# Structure and molecular dynamics of $Ru_2(CO)_6(\mu\text{-}PCy_2)_2$: an unusual case of cyclohexyl rearrangement

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Received 17 May 1996; revised 27 June 1996

## Abstract

The dinuclear complex $Ru_2(CO)_6(\mu\text{-}PCy_2)_2$ (Cy = Cyclohexyl) was studied in the solid state by X-ray crystallography and in solution by NMR spectroscopy. The variable-temperature ^{13}C and ^{31}P NMR studies reveal two interconverting isomers to be present in solution, in contrast to the unique isomer found in the crystal.

*Keywords:* Ruthenium; X-ray diffraction; Nuclear magnetic resonance; Cyclohexyl

## 1. Introduction

The dinuclear phosphido-bridged complex $Ru_2(CO)_6(\mu\text{-}PPh_2)_2$ has been known since 1972 [1]; its structure was elucidated in 1990 [2]. A serious drawback in investigating the chemistry of this compound was its poor accessibility, all synthetic methods reported before 1992 gave only low yields, or even trace amounts [1–8]. Four high-yield routes were developed in 1992: whereas Mathieu and coworkers obtained $Ru_2(CO)_6(\mu\text{-}PPh_2)_2$ from $Ru_3(CO)_{12}$ and $P_2Ph_4$ [9], we found this compound to be easily accessible from $Ru_3(CO)_{12}$, $HPPh_2$ and CO, from $Ru_3(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}H)_2$ and CO, and from $Ru_2(CO)_4(\mu\text{-}OOCEt)_2(PPh_2H)_2$ and CO [10]. The last method can easily be extended to other phosphido derivatives: from $Ru_2(CO)_4(\mu\text{-}OOCEt)_2(PCy_2H)_2$ and carbon monoxide we obtained the new cyclohexyl analogue $Ru_2(CO)_6(\mu\text{-}PCy_2)_2$ (1) [11] which, in contrast to the phenyl derivative, appeared to exist in two isomeric forms in solution, as shown by the ^{31}P NMR spectra [11].

In this paper we report a single-crystal X-ray structure analysis of 1, and a detailed analysis of the ^{13}C NMR spectra and of the variable-temperature ^{31}P spectra, as well as the kinetic and thermodynamic parameters of the equilibria between the two isomers of 1 in solution.

## 2. Experimental

### 2.1. Synthesis

Complex 1 was synthesized as described previously [11].

### 2.2. Spectroscopy

^{13}C and ^{31}P NMR spectra were measured on Bruker AMX 400, AMX 500, or AMX 600 spectrometers, at 100.62 (223 K, 243 K, 273 K and room temperature), 125.77, 150.90 MHz (^{13}C) and 162.0 MHz (^{31}P). The attributable ^{13}C NMR signals are given in Section 3 and Table 2.

### 2.3. X-ray analysis

Suitable crystals of 1 were grown from pentane as pale green blocks. Intensity data were collected at room temperature on a Stoe AED2 four-circle diffractometer using MoKα graphite monochromated radiation ($\lambda = 0.71073$ Å) with ω–Θ scans in the 2Θ range 3–55°.
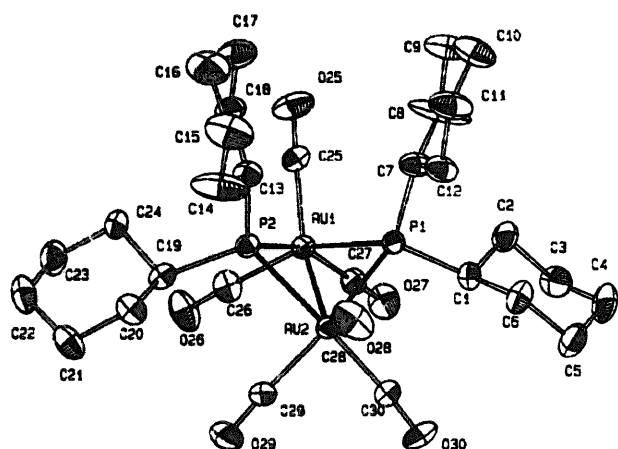
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Fig. 1. Molecular structure of Ru₂(CO)₆( μ-PCy₂)₂ (1). ZORTEP [14] drawing (ellipsoids with 30% probability; hydrogen atoms removed for clarity).

### 3. Results and discussion

In order to determine the conformation of the four cyclohexyl rings of complex $Ru_2(CO)_6( \mu\text{-PCy}_2)_2$ (1) in the solid state, an X-ray analysis was carried out. The molecular structure of 1 is displayed in Fig. 1. Selected bond distances, bond angles and torsion angles are given in Table 1.

In the solid state, complex 1 has approximate $C_2$ symmetry; its structure is analogous to the known phenyl complex $Ru_2(CO)_6( \mu\text{-PPh}_2)_2$ [2]. Each ruthenium atom is coordinated almost octahedrally. Each cyclohexyl ring adopts the 'chair' conformation, the four cycles being bound equatorially to the phosphorus atoms. The interatomic distance Ru–Ru is 2.845 Å; this compares well with the same distance in the phenyl analogue (2.820 Å) [2]. The slight difference is probably due to the larger steric hindrance of the cyclohexyl groups. The angles Ru–P–Ru vary between 52 and 53°, the dihedral angle between the Ru₂P planes is 68.7° (phenyl analogues: 75.1° [2]).

As shown by the X-ray analysis, complex 1 is symmetrical with respect to the Ru–Ru bond; hence, only one $^{31}P$ NMR signal is expected. However, the $^{31}P$ NMR spectrum measured at room temperature in $d_8$-toluene reveals three broad signals at $\delta = 146.9$, 139.7 and 138.6. Furthermore, the $^{13}C$ NMR spectrum shows more than four distinct cyclohexyl signals at $\delta = 56.5$ (C-1a), 35.2 (C-2a), 28.1 (C-3a), and 26.3 (C-4a) (Scheme 1), as well as three carbonyl signals at $\delta = 201.3$, 200.9, and 199.2. The results indicate that 1 exists in solution as an equilibrium mixture of two species, one of which has the same symmetrical conformation of that in the solid state.

$^{31}P$ NMR measurements were obtained over the temperature range 203–353 K. The three broad $^{31}P$ NMR signals observed at room temperature gradually broadened on increasing the temperature and coalesced at ca. 350 K to one signal at $\delta = 142$. At 273 K the three signals were shifted slightly downfield and became sharper (a singlet at $\delta = 139.5$ and two doublets at

The structure was solved by direct methods using the program SHELXS-86 [12]. The refinement and all further calculations were carried out using SHELXL-93 [13]. The H atoms were refined isotropically and the non-hydrogen atoms anisotropically, using weighted full-matrix least squares on $F^2$. Crystal data for 1: $C_{30}H_{44}O_6P_2Ru_2$, monoclinic, space group $P2_1/c$, $a = 9.674(1)$, $b = 20.276(2)$, $c = 17.042(1)$ Å, $\beta = 90.11(1)°$, $Z = 4$, 7688 independent reflections, 7677 observed reflections ($I > 2\sigma(I)$), final $R = 0.064$, $R_w = 0.108$, goodness-of-fit 1.09, residual density max./min. $0.633/-0.518$ e Å$^{-3}$. Absorption coefficient $\mu = 1.04$ mm$^{-1}$; no correction for absorption was applied. Selected bond distances and angles, and torsion angles are given in Table 1. The molecular structure of 1 is illustrated in the ZORTEP [14] drawing, Fig. 1. Full tables of atomic parameters and bond lengths and angles may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (UK) on quoting the full journal citation.

Table 1

Important distances (Å), bond angles (deg) and torsion angles (deg) of Ru₂(CO)₆( μ-PCy₂)₂ (1)

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.8452(8) | Ru(2)–C(28) | 1.907(9) |
| Ru(1)–P(1) | 2.355(2) | Ru(2)–C(29) | 1.914(9) |
| Ru(1)–P(2) | 2.379(2) | P(1)–C(1) | 1.849(8) |
| Ru(2)–P(1) | 2.379(2) | P(1)–C(7) | 1.855(6) |
| Ru(2)–P(2) | 2.355(2) | P(2)–C(13) | 1.875(8) |
| P(2)–C(19) | 1.853(8) | P(1)–Ru(1)–P(2) | 82.57(7) |
| Ru(1)–Ru(2)–P(1) | 53.45(5) | Ru(1)–Ru(2)–P(1)–C(1) | −112.1(3) |
| Ru(1)–Ru(2)–P(2) | 52.66(5) | Ru(1)–Ru(2)–P(1)–C(7) | 115.9(3) |
| Ru(1)–P(1)–Ru(2) | 73.89(6) | Ru(2)–Ru(1)–P(2)–C(13) | 115.5(3) |
| Ru(1)–P(2)–Ru(2) | 73.89(6) | Ru(2)–Ru(1)–P(2)–C(19) | 112.1(3) |

**1a**                                              **1b**
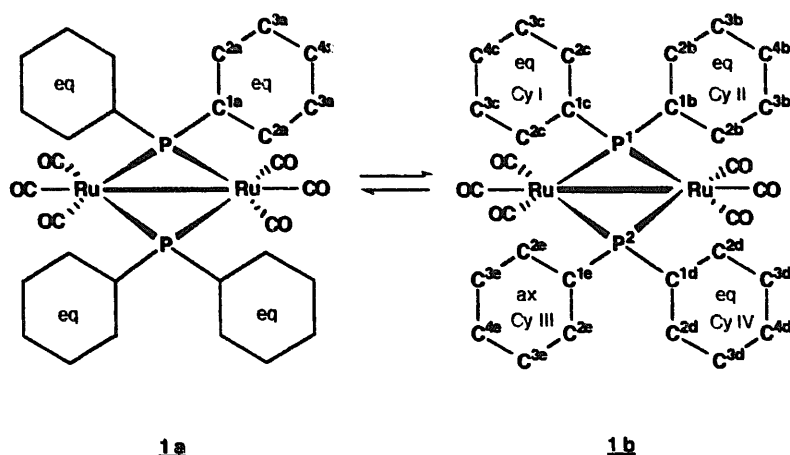
Scheme 1. Proposed equilibrium for the isomerization of complex **1**. Isomer **1a**: four equatorial rings; isomer **1b**: one axial and three equatorial rings.

$\delta$ = 147.0 and 138.0); no radical difference in the chemical shift and the shape of these signals was observed down to 203 K.

Examination of a tridimensional ball-and-stick model of **1** suggested a spatial constraint between both Cy(I) and Cy(III) substituents (Fig. 1). Transformation of either of these groups to an axial position could relieve this constraint and thus lead to a number of isomers. As one or more of the cyclohexyl groups changes from an equatorial to an axial position, the symmetry of the molecule is perturbed, resulting in chemically nonequivalent cyclohexyl $^{13}$C signals, and five sets of $^{13}$C signals for each C-1, C-2, C-3 and C-4 are expected; one set for the symmetrical isomer (namely **1a**), and the

other four for the equilibrating, unsymmetrical isomer (namely **1b**) (Scheme 1). This interpretation is in accordance with the $^1$H- and $^{31}$P- decoupled $^{13}$C NMR spectra at $-30°C$, as well as with a heteronuclear $J$-resolved experiment which, altogether, revealed 20 $^{13}$C signals in the cyclohexyl region, a missing cross-peak at $\delta$ = 43 not being visible under the recording conditions (Fig. 2). In determining which isomers were present, the number of C-3 $^{13}$C signals from the equatorially disposed $PCy_2$ group was first identified. The chemical shift and $^{13}C-^{31}P$ coupling of phosphono-cyclohexanes **2a** and **2b** (Fig. 3) with known stereochemistry of the C(1)–P bond, have been measured [15–17]. It was found that the C-1, C-3 and C-5 $^{13}$C
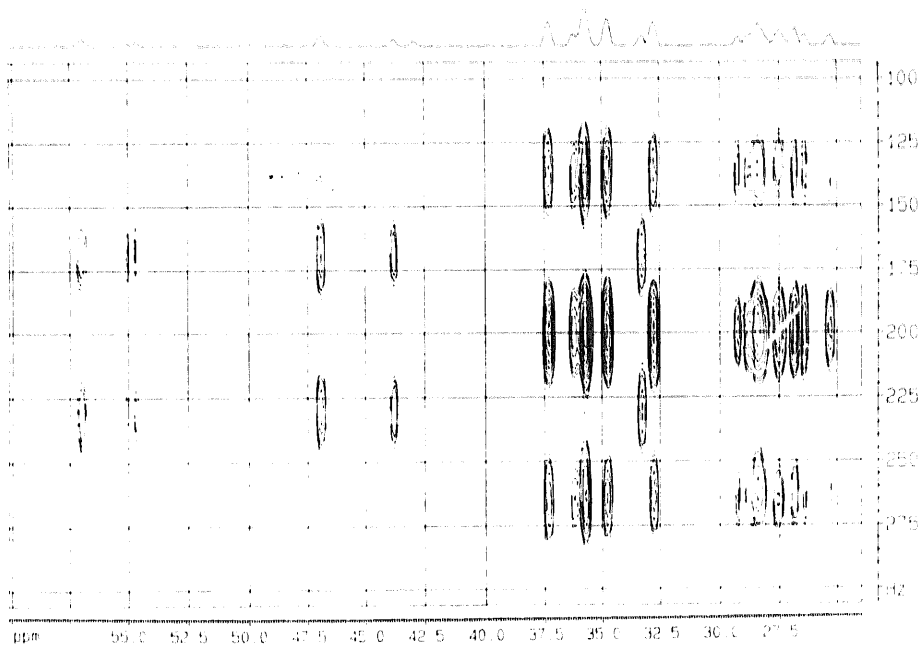


Fig. 2. $^{13}$C,$^1$H $J$-resolved NMR spectrum of **1** (100 MHz, CDCl$_3$, 243 K).

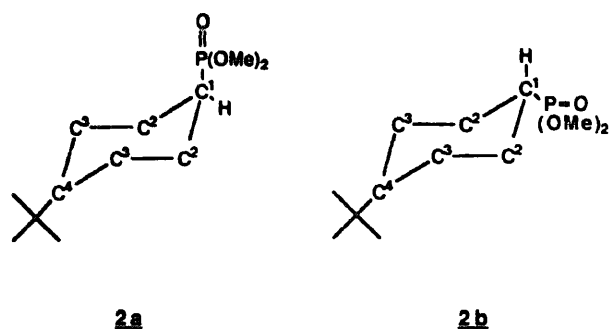Fig. 3. Couple of isomeric phosphonocyclohexanes [15–17]. Isomer 2a: axial P–C bond; isomer 2b: equatorial P–C bond.

Table 2
Assignment of the $^{13}$C NMR signals to both isomers of 1 ($\delta$, see Scheme 1)

|   | C$^1$ | C$^2$ | C$^3$ | C$^4$ |
|---|---|---|---|---|
| a | 56.5 | 35.2 | 28.1 | 26.3 |
| b | 54.4 |  | 27.3 |  |
| c | 42.8 |  | 27.6 |  |
| d | 46.0 |  | 26.7 |  |
| e | 32.2 |  |  |  |

signals for **2a** were slightly more upfield than those of **2b**. The $^3J(^{13}C-^{31}P)$ for the axially disposed $PCy_2$ group of **2a** was only 0.6 Hz, while the equatorial counterpart **2b** displayed a comparatively strong $W$ coupling of 16.2 Hz.

Comparison of the $^1$H-decoupled $^{13}$C NMR and $^1$H-, $^{31}$P-decoupled $^{13}$C NMR spectra reveals that four signals have high $^3J(^{13}C-^{31}P)$ values: $\delta = 28.1$ (d, $J =$ 10.7 Hz), $\delta = 27.6$ (d, $J = 10.8$ Hz), $\delta = 27.3$ (d, $J = $ 12.4 Hz), and $\delta = 26.7$ (d, $J = 10.0$ Hz), indicating that the conformation proposed for isomer **1b** is correct. The assignment of the four C-3 carbons is as follows: $\delta = $ 28.1 to C-3a, based on the room temperature $^{13}$C NMR measurement; $\delta = 27.3$ to C-3b, which has the largest $^3J(^{13}C-^{31}P)$ value and is oriented away from the other three Cy groups, allowing the maximum angle between C-3 and P; $\delta = 27.6$ to C-3c, and $\delta = 26.7$, as being shielded by the cycle III. In assigning the C-1 chemical shifts for **1b**, both heteronuclear $J$-resolved and triple resonance $^{13}$C NMR spectra were analysed. The following CH resonances were found: $\delta = 54.4$ (d, $J = $ 31.7 Hz), 46.0 (d, $J = 8.1$ Hz), 42.8 (s), and 32.2 (d, $J = 8.3$ Hz). The multiplicity can be attributed to
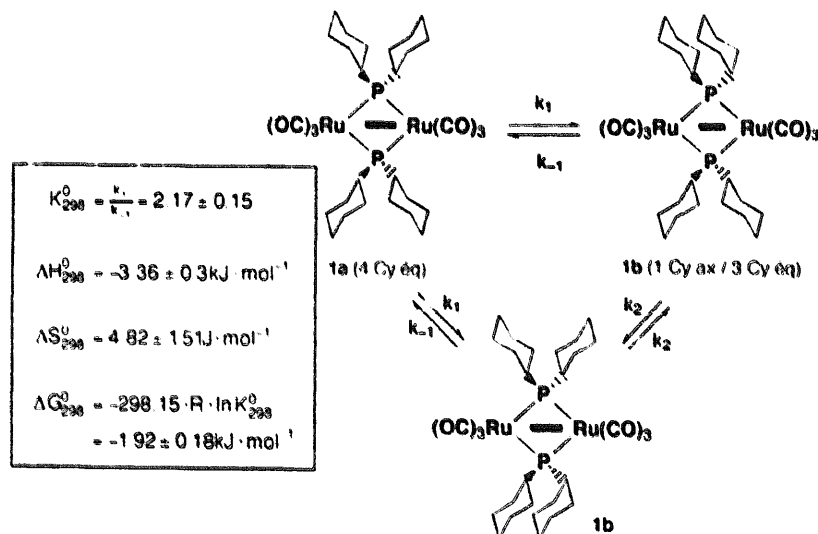
$^3J(^{13}C-^{31}P)$, following the C–P–Ru–P path. Thus C-1b and C-1d are expected to have a pseudo $W$ conformation, while no such conformation was indicated for C-1c. Following this argument, the signal at $\delta = 54.4$ is attributed to C-1b, that at $\delta = 46.0$ to C-1d, and $\delta = 42.8$ to C-1c. Finally, the signal at $\delta = 32.2$ is assigned to C-1e. The assignment of the C-2 signals was based on the coupling constants $^1J(^{13}C-^1H)$ derived from the $J$-resolved experiments, and these assumptions could not be verified by other NMR experiments. The C-2 carbons from equatorially disposed cyclohexyls (i.e. C-1b–d), $\delta = 36.3$ (132 Hz), 34.7 (130 Hz) and 31.7 (129.2 Hz) are assumed to have virtually the same $^1J(^{13}C-^1H)$ values. In contrast, the C-2e signal is expected at $\delta = 33.9$ (121.4 Hz), based on its lower $^1J(^{13}C-^1H)$ value. Furthermore, all three proposed C-2 signals appear as doublets of the same intensity having $^2J(^{13}C-^{31}P)$ values of around 4 Hz, while the proposed C-2e signal is a sharp singlet. The remaining $^{13}$C signals at $\delta = 28.3, 28.0, 25.9, 25.7, 25.6$ and 24.4, account for the C-3e and C-4b–e cyclohexyl carbons. Table 2 shows a summary of the $^{13}$C assignments of the cyclohexyl carbons.

A $^{31}$P-NOESYTP [18] experiment at 243 K (CDCl$_3$) showed an exchange between the singlet at $\delta = 118.5$ (isomer **1a**) and the two doublets at $\delta = 126.1$ and



$K^0_{298} = \dfrac{k_1}{k_{-1}} = 2.17 \pm 0.15$

$\Delta H^0_{298} = -3.36 \pm 0.3 \text{ kJ mol}^{-1}$

$\Delta S^0_{298} = 4.82 \pm 1.51 \text{ J mol}^{-1}$

$\Delta G^0_{298} = -298.15 \cdot R \cdot \ln K^0_{298}$
$\quad = -1.92 \pm 0.18 \text{ kJ mol}^{-1}$

Scheme 2. Isomerization **1a** → **1b** (rate constant $k_1$), and intramolecular P exchange in isomer **1b** (rate constant $k_2$).
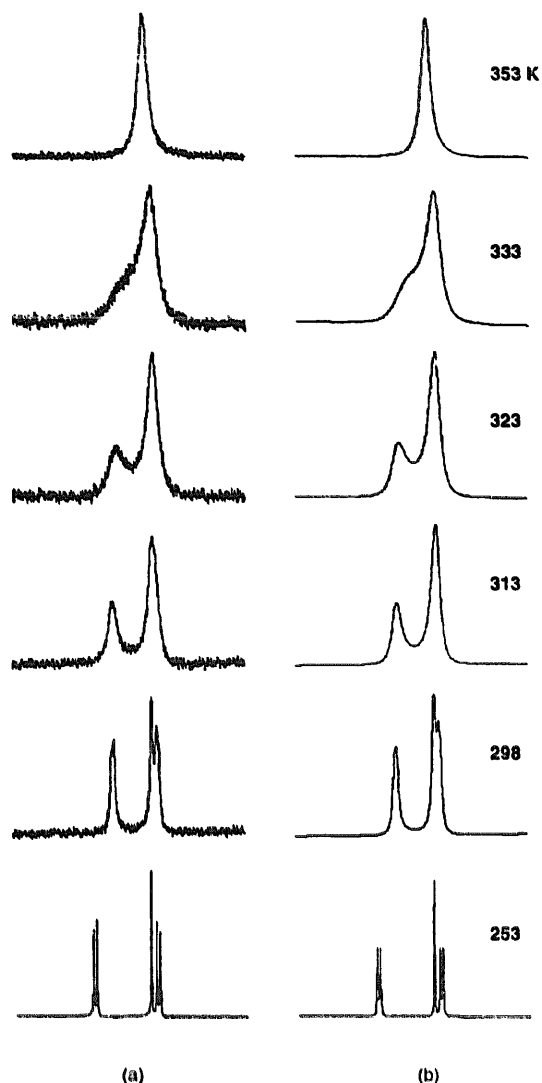
Fig. 4. Variable-temperature $^{31}$P NMR spectra of 1. (a) Measured ($d_8$-toluene, 162 MHz). (b) Calculated: SIMUL program [19–23].

Table 3

Observed rate constants for isomerization 1a → 1b ($k_1$) and the intramolecular P exchange in 1b ($k_2$)

| $T/K$ | $k_1/s^{-1}$ | $k_2/s^{-1}$ |
|---|---|---|
| 253.2 | 4.56 | |
| 313.2 | 379.9 | 1136 |
| 232.2 | 1272 | 2516 |
| 333.2 | 1702 | 4440 |
| 343.2 | 2131 | 9147 |
| 353.2 | 3718 | 44826 |

$[P(1a),P_1(1b)] = [P(1a),P_2(1b)] = k_1$, $[P_2(1b),P(1a)] = [P_1(1b),P(1a)] = k_1/2K$, $[P_2(1b),P_1(1b)] = [P_1(1b),P_2(1b)] = k_2$, where $k_1$ and $k_2$ are the rate constants of isomerization 1a → 1b and of the intra-
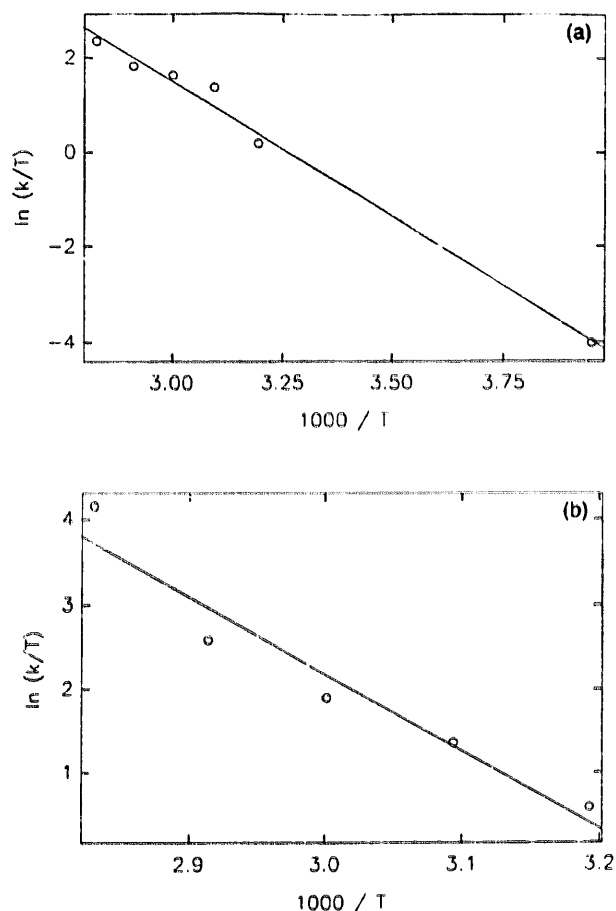


Fig. 5. Eyring plots: (a) $k_1$, isomerization 1a → 1b; (b) $k_2$, intramolecular P exchange in 1b.

117.5 (isomer 1b), and also between the doublets due to the two non-equivalent P-atoms of 1b. The population ratio $K = [1b]/[1a]$ was calculated from the integrals of the corresponding $^{31}$P signals between 193 and 323 K, and a linear regression of ln K vs. $1/T$ gave the thermodynamic parameters reported in Scheme 2. Knowing the population ratio of the two isomers at each temperature, the calculated spectra were fitted to the variable-temperature $^{31}$P NMR spectra by line-shape analysis, using the following exchange matrix elements: $[P(1a),P(1a)] = k_1$, $[P_1(1b),P_1(1b)] = [P_2(1b),P_2(1b)] = -(k_1/2K) - k_2$,

Table 4

Rate constants and associated kinetic parameters for $k_1$ and $k_2$ (data extrapolated to 298 K)

| | $k_{298}/s^{-1}$ | $\Delta S_{298}^\ddagger/J\,K^{-1}\,mol^{-1}$ | $\Delta H_{298}^\ddagger/kJ\,mol^{-1}$ | $\Delta G_{298}^\ddagger/kJ\,mol^{-1}$ |
|---|---|---|---|---|
| Isomerization | 174 ± 24 | −41 ± 8 | 48 ± 3 | 60.2 ± 0.3 |
| P exchange | 205 ± 124 | 55 ± 41 [a] | 76 ± 14 | 59.8 ± 1.5 |

[a] Estimated value.

molecular P exchange in isomer **1b** respectively (Fig. 4). The kinetic parameters are collected in Tables 3 and 4 and were calculated by linear regression of the graphs $\ln(k/T)$ vs. $1/T$ (Fig. 5).

Process **1a** → **1b** is exothermic and about as rapid as the intramolecular site exchange in **1b** at 298 K. The $^{13}C$ NMR spectra clearly show that the non-equivalence of the P atoms in **1b** is due to one axial Cy group (not two) and three equatorial Cy groups (Fig. 2). Therefore, the isomerization process is due to the equatorial–axial conformation exchange of one Cy substituent. Examination of the molecular structure of **1a** (Scheme 1) suggests that the intramolecular process in **1b** is a simultaneous axial–equatorial conformation change on P-1 and the reverse conformation change on P-2 (Scheme 2).

## 4. Conclusions

The dinuclear complex $Ru_2(CO)_6(\mu\text{-PCy}_2)_2$ (1), which shows an all-equatorial arrangement of the four cyclohexyl substituents at the two phosphorus atoms in the solid state, isomerizes in solution by an intramolecular axial–equatorial rearrangement of one cyclohexyl ring, simultaneous at both phosphorus atoms. To our knowledge, this is the first example of such a simultaneous rearrangement of cyclohexyl groups in a complex molecule.

## Acknowledgements

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