Journal of Organometallic Chemistry 695 (2010) 156–161

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Reaction of the diyne complex $[Os_3(\mu\text{-}CO)(CO)_9\{\mu_3\text{-}\eta^2\text{-}Me_3SiCCC{\equiv}CSiMe_3\}]$ with phosphines and phosphites: Characterization of monophosphine substituted clusters $[Os_3(\mu\text{-}CO)(CO)_8(PR_3)\{\mu_3\text{-}\eta^2\text{-}Me_3SiCCC{\equiv}CSiMe_3\}]$ (PR_3 = PPh_3, $P(OEt)_3$, PEt_3, $PHPh_2$ and $Ph_2PCH_2PPh_2$)

Indira Torres-Sandoval [a], Simon K. Brayshaw [b], Paul R. Raithby [b,*], María J. Rosales-Hoz [a,*]

[a] Departamento de Química, Centro de Investigación y de Estudios Avanzados, Av. Instituto Politécnico Nacional 2508, Col. San Pedro Zacatenco, México 07360, D.F., Mexico
[b] Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

ARTICLE INFO

Article history:
Received 29 July 2009
Received in revised form 15 October 2009
Accepted 16 October 2009
Available online 25 October 2009

Keywords:
Osmium cluster carbonyl
Diyne
Phosphine
Phosphite
X-ray crystallography

ABSTRACT

The reactions of $[Os_3(\mu\text{-}CO)(CO)_9\{\mu_3\text{-}\eta^2\text{-}Me_3SiCCC{\equiv}CSiMe_3\}]$ with phosphorus donor ligands (PPh_3, PEt_3, $P(OEt)_3$, $PHPh_2$ and a diphosphine; $Ph_2PCH_2PPh_2$ (dppm)) afford carbonyl mono-substitution products $[Os_3(\mu\text{-}CO)(CO)_8(L)\{\mu_3\text{-}\eta^2\text{-}Me_3SiC_2C_2SiMe_3\}]$ even in the case of the bidentate phosphine dppm. All the complexes have been characterized by IR and multinuclear NMR spectroscopy and for **2** (L = PPh_3), **3** (L = PEt_3), **4** (L = $P(OEt)_3$) and **5** (L = η^1-dppm) the structures have been confirmed by single-crystal X-ray analysis. The structural analyses show that in all four clusters the substitution has occurred at one of osmium equatorial sites that is σ-bonded to the $\mu_3\text{-}\eta^2$-alkyne.

© 2009 Published by Elsevier B.V.

1. Introduction

There has been an ongoing interest in the reactions between transition metal carbonyl clusters and hydrocarbon containing ligands for the last four decades because of the range of coordination modes that are adopted by the organic groups and by the possibility of both ligand rearrangements on the cluster core and cluster build up processes [1]. Alkynes and diynes, as ligands, in ruthenium and osmium cluster chemistry are particularly interesting because of the versatility of their chemistry that leads to a range of products involving carbon–carbon bond formation, carbonyl insertion and a range of hydrogenated products depending on whether $[M_3(CO)_{12}]$ (M = Ru, Os), $[M_3(CO)_{10}(NCMe)_2]$ or $[Os_3H_2(CO)_{10}]$ is used as the cluster starting material [2]. Despite the plethora of cluster carbonyl complexes that contain diynes or their derivatives relatively little reaction chemistry has been carried out on the substituted complexes despite the presence of the diyne apparently activating the complex by comparison to the binary carbonyls [3–7]. In reported reactions of diyne-substituted cluster complexes decarbonylation as well as ligand rearrangement paths can occur. In addition, in clusters where a free alkyne moiety is present, there is the possibility of carrying out further reactions with this fragment, as exemplified by the reaction of $[Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2C{\equiv}CSiMe_3)]$ with $[Co_2(CO)_8]$ where the complex $[Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2C_2SiMe_3)\{Co_2(CO)_6\}]$ was formed by coordination of the dicobalt fragment to the C≡C triple bond adjacent to the $SiMe_3$ group [8]. When the ruthenium complex is used, a bow-tie cluster is formed by the insertion of the cobalt species into a Ru–Ru bond [9].

Reactions of diyne-cluster derivatives with Me_3NO–MeCN have also been carried out in order to further enhance the activation of the metal cluster and the derivatives $[Os_3(CO)_8(MeCN)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}\{(MeC_2)C_2(Me)\}_2CO)]$ and $[Os_3(CO)_8(NMe_3)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}\{(MeC_2)C_2(Me)\}_2CO)]$ have been isolated [10]. The related clusters $[Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}\eta^2\text{-}MeC_2C{\equiv}CMe)]$ and $[Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$ also react with Me_3NO–MeCN, presumably to form MeCN derivatives, and then with water to form a 50-electron cluster containing a μ-OH group [10]. Previously, the reaction of diyne derivatives of trinuclear osmium and ruthenium clusters with phosphines appears to have been restricted to the reaction of $[Ru_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$ with the chelating phosphine $Ph_2PCH_2PPh_2$ (dppm), in tetrahydrofuran, under reflux, to give $[Ru_3(\mu\text{-}CO)(CO)_7(dppm)(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$ [3].

---

[*] Corresponding authors. Tel.: +55 57 47 37 16; fax: +55 57 47 37 89 (M.J. Rosales-Hoz).

E-mail addresses: P.R.Raithby@bath.ac.uk (P.R. Raithby), mrosales@cinvestav.mx (M.J. Rosales-Hoz).

0022-328X/$ - see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.jorganchem.2009.10.018

We have recently observed the facile cleavage of C–Si bonds in trinuclear-acetylide derivatives [11]. This led us to explore the reactivity of $[Os_3(\mu\text{-}CO)(CO)_9\{\mu_3\text{-}\eta^2\text{-}Me_3SiCCC{\equiv}CSiMe_3\}]$; **1** (Scheme 1); where there are two different C–Si bonds adjacent to the coordinated and uncoordinated alkyne groups, respectively. In this paper we report the reaction of compound **1** with several phosphines and a phosphite and show that, in all cases, mono-substitution of a carbonyl group in the plane of the Os_3 triangle occurs and that the diyne group does have an influence on the rate of substitution, preventing coordination of bulky phosphines, but not on the position of substitution.

2. Results and discussion

The reactions of $[Os_3(\mu\text{-}CO)(CO)_9\{\mu_3\text{-}\eta^2\text{-}Me_3SiCCC{\equiv}CSiMe_3\}]$ **1** with a series of phosphines and phosphites in hexane, under reflux, affords as the only products that could be isolated, the clusters $[Os_3(\mu\text{-}CO)(CO)_8(L)\{\mu_3\eta^2\text{-}Me_3SiCCC{\equiv}CSiMe_3\}]$ (**2**, L = PPh_3, **3**, L = PEt_3, **4**, L = $P(OEt)_3$, **5**, L = $Ph_2PCH_2PPh_2$ (dppm) and **6**, L = $PHPh_2$) where substitution of a carbonyl group took place. Reactions with other, bulkier phosphines (PCy_3 and bis(dicyclohexylphosphino)ethane) [12] were also carried out. Interestingly, for these only unreacted starting material was recovered, even after prolonged heating, indicating that steric factors were important in the reaction pathway. However, the basicity of the phosphine [13] may also play a role. In the reaction with the most basic and the sterically least demanding phosphine, PEt_3 in the series, the starting material is consumed most quickly. Since all the reactions were carried out for the same period of time, the yields of the mono-substituted products obtained under similar conditions, given in the Section 4, may reflect the rate of reaction. These results are in general agreement with the work of Poë et al. on the kinetics of associative reactions of metal carbonyl clusters [14]. Spectroscopic data for **2**–**6** is consistent with the presence of both the phosphine/phosphite and the diyne ligands in the reaction products. The similarity of the IR spectra, in the carbonyl region, of all the complexes suggests the symmetry and distribution of the carbonyl groups is similar for all of them. All the IR spectra have a signal below 1900 cm^{-1} consistent with the fact that the bridging carbonyl group in **1** [15] is retained in the products. ^1H NMR spectra for the five compounds **2–6**, show the $SiMe_3$ signals, at similar values than in **1** [15], as well as those corresponding to the groups bonded to the phosphorus centres. The spectrum of **5** shows two doublets of doublets in the methylene region, indicating that the two hydrogen atoms in the CH_2 group of the dppm ligand are not equivalent.

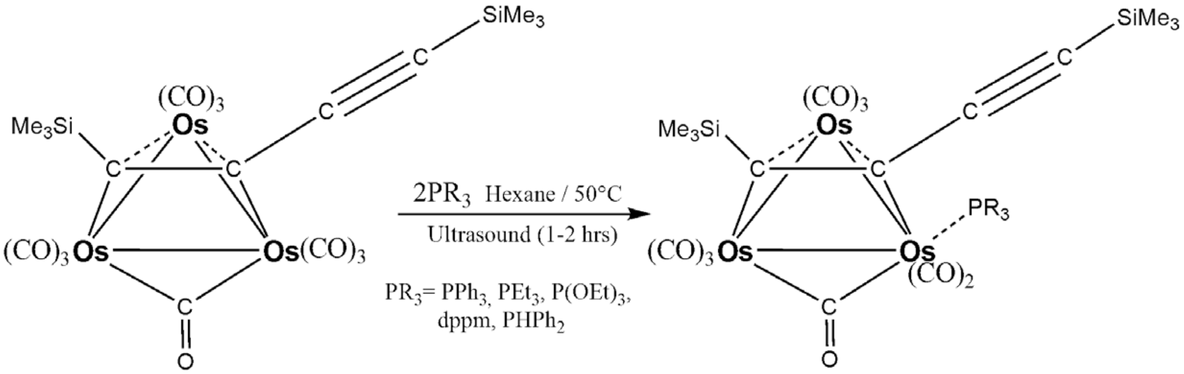
^{31}P NMR spectra of **2**–**6** show the shift of the signals to higher frequencies than those observed in the free phosphine with the exception of the case of the $P(OEt)_3$ ligand which moves to lower frequency. This behavior is similar to that observed in other complexes of these ligands although the effect is less marked in other cases such as $[Os_3(CO)_{11}(PPh_3)]$ where there is a $\Delta\delta$ shift of free phosphine to coordinated phosphine of only +2.74 ppm in comparison to +18.42 ppm in **2** [16]. In the case of compound **5**, the spectrum shows two singlets; one at 2.79 ppm, which is assigned to the coordinated PPh_2 group, and another one at −26.37 ppm, more similar to the value of the free phosphine (−21.24 ppm), assigned to a non-coordinated phosphorus centre.

The ^{13}C NMR spectra of compounds **2**–**5** were obtained. The corresponding spectrum for compound **1** had not been reported but we also obtained it; signals are observed in 125.10 ppm for C(1), in 139.43 ppm for C(2), in 117.84 ppm for C(3) and in 100.15 ppm for C(4).

The assignment of the different signals of compounds **2**–**5** was thus made by comparison with the spectrum of **1** as well as the shifts observed for $[Os_3(CO)_{10}(HC{\equiv}CSiMe_3)]$ [17] and $Mo_2(\mu\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(CO_4)(Cp)_2$ [18]. The signals observed between 120 and 127 ppm in the four compounds, are assigned to C(1), the terminal carbon atom of the coordinated alkyne moiety while the signals between 157 and 160 ppm are assigned to C(2), the other carbon atom of the coordinated alkyne. C(3) is believed to show signals between 113 and 117 ppm while C(4) shows signals at slightly lower frequencies 93 ppm; these last two carbon atoms were assigned to the alkyne that is not coordinated to the cluster, by comparison with the trends observed in the experimental spectrum of the free ligand in which C(1) and C(4) are observed at 86.00 ppm and C(2) and C(3) are observed at 88.05 ppm. The very similar chemical shifts of the carbon atoms in the organic chains in compound **2**–**5** indicate that the electronic properties of the diyne group are not significantly affected by the variation of the phosphine or phosphite ligand.

X-ray crystal structures of compounds **2–5** were obtained and the molecular structures are shown in Figs. 1–4, respectively, while some selected bond lengths and angles are given in Table 1. The four structures show that, as proposed, substitution of one carbonyl group by a phosphine or phosphite group occurred, even in the case of the bidentate phosphine dppm where one of the phosphorus atoms remains uncoordinated. Apart from **3**, where there are two independent but structurally similar molecules in the asymmetric unit, each structure crystallizes with one independent molecule in the asymmetric unit. There are no short intermolecular contacts and the molecules within the crystal are separated by normal van der Waals distances.

The overall core geometry in each structure is very similar and reminiscent of that in the parent cluster **1** and the related species $[Os_3(\mu\text{-}CO)(CO)_9\{\mu_3\text{-}\eta^2\text{-}PhCCC{\equiv}CPh\}]$ [19]. In each structure **2**–**5** the osmium atoms form an isosceles triangle the longest edge of



Scheme 1.

Download English Version:

https://daneshyari.com/en/article/1322695

Download Persian Version:

https://daneshyari.com/article/1322695

Daneshyari.com