Journal of Organometallic Chemistry, 276 (1984) 241–248
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE SYNTHESIS AND STRUCTURE OF BIS{2-[(DIPHENOXYPHOSPHINO)OXY]PHENYL-*C*,*P*}BIS(TRIPHENYLPHOSPHITE-*P*)RUTHENIUM, $[(C_6H_5O)_2\overline{POC_6H_4]_2Ru}[P(OC_6H_5)_3]_2$

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(Received May 11th, 1984)

Summary

The reaction of $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4Ru}Cl$ (I) with phenoxides yields the title compound, II. This represents a new synthesis of compound II. Crystals of II were obtained from hexane/toluene. II crystallizes in the monoclinic $P2_1/c$ space group with a 15.39(1), b 15.33(1), c 27.16(1) Å, β 94.32(5)°, $Z = 4$, D_x 1.39 g/cm^3. The structure was solved at ambient temperature using Mo-K_α radiation with μ 4.1 cm^{-1}, $F(000) = 2767.70$ and $R = 0.0780$, ($R_w = 0.0718$). There were 4991 unique observed reflections. The main feature of the structure is the presence of two orthometallated triphenylphosphite ligands and two conventional triphenylphosphite ligands leading to the presence of *cis*-aryl linkages about ruthenium. The mechanism of formation of II from I is discussed.

Introduction

In 1969, Parshall [1] and coworkers reported the synthesis of the complex $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4Ru}Cl$ (I). Most intriguing was the fact that this molecule catalyzed selective H–D exchange on phenol. The reaction between I and phenoxide was studied in order to determine if phenoxide played a direct role in the H–D exchange mechanism. The result of the present work was the synthesis of the title compound, II, from the reaction of I and phenoxide. This paper discusses the synthesis, structure, and mechanism of formation of II.

Experimental

The solvents THF and toluene were dried over Na benzophenone ketyl then vacuum transferred. Hexane was dried over P_4O_{10} and vacuum transferred.

Compound I, $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4Ru}Cl$, was synthesized according to the method of Parshall [1]. II, $[(C_6H_5O)_2\overline{P(OC_6H_4)]_2Ru}[P(OC_6H_5)_3]_2$, was prepared by combining I (0.21 g, 0.15 mmol) and $NaOC_6H_5$ (0.020 g, 0.17 mmol) in 15 ml THF and gently refluxing for 1 h. The identical product, II, was obtained when the phenoxides p-$OC_6H_4CH_3$ and 2,6-$OC_6H_3(C(CH_3)_3)_2$ were substituted for

0022-328X/84/$03.00

TABLE 1

CRYSTALLOGRAPHIC DATA FOR $[(C_6H_5O)_3P]_2[(C_6H_5O)_2\overline{P(OC_6H_4)]_2Ru}$

Chemical formula	$C_{72}H_{58}O_{12}P_4Ru$
Crystal description	Off white prisms
Dimension, mm	0.2 × 0.2 × 0.3
Lattice constants	
a, Å	15.39(1)
b, Å	15.33(1)
c, Å	27.16(1)
β, deg	94.32(5)
Radiation wavelength, Å	Monochromated Mo-K_α, 0.71069
Temperature of collection	Ambient
Space group	$P2_1/c$
μ, cm^{-1}	4.1
2θ range, deg	$3 < 2\theta < 45$
Type of diffractometer	Nicolet P3F
Conditions for collecting reflections	$+h$, $+k$, $\pm l$
Number of reflections measured	8033
Unique observed reflections with $F > 2.5\sigma(F)$	4991

$NaOC_6H_5$. The refluxed solution was filtered in the glove box and the THF removed in vacuo. The yield of II was essentially quantitative as measured by $^{31}P\{^1H\}$ NMR. The dried residue was recrystallized by slow diffusion of hexane into a toluene solution of the residue. An off-white crystal was sealed in a 0.2 mm glass capillary under argon.

Reaction with $AgPF_6$

I (0.205 g, 0.149 mmol) was dissolved in 10 ml of toluene, $AgPF_6$ (0.042 g, 0.166 mmol) was added, and the solution stirred for 15 min. The solution was filtered and the solvent removed under vacuum. The $^{31}P\{^1H\}$ NMR of the dried filtrate was obtained in $CDCl_3$ solution on a Varian XL 300 (121.5 MHz) NMR spectrometer.

Crystallography

The crystallographic data are summarized in Table 1. The structure was solved using the SHELXTL [2] program package. The Ru position was located from a Patterson map. Other atoms were identified from difference Fourier synthesis. In later stages of the refinement, H atoms were included with fixed bond lengths and temperature factors of 0.96 Å and 0.06 Å [2], respectively. All non-hydrogen atoms were refined anisotropically. A total of 802 parameters were refined resulting in $R_w = 0.0718$ and $R = 0.0780$. The weighting scheme employed was $w = 1/[\sigma^2(F) + 0.001F^2]$. The final difference Fourier map had minimum and maximum values of -0.57 e/A^3 and $+0.57$ e/A^3, respectively. Table 2 lists the atom coordinates and temperature factors for II. Bond distances and angles are given in Tables 3 and 4, respectively. Tables 2–4 can be found in the supplementary material *. Also

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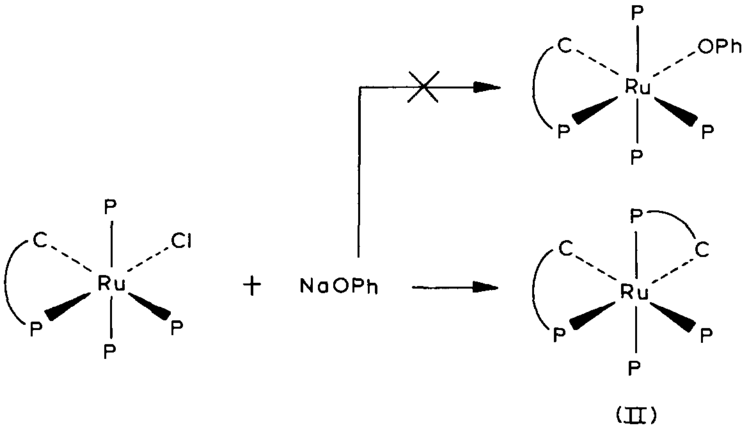
* Please send requests for supplementary material to Larry Lewis, General Electric Research and Development Center, Building K-1, Room 5B10, P.O. Box 8, Schenectady, NY 12301, U.S.A. Send self-addressed stamped envelope.

included are the anisotropic temperature factors, Table 5, and the observed and calculated structure factors, Table 6.

Results and discussion

The anticipated result of treating a phenoxide with I was the formation of a Ru–phenoxide (oxygen) bond. As shown in eq. 1, this was not the case, rather eq. 1 was a new route to II which had been previously synthesized [3,4].



(1)

(II)

II was identified by comparing the $^{31}P\{^1H\}$ NMR spectrum to the reported spectrum [3,4] for this compound. In addition, II was synthesized by a literature procedure [3], and the $^{31}P\{^1H\}$ NMR spectrum of this material was identical to that of the product of eq. 1. The field desorption mass spectrum of II shows M^+ with a cluster of peaks centered at 1340 amu. II was proposed [3] to contain two *cis*-Ru–C linkages. It was of interest to determine the structure of II and compare II to that reported [5] for the analogous iridium system, $[(C_6H_5O)_3P(C_6H_5O)_2\overline{POC_6H_4]_2Ir}Cl$, since II is completely substituted in phosphites. The increased steric crowding about the metal by replacing a chloride by a triphenylphosphite might result in some unusual structural effects. Crystals of the compound were grown and submitted for X-ray structural analysis.

Description of the structure

Figure 1 shows the numbering scheme for II. A three dimensional stereo view (thermal ellipsoids) is given in Fig. 2. The molecule is composed of a ruthenium bound by two conventional triphenylphosphite ligands (P(1) and P(4)) and two triphenylphosphite ligands (P(2) and P(3)) in which orthometallation has occurred thus forming two metal carbon bonds. The structure of II generally derives from that proposed for I wherein the Cl ligand has been replaced by a second metal carbon bond [1].

The complex is a distorted octahedron. The smallest angles about ruthenium are formed between the phosphorus atoms and their ring carbon attached to the metal: P(3)–Ru–C(38) 77.5°, P(2)–Ru–C(20) 79.2°. The widest angle is P(2)–Ru–P(4) 105.9°; this angle is *trans* to the C(20)–Ru–C(38) angle. The angles about phosphorus are reduced by orthometallation as well. Thus the smallest Ru–P–O angles occur for the two orthometallated ring systems Ru–P(2)–O(4) 108.2° and Ru–P(3)–O(7) 108.8°. This compares with a similar contraction observed in the structure of other orthometallated systems [5,6]. No significant change in the P–O or

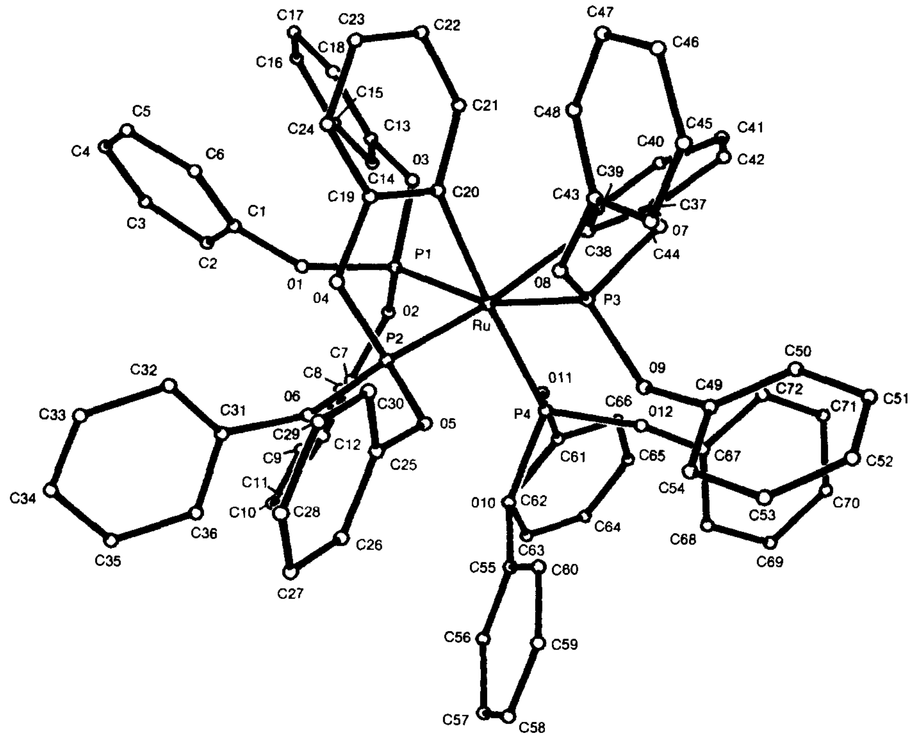


Fig. 1. Numbering scheme for $[(C_6H_5O)_2\overline{POC_6H_4]_2Ru}[P(OC_6H_5)_3]_2$, II.

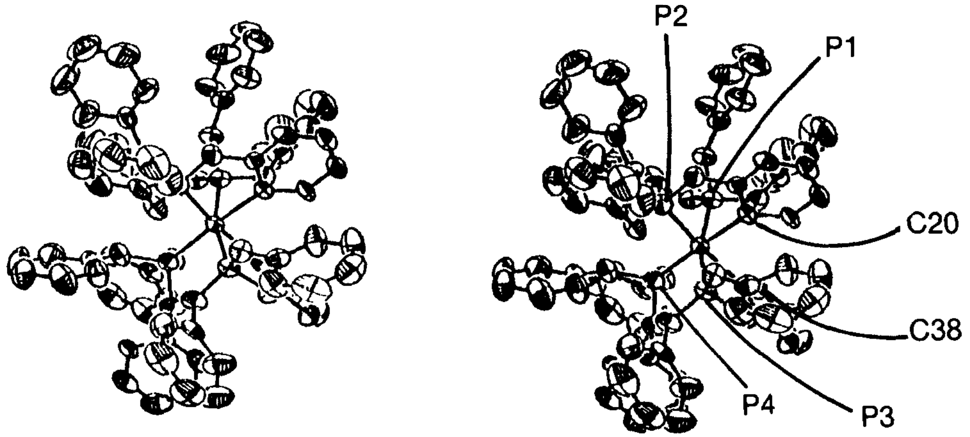


Fig. 2. Three dimensional ORTEP drawing of II. Phosphites P(1) and P(3) bend to distort the octahedron about the central ruthenium atom.

C–O distances was observed upon chelation here or in other similar structures. The two Ru–P bonds shorten upon orthometallation. Thus, Ru–P(2) and Ru–P(3) are 2.245 and 2.264 Å, respectively, whereas Ru–P(1) and Ru–P(4) are 2.312 and 2.288 Å, respectively, for an average reduction in bond distance of 0.045 Å or 5σ.

The main feature of the structure is the presence of two *ortho*-ring carbon to metal linkages. These linkages form planar five-membered rings. The presence of the two linkages produces a molecule which is diastereotopic. Figure 3 is a "stripped down" packing diagram which shows both diastereomers. Deviation of the atoms from either plane 1 [Ru–P(3)–O(7)–C(37)–C(38)] or plane 2 [Ru–P(2)–O(4)–C(19)–C(20)] is small, as can be seen in Table 7. The standard deviations of planes 1 and 2 of 0.09 and 0.01 Å agree well with the 0.05 Å average deviation from planarity for the analogous five membered rings in $[(C_6H_5O)_3P][(C_6H_5O)_2\overline{POC_6H_4]_2Ir}Cl$ [5].

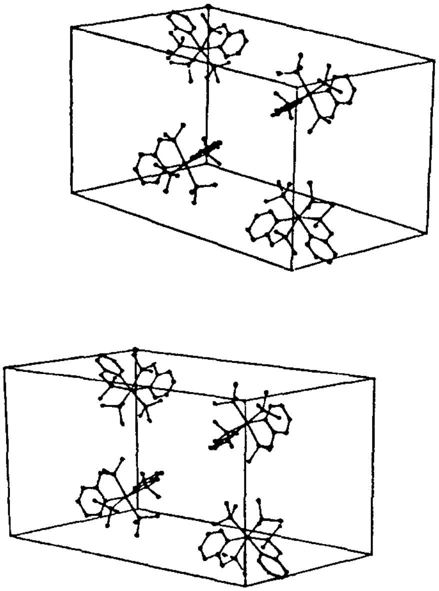


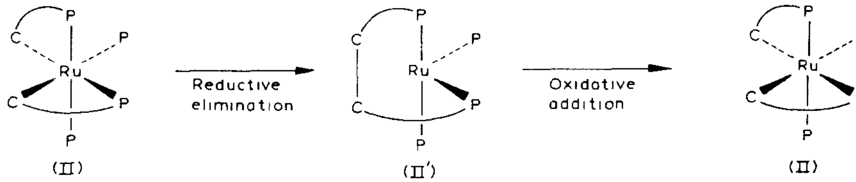
Fig. 3. Three dimensional packing diagram of II. The molecules have been "stripped down" in order that the two pairs of diastereomers can be seen. Ruthenium, P(1)–P(4), O(1)–O(12) and the carbons of the orthometallated rings, C(19)–C(24) and C(37)–C(42) are included in the drawing.

TABLE 7

DEVIATIONS (Å) FROM LEAST SQUARES PLANES

Plane	1		2
Ru	−0.08	Ru	−0.01
P(3)	+0.12	P(2)	+0.01
O(7)	−0.12	O(4)	0
C(37)	+0.02	C(19)	−0.01
C(38)	+0.06	C(20)	+0.01

What is most remarkable is the stability (m.p. 250°C) of II in light of the presence of the *cis*-Ru–C bonds. The distance between C(20) and C(38) is 3.01 Å while the angle C(20)–Ru–C(38) is 89.4°. In the analogous iridium complex referred to above, the C–C distance is 2.951 Å. In the octahedral complex, *cis*-$Cr(bipy)_2Ph_2$ where the C–Cr–C angle is large (93.7°), the carbon–carbon distance is 3.05 Å [7]. The bipy ligand is sterically less demanding than the phosphites of II. In the square planar complex, *cis*-$PtPh_2(Ph_2PCH_2PPh_2)$, the metal bound carbon–carbon distance is 2.82 Å (angle C–Pt–C 87°) [8]. The analogous palladium system, *cis*-$Pd(CH_3)_2(PPh_3)_2$, is known to reductively eliminate ethane upon heating. This appears to be a general reaction for *cis*-L_2MR_2 square planar complexes, R = alkyl or aryl, which have a propensity toward reductive elimination and concomitant C–C bond formation [9]. The lack of such reactivity in II may be related to the high activation energy associated with C–C bond formation. In other bis-alkylmetals where reductive elimination occurs, the organic moiety produced is often soluble in the reaction medium or is a gas which is given off, thus release of the R–R species from $M\genfrac{}{}{0pt}{}{R}{R}$ is often favored thermodynamically. In II there is a chelate effect which holds the newly formed C–C bond in place near the metal (eq. 2).

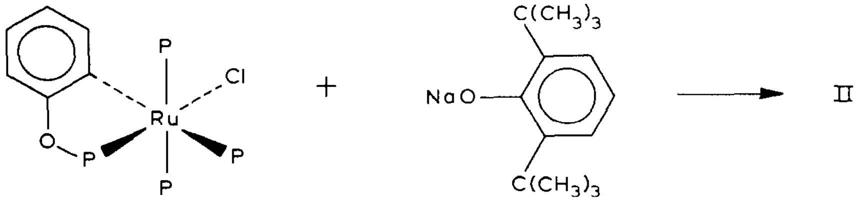


(2)

Oxidative addition of the C–C bond II′ to reform II is probable due to the closeness of the bond to the metal. In addition, there may also be a kinetic barrier to formation of the C–C bond in II′ in the first place. The two phosphorus atoms which contain the orthometallated groups may not be able to move close enough, for steric reasons, to bring the two metal–carbon units within bonding distance.

Formation of II

Reaction 1 was further probed in order to ascertain if a ruthenium phenoxide intermediate was responsible for production of II. A few Group VIII metal alkoxides have been reported [10], but there are no known terminal phenoxide complexes for this group. A ruthenium phenoxide intermediate was ruled out by the reaction of I with 2,6-di-t-butyl phenoxide (eq. 3).

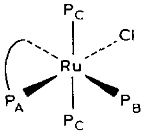


(3)

It is unlikely that the oxygen on this bulky phenol could approach ruthenium to form a bond. Thus, phenoxide acted simply as a base for abstraction of the

TABLE 8

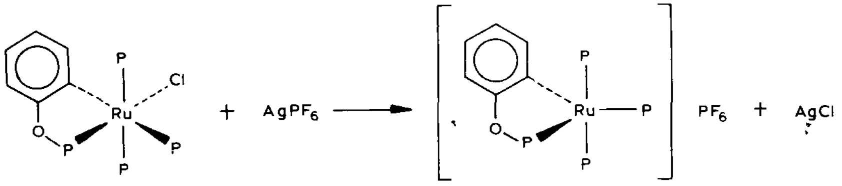
$^{31}P\{^1H\}$ NMR SPECTRA OF I AND III



Chemical shifts ^{a}			Coupling constants (Hz)	
I	A	155.24	J_{AB}	43.0
	B	123.92	J_{AC}	61.2
	C	116.52	J_{BC}	50.5
III	A	151.86	J_{AB}	44.3
	B	120.18	J_{AC}	68.4
	C	111.56	J_{BC}	49.5

^{a} Chemical shifts relative to external 85% H_3PO_4, decreasing field is positive solvent, $CDCl_3$.

ortho-ring hydrogen to form phenol and II without ruthenium phenoxide formation. This mechanism was further supported by the result of the reaction of I with $AgPF_6$ (eq. 4). The $^{31}P\{^1H\}$ NMR spectrum of the product III of this reaction was similar to that for I (Table 8) except that each resonance of III was shifted upfield. This was consistent with III being a cation [11], structurally related to I.



(4)

(III)

In conclusion, a new synthesis of the title compound has been found from I and phenoxide. The reaction does not involve precoordination of phenoxide to ruthenium, rather a metathetical loss of Cl followed by base abstraction of an *ortho*-ring C–H hydrogen by phenoxide. The outstanding feature of II is the presence of two orthometallated phosphite ligands which results in two aryl carbon to ruthenium bonds *cis* to each other.

Acknowledgments

Liz Williams and Paul Donahue are thanked for recording the $^{31}P\{^1H\}$ NMR spectra. Jack Hallgren is thanked for helpful discussions.

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