Diphosphines with large natural bite angles lead to the formation of non-classical *cis*-(diphosphine)$_2$Ru(H)(H$_2$)$^+$ complexes

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The application of diphosphine ligands with large natural bite angles leads to the formation of thermo-labile, non-classical *cis*-(diphosphine)$_2$Ru(H)(H$_2$)$^+$ complexes.

The discovery of the first η^2-dihydrogen complex by Kubas *et al.*[1] has led to numerous studies on the factors determining the properties of such complexes. The bond between the transition metal and the H$_2$ ligand is a subtle balance between σ donation and π back-donation. Morris and coworkers have reported several studies on the effect of electronic modifications in diphosphine ligands on the stability of ruthenium dihydrogen complexes and on the acidity of the H$_2$ ligand.[2–9]

So far, few detailed studies have dealt with the effect of geometrical changes on the nature and reactivity of η^2-dihydrogen complexes.

Recently, Morokuma and coworkers reported that, with an increasing bite angle of the diphosphine, the nature of the (diphosphine)$_2$Ru('H$_3$')$^+$ complexes changes from *trans*-hydrido–dihydrogen to classical trihydride and to *cis*-hydrido–dihydrogen complexes.[10]

We recently developed[11] diphosphines based on xanthene-like backbones that allow the investigation of the effect of large bite angles on the properties of transition-metal complexes (Fig. 1). Here, we report that the geometrical constraints of these rigid bidentate phosphine ligands have a large effect on the structure and stability of ruthenium dihydrogen complexes.

cis-(Diphosphine)$_2$RuH$_2$ complexes **1** were prepared from Ru(cod)(cot) (cod = cycloocta-1,5-diene, cot = cycloocta-1,3,5-triene) and 2 equiv. of the diphosphine under 5 kPa H$_2$ (Fig. 2).†

Protonation of (thixantphos)$_2$RuH$_2$ **1a** at 176 K with HBF$_4$·OEt$_2$‡§ results in one product, which exhibits a broad symmetric signal in the ^{1}H NMR spectrum at δ −6.7 and a double triplet in the ^{31}P{^{1}H} NMR spectrum. Based on the ^{31}P NMR spectrum and the T_1(min) for the hydride signal in the high-field region of the ^{1}H NMR spectrum (17 ms at 240 K), we assign these signals to a *cis*-Ru(H$_2$)H species (**2a**). Upon raising the temperature slowly from 220 to 260 K, the signals from **2a** decrease and signals of a new species appear (Fig. 3). This new component gives rise to a sharp 14 line signal centred at δ −6.28 in the high-field region of the ^{1}H NMR spectrum, and an ABMX splitting in the ^{31}P{^{1}H} NMR spectrum. At 260 K this is the only species present. The nature of this new species was unambiguously determined by measurement of selective hydride-coupled ^{31}P NMR as the cationic species (thixantphos)$_2$RuH$^+$ **3a**, resulting from the evolution of H$_2$ [T_1 (240 K) 242 ms]. The vacant site probably interacts with the counter ion or a solvent molecule (L).

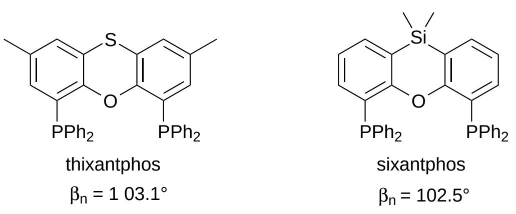


Fig. 1 Structure and natural bite angles of the ligands. Bite angles calculated using molecular mechanics (CAChe WorkSystem),[12] with a P–Ru bond length of 2.424 Å[10] and a P–Ru–P angle bending force constant of 0 mdyn Å rad^{-1} (1 dyn = 1 × 10^{-5} N). The natural bite angle is defined as the preferred chelation angle determined only by ligand backbone constraints and not by metal valence angles.[13]

Upon protonation of (sixantphos)$_2$RuH$_2$ **1b** at 176 K three products are formed as concluded from ^{1}H and ^{31}P NMR. In the high-field region of the ^{1}H NMR spectrum one sharp 14 line multiplet centred at δ −5.6, similar to the signal observed for **3a**, and two broad signals located at δ −6.9 (major) and at δ −6.6 (minor) are present. Based on the ^{31}P NMR spectrum and the T_1(min) value of the combined ^{1}H signals at −6.9 to −6.6 (23 ms at 200 K), these signals are assigned to two *cis*-Ru(H$_2$)H isomers, **2b** and **2b′**. The ratio of these complexes is 1 (**2b′**) : 4 (**2b**) : 9 (**3b**). Increasing the temperature to 200 K results in a slight decrease of the amount of **2b**, **b′** and an increase of **3b** and at 210 K only the 14 line hydride signal of **3b** remains [T_1 (200 K) = 622 ms].

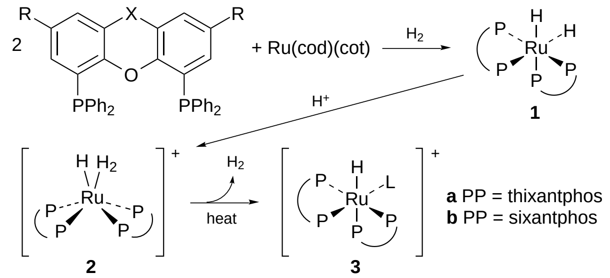


Fig. 2 Reaction sequence leading to the products investigated

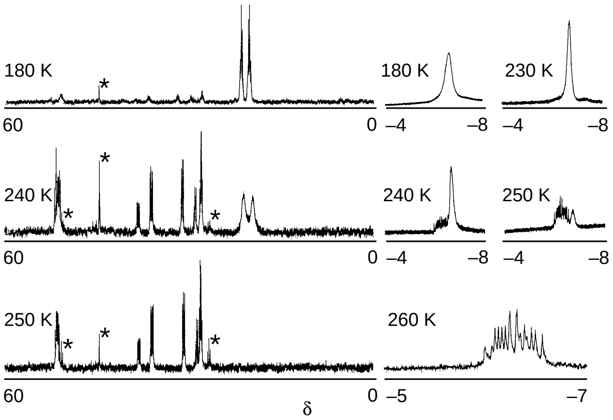


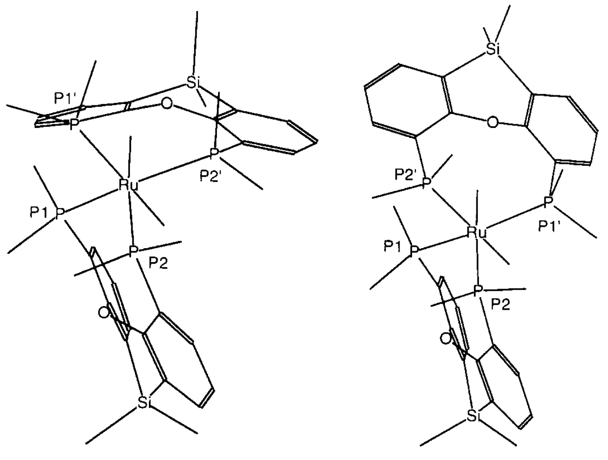
Fig. 3 Change with temperature of the ^{31}P{^{1}H} and high-field region of the ^{1}H NMR spectra of the reaction mixture arising from protonation of **1a** with HBF$_4$·OEt$_2$; * denotes an impurity

The short T_1 values observed for **2** are indicative of the presence of short H–H distances (0.84 Å and 0.89 Å for **2a** and **2b** respectively as calculated from $T_1(H_2)$ and $T_1(H)$: see ef. 6.

Comparison of the $^{31}P\{^1H\}$ NMR spectra obtained for **2a** and **2b** reveals a notable difference in geometry for the complexes of these similar ligands. We used molecular modelling to investigate the possible geometries for these $(diphosphine)_2Ru(H)(H_2)^+$ complexes. The relative orientation of the backbones of the diphosphines when coordinated to the metal centre allows us to distinguish two types of complexes (Fig. 4). In complexes of type **A**, every P nucleus has a different environment, therefore all P nuclei are magnetically inequivalent and an ABMX splitting in the ^{31}P NMR spectrum is expected. In complexes of type **B**, we can distinguish two pairs of magnetically different P nuclei and an A_2B_2 splitting in the ^{31}P NMR spectrum is expected. In type **A** complexes the aromatic rings are more densely packed, compared to type **B** complexes, resulting in energetically favourable π-stacking interactions. This would be the favoured product (as seen in **2b**), but for thixantphos these stabilizing interactions are hampered by the methyl groups on the backbone, resulting in the formation of type **A** only.

The low thermal stability of **2a** and **2b** compared to other $(diphosphine)_2RuH_3^+$ complexes may be explained by the fact that the xantphos-type diphosphines enforce large bite angles, and therefore induce significant distortion of the octahedral ruthenium complex. INDO/1 calculations show that this distortion of the octahedral geometry induced by the xantphos-type diphosphines can lead to less optimal orbital overlap, resulting in decomplexation of H_2. Experimentally, for all three $(diphosphine)_2RuH_3^+$ complexes presented here, there is one signal corresponding to the 'H_3' in the ^1H NMR spectra, indicating very rapid exchange as a result of the *cis* relative position of the hydride and dihydrogen ligands, unlike other $(diphosphine)_2MH_3^+$ complexes (M = Fe, Ru, Os), which only coalesce at higher temperatures.[2–7,9,14–17] Addition of CF_3CO_2D to **1** leads for the product to the same ^1H and $^{31}P\{^1H\}$ NMR spectra as for protonation with $HBF_4{\cdot}OEt_2$. There is no resolvable H–D coupling, but in the $^{31}P\{^1H\}$ NMR spectrum all signals have small shoulders due to downfield isotopic shifts.

The application of diphosphines with large bite angles in the synthesis of $(diphosphine)_2Ru(H)(H_2)^+$ complexes emphasises the delicate nature of the bonding of H_2 to a transition metal. The distortion of the octahedral geometry of the complex favours the hydrogen atom exchange and destabilises the bond of H_2 to the metal centre by reducing the back-donation to the H_2 ligand. The results reported here provide experimental evidence for the predictions by Morokuma and coworkers[10] that an increase of the P–Ru–P bite angle might lead to a change from *trans*-hydride–dihydrogen complexes[14] to equilibria between *cis* and *trans* complexes,[15] and further to *cis* complexes. Furthermore these results show that tuning a steric parameter such as the natural bite angle of diphosphines dramatically influences the electronic properties of a transition-metal complex.



A B

Fig. 4 Two types of isomer for **2b**. Only C_{ipso} atoms of phenyl groups are shown for clarity.

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Footnotes

† *Synthesis* of starting material: 0.120 g of Ru(cod)(cot) (0.381 mmol) and 2 equiv. of diphosphine were added to a Fisher–Porter bottle. The flask was flushed with argon, and 10 cm³ of thf was added. Upon stirring a bright yellow solution formed, which was flushed with H_2, then pressurized to 5 kPa, and heated to 433 K for 20 h, during which time the reaction mixture turned dark brown. After cooling to room temp., the solvent was evaporated, and an extensive washing procedure yielded the pure product **1** (50–60%).

‡ *Protonation experiments*: a solution of **1** (*ca.* 0.01 g, *ca.* 7 µmol) in 0.5 cm³ of CD_2Cl_2 was frozen in liquid N_2. $HBF_4{\cdot}Et_2O$ was added (3 mm³, 35 µmol). The NMR tube was allowed to warm just to the melting point of the solution, shaken to dissolve the frozen $HBF_4{\cdot}Et_2O$, then immediately lowered into the NMR probe at 180 K. The first ^1H and $^{31}P\{^1H\}$ NMR spectra and the T_1 measurements were performed at this temperature. Subsequent measurements were performed at 10 K intervals up to 300 K.

§ *Selected NMR data*: ^1H and $^{31}P\{^1H\}$ NMR spectra measured in CD_2Cl_2 at 300 and 121.5 MHz respectively, except for **3a**, for which a separate experiment was performed in $(CD_3)_2CO$ with ^1H and $^{31}P\{^1H\}$ NMR spectra at 400 and 160 MHz, respectively. The ^1H data refers to the hydride region. **1a**; δ −8.32 (dt); $^{31}P\{^1H\}$, δ 36.3 (t), 33.5 (t). **2a**; ^1H, δ −6.69 [br, T_1(min) 17 ms (240 K)]; $^{31}P\{^1H\}$, δ 21.7 (apparent t), 20.3 (apparent t). **3a**; ^1H, δ −6.15 (m); $^{31}P\{^1H\}$, δ 33.5 (m), 35.0 (m), 42.5 (m), 57.2 (m).

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