Inorganica Chimica Acta 392 (2012) 241-245

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Insertion of a phospholide unit into a metal–metal bond: Synthesis and X-ray structure of $[Ru_3(CO)_9(\mu:\eta^1:\eta^5-PC_4H_2Me_2)(\eta^1-C_6H_5)]$

Alejandro J. Arce, Ysaura De Sanctis, María Cristina Goite, Ruben Machado, Yomaira Otero*, Teresa Gonzalez

Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela

ARTICLE INFO

Article history: Received 31 October 2011 Received in revised form 13 January 2012 Accepted 18 January 2012 Available online 2 February 2012

Keywords: Triruthenium clusters Triosmium clusters Phospholes Phospholide

ABSTRACT

The reaction of $[Ru_3(CO)_{12}]$ with 3,4-dimethyl-1-phenylphosphole under mild conditions affords three derivatives which were identified by means of spectroscopic methods as the substitution compounds $[Ru_3(CO)_{12-x}(PhPC_4H_2Me_2)_x]$ (x = 1, 2, 3) in which the phosphole ligand acts as a tertiary phosphine bonded through the phosphorus atom. Thermolysis of the monosubstituted $[Ru_3(CO)_{11}(PhPC_4H_2Me_2)_1]$ in cyclohexane affords two new clusters, characterised as $[Ru_3(CO)_9(\mu^3:\eta^2:\eta^2:\eta^2:\eta^2-PhPC_4H_2Me_2)]$ and $[Ru_3(CO)_9(\mu:\eta^1:\eta^5-PC_4H_2Me_2)(\eta^1-C_6H_5)]$, where the phosphole ring behaves as a six- and sevenelectron donor ligand respectively. The reaction with $[Os_3H_2(CO)_{10}]$ gives the new species $[Os_3(\mu-H)(CO)_9(\mu^3:\eta^1:\eta^1:\eta^2-PhPC_4H_3Me_2)]$ in which the ligand behaves as a five-electron donor.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Five-membered rings containing phosphorus atoms have been synthesised since 1959, however nearly 75% of all known rings of this kind were prepared in the last 20 years. Regarding organome-tallic chemistry, phospholes offer a wide versatility of coordination modes and reactivity patterns [1]. Structural diversity of their transition metal complexes has been facilitated by the ability of the phospholyls to coordinate metals in σ , π , and mixed bonding modes. The coordination chemistry of phosphole is still a fertile area for further research and many of the complexes now known have obvious potential as catalytic systems and multifunctional materials for OLEDs [2].

In an earlier work we have shown that phospholes react with triosmium carbonyl clusters [3] giving rise not only to simple substitution complexes but also to a series of derivatives containing ring-opened ligands. In this paper we describe the synthesis and spectroscopic characterisation of the products from the reaction of ruthenium and osmium carbonyl clusters with 3,4-dimethyl-1phenylphosphole and to the best of our knowledge, the first example of the insertion of a phospholide unit into a Ru–Ru bond is reported.

2. Experimental

2.1. Ruthenium

A solution of $[Ru_3(CO)_{12}]$ (250 mg, 0.391 mmol) and 3,4-dimethylphenylphosphole [4] (73.5 mg, 0.391 mmol) in dried cyclohexane (40 mL) was taken to reflux under nitrogen for 40 min. After evaporation of the solvent, TLC (SiO₂) of the orange-yellow residue (eluant pentane:dichloromethane, 4:1 v:v) gave five main bands: $[Ru_3(CO)_{11}(PhPC_4H_2Me_2)]$ (1) was obtained as pale-yellow crystals from *n*-hexane (25% yield); $[Ru_3(CO)_{10}(PhPC_4H_2Me_2)_2]$ (2) was isolated as a yellow solid (18% yield); $[Ru_3(CO)_9(PhPC_4H_2Me_2)_3]$ (3) (12% yield) was obtained as orange crystals from cyclohexane; $[Ru_3(CO)_9(\mu^3;\eta^2;\eta^2;\eta^2-PhPC_4H_2Me_2)]$ (4) (7% yield) and $[Ru_3(CO)_9(\mu;\eta^1;\eta^5-PC_4H_2Me_2)(\eta^1-C_6H_5)]$ (5) (7% yield) were both isolated as yellow solids.

Thermolysis of 1 (75 mg) in 50 mL of dried cyclohexane under reflux under nitrogen for 3 h gave two yellow bands (eluant pentane:dichloromethane, 10:1 v:v). The first one gave unreacted 1 (35% yield), an the other one gave compound 5 (60% yield), from which pale yellow crystals were obtained from slow evaporation of a cyclohexane solution.

2.2. Osmium

A solution of $[Os_3(\mu-H)_2(CO)_{10}]$ (250 mg, 0.293 mmol) and 3,4dimethylphenylphosphole (55.1 mg, 0.293 mmol) in dried cyclohexane (40 mL) was taken to reflux under nitrogen for 6 h. After evaporation of the solvent, TLC (SiO₂) of the yellow residue

E-mail address: ysantis@ivic.gob.ve (Y. De Sanctis).

Corresponding author.





(eluant pentane) gave one main band: $[Os_3(CO)_9(\mu-H)(\mu^3:\eta^1:\eta^1:\eta^2-PhPC_4H_3Me_2)]$ (**6**) was obtained as yellow crystals from *n*-hexane (35% yield).

¹H, ¹³C and ³¹P NMR spectra were recorded on Bruker Avance 300 and 500 MHz spectrometers and IR spectra were recorded on a Nicolet 5DXC.

3. Results and discussion

The substitution compounds $[Ru_3(CO)_{12-x}(PhPC_4H_2Me_2)_x]$ (x = 1, 2 or 3; 1, 2 and 3, respectively) are obtained under very mild reaction conditions as well as minor quantities of $[Ru_3(-CO)_9(\mu^3:\eta^2:\eta^2:\eta^2-PhPC_4H_2Me_2)]$ (4) and $[Ru_3(CO)_9(\mu:\eta^1:\eta^5-PC_4H_2Me_2)(\eta^1-C_6H_5)]$ (5) (Scheme 1), easily separated by thin layer chromatography on SiO₂. Compounds 1–3 are closely related spectroscopically to their known tertiary phosphine analogues [5,6]

Table 1

Spectroscopic data for compounds 1-6.

and as shown by X-ray crystal structure determinations [7] the phosphole ligand is coordinated only through the phosphorus atom. As in the case of other tertiary phosphine analogues, only one isomer of the decacarbonyl cluster is formed, the 1,2- $[Ru_3(CO)_{10}(PhPC_4H_2Me_2)_2]$ (2), as no evidence for the 1,1-isomer was obtained. The ³¹P NMR sprectrum of 2 shows two equal-intensity singlets for the unsymmetrycal isomer with non-equivalent phosphole ligands at δ = 26.4 and 26.1 ppm (Table 1). The trisubstituted derivative 3 shows only one singlet in the ³¹P NMR sprectrum as expected for three equivalent phosphorus atoms.

A single crystal X-ray structure determination was carried out for cluster **3**, its ORTEP diagram is shown in Fig. 1 and selected bond lengths and angles are shown in Table 2. The structure consists of a triangular Ru₃ core with three nearly equal Ru–Ru bonds showing an average length of 2.858 Å as observed for $[Ru_3(-CO)_9(PPh_3)_3]$ [8], in which the three phosphole ligands take up

Compound	$v(CO)^{a} (cm^{-1})$	NMR ^b (δ, pj	NMR^{b} (δ , ppm)			J (Hz)	
		${}^{31}P{}^{1}H{}$	¹³ C{ ¹ H}	¹ H			
[Ru ₃ (CO) ₁₁ (PhPC ₄ H ₂ Me ₂)] (1)	2095 s 2042 s 2028 s 2012 s 1995 w 1985 m 1960 w	25.8 s	150.2 d, C ² 132.8 d, C ⁴ 130.4 d, C ⁵ 130.3 s, C ⁷ 128.9 d, C ⁶ 127.6 d, C ¹ 17.3 d, C ³	7.49 m, H ⁵ 7.41 m, H ⁶ , H ⁷ 6.54 d, H ¹ 2.07 s, Me	P-H ¹ 36.5 P-C ¹ 48.7 P-C ² 10.2 P-C ³ 12.5	P-C ⁴ 48.7 P-C ⁵ 10.7 P-C ⁶ 10.7	
$[Ru_3(CO)_{10}(PhPC_4H_2Me_2)_2]$ (2)	2071 w 2018 s 2002 w 1990 m 1973 w	26.4 s 26.1 s	149.3 d, C^2 130.4 d, C^5 129.8 d, C^4 128.7 s, C^6 128.6 s, C^7 128.3 d, C^1 17.2 d, C^3	7.50 m, H ⁵ 7.37 m, H ⁶ , H ⁷ 6.50 d, H ¹ 2.04 d, Me	P-H ¹ 36.2 P-Me 5.5 P-C ¹ 47.0 P-C ² 10.1	P-C ³ 12.1 P-C ⁴ 10.0 P-C ⁵ 10.6	
[Ru ₃ (CO) ₉ (PhPC ₄ H ₂ Me ₂) ₃] (3)	2043 w 1983 s 1971 s 1949 m	26.8 s	148.4 d, C^2 134.4 d, C^4 130.5 d, C^5 129.3 s, C^7 129.0 d, C^1 128.4 d, C^6 17.2 d, C^3	7.48 m, H ⁵ 7.32 m, H ⁶ , H ⁷ 6.41 d, H ¹ 1.99 s, Me	P-H ¹ 35.7 P-C ¹ 45.3 P-C ² 9.8 P-C ³ 12.1	P-C ⁴ 44.9 P-C ⁵ 10.7 P-C ⁶ 10.5	
[Ru ₃ (CO) ₉ (μ ³ :η ² :η ² :η ² -PhPC ₄ H ₂ Me ₂)] (4)	2062 w 2022 s 1996 m 1980 m 1924 w	28.9 s	142.6 d, C^4 130.3 s, C^7 129.1 d, C^6 127.3 d, C^5 92.7 d, C^2 32.6 d, C^1 15.4 d, C^3	7.56 m, Ph 2.34 s, Me 2.07 d, H ¹	P-H ¹ 31.2 P-C ¹ 52.4 P-C ² 10.2 P-C ³ 6.2	P-C ⁴ 9.2 P-C ⁵ 14.4 P-C ⁶ 10.6	
[Ru ₃ (CO) ₉ (μ:η ¹ :η ⁵ -PC ₄ H ₂ Me ₂)(η ¹ -C ₆ H ₅)] (5)	2108 s 2068 s 2042 s 2026 s 2019 m 1998 m 1986 w 1950 s 1918 w	88.6 s	$\begin{array}{c} 145.5 \ d, \ C^5 \\ 142.8 \ d, \ C^4 \\ 127.8 \ s, \ C^6 \\ 123.9 \ s, \ C^7 \\ 102.0 \ d, \ C^{2a} \\ 100.6 \ d, \ C^{2a} \\ 60.0 \ d, \ C^{1a} \\ 57.7 \ d, \ C^{1b} \\ 15.6 \ d, \ C^{3a} \\ 15.4 \ d, \ C^{3b} \end{array}$	7.38 d, H^5 6.86 dd, H^6 6.79 d, H^7 2.95 d, H^{1a} 2.79 d, H^{1b} 2.42 s, Me^a 2.41 s, Me^b	H ⁵ -H ⁶ 7.3 H ⁶ -H ⁷ 7.2 P-H ^{1a} 30.7 P-H ^{1b} 33.9 P-C ^{1a} 17.4 P-C ^{1b} 19.5	$\begin{array}{l} P-C^{2a} \ 4.3 \\ P-C^{2b} \ 5.6 \\ P-C^{3a} \ 6.3 \\ P-C^{3b} \ 6.6 \\ P-C^4 \ 13.2 \\ P-C^5 \ 5.9 \end{array}$	
[Os ₃ (CO) ₉ (μ-H)(μ ³ :η ¹ :η ¹ :η ² -PhPC ₄ H ₃ Me ₂)] (6)	2082 s 2053 s 2023 s 2011 m 1986 m 1975 w 1965 w 1949 w	–23.5 s	$\begin{array}{c} 139.5 \text{ d}, \ C^4 \\ 131.0 \text{ d}, \ C^7 \\ 129.1 \text{ d}, \ C^6 \\ 128.1 \text{ d}, \ C^5 \\ 123.0 \text{ d}, \ C^{2a} \\ 66.1 \text{ d}, \ C^{2b} \\ 39.4 \text{ d}, \ C^{1a} \\ 29.4 \text{ s}, \ C^{3a} \\ 18.8 \text{ d}, \ C^{3b} \\ -12.5 \text{ d}, \ C^{1b} \end{array}$	7.44 m, H^6 , H^7 7.34 m, H^5 3.73 dq, H^{1b} 3.57 d, H^{1a} 2.41 s, Me^a 2.33 s, H^2 0.79 d, Me^b -17.9 d, OsH	H ^{1b} -Me ^b 6.8 P-H ^{1a} 23.9 P-H ^{1b} 37.9 P-H(Os) 12.7 P-C ^{1a} 48.0 P-C ^{1b} 14.8	$\begin{array}{l} P-C^{2a} \ 16.2 \\ P-C^{2b} \ 4.3 \\ P-C^{3b} \ 6.8 \\ P-C^4 \ 6.0 \\ P-C^5 \ 11.3 \\ P-C^6 \ 9.0 \\ P-C^7 \ 2.4 \end{array}$	



Fig. 1. Molecular structure of the cluster [Ru₃(CO)₉(PhPC₄H₂Me₂)₃] (3).

positions that are as far apart as possible, each equatorially bonded to one ruthenium atom. The nine carbonyl ligands are terminal, six occupying axial positions while the other three are alternated with the phosphole ligands in one of the two equatorial positions for each ruthenium atom. The Ru–P distances are similar to the ones found for analogue triruthenium derivatives [8] with an average bond length of 2.321 Å.

Two new species were also obtained in low yields, for which their IR spectra in the carbonyl stretching region indicate the presence of nonacarbonyl compounds (Table 1). These clusters were characterised as $[Ru_3(CO)_9(\mu^3:\eta^2:\eta^2:\eta^2:PhPC_4H_2Me_2)]$ (4), show-

Selected bond lengths (Å) and angles ($^\circ)$ for compound 3.

Ru1-Ru2	2.8599 (5)	Ru1-P1	2.3226 (11)
Ru1-Ru3	2.8680 (6)	Ru2-P2	2.3160 (10)
Ru2-Ru3	2.8448 (6)	Ru3-P3	2.3233 (12)
Ru2-Ru1-Ru3	59.557 (14)	C21A-Ru2-C23A	95.08 (19)
C11A-Ru1-C12A	174.60 (18)	C22A-Ru2-C23A	92.50 (18)
C13A-Ru1-C12A	91.1 (2)	Ru1-Ru3-Ru2	60.079 (14)
C11A-Ru1-C13A	93.2 (2)	C31A-Ru3-C32A	95.05 (18)
Ru1-Ru2-Ru3	60.363 (15)	C31A-Ru3-C33A	171.62 (18)
C21A-Ru2-C22A	172.17 (19)	C32A-Ru3-C33A	93.07 (18)



Fig. 2. Molecular structure of the cluster $[Ru_3(CO)_9(\mu;\eta^1;\eta^5-PC_4H_2Me_2)(\eta^1-C_6H_5)]$ (5).

ing an IR similar to the one found for $[Os_3(CO)_9(C_6H_6)]$ [9] and $[Ru_3(CO)_9(\mu;\eta^1;\eta^5-PC_4H_2Me_2)(\eta^1-C_6H_5)]$ (5) for which was observed an IR pattern resembling the one for $[Ru_3(CO)_{10}(\mu;\eta^1;\eta^5-C_5H_4)]$, obtained from the reaction of $[Ru_3(CO)_{12}]$ and diazocyclopentadiene $(C_5H_4N_2)$ [10].

The ¹H NMR spectrum of **4** (Table 1) is similar to that of the rhenium nonacarbonyl [Re₃(CO)₉(PhPC₄H₂Me₂)] isolated from the reaction of [Re₂(CO)₈(MeCN₂)] and 3,4-dimethyl-1-phenylphosphole [7], where in both cases the ligand acts as a six-electron donor. We were unable to obtain suitable crystals for the X-ray diffraction analysis of **4**, however based on the spectroscopic evidence and comparison with its osmium analogue [Os₃(CO)₉ (PhPC₄H₂Me₂)] [7] the structure shown for **4** in Scheme 1 is the most likely.

Thermal treatment of $[Ru_3(CO)_{11}(PhPC_4H_2Me_2)]$ (1) for 3 h in cyclohexane leads in very high yield to cluster **5** (60%). Its single crystal X-ray structure determination (Fig. 2, Table 3) revealed the structural type of an open Ru₃ cluster with two metal–metal bonds bridged by a $(\eta^1:\eta^5-PC_4H_2Me_2)$ unit, obtained by double decarbonylation of **1**, cleavage of a Ru–Ru bond and insertion of a Ru(CO)₃ unit into the P-Aryl bond, where the PhPC₄H₂Me₂ moiety is coordinated as a phospholide to two metal atoms acting as a seven-electron donor. Shift to higher values of the IR v(CO) frequen-

able 3						
elected bond	lengths (Å) and	angles (°)	for c	ompound	5.

Ru1-Ru2	2.9365 (9)	Ru1-C4	2.243 (4)
Ru2-Ru3	2.9855 (8)	P1-C1	1.777 (4)
Ru1-P1	2.4864 (13)	P1-C4	1.769 (5)
Ru3-P1	2.2749 (13)	C1-C2	1.422 (6)
Ru1-C1	2.244 (4)	C2-C3	1.432 (6)
Ru1-C2	2.225 (4)	C3-C4	1.411 (6)
Ru1-C3	2.234 (4)		
Ru2-Ru1-P1	56.67 (3)	Ru1-P1-C4	60.87 (15)
Ru1-Ru2-Ru3	100.73 (2)	Ru3-P1-C4	131.89 (16)
Ru2-Ru3-P1	55.93 (3)	C1-P1-C4	89.3 (2)
P1-Ru3-C7	88.38 (11)	P1-C1-C2	112.8 (3)
P1-Ru3-C31	159.08 (17)	P1-C4-C3	113.6 (3)
Ru1-P1-Ru3	146.59 (5)	C1-C2-C3	112.1 (4)
Ru1-P1-C1	60.83 (13)	C2-C3-C4	111.9 (4)

cies as expected for an anionic Ru₃ species was not observed for **5**, so an eight-electron donating ligand can not be considered in this case, which makes compound **5** a 50-electron cluster. The Ru₃-P bond length in **5** is sligthly shorter than that of the Ru–P(η^1 -phosphole) bond for **3** (2.275 Å versus 2.321 Å, respectively); the Ru–phosphole π -interaction involved in the η^5 -coordination in **5**





Fig. 3. Molecular structure of the cluster $[Os_3(CO)_9(\mu-H)(\mu^3:\eta^1:\eta^1:\eta^2-PhPC_4H_3Me_2)]$ (6).

Table 4

Selected bond lengths (Å) and angles (°) for compound 6.

Os1-Os2	2.9767 (14)	Os3-C2	2.544 (9)
Os1-Os3	2.8517 (11)	P1-C1	1.776 (9)
Os2-Os3	2.9053 (16)	P1-C4	1.810 (10)
Os2-P1	2.338 (2)	C1-C2	1.396 (13)
Os1-C4	2.207 (8)	C2-C3	1.507 (14)
Os3-C1	2.331 (8)	C3-C4	1.535 (13)
Os2-Os1-Os3	59.75 (3)	Os2-Os3-C1	76.4(2)
Os3-Os1-C4	78.9 (2)	Os2-Os3-C2	101.3(2)
Os1-Os2-Os3	57.99 (2)	C1-P1-C4	93.9 (4)
Os1-Os2-P1	70.27 (6)	P1-C1-C2	110.1 (7)
Os3-Os2- P1	69.65 (6)	P1-C4-C3	105.3 (6)
Os1-Os3-Os2	62.26 (3)	C1-C2-C3	114.6 (8)
Os1-Os3-C1	93.6 (2)	C2-C3-C4	106.8 (7)

is similar to the one observed for the $C_5H_4N_2$ derivative [Ru₃(-CO)₁₀(μ : η^1 : η^5 - C_5H_4)] [10] as are the values obtained for the mean Ru– C_n (phosphole) bond lengths in **5** (2.237(4) Å) compared to the

mean Ru– C_n bond distance (n = 2-5) of 2.231(7) Å for the cyclopentadienyl derivative.

The reaction of the unsaturated triosmium cluster $[Os_3(\mu-H)_2(CO)_{10}]$ with 3,4-dimethyl-1-phenylphosphole gave one main compound characterised as $[Os_3(CO)_9(\mu-H)(\mu^3;\eta^1;\eta^1;\eta^2-PhPC_4H_3Me_2)]$ (**6**) (Scheme 2) where the phosphole ligand lies over the plane of the metal skeleton in a partially hydrogenated form, behaving as a five-electron donor. The compound was characterised by IR, ³¹P, ¹H and ¹³C NMR and X-ray studies, and its structure is shown in Fig. 3. The C3–C4 bond distance of 1.535(13) Å (Table 4) is characteristic of a simple bond while C1–C2 = 1.396(1) Å, corresponds to a C–C double bond distance.

In conclusion we have found that $[Ru_3(CO)_9(\mu;\eta^1:\eta^5-PC_4H_2Me_2)(\eta^1-C_6H_5)]$ (**5**) is the first example of a phospholide unit inserted into a metal–metal bond. This procedure opens up the possibility for a facile access to new ruthenium and maybe other metal complexes with $(\mu:\eta^1:\eta^5-PC_4R_4)$ units as bridging ligands.

Acknowledgements

We thank FONACIT for Project G-20050000447.

Appendix A. Supplementary material

CCDC 7308, 10908 and 13908 contain the supplementary crystallographic data for compounds **3**, **5** and **6**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2012.01.033.

References

- F. Mathey (ed.), Phosphorus-carbon heterocyclic chemistry: the rise of a new domain, Pergamon, 2001.
- [2] J. Crassous, R. Réau, Dalton Trans. (2008) 6865.
- [3] A.J. Deeming, N.I. Powell, A.J. Arce, Y. De Sanctis, J. Manzur, J. Chem. Soc., Dalton Trans. (1991) 3381.
- [4] A. Breque, F. Mathey, P. Savignac, Synthesis (1981) 983.
- [5] A.J. Deeming, Adv. Organomet. Chem. 26 (1986) 1.
- [6] A.J. Deeming, B.F.G. Johnson, J. Lewis, J. Chem. Soc. A (1970) 987.
- [7] A. Arce, Y. De Sanctis, R. Machado, Y. Otero, unpublished results.
- [8] Z.R. Bell, R.H. Laye, M.D. Ward, Acta Crystallogr., Sect. E58 (2002) m165.
- [9] M.D. Gómez-Sal, B.F.G. Johnson, J. Lewis, P.R. Raithby, A.H. Wright, Chem. Commun. (1985) 1682.
- [10] A.J. Arce, Y. De Sanctis, J. Manzur, M.V. Capparelli, Angew. Chem., Int. Ed. Engl. 33 (1994) 2193.