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Synthesis, Characterization, and Reactivity Studies of Electrophilic Ruthenium(II) Complexes: Study of H_2 Activation and Labilization

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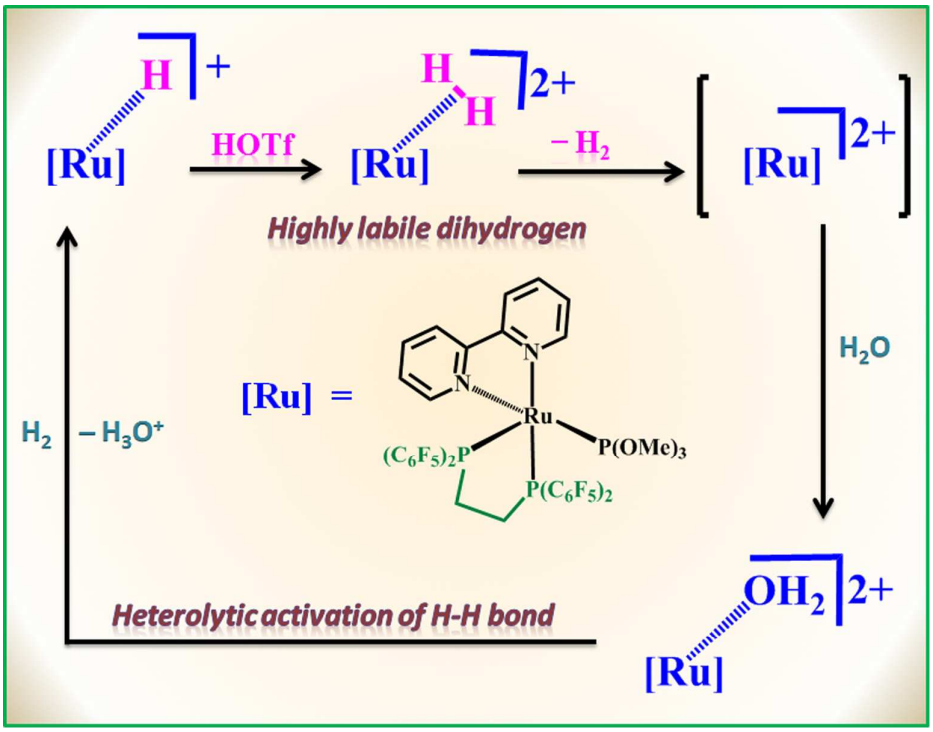
Graphical Abstract

Synthesis of some new highly electrophilic ruthenium complexes bearing 1,2-bis(dipentafluorophenyl phosphino)ethane ligand and their reactivity studies towards activation and labilization of molecular hydrogen are reported.



Cite this: DOI: 10.1039/c0xx00000x

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Synthesis, Characterization and Reactivity Studies of Electrophilic Ruthenium(II) Complexes: Study of H_2 Activation and Labilization

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Abstract: Reaction of 2,2'-bipyridine (bpy) with dinuclear complexes [RuCl(dfppe)(μ-Cl)$_3$Ru(dmso-S)$_3$] (dfppe = 1,2-bis(dipentafluorophenyl phosphino)ethane, $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$; dmso = dimethyl sulfoxide) (1) or [RuCl(dfppe)(μ-Cl)$_3$RuCl(dfppe)] (2) affords the mononuclear species *trans*-[RuCl$_2$(bpy)(dfppe)] (3). Using this precursor complex (3), a series of new cationic Ru(II) electrophilic complexes [RuCl(L)(bpy)(dfppe)][Z] (L = P(OMe)$_3$ (5), PMe$_3$ (6), CH$_3$CN (7), CO (8), H$_2$O (9); Z = OTf (5, 6, 7, 8), BAr^F_4 (9) have been synthesized via abstraction of chloride by AgOTf or BAr^F_4Na in the presence of L. Complexes 5 and 6 were converted into the corresponding isomeric hydride derivatives [RuH(PMe$_3$)(bpy)(dfppe)][OTf] (10a, 10b) and [RuH(P(OMe)$_3$)(bpy)(dfppe)][OTf] (11a, 11b) respectively, when treated with NaBH$_4$. Protonation of the cationic monohydride complex (11a) with HOTf at low temperature resulted in H$_2$ evolution accompanied by the formation of either solvent or triflate bound six coordinated species [Ru(S)(P(OMe)$_3$)(bpy)(dfppe)][OTf]$_n$ [(S = solvent (n =2), triflate (n = 1)] (13a/13b); these species have not been isolated and could not be established with certainty. They (13a/13b) were not isolated, instead, the six-coordinated isomeric aqua complexes *cis*-[Ru(bpy)(dfppe)(OH$_2$)(P(OMe)$_3$)][OTf]$_2$ (14a/14b) were isolated. Reaction of the aqua complexes (14a/14b) with 1 atm of H$_2$ at room temperature in acetone-d$_6$ solvent resulted in a heterolytic cleavage of the H-H bond. Results of the studies on H$_2$ lability and heterolytic activation using these complexes are discussed. The complexes 3, 5, 11a, and 14a have been structurally characterized.

Introduction

Activation and the subsequent cleavage of the strong H-H bond in molecular hydrogen are of immense significance in chemistry[1,2] and biology[3,4] and are of great utility in industrial applications. Enzymes such as hydrogenases, nitrogenases and enzymatic mimics are believed to bring about the activation of dihydrogen in a heterolysis fashion at a metal center during sequential proton-electron transfer steps.[5-8] The relative stability and the acidity of the H$_2$ ligand bound to a metal center could vary widely depending upon the metal and the ancillary ligand environment. Generally, highly electron deficient metal centers bring about the heterolytic activation of H$_2$.[8,9] In addition to H$_2$, the heterolysis of H-X (X = Si, B, C) bonds could also be achieved by employing highly electrophilic or superelectrophilic metal complexes.[10,11] We previously reported the synthesis of an air-stable superelectrophilic, five-coordinated species [Ru(P(OH$_3$)(dppe$_2$)]$^{2+}$ (dppe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) which has the propensity to activate the H-X (X = H, Si, B, C) bonds in small molecules in a heterolytic fashion.[10,12] In continuation of these studies, we intend to build systems that are even more electrophilic than our previous systems and capable of exhibiting greater reactivity towards heterolytic activation of strong sigma bonds in small molecules. By having fluorine substituents on the phosphorus ligands, e.g., $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ which upon complexation with a metal center could drain out electron density from the metal center.[13-15] The resulting metal complexes with this ligand would be highly electrophilic.[16-19] In addition to having $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ ligand, the metal center could be rendered superelectrophilic by employing phosphite ligands which are very good π-acceptors.

Herein, we report the synthesis and structural characterization of a series of new, electrophilic cationic Ru(II) complexes bearing a chelating phosphine ligand - bis(dipentafluorophenylphosphino)ethane, $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe). An attempt to prepare a highly acidic dihydrogen complex of the type *cis*-[Ru(bpy)(dfppe)(H$_2$)(P(OMe)$_3$)][OTf]$_2$ (bpy = 2,2-bipyridyl; OTf = trifluoromethane sulfonate), via protonation of the precursor hydride complex *cis*-[Ru(H)(bpy)(dfppe)(P(OMe)$_3$)][OTf] using HOTf surprisingly resulted in H$_2$ evolution and formation of either solvent or OTf bound six coordinated species which were not isolated and could not be established with certainty. Reaction of an aqua complex *cis*-[Ru(bpy)(dfppe)(OH$_2$)(P(OMe)$_3$)][OTf]$_2$ with H$_2$ however, resulted in the heterolytic activation of the H-H bond and the concomitant protonation of O-H to give the corresponding hydride complex *cis*-[Ru(H)(bpy)(dfppe)(P(OMe)$_3$)][OTf] and H_3O^+. The results of these studies are also described in this report.

Experimental Section

General Procedures

All the reactions were carried out under an atmosphere of dry and oxygen-free N_2 or Ar at room temperature using standard Schlenk techniques unless otherwise specified.[20,21] The ^1H, ^{31}P, and ^{19}F NMR spectral data were obtained using an Avance Bruker 400 MHz instrument. All the ^{31}P NMR spectra were proton decoupled unless otherwise stated and have been measured relative to 85% H_3PO_4 in CD_2Cl_2. ^{19}F NMR spectra were recorded with respect to $CFCl_3$ in CD_2Cl_2. High pressure NMR tubes fitted with Swagelok fittings were procured from Wilmad Glass and reactions under high pressures of H_2 were carried out on a home-built manifold made of Swagelok parts. Mass spectral analyses were carried out using a Micromass Q-TOF instrument at the Department of Organic Chemistry, I.I.Sc. Elemental analysis was carried out on a Thermo Scientific Flash 2000 Organic Elemental Analyzer. Solvents were dried and degassed by refluxing over standard drying agents under an inert atmosphere and were freshly distilled prior to use. 1,2-Bis(dipentafluorophenyl phosphino)ethane (dfppe),[22] cis-$[RuCl_2(DMSO)_4]$,[23] and $[RuCl_2(PPh_3)_3]$[24] were prepared using literature procedures.

Preparation of $[RuCl(dfppe)(\mu\text{-}Cl)_3Ru(dmso\text{-}S)_3]$, 1

To a solution of cis-$[RuCl_2(DMSO)_4]$ (0.250 g, 0.516 mmol) in CH_2Cl_2 (10 mL) was added dfppe (0.194 g, 0.516 mmol). The reaction mixture was stirred at room temperature for 12 h. The resulting orange yellow suspension was filtered through a Celite pad on a filter frit and the solvent from the filtrate was removed in vacuo. The product of $[RuCl(dfppe)(\mu\text{-}Cl)_3Ru(dmso\text{-}S)_3]$ 1 was crystallized from CH_2Cl_2/Et_2O at room temperature. Yield, 0.165 g (47%). ^1H NMR ($CDCl_3$, 298 K): € 2.44 (br m, 2H, $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$), 3.54 (br m, 2H, $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$)), 3.44 (brs, 6H, $(CH_3)_2S{=}O$), 3.47 (br s, 12H, $(CH_3)_2S{=}O$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): € 65.3 (s, 2P, dfppe). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 298 K): € ,125.7 (br s, 4F, ortho-F ArF), ,125.9 (br s, 4F, ortho-F ArF), ,146.6 (m, 2F, para-F ArF), ,148.2 (br s, 2F, para-F ArF), ,158 .6 (m, 4F, meta-F ArF), ,159.6 (m, 4F, meta-F ArF). Anal. Calc. for $C_{32}H_{22}Cl_4F_{20}O_5P_2Ru_2S_3$·$(CH_3)_2SO$·$H_2O$: C, 28.50; H, 2.11; S, 8.95 Found: C, 28.78; H, 2.23; S, 9.12%.

Preparation of $[RuCl(dfppe)(\mu\text{-}Cl)_3RuCl(dfppe)]$, 2

A mixture of $[RuCl_2(PPh_3)_3]$ (0.953 g, 1 mmol) and dfppe (0.758 g, 1 mmol) was dissolved in 30 mL of acetone and was stirred at room temperature for 1 h. The brick red colored solution turned red during this time. The solution was then filtered through a filter frit and the solvent was removed in vacuo. The residue was washed several times with n-hexanes and dried to afford the product of $[RuCl(dfppe)(\mu\text{-}Cl)_3RuCl(dfppe)]$, 2 which was crystallized from acetone/n-hexanes at room temperature. Yield, 0.445 g (45%). ^1H NMR ($CDCl_3$, 298 K): € 2.71 (br s, 4H, $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$), 3.25 (br s, 4H, $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): € 64.47 (s, 4P, dfppe). Anal. Calc. for $C_{52}H_8Cl_5F_{40}O_3P_4Ru_2$·$(CH_3)_2C(OH)CH_2COCH_3$·$H_2O$: C, 34.32; H, 1.09 Found: C, 34.78; H, 1.23%.

Preparation of trans-$[RuCl_2(bpy)(dfppe)]$, 3

To a solution of compound 1 (0.250 g, 0.187 mmol) in CH_2Cl_2 (10 mL) was added 2,2'-bipyridine (0.029 g, 0.187 mmol). The resulting solution was stirred at room temperature for 1 day and then its volume was reduced to 1 mL and stored at room temperature for another day. Orange red crystals of compound 3 that were formed were filtered from the solution and dried under vacuum. Yield, 0.030 g (30%). NMR spectral data of compound 3 have been summarized in Tables 1 and 2.

A much better yield was obtained by reacting compound 2 (0.1 g, 0.527 mmol) with 2 equiv of 2,2'-bipyridine (bpy) (0.164 g, 1.054 mmol) in CH_2Cl_2 (30 mL) at room temperature for 1 h. Reduction of the solution volume to 3 mL and addition of excess Et_2O caused the precipitation of a deep red solid of the product. It was washed repeatedly with Et_2O and dried in vacuo. Crystallization from CH_2Cl_2/Et_2O at room temperature gave the product in a yield of 70% (0.400 g). Anal. Calc. for $C_{36}H_{12}Cl_2F_{20}N_2P_2Ru$·$3CHCl_3$: C, 32.43; H, 1.05; N, 1.94, Found: C, 32.73; H, 1.08; N, 2.01%.

Preparation of trans-$[RuCl_2(phen)(dfppe)]$, 4

Compound 4 was prepared in an analogous manner to that of compound 3 starting from compound 2 (0.100 g, 0.052 mmol) and phenanthroline (phen) (0.022 g, 0.104 mmol). Yield, 0.04 g (70%). NMR spectral data of compound 4 have been listed in Tables 1 and 2. Anal. Calc. for $C_{38}H_{12}Cl_2F_{20}N_2P_2Ru$·$0.5CH_3OH$·$H_2O$: C, 40.40; H, 1.41; N, 2.45, Found C, 40.26; H, 1.34; N, 2.52%.

Preparation of $[RuCl(P(OMe)_3)(bpy)(dfppe)][OTf]$, 5

To a CH_2Cl_2 solution (15 mL) of complex 3 (0.500 g, 0.460 mmol) was added AgOTf (0.115 g, 0.460 mmol) with stirring and then it was left at room temperature for 10 min during which time, the color turned orange yellow from red. Then, $P(OMe)_3$ (55 µL, 0.460 mmol) was added to this mixture and stirred for ½ h. The reaction mixture was filtered and the filtrate was concentrated to ca. 1 mL. Addition of Et_2O (10 mL) caused the precipitation of a lemon-yellow solid of 5. The supernatant was decanted and the product was washed with Et_2O and dried in vacuo. Yield, 0.460 g (73%). NMR spectral data of complex 5 have been summarized in Tables 1 and 2. Anal. Calc. for $C_{40}H_{21}ClF_{23}N_2O_6P_3RuS$·$0.5CH_2Cl_2$·$0.5H_2O$: C, 35.36; H, 1.69; N, 2.04, S, 2.33 Found: C, 34.99; H, 1.35; N, 2.13, S, 2.32%.

Preparation of $[RuCl(PMe_3)(bpy)(dfppe)][OTf]$, 6

Complex 6 was prepared in a similar manner to that of 5 starting from complex 3 (0.300 g, 0.276 mmol), AgOTf (0.069 g, 0.276 mmol), and PMe_3 (0.27 µL, 0.270 mmol). Yield, 0.300 g (85%). NMR spectral data of complex 6 have been listed in Tables 1 and 2. Anal. Calc. for $C_{40}H_{21}ClF_{23}N_2O_3P_3RuS$·$C_6H_{14}$·$H_2O$: C, 40.03; H, 2.70; N, 2.03; S, 2.32 Found: C, 40.21; H, 2.62; N, 2.19; S, 2.21%.

Preparation of $[RuCl(CH_3CN)(bpy)(dfppe)][OTf]$, 7

Complex 7 was prepared in an analogous manner to that of complex 5 starting from complex 3 (0.200 g, 0.184 mmol), AgOTf (0.046 g, 0.184 mmol), and CH_3CN (9.6 µL, 0.184 mmol). Yield of complex 7, 0.150 g (75%). NMR spectral data of compound 7 have been summarized in Tables 1 and 2. Anal. Calc. for $C_{39}H_{15}ClF_{23}N_3O_3P_2RuS$: C, 37.74; H, 1.22; N, 3.39; S,

2.58 Found: C, 37.52; H, 1.43; N, 3.42, S, 2.60%.

Preparation of [RuCl(CO)(bpy)(dfppe)][OTf], 8

Complex 3 (0.055 g, 0.05 mmol) was dissolved in CH_2Cl_2 (6 mL) and then AgOTf (0.013 g, 0.05 mmol) was added and stirred for about 10 min at room temperature. During this time, the color turned from orange red to orange yellow. To this solution, CO gas was bubbled at a steady rate for 10 min. The solution was then filtered and the filtrate was concentrated to ca. 1 mL. Addition of Et_2O (10 mL) resulted in the precipitation of complex 8 in a yield of 31% (0.020 g). NMR spectral data of compound 8 have been summarized in Tables 1 and 2. Anal. Calc. for $C_{38}H_{13}ClF_{23}N_2O_4P_2RuS$: C, 37.14; H, 1.07; N, 2.28; S, 2.61 Found: C, 37.24; H, 1.27; N, 2.43, S, 2.51%.

Preparation of $[RuCl(OH_2)(bpy)(dfppe)][BAr^F_4]$, 9

Compound 9 was prepared in a similar manner to that of complex 8. Instead of AgOTf, $NaBAr^F_4$ (BAr^F_4 = tetrakis[(3,5-trifluoromethyl)phenyl]borate) (0.040 g, 0.046 mmol) and instead of CO gas, water (ca. 2 µL, 0.09 mmol) were used. Yield, 0.061 g (69%). NMR spectral data of compound 9 have been summarized in Tables 1 and 2. Anal. Calc. for $C_{68}H_{24}BClF_{44}N_2OP_2Ru \cdot H_2O$: C, 41.88; H, 1.45; N, 1.44; Found: C, 41.63; H, 1.64; N, 1.33%.

Preparation of [RuH(PMe$_3$)(bpy)(dfppe)][OTf], 10a, 10b

Sodium borohydride (0.002 g, 0.053 mmol) was added to a solution of [RuCl(PMe$_3$)(bpy)(dfppe)][OTf] (6) (0.070 g, 0.053 mmol) in EtOH (5 mL) and the reaction mixture was stirred at room temperature for 20 min during which time, the color turned from yellow to orange. Solvent was removed in vacuo and the resulting residue was extracted with CH_2Cl_2 and dried under vacuum. Yield, 0.050 g (73%). In this reaction, we noted the formation of two isomers, 10a and 10b), one of them, 10a could be deciphered using NMR spectroscopy. NMR spectral data of isomer 10a have been summarized in Tables 3 and 4. Anal. Calc. for $C_{40}H_{22}F_{23}N_2O_3P_3RuS \cdot C_2H_5OH \cdot 3H_2O$: C, 37.60; H, 2.55; N, 2.09; S, 2.39 Found: C, 37.34; H, 2.42; N, 2.19, S, 2.34%.

Preparation of [RuH(P(OMe)$_3$)(bpy)(dfppe)][OTf], 11a, 11b

The two isomers 11a and 11b were obtained using a similar procedure to that of 10 starting from [RuCl(P(OMe)$_3$)(bpy)(dfppe)][OTf] (5) (0.560 g, 0.409 mmol) and $NaBH_4$ (0.016 g, 0.409 mmol). Yield, 0.350 g (64%) (isomer 11a, 95% and isomer 11b, 5% as found from NMR spectroscopy). The spectral data have been given in Tables 3 and 4. Anal. Calc. for $C_{40}H_{22}F_{23}N_2O_6P_3RuS \cdot CH_3OH \cdot 2H_2O$: C, 36.27; H, 2.23; N, 2.06, S, 2.36 Found: C, 36.23; H, 2.33; N, 1.92, S, 2.34%.

Isomerization of complex 11a to 11c

A 5 mm NMR tube charged with 11a (0.020 g, 0.015 mmol) in acetone-d_6 (0.6 mL) was allowed to shake at room temperature on a rotary shaker for a week. During this time, complex 11a underwent isomerization to 11c. The NMR spectral characteristics of isomer 11c have been summarized in Tables 3 and 4. Satisfactory elemental analysis for compound 11c was not obtained.

Attempt to prepare [Ru(η^2-H_2)(P(OMe)$_3$)(bpy)(dfppe)][OTf]$_2$, 12

A flame-dried 5 mm Schlenk NMR tube was charged with 11a (0.020 g, 0.015 mmol) and dissolved in CD_2Cl_2 (0.6 mL). It was then cooled to 77 K and then ca. 1.3 (1 equiv) of HOTf was added under N_2 flow. After the addition, the NMR tube was flame sealed. It was then inserted into the NMR probe precooled to 193 K and the spectral data was acquired at this temperature. No evidence of the dihydrogen complex 12 was apparent, instead we noted a signal for free H_2 in the ^{1}H NMR spectrum (4.6 ppm) together with solvent or OTf bound six-coordinate species [Ru(S)(P(OMe)$_3$)(bpy)(dfppe)][OTf]$_n$ [(S = solvent (n =2), triflate (n = 1)], 13a, 13b. These species were not isolated.

In a separate experiment aimed at obtaining the dihydrogen complex [Ru(η^2-H_2)(P(OMe)$_3$)(bpy)(dfppe)][OTf]$_2$, 12 we carried out the reaction of complex 11a (0.020 g, 0.015 mmol) and HOTf (20 µL, 10 equiv) in CD_2Cl_2 (0.6 mL) in a 5 mm NMR tube capped with a septum. The NMR tube was saturated with H_2 prior to addition of HOTf and also cooled to 193 K. It was then inserted into an NMR probe precooled and maintained at 193 K. In this case as well, no evidence of a dihydrogen complex 12 was apparent; NMR spectral signals due to free H_2 and the isomeric six-coordinate species 13a, 13b were noted. The NMR spectral data for compound 13a, 13b are summarized in Tables 1 and 2.

Preparation of [Ru(H_2O)(P(OMe)$_3$)(bpy)(dfppe)][OTf]$_2$ (isomers 14a, 14b)

To a sample of 11a (0.200 g, 0.149 mmol) in CH_2Cl_2 (5 mL) was added 1 equiv (14 µL) of HOTf. To this solution, excess H_2O (0.1 mL) was added and the mixture was stirred for 15 min. When the volume of the solution was concentrated to a few millilitres, a light yellow solid separated out. The solid product (isomers 14a, 14b) was filtered and washed with Et_2O. It was then collected and dried in vacuo. Yield, 0.158 g (71%). (isomer 14a (85%) and isomer 14b (15%) as found from NMR spectroscopy). The NMR spectral data for this (isomers 14a, 14b) are summarized in Tables 1 and 2. Anal. Calc. for $C_{41}H_{23}ClF_{26}N_2O_{10}P_3RuS_2 \cdot 0.5CH_2Cl_2 \cdot H_2O$: C, 32.49; H, 1.84; N, 1.83; S, 4.18, found: C, 32.93; H, 1.61; N, 1.63; S, 4.34%.

Reaction of [Ru(H_2O)(P(OMe)$_3$)(bpy)(dfppe)][OTf]$_2$ (isomers 14a, 14b) with H_2

The isomeric mixture of 14a and 14b was dissolved in acetone-d_6 (0.6 mL) in a 5 mm NMR tube fitted with a Teflon valve. Next, H_2 (1 atm) was introduced into the tube using a Swagelok setup for 3 min. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the sample were recorded at frequent time intervals at 298 K which gave evidence for the formation of compound 11a.

Preparation of [Ru(CH_3CN)(P(OMe)$_3$)(bpy)(dfppe)][OTf]$_2$, 15

To a sample of 11a (0.050 g, 0.037 mmol) in CH_2Cl_2 (5 mL) was added 1 equiv (2 µL) of HOTf. To this solution, CH_3CN (0.5 mL) was added and the mixture was stirred for 15 min. When the volume of the solution was concentrated to a few millilitres, a creamy-yellow solid separated out. The solid product 15 was filtered and washed with Et_2O. It was then collected and dried in vacuo. Yield, 0.046 g (83%). The NMR spectral data for compound 15 have been summarized in Tables 1 and 2.

X-ray Crystallographic Study

Details of X-ray crystal structure data collection, solution, and refinement for 3, 5, 11a and 14a have been collected in Table 5. Data for the other compounds 1, 2, 4, 6, 9, 10a and 11c have been deposited in the ESI. Single crystal X-ray diffraction data for the complexes 1, 2, 3, 4, 5, 6, 9, 10a, 11a, 11c, and 14a were collected on a Bruker SMART APEX CCD diffractometer using graphite monochromatized Mo (K_α) radiation (0.71073 Å). The structures were solved by direct methods using the SHELX[35] The WinGX[26] package was used for refinement and production of data tables and ORTEP-3[27] for structure visualization and making the molecular representations. Empirical absorption corrections were applied with SADABS.[28] The hydrogen atoms of the main molecule were geometrically fixed and allowed to ride while those of solvents wherever possible they were geometrically fixed and in few cases they were neither fixed nor located. In general, in few of the structures the fluorine atoms exhibit high thermal vibrations.

In few of the structures though the hydrogen atoms of the solvents and the water molecules were neither located nor geometrically fixed, they were accounted for in the molecular formula of the CIF file. Compounds 1, 2, 4, 5, 6, 11c and 14a contain diffuse electron density associated with disordered solvents in the voids which could not be modeled appropriately therefore SQUEEZE option was applied.[29] The details of the refinements for individual structures are as follows.

The structure of 1 contains disordered solvent dimethyl sulfoxide along with a water molecule. The DMSO molecule was modeled with one carbon atom sharing the Site Occupancy of 0.5 and the water molecule was removed with Platon SQUEEZE. It accounted for 10 electron counts per unit cell i.e., 0.5 H_2O per asymmetric unit. The formula unit and the molecular formula in the INS file were modified accordingly. The hydrogen atoms bound to the carbon of the DMSO were neither located nor fixed from the difference Fourier map.

Compound 2 contains two water molecules and two diacetone alcohol molecules in the unit cell which are disordered and could not be modelled successfully. Therefore, their contributions were removed using the SQUEEZE procedure.[29]

The structure of 4 contains a methanol molecule, the oxygen atom of which is sitting in the inversion center and is highly disordered as well as the water molecules. Few residual electrons of the order of 1.7 e/Å^3 appear near the methanol which could not be modelled satisfactorily. Therefore, SQUEEZE procedure was applied.[29]

The structure of complex 5 contains combinations of disordered solvents, likely to be MeOH, water and hexane. These could not be assigned unambiguously. Therefore, SQUEEZE procedure was applied.[29]

The complex 6 having combinations of disordered solvents, likely to be propanol, 2-butanol and water could not be assigned unambiguously. Therefore, SQUEEZE procedure was applied.[29] The triflate ion was disordered and was modeled appropriately.

In complex 9, CF_3 of the anionic moiety exhibits high thermal vibration and the fluorine atoms (F38, F44) bound to this group were found to be thermally disordered. Moreover, the disordered water molecules were modeled and their Site Occupancies were refined so that the combined occupancy is unity. The refined isotropic thermal factors for the shared water molecule are comparable.

The structure of complex 10a has disordered water and triflate ion. Thus the water and triflate were modeled with the sharing of site occupancies and proper distance constraints.

In 11a, the disordered triflate group was modeled. In addition, the disordered water molecules O7A, O7B and O8A, O8B were modeled in such a way so as to maintain the same isotropic temperature factors by adjusting the Site Occupancy Factors and the refinements is completed.

The structure of 11c, due to poor quality of crystal diffraction, completeness of the structure and diffraction measured fraction theta are low. Hence, the hydride near the ruthenium center was not located. In addition, compound 11c contains diffuse electron density associated with disordered solvents likely to be CH_2Cl_2, MeOH and water in the voids which could not be modeled appropriately therefore SQUEEZE was applied.[29]

In 14a, due to poor diffraction of the crystal, data quality was not good resulting in high R1 (0.1132) and wR (0.3330) values. The triflate ion containing S(2) was modeled as per the previous model used in complex 8 but was not useful. The short contacts of halogens viz. F….F and F…Cl although weak have been observed in several instances earlier.[29a] Such contacts are caused by close packing and do not form stabilizing interactions. The solvent oxygen molecules with short contacts were found to be disordered and were squeezed out with the help of Platon Squeeze.[29]

Results and Discussion

Preparation of [RuCl(dfppe)(μ-Cl)$_3$Ru(dmso-S)$_3$], 1

Treatment of *cis*-[$RuCl_2$(dmso)$_4$] with 1 or 2 equiv of 1,2-bis(dipentafluorophenyl phosphino)ethane, $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe) in CH_2Cl_2 afforded the dinuclear ruthenium complex with three chloride bridging ligands between the two ruthenium centers and an unsymmetrical arrangement of the chelating phosphine and dmso ligands, as orange microcrystals (eq 1). The methyl groups of the coordinated DMSO molecules appear as two sets of singlets at 3.47 ppm and 3.44 ppm in the ^{1}H NMR spectrum. The ^{31}P{^{1}H} NMR spectrum is comprised of a singlet at 65.3 ppm for the chelating phosphine ligand. Complex 1 was structurally characterized and the details including the ORTEP diagram have been deposited in the ESI.

Preparation of [RuCl(dfppe)(μ-Cl)$_3$RuCl(dfppe)], 2

Reaction of $RuCl_2(PPh_3)_3$ with 1 equiv of dfppe resulted in the formation of the mixed valence, trichloro-bridged Ru(II, III) complex as an air-stable red-brown solid (eq 2). The compound was purified and crystallized from an acetone-hexanes solution. We noted that this reaction to afford complex 2 undergoes only in acetone solvent. When the reaction was performed in CH_2Cl_2, THF, or toluene, we did not obtain complex 2. The ^{31}P{^{1}H} NMR spectrum showed a singlet at 65.3 ppm for both the chelating phosphine ligands evidencing that the two phosphorus atoms are equivalent. Complex 2 was also structurally characterized and the details have been deposited in the ESI.

Preparation of trans-[$RuCl_2$(bpy)(dfppe)], 3

Table 1 ^{1}H NMR Spectral Data (€) of [RuCl(L)(bpy)(dfppe)]$^{n/n'/n''/n'''+}$ Complexes[a]

L(compd no)	€ (CH_2-CH_2)	€ (L)	€ (bpy)[e]
Cl(3)	3.17 (br d, 4H)		7.31 (t, 2H), 7.89 (t, 2H), 8.13 (d, 2H), 9.10 (br d, 2H)
Cl(4)[d]	3.24 (br d, 4H)		7.69 (m, 2H), 7.95 (s, 2H), 8.41 (d, 2H), 9.45 (br s, 2H)
$P(OMe)_3$(5)	2.67 (m, 2H) 4.04(m, 2H)	3.26(d, 9H)	7.26 (t, 1H), 7.50 (t, 1H), 8.05 (t, 1H), 8.25 (d, 1H), 8.27 (t, 1H), 8.59 (d, 1H), 8.69 (d, 1H), 8.91 (br s, 1H)
PMe_3(6)	2.01 (m, 2H) 4.07 (m, 2H)	0.51 (d, 9H)	7.39 (t, 1H),7.44 (t, 1H), 8.17 (t, 1H), 8.28 (t, 1H), 8.43 (d, 1H), 8.63 (br s, 1H) 8.79 (d, 1H), 8.83 (d, 1H)
CH_3CN(7)	2.91 (m, 2H) 4.10 (m, 2H)	2.13(s, 3H)	7.30 (t, 1H), 7.44 (t, 1H), 7.79 (m, 2H), 8.21 (m, 2H), 8.42 (d, 1H) 9.72 (br s, 1H)
CO(8)	3.3 (m, 2H) 4.22 (m, 2H)		7.26 (t, 1H), 7.62 (t, 1H), 7.84 (m, 2H), 7.95 (t, 1H), 8.32 (d, 1H) 8.46 (br s, 1H) 9.74 (br s, 1H)
H_2O(9)	2.53 (m, 2H) 4.15 (m, 2H)		6.84(t, 1H), 7.80 (t, 1H), 7.85 (m, 1H), 7.88 (t, 1H), 8.09 (d, 1H) 8.24 (br s, 2H) 9.75 (br s, 1H)
$P(OMe)_3$(13a)[b]	2.64 (m, 2H) 4.20 (m, 2H)	3.73 (d, 9H)	7.37 (t, 1H), 7.72 (t, 1H), 7.92 (t, 1H), 8.01 (d, 1H), 8.14 (d, 1H), 8.31 (d, 1H), 8 (d, 1H), 10.16 (br s, 1H)
$P(OMe)_3$(13b)[b]	2.82 (m, 2H) 3.61 (m, 2H)	3.39 (d, 9H)	7.76(t, 2H), 8.49 (t, 2H), 8.58 (d, 2H), 8.75 (br s, 2H)
H_2O /$P(OMe)_3$(14a)[c]	3.05 (m, 2H) 4.58 (m, 2H)	5.75 (s, 2H) 3.95 (d, 9H)	7.60(t, 1H), 8.13 (t, 1H), 8.26 (d, 1H), 8.47 (d, 1H), 8.70 (d, 1H), 8.80 (br s, 2H) 10.08 (s, 1H)
H_2O /$P(OMe)_3$(14b)[c]	2.99 (m, 2H) 4.58 (m, 2H)	5.79 (s, 2H) 3.94 (d, 9H)	7.65(t, 1H), 7.75 (t, 1H), 8.19 (t, 1H), 8.43 (t, 1H), 8.59 (d, 1H), 8.82 (br s, 2H) 10.28 (s, 1H)
$NCCH_3$/$P(OMe)_3$(15)[c]	3.10 (m, 2H) 4.28 (m, 2H)	2.47 (s, 3H) 3.97 (d, 9H)	7.55 (t, 1H), 8.15 (t, 1H), 8.28 (t, 1H), 8.52 (d, 1H), 8.64 (s, 1H),8.76 (d, 1H), 8.8 (d, 1H), 10.01 (br s,1H)

[a] In $CDCl_3$ solution, [b] in CD_2Cl_2 solution,(13a recorded at 233 K), [c] in acetone-d_6 solution, [d] trans-$[RuCl_2(phen)(dfppe)]$, for 3, 4 (n = 0);5, 6, 7, 8 (n' = +1, counter anion= [OTf]);9 (n'' = +1, counter anion=BAr^{F}_4) and13a, 13b, 14a, 14b, 15 (n''' = +2, counter anion = [OTf]);[e] all coupling constants for bpy (2, 2'-bipyridine) and phen (1,10-phenanthroline) proton resonance were about 8 Hz.

Reaction of complex 1 or 2 with 2,2'-bipyridine at room temperature resulted in the formation of trans-$[RuCl_2(bpy)(dfppe)]$,3 (eq 3) In case of reaction of 1 with 2,2'-bipyridine we obtained cis-$[RuCl_2(dmso)_4]$ as a side product. In addition, reaction of 2 with 2,2'-bipyridine resulted as complex 3 in good yield. Generally, dichloride metal complexes are very good precursors for preparing five coordinate complexes.[30,31] The $^{31}P\{^{1}H\}$ NMR spectrum of complex 3 gave a singlet at † 68.9 ppm which is consistent with a structure in which the two chloride ligands are mutually trans-disposed. In addition, the ^{1}H NMR spectrum evidenced the presence of two equivalent ortho hydrogen atoms on the bipyridyl ligand at † 9.10 ppm which lends further support for the trans geometry of the two chloride ligands. The structure of complex 3 was unambiguously established by X-ray crystallographic study. The ORTEP view of the complex is shown in Figure 1 and the pertinent bond lengths and angles have been summarized in Table 6. The structure consists of a ruthenium(II) center in a distorted octahedral geometry with the two chelating ligands, bpy and dfppe taking up the four coordination sites in the equatorial plane, whereas the two chloride ligands are trans-disposed to each other and occupy the axial sites. The bite angle P1•Ru1•P2 is 84.91°(2) and that of N1•Ru1•N2 is 76.33°(8). The Ru1•Cl1 and •Cl2, Ru1•N1 and •N2, and Ru1•P1 and •P2 bond distances are in the typical range found for certain analogous ruthenium derivatives trans-$[RuCl_2(P\text{-}P)(N\text{-}N)]$[32-34] (P-P = dppf, dppb; N-N = en, py (pyridine), dimen (N,N'-dimethyl(ethylenediamine)) reported in the literature. The Cl1•Ru1•Cl2 bond angle is 175.28°(2) which evidences that the chloride ligands are bent slightly away from their axial positions towards the bpy ligand due to steric encumbrance of the fluorophenyl moieties of the ligand dfppe. X-ray crystal structure of the phenanthroline derivative has also been established and the details have been deposited in the ESI.

Preparation and Characterization of [RuCl(L)(bpy)(dfppe)][Z] (L = $P(OMe)_3$ (5), PMe_3 (6), CH_3CN (7), CO (8), H_2O (9); Z = OTf (5, 6, 7, 8), BAr^{F}_4 (9) Complexes

Table 2. $^{31}P\{^{1}H\}$ and ^{19}F NMR Spectral Data (€) of $[RuCl(L)(bpy)(dfppe)]^{n/n'/n''/n'''+}$ Complexes[a]

		€ (P)			€ (F)	
Compd no	L	dfppe	$J(P,P_{trans})$, Hz	$J(P,P_{cis})$, Hz	dfppe	OTf
3		68.89 (s, 2P)			,122.05 (br s, 8F, o-F), ,147.63 (m, 4F, p-F), ,158.76 (m, 8F, m-F)	
4[d]		68.37 (s, 2P)			,122.31 (br s, 8F, o-F), ,147.64 (m, 4F, p-F), ,158.89 (m, 8F, m-F)	
5	110.32 (dd, 1P)	46.92 (br s, 1P), 25.7 (dd, 1P)	546.26	46	,125.45 (br m, 8F, o-F), ,145.92 (four t, 4F, p-F), ,158.22 (br m, 8F, m-F)	,78.49 (s, 3F)
6	,3.05 (dd, 1P)	44.44(br s, 1P), 30.7 (dd, 1P)	346.16	30	,127.87 (br m, 8F, o-F), ,145.06 (four t, 4F, p-F), ,157.35 (br m, 8F, m-F)	,78.37(s, 3F)
7		59.74(s, 1P), 53.17 1P)			,124.87 to ,130.76 (four d, 8F, o-F), ,1 43.77 to ,147.77 (three t, 4F, p-F), ,156.94 to ,159.14 (four d, 8F, m-F)	
8		49.02(s, 1P), 20.09 1P)				
9		60.52(s, 1P), 54.67 1P)			,124.86 to ,134.25 (m, 8F, o-F), ,143.17 to ,148.13 (three t, 4F, p-F), ,157.85 to ,160.40 (four d, 8F,m-F)	
13a[b]	118.71 (t, 1P)	62.63(d, 1P), 51.19 (1P)		60.60		
13b[b]	119.42 (t, 1P)	50.92 (d, 2P)		54.80		
14a[c]	120.84 (t, 1P)	52.01 (d, 1P), 60.11 (d 1P)		60.52		
14b[c]		52.28(d, 1P), 62.66 (1P)		61.87		
15	120.18 (t, 1P)	51.53 (d, 1P), 539.8(d, 1P)		59.81	,125.54 to ,135.43 (four d, 8F, o-F), ,147.55 to ,147.94 (m, 4F, p-F), ,159.05 to ,161.82 (m, 8F, m-F)	,78.90 (s, 6F)

[a] In $CDCl_3$ solution, [b] in CD_2Cl_2 solution, (13a recorded at 233 K), [c] in acetone-d_6 solution, [d] trans-$[RuCl_2(phen)(dfppe)]$ for 3, 4 (n = 0); 5, 6, 7, 8 (n' = +1, counter anion = [OTf]); 9 (n'' = +1, counter anion = BAr^f_4) and 13a, 13b, 14a, 14b, 15 (n'' = +2, counter anion = [OTf])

Table 3. ^{1}H NMR Spectral Data (€) of $[RuCl(L)(bpy)(dfppe)][OTf]$ Complexes[a]

L(compd no)	€ (Ru-H)	$J(H,P_{trans})$, Hz	$J(H,P_{cis})$, Hz	€ (CH_2-CH_2)	€ (L)	€ (bipy)[e]
PMe_3 (10a)	, 15.80 (q, 1H)		24.22	3.07 (m, 2H), 3.48 (m, 1H), 4.28 (m 1H)	0.66 (d, 9H)	7.26 (t, 2H), 7.48 (t, 2H) 8.15 (d,2H), 8.64 (d, 2H)
$P(OMe)_3$ (11a)	, 6.32 (dtt,1H)	145	28	2.55 (m, H), 4.12 (m, 2H)	3.52 (d, 9H)	7.13 (t, 1H), 7.86 (t, 1H 8.08 (d, 1H), 8.22 (br s, 1H), 8.30 (t, 1H), 8.64 (1H), 8.74 (d, 1H), 9.88 (s, 1H)
$P(OMe)_3$ (11b)	, 6.26 (dt, 1H)	145	28	2.53 (m, 2H), 4. (m, 2H)	3.53 (d,9H)	6.85 (t, 1H), 7.21 (t, 1H 7.58 (t, 1H), 7.86 (t, 1H 8.09 (d, 1H), 8.29 (d, 1H 8.40 (d, 1H), 9.64 (br s, 1H)
$P(OMe)_3$ (11c)[c]	, 15.22 (q, 1H)		24.55	2.43 (m, 2H), 3.8 (m, 2H)	3.23 (d, 9H)	7.47 (t, 1H), 7.67 (t, 1H 8.23 (br s, 2H), 8.35 (1H), 8.71 (d, 2H), 8.97 (br s, 1H)

[a] In $CDCl_3$ solution, [c] in acetone-d_6 solution, [e] all coupling constants for bpy (2, 2'-bipyridine) proton resonance were about 6 Hz.

The new ruthenium monocationic complexes $[RuCl(L)(bpy)(dfppe)][Z]$ were prepared from trans-$[RuCl_2(dfppe)(bpy)]$ via the substitution of one of the chloride ligands with L (L = $P(OMe)_3$, PMe_3, CH_3CN, CO) in presence of AgOTf (eq 4). In the case of L = H_2O, complex 3 was treated with $NaBAr^F_4$. All the reactions afforded the products in fairly good yields. The products are all yellow colored solids except for complex 8, which is off-white. They were all purified by crystallization from CH_2Cl_2/n-hexanes solutions. The $^{31}P\{^{1}H\}$ NMR spectrum of $[RuCl(P(OMe)_3)(bpy)(dfppe)][OTf]$, 5 is comprised of a doublet of doublets at † 24.1 ppm for the dfppe phosphorus nucleus due to trans phosphite and cis phosphine-phosphite couplings of 550 Hz and 46 Hz, respectively. Another doublet of doublets for the phosphite phosphorus nucleus was obtained † at 108.4 ppm with the same magnitudes of trans- and cis-coupling constants. Another broad multiplet at † 47.7 ppm was also noted for the dfppe phosphorus nucleus that is cis disposed to both phosphite phosphorus and the other dfppe phosphorus atoms. Structure of complex 5 was established by X-ray crystallographic study. The ORTEP view of

Table 5. Crystallographic Data for Complexes 3, 5, 11a, and 14a

	3	5	11a	14a
Formula	$C_{39}H_{15}Cl_{11}F_{20}N_2P_2Ru$	$C_{41}H_{28}ClF_{23}N_2O_{8.50}P_3RuS$	$C_{41}H_{30}F_{23}N_2O_9P_3RuS$	$C_{83}H_{58}Cl_2F_{52}N_4O_{25}P_6Ru_2S_4$
Formula weight	1444.49	1383.14	1357.71	3086.43
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	P21/n	P21/c
a (Å)	11.9861(9)	16.1027(5)	13.5067(19)	12.4013(9)
b (Å)	14.4311(11)	18.6460(5)	15.1532(19)	40.588(3)
c (Å)	16.8372(12)	21.5432(6)	24.670(3)	21.9501(15)
„ (‡)	71.256(4)	113.439(3)	90	90
ˆ (‡)	70.570(4)	93.612(2)	104.488(7)	100.534(3)
‰ (‡)	67.871(4)	112.231(3)	90	90
V (Å^{-3})	2479.3(3)	5317.1(3)	4888.6(11)	10862.2(13)
Z	2	4	4	4
D_{calc}(g/cm^{-3})	1.935	1.728	1.845	1.887
T (K)	100 2)	110(2)	100 (2)	293(2)
Š (Å)	0.71073	0.71073	0.71073	0.71073
µ (mm^{-1})	1.085	0.607	0.606	0.655
R[a]	0.0598	0.0394	0.0534	0.1132
R_w[a]	0.1626	0.0988	0.1526	0.3330

[a] [a]R = ‹(| Fo| ð-|Fc|)/k| Fo|, Rw = [‹ w(|Fo| ð-|Fc|)2/‹ w|Fo|2]1/2 (based on reflections with I> 2Ei(I)).

Table 6. Selected Bond Distances (Å) and Angles (°) for Complexes 3, 5, 11a, and 14a

	3	5	11a	14a
Ru(1)-X1	2.4009(6)	2.4282(7)	1.61(6)	2.1917
Ru(1)-X2	2.4085(6)	2.3073(7)	2.2549(10)	2.282(3)
Ru(1)-N(1)	2.128(2)	2.108(2)	2.157(3)	2.176(8)
Ru(1)-N(2)	2.138(2)	2.071(2)	2.160(3)	2.159(8)
Ru(1)-P(1)	2.2844(7)	2.4213(7)	2.2628(9)	2.290(3)
Ru(1)-P(2)	2.2810(6)	2.3304(7)	2.3853(9)	2.350(2)
N(1)-Ru(1)-N(2)	76.33(8)	77.91(9)	75.88(12)	76.2(3)
P(2)-Ru(1)-P(1)	84.91(2)	81.51(2)	85.66(3)	85.92(9)
N(1)-Ru(1)-P(1)	174.98(5)	91.43(6)	95.87(9)	87.9(2)
X2-Ru(1)-P(2)	89.04(2)	100.92(2)	93.94(3)	87.94(9)
X2-Ru(1)-P(1)	94.58(2)	168.75(3)	88.76(3)	93.16(10)
X1-Ru(1)-P(1)	89.21(2)	83.97(2)	85.78(3)	178.29(18)

[a] X1, X2 represents the atoms of the monodentate ligand coordinated to Ru, X1 = Cl1(3, 5), H1(11a), O1(14a); X2 = Cl2(3), P(OMe)2(5, 11a, 14a).

the cation of complex 5 is shown in Figure 2. Selected bond distances and angles have been summarized in Table 6. The structure consists of distorted octahedral coordination geometry around the metal center. We noted two molecules crystallographically in the asymmetric unit. The chelating phosphine phosphorus atoms, phosphite phosphorus atom, and one of the nitrogen atoms of the bipyridyl ligand form the equatorial plane while the second nitrogen atom of the bipyridyl moiety and the chloride that are mutually trans to one another occupy the axial sites around the ruthenium. The Ru-P3 (phosphite phosphorus) bond length is 2.3073(7) Å. This distance is comparable to that of Ru-P (phosphite phosphorus) (2.337(2) Å) bond in trans-[RuH(P(OMe)2)(dppe)2][BF4][35] but longer with respect to those in trans-[RuH(PF(OMe)2)(dppe)2][BF4] (2.264(2) Å)[35] trans-[RuH(PF3)(dppe)2][BF4] (2.206(2) Å)[36] [Ru(P(OH)2(OMe))(dppe)2][OTf]2 (2.2016(9) Å)[37] and [Ru(P(OH)3)(dppe)2][OTf]2 (2.2011(9) Å).[10] Two aspects of the structure of complex 5 are important in this context: (a) phosphite moiety lies in the equatorial plane and trans to one of the phosphorus atoms of the chelating phosphorus which is a manifestation of the relief in the steric strain and (b) although phosphite phosphorus is trans to phosphine bearing C6F5 substituent, the Ru-P (phosphite phosphorus) bond length is not shortened as one would have expected, which is a manifestation of electronic influence of the monocationic nature of the complex. There are large differences in the Ru(1)-P(1) (2.4213(7) Å) and Ru(1)-P(2) (2.3304(7) Å) distances of 5. The notable lengthening of the former bond arises from differing trans influences of the phosphite (P3) when compared to bpy(N1). The bite angles of dfppe and bpy are 81.51(2)°, 77.91(9)°, respectively and those in [RuCl(H2O)(bipy)(dfppe)][BArF4] (9) are P(2)-Ru(1)-P(1) 85.39(4)°, N(2)-Ru(1)-N(1) 78.57(15)° respectively. In comparison of compound 9 with 5 the reduction in the bite angle of dfppe and bpy in 5 is due to the better π-accepting nature of the P(OMe)3 ligand. In a similar manner, complex 6, 7 and 8 were prepared and characterized; the structural data of these derivatives have been deposited in the ESI.

In order to prepare the five coordinate [RuCl(bpy)(dfppe)][BArF4] complex from 3 we used non-coordinating anion salt NaBArF4 instead of AgOTf for the abstraction of chloride. Because of the high instability of the five coordinate species, upon chloride abstraction, it immediately reacts with trace amount of water present in the NaBArF4 or solvent and affords complex 9. The ^{1}H NMR spectrum of 9 in $CDCl_3$ shows a singlet at δ 3.52 for the coordinated water, while two singlet resonances in the ^{31}P{^{1}H} NMR spectrum which indicates that the two ends of the dfppe ligand are in different environments. In addition, the structure of complex 9 was established by X-ray crystallographic study and the details have been deposited in the ESI.

Preparation and Characterization of [RuH(PMe3)(bpy)(dfppe)][OTf], 10a, 10b

Reaction of [RuCl(PMe3)(bpy)(dfppe)][OTf] with $NaBH_4$ in EtOH gave yellow colored isomeric mixture of cationic monohydride [RuH(PMe3)(bpy)(dfppe)][OTf] complexes 10 (10a, 10b) (eq 5). In an attempt to obtain a single isomer we carried out the reaction of 6 with KHBSBu3 (K-selectride) in THF which

resulted in an incomplete reaction even under reflux conditions.

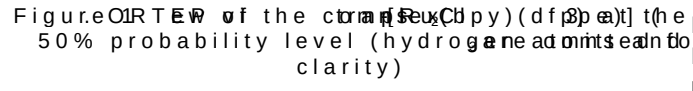


Figure 1. ORTEP view of the complex [RuCl(bpy)(dfppe)][OTf] (the 50% probability level (hydrogen atoms omitted and solvent of crystallization CHCl$_3$ omitted for clarity))

However, in the case of reaction of compound 6 with $NaBH_4$ in EtOH, we noted rapid reaction that was complete within 5 min; continuation of the reaction at 298 K led to isomerization. The two hydride isomers 10a and 10b are stable in solution as well as in the solid state in air. They contain mutually trans-phosphines with the hydride trans to the nitrogen of bpy ligand as deduced from their solution ^1H and $^{31}P\{^1H\}$ NMR spectra. The ^1H NMR spectral signals of these isomers exhibit nearly similar chemical shifts and the coupling constants are also quite similar. The isomer 10a displays a quartet at δ 15.80 ppm for the hydride ligand due to coupling with the three cis-phosphorus atoms (dfppe and PMe_3). The $J(H,P_{cis})$ is on the order of 24 Hz. On the other hand, extracting useful NMR spectral information for 10b was rendered difficult due to similar chemical shifts and coupling constants. The $^{31}P\{^1H\}$ NMR spectrum consists of two doublet of doublets ($J(P,P_{trans})$ = 348 Hz) at δ 45.1 and, 7.4 ppm for the dfppe and PMe_3 phosphorus nuclei, which suggests that both the phosphines are trans to each other and another broad singlet at δ 37.1 ppm for the other dfppe P atom. The X-ray crystal structure of complex 10a has been determined and the details have been deposited in the ESI.

Preparation and Characterization of [RuH(P(OMe)$_3$)(bpy)(dfppe)][OTf], 11a, 11b

Reaction of [RuCl(P(OMe)$_3$)(bpy)(dfppe)][OTf] with $NaBH_4$ in EtOH gave yellow colored diastereomeric mixture of cationic monohydride [RuH(P(OMe)$_3$)(bpy)(dfppe)][OTf] complexes (11a, 11b) (eq 6). Like the isomers 10a and 10b, these hydride complexes are also stable in solution as well as in the solid state in air. Isomer 11a contains mutually cis phosphine/phosphite with the hydride trans to one of the phosphorus atoms of dfppe, as deduced by its solution NMR spectrum. The ^1H NMR spectrum of 11a consists of a pair of triplets of a triplet centered at δ 6.26 ppm for the hydride ligand due to coupling with the trans phosphorus of dfppe and the cis phosphorus of dfppe/phosphite. The $J(H,P_{trans})$ is on the order of 145 Hz (coupling with dfppe P) whereas the $J(H,P_{cis})$, on the order of 27 Hz (coupling with cis dfppe/phosphite). In addition, we also observed J(H,F) coupling of 10 Hz. On the other hand, the $^{31}P\{^1H\}$ NMR spectrum consists of a doublet of doublet at 145.0 ppm for the phosphite P atom with $J(P,P_{cis})$ of 65 Hz due to coupling with the cis phosphine phosphorus, a broad doublet at δ 65.0 ppm for one of the dfppe P nucleus which is due to coupling with phosphine/phosphite, and another broad singlet at

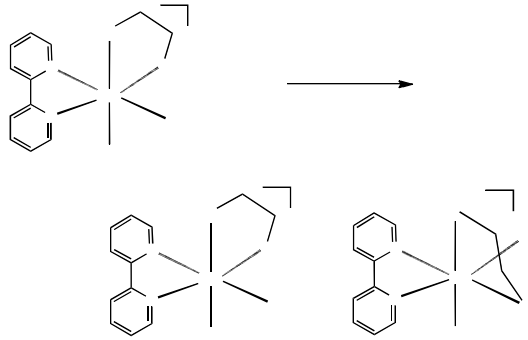
25.0 ppm for the other dfppe P atom. The isomeric hydride complexes of **11a** and **11b** exhibit very similar NMR spectral characteristics (both chemical shifts and coupling constants). Recrystallization of the isomeric mixture in CH_2Cl_2/n-hexanes resulted in the separation of the major isomer **11a**. The structure of complex **11a** was established unambiguously by X-ray crystallography.

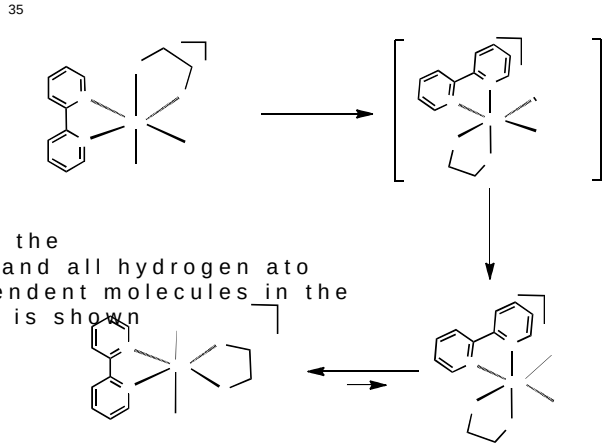
The ORTEP view of the monocation **11a** is shown in Figure 3 and the important bond lengths and angles have been summarized in Table 6. In addition to a discrete OTf counterion, two molecules of H_2O were also found. The Ru-P3 (phosphite) bond distance of 2.2549(10) Å in complex **11a** is shorter than that in *trans*-[RuH(P(OMe$_3$)(dppe)$_2$][BF_4] (2.337(2) Å).[35] This is a manifestation of the presence of nitrogen of the bpy ligand *trans* to P(OMe$_3$) in complex **11a** as opposed to a hydride in *trans*-[RuH(P(OMe$_3$)(dppe)$_2$][BF_4]. A hydride is a stronger *trans* directing ligand compared to bpy.[38] The P-O bond distances of the phosphite moiety fall in the range 1.577(7)-1.629(8) Å. The dfppe and bpy bite angles P1-Ru1-P2 and N1-Ru1-N2 are 85.66(3)° and 75.8(12)°, respectively.

Isomerization of [RuH(P(OMe$_3$)(bpy)(dfppe)][OTf], **11a**

We found that the complex **11a** slowly isomerizes to **11c** in solution (acetone or CH_2Cl_2); the isomerization that takes place is a conformational rearrangement of ligands around the metal center as shown in (eq 7). The structure of complex **11c** was not only deduced from its solution NMR spectral study but also X-ray crystallography (structural data have been deposited in the ESI). The ^{1}H NMR spectrum of complex **11c** shows a quartet at δ -15.22 ppm for the hydride ligand, indicating that it is cis to all the phosphorus ligands and trans to nitrogen of bpy. On the other hand, the ^{31}P{^{1}H} NMR spectrum consists of a doublet of doublet at δ 137.1 ppm for the phosphite P with J(P,P$_{trans}$) of 65 Hz due to coupling with the *trans* phosphine phosphorus, a broad doublet at δ 32.7 ppm for one of the dfppe P which is due to coupling with phosphine/phosphite, and another broad singlet at δ 47.7 ppm for the other dfppe P atom.

Figure 2 ORTEP view of the [Ru(bpy)(dfppe)(P(OMe$_3$)$_3$)H][OTf] cation at the 50% probability level. Solvent, disorder, and all hydrogen atoms omitted for clarity. There are two independent molecules in the asymmetric unit; only one molecule is shown



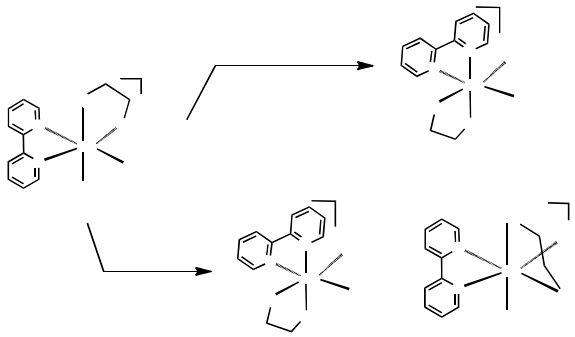


Protonation Reaction of [RuH(P(OMe$_3$)(bpy)(dfppe)][OTf] **11a**

In an attempt to prepare the dihydrogen complex [Ru(η^2-H$_2$)(P(OMe$_3$)(bpy)(dfppe)][OTf]$_2$ **12** starting from [RuH(P(OMe$_3$)(bpy)(dfppe)][OTf] species and also to get an insight into the electrophilicity of the metal center in such a complex, we carried out protonation of complex **11a**. In the first experiment, we carried out the protonation of complex **11a** using HOTf at 77 K. The NMR tube containing a mixture of the starting hydride complex **11a** and HOTf in CD_2Cl_2 at 77 K was inserted into the NMR probe precooled to and maintained at 193 K. We detected a signal corresponding to free H_2 at δ 4.6 ppm in the ^{1}H NMR spectrum and complex **13a** which is either solvent or triflate coordinated six coordinated species [Ru(S)(P(OMe$_3$)(bpy)(dfppe)][OTf]$_n$ [(S = solvent (n =2), triflate (n = 1)] exhibiting a geometry shown in eq 8. Upon raising the temperature of the sample from 243 K to 298 K, the geometry of **13a** changes to another isomer **13b** (eq 8). These species were not isolated but observed in solution. If the metal center is highly electrophilic, the propensity of the bound H_2 ligand to undergo heterolysis increases tremendously; in this scenario, excess protonating agent is required to protonate the starting hydride complex to be able to observe and also to stabilize the corresponding η^2-H_2 moiety bound to the metal. We carried out

an experiment in which we used excess HOTf in an effort to observe the η^2-H_2 moiety. Under these conditions as well, we did not observe an H_2 ligand

Figure 3 ORTEP view of the [Ru(H)(η²-H₂)(bpy)(dfppe)][OTf] cation at the 50% probability level. Solvent, triflate anions and H atoms (except the Ru-H and H-H) are omitted for clarity



Scheme 1

bound to the metal, instead we noted free H_2 evolution. This indicates the extreme labile ability of H_2 that is formed in situ. Protonation of complex 11a using excess HOTf under 1 atm of H_2(g) also did not afford the dihydrogen complex even at 193 K only free H_2 and complex 13a were formed.

The relative strength and stability of dihydrogen complexes depends on both σ donation and π back donation components. In case of cationic dihydrogen complexes π back bonding takes prominence in stabilizing the H-H bond interaction with the metal center whereas σ donation from the H_2 bonding MOs to an empty metal d orbital dominates in the case of dicationic dihydrogen complexes wherein the metal center is highly electrophilic.[8] In our case, the electron withdrawing nature of the dfppe ligand trans to H_2 moiety in the expected dihydrogen complex [Ru(η^2-H_2)(P(OMe)$_3$)(bpy)(dfppe)][OTf]$_2$ 12 and the dicationic nature of the metal center, results in a reduction of back donation from the metal to H_2. In such instances σ donation component should take prominence resulting in a stable and observable dihydrogen complex. Surprisingly in our case, the postulated dihydrogen complexes were not observed, but free H_2 was detected in all our experiments.

Highly acidic dihydrogen complexes with pK$_a$ < 0 are very labile with respect to H_2 loss.[39] There have been reports of only labile dihydrogen complexes in the literature.[40-43] Bianchini and his co-workers reported [Ir(H)$_2$(H$_2$)(triphos)][BPh$_4$] complex that contains dihydrogen ligand which is quite labile. They characterized the complex with the bound H_2 ligand using high pressure NMR spectroscopy technique. In a similar manner, we

Figure 4 ORTEP view of [Ru(H)(P(OMe)$_3$)(bpy)(dfppe)] (cation) at the 50% probability level. Solvent, triflate anions and H atoms are omitted for clarity. There are two independent molecules in the asymmetric unit; only one molecule is shown

Figure 5 ^{1}H NMR (recorded 400 MHz) spectral stack plot for reaction of [Ru(H)(P(OMe)$_3$)(bpy)(dfppe)][OTf] (11a) with H$_2$

attempted the protonation of complex 11a using HOTf under 5 bar of H_2 pressure at room temperature. The sample was then analyzed by NMR spectroscopy in the temperature range of 298 K to 183 K. Even in these circumstances, no evidence of H_2 bound to the metal center was noted. We obtained only H_2 loss product. Interestingly, upon H_2 loss, the species that results, 13a could be either solvent or triflate bound six coordinate complex [Ru(S)(P(OMe)$_3$)(bpy)(dfppe)][OTf]$_n$ [(S = solvent (n =2), triflate (n = 1)]. Upon raising the temperature of the sample from 243 K to 298 K, the geometry of 13a changes to another isomer 13b (eq 8). These compounds were not isolated but observed in solution. The geometries 13a and 13b were established by VT ^{1}H and ^{31}P{^{1}H} NMR spectroscopy (spectral data have been deposited in the ESI). From 193 K to 243 K, complex 13a displays three inequivalent phosphorus atoms with shifts at δ 118.7, 62.7, and 51.3 ppm, respectively in the ^{31}P{^{1}H} NMR spectrum. The ^{1}H NMR spectrum is comprised of 8 signals for the bpy moiety for the proposed 13a geometry.

When the temperature of the sample was raised, all the signals broadened which is due to a dynamic exchange of isomers 13a and 13b. At 243 K, complex 13b shows two inequivalent $^{31}P\{^1H\}$ NMR spectral signals, doublet at δ 50.8 ppm and triplet at 119.7 ppm for the dfppe and $P(OMe)_3$ which are cis to each other with about J(P,P) = 56 Hz and also bipyridine shows 4 signals corresponding to eight protons which supports its proposed 13b geometry.

We carried out a preparatory scale experiment in an attempt to isolate and characterize the proposed 13a/13b species. Protonation of complex 11a with HOTf at room temperature under Ar atmosphere resulted in H_2 evolution. Workup of the reaction mixture gave a residue that was insoluble in CH_2Cl_2 and THF but soluble in only acetone and methanol. It was found to be highly moisture sensitive. Dissolution in acetone-d_6 followed by NMR spectral characterization of the product evidenced it to be an isomeric mixture of aqua complexes $[Ru(H_2O)(P(OMe)_3)(bpy)(dfppe)][OTf]_2$ (14a, 14b) (Scheme 1). ^1H NMR spectrum features two sharp singlets at † 5.76 and 5.80 ppm which are attributable to the coordinated water of the major (14a) and the minor (14b) isomers. Aqua complexes having combination of soft P donors and hard nitrogen ligands, e.g. $[Ru(OH_2)(PEt_3)_2(terpy)]^{2+}$ (terpy = 2,2':6',2''-terpyridine)[44] and $[Ru(OH_2)(dppe)(TpiPr)]$ (TpiPr = hydridotris(3,5-diisopropylpyrazolyl)borato)[45] have been reported. The IR spectrum of (14a, 14b) (KBr) shows a broad band around 3520 cm^{-1} attributable to the stretching mode of coordinated water (the spectrum has been deposited in the ESI). In case of complexes $[RuH(CO)(PPh_3)_3(H_2O)][BF_4]\cdot H_2O$[46] and $[Mo(CO)_3(PCy_3)_2(H_2O)]\cdot 2H_2O$,[47] bound water ligand gives a band at 3600 and 3308–3560 cm^{-1}, respectively. In addition, complex 14a has been structurally characterized.

Crystals of complex 14a were obtained via slow evaporation from its saturated methanol solution. The ORTEP view of the dication of complex 14a is shown in Figure 4 and the important bond lengths and angles have been summarized in Table 5. The asymmetric unit contains two distinct complex dications, $[Ru(H_2O)(P(OMe)_3)(bpy)(dfppe)]^{+2}$ and a total of four $[OTf]^-$ counteranions. The structure consists of a distorted octahedral coordination around the metal with water molecule and one of the phosphorus atoms of dfppe are trans to each other. The Ru–N and Ru–P distances are comparable to those in complex 9 and 11a. The Ru1–O1 bond distance is 2.191(7) Å, which is slightly longer than that in 9 (2.187(3) Å) and comparable to that reported in the literature such as *trans*-$[RuCl_2(PEt_3)_2(CO)(H_2O)]$ (2.189(2)Å),[48] and $[Ru(bpc)(bpy)OH_2]^+$ (bpc = 2,2'-bipyridine-6-carboxylate) (2.112(2)Å).[49] The difference in bond lengths of Ru1–P1 (2.290(3) Å) and Ru–P2 (2.350(2)Å) is due to the different trans influence of O1(H_2O) and N2(bpy) ligands.

The dihydrogen ligand in complex 12 is extremely labile and can be easily replaced by ligands such as CH_3CN and H_2O. When complex 11a was protonated in CH_2Cl_2 in presence of water or CH_3CN under N_2 atmosphere, complexes 14a, 14b and 15 were obtained, respectively presumably through the intermediacy of the dihydrogen complex 12 (Scheme 1). Complex 15 shows three inequivalent ^{31}P NMR spectral signals at † 120.1, 51.5, 53.3, respectively for the $P(OMe)_3$ and dfppe ligands. In the ^1H NMR spectrum, the coordinated acetonitrile appears at † 2.47 ppm, up field shifted with respect to free acetonitrile († 2.1 ppm) which is generally the case of the cationic acetonitrile complexes.

Reaction of $[Ru(H_2O)(P(OMe)_3)(bpy)(dfppe)][OTf]_2$ (14a, 14b) with H_2

Reaction of the diastereomeric mixture of $[Ru(H_2O)(P(OMe)_3)(bpy)(dfppe)][OTf]_2$ (14a, 14b) complexes with H_2 at 1 atm in acetone-d_6 at room temperature resulted in the heterolytic cleavage of H_2. The two isomeric hydride complexes $[RuH(P(OMe)_3)(bpy)(dfppe)][OTf]$ (11a, 11b) together with H_3O^+ were obtained. Figure 5 shows a partial ^1H NMR spectral stack plot of the formation of the hydride complexes as a function of time. We believe that the formation of the hydride complexes 11a and 11b and H_3O^+ proceeds through the intermediacy of the dihydrogen complex 12. Attempts to observe the dihydrogen complex 12 via reaction of 14a and 14b with H_2 at 1 atm using VT NMR spectroscopy (183–293 K) were not successful. Instead, isomers 14a and 14b having coordinated water molecule to one of the phosphorus atoms of dfppe were only obtained. By virtue of the trans effect of dfppe on the bound water molecule, the water molecule becomes labile. Similar trans influence of phosphines on coordinated water molecules was noted by Mezzetti and co-workers.[30,50] Due to lability of the bound water ligand, H_2 can easily replace it and form the corresponding dihydrogen complex $[Ru(\eta^2\text{-}H_2)(P(OMe)_3)(bpy)(dfppe)][OTf]_2$ 12. This species is quite short-lived and the bound H_2 ligand undergoes heterolytic cleavage which is triggered by the presence of an acceptor of the proton equivalent, here H_2O. In the absence of any proton acceptor, we noted only H_2 evolution. Upon heterolysis, the isomeric hydride complexes 11a and 11b were obtained. We were unable to observe H_3O^+ in solution which is due to rapid H/D exchange with residual free water present in the solution. Apparently, H_2 undergoes HD exchange with acetone-d_6 to give HD and D_2 which results in the formation of the deuteride complex $[RuD(P(OMe)_3)(bpy)(dfppe)][OTf]$ (11a-d and 11b-d). We noted a signal for the hydride ligand of complex 11a in acetone-d_6 solution at δ 6.23 ppm in the ^1H NMR spectrum, the intensity of which remained unaltered over an extended period of time at room temperature. This suggests that the hydride ligand does not undergo H/D exchange with the deuterated solvent. However, the reaction of isomeric aqua complexes with H_2 the ^1H NMR spectrum of 11a and 11b over a period of ca. 3 h showed the disappearance of the hydride signal whereas, all the other ^1H and ^{31}P NMR spectral signals of the complex remained unchanged. This is indicative of reaction of only the hydride ligand of 11a and 11b. We also noted that the amount of isomer 11b formed is quite less whereas 11a is the major one. We propose that the H_3O^+ formed in solution slowly reacts with complexes 11a and 11b and forms the corresponding dihydrogen complex which rather has a fleeting existence. The bound H_2 ligand gets substituted by HD in a facile manner. The HD isotopomer of complex 12 undergoes deprotonation in presence of H_2O to form the Ru–D complex. The presence of the deuteride was confirmed by ^2H NMR spectroscopy, which showed a signal at δ 6.11 ppm (spectrum has been deposited in the ESI). After one week, the Ru–D isomer slowly isomerizes to 11c-d which was confirmed by NMR spectroscopy (see ESI). Isotopic H/D exchange in metal-H_2 complexes is a most commonly observed process in presence of deuterated solvents.[51]

For example, Morris and his co-workers observed reaction of acetone-d_6 with $[RuCl(H_2)(dppe)_2]^+$ to give the HD isotopomer in 20 min.[52]

Conclusions

A series of new cationic Ru(II) complexes of the type [RuCl(L)(bpy)(dfppe)][Z] (L = $P(OMe)_3$ (5), PMe_3 (6), CH_3CN (7), CO (8), H_2O (9); Z = OTf (5, 6, 7, 8), BAr^F_4 (9) have been synthesized starting from *trans*-$[RuCl_2(bpy)(dfppe)]$ (3) via abstraction of one of the chloride ligands using AgOTf or $NaBAr^F_4$ in the presence of L. By virtue of the presence of electron withdrawing dfppe ligand and the cationic nature of the complex, these derivatives are quite electrophilic. Protonation reaction of the hydride complex $[RuH(P(OMe)_3)(bpy)(dfppe)][OTf]$ with HOTf at low temperature gave free H_2 and formation of $[Ru(S)(P(OMe)_3)(bpy)(dfppe)][OTf]_n$ [(S = solvent (n =2), triflate (n = 1)], 13a/b which could be either solvent or triflate bound six coordinated species; these species were not isolated and their formulation and geometry are not known with certainty. Surprisingly, in this reaction we obtained dihydrogen complex (unobserved) in which the H_2 ligand was found to be highly labile. The aqua complex *cis*-$[Ru(bpy)(dfppe)(OH_2)(P(OMe)_3)][OTf]_2$ on the other hand reacts readily with H_2 under ambient conditions and brings about heterolytic cleavage of the H–H bond in H_2 molecule.

Acknowledgements

We are grateful to the Department of Science & Technology, India (Science & Engineering Research Board) for the financial support.

Notes and references

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• Electronic Supplementary Information (ESI) available: Crystallographic data, ORTEP view of the complexes, IR and NMR spectral data for the complexes. CCDC reference numbers 936512-936522. See DOI: 10.1039/b000000x/

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