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16-Electron Elongated Dihydrogen Complex Stabilized by Agostic Interaction

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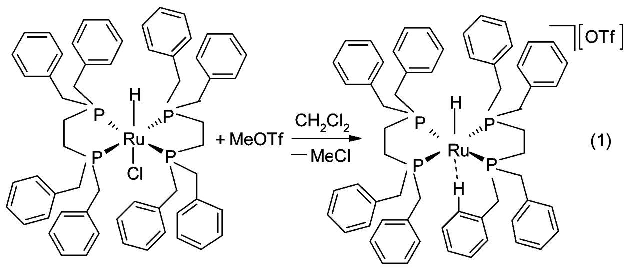
A 16-electron dicationic dihydrogen complex [Ru(η^2-H•••H)(PP)$_2$][OTf]$_2$ [**4**; PP = $(C_6H_5CH_2)_2PCH_2CH_2P(CH_2C_6H_5)_2$] has been prepared and characterized by protonating the precursor hydride complex [Ru(H)(PP)$_2$)][OTf] (**2**) using HOTf. The hydride and dihydrogen complexes are stabilized via agostic interaction of the ortho C–H fragment of the phenyl ring on the benzyl group. The intact nature of the H–H bond in this derivative was established from the short spin–lattice relaxation time and the observation of a substantial *J*(H,D) of 22.0 Hz for the HD isotopomer. The H–H bond distance calculated from *J*(H,D) is 1.05 Å, which falls under the category of *elongated* dihydrogen ligands.

The binding of molecular hydrogen to a transition-metal center leads to the elongation of the H−H bond along the reaction coordinate for the oxidative addition of dihydrogen. While a large number of dihydrogen complexes reported to date have H−H distances (d_{HH}, Å) between 0.8 and 1.0 Å, there are fewer examples of complexes that possess *elongated* dihydrogen moieties (d_{HH} between 1.0 and 1.5 Å).[1,2] The elongated dihydrogen complexes represent arrested intermediates in the important process of oxidative addition of dihydrogen to a metal center. We recently started a program to study the smooth gradation of the H−H distances in certain ruthenium dihydrogen complexes along the reaction coordinate for the oxidative addition of dihydrogen. In this Communication, we report an unprecedented example of a 16-electron, dicationic elongated dihydrogen complex of ruthenium that is stabilized by an agostic Ru•••H−C interaction.



1 **2**

(1)

Treatment of *trans*-[Ru(Cl)H(PP)$_2$][3] [**1**; PP = $(C_6H_5CH_2)_2PCH_2CH_2P(CH_2C_6H_5)_2$] with 1 equiv of MeOTf in CH_2Cl_2 at room temperature resulted in the unexpected elimination of MeCl instead of CH_4, accompanied by the formation of a new 16-electron hydride complex, [Ru(H)(PP)$_2$][OTf] (**2**; eq 1).[4] The ^{1}H NMR spectrum of this species shows a quintet at δ −25.44 for the hydride moiety. The benzyl CH_2 hydrogens appear as four independent doublets at δ 3.68, 3.29, 3.22, and 2.90, with three of the geminal ^2J(H,H) of 14.6 Hz and the fourth 12.6 Hz. In addition, the spectrum shows a well-resolved doublet at δ 6.67 (integrates to 8H) that is upfield-shifted from the phenyl resonances (δ 6.92−7.36), with a ^3J(H,H) = 6.8 Hz. The ^{19}F NMR spectrum shows a single resonance at δ −79.83 for the OTf$^-$ counterion. These spectral features and the observation of the elimination of MeCl points to the formation of a five-coordinate, 16-electron hydride complex, which is stabilized by a Ru•••H−C agostic interaction in the sixth coordinate site on the metal center.[5] A similar agostic benzyl interaction

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(3) To a 2-propanol solution (10 mL) of [RuH(Cl)(PPh$_3$)$_3$] (0.100 g, 0.108 mmol) was added $(C_6H_5CH_2)_2PCH_2CH_2P(CH_2C_6H_5)_2$ (0.098 g, 0.216 mmol), and the reaction mixture was refluxed for 2 h, during which time a yellow product precipitated out. The solution was filtered after it had cooled to room temperature, and the precipitate containing the product *trans*-[RuH(Cl)((($C_6H_5CH_2)_2PCH_2CH_2P(CH_2C_6H_5)_2)_2$)] (**1**) was washed with ^{i}PrOH (5 mL) and dried in vacuo. Yield: 0.065 g (57.0%). QTOF-MS: *m/z* = 1011 [M$^+$ − Cl$^-$]. ^{1}H NMR (CD_2Cl_2): δ −19.63 (qnt, 1H, Ru−*H*, *J*(H,P) = 19.5 Hz), 0.60 (br s, 4H, PCH_2CH_2P), 1.10 (br s, 4 H, PCH_2CH_2P), 2.89 (d, 4H, C$H_2C_6H_5$, *J*(H,H) = 13.6 Hz), 3.13 (d, 4H, C$H_2C_6H_5$, *J*(H,H) = 13.6 Hz), 3.22 (d, 4H, C$H_2C_6H_5$, *J*(H,H) = 13.7 Hz), 4.33 (d, 4H, C$H_2C_6H_5$, *J*(H,H) = 14.6 Hz), 7.14−7.56 (m, 40H, C_6H_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 63.1 (s, 4P).

(4) Characterization of [Ru(H)((($C_6H_5CH_2)_2PCH_2CH_2P(CH_2C_6H_5)_2)_2$)][OTf] (**2**). QTOF-MS: *m/z* = 1009 [M$^+$ − (H_2 + OTf$^-$)], 555 [M$^+$ − ((($C_6H_5CH_2)_2PCH_2CH_2P(CH_2C_6H_5)_2$) + OTf$^-$)]. ^{1}H NMR ($CD_2Cl_2$): δ −25.44 (qnt, 1H, Ru−*H*, *J*(H,P) = 20.2 Hz), 0.75 (br s, 4H, PCH_2CH_2P), 1.19 (br s, 4 H, PCH_2CH_2P), 2.90 (d, 4H, C$H_2C_6H_5$, *J*(H,H) = 14.6 Hz), 3.22 (d, 4H, C$H_2C_6H_5$, *J*(H,H) = 12.7 Hz), 3.29 (d, 4H, C$H_2C_6H_5$, *J*(H,H) = 14.6 Hz), 3.68 (d, 4H, C$H_2C_6H_5$, *J*(H,H) = 14.6 Hz), 6.67 (d, 8H, Ru•••*H*−C, *J*(H,H) = 6.8 Hz), 6.92−7.36 (m, 32H, C_6H_5, and hydrogens of nonagostic phenyl rings). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 59.0 (s, 4P). ^{19}F (CD_2Cl_2): δ −79.83 (s, OTf).

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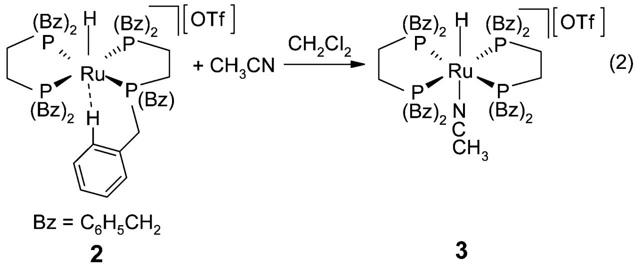
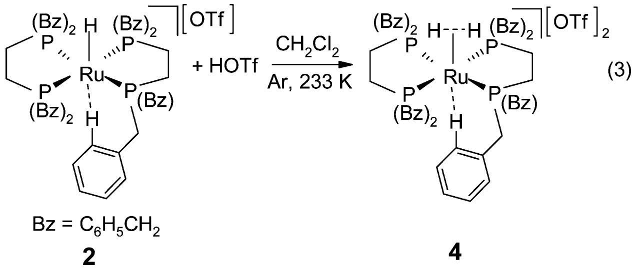
was reported earlier by Luo et al.[5b] In contrast to [RuH(dppp)$_2$] [dppp = Ph$_2$P(CH$_2$)$_3$PPh$_2$] reported by Saburi et al.,[5a] which has the hydride in the cis position with respect to the agostic site, in complex **2**, the hydride and the agostic site are mutually trans to one another. This is based on the observation of a single resonance for all of the four phosphine phosphorus atoms in the ^{31}P{^{1}H} NMR spectrum (δ 59.0) The H−C moiety on the ortho position of the phenyl ring is the donor for this agostic interaction.

The variable-temperature (VT) ^{1}H NMR spectroscopy of this sample resulted in the broadening of the doublet signal (agostic hydrogen) at low temperature, eventually becoming a broad singlet and at the same time shifted upfield in the temperature range of 293−223 K. The four sets of doublets for the benzyl CH$_2$'s also underwent line broadening at low temperatures. Further cooling to 183 K resulted in decoalescence of the signal due to the agostic hydrogen into two broad singlets at δ 6.37 and 6.64 signaling the freezing of the *o*-hydrogen exchange process. This complex is stable in the solid state; however, it is only moderately stable in solution at 293 K. In the CH$_2$Cl$_2$ solvent, it picks up a chloride from the solvent to give chloride hydride complex **1** over a period of 12 h. It is only partially soluble in most solvents, thus causing difficulty in growing crystals. To establish the agostic interaction with certainty, we reacted the hydride complex **2** with 1 equiv of CH$_3$CN. The reaction mixture immediately turned colorless from yellow, and yet another new hydride derivative was obtained, *trans*-[Ru(H)(CH$_3$CN)(PP)$_2$][OTf] (**3**; eq 2).[6] The hydride signal of complex **2** at δ −25.44 disappeared, whereas a new quintet for the hydride ligand of the acetonitrile complex formed at δ −17.52 in the ^{1}H NMR spectrum. CH$_3$CN appears as a singlet at δ 2.32.



Protonation of **2** using 1 equiv of HOTf in CD$_2$Cl$_2$ resulted in a new dicationic dihydrogen complex [Ru(η^2-H⋯H)(PP)$_2$][OTf]$_2$ (**4**; eq 3).[7] The dihydrogen ligand appears as a broad singlet in the ^{1}H NMR spectrum at δ −17.97. Remarkably enough, the agostic interaction was left undisturbed upon protonation. The Ru⋯H−C agostic hydrogen appears as a doublet [^2J(H,H) = 6.8 Hz] at δ 6.77, upfield from the remaining phenyl resonances (δ 6.83−7.86). The dihydrogen ligand and the agostic site are trans-disposed as evidenced by ^{31}P{^{1}H} NMR spectroscopy (δ 54.0, singlet). The ^{19}F NMR spectrum of **4** shows only one signal at δ −79.71. The observation of only one signal in the ^{19}F NMR spectrum and the signals for the benzyl agostic interaction in the ^{1}H NMR spectrum, along with the formation of the CH$_3$CN complex (eq 2), strongly suggests that a potential coordinating anion like the triflate is not bound to the metal in the sixth coordination site. The complex **4** has limited stability, thus precluding further reactivity studies. With time, it picks up a chloride from the solvent, resulting in a dihydrogen chloride complex that we are currently attempting to isolate and characterize.



To establish the intact nature of the H−H bond in this derivative, we carried out the VT ^{1}H spin−lattice relaxation time (T_1, ms) measurements for the bound dihydrogen.[8] A T_1 (min) (400 MHz) of 23.1 ms was obtained at 253 K from which the H−H bond distances for the fast- and slow-spinning regimes were calculated to be 0.90 and 1.14 Å, respectively.[9] Unambiguous establishment of the intact nature of the H−H bond was achieved by the partial incorporation of deuterium to form the HD isotopomer of complex **4** and measurement of J(H,D). This was done by reacting **2** with 1 equiv of DOTf at 233 K to generate a mixture of [Ru(η^2-H⋯D)(PP)$_2$][OTf]$_2$ (major) and **4** (minor) derivatives. We recorded the ^{1}H NMR spectrum of the HD isotopomer in the temperature range 293−223 K by nullifying the residual signal of the η^2-H$_2$ species by an inversion−recovery pulse (Figure 1).[10] At 293 K, the ^{1}H NMR spectrum in the hydride region shows a very well-resolved 1:1:1 triplet due to H−D coupling at δ −18.00; each one of the 1:1:1 triplet signals was further split into a quintet as a result of HD−P coupling.

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(5) Previous instances of the observation of agostic interactions in somewhat similar systems: (a) Saburi, M.; Fujii, T.; Shibusawa, T.; Masui, D.; Ishii, Y. *Chem. Lett.* **1999**, 1343−1344 and references cited therein. (b) Luo, X.-L. L.; Kubas, G. J.; Burns, C. J.; Eckert, J. *Inorg. Chem.* **1994**, *33*, 5219−5229. (c) King, W. A.; Scott, B. L.; Eckert, J.; Kubas, G. J. *Inorg. Chem.* **1999**, *38*, 1069−1084 and references cited therein.

(6) Characterization of *trans*-[Ru(H)(CH$_3$CN)(((C$_6$H$_5$CH$_2$)$_2$PCH$_2$CH$_2$P(CH$_2$C$_6$H$_5$)$_2$)$_2$)][OTf] (**3**). ^{1}H NMR (CD$_2$Cl$_2$): δ −17.52 (qnt, 1H, Ru−*H*, J(H,P) = 20.4 Hz), 0.91 (br s, 4H, PC*H*$_2$C*H*$_2$P), 1.23 (br s, 4 H, PC*H*$_2$C*H*$_2$P), 2.32 (s, 3H, C*H*$_3$CN), 2.82 (d, 4H, C*H*$_2$C$_6$H$_5$, J(H,H) = 13.6 Hz), 3.00 (d, 4H, C*H*$_2$C$_6$H$_5$, J(H,H) = 13.6 Hz), 3.29 (d, 4H, C*H*$_2$C$_6$H$_5$, J(H,H) = 13.6 Hz), 3.39 (d, 4H, C*H*$_2$C$_6$H$_5$, J(H,H) = 13.6 Hz), 6.81−7.75 (m, 40H, C$_6$*H*$_5$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 55.0 (s, 4P). ^{19}F (CD$_2$Cl$_2$): δ −79.84 (s, OTf).

(7) Characterization of [Ru(η^2-H⋯H)(((C$_6$H$_5$CH$_2$)$_2$PCH$_2$CH$_2$P(CH$_2$C$_6$H$_5$)$_2$)$_2$)][OTf]$_2$ (**4**). ^{1}H NMR (CD$_2$Cl$_2$): δ −17.97 (br s, 2H, Ru−η^2*H*$_2$), 0.80 (br s, 4H, PC*H*$_2$C*H*$_2$P), 0.94 (br s, 4 H, PC*H*$_2$C*H*$_2$P), 2.63 (d, 4H, C*H*$_2$C$_6$H$_5$, J(H,H) = 14.7 Hz), 2.95 (d, 4H, C*H*$_2$C$_6$H$_5$, J(H,H) = 14.7 Hz), 3.94 (d, 4H, C*H*$_2$C$_6$H$_5$, J(H,H) = 14.7 Hz), 4.04 (d, 4H, C*H*$_2$C$_6$H$_5$, J(H,H) = 13.7 Hz), 6.77 (d, 8H, Ru⋯*H*−C, J(H,H) = 6.8 Hz), 6.83−7.86 (m, 32H, C$_6$*H*$_5$, and hydrogens of nonagostic phenyl rings). ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$): δ 54.0 (s, 4P). ^{19}F (CD$_2$Cl$_2$): δ −79.71 (s, OTf$^-$).

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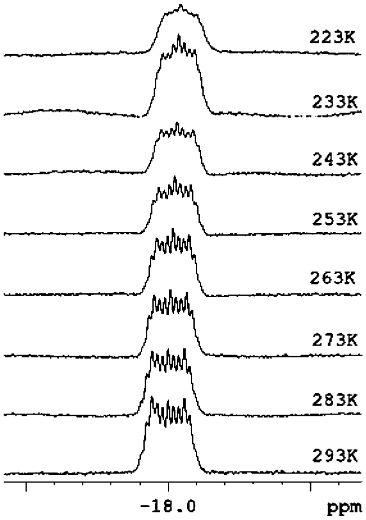

Figure 1. VT ^{1}H NMR spectral stack plot of the hydride region of [Ru(η^2-H$\cdots$D)(PP)$_2$][OTf]$_2$ in CD_2Cl_2.

J(H,D) was found to be 22.0 Hz,[11] which gives a H$-$H distance (d_{HH}) calculated from the inverse relationship between d_{HH} and J(H,D) of 1.05 Å.[12] This distance seems to be more consistent with the slow than the fast rotation regime of the bound dihydrogen.[9] J(HD,P$_{cis}$) was found to be 8.0 Hz, which is within the range (7.2$-$8.0 Hz) reported for complexes of the type *trans*-[RuCl(η^2-HD)(diphosphine)$_2$]$^+$ by Morris et al.[10b]

In the family of complexes of the type *trans*-[Ru(η^2-H$_2$)(H)(PP)$_2$]$^+$ (PP = dppe, depe) reported by Morris et al.,[13] J(H,D) was found to be in the range 32$-$33 Hz, which gives a d_{HH} of 0.88$-$0.86 Å. On the other hand, in complexes with a good π donor like chloride, *trans*-[RuCl(η^2-HD)(PP)$_2$]$^+$, d_{HH} was found to be 1.15 Å (PP = dcype), 1.04 Å (PP = depe), and 0.98 Å (PP = dppe). The decrease in d_{HH} reflects a decrease in the donor abilities of the diphosphine ligands from dcype to depe to dppe. On the basis of the T_1 data, Mezzetti et al. reported that the bound dihydrogen ligand in [RuX(η^2-H$_2$)(PP)$_2$]$^+$ (PP = dppp) complexes was elongated.[14] Our group reported several examples of dicationic dihydrogen complexes with the [Ru(PP)$_2$] backbone of the type [Ru(η^2-H$_2$)(L)(PP)$_2$]$^{2+}$ (L = RCN, P(OR)$_3$, PF(OR)$_2$, PF$_3$; PP = dppm, dppe), and in all of those cases, d_{HH} was found to be less than 1.0 Å.[15]

The dihydrogen complex **4** belongs to the class of *elongated* dihydrogen complexes. The ruthenium fragment is dicationic and is formally a 16-electron center stabilized via an agostic interaction (trans to the bound dihydrogen) with the H$-$C fragment on the ortho position of the phenyl ring. We also studied the temperature dependence of J(H,D) in [Ru(η^2-H$\cdots$D)(PP)$_2$][OTf]$_2$ and found a modest variation, increasing from 22.0 Hz at 293 K to 24.0 Hz at 233 K. This behavior has been observed for other elongated dihydrogen complexes as well.[2]

Chaudret et al.[16] reported certain 16-electron ruthenium complexes of the type [Ru(H)X(η^2-H$_2$)(PR$_3$)$_2$]. d_{HH} in this series of compounds was found to be in the range 1.0$-$1.03 Å. In one of the complexes, [RuH(H$_2$)(o-C$_6$H$_5$py)(PR$_3$)$_2$][BArf], Ru$\cdots$H$-$C (H$-$C of the phenyl) agostic interaction was noted.[16a] This compound was isolated and characterized by NMR spectroscopic, X-ray crystallographic, and theoretical studies.

In summary, we synthesized and characterized a dicationic dihydrogen complex **4** in which the H$-$H bond is elongated (1.05 Å). This species is stabilized by an agostic interaction trans to the dihydrogen ligand. It is of interest to note that, although the metal fragment is dicationic and formally a 16-electron center, the bound dihydrogen is significantly elongated, which is contrary to what one would expect based on the bonding principles of these types of novel molecules.[1] In addition, a potential coordinating anion like OTf$^-$ remains as a counterion rather than binding to the metal. Recently, Pons and Heinekey reported an elongated dihydrogen complex of iridium [Ir(Cp*)(η^2-H$_2$)(dppm)]$^{2+}$ (dmpm = Me$_2$PCH$_2$PMe$_2$) wherein the metal fragment is dicationic.[17] Efforts are underway to systematically study the effect of increasing the electron donor ability of the diphosphine ligand on d_{HH} with a view to realize complexes with even more elongated dihydrogen ligands.

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Supporting Information Available: Synthesis and characterization details for the compounds, VT T_1 data, J(H,D) data, NMR spectra of the reactions, and mass spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The ^{1}H{^{31}P} NMR spectrum of the HD isotopomer gave a 1:1:1 triplet with a J(H,D) of 22.0 Hz, consistent with that obtained in the ^{1}H NMR spectrum. See the Supporting Information.

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