Ab Initio MO and MM Study on the Nature of $[Ru(P\text{-}P)_2``H_3"]^+$ (P-P = dppb, diop, dpmb, dppe) Complexes

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A theoretical study has been carried out on $[Ru(P\text{-}P)_2``H_3"]^+$ (P-P = dppb, diop, dpmb, dppe) complexes with the goal of clarifying the wide differences observed in their experimental NMR spectra. Electronic effects are evaluated through ab initio molecular orbital calculations at the MP2 and MP4 levels on the $[Ru(PH_3)_4``H_3"]^+$ model, while steric effects are quantified through molecular mechanics calculations on the $[Ru(P\text{-}P)_2]$ (P-P = dppb, diop, dpmb, dppe) model. The results suggest that the dominant species in solution are six-coordinate dihydrogen hydride $[Ru(P\text{-}P)_2H(H_2)]^+$ complexes. Two different isomers of this complex seem possible, an octahedral trans species and a very distorted cis species, their relative energies depending on the particular diphosphine ligand. A trihydride complex is also found to play a substantial role as an intermediate in $[Ru(diop)_2``H_3"]^+$.

Introduction

A considerable amount of research effort has been invested in recent years by many authors in the study of $[M(P\text{-}P)_2H(H_2)]^+$ (M = Fe, Ru, Os; P-P = chelating diphosphine) complexes,[1–4] and closely related compounds.[5–7] One of the interesting features of these complexes is the frequent existence of an exchange reaction between the atoms of the (usually trans) hydride and dihydrogen ligands which leads to their equivalence in NMR spectra at room temperature. The mechanism of this process, which could have far-reaching implications in the general field of σ-bond activation,[8] is still poorly understood.

The most complete experimental work available in the literature on these bis(diphosphine) complexes is probably that of Morris and co-workers.[1,2] From their study of a large series of these complexes, they postulate that the exchange reaction must start with oxidative addition of the molecular hydrogen ligand to give rise to a seven-coordinate trihydride complex, which then would undergo a fluxional process. The need for oxidative addition could be called into question on diverse grounds, such as the presence of exchange also in similar dihydride complexes,[9] a study on $[ReH_2(H_2)(CO)(PMe_2Ph)_3]^+$ complexes which demonstrates the existence of a non-dissociative path different from oxidative addition,[10] and theoretical RHF results on the model system *cis*-$[Fe(PH_3)_4H(H_2)]^+$.[11] In summary, the topic cannot be considered as settled, either on experimental or on theoretical grounds.

In this context, some recent experimental results by Saburi and co-workers on ruthenium complexes seem especially exciting.[4,12] Of particular interest are their results with systems where the chelating ligands are 1,4-bis(diphenylphosphino)butane (dppb) and the closely related (*R,R*)-4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane (diop) and 1,2-bis((diphenylphosphino)methyl)benzene (dpmb). The shapes of these three ligands are shown in Chart 1, together with that of the more frequently used 1,2-bis(diphenylphosphino)ethane (dppe). Despite the formal resemblance between dppb, diop, and dpmb ligands, the low-temperature ^{31}P and high-field ^1H NMR spectra of the $[Ru(dppb)_2``H_3"]^+$, $[Ru(diop)_2``H_3"]^+$, and $[Ru(dpmb)_2``H_3"]^+$ systems are

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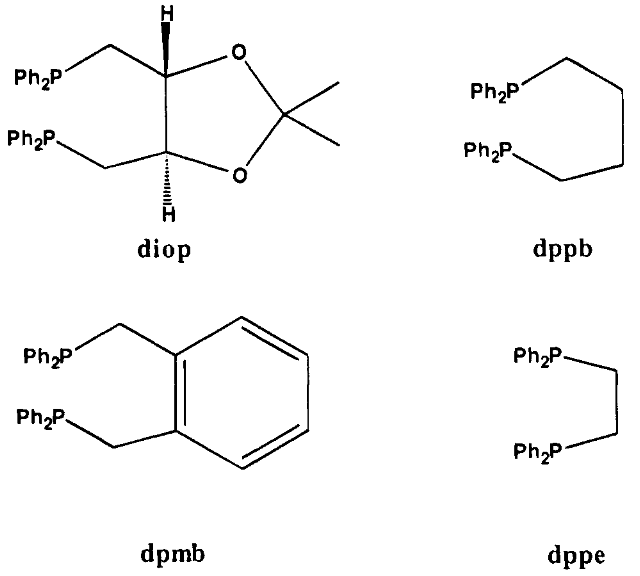
Chart 1



diop **dppb**

dpmb **dppe**

clearly different. For the dppb system the spectra show a complicated pattern, which can be attributed to the presence of different trans dihydrogen hydride isomers associated with different arrangements of the dppb rings. In the case of the dpmb ligands, there is one single signal in the ^{1}H case and two in the ^{31}P spectrum. This could be tentatively assigned to the presence of the cis dihydrogen hydride complex. The case of the diop ligand has no obvious explanation. There are two different species in equilibrium, one of them being the trans dihydrogen hydride complex, the other of unknown nature. This "unknown" species is especially puzzling, showing one single signal in both the ^{1}H and ^{31}P spectra. Furthermore, since it has a relaxation time T_1 value incompatible with trihydridic nature, it could even be the first example of a trihydrogen ligand, which has been previously postulated theoretically.[13]

In order to shed some light on the nature of this [Ru(diop)$_2$"H$_3$"]$^+$ species, as well on the reasons for the different behavior of this group of apparently similar complexes, theoretical calculations have been performed both at the ab initio and molecular mechanics levels, the results being presented in the following sections. A similar combination of ab initio and MM methods has been applied before to related systems, although they dealt with a different problem.[14]

Computational Details

Calculations concerning electronic effects, for an understanding of the direct bond interactions between metal and ligands, have been carried out on the model system [Ru(PH$_3$)$_4$"H$_3$"]$^+$ with the ab initio molecular orbital (MO) methodology using the Gaussian program.[15] Effective core potentials including relativistic contributions are used to represent the 28 innermost (up to 3d) electrons of the ruthenium atom.[16] The basis set is of valence double-ζ quality. For the Ru atom, it is that associated with the effective core potential,[16] with the (341/321/31) contraction built-in in the Gaussian program.[15] The other atoms are described with the standard 3-21G basis set.[17] Geometry optimizations have been done at the correlated MP2 level,[18] which takes the electron correlation into account with the second-order perturbation and has been demonstrated to give a good characterization of this kind of system.[19] Additionally, single-point energy-only calculations have been carried out at the more reliable, higher MP4 level of theory, including single, double, triple, and quadruple excitations. All these MP calculations use the frozen core approach, considering excitations involving only the 42 outermost valence electrons. MO geometry optimizations are full except that in phosphine ligands P—H distances are frozen to 1.42 Å, and angles about the phosphorus atoms are assumed to be tetrahedral.

Steric effects, essentially of a ligand–ligand nature, have been introduced through molecular mechanics (MM) calculations with the MM2 program[20] on [Ru(P-P)$_2$] systems. While the diphosphine ligands are considered explicitly in its experimental form, a very simplistic modelization of the metal atom is done, and the hydrogen atoms directly attached to it are simply neglected. The rationale behind this approach is that steric effects are expected to involve essentially the organic part of the diphosphine ligands, far away from the ruthenium atom, and that in any case, the molecular mechanics scheme applied cannot be expected to account properly for the subtleties of the dihydrogen/dihydride bonding to the metal atom. In line with this, in MM calculations the Ru—P distance is frozen at a value of 2.4237 Å, the average of the optimized values in the MO calculations for the trans hydride dihydrogen complex (vide infra). Constants for bond angles and dihedral angles centered at the metal atom (i.e., A—Ru—B, A—Ru—B—C) are considered to be zero, consequently giving complete freedom to these geometrical parameters. For bond angles and dihedral angles where the ruthenium atom occupies a terminal position (i.e., A—B—Ru, A—B—C—Ru), the values used are those corresponding to a lone pair. In any case, a set of van der Waals parameters is used for the ruthenium atom.[21]

Results and Discussion

Electronic Effects. The electronic effects on the experimental systems have been evaluated through ab initio MO calculations on the [Ru(PH$_3$)$_4$"H$_3$"]$^+$ model system. Other MO calculations have been previously published on the closely related [Fe(PH$_3$)$_4$H(H$_2$)]$^+$ systems,[11,22,23] where geometry optimization was carried out only at the lower HF level without electron correlation. In addition to the difference in the metal, the calculations presented here involve full optimization at the more reliable correlated MP2 level and consider a larger scope of possible geometries.

Figure 1 shows the two species with a trans disposition of the hydrogen atoms around the metal. Species **1**, the absolute minimum of the system, is the trans

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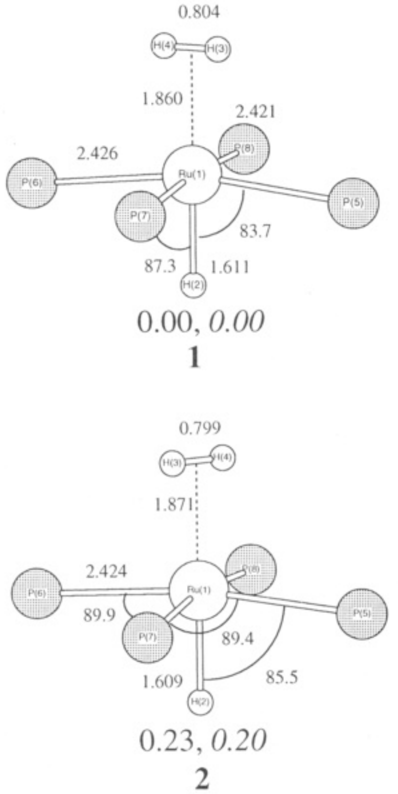

Figure 1. MP2 optimized geometries (in Å and deg) of equilibrium structure **1** (C_{2v}) and transition state **2** (C_{2v}), related to *trans*-$[Ru(PH_3)_4H(H_2)]^+$. The relative energies (in kcal/mol) indicated above the structure number in Roman type are at the MP2 level, while those in italics are at the MP4 level. Hydrogen atoms on phosphine ligands are omitted for clarity.

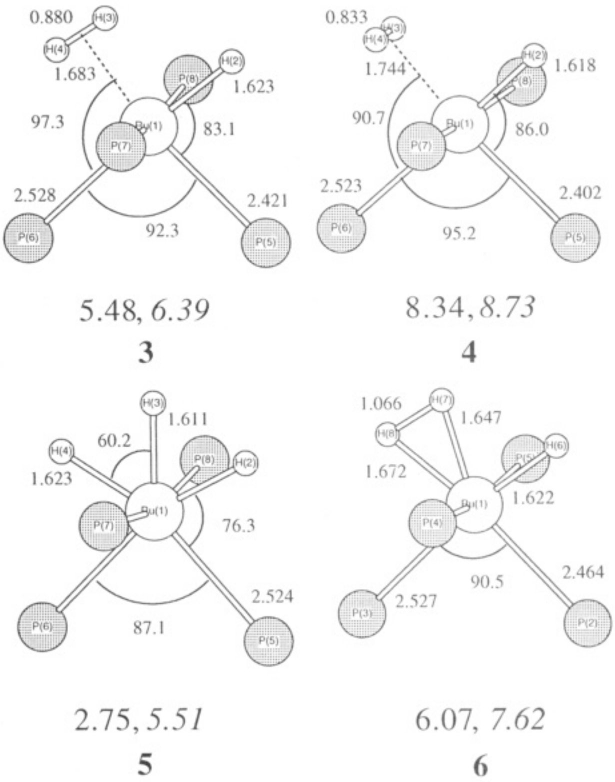

Figure 2. MP2 optimized geometries (in Å and deg) of equilibrium structure **3** (C_S), transition state **4** (C_S), equilibrium structure **5** (C_S), and transition state **6** (C_S), related to *cis*-$[Ru(PH_3)_4H(H_2)]^+$. Energies (in kcal/mol) indicated above the structure number in Roman type are for the MP2 level and with italics for the MP4 level, relative to **1**. Hydrogen atoms on phosphine ligands are omitted for clarity.

dihydrogen hydride complex, which is indeed usually considered to be the most stable isomer for this kind of system.[1,2] Although there are no neutron diffraction data available for any of these ruthenium species to check the optimized geometries, the geometry of the absolute minimum **1** is reasonable. The metal–phosphine distances of 2.426 and 2.421 Å are quite close to experimental average values (exemplified by 2.307 Å for Ru–PMe_3, 2.370 Å for Ru–PPh_3, or 2.396 Å for Ru–PPh_2Me).[24] For the Ru–H distance, although there are no experimental data for ruthenium itself, the value of 1.609 Å is in reasonable agreement with 1.609 Å for Fe–H and 1.659 Å for Os–H.[24] As for the dihydrogen ligand, the H–H distance of 0.804 Å is well in line with the usual values for dihydrogen complexes.[8,25] Finally, the general shape of the molecule, a distorted octahedron with a global C_{2v} symmetry, has a good resemblance to the available picture on analogous iron systems.[22,26]

Species **2**, also presented in Figure 1, is the transition state for the rotation of the hydrogen molecule around the Ru–mid(H_2) axis. The major geometrical difference between **1** and **2** is in the orientation of the H(3)–H(4) unit. In **1**, it is aligned in the P(5)–Ru(1)–P(6) direction, while in **2** it is parallel to the bisector of P(5)–Ru(1)–P(8). The most remarkable feature of transition state **2** is its relative energy of only 0.20 kcal/mol above the minimum, which would vanish, should zero-point energy correction be taken into account. This value, smaller than reported experimental values of ca. 1 kcal/mol for other complexes,[27] might be underestimated because of the full relaxation of the phosphine ligands allowed in our calculation on this model compound, whereas it may not be allowed in experimental ligands. At any rate, the very low rotational barrier is fully consistent with the experimental NMR equivalence always associated with the atoms in the dihydrogen unit. Moreover, it also points to the equivalence of phosphorus atoms in the corresponding NMR spectrum.

Figure 2 shows species where the hydrogen atoms are in a cis disposition. Species **3** is the octahedral cis dihydrogen hydride complex. This complex has a C_S symmetry, with the symmetry plane defined by the metal and the three hydrogen atoms attached to it. This same geometry was obtained using nonsymmetric orientations as starting points, being therefore a local minimum in the potential hypersurface. Although it may not be easily seen in the figure, the molecule presents the expected asymmetry in the bonding of the hydrogen molecule to the metal; the Ru(1)–H(3) and Ru(1)–H(4) distances are nearly equal, 1.73 vs 1.75 Å, the shorter distance corresponding to the atom closer to the hydride ligand.[22,28] Species **4** is the transition state for the rotation of the dihydrogen unit around the

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metal–mid(H_2) axis for the cis isomer. The energy barrier for this process, 2.86 kcal/mol (2.34 kcal/mol at the more reliable MP4 level), higher than for the trans isomer, can be viewed as a proof of cis interaction between hydride and dihydrogen ligands.[22,28] Geometry changes between **3** and **4**, H(3)–H(4) going from 0.880 to 0.833 Å and Ru(1)–H_2 from 1.683 to 1.744 Å, are also substantially larger than those between **1** and **2**, 0.804 to 0.799 Å and 1.870 to 1.871 Å for the same parameters, in agreement with the larger energy difference associated with the cis influence of the hydride ligand on the binding of dihydrogen to the metal.

Species **5** and **6** provide the path for the exchange reaction between dihydrogen and hydride ligands. Species **5** can be described as an intermediate, a pentagonal-bipyramidal seven-coordinate trihydride complex, with the trihydride ligands in equatorial positions. Species **6** is the transition state connecting **3** and **5**. The presence of a trihydride complex in the path of this exchange represents a significant difference from previous RHF results on the analogous complex of Fe.[11] The trihydride complex, which had been ruled out as very high in RHF energy for Fe,[11] appears here as a local minimum at the more reliable MP2 level. These calculations cannot answer the question as to whether this is a genuine difference between the behavior of the two metals or a reflection of the overstabilization of dihydrogen complexes relative to dihydride complexes in RHF calculations.[19] Though the MP4 single-point calculations at MP2 optimized geometries are considered to be quite reliable, a small energy span of the species **3**–**6**, 3.22 kcal/mol at the MP4 level (5.62 kcal/mol at the MP2 level), does not warrant a decisive conclusion as to the real nature of the cis minima. Nevertheless, for the discussion under way it seems sufficient to observe that these species are close in energy. This result alone makes a strong case for the NMR equivalence of hydrogen atoms of hydride and dihydrogen ligands when they are in cis equivalent positions as in this case. This also suggests two clearly differentiated signals in the ^{31}P NMR spectra.

Stationary points presented in Figures 1 and 2 could provide satisfactory explanations for the low-temperature NMR spectra of species [Ru(dppb)$_2$"H$_3$"]$^+$ as a trans dihydrogen hydride complex and [Ru(dpmb)$_2$"H$_3$"]$^+$ as a cis dihydrogen hydride complex. Nevertheless, the species in equilibrium with the trans complex in the [Ru(diop)$_2$"H$_3$"]$^+$ system, having single signals in both high-field ^1H and ^{31}P spectra, remains unexplained. Some other species which appeared possibly relevant to the spectra are presented in Figure 3.

Species **7** is a trihydrogen complex with a triangular trihydrogen ligand. Several variations of this complex, with different orientations of phosphine ligands, were examined. The energies of this kind of complex, assuming an initial H–H distance of around 1.0 Å, were found in all cases to be above that of the most stable complex **1** by more than 50 kcal/mol at the MP2 level. MP4 calculations did not lead to substantial changes. Even worse, in no case was this coordination mode found to be a local minimum, even when restrictions to the position of the phosphine ligands were introduced. As for possible linear trihydrogen species, relative energies are much lower, but the structures correspond in all the cases to "transition states", or possibly higher order tops (having more than one imaginary vibrational frequency), on the potential energy hypersurface, breaking the trihydrogen unit into hydride and dihydrogen, in agreement with the RHF results for [Fe(PH$_3$)$_4$H(H$_2$)]$^+$.[11] In summary, despite the appealing features that a trihydrogen ligand could account for experimental results with the diop ligand, these theoretical results suggest strongly that its existence is not likely for this system.

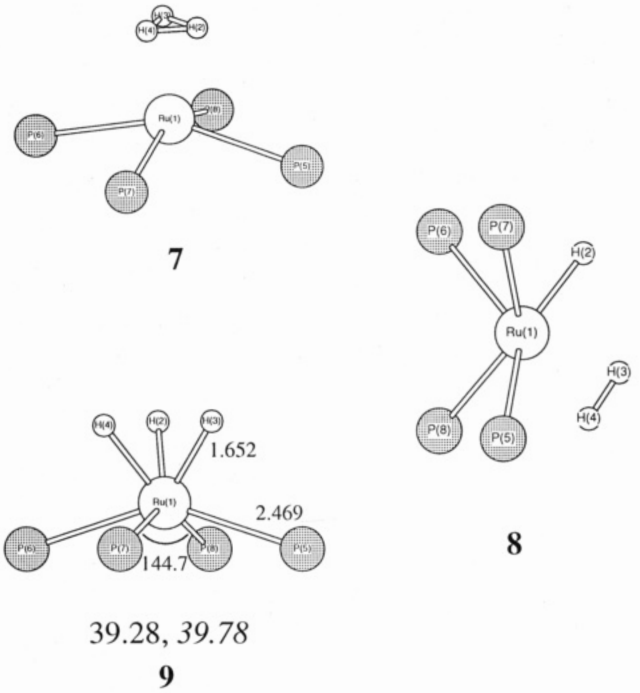

Figure 3. Geometries (in Å and deg) which were considered in calculations on the [Ru(PH$_3$)$_4$"H$_3$"]$^+$ system but did not correspond to stationary points in the potential hypersurface at the MP2 level. Energies (in kcal/mol) for complex **9** are indicated above the structure number in Roman type for the MP2 level and with italics for the MP4 level, relative to **1**. Hydrogen atoms on phosphine ligands are omitted for clarity.

Complex **8** has a six-coordinate trigonal prism geometry with C_S symmetry. Again, the relative energy is around 50 kcal/mol higher than in complex **1**. Optimization leads in all cases to one of the cis octahedral complexes in Figure 2. When this is precluded by forcing the metal atom and the three hydrogens attached to it to stay in the plane defined by the bisectors of the P(5)–Ru(1)–P(8) and P(5)–Ru(1)–P(6) angles, the outcome is the elimination of the hydrogen molecule, resulting in [Ru(PH$_3$)$_4$H]$^+$ + H_2. This trigonal prism species would have been of interest because it would be the formally simplest transition state for an octahedral fluxionality which would lead to equivalence of the phosphine ligands in the cis complex **3**. The present result simply justifies the well-known lack of fluxionality of octahedral complexes; such a fluxionality can only take place in the presence of substantial steric effects.[9]

Finally, complex **9** is the result of a geometry optimization with the RuP$_4$ fragment restricted to a local C_{4v} symmetry while the three hydrogen atoms are in a cis disposition. The resulting species is the trihydride complex presented in Figure 3. The RuH$_3$ fragment adopts spontaneously a C_{3v}-like geometry, resulting in

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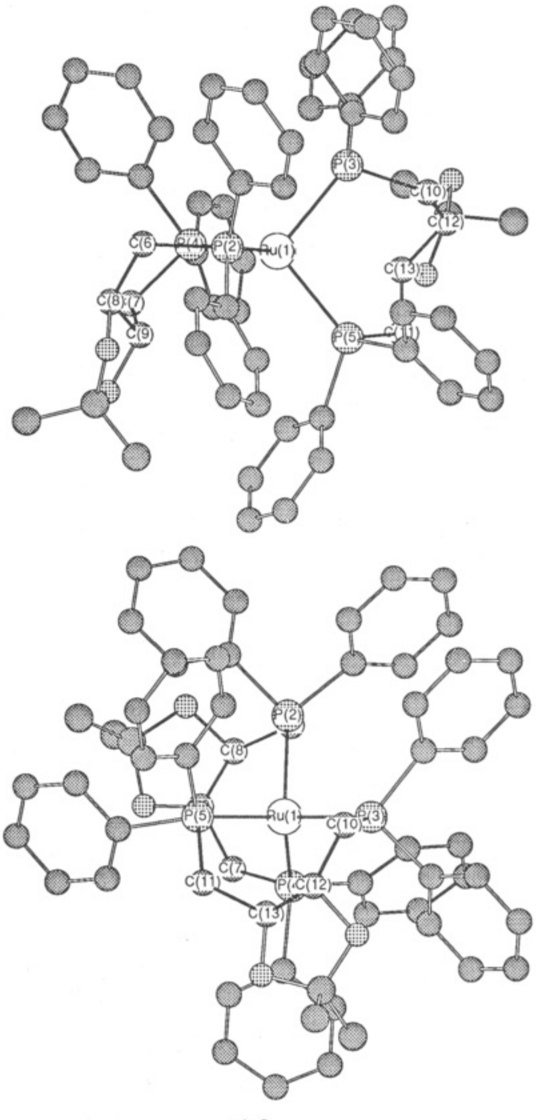
a type of seven-coordinate geometry that has been labeled as 3 + 4 by other authors.[29] This species could also be viewed as similar to the expected transition state for the fluxionality by turnstile rotation of a seven-coordinate complex.[30] In any case, the high relative energy of 39 kcal/mol at the MP4 level makes isomer **9** a poor candidate for playing any role in the chemistry of this system, unless the steric stabilization to be considered in the next section changes the situation.

The species presented in Figure 3 do not, therefore, seem to provide any clue to the identity of the unknown species in the $[Ru(diop)_2\text{“}H_3\text{”}]^+$ system. Other pentagonal-bipyramidal seven-coordinate trihydride complexes have not been considered because a fast equilibrium which involved them would likely lead to the scrambling of all the ligands in the system and would be incompatible with the existence of an equilibrium with a trans dihydrogen hydride complex as shown by experiment. In summary, the problem seems unsolvable within the framework of electronic effects alone, and steric effects must be taken into consideration.

Steric Effects. The steric energy has been evaluated for different arrangements of the phosphorus atoms around the metal in MM calculations on the $[Ru(P\text{-}P)_2]$ model system (omitting the hydrogen atoms attached to the metal, as explained in Computational Details) for each of the four diphosphine ligands presented in Chart 1: dppb, dpmb, diop, and dppe. Four of the arrangements considered (**1**, **3**, **5**, and **9**) are taken from the geometries of the corresponding model complex $[Ru(dppb)_2\text{“}H_3\text{”}]^+$ optimized with the ab initio MP2 level in the previous section. The RuP_4 skeleton is fixed at the ab initio result, with the only change of using for all Ru—P bonds the same distance, 2.4237 Å, which is the average of the computed values for the most stable structure **1**. The other two arrangements, **10** and **11**, are not ab initio local minima but local minima obtained through optimization of the position of the phosphorus atoms at the MM level, starting from different initial guesses. The first of them, **10**, corresponds to an approximately tetrahedral arrangement of the phosphorus atoms around the ruthenium center. The starting point of the second MM optimized geometry, **11**, is **3**, the cis dihydrogen hydride complex, which happens to be quite unstable at the MM level. Both geometries are presented for the particular case of the diop ligand in Figures 4 and 5, respectively. The corresponding MM geometry optimization from isomer **1** leads to no qualitative change from the starting geometry, with energy improvements always less than 6 kcal/mol. MM geometry optimizations from **5** and **9** lead to the same structures as those from **3** and **1**, respectively.

The energetics resulting from these calculations are collected in Table 1. Although these steric energies have to be added to the electronic energies for the total energy discussion, which will be done in the next section, some comments can be advanced here. For instance, the steric difference between the trans and cis dihydrogen hydride complexes **1** and **3** favors in all the cases the trans complex, always with a similar value between 7.3 and 10.9 kcal/mol. The pentagonal-bipyramidal trihydride **5** has a steric energy close to that of the cis octahedral complex **3**, with a maximum difference of 4 kcal/mol, as expected from the similarity in the geometries. A similar trend is observed for the species **9** relative to **1**. Substantial differences in the steric energy are, however, found among various diphosphine ligands for species **10** and **11**.



10

Figure 4. MM optimized geometry for isomer **10** of the $[Ru(diop)_2]$ model seen in two different orientations. The Ru—P—C—C—C—C—P fragments are highlighted by labeling only these atoms and drawing the connecting bonds in solid lines. All hydrogen atoms are omitted for clarity.

Species **10** retains an approximately tetrahedral disposition of the phosphorus atoms, as can be seen in Figure 4. The average values for the P—Ru—P angles of the chelating diphosphine ligands are 99.8° for dppb, 102.0° for diop, 99.6° for dpmb, and 77.9° for dppe. The dppe ligand, with a substantially smaller bite angle, is likely to gain less stabilization energy as one goes to the less constrained tetrahedral structure **10**. This is indeed confirmed by the energetics, which depends in this case strongly on the nature of the diphosphine ligand. A very small stabilization energy of 1.3 kcal/mol relative to **1** is found for dppe, while a substantial value of 21.8 kcal/mol is obtained for diop. Values for dppb and dpmb stay between, around 14 kcal/mol.

The geometry of species **11**, the result of MM geometry optimization from the cis complex **3**, is clearly less symmetric than that of **10**, as can be readily observed

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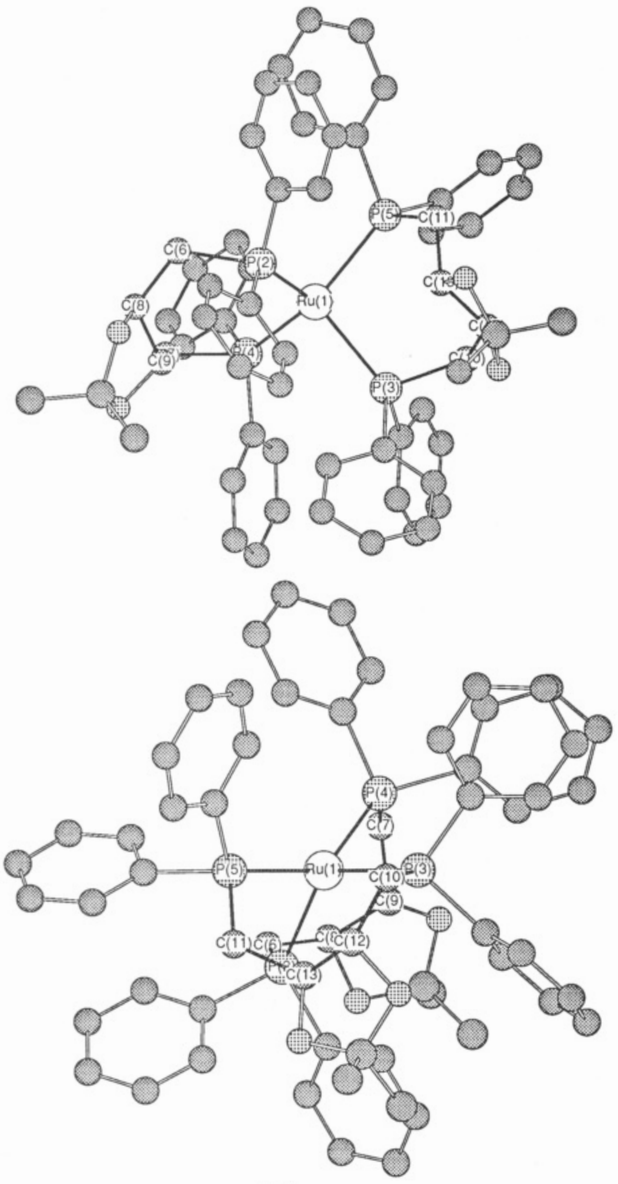
[29] Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511–522.

[30] Riehl, J.-F.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 5414–5424.



11

Figure 5. MM optimized geometry for isomer **11** of the [Ru(diop)$_2$] model seen in two different orientations. The Ru–P–C–C–C–C–P fragments are highlighted by labeling only these atoms and drawing the connecting bonds in solid lines. All hydrogen atoms are omitted for clarity.

Table 1. Relative Steric Energies (in kcal/mol) Computed for the Different Diphosphine Ligands in Different Isomers of the Model System [Ru(P-P)$_2$]

	1	3	5	9	10	11
dppb	0.0	+7.3	+8.9	+3.1	−14.1	−7.9
diop	0.0	+10.4	+11.9	+5.5	−21.8	−18.0
dpmb	0.0	+10.1	+12.1	+0.5	−14.8	−14.4
dppe	0.0	+10.9	+6.9	−1.4	−1.3	−7.1

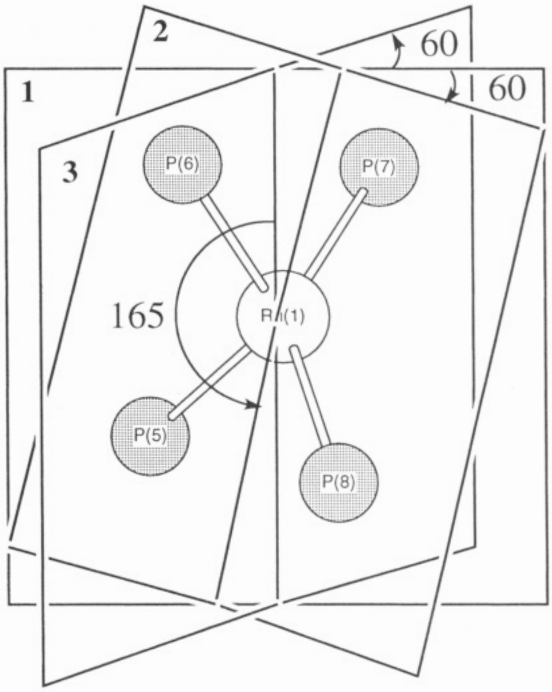


Figure 6. Illustration of the angles defining the fixed orientation of the RuP$_4$ skeleton in the ab initio calculations of isomer **11** for the [Ru(dppb)$_2$], [Ru(diop)$_2$], and [Ru(dpmb)$_2$] species. Plane 1 is defined by the bisectors of the P(5)–Ru(1)–P(8) and P(6)–Ru(1)–P(7) angles. Plane 2 contains Ru(1), P(5), and P(8), and plane 3 contains Ru(1), P(6), and P(7). The chelating ligands are P(5)–P(8) and P(6)–P(7).

in Figure 5. This structure can probably be better understood by considering its genesis in the geometry optimization from isomer **3**, using the angles shown in Figure 6. A plane can be defined by the metal atom and the bisectors of the P–Ru–P angles corresponding to each of the biphosphines. The angle between the P–Ru–P planes of each biphosphine and this plane of the bisector lines is essentially conserved between the "electronic" isomer **3** (average value of 53.3°) and the different "steric" isomers **11** (average values of 58.3° for dppb, 59.6° for diop, 58.4° for dpmb, and 53.7° for dppe). The large changes appear in the angles between the two bisector lines, which are 127.0° for **3**, 158.8° for **11**-dppb, 169.7° for **11**-diop, 168.6° for **11**-dpmb, and 136.3° for **11**-dppe. Again, the dppe ligand shows a significantly different behavior from that of the other chelating biphosphines; the angles for dppe are much closer to that for PH$_3$ than to those for chelating phosphines. Optimized bite angles P–Ru–P are similar to those of the "tetrahedral" species **10**. As for the energetics, fairly large stabilization energies (−18.0 and −14.4 kcal/mol) are found for diop and dpmb, while smaller values (−7.9 and −7.1 kcal/mol) are associated with dppb and dppe. The larger (more negative) values associated with diop and dpmb can be tentatively assigned to the combination they present of a large bite angle (absent in dppe) and a rather rigid organic chain connecting the phosphorus atoms (absent in dpmb). The more free butane ring of dppb would occupy too much space to allow for a similar stabilization energy in this diphosphine.

An explanation of these results for isomer **11** is not as straightforward as for species **10**, and interactions between the two different diphosphine ligands are probably also playing some significant role in this case. Especially puzzling is the clearly larger stability (5.8 kcal/mol) of **11** over **10** in the case of dppe; this has to be associated with a stabilizing interaction between the phenyl rings attached to different phosphorus atoms. In any case, the result which is probably more significant in the context of this paper is the substantial steric energy improvement as one goes from species **3** to **11**. Certainly, energy differences between these two species range between 15.2 and 28.4 kcal/mol. This result for the cis complex **3**, not matched by the trans complex **1**, suggests a much larger margin of steric stabilization for the former, for the which the geometry obtained from

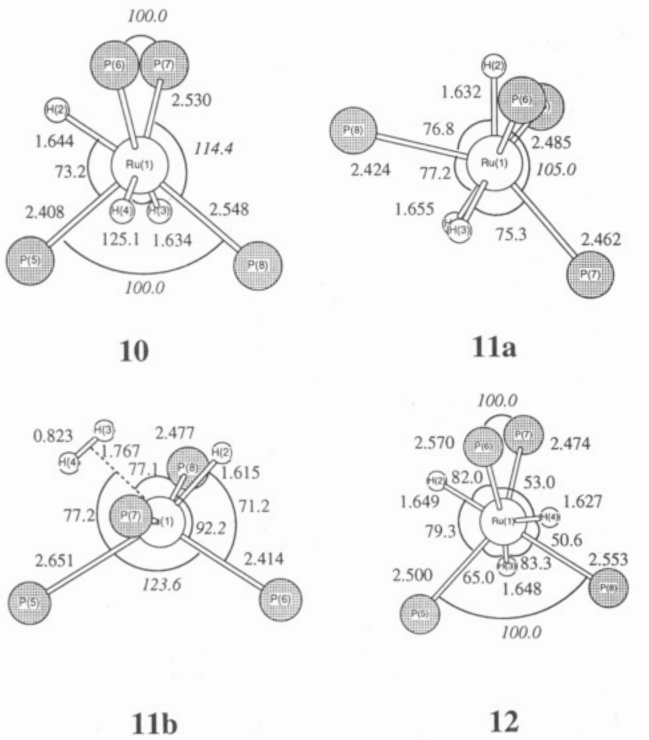


Figure 7. Structures proposed (in Å and deg) from ab initio and MM calculations for the equilibrium structures **10** (C_S), **11a** (C_1), and **11b** (C_1) and the transition state **12** (C_1). Substituents on phosphine ligands are omitted for clarity. Bond angles relating the phosphine ligands, which are not optimized in the ab initio calculation, are indicated in italics. The chelating ligands are P(5)—P(8) and P(6)—P(7).

the mere consideration of electronic effects may not be accurate enough.

Steric plus Electronic Energy. This section presents the total energies of the different isomers estimated as a sum of those presented in Figures 1–3 at the ab initio MP4 level for the $[Ru(PH_3)_4\text{“}H_3\text{”}]^+$ model system and those presented in Table 1 at the MM level for varieties of ligands. Some additional ab initio calculations are necessary to assign electronic energies to species **10** and **11**, which were obtained by the MM calculation. In order to minimize the number of computationally expensive ab initio calculations, an approximate average of the MM diphosphine geometries corresponding to dppb, diop, and dpmb ligands is assumed. In the case of the “tetrahedral” isomer **10**, this means a D_{2d} disposition for the RuP_4 fragment with bit angles of 100°. In the case of the species **11** of lower symmetry, as illustrated in Figure 6, the values assumed are 105° for the bite angle, 165° for the angle between the bisectors of the P—Ru—P angles of each diphosphine ligand, and 60° for the dihedral angle between the folding plane and the P—Ru—P planes. Corresponding calculations for the dppe case, which require a different set of coordinates, have not been performed in the case of isomer **10** because of the high steric energy for this ligand. In the case of the isomer dppe-**11**, the values used are 80° for the bite angle, 135° for the angle between bisectors, and 60° for the dihedral angles.

The geometry optimized by the ab initio calculation with the above geometrical constraints without symmetry constraint converged to C_s symmetry for isomer **10** and is shown in Figure 7. It is clearly a trihydride complex, with the shortest H—H distance of 2.60 Å. The geometry of this seven-coordinate species can be probably better viewed as an eight-coordinate dodecahedron[31] where one of the ligands in the B sites is missing. In particular, the missing ligand should be about the center of the triangle defined by the atoms P(6), P(7), and P(8). Of the two sets of four equivalent sites associated with dodecahedral coordination, all of the A sites are occupied by the phosphine ligands, while the B sites contain three hydride ligands and a lone pair. Remarkably, the geometry of the RuP_4 skeleton of this **10** isomer is in good agreement with that reported in an X-ray study on $[Ru(dppf)_2H_3]^+$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene).[32] Furthermore, although the hydrogen atoms could not be located by X-ray diffraction, this complex was predicted to be a trihydride complex from its NMR spectral properties.[31]

Table 2. Total Relative Energies (in kcal/mol), Estimated by Addition of Electronic and Steric Contributions, for the Different Diphosphine Ligands in Different Isomers of the $[Ru(P\text{-}P)_2\text{“}H_3\text{”}]^+$ System

	1	3	5	9	10	11a	11b	“13”
dppb	0.0	+13.7	+14.4	+42.9	+16.1	+15.6	+27.6	+12.4
diop	0.0	+16.8	+17.4	+45.3	+8.4	+5.5	+17.5	+7.9
dpmb	0.0	+16.5	+17.6	+40.3	+15.4	+9.1	+23.1	+10.5
dppe	0.0	+17.3	+12.4	+38.4		+29.9	+7.9	

As for **11**, things are complicated by two qualitatively different local minima, labeled as **11a** and **11b**, obtained by ab initio optimization with the above-mentioned geometry constraints. They do not have symmetry because the arrangement of the phosphines does not allow them to. For instance, in **11a**, while the P(7)—Ru(1)—P(6) angle is 105.0°, P(7)—Ru(1)—P(5) is 92.2°. These species correspond to different arrangements of the hydrogen atoms in this particular shape of the RuP_4 skeleton, as can be seen in Figure 7. Structure **11a** can be better described as a seven-coordinate capped-octahedral[33] trihydride complex, the capping ligand being the hydride labeled as H(2). Structure **11b** corresponds instead to a six-coordinate dihydrogen hydride complex. Its shape could be regarded as being roughly octahedral, although heavily distorted because of the fixed orientation of the phosphine ligands.

The total relative energies, calculated as a sum of the electronic energies from ab initio calculation of the model $[Ru(PH_3)_2H_3]^+$ complex and the steric energy in Table 1, are presented in Table 2. The trans complex **1** is the absolute minimum in all cases. Species **9**, with three equivalent hydride and four equivalent phosphine ligands, can be readily discarded because of its high energy of about 40 kcal/mol. Species **3** and **5**, the “electronic” cis dihydrogen hydride octahedral complex and its associated trihydride, also reach relative energies of over 10 kcal/mol when steric effects are introduced. The first unexpected result presented in Table 2 is probably the presence of a relatively low energy (8.4 kcal/mol) isomer **10** that exists only in the case of the diop ligand. It is interesting to check whether this

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[31] (a) Hoard, J. J.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235–243. (b) Drew, M. G. B. *Coord. Chem. Rev.* **1977**, *24*, 179–245. (c) Burdett, J. K.; Hoffmann, R.; Fay, R. C. *Inorg. Chem.* **1978**, *17*, 2553–2568.

[32] Saburi, M.; Aoyagi, K.; Kodama, T.; Takahashi, T.; Uchida, Y.; Kozawa, K.; Uchida, T. *Chem. Lett.* **1990**, 1909–1912.

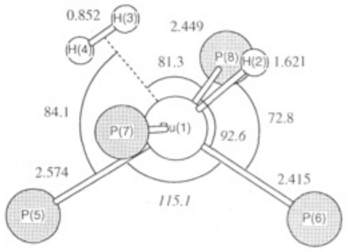
[33] (a) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67–210. (b) Kouba, J. K.; Wreford, S. S. *Inorg. Chem.* **1976**, *14*, 1463–1465. (c) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511–522.

isomer can be related to the NMR equivalence of the ligands. Such an equivalence could be accomplished if the shift reaction of one hydride ligand to the empty coordination sites were faster than the NMR time scale.

This shift reaction of one hydride ligand in complex **10** is expected to be feasible with a small energy barrier, since it is present in the experimental analog mentioned above.[31] The possible nature of the transition state is explored in some detail. As a first approach, its geometry is optimized without symmetry restriction at the ab initio level with the RuP$_4$ fragment frozen at the "tetrahedral" orientation of **10**. The resulting transition state has a high relative energy of 28.4 kcal/mol over the corresponding reactant local minimum **10** at the MP2 level. This barrier is somehow lowered through steric relaxation in the position of the phosphine ligands. For instance, a simple movement of the frozen bite angles within their respective P—M—P planes yields a stabilization of 3.2 kcal/mol. The resulting geometry, which is labeled as **12**, is included in Figure 7. This C_1 transition state is a trihydride complex, with H(4) shifting from the P(5)—P(6)—P(8) triangle in **10** to the P(6)—P(7)—P(8) triangle. Whenever more restrictions are relaxed, the ab initio calculation leads to a qualitatively different geometry similar to that of the trihydride complex **5** presented before. It seems reasonable to assume that a simultaneous consideration of steric and electronic effects should lead to a transition state, with the geometry somewhere between **12** and **5**, of substantially lower energy.

The fact that the trihydride complex **10** has a quite low relative energy only in the case of the diop ligand, coupled with its expected easy fluxionality, looks like a promising explanation of the experimental peculiarities of [Ru(diop)$_2$"H$_3$"]$^+$. Certainly, the NMR spectra to be expected from species **10** would be one single signal in both high-field ^{1}H and ^{31}P NMR spectra, since the two sets of ligands would be made equivalent by fluxionality. However, a serious objection to the assignment of the unknown species to isomer **10** is the value of the relaxation time T_1 for this complex. Although the minimum of this temperature-dependent parameter has not been determined,[12] values observed between 213 and 303 K can become as low as 31 ms.[4,12] This seems too low for a trihydride complex, especially taking into account that the analogous [Ru(dppf)$_2$H$_3$]$^+$ system has values always above 200 ms in the same range of temperatures.[31]

Other interesting results contained in Table 2 are the energetics of species **11a** and **11b**. The capped-octahedral trihydride complex **11a** presents remarkably low energies in the cases of the ligands diop (5.5 kcal/mol) and dpmb (9.1 kcal/mol), while the dihydrogen hydride complex **11b** has a low energy of 7.9 kcal/mol for the dppe ligand. As a first impression, these results seem to be at odds with the experimental data. Complex **11a** should present two different ^{1}H signals and three different ^{31}P NMR signals, and there are no obvious paths available for fluxionality. Moreover, as a trihydride complex, it should have a high T_1 value. On the other hand, **11b**, which as a cis dihydrogen hydride complex could have appealing features to explain original spectral properties, has low energy only in the case of dppe, which is known to give rise only to a trans dihydrogen hydride complex in solution. Nevertheless, the fact that the low energy of dppe-**11b** is clearly associated with the relatively small distortion of the RuP$_4$ skeleton from the "electronic" cis complex **3** provides a first clue to a possible explanation.



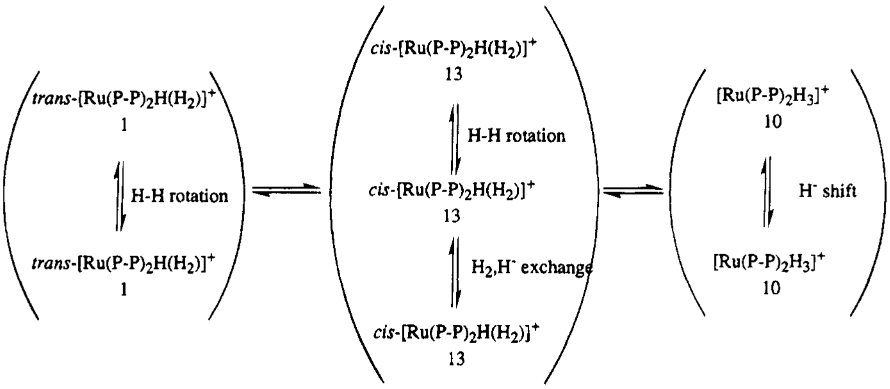
"13"

Figure 8. Structure (in Å and deg) obtained in the estimation of the shape of isomer **13** (C_1) from ab initio calculations. Substituents on phosphine ligands are omitted for clarity. Bond angles relating the phosphine ligands, which are not optimized in the ab initio calculation, are indicated in italics. The chelating ligands are P(5)—P(8) and P(6)—P(7).

Certainly, the experimental data point to the existence of a dihydrogen hydride complex different from **1** for the cases of the diop and dpmb ligands. This cannot be either the "electronic" species **3** or the "steric" species **11b**, which present relative energies over 15 kcal/mol for these two ligands. However, it could be some species with an intermediate geometry, which is perfectly reasonable if one realizes how substantially different are the arrangements of the phosphine ligands around the metal in both isomers. Unfortunately, the location of this hypothetical species, which we can label as **13**, would require the simultaneous consideration of electronic and steric effects, which is out of the reach of the applied methodology. Still, an estimative calculation can be performed, by assuming an arbitrary distribution of the RuP$_4$ skeleton intermediate between those associated with **3** and **11b**. This arbitrary distribution, labeled as **"13"**, consists of bite angles of 100°, a bisector—metal—bisector angle of 150°, and dihedral angles of 60° between the P—Ru—P planes and the folding plane. The energy of this species **"13"** is evaluated with the same algorithm followed throughout the section: ab initio optimization of the position of the hydride ligands and MM optimization of the real substituents in the chelating phosphines, always with a rigid RuP$_4$ skeleton. The resulting geometry for the RuP$_4$"H$_3$" part is presented in Figure 8. The energy calculated this way for **"13"**, presented in Table 2, is lower than those of **3** and **11b** for each of the three diphosphine ligands dppb, dpmb, and diop. Therefore, it is justified to assume the existence of the lower energy cis dihydrogen hydride complex **13**, although its geometry and energy cannot be located with the method employed. Moreover, this isomer should have a lower energy in the cases of the diop and dpmb ligands.

Once the existence of the cis dihydrogen, hydride isomer **13** is accepted for the cases of [Ru(diop)$_2$"H$_3$"]$^+$ and [Ru(dpmb)$_2$"H$_3$"]$^+$ complexes, a mechanism accounting for all the experimental and theoretical results can be proposed, as shown in Scheme 1. There are three possible chemically different stable species, the trans dihydrogen hydride complex **1**, the cis dihydrogen hydride complex **13**, and the trihydride **10**. Each of these three complexes is subject to low barrier fluxional processes depicted by the vertical lines, which give rise

Scheme 1



to different NMR equivalences. For the trans complex **1**, the result is two signals in ^{1}H and one in ^{31}P spectra. For the cis complex **13**, the result is one kind of hydrogen and two kinds of phosphorus signals. Finally, for the trihydride complex **10**, the corresponding spectra consist of one signal for each of the two elements. The energy barrier between trans and cis complexes **1** and **13** is always too high for fluxionality at low temperature, allowing separation of the two species when they coexist in solution, which would be the case for [Ru(diop)$_2$"H$_3$"]$^+$. In the other cases, only one of the isomers would be present in solution, trans for P-P = dppb, dppe and cis for P-P = dpmb. The difference between diop and dpmb ligands in the behavior of the cis isomers **13** comes from the equilibrium with the trihydride **10**, which exists and has a low energy barrier only in the case of diop. The existence of **1** for diop but not for dpmb is in contradiction with the relative energies of **1** and "**13**" shown in Table 2. Again, this can also be attributed to the lack of accuracy in the quantitative characterization of isomer **13**.

The weak point of the reasoning in the previous paragraph is, of course, the failure of the calculations presented here to theoretically find the cis complex **13**. This failure can be justified nevertheless by the limitations of the approach applied. The separate consideration of steric and electronic effects works properly when one of the two is clearly dominant. Electronic effects define the structure of species **1**, while steric effects play the main role in **10**. If species **13** were the product of a subtle compensation between electronic and steric effects, the determination of its structure and energy would lie out of the range of the present methodology of simply combining ab initio and MM results. The existence of such a species can find some indirect backing from the highly distorted experimental structure of the six-coordinate dihydride complex [Fe(P(OEt)$_2$Ph)$_4$H$_2$].[34]

Conclusions

The combined application of the ab initio and molecular mechanics methods to the series of [Ru(P-P)$_2$"H$_3$"]$^+$ (P-P = dppb, diop, dpmb, dppe) complexes sheds some light on the complicated nature of these species in solution. The mechanism in Scheme 1, which seems better fitted to all the available experimental and theoretical results, postulates as the main species an essentially octahedral six-coordinate trans dihydrogen hydride complex and a fairly distorted six-coordinate cis dihydrogen hydride complex. A third species, a trihydride complex with essentially tetrahedral disposition of the phosphorus atoms, would also exist as an intermediate in the case of the [Ru(diop)$_2$"H$_3$"]$^+$ system. Although the calculations reported here cannot rule out all other possible mechanisms, they do provide a strong argument against the existence in this system of intermediates containing triangular trihydrogen H$_3$ as a ligand. A six-coordinate species with trigonal-prism shape is also unlikely.

The peculiar behavior of complexes with diphosphine ligands derived from dppb, such as diop and dpmb, seems to be associated with their relatively large bite angles. Optimal values determined here of around 100° are clearly different from the optimal value around 80° computed for the more common ligand dppe. The larger value is likely to make the system more sensitive to steric effects, which favor the cis complex. The ligand with a larger tendency to open the P—Ru—P angle, diop, is proposed to be the only one that gives rise to the trihydride complex with the phosphines in a tetrahedral disposition.

Finally, it must be said that these results do not pretend to provide a definite answer to all the questions concerning the true nature in solution of [M(P-P)$_2$"H$_3$"]$^+$ complexes. They could hardly do so, since only a very particular series of complexes has been studied, and some fundamental processes, such as the equilibrium itself between the trans and cis complexes, have not even been considered. The goal of this work is, rather, the presentation of a series of theoretical results and, based on them, the construction of a plausible mechanism, the validity of which will have to be monitored with future experimental and theoretical studies in this field.

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