Pincer ligand coordination at a triosmium cluster: X-ray structures of 1,2-Os$_3$(CO)$_{10}$[4,6-bis(diphenylphosphinomethyl)-m-xylene] and 1,2-Os$_3$(CO)$_{10}$[1-diphenylphosphino-1-{(2,4-dimethyl-5-diphenylphosphinomethyl)phenyl}-propan-2-ol]

Vladimir Nesterov [a,*], Bhaskar Poola [b], Xiaoping Wang [b,*], Michael G. Richmond [b,*]

[a] *Department of Chemistry, New Mexico Highlands University, Las Vegas, NM 87701, United States*
[b] *Department of Chemistry, University of North Texas, P.O. Box 305070, Denton, TX 76203-5070, United States*

Dedicated to Prof. Gulya Palyi for his lifetime contributions in organometallic chemistry on occasion of his 70th birthday.

Abstract

The reaction between the triosmium cluster 1,2-Os$_3$(CO)$_{10}$(MeCN)$_2$ and the diphosphine pincer ligand 4,6-bis(diphenylphosphinomethyl)-m-xylene (dppx) has been examined and found to yield the pincer-bridged cluster 1,2-Os$_3$(CO)$_{10}$(dppx) (**2**) as the major product, in addition to the pincer-bridged cluster 1,2-Os$_3$(CO)$_{10}$[1-diphenylphosphino-1-{(2,4-dimethyl-5-diphenylphosphinomethyl)phenyl}-propan-2-ol] (**3**) in trace amounts (<2% yield). Both cluster products have been isolated and their molecular structures determined by crystallographic analyses. The structural highlights of compounds **2** and **3**, which represent the first examples of pincer-ligated metal clusters, are discussed. The origin of the functionalized diphosphine ligand in **3** is traced to the ethanol solvent that was used in the recrystallization of the dppx ligand.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Pincer ligands; Diphosphine ligands; Osmium clusters; Diphosphine ligand activation; Ligand substitution

1. Introduction

The last two decades have witnessed the synthesis of a multitude of terdentate-coordinated organometallic compounds based on PCP, NCN, and PNP pincer-ligand platforms [1]. Literally scores of new pincer-ligated metal compounds have been prepared and structurally characterized. The study of the reactivity exhibited by such pincer-based complexes continues to receive attention with respect to C–H and C–C bond activation due to the potential commercial benefits associated with the production of commodity chemicals using abundant but unreactive alkane/arene feedstocks [2]. Truly impressive are the reports of catalytic alkane dehydrogenation and the activation of ammonia, as exemplified by the two reactions [3,4].
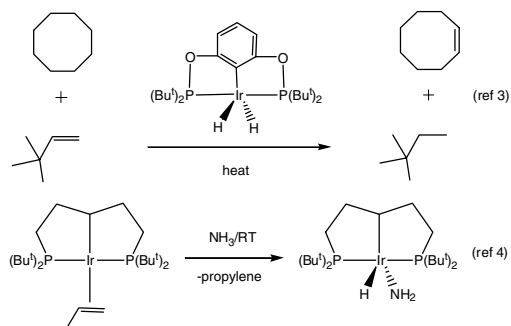
* Corresponding authors. Tel.: +1 505 454 3464; fax: +1 940 565 4318 (V. Nesterov), tel.: +940 369 8489 (X. Wang), tel.: +940 565 3548 (M.G. Richmond).
E-mail addresses: vnesterov@nmhu.edu (V. Nesterov), xpwang@unt.edu (X. Wang), cobalt@unt.edu (M.G. Richmond).

In comparison to the myriad pincer-ligated mononuclear complexes known, no examples exist, to our knowledge, for the coordination of this genre of ligand to a polynuclear entity. The coordination mode that would be exhibited by such pincer ligands at a metal cluster is not immediately obvious since the pincer could function as a 4e-bridging or chelating ligand via binding of the two phosphine or amine moieties in the case of the xylene-based pincer ligands 1,3-$(R_2PCH_2)_2C_6H_4$ and 1,3-$(RNCH_2)_2C_6H_4$. Accompanying this P,P/N,N coordination uncertainty is the possible promotion of aryl cyclometalation and the generation of a meridionally tethered pincer ligand through use of one of the metal–metal bonds. While it would be premature to extol excessively any reactivity advantages associated with the corresponding terdentate-derived polynuclear systems, pincer-substituted metal clusters have the potential to facilitate multisite substrate activation unlike their mononuclear counterparts.

We have recently initiated substitution studies with the pincer ligand 4,6-bis(diphenylphosphinomethyl)-*m*-xylene (dppx) with different metal clusters. Depending on the reaction conditions and the nature of the starting cluster, our preliminary data indicate that the dppx ligand can coordinate one cluster unit at each phosphine group in an η^1 fashion or act as a bridging ligand and bind adjacent metal centers. For example, the reaction between dppx and the tricobalt cluster PhCCo$_3$(CO)$_9$ gives the bis(cluster) compound [PhCCo$_3$(CO)$_8$]$_2$(dppx) while the use of the hexaruthenium cluster Ru$_6$(μ_6-C)(CO)$_{17}$ yields the bis(cluster) compound [Ru$_6$(μ_6-C)(CO)$_{16}$]$_2$(dppx) and the pincer-bridged cluster Ru$_6$(μ_6-C)(CO)$_{15}$(dppx) [5]. Herein we present our findings for the reaction of the dppx ligand with the triosmium cluster 1,2-Os$_3$(CO)$_{10}$(MeCN)$_2$. The replacement of the two MeCN groups by the dppx ligand furnishes the diphosphine-bridged cluster 1,2-Os$_3$(CO)$_{10}$-(dppx) (**2**) as the predominant product, along with trace amounts of the cluster compound 1,2-Os$_3$(CO)$_{10}$[1-diphenylphosphino-1-{(2,4-dimethyl-5-diphenylphosphinomethyl)phenyl}-propan-2-ol] (**3**). The identities of both **2** and **3** have been established by X-ray analyses. Preliminary NMR data from near-UV irradiation experiments with cluster **2** confirm the facile activation of **2** and suggest the formation of phosphido-bridged Os$_3$ clusters.

2. Experimental

2.1. General

High-pressure carbonylation of OsO$_4$ afforded Os$_3$(CO)$_{12}$ [6], which was then used in the synthesis of the labile cluster 1,2-Os$_3$(CO)$_{10}$(MeCN)$_2$ [7]. The pincer ligand dppx was synthesized according to the published procedure using 1,3-bis(chloromethyl)-4,6-dimethylbenzene and Ph$_2$PLi [8,9] and initially purified by recrystallization from EtOH. The chemicals Me$_3$NO · *n*H$_2$O and *m*-xylene were purchased from Aldrich Chemical Co., with the former chemical dried by azeotropic distillation from

benzene. All reaction, IR, and NMR solvents were of reagent grade and were either degassed with argon prior to their use or distilled from a suitable drying agent and stored in Schlenk vessels equipped with Teflon stopcocks [10]. The combustion analysis was performed by Atlantic Microlab, Norcross, GA.

The reported infrared spectral data were recorded on a Nicolet 20 SXB FT-IR spectrometer in a 0.1 mm NaCl cell, using PC control and OMNIC software. The ^{1}H NMR data were recorded at 200 MHz on a Varian Gemini-200 spectrometer, and the ^{31}P NMR data were recorded at 121 MHz on a Varian 300-VXR spectrometer. The reported ^{31}P chemical shifts were acquired in the proton-decoupled mode and referenced to external H$_3$PO$_4$ (85%), taken to have $\delta = 0$. The ESI-APCI mass spectral data for cluster **3** and the two diphosphine ligands were obtained at the UC San Diego Mass Spectrometry Center.

2.2. Synthesis of 1,2-Os$_3$(CO)$_{10}$(dppx) and 1,2-Os$_3$(CO)$_{10}$[1-diphenylphosphino-1-{(2,4-dimethyl-5-diphenylphosphinomethyl)phenyl}-propan-2-ol]

To 0.30 g (0.32 mmol) of 1,2-Os$_3$(CO)$_{10}$(MeCN)$_2$ in 40 mL of CH$_2$Cl$_2$ under argon was added 0.16 g (0.32 mmol) of dppx. The reaction solution was stirred at room temperature and monitored by TLC using a 1:1 mixture of CH$_2$Cl$_2$/hexane as the eluent, which confirmed the complete consumption of the starting cluster after 2 h and the presence of one spot corresponding to cluster **2** ($R_f = 0.65$) and a trace amount of a slower moving spot for cluster **3** ($R_f = 0.10$). The solvent was concentrated under vacuum and subjected to column chromatography over silica gel using CH$_2$Cl$_2$/hexane (3:7). Cluster **2** was obtained as an air-stable yellow solid that was recrystallized from CH$_2$Cl$_2$/hexane in 79% yield (0.34 g). Cluster **2**: IR (CH$_2$Cl$_2$): v(CO) 2088 (s), 2051 (m), 2023 (s), 2004 (vs), 1969 (m), 1949 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.67 (s, 6H, Me), 3.57 (d, 4H, benzylic, $J_{P–H} = 11$ Hz), 6.61 (s, 1H, aryl), 7.20–7.65 (m, 20H, aryl), 7.80 (s, 1H, aryl). ^{31}P (CDCl$_3$): δ −0.76 (s). Anal. Calc. (found) for C$_{44}$H$_{32}$Os$_3$-O$_{10}$P$_2$ · CH$_2$Cl$_2$: C, 37.58 (37.46); H, 2.38 (2.36). Cluster **3**: IR (CH$_2$Cl$_2$): v(CO) 2078 (s), 2063 (s), 2051 (s), 2027 (vs), 2009 (vs), 1997 (vs), 1970 (sh) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.90 (s, 3H, Me), 2.02 (b, 3H, Me), 2.15 (s, 3H, Me), 3.35–3.65 (b, 4H, benzylic hydrogens and C*H*(OH) methine hydrogen), 6.58 (s, 1H, aryl), 7.10–7.80 (bm, 21H, aryl). ESI-APCI MS (m/z): 1399.55 [**3**+H]$^+$.

2.3. X-ray diffraction structure for clusters 2 and 3

Single crystals of clusters **2** and **3** suitable for X-ray crystallography were grown from a CH$_2$Cl$_2$ solution containing each cluster that had been layered with hexane. The X-ray data for **2** · CH$_2$Cl$_2$ (NMHU) and **3** (UNT) were collected on APEX II CCD-based diffractometers at 295 K and 100 K, respectively. The frames were integrated with the available SAINT [11] and APEX2 [12] software packages using

a narrow-frame algorithm, and each structure was solved and refined using the SHELXTL program package [13]. The molecular structures were checked using PLATON [14], and all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were assigned calculated positions and allowed to ride on the attached heavy atom. The refinement for **2** converged at $R = 0.0747$ and $R_w = 0.1746$ for 11 005 independent reflection with $I > 2\sigma(I)$ and for **3** at $R = 0.0296$ and $R_w = 0.0566$ for 8664 independent reflection with $I > 2\sigma(I)$. Tables 1 and 2 summarize the pertinent X-ray data.

3. Results and discussion

3.1. Synthesis and molecular structures for clusters 2 and 3

Treatment of 1,2-$Os_3(CO)_{10}(MeCN)_2$ with an equimolar amount of dppx in CH_2Cl_2 at room temperature leads to a rapid substitution reaction and formation of cluster **2** as the predominant product, as assessed by TLC analysis. Besides **2**, TLC also revealed the presence of a slow moving yellow spot that suggested the formation of another osmium containing product. Both cluster products were subsequently isolated by column chromatography over sil-

Table 1
X-ray crystallographic data and processing parameters for clusters **2** and **3**

Compound	**2**	**3**
CCDC entry number	616 548	616 547
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.183(3)	12.6828(6)
b (Å)	12.424(3)	13.0300(6)
c (Å)	19.616(4)	15.3073(8)
α (°)	82.388(6)	93.362(1)
β (°)	80.807(4)	103.088(1)
γ (°)	73.278(4)	114.539(1)
V (Å^3)	2336.4(1)	2207.9(2)
Molecular formula	$C_{44}H_{32}O_{10}Os_3P_2 \cdot CH_2Cl_2$	$C_{46}H_{36}O_{11}Os_3P_2$
Formula weight	1438.16	1397.29
Formula units per cell (Z)	2	2
D_{calcd} (Mg/m^3)	2.044	2.102
λ (Mo Kα) (Å)	0.71073	0.71073
Absorption coefficient (mm^{-1})	8.375	8.744
R_{merge}	0.0496	0.0388
Absorption correction, max/min	Multi-scan, 0.8504/0.4880	Multi-scan, 0.5796/0.2611
Total reflections	23 211	18 941
Independent reflections	11 005	8664
Data/res/parameters	11 005/1/561	8664/0/562
[a]R	0.0747	0.0296
[b]R_w	0.1746	0.0566
[c]Goodness-of-fit on F^2	0.998	1.015
Largest difference in peak and hole (e/Å^3)	2.801, −1.257	1.873, −1.188

[a] $R = \sum \|F_o| - |F_c\|/\sum |F_o|$.

[b] $R_w = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \right\}^{1/2}$, where $w = 1/|\sigma^2(F^2) + (aP)^2 + bP|$ and $P = [2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

[c] $\text{GOF} = \left\{ \sum [w(F_o^2 - F_c^2)^2]/(n - p) \right\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

Table 2
Selected bond distances (Å) and angles (°) for clusters **2** and **3**

Bond distances			
Cluster **2**		Cluster **3**	
Os(1)–Os(2)	2.9743(9)	Os(1)–Os(2)	2.9802(3)
Os(2)–Os(3)	2.898(1)	Os(2)–Os(3)	2.8962(3)
Os(1)–Os(3)	2.8862(9)	Os(1)–Os(3)	2.8789(3)
Os(1)–P(1)	2.356(4)	Os(1)–P(1)	2.359(1)
Os(2)–P(2)	2.348(4)	Os(2)–P(2)	2.368(2)
P(1)···P(2)	5.530(8)	P(1)···P(2)	5.539(2)
Bond angles			
P(1)–Os(1)–Os(3)	177.7(1)	P(1)–Os(1)–Os(3)	175.79(4)
P(2)–Os(2)–Os(3)	173.45(9)	P(2)–Os(2)–Os(3)	176.76(4)
C(9)–P(1)–Os(1)	119.6(5)	C(11)–P(1)–Os(1)	120.0(2)
C(22)–P(2)–Os(2)	121.9(5)	C(20)–P(2)–Os(2)	128.5(2)
C(2)–C(9)–P(1)	113(1)	C(12)–C(11)–P(1)	111.5(4)
C(6)–C(22)–P(2)	120(1)	C(14)–C(20)–P(2)	116.8(4)

ica gel as air-stable solids. The structures for these two clusters are
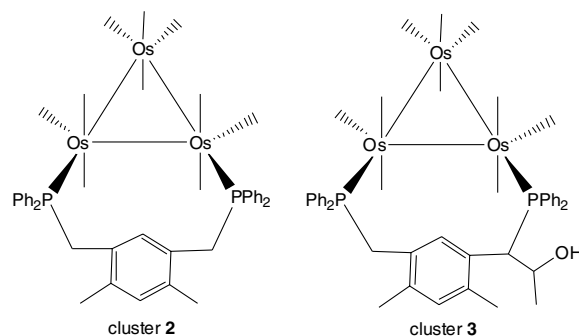
cluster **2**　　　　cluster **3**

The major product corresponds to the dppx-bridged cluster **2**, which was isolated in 79% yield and characterized in solution by IR and NMR spectroscopies, elemental analysis, and X-ray crystallography. The ^{1}H NMR spectrum of **2** displays resonances at δ 1.67 and 3.57 for the pairwise equivalent methyl and benzylic hydrogens, respectively, with the aromatic hydrogens of the Ph_2P moieties appearing as a multiplet from δ 7.20 to 7.65. The two singlets that integrate for 1H each at δ 6.61 and 7.80 are readily assigned to the unique aryl hydrogens on the xylene platform. These data confirm that cyclometalation of the dppx ligand has not occurred. The high-field ^{31}P singlet recorded at δ −0.76 for **2** is in accord with the proposed structure and the NMR data reported by us for other diphosphine-bridged Os_3 clusters [15]. The molecular structure for **2** is shown in Fig. 1. Cluster **2** contains 48-valence electrons and is electronically saturated, with the bridging of the Os(1) and Os(2) centers by the dppx ligand structurally confirmed. The Os–Os bond distances range from 2.8862(9) Å [Os(1)–Os(3)] to 2.9743(9) Å [Os(1)–Os(2)], with a mean distance of 2.9195 Å that is consistent with those distances found in simple triosmium clusters and related diphosphine-bridged $Os_3(CO)_{10}(P–P)$ clusters [14,16]. The internuclear P(1)···P(2) distance is 5.530(8) Å and the two equatorially disposed phosphine moieties are
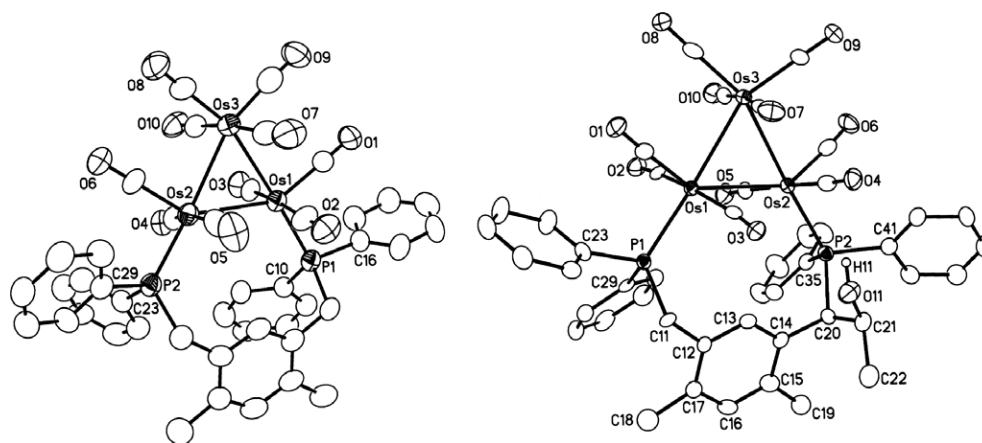
Fig. 1. Thermal ellipsoid plots of 1,2-Os$_3$(CO)$_{10}$(dppx) (left: **2**; 30% probability level) and 1,2-Os$_3$(CO)$_{10}$[1-diphenylphosphino-1-{(2,4-dimethyl-5-diphenylphosphinomethyl)phenyl}-propan-2-ol] (right: **3**; 50% probability level). With the exception of the H(11) atom in the latter structure, all hydrogen atoms have been omitted for clarity.

situated essentially *trans* to the non-bridged Os–Os bonds based on the observed bond angles of 177.7(1)° and 173.45(9)° for the P(1)–Os(1)–Os(3) and P(2)–Os(2)–Os(3) linkages, respectively. The nine-membered ring formed by the coordination of the dppx ligand to the Os(1)–Os(2) vector core exhibits a "terraced" motif with the planes defined by the xylene ring and trimetallic plane representing adjacent terrace steps.

The slower moving spot obtained from the chromatographic separation was characterized in solution by IR and ^{1}H NMR spectroscopies and ESI mass spectrometry. These data were consistent with the formation of an Os$_3$ cluster containing a dppx-derived ligand. The unequivocally identity of this minor product was subsequently established by X-ray diffraction analysis. The structure for cluster **3** is given in the right-hand portion of Fig. 1. Of surprise to us was the "HOCHCH$_3$" appendage at the benzylic C(20) center in **3**. The coordination of the functionalized dppx ligand (also referred to as dppx′ for convenience) to the Os$_3$ frame in **3** is analogous to that already described for cluster **2**. The diphosphine-bridged Os(1)–Os(2) bond is slightly longer (ca. 0.093 Å) than the non-bridged Os–Os bonds, whose mean length is 2.8876 Å. The internuclear P(1)···P(2) distance of 5.539(2) Å agrees well with that distance found in cluster **2**.

Since we had recrystallized the dppx ligand from EtOH [17], it seemed reasonable to assume that the recrystallization solvent was activated by the diphosphine ligand. This premise was subsequently verified by NMR and mass spectral analyses of the recrystallized dppx ligand. The ^{1}H NMR spectrum of the "purified" ligand revealed resonances for the dppx ligand in agreement with the data reported by Milstein and coworkers that accounted for >95% of the material [8]. Further careful inspection of the ^{1}H NMR spectrum revealed broadened baselines about the methyl and benzylic singlets belonging to the dppx ligand, along with a broadened AB quartet at δ 3.50, which in hindsight would be in agreement with the diastereotopic hydrogens at the non-activated benzylic site on the dppx′ ligand. Unequivocal evidence for the presence of dppx′ in the recrystallized sample of the diphosphine ligand was also provided by electrospray mass spectrometry in the positive ionization mode. A sample of the diphosphine ligand in MeOH solvent exhibited m/z peaks at 535.25 and 557.27 for [dppx+MeOH+H]$^+$ and [dppx+MeOH+Na]$^+$ in excellent agreement with the calculated m/z values of 535.60 and 557.22, respectively. Moreover, the small m/z value recorded at 601.17 provided proof for the presence of the functionalized ligand 1-diphenylphosphino-1-{(2,4-dimethyl-5-diphenylphosphinomethyl)phenyl}-propan-2-ol in the dppx ligand sample based on the calculated m/z value of 601.24 for [dppx′+MeOH+Na]$^+$. Both analytical techniques indicate that the dppx′ ligand was present from the start and carried along in the reaction with cluster **1**. Finally, independent thermolysis of dppx in EtOH solvent gives the functionalized ligand dppx′ in low yields, as judged by NMR analysis (Eq. 1). The details associated with this unexpected reaction and its generality are under study and will be published in due course. Suffice it to say, the inert behavior that is generally ascribed to this genre of pincer ligand needs to be viewed with caution given the mild conditions under which dppx reacts with EtOH.

$$\text{(1)}$$
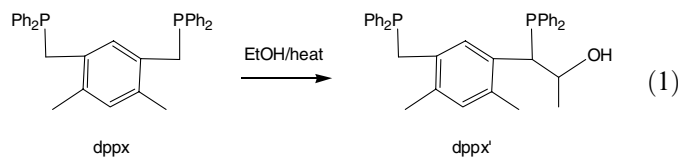
3.2. Activation of the dppx ligand in cluster 2

Due to our long-term interest in the study of the degradation pathways available to cluster-bound diphosphine ligands [14,18], we have carried out preliminary studies on the photochemical and thermal stability of cluster **2**. Irradiation of sealed NMR tubes of **2** in C$_6$D$_6$ with 366 nm light leads to the complete consumption of **2** over the course of several days and the formation of two new

species based on the appearance of ^{31}P NMR resonances at δ 16.90, 18.72, 36.70, and 38.36. The ^1H NMR spectrum also exhibits two sets of singlets at δ 1.45, 2.15 and 1.74, 2.40 for the xylene-based methyl groups in support of the formation of two major products. Careful inspection of the high-field region of the NMR spectrum confirms the absence of metal hydride resonances, which in turn rules out an *ortho*-metalation reaction involving the different aromatic rings and supports to the formation of phosphido-bridged osmium clusters.

Samples of **2** in C_6D_6 in sealed NMR tubes were found to be stable at temperatures up to 75 °C for a period of several days (<5% conversion). However, thermolysis at 100 °C led to the slow consumption of cluster **2** and the formation of three new hydride-bridged clusters based on the presence of bridging hydride resonances at δ −14.23 (d, $J_{P-H} = 26$ Hz), −16.52 (dd, $J_{P-H} = 10$, 8 Hz), −17.84 (dd, $J_{P-H} = 8$, 6 Hz). Our data suggest that heating cluster **2** most likely leads to *ortho*-metalation of the dppx ligand. Similar *ortho*-metalation reactivity has been reported in the thermolysis of the diphosphine-substituted cluster compounds $Os_3(CO)_{10}(P–P)$ (where P–P = dppm, dppe, dppp) [19]. Our future research efforts will be directed towards the isolation and characterization of these new activation products.

4. Conclusions

The substitution reaction of the well-known pincer ligand dppx with $1,2-Os_3(CO)_{10}(MeCN)_2$ has been investigated. The two acetonitrile ligands in **1** are replaced by the dppx ligand to afford the diphosphine-bridged cluster $1,2-Os_3(CO)_{10}(dppx)$ as the major product. We have also succeeded in isolating and characterizing the cluster compound $1,2-Os_3(CO)_{10}[1-diphenylphosphino-1-\{(2,4-dimethyl-5-diphenylphosphinomethyl)phenyl\}-propan-2-ol]$. The origin of this new dppx-derived ligand in cluster **3** has been traced to the EtOH solvent that was used in the recrystallization of the dppx ligand. The generality associated the unexpected reaction between the dppx ligand and EtOH is currently under investigation. It is hoped that our fortuitous uncovering of this latter reaction may serve as an entry point into the synthesis of more exotic diphosphine ligands based on dppx.

Acknowledgments

Appendix A. Supplementary material

X-ray crystallographic files, in CIF format, for the structure determination of both clusters **2** (#616548) and **3** (#616547) have been deposited with the Cambridge Crystallographic Data Center, CCDC 260091 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit @ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.021.

References

[1] (a) For several reviews on this subject, see: P. Steenwinkel, R.A. Gossage, G. van Koten, Chem. Eur. J. 4 (1998) 759;
(b) C.M. Jensen, Chem. Commun. (1999) 2443;
(c) B. Rybtchinski, D. Milstein, Angew. Chem., Int. Ed. 38 (1999) 871;
(d) A. Vigalok, D. Milstein, Acc. Chem. Res. 34 (2001) 798;
(e) M. Albrecht, G. van Koten, Angew. Chem., Int. Ed. 40 (2001) 3751;
(f) M.E. van der Boom, D. Milstein, Chem. Rev. 103 (2003) 1759.

[2] (a) F. Liu, E.B. Pak, B. Singh, C.M. Jensen, A.S. Goldman, J. Am. Chem. Soc. 121 (1999) 4086;
(b) K.B. Renkema, Y.V. Kissin, A.S. Goldman, J. Am. Chem. Soc. 125 (2003) 7770;
(c) X. Zhang, T.J. Emge, R. Ghosh, K. Krogh-Jespersen, A.S. Goldman, Organometallics 25 (2006) 1303;
(d) A.C. Sykes, P. White, M. Brookhart, Organometallics 25 (2006) 1664.

[3] I. Göttker-Schnetmann, P. White, M. Brookhart, J. Am. Chem. Soc. 126 (2004) 1804.

[4] J. Zhao, A.S. Goldman, J.F. Hartwig, Science 307 (2005) 1080.

[5] Unpublished results.

[6] S.R. Drake, P.A. Loveday, Inorg. Synth. 28 (1990) 230.

[7] J.N. Nicholls, M.D. Vargas, Inorg. Synth. 26 (1989) 289.

[8] R. Cohen, M.E. van der Boom, L.J.W. Shimon, H. Rozenberg, D. Milstein, J. Am. Chem. Soc. 122 (2000) 7723.

[9] M. Gerisch, J.R. Krumper, R.G. Bergman, T.D. Tilley, Organometallics 22 (2003) 47.

[10] D.F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, 1969.

[11] SAINT Version 6.02, Bruker Analytical X-ray Systems, Inc. Copyright 1999, Madison, WI.

[12] APEX2 Version 2.02, Bruker Analytical X-ray Systems, Inc. Copyright 2005, Madison, WI.

[13] SHELXTL Version 6.14, Bruker Analytical X-ray Systems, Inc. Copyright 2003, Madison, WI.

[14] PLATON – A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, Spek, A.L., 2001.

[15] W.H. Watson, G. Wu, M.G. Richmond, Organometallics 24 (2005) 5431;
Organometallics 25 (2006) 930.

[16] (a) V.M. Hansen, A.K. Ma, K. Biradha, R. Pomeroy, M.J. Zaworotko, Organometallics 17 (1998) 5267;
(b) M.R. Churchill, B.G. DeBoer, Inorg. Chem. 16 (1977) 878;
(c) M.I. Bruce, P.A. Humphrey, G. Melino, B.W. Skelton, A.H. White, N.N. Zaitseva, Inorg. Chim. Acta 358 (2005) 1453;
(d) W.K. Leong, Y. Liu, J. Organomet. Chem. 584 (1999) 174;
(e) S. Cartwright, J.A. Clucas, R.H. Dawson, D.F. Foster, M.M. Harding, A.K. Smith, J. Organomet. Chem. 302 (1986) 403;
(f) J.A. Clucas, R.H. Dawson, P.A. Dolby, M.M. Harding, K. Pearson, A.K. Smith, J. Organomet. Chem. 311 (1986) 153;
(g) A.J. Deeming, S. Donovan-Mtunzi, K.I. Hardcastle, S.E. Kabir, K. Henrick, M. McPartlin, J. Chem. Soc., Dalton Trans. (1988) 579.

[17] (a) One of the more common methods employed in the purification of solid triarylphosphines involves recrystallization from EtOH. For

example, see: V.D. Bianco, S. Doronzo, Inorg. Synth. 18 (1978) 169;
(b) H. Schmidbaur, A. Stützer, E. Herdtweck, Chem. Ber. 124 (1991) 1095;
(c) D.N. Kazul'kin, A.N. Ryabov, V.V. Izmer, A.V. Churakov, I.P. Beletskaya, C.J. Burns, A.Z. Voskoboynikov, Organometallics 24 (2005) 3024.

[18] (a) K. Yang, J.M. Smith, S.G. Bott, M.G. Richmond, Organometallics 12 (1993) 4779;
(b) S.G. Bott, K. Yang, K.A. Talafuse, Organometallics 22 (2003) 1383;

(c) S.G. Bott, K. Yang, M.G. Richmond, J. Organomet. Chem. 690 (2005) 3067;
(d) S.G. Bott, H. Shen, M.G. Richmond, J. Organomet. Chem. 690 (2005) 3838;
(e) W.H. Watson, S.G. Bodige, K. Ejsmont, J. Liu, M.G. Richmond, J. Organomet. Chem. 691 (2006) 3609.

[19] (a) J.A. Clucas, D.F. Foster, M.M. Harding, A.K. Smith, J. Chem. Soc., Chem. Commun. (1984) 949;
(b) A.J. Deeming, K.I. Hardcastle, S.E. Kabir, J. Chem. Soc., Dalton Trans. (1988) 827.