A DFT study of germane activation in ruthenium complexes. σ-Coordination *versus* oxidative addition

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The coordination of GeH_4 to the ruthenium complex $RuH_2(\eta^2\text{-}H_2)_2(PH_3)_2$ can lead to oxidative addition or σ-bond coordination of the germane. The corresponding germyl or σ-isomers have been optimized by DFT using the B3LYP hybrid functional. The most stable isomer corresponds to a germyl bis(dihydrogen) complex $RuH(GeH_3)(\eta^2\text{-}H_2)_2(PH_3)_2$ (**1T-b1**) with *trans* phosphines. It is only 2 kcal mol^{-1} below the σ-isomer $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}H–GeH_3)(PH_3)_2$ (**1C-a1**). This is in contrast to what has been previously observed in the corresponding silane chemistry, in which σ-coordination was favoured. However, calculated binding energies for GeH_4 or SiH_4 to the $RuH_2(H_2)(PH_3)_2$ fragment are very similar (−21.3 and −22.2 kcal mol^{-1}, respectively). The nature of the metal–germane interaction is analysed by natural bond orbital (NBO) calculations.

Introduction

The activation of σ-H–E bonds (E = H, C, Si) as a result of the reactivity of dihydrogen, alkanes or silanes with transition metal complexes has been extensively studied both experimentally and theoretically.[1] Several types of complexes can be obtained depending on the degree of activation of the σ-H–E bond, among which the corresponding σ-complex and the species resulting from oxidative addition of the substrate represent the more important species. However, it is sometimes difficult to discriminate between these two limiting compounds. This has been the case for many years for the dihydrogen formulation *versus* its polyhydride analog.[1a,2] More recently, the existence of secondary interactions playing a major role in silane chemistry has been evidenced.[3] In this context, theoretical studies represent a tool of major importance.

It is noteworthy that the chemistry related to the analogous germane compounds is less documented by far.[1a] Some of us have previously reported one example of a ruthenium complex resulting from the activation of $HGePh_3$.[4] The complex $RuH_2(\eta^2\text{-}H_2)(HGePh_3)(PCy_3)_2$ was obtained by addition of the germane to the bis(dihydrogen) complex $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$. It was tentatively formulated as a dihydrogen (germane) complex on the basis of NMR data. In the more recent years, we have been able to fully characterize the analogous silane complex $RuH_2(\eta^2\text{-}H_2)(HSiPh_3)(PCy_3)_2$, in particular by X-ray and theoretical data.[5] We now report a theoretical study on the coordination of a germane to a ruthenium complex leading to the dihydrogen or dinitrogen species $RuH_2(L)(GeH_4)(PH_3)_2$ (L = H_2 or N_2). We have used GeH_4 and $RuH_2(\eta^2\text{-}H_2)_2(PH_3)_2$ as models of the starting experimental compounds $HGePh_3$ and $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$, respectively. This study allows a direct comparison between silane and germane activation.

Computational details

The theoretical treatment of the different systems included in this work was performed by using the DFT/B3LYP approach implemented in the Gaussian98 series of programs.[6] The B3LYP hybrid functional[7] has been found to be quite reliable in describing potential energy surfaces (PES) and binding energies in ruthenium complexes.[3,5,8]

For ruthenium, the core electrons were represented by a relativistic small-core pseudopotential determined according to the Durand–Barthelat method.[9] The sixteen electrons corresponding to the 4s, 4p, 4d, and 5s atomic orbitals were described by a (7s, 6p, 6d) primitive set of Gaussian functions contracted to [5s, 5p, 3d]. Standard pseudopotentials developed in Toulouse were used to describe the atomic cores of nitrogen, germanium and phosphorus.[10] A double-zeta plus polarization valence basis set was employed for each atom (d-type function exponents were 0.95, 0.25 and 0.45, respectively). For hydrogen, a standard (4s) primitive basis contracted to [2s] was used. A p-type polarization function (exponent 0.90) was added for the hydrogen atoms directly bound to ruthenium. The geometries of the different species under consideration were optimized using analytic gradient. The harmonic vibrational frequencies of the different stationary points of the PES have been calculated at the same level of theory in order to identify the local minima as well as to estimate the corresponding zero-point vibrational energy (ZPE). Binding energies of the GeH_4 ligand on the unsaturated fragment $RuH_2(L)(PH_3)_2$ (L = H_2, N_2) were also calculated.

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The nature of the metal–germane interaction was analyzed using natural bond orbital (NBO) calculations.[11]

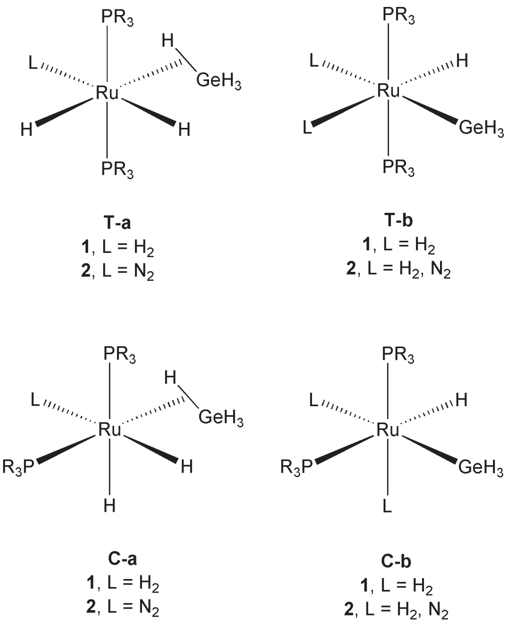
Results and discussion

We will adopt a systematic numbering for isomers of the type $RuH_2(L)(GeH_4)(PH_3)_2$with $L = H_2$ or N_2 (see Scheme 1). These isomers contain six ligands which can be arranged around the ruthenium in a pseudo-octahedral structure. They will be denoted **1** for H_2 isomers and **2** for N_2 isomers. The letters **T** and **C** are used to represent the phosphine positions, *i.e.* **T** for *trans* and **C** for *cis* position. We have examined the two different types of activation of the Ge–H bond leading either to σ-complexation or oxidative addition. We will attribute the letter **a** or **b** to these two possibilities, respectively. So we will have the series **1T-a**, **1T-b**, **1C-a**, **1C-b** for $L = H_2$ and **2T-a**, **2T-b**, **2C-a**, **2C-b** for $L = N_2$. In each series, we can add a serial number corresponding to the relative position of the other ligands in the equatorial plane. When an isomer of the series **nC** differs from another only by rotating the Ge–H bond in the equatorial plane, we add a prime to its name. We do the same in the series **2** in the case of two isomers containing a dihydrogen and a dinitrogen ligand, which differ only by the interchange of these two ligands.

All the described isomers are local minima on their respective potential energy surfaces. We will begin by a description of the B3LYP-optimized geometry of all isomers for each series. We will conclude by a comparative analysis of germane *versus* silane activation.

Optimized geometries and relative stabilities

Dihydrogen isomers. Optimized geometries are depicted in Fig. 1 for isomers with *trans* phosphines and in Fig. 2 for isomers with *cis* phosphines. Values of selected geometrical parameters are listed in Tables 1 and 2. Relative energies as well as corrections of zero point energy, thermal enthalpy and free energy differences for the different isomers are gathered in Table 3. The most stable isomer $RuH(GeH_3)(\eta^2\text{-}H_2)_2(PH_3)_2$ (**1T-b1**) is characterized by a *trans* position of the two phosphines. It is a bis(dihydrogen) complex resulting from the oxidative addition of the germane to produce a hydrido(germyl) species. It is remarkable that the most stable isomers are germyl species (series **b**) whereas the most stable isomer of the **a** series is $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}H\text{–}GeH_3)(PH_3)_2$ (**1C-a1**). In the case of the corresponding silane complexes, the situation is reversed as the most stable isomer $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}H\text{–}SiH_3)(PH_3)_2$ is 1.9 kcal mol^{-1} below the silyl species $RuH(SiH_3)(\eta^2\text{-}H_2)_2(PH_3)_2$.[5] In that case, the X-ray structure was in total agreement with an isomer of type **C-a1** with the phosphines in *cis* position.



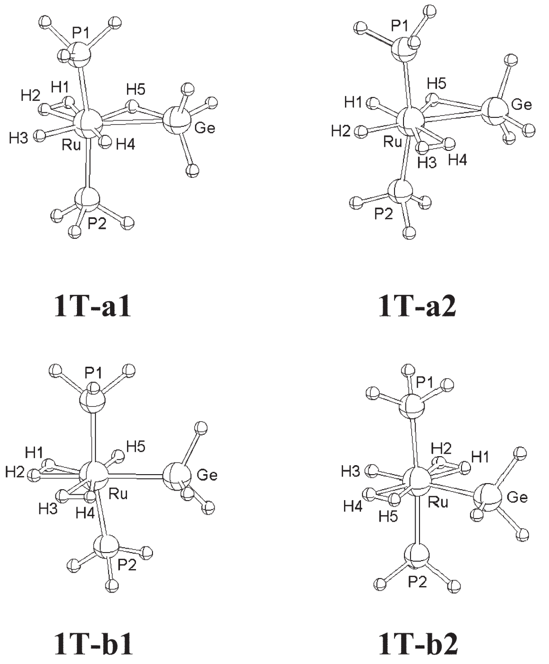
T-a
1, $L = H_2$
2, $L = N_2$

T-b
1, $L = H_2$
2, $L = H_2$, N_2

C-a
1, $L = H_2$
2, $L = N_2$

C-b
1, $L = H_2$
2, $L = H_2$, N_2

Scheme 1 Systematic numbering of the various isomers.



1T-a1 **1T-a2**

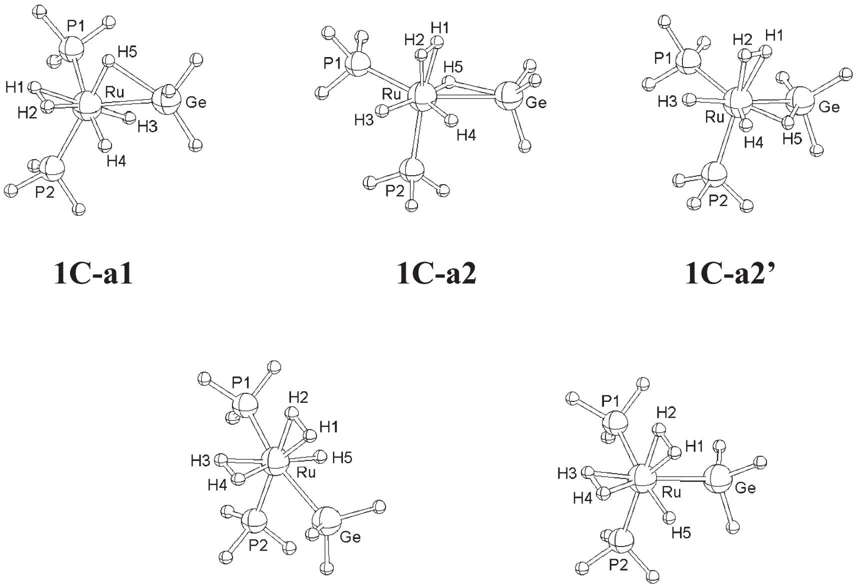
1T-b1 **1T-b2**

Fig. 1 DFT/B3LYP optimized geometries of *trans* isomers of $RuH_2(H_2)(GeH_4)(PH_3)_2$ (**1T**).

In the **a** series, the (η^2-H–Ge) coordination mode is confirmed by a significant lengthening of the Ge–H5 bond compared to the Ge–H bond length in free GeH_4 (1.565 Å) calculated at the same level of theory. This lengthening is equal to 30.5% and 27.8% for the **1C-a1** and **1C-a2** isomers, respectively, and reaches a value of 42.5% for **1C-a2′**. Note that a comparable value of 30.6% has been calculated for the Si–H lengthening in the silicon analog of **C-a1** type. This testifies to a comparable activation of the E–H bond (E = Si, Ge) by the complexation process in the most stable isomer of the **a** series. Less important elongations have been obtained for the **1T-a1** (15.8%) and **1T-a2** (17.6%) isomers which are slightly higher in energy with respect to **1C-a1** by 1.5 and 1.9 kcal mol^{-1}, respectively (see Table 3 for ΔG^0 values).

The greatest stability of the *cis* isomer **1C-a1** among the **a** isomers can be easily understood if we remark that the geometry of this isomer allows the two other hydrides H3 and H4 to be at a distance from the germanium atom shorter than the sum of the van der Waals radii of hydrogen and germanium. Although not exactly known, a reasonable value of 2.15 Å for the van der Waals radius of Ge can be inferred from the values of 2.10 Å and 2.17 Å given for silicon and tin atoms,[12] respectively. Indeed the calculated Ge···H3 and Ge···H4 distances, 2.292 Å and 2.246 Å, respectively, are much shorter than the sum of the van der Waals radii (3.35 Å). These weak secondary interactions between Ge and the hydrides H3 and H4 are responsible for the *cis* geometry of the two phosphines. Such interactions are precluded or at least reduced in the other **a** isomers. A similar role of secondary interactions has been evidenced in silane complexes (SISHA interactions).[3b]

All isomers of the **a** series bear two different η^2-coordinated σ bonds, a Ge–H bond and a H–H bond. The dihydrogen ligand is characterized by a bond length ranging from 0.840 Å (**1T-a1**) to 0.893 Å (**1C-a2**). This increase in the H–H distance under complexation is quite comparable to that



1C-a1 **1C-a2** **1C-a2’**

1C-b1 **1C-b2**

Fig. 2 DFT/B3LYP optimized geometries of *cis* isomers of $RuH_2(H_2)(GeH_4)(PH_3)_2$ (**1C**).

calculated in $RuH_2(H_2)_2(PH_3)_2$ (0.854 Å)[2b] and is in agreement with an unstretched dihydrogen complex. We can conclude that the substitution of one dihydrogen by a germane ligand has no significant effect on the activation of the other dihydrogen. Isomers of the **b** series contain two dihydrogen ligands with comparable values of H–H bond lengths. These H_2 ligands are equally activated.

In the present system, PH_3 models PCy_3 used experimentally. In order to study the effect of the phosphine ligands on the geometries and the relative stabilities of the lowest isomers, we have optimized the analogs of **1T-b1** and **1C-a1** using as a more realistic model of PCy_3, the trimethylphosphine. The calculated free energy difference (5.0 kcal mol^{-1}) between the two isomers remains in favour of the germyl *trans* species $RuH(GeH_3)(\eta^2\text{-}H_2)_2(PMe_3)_2$. We can notice that in the η^2-H–Ge *cis* complex, the activated Ge–H bond undergoes a lengthening of 32.3% very similar to that observed in the **1C-a1** isomer. As previously, the two hydrides H3 and H4 are located at 2.321 Å and 2.216 Å, respectively, from germanium, indicating the presence of weak secondary interactions.

Dinitrogen isomers

For the dinitrogen species, twelve isomers have been identified on the corresponding PES. The optimized geometries of the four isomers with *trans* phosphines are shown in Fig. 3 and those of the eight isomers with *cis* phosphines are gathered in Fig. 4. Values of the most important bond lengths and angles are presented in Tables 4 and 5. Relative energies for all isomers are listed in Table 6. As in the previous dihydrogen germane complex, the most stable isomers are germyl species

Table 1 B3LYP optimized geometrical parameters[a] for the *trans* isomers of $RuH_2(H_2)(GeH_4)(PH_3)_2$

	1T-a1	1T-a2	1T-b1	1T-b2
Ru–H1	1.835	1.610	1.759	1.709
Ru–H2	1.804	1.632	1.786	1.701
Ru–H3	1.640	1.797	1.820	1.656
Ru–H4	1.611	1.828	1.791	1.712
Ru–H5	1.715	1.664	1.618	1.719
Ru–Ge	2.622	2.667	2.543	2.593
Ge···H3	4.104	3.393	3.496	4.247
Ge···H4	2.541	2.667	2.791	3.473
Ge–H5	1.813	1.840	2.737	2.718
H1–H2	0.840	2.014	0.868	0.924
H2···H3	2.084	2.080	2.139	2.026
H3–H4	2.063	0.850	0.852	2.025
H4–H5	2.767	3.000	3.341	0.907
Ru–P1	2.319	2.319	2.324	2.331
Ru–P2	2.319	2.319	2.324	2.331
P1–Ru–P2	164.3	165.8	169.0	175.1
Ru–H5–Ge	95.9	99.0	65.7	67.2
H1–Ru–H2	26.7	76.8	28.3	31.4
H2–Ru–H3	74.3	74.5	72.8	74.2
H3–Ru–H4	78.8	27.1	27.3	73.9

[a] Distances are in Å and angles in degrees. See Fig. 1 for labelling of the atoms.

Table 2 B3LYP optimized geometrical parameters[a] for the *cis* isomers of $RuH_2(H_2)(GeH_4)(PH_3)_2$

	1C-a1	C-a2	1C-a2′	1C-b1	1C-b2
Ru–H1	1.802	1.739	1.736	1.723	1.722
Ru–H2	1.778	1.710	1.722	1.744	1.755
Ru–H3	1.627	1.651	1.644	1.814	1.786
Ru–H4	1.639	1.616	1.604	1.791	1.760
Ru–H5	1.645	1.673	1.618	1.616	1.627
Ru–Ge	2.513	2.565	2.591	2.558	2.535
Ge–H3	2.292	4.034	4.206	3.540	4.317
Ge–H4	2.246	2.460	3.701	2.841	4.204
Ge–H5	2.042	2.00	2.230	2.801	2.756
H1–H2	0.855	0.893	0.885	0.887	0.876
H3–H4	2.295	2.047	1.890	0.856	0.870
Ru–P1	2.367	2.390	2.392	2.350	2.384
Ru–P2	2.360	2.310	2.310	2.307	2.304
P1–Ru–P2	98.3	96.7	96.1	93.6	95.1
Ru–H5–Ge	85.2	88.1	83.0	64.4	64.8
H1–Ru–H2	27.6	30.0	29.7	29.6	29.2
H2–Ru–H3	162.1	72.9	76.1	87.0	86.2
H3–Ru–H4	89.3	77.6	71.2	27.5	28.4
H4–Ru–H5	98.7	118.3	63.4	160.2	76.5

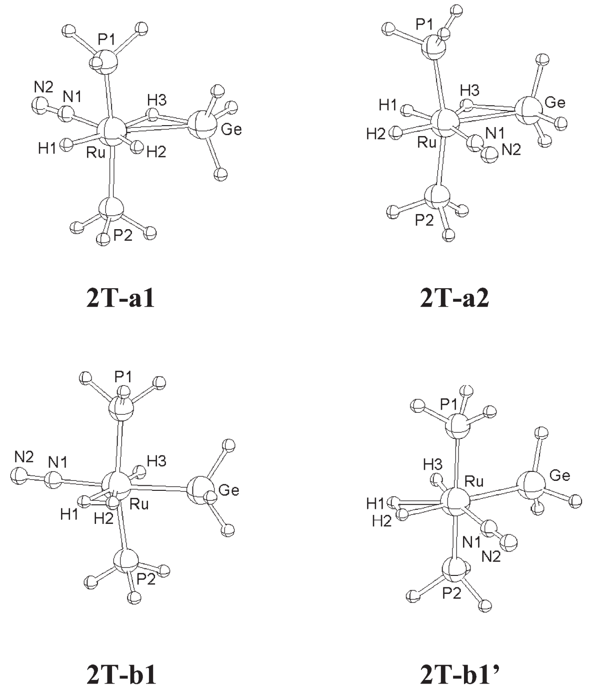
[a] Distances are in Å and angles in degrees. See Fig. 2 for labelling of the atoms.

Table 3 Relative energies (kcal mol^{-1}) of $RuH_2(H_2)(GeH_4)(PH_3)_2$ isomers calculated at the DFT/B3LYP level

Isomer	ΔE	ΔE + ZPE	$\Delta H°$	$\Delta G°$
1T-b1	0.0	0.0	0.0	0.0
1C-b1	1.3	1.8	1.7	2.1
1C-b2	1.8	1.8	1.8	2.5
1C-a1	2.0	1.8	1.6	2.0
1C-a2′	3.9	3.4	3.3	3.5
1T-a1	4.3	3.8	3.9	3.5
1T-a2	4.7	4.0	4.0	3.9
1C-a2	4.9	4.5	4.4	4.6
1T-b2	6.5	5.9	6.1	5.1

and can be formulated as $RuH(GeH_3)(\eta^2\text{-}H_2)(N_2)(PH_3)_2$. Among these **b** isomers, the two isomers with the phosphines in *trans* position (isomer of **T** type) are slightly more stable than the others. Isomers **2T-b1′** and **2T-b1** are quasi-degenerated in energy, the latter being only 1 kcal mol^{-1} above **2T-b1′**. They differ by the position of the germyl ligand which is *trans* to the dinitrogen in **2T-b1** and *trans* to the dihydrogen in **2T-b1′**.

The most stable isomer of the **a** series (**2C-a1**) is only 1.7 kcal mol^{-1} above **2T-b1′**. The geometry of this isomer is characterized by a *cis* position of the phosphines with the three hydrogen atoms oriented toward germanium, two of them being at the same distance from this atom (Ge–H2 = 2.097 Å and Ge–H3 = 2.099 Å). These distances correspond to a lengthening of the two Ge–H bonds by 34%, indicating the presence of two bridging Ru–H–Ge interactions. The third hydride H1 is at a distance from the germanium center significantly greater than H2 and H3, but shorter than the sum of the van der Waals radii of H and Ge (Ge···H1 = 2.339 Å), suggesting one weak secondary interaction in isomer **2C-a1**. The molecular structure of **2C-a1** can be viewed as an intermediate structure between two bonding situations, the first one with two hydrides and an η^2-H–Ge bond and the second one with a dihydrogen and a germyl ligand as in isomer **2C-b1**.



2T-a1 **2T-a2**

2T-b1 **2T-b1’**

Fig. 3 DFT/B3LYP optimized geometries of *trans* isomers of $RuH_2(N_2)(GeH_4)(PH_3)_2$(**2T**).

The *trans* isomers **2T-a1** and **2T-a2** are above **2C-a1** by 2.7 kcal mol^{-1} and 2.0 kcal mol^{-1}, respectively. They present a lesser activation of the Ge–H bond. The two other *cis* isomers of the **a** series, *i.e.* **2C-a2** and **2C-a2′**, are the highest in energy (5.2 kcal mol^{-1} and 6.0 kcal mol^{-1} above **2T-b1′**, respectively). This can be easily understood if we remark that in **2C-a2**, the Ge–H3 bond is lesser elongated (by 17.5%) and that it remains only one weak secondary interaction Ge···H2. In the case of **2C-a2′**, the Ge–H3 bond is elongated by 33% as usual, but there is no secondary interaction between the two hydrides H1 and H2 and germanium.

In all isomers, dinitrogen is end-on coordinated to ruthenium as it is usual in ruthenium dinitrogen complexes.[14] The N–N bond is lengthened by about 1%, indicating a weak activation of the N_2 ligand in these mixed complexes.

Thermodynamic analysis

Binding energies. In order to compare silane *versus* germane activation, we will calculate the binding energy of GeH_4 on the $RuH_2(L)(PH_3)_2$ fragment in the most stable σ-germane isomers **1C-a1** (L = H_2) and **2C-a1** (L = N_2). We will note Δ_rE the energy difference associated with the following equation:

$$RuH_2(L)(PH_3)_2 + GeH_4 \rightarrow RuH_2(L)(\eta^2\text{-}H\text{–}GeH_3)(PH_3)_2$$

The Δ_rE values as well as the zero point energy corrected values and the thermal enthalpies at the standard conditions (298.15 K and 1 atm) have been calculated. The Δ_rE values calculated for **1C-a1** and **2C-a1** are −21.3 and −19.1 kcal mol^{-1} respectively (−20.6 and −17.4 kcal mol^{-1} with ZPE corrections). We can see that the binding energy of GeH_4 is slightly weaker in the case of L = N_2. The same tendency can be observed with the Δ_rH^0 values (−19.6 and −17.7 kcal mol^{-1}). This indicates that the presence of dinitrogen as spectator ligand does not reinforce the GeH_4 binding.

This binding energy of GeH_4 can be compared with the binding energy calculated for SiH_4 coordinated to the same metallic fragment $RuH_2(H_2)(PH_3)_2$ using the same theoretical procedure[13] (Δ_rE value of −22.2 kcal mol^{-1} and Δ_rH^0 value of −20.4 kcal mol^{-1}). We can conclude that the bonding mode of the germane and silane ligands are quite similar.

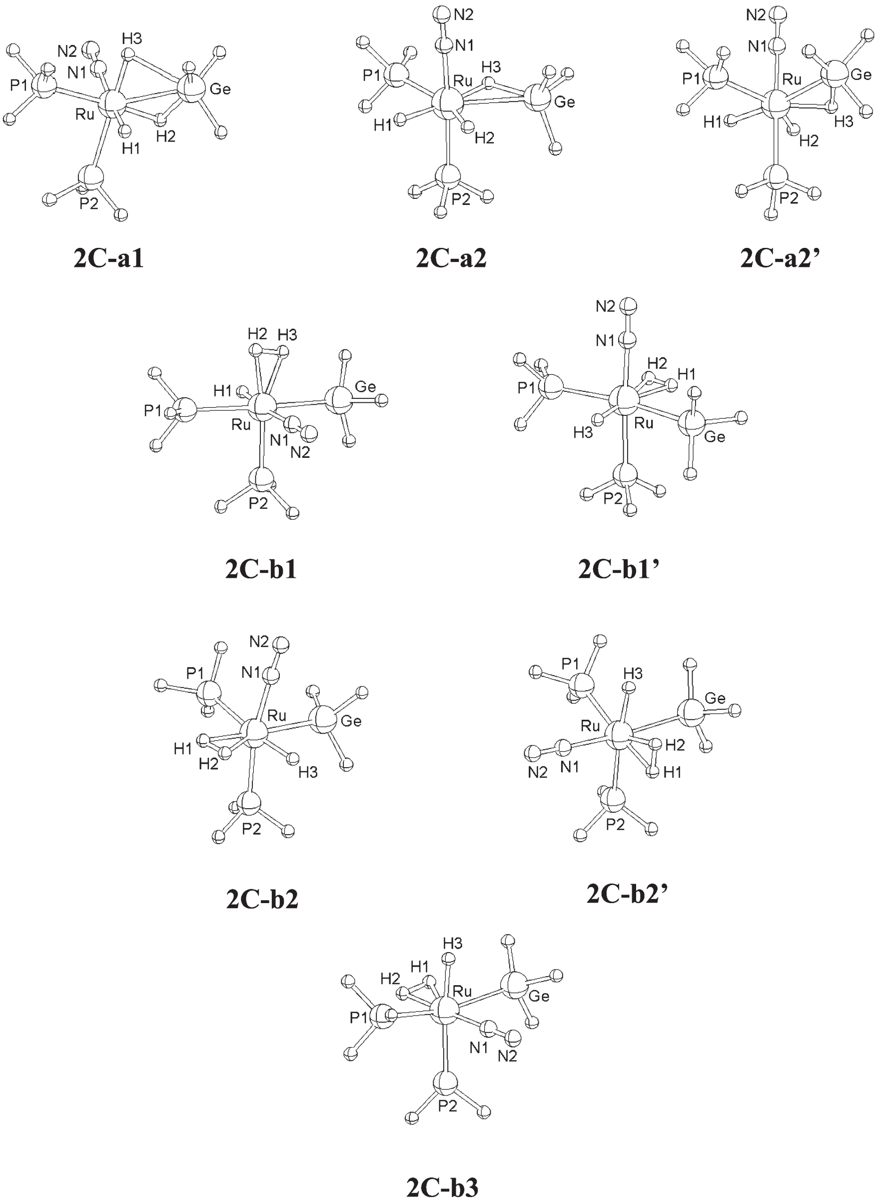
Substitution reactions

One of the dihydrogen ligands of $RuH_2(\eta^2\text{-}H_2)_2(PH_3)_2$ can be replaced by a σ Ge–H bond according to the following equation:

$$RuH_2(\eta^2\text{-}H_2)_2(PH_3)_2 + H\text{–}GeH_3 \rightarrow RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}H\text{–}GeH_3)(PH_3)_2 + H_2$$

This substitution reaction leads to **1C-a1** which is not the most stable isomer. Then oxidative addition of the η^2-H–Ge bond can take place leading to the bis(dihydrogen) germyl isomer **1T-b1**. The B3LYP calculated thermodynamic quantities associated with the entire process are: $\Delta_rE = -5.3$ kcal mol^{-1}, $\Delta_rH^0 = -5.9$ kcal mol^{-1} and $\Delta_rG^0 = -4.4$ kcal mol^{-1}. These negative values indicate that the reaction is exothermic. This is in agreement with the experimental observation since this reaction is a model for the synthesis of the complex obtained by addition of $HGePh_3$to $RuH_2(H_2)_2(PCy_3)_2$.[4]

The same thermodynamic quantities have been calculated for the substitution of one dihydrogen of $RuH_2(\eta^2\text{-}H_2)_2$-$(PH_3)_2$ by a η^2-H–Si bond, leading to the silane analog of **1C-a1**. Recall that in that case, the η^2-complex is the most stable isomer. The B3LYP calculated values are: $\Delta_rE = -4.1$ kcal mol^{-1}, $\Delta_rH^0 = -5.0$ kcal mol^{-1}. The same conclusion can be deduced on the ease of dihydrogen elimination from $RuH_2(\eta^2\text{-}H_2)_2(PH_3)_2$ to coordinate a H–Si bond.



2C-a1 2C-a2 2C-a2’

2C-b1 2C-b1’

2C-b2 2C-b2’

2C-b3

Fig. 4 DFT/B3LYP optimized geometries of *cis* isomers of $RuH_2(N_2)(GeH_4)(PH_3)_2$ (**2C**).

We have also considered a substitution reaction with dinitrogen. The bis(dihydrogen) germyl compex (**1T-b1**) can react with dinitrogen to form a mixed complex in which one dihydrogen is replaced by dinitrogen (**2T-b1′**):

$$\mathrm{RuH(H_2)_2(GeH_3)(PH_3)_2 + N_2 \rightarrow RuH(H_2)(N_2)(GeH_3)(PH_3)_2 + H_2}$$

The thermodynamic quantities associated with this substitution reaction are: $\Delta_r E = 0.5$ kcal mol^{-1}, $\Delta_r H^0 = -0.6$ kcal mol^{-1} and $\Delta_r G^0 = 0.8$ kcal mol^{-1}. The $\Delta_r G^0$ value is close to zero, indicating that this reaction is reversible. We have observed the same behavior[14] for the direct substitution reaction of dihydrogen by dinitrogen in $RuH_2(\eta^2\text{-}H_2)_2(PH_3)_2$.

NBO analysis

We have reported in Table 7 the natural charges q, the Wiberg bond indices[15] W and the natural orbital occupancies for $RuH_2(H_2)(GeH_4)(PH_3)_2$ (isomers **1C-a1** and **1T-b1**) and for $RuH_2(N_2)(GeH_4)(PH_3)_2$ (isomers **2C-a1** and **2T-b1′**). We will discuss the conventional indices which are frequently used to characterize the bonding situation in complexes, *i.e.* atomic charges and bond orders. The calculated charge distribution shows that ruthenium always carries a negative charge while the Ge atom is positively charged. In free GeH_4, each Ge–H bond is polarized ($^{+0.61}$Ge–H$^{-0.15}$). We can notice that both in **1C-a1** and **2C-a1**, the positive charge of Ge is increased to +0.74 under complexation so that the GeH_4 ligand becomes positively charged (net charge of +0.17). This indicates an overall electron transfer from GeH_4 toward the metallic fragment $RuH_2(L)(PH_3)_2$. If we suppose that the bonding mode of GeH_4 is identical to that already reported for SiH_4, this global electron transfer is the result of two transfers, *i.e.* a σ-donation from a σ Ge–H bond orbital to the ruthenium and a back-bonding from an adequate *d* orbital of the metal to the σ* Ge–H orbital. We can conclude that in our **a** isomers, σ-donation is more important than back-bonding. The relative values of these two transfers can indeed be deduced from the NBO orbital occupancies. For isomers **1C-a1** and **2C-a1**, the Ge–H σ bond lost 0.59 and 0.62 electron, respectively, meanwhile the σ* orbital presents an occupancy of 0.32 and 0.35 electron. This result is coherent with the positive charge of the GeH_4 ligand.

For isomer **1C-a1**, the Wiberg bond index associated with the η^2-Ge–H5 bond is strongly decreased compared to free

Table 4 B3LYP optimized geometrical parameters[a] for the *trans* isomers of $RuH_2(N_2)(GeH_4)(PH_3)_2$

	2T-a1	**2T-a2**	**2T-b1**	**2T-b1′**
Ru–H1	1.634	1.603	1.841	1.765
Ru–H2	1.611	1.638	1.802	1.803
Ru–H3	1.735	1.642	1.615	1.614
Ge–H1	4.144	3.584	3.494	4.208
Ge–H2	2.568	4.267	2.790	4.339
Ge–H3	1.760	1.912	2.783	2.782
H1–H2	2.097	1.988	0.843	0.860
Ru–N1	2.083	2.083	2.055	2.080
Ru–Ge	2.650	2.640	2.539	2.538
N1–N2	1.117	1.117	1.119	1.118
Ru–P1	2.320	2.324	2.327	2.327
Ru–P2	2.320	2.324	2.327	2.326
P1–Ru–P2	161.8	165.9	167.3	166.7
H1–Ru–H2	80.5	75.7	26.7	27.9
H2–Ru–H3	110.3	142.5	158.8	102.5
H3–Ru–H1	169.2	66.9	174.5	74.7
Ru–N1–N2	176.6	176.7	177.3	177.8

[a] Distance are in Å and angles in degrees. See Fig. 3 for labelling of the atoms.

GeH_4 (0.28 *versus* 0.96). This is correlated with the important elongation of the Ge–H5 bond already mentioned. It is interesting to note that the Wiberg bond indices corresponding to the secondary interactions Ge···H3 and Ge···H4 (0.15 and 0.19, respectively) have smaller but non zero values, indicating the presence of electrostatic interactions between the classical hydrides and the positively charged Ge atom. The situation is comparable in the **2C-a1** isomer. The Wiberg bond index of the η^2-Ge–H3 activated bond is equal to 0.29. However the value of the bond index corresponding to the Ge···H2 secondary interaction is of the same order of magnitude (0.25), showing that it would be better to consider that in this complex, H2 and H3 play a similar role.

Isomer **1C-a1** is a mixed σ-(H–H) and σ-(H–Ge) complex, thus allowing the comparison of the bonding nature of a dihydrogen and a germane coordinated to the same ruthenium atom. For the η^2-H_2 bond, while σ-donation involves 0.27 electron, the back-bonding from the occupied d orbital of Ru to the σ* orbital of H_2 concerns only 0.10 electron. This observation is in line with the positive net charge (+0.15) of the η^2-coordinated H_2. Both H_2 and GeH_4 behave more as an electron donor than as an electron acceptor. On the other hand, the Ge–H bond appears to be a better acceptor than H–H.

In the case of isomer **1T-b1**, the NBO charges of Ru and Ge are −0.89 and 0.52, respectively, which results in a highly polar bond. This is reflected by the reduced value of the Ru–Ge bond index (0.58), thus lower than 1. The same remark can be made concerning the Ru–Ge bond in **2T-b1′**. With respect to the two η^2-H_2 bonds in **1T-b1**, it can be seen that the presence of the germyl ligand has no effect on the relative values of σ-donation and σ* back-bonding.

Conclusion

We have reported a theoretical analysis of germane activation by the ruthenium complex $RuH_2(\eta^2\text{-}H_2)_2(PH_3)_2$. Several isomers have been optimized at the DFT/B3LYP level. Two series can be distinguished as a result of the complexation process: series **a** for the σ-germane isomers and series **b** for the germyl isomers resulting from oxidative addition. The most stable isomer is the germyl bis(dihydrogen) complex $RuH(GeH_3)(\eta^2\text{-}H_2)_2(PH_3)_2$ (**1T-b1**) but it is noteworthy that the σ-isomer $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}H\text{–}GeH_3)(PH_3)_2$ (**1C-a1**), is only 2.0 kcal mol^{-1} above **1T-b1**. In the corresponding silane chemistry, the reverse situation is observed as the σ-silane complex is 1.9 kcal mol^{-1} below the silyl bis(dihydrogen) complex. The formulation of a σ-silane coordination was also confirmed by X-ray diffraction.[5] In the germane case, in the absence of any X-ray data and of more experimental information, it is difficult to reach a conclusion. Indeed, the effect of substituents on the germanium could have enough influence to modify the stability order of the different isomers as we have found them very close in energy. It is noteworthy that using PMe_3 instead of PH_3 increases the free energy difference between **1T-b1** and **1C-a1**. As recently pointed out on a molybdenum system,[1a,16] in our system, slightly higher activation toward oxidative addition for a germane is observed compared to the silane congener. NBO studies and analysis of the optimized geometrical parameters of the different isomers indicate, as in silane chemistry,[3b] the presence of stabilising secondary interactions between the classical hydrides and the positively charged Ge atom. This results in the **a** series to a *cis* position of the phosphines. Substitution of one dihydrogen ligand by a dinitrogen does not lead to any significant difference on the relative energies between the corresponding isomers. The binding energies associated with the σ-coordination of GeH_4 or SiH_4 to the same metallic fragment $RuH_2(H_2)(PH_3)_2$ are very similar.

Table 5 B3LYP optimized geometrical parameters[a] for the *cis* isomers of RuH2(N2)(GeH4)(PH3)2

	2C-a1	**2C-a2**	**2C-a2′**	**2C-b1**	**2C-b1′**	**2C-b2**	**2C-b2′**	**2C-b3**
Ru–H1	1.622	1.641	1.645	1.724	1.796	1.791	1.758	1.689
Ru–H2	1.645	1.618	1.607	1.746	1.823	1.763	1.721	1.711
Ru–H3	1.645	1.709	1.63	1.611	1.617	1.625	1.628	1.623
Ge–H1	2.339	4.115	4.221	2.526	2.845	4.327	3.014	2.494
Ge–H2	2.097	2.578	3.683	3.309	3.543	4.207	2.898	3.293
Ge–H3	2.099	1.839	2.082	2.844	2.772	2.75	2.815	2.821
H1–H2	2.364	2.07	1.919	0.888	0.854	0.87	0.878	0.909
H2–H3	2.523	2.804	1.792	2.304	3.434	2.093	1.923	2.335
Ru–N1	2.067	2.013	2.02	2.082	2.012	2.013	2.064	1.993
Ru–Ge	2.515	2.618	2.601	2.559	2.554	2.538	2.528	2.553
N1–N2	1.117	1.118	1.117	1.118	1.118	1.118	1.119	1.119
Ru–P1	2.366	2.399	2.295	2.355	2.367	2.401	2.307	2.363
Ru–P2	2.366	2.293	2.398	2.309	2.298	2.297	2.391	2.407
P1–Ru–P2	95.2	95.4	95.2	94	93.9	95.7	95.8	102.7
H1–Ru–H2	92.7	78.9	72.3	29.6	27.3	28.3	29.2	31
H2–Ru–H3	100.2	114.9	67.3	86.6	173.2	76.2	70.1	80.9

[a] Distances are in Å and angles in degrees. See Fig. 4 for labelling of the atoms.

Finally, GeH_4 as H_2 is a better electron donor than an electron acceptor, but the Ge–H bond appears to be a better acceptor than H–H.

Table 6 Relative energies (kcal mol^{-1}) of $RuH_2(N_2)(GeH_4)(PH_3)_2$ isomers calculated at the DFT/B3LYP level

Isomer	ΔE	ΔE + ZPE	$\Delta H°$	$\Delta G°$
2T-b1′	0.0	0.0	0.0	0.0
2T-b1	0.9	1.0	1.0	1.0
2C-b1	1.4	1.7	1.6	2.0
2C-b1′	1.5	1.9	1.7	2.2
2C-a1	1.7	1.6	1.3	1.7
2C-b2	1.8	2.0	1.8	2.9
2C-b2′	2.9	2.9	2.8	3.5
2T-a2	4.0	3.7	3.7	3.7
2T-a1	4.2	4.2	4.1	4.4
2C-b3	4.8	4.8	4.7	5.0
2C-a2′	5.1	4.8	4.6	5.2
2C-a2	5.7	5.6	5.4	6.0

Table 7 Natural charges q, Wiberg bond indices W and natural orbital occupancies for **1C-a1** and **1T-b1** isomers of $RuH_2(H_2)(GeH_4)(PH_3)_2$, and for **2C-a1** and **2T-b1′** isomers of $RuH_2(N_2)(GeH_4)(PH_3)_2$.[a]

	1C-a1	**1T-b1**	**2C-a1**	**2T-b1′**
q(Ru)	−0.91	−0.89	−0.72	−0.70
q(H1)	0.06	0.08	−0.04	0.08
q(H2)	0.09	0.05	−0.04	0.05
q(H3)	−0.01	0.05	−0.04	−0.04
q(H4)	−0.04	0.08	—	—
q(H5)	−0.03	−0.01	—	—
q(N1)	—	—	−0.04	−0.06
q(N2)	—	—	0.04	0.04
q(Ge)	0.74	0.52	0.74	0.52
q(P1)	0.34	0.37	0.34	0.37
q(P2)	0.35	0.37	0.34	0.37
W(Ru–H1)	0.18	0.20	0.60	0.19
W(Ru–H2)	0.18	0.18	0.46	0.18
W(Ru–H3)	0.56	0.16	0.46	0.63
W(Ru–H4)	0.48	0.16	—	—
W(Ru–H5)	0.46	0.61	—	—
W(Ge–H1)	0.01	0.07	0.14	0.07
W(Ge–H2)	0.0	0.10	0.25	0.10
W(Ge–H3)	0.15	0.01	0.29	0.10
W(Ge–H4)	0.19	0.04	—	—
W(Ge–H5)	0.28	0.08	—	—
W(Ru–N1)	—	—	0.39	0.38
W(Ru–Ge)	0.30	0.58	0.29	0.59
W(N1–N2)	—	—	2.82	2.81
σ(Ge–H3)	—	—	1.38	—
σ(Ge–H5)	1.41		—	—
σ(H1–H2)	1.73	1.74	—	1.75
σ(H3–H4)	—	1.75	—	—
Lp(N1)[b]	—	—	1.78	1.79
Lp(N2)[b]	—	—	1.98	1.98
σ*(Ge–H3)	—	—	0.35	—
σ*(Ge–H5)	0.32	—	—	—
π_1*(N–N)	—	—	0.10	0.10
π_2*(N–N)	—	—	0.10	0.11
σ*(H1–H2)	0.10	0.10	—	—
σ*(H3–H4)	—	0.10	—	—

[a] See Figs. 1–4 for labelling of the atoms. [b] Lp = lone pair

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