picoline, and 4-(dimethylamino)-pyridine (Aldrich) were used as received. $ReH_7(PPh_3)_2$ was prepared according to the literature method.[9]

^1H and ^{31}P NMR spectra were recorded on a GE Omega 300 and for **1b** also on a Bruker AMX 500 spectrometer; chemical shifts were measured relative to residual solvent (^1H NMR) or to external 85% H_3PO_4 (^{31}P NMR). The $^1H\{^{31}P\}$ ROESY[7] spectrum was recorded using a phase-alternated spin-lock of 120 ms duration employing a rf field strength of 9.2 kHz. One-dimensional $^1H\{^{31}P\}$ COSY spectra[10] were measured by selectively exciting one of the hydride resonances with a Guassian-shaped pulse of 20 ms duration followed by a fixed evolution period of 5 ms and the usual mixing. In both the ROESY and COSY experiments, additional ^{31}P CW decoupling was employed.

IR spectra were collected on a MIDAC FT-IR spectrometer. Elemental microanalyses were performed by Atlantic Microlabs.

Preparation of 4-Carbomethoxypyridine. A mixture of isonicotinoyl chloride hydrochloride (770 mg, 4.325 mmol) and 2 mL of pyridine was stirred in 8 mL of MeOH at ambient temperature for 10 min, and the volatile materials were removed *in vacuo*. The solid residue was extracted into THF (3 × 4 mL), the extract was filtered through a basic alumina column, and the solvent was removed from the clear filtrate under reduced pressure, leaving 410 mg (85%) of a colorless liquid. ^1H NMR ($CDCl_3$, 298 K): δ 3.96 (3H, s, Me), 7.84 (2H, d, $J = 6$ Hz, aromatic C−H), 8.78 (2H, br s, aromatic C−H). IR (Nujol): $\nu_{C=O}$ 1741 cm^{-1}.

Pentahydridobis(triphenylphosphine)(4-carbomethoxypyridine)-rhenium(V) (1a). $ReH_7(PPh_3)_2$ (141 mg, 0.196 mmol) was stirred with 4-carbomethoxypyridine (64 mg, 0.576 mmol) in 12 mL of benzene at ambient temperature for 24 h, during which the color changed from pale yellow to dark purple. The volume of the solution was reduced to about 6 mL under reduced pressure, and a mixture of hexanes (9 mL) was slowly added to precipitate dark purple microcrystals. The product was filtered off, washed with hexanes (2 × 2 mL), and dried *in vacuo* (126 mg, 78%). ^1H NMR (CD_2Cl_2, 298 K): δ −4.43 (5H, br s, Re−H), 3.38 (3H, s, Me), 6.53 (2H, d, $J = 6.3$ Hz, aromatic protons on pyridine ring), 7.19 (18H, br s, Ph), 7.62 (12H, br s, Ph), 8.29 (2H, d, $J = 6.3$ Hz, aromatic protons on pyridine ring). ^{31}P\{selectively hydride-coupled\} NMR (CD_2Cl_2, 298 K): δ 44.49 (br s). IR (KBr): $\nu_{C=O}$ 1726 (s), ν_{Re-H} 1999 (w), 1950 (w), 1821 cm^{-1} (w). Anal. Calc for $C_{39}H_{42}NO_2P_2Re$: C, 58.20; H, 3.98; N, 1.74. Found: C, 58.54; H, 4.17; N, 1.61. The complex can be recrystallized from CH_2Cl_2/hexanes.

Pentahydridobis(triphenylphosphine)(pyridine)rhenium(V) (1b). $ReH_7(PPh_3)_2$ (170 mg, 0.196 mmol) was stirred with pyridine (76 mg, 0.973 mmol) in 15 mL of benzene at ambient temperature for 16 h, during which the color changed from pale yellow to bright yellow. The solution was filtered through Celite, the volume of the filtrate was reduced to 5 mL under reduced pressure, and a mixture of hexanes (10 mL) was slowly added to precipitate a bright yellow solid. The product was filtered off, washed with hexanes (2 × 2 mL), and dried *in vacuo* (158 mg, 84%). ^1H NMR (CD_2Cl_2, 298 K): δ −4.51 (5H, br s, Re−H), 6.10 (2H, t, $J = 6.9$ Hz, *m*-H, pyridine), 6.90 (1H, t, $J = 7.8$, *p*-H, pyridine), 7.20 (18H, m, Ph), 7.61 (12H, m, Ph), 8.16 (2H, d, $J = 5.1$ Hz, *o*-H, pyridine). IR (KBr): ν_{Re-H} 2027 (w), 1997 (w), 1969 (w), 1931 (m), 1873 cm^{-1} (m). Anal. Calc for $C_{37}H_{39}NP_2Re$: C, 61.95; H, 5.07; N, 1.76. Found: C, 62.22; H, 5.23; N, 1.62.

Pentahydridobis(triphenylphosphine)(4-methylpyridine)rhenium-(V) (1c). $ReH_7(PPh_3)_2$ (162 mg, 0.226 mmol) was stirred with 4-picoline (63 mg, 0.676 mmol) in 8 mL of benzene at ambient temperature for 19 h, during which a yellow precipitate formed; a mixture of hexanes (9 mL) was then added to complete precipitation. The product was filtered off, washed with hexanes (2 × 2 mL), and dried *in vacuo* (124 mg, 68%). ^1H NMR (CD_2Cl_2, 298 K): δ −4.64 (5H, br s, Re−H), 2.00 (3H, s, Me), 5.95 (2H, d, $J = 6.6$ Hz, aromatic protons on pyridine ring), 7.20 (18H, br s, Ph), 7.61 (12H, br s, Ph), 7.99 (2H, d, $J = 6.6$ Hz, aromatic protons on pyridine ring). ^{31}P\{selectively hydride-coupled\} NMR (CD_2Cl_2, 298 K): δ 46.04 (br s). IR (KBr): ν_{Re-H} 2024 (w), 1996 (w), 1928 (w), 1873 cm^{-1} (w). Anal. Calc for $C_{42}H_{42}NP_2Re$: C, 62.36; H, 5.23; N, 1.73. Found: C, 62.66; H, 5.47; N, 1.59.

Pentahydridobis(triphenylphosphine)(4-(dimethylamino)pyridine)rhenium(V) (1d). $ReH_7(PPh_3)_2$ (180 mg, 0.251 mmol) was stirred with 4-(dimethylamino)pyridine (92 mg, 0.753 mmol) in 15 mL of benzene at ambient temperature for 17 h, during which a pale yellow precipitate formed; a mixture of hexanes (10 mL) was then added to complete precipitation. The product was filtered off, washed with hexanes (2 × 2 mL), and dried *in vacuo* (148 mg, 70%). ^1H NMR (CD_2Cl_2, 298 K): δ −4.70 (5H, br s, Re−H), 2.72 (6H, s, Me), 5.40 (2H, d, $J = 6.9$ Hz, aromatic protons on pyridine ring), 6.49 (1H, d, $J = 6.9$ Hz, aromatic proton on pyridine ring), 7.20 (18H, br s, Ph), 7.62 (12H, m, Ph), 8.36 (1H, d, $J = 7.8$ Hz, aromatic protons on pyridine ring). ^{31}P\{selectively hydride-coupled\} NMR (CD_2Cl_2, 298 K): δ 46.63 (br s). IR (KBr): ν_{Re-H} 2007 (w), 1979 (w), 1964 (w), 1831 cm^{-1} (m). Anal. Calc for $C_{43}H_{45}N_2P_2Re$: C, 61.63; H, 5.41; N, 3.34. Found: C, 62.01; H, 5.73; N, 3.20.

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