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Inorganica Chimica Acta 344 (2003) 123-127

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Reactions of the clusters [Os₃(CO)₁₀(MeCN)₂)] and [Ru₃(CO)₁₂] with (2-aminophenyl)phosphine P(2-NH₂C₆H₄)H₂. A comparison of the reactivity of amino and phosphino groups with clusters

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Received 24 May 2002; accepted 2 August 2002

Abstract

The reaction of (2-aminophenyl)phosphine P(2-NH₂C₆H₄)H₂ with $[Os_3(CO)_{10}(MeCN)_2]$ gives the compounds $[Os_3(CO)_{11}{P(2-NH_2C_6H_4)H_2}]$ (1), $[1,2-Os_3(CO)_{10}{P(2-NH_2C_6H_4)H_2}_2]$ (2) and $[Os_3(\mu-H)(CO)_{10}{\mu-P(2-NH_2C_6H_4)H}]$ (3). Thermolysis of compounds 1 and 3 in cyclohexane affords in quantitative yields $[Os_3(\mu-H)_2(CO)_9{\mu_3-P(2-NH_2C_6H_4)}]$ (4). However, the direct reaction of P(2-NH_2C_6H_4)H_2 with [Ru₃(CO)_{12}] yields only the nonacarbonyl species $[Ru_3(\mu-H)_2(CO)_9{\mu_3-P(2-NH_2C_6H_4)}]$ (5). The phosphino group coordinates more favorably than the amino group and P–H bond activation is favored over amino coordination. \bigcirc 2002 Elsevier Science B.V. All rights reserved.

Keywords: Osmium; Ruthenium; Oxidative addition; 2-Aminophenylphosphine; Carbonyl clusters

1. Introduction

The chemistry of phenylphosphine-containing ligands with mixed functionality has received less attention than that of their unsubstituted phosphine counterparts. There are some studies of complexes of transition metals with ligands such as (2-hydroxophenyl)diphenylphosphine [1] and (2-aminophenyl)diphenylphosphine [2-4]. The reactions of (2-aminophenyl)diphenylphosphine $P(2-NH_2C_6H_4)R_2$ (R = C₆H₅) with $[Os_3(CO)_{12-x} (MeCN)_x$ (x = 1, 2) have been reported to give the clusters $[Os_3(CO)_{11}{P(2-NH_2C_6H_4)R_2}]$ and $[HOs_3(CO)_9{P(2-NHC_6H_4)R_2}]$ where the latter shows the ligand bridging one edge of the Os₃ triangle by the amido nitrogen shared between two Os atoms, and the phosphorus atom coordinated to one of these metals [5]. In this paper we describe the synthesis and characterization of four triosmium clusters derived from the reaction of (2-aminophenyl)phosphine P(2-NH₂C₆H₄)H₂ and [Os₃(CO)₁₀(MeCN)₂]. Also we report here the direct reaction with [Ru₃(CO)₁₂] to give exclusively the cluster [Ru₃(μ -H)₂(CO)₉{ μ_3 -P(2-NH₂C₆H₄)}]. Reactions occur exclusively at the PH₂ rather than at the NH₂ group, which remained non-coordinated in all the new clusters obtained.

2. Experimental

2.1. Synthesis of compounds 1–5

All the reactions were performed under nitrogen atmosphere. Solvents were purified by standard methods and distilled prior to use. $[Os_3(CO)_{10}(MeCN)_2]$ [6] and (2-aminophenyl)phosphine [7] were prepared by published procedures. $[Ru_3(CO)_{12}]$ was purchased from Strem Chem. IR spectra were recorded in cyclohexane and ¹H and ³¹P NMR spectra were obtained at 300

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Table 1

MHz. Synthesis of 1, 2 and 3: $[Os_3(CO)_{10}(MeCN)_2]$ (0.1 g, 0.11 mmol) was added to a refluxing solution of (2-aminophenyl)phosphine (0.027 g, 0.22 mmol) in 50 ml of THF. The solution was refluxed for 45 min (IR monitoring), during which time the color changed from pale yellow to orange. Low-pressure removal of the volatiles and TLC of the residue (SiO₂, n-C₆H₁₄– CH₂Cl₂ 7/3, v/v), yielded $[Os_3(CO)_{11}{P(2-NH_2C_6H_4)H_2}]$ (1), (0.010 g, 9%) and $[Os_3(CO)_{10}{P(2-NH_2C_6H_4)H_2}]$

IR and NMR data for the new complexes

 $NH_2C_6H_4)H_2\}_2$] (2) (0.010 g, 9%) both as yellow solids, and $[Os_3(\mu-H)(CO)_{10}\{\mu-P(2-NH_2C_6H_4)H\}]$ (3) as yellow crystals from $n-C_6H_{14}-CH_2Cl_2$ (0.022 g, 20%). *Thermal treatment of compound* 3: $[Os_3(\mu-H)(CO)_{10}\{\mu-P(2-NH_2C_6H_4)H\}]$ (3) (0.015 g) were dissolved in 30 ml of cyclohexane and heated under reflux for 48 h (IR monitoring). TLC as above gave a high yield of $[Os_3(\mu-H)_2(CO)_9\{\mu_3-P(2-NH_2C_6H_4)\}]$ (4) (0.012 g, 80%). *Synthesis of* 5: (2-Aminophenyl)phosphine (0.04)

Compound	ν (CO) ^a (cm ⁻¹)	¹ H NMR ^b (δ , ppm)	J (Hz)	³¹ P{ ¹ H} NMR ^b (δ , ppm)
$[Os_{3}(CO)_{11}\{P(2-NH_{2}C_{6}H_{4})H_{2}\}] (1)$	2109w, 2056s, 2036s, 2020vs, 1988ms	7.35 (ddd, H ⁴) 7.30 (m, H ²) 6.90 (m, H ³) 6.80 (m, H ¹) 6.20 (d, PH ₂) 3.97 (brs, NH ₂)	$H^{2}H^{3} = 7.5$ $H^{2}H^{4} = 1.4$ $H^{3}H^{4} = 7.6$ $H^{3}P = 7.6$ $H^{4}P = 17$ $H_{2}P = 376$	-130.5
$[Os_3(CO)_{10}\{P(2\text{-}NH_2C_6H_4)H_2\}_2] \ \textbf{(2)}$	2090w, 2033s, 2004vs, 1968s	7.35 (ddd, H ⁴) 7.32 (m, H ²) 6.90 (m, H ³) 6.75 (m, H ¹) 6.20 (d, PH ₂) 3.97 (brs, NH ₂)	$H^{2}H^{3} = 7.5$ $H^{2}H^{4} = 1.5$ $H^{3}H^{4} = 7.6$ $H^{3}P = 7.6$ $H^{4}P = 15$ $H_{2}P = 372$	-129.5
$\label{eq:1.1} \begin{split} &[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}P(2\text{-}NH_2C_6H_4)H\}] \ \textbf{(3)} \end{split}$	2105m, 2062vs, 2055sh, 2021s,2008s, 1994s	7.24 (dd, H ³) 7.20 (dd, P <i>H</i>) 7.12 (ddd, H ⁴) 6.83 (ddbr, H ²) 6.65 (dd, H ¹) 4.12 (brs, N <i>H</i> ₂) -19.4 (dd, Os <i>H</i>)	$H^{1}H^{2} = 7.5$ $H^{2}H^{3} = 7.6$ $H^{2}H^{4} = 1.3$ $H^{3}H^{4} = 7.8$ $H^{1}P = 7.9$ $H^{4}P = 17$ $(OsH)P = 17.9$ $(OsH)PH = 4$ $HP = 407$	-70.9
$\label{eq:constraint} \begin{split} & [Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}P(2\text{-}NH_2C_6H_4)\}] \ \textbf{(4)} \end{split}$	2105m, 2076vs, 2049vs, 2032vs, 2012vs, 1988s, 1974s °	7.79 (dddd, H^4) ^d 7.38 (m, H^2) 6.95 (dddd, H^1) 6.79 (m, H^3) 4.52 (brs, NH_2) -22.1 (d, OsH)	$\begin{split} H^1 H^2 &= 8.3 \\ H^1 H^3 &= 1.2 \\ H^1 H^4 &= 0.5 \\ H^2 H^3 &= 7.2 \\ H^2 H^4 &= 1.6 \\ H^3 H^4 &= 7.8 \\ H^1 P &= 6.8 \\ H^2 P &= 1.9 \\ H^3 P &= 2.3 \\ H^4 P &= 17.9 \\ (OsH_2) P &= 12 \end{split}$	88.8
$\label{eq:constraint} \begin{split} & [Ru_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}P(2\text{-}NH_2C_6H_4)\}] \ \textbf{(5)} \end{split}$	2105m, 2075s, 2048vs, 2033m, 2019vs, 1997s, 1984s °	7.76 (ddd, H ⁴) 7.36 (m, H ¹) 6.83 (m, H ² , H ³) 3.73 (brs, N <i>H</i> ₂) -19.2 (d, Ru <i>H</i>)	$\begin{split} H^{1}H^{2} &= 7.5 \\ H^{1}H^{3} &= 1.5 \\ H^{2}H^{4} &= 1.5 \\ H^{3}H^{4} &= 7.9 \\ H^{1}P &= 7.5 \\ H^{4}P &= 16.1 \\ (RuH_{2})P &= 15 \end{split}$	245

 a In CH₂Cl₂.

^b In CDCl₃, 300 MHz, 296 K.

^c In C₆H₁₂.

^d In CD₃COCD₃.

g, 0.32 mmol) was added to a refluxing solution of $[Ru_3(CO)_{12}]$ (0.2 g, 0.32 mmol) in 50 ml of $C_6H_5CH_3$. The solution was refluxed for 30 min (IR monitoring). TLC separation (SiO₂, n-C₆H₁₄-CH₂Cl₂ 4/1, v/v), gave $[Ru_3(\mu-H)_2(CO)_9{\mu_3}-P(2-NH_2C_6H_4)]$ (5) as orange crystals from n-C₆H₁₄-CH₂Cl₂ (0.043 g, 20%).

2.2. X-ray analysis for 3 and 5

Selected crystals were mounted on fiberglass and placed on a Rigaku AFC7S diffractometer using graphite monochromated Mo Ka radiation. Data were collected at room temperature using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 50°. In both cases the cell was refined using 25 carefully centered reflections by full-matrix least-squares techniques. Instrument and crystals stabilities were checked by measuring three standard reflections periodically. Data were corrected for Lp effects and for absorption based on empirical (DIFABS) for 3 and ψ -scans methods for 5. The structures were solved by direct methods (SHELXTL-PLUS v. NT 5.1) and refined by full-matrix least-squares. For both complexes, crystal parameters, data collection and structure refinements are given in Table 4. All nonhydrogen atoms were refined anisotropically, and hydrogen atoms were added at calculated positions, except for the H atom on the phosphorous in 3 which was located and refined by using a riding model. Positions of the hydride atoms were observed in the last residual density map and were included without any further refinement. Full-matrix least-squares refinement was based on F^2 .

3. Results and discussion

The labile cluster $[Os_3(CO)_{10}(MeCN)_2]$ reacts readily with 2 equiv. of the substituted phenyl phosphine P(2- $NH_2C_6H_4)H_2$ to yield three products including the monophosphine cluster $[Os_3(CO)_{11}{P(2-NH_2C_6H_4)H_2}]$ (1) which possibly derived from [Os₃(CO)₁₁(MeCN)] impurity in [Os₃(CO)₁₀(MeCN)₂]. Compound 1 is air stable and has been characterized spectroscopically. The IR spectrum contains only four v(CO) bands between 2100 and 1900 cm⁻¹ (Table 1), a very similar IR spectrum to those of tertiary phosphine clusters of the type $[Os_3(CO)_{11}(PR_3)]$ [8]. Phosphine rather than amine coordination is supported by the low-field shift of the ³¹P{¹H} NMR signal in 1 (δ –130.5) from that of the free ligand (δ +151.4) as found in the coordinated phosphines $[Os_3(CO)_{11}(PR)H_2]$ (R = Ph, C_6H_{11} , $C_6H_4OCH_3$ [9]. The ligand acts as a two electron-donor at just one coordination site in the triosmium frame as observed for monodentate phosphines. Two more derivatives are obtained, one is the disubstituted cluster $[1,2-Os_3(CO)_{10}{P(2-NH_2C_6H_4)H_2}_2]$ (2); the IR specScheme 1. trum in the carbonyl region shows only four ν (CO) absorption bands, very similar to those of other disubstituted clusters with tertiary phosphines [8]. Based upon spectroscopic evidence, the structure depicted by **2** in Scheme 1 is the most likely. The single broad ³¹P{¹H} NMR signal at room temperature (δ –129.5 ppm) gives three different signals at 213 K, two of equal intensity (–129.5 and –134.7 ppm) and a lower intensity signal at –131 ppm, suggesting the presence of two isomers in solution rapidly exchanging at room temperature, as found for [Os₃(CO)₁₀(PMe₂Ph)₂] [10].

Fig. 1. An ortep drawing of the molecular structure of $[Os_3(\mu + H)(CO)_{10}\{\mu - P(2 - NH_2C_6H_4)H\}]$ (3).



NH

 $(CO)_3$

 $(CO)_4O$

3

1

Os

 $(CO)_4$

(CO)3

Os(CO)₄

Os(CO):

Δ

Δ

Os(CO)₃

[Os₃(CO)₁₀(CH₃CN)₂]

 $[1,2-Os_3(CO)_{10}{P(2-NH_2C_6H_4)H_2}_2]$

(CO)₃

2

4

Table 2 Selected bond lengths (Å) and angles (°) for compound ${\bf 3}$

Bond lengths		Bond angles	
Os(1)-Os(2)	2.891(2)	Os(1) - Os(2) - P(1)	84.5(1)
Os(1) - Os(3)	2.894(1)	Os(1) - Os(3) - P(1)	84.2(1)
Os(2) - Os(3)	2.911(1)	Os(2) - P(1) - C(1)	122.5(8)
Os(2)–(P1)	2.366(5)	Os(3) - P(1) - C(1)	121.0(7)
Os(3) - P(1)	2.380(6)	Os(2) - P(1) - Os(3)	75.7(2)
C(1)–P(1)	1.80(2)		

Also from this reaction, the oxidative addition compound $[Os_3(\mu-H)(CO)_{10}\{\mu-P(2-NH_2C_6H_4)H\}]$ (3) was obtained; its ${}^{31}P{}^{1}H$ NMR spectrum shows a low field signal at $\delta = -70.9$ ppm typical for a P atom bridging an Os-Os bond. The hydride signal in the ¹H NMR spectrum at $\delta = -19.4$ ppm, with J(Os-H)P =17.9 and J(Os-H)PH = 4 Hz, confirms the presence of the bridging hydride in the same edge of the osmium triangle bridged by the phosphido group. In the formation of 3, deprotonation of the phosphine occurs by hydrogen atom transfer to the metal centers; no activation of the NH₂ group has been observed based on the ¹H NMR spectrum (Table 1). This arrangement has been confirmed by single-crystal X-ray diffraction analysis. The X-ray crystal structure of compound 3 (Fig. 1) shows that the (2-aminophenyl)phosphido ligand behaves as a three electron-donor through the phosphorus atom and no bonding interaction of the amine moiety with the metal triangle is observed, which is in contrast to the bonding mode found on the product from the reaction of [Os₃(CO)₁₀(MeCN)₂] and (2aminophenyl)diphenylphosphine, where the nitrogen and phosphorus atoms are both coordinated [5].

The molecular structure of **3** is based on a triangle of three osmium atoms, with two short Os–Os bonds, Os(1)-Os(2) = 2.891(2), Os(1)-Os(3) = 2.894(1) Å and one longer bond, Os(2)-Os(3) = 2.911(1) Å, bridged by the hydride and the phosphido group with Os(2)-P(1) = 2.366(5) and Os(3)-P(1) = 2.380(6) Å (Table 2). The 2-aminophenyl group points away from the $Os(CO)_4$ group and there is no short distance between the NH₂ group and either CO or metal. Its configuration is the same found for related clusters such as





Fig. 2. An ORTEP drawing of the molecular structure of $[Ru_3(\mu-H)_2(CO)_9{\mu_3-P(2-NH_2C_6H_4)}]$ (5).

 $[M_3H(CO)_{10}(PHPh)]$ (M = Ru, Os) [11]. In 3, the 2aminophenyl group is approximately perpendicular to the Os₃ triangle (dihedral angle between the Os₃ plane and C₆ ring = 94.3°).

Thermolysis of either compound $[Os_3(CO)_{11}{P(2-NH_2C_6H_4)H_2}]$ (1) or $[Os_3(\mu-H)(CO)_{10}{\mu-P(2-NH_2C_6H_4)H}]$ (3) in cyclohexane affords in quantitative yields the nonacarbonyl species $[Os_3(\mu-H)_2(CO)_9{\mu_3-P(2-NH_2C_6H_4)}]$ (4). Based on the IR, ¹H and ³¹P NMR spectra, we conclude that a phosphinidene moiety is present, and the structure depicted by 4 in Scheme 1 is the most likely; there is no spectroscopic evidence for any interaction of the amino group with any other part of the cluster.

The direct reaction of $[Ru_3(CO)_{12}]$ and 2-aminophenylphosphine in refluxing toluene gives only $[Ru_3(\mu-H)_2(CO)_9{\mu_3-P(C_6H_4NH_2)}]$ (5) in high yield (Scheme 2).

The ³¹P{¹H} NMR spectrum displays a singlet at δ = 245 ppm, indicating the presence of a phosphinidene moiety. In the ¹H NMR spectrum the broad signal at δ = 3.73 ppm is assigned to the NH₂ protons and the doublet at δ = -19.2 ppm to the 2 equiv. hydrides. The close similarity of the IR spectra in the carbonyl region

Table 3 Selected bond lengths (Å) and angles (°) for compound ${\bf 5}$

Bond lengths		Bond angles	Bond angles		
Ru(1)-Ru(2)	2.8264(8)	Ru(1) - P(1) - Ru(2)	76.20(3)		
Ru(1)-Ru(3)	2.9298(9)	Ru(1) - P(1) - Ru(3)	78.85(3)		
Ru(2)-Ru(3)	2.9402(9)	Ru(2) - P(1) - Ru(3)	78.89(3)		
Ru(1) - P(1)	2.2832(9)	Ru(1)-P(1)-C(1)	132.1(1)		
Ru(2) - P(1)	2.298(1)	Ru(2)-P(1)-C(1)	142.3(1)		
Ru(3) - P(1)	2.330(1)	Ru(3)-P(1)-C(1)	125.1(1)		
C(1)–P(1)	1.797(3)				

Scheme 2.

Table 4

Crystal data, data collection and refinement parameters for the structures of $[Os_3(\mu-H)(CO)_{10}\{\mu-P(2-NH_2C_6H_4)H\}]$ (3), and $[Ru_3(\mu-H)_2(CO)_9\{\mu_3-P(2-NH_2C_6H_4)\}]$ (5)

Crystal parameters	3	5	
Empirical formula	C ₁₆ H ₈ NO ₁₀ O-	C _{15.5} H ₉ ClNO ₉ -	
	s ₃ P	PRu ₃	
Formula weight	975.80	722.87	
Crystal color, habit	Yellow prism	Yellow prism	
Crystal system	monoclinic	triclinic	
Space group	C2/c	ΡĪ	
a (Å)	25.704(5)	8.822(2)	
b (Å)	8.770(2)	10.617(3)	
<i>c</i> (Å)	19.576(4)	12.716(3)	
α (°)	90.00	82.60(2)	
β (°)	99.45(3)	74.389(17)	
γ(°)	90.00	85.64(2)	
V (Å ³)	4353.0(15)	1136.5(5)	
Z	8	2	
$D_{\text{calc}} (\text{g cm}^{-3})$	2.978	2.112	
$\mu ({\rm mm}^{-1})$	17.596	2.200	
F(000)	3472	690	
Crystal size (mm)	$0.44 \times 0.40 \times$	$0.42 \times 0.42 \times$	
•	0.38	0.25	
2θ Range (°)	4.22-50.00	4.80-53.0	
Data collection and			
refinement			
Absorption correction	Empirical (DI-	Psi-scan	
*	FABS)		
Reflections measured	3927	4955	
Observed reflections	3046	4253	
[criterion: $F_0 > 4\sigma(F_0)$]			
Unique reflections	3835	4692	
Max/min transmission	0.0572/0.0400	0.5770/0.4340	
Data-to-parameter ratio	13.6:1	16.8:1	
R _{int}	0.0756	0.0090	
R, wR, all data	0.0958. 0.2700	0.0258, 0.0591	
<i>R</i> . <i>wR</i> . unique reflections	0.0787. 0.2573	0.0219. 0.0575	
Largest features in final difference	2.242/-2.137	1.035/-0.670	
map (max/min e Å ^{-3})	,,		

of 4 and 5 (Table 1) shows that these are isostructural. To confirm the mode of bonding of the ligand, an X-ray structure analysis for compound 5 was undertaken. Its molecular structure is shown in Fig. 2, and some relevant bond lengths and angles are summarized in Table 3.

The molecular structure of **5** relates closely to that of $[Ru_3(\mu-H)_2(CO)_9(\mu_3-PPh)]$ [9] and it is as expected for a μ_3 -phosphinidene complex with two long Ru–Ru dis-

tances Ru(1)-Ru(3) = 2.9298(9) and Ru(2)-Ru(3) = 2.9402(9) Å supporting the bridging hydrides, while the short edge Ru(1)-Ru(2) = 2.8264(8) Å carries no hydride.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 179300 and 179301 for compounds **3** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the British Council for support through a British Council Academic Link between UCL and IVIC groups and to FONACIT, Venezuela, for projects S1-95000578, S1-96001062 and LAB-97000665.

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