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Piano-stool inversion in arene complexes of Ru(II): modelling the transition state

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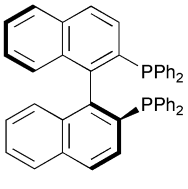
In the solid-state, the [RuH(arene)(Binap)]CF$_3$SO$_3$, complexes, 1, arene = η^6-benzene and 2, arene = η^6-toluene, distort markedly from a classical three-legged piano-stool structure with the former having the P–Ru–P plane approximately perpendicular to the plane of the arene; this structure for 1 is what one would expect for a transition state leading from one diastereomer to another *via* inversion at ruthenium.

The atropoisomeric chiral bidentate Binap is an excellent chiral auxiliary and is often employed in homogeneously catalysed reactions. It is perhaps best known in connection with Ru-assisted homogeneous hydrogenation chemistry,[1] and consequently a number of solid-state structures of Ru-Binap complexes have appeared.[2]



Binap

Often, the ruthenium precursor used in the catalysis involves an 18-electron η^6-arene complex of Ru(II). These arene compounds are known to have classical, but distorted, three-legged piano-stool structures, *e.g.* [RuCl(arene)(Binap)]$^+$,[3] [RuH-(η^6-benzene or η^6-toluene)(PPh$_3$)$_2$]$^+$ [4] or [RuH(η^6-benzene)-(dippe)]$^+$ [dippe = bis(diisopropylphosphino)ethane].[5] This structural type has been considered[6] *via* computational methods and electronic effects are thought to contribute to the distortion of the piano-stool. We show here that the Binap complexes [RuH(η^6-arene)(Binap)]CF$_3$SO$_3$, **1** and **2**, both distort markedly from a classical three-legged piano-stool and, for **1**, can reach a trigonal structure.

The complexes were prepared by reacting Ru(OAc)$_2$(Binap) with either benzene or toluene and triflic acid in methanol to afford **1** and **2** respectively.[7] The molecular structures for **1** and **2** were determined *via* X-ray diffraction methods[8] and ORTEP[9] views of these molecules are given in Fig. 1. Selected bond distances and bond angles are given in the caption. In both structures the bond lengths and angles are very similar and fall in the expected range. The major differences between the two structures lie in a) the values of the dihedral angle between the planes defined by atoms P1–Ru–P2 and the C1–C6 ring [89.7(1)° for **1** and 79.6(1)° for **2**, respectively] and b) the extremely large value of the anisotropic displacement parameters (ADPs) for the Ru atom in **1**. The two Ru–P distances are equal in **1** and slightly different in **2**.

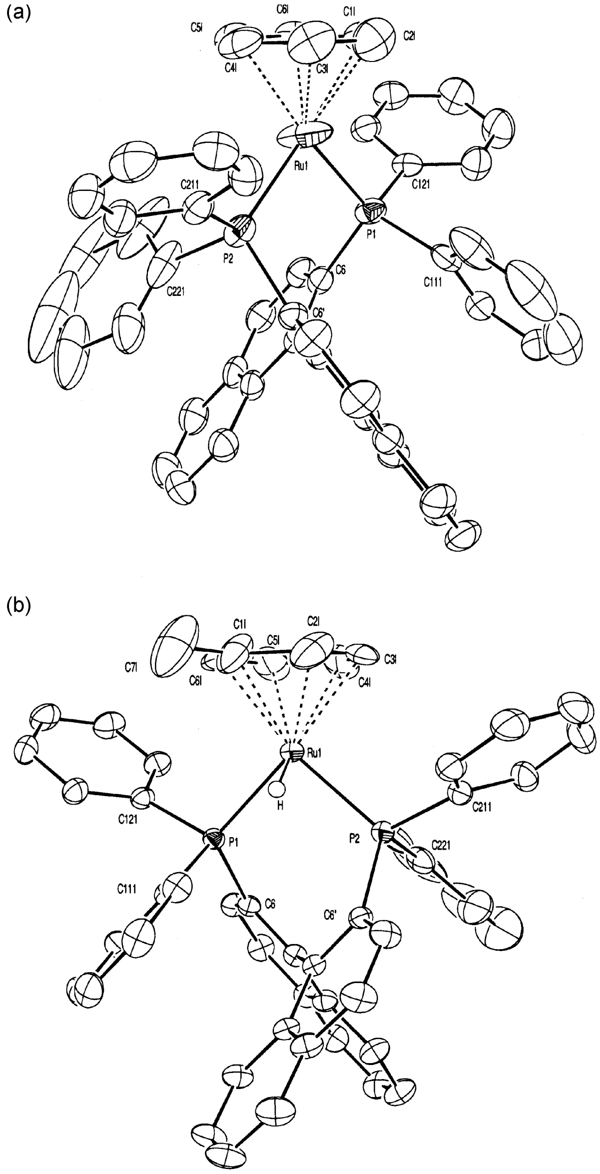


Fig. 1 (a) Selected bond lengths (Å) and angles (°) for compound **1**·CH$_2$Cl$_2$: Ru–P1 2.290(1), Ru–P2 2.290(2), Ru–C11 2.247(6), Ru–C21 2.268(8), Ru–C31 2.271(7), Ru–C41 2.260(6), Ru–C51 2.275(6), Ru–C61 2.262(6), P1–C6 1.843(6), P2–C6′ 1.843(5); P1–Ru–P2 90.57(5) and (b) for compound **2**: Ru–P1 2.299(1), Ru–P2 2.280(1), Ru–C11 2.272(5), Ru–C21 2.235(5), Ru–C31 2.245(5), Ru–C41 2.259(5), Ru–C51 2.282(5), Ru–C61 2.268(4), P1–C6 1.838(4), P2–C6′ 1.835(4), Ru–H 1.62(7); P1–Ru–P2 90.58(3).

In **1** the ruthenium ADPs show a very large amplitude of displacement in one direction (≈0.2 Å) (see Figs. 1 and 2) compared to compound **2**, where a much smaller elongation of the ADPs is observed (≈0.04 Å). This large displacement may be the result of the metal atom undergoing a large amplitude motion or it may be caused by static disorder due to the superimposition of two conformations each having the Ru sitting at each end of the observed displacement. Thus the observed "trigonal" geometry at the metal centre in **1** may be seen as an average structure consistent with the molecule sitting in a *very shallow* single minimum potential. For **1**, the P-atoms, the

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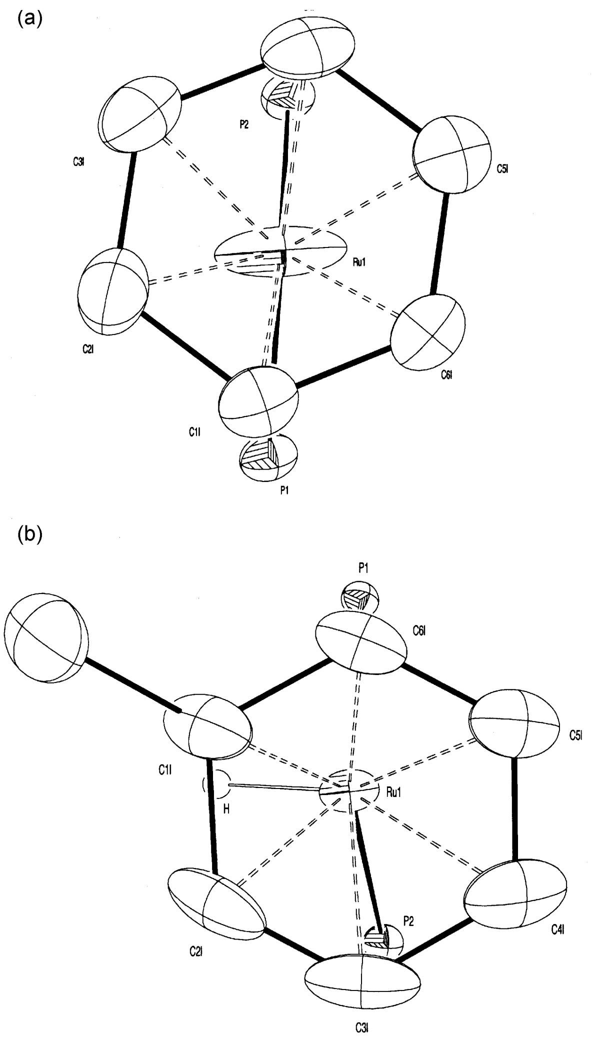
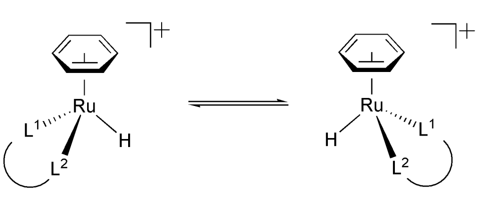


Fig. 2 (a) View of **1** from behind the arene looking towards the metal. Only the P–Ru–P atoms of the Ru(Binap) fragment are shown. The approximately perpendicular arrangement of the two planes is clear. (b) View of **2** from behind the arene looking towards the metal. Only the P–Ru–P atoms of the Ru(Binap) fragment are shown. The slight deviation, *ca.* 10°, is noticable.

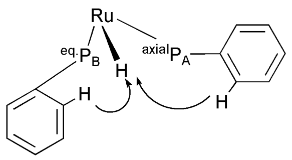
C-atoms of the Binap core and those of the η^6-benzene do not show the same large amplitude displacements of the Ru atom. This is consistent with the observation that, in the fluxional process, the ligands do not move. *Thus it may be assumed that the observed structure of* **1** is in fact a static picture of the reaction path leading from one piano-stool conformation to the opposite through the trigonal transition state [see eqn. (1)].



(1)

In both compounds two P bonded phenyl rings are also disordered but this may not be related to the fluxional process.

The ^{31}P spectra for **1** and **2** in CD_2Cl_2 reveal dynamic character. At ambient temperature one finds AB spectra which collapse to broad singlets at *ca.* 240 K and *ca.* 260 K, respectively, and then reappear as two new AB spectra upon lowering the temperature. The two resonances for **1** are separated by < 0.7 ppm between 195 K and 298 K. The ^{1}H-hydride resonance is sharp throughout the entire temperature range and appears as the X part of an ABX spin system. One finds NOEs from the hydride signals to the two non-equivalent sets of P-phenyl *ortho* protons: one from P_A (phenyl axial) and one from P_B (phenyl equatorial) *i.e.*,



Detailed ^{1}H NMR studies suggest that the observed dynamics stem from restricted rotation around P–C(phenyl) bonds and not the inversion of eqn. (1). These NMR results are consistent with non-equivalent but very similar P-donors. A solid-state ^{31}P NMR spectrum was obtained but, due to the substantial line width, was not informative.

The chemistry of eqn. (1) can (but need not be) facile and there is substantial discussion by Brunner and co-workers,[10] amongst others,[11] on this subject. Our result for **1** presents the first example of a structure confirming that the barrier need not be very high.

Acknowledgements

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8 Crystal data for compound **1**·CH_2Cl_2: $C_{52}H_{41}Cl_2F_3O_3P_2RuS$, M = 1037.83, monoclinic, space group $P2_1/n$ (no. 14), a = 11.2603(5), b = 30.441(1), c = 13.3700(6) Å, β = 100.537(2)°, U = 4505.7(3) Å^3, Z = 4, μ = 6.41 cm^{-1}, T = 223 K. All atoms were refined anisotropically by full-matrix least squares on F^2. Final agreement factors are: $R1$ = 0.090 [for 7213 unique reflections having $I > 2\sigma(I)$], 0.126 (for all 10642 independent reflections). The terminal hydride was not located unambiguously. Crystal data for compound **2**: $C_{52}H_{40}F_3O_3P_2RuS$, M = 964.91, monoclinic, space group $P2_1/n$ (no. 14), a = 11.7605(2), b = 21.0232(5), c = 17.2739(5) Å, β = 91.247(1)°, U = 4269.9(2) Å^3, Z = 4, μ = 5.50 cm^{-1}, T = 200 K. All atoms were refined anisotropically by full-matrix least squares on F^2. Final agreement factors are: $R1$ = 0.060 [for 8198 unique reflections with $I > 2\sigma(I)$], 0.073 (for all 9764 independent reflections). The hydride ligand was located on a difference Fourier map and refined without constraints using an isotropic temperature factor. CCDC reference numbers 182445 and 182446. See http://www.rsc.org/suppdata/dt/b2/b202630a/ for crystallographic data in CIF or other electronic format.

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