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Synthesis and NMR T_1 Relaxation Study of Rhenium and Manganese Hydride Complexes

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Some new and known hydride complexes of manganese ($MnH(NO)_2(PEt_3)_2$, $MnH(CO)_3(PEt_3)_2$) and rhenium ($ReH(CO)_n(PMe_3)_{5-n}$, $n = 1, 2, 3$; $ReH_2(CO)(NO)(PR_3)_2$) were prepared. ^1H selective and nonselective relaxation times were determined as a function of temperature for each compound. From the measurements, the contributions of the M–H dipole–dipole interaction to the relaxation times of the H ligands were isolated, and the M–H bond lengths were calculated using the model of an isotropic motion. In all cases reasonable M–H bond distances from 1.60 (Mn–H) to 1.77 Å (Re–H) have been obtained in spite of clear evidence for an anisotropic rotation of the investigated hydrides. Possible errors in such calculations (<4%) have been examined by an analysis of anisotropic effects using Woessner's equation and an approach based on a distribution of molecular correlation times. Thus the isotropic motion approach, even though not strictly correct, is of high potential value in the elucidation of structural features of mononuclear hydride complexes in solution.

Introduction

In recent years, ^1H T_1 relaxation time measurements have often been used to obtain quantitative and semiquantitative information about the distances for metal bound hydrogen ligands, in particular about the M–H or H–H bond lengths in metal hydrides of the type L_nMH_m.[1] The increasing popularity of this T_1 approach is obviously due to the possibility to carry out the measurements on common NMR spectrometers and due to an easy interpretation of the resulting relaxation data. In the meantime, the reliability of the structural information based on T_1 data became however subjected to criticism.[2] The latest theoretical and experimental studies have revealed that in some cases the traditional way of T_1 relaxation time analyses implying an isotropic motion of hydride complexes in solution is seemingly incorrect[1f,3] and has to be considered a source of serious errors.[3] A significant discrepancy was found in the case of $IrH_5(PPr^i_3)_2$ where the observed T_{1min} value of 599 ms (500 MHz) strongly differed from calculated 161 ms.[3] Similar observations were made for some other polyhydrides such as $(ReH_8(PPh_3))^-$, $WH_6(PMe_2Ph)_3$, and $ReH_7(dppe)$ and were explained by significantly anisotropic rotation of the molecules in solution.[3]

In this work we report on the studies of ^1H selective and nonselective relaxations in some known and new rhenium and manganese hydride complexes. The experimental data allow the determination of the contributions of the M–H dipole–dipole interaction (MHDDI)[1a,b,3] to the relaxation rates of the H ligands and the calculation of the Re–H and Mn–H bond lengths using the model of isotropic motion.

In spite of clear evidence obtained for an anisotropic rotation of the hydrides treated in this work, reasonable M–H bond distances have been calculated in all cases. Possible errors in such determinations of the bond lengths have been examined and are unlikely to be greater than 4%. The distances between the H ligands have been calculated for three rhenium dihydrides from the cross-relaxation rates derived from the observed selective (T_{1s}) and biselective (T_{1bs}) relaxation times.

Thus, we believe that the isotropic motion approach, even though not strictly correct, is of high potential value in the elucidation of the structural features of mononuclear hydride complexes.

Experimental Section

All manipulations were performed under a dry nitrogen atmosphere by standard Schlenk-tube techniques. Solvents were dried and deoxygenated by using conventional procedures and were freshly distilled before use.

IR spectra were recorded in solution on a Biorad FTS-45 instrument. Mass spectra were run on a Finnigan MAT-8230 mass spectrometer, m/e based on ^{187}Re.

NMR data were obtained on Bruker WP 200 SY, Varian Gemini-200 and Varian Gemini-300 spectrometers. The conventional inversion-recovery method (180–τ–90) was used to determine T_1. T_{1s} and T_{1bs} relaxation times were measured by applying a selective 180° pulse provided by the decoupler with the pulse sequences described previously.[4] The calculation of the relaxation times was made using the nonlinear three-parameter fitting routine of the spectrometers. In each experiment, the waiting period was 5 times the expected relaxation time and 11 variable delays were employed. The duration of the pulses were controlled at every studied temperature. The temperature was calibrated by ^1H NMR with a standard methanol sample.

For the studied complexes, four ($ReH_2(CO)(NO)(PCy_3)_2$) or five (the others) values of T_{1s} and T_{1bs} were measured at different temperatures where the extreme narrowing condition, $\omega^2\tau^2 \ll 1$, seemed to hold. Consequently, four or five values of k (see below, eq 4) were calculated. The mean values of k were used to obtain the M–H distances presented in Table I. The errors (at a confidence level of 95%) were estimated according to a common approach,[5] using eq 7 for calculation of r_{M-H} for each experimental value of k.

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Table I. Results of Relaxation Time Measurements and of the Fitting of Experimental T_1 Values to eq 5 for the Complexes **1–8**

complex	ν_H, MHz	δ(M–H) (C_6D_6)	E_a, kcal/mol	τ_0, 10^{-13} s	T_{1min}^{-1},[a] s^{-1}	k	T_{1min}^{-1}(MH),[b] s^{-1}	r_{M-H}, Å
1[c]	300	–0.49	2.8	1.5	7.28 (178 K)	0.7	5.96	1.59 ± 0.02
2[c]	300	–8.50	2.8	1.5	6.77 (172 K)	0.9	5.32	1.62 ± 0.02
3[d]	200	–6.17	3.3	1.8	6.21 (200 K)	0.9	4.95	1.71 ± 0.05
3[d]	300		2.8	3.9	4.29 (203 K)	1.1	3.18	1.72 ± 0.01
3[d]	300		3.0	2.5	4.35 (205 K)	1.0	3.28	1.71 ± 0.05
4[c]	300	–5.08	2.6	1.9	3.83 (167 K)	0.9	3.08	1.73 ± 0.03
5a[c]	300	–7.04	2.6	1.7	4.55 (165 K)	1.0	3.53	1.69 ± 0.03
5b[c]	300	–6.38	2.6	2.5	3.89 (172 K)	1.5	2.68	1.77 ± 0.05
6[e]	200	–0.81	2.5	1.7	6.87 (153 K)	1.4	4.78	1.72 ± 0.04
		–4.24	2.5	1.9	6.52 (152 K)	1.7	4.28	1.75 ± 0.05
								2.25 ± 0.15[f]
7[d]	200	–1.00	2.5	15	10.42 (207 K)	3.5	4.87	1.71 ± 0.08
		–4.90	2.4	16	10.68 (206 K)	4.6	4.38	1.74 ± 0.04
								2.34 ± 0.37[f]
8[d]	200	–1.51	3.2	1.5	7.95 (194 K)	2.3	4.73	1.72 ± 0.05
		–4.78	3.0	2.0	7.78 (188 K)	1.8	5.10	1.70 ± 0.08
								2.28 ± 0.12[f]
8[d]	300	–1.51	3.3	1.4	5.09 (204 K)	1.5	3,53	1.69 ± 0.03
		–4.78	3.2	1.6	4.75 (202 K)	1.5	3.29	1.71 ± 0.03

[a] The values are from the theoretical curves obtained by fitting the experimental temperature-dependent T_1 data to eq 5. [b] Calculated with the M–H distances by eq 3c. [c] In CD_2Cl_2. [d] In toluene-d_8. [e] In a mixture of toluene-d_8 (95%) and CD_2Cl_2. [f] The r(H···H) distances.

The following compounds were prepared as described in the literature: $MnBr(CO)_3(PEt_3)_2$,[6] $MnCl(NO)_2(PEt_3)_2$,[7] $ReCl(CO)_3(POPr^i_3)_2$,[8] $ReCl(CO)_2(PMe_3)_3$,[8] and $ReH_2(CO)(NO)L_2$ (L = PMe_3, PCy_3, $POPr^i_3$).[9]

$ReCl_3(CO)_2(PMe_3)_3$ was prepared in a manner similar to that described by Shaw et al. for $ReCl_3(CO)_2(PMe_2Ph)_3$:[10] 3 mL of a saturated solution of Cl_2 in CCl_4 was added dropwise to a chloroform solution of $ReCl(CO)_2(PMe_3)_3$. After 30 min the yellow reaction mixture was filtered through Celite and was evaporated to dryness, yielding a lemon yellow powder. The compound was used without further purification. IR ($CHCl_3$): ν_{CO} 1862.1 cm^{-1}. MS (EI): *m/e* 550 (M^+), 522 (M^+ – CO), 482 (M^+ – Cl_2), 474 (M^+ – PMe_3), 446 (M^+ – CO – PMe_3).

$MnH(NO)_2(PEt_3)_2$ (1). $NaBH_4$ (0.05 g, 1.1 equiv) was added over a period of 15 min to a solution of $MnCl(NO)_2(PEt_3)_2$ (0.5 g, 1.3 mmol) in ethanol (70 mL) cooled to –30 °C. The temperature was then slowly increased to 0 °C. After 2 h, the solvent was evaporated under reduced pressure. The remaining solid residue was dissolved in hexane (1 mL) and chromatographed on silica gel using a mixture of hexane/ether (2/1) as eluent. A pale yellow fraction was collected and evaporated, affording a lemon yellow solid. Yield: 0.4 g (89%). Anal. Calcd for $C_{12}H_{31}MnN_2O_2P_2$: C, 40.91; H, 8.81. Found: C, 40.76; H, 8.84. IR (diethyl ether): ν_{NO} 1669 (s), 1634 cm^{-1} (vs). MS (EI): *m/e* 352 (M^+), 322 (M^+ – NO), 292 (M^+ – 2NO), 204 (M^+ – NO – PEt_3), 174 (M^+ – 2NO – PEt_3). ^1H NMR (C_6D_6, 298 K): δ 1.55 (quint, $^3J_{HH}$ = 7.7 Hz, $^2J_{PH}$ = 7.7 Hz, 12 H, CH_2), 1.01 (quint, $^3J_{HH}$ = 7.7 Hz, $^3J_{PH}$ = 16.3 Hz, 18 H, CH_3), –0.49 (t, $^2J_{PH}$ = 101.1 Hz, 1 H, MnH). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): δ 66.8. $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ 22.1 (t, $^1J_{PC}$ = 27.6 Hz, CH_2), 7.9 (s, CH_3).

$MnH(CO)_3(PEt_3)_2$ (2). In a manner similar to a published method,[11] a solution of $MnBr(CO)_3(PEt_3)_2$ (0.5 g, 1.1 mmol) and PEt_3 (0.15 ml, 0.3 mmol) in THF (100 mL) and an excess of sodium amalgam (0.25 g in 1.9 mL of Hg) were stirred vigorously for 4 h. After filtration through Celite and cooling to –80 °C, acetic acid (62 μL, 1 equiv) was added. The mixture was allowed to warm slowly to room temperature and was stirred for another hour. Volatiles were removed under reduced pressure and the residue was extracted with hexane (70 mL). The yellow extract was filtered and the solvent evaporated to yield a yellow oil. Yield: 0.3 g (85%). Anal. Calcd for $C_{15}H_{31}MnO_3P_2$: C, 47.87; H, 8.24. Found: C, 47.69; H, 8.28. IR (hexane): ν_{CO} 1900 cm^{-1}. MS (EI): *m/e* 376 (M^+), 375 (M^+ – H), 347 (M^+ – H – CO), 319 (M^+ – H – 2CO), 292 (M^+ – 3CO), 291 (M^+ – H – 3CO), 174 (M^+ – 3CO – PEt_3), 173 (M^+ – H – 3CO – PEt_3). ^1H NMR (C_6D_6, 298 K): δ 1.52 (quint, $^3J_{HH}$ = 7.6 Hz, $^2J_{PH}$ = 7.6 Hz, 12 H, CH_2), 1.01 (quint, $^3J_{HH}$ = 7.6 Hz, $^3J_{PH}$ = 15.0 Hz, 18 H, CH_3), –8.50 (t, $^2J_{PH}$ = 31.3 Hz, 1 H, MnH). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): δ 62.6. $^{13}C\{^1H\}$ NMR (C_6D_6, 298K): δ 225.6 (t, $^2J_{PC}$ = 15.1 Hz, 1 CO), 225.2 (t, $^2J_{PC}$ = 20.6 Hz, 2 CO), 22.8 (d, $^1J_{PC}$ = 25.3 Hz, CH_2), 8.1 (s, CH_3).

$ReH(CO)_3(POPr^i_3)_2$ (3). A solution of $ReCl(CO)_3(POPr^i_3)_2$ (1 g, 1.4 mmol) in THF was added to slices of sodium (0.5 g, 15 equiv) in THF, and the mixture was stirred for 18 h at room temperature. After filtration through Celite, water (28 mL, 1.1 equiv) was added and the solution evaporated to dryness. The product was extracted with hexane (50 mL) and the solvent removed under reduced pressure affording a colorless oil. Yield: 0.7 g (73%). Anal. Calcd for $C_{21}H_{43}O_9P_2Re$: C, 36.60; H, 6.25. Found: C, 35.95; H, 6.21. IR (hexane): ν_{CO} 2052 (w), 1948 (s), 1927 cm^{-1}(m). MS (EI): *m/e* 688 (M^+), 660 (M^+ – CO), 628 (M^+ – C_3H_{80}). ^1H NMR (C_6D_6, 298 K): δ 4.80 (m, 6 H, CH), 1.26 (d, $^3J_{HH}$ = 6.1 Hz, 36 H, CH_3), –6.17 (t, $^2J_{PH}$ = 22.7 Hz, 1 H, ReH). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): δ 126.8. $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ 194.7 (t, $^2J_{PC}$ = 13.2 Hz, 2 CO), 194.5 (t, $^2J_{PC}$ = 9.3 Hz, 1 CO), 69.9 (s, CH), 24.0 (s, CH_3).

$ReH(CO)_2(PMe_3)_3$ (4). A solution of $ReCl(CO)_2(PMe_3)_3$ (1.2 g, 2.4 mmol) in 150 mL of THF was treated with small pieces of sodium (0.4 g, 8 equiv). The reaction mixture was stirred for 48 h at room temperature. After filtration through Celite, water (1.5 mL) was added dropwise at 0 °C. After 30 min the solvent was removed under reduced pressure. The colorless product was extracted with hexane and filtered through Lichroprep. A white powder was obtained after removing the solvent in vacuo. Yield: 1.0 g (91%) Anal. Calcd for $C_{11}H_{28}O_2P_3Re$: C, 27.97; H, 5.93. Found: C, 27.92; H, 5.87. IR (diethyl ether): ν_{CO} 1921 cm^{-1}, 1858 cm^{-1}. MS (EI): *m/e* 472 (M^+), 444 (M^+ – CO), 396 (M^+ – PMe_3), 368 (M^+ – CO – PMe_3). ^1H NMR (C_6D_6, 298 K): δ 1.46 (apparent t, J_{PH} = 6.5 Hz, 18 H, CH_3), 1.20 (d, $^2J_{PH}$ = 6.9 Hz, 9 H, CH_3), –5.08 (dt, $^2J_{PH}$ = 27.9 Hz, $^2J_{PH}$ = 23.8 Hz, 1H, ReH). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): δ –42.1(d, $^2J_{PP}$ = 28.4 Hz, 2 P), –45.7 (t, 1 P). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ 203.5 (dt, $^2J_{PC}$ = 48.3 Hz, $^2J_{PC}$ = 10.1 Hz, CO trans to PMe_3), 201.9 (dt, $^2J_{PC}$ = 10.1 Hz, $^2J_{PC}$ = 6.3 Hz, CO), 24.8 (dt, $^3J_{PC}$ = 2.1 Hz, $^1J_{PC}$ = 31.0 Hz, 2 CH_3), 23.7 (dt, $^1J_{PC}$ = 26.3 Hz, $^3J_{PC}$ = 3.5 Hz, 1 CH_3).

$ReH_3(CO)(PMe_3)_3$. In a procedure similar to that described by Crabtree and Luo[12] $LiAlH_4$ (0.4 g, 8 equiv) was added to a solution of $ReCl_3(CO)(PMe_3)_3$ (0.7 g, 1.5 mmol) in diethyl ether (50 mL), and the suspension was kept under reflux for 24 h. The solution was filtered through a small amount of Celite, cooled to 0 °C, and diluted with 100 mL of THF, and then 1.5 mL of water was added slowly to it. After 20 min the volatiles were removed under reduced pressure and the remaining solid was extracted with diethyl ether (3 × 50 mL). Removal of the solvent leads to a white solid. Yield: 0.6 g (93%) Anal. Calcd for $C_{10}H_{30}OP_3Re$: C, 26.91; H, 6.73. Found: C, 26.95; H, 6.69. IR (diethyl ether): ν_{CO} 1861 cm^{-1}. MS (CI): *m/e* 446 (M^+), 444 (M^+ – H2). ^1H NMR (THF-d_8, 298 K): δ 1.60 (d, $^2J_{PH}$ = 8.1 Hz, 27 H, PMe_3), –6.28 (q, $^2J_{PH}$ = 23.0 Hz, 3 H, ReH). ^1H NMR (THF-d_8, 193 K): δ 1.67 (d, $^2J_{PH}$ = 7.6 Hz, 18 H, PMe_3), 1.46 (d, $^2J_{PH}$ = 6.8 Hz, 9 H, PMe_3), –6.17

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(m, 2 H, ReH), –6.80 (tdt, $^2J_{PH}$ = 44.9 Hz, $^2J_{PH}$ = 16.0 Hz, $^2J_{HH}$ = 6.1 Hz, 1 H, ReH). $^{31}P\{^1H\}$ NMR (THF-d_8, 193 K): δ –27.8 (d, $^2J_{PP}$ = 25.1 Hz, 2 P), –44.9 (t, $^2J_{PP}$ = 25.1 Hz, 1P). $^{31}C\{^1H\}$ NMR (THF-d_8, 298 K): δ 203.0 (q, $^2J_{PC}$ = 9.2 Hz, CO), 27.7 (d, $^1J_{PC}$ = 30.6 Hz, PMe$_3$). $^{13}C\{^1H\}$ NMR (THF-d_8, 193 K): δ 203.0 (dt, $^2J_{PC}$ = ±51.0 Hz, $^2J_{PC}$ = ∓11.7 Hz, CO), 27.2 (apparent t, J_{PC} = 34.0 Hz, 2 PMe$_3$), 26.3 (d, J_{PC} = 25.4 Hz, 1 PMe$_3$).

***cis*-ReH(CO)(PMe$_3$)$_4$ (5a).** Similar to the previously published method for *trans*-ReH(CO)(PMe$_2$Ph)$_4$,[13] PMe$_3$ (0.26 ml, 2.5 equiv) was added to ReH$_3$(CO)(PMe$_3$)$_3$ (0.5g, 1.1 mL) in THF (80 mL). The resulting solution was refluxed for 2 h. After filtration through Celite and evaporation to dryness, a gray solid remained that was extracted with hexane and again filtered through Celite. After partial evaporation of the solvent the solution was chilled to –30 °C, which afforded white crystals. Yield: 0.55 g (97%). IR, MS, and ^1H NMR data at room temperature are consistent with those described earlier.[14] $^{31}P\{^1H\}$ NMR (THF-d_8, 297 K): δ –41.1 (br d, $^2J_{PP}$ = 26.4 Hz, 2 P), –44.3 (q, $^2J_{PP}$ = 28.8 Hz, 1 P), –45.3 (br d, $^2J_{PP}$ = 26.5 Hz, 1 P). $^{31}P\{^1H\}$ NMR (THF-d_8, 183 K): δ –40.9 (dd, $^2J_{PP}$ = 29.4 Hz, $^2J_{PP}$ = 10.4 Hz, 2 P), –44.2 (q, $^2J_{PP}$ = 29.4 Hz, 1P.), –45.0 (dt, $^2J_{PP}$ = 29.4 Hz, $^2J_{PP}$ = 10.4 Hz, 1 P). $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 297 K): δ 205.8 (apparent dt, $^2J_{PC}$ = 44.7 Hz, $^2J_{PC}$ = 10.2 Hz, CO), 28.4 (d, $^1J_{PC}$ = 21.3 Hz, 1 PMe$_3$), 28.2 (apparent tt, J_{PC} = 27.2 Hz, J_{PC} = 2.0 Hz, 2 PMe$_3$), 26.5 (dq, J_{PC} = 22.1 Hz, J_{PC} = 4.5 Hz, 1 PMe$_3$).

***trans*-ReH(CO)(PMe$_3$)$_4$ (5b).** Purified NaH (0.06 g, 3 equiv) was added to a solution of [ReH$_2$(CO)(PMe$_3$)$_4$][BPh$_4$][15] (0.8 g, 0.9 mmol) in 10 mL of THF and the gray suspension was stirred vigorously. After 10 min the suspension was filtered through Celite and the filtrate rinsed with diethyl ether (50 mL). The resulting solution was evaporated to dryness and the residue extracted with hexane (100 mL). The colorless solution was filtered, concentrated, and chilled to –30 °C upon which white crystals precipitated. Yield: 0.44 g (90%). Anal. Calcd for C$_{13}$H$_{37}$OP$_4$Re: C, 30.01; H, 7.12. Found: C, 29.92; H, 7.14. IR (diethyl ether): ν_{CO} 1823 cm^{-1}. MS (EI): *m/e* 520 (M$^+$), 443 (M$^+$ – PMe$_3$ – H). ^1H NMR (CD$_2$Cl$_2$, 297 K): δ 1.58 (apparent t, J_{PH} = 5.0 Hz, 36 H, PMe$_3$), –6.38 (quint, $^2J_{PH}$ = 23.6 Hz, 1 H, ReH). ^1H NMR (CD$_2$Cl$_2$, 168 K): δ 1.45 (br s, 36 H, PMe$_3$), –6.75 (m, 1 H, ReH). Hydride-coupled ^{31}P NMR (CD$_2$Cl$_2$, 297 K): δ –38.8 (d, $^2J_{PH}$ = 23.6 Hz). $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$, 168 K): δ –37.0 (t, $^2J_{PP}$ = 21.7 Hz, 2 P), –40.1 (t, 2 P). $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 297 K): δ 204.6 (quint, $^2J_{PC}$ = 8.9 Hz, CO), 26.9 (m, $^1J_{PC}$ = 33.8 Hz, PMe$_3$).

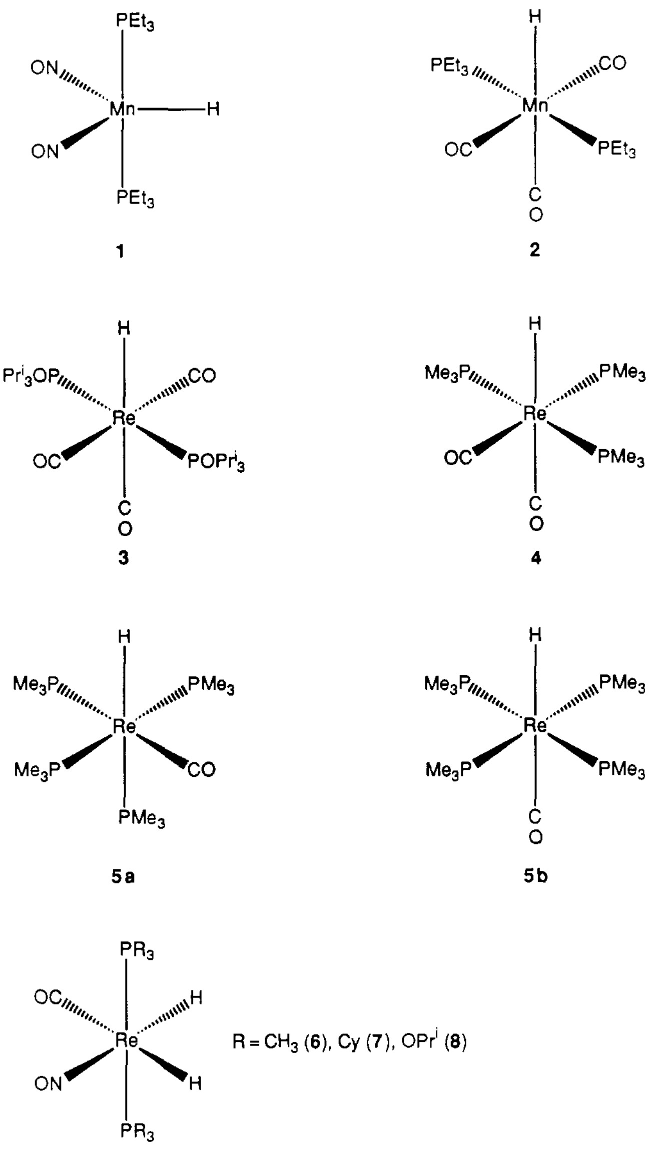
Synthesis and Characterization of *trans*-MnH(NO)$_2$(PEt$_3$)$_2$ (1), *mer,trans*-MnH(CO)$_3$(PEt$_3$)$_2$ (2), *mer,trans*-ReH(CO)$_3$(POPr$^i_3$)$_2$ (3), *cis,mer*-ReH(CO)$_2$(PMe$_3$)$_3$ (4), ReH$_3$(CO)(PMe$_3$)$_3$, *cis*-ReH(CO)(PMe$_3$)$_4$ (5a), and *trans*-ReH(CO)(PMe$_3$)$_4$ (5b). The method of preparation of MnH(NO)$_2$(PPh$_3$)$_2$ described by Hieber and Tengler[7a] and improved by Schweiger and Beck[7b] was unsuccessful for the preparation of compounds with aliphatic phosphanes. Therefore a new route has been developed. Treatment of MnCl(NO)$_2$(PEt$_3$)$_2$ with NaBH$_4$ in ethanol at –30 °C affords MnH(NO)$_2$(PEt$_3$)$_2$ (1) as a yellow solid in good yield. 1 was characterized by a correct elemental analysis, and its structure was assigned spectroscopically.

The ^1H NMR spectrum of 1 shows two quintets for the PEt$_3$ ligands and a triplet hydride resonance with $^2J_{PH}$ = 101.1 Hz. In the $^{13}C\{^1H\}$ spectrum triplet and singlet signals are observed for the PEt$_3$ groups, which indicate that the phosphorus ligands of 1 are chemically equivalent. The IR spectrum of 1 in diethyl ether exhibits two ν_{NO} bands of unequal intensities at 1669 and 1634 cm^{-1}, which are consistent with an angle <180° between the NO groups. Taking all these data into account, we suggest a trigonal bipyramidal structure for 1 with the phosphorus donors in axial positions and the nitrosyl and the hydride ligands in equatorial positions (see Chart I).

MnH(CO)$_3$(PEt$_3$)$_2$ (2) was prepared in a manner similar to that described for MnH(CO)$_3$L$_2$ (L = phosphite)[11] by reduction of MnBr(CO)$_3$(PEt$_3$)$_2$ in THF with an excess of sodium amalgam and subsequent protonation of the anionic intermediate with acetic acid. The compound was isolated as a yellow oil. Following a similar procedure, the rhenium hydride ReH(CO)$_3$(POPr$^i_3$)$_2$ (3) was obtained by reduction of the corresponding chloride with sodium and subsequent acidification.

The ^1H NMR spectra of compounds 2 and 3 both show a triplet resonance in the hydride region. In the $^{13}C\{^1H\}$ NMR spectra of 2 and 3, the CO ligands are observed as two triplets with $^2J_{PC}$ values typical of a cis position with regard to the phosphorus ligands. Therefore all CO groups of 2 and 3 are arranged meridionally at the metal center (Chart I). The IR spectra of 2 and 3 in hexane show one strong ν_{CO} band at 1900 cm^{-1} (2) and three ν_{CO} bands of very different intensities at 2052 (w), 1948 (vs), and 1927 (s) cm^{-1} (3), also supporting the meridional CO substitution pattern.

Chart I



ReH(CO)$_2$(PMe$_3$)$_3$ (4) was obtained following the same procedure as for 3. The ^1H NMR spectrum of 4 reveals a triplet of doublets in the hydride region. The $^2J_{PH}$ values of 23.8 and 27.9 Hz suggest that all PMe$_3$ ligands are located cis to the metal bound hydrogen atom (Chart I). This is confirmed by the $^{31}P\{^1H\}$ NMR spectrum in which an AM$_2$ pattern is observed. In the $^{13}C\{^1H\}$ NMR spectrum of 4 the CO ligands appear as two triplets of doublets at δ 203.5 ($^2J_{PC}$ = 10.1 and 48.3 Hz) and δ 201.9 ($^2J_{PC}$ = 6.3 and 10.1 Hz). On the basis of the large doublet coupling, the former signal is assigned to the CO group trans to a PMe$_3$ ligand. The IR spectrum in diethyl ether shows two intense ν_{CO} bands at 1921 and 1858 cm^{-1}, consistent with the presumed cis arrangement of the two CO ligands.

ReH$_3$(CO)(PMe$_3$)$_3$ was prepared as described for ReH$_3$(CO)(PMe$_2$Ph)$_3$ by refluxing ReCl$_3$(CO)(PMe$_3$)$_3$ with LiAlH$_4$ in diethyl ether.[12] Subsequent hydrolysis with H$_2$O/THF affords a colorless solid isolated in good yield by crystallization from hexane.

The ^1H NMR spectrum of ReH$_3$(CO)(PMe$_3$)$_3$ at 298 K is characterized by a quartet resonance for the hydride ligands and a doublet resonance for the PMe$_3$ groups as result of the fluxional behavior of this molecule. On cooling, two doublet signals with an intensity ratio of 1:2 have evolved for the PMe$_3$ groups (193 K), while in the hydride region a multiplet and

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a triplet of doublets of triplets have appeared (1:2 integral ratio). It should be noted that at this temperature the $^{31}P\{^1H\}$ NMR spectrum of $ReH_3(CO)(PMe_3)_3$ displays an AM_2 type pattern with $^2J_{PP} = 25.1$ Hz. A quartet CO resonance (δ 203.0, $^2J_{PC} = 9.2$ Hz), observed in the $^{13}C\{^1H\}$ NMR spectrum of $ReH_3(CO)(PMe_3)_3$ at room temperature, transforms to a doublet of triplets with $^2J_{PC}$ values of ± 51.0 Hz and ∓ 11.7 Hz indicating the CO ligand to be trans to one of the PMe_3 groups. The IR spectrum of $ReH_3(CO)(PMe_3)_3$ in diethyl ether as expected shows one strong ν_{CO} band at 1861 cm^{-1}.

Boiling of a THF solution of $ReH_3(CO)(PMe_3)_3$ in the presence of PMe_3 under reflux in a manner identical to the preparation of *trans*-$ReH(CO)(PMe_2Ph)_4$[13] led to formation of the cis isomer of $ReH(CO)(PMe_3)_4$ (**5a**). The IR and room temperature ^1H NMR data of 5a are consistent with those described previously.[14] The $^{31}P\{^1H\}$ NMR spectrum at 183 K reveals a well-resolved A_2BM pattern with $^2J_{PP}$ values of 10.4 and 29.4 Hz. At 193 K the $^{13}C\{^1H\}$ NMR spectrum shows a apparent doublet of triplets for the CO ligand with $^2J_{PC}$ values of 44.7 and 10.2 Hz, indicating a pseudooctahedral geometry with one PMe_3 group trans to the CO ligand (Chart I).

Treatment of $[ReH_2(CO)(PMe_3)_4][BPh_4]$[15] with NaH in a small amount of THF for 10 min resulted in the formation of *trans*-$ReH(CO)(PMe_3)_4$ (**5b**), which was isolated in good yield as white crystals from hexane. Increasing the reaction time causes isomerization of **5b** into **5a**, which is accelerated upon heating.

At 297 K the ^1H NMR spectrum of 5b displays a quintet hydride resonance with a $^2J_{PH}$ value of 23.6 Hz and one resonance for the four chemically equivalent PMe_3 ligands. The hydride-coupled ^{31}P NMR spectrum of **5b** shows a doublet resonance with $^2J_{PH} = 23.6$ Hz. At 297 K the $^{13}C\{^1H\}$ NMR spectrum of **5b** displays a quintet in the CO region at δ 204.6 with a $^2J_{PC}$ value of 8.9 Hz. The IR spectrum in diethyl ether exhibits a strong ν_{CO} band at 1823 cm^{-1}, and at 168 K the $^{31}P\{^1H\}$ NMR spectrum displays an A_2B_2 pattern with a small $^2J_{PP}$ constant of 21.7 Hz. The latter can be rationalized in terms of a distortion of the P_4Re coordination plane leading to pairwise equivalent PMe_3 ligands.

Theory

Intramolecular proton–proton and proton–metal dipole–dipole interactions (HHDDI and HMDDI) dominate the T_1 relaxation of hydride ligands in rhenium and manganese phosphane complexes:[1c–f,3]

$$1/T_1 = 1/T_1(\text{H–M}) + 1/T_1(\text{H}\cdots\text{H}) \qquad (1)$$

The contributions, $1/T_1(\text{H–M})$ and $1/T_1(\text{H}\cdots\text{H})$, were separated experimentally for $ReH(CO)_3(PPh_3)_2$ by using perdeuterated ligands.[1e] In the present work another approach has been utilized to determine $1/T_1(\text{H–M})$, based on measurement of selective relaxation time (T_{1s})[4,16] (eq 2). If $\omega_H{}^2\tau_c{}^2 \ll 1$ (the fast

$$1/T_{1s} = 1/T_1(\text{H–M}) + 1/T_{1s}(\text{H}\cdots\text{H}) \qquad (2)$$

motion regime), it follows from the well-known eqs 3 (where γ_H

$$1/T_1(\text{H}\cdots\text{H}) = C_1(\tau_c/(1 + \omega_H{}^2\tau_c{}^2) + 4\tau_c/(1 + 4\omega_H{}^2\tau_c{}^2)) \qquad (3a)$$

$$1/T_{1s}(\text{H}\cdots\text{H}) = C_1(\tau_c/(1 + \omega_H{}^2\tau_c{}^2) + 2\tau_c/(1 + 4\omega_H{}^2\tau_c{}^2) + \tau_c/3) \qquad (3b)$$

$$C_1 = 0.3\gamma_H{}^4\hbar^2/r_{\text{H}\cdots\text{H}}{}^6$$

$$1/T_1(\text{M–H}) = C_2(3\tau_c/(1 + \omega_H{}^2\tau_c{}^2) + 6\tau_c/(1 + (\omega_H + \omega_M)^2\tau_c{}^2) + \tau_c/(1 + (\omega_H - \omega_M)^2\tau_c{}^2)) \qquad (3c)$$

$$C_2 = 2\gamma_H{}^2\gamma_M{}^2\hbar^2 I(I + 1)/15r_{\text{H–M}}{}^6$$

and γ_M are the ^1H and metal gyromagnetic ratios, τ_c is the correlation time for molecular reorientation, and ω_H and ω_M are the Larmor frequencies)[4,16,17] that

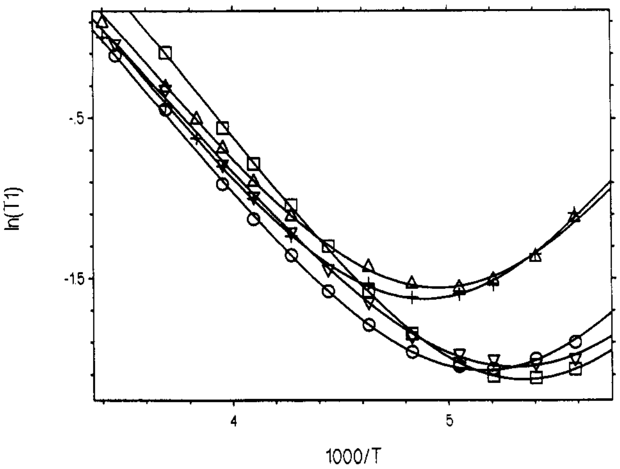

Figure 1. Variable-temperature T_1 data for $ReH_2(CO)(NO)(POPr^i{}_3)_2$. 200 MHz: ○, ReH ($\delta$ –1.51); ▽, ReH (δ –4.78); □, CH_3. 300 MHz: +, ReH (δ –1.51); △, ReH (δ –4.78).

$$k = C_1/C_2 = (f - 1)/(0.5 - f/3) \text{ where } f = T_{1s}/T_1. \qquad (4)$$

Thus, eq 1 in combination with eqs 2 and 4 takes the form

$$1/T_1 = C_2((3 + k)\tau_c/(1 + \omega_H{}^2\tau_c{}^2) + 4k\tau_c/(1 + 4\omega_H{}^2\tau_c{}^2) + 6\tau_c/(1 + (\omega_H + \omega_M)^2\tau_c{}^2) + \tau_c/(1 + (\omega_H - \omega_M)^2\tau_c{}^2)) \qquad (5)$$

Thus, by measuring T_{1s} and the temperature dependence of T_1, the latter can be fitted to eq 5, using least-squares linear regression programs applied in analyses of relaxation data.[1a,b,f] In the present case such an approach allows one to determine the proton–metal bond distance ($r_{\text{H–M}}$), the activation energy for molecular reorientation (E_a), and the correlation constant (τ_0), assuming that the correlation time obeys the Arrhenius equation:

$$\tau_c = \tau_0 \exp(E_a/RT)$$

The least-squares fits for all three parameters $r_{\text{H–M}}$, E_a, and τ_0 were carried out twice for each complex studied in this work. For the first fit the values of k were calculated from eq 4 assuming $\omega^2\tau_c{}^2 \ll 1$. For the second fit, k values were obtained using τ_c values determined from E_a and τ_0 provided by the first fit. In all cases the changes in $r_{\text{H–M}}$ were demonstrated to be less than 0.03 Å after the second fit. The activation energy and the correlation constant were retained practically unchanged along this procedure.

Biselective relaxation times (T_{1bs}) can be employed in the determination of the distances between nonequivalent H ligands in dihydride complexes. The difference $1/T_{1s} - 1/T_{1bs}$ yields the cross-relaxation term σ_{ij}[4,16] (eq 6) between the protons i and j

$$(1/T_{1s} - 1/T_{1bs})_i = (1/T_{1s} - 1/T_{1bs})_j = \sigma_{ij}$$

$$\sigma_{ij} = 0.1\gamma_H{}^4\hbar^2 r_{ij}{}^{-6}(6\tau_c/(1 + 4\omega_H{}^2\tau_c{}^2) - \tau_c) \qquad (6)$$

subjected to excitation with selective 180° pulses, from which r_{ij} can be calculated when τ_c is known.

Results and Discussion

The experimental relaxation data and calculated distances ($r_{\text{M–H}}$ and $r_{\text{H}\cdots\text{H}}$) for complexes **1–8** are collected in Table I. Figures 1 and 2 show the experimental and calculated temperature-dependent T_1 data for the hydride ligands of **8** and **3**. The plots, being typical for all the other hydrides studied in this work, give

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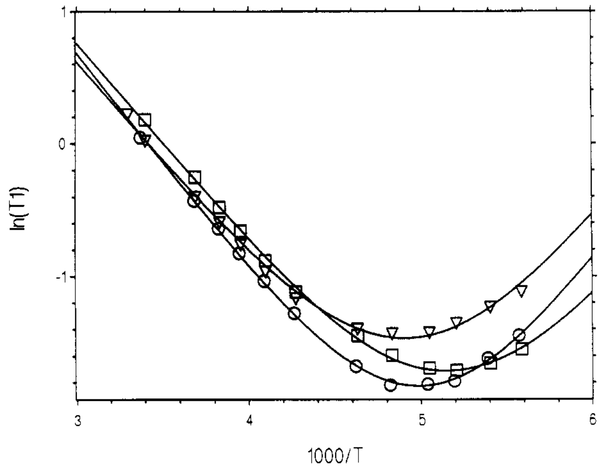

Figure 2. Variable-temperature T_1 data for $ReH(CO)_3(POPr^i_3)_2$. 200 MHz: ○, ReH. 300 MHz: ▽, ReH; □, CH_3.

evidence for a good agreement between the theoretical and experimental data.

It follows from eq 5 that the T_1 times of hydride ligands in Re and Mn complexes have to reach a minimum when the rotational correlation time τ_c lies between $0.62/\omega_H$ and $0.93/\omega_H$, depending on the strength of MHDDI.[1a,d] According to our data T_{1min} values for **1–8** actually fall into the range between $0.75/\omega_H$ ($ReH_2(CO)(NO)(PCy_3)_2$, $k = 4.6$, 41% MHDDI) and $0.88/\omega_H$ ($MnH(NO)_2(PEt_3)_2$, $k = 0.67$, 82% MHDDI). Substituting these values of τ_c(min) into eq 5 and evaluating the constants yields eq 7, relating

$$r_{H-M}\ (\text{Å}) = c((1.4k + 4.47)T_{1min}/\nu)^{1/6} \qquad (7)$$

T_{1min} and the internuclear distance where ν is the ^1H NMR resonance frequency (MHz) and $C = 10^7(\gamma_H{}^2\gamma_M{}^2\hbar^2 I(I+1)/15\pi)^{1/6}$ (Re, $C = 4.20$; Mn, $C = 4.31$). Similar expressions allowing the calculation of proton–proton distances were obtained from eq 3a for T_1 relaxation due to HHDDI.[3,18] It should be noted that in spite of its approximate character eq 7 gives fairly accurate M–H distances deviating by less than 0.005 Å from those obtained by the fitting procedure described above (see Table I).

Equation 7 makes it easy to estimate the possible errors in the determination of r_{H-M} resulting from inaccuracy in the relaxation times. It seems to be realistic to assume a 5% experimental error for T_1 measurements on modern NMR spectrometers which corresponds to the reproducibility of the relaxation data under investigation. Consequently, as it follows from eq 7, the assumed error in T_{1min} causes a negligibly small error in the bond distance r_{H-M}. For the present approach based on measurement of T_{1s}, the only experimental parameter appreciably influencing r_{H-M} is the ratio $T_{1s}/T_1 = f$. It is instructive to examine the two cases when $f_1 = 1.125$ ($k_1 = 1$) and $f_2 = 1.312$ ($k_2 = 5$). Simple calculations (eq 7) show that a change in r_{H-M} by 1.5–2% ($\Delta r \cong 0.03$ Å, if $r = 1.7$ Å) is followed by changes in k_1 and k_2 by 40 and 15%, respectively. However, while the significant error in k seems to be not dramatic for the calculation of the r_{M-H} distance, the real accuracies needed when determining f_1 and f_2 have to be 1.5 and 3%, respectively, that constitutes a quite rigorous condition.

Practically all distances in Table I were obtained with k averaged on five experimental values. This approach seemingly provides satisfactory accuracy, since the r_{H-M} distances in 3 and **8** were reproduced with errors ≤0.03 Å and similar errors (0.02–0.05 Å) were estimated (at the confidence level of 95%) for most of the other complexes.

In the calculations of internuclear distances from T_1 relaxation data another principal error can be caused by anisotropic molecular motion in solution. Note, that eqs 3 and 5–7 are valid only when reorientations of the internuclear vectors with respect to the external magnetic field can be characterized by a single correlation time, τ_c. Recent studies have revealed several examples of hydride complexes that apparently violate this condition.[1f,2d,3] The plots in Figures 1 and 2 also call into question the validity of the common approach implying isotropic molecular motions.

Both Figures 1 and 2 clearly show that the CH_3 relaxation in 3 and **8** does not go through a minimum at a temperature higher than those at which T_1 of the H ligands are minimal. This obviously contradicts eqs 3 and 5.[1e,17] The observation that for the hydride ligands of **8** the temperature dependencies of T_1 go through minima at different temperatures (Figure 1) is in addition difficult to rationalize in terms of a model of isotropic molecular motion (IMM).

An anisotropic motion is characteristic of macromolecules or sometimes even small molecules in solution, especially in viscous media. In such cases it is useful to modify the expressions for T_1 by introducing in an appropriate manner a distribution of molecular correlation times (DCT). Thus τ_c becomes a center of the distribution, the width of which being represented by a distribution parameter.[19a,b]

Symmetric and asymmetric distributions are the most typical cases of DCT. While the latter is known to have insignificant influence on T_{1min},[19b,c] the former commonly results in substantial underestimation of E_a and overestimation of T_{1min} values when analyzing the temperature-dependent T_1 data in terms of IMM.[19b] Consequently, if DCT is not taken into account, there is a chance of overestimation of internuclear distances.

Empirical density functions suggested by Cole and Cole (C–C DCT),[20a] and Fouss and Kirkwood (F–K DCT)[20b] are quite successful models for the symmetric DCT and allow a qualitative consideration of the hydride relaxation.

It is known[19b] that when C–C or F–K DCT are valid, the limiting values of the slopes of ln T_1 against $1/T$ curves, i.e. $E_a(\text{obs})/R$, are proportional to the distribution parameters γ or β, respectively, i.e.

$$E_a(\text{obs}) = \gamma E_a\ (\text{or } \beta E_a)$$

where E_a and E_a(obs) are the real and experimentally determined activation energies, respectively, and $0 < (\gamma \text{ or } \beta) \leq 1$.

The E_a(obs) values for the Re and Mn complexes in Table I amount to 2.6–2.8 kcal/mol in CD_2Cl_2 and 2.4–3.3 kcal/mol in toluene. These energies can be compared with those known for the cases where IMM is evident for geometrical reasons ($HMn(CO)_5$, THF-d_4–CD_2Cl_2 (5%), $E_a = 2.52$ kcal/mol)[1a] or when it follows from the experimental data ($OsH_4(PTol_3)_3$, (CD_2Cl_2), 2.53 kcal/mol; ($Fe(\eta^2\text{-}H_2)(H)(dppe)_2)BF_4$, acetone-$d_6$, 2.6 kcal/mol; ($Ru(\eta^2\text{-}H_2)(H)(dppe)_2)BF_4$, acetone-$d_6$, 2.5 kcal/mol; ($Os(\eta^2\text{-}H_2)(H)(depe)_2)BPh_4$, (acetone-$d_6$), 2.9 kcal/mol).[1b,3] This comparison demonstrates that among complexes **1–8** one does not likely deal with a case which could be substantially affected by a distribution of correlation times.

To make the consideration more quantitative we can suggest that the values of γ and β of 0.6–0.7 determined for macromol-

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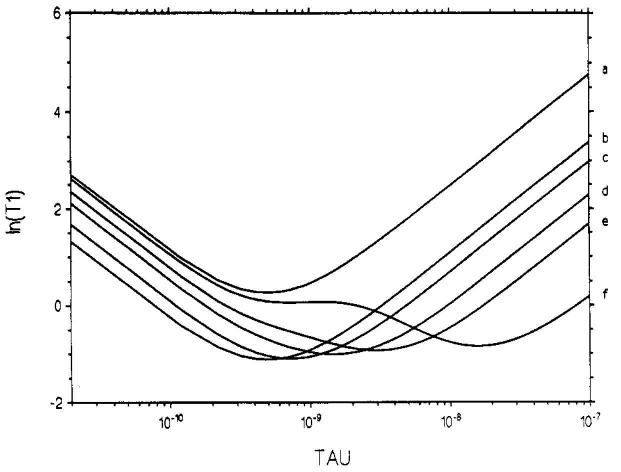

Figure 3. Effect of variation of ρ on T_1 relaxation (eq 8) of a pair of protons fixed in a symmetric ellipsoid with the internuclear distance of 2 Å at 200 MHz. The angle between the internuclear vector and the long axis of the ellipsoid, α, is 90°. (a) $\rho = \infty$, (b) $\rho = 1$, (c) $\rho = 2$, (d) $\rho = 5$, (e) $\rho = 10$, and (f) $\rho = 50$.

ecules (polyethylene glycol 200 and polyoxymethylene)[19b] could be the reasonable limiting values for the distribution parameters of complexes **1**–**8** or those of similar structure in the presence of symmetric DCT. Using the known equation for F–K DCT with β of 0.7, we have calculated that the distribution results in overestimation of $T_{1\min}$ values by 25%; i.e., for example, for r_{M-H} of 1.7 Å, the "observed" distance must be equal to 1.76 Å. Thus, even in such a quite unrealistic situation the error in $T_{1\min}$ and r_{M-H} (the latter is less then 4%) does not seem to be dramatic.

Some of the complexes studied in this work have two trans PR_3 ligands and their rotational motion is similar to that of an ellipsoid in a continuous medium. Woessner has presented a detailed discussion of the T_1 relaxation in the idealized case of two identical nuclei of spin $I = {}^1/_2$ fixed in a symmetric ellipsoid undergoing anisotropic rotational diffusion.[21] In contrast to the isotropic case, the anisotropic relaxation depends both on the orientation of the internuclear vector in the ellipsoid and on the ratio of the rotational diffusion coefficients, $\rho = D_\parallel/D_\perp$. The main anisotropy effect is expressed in an increase of T_1 times and when the ratio becomes very large and the internuclear vector is perpendicular to the motional axis of symmetry ($\alpha = 90°$), the anisotropy effect amounts to a maximum: $T_1(\text{aniso}) = 4T_1(\text{iso})$.

For $IrH_5(PPr^i_3)_2$, which is similar to a symmetric top, a crude calculation of the moments of inertia has yielded $I_\parallel/I_\perp = 0.41$.[3] This means that for a typical *trans*-bis(phosphane) complex the ratio, ρ, can not be large and $\rho = 5$ could be treated as the upper limit. In this case, if $\omega_H{}^2\tau^2 \ll 1$ ($\tau = 1/6D_\perp$), the anisotropy effect ($T_1(\text{iso})/T_1(\text{aniso}) = 0.58$ and 0.45 when α is 45 and 90°, respectively[21]) is substantial and has to be taken into account.

To understand the influence of the anisotropic motion on the ratio between $T_{1\min}(\text{iso})$ and $T_{1\min}(\text{aniso})$ we have investigated eq 8 obtained by using Woessner expressions for the spectral densities[21] with $\alpha = 90°$, where $a = (2\rho + 1)/3$ and $\tau = 1/6D_\perp$.

$$1/T_1 = (3/40)\gamma_H{}^4\hbar^2 r_{H-H}{}^{-6}\tau(1/(1 + \omega_H{}^2\tau^2) + 4/(1 + 4\omega_H{}^2\tau^2) + 3a/(a^2 + \omega_H{}^2\tau^2) + 12a/(a^2 + 4\omega_H{}^2\tau^2)) \quad (8)$$

Figure 3 shows the ln T_1 vs τ curves for $\omega = 2\pi(200\ \text{MHz})$, $r_{H-H} = 2$ Å and ρ of 1 (the isotropic case), 2, 5, 10, 50, and ∞. The theoretical dependencies go through the corresponding $T_{1\min}$'s of 330, 336, 367, 396, 430, and 1320 ms. Consequently, when $\rho = 5$ for a real symmetric toplike complex, the distance of 2.035 Å could be calculated from $T_{1\min}$ by using the common approach.

It follows from the presented analysis that $T_{1\min}$ is a very reliable parameter which is quite insensitive to the character of molecular motion. In this context it should be pointed out that the 4-fold difference between the experimental and theoretical $T_{1\min}$ values found[3] for $IrH_5(PPr^i_3)_2$ and $(ReH_8(PPh_3))^-$ could not be explained by an anisotropy of molecular tumbling. An alternative reason for the observed phenomenon can be a very fast intramolecular motion of the hydride ligands. It can, for example, be imagined that a fast rotation of the pentahydride "ring" in $IrH_5(PPr^i_3)_2$ around the P–Ir–P axis occurs, which indeed could cause a strong increase of the relaxation time. This would certainly be a matter for separate studies.

Figure 3 reveals another interesting fact: the position of the $T_{1\min}$ time, $\tau_{\min}$, changes substantially with ρ. In addition, there should also be a dependence of $\tau(\min)$ on α. According to the results of our calculations the minima occur at 2.06τ (min, iso) and 3.02τ (min, iso), if $\rho = 5$ and $\alpha =$ to 45 and 90°, respectively (τ(min, iso) is the value for the isotropic case, $\rho = 1$). Thus, when treating the relaxation in a symmetric ellipsoid and assuming an isotropic motion, the value of E_a can still be meaningful, while the correlation time constant τ_0 becomes a fictitious parameter.

The major part of the Re–H distances calculated in this work (1.69–1.74 Å) is in fairly good agreement with the data from neutron diffraction studies on other rhenium hydride complexes, for which the typical Re–H bond lengths were determined to be between 1.67 and 1.69 Å.[22] The NMR distances seem to be a little longer than those from neutron diffraction data. But most likely, as in the case for $ReH(CO)_3(PPh_3)_2$, where the r_{Re-H} value of 1.75 Å has been estimated by NMR,[1c] the elongation found in some of our complexes could be attributed to real chemical factors like the low oxidation state of rhenium center or possibly to the high trans influence of the CO ligand. Probably the latter is the reason for the shorter Re–H bond in the cis isomer of $ReH(CO)(PMe_3)_4$ (**5a**). It is interesting to note that the longer Re–H bond of the trans isomer **5b** would be in accord with the substantially higher reactivity toward insertions of small unsaturated molecules.[23]

The Mn–H bond lengths calculated for **1** (1.59 ± 0.02 Å) and **2** (1.62 ± 0.02 Å) constitute very reasonable values, which are approximately 0.1 Å shorter than r_{Re-H} and which agree well with the neutron diffraction[24] and NMR[1a] data obtained for $MnH(CO)_5$ (1.60 ± 0.03 and 1.65 ± 0.05 Å, respectively).

Table I lists the distances between the H ligands in dihydrides **6**–**8** calculated from the selective and biselective relaxation times. All values obtained are practically identical and correspond to an H–Re–H angle of about 80°.

As seen from Table I the differences within the series of Mn–H or Re–H bond distances are quite small. It can therefore be concluded that the M–H bond lengths are obviously dependent on the size of the transition metal center, but are not so strongly affected by even substantial chemical changes in the ligand sphere.

Thus, this work provides experimental and theoretical evidence that in mononuclear hydride complexes containing two, three, or four PR_3 ligands, ^1H T_1 relaxation, effected by HHDDI and MHDDI in the absence of a very fast intramolecular motion of H ligands, can be successfully treated by assuming an isotropic molecular motion causing an error in the determination of the internuclear distances of less than 4%.

Acknowledgment. We thank the Swiss National Science Foundation for financial support.

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Appendix

Equations 1 and 2 can be written as

$$1/T_1 = aC_1\tau_c + bC_2\tau_c \qquad \text{(A1)}$$

$$1/T_{1s} = cC_1\tau_c + bC_2\tau_c \qquad \text{(A2)}$$

where $a = 1/(1 + \omega_H^2\tau_c^2) + 4/(1 + 4\omega_H^2\tau_c^2)$, $b = 3/(1 + \omega_H^2\tau_c^2) + 6/(1 + (\omega_H + \omega_M)^2\tau_c^2) + 1/(1 + (\omega_H - \omega_M)^2\tau_c^2)$, and $c = 1/(1 + \omega_H^2\tau_c^2) + 2/(1 + 4\omega_H^2\tau_c^2) + {}^1/_3$.

Then

$$T_{1s}/T_1 = (aC_1\tau_c + bC_2\tau_c)/(cC_1\tau_c + bC_2\tau_c) = f \qquad \text{(A3)}$$

$fcC_1 + fbC_2 = aC_1 + bC_2$ and $fcC_1/C_2 + fb = aC_1/C_2 + b$.

If $C_1/C_2 = k$ the latter can be written as $kfc - ka = b - fb$ and $k = b(f - 1)/(a - cf)$.

When $\omega_H^2\tau_c^2$, $(\omega_H + \omega_M)^2\tau_c^2$, and $(\omega_H - \omega_M)^2\tau_c^2 \ll 1$ (the fast motion regime) $a = 5$, $b = 10$, and $c = {}^{10}/_3$.

Then $k = 10(f - 1)/(5 - 10f/3) = (f - 1)/(0.5 - f/3)$.