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Review

Dihydrogen, dihydride and in between: NMR and structural properties of iron group complexes

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Abstract

Tabulating the structures and characteristic NMR properties of 17 iron complexes, 98 ruthenium complexes and 70 osmium complexes that contain dihydrogen or compressed dihydride ligands reveals a variety of trends. The H—H bond lengths increase from similar Fe(II) to Ru(II) to Os(II) complexes. Iron(II) displays a narrow range of H—H distances for stable complexes. Electronegative atoms Cl and O, when attached on the metal trans to the dihydrogen ligand, result in elongation of the H—H bond relative to more electropositive atoms H, C, P and N. The family of cyclopentadienyl ligands also causes this elongating effect. The dihydrogen ligands with short H—H distances and weak interactions with the metal, especially on iron and ruthenium are in the fast spinning regime. One exception is the biporphyrin complex of ruthenium with the side-on bridging H_2 ligand which has an H—H distance of 118 pm but is in the fast spinning regime. There are some ruthenium complexes with H—H distances greater than 110 pm that are in the slow motion regime and several complexes of osmium with H—H distances greater than 130 pm that

Abbreviations: binap, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; bpy, bipyridine; bpzm, bis(pyrazol-1-yl)methane; cod, 1,5-cyclooctadiene; dach, *trans*-1,2-diaminocyclohexane; dcpp, $PCy_2CH_2CH_2CH_2PCy_2$; dcype, $PCy_2CH_2CH_2PCy_2$; DFT, density functional theory; dppip, 2,2-bis(diphenylphosphino)propane; diphos, chelating bis(diphosphino)ligand; dmpe, $PMe_2CH_2CH_2PMe_2$; dmpm, $PMe_2CH_2PMe_2$; dmpm, bis-dimethylphosphinomethane; dpen, 1,2-diphenylethylenediamine; dippach, $P^iPr_2NHC_6H_{10}NHP^iPr_2$; dippae, $P^iPr_2NHCH_2CH_2NHP^iPr_2$; dppe, $PPh_2CH_2CH_2PPh_2$; dppp, $PPh_2CH_2CH_2CH_2PPh_2$; dppm, $PPh_2CH_2PPh_2$; $HBPz_3^-$, hydridotris(pyrazolyl)borate; HCn, 1,4,7-triazacyclononane; imid*, 1-*tert*-butyl-3-phenyl-imidazole; INS, inelastic neutron scattering; MeCN, 1,4,7-trimethyl-1,4,7-triazacyclononane; *meso*-tetraphos-1, $PPh_2CH_2CH_2PPhCH_2CH_2PPhCH_2CH_2PPh_2$; oep, octaethylporphyrin; OTf^-, $CF_3SO_3^-$; pcp, $[C_6H_3(CH_2PPh_2)_2\text{-}2,6]^-$; Pcyp3, tris(cyclopentyl)phosphine; $pybuS_4^{2-}$, 2,6-$\{2,5\text{-}^t$Bu-6-$S^-\text{-}C_6H_2SCH_2\}_2C_5H_3N$; Spy^-, 2-mercaptopyridine anion; QEC, quantum mechanical exchange coupling; tpm, tris(pyrazolyl)methane.

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are in this regime. The large J_{HH} due to quantum mechanical exchange coupling are observable for some of these osmium complexes with H–H distances in the range of 140–160 pm. The dihydrogen ligands in many complexes appear to have librational motions or other motions that place them in the intermediate motion regime. New equations to correlate J_{HD} with H–H distances for ruthenium dihydrogen complexes and for osmium dihydrogen complexes are introduced here.

Keywords: Iron; Ruthenium; Osmium; Hydride; Dihydrogen; NMR; Coupling constant; T_1

1. Introduction

Kubas has defined dihydrogen complexes as transition metal complexes with a side-on bonded dihydrogen ligand with an H–H bond distance in the range from 80 to 120 pm [1]. Compounds with metal–hydrogen bonds and with longer H–H distances are defined as compressed dihydrides (120–160 pm) or dihydrides (>160 pm). There is not a definite transition from one form to another in this continuum of structures and so these definitions are somewhat arbitrary. Dihydrogen ligands with H–H distances greater than about 100 pm have also been referred to as elongated or stretched dihydrogen ligands. The chemistry of such compounds is of direct relevance to the action of the hydrogenase enzymes in biology, to the mechanism of catalytic reactions involving hydrogen or element–hydrogen bonds in industry and academia, and to the design of hydrogen storage materials in the energy sector.

Nuclear magnetic resonance played a key role in the identification of the first stable dihydrogen complexes of transition metals. The observation of a large ^1H–^2H coupling in the high field resonance in the ^1H NMR spectrum of the complex $W(HD)(P^iPr_3)_2(CO)_3$ was convincing evidence that such a sigma complex could exist in a stable form [2]. This has turned out to be the most useful diagnostic for the presence of H–H bonding in solution [1,3–6]. Another useful diagnostic for complexes in solution is the minimum with respect to temperature of the spin-lattice relaxation time (T_1^{min}) of the ^1H NMR resonance of the hydrogens [7–10]. The short H–H distance of dihydrogen complexes result in short T_1 times, a characteristic property of the dihydrogen ligand. Much data has been collected but its quantitative interpretation has been a challenge since the motion of the dihydrogen ligand modifies this property in complex ways [11].

The triad of elements iron, ruthenium and osmium provides the largest range of known dihydrogen complexes. The formal oxidation states are typically Fe(II), Ru(II) and Os(II) or Os(IV). The objective of this review is to tabulate J_{HD}, T_1^{min} and H–H distances (d_{HH}) for such complexes in the literature and to categorize the structures on the basis of their approximately octahedral structure (except for 5 and 7 coordination complexes). This allows an overview of the obscure effects that the ligand structure and electronics have on the dihydrogen or compressed dihydride H–H distance and NMR properties. In addition it makes use of abundant T_1 data to constrain the possible d_{HH} values of dihydrogen complexes. This helps to obtain new d_{HH} versus J_{HD} correlations for individual metals, ruthenium and osmium, in the case of this article. The data for several polyhydride complexes of the iron group have been omitted because of the difficulty in relating NMR properties to possible structures of these [9]. The ^2H NMR and ^3H NMR properties both in solution and the solid state of dihydrogen complexes labelled with isotopes ^2H [12–18] and ^3H [19–22] have also proven informative but will only be mentioned briefly in this review.

2. Equations relating the hydrogen–hydrogen distance (d_{HH}) in a dihydrogen or dihydride complex and the coupling constant J_{HD} of its deuterated isotopomer

2.1. The dihydrogen regime where J_{HD} is greater than 15 Hz

Dihydrogen complexes have been arbitrarily defined above to have H–H distances of less than 120 pm. The HD isotopomer of such complexes will usually have $^1J_{HD}$ values of greater than approximately 15 Hz. Preparing the HD isotopomer of a dihydrogen complex and measuring its $^1J_{HD}$ coupling constant is usually a straightforward process [1,5,6]. In some cases rapid intramolecular exchange of hydrogen isotopes in deuterated hydride(dihydrogen) complexes results in an averaged J_{HD} value. In these cases only approximate $^1J_{HD}$ values can be obtained by making assumptions about the nature of the averaging process, the magnitude of coupling constants for pairs of isotopes and the nature of the distribution of isotopes in the isotopomers of the complex [5,23,24]. In a few cases, the $^1J_{HD}$ value is temperature dependent [20,22,25–27]. In two cases, the dihydrogen complex has sufficient diamagnetic anisotropy to partially align in the magnetic field of the NMR magnet, especially at high fields. This leads to residual H–D dipolar couplings added [28] or subtracted [29] from the scalar $^1J_{HD}$ value. Tables 1 and 2

report the scalar values.

Obtaining correct H–H distances for dihydrogen complexes in solution is a challenge. A successful approach is to correlate the H–H distance observed in solid-state structures with HD coupling constants for the HD isotopomers in solution with the assumption that the structure does not change from the solid to the solution. The first correlations proposed made use of distances determined by single crystal neutron diffraction, solid-state NMR, X-ray diffraction and T_1 measurements. The Morris group proposed Eq. (1) (converted here from Å to pm) on the basis of 79 J_{HD} values determined for solutions of HD complexes matched with 15 distances from solid-state measurements, and 64 approximate distances from T_1 measurements for solutions

Table 1
Properties of osmium complexes

	Complex $[Os(H_2)(L^t)(L^{cis})_m]^{n+}$	$n+$	L^t	L^{cis}	$J_{HD,obs}$ (Hz)	$J_{HD,cor}$ (Hz)	$T_{1,obs}$ (ms)	$T_{1,HH}^{min}$ (ms)	ν (MHz)	d_{HH}^{slow} (pm)	d_{HH}^{fast} (pm)	J_{HH} (Hz)	d_{HH} other[a] (pm)	$d_{HH,av}$ (pm)	d_{HH}^{eq15}	Ref.
1	$Os(H_2)CO(H)Cl(P^iPr_3)_2$	0	H	P_2CCl	30.9	30.9	6	6	300	96	76			86	91	[71–73]
2	$Os(H_2)CO(H)I(P^iPr_3)_2$	0	H	P_2IC	29.9	29.9	7	7	300	98	78			88	93	[73]
3	$OsH(H_2)(CO)[2,6\text{-}(CH_2P^tBu_2)_2C_6H_3]$	0	H	P_2C_2	29.8	29.8	7.9	7.9	300	100	79			90	93	[74]
4	$Os(H_2)(H)_2(CO)(P^tBu_2Me)_2$	0	H	P_2CH	4.3	22.6	24	14.2	300	110				110	107	[73]
5	$[Os(H_2)H(PPh_3)\{PPh_2CH_2\text{-}C_5H_3NCH(CPh{=}CH_2\}PPh_2]BF_4$ Isomer 1	1	H	P_3N	30	30	14.5	14.5	300	111	88			99	92	[75]
6	$[Os(H_2)H(PPh_3)\{PPh_2CH_2C_5H_3NCH\text{-}(CPh{=}CH_2\}PPh_2]BF_4$ Isomer 2	1	H	P_3N	29.7	29.7		15.2	300	112	89			100	93	[75]
7	$[Os(H_2)H(meso\text{-tetraphos-1})]^+$, *trans*	1	H	P_4	26.4	26.4	32	32	400		96			96	99	[47]
8	$[Os(H_2)H(P(C_6H_4CF_3)_2CH_2CH_2\text{-}P(C_6H_4CF_3)_2)_2]^+$ *trans*	1	H	P_4	25.5	25.5	15	15	200		95			95	101	[76]
9	$[Os(H_2)H(dppe)_2](BF_4$ or $PF_6)$ *trans*	1	H	P_4	25.5	25.5	40	40	400		99			99	101	[10]
10	$[Os(H_2)(H)(PPh_2OEt)_4]^+$	1	H	P_4	20	20	10	11	200	113				113	112	[77]
11	$[Os(H_2)H(depe)_2]BPh_4$ *trans*	1	H	P_4	10.5–11.4	10.5–11.4	69	80	400	141	111			126	130	[10]
12	$[OsH_3(dcype)_2]BPh_4$	1	H	P_4	0	0	35		80	160				144	150	[78]
13	$[Os(H_2)H(P(CH_2CH_2PPh_2)_3)]BPh_4$ *cis*	1	P	P_3H	7.5–8.3	22.5	22	18	300	115	91			106	107	[54]
14	$[Os(H_2)CO(dppp)_2](O_3SCF_3)_2$	2	C	P_4	32	32	5.5	6	200	102	81			92	89	[79]
15	$[Os(H_2)(^{13}CNH)(dppp)_2](OTf)_2$, *trans*	2	C	P_4		28.8	7	7.6	200	107	84			96	95	[80]
16	$[Os(H_2)(^{13}CNH)(dppe)_2](OTf)_2$, *trans*	2	C	P_4		29.1	14	14	300	110	87			99	94	[80]
17	$[Os(H_2)(CN)(dppe)_2]BF_4$, *trans*	1	C	P_4		28.7	14.7	14.7	300	111	88			100	95	[80]
18	$[Os(H_2)(^{13}CN)(depe)_2](OTf)$, *trans*	1	C	P_4		25.4	16	16	300	113	89			101	101	[80]
19	$[Os(H_2)(PPh_3)\{2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N\}]BF_4$	1	C	P_3N		29.7	16.2	16.2	300	113	90			101	93	[75]
20	$[Os(C_5Me_5)(CO)_2(H_2)][B(C_6F_5)_4]$	1	C	C_4		24.5	24	24	500	111	88			99	103	[55]
21	$[Os(C_5H_5)(dppm)H_2][B(C_6F_5)_4]$	1	C	P_2C_2		3		240	500	163		133–176		163	144	[55]
22	$[Os(C_5Me_5)(PPh_3)H_2(H_2)][BF_4]$	1	C	PH_2C_2	3.6	16.6–26.6	99	77	500		107		78(8) X, 101(1) N,105 (94 with BF_4^-) D	98	99–118	[24]
23	$[Os(C_5Me_5)(AsPh_3)H_2(H_2)][BF_4]$	1	C	AsH_2C_2	2.8	11.8–21.8	130		500		116		108(1) N	120	108–127	[24]
24	$[Os(C_5Me_5)(PCy_3)H_2(H_2)][BF_4]$	1	C	PH_2C_2	3.4	15.4–25.4	41		500	112			114(7) X, 131(3) N, 168, 155 with BF_4^- D	132	101–120	[24]
25	$Os(H_2)(CO)(eta\text{-}2\text{-}S_2CH)(P^iPr_3)_2$	0	S	P_2CS	25.1	25.1	8	8	300	100				100	102	[56]
26	$Os(H_2)(pybuS_4)$	0	N	S_4	31.2	31.2	6	6	270	97	77			87	90	[58]
27	$[Os(H_2)(\kappa^1\text{-}OCMe_2)(P^iPr_3)(HBPz_3)]BF_4$	2	N	PON_2^-			19	19	300		92		80(10) X, 92 D	92		[59]
28	$[Os(H_2)_2(P^iPr_3)(HBPz_3)]BF_4$	2	N	$P(H_2)N_2^-$			12	12	300	107	85		84(1), 111(1) X, 91 D	96		[59]
29	$[Os(H_2)(PPh_3)_2(bpy)(CO)](OTf)_2$	2	N	P_2CN	25.3	25.3	15	15.2	500	103	81			92	101	[81]
30	$[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$	2	N	P_2CN	25.5	25.5	6.3	6.3	200	103				103	101	[81]
31	$[Os(H_2)(PMePh_2)_2(bpy)(CO)]^{2+}$	2	N	P_2CN	25.5	25.5	16.5	16.5	500	104				104	101	[81]
32	$[Os(H_2)(CH_3CN)_3(P^iPr_3)_2]^{2+}$	2	N	P_2N_2	25.5	25.5	12	12	300	107	85			96	101	[82]
33	$[Os(H_2)(PPh_3)_2(HBPz_3)]BF_4$	2	N	$P_2N_2^-$	24.8	24.8	31	31	400	120	95			108	102	[83]
34	$[Os(H_2)(CH_3CN)(dppe)_2]^{2+}$ *trans*	2	N	P_4	21.4	21.4	28	28	400	118	94			106	109	[57]
35	$[Os(H_2)(PPh_3)_2(pyS)(CO)]BF_4$	1	N	P_2CS	21	21	16	17	400	108				108	110	[84]
36	$[Os(H_2)(=CCH_2CH_2CH_2CH_2O)(NH_3)_4]^{2+}$ *cis*	2	N	CN_3	22.7	22.7	21	21	400	112	89			101	106	[85]
37	$[Os(H_2)(pyrazine)(NH_3)_4]^{2+}$ *trans*	2	N	N_4	23.4	23.4	24	24	400	115	91			103	105	[85]
38	$[Os(H_2)(py)(en)_2]^{2+}$ *cis*	2	N	N_4	18	18	27	27	400	117	93			105	115	[86]
39	$[Os(H_2)(py)(NH_3)_4]^{2+}$ *cis*	2	N	N_4	20.2	20.2	28	28	400	118	94			106	111	[40,87]
40	$[Os(H_2)(py)(en)_2]^{2+}$ *trans*	2	N	N_4	19	19	32	32	400	121	96			108	114	[86]
41	$[Os(H_2)(CH_3CN)(en)_2]^{2+}$	2	N	N_4	17.7	17.7	32	32	400	121	96			108	116	[86]
42	$[Os(H_2)(py)(NH_3)_4]^{2+}$ *trans*	2	N	N_4	19.6	19.6	38	38	400	124	98			111	112	[40,87]
43	$[Os(H_2)(imid)(NH_3)_4]^{2+}$ *trans*	2	N	N_4	17.1	17.1	63	63	400	135	107			121	117	[40,87]

Table 1(*Continued*)

	Complex $[Os(H_2)(L^t)(L^{cis})_m]^{n+}$	n+	L^t	L^{cis}	$J_{HD,obs}$ (Hz)	$J_{HD,cor}$ (Hz)	$T_{1,obs}$ (ms)	$T_{1,HH}^{min}$ (ms)	ν (MHz)	d_{HH}^{slow} (pm)	d_{HH}^{fast} (pm)	J_{HH} (Hz)	d_{HH} other[a] (pm)	$d_{HH,av}$ (pm)	d_{HH}^{eq17}	Ref.
44	$[Os(H_2)H(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(P^iPr_3)_2]BF_4$	1	N	$P_2(CC)H$	4.7	4.7	48	48	300	135				135	141	[60]
45	$Os(H_2)(NC_5H_4\text{-}o\text{-}CH{=}CH)Cl(P^iPr_3)_2$	0	N	P_2CCl	6.3	6.3	39	39	300	131				131	138	[60]
46	$Os(H_2)Cl(NH{=}C(Ph)C_6H_4)(P^iPr_3)_2$	0	N	P_2CCl	6.3	6.3	49	49	300	141		9700–12,000	146 D	144	138	[61]
47	$Os(H_2)(P^iPr_3)_2Cl_2(CO)$	0	Cl	P_2CCl	20.1	20.1	15	15	300	112	88			100	111	[88,89]
48	$[Os(H_2)Cl(PPh_3)\{2,6\text{-}(PPh_2CH_2)_2C_5H_3N)\}]BF_4$	1	Cl	P_3N	17.7	17.7	39	43	300	133	105			119	116	[90]
49	$[Os(H_2)Cl(dppe)_2]PF_6$	1	Cl	P_4	13.6	13.6	53	66	400	136	108		115–122(3) N, 111 (PF_6) 135 (no PF_6) D	122	124	[30,33]
50	$[Os(H_2)Cl(depe)_2]^+$	1	Cl	P_4	13.1	13.1	60	68	400	138	108			123	125	[30]
51	$[Os(H_2)Cl(dcype)_2]^+$	1	Cl	P_4	10.5	10.5	10	10	80	130				130	130	[78]
52	$OsCl_2(H_2)(NH{=}CPh_2)(P^iPr_3)_2$	1	Cl	P_2NCl	10.5	10.5	32	32	300	127			129 X	128	130	[91]
53	$Os(H_2)Cl(PPh_3)(pcp)$	0	Cl	P_3C	9	9	48	48	300	135				135	133	[92]
54	$Os(H_2)H(Cl)(PPh_3)_3$	0	Cl	P_3H			<26		300				148 N	148		[62]
55	$[Os(H_2)(OAc)(PPh_3)_3]^+$	1	O	P_3O	13.7	13.7	41	41	400	126	100			113	124	[93]
56	$[Os(H_2)(en)_2(OAc)]PF_6$	1	O	N_4	9	9	61	61	400	134			134(2) N, 128 D	132	133	[33,40,94]
57	$[Os(H_2)(D_2O)(NH_3)_4]^{2+}$ *trans*	2	O	N_4	8.1	8.1	77	77	400	140				140	134	[40,87]
58	$[Os\{C_6H_4C(O)CH_3\}Cl(H_2)(P^iPr_3)_2]BF_4$	1	O	P_2CCl	4.5	4.5	50	50	300	136			149 D	143	141	[95]
59	$Os\{C_6H_4C(O)CH_3\}F(H_2)(P^iPr_3)_2$	1	O	P_2CF			64	64	300	142			134 X, 154 D	143		[95]
60	$[Os\{C_6H_4C(O)CH_3\}(H_2)\{\kappa^1\text{-}(CH_3)_2CO\}(P^iPr_3)_2]BF_4$	1	O	P_2CO			48	48	300	136			149 X	143		[95]
61	$OsH_2(SnPh_2Cl)\{2,5\text{-}C_6H_3(OCH_3)C(O)H\}(P^iPr_3)_2$	0	O	P_2SnC			74	76	300	146		48		146		[96]
62	$OsH_2(SnPh_2Cl)\{C_4(O)H_2C(O)H\}(P^iPr_3)_2$	0	O	P_2SnC			60	62	300	141		267	141 X	141		[96]
63	$OsH_2(SnPh_2Cl)\{2,6\text{-}C_6H_3(OCH_3)C(O)H\}(P^iPr_3)_2$	0	O	P_2SnC			66	68	300	143		56	141 X	142		[96]
64	$OsH_2(SnPh_2Cl)\{C_6H_3(CF_3)C(O)H\}(P^iPr_3)_2$	0	O	P_2SnC			73	75	300	145		38		145		[96]
65	$OsH_2(SnPh_2Cl)\{C_6H_4C(O)H\}(P^iPr_3)_2$	0	O	P_2SnC			78	80	300	147		42	146 X	147		[96]
66	$OsH_2(SnPh_2Cl)\{C_6H_3(CF_3)C(O)H\}(P^iPr_3)_2$	0	O	P_2SnC			86	90	300	150		42		150		[96]
67	$OsCl\{OC(Ph)OSnPh_2\}(H_2)(P^iPr_3)_2$	0	O	P_2SnCl			80	90	300	150		303	139(9) X	145		[97]
68	$OsCl\{OC(Ph)OSn(\kappa^2\text{-}O_2CPh)Ph\}(H_2)(P^iPr_3)_2$	0	O	P_2SnCl			64	66	300	146			152(5) X	149		[97]
69	$Os(SnPh_2Cl)(\kappa^2\text{-}O_2CPh)(H_2)(P^iPr_3)_2$	0	O	P_2SnO			74	90	300	150		243		150		[97]
70	$OsH_2Cl[CH(C_2H_4P^tBu_2)_2]$	0	-	P_2CCl		0	109		300	168			157(3) X	163		[63]

[a] (X) X-ray, (N) neutron, (D) DFT.

Table 2
Properties of ruthenium complexes

	Complex $[Ru(H_2)(L^t)(L^{cis})_m]^{n+}$	n+	L^t	L^{cis}	$J_{HD,cor}$ (Hz)	$T_{1,obs}$ (ms)	$T_{1,HH}^{min}$ (ms)	ν (MHz)	d_{HH}^{slow} (pm)	d_{HH}^{fast} (pm)	d_{HH} other[a] (pm)	$d_{HH,av}$ (pm)	d_{HH}^{eq16} (pm)	Ref.
1	$Ru(H_2)(H)_2(HSiPh_3)(PCy_3)_2$	0	H	$P_2(HSi)H$							82(2) X, 85 D	83		[98]
2	$Ru(H_2)_2H_2(PCyp_3)_2$	0	H	$P_2(H_2)H$		<95	<67	500		<110	70(4) X, 0.83(1) N, 85 D	85		[99]
3	$Ru(H_2)H_2(\eta^2\text{-HBpin})(PCy_3)_2$	0	H	$P_2(HB)H$		40	18	300		91	79(3) X, 86 D	88		[100]
4	$Ru(H_2)H_2(\eta^2\text{-HBcat})(PCy_3)_2$	0	H	$P_2(HB)H$		47	21	300		94	77(3) X, 86 D	90		[100]
5	$Ru(H_2)_2H_2(P^iPr_3)_2$	0	H	$P_2(H_2)H$	30	60	40	500		95		95	94	[101]
6	$Ru(H_2)(CO)(H)_2(P^iPr_3)_2$	0	H	P_2CH	32.4	15	8	200	108	85		96	90	[102]
7	[Ru(H2)(dcpp)(*m*-H)3Ru(dcpp)]	0	H	P_2H_2		53	20	400		88	83 X	88		[103]
8	$Ru(H_2)H_2(PCy_3)_2$(L1) L1 = 2-phenyl-3,4-dimethylphosphaferrocene	0	H	P_3H	30	37	20	400.1		88	88(3) X	88	94	[104]
9	$Ru(H_2)H_2(PPh_3)_3$	0	H	P_3H	16.2	20	11	200	113			113	115	[7,9,105]
10	$[Ru(H_2)H((R)\text{-binap})((R,R)\text{-dpen})]^+$ *trans*	1	H	P_2N_2	37								84	[106]
11	$[Ru_2(H_2)(S_2C_3H_6)(H)(CO)_3(PCy_3)_2]^+$	1	H	PCS_2	31	30	30	500		91		91	93	[107]
12	$[Ru(H_2)H(P(C_6H_4CF_3)_2CH_2CH_2P(C_6H_4CF_3)_2)]^+$ *trans*	1	H	P_4	33.1	10	10	200		88		88	89	[76]
13	$[Ru(H_2)H(meso\text{-tetraphos-1})]^+$, *trans*	1	H	P_4	33.5	20	20	400		88		88	89	[47]
14	$[Ru(H_2)H(dppe)_2]BPh_4$	1	H	P_4	32	21	21	400		89	82–94(3) N	89	91	[16,46]
15	$[Ru(H_2)H(P(C_6H_4OMe)_2CH_2CH_2P(C_6H_4OMe)_2)_2]^+$ *trans*	1	H	P_4	31	11	11	200		90		90	93	[76]
16	$[Ru(H_2)(H)(PPhOEt_2)_4]^+$ *trans*	1	H	P_4	32	5	5	80		92		92	91	[108]
17	$[Ru(H_2)H(dcype)_2]^+$ *trans*	1	H	P_4	31.5	3	3	80	106	84		95	92	[78]
18	$[Ru(H_2)H(depe)_2]^+$ *trans*	1	H	P_4	32	16	16	400	108	85		96	91	[46]
19	$[Ru(H_2)(DMeOPrPE)_2H]^+$ *trans*	1	H	P_4	32.1	21	21	500	108	86		97	91	[109]
20	$[Ru(H_2)H(duphos\text{-}Me)_2]PF_6$ *trans*	1	H	P_4	30	9	10	400	99	79	80(20) X	93	94	[110]
21	$[Ru(H_2)(bpy)_2\{P(OEt)_3\}]^{2+}(CF_3SO_3^-)_2$	2		N_4	32.8	7	7	200	105	83		94	90	[111]
22	$[Ru(H_2)(bpy)_2\{PPh_2(OEt)\}]^{2+}(CF_3SO_3^-)_2$	2	P	N_4	31.7	7.2	7.2	200	106	84		95	91	[111]
23	$[Ru(H_2)(bpy)_2\{PPh(OEt)_2\}]^{2+}(CF_3SO_3^-)_2$	2	P	N_4	31.2	7.6	7.6	200	107	85		96	92	[111]
24	$[Ru(H_2)(bpy)\{P(OEt)_3\}_3]^{2+}(CF_3SO_3^-)_2$	2	P	P_2N_2	29.9	4.9	4.9	200	99	79		89	94	[111]
25	$[Ru(H_2)(bpy)\{PPh_2(OEt)\}_3]^{2+}(CF_3SO_3^-)_2$	2	P	P_2N_2	28.9	5.1	5.1	200	100	79		89	96	[111]
26	$[Ru(H_2)(bpy)\{PPh(OEt)_2\}_3]^{2+}(CF_3SO_3^-)_2$	2	P	P_2N_2	30.1	6.1	6.1	200	103	81		92	94	[111]
27	$[Ru(H_2)(phen)\{PPh_2(OEt)\}_3]^{2+}(CF_3SO_3^-)_2$	2	P	P_2N_2	29.4	5.9	5.9	200	102	81		92	95	[111]
28	$[Ru(H_2)(P(OH)_3)(dppe)_2][OTf]_2$ *trans*	2	P	P_4	33.3	14.4	14.4	400	106	84	82 D	88	89	[112]
29	$[Ru(H_2)(dppe)_2(P(OH)_2(OMe))][OTf]_2$ *trans*	2	P	P_4	32.8								90	[113]
30	$[Ru(H_2)(PF(OMe)_2))(dppe)_2][BF_4]_2$ *trans*	2	P	P_4	29	16.6	16.6	400	108	86		97	96	[114,115]
31	$[Ru(H_2)(PF(OEt)_2))(dppe)_2][BF_4]_2$ *trans*	2	P	P_4	28	17	17	400	109	86		97	97	[115]
32	$[Ru(H_2)(dppe)_2(PF(O^iPr)_2))][BF_4]_2$ *trans*	2	P	P_4	27	17	17	400	109	86		97	99	[115]
33	$[Ru(H_2)H(PMe_3)_4]^+$ *cis*	1	P	P_3H	31.5	10	7	300	98	78		88	92	[116]
34	$[Ru(H_2)H(P(CH_2CH_2PPh_2)_3)]^+$ *cis*	1	P	P_3H	29.7	6	6	300	96			96	94	[117]
35	$[Ru(H_2)H(P(CH_2CH_2PCy_2)_3)]^+$ *cis*	1	P	P_3H	28	24	24	400	115	91		103	97	[118]
36	$[Ru(H_2)H(homoxantphos)_2]^+$ *cis*	1	P	P_3H		18	18	300	115	91		103		[119]
37	$Ru(H_2)H(phpz)(PiPr_3)_2$	0	C	P_2NH							90 D (J_{HH} 310 at 213 K)	90		[120]
38	$[Ru(H_2)(CNH)(dppe)_2][OTf]_2$ *trans*	2	C	P_4	32.4	13.6	13.6	300		87		87	90	[121]
39	$[Ru(H_2)(CNH)(dppe)_2](TfO\text{-}HOTf)_2$ *trans*	2	C	P_4	32.4	13.6	13.6	300		87		87	90	[80]
40	$[Ru(H_2)(CNH)(dppp)_2](OTf)_2$	2	C	P_4	31.8	5.9	5.9	200	102	81		92	91	[80]
41	$[Ru(H_2)(CNH)(dppm)_2](OTf)_2$ *trans*	2	C	P_4	32.2	6.4	6.4	200	104	82		93	91	[80]
42	$[Ru(H_2)(CN)(dppe)_2](TfO\text{-}HOTf)$ *trans*	1	C	P_4	32	12.4	12.4	300		86		86	91	[80]
43	$[Ru(H_2)(CN)(dppe)_2](OTf)$ *trans*	1	C	P_4	32.5									[80]
44	$[Ru(H_2)(CN)(dppm)_2](OTf)$ *trans*	1	C	P_4	32	5.8	5.8	200	102	81		91	91	[80]
45	*trans*-$[Ru(H_2)(CN)(dppp)_2](OTf)$	1	C	P_4	31.6	5.4	5.4	200	101	80		90	92	[80]
46	$[Ru(H_2)(CN)(dppe)_2][HOTf\text{-}OTf]$ *trans*	1	C	P_4	32	12.4	12.4	300	108	86		97	91	[121]
47	$[Ru(H_2)(C_5Me_5)(COD)]BF_4$	1	C	C_4	29.3	12	12	300.1	108	85		96	95	[122]
48	$[Ru(H_2)(CO)(PCy_3)(C_5H_5)]OC(CF_3)_3$	1	C	PC_3		11	11	400	101	80		91		[123]
49	$[Ru(H_2)(C_5H_5)(CO)(PCy_3)]^+$	1	C	PC_3	28.5						97 S, 93 D	95	96	[33,43,65]
50	$[Ru(H_2)(C_5H_5)(CO)(P^iPr_3)]^+$	1	C	PC_3	28.5	6	6	300	96			96	96	[124]
51	$[Ru(H_2)(dppe)(\eta^5\text{-}C_9H_7)]CF_3SO_3$	1	C	P_2C_2	29.4	16	16	400	108	85		96	95	[125]
52	$[Ru(H_2)(dppp)(\eta^5\text{-}C_9H_7)]CF_3SO_3$	1	C	P_2C_2	27.4	15	15	400	106	84		95	98	[125]
53	$[Ru(H_2)(C_5H_5)(dippae)]^+$	1	C	P_2C_2	26	20	20	400	112	88		100	100	[126]
54	$[Ru(H_2)(\eta^5\text{-}C_9H_7)(dppm)]CF_3SO_3$	1	C	P_2C_2	25.9	13	13	400	104			104	100	[125]
55	$[Ru(H_2)(C_5H_5)(dmpe)]^+$	1	C	P_2C_2	22.1						102 S, 99 D	101	106	[33,43,66]

Table 2 (*Continued*)

	Complex $[Ru(H_2)(L^t)(L^{cis})_m]^{n+}$	$n+$	L^t	L^{cis}	$J_{HD,cor}$ (Hz)	$T_{1,obs}$ (ms)	$T^{min}_{1,HH}$ (ms)	ν (MHz)	d^{slow}_{HH} (pm)	d^{fast}_{HH} (pm)	d_{HH} other[a] (pm)	$d_{HH,av}$ (pm)	d^{eq16}_{HH} (pm)	Ref.
56	$[Ru(H_2)(C_5Me_5)(dppm)]BF_4$	1	C	P_2C_2	22–23.8	19.3	19.3	500	107		108–110(3) N, 91 D, 98 D	106	105	[20,21,25,33]
57	$[Ru(H_2)(C_5Me_5)(PEt_3)_2][BF_4]$	1	C	P_2C_2	21.5	17.5	17.5	400	109			109	107	[127]
58	$[RuH_2(dppip)(C_5Me_5)]^+$	1	C	P_2C_2	18.6								111	[21]
59	$[RuH_2(C_5Me_5)(dmpm)][B(C_6H_3(CF_3)_2)_4]$	1	C	P_2C_2	15.9								115	[21]
60	$[Ru(H_2)(H)_2(C_5Me_5)](((CF_3)_3CO{-}HOC(CF_3)_3)$	1	C	C_2H_2			18	500	106	84		95		[128]
61	$Ru(H_2)H(o\text{-}C_6H_4C_5H_4N)(P^iPr_3)_2$	0	C	P_2NH		<23	<16	400	107	85	(J_{HH} 308–114 Hz)	96		[64]
62	$[Ru(H_2)(CH_3CN)(PPh_3)(HBPz_3)]BF_4$	2	N	PN_3	33	16	16	400		85		85	90	[129,130]
63	$[Ru(H_2)(PPh_3)_2(tpm)](BF_4)_2$	2	N	P_2N_2	31.1	24	24	400		91	81 D	86	92	[131]
64	$[Ru(H_2)(PPh_3)_2(HBPz_3)]BF_4$	2	N	$P_2N_2{}^-$	32	21	21	400		89		89	91	[129,130]
65	$[Ru(H_2)(dppe)(HBPz_3)]BF_4$	2	N	$P_2N_2{}^-$	32.5	14	14	400	105	83		94	90	[129]
66	$[Ru(H_2)(dippae)(HBPz_3)][B(C_6H_3(CF_3)_2)_4]$	2	N	$P_2N_2{}^-$	29	16.5	16.5	400	108	86	69(4) X	97	96	[132]
67	$[Ru(H_2)(R,R\text{-}dippach)(HBPz_3)][B(C_6H_3(CF_3)_2)_4]$	2	N	$P_2N_2{}^-$	30	20	20	400	112	88		100	94	[132]
68	$[Ru(H_2)(PPh_3)_2(HCn)](BF_4)_2$	2	N	P_2N_2	29.4	20	20	400	112	88		100	95	[129]
69	$[Ru(H_2)(CO)(PPh_3)MeCn](PF_6)(CF_3SO_3)$	2	N	PCN_2	31	12	12	400	103	81		92	93	[129]
70	$[Ru(H_2)(CO)(PPh_3)(HCn)](BF_4)_2$	2	N	PCN_2	31.8	14	14	400	105	83		94	91	[129]
71	$[Ru(H_2)(dppe)MeCn](CF_3SO_3)_2$	2	N	P_2N_2	29.4	24	24	400		91		91	95	[129]
72	$[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}(OTf^-)_2$	2	N	P_2CN	31	3.9	3.9	200	95			86	93	[81]
73	$Ru(H_2)_2H(HB(Pz\text{-}3,5\text{-}Me_2)_3)$	1	N	$(H_2)HN_2{}^-$	27	26	21	250		96		96	99	[133]
74	$Ru(H_2)H(py)(HB(Pz\text{-}3,5\text{-}Me_2)_3)$	1	N	N_3H^-	26.7	19	13	250	112	89		101	99	[133]
75	$[Ru(H_2)H(o\text{-}C_6H_5py)(PiPr_3)_2][B(C_6H_3(CF_3)_2)_4]$	1	N	$P_2(HC)H$	23	16	11	300	106		82 (4) X, 89 D	97	105	[134]
76	$Ru_2(H_2)(biporphyrin)(imid^*)_2$	0	N	N_4	15.2	132	132	400		121	118 (R)	120	116	[29]
77	$Ru(H_2)H(HPNP\text{-}^tBu)Cl$	0	N	P_2ClH							112(3) X, 95 D	104		[135]
78	$Ru(H_2)H(HPNP\text{-}Cy)Cl$	0	N	P_2ClH		59	43	300	132	105		113		[135]
79	$[Ru(H_2)H(bipy)(PCy_3)_2](HC(SO_2CF_3)_2)$	1	N	P_2NH	19								111	[136]
80	$[Ru(H_2)(THF)(o\text{-}C_6H_4py)(PiPr_3)_2][B(C_6H_3(CF_3)_2)_4]$	1	N	P_2OC	27	11	11	300	106	84		95	99	[134]
81	$Ru(H_2)H(PCy_3)(B(Pz\text{-}3,5\text{-}Me_2)_3)$	1	N	PN_2H^-	21	15	15	250	115	91		103	108	[133]
82	$Ru(H_2)(P^iPr_3)(N_2Me_2S_2)$	0	N	PNS_2	26						92 X	92	100	[137]
83	$[Ru(H_2)(PCy_3)(N_2Me_2S_2)]$	0	N	PNS_2	25.9						99 X	99	100	[137]
84	$Ru(H_2)H(SC_4H_8)(B(Pz\text{-}3,5\text{-}Me_2)_3)$	1	N	$SHN_2{}^-$	24.3		13	250	112	89		101	103	[133]
85	$[Ru(H_2)(H_2O)_5]^{2+}$	2	O	O_4	31.2						94 D	94	92	[67,68]
86	$Ru(H_2)(oep)(THF)$	0	O	N_4	29.5	25	25	400		92		92	95	[29]
87	$[Ru(H_2)Br\{PPh(OEt)_2\}_4]^+$	1	Br	P_4		9	9	200	110	87		98		[138]
88	$Ru(H_2)(dppb)(\mu\text{-}Cl_3)RuCl(dppb)$	0	Cl	P_2Cl_2	29.4	12	12	300	108	85		96	95	[139,140]
89	$[Ru(H_2)Cl(dach)(PPh_3)_2]BF_4$	1	Cl	P_2N_2	28.5						78(6) X		96	[141]
90	$[Ru(H_2)Cl(dppe)_2]^+$	1	Cl	P_4	25.9	25	25	400	116	92		104	100	[142]
91	$[Ru(H_2)Cl(depe)_2]^+$	1	Cl	P_4	25.2	28	28	400	118	94		106	101	[142]
92	$Ru(H_2)Cl(PCy_3)_2(CO)$	0	–	P_2CCl	29.3								95	[143]
93	$[Ru(H_2)\{(C_6H_5CH_2)_2PCH_2CH_2P(CH_2C_6H_5)_2\}_2][OTf]_2$	2	–	P_4	22	23.1	23.1	400	114	91		102	106	[144]
94	$Ru(H_2)Cl_2(PCy_3)_2$	0	–	P_2Cl_2	22.4	18.8	18.8	500	106			106	105	[145]
95	$Ru(H_2)H(PNP\text{-}Cy)$	0	N	P_2H	15	45	32	300	127		95 D	111	117	[135]
96	$Ru(H_2)Cl(SiMeCl_2)(PCy_3)_2$	0	Cl	P_2Si	17.5	27	27	400.1	117		105 X, 107 D	112	113	[146]
97	$Ru(H_2)Cl(SiCl_3)(PCy_3)_2$	0	Cl	P_2Si	18.9	23	23	400.1	114			114	111	[146]
98	$Ru(H_2)Cl(SiMe_2Cl)(PCy_3)_2$	0	Cl	P_2Si	12	29	29	400.1	119		139 D	129	121	[146]

[a] (X) X-ray, (N) neutron, (D) DFT, (S) solid-state ^1H NMR, (R) residual dipolar coupling in solution.

of dihydrogen complexes of several transition metals [30].

$$d_{HH}^{eq1} = 142 - 1.67 J_{HD} \quad (1)$$

It was acknowledged that a plot of d_{HH} versus J_{HD} would curve to higher values of d_{HH} for *cis*-dihydrides with small J_{HD} values so that the linear Eq. (1) would not be applicable for these compounds.

Heinekey and Luther proposed a very similar equation (Eq. (2)), shown here with units of pm, based on 10 well-determined H–H distances in solid samples [31].

$$d_{HH}^{eq2} = 144 - 1.68 J_{HD} \quad (2)$$

This equation gives distances that are 2 pm greater than d_{HH}^{eq1} but still within the errors of experimental measurements (about ±4 pm).

Hush made use of DFT methods to calculate HD coupling constants, first for certain osmium dihydrogen complexes [32], and found a linear relationship with d_{HH} for these and for other closed shell 18-electron dihydrogen complexes.

$$d_{HH}^{eq3} = 148 - 1.7 J_{HD} \quad (3)$$

This equation gives distances that are 5–6 pm greater than d_{HH}^{eq1}.

More recently Gusev has calculated J_{HD} and d_{HH} values for a variety of dihydrogen and dihydride systems using DFT methods [33]. He showed that Eq. (4) fits existing data a little better than the equations above for dihydrogen complexes with J_{HD} greater than 10 Hz and that none of the equations could account for the scatter of experimental data for J_{HD} less than 10 Hz, the couplings found in compressed dihydride and dihydride complexes. He recommends calculating J_{HD} and d_{HH} from first principles. He points out that the calculated d_{HH} will not usually match the observed d_{HH} because the latter have undergone averaging due to vibrations, usually in an anharmonic potential well. Other recent work in this regard shows that it is challenging to calculate J_{HD} from first principles and that corrections for the effects of vibrations are important, particularly for elongated dihydrogen complexes that have flat potential surfaces over a wide range of H–H distances [27]. It is also important to take into account the effect of counter anions that can interact with the H_2 ligand and perturb the H–H interaction significantly [33]. This latter effect can cause significant differences between the solid state and solution structures as reported for $[Os(H_2)H_2(C_5Me_5)(PPh_3)]BF_4$ [24]. The different structures of $Ir(H_2)H(Cl)_2(P^iPr_3)_2$ in solution and in the solid state can also be attributed to an intermolecular IrCl···(H_2)Ir hydrogen bond [30,33,34].

$$d_{HH}^{eq4} = 147 - 1.75 J_{HD} \quad (4)$$

2.2. The compressed dihydride regime where J_{HD} is less than 15 Hz

To account for the transition from dihydrogen to dihydride, Limbach and co-workers [35] used a bond-valence bond-length method and derived Eq. (5) to express the relationship between the $J_{LL'}$ coupling constant (L, L′ = H, D, T) and the p_{HH} bond order.

$$J_{LL'} = \frac{J_{HH}\gamma(L)\gamma(L')}{\gamma(H)^2} = {}^1J^{\circ}_{LL'} p_{HH} + {}^2J^{\circ}_{LL'}(1 - p_{HH})^2 \quad (5)$$

with

$$p_{HH} = \exp\{-(d_{HH} - 0.74)/b\} \quad (6)$$

The γ(L) and γ(L′) in Eq. (5) refer to the magnetogyric ratios of the isotopes H, D or T while ${}^1J^{\circ}_{LL'}$ refers to the coupling constants in the appropriate L–L′ (gas) and ${}^2J^{\circ}_{LL'}$, in the *trans*-L–M–L′ compound. For example, the ${}^2J_{HD}$ value is proposed to be −2.8 Hz as observed for the *trans*-hydridedeuteride FeHD(*meso*-tetraphos-1) [47]. Corresponding metal–hydrogen bond orders ($p_{MH} = 1 - p_{HH}$) can also be calculated. The parameters 0.74 and b in Eq. (6) refer to the H–H distance in dihydrogen gas (in Å) and the sensitivity to a change in bond order with respect to distance for N–H···N hydrogen-bonded systems ($b = 0.404$). These parameters may actually vary from one metal to another and this might explain the scatter of experimental data referring to dihydrogen complexes of different transition metals. When Eq. (5) is solved for d_{HH} (in pm) in terms of J_{HD} the equation becomes [26]:

$$d_{HH}^{eq7} = 74 - b \ln\left\{\frac{2 - 43/{}^2J_{HD} - \sqrt{(2 - 43/{}^2J_{HD})^2 - 4(1 - {}^1J_{HD}/{}^2J_{HD})}}{2}\right\} \quad (7)$$

This equation gives d_{HH}^{eq7} values that are less than d_{HH}^{eq1} when J_{HD} is greater than 12 Hz, but greater when J_{HD} is less than 12 Hz. It accounts, approximately, for the small J_{HD} of *cis* dihydrides and the small, negative J_{HD} of *trans* dihydrides where Eqs. (1)–(3) do not apply. Interestingly hydrogen–hydrogen bond orders are proposed to have finite values even at distances greater than 200 pm.

Eq. (7) gives values of d_{HH} that are somewhat low compared to some experimental data points for J_{HD} in the range 20–30 Hz. Gelabert et al. [36] propose empirical values of $b = 0.494$ and ${}^2J_{HD} = 3.03$ that appear to fit existing experimental data more closely. The values from this modified Eq. (8) give d_{HH}^{eq8} values that are similar to d_{HH}^{eq1} for J_{HD} greater than 23 Hz but larger values for J_{HD} less than 23 Hz.

$$d_{HH}^{eq8} = 74 - 49.4 \ln\left\{8.096 - 0.5\sqrt{258.2 - 1.32 J_{HD}}\right\} \quad (8)$$

There is some evidence that J_{HD} refers to an H–D distance in the HD isotopomer that is shorter than the corresponding H–H distance in the HH complex. This discrepancy is likely to be largest for certain complexes with very flat potential surfaces with H–H distances between 100 and 140 pm [37].

3. Determining H–H distances by use of the T_1 method

3.1. Regime of slow motion of the dihydrogen or compressed dihydride ligand

Hamilton and Crabtree proposed the measurement of the minimum T_1 value of the ^{1}H NMR signal for the H_2 ligand as another means of detecting H–H bonding in solution [7]. Here there is the promise of the direct measurement of the H–H distance by use of equations describing dipolar relaxation as long as the correlation time for dihydrogen ligand motion (τ_{HH}) is significantly longer than that of the molecule (τ_{mol}). At the temperature of the minimum spin lattice relaxation time of the protons of the dihydrogen ligand it can be shown [10] that the H–H distance can be given as:

$$d_{HH}^{slow} = 58.15\sqrt[6]{\frac{T_{1,HH}^{min}}{\nu}} \quad (9)$$

with d_{HH} in pm, $T_{1,HH}^{min}$ in s and ν, the spectrometer frequency, in MHz. The distance d_{HH}^{slow} indicates that this equation applies when $\tau_{HH} \gg \tau_{mol}$. The $T_{1,HH}^{min}$ notation indicates that other possible contributions of relaxation to the observed $T_{1,obs}$ have been accounted for according to Eq. (10).

$$\frac{1}{T_{1,HH}} = \frac{1}{T_{1,obs}} - \frac{1}{T_{1,L}} - \frac{1}{T_{1,M}} \quad (10)$$

In Eq. (10), $1/T_{1,L}$ refers to the total contribution to relaxation of the dihydrogen nuclei by ligand nuclei that are near (<300 pm) to the dihydrogen nuclei, and $1/T_{1,M}$, from a dipolar metal (e.g. Mn, Re, Tc, Co, Pt), as calculated by the method suggested by Desrosiers et al., for example, [9].

A criterion for slow H_2 or dihydride motion is that the d_{HH}^{slow} value should be approximately equal to the d_{HH} value obtained from solid-state methods or from the J_{HD} correlations listed above (Eq. (11)) [11].

Criterion for slow H_2 motion ($\tau_{HH} \gg \tau_{mol}$):

$$\frac{d_{HH}^{from\ JHD}}{581.5\sqrt[6]{T_{1,HH}^{min}/\nu}} \cong 1.0 \quad (11)$$

Other evidence for slow motion of the two hydrogen atoms is the observation of magnetic or chemical inequivalence of their two nuclei.

3.2. Regime of rapid spinning of the dihydrogen ligand

Distances determined by neutron diffraction methods [2,25,30,34,38–42] and by solid-state NMR [43–45] are usually found to be shorter than the distance calculated from ^{1}H NMR $T_{1,HH}$ data on the assumption of slow internal motion of the H_2 ligand, d_{HH}^{slow} [11]. The Morris group provided evidence that the complexes *trans*-$[M(H_2)H(dppe)_2]^+$ [8,10,46] and $[M(H_2)H(meso\text{-tetraphos})_2]^+$, M = Fe, Ru, Os [47], have rapidly spinning dihydrogen ligands with $\tau_{HH} \ll \tau_{mol}$. In this case, spin-lattice relaxation of the dihydrogen nuclei is four times less efficient and Eq. (12) must be used to calculate the H–H distance, denoted d_{HH}^{fast} [8,46].

$$d_{HH}^{fast} = 461\sqrt[6]{\frac{T_{1,HH}^{min}}{\nu}} \quad (12)$$

where the relationship between Eqs. (9) and (11) is shown in Eq. (13).

$$\frac{d_{HH}^{fast}}{d_{HH}^{slow}} = \sqrt[6]{0.25} = 0.7937 \quad (13)$$

Later Collman et al. [29] reported a dimeric ruthenium complex, $Ru_2(H_2)$(biporphyrin)$(imid^*)_2$, where its d_{HH} of 118 pm as determined in solution by analysis of residual dipolar couplings is only consistent with d_{HH}^{fast} as calculated from the $T_{1,HH}^{min}$ value (entry 76 Table 2). This is a unique complex with a dihydrogen ligand spinning parallel to, and bridging between, the two porphyrin planes containing ruthenium(II) with Ru–H distances of about 190 pm (Fig. 1).

Several other dihydrogen complexes with fast-spinning ligands have been identified (32 complexes previously [11] and see below) when the ratio of d_{HH}^{eq1} (calculated from J_{HD}) to d_{HH}^{slow} (calculated by use of the $T_{1,HH}$) is equal to approximately 0.794 (Eq. (14)) [11].

Criterion for fast spinning or four-fold hopping ($\tau_{HH} \ll \tau_{mol}$):

$$\frac{d_{HH}^{eq1}}{581.5\sqrt[6]{T_{1,HH}^{min}/\nu}} = 0.794 \quad (14)$$

Typically the dihydrogen ligand is situated *trans* to a hydride ligand or has a pseudo C_4 axis running through the midpoint of the H–H bond and the metal. Eq. (14) applies to a rapid rotation of H_2 as a free rotor but could equally well apply to a rapid hopping of the two H between four fold sites of equal population. This naturally implies that there is a low energy barrier to rotation; this has been verified by use of the inelastic neutron scattering (INS) method [41,48–50]. In addition the H–H distance is usually less than 100 pm (except for the case the unusual bridging dihydrogen ligand shown in Fig. 1). Thus the d_{HH} from Eqs. (2), (4) or (8) could be used equally well in Eq. (14) since they all give approximately the same value when $J_{HD} > 29$ Hz.

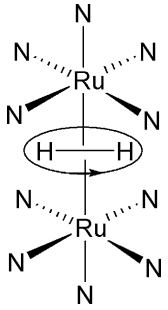

Fig. 1. The confacial biporphyrin complex with a bridging dihydrogen ligand.

3.3. Intermediate motion regime

In 1997 it was reported that 35 dihydrogen complexes have ratios that fall between 1.0 and 0.794, those of the two criteria of Eqs. (11) and (14) [11]. There are a variety of possible causes for this. Rapid motions of dihydrogen such as a tortional oscillation (libration) or hopping between sites of unequal population can result in ratios between these limits. The Morris and Koetzle groups provided evidence that the complexes *trans*-[Os(H$_2$)X(dppe)$_2$]PF$_6$, X = Cl, Br have elongated dihydrogen ligands with correlation times similar to the ^{1}H Larmor frequency; this also results in a ratio falling between the two limits and distorted ln(T_1) versus 1/T plots [30]. In the survey below I will use the average of d_{HH}^{fast} and d_{HH}^{slow} for complexes that fall between these limits.

4. NMR properties and H–H distances of iron-group dihydrogen and compressed dihydride complexes

4.1. Osmium complexes

Table 1 lists the properties of 70 dihydrogen or compressed dihydride complexes of osmium where the J_{HD} and $T_{1,obs}^{min}$ values have been reported, or where at least one of these measurements along with d_{HH} from other sources are available. Table 1 lists the complexes in the approximate order of increasing estimated d_{HH}, but they are grouped according to the atom on the ligand, L^t, *trans* to the dihydrogen ligand. The nature of the *trans* ligand has a large influence on the dihydrogen ligand and its properties. Typically the less electronegative atoms H, P, C, S and N cause less H–H bond lengthening than Cl and O although the effect of the *cis* ligands is also important. Lists of similar atoms on L^{cis} are then grouped together in order to reveal any electronic and steric influences of these on d_{HH}. Next are listed the observed $J_{HD,obs}$ value and the one corrected for exchange with *cis* H or D nuclei ($J_{HD,cor}$) and residual dipolar couplings. The $T_{1,obs}$ and $T_{1,HH}$ have been defined in Section 3.1. The values of d_{HH}^{slow} and d_{HH}^{fast} are calculated using Eqs. (9) and (12), respectively. Only the d_{HH}^{slow} value is reported if the criterion of Eq. (11) holds as reported in the literature or as classified in this work. Only the d_{HH}^{fast} value is reported if the criterion of Eq. (14) is true. Otherwise both values are reported. The $d_{HH,av}$ distance is obtained by averaging the d_{HH} derived from the $T_{1,HH}^{min}$ value and other sources of d_{HH} but not from $J_{HD,cor}$. This is done so that $d_{HH,av}$ and $J_{HD,cor}$ can be plotted as relatively independent variables to check the correlation against those listed in Sections 2.1 and 2.2.

Table 1 lists large J_{HH} values where reported. These are caused by the phenomenon of quantum mechanical exchange coupling (QEC) [5,19,43,51–53]. They are observed when the barrier to incoherent exchange of the two H atoms is near to 10 kcal/mol. Typically H–H distances are around 140–170 pm and so this is a signal that a compressed dihydride is present. In this case d_{HH}^{slow} should be used to calculate the H–H distance from $T_{1,HH}$.

Other d_{HH} that have been determined by X-ray (X) or neutron (N) diffraction, DFT methods (D), solid-state ^{1}H NMR (S) and residual dipolar coupling (R) are also listed.

The first 12 entries of Table 1 have dihydrogen *trans* to hydride. Most have large J_{HD} couplings and short H–H distances due to the strong H–H bonding and with Os–H$_2$ bonding weakened by the *trans* influence of the hydride. The first four are neutral complexes containing π-acid CO ligands that reduce backdonation into the dihydrogen ligand, resulting in short d_{HH}. The cationic complexes with *cis* aryl phosphine ligands have shorter d_{HH} than those with alkyl substituents. The alkyl substituents enhance π-backdonation into the σ* orbital of the H$_2$ ligand, causing a lengthening of the H–H bond. At least three of the complexes, with H$_2$ *trans* to H, i.e. *trans*-[Os(H$_2$)H(*meso*-tetraphos-1)]$^+$ and *trans*-[Os(H$_2$)H(PAr$_2$CH$_2$CH$_2$PAr$_2$)$_2$]$^+$, Ar = aryl (entries 7–9), have fast-spinning dihydrogen ligands while the others have ambiguous H$_2$ motion. The rapid spinning of the D$_2$ ligand in *trans*-[Os(D$_2$)D(dppe)$_2$]PF$_6$ affects the $T_{1,DD}^{min}$ of the deuterium in the D$_2$ ligand and results in the calculation of a motion-reduced quadrupole coupling constant of only about 30 kHz [16]. The motion of other ruthenium and osmium dideuterium complexes have been reviewed by Bakhmutov [17].

Cis-[Os(H$_2$)H(P(CH$_2$CH$_2$PPh$_2$)$_3$)]BPh$_4$, entry 13, has H$_2$ *trans* to phosphorus in a tetradentate phosphine ligand [54]. The observed J_{HD} value is reduced by averaging due to exchange with a *cis* D ligand. Similarly the $T_{1,obs}$ value is lengthened by averaging due to the exchange with a *cis* H ligand. In general the d_{HH} for entries with H appearing in the list of L^{cis} (entries 4, 13, 22, 23, 24, 28, 44, 54) are less reliable due to unknowns in the way the J_{HD} and $T_{1,obs}$ values are averaged.

Entries 14–20 have H$_2$ *trans* to carbon in osmium(II) complexes. The $d_{HH,av}$ range from 90 to 100 pm. In general η^5-C$_5$Me$_5$ ligands promote H–H bond lengthening, but in [Os(C$_5$Me$_5$)(CO)$_2$(H$_2$)][B(C$_6$F$_5$)$_4$] (entry 20, [55]), π-acid CO ligands are present to counteract this effect. [Os(C$_5$H$_5$)(dppm)H$_2$][B(C$_6$F$_5$)$_4$] (entry 21, [55]) is a dihydride with the dppm ligand replacing the CO of entry 20. It displays QEC with large J_{HH}.

The elongated dihydrogen ligands in the osmium(IV) complexes [Os(C$_5$Me$_5$)(L)H$_2$(H$_2$)][BF$_4$] (L = PPh$_3$, AsPh$_3$ and PCy$_3$, entries 22–24) have been characterized by single crystal neutron diffraction, DFT calculations and ^{1}H NMR by Girolami and co-workers [24]. Entries 22 and 23 are thought to have fast-spinning H$_2$ ligands although the interpretation of the NMR data is difficult due to the exchange with the *cis* H (D) ligands. The uncertainties arising from the averaging of coupling constants and relaxation rates of hydrogen or deuterium ligands caused by exchange have been carefully analyzed in this work.

The complex Os(H$_2$)(CO)(η^2-S$_2$CH)(P^{i}Pr$_3$)$_2$ (entry 25, [56]) is a rare complex that has H$_2$ *trans* to sulfur. The NMR data are consistent with a slow spinning dihydrogen with an H–H distance of 100 pm. An isomer of the complex [Os(H$_2$)(CO)(Spy)(PPh$_3$)$_2$] with H$_2$ *trans* to S has also been reported [57].

There is a particularly large range of d_{HH} for complexes with dihydrogen *trans* to nitrogen (entries 26-46). Sellmann's pybuS$_4^{2-}$ ligand produces a dihydrogen complex Os(H$_2$)(pybuS$_4$) with an unusually short H–H distance (approximately 87 pm) [58]. Dications with dihydrogen *trans* to N

generally produce H–H distances in the range 92–110 pm with complexes containing some *cis*-P donors giving the shorter distances than those containing all N-donors. Three pyrazolylborate complexes (entries 27, 28 and 33) are treated as part of this group of dications at the metal, with the negative charge located on the borate group of the ligand. Only $[Os(H_2)(\kappa^1\text{-}OCMe_2)(P^iPr_3)(HBPz_3)]BF_4$ (entry 27, [59]) has a fast-spinning dihydrogen ligand on the basis of the match of the d_{HH}^{fast} value calculated from the $T_{1,HH}$ with the d_{HH} from X-ray and DFT calculations. The rest of this class of H_2 *trans* to N have H_2 either in the intermediate or slow motion regimes, consistent with a strong interaction of the H_2 unit with osmium (with shorter Os–H bonds than in those complexes with H_2 *trans* to H that were described above). The monocation $[Os(H_2)H(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(P^iPr_3)_2]BF_4$ (entry 44, [60]) and the neutral complexes (entries 45 and 46) have *trans*-P^iPr_3 ligands. These have unusually long H–H distances (130–150 pm) and one of these, $Os(H_2)Cl(NH{=}C(Ph)C_6H_4)(P^iPr_3)_2$, displays huge J_{HH} couplings [61]. As compressed dihydrides, these complexes have d_{HH}^{slow} values that agree with the d_{HH}^{eq7} calculated from the J_{HD} values and with the d_{HH} from DFT calculations.

A *trans* chloride ligand causes a noticeable elongation of the H–H distance (entries 47–54) in the range of 100–150 pm. The H–H distance of two of these complexes, $[Os(H_2)Cl(dppe)_2]PF_6$ [30] and $Os(H_2)H(Cl)(PPh_3)_3$ [62] have been determined by use of single crystal neutron diffraction, thus definitively establishing the elongated H–H distance. The former complex has dihydrogen with frequency of motion near to that of the Larmor frequency of ^1H nuclei (see above) and with an H–H distance of about 120 pm while the latter has an H–H distance of 148 pm. Entries 51–53 have compressed dihydrides in the slow motion regime according to the $T_{1,HH}^{min}$ values.

Oxygen donors *trans* to dihydrogen (entries 55–69) consistently cause an elongation and all of the complexes except perhaps for $[Os(H_2)(OAc)(PPh_3)_3]^+$ are compressed dihydrides or dihydrides. Several of these with H–H in the range of 145–150 pm have observable, large J_{HH} values due to QEC.

The 5-coordinate complex $OsH_2Cl[CH(C_2H_4P^tBu_2)_2]$ (entry 70, [63]) has two hydrides that are separated by about 160 pm and, together, are *trans* to a vacant site.

A rough correlation with much scatter is obtained (Fig. 2) when the d_{HH}^{av} values that are obtained from T_1 and methods other than the use of J_{HD} are plotted against $J_{HD,cor}$. The Eq. (15) of best fit gives an correlation coefficient r^2 of 0.88 for 56 data points.

$$d_{HH}^{eq15} = 150 - 1.92 J_{HD,Os} \quad (15)$$

Therefore osmium appears to have a correlation with a greater negative slope compared to previous equations (Eqs. (1)–(4)) that were derived from correlations involving complexes of several transition metals. The d_{HH}^{eq15} values are listed next to the d_{HH}^{av} values in Table 1. In general the agreement is very good. Due to the scatter of points for this data set, the use of a more complex equation such as that proposed by Limbach et al. (see Eq. (5) above) for the correlation is not justified.

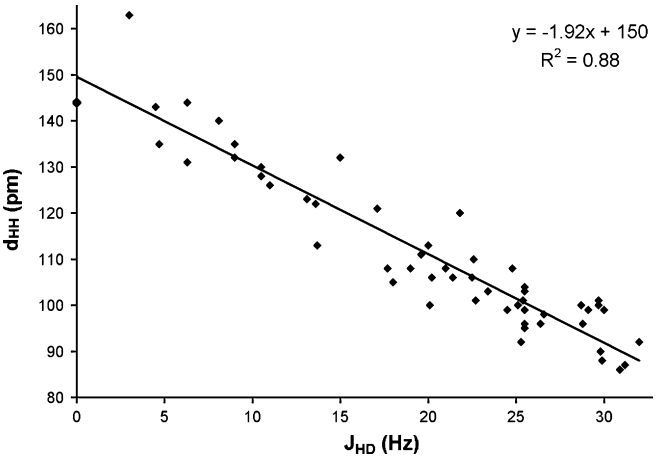

Fig. 2. Plot of d_{HH}^{av} versus J_{HD} for the osmium dihydrogen and compressed dihydride complexes.

4.2. Ruthenium complexes

Table 2 compiles the data for 98 ruthenium complexes. In general the H–H distances are shorter for a ruthenium complex than its osmium analogue. Ruthenium(II) forms weaker M–H bonds than osmium(II) and ruthenium(II) has lower energy d electrons with poorer capability for backdonation into the σ^* orbital of the dihydrogen compared to Os(II). Compare, for example, the following pairs of entries in Tables 1 and 2, respectively *trans*-$[M(H_2)H(meso\text{-tetraphos-1})]^+$ (96 pm for Os versus 88 pm for Ru), $[M(H_2)(H)(dppe)_2]^+$ (99 pm versus 89 pm), $[M(H_2)H(depe)_2]^+$ (126 pm versus 96 pm), $[M(H_2)H(P(CH_2CH_2PPh_2)_3)]BPh_4$ (106 pm versus 96 pm), $[M(H_2)(CNH)(diphos)_2]^{2+}$ (96–99 pm versus 87–92 pm), $[M(H_2)(PPh_3)_2(bipy)(CO)]^{2+}$ (92 pm versus 86 pm), $[M(H_2)(PPh_3)_2(HBPz_3)]^+$ (108 pm versus 89 pm), $[M(H_2)Cl(dppe)_2]^+$ (122 pm versus 104 pm), $[M(H_2)Cl(depe)_2]^+$ (123 pm versus 105 pm).

A plot of $d_{HH,av}$ versus J_{HD} is shown in Fig. 3. The best fit Eq. (16) has a correlation coefficient r^2 of 0.80, poorer than that

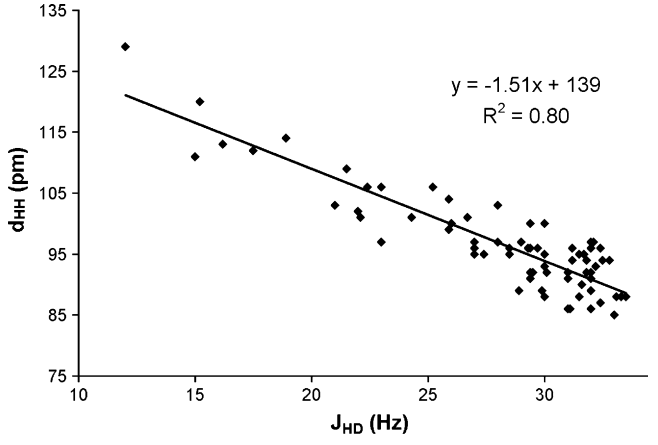

Fig. 3. A plot of d_{HH}^{av} versus J_{HD} for ruthenium dihydrogen and compressed dihydride complexes.

of osmium.

$$d_{HH}^{eq16} = 139 - 1.51 J_{HD,Ru} \quad (16)$$

There is good agreement between the d_{HH}^{av} and d_{HH}^{eq16} listed in Table 2.

Entries 1–20 of Table 2 are ruthenium dihydrogen complexes with H_2 *trans* to H (hydride). There is a narrow range of short H–H distances observed, 84–94 pm, despite large changes in the *cis* ligands. When there are *cis* hydrides, there is rapid exchange so that there is more uncertainty in these distances. Most of these complexes have dihydrogen in the fast spinning regime. This has been established with certainty for the complex *trans*-$[Ru(H_2)H(dppe)_2]BPh_4$ which has an H–H distance of approx. 90 pm according to single crystal neutron diffraction [41], d_{HH}^{fast} and d_{HH}^{eq16}. Inelastic neutron scattering shows that the barrier to rotational tunnelling is very low at 1.4 kcal/mol [41]. The rapid spinning of the D_2 ligand in *trans*-$[Ru(D_2)D(dppe)_2]BPh_4$ affects the $T_{1,DD}^{min}$ of the deuterium in the D_2 ligand in solution and in the solid state and results in the calculation of a motion-reduced quadrupolar coupling constant of only 20 kHz for the solution and 48 kHz in the solid state [16].

The complexes with dihydrogen *trans* to phosphorus (entries 21–36) also have a narrow range of distances: 88–97 pm when there is no *cis* hydride. These have motions in the intermediate regime.

The complexes with dihydrogen *trans* to carbon when not in a cyclopentadienyl ring (entries 37–46, 61) also have a narrow range of distances 86–97 pm. Entries 37 and 61 are a unique complexes displaying a large exchange coupling between the dihydrogen nuclei and the *cis* hydride nucleus [64].

The complexes with cyclopentadienyl and indenyl ligands (entries 47–60) have H–H distances that are more sensitive to the nature of the *cis* ligands. The *cis*-π-acid ligands CO and COD cause short H–H distances (91–96 pm) while P donors produce elongated H–H distances (96–115 pm). Replacing aryl groups with alkyl groups on the P donors results in an elongation and C_5Me_5 complexes have longer H–H distances than their C_5H_5 analogues. The H–H distances of $[Ru(H_2)(C_5H_5)(CO)(PCy_3)]^+$ [65] and $[Ru(H_2)(C_5H_5)(dmpe)]^+$ [43,66] have been verified by solid-state NMR methods while that of $[Ru(H_2)(C_5Me_5)(dppm)]^+$ has been determined by single crystal neutron diffraction [25]. Several of these complexes have H_2 in the slow motion regime and some are in the intermediate motion regime caused by directional d_π–σ^* bonding in these piano stool complexes [25].

There is an interesting range of complexes with dihydrogen *trans* to nitrogen (entries 62–84). The dicationic complexes (the pyrazolyl ligands are treated as monoanionic ligands) have H–H distance of 85–100 pm. The monocationic and neutral complexes of this type have longer H–H distances, in the range 95–120 pm, with the diruthenium complex of Fig. 1 having the longest distance of this range. This effect of charge can be explained by the increase in $d_\pi(Ru)$–$\sigma^*(H_2)$ backdonation with a reduction in positive charge.

The oxygen donors in $[Ru(H_2)(OH_2)_5]^{2+}$ [67,68] and $Ru(H_2)$(octaethylporphyrin)(THF) [29] (entries 85 and 86) do

Table 3
Properties of iron complexes

	Complex $[Fe(H_2)(L^t)(L^{cis})_4]^{n+}$	$n+$	L^t	L^{cis}	$J_{HD,cor}$ (Hz)	$T_{1,HH}^{min}$ (ms)	ν (MHz)	d_{HH}^{slow} (pm)	d_{HH}^{fast} (pm)	d_{HH} other[a] (pm)	$d_{HH,av}$ (pm)	d_{HH}^{eq1} (pm)	Ref.
1	$[Fe(H_2)H(P(C_6H_4CF_3)_2CH_2CH_2P(C_6H_4CF_3)_2)_2]^+$ *trans*	1	H	P_4	32	15	400		84		84	89	[76]
2	$[Fe(H_2)H(dppe)_2]BPh_4$	1	H	P_4	32	17	400		86	82–85(2) N	85	89	[39,46]
3	$[Fe(H_2)H(meso\text{-tetraphos-1})]^+$, *trans*	1	H	P_4	32	18	400		87		87	89	[47]
4	$[Fe(H_2)(PNP)(dmpm)H]^+$	1	H	P_4	30.8	20.7	400		89		89	91	[147]
5	$Fe(H_2)H(dmpe)_2]^+$	1	H	P_4	31	8	270	103	81		91	90	[148–150]
6	$[Fe(H_2)(CO)(dppe)_2][OTf]_2$	2	C	P_4	33.1	11	300		84		84	87	[151]
7	$[Fe(H_2)(CO)(depe)_2][SbF_6]_2$	2	C	P_4	33	10	300		83		83	87	[151]
8	$[Fe(H_2)(CN)(dppe)_2](OTf)$ *trans*	1	C	P_4	32.5	11.7	300		85		85	88	[80]
9	$[Fe(H_2)(CNH)(dppe)_2][OTf]_2$ *trans*	2	C	P_4	32.5	21.5	500		86		86	88	[152]
10	$[Fe(H_2)(CN)(depe)_2](BF_4)$ *trans*	1	C	P_4	31.6	15.2	400		85		85	89	[80]
11	$[Fe(H_2)(dppe)(C_5Me_5)]BF_4$	1	C	P_2C_2	27	9.6	400	99		94 D	96	97	[153,154]
12	$[Fe(H_2)(bpy)\{PPh(OEt)_2\}_3]^{2+}$	2	N	P_3N	32.5	3.6	200	94			94	88	[155]
13	$[Fe(H_2)(phen)\{PPh(OEt)_2\}_3]^{2+}$	2	N	P_3N	32	3.1	200	92			92	89	[155]
14	$[Fe(H_2)(bpy)\{P(OEt)_3\}_3]^{2+}$	2	N	P_3N	31.5	3.1	200	92			92	89	[155]
15	$[Fe(H_2)(phen)\{P(OEt)_3\}_3]^{2+}$	2	N	P_3N	31.2	3.3	200	93			93	90	[155]
16	$[Fe(H_2)H(P(CH_2CH_2PMe_2)_3)]^+$	1	P	P_3H	31.1	12.8	400	104	82		93	90	[156]
17	$Fe(H_2)H(P(CH_2CH_2PPh_2)_3)]^+$ *cis*	1	P	P_3H	28.5	6	300	96			96	94	[157]

[a] (N) Neutron, (D) DFT.

not cause the large elongation of the H–H distance that is observed for the osmium complexes with oxygen *trans* to dihydrogen. These two ruthenium complexes have H–H distances of about 93 pm.

As with osmium complexes, the ruthenium complexes with halide *trans* to dihydrogen show some elongation of the H–H distances. Entries 87–91 have H–H distances in the range 96–106 pm. The H_2 ligands are in the intermediate motion regime. The complex *trans*-$[Ru(D_2)Cl(dppe)_2]PF_6$ has been studied extensively by solid-state ^2H NMR [16,69]. One of these studies provided the only known example of coherent rotational tunneling in a solid dideuteride complex [69]. The barrier for D–D rotation was found to be about 6 kcal/mol.

The last entries (92–98) are five-coordinate ruthenium complexes. These have elongated H–H distances of 100–130 pm. This shows ruthenium's high propensity to remain as a Ru(II) dihydrogen complex instead of as a Ru(IV) dihydride.

4.3. Iron dihydrogen complexes

There is little variation in the H–H distance of dihydrogen complexes of iron (Table 3). Dihydrogen ligands *trans* to hydride or *trans* to carbon (except when *trans* to C_5Me_5) are in the fast spinning regime with H–H distances of 84–91 pm. Dihydrogen ligands *trans* to C_5Me_5, nitrogen or phosphorus are in the slow motion regime with distances of 90–96 pm. Eqs. (1), (2) or (4) are adequate for calculating d_{HH} from J_{HD} for these compounds.

5. Conclusions

Tabulating the structures and characteristic NMR properties of 17 iron complexes, 98 ruthenium complexes and 70 osmium complexes that contain dihydrogen or compressed dihydride ligands has revealed more clearly a variety of trends that have been alluded to in the past [1,3,5,6,70]. The H–H bond lengths increase from similar Fe(II) to Ru(II) to Os(II) complexes. Iron(II) displays a narrow range of H–H distances for stable complexes. There are a variety of factors that cause these trends including the smaller size of iron and its valence orbitals, the extent of donation to the metal of the σ electrons of the dihydrogen ligand and the extent of backdonation from a filled d orbital of the metal into the σ^* orbital of the dihydrogen ligand. Electronegative atoms Cl and O result in elongation of the H–H bond relative to more electropositive atoms H, C, P and N. This is attributed to filled p to filled d repulsions for Cl and O ligands which results in an increase in backdonation from the metal into the σ^* orbital of the dihydrogen. The cyclopentadienyl family of ligands also causes this elongating effect.

The dihydrogen ligands with short H–H distances and weak interactions with the metal, especially on iron and ruthenium are in the fast spinning regime. They typically have H–H distances less than 95 pm for ruthenium and 91 pm for iron. One exception is the biporphyrin complex of ruthenium with the side-on bridging H_2 ligand which has an H–H distance of 118 pm but is in the fast spinning regime. There are some ruthenium complexes with H–H distances greater than 110 pm that are in the slow motion regime and several complexes of osmium with H–H distances greater than 130 pm that are in this regime. The large J_{HH} due to quantum mechanical exchange coupling are observable for some of these osmium complexes with H–H distances in the range of 140–160 pm. The dihydrogen ligands in many complexes appear to have librational motions or other motions that place them in the intermediate motion regime.

Introduced here are new equations to correlate J_{HD} with H–H distances for ruthenium complexes and for osmium complexes. As a reviewer points out, these correlations must be used with caution since so many factors are changing when comparing one complex with another. The correlation coefficients (r^2) for these equations are only 0.9 for osmium and 0.8 for ruthenium. However they do provide a much needed estimate of the H–H distance for such complexes in solution. Such analysis can also be conducted for dihydrogen complexes of other elements once there is sufficient data.

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