Synthesis, Structure and Structural Dynamics of Ruthenium(II) Bis(2-diphenylphosphinoethyl)phenylphosphine Dichloride

ROSALVINA R. GUIMERANS*, EVA C. HERNANDEZ
Universidad Simon Bolivar, Departamento de Quimica, Apartado 89000, Caracas 1080-A (Venezuela)
MARILYN M. OLMSTEAD and ALAN L. BALCH
University of California, Department of Chemistry, Davis, CA 95616 (U.S.A.)

(Received February 10, 1989)

Abstract

Treatment of $RuCl_2(PPh_3)_3$ with $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$ (TRIPHOS) yields yellow $RuCl_2(TRIPHOS)_2$. $RuCl_2\{[Ph_2P(CH_2)_2]_2PPh\}_2 \cdot CHCl_3 \cdot (C_2H_5)_2O$ crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 12.850(3)$, $b = 16.131(5)$, $c = 16.990(5)$ Å, $\alpha = 95.77(2)°$, $\beta = 98.56(2)°$, $\gamma = 94.96(2)°$, $V = 3446(2)$ Å^3 and $Z = 2$ at 130 K. Refinement yielded $R = 0.05$ for 6635 reflections with $I > 2\sigma(I)$ and 781 parameters. The ruthenium atom is octahedral with *trans* chloride ligands, one meridional chelating phosphine, and one monodentate TRIPHOS which bonds through the central phosphorus. ^{31}P NMR data shows hindered rotation of the monodentate TRIPHOS about the Ru–P bond.

Introduction

There is interest in ruthenium/phosphine complexes due to their activity in catalytic processes, particularly hydrogenation and the oxo reactions [1]. Most of these catalysts are ruthenium monomers with triphenylphosphine as ligands [2, 3]. There has been a great interest in varying the phosphine ligands in these ruthenium compounds to see how the activity of the catalyst will vary. Triphenylphosphine ligands have been exchanged for other monomeric phosphines [4] and symmetric [5, 6] or asymmetric [7] diphosphines. In this way, some or all the triphenylphosphine ligands have been replaced. A few examples of substitution of triphosphine ligands [5, 8] have been reported for these ruthenium compounds.

Bis(2-diphenylphosphinoethyl)phenylphosphine (TRIPHOS) has been used to prepare different metallic compounds. TRIPHOS has been reported to chelate the metal by a terminal and a central phosphorus [9] in a platinum compound or with all the phosphorus in a facial arrangement in a cobalt complex [10]. It was suspected that these were the only likely binding possibilities for TRIPHOS, and that the meridional form was excluded because the length of the chain between the phosphorus atoms would produce significant strain in the *trans* P–M–P angle [10].

In the present work, the ligand bis(2-diphenylphosphinoethyl)phenylphosphine has been exchanged for the triphenylphosphine ligands of $RuCl_2(PPh_3)_3$. The monomeric ruthenium product has its two TRIPHOS bound in different ways.

Experimental

Preparation of Compounds

Bis(2-diphenylphosphinoethyl)phenylphosphine (Strem) was used without further purification. $RuCl_2(PPh_3)_3$ was synthesized according to an established procedure [11]. All solvents were dried and purged under nitrogen before use.

$RuCl_2\{[Ph_2P(CH_2)_2]_2PPh\}_2 \cdot CHCl_3 \cdot (C_2H_5)_2O$ (1)

A slurry of brown $RuCl_2(PPh_3)_3$ (0.468 g, 0.471 mmol) and TRIPHOS (0.513 g, 0.960 mmol) was prepared in 40 ml of hexane. This mixture was heated for 5 h under nitrogen. During this time a yellow solid formed. The suspension was cooled and the precipitate collected by filtration and washed with ether. The product was recrystallized from chloroform–ether to give 64% yield. *Anal.* Calc. for $C_{73}H_{77}Cl_5OP_6Ru$: C, 61.12; H, 5.41. Found: C, 61.35; H, 5.25%.

Spectroscopic Measurements

The ^{31}P spectra were recorded proton decoupled at 81 MHz on a Nicolet NT200 Fourier Transform spectrometer. Phosphoric acid 85% was used as external reference. The high-frequency positive convention, recommended by IUPAC, has been used to report all chemical shifts.

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*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

X-ray Data Collection

Orange–yellow crystals of **1** were formed by vapor diffusion of diethyl ether into a chloroform solution of the compound. The crystals were removed from the vial and quickly covered with a light hydrocarbon oil to protect them from the atmosphere. The lattice was found to be triclinic by standard procedures using the software of the Syntex $P2_1$ diffractometer. The data were collected at 130 K using a locally modified LT-1 apparatus on the diffractometer. No decay in the intensities of two standard reflections was observed during the course of data collection. The data were corrected for Lorentz and polarization effects. Data collection parameters are summarized in Table 1.

Solution and Refinement of the Structure

All structure determination calculations were done on a Data General Eclipse MV/10000 computer using the SHELXTL version 5 software package. The position of the ruthenium atom was found from the Patterson map. Other atoms positions were located from successive difference Fourier maps. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. The final R value of 0.05 was computed from 781 least-square parameters and 6635 reflections. Hydrogen atoms were included at calculated positions using a riding model with C–H vector fixed at 0.96 Å and the thermal parameter for each hydrogen atom was set 1.2 times the value for the carbon atom to which it was bonded. The largest feature on a final difference map was 0.82 $e\text{Å}^{-3}$ in height in the vicinity of the molecule of diethyl ether. The largest shift in the final cycle of refinement was 0.13 for y of C(9). Corrections for absorption [2]* were applied. Neutral-atom scattering factors [13] were taken from reported values.

Results

An orange–yellow solid was obtained, after recrystallization, from the reaction between $RuCl_2(PPh_3)_3$ and TRIPHOS. The exchange of the phosphine ligands was a clean reaction, no other side products were detected. Compound **1** is very soluble

TABLE 1. Crystal data collection parameters for $RuCl_2\{[Ph_2P(CH_2)_2]_2PPh\}_2 \cdot CHCl_3 \cdot (C_2H_5)_2O$

Formula	$C_{73}H_{77}Cl_5OP_6Ru$
Formula weight	1434.59
Color and habit	orange–yellow parallelepipeds
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	12.850(3)
b (Å)	16.131(5)
c (Å)	16.990(5)
α (°)	95.77 (2)
β (°)	98.56(2)
γ (°)	94.96(2)
V (Å^3)	3446(2)
T (°)	130 K
Z	2
Crystal dimensions (mm)	0.22 × 0.22 × 0.22
D_{calc} (g cm^{-3})	1.38
Radiation (Å)	Mo Kα (λ = 0.71069)
μ (Mo Kα) (cm^{-1})	5.97
Range of transmission factors	0.86–0.89
Diffractometer	$P2_1$, graphite monochromator
Scan method	ω, 1.5° range, 1.2° offset for background
Scan speed (° min^{-1})	15.0
2θ range (°)	0–45
Octants collected	$h, \pm k, \pm l$
No. data collected	9011
No. unique data	9011 [R(merge) = 0.005]
No. data used in refinement	6635 [$I > 2\sigma(I)$]
No. parameters refined	781
R^a	0.050
$R_w{}^a$	0.049 [$w = 1/\sigma^2(F_o)$]

$^a R = \Sigma||F_o| - |F_c||/|F_o|$ and $R_w = \Sigma||F_o| - |F_c||w^{1/2}/\Sigma|F_o w^{1/2}|$.

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*The method obtains an empirical absorption tensor from an expression relating F_o and F_c.

TABLE 2. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for $RuCl_2\{[Ph_2P(CH_2)_2]_2PPh\}_2 \cdot CHCl_3 \cdot (C_2H_5)_2O$

	x	y	z	U
Ru	2302(1)	10050(1)	2516(1)	13(1)*
Cl(1)	1792(1)	10239(1)	1112(1)	19(1)*
Cl(2)	2816(1)	9881(1)	3914(1)	19(1)*
P(1)	509(1)	10244(1)	2641(1)	17(1)*
P(2)	1609(1)	8679(1)	2175(1)	18(1)*
P(3)	3802(1)	9504(1)	2101(1)	16(1)*
P(4)	2319(1)	13480(1)	4650(1)	29(1)*
P(5)	3044(1)	11483(1)	2814(1)	16(1)*
P(6)	2316(1)	13259(1)	1005(1)	26(1)*
C(1)	−185(4)	10955(3)	2013(3)	16(2)*
C(2)	−364(4)	11751(4)	2354(4)	21(2)*
C(3)	−831(5)	12304(4)	1873(4)	24(2)*
C(4)	−1135(5)	12078(4)	1061(4)	27(2)*
C(5)	−988(4)	11288(4)	724(4)	23(2)*
C(6)	−513(4)	10732(4)	1195(3)	19(2)*
C(7)	−10(4)	10499(4)	3576(3)	19(2)*
C(8)	−1093(5)	10384(4)	3597(4)	24(2)*
C(9)	−1490(5)	10596(4)	4284(4)	31(2)*
C(10)	−840(5)	10962(4)	4971(4)	31(2)*
C(11)	236(5)	11090(4)	4968(4)	27(2)*
C(12)	655(5)	10838(3)	4279(4)	22(2)*
C(13)	−291(4)	9229(4)	2253(4)	22(2)*
C(14)	241(4)	8680(4)	1682(4)	21(2)*
C(15)	1483(5)	7926(4)	2904(4)	21(2)*
C(16)	2397(5)	7812(4)	3429(4)	25(2)*
C(17)	2375(5)	7220(4)	3961(4)	28(2)*
C(18)	1448(6)	6749(4)	4008(4)	35(3)*
C(19)	542(6)	6883(4)	3522(4)	39(3)*
C(20)	552(5)	7459(4)	2968(4)	33(2)*
C(21)	2348(5)	8119(4)	1458(4)	22(2)*
C(22)	3259(4)	8687(4)	1260(3)	20(2)*
C(23)	4662(4)	8958(4)	2795(3)	20(2)*
C(24)	4833(5)	8125(4)	2634(4)	27(2)*
C(25)	5530(5)	7762(4)	3168(4)	35(3)*
C(26)	6065(5)	8224(4)	3860(4)	35(3)*
C(27)	5889(5)	9054(4)	4032(4)	27(2)*
C(28)	5180(4)	9417(4)	3508(3)	21(2)*
C(29)	4772(4)	10110(3)	1637(3)	18(2)*
C(30)	5861(5)	10191(4)	1925(4)	23(2)*
C(31)	6567(4)	10666(4)	1556(4)	23(2)*
C(32)	6191(5)	11054(4)	902(4)	26(2)*
C(33)	5117(5)	10978(4)	606(4)	27(2)*
C(34)	4413(5)	10511(4)	976(3)	21(2)*
C(35)	3041(5)	14520(4)	4915(4)	30(2)*
C(36)	3008(5)	14909(4)	5678(4)	46(3)*
C(37)	3541(6)	15696(5)	5942(5)	52(3)*
C(38)	4085(5)	16102(4)	5433(5)	45(3)*
C(39)	4143(6)	15731(4)	4671(5)	48(3)*
C(40)	3618(5)	14928(4)	4419(4)	35(2)*
C(41)	1053(5)	13748(4)	4131(4)	25(2)*
C(42)	971(5)	14358(4)	3605(4)	33(2)*
C(43)	2(5)	14536(4)	3239(4)	38(3)*
C(44)	−917(5)	14114(4)	3382(4)	42(3)*
C(45)	−863(5)	13506(5)	3892(4)	47(3)*
C(46)	115(5)	13316(4)	4272(4)	36(3)*
C(47)	2918(5)	13035(4)	3785(4)	23(2)*
C(48)	2443(5)	12126(3)	3540(4)	21(2)*
C(49)	4433(4)	11644(3)	3297(4)	20(2)*
C(50)	5261(5)	11874(4)	2885(4)	23(2)*
C(51)	6300(5)	11981(4)	3276(4)	29(2)*
C(52)	6535(5)	11851(4)	4071(4)	29(2)*
C(53)	5724(5)	11612(4)	4482(4)	30(2)*
C(54)	4693(5)	11521(4)	4094(4)	24(2)*
C(55)	3071(4)	12150(4)	1998(3)	20(2)*
C(56)	2019(5)	12454(4)	1663(4)	23(2)*
C(57)	1024(5)	13532(4)	591(4)	28(2)*
C(58)	451(5)	13955(4)	1103(4)	37(3)*
C(59)	−517(6)	14228(4)	822(5)	45(3)*
C(60)	−922(5)	14103(4)	14(4)	40(3)*
C(61)	−358(5)	13690(4)	−510(4)	37(3)*
C(62)	588(5)	13407(4)	−219(4)	31(2)*
C(63)	2727(5)	12659(4)	155(4)	26(2)*
C(64)	2344(5)	11833(4)	−108(4)	25(2)*
C(65)	2703(5)	11388(4)	−740(4)	29(2)*
C(66)	3413(6)	11777(4)	−1138(4)	43(3)*
C(67)	3815(6)	12591(5)	−885(5)	51(3)*
C(68)	3480(6)	13025(4)	−231(4)	41(3)*
Cl(4)	4793(2)	5211(2)	2511(2)	78(1)*
Cl(5)	3896(2)	5787(2)	1033(2)	90(1)*
Cl(3)	2773(2)	5879(2)	2370(2)	80(1)*
C(69)	3611(6)	5319(5)	1877(5)	50(3)*
O	7127(4)	4704(4)	1792(4)	68(2)*
C(70)	7943(8)	6124(6)	2125(7)	97(5)*
C(71)	7245(7)	5506(5)	1513(6)	77(4)*
C(72)	6449(8)	4117(6)	1195(5)	82(4)*
C(73)	6289(8)	3331(5)	1553(7)	85(5)*

Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

in chloroform and methylene chloride and moderately soluble in toluene. $RuCl_2(TRIPHOS)_2$ is air stable as solid or in solution.

X-ray Crystal Structure of $RuCl_2(TRIPHOS)_2$

Final atomic positional and thermal parameters are given in Table 2 while selected interatomic distances and angles are in Table 3. One molecule of **1** crystallizes along with one molecule of chloroform and one of diethyl ether in the asymmetric unit. There are no unusual contacts between these entities.

From Fig. 1 can be seen that the ruthenium atom in **1** has six atoms bound to it, forming an almost perfect octahedron. The two chlorine atoms are at equal distance from the metal. The four coordinated phosphorus, the central one of a TRIPHOS and the three of the other phosphine, lie in a plane that is perpendicular to the Cl–Ru–Cl axis. The terminal phosphorus atoms of the chelate TRIPHOS and the central of the other phosphine, P(5), have Ru–P bond distances between 2.358–2.397 Å, while the central phosphorus of the chelate TRIPHOS, P(2),

TABLE 3. Selected interatomic distances (Å) and angles (°) for $RuCl_2\{[Ph_2P(CH_2)_2]_2PPh\}_2 \cdot CHCl_3 \cdot (C_2H_5)_2O$

Distances			
Ru–Cl(1)	2.436(1)	Ru–Cl(2)	2.418(1)
Ru–P(1)	2.390(2)	Ru–P(2)	2.296(1)
Ru–P(3)	2.358(2)	Ru–P(5)	2.397(1)
P(1)–C(13)	1.860(5)	P(2)–C(14)	1.831(6)
P(2)–C(21)	1.863(6)	P(3)–C(22)	1.851(5)
P(4)–C(47)	1.868(7)	P(5)–C(48)	1.833(6)
P(5)–C(55)	1.841(6)	P(6)–C(56)	1.849(7)
Angles			
Cl(1)–Ru–Cl(2)	179.3(1)	Cl(1)–Ru–P(1)	85.6(1)
Cl(1)–Ru–P(2)	86.9(1)	Cl(1)–Ru–P(3)	85.2(1)
Cl(1)–Ru–P(5)	90.9(1)	Cl(2)–Ru–P(1)	94.5(1)
Cl(2)–Ru–P(2)	93.9(1)	Cl(2)–Ru–P(3)	94.9(1)
Cl(2)–Ru–P(5)	88.3(1)	P(1)–Ru–P(3)	161.9(1)
P(2)–Ru–P(5)	177.5(1)	P(1)–Ru–P(2)	82.5(1)
P(1)–Ru–P(5)	98.6(1)	P(2)–Ru–P(3)	81.4(1)
P(3)–Ru–P(5)	97.2(1)	Ru–P(1)–C(13)	106.8(2)
Ru–P(2)–C(14)	107.5(2)	Ru–P(2)–C(21)	111.5(2)
Ru–P(3)–C(22)	104.7(2)	Ru–P(5)–C(48)	115.6(2)
Ru–P(5)–C(55)	119.7(2)		

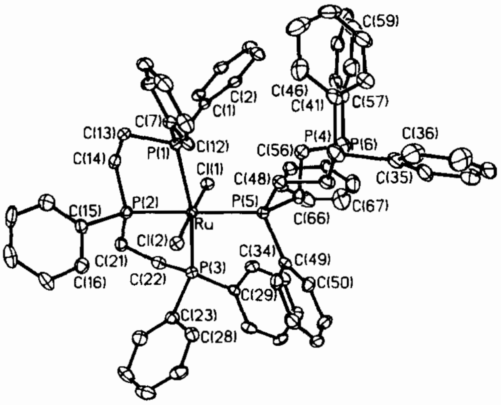

Fig. 1. A perspective view of the labelled molecule of $RuCl_2\{[Ph_2P(CH_2)_2]_2PPh\}_2$ (**1**).

has a shorter Ru–P bond, 2.2296 Å. The terminal phosphorus atoms, P(1) and P(3), are tilted toward P(2) with P–Ru–P(2) angles of 81.4° and 82.5°. As a consequence, the P(1)–Ru–P(3) angle is 161.9° while the unconstrained P(2)–Ru–P(4) angle is 177.5°. The P(1)–Ru–P(3) angle is below the limit of 166° predicted previously for TRIPHOS in a meridional geometry [14]. Phosphorus atoms P(4) and P(6) show no interaction with the ruthenium atom as seen best in Fig. 2. The bond distances between all the aliphatic carbons and the phosphorus are within 1.831–1.868 Å and the angles are between 103.4–119.7°. The conformation of the chelating TRIPHOS can be clearly seen in Fig. 3. The geometric constraints of this ring are quite severe. The four

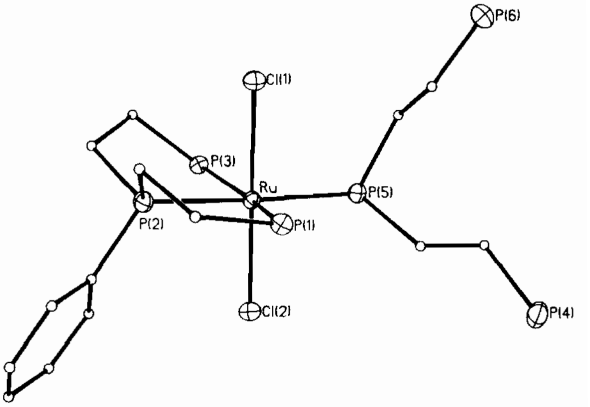

Fig. 2. A perspective view of the inner ruthenium coordination in $RuCl_2(TRIPHOS)_2$ with phenyl groups omitted.

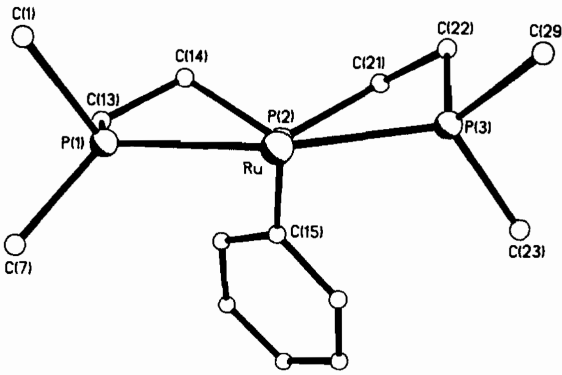

Fig. 3. A view of the chelate ring conformations in $RuCl_2(TRIPHOS)_2$.

methylene carbons are forced to lie on one side of the P(3)–Ru plane while the phenyl ring attached to P(2) lies on the opposite side. Each of the five-membered chelate rings adopts an asymmetric envelope conformation rather than the more usual symmetric skew conformation [15].

^{31}P NMR Spectral Studies

Figure 4 shows the ^{31}P NMR spectra of **1** over the temperature range 24 to –75 °C. These spectra indicate that a fluxional process occurs in solution. At room temperature four signals can be observed: two doublets at 106.2 and 23.6 ppm and two singlets at 51.2 and –0.7 ppm. As the temperature is lowered the two singlets broaden and at –75 °C the low field signal has split into two, 3.6 and –4.4 ppm. At –75 °C the signal at *c.* 50 ppm appears as an AB quartet with $J(P,P)$ of 303.7 Hz.

The signal at 106.2 ppm is assigned to the central phosphorus of the chelate TRIPHOS, while the one at 23.6 ppm is assigned to the central phosphorus of the other TRIPHOS. Those two signals show coupling [6] consistent with a *trans* P–Ru–P′ unit ($^2J(P–P)$ 296.7 Hz). The signal at about 50 ppm is

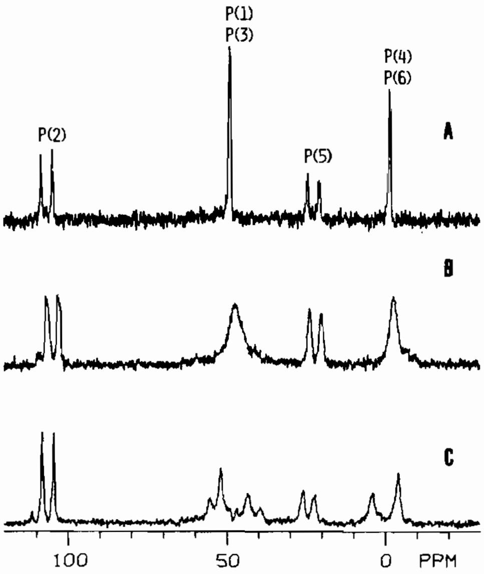

Fig. 4. The experimental $^{31}P\{^1H\}$ NMR of a solution of $RuCl_2(TRIPHOS)_2$ in methylene chloride at: 24 °C (A), −50 °C (B), −75 °C (C).

assigned to the terminal phosphorus bound to the ruthenium while the signal around −1 ppm is assigned to the free terminal phosphorus.

Discussion

The substitution of the triphenylphosphines in $RuCl_2(PPh_3)_3$ by TRIPHOS took place cleanly to yield $RuCl_2(TRIPHOS)_2$ in good yield. As in most of the polyphosphines substitutions [5, 7] on ruthenium triphenylphosphine compounds, the product is an octahedral monomer with *trans* chloride ligands. This synthetic substitution reaction was preferred because it always seems to afford monomers, something that does not always happen when starting with $RuCl_3$ and polyphosphines [8].

From the X-ray of $RuCl_2(TRIPHOS)_2$, the Ru–Cl and Ru–P distances fall within normal ranges [16] as can be seen in Table 3 and these distances are very similar to those in $RuCl_2(PPh_3)_3$ [16].

The chelate TRIPHOS of **1** is in a meridional arrangement that is quite unusual for this ligand which usually adopts facial configuration [10, 17]. In this chelate ligand, the two terminal phosphorus atoms have slightly longer Ru–P bonds (0.06 and 0.09 Å) than the central one. The same pattern of a longer terminal phosphorus–metal bond than the central phosphorus–metal bond has been reported for rhodium [17] in which bis(3-diphenylphosphinopropyl)phenylphosphine is the meridional chelate ligand. The phosphorus *trans* effect and the chelate meridional position adopted by the ligand are the reasons given for this difference in the rhodium compounds. In the case of **1**, the linear chelate position of the ligand should be taken more into consideration as a cause for this bond length difference, since it is not only TRIPHOS in a meridional position but each ring has five members. The chelate size too is a probable cause for the deviation of the phosphorus–metal–phosphorus bond (Table 3) making the terminal phosphorus atom look tilted toward the central one, Fig. 3. This deviation in the angles is not observed in the meridional chelated [14, 17] complexes with bis(3-diphenylphosphinopropyl)phenylphosphine.

From the ^{31}P NMR spectra at different temperatures, Fig. 4, it should be noted that only two signals undergo signs of exchange. The other two, at 106.2 and 23.6 ppm, remain effectively unaltered. If exchange of free and bound terminal phosphorus atoms was taking place, a new signal due to a different kind of central phosphorus should have appeared. Since a new signal does not appear, and there is a lack of change in the signal of the central phosphorus atoms, P(2) and P(5), the fluxional process leaves the P(2)–Ru–P(5) unit intact. However, the observed changes are consistent with the rotation of the monodentate TRIPHOS about the central Ru–P(5) bond. A similar example of changes of ^{31}P spectra upon rotation of a ligand about a Pb–P bond was reported for a lead compound [18]. At 24 °C this rotation renders P(6) equivalent with P(4) and P(1) equivalent with P(3). However, at −75 °C this rotation is slowed and these phosphorus atoms are no longer pairwise equivalent. Rather they are frozen into a geometry that is probably like that seen in the solid state where P(6) and P(4) are different because of their location relative to the chelating ligand and in particular the phenyl ring attached to P(2). This is readily seen in Fig. 2. Likewise when rotation about the Ru–P(5) bond is stopped, P(1) and P(3) become inequivalent because of their relationship to the monodentate TRIPHOS. This is clearly apparent in Fig. 1. Since P(1) and P(3) are *trans* to one another, a *trans*-P–P coupling constant of *c*. 300 Hz is expected and that is exactly what is seen in the AB pattern at *c*. 50 ppm in the −75 °C spectrum (trace C of Figure 4).

Conclusions

The new compound $RuCl_2(TRIPHOS)_2$ was synthesized from $RuCl_2(PPh_3)_3$ and TRIPHOS. The X-ray structure shows an unique meridional chelate arrangement for one TRIPHOS ligand, while only the central phosphorus of the second ligand is bound to the metal. Few examples are known of metal/polyphosphine complexes were two molecules of the same ligand will bond in different ways to the metal center

[19, 20]. ^{31}P NMR data indicated that in solution the monocoordinated TRIPHOS rotates around the ruthenium–phosphorus bond.

The catalytic activity of this ruthenium–TRIPHOS compound is now under study as well the possible reactions of it with other metals through the free phosphorus atoms.

Supplementary Material

A stereoview of **1** and listings of all bond lengths, bond angles, anisotropic thermal parameters for **1** (6 pages); and listings of H atom coordinates and isotropic thermal parameters for **1** (2 pages) are available from the author on request.

Acknowledgements

R. Guimerans thanks CONICIT (Grant S1-1680) and U.S.B. for their support. A. L. Balch thanks the U.S. National Science Foundation for support.

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