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Review

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

Robert H. Morris *

Davenport Laboratories, Department of Chemistry, University of Toronto,
80 St. George Street, Toronto, Ont., Canada M5S 3H6

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Contents

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

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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, $[C_6H_3(CH_2PPh_2)_2\text{-}2,6]^-$; $Pcyp_3$, tris(cyclopentyl)phosphine; $pybuS_4^{2-}$, 2,6-$\{2,5\text{-}^tBu\text{-}6\text{-}S^-\text{-}C_6H_2SCH_2\}_2C_5H_3N$; Spy^-, 2-mercaptopyridine anion; QEC, quantum mechanical exchange coupling; tpm, tris(pyrazolyl)methane.

* Tel.: +1 416 978 6962.
E-mail address: rmorris@chem.utoronto.ca.

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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