

# Separating the Re-H and H-H Dipole-Dipole Contributions to the $^1\text{H}$ NMR Spin-Lattice Relaxation Rate of the Hydride Ligand in *mer,trans*- $\text{ReH}(\text{CO})_3(\text{PPh}_3)_2$ by Deuteration

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The reaction of *mer,trans*- $\text{ReCl}(\text{CO})_3(\text{PPh}_3)_2$  with  $\text{LiAlH}_4$  in THF at room temperature gives *mer,trans*- $\text{ReH}(\text{CO})_3(\text{PPh}_3)_2$  (**1**). The temperature dependence of the  $^1\text{H}$  NMR spin-lattice ( $T_1$ ) relaxation rate of the hydride resonance of **1** is studied to try to understand the excess  $T_1$  relaxation often found for rhenium hydride complexes. Our previous assumption that the dipole-dipole relaxation mechanism is dominant is confirmed. Two main dipole-dipole contributions are identified. One is from the usual proton-proton dipole-dipole (HHDD) relaxation between the hydride ligand and the protons of the phosphine ligands, and the other from the rhenium-hydride dipole-dipole (ReHDD) relaxation. The two contributions can be separated by studying *mer,trans*- $\text{ReH}(\text{CO})_3(\text{PPh}_3-d_{15})_2$  (**1-d<sub>30</sub>**). The two components come to a minimum  $T_1$  value at different temperatures. The  $T_1(\text{min})$  value observed for the ReHDD relaxation in **1-d<sub>30</sub>** is consistent with an Re-H bond distance of 1.75 Å, which is in satisfactory agreement with those determined by neutron diffraction studies on other rhenium hydride complexes.

## Introduction

Interest in the synthesis and characterization of transition-metal hydride complexes has greatly increased as the result of the discovery of nonclassical dihydrogen ( $\eta^2\text{-H}_2$ ) complexes.<sup>1</sup> The difficulty of obtaining neutron diffraction data has made NMR spectroscopy the most common method of characterization. We previously suggested a solution  $^1\text{H}$  NMR spin-lattice ( $T_1$ ) relaxation method for distinguishing classical from nonclassical hydride complexes.<sup>2</sup> The method is based on the fact that proton-proton dipole-dipole (HHDD) interactions dominate  $T_1$  relaxation in small diamagnetic molecules in which the protons are close together (<2 Å). By this mechanism, the relaxation rate,  $T_1^{-1}$ , increases with the inverse sixth power of the H-H distance. A short H-H distance, such as is present in an  $\eta^2\text{-H}_2$  complex, leads to a short  $T_1(\text{min})$  value.

Work by Morris et al.<sup>3</sup> and ourselves<sup>1c,4,5a</sup> has shown that where the structural and  $T_1(\text{min})$  data are both available, the  $T_1(\text{min})$  data can in most cases be quantitatively interpreted by summing the HHDD interactions from all H-H vectors in the molecule. In some other cases, many of which involve rhenium hydride complexes, somewhat faster relaxation rates have been observed than predicted from the HHDD mechanism.<sup>5-7</sup> Several explanations have been suggested, including metal-hydride dipole-dipole (MHDD) relaxation and scalar relaxation,<sup>6</sup> but these have not yet been thoroughly tested by experiment.

**Table I.** Variable-Temperature  $^1\text{H}$  NMR  $T_1$  Data for the Hydride Resonances of *mer,trans*- $\text{ReH}(\text{CO})_3(\text{PPh}_3)_2$  (**1**) and *mer,trans*- $\text{ReH}(\text{CO})_3(\text{PPh}_3-d_{15})_2$  (**1-d<sub>30</sub>**) in  $\text{CD}_2\text{Cl}_2$  at 250 MHz

temp, K	$T_1$ , ms		$T_1(\text{HHDD}),^a$ ms
	<b>1</b>	<b>1-d<sub>30</sub></b>	
298	712	1210	1730
268	441	803	978
248	317	636	632
228	222	441	447
208	177	311	411
198	177	290	454
188	196	281	648
178	245	336	905

<sup>a</sup>The  $T_1(\text{HHDD})$  values are calculated from eq 1 by subtracting the relaxation rates for **1-d<sub>30</sub>** from those for **1**:  $1/T_1(\text{HHDD}) = 1/T_1(\mathbf{1}) - 1/T_1(\mathbf{1-d}_{30})$ .

Farrar and Quinting<sup>8</sup> identified the MHDD contribution to hydride relaxation in  $\text{MnH}(\text{CO})_5$  and used the data to calculate the Mn-H bond distance. Halpern et al.,<sup>9</sup> Bakhmutov et al.,<sup>10</sup> and we<sup>11</sup> have suggested that the MHDD relaxation can also be an important contributor to  $T_1$  relaxation in hydride complexes of transition metals such as rhenium and cobalt, which have both a high gyromagnetic ratio ( $\gamma$ ) and a high nuclear spin ( $I$ ). Better agreement between calculated and observed  $T_1(\text{min})$  values is therefore obtained by including the MHDD contribution.

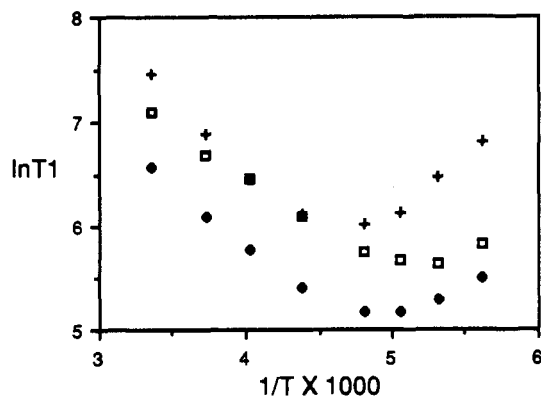
Fast  $T_1$  relaxation has been found in  $\text{CoH}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ ,  $[\text{CoH}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$ , and  $\text{CoH}(\text{CO})(\text{PPh}_3)_3$ , consistent with a significant contribution from Co-H dipole-dipole (CoHDD) relaxation.<sup>10</sup> Definitive experimental evidence has been lacking for the presence of Re-H dipole-dipole (ReHDD) relaxation in rhenium hydride complexes. We have therefore studied *mer,trans*- $\text{ReH}(\text{CO})_3(\text{PPh}_3)_2$  (**1**) and *mer,trans*- $\text{ReH}(\text{CO})_3(\text{PPh}_3-d_{15})_2$  (**1-d<sub>30</sub>**) to identify any ReHDD relaxation and study its magnitude and properties.

## Results and Discussion

**Synthesis and Characterization of *mer,trans*- $\text{ReH}(\text{CO})_3(\text{PPh}_3)_2$  (**1**) and *mer,trans*- $\text{ReH}(\text{CO})_3(\text{PPh}_3-d_{15})_2$  (**1-d<sub>30</sub>**).** Complex **1** has been prepared by Jones et al. from the carbonylation of  $\text{ReH}_3(\eta^4\text{-C}_5\text{H}_6)(\text{PPh}_3)_2$  under a high pressure of CO.<sup>12</sup> A better

- (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (c) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.
- (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. (c) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 3124. (d) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.
- Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. A.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031.
- Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 2788.
- (a) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 4813. (b) Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3775. (c) Luo, X.-L.; Baudry, D.; Boydell, P.; Charpin, P.; Nierlich, M.; Ephritikhine, M.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 1511. (d) Hamilton, D. G.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3198. (e) Luo, X.-L.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1990**, 189. (f) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912. (g) Luo, X.-L.; Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **1991**, 587. (h) Luo, X.-L.; Michos, D.; Crabtree, R. H. *Inorg. Chem.*, in press. (i) Luo, X.-L.; Michos, D.; Crabtree, R. H. *Organometallics*, in press.
- (a) Cotton, F. A.; Luck, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5757. (b) Cotton, F. A.; Luck, R. L.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 43. (c) Cotton, F. A.; Luck, R. L.; *Inorg. Chem.* **1989**, *28*, 6. (d) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 2181.
- Antoniutti, S.; Albertin, G.; Amendola, P.; Bordignon, E. *J. Chem. Soc., Chem. Commun.* **1989**, 229.

- (8) Farrar, T. C.; Quinting, G. R. *J. Phys. Chem.* **1986**, *90*, 2834.
- (9) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173.
- (10) Gusev, D. G.; Vymontis, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1991**, *30*, 3116.
- (11) Luo, X.-L.; Howard, J. A. K.; Crabtree, R. H. *Magn. Reson. Chem.*, in press.
- (12) Jones, W. D.; Maguire, J. A. *Organometallics* **1987**, *6*, 1728.



**Figure 1.** Plots of  $\ln T_1$  vs  $1/T$ : ( $\blacklozenge$ ) net relaxation,  $\ln T_1(\mathbf{1})$  vs  $1/T$ ; ( $\square$ ) ReHDD component,  $\ln T_1(\mathbf{1-d}_{30})$  vs  $1/T$ ; (+) HHDD component by subtraction (eq 1),  $\ln T_1(\text{HHDD})$  vs  $1/T$ .

synthetic route to the **1** and **1-d**<sub>30</sub> was required for use with the expensive deuterated triphenylphosphine.

Complex *mer,trans*-ReCl(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>, the precursor to **1**, is prepared from the carbonylation of ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub><sup>13</sup> in the presence of SbPh<sub>3</sub> as a reducing reagent in refluxing toluene. This is a modification of the literature method described by Chatt et al.<sup>14</sup> The original method used PPh<sub>3</sub> as the reducing reagent and gave an impure pink product which required recrystallization from benzene/methanol in the presence of KOH. Our modified method gives high yields of an off-white product, which is sufficiently pure to be used without recrystallization.

Treatment of *mer,trans*-ReCl(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> with LiAlH<sub>4</sub> in THF at room temperature followed by hydrolysis yields **1**. The spectroscopic and microanalytical data of **1** are in good agreement with those reported in the literature.<sup>12</sup> In addition, the selectively hydride-coupled <sup>31</sup>P NMR spectrum of **1** in CD<sub>2</sub>Cl<sub>2</sub> shows a doublet ( $\delta$  21.88, <sup>2</sup>J<sub>PH</sub> = 17.6 Hz), confirming the presence of only one hydride ligand.

The ligand replacement reaction of ReOCl<sub>3</sub>(SbPh<sub>3</sub>)<sub>2</sub><sup>15</sup> with the commercially available PPh<sub>3-d</sub><sub>15</sub> occurs readily in CH<sub>2</sub>Cl<sub>2</sub> to form ReOCl<sub>3</sub>(PPh<sub>3-d</sub><sub>15</sub>)<sub>2</sub>, which after carbonylation gives *mer,trans*-ReCl(CO)<sub>3</sub>(PPh<sub>3-d</sub><sub>15</sub>)<sub>2</sub>. Treatment of the latter with LiAlH<sub>4</sub> affords *mer,trans*-ReH(CO)<sub>3</sub>(PPh<sub>3-d</sub><sub>15</sub>)<sub>2</sub> (**1-d**<sub>30</sub>).

**Variable-Temperature <sup>1</sup>H NMR  $T_1$  Measurements on **1** and **1-d**<sub>30</sub>.** The monohydride complex **1** is a good candidate for studying any ReHDD contribution to  $T_1$  relaxation of hydride ligands, because the HHDD interactions between the hydride ligand and phosphine ligand protons can be eliminated in **1-d**<sub>30</sub>. <sup>1</sup>H NMR (250 MHz)  $T_1$  values of the hydride resonances of **1** and **1-d**<sub>30</sub> in CD<sub>2</sub>Cl<sub>2</sub> were measured as a function of the temperature. The data are listed in Table I and plotted in Figure 1.

Complex **1** shows a minimum  $T_1$  value of 177 ms at ca. 203 K, corresponding to a relaxation rate of 5.65 s<sup>-1</sup>. In contrast, **1-d**<sub>30</sub> exhibits a minimum of 281 ms near 188 K, equivalent to a rate of 3.56 s<sup>-1</sup>. Since H-H vectors involving the phosphine protons are removed in **1-d**<sub>30</sub>, essentially all HHDD relaxation is eliminated. In spite of this, more than half the relaxation in **1** remains in **1-d**<sub>30</sub>. This indicates that there is a substantial non-HHDD contribution which we assign mainly to ReHDD relaxation (vide infra).

By subtracting the relaxation rates for **1-d**<sub>30</sub> from those for **1** (eq 1) we can estimate the HHDD contribution to the overall relaxation in **1**.  $T_1(\text{HHDD})$ , plotted in the form of crosses in

$$1/T_1(\text{HHDD}) = 1/T_1(\mathbf{1}) - 1/T_1(\mathbf{1-d}_{30}) \quad (1)$$

Figure 1, goes through a minimum of 411 ms (2.43 s<sup>-1</sup> in rate) at ca. 208 K. This shows that the HHDD relaxation goes through

a minimum  $T_1$  at a higher temperature than the proposed ReHDD relaxation in **1-d**<sub>30</sub>. Using the dipole-dipole relaxation theory, it can be easily predicted that  $T_1(\text{HHDD})$  should be a minimum when the rotational correlation time  $\tau_c$  is 0.62/ $\omega_H$ , whereas  $T_1$ - (ReHDD) should be so when  $\tau_c$  is 0.93/ $\omega_H$ .<sup>9-11</sup> Since  $\tau_c$  decreases with increasing temperature,<sup>16</sup> the smaller value of  $\tau_c$  in the former case corresponds to a higher temperature, which is indeed confirmed by our experiment.

We can be more quantitative in our approach. The temperature dependence of the correlation time can be described by the Arrhenius equation,  $\tau_c = \tau_0 e^{E_a/RT}$ , where  $E_a$  is the activation energy for rotational diffusion in the solvent.<sup>16</sup> The correlation times,  $\tau_c$  and  $\tau_c'$ , at the  $T_1(\text{HHDD})$  and  $T_1(\text{ReHDD})$  minima should thereby be related to the temperatures  $T$  and  $T'$  of the minima by eq 2. This indicates that the temperature difference between

$$\ln(\tau_c/\tau_c') = (E_a/R)(1/T - 1/T') \quad (2)$$

the  $T_1(\text{HHDD})$  and  $T_1(\text{ReHDD})$  minima will depend upon  $E_a$  and accordingly upon the solvent chosen. Substituting the data ( $\tau_c = 0.62/\omega_H$ ,  $\tau_c' = 0.93/\omega_H$ ,  $T = 208$  K, and  $T' = 188$  K) into eq 2 leads to an  $E_a$  value of 1.56 kcal mol<sup>-1</sup>, which is in satisfactory agreement with the literature value of 1.49 kcal mol<sup>-1</sup> for viscous flow for dichloromethane.<sup>17</sup>

The second feature of the ReHDD relaxation that we can test is its magnitude. This can be done at the temperature (208 K) where  $T_1(\text{HHDD})$  is a minimum; i.e.,  $\tau_c$  is 0.62/ $\omega_H$ . At this temperature, we<sup>11</sup> previously showed that the ReHDD relaxation rate,  $1/T_1(\text{ReHDD})$ , at 250 MHz is related to the HHDD relaxation rate,  $1/T_1(\text{HHDD})$ , for the same internuclear distance  $r$  by eq 3. Substituting the observed  $T_1(\text{ReHDD})$  value of 311

$$1/T_1(\text{ReHDD}) = 0.5976[1/T_1(\text{HHDD})] = 92.74r^{-6} \quad (3)$$

ms for **1-d**<sub>30</sub> at 208 K into eq 3 leads to an estimated Re-H bond distance of 1.75 Å. This is only slightly longer than the values determined by neutron diffraction studies on other rhenium hydride complexes.<sup>18</sup> The lengthening may be attributed to the high trans influence of the CO ligand as well as the low oxidation state of rhenium in **1**. The  $T_1$  data of **1-d**<sub>30</sub> is therefore consistent with the assignment of the  $T_1$  relaxation to the ReHDD interaction.

There are two sources of relaxation of which we have not yet taken account: proton-deuteron dipole-dipole (HDDD) relaxation in **1-d**<sub>30</sub> and proton-phosphorus dipole-dipole (HPDD) relaxation in both **1** and **1-d**<sub>30</sub>. We will now look at these qualitatively. We assume an ideal octahedral structure with a trans disposition of the two phosphine ligands and Re-P and Re-H distances of 2.10 and 1.70 Å, respectively.

Thanks to the small magnitude of  $\gamma_D$  versus  $\gamma_H$  and the dependence of the HDDD relaxation rate on  $\gamma_D^2$ , it can be easily shown that the HDDD relaxation rate is reduced by a factor of ca. 16 relative to the HHDD relaxation rate on the assumption that the internuclear distances are unchanged by isotopic substitution. This relation leads to a small HDDD relaxation rate of 0.15 s<sup>-1</sup> for **1-d**<sub>30</sub>. The subtraction procedure (eq 1) leads to an underestimate of the HHDD contribution by this amount. The HPDD relaxation rate in **1** and **1-d**<sub>30</sub> can be estimated from the Re-H and Re-P distances to be only 0.12 s<sup>-1</sup>, and so it is also insignificant. By neglecting the HDDD and HPDD contributions and assigning the relaxation in **1-d**<sub>30</sub> solely to the ReHDD relaxation, we have overestimated the ReHDD contribution only by 0.27 s<sup>-1</sup>. The adjusted  $T_1(\text{ReHDD})$  value corresponds to an Re-H bond distance of 1.77 Å.

(16) Farrer, T. C.; Becker, E. D. *Pulse and Fourier NMR*; Academic Press: New York, 1971; Chapter 4.

(17) Griffing, V.; Cargyle, M. A.; Corvese, L.; Eby, D. J. *Phys. Chem.* **1954**, *58*, 1054.

(18) (a) Brammer, L.; Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L.; Stringer, A. M. *J. Chem. Soc., Chem. Commun.* **1991**, 241. (b) Howard, J. A. K.; Mason, S. A.; Johnson, O.; Diamond, I. C.; Crennel, S.; Keller, P. A.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1988**, 1502. (c) Enge, T. J.; Koetzle, T. F.; Bruno, J. W.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 4012. (d) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872. (e) Abrahams, S. C.; Ginsberg, A. P.; Knox, K. *Inorg. Chem.* **1964**, *3*, 558.

(13) Chatt, J.; Rowe, G. A. *J. Chem. Soc.* **1962**, 4019.

(14) Chatt, J.; Dilworth, J. R.; Gunz, H. P.; Leigh, G. J. *J. Organomet. Chem.* **1974**, *64*, 245.

(15) Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. J. *J. Chem. Soc.* **1964**, 1054.

**Consequences of MHDD Relaxation for Using the  $T_1$  Method.** The HHDD and MHDD contributions will in general reach their  $T_1$  minima at different temperatures. If the HHDD contribution dominates, as will normally be the case for dihydrogen complexes or polyhydride complexes containing a large number of hydride ligands, then the observed  $T_1(\text{min})$  value and the corresponding temperature will lie close to those dictated by the HHDD contribution alone. The rotational correlation time  $\tau_c$  at the observed  $T_1$  minimum can therefore be taken as being equal to  $0.62/\omega_H$  and the effect of the MHDD contribution treated as a perturbation. In the case of classical hydride complexes, especially those having only one or two hydride ligands, the HHDD and MHDD contributions may have comparable magnitudes, just as we have seen for **1**. As a result, the temperature at which  $T_1$  is a minimum will lie somewhere between the temperatures at which the HHDD and the MHDD contributions reach their  $T_1$  minima. Nevertheless, as shown by Halpern,<sup>9</sup> Bakhmutov,<sup>10</sup> and us,<sup>11</sup> assuming that  $\tau_c$  at the  $T_1$  minimum is still  $0.62/\omega_H$  introduces only relatively small error. Good agreement between calculated and observed  $T_1(\text{min})$  values can therefore still be obtained in such cases by including the MHDD contribution.

### Conclusion

This work provides direct experimental evidence that MHDD relaxation can be a significant contributor to  $T_1$  relaxation in rhenium hydride complexes as a result of the relatively high gyromagnetic ratio and nuclear spin of the two rhenium isotopes. The MHDD and HHDD contributions to  $T_1$  relaxation in a monohydride such as **1** can be separated by using perdeuterated ligands, which allows us to show that both are operative and have comparable magnitudes. As predicted by the dipole-dipole relaxation theory and now confirmed by our experiment, the MHDD and HHDD contributions come to their  $T_1$  minima at different temperatures. For "pure" dihydrogen complexes  $L_xM(\eta^2-H_2)_y$ , i.e., those containing one or more  $\eta^2-H_2$  ligands but no terminal hydride ligands, since the short H-H distances of the  $\eta^2-H_2$  ligands give rise to very large HHDD relaxation, the effect of MHDD relaxation is relatively small. Nevertheless, for quantitative evaluation, the MHDD contribution cannot be neglected. In the case of classical hydrides or nonclassical polyhydrides which contain both  $\eta^2-H_2$  and terminal hydride ligands, the MHDD relaxation can make a significant contribution to the overall  $T_1$  relaxation. Thus, good agreement between calculated and observed  $T_1(\text{min})$  values can be obtained only if the MHDD contribution is included. Scalar relaxation does not seem to be a significant contributor to hydride relaxation.

### Experimental Section

**General Procedures.** All manipulations were performed under a dry  $N_2$  atmosphere by standard Schlenk-tube techniques. Diethyl ether, hexane, toluene, and tetrahydrofuran were distilled from Na/Ph<sub>2</sub>CO;

dichloromethane was distilled from CaH<sub>2</sub>. All solvents were stored under  $N_2$  over 4-Å molecular sieves.  $ReOCl_3(PPh_3)_2$ <sup>13</sup> and  $ReOCl_3(SbPh_3)_2$ <sup>15</sup> were prepared according to the literature methods.

<sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker WM 250 or WM 500 spectrometer; <sup>1</sup>H shifts were measured with the residual solvent resonance as reference; <sup>31</sup>P chemical shifts were measured with external 85% H<sub>3</sub>PO<sub>4</sub> as reference. IR spectra were recorded on a Nicolet 5-SX FT-IR spectrometer. <sup>1</sup>H NMR  $T_1$  measurements were carried out at 250 MHz by the inversion-recovery method using a standard 180- $\tau$ -90° pulse sequence.

**Oxotrichlorobis(triphenylphosphine- $d_{15}$ )rhenium(V).**  $PPh_3-d_{15}$  (0.601 g, 2.166 mmol) was added to a solution of  $ReOCl_3(SbPh_3)_2$  (1.000 g, 0.986 mmol) in  $CH_2Cl_2$  (40 mL). The mixture was stirred at room temperature for 5 h. The solvent volume was reduced in vacuo to ca. 5 mL, and Et<sub>2</sub>O (40 mL) was added. The resulting green solid was filtered off, washed with Et<sub>2</sub>O (4 × 10 mL), and dried in vacuo. Yield: 0.825 g (97%). IR (Nujol):  $\nu_{Re=O}$  962 cm<sup>-1</sup>.

**mer,trans-Chlorotricarbonylbis(triphenylphosphine)rhenium(I).** A stream of CO was bubbled for 3 h through a boiling suspension of  $ReOCl_3(PPh_3)_2$  (0.500 g, 0.600 mmol) and  $SbPh_3$  (0.500 g, 1.416 mmol) in toluene (50 mL). The volume of the resulting greenish yellow solution was reduced in vacuo to ca. 3 mL. Addition of Et<sub>2</sub>O (40 mL) resulted in the precipitation of an off-white solid, which was filtered off, washed with Et<sub>2</sub>O (4 × 10 mL), and dried in vacuo. Yield: 0.473 g (95%). IR (Nujol):  $\nu_{CO}$  2040, 1942, 1892 cm<sup>-1</sup>.

**mer,trans-Chlorotricarbonylbis(triphenylphosphine- $d_{15}$ )rhenium(I).** This complex was prepared by the above procedure except that  $ReOCl_3(PPh_3-d_{15})_2$  was used instead of  $ReOCl_3(PPh_3)_2$ . Yield: 95%. IR (Nujol):  $\nu_{CO}$  2041, 1944, 1893 cm<sup>-1</sup>.

**mer,trans-Hydridotricarbonylbis(triphenylphosphine)rhenium(I) (1).**  $LiAlH_4$  (0.110 g, 2.89 mmol) was added to a suspension of *mer,trans-ReCl(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>* (0.300 g, 0.361 mmol) in THF (20 mL). The mixture was stirred at room temperature for 15 min. The resulting yellow suspension was cooled to 0 °C and hydrolyzed by dropwise addition of H<sub>2</sub>O (0.200 mL) in 5 mL of THF. The mixture was dried with 3 g of anhydrous Na<sub>2</sub>SO<sub>4</sub> for 15 min and filtered through Celite. The yellow filtrate was evaporated in vacuo to ca. 1 mL. Addition of hexane (25 mL) resulted in the precipitation of a white solid, which was filtered off, washed with hexane (4 × 10 mL), and dried in vacuo. Yield: 0.183 g (64%). Anal. Calcd for C<sub>39</sub>H<sub>31</sub>O<sub>3</sub>P<sub>2</sub>Re: C, 58.86; H, 3.93. Found: C, 59.03; H, 4.01. IR (Nujol):  $\nu_{Re-H}$  2018 cm<sup>-1</sup>;  $\nu_{CO}$  1940, 1915, 1889 cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  7.57 (m, 12 H, Ph), 7.40 (m, 18 H, Ph), -5.125 (t, <sup>2</sup>J<sub>PH</sub> = 18.2 Hz, 1 H, Re-H). Selectively hydride-coupled <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  21.88 (d, <sup>2</sup>J<sub>PH</sub> = 17.4 Hz).

**mer,trans-Hydridotricarbonylbis(triphenylphosphine- $d_{15}$ )rhenium(I) (1- $d_{30}$ ).** This complex was similarly prepared by the above procedure except that *mer,trans-ReCl(CO)<sub>3</sub>(PPh<sub>3</sub>- $d_{15}$ )<sub>2</sub>* was used instead of *mer,trans-ReCl(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>*. Yield: 62%. IR (Nujol):  $\nu_{Re-H}$  2019 cm<sup>-1</sup>;  $\nu_{CO}$  1941, 1917, 1890 cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  -5.136 (t, <sup>2</sup>J<sub>PH</sub> = 18.3 Hz, Re-H). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  21.16 (d, <sup>2</sup>J<sub>PH</sub> = 18.0 Hz).

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