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Research paper

Electrochemistry of transition metal hydride diphosphine complexes trans-MH(X)(PP)₂ and trans-[MH(L)(PP)₂]⁺, M = Fe, Ru, Os; PP = chelating phosphine ligand

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Dedicated to Professor Maurizio Peruzzini

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ABSTRACT

A series of over 30 iron, ruthenium, and osmium hydride phosphine complexes are reported, along with their $M^{III/II}$ redox potentials. The complexes are of the type $MH(PP)_n(X)$ or $[MH(PP)_n(L)]^+$, where PP is one of the following bidentate phosphine ligands: dppe, dtpe, depe, and dtfpe, with n = 2; or the tetradentate phosphine ligand meso-tet-1, with n = 1. The electrochemical data of these complexes and those from the literature are used to determine the Lever E_L parameter of -0.65 V for the hydride ligand for iron and ruthenium. For osmium, however, the E_L value for the hydride ligand is found to be more positive at only -0.37 V, an increase which is attributed to Os-H σ bond strengthening due to relativistic effects. The correlation holds for irreversible oxidations as well as reversible ones. These E_L values can now be used along with Lever's equations to predict redox potentials of other iron-group hydride complexes.

1. Introduction

There has been considerable interest in correlating electrochemical potentials with the effects of ligand substitution [1–10]. Electrochemical potentials have been related to a variety of properties of transition metal complexes such as charge-transfer transition energies, infrared stretching frequencies of ligands, HOMO energies ligand substitution effects [1] and the stability of dihydrogen complexes [4]. However, the electrochemistry of transition metal hydride complexes has not been studied systematically. Understanding the electronic nature of these hydride complexes is an important handle in the rational development of catalysts for such processes as carbon dioxide reduction and hydrogen evolution [11,12]. In this paper the electrochemical properties of a series of metal hydride complexes, formulated as trans-MH(X)(PP)2 and *trans*- $[MH(L)(PP)_2]^+$ (M = Fe, Ru and Os; PP = dppe, depe, dtpe, dtfpe, 1/2 meso-tet-1; X = anionic ligands and L = neutral monodentate ligands) will be reported. This data will be used in conjunction with literature data to determine the Lever electronic parameter for the hydride ligand for Fe, Ru and Os complexes.

The electrochemical potential of a compound is valuable in the un-

derstanding of its chemical reactions [3,13]. Pickett and co-workers found that the $E_{1/2 \text{ ox}}$ of Cr(CO)₅L was very sensitive to the nature of L and they developed a series of ligand constants, P_L , by the use of Eq. (1) [14].

$$P_{L} = E_{1/2}^{ox} [Cr(CO)_{5}L] - E_{1/2}^{ox} [Cr(CO)_{6}]$$
(1)

The ligand parameters, P_L, represent the change in energy of the HOMO of Cr(CO)₆ when one CO ligand is replaced by a ligand, L. In some cases, in addition to HOMO energies, structural re-organization energies would have to be included as well. Ligands with the weakest σ -donor and strongest π -acceptor properties such as CO and N₂ have the most positive P_L constants while strong σ -donor and π -donor ligands such as the halides and pseudo-halides have the most negative P_L. Thus P_L appears to reflect the net donor properties (σ -and π -donor + π -acceptor) of the ligand L. Pickett also applied the P_L parameter to other metal systems by graphing E^{0X}_{1/2} versus P_L for a series of complexes [ML'₅L]. The linear correlation produced is shown in eq (2), where E_s equals to the E_{1/2} of the complex M(CO)₆ and β is the slope of the E^{0X}_{1/2} vs. P_L plot [14,15].

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Table 1

Selected	F.	values	Unless	specified	the data	a ic	from	ref	[2]	é
SCIECTER	L'II.	values.	Unicss	specifieu,	uic uala	1 15	nom	ICI.	141	

Ligand	E _L (V)	Ligand	E _L (V)	Ligand	E _L (V)	Ligand	E _L (V)	Ligand	E _L (V)	Ligand	E _L (V)
со	0.99	P(OMe) ₃	0.42	depe ^b	0.27	MeIm	0.08	Cl-	-0.24	SPh ⁻	-0.53
N ₂	0.68	meso-tet-1	0.35	PMe ₂ Ph	0.34	CN	0.02	NCO	-0.25	S'Bu	-0.55
P(OPh) ₃	0.58	dtpe ^b	0.34	MeCN	0.34	NCS ^{- c}	-0.06	N ₃	-0.30	H^{-} (Fe, Ru) ^b	-0.65
dtfpe ^b	0.52	dppe	0.36	PMe_3	0.33	Br^{-}	-0.22	H ⁻ (Os) ^b	-0.37		

^a See table S4 for a complete list. ^b E_L value is derived here. ^c The E_L for NCS⁻ refers to the nitrogen-bound ligand, which is applicable for the complexes studied here. See ref. [16] for a crystal structure of nitrogen-bound NCS⁻ of the related iron complex Fe(NCS)₂(PPh₂(CH₂)₂PPh(CH₂)₂PPh(CH₂)₂PPh₂)

Table 2 The slope, intercept data, and equations for $E_{1/2}(d^5/d^6)$ (V vs. NHE) versus ΣE_L for low spin six coordinate iron group complexes in organic solvents.

Couple	Source	Slope S _M /S _D	Intercept I _M /S _D	R ²	$\begin{array}{l} E_{1/2} = \\ S_M \Sigma E_L + I_M \end{array}$	EL of Hydride / Error
Fe ^{III/II}	Lever ^a	1.10 / 0.05	-0.43 / 0.12	0.99	$\begin{array}{l} E_{calc} = \\ 1.10\Sigma E_L - \\ 0.43 \end{array}$	-
Ru ^{III/II}	Lever	0.97 / 0. 01	0.04 / 0.03	0.99	$\begin{array}{l} E_{calc} = \\ 0.97\Sigma E_L + \\ 0.04 \end{array}$	-
Os ^{III/II}	Lever	1.01 / 0.02	-0.40 / 0.11	0.98	$\begin{array}{l} E_{calc} = \\ 1.01\Sigma E_L - \\ 0.40 \end{array}$	-
Fe ^{III/II}	this work ^b	1.08 / 0.05	-0.46 / 0.05	0.91	$\begin{array}{l} E_{obs} = \\ 1.08\Sigma E_L - \\ 0.46 \end{array}$	-0.65 / 0.02
Ru ^{III/II}	this work	0.77 / 0.05	0.15 / 0.03	0.84	$\begin{array}{l} E_{obs} = \\ 0.77\Sigma E_L + \\ 0.15 \end{array}$	-0.65 / 0.02
Os ^{III/II}	this work	1.04 / 0.10	-0.44 / 0.11	0.88	$\begin{array}{l} E_{obs} = \\ 1.04\Sigma E_L - \\ 0.44 \end{array}$	-0.37 / 0.04

^a Lever refers to Lever's equations discussed in ref. [2]. ^b Refers to the hydride plots discussed in this work.

$$E_{1/2}^{ox} = E_s + \beta P_L \tag{2}$$

A more general additive ligand method has been proposed by Lever based on the change in the ruthenium(III)/ruthenium(II) couple as a function of bound ligands in organic solvents [2]. He defined an additive ligand parameter E_L , which represents a separate contribution for each ligand of the complex. For example, the E_L contribution of byy in the complex [Ru(bpy)₃]²⁺ ($E_{1/2} = 1.53$ V vs. NHE) is defined to be 1.53/6 or 0.255 V because the complex contains six identical Ru-N bonds. In this fashion the E_L values for over 200 ligands were defined (Table 1 lists some of these values in order of decreasing potential which will be used in this study). Therefore, the electrochemical potential of the general complex, RuX_xY_yZ_z, can be calculated by using the E_L values as in Eq. (3) or its abbreviated form [2].

$$E_{calc} = xE_L(X) + yE_L(Y) + zE_L(Z) = \Sigma E_L$$
(3)

Lever has also demonstrated that the E_L ligand parameters can be used for many other metal ions in a given oxidation state [2]. Plots of the observed potentials for certain complexes (MXxYyZz) against $\sum E_L$ were linear as expressed in Eq. (4).

$$E_{obs} = S_M[\Sigma E_L] + I_M \tag{4}$$

The slope, S_M and intercept, I_M data for the metal ion being studied should reflect the specific M(n)/M(n-1) couple. The values of the slope (S_M) and intercept (I_M) constants determined by Lever for the M(III)/M (II) couple of the iron group d⁶ complexes $MX_xY_yZ_z$, M = Fe, Ru, Os are summarized in Table 2. Also in table 2 is the hydride data from this work, which is discussed later. These slope and intercept data can be used to predict unknown electrochemical potentials. Conversely, observed potentials may be used to calculate as yet unknown E_L values.

Lever suggested that the E_L of the hydride, -0.30, which was derived

from the Picket/Pletcher ligand parameter, might be too low [2]. The E_L of the hydride was calculated to be -0.76 V using the computed ligand electronic parameter (CEP) method, via an equation that relates the CEP to the Lever electronic parameter [8]. In our work, experimental data is used to calculate an E_L value for the hydride ligand based on iron-group data. Up to now, the electrochemical behavior of ReCl(L)(diphos)₂, [MoXL(diphos)₂]^{*n*+}, [RuL(NH₃)₅]^{*n*+}, [ReLN₂(dppe)₂]²⁺, [FeH(L) (dppe)₂]⁺, and multi- and mono- nuclear complexes of the type [FeH (CN)(dppe)₂] with a bridging cyanide or with benzoyl isocyanide, have been examined by Pickett et al. [15,17] and Almeida et al. [18] respectively. Here we extend the study to other ditertiaryphosphines as well as to other transition metals Ru and Os.

2. Experimental

2.1. Materials and methods

Abbreviations: MeIm = 1-methylimidazole, dppe = 1,2-bis(diphenylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dtpe = 1,2-bis(di(*para*-tolyl)phosphino)ethane, diphos = bistertiarylphosphines, *meso*-

 $\begin{array}{l} tet-1 = (R,S)\text{-}PPh_2(CH_2)_2P(Ph)(CH_2)_2P(Ph)(CH_2)_2PPh_2, dtfpe = 1,2-\\ bis(di(para-trifluorotolyl)phosphino)ethane, bpy = 2,2'-bipyridine,\\ THF = tetrahydrofuran, MeOH = methanol, CH_2Cl_2 = dichloromethane,\\ NBA = 4-nitrobenzyl alcohol, NPOE = 2-nitrophenyloctylether, FAB MS = Fast atom bombardment mass spectrometry, <math>E_{pa}$ = anodic peak potential of an irreversible oxidation wave; Fc^+/Fc = ferrocenium/ferrocene couple, NHE = Normal Hydrogen Electrode.

All operations were conducted in an argon atmosphere by use of Schlenk line techniques, or in a purified nitrogen atmosphere using a Vacuum Atmospheres glove box. All solvents were dried over appropriate reagents and distilled under N2 before use. Benzene, THF, diethyl ether, and hexanes were dried over and distilled from sodiumbenzophenone ketyl. MeOH was dried over magnesium methoxide, and ethanol over magnesium ethoxide. Acetone was dried over potassium carbonate. CH₂Cl₂ was distilled from calcium hydride. Deuterated solvents were dried over Linde type 4 Å molecular sieves and degassed with argon using several evacuate/refill cycles. Reagent-grade chemicals were used as purchased from Aldrich Chemical Company, Inc. unless otherwise stated. Phosphine ligands, dppe, depe and Cl₂PCH₂CH₂PCl₂ were purchased from Strem Chemical Co. or Digital Specialty Chemicals Ltd. Sodium thiophenoxide, NaSPh, was prepared in 93% yield from thiophenol and sodium hydride using a Et₂O/THF (7/ 3 v/v) solvent and 1.75 h reaction time; the white solid was filtered and washed with Et₂O. Sodium thio-*tert*-butoxide was prepared from HS^tBu and NaH in THF. Infrared spectra were recorded as Nujol mulls on NaCl plates using a Nicolet 5DX FTIR spectrometer. NMR spectra were recorded on Varian XL-400 (400 MHz for ¹H, 162 MHz for ³¹P), Varian Gemini 200 (200 MHz for ¹H) or Varian Gemini 300 (300 MHz for ¹H, 120.5 MHz for ³¹P) spectrometers. Chemical shifts refer to room temperature conditions (20 °C) unless specified otherwise. ³¹P chemical shifts were measured in the proton decoupled mode and referenced either internally or externally to 1% P(OMe)3 in C6D6 sealed in coaxial capillaries, but are reported relative to 80% H_3PO_4 by use of δ (P $(OMe)_3) = 140.4$ ppm. ¹H chemical shifts were measured relative to

Table 3

Lever additive electrochemical parameters, ΣE_L , calculated $E_{1/2}(d^5/d^6)$ and observed $E_{1/2}$ (or E_{pa}) values for the complexes *trans*-[MH(L)(PP)₂]⁺ and *trans*-MH(X)(PP)₂; THF solvent, 0.2 M NBu₄PF₆, 250 mV s⁻¹ scan rate.

No.	Metal	Bisphosphine	L or X^-	ΣE_L^a	$E_{\rm calc}$ V vs. NHE $^{\rm b}$	E_{obs} V vs. Fc $^+/Fc^c$	$E_{\rm obs}$ V vs. NHE $^{\rm d}$
1a	Fe	depe	N_3^-	0.13	-0.29	-0.98	-0.33
1b	Fe	depe	NCO ⁻	0.18	-0.23	-0.96	-0.31
1c	Fe	depe	Cl^{-}	0.19	-0.22	-0.98	-0.33
1d	Fe	depe	Br ⁻	0.21	-0.20	-0.95	-0.30
1e	Fe	depe	NCS ⁻	0.37	-0.02	-0.75	-0.10
1f	Fe	depe	N ₂	1.11	0.79	0.31	0.96
1h	Fe	depe	CO	1.42	1.13	0.76	1.41
1j	Fe	dtpe	NCO ⁻	0.47	0.09	-0.68	-0.03
1k	Fe	dtpe	Cl ⁻	0.46	0.08	-0.72	-0.07
11	Fe	dtpe	NCS ⁻	0.65	0.29	-0.43	0.22
1m	Fe	dtpe	CN^{-}	0.73	0.37	-0.32	0.33
1n	Fe	dtpe	NCMe	1.05	0.73	-0.06	0.59
10	Fe	dtpe	H ₂	1.31	1.01	(0.65)	(1.30)
1p	Fe	dtpe	CO	1.70	1.44	(0.43)	(1.08)
1r	Fe	dtfpe	NCO ⁻	1.18	0.87	(0.24)	(0.89)
1t	Fe	dtfpe	NCS ⁻	1.37	1.08	(0.36)	(1.01)
1u	Fe	dtfpe	CN^{-}	1.45	1.17	(0.38)	(1.03)
1v	Fe	dtfpe	MeCN	1.77	1.52	(0.53)	(1.18)
1w	Fe	dtfpe	H ₂	2.03	1.80	(-0.03) ^e	(0.62)
2a	Ru	depe	S ^t Bu ⁻	-0.12	-0.08	-0.90	-0.25
2b	Ru	depe	H^{-}	-0.22	-0.17	-0.50	0.15
2c	Ru	depe	NCO ⁻	0.18	0.21	-0.40	0.25
2d	Ru	depe	Cl^{-}	0.19	0.22	-0.30	0.35
2e	Ru	depe	Br^{-}	0.21	0.24	-0.38	0.27
2f	Ru	depe	NCS ⁻	0.37	0.40	-0.27	0.38
2g	Ru	depe	NCMe	0.77	0.79	0.27	0.92
2h	Ru	meso-tet-1	H^{-}	0.10	0.14	-0.47	0.18
2i	Ru	meso-tet-1	Cl^{-}	0.51	0.53	-0.35	0.30
2j	Ru	meso-tet-1	MeIm	0.83	0.85	-0.10	0.55
2k	Ru	meso-tet-1	PMe ₂ Ph	1.09	1.10	0.42	1.07
21	Ru	meso-tet-1	NCMe	1.09	1.10	0.46	1.11
2m	Ru	dtfpe	$S^{t}Bu^{-}$	0.88	0.89	0.48	1.13
20	Ru	dtfpe	NCS ⁻	1.37	1.37	(0.67)	(1.24)
2p	Ru	dtfpe	MeCN	1.77	1.76	(0.59)	(1.32)
3a	Os	dppe	S ^t Bu ⁻	0.52	0.13	-0.77	-0.12
3b	Os	dppe	SPh ⁻	0.54	0.15	-0.65	0.00
3e	Os	dppe	Br ⁻	0.85	0.46	-0.11	0.54
3f	Os	dppe	MeIm	1.15	0.76	0.31	0.96
3g	Os	dppe	PMe ₃	1.40	1.01	0.68 ^f	1.33
3h	Os	dppe	MeCN	1.43	1.04	0.58 ^f	1.23
3i	Os	dppe	P(OMe) ₃	1.49	1.10	(0.97)	(1.62)
3j	Os	dppe	P(OPh) ₃	1.65	1.27	>1.2 ^g	>1.85

 ${}^{a}\Sigma E_{L} = 4 E_{L}(PP) + E_{L}(L) + E_{L}(H^{-})$. ^b Lever's calculated equations for Fe, Ru and Os are listed in Table 2. ^c ±0.05 V. Values in brackets represent irreversible processes which are reported as E_{pa} peak potentials. ^d Converted from Fc⁺/Fc reference to the NHE reference by adding 0.65. ^e E_{pa} value in CH₂Cl₂ solvent is 0.48 V vs. Fc⁺/Fc, or 1.13 V vs NHE. ^f CH₂Cl₂ solvent. ^g No OS^{III/II} redox processes were observed in the electrochemical window.

partially deuterated solvent peaks, but are reported relative to tetramethylsilane. FAB-MS spectra were obtained with a VG 70-250S mass spectrometer using a NBA or NPOE matrix. Microanalyses were performed on a sample handled under an inert atmosphere by Canadian Microanalytical Services, Vancouver. Electrochemical Apparatus: Electrochemical measurements were made on a Princeton Applied Research Model 273 Potentiostat/Galvanostat (without IR compensation). All cyclic voltammograms were obtained using an electrochemical cell consisting of a platinum working electrode, tungsten secondary electrode and silver wire reference electrode in a Luggin-Haber probe capillary. All measurements were made under Ar gas using 0.2 M NBu₄PF₆ in freshly distilled THF or CH₂Cl₂ as the electrolyte solution. The cyclic voltammograms were collected as two cycles of negative to positive to negative potential sweeps. The applied potential was varied over a 2 V range: -0.8 to 1.2 V vs. Ag⁺/Ag for THF solutions, or -0.3 to 1.7 V vs. Ag^+/Ag for CH_2Cl_2 solutions. The $E_{1/2}$ and E_{pa} values are reported relative to the ferrocenium/ferrocene couple. Initially, a background scan of 6 mL of the electrolyte solution was made in order to insure that no oxygen or water was present. Under a positive pressure of argon, approximately 10 mg of the complex were added to the electrolyte. A small amount of solution was drawn up around the reference electrode and the argon was turned off. The electrochemistry cell was

enabled and the acquisition program started. After the initial measurement, a small amount of ferrocene was added and the process was repeated. All the $E_{1/2}$ values for the complexes *trans*-MH(X)(PP)₂ and *trans*-[MH(L)(PP)₂]⁺ are summarized in Table 3.

2.2. Synthesis

Preparations of the ligands dtpe [19], *meso*-tet-1 [20] and dtfpe [19] have been reported. (NH₄)₂[OsBr₆] was prepared from OsO₄ according to the literature method [21]. The following complexes were prepared by previously reported methods: FeCl₂(depe)₂ [22], *trans*-FeHCl(PP)₂ (**1k**: PP = dtpe [23]; **1s**: dtfpe [23]; **1c**: depe [24]), Ru(cod)(cot) [25], *cis*- and *trans*-Ru(H)₂(depe)₂ [26], *trans*-RuH(Cl)(depe)₂ [24], RuH(X) (*meso*-tet-1) (**2 h**: X⁻ = H⁻; **2i**: X⁻ = Cl⁻) and [RuH(L)(*meso*-tet-1)]⁺ (**2j**: L = MeIm; **2k**: L = PMe₂Ph; **2 l**: L = NCMe) [20].

trans-FeH(X)(depe)₂, **1a**, **1b**, **1d**, **1e**: The complex FeHCl(depe)₂ (0.2 g, 0.4 mmol) and a slight excess of NaX ($X^- = N_3^-$, NCO⁻, NCS⁻, Br⁻) were stirred overnight in acetone (20 mL). The fine sodium salts that formed were filtered off through Celite and the filtrate taken to dryness. The solid was dissolved in benzene (5 mL) and hexanes (5 mL) added. The volume of this solution was reduced under vacuum and placed in the refrigerator. The solid that formed was filtered off and the filtrate was

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slowly taken to dryness to leave the product as needles. *trans*-FeH(N₃) (depe)₂ (**1a**): ¹H NMR(C₆D₆): -30.8 ppm (quint, ²J_{HP} = 47.6 Hz, FeH); ³¹P{¹H} NMR(THF) 89.5 ppm (s). FAB MS calc. for C₂₀H₄₉FeN₃P₄ : 511; obs. 511 (M⁺). *trans*-FeH(NCO)(depe)₂ (**1b**): ¹H NMR(acetone-*d*₆): -28.7 ppm (quint, ²J_{HP} = 47.1 Hz, FeH); ³¹P{¹H} NMR(THF) 89.5 ppm (s). FAB MS calc. for C₂₁H₄₉FeNOP₄ : 511; obs. 511 (M⁺). *trans*-FeH(Br) (depe)₂ (**1d**): ¹H NMR(acetone-*d*₆): -31.5 ppm (quint, ²J_{HP} = 50.9 Hz, FeH); ³¹P{¹H} NMR(THF) 85.2 ppm (s). FAB MS: calc. for C₂₀H₄₉FeP₄Br : 548; obs. 548 (M⁺). *trans*-FeH(NCS)(depe)₂ (**1e**): ¹H NMR(acetone-*d*₆): -25.7 ppm (quint, ²J_{HP} = 47.3 Hz, FeH); ³¹P{¹H} NMR(THF) 89.1 ppm (s). FAB MS calc. for C₂₁H₄₉FeNP₄S : 527; obs. 527 (M⁺).

trans-[FeH(L)(depe)₂]BF₄ (**1f**, **1h**): The complexes were prepared by the method of Bancroft and Mays [27] except that NaBF₄ was used instead of NaBPh₄. *trans*-[FeH(N₂)(depe)₂]BF₄ (**1f**): ¹H NMR(acetone-*d*₆): -18.2 ppm (quint, ²J_{HP} = 47.3 Hz, FeH); ³¹P{¹H} NMR(THF) 80.8 ppm (s). *trans*-[FeH(CO)(depe)₂]BF₄ (**1h**): ¹H NMR(acetone-*d*₆): -10.9 ppm (quint, ²J_{HP} = 47.8 Hz, FeH); ³¹P{¹H} NMR(THF) 65.7 ppm (s). FAB MS calc. for C₂₁H₄₉FeOP₄: 497; obs. 497 (M⁺).

trans-FeH(X)(dtpe)₂, **1j**, **11**, **1m**: The complexes **1j**-**1m** were obtained by the same procedure as described in preparation of **1a** by using FeHCl (dtpe)₂ as the starting material. *trans*-FeH(NCO)(dtpe)₂, **1j**: orange solid, yield 60%. ¹H NMR(acetone-*d*₆): –26.5 ppm (quint, ²J_{HP} = 46.3 Hz, FeH); ³¹P{¹H} NMR(THF) 82.9 ppm (s). FAB MS calc. for C₆₁H₆₅Fe-NOP₄: 1007; obs. 1007 (M⁺). *trans*-FeH(NCS)(dtpe)₂, **1l**: orange solid, yield 59%. ¹H NMR(C₆D₆): –24.4 ppm (quint, ²J_{HP} = 43.9 Hz, FeH); ³¹P {¹H} NMR(THF) 83.5 ppm (s). FAB MS calc. for C₆₁H₆₅FeNP₄S: 1023; obs. 1023(M⁺). *trans*-FeH(CN)(dtpe)₂, **1m**: yellow solid, yield 59%. IR: 2056 (*v*CN). ¹H NMR(acetone-*d*₆): –15.1 ppm (quint, ²J_{HP} = 44.2 Hz, FeH); ³¹P{¹H} NMR(THF) 89.1 ppm (s). FAB MS calc. for C₆₁H₆₅FeNP₄: 991; obs. 991 (M⁺).

trans-[FeH(NCMe)(dtpe)₂]BPh₄ , **1n**: *trans*-Fe(H)(Cl)(dtpe)₂ (0.10 g, 0.10 mmol) was stirred for 5 h in 10 mL acetonitrile with NaBPh₄ (0.05 g, 0.44 mmol). The solution was filtered through THF saturated Celite. The solvent was removed under vacuum. Methanol (10 mL) was added and the resulting yellow solid was filtered off and washed with methanol. **1n** (0.16 g, yield 86%) was obtained. ¹H NMR(acetone-*d*₆): -20.8 ppm (quint, ²J_{HP} = 48.1 Hz, FeH); ³¹P{¹H} NMR(THF) 80 ppm (s). FAB MS calc. for C₆₂H₆₈FeNP₄: 1006; obs. 965 (M⁺- MeCN).

trans-[FeH(CO)(dtpe)₂]BF₄, **1p**: trans-[FeH(Cl)(dtpe)₂] (0.15 g, 0.15 mmol) was dissolved in 20 mL acetone under a CO atmosphere to give a dark red solution. NaBF₄ (0.016 g, 0.15 mmol) was then added and the mixture was stirred overnight. This pale yellow solution was filtered through acetone-saturated Celite. The solvent was evaporated to 3 mL and the addition of 15 mL diethyl ether caused the precipitation of a pale yellow solid which was filtered off and washed with diethyl ether. The yield was 0.15 g (93%). IR: 1940 (ν CO). ¹H NMR(acetone-*d*₆) –8.05 ppm (quint, ²J_{HP} = 47.6 Hz, FeH); ³¹P{¹H} NMR(THF) 82.9 ppm (s). FAB MS calc. for C₆₁H₆₄FeOP₄: 993; obs. 993 (M⁺).

trans-FeH(X)(dtfpe)₂, **1r**, **1 t**, **1u**: The complexes **1r**, **1t** and **1u** were obtained by the same procedure as described in the preparation of **1a** by using FeHCl(dtfpe)₂ as the starting material. *trans*-FeH(NCO)(dtfpe)₂, **1r**: orange solid, yield: 53%. ¹H NMR(acetone-*d*₆): –26.2 ppm (quint, ²J_{HP} = 44.2 Hz, FeH); ³¹P{¹H} NMR(THF) 81.7 ppm (s). FAB MS calc. for C₆₁H₄₁F₂₄FeNOP₄: 1439; obs. 1439 (M⁺). *trans*-FeH(NCS)(dtfpe)₂, **1t**: orange solid, yield: 54%. ¹H NMR(C₆D₆): –24.9 ppm (quint, ²J_{HP} = 42.8 Hz, FeH); ³¹P{¹H} NMR(THF) 85.6 ppm (s). FAB MS calc. for C₆₁H₄₁F₂₄FeNP₄S: 1455; obs. 1455 (M⁺). *trans*-FeH(CN)(dtfpe)₂, **1u**: yellow solid, yield: 56%. IR: 2083 (ν CN). ¹H NMR(C₆D₆): –15.3 ppm (quint, ²JHP = 46 Hz, FeH); ³¹P{¹H} NMR(THF) 91.5 ppm (s). FAB MS calc. for C₆₁H₄₁F₂₄FeNP₄: 1423; obs. 1423 (M⁺).

trans-[FeH(NCMe)(dtfpe)₂]BF₄, **1v**: The complex **1v** (yellow solid, yield 80%) was obtained by the same procedure as described in preparation of **1n** by using FeHCl(dtfpe)₂ as the starting material. ¹H NMR (acetone-*d*₆): -21.3 ppm (quint, ²J_{HP} = 43.5 Hz, FeH); ³¹P{¹H} NMR (THF) 84.1 ppm (s). FAB MS calc. for C₆₂H₄₄F₂₄FeNP₄: 1438; obs. 1397 (M⁺- MeCN).

trans-[FeH(CO)(dtfpe)₂]BF₄, **1x**: The pale yellow powder, *trans*-[FeH (H₂)(dtfpe)₂]BF₄, was placed in a flask under argon. The flask was evacuated and heated in vacuum for 3 min with a heat gun at approximately 170 °C. The pale yellow solid turned navy blue. The powder was then placed under 1 atm CO(g) and the color immediately changed to pale yellow (100% yield). IR: 1967 (ν CO). ¹H NMR(acetone-*d*₆): -7.64 ppm (quint, ²J_{HP} = 47.3 Hz, FeH); ³¹P{¹H} NMR(acetone-*d*₆) 90.7 ppm (s). FAB MS calc. for C₆₁H₄₁F₂₄FeOP₄: 1425; obs. 1425 (M⁺).

trans-RuHX(depe)2, 2a, 2c, 2e, 2f: The complexes 2a, 2c, 2e, 2f were obtained by the same procedure as described for the preparation of 1a by using RuHCl(depe)₂ as starting material. *trans*-RuH(S^tBu)(depe)₂, **2a**: yellow solid, yield 80%. ¹H NMR(acetone- d_6): -18.4 ppm (quint, ²J_{HP} = 21.1 Hz, RuH); ³¹P{¹H} NMR(THF) 61.8 ppm (s). FAB MS: calcd for $C_{24}H_{58}P_4RuS: 604; obs.: 547 (M^+-{}^{t}Bu), 546 (M^+-{}^{t}Bu,H). trans-RuH$ (NCO)(depe)₂, **2c**: yellow solid, yield 80%. ¹H NMR(acetone-*d*₆): -17.8 ppm (quint, ${}^{2}J_{HP} = 18.9$ Hz, RuH); ${}^{31}P{}^{1}H}$ NMR(THF) 65.2 ppm (s). FAB MS: calcd for C₂₁H₄₉NOP₄Ru: 557; obs.: 556 (M⁺-H), 515 (M⁺-H, NCO). trans-RuHBr(depe)₂, 2e: pale yellow solid, yield 80%. ¹H NMR (acetone- d_6): -20.0 ppm (quint, ${}^{2}J_{HP} = 19.6$ Hz, RuH); ${}^{31}P{}^{1}H$ NMR (THF) 61.7 ppm (s). FAB MS calcd for C₂₀H4₉BrP₄Ru: 594; obs.: 594 (M⁺), 515 (M⁺-Br). trans-RuH(NCS)(depe)₂, 2f: yellow solid, yield 80%. ¹H NMR(acetone- d_6): -19.0 ppm (quint, ²J_{HP} = 19.5 Hz, RuH); ³¹P {¹H} NMR(THF) 64.7 ppm (s). FAB MS calcd for C₂₁H₄₉NP₄RuS: 573; obs.: 572 (M⁺-H), 515 (M⁺-HNCS).

trans-[RuH(NCMe)(depe)₂]BF₄, **2g**: The complex **2g** (yellow solid, yield 80%) was obtained by the same procedure as described in the preparation of **1n** by using RuHCl(depe)₂ as the starting material. ¹H NMR(acetone-*d*₆): -18.2 ppm (quint, ²J_{HP} = 19.7 Hz, RuH); ³¹P{¹H} NMR(THF) 62.2 ppm (s). FAB MS calcd for C₂₂H₅₂NP₄Ru: 556; obs.: 515 (M⁺-MeCN).

trans-[Ru(H)(MeIm)(meso-tet-1)]BF₄, **2j**: The complex **2j** (cream colored solid, 0.035 g, 60%) was made by the same procedure as described in the preparation of **1n** by using *trans*-RuHCl(*meso*-tet-1) as the starting material. ¹H NMR(acetone-*d*_6): 8.0–6.5 (m, PC₆H₅); 6.6, 6.1, 5.95 (3 m, –CHCHNCH-); 3.0–1.1 (6 m, PCH₂CH₂P); 3.05 (s, –NCH₃); –19.5 (quint, ²J_{HP} = 20.1 Hz, RuH). ³¹P{¹H} NMR(THF) 98.7 (dm), 59.1 (dm), ²J_{PP} = 230.1 Hz. FAB MS calcd for C₄₆H₄₉N₂P₄Ru: 855; obs.: 772 (M⁺–H,MeIm).

trans-RuH(X)(dtfpe)₂, **2m**, **2o**: A mixture of [RuH(dtfpe)₂]BF₄ (0.2 g) and an excess amount of MX (KNCS for **2o**, NaS^tBu for **2 m**) in MeOH (10 mL) was stirred at room temperature for 5 min to give a colorless solution. The MeOH was removed completely under vacuum. The residue was extracted with CH₂Cl₂ (10 mL). Addition of hexane (20 mL) produced a white solid. *trans*-RuH(S^tBu)(dtfpe)₂, **2m**: white solid, yield 80%. ¹H NMR(C₆D₆): -18.9 ppm (quint, ²J_{HP} = 19.1 Hz, RuH); ³¹P{¹H} NMR(THF) 62.2 ppm (s). FAB MS calcd for C₆₄H₅₀F₂₄RuP₄S: 1532; obs.: 1532 (M⁺). *trans*-RuH(NCS)(dtfpe)₂, **2o**: ¹H NMR(CD₂Cl₂): -17.1 ppm (quint, ²J_{HP} = 20.7 Hz, RuH); ³¹P{¹H} NMR(THF) 65.6 ppm (s). FAB MS calcd for C₆₁H₄₁F₂₄RuNP₄S: 1501; obs.: 1501 (M⁺).

trans-[RuH(NCMe)(dtfpe)₂]BF₄, **2p**: The complex **2p** (white solid, yield 80%) was obtained from same procedure as described in preparation of **1n**. ¹H NMR(acetone- d_6): -15.9 ppm (quint, ²J_{HP} = 18.8 Hz, RuH); ³¹P{¹H} NMR(THF) 62.6 ppm (s). FAB MS calcd for C₆₂H₄₄F₂₄RuNP₄: 1471; obs.: 1471 (M⁺)

trans-[RuH(CO)(dtfpe)₂], **2q**: The complex **2q** (white solid, yield 80%) was obtained from same procedure as described in preparation of **1h** by using [RuH(dtfpe)₂]BF₄ as the starting material. ¹H NMR(CD₂Cl₂): -7.1 ppm (quint, ²J_{HP} = 19.7 Hz, RuH); ³¹P{¹H} NMR(THF) 63.2 ppm (s). FAB MS calcd for C₆₁H₄₁F₂₄RuOP₄: 1484; obs.: 1484 (M⁺)

trans-OsHCl(depe)₂: The complex was prepared using a modified version of Chatt and Hayter's method [24] which is described in reference [28]. NMR data were not given when this complex was first described. ¹H NMR(C₆D₆) –22.8 (quint, ²J_{HP} = 15.3 Hz); ³¹P{¹H} NMR (acetone) 33.4 (s).

trans-OsH(S^tBu)(dppe)₂, **3a**: The complex was prepared from trans-OsHBr(dppe)₂ (0.122 g, 0.144 mmol) and NaS^tBu (0.07 g, 0.62 mmol) in

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THF (20 mL). See below for the preparation of the OsHBr(dppe)₂ complex. The reaction mixture was refluxed for 2 h. After completion of the reaction, the reaction mixture was slowly filtered through THF-saturated Celite. Solvents were removed from the bright yellow filtrate by vacuum distillation. Acetone (~4 mL) was added to the orange-yellow residue, and the tangerine orange solid was filtered and dried in vacuum. Yield was 33% (0.40 g). IR: 2040 (br w, ν OsH). ¹H NMR (C₆D₆): 7.6 to 6.8 (m, 40H, Ph), 2.89 (m, 4H, CH₂), 2.06 (m, 4H, CH₂), 1.08 (s, 9H, tBu), -17.8 (quint, ¹H, ²J_{HP} = 16.7 Hz, OsH). ³¹P{¹H} NMR (THF) 24.4 ppm (s). FAB MS calcd for C₅₆H₅₈SP₄Os: 1078; obs. 1079 (weak, MH⁺), 990 (MH⁺ -^tBuS), 988 (MH⁺ -^tBuS, 2H).

trans-OsH(SPh)(dppe)₂, 3b: A slurry of trans-OsHBr(dppe)₂ (0.218 g, 0.204 mmol), NaSPh (0.048 g, 0.36 mmol) and THF (10 mL) was stirred for 3 h, and the ³¹P NMR spectrum recorded; trans-OsHBr(dppe)₂ was the major species present. More NaSPh was added (0.050 g, 0.038 mmol) and the reaction mixture was refluxed for 3 h and then stirred for 50 h. The ³¹P NMR spectrum showed that the reaction was complete. The suspension was chilled, filtered through THF-saturated Celite, and the solvent was removed from the yellow filtrate under reduced pressure. The resulting bright yellow powder was precipitated from THF (3 mL) by addition of cold Et₂O (10 mL) to give 0.277 g of crude product. This was dissolved in benzene (20 mL) and the salts were removed by filtering through benzene-saturated Celite. The volume of the filtrate reduced in vacuum to 2 mL, Et₂O (4 mL) were added, and the mixture briefly cooled. The bright yellow solid (0.181 g, 80% yield) was filtered, washed with Et₂O (5 mL) and dried in vacuum. IR: 2020 (m, ν OsH). ¹H NMR(C₆D₆⁶): 7.5 to 6.75 (m, 40H, PC₆H₅), 6.63 (m, 2H, SC₆H₅), 6.26 (m, 3H, SC₆H₅), 2.80 (m, 4H CH₂), 2.08 (m, 4H, CH₂), 16.6 (quint, ¹H, ²J_{HP}) = 16.6 Hz, OsH). ${}^{31}P{}^{1}H{}$ NMR(C₆D₆) 28.0 ppm (s). FAB MS calcd for C₅₈H₅₄SP₄Os: 1098; obs. 1098 (M⁺), 989 (M⁺ -SPh).

trans-OsHCl(dppe)₂ **3d**: This complex was prepared by reacting *trans* $[Os(\eta^2-H_2)H(dppe)_2]PF_6$ with LiCl as described in reference [28]. NMR data were not given when this complex was first described [24]. ¹H NMR (C₆D₆) 7.6 to 6.8 (m, 40H, Ph), 2.57 (m, 4H, CH₂), 2.00 (m, 4H, CH₂), -20.4 (quint, ¹H, ²J_{HP} = 15.4 Hz, OsH); ³¹P{¹H} NMR(C₆D₆) 30.5 (s).

trans-OsHBr(dppe)₂ **3e**: This complex was prepared from $(NH_4)_2[OsBr_6]$ and 2.2 equivalents of dppe as described in reference [28]. ³¹P{¹H} NMR(CH₂Cl₂) 28.7 (s). ¹H NMR(CD₂Cl₂) 7.35 to 6.95 (m, 40H, Ph), 2.66 (m, 4H, CH₂), 2.10 (m, 4H, CH₂), -20.4 (quint, ²J_{HP} = 15.3 Hz, OsH)

trans- $[Os(\eta^2-H_2)H(dppe)_2]PF_6$: The complex was prepared in 92% yield from $OsH_2(dppe)_2$ (0.660 g in 40 mL Et₂O) and 0.35 mL of 60–65 wt% HPF₆(aq), using a method analogous to that described for the BF₄ salt [26]. After 15 min of reaction the solvent was decanted from the white product, and the solid was treated with 2x40 mL of Et₂O (stirring followed by decantation). The product was filtered, washed with 3x15 mL of Et₂O and dried in vacuo; 0.696 g were obtained. The complex is air-stable enough to be filtered through the air, though long term storage (weeks) requires a N₂ or Ar atmosphere. ¹H and ³¹P NMR(acetone or dichloromethane solvents) as described for *trans*- $[Os(\eta^2-H_2)H(dppe)_2]$ BF₄; a PF₆⁻ resonance is also observed by ³¹P NMR.

trans-[OsH(L)(dppe)₂]PF₆, **3f-3j**: *trans*-[Os(H)(H₂)(dppe)₂]PF₆ (0.106 g, 0.093 mmol) was dissolved in 10 mL of acetone and a slight excess amount of L was added. The solution was refluxed for 50 min; a ³¹P NMR spectrum indicated that the reaction was complete. The solvent was removed under reduced pressure, and the white residue dissolved in 3 mL of CH₂Cl₂. Three volumes of Et₂O were added, and the solution was cooled for 30 min, followed by stirring to produced a white solid. The volume was reduced in vacuum by one third and the solid was filtered, washed with 2 mL of Et₂O and dried in vacuum.

trans-[OsH(MeIm)(dppe)₂]PF₆, **3f**: yellow solid, 0.089 g, yield 75%. IR: 2066 (w, ν OsH). ¹H NMR(acetone- d_6) 7.7 to 6.7 (m, 40H, Ph), 6.46, 6.21, 6.08 (s, –CHCHNCH-), 3.07 (s, 3H, NMe), 2.79 (m, 4H, CH₂), ~2.0 (m, ~4H, CH₂), -18.4 (quint, ¹H, ²J_{HP} = 16.6 Hz, OsH). ³¹P{¹H} NMR (acetone) 34.8 ppm (s). Anal. Calcd for C₅₆H₅₅F₆N₂OsP₅: C, 55.35; H, 4.56. Found: C, 55.69; H, 4.87. FAB MS calcd for C₅₆H₅₅N₂OsP₄: 1071;

Table 4

List	of ³¹ P	NMR	chemical	shifts	of some	complexes	trans-[MH(L)(PP) ₂] ⁺	and
tran	s-MH(X	(PP)	$_{2}$ (M = Fe,	Ru ar	nd Os).			

Р—Р	L or X^-	δ (PFe)	δ (PRu)	δ (POs)	∆ (Fe- Ru)	Δ (Ru- Os)	Δ (Fe- Os)
dppe ^a	H_2	92.5	68.6	37.5	23.9	31.1	55
dppe ^{a,c}	H^{-}	_	83.4	49.8	-	33.6	-
dppe	SPh^{-}	-	62.3	28	-	34.3	-
dppe	NCMe ^b	84.3 ^a	-	33	-	-	51.3
dppe	Cl^{-}	_	62.5 ^d	30.5	_	32.0	-
depea	H_2	92.9	68.7	30.7	24.2	38.0	62.2
depe ^{a,c}	H^{-}	-	84.4	48.3		36.1	-
depe	Cl^{-}	87.2	64.4	32.0	22.8	32.4	55.2
depe	Br^{-}	85.2	61.7	-	23.5	-	-
depe	NCS^{-}	89.1	64.7	-	24.4	-	-
depe	MeCN	89.1	62.2	-	26.9	-	-
depe	S ^t Bu ⁻	89.1	61.8	-	27.3	-	-
dtfpe ^a	H_2	94.7	71.4	39.9	23.3	31.5	54.8
dtfpe ^{a,c}	H^{-}	-	84.8	52.2	-	32.6	-
dtfpe	NCS^{-}	85.6	65.6	-	20.0	-	-
dtfpe	MeCN	84.1	62.6	-	21.5	-	-
dtfpe	CO	90.7	63.2	-	27.5	-	-
Average					24.1	33.5	56.5

^a Ref. [23]. ^bNo NMR data were given by Chatt et al. [15] when this complex was first described. ^c Data for trans isomer is given; ^d Ref. [33].

obs. 1071 (weak, M⁺), 989 (M⁺-MeIm). trans-[OsH(PMe₃)(dppe)₂]PF₆, **3g**: vellow solid, 0.07 g, vield 66%, IR: 2038 (w, ν OsH), ¹H NMR(acetone-d₆) 7.4 to 6.9 (m, 40H, Ph), 2.64 (m, 4H, CH₂), 2.30 (m, 4H, CH₂), 0.49 (d, 9H, ${}^{2}J_{HP} = 7$ Hz, Me), -11.9 (d quint, 1H, ${}^{2}J_{HP} = 41.7$, 19.2 Hz, OsH). ³¹P{¹H} NMR(acetone-*d*₆): 29.4 (d, dppe), 73.9 (quint, PMe₃, ²J_{PP} = 14.2 Hz). FAB MS calcd for C₅₅H₅₈P₅Os: 1065.3; obs. 1065.2 (M⁺), 989 (M⁺-PMe₃) and 987 (M⁺ -PMe₃,2H). trans-[OsH(NCMe)(dppe)₂] PF₆, **3h**: white solid, 0.045 g, yield 70%. IR: 2066 (w, vOsH), 2267 (w, ν CN). ¹H NMR(CD₂Cl₂): 7.4 to 7.1 (m) and 6.7 (br s) (40H, Ph), 2.54 (m, 4H, CH₂), 2.06 (m, 4H, CH₂), 1.81 (s, 3H, NCMe), 16.6 (quint, 1H, ²J_{HP} = 16.2 Hz, OsH). ${}^{31}P{}^{1}H}$ NMR(CH₂Cl2) 33.0 ppm (s). FAB MS calcd for C54H52NP4Os: 1030; obs. 1030 (weak, M⁺), 989 (M⁺ -NCMe), 987 (M⁺ -NCMe, 2H). trans-[OsH(P(OMe)₃)(dppe)₂]PF₆, 3i: white solid, 0.08 g, yield 75%. IR: 2002 (w, vOsH). ¹H NMR(CD₂Cl₂): 7.45 to 7.0 (m) and 6.8 (br s) (40H, Ph), 2.76 (m, 4H, CH₂), 2.38 (m, 4H, CH₂), 2.86 (d, 9H, ²J_{HP} = 10.4 Hz, Me), -10.6 (d quint, 1H, ${}^{2}J_{HP} = 86.7$, 19.0 Hz, OsH). ${}^{31}P{}^{1}H{}$ NMR(acetone-*d*₆) 28.1 (d, dppe), 91.7 (quint, P(OMe)₃, ²J_{PP} = 23.0 Hz). FAB MS calcd for C55H58O3P5Os: 1113; obs. 1113 (M⁺), 987 (M⁺ -P (OMe)₃).

trans-[OsH(P(OPh)₃)(dppe)₂]PF₆, **3***j*: white solid, 0.08 g, yield 77%. IR 2062, 2013 (w). ¹H NMR(acetone-*d*₆): 7.4 to 6.9 (m, 40H, PC₆H₅), 6.84 and 6.23 (m, 15H, OPh), 3.02 (m, 4H, CH₂), 2.64 (m, 4H, CH₂), -10.4 (d quint, 1H, ²J_{HP} = 108.9, 19.8 Hz, OsH). ³¹P{¹H} NMR (acetone/THF: 3/2 v/v) 25.3 (d, dppe), 76.5 (quint, ²J_{PP} = 22.1 Hz, P (OPh)₃). Anal. Calcd for C₇₀H₆₄F₆P₆Os: C, 58.25; H, 4.47. Found: C, 57.81; H, 4.66. FAB MS calcd for C₇₀H₆₄P₅Os: 1299; obs. 1299 (M⁺), 989 (M⁺ -P(OPh)₃) and 987 (M⁺ -P(OPh)₃, 2H).

3. Results and discussion

3.1. Synthesis and characterization

The complexes *trans*-MH(X)(PP)₂ (M = Fe, PP = depe, dtpe and dtfpe, X = NCS⁻, NCO⁻, N₃⁻, CN⁻, Br⁻; M = Ru, PP = depe, 1/2 *meso*-tet-1, X = Cl⁻, Br⁻, NCS⁻, NCO⁻, S^tBu⁻; M = Os, PP = dppe, X = StBu⁻, SPh⁻) were prepared in high yield from the starting complexes *trans*-MH (X)(PP)₂ (X = Cl⁻ or Br⁻) and an excess of the appropriate potassium or sodium salt in acetone at 20 °C in 4 h as shown in Eq. (5). The ³¹P NMR data for some of these complexes and ones described below are listed Table 4 to illustrate the trend δ Fe > δ Ru > δ Os.



Field and co-workers have reported the preparation of structurally similar thiolate iron hydride complexes MH(SR)(dmpe)₂ [29,30]. The dihvdride complexes $M(H)_2(dmpe)_2$ (M = Fe, Ru) are protonated by arene or alkanethiols in THF to initially yield the molecular hydrogen complexes [MH(H₂)(dmpe)₂]⁺ which react with the thiolate to give a mixture of cis and trans-MH(SR)(dmpe)2. These thiolate complexes react with HBF₄•Et₂O to form protonated thiol complexes, rather than dihydrogen complexes [31]. The thiolate complex trans-RuH(SPh)(dppe)₂ was reported to crystallize with the thiolate trans to the hydride [31]. Some literature data for thiolate complexes are included in the Supporting Information (SI).

The complexes trans- $[MH(L)(PP)_2]BF_4$ (M = Fe, PP = depe, dtpe, dtfpe, L = NCMe, CO, N₂, H₂; M = Ru, PP = depe, 1/2 meso-tet-1, L = NCMe, CO, H₂, PMe₂Ph, MeIm) were also prepared from trans-MHCl $(PP)_2$ by direct ligand substitution in the presence of NaBF₄ as Eq. (6) shows. Analogous iron nitrile complexes have been prepared in a similar fashion; these complexes tend to crystallize in a trans configuration [32]. The electrochemistry of these complexes has been reported by Lee et al. [32] and is included in the SI.

The five-coordinate ruthenium hydride complex [RuH(dtfpe)₂]BF₄ of unknown stereochemistry can also be used to prepare trans-RuH(X) $(dtfpe)_2 (X = S^tBu^- and NCS^-)$ and trans- $[RuH(NCMe)(dtfpe)_2]^+$ in high yield as Eq. (7) shows.

$$\begin{bmatrix} P_{M_{n}} \stackrel{H}{\underset{p}{\checkmark}} \stackrel{\bigoplus}{\underset{p}{\checkmark}} \stackrel{\bigoplus}{\underbrace{\operatorname{L} \text{ or } X^{*} (\operatorname{excess})}} \begin{bmatrix} P_{M_{n}} \stackrel{H}{\underset{p}{\checkmark}} \stackrel{\bigoplus}{\underset{p}{\checkmark}} \stackrel{\bigoplus}{\underset{p}{\rightthreetimes}} \stackrel{\bigoplus}{\underset{p}{\underset{p}{\rightthreetimes}} \stackrel{\bigoplus}{\underset{p}{\atop}} \xrightarrow{\bigoplus}} \stackrel{\bigoplus}{\underset{p}{\atop}} \stackrel{\bigoplus}{\underset{p}{\atop}} \xrightarrow{\bigoplus}} \stackrel{\bigoplus}{\underset{p}{\atop}} \xrightarrow{\bigoplus}} \stackrel{\bigoplus}{\underset{p}{\atop}} \xrightarrow{\bigoplus}$$

The complexes trans-[MH(L)(PP)₂]⁺ and trans-MH(X)(PP)₂ prepared in this work were shown by ¹H and ³¹P NMR spectroscopy to exist solely as the trans isomer. In preparing the cationic members of the series trans- $[MH(L)(dppe)_2]^+$, tetraphenylborate (BPh₄⁻) was avoided as a counterion because it is redox active in the electrochemical potential region of interest. Tetrafluoroborate (BF_4^-) or hexafluorophosphate (PF_6^-) are appropriate counter-ions.

Some complexes trans- $[MH(L)(PP)_2]^+$ and trans- $MH(X)(PP)_2$ (M = Fe, PP = dtfpe, L = CO; M = Ru, PP = dppe, $X = SPh^{-}$; M = Os, PP =dppe, $X = Cl^{-}$, $S^{t}Bu^{-}$, L = MeIm, NCMe, PMe₃, P(OMe)₃, P(OPh)₃) can be prepared from their dihydrogen precursors in acetone as shown in Eq. (8). Similar iron-group dihydrogen complexes have been synthesized, and it has been shown that the dihydrogen can be substituted with triflate [34]. The complex trans-OsH(Br)(dppe)₂, however, is prepared directly from (NH₄)₂[OsBr₆] and dppe in refluxing MeOH/EtOH [28].



The advantage of this route is that the precursor materials, trans-[MH



Fig. 1. Cyclic voltammograms of trans-OsH(SPh)(dppe)₂ in THF solution containing 0.2 M NBu₄PF₆, at scan rates (n) of 50 and 500 mVs⁻¹.

 $(\eta^{2}-H_{2})(PP)_{2}]PF_{6}$ (M = Fe, Ru, Os) are prepared in a pure form in high yield. The pathway for the substitution reaction is likely via a five coordinate hydride species. Once the electron-deficient five-coordinate metal hydride is formed, the substitution goes quickly. Preparation of the carbonyl derivative of trans-[FeH(H2)(dtfpe)2]BF4, however, required generation of the five coordinate intermediate in the solid state, as Eq. (9) shows.

$$\begin{bmatrix} P_{H_{2}}, P_{1}, P_{2}, P_{1} \\ P_{p} & F_{p} \\ P_{p} & F$$

The FAB MS results show that for anionic ligands, complexes trans-MH(X)(PP)₂ can either lose H⁻ or X⁻ to give five-coordinate fragments $[MH(PP)_2]^+$ or $[MX(PP)_2]$ whereas for the neutral ligands, the complexes trans-[MH(L)(PP)₂]⁺ lose the neutral ligand to give fragments [MH(PP)₂]⁺. The observation of the unsaturated complexes support the proposal that they are intermediates in the substitution reactions represented by Eqs. (8) and (9).

However, it is noteworthy that if the ligand X⁻ is basic enough, the deprotonation of the dihydrogen complex may occur. For example, the reaction of trans-[OsH(H₂)(dppe)₂]PF₆ and excess NaS^tBu gives a mixture of cis and trans-Os(H)₂(dppe)₂ (94%) and trans-OsH(S^tBu) $(dppe)_2$ (6%). That the pK_a of the dihydrogen complex is about 13 while the p K_a of HS^tBu is about 10 in water, but higher in less polar solvents gives a reasonable explanation [23].

Dichloromethane was not used to prepare solutions of the electron rich thiolate complexes trans-MH(SR)(dppe)2 because this solvent reacts with these compounds. Most of these metal hydride complexes are very soluble in most organic solvents.

All of the products were characterized by ³¹P, ¹H NMR, FAB MS and electrochemistry. The ³¹P NMR data (Table 4) show systematic trends where for complexes with the same ligands but different metals, the ruthenium chemical shifts are 20 to 30 ppm downfield of the those of iron while the osmium chemical shifts are 51 to 62 ppm downfield of he ruthenium ones. There is a good correlation between the ³¹P chemical shifts of ruthenium and osmium (Figure S4) but a poor correlation between those of iron and ruthenium or iron and osmium.

3.2. Electrochemistry of trans- $[MH(L)(PP)_2]^+$ and trans- $MH(X)(PP)_2$

Since we are interested in the oxidation of the M(II) state, the region between -1 to 1.6 V vs. Fc⁺/Fc was examined. The cyclic voltammograms of most of the metal hydride complexes showed pseudo-reversible



Fig. 2. Plot of anodic and cathodic peak currents (i_{pa} and i_{pc}) versus scan rate $\nu^{1/2}$ for a solution of OsH(SPh)(dppe)_2.

waves in this region. A typical cyclic voltammogram is shown in Fig. 1.

The cyclic voltammograms (CVs) of the complex *trans*-OsH(SPh) (dppe)₂ were obtained by cycling the potential of the working electrode, relative to Fc⁺/Fc, between -0.8 and 0.7 V at a scan rate of 50 or 500 mVs⁻¹. An oxidation wave at the anionic potential peak E_{pa} is observed in the forward scan and a reduction wave at the cathodic potential peak E_{pc} is displayed in the reverse scan. The current height at E_{pa} or E_{pc} is proportional to the square root of the scan rate, $\nu^{1/2}$, and the i_{pa}/i_{pc} ratio is one (see Fig. 2). Both of these characteristics are expected for reversible redox processes. However, the separation between E_{pa} and E_{pc} (ΔE_p) increases as the scan rate increases (see Table 5), and is not equal to 59 mV/n (n = electron stoichiometry) as expected for a reversible process. This is attributed to an increase in double layer capacitance with increasing scan rate, and the uncompensated high resistance of the solvent mixture.

It is interesting to note that at more positive potentials (potential is increased from -0.1 to 0.4 V vs. Fc⁺/Fc) a second set of E_{pa} and E_{pc} peaks is observed for *trans*-OsH(SPh)(dppe)₂ due to the d⁴/d⁵ couple (see Table 5). The $E_{1/2}$ values for the complexes *trans*-[MH(L)(PP)₂]⁺ and *trans*-MH(X)(PP)₂ are obtained as the potential half-way between the oxidation (E_{pa}) and the reduction (E_{pc}) potentials.

The redox behavior of several complexes, such as *trans*-[FeH(L) $(dtpe)_2]^+$ (L = H₂, CO), *trans*-FeH(X)(dtfpe)₂, *trans*-[FeH(L)(dtfpe)₂]⁺, *trans*-[Ru(H)(NCMe)(dtfpe)₂]⁺ and *trans*-[OsH(P(OMe)₃)(dppe)₂]⁺, are irreversible. Anodic peak potentials (E_{pa}) have been reported in Table 3 for these complexes. A typical cyclic voltammogram of an irreversible redox process for the iron group hydride complexes is shown in Fig. 3. This irreversibility can generally be rationalized by investigating the acidity of the oxidized complex, as discussed elsewhere [35], with use of the ligand acidity constant (LAC) method. For reversible voltammograms, generally the calculated pK_a^{LAC} for the oxidized complex is

relatively high, which makes the oxidized complex stable to proton loss. For example , the Fe^{III} complex [FeH(Cl)(depe)₂]⁺ has a pK_a^{LAC} of 19, which is too high to be acidic enough for proton loss, and the voltammogram is reversible. Conversely, complexes that are irreversibly oxidized tend to have more acidic metal hydrides upon oxidation. For example, the Fe^{III} complex [FeH(CO)(dtpe)₂]²⁺ has a pK_a^{LAC} value of -1, and the complex is irreversibly oxidized. The oxidation is irreversible likely because the complex loses a proton upon oxidation. On the same grounds, some reversible voltammograms are expected to be irreversible, yet display partially reversible behavior, possibly due to slow proton loss.

The dihydrogen complexes in Table 3 (entries 10 and 1w) also display irreversible oxidations. In these cases, the complex likely loses dihydrogen upon oxidation, as discussed elsewhere [35].

The E_L values for the depe, dtpe, and *meso*-tet-1 ligands were not reported by Lever, and are determined here from experimental data. The E_L values of all of these ligands are included in Table 1.

It is generally agreed that a less donating ligand gives rise to a more electron poor metal center M which, in turn, is more difficult to oxidize. For example, the complexes *trans*-[FeH(L)(dtfpe)₂]⁺, with an electron-withdrawing CF₃ substituents on the aryl groups, have more positive electrochemical potentials than the analogous dtpe complexes with CH₃ substituents or depe complexes with Et groups on phosphorus (see table 2). For a given metal and PP ligand, the $E_{1/2}$ of the complexes *trans*-[MH(L)(PP)₂]⁺ and *trans*-MH(X)(PP)₂ are generally shifted to more positive potentials as the E_L value of the X⁻ or L ligand increases; exceptions to this ordering can be accounted for by the experimental error



Fig. 3. Cyclic voltammogram of complex *trans*- $[OsH(P(OMe)_3)(dppe)_2]^+$ with 50 mV/s scan rate in CH₂Cl₂ containing 0.2 M NBu₄PF₆ solution.

Table 5

Measured $E_{1/2}$ values (V, vs. Fc^+/Fc) of the d^5/d^6 couple (unless noted otherwise) for the d^6 complexes *trans*-[OsH(L)(dppe)₂]⁺ in 0.2 M NBu₄PF₆ solution at the noted scan rates.

Ligand	$E_{1/2 obs}$ at scan rate, ν (mVs ⁻¹)							
	$\nu = 50$	ΔE , mV	$\nu = 250$	$\Delta E, mV$	$\nu = 500$	$\Delta E, mV$		
S ^t Bu ⁻			-0.769	38 ^a	-0.771	55 ^a	THF	
SPh ⁻	-0.664	109	-0.646	143	-0.649	173	THF	
SPh ⁻	0.245^{b}	72	0.262^{b}	137	$0.277^{\rm b}$	158	THF	
Cl ⁻	-0.126	82	-0.131	110	-0.124	142	THF	
Br ⁻	-0.101	99	-0.104	123	-0.116	128	THF	
MeIm	0.311	99	0.311	118	0.311	143	THF	
PMe ₃	0.673	108	0.681	143	0.683	158	CH_2Cl_2	
NCMe	0.584	74	0.584	84	0.587	89	CH_2Cl_2	
P(OMe) ₃			0.97 ^c		0.97 ^c		CH_2Cl_2	
P(OPh) ₃			>1.2 ^d				CH_2Cl_2	

^a Small ΔE_p indicates possible 2e⁻ process; also observed: waves at -0.52 V, -0.14 V and an irreversible wave with E_{pa} of $0.23 \pm 0.02 \text{ V}$. ^b d⁴/d⁵ couple. ^c E_{pa} value. ^d The triphenylphosphite derivative is more difficult to oxidize than the dichloromethane solvent employed, and no redox potential was obtained for this complex.



Fig. 4. Plots of E_{obs} vs. ΣE_L for the group 8 metal hydride complexes. The solid blue line corresponds to the line of best fit for the data. The dashed orange line is from Lever's equations [2]. (a) $Fe^{III/II}$ couple, $E_{obs} = 1.08\Sigma E_L - 0.46$. (b) $Ru^{III/II}$ couple, $E_{obs} = 0.77\Sigma E_L + 0.15$ and (c) $Os^{III/II}$ couple, $E_{obs} = 1.04\Sigma E_L - 0.44$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of the $E_{1/2}$ measurements. As the ligands change from σ and π -donor to σ -donor and π -acceptor as the value of the E_L parameter increases, the σ -donor and π -acceptor ligands (such as N_2 , CO and H_2) make the metal complex more oxidizing.

The solvent influence on E_{obs} is probably small. For example, the complex *trans*-[FeH(L)(dtpe)₂]⁺, where $L = H_2$, NCMe, showed similar $E_{1/2}$ values in THF and CH₂Cl₂. Thus we assume that the potentials that we are measuring in this study are independent of the solvent system. One notable exception, however, is the dihydrogen complex *trans*-[FeH (H₂)(dtfpe)₂]⁺ which exhibits a solvent dependent E_{pa} (see Table 3, entry 1w): $E_{pa} = -0.03$ V in THF; $E_{pa} = +0.48$ V in CH₂Cl₂) the values of which are surprisingly lower than observed for the more basic complex

trans-[FeH(H₂)(dtpe)₂]⁺ (pK_a = 12.6 ± 0.4) [23]. The unexpected electrochemical behavior of *trans*-[FeH(H₂)(dtfpe)₂]⁺ may be due to its acidic nature (pK_a = 7.8 ± 0.3) [23]. It is plausible that this acidic dihydrogen complex, which is in low concentration relative to the electrolyte NBu₄PF₆ (0.2 M), exists as a solvent-dependent equilibrium between the protonated and the deprotonated forms:

$$\mathbf{B} + [\mathbf{FeH}(\mathbf{H}_2)(\mathbf{dtfpe})_2]\mathbf{PF}_6 \rightleftharpoons \mathbf{Fe}(\mathbf{H})_2(\mathbf{dtfpe})_2 + \mathbf{HB}^+\mathbf{PF}_6^-$$
(10)

The nature of the base, B, remains uncertain but its acid form, BH⁺, must have a pK_a near 8. It is likely that the electrolyte, NBu₄PF₆, is responsible for the deprotonation. Tilset and Parker have observed that electrolytes commonly used for electrochemical studies are sufficiently basic to cause the deprotonation of some acidic hydride complexes [36,37]. For example, the acidic hydride $[CpW(CO)_2(PMe_3)H_2]^+$ is quite stable in dry acetonitrile but undergoes spontaneous deprotonation in acetonitrile/0.1 M NBu₄PF₆ [36,37]. The unexpectedly low, solventdependent E_{pa} value for [FeH(H₂)(dtfpe)₂]BF₄, therefore, reflects the presence of the dihydride species. As further support for this argument, when Fe(H)₂(dtfpe)₂ was combined with an equal weight of [FeH(H₂) (dtfpe)₂]BF₄, the anodic wave (for the dichloromethane solution) appeared at +0.05 V instead of +0.48 for the dihydrogen complex alone. The oxidation potential for the dihydrogen complex is sensitive to the presence of the dihydride species in solution as expected on the basis of the Nernst equation.

3.3. Electrochemistry of literature-reported iron-group hydrides

A more extensive collection of literature reported cyclic voltammograms (CVs) of iron-group hydrides is included in the Supporting Information. A part of the tables in the SI is copied from a previous paper [35]. The data includes both reversible and irreversible oxidations of M (II) hydride complexes, where M = Fe, Ru, and Os. Where multiple papers report the same data, all data is included. Some E_L values are determined here, while others are found in Lever's paper [2]. All E_L values used are listed in Table S5.

The literature iron voltammetry data is presented in Table S1. Fig. 4a shows the Fe^{III/II} Lever plot for the combined data measured in this work (Table 3) and from the literature, 43 data points in all. In order to generate this plot the E_L value of the hydride was varied within the sum of the E_L values of ligands until the optimum fit to the data was obtained. With $E_L(H) - 0.65 \pm 0.02$ V, the correlation was good at 0.91 The equation of the line is the same, within error, as Lever's equation for iron complexes as shown in Table 2. This E_L value is somewhat near to the value calculated using the computed electronic parameter method, which is -0.76 [8].

The plot for just the 17 iron complexes measured in the current work (Table 3) is shown in Figure S1. The correlation is improved to 0.94, and the slope and intercept are also close to Lever's equation for iron data shown in Table 2. The same E_L value of -0.65 V is obtained for hydride from this subset of data. Note that the two dihydrogen complexes were omitted from this analysis.

The literature ruthenium data is presented in Table S2; Fig. 4b shows the Ru^{III/II} Lever plot for the combined data (49 data points) from the literature and the current work (Table 3). The correlation is modest at 0.84. The E_L value for the hydride is found to be -0.65 V which is the same as the iron data. The equation of the line deviates somewhat from Lever's equation for ruthenium complexes as shown in Table 2. This deviation is attributed to the relatively poor correlation. Note that the correlation does not improve if irreversible CVs are excluded.

The plot for just the 15 ruthenium complexes presented in Table 3 is shown in Figure S2. The correlation is improved to 0.87, but the slope and intercept are still somewhat different from Lever's equation for ruthenium data shown in Table 2. The same E_L value of -0.65 V is obtained for the hydride ligand from this subset of data.

The literature osmium data is presented in Table S3; Fig. 4c shows

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the Os^{III/II} Lever plot for the combined data (19 data points) from the literature and this work (Table 3). The correlation is modest at 0.88, and the E_L value for the hydride is found to be -0.37 ± 0.05 V. This E_L for the hydride is more positive for Os than for Ru and Fe. This variation is attributed to stronger M-H σ bonding due to relativistic effects associated with osmium. For the Lever plot shown, the equation of the line is within error of Lever's equation for osmium complexes shown in Table 2.

The plot for just the 8 osmium complexes of Table 2 is shown in Figure S3. The correlation is improved to 0.93, but the slope and intercept deviate from Lever's equation for osmium complexes shown in Table 2. The same E_L value of -0.37 V is obtained for the hydride ligand from this subset of data.

Overall, the literature data agrees with the data reported here, although there is more scatter in the literature data. This scatter may be due to the use of different referencing systems, different solvents, errors in $E_{1/2}$ values due to irreversibility, and slightly erroneous E_L values.

4. Conclusions

The $M^{III/II}$ electrochemistry of a series of group 8 metal hydride phosphine complexes was presented. An E_L value for the hydride ligand was calculated based on the iron group phosphine complexes $MHX(PP)_2$ and $MHL(PP)_2^+$, and a collection of literature data . Based on the ruthenium and iron data, an E_L value of -0.65 V was obtained. The osmium data had an E_L value of only -0.37 V; this variation between iron/ruthenium and osmium is attributed to stronger M-H bonding in the 5d metal compared to the 3d and 4d metals. Ongoing work is focused on obtaining an E_L value for the hydride ligand for other metals.

Credit authorship contribution statement

All of the authors contributed equally to this research.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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