

The Synthesis and Structure of Hexakis(dimethylphenylphosphonite)-ruthenium(II) bis[tetraphenylborate(−1)]

Samson O. Owalude,^{*,[a]} Ezekiel O. Odebunmi,^[a] Uche B. Eke,^[a] Adedibu C. Tella,^[a] Arnold L. Rheingold,^[b] and Steven L. Suib^[c]

Keywords: Dimethylphenylphosphonite; Ruthenium; Tetraphenylborate; X-ray crystallography; Spectroscopic analysis

Abstract. Treatment of the hydrazine salt $[\text{Ru}(\text{COD})(\text{H}_2\text{NNH}_2)_4][\text{BPh}_4]_2$ with excess of $\text{P}(\text{OMe})_2\text{Ph}$ in acetone gave a homoleptic complex $\text{trans-}[\text{Ru}\{\text{P}(\text{OMe})_2\text{Ph}\}_6][\text{BPh}_4]_2$, which was characterized by IR, $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, and ^1H NMR spectroscopy, elemental analysis, and

X-ray crystallography. The ruthenium in the complex has distorted octahedral coordination arrangement and bonded to all the six $\text{P}(\text{OMe})_2\text{Ph}$ molecules through the phosphorus atoms.

Introduction

There is continued interest in research into the coordination chemistry of Ru^{II} -phosphine complexes due to their wide application in homogeneous catalysis.^[1] Interest in homoleptic Ru^{II} -phosphorus donor complexes in particular is not only due to their rich structural chemistry and reactivity but also to their unusual redox properties.^[2] Such complexes often contain weakly-bonded anions making them highly suitable in mechanistic studies.^[3] They are also very useful as precursors in synthesis and they may readily give active sites in catalysis.^[3] In this regard, a vast number of Ru^{II} -phosphine complexes have been prepared including very few reports on homoleptic Ru^{II} phosphorus-donor complexes.^[4] Such stable and isolable complexes have been obtained for three molecules of a bidentate diphosphine, 1,1-bis(diphenylphosphanyl)ethane, surrounding a Ru^{II} ion to form hexacoordinate complexes.^[2–5] Other examples in the literature are for mixed bidentate (L-L) and monodentate (L) ligands. Reported examples of this type of homoleptic compounds are for $[\text{Ru}(\text{P-P})_2(\text{L})_2]^{2+}$ [$\text{P-P} = \text{dppe}$; $\text{L} = \text{P}(\text{OMe})_3$ and PMe_3].^[2,4] So far there has been no crystal structure report of homoleptic Ru^{II} compounds bearing only monodentate phosphorus donor ligands. While the inability to prepare homoleptic Ru^{II} -diphosphine complexes with arylidiphosphines has been attributed to steric constraints,^[3,4] the

reason for unsuccessful attempts to prepare monodentate homoleptic Ru^{II} -phosphorus donor complexes remain unraveled. We wish to report herein the successful isolation and characterization of a homoleptic Ru^{II} complex with six monodentate phosphine ligands prepared by treatment of the hydrazine salt $[\text{Ru}(\text{COD})(\text{H}_2\text{NNH}_2)_4][\text{BPh}_4]_2$ in acetone with excess dimethylphenylphosphonite $[\text{P}(\text{OMe})_2\text{Ph}]$.

Applications of the polymer $[\{\text{RuCl}_2(\text{COD})\}_x]$ (**1**) ($\text{COD} = \text{cyclo-octa-1,5-diene}$) as a useful synthetic precursor to a wide range of ruthenium compounds has been documented.^[5,6] Due to high insolubility of this polymer in most organic solvents, reactions with it are usually carried out under extreme conditions, which require filtration steps and long reaction times.^[7] Most often products from these reactions are obtained in moderate to low yields.^[8] However, suspensions of this polymer in methanol have been found to react rapidly with hydrazines to produce clear solutions, from which cationic ruthenium(II) salts were isolated in quantitative yield on addition of suitable counter anions.^[9] Such derivatives of the polymer contain labile hydrazine groups in solution making them ideal precursors for the synthesis of an extensive range of ruthenium(II) salts.^[7,9] The most commonly applied among these hydrazine derivatives is the ruthenium(II) hydrazine salt $[\text{Ru}(\text{COD})(\text{NH}_2\text{NH}_2)_4][\text{BPh}_4]_2$ (**2**) and we have recently demonstrated the use of readily available and non-regulated hydrazine hydrate to produce **2** instead of pure anhydrous hydrazine usually employed in this reaction.^[10]

We have now found that the reaction of **2** with excess $\text{P}(\text{OMe})_2\text{Ph}$ in acetone did not give the Ru^{II} -bishydrazone salts as reported in the literature^[11,12] but a homoleptic ruthenium(II)-phosphorus donor complex $[\text{Ru}\{\text{P}(\text{OMe})_2\text{Ph}\}_6][\text{BPh}_4]_2$ (**3**). An X-ray diffraction study of a suitable crystal of **3** was therefore undertaken to confirm the structure. This complex is the first example ever of a homoleptic ruthenium(II)-phosphorus donor complex. The crystallographic structure of a homoleptic Ru^{II} -phosphorus donor com-

* Dr. S. O. Owalude
E-Mail: owalude1412@yahoo.com; owalude@unilorin.edu.ng

[a] Department of Chemistry
University of Ilorin

P.M.B. 1515, Ilorin, Nigeria

[b] Department of Chemistry and Biochemistry
University of California, San Diego
La Jolla CA, 92093-0358, USA

[c] Department of Chemistry
University of Connecticut, U-3060
55 North Eagleville Road
Storrs, 06269-3060, USA

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/zaac.201300422> or from the author.

plex with two chelating 1,1-bis(diphenylphosphanyl)ethane and two P(OMe)_3 ligands has, however, been reported.^[12]

Results and Discussion

Treatment of the hydrazine salt **2** with excess $\text{P(OMe)}_2\text{Ph}$ in refluxing acetone for 19 h gave in good yield a product of stoichiometry $[\text{Ru}\{\text{P(OMe)}_2\text{Ph}\}_6][\text{BPh}_4]_2$. The complex was of limited stability and was therefore stored in an inert atmosphere. The complex is soluble in CHCl_3 , CH_2Cl_2 , DMF, and DMSO solvents but not in methanol, ethanol, hexane, pentane, THF, and diethyl ether.

Spectroscopic Analyses

In order to study the bonding mode of ligand to metal in the new compound, the IR and the ^1H NMR spectra of both the precursor **2** and those of complex **3** were compared. The complex has a new $\nu(\text{Ru-P})$ band at 528 cm^{-1} ,^[13] while all the other characteristic IR bands observed in **2**^[10] were completely absent. The ^1H NMR spectrum of **3** contains a singlet at $\delta = 3.26\text{ ppm}$, which was assigned to the protons on the methoxy groups of $\text{P(OMe)}_2\text{Ph}$ but lacks the proton resonances of coordinated COD and hydrazine. The phenyl protons on the BPh_4 molecule were observed as multiplets in the expected ratio of 2:2:1 between 6.80–7.2 ppm, while those on the $\text{P(OMe)}_2\text{Ph}$ were also observed as multiplets between 7.30–7.90 ppm. The ^{13}C spectrum of **3** in DMSO gave a series of lines in the region 122–136 ppm, which were assigned to the aromatic carbon atoms of the phenyl rings, while the presence of methoxy carbon atoms were observed as a single line at $\delta = 57.22\text{ ppm}$. The $^3\text{P}\{^1\text{H}\}$ NMR spectrum of **3** is a singlet at $\delta = 154.81\text{ ppm}$, which indicates that all the phosphorus atoms in the complex are chemically equivalent.^[14] The ^{31}P chemical shift of free $\text{P(OMe)}_2\text{Ph}$ has been reported at $\delta +165.09\text{ ppm}$.^[15] The coordination shift is therefore 11 units upfield when the free $\text{P(OMe)}_2\text{Ph}$ becomes coordinated to the ruthenium in $[\text{Ru}\{\text{P(OMe)}_2\text{Ph}\}_6]^{2+}$ complex.

X-ray Crystallography Diffraction Analyses

Crystals of $[\text{Ru}\{\text{P(OMe)}_2\text{Ph}\}_6][\text{BPh}_4]_2$ (**3**) suitable for X-ray diffraction studies were obtained by a slow diffusion of diethyl ether into a solution of the complex in CH_2Cl_2 . The structure consists of two tetraphenylborate anions (not shown)

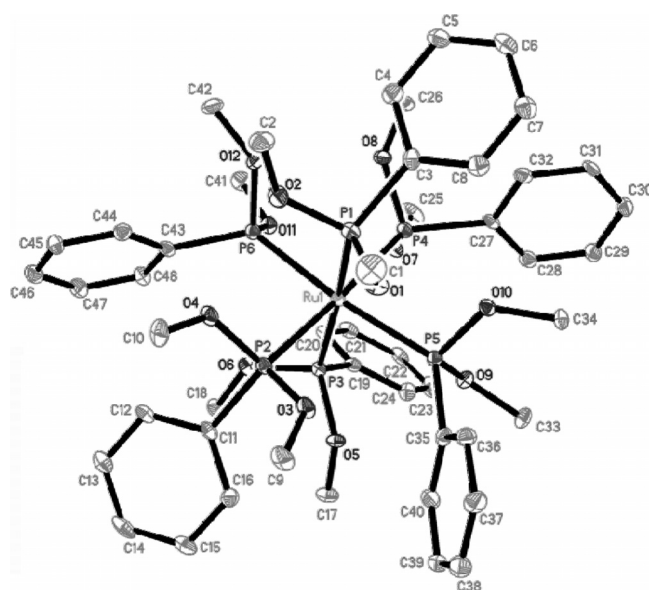


Figure 1. ORTEP view of the structure of the $[\text{Ru}\{\text{P(OMe)}_2\text{Ph}\}_6]^{2+}$ cation with numbering scheme adopted. The BPh_4^- anions and hydrogen atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level.

and a cation shown in the ORTEP diagram in Figure 1. The structure shows six P-bonded $\text{P(OMe)}_2\text{Ph}$ ligands coordinated in a distorted octahedral arrangement to the central Ru^{2+} cation with two BPh_4^- anions outside the coordination sphere. The average Ru-P-C bond angle of $127.28(14)^\circ$ in **3** indicates that the $\text{P(OMe)}_2\text{Ph}$ ligands bind to the ruthenium with the phenyl ring significantly bent. The P-Ru-P angles between mutually *trans* $\text{P(OMe)}_2\text{Ph}$ ligands are 176.52 , 171.72 , and $171.9(4)^\circ$. The angles around the ruthenium atom are all close to 90° (mean = 87°) in line with the octahedral coordination arrangement. The six phenyl rings in the structure have the average C–C bond length of $1.393(6)\text{ \AA}$ and C–C–C bond angles of 120.1° , which are within the accepted values of $1.394\text{ \AA}$ and 120° for phenyl rings.^[16] Mean P–O and O–C distances are $1.596(3)$ and $1.450(5)\text{ \AA}$ and are normal.^[17] The mean Ru–P distance in **3** ($2.3714\text{ \AA}$) (Table 1) is significantly longer than the average Ru–P bond length of $2.31\text{ \AA}$ reported for 14 sterically crowded complexes containing *trans*- $[\text{Ru}^{\text{II}}(\text{dmpe})_2]$ moieties^[4,18] suggesting some steric crowding in **3**.^[12,4] In solution, the hydrazine groups probably become destabilized due to the dominant steric interactions of the $\text{P(OMe)}_2\text{Ph}$ ligands, which explains the formation of the homoleptic complex **3** in prefer-

Table 1. Major bond lengths / $\text{\AA}$ and bond angles $^\circ$ of the ruthenium complex $[\text{Ru}\{\text{P(OMe)}_2\text{Ph}\}_6][\text{BPh}_4]_2$.

Ru1–P1	2.4042(12)	P1–O1	1.600(3)	P4–C27	1.824(4)
Ru1–P2	2.3498(11)	P2–O3	1.570(3)	P5–C35	1.816(4)
Ru1–P3	2.3554(11)	P3–O6	1.594(3)	P6–C43	1.817(4)
Ru1–P4	2.3814(11)	P4–O4	1.556(3)	C3–C4	1.412(4)
Ru1–P5	2.3493(11)	P5–O9	1.607(3)	C3–C8	1.394(4)
Ru1–P6	2.3881(11)	P6–O11	1.599(3)	C15–C16	1.401(4)
P2–Ru–P4	87.72(4)	P2–Ru–P4	176.12(4)		
P3–Ru–P6	89.47(4)	P2–Ru–P6	93.28(4)		
P1–Ru–P3	171.72(4)	P5–Ru–P6	171.90(4)		
P2–Ru–P3	87.72(4)	P1–Ru–P2	84.12(4)		

ence to the hydrazone.^[19] The arrangement of the tetraphenylborate ions is in agreement with that found in other structures^[20,21] and no interactions was found between these ions and the ruthenium(II) core.

Conclusions

The complex $[\text{Ru}\{\text{P}(\text{OMe})_2\text{Ph}\}_6][\text{BPh}_4]_2$ (**3**) was synthesized from $[\text{Ru}(\text{COD})(\text{H}_2\text{NNH}_2)_4][\text{BPh}_4]_2$. A distorted octahedral structure was assigned to the complex by analyzing elemental, spectral, and single-crystal X-ray crystallographic data. The X-ray crystallography analysis revealed that complex **3** is hexacoordinate with six $\text{P}(\text{OMe})_2\text{Ph}$ ligands and two tetraphenylborate anions outside the coordination sphere. No interaction between the central ruthenium(II) atom and the tetraphenylborate anion was observed. Work is in progress to expand the scope of this research to other monodentate phosphines and phosphites and also to extend the study to investigation of the redox and spectroscopic properties of the resulting complexes.

Experimental Section

Synthesis of Hexakis(dimethylphenylphosphonite)ruthenium(II) bis[tetraphenylborate(−1)]: $[\text{Ru}(\text{COD})(\text{H}_2\text{NNH}_2)_4][\text{BPh}_4]_2$ (**2**) (1.26 g, 1.20 mmol) was dissolved in acetone (50 mL). The acetone was degassed by three freeze thaw-cycles. An excess of dimethylphenylphosphonite (1.30 g, 7.60 mmol) was added and the solution was refluxed in an argon atmosphere for 19 h. A yellowish precipitate separated out of the solution after this period, which was collected and dried under vacuum to obtain a colorless crystalline solid. The compound was then recrystallized by slow diffusion of Et_2O into the solution of the complex in CH_2Cl_2 . Yield: 1.36 g, 65%. M.p.: decomp $> 240^\circ\text{C}$. IR: $\tilde{\nu} = 528 \text{ v}(\text{Ru}-\text{P}) \text{ cm}^{-1}$. ^1H NMR (CD_2Cl_2): $\delta = 3.26$ (s, OCH_3), 6.79–7.20 [m, $\text{B}(\text{C}_6\text{H}_5)_4$], 7.30–7.90 (m, C_6H_5) ppm. ^{13}C NMR (CD_2Cl_2): $\delta = 122$ – 136 (m, C_6H_5) ppm. ^{31}P NMR (CD_2Cl_2): $\delta = 154.81$ ppm. $\text{C}_{96}\text{H}_{106}\text{B}_2\text{O}_{12}\text{P}_6\text{Ru}$: calcd. C 65.49; H 6.03%; found: C 64.86; H 5.72%.

Supporting Information (see footnote on the first page of this article): Experimental procedures as well as details of the X-ray single crystal structure refinement are given.

Acknowledgements

This work was supported by the United States' Institute of International Education (IIE). The authors would like to thank University of Connecticut for the facilities to carry out the research work and the University of California, San Diego for the X-ray diffraction analysis.

The financial support from The World Bank assisted Science and Technology Education Post Basic (STEP-B) Project is also gratefully acknowledged for a grant of IOT Award to SOO.

References

- [1] a) S. P. Nolan, T. R. Belderrain, R. H. Grubbs, *Organometallics* **1997**, *16*, 5569–5571; b) Y. Nishibayashi, I. Takei, S. Uemura, M. Hidai, *Organometallics* **1998**, *17*, 3420–3422; c) H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A. F. England, T. Ikariya, R. Noyori, *Angew. Chem. Int. Ed.* **1998**, *37*, 1703–1707.
- [2] J. F. Bickley, A. A. La Pensée, S. J. Higgins, C. A. Stuart, *Dalton Trans.* **2003**, 4663–4668.
- [3] J. F. Bickley, S. J. Higgins, C. A. Stuart, A. Steiner, *Inorg. Chem. Commun.* **2000**, *3*, 211–213.
- [4] A. A. La Pensée, J. Bickley, S. J. Higgins, M. Marcaccio, F. Paolucci, S. Roa, J. M. Charnock, *J. Chem. Soc. Dalton Trans.* **2002**, 4095–4104.
- [5] J. J. Pérez-Torrente, C. Cunchillos, D. Gómez-Bautista, M. V. Jiménez, R. Castarlenas, F. J. Lahoz, L. A. Oro, *J. Coord. Chem.* **2012**, *65*, 2981–2991.
- [6] *Comprehensive Organometallic Chemistry*, vol. 4, (Ed.: G. Wilkinson), Pergamon Press, Oxford, **1982**, pp. 748–750.
- [7] S. O. Owolude, E. O. Odebunmi, U. B. Eke, A. L. Rheingold, N. Opembe, S. L. Suib, *J. Organomet. Chem.* **2013**, *739*, 21–25.
- [8] B. M. Barney, H. I. Lee, P. C. Dos Santos, B. M. Hoffman, D. R. Dean, L. C. Seefeldt, *Dalton Trans.* **2006**, 2277–2284.
- [9] T. V. Ashworth, E. Singleton, J. J. Hough, *J. Chem. Soc. Dalton Trans.* **1977**, 1809–1815.
- [10] S. O. Owolude, E. O. Odebunmi, U. B. Eke, R. Meijboom, V. N. Nesterov, E. Singleton, N. J. Coville, *Bull. Chem. Soc. Ethiop.* **2013**, *27*, 405–411.
- [11] E. Singleton, H. E. Swanepoel, *Inorg. Chim. Acta* **1982**, *57*, 217–221.
- [12] H. E. Oosthuizen, E. Singleton, J. S. Field, G. C. Van Niekerk, *J. Organomet. Chem.* **1985**, *279*, 433–446.
- [13] M. Ashok, A. V. Prasad, V. Ravinder, *J. Braz. Chem. Soc.* **2007**, *18*, 1492–1499.
- [14] Z. L. Lu, K. Eichele, I. Warad, H. A. Mayer, E. Lindner, Z. J. Jiang, V. Schurig, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1308–1315.
- [15] K. V. Rajendran, D. G. Gilheany, *Chem. Commun.* **2012**, *48*, 10040–10042.
- [16] G. I. Lamprecht, C. P. van Biljon, J. G. Leipoldt, *Inorg. Chim. Acta* **1986**, *119*, L1–L4.
- [17] A. M. Z. Slawin, P. G. Waddell, J. D. Woollins, *Acta Crystallogr. Sect. E* **2007**, *63*, m2017.
- [18] D. A. Fletcher, R. F. McMeeking, D. Parkin, *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746–749.
- [19] K. S. Hagen, *Inorg. Chem.* **2000**, *39*, 5867–5869.
- [20] T. L. Blundell, H. M. Powell, *Acta Crystallogr., Sect. B* **1971**, *27*, 2304–2310.
- [21] M. D. Vaira, A. B. Orlandini, *J. Chem. Soc. Dalton Trans.* **1972**, 1704–1712.

Received: August 20, 2013
Published Online: November 13, 2013