Table XII. ^{19}F and ^{29}Si Chemical Shift Differences $|\delta(RR'SiF_3) - \delta(RR'SiF_2)|$[a] and Si–F Coupling Constant Differences $J_{RR'SiF_2} - J_{RR'SiF_3^-}$[b]

R, R'	$\Delta\delta(^{19}F)$,[c] ppm	$\Delta\delta(^{29}Si)$, ppm	ΔJ_{SiF},[c] Hz
$(CH_2)_4$	29.0	82.7	66.5
$(CH_2)_5$	40.5	76.0	67.7
MePh	36.9	69.1	49.7
o-Tol, *o*-Tol	40.4	67.7	51.3
Mes, Mes	28.1	69.2	51.3
t-Bu, Ph	32.5	69.2	45.7
Ph, Ph	33.2	77.6	52.5
BiPh	44.7	69.0	70.2
BiBz	41.5	77.3	56.5

[a] The difference in chemical shifts (Δ) is an absolute value. The ^{19}F chemical shift moves downfield upon pentacoordination while the ^{29}Si chemical shift moves upfield upon pentacoordination. [b] The difference in coupling constants is a positive value. [c] All values are averages; i.e., $\Delta\delta(^{19}F)$ and ΔJ_{SiF} are obtained from the low-temperature NMR spectral parameters for "stopped" exchange where the weighted averages were calculated for the $RR'SiF_3^-$ derivatives and subtracted from the respective values for the $RR'SiF_2$ derivatives except for $[(CH_2)_4SiF_3]^-$ where exchange did not slow. In this case, the NMR parameters obtained at −58.3 °C were used.

for pentacoordinated anionic silicates relative to the isoelectronic phosphoranes. The latter is reasonable in terms of a reduction in the inherent difference in energy for the normally higher energy SP relative to the ground-state TBP expected for a "looser" structure implied for silicon with its greater charge dispersal as a result of the lower nuclear charge on silicon. Ab initio calculations performed on the TBP–SP energy difference between PF_5 and SiF_5^- support this conclusion showing a smaller energy difference for the anionic pentafluorosilicate compared to that for PF_5.[48]

The cyclic silicate $(CH_2)SiF_3^-$ also shows a lower barrier relative to the analogous phosphoranes, $(CH_2)_nPF_3$ (n = 4, 5). For the anionic silicate with the five-membered ring, ^{19}F NMR indicates that exchange is not stopped at −70 °C, whereas a low-temperature pattern results for the respective phosphorane[49] at this temperature consistent with "stopped" exchange. For the derivatives with the six-membered ring, the cyclic phosphorane shows no evidence for any exchange process by ^{19}F NMR[49] while the analogous silicate undergoes intramolecular exchange at room temperature and requires a reduction to −97 °C to sufficiently slow the process to see the limiting spectrum. Ring strain relief as suggested for the phosphoranes[49,50] appears to be the principal factor causing lower barriers for the five-membered silicate relative to the six-membered derivative. Ground state A of Figure 7 should be of higher energy for the five-membered ring compound. A reduction of ring strain in forming intermediate E of Figure 7b encountered during pseudorotation by this route[45] would cause a decrease in the exchange barrier, more so for the five-membered ring compared to the six-membered ring derivative.

NMR Parameters. Table XI summarizes the ^{19}F and ^{29}Si NMR parameters for the diorganodifluorosilanes[6,10,51-54] used in this study. They show discrete ranges in chemical shifts and coupling constants relative to those for the anionic silicates (Table VIII). These differences between the two series are presented in Table XII. Similar to those for the members of the tetrafluorosilicate series $RSiF_4^-$, the ^{19}F chemical shifts for the $R_2SiF_3^-$ derivatives move downfield upon pentacoordination opposite to the movement of the ^{29}Si chemical shifts upon increased coordination. Unlike the $RSiF_4^-$ series, where a steric effect was implied in the ordering, none is discernible here (Table VIII).

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Supplementary Material Available: Thermal parameters, additional bond lengths and angles, and hydrogen atom parameters for **1** (Tables S1–S3), for **2** (Tables S4–S6), and for **3** (Tables S7–S9) (12 pages); tables of calculated and observed structure factors (27 pages). Ordering information is given on any current masthead page.

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(48) Deiters, J. A.; Holmes, R. R. Unpublished work.

(49) Muetterties, E. L.; Mahler, W.; Schmutzler, R. *Inorg. Chem.* **1963**, *2*, 613.

(50) Cited in ref 32, pp 160–161.

(51) Dabbit, O.; Sutcliffe, L. H. *Org. Magn. Reson.* **1983**, *21*, 412.

(52) Laane, J. *J. Am. Chem. Soc.* **1967**, *89*, 1144.

(53) Auner, N.; Grobe, J. *Z. Anorg. Allg. Chem.* **1982**, *485*, 53.

(54) Marsmann, H. C. *Chem.-Ztg.* **1972**, *96*, 288.

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The First Polyhydrides Stabilized Only by N-Donor Ligands, $[\{HB(pz)_3\}ReH_6]$ and $[\{CH_2(pz)_2\}ReH_7]$

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$TpReH_6$ (**1**), $TpReH_4(PPh_3)$ (**2**), and $BpReH_7$ (**4**) (Tp = tris(pyrazolyl)borate; Bp = bis(pyrazolyl)methane) have been synthesized and characterized. The question of degradation-resistant ligands for use in transition-metal catalysts, especially for alkane conversion, is discussed; neither Tp nor Bp is found to be satisfactory in this respect. **1** and **4** are the first transition-metal polyhydride complexes stabilized only by N-donor ligands. Variable-temperature ^1H NMR T_1 data and isotope shifts of hydride resonances upon deuterium substitution indicate that all three complexes have classical structures without direct H–H bonds. These complexes show the shortest T_1's so far reported for classical polyhydrides, which may be ascribed to close nonbonding H···H contacts required by the high coordination number. **4** undergoes decoalescence of the hydride resonance on cooling, which is the first example for a nine-coordinate polyhydride. One hydride resonates at δ +3.14, a much lower field than is usual for hydrides.

Polyhydride complexes[1] are of current interest, particularly as alkane conversion catalysts[2] and as examples of molecular hydrogen complexes.[3-6] Polyhydrides of rhenium are particularly extensive and important.[1] Up to now, only three classes of po-

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lyhydrides $[L_nMH_x]$ ($x > 3$) have been described: (i) homoleptic hydrides, such as $[ReH_9]^{2-}$,[7] in which there are no L ligands, (ii) hydrides in which L is a 3° phosphine,[1] and (iii) hydrides in which L is a cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) group,[8-12] such as Herrmann and Okuda's Cp^*ReH_6.[8]

Only complexes of the second class, i.e., phosphine-supported polyhydrides, are common, but it is not clear why this should be so. As recently as 1985[1] it had seemed that the role of the ligand L was limited to (a) remaining tightly bound to prevent decomposition by M–H–M bridging between metals and (b) favoring the formation of strong M–H bonds. This second requirement ensures that the polyhydride is stable to reductive elimination of H_2 and helps explain why polyhydrides are so much more common with the third-row elements, where M–H bond strengths in general are high.

It has recently become clear that some polyhydrides have nonclassical structures in which dihydrogen ligands are present along with terminal hydrides. T_1 evidence for such a structure is strong for $RuH_2(H_2)(PPh_3)_3$,[4] but in the case of $[ReH_7(PPh_3)_2]$,[5] the averaging of the T_1 over seven sites rather than the four in the Ru species makes an unequivocal distinction difficult on the basis of T_1 data alone.

The existence of nonclassical polyhydrides means that a metal can form a polyhydride without having to form many strong M–H single bonds; it is sufficient that the $M-(\eta^2-H_2)$ binding energy be on the order of 30 kcal/mol for the complexes to be thermally stable, air-stable, and isolable species. This should be possible with only relatively modest back-donation from an $M(d_\pi)$ orbital to an $H-H(\sigma^*)$ orbital.

In attempts to prepare polyhydrides without phosphines or cyclopentadienyl groups, aromatic N-donor ligands seemed to provide the best coordination environment. We chose tris(pyrazolyl)borate (Tp) because many Tp complexes are known in cases where the analogous Cp complexes also exist.[13,14]

Degradation-Resistant Ligands

There was also a second reason for studying these complexes. Tertiary-phosphine-containing polyhydrides have proved to be effective alkane conversion catalysts,[2] but they rapidly deactivate in a number of ways under the relatively harsh conditions of typical alkane activation reactions, most notably via P--C bond hydrogenolysis.[15,16] An exception is Tanaka's[17] use of $[RhCl(CO)(PMe_3)_2]$ in alkane photodehydrogenation and related reactions. The development of a range of degradation-resistant ligands will probably be of importance in the future development of alkane conversion chemistry.[16]

With ligands such as 1-phosphaadamantane[18] or 1-phospha-3,5,7-triazaadamantane,[19] we have not observed alkane conversion.[20] We were attracted to tris(pyrazolyl)borate (Tp) because of its conformational rigidity and especially because Graham[21] has shown that $Tp^*Rh(CO)_2$ (Tp* = tris(3,5-dimethylpyrazolyl)borate) is active for stoichiometric photochemical activation of alkanes presumably via photoexpulsion of CO.

The existence of Cp^*ReH_6[8] suggested that $TpReH_6$ might also be stable, and so we made this our first objective.

Results and Discussion

$TpReH_6$ (1) and $TpReH_4(PPh_3)$ (2). A possible precursor to $TpReH_6$, the complex $TpReOCl_2$, is known.[22] We now find that treatment of $TpReOCl_2$ with $LiAlH_4$ (5 mol equiv) in THF at 25 °C followed by hydrolysis with H_2O in toluene at 0 °C gives the new polyhydride $TpReH_6$ (**1**, 40%, eq 1). The IR spectrum

$$TpReOCl_2 \xrightarrow{\text{(i) LiAlH}_4\text{, (ii) H}_2\text{O}} \underset{\mathbf{1}}{TpReH_6} \qquad (1)$$

shows both B–H (2492 cm^{-1} (s)) and Re–H vibrations (2111 (w), 2042 (w), 2021 cm^{-1} (s)). The ^1H NMR spectrum of **1** in CD_2Cl_2 at 298 K exhibits a singlet hydride resonance of intensity 6 at δ −2.67 (Figure 1). On cooling, the hydride resonance becomes somewhat broad ($\omega_{1/2}$ = 11 Hz at 185 K).

We previously developed a ^1H NMR T_1 method for the characterization of η^2-H_2 complexes.[3] The method is based on the fact that the dipole–dipole mechanism dominates the proton–proton relaxation in small diamagnetic molecules in which the protons are close together (<2 Å). By this mechanism, the relaxation rate increases with the inverse sixth power of the H···H distance. The H···H distance in an η^2-H_2 ligand is exceptionally short, and so the corresponding relaxation rate is very fast and gives rise to a very short T_1. Fluxional processes in polyhydrides are usually so fast that it is not possible to freeze out the fluxionality in ^1H NMR spectra and to measure directly the integrals and the T_1's of the different types of hydrides. However, in a fluxional nonclassical polyhydride containing one or more η^2-H_2 ligands, the average T_1 should be shorter than would be expected for a classical structure. The T_1 goes through a minimum as the temperature is lowered, and T_1(min), which scales with spectrometer field, is the best structural criterion.[4,5]

Variable-temperature T_1 measurements were carried out for the hydride resonance of **1**. The T_1 value is 63 ms at 200 K, and 250 MHz. We were not able to observe a T_1 minimum, no doubt as a result of the low moment of inertia of **1**.[5] Since we originally assigned a nonclassical structure[5] to ReH_7L_2 (L = PPh_3 and $^1/_2$ $Ph_2PCH_2CH_2PPh_2$) on the basis of T_1(min) values in the range 55–70 ms at 250 MHz, a nonclassical structure, $TpReH_4(\eta^2-H_2)$, might seem reasonable for **1**, but isotope shift data, described later, argue for a classical formulation both for **1** and for the phosphine polyhydrides, ReH_7L_2. In cases where there is strong evidence that H_2 ligands are present, such as $FeH_2(\eta^2-H_2)(PEt_2Ph)_3$ and $RuH_2(\eta^2-H_2)(PPh_3)_3$, T_1(min) values below 35 ms at 250 MHz are observed.[4,5]

Herrmann and Okuda[8] have described the closely related classical species Cp^*ReH_6, which contains one axial hydride and five equatorial hydrides in a C_{5v} structure, as suggested by the low-temperature-limiting ^1H NMR spectrum. T_1 measurements[5] on a sample kindly provided by Herrmann and Okuda have shown rather long T_1 values for the two hydride resonances (δ −5.04, sextet, axial Re–H, T_1 = 290 ms; δ −6.90, doublet, equatorial

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(1) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1.

(2) (a) Baudry, D.; Ephritikine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243. (b) Baudry, D.; Ephritikine, M.; Felkin, H.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1235. (c) Baudry, D.; Ephritikine, M.; Felkin, H.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 788. (d) Felkin, H.; Fillebeen-Khan, T.; Gault, Y.; Holmes-Smith, R.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, 1279. (e) Baudry, D.; Ephritikine, M.; Felkin, H.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, 1283.

(3) (a) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661. (b) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

(4) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3321.

(5) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 4126.

(6) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.

(7) Ginsberg, A. P. *Inorg. Chem.* **1964**, *3*, 567.

(8) Herrmann, W. A.; Okuda, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1092.

(9) Mayer, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 2157.

(10) Mayer, J. M.; Wolczanski, P. T.; Santarsiero, B. D.; Olsen, W. A.; Bercaw, J. E. *Inorg. Chem.* **1983**, *22*, 1149.

(11) Holmes, S. J.; Schrock, R. R. *Organometallics* **1983**, *2*, 1463.

(12) Gilbert, T. M.; Bergman, R. G. *Organometallics* **1983**, *2*, 1458.

(13) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988; p 112.

(14) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115–210.

(15) Burk, M. J.; Crabtree, R. H.; McGrath, D. V. *J. Chem. Soc., Chem. Commun.* **1985**, 1829. Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025.

(16) Garrou, P. *Chem. Rev.* **1985**, *85*, 171–86.

(17) Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1987**, 758.

(18) Meuwissen, H. J.; Van der Knapp, T. A.; Bickelhaupt, F. *Tetrahedron* **1983**, *39*, 4225–8.

(19) Daigle, D. J. U.S. Pat. Appl. 391189, Aug 24, 1973.

(20) Crabtree, R. H.; Uriarte, R. Unpublished results, 1981.

(21) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726–7.

(22) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125.

Re–H, T_1 = 618 ms in toluene-d_8 at 200 K and 250 MHz). A T_1(min) could not be obtained, and the moment of inertia is expected to be even lower than that for **1**. The data for Cp*ReH$_6$ are therefore not directly comparable to those for **1**, because the Cp* complex must be further from the T_1 minimum at comparable temperatures.

1 is relatively unreactive. It cannot be protonated by PhCH(SO$_2$CF$_3$)$_2$ and does not undergo H/D exchange with D$_2$ at 25 °C. It also fails to undergo substitution reaction with PPh$_3$ even in refluxing toluene. The expected substitution product, TpRe(PPh$_3$)H$_4$ (**2**), is stable and can be prepared by treatment of the known TpReCl$_2$(PPh$_3$)[22] with LiAlH$_4$ (eq 2).

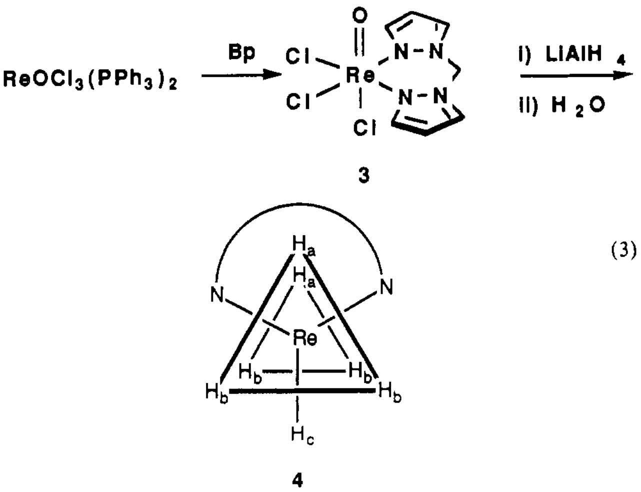
$$\mathrm{TpReOCl_2} \xrightarrow{\mathrm{PPh_3}} \mathrm{TpReCl_2(PPh_3)} \xrightarrow{\mathrm{LiAlH_4}} \underset{\mathbf{2}}{\mathrm{TpRe(PPh_3)H_4}} \quad (2)$$

The ^{1}H NMR spectrum of **2** in CD$_2$Cl$_2$ at 298 K shows a doublet hydride resonance of intensity 4 at δ –4.48 (J_{HP} = 27.2 Hz, Figure 2). No change in the spectrum was apparent upon cooling the sample to 193 K. The selectively hydride-coupled ^{31}P NMR spectrum displays a binomial quintet at δ 4.6 (J_{HP} = 26.6 Hz), which also demonstrates the presence of four hydride ligands.

The ^{1}H NMR T_1(min) value of the hydride resonance of **2** is low, 55 ms at 220 K in toluene-d_8 at 250 MHz. We believe that close nonbonding H···H contacts in this eight-coordinate structure may be responsible for the short T_1. Only terminal ν_{Re-H} stretching frequencies are clearly apparent in the IR spectrum at 2060 (w), 2026 (w), and 2000 cm^{-1} (s). Isotope shift data, discussed later, again provide key evidence for a classical structure.

BpReH$_7$ (4). Our success in the synthesis of **1** suggested that other N-supported polyhydrides might also be accessible. Since ReH$_7$(PPh$_3$)$_2$ is an effective alkane conversion catalyst,[2] we looked for N-donor ligands that might give analogous complexes. Bis(pyrazolyl)methane (Bp) seemed most suitable. It also has the advantage of containing the less labile C–H and C–N bonds in place of the B–H and B–N bonds of Tp.

Bp complexes of rhenium suitable for use as precursors are not available, and so we were forced to investigate synthetic routes to possible halide and oxohalide complexes. We found that the readily available ReOCl$_3$(PPh$_3$)$_2$[23] reacts with Bp in refluxing toluene over 5 min to give a new blue-green compound, which is probably BpReOCl$_3$ (**3**), in quantitative yield. It can only be recrystallized from DMSO, the only common organic solvent in which it is soluble, and we were never able to obtain an analytically pure sample. The IR band at 973 cm^{-1} is assigned to the Re=O vibration, and ^{1}H NMR resonances at δ 6.98, 8.65, and 8.72 are assigned to the pyrazolyl ring protons. Each of the two methylene protons resonates separately at δ 6.93 and 7.32, with a $J_{HH'}$ of 15 Hz appropriate for geminal HH′ coupling. This suggests that the complex adopts the stereochemistry shown in eq 2, in which the two faces of the ligand are inequivalent. A similar structure has been reported for [ReOCl$_3$(PEt$_3$)$_2$].[24]

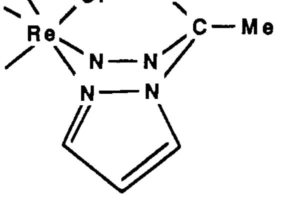


3

(3)

4

In attempts to prepare analogues that might be more tractable, we found that species of the type ReOCl$_3$L$_2$ could only be obtained for MeCH(pz)$_2$ and not Me$_2$C(pz)$_2$. Possibly these compounds all adopt a boat conformation, as found in a recent crystallographic study.[25] Stable species may only be obtained when the bridgehead carbon carries at least one H, which may occupy the axial position to avoid destabilizing 1,3-diaxial repulsion between Re–*Cl* and C–*Me*, as would be inevitable for the 2,2-bis(pyrazolyl)propane, as shown in the following diagram:



The polyhydride BpReH$_7$ (**4**) was prepared in low, but reproducible, yield (8%) by treatment of the blue-green material, obtained above, with LiAlH$_4$ in THF, followed by hydrolysis. The ^{1}H NMR spectrum of this heptahydride shows a resonance at δ –2.52 of intensity 7. On cooling, this resonance broadens and decoalesces into two broad resonances at 178 K, one at δ +3.14 and the other at δ –5.00, integrating for ca. 2 and 5 protons, respectively. The integration is confirmed by the fact that a ratio of 2:5 is the only set that can give a weighted average chemical shift consistent with that of the room-temperature hydride resonance.

Decoalescence of the resonance with the two peaks having a 2:5 intensity ratio at first sight suggests a nonclassical structure, i.e., BpReH$_5$(η^2-H$_2$). However, a 2:5 ratio is also expected for the nine-coordinate tricapped trigonal-prismatic structure shown in eq 2 if the H$_b$ and H$_c$ hydrides exchange with each other but not with H$_a$ hydrides. The alternate structure with Bp nitrogens occupying eclipsed axial positions would also account for the 2:5 ratio.

The T_1 minimum of **4** was not observed, no doubt because of the low moment of inertia of the molecule. The T_1 values for both hydride resonances are 75 ms at the lowest accessible temperature, 178 K. This does not mean that the two sites have the same intrinsic T_1 because an exchange rate that is insufficiently rapid to cause coalescence can still be fast enough to make the T_1 values the same. As discussed more fully elsewhere,[5] in the case of a fluxional complex, the short T_1 of the nonclassical site tends to lower the observed T_1 of the classical site if exchange is fast relative to the T_1 of the classical site.

4 did not undergo H/D exchange with D$_2$ and failed to react with PPh$_3$ in refluxing toluene. The protonation of **4** in CD$_2$Cl$_2$ with PhCH(SO$_2$CF$_3$)$_2$ resulted in hydrogen evolution, but we were unable to characterize the product.

Isotope Shifts in ^{1}H NMR Hydride Resonances

The structures of **1**, **2**, and **4** were still unresolved, and so we turned to the IPR (isotopic perturbation of resonance) method. First developed by Saunders,[26] the IPR technique has been successfully used for the study of agostic M···H–C interactions,[27] a

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(23) (a) Chatt, J.; Rowe, G. A. *J. Chem. Soc.* **1962**, 4019. (b) Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *Inorg. Synth.* **1967**, *9*, 145.

(24) Fergusson, J. E.; Heveldt, P. F. *J. Inorg. Nucl. Chem.* **1976**, *38*, 223.

(25) Jansen, J. C.; van Konigsveld, H.; van Ooijen, J. A. C.; Reedijk, J. *Inorg. Chem.* **1980**, *19*, 170.

(26) (a) Saunders, M.; Jaffe, M. H.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2558. (b) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070.

(27) (a) Calvert, B. R.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (c) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. *J. Chem. Soc., Chem. Commun.* **1981**, 506. (d) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134. (e) Dawkins, G. M.; Green, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 41. (f) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117.

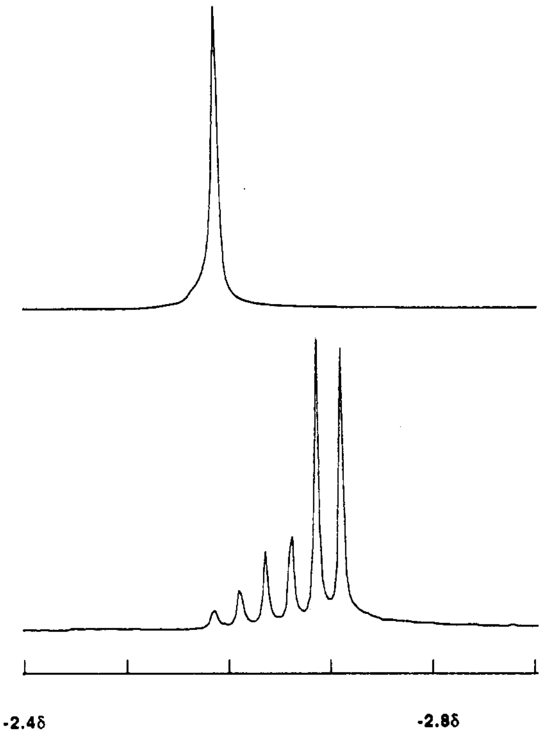

Figure 1. Hydride region of the ^1H NMR spectrum of $TpReH_6$ (upper trace) and $TpReH_{6-x}D_x$ (lower trace), showing the secondary isotope effect. The data were recorded in CD_2Cl_2 at 298 K.

situation very similar to the one studied here. The method is based on the isotopic fractionation between different sites due to the difference in zero-point energies.

If an isotopomer mixture, i.e., $ReH_xD_yL_z$, of a fluxional classical polyhydride with all terminal M–H bonds is examined by ^1H NMR, the isotope shift of per D substitution of the hydride resonance should be small.[28] On the other hand, for a nonclassical polyhydride containing both terminal hydrides and one or more η^2-H_2 ligands, the different zero-point energies of Re–H versus Re–D and of Re(H–H) versus Re(H–D) bonds ($\Delta\Delta E$) should lead to an isotopic fractionation between the different types of sites. If these sites have different chemical shifts ($\Delta\delta$), each isotopomer should show a distinctive hydride resonance in the fast-exchange-limiting ^1H NMR spectrum. The isotope shifts upon successive deuteration are not expected[26,27] to be the same [i.e., $\{\delta(ReH_7) - \delta(ReH_6D) \neq \delta(ReH_6D) - \delta(ReH_5D_2)\}$]. In addition, a true IPR shift should show a strong temperature dependence as a result of the Boltzmann equilibrium operating on the isotopic fractionation between the two sites. Both the chemical shift difference, $\Delta\delta$, and the isotopic fractionation between the two sites, measured by $\Delta\Delta E$, have to be nonzero for a significant IPR effect to be seen. Experimentally, there is little or no IPR for any Re polyhydride we have examined, but the chemical shift difference, $\Delta\delta$, of the two sites might be close to zero, although the isotopic fractionation, $\Delta\Delta E$, is unlikely to be zero.

The importance of $BpReH_7$ (**4**) is that it is the first rhenium heptahydride in which the decoalescence of the hydride resonance has been observed. If the complex is nonclassical with the hydride resonance at δ 3.14 assigned to Re(η^2-H_2) and the other at δ –5.00 assigned to the five classical hydrides, the chemical shift difference between the classical Re–H sites and the nonclassical sites is therefore known and equal to 8.14 ppm. This large number means that a very substantial IPR shift should be observed. Experimentally, we find a very small isotope shift (<0.002 ppm) at 298 K. We are therefore forced to conclude that **4** is classical.

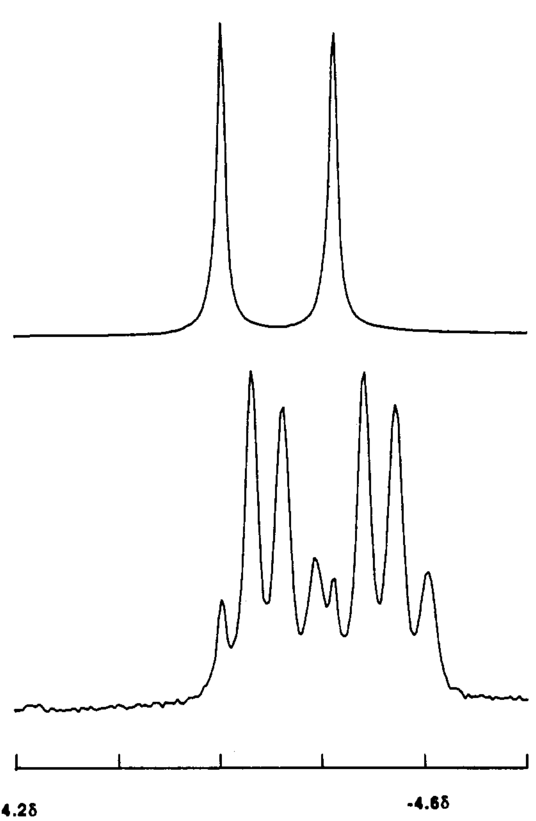

Figure 2. Hydride region of the ^1H NMR spectrum of $TpReH_4(PPh_3)$ (upper trace) and $TpReH_{4-x}D_x(PPh_3)$ (lower trace), showing the secondary isotope effect. J_{PH} remains the same for each isotopomer. The data were recorded in CD_2Cl_2 at 298 K.

In view of these results, Luo and Crabtree[29] have made several new complexes of the ReH_7L_2 type and have found that the hydride resonance of ReH_7(dppb) (dppb = 1,4-bis(diphenylphosphino)butane) also decoalesces at low temperature into two separate resonances in a ratio of 2:5. The T_1 of the intensity 2 site is longer than that of the other resonance, which is inconsistent with a nonclassical structure. They have also found that isotope shifts are very small for this and other complexes of the ReH_7L_2 type. These complexes are therefore probably also classical. We will defer a detailed discussion of how a classical hydride comes to have so short a T_1 to the paper[29] that reports the results for the rhenium phosphine heptahydrides, but it appears to be the nine-coordination of ReH_7L_2 that leads to the presence of several relatively short H···H contacts in the molecule.

An interesting feature of **4** is the position of the low-field hydride resonance. In almost all previous cases, hydride resonances have been found upfield from TMS. The appearance of a hydride resonance at such a low field in **4** emphasizes the relatively inefficient shielding of hydride protons by a d^0 metal, possibly also accentuated by the anisotropic effects of the aromatic ring currents in the Bp ligand.

The hydride region of the ^1H NMR spectrum of a isotopomeric mixture of $TpReH_6$ (**1**) in CD_2Cl_2 at 298 K, shown in Figure 1, displays six distinct, equally spaced hydride resonances assignable to $TpReH_{6-x}D_x$ (x = 0–5) and separated by an upfield isotope shift of –0.025 ppm/D. The isotope shift increases as the temperature is lowered, but even at 203 K, it is only –0.035 ppm/D. At each temperature the lines remain equally spaced and the shift is small, unlike the situation for a true IPR. The observed isotope shifts are probably normal geminal deuterium isotope effects. These usually give rise to upfield isotope shifts of –0.01 to –0.03 ppm/D for geminal substitution of H by D in second-row main-group elements.[30a–f] Although there has been little study of the

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[28] No data on isotope shifts of hydride resonances of polyhydrides have been reported in the literature. A very small and temperature-independent isotope shift (ca. 0.01 ppm/D)[29] was observed for $ReH_7(PPh_3)_2$.[5] In six-coordinate complexes containing two or three hydride ligands, the isotope shift for H cis to D is less than 0.02 ppm, while the value for H trans to D can be as large as 0.05–0.1 ppm[30,31] as a result of the relatively large differential isotopic trans effects of H and D.[32]

[29] Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.*, in press.

temperature dependence of the ^{1}H NMR isotope shifts in the literature, Brey et al.[30i] have observed larger ^{19}F NMR isotope shifts due to chlorine isotope (^{37}Cl and ^{35}Cl) as well as carbon isotope substitution (^{13}C and ^{12}C) at low temperature. Thus, our observation of the temperature dependence of the isotope shift of **1** does not necessarily mean that the isotope shift originates from the temperature-dependent isotopic fractionation between classical and nonclassical sites. In conclusion, **1** is a classical polyhydride based on the isotope shift data.

As shown in Figure 2, four separate and equally spaced doublet hydride resonances, assignable to $TpReH_{4-x}D_x(PPh_3)$ (x = 0–3), are present in the hydride region of the ^{1}H NMR spectrum of the isotopomeric mixture. As in the case of **1**, we see a small isotope shift, which is linearly temperature dependent, ranging from −0.030 ppm/D at 298 K to −0.047 ppm/D at 203 K. Here we can also measure the $^2J_{HP}$ values associated with each isotopomer. If we were dealing with a nonclassical hydride, the $^2J_{HP}$ values for the Re(η^2-H$_2$) sites would be much smaller than those for the Re–H sites, on the basis of literature data showing low $^2J_{HP}$ couplings to H_2 ligands.[6] This would mean that an isotopic perturbation of the coupling constant would be observed and each isotopomer would show a different $^2J_{HP}$ in the fast-exchange-limiting spectrum. In fact, the coupling constants for all the isotopomers are the same within experimental error in the whole temperature range we studied. The small upfield isotope shift of **2** is unlikely to arise from an isotopic fractionation between Re(η^2-H$_2$) and Re–H sites but can be ascribed to the geminal isotope effect. The data are therefore consistent with a classical structure for **2**.

Fast T_1 Relaxation in Classical Hydrides

We observe T_1 values in the range 55–80 ms at 250 MHz for the N- and P-donor classical polyhydrides, $TpReH_6$, $TpReH_4(PPh_3)$, and ReH_7L_2 (L = PPh_3, $^1/_2$ dppb, $^1/_2$ Bp). Values in this range cannot therefore be automatically associated with a nonclassical structure as we had previously assumed.[4,5]

On the other hand, literature reports of T_1 data must be interpreted critically. The very short T_1 values in the range 60–90 ms measured by Bordignon et al.[31] for classical hydrides cannot be directly compared with the above data, because Bordignon et al. obtained their data at 80 MHz. Assuming that their values refer to the minimum, these numbers translate to a range of 190–270 ms at 250 MHz. To the extent that the observed T_1 was greater than T_1(min), the range cited for 250 MHz would move to shorter T_1 values. We will discuss the problems of interpretation of T_1 data in more detail in a future paper.[29]

Attempts To Observe Alkane Conversion

We tried **1** and **4** as catalysts for cyclooctane dehydrogenation with t-BuCH=CH$_2$ as hydrogen acceptor at 70–110 °C but were not successful. It seems likely that the Tp ligand is too fagile; loss of pyrazole takes place at ca. 100 °C and below the temperature necessary for reaction with the alkane. The Bp ligand seems to be more stable to decomposition, but the complex was still inactive. Possibly, any open sites generated by H_2 loss are blocked by formation of Re–H–Re bridges, although we were unable to characterize any of the products of thermolysis. Perhaps we need ligands that are somewhat more bulky in the region of space removed from the metal to prevent oligomerization, while leaving the immediate coordination sphere of the metal unhindered for approach and activation of the alkane.

Conclusion

We have prepared and characterized the unusual rhenium polyhydrides $TpReH_6$ (**1**), $TpReH_4(PPh_3)$ (**2**), and $BpReH_7$ (**4**). **1** and **4** are the first such species supported only by N-donor ligands, and **4** is the first nine-coordinate polyhydride in which the hydride ^{1}H NMR signal has been found to undergo decoalescence on cooling. The isotope effects of deuterium substitution on the hydride chemical shift and on J_{HP} have led us to propose that **1**, **2**, and **4** are all classical polyhydrides. The observed short T_1's probably arise from close nonbonding H···H contacts as a result of the high coordination number. Tp and Bp do not seem to be satisfactory as degradation-resistant ligands.

Experimental Section

Bis(pyrazolyl)methanes were obtained by the literature method from potassium pyrazolate and the appropriate 1,1-diiodide in THF followed by sublimation.[32] Other materials were purchased from Aldrich Chemical Co. Reactions were carried out under a dry N_2 atmosphere by standard Schlenk techniques.

Microanalyses were carried out by Desert Analytic Co. ^{1}H NMR Spectra were recorded on a Bruker WM 250 spectrometer; chemical shifts were measured with reference to the residual solvent resonance. ^{31}P NMR spectra were recorded on a Bruker WM 500 spectrometer; chemical shifts were measured with reference to external 85% H_3PO_4. IR spectra were recorded on a Nicolet 5-SX FT-IR instrument.

(Tris(pyrazolyl)borato)hexahydridorhenium(VII) (1). To a solution of $TpReOCl_2$[22] (700 mg, 1.44 mmol) in thf (25 mL) at 25 °C was added $LiAlH_4$ (266 mg, 7 mmol) with stirring under Ar at 25 °C. After 2 h, the solvent was removed in vacuo, and the light yellow residue was suspended in toluene (15 mL). Hydrolysis by slow addition of degassed H_2O (0.5 mL) at 0 °C led to the formation of the title polyhydride, which was isolated as a colorless powder by evaporation of the toluene, extraction of the residue with CH_2Cl_2 (3 × 5 mL), and evaporation of the CH_2Cl_2 solution leading to recrystallization. Traces of grease were removed with $CFCl_3$ (5 mL) to give the analytically pure material. Yield: 241 mg, 41%. Anal. Calcd for $C_9H_{16}BN_6Re$: C, 26.67; H, 3.95; N, 20.74. Found: C, 26.80; H, 4.00; N, 20.85. ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.81 (d, J_{HH} = 2.5 Hz, 3 H, pz), 7.67 (d, J_{HH} = 2.5 Hz, 3 H, pz), 6.21 (t, J_{HH} = 2.5 Hz, 3 H, pz, 4-proton), −2.59 (s, 6 H, Re–H, T_1 = 63 ms, 200 K, 250 MHz). IR (Nujol): ν_{Re-H} 2111 (w), 2042 (w), 2021 cm^{-1} (s); ν_{B-H} 2492 cm^{-1} (s).

(Tris(pyrazolyl)borato)tetrahydrido(triphenylphosphine)rhenium(V) (2). To a red-orange solution of $TpRe(PPh_3)Cl_2$[22] (260 mg, 0.35 mmol) in thf (25 mL) at 25 °C was added $LiAlH_4$ (3 mL of 1 M solution in thf). After 2 h, the solvent was removed in vacuo, and the dark red residue was suspended in toluene (15 mL). Hydrolysis as above led to the formation of the title polyhydride, which was isolated as a yellow powder by evaporation of the toluene, extraction of the residue with CH_2Cl_2 (10 mL) followed by filtration through Celite, reduction of the volume of the CH_2Cl_2 solution to 2 mL, and precipitation of the analytically pure material by adding Et_2O (15 mL). Yield: 101 mg, 43%. Anal. Calcd for $C_{27}H_{28}BN_6PRe$: C, 48.80; H, 4.24; N, 12.64. Found: C, 48.79; H, 4.45; N, 12.25. ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.56 (d, J_{HH} = 2.2 Hz, 3 H, pz), 7.2–7.4 (c, 15 H, Ph), 7.15 (d, J_{HH} = 2.2 Hz, 3 H, pz), 5.91 (t, J_{HH} = 2.2 Hz, 3 H, pz, 4-proton), −4.48 (d, J_{PH} = 27 Hz, 4 H, Re–H). Selectively hydride-coupled ^{31}P NMR (CD_2Cl_2, 298 K): δ 4.6 (quintet, J_{HP} = 26.6 Hz). IR (Nujol): ν_{Re-H} 2060 (w), 2026 (w), 2000 cm^{-1} (s); ν_{B-H} 2454 cm^{-1} (s).

(Bis(pyrazolyl)methane)oxotrichlororhenium(V) (3). $ReOCl_3(PPh_3)_2$ (2 g, 2.41 mmol) and bis(pyrazolyl)methane (1.3 g, 8.8 mmol) were stirred in toluene (50 mL) for 5 min. The title complex was filtered off and washed with toluene (5 × 10 mL) and Et_2O (2 × 10 mL). Yield: 1.09 g, 95%. Recrystallization of the product may be carried out from DMSO (5 mL) by adding CH_2Cl_2 (40 mL). ^{1}H NMR (DMSO-d_6, 298 K): δ 8.72 (d, J_{HH} = 2.2 Hz, 2 H, pz), 8.65 (d, J_{HH} = 2.2 Hz, 2 H, pz), 7.32 (d, J_{HH} = 15.0 Hz, 1 H, CH_2), 6.98 (t, J_{HH} = 2.2 Hz, 2 H, pz, 4-proton), 6.93 (d, J_{HH} = 15.0 Hz, 1 H, CH_2). IR (Nujol): ν_{Re-O} 973 cm^{-1}. The analogous 1,1-bis(pyrazolyl)ethane complex was obtained in similar yield by substituting $MeCH(pz)_2$ in the above preparation. Two isomers in a 3:1 ratio were obtained, as judged by ^{1}H NMR spectroscopy. After recrystallization from DMSO as described above, only the major isomer remained. ^{1}H NMR (DMSO-d_6, 298 K): δ 9.02 (d, J_{HH} = 2.7 Hz, 2 H, pz), 8.83 (d, J_{HH} = 2.7 Hz, 2 H pz), 7.28 (q, J_{HH} = 6.3 Hz, 1 H, CH), 7.06 (t, J_{HH} = 2.7 Hz, 2 H, pz), 2.07 (d, J_{HH} = 6.3 Hz, 3 H, CH_3). The complexes were never obtained in analytically pure form.

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(30) (a) Tiers, G. V. D. *J. Chem. Phys.* **1958**, *29*, 963. (b) Gutowsky, H. S. *J. Chem. Phys.* **1959**, *31*, 1683. (c) Saunders, M.; Plostnieks, P. S.; Wharton, P. S.; Wasserman, H. H. *J. Chem. Phys.* **1960**, *32*, 317. (d) Bernheim, R. A.; Batiz-Hernandez, H. *J. Chem. Phys.* **1964**, *40*, 3446. (e) Bernheim, R. A.; Lavery, B. J. *J. Chem. Phys.* **1965**, *42*, 1464. (f) Bernheim, R. A. *J. Chem. Phys.* **1966**, *45*, 2261. (g) Batiz-Hernandez, H.; Bernheim, R. A. *Prog. Nucl. Magn. Reson. Spectrosc.* **1967**, *3*, 63. (h) Lambert, J. B.; Greifenstein, L. G. *J. Am. Chem. Soc.* **1974**, *96*, 5120. (i) Brey, W. S.; Ladner, K. H.; Block, R. E.; Tallon, W. A. *J. Magn. Reson.* **1972**, *8*, 406.

(31) Antoniutti, B.; Albertin, G.; Amendola, P.; Bordignon, E. *J. Chem. Soc., Chem. Commun.* **1989**, 229.

(32) Claramunt, R. M.; Hernandez, H.; Elguero, S.; Julia, S. *Bull. Soc. Chim. Fr.* **1983**, 5.

(Bis(pyrazolyl)methane)heptahydridorhenium(VII) (4). To a suspension of $BpReOCl_3$ (1.09 g, 3 mmol) in thf (30 mL) at 25 °C was added $LiAlH_4$ (900 mg, 24 mmol). After 2 h, the solvent was removed in vacuo, and the light yellow residue was suspended in toluene (30 mL). Hydrolysis by slow addition of water (0.5 mL) at 0 °C led to the formation of the title complex (**4**), which was isolated by evaporation of the toluene, extraction of the residue with CH_2Cl_2, reduction of the volume of the CH_2Cl_2 solution, and precipitation of the analytically pure material with diethyl ether. Yield: 83 mg, 8%. Anal. Calcd for $C_7H_{15}N_6N_4Re$: C, 24.61; H, 4.40; N, 16.41. Found: C, 24.87; H, 4.38; N, 16.26. ^1H NMR (CD_2Cl_2, 298 K): δ 8.00 (d, $J_{HH} = 2.3$ Hz, 2 H, pz), 7.73 (d, $J_{HH} = 2.3$ Hz, 2 H, pz), 6.49 (s, 2 H, CH_2), 6.35 (t, $J_{HH} = 2.3$ Hz, 2 H, pz, 4-proton), −2.52 (s, 7 H, Re–H). ^1H NMR (CD_2Cl_2/CF_3Cl, 178 K): δ 7.90 (br s, 2 H, pz), 7.60 (br s, 2 H, pz), 6.33 (s, 2 H, CH_2), 6.35 (br s, 2 H, pz, 4-proton), 3.14 (br s, 2 H, Re–H, $T_1 = 75$ ms), −5.00 (br s, 5 H, Re–H, $T_1 = 75$ ms). IR (Nujol): ν_{Re-H} 2128 (m), 2024 (m), 2000 (s), 1922 cm^{-1} (w).

T_1 and Isotope Shift Measurements

T_1 measurements were made as described in ref 5, at 250 MHz in CD_2Cl_2 at 200 K. T_1 minima were not observed for either **1** or **4** in the accessible temperature range.

The isotopomeric mixtures of **1**, **2**, and **4** were prepared by treatment of the corresponding precursors with $LiAlH_4/LiAlD_4$ (1:4 molar ratio) followed by hydrolysis with H_2O/D_2O (1:4 molar ratio). The isotope shifts, defined as $\Delta\delta = \delta_{ReH_{x-1}D_{y+1}L_z} - \delta_{ReH_xD_yL_z}$, are reported as follows: temperature (K), isotope shifts (in ppm/D and in Hz/D at 250 MHz). No isotope effect (<0.002 ppm/D) could be observed for **4**.

1: 298, −0.0247, −6.18; 293, −0.0253, −6.32; 283, −0.0265, −6.62; 273, −0.0271, −6.77; 263, −0.0282, −7.06; 253, −0.0294, −7.35; 2438 −0.0303, −7.54; 233, −0.0311, −7.79; 223, −0.0323, −8.09; 213, −0.0338, −8.46; 203, −0.0353, −8.82. **2**: 298, −0.0304, −7.72; 283, −0.0323, −8.09; 273, −0.0341, −8.53; 263, −0.0360, −9.01; 253, −0.0379, −9.53; 243, −0.0397, −10.00; 233, −0.0416, 10.48; 223, −0.0434, −10.88; 213, −0.0453, −11.33; 203, −0.0470, −11.76.

Attempts To Observe Alkane Conversion

Alkane activation experiments with **1** and **4** were performed as described in ref 15, with cyclooctane as substrate and solvent and *t*-$BuCH{=}CH_2$ as hydrogen acceptor at 25, 80, and 130 °C in a sealed glass vessel. No cyclooctene was detected, and decomposition of the complexes occurred at 130 °C, forming black precipitates.

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Reactions of the Dirhenium(II) Complexes $Re_2Cl_4(PR_3)_4$ with Lithium Aluminum Hydride. A Convenient Synthetic Route to the Dirhenium Octahydride Complexes $Re_2H_8(PR_3)_4$

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A general synthetic method has been developed for the preparation of dirhenium octahydride complexes of the type $Re_2H_8(PR_3)_4$ that is adaptable to PR_3 being a trialkylphosphine, a mixed alkylarylphosphine, or a bidentate phosphine; i.e., PR_3 = PMe_3, PEt_3, P-*n*-Pr_3, PMe_2Ph, PEt_2Ph, $PMePh_2$, $Ph_2PCH_2PPh_2$ (dppm), or $Ph_2PCH_2CH_2PPh_2$ (dppe). This procedure involves the reaction of the triply bonded species $Re_2Cl_4(PR_3)_4$ with $LiAlH_4$ in glyme (or THF) at room temperature, followed by hydrolysis of the reaction mixture. These reactions probably proceed by a mechanism that involves the retention of the dirhenium unit throughout. The formation of the mononuclear heptahydride complexes $ReH_7(PR_3)_2$ as byproducts in some of these reactions can be attributed to the further reaction of $LiAlH_4$ with $Re_2H_8(PR_3)_4$ with resulting disruption of the dimetal unit. In the case of the PMe_3 complex, this is a convenient method for preparing $ReH_7(PMe_3)_2$. The crystal structure and NMR spectral properties of the dppm derivative are consistent with the structure $Re_2(\mu\text{-}H)_2H_6(\mu\text{-dppm})_2$, rather than $Re_2(\mu\text{-}H)_4H_4(\mu\text{-dppm})_2$. The complex of stoichiometry $Re_2H_8(dppm)_2$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.962$ (3) Å, $b = 12.002$ (8) Å, $c = 14.979$ (4) Å, $\beta = 112.30$ (2)°, $V = 2156$ (3) Å^3, and $Z = 2$. The structure, which was refined to $R = 0.048$ ($R_w = 0.057$) for 2470 data with $I > 3.0\sigma(I)$, reveals an unexpectedly long Re–Re bond (2.933 (1) Å) and a P–Re–P angle (164.1 (1)°) much larger than is observed in structurally characterized derivatives with monodentate phosphines. The complex $Re_2H_8(dppe)_2$ probably contains chelating phosphine ligands but is otherwise closely related structurally to the complexes that contain monodentate phosphines.

Introduction

The syntheses of the dirhenium octahydride complexes $Re_2H_8(PR_3)_4$ (PR_3 = PEt_2Ph or PPh_3) were first reported by Chatt and Coffey in 1969,[1] and the diethylphenylphosphine derivative was structurally characterized as $Re_2(\mu\text{-}H)_4H_4(PEt_2Ph)_4$ by Bau et al.[2] in 1977. Since that time, a few additional derivatives of this type have been prepared, most notably $Re_2H_8(PMe_2Ph)_4$,[3] but no uniform synthetic strategy has been developed. The original Chatt and Coffey procedure,[1] namely the thermal decomposition of the corresponding mononuclear heptahydride complexes $ReH_7(PR_3)_2$, requires that these heptahydride starting materials be available and that they not be thermally resistant to loss of H_2 and dimerization, a condition that is not always met.[4] Several other reactions have been described in which dirhenium octahydride complexes are formed: (1) the reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ or $Re_2Cl_6(PPh_3)_2$ with $NaBH_4$ and PPh_3 in ethanol to give $Re_2H_8(PPh_3)_4$;[5,6] (2) the photolysis of $ReH_5(PR_3)_3$ or $ReH_7(PR_3)_2$ (PR_3 = PPh_3, $PMePh_2$, or PMe_2Ph) to give $Re_2H_8(PR_3)_4$, along with several other products;[7,8] (3) the chemical oxidation of $K[ReH_6(PMePh_2)_2]$ to form $Re_2H_8(PMePh_2)_4$;[9] (4)

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(1) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963.

(2) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

(3) The complex $Re_2H_8(PMe_2Ph)_4$ has been extensively studied by Professor K. G. Caulton and his group. It is prepared via the Chatt and Coffey method, which involves the thermolysis of $ReH_7(PMe_2Ph)_2$. See: Green, M. A. Ph.D. Thesis, Indiana University, 1982.

(4) An interesting example is the thermal stability of $ReH_7[P(C_6H_{11})_3]_2$: Zeiher, E. H. K.; DeWit, D. G.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 7006.

(5) Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2674.

(6) Cameron, C. J.; Moehring, G. A.; Walton, R. A. *Inorg. Synth.*, in press.

(7) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695.

(8) Roberts, D. A.; Geoffroy, G. L. *J. Organomet. Chem.* **1981**, *214*, 221.

(9) Bruno, J. W.; Caulton, K. G. *J. Organomet. Chem.* **1986**, *315*, C13.

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