Unprecedented Coordination of 4,4′,5,5′-Tetramethyl-2,2′-biphosphinine Doubly Bridging over an Open Triosmium Core

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The crystal structure of the novel cluster $[Os_3(CO)_{10}$(4,4′,5,5′-tetramethyl-2,2′-biphosphinine)] reveals an unprecedented coordination mode of the biphosphinine ligand that occupies a doubly-bridging position spanning the open osmium triangle. The cluster is photostable, pointing to a localization of the lowest-energy electronic transition largely on the negatively charged biphosphinine ligand.

Introduction

Clusters of the type $[Os_3(CO)_{10}$(α-diimine)] exhibit a very diversified photochemical and redox behaviour which is controlled by the tuneable electronic and steric properties of the α-diimine ligand. Such ligands include 4,4′-di-R-2,2′-bipyridine and pyridine-2-carbaldehyde-*N*′-R-imine (R = alkyl).[1–3] In comparison with σ*N*,σ*N*′-chelated 2,2′-bipyridine, its aromatic phosphorus derivative 4,4′,5,5′-tetramethyl-2,2′-biphosphinine (tmbp) binds as a fairly strong π-acceptor ligand in a variety of mononuclear complexes, and better stabilizes low oxidation states of the metal in the M(σ*P*,σ*P*′-tmbp) chelate ring.[4,5] In addition, it may bind as a cyclophosphahexatriene with localized double bonds, for example in $[Mn_2(CO)_6$(tmbp)] where it chelates to one $Mn(CO)_3$ moiety through the P lone pairs and to the other metal centre through the internal P=C bonds.[6]

The growing interest in biphosphinine complexes prompted us to attempt the synthesis of the cluster $[Os_3(CO)_{10}$(σ*P*,σ*P*′-tmbp)], with the aim of performing a comparative study of its spectroscopic, photochemical and redox properties. Nevertheless, as often encountered in cluster chemistry, our synthetic efforts instead yielded a structural isomer of the intended product, which presents the first example of the biphosphinine coordinated to three transition metal centres as a doubly bridging ligand. Herein we report the synthesis, X-ray crystal structure and brief characterization of this unusual triosmium cluster.

Results and Discussion

The precursor cluster $[Os_3(CO)_{10}(MeCN)_2]$ reacts with tmbp in THF at room temperature to give purple $[Os_3(CO)_{10}(\mu_2P,\mu_2P'$-tmbp)] (**1**, Figure 1). The cluster **1** was isolated and spectroscopically characterized. The X-ray crystal structure is shown in Figure 2. Similarly to the four-electron donor 2,2′-bipyridine in $[Os_3(CO)_{10}$(bpy)], the biphosphinine ligand is chelated at Os(1). In addition, each phosphorus atom forms a bridge between Os(1) and one of the other two osmium centres. The double μ_2-P bridging of tmbp causes cleavage of the Os(1)–Os(2) bond and opening of the osmium triangle [Os(1)–Os(3)–Os(2) = 85.93(2)°]. Secondly, the tmbp ligand becomes strongly distorted and its aromaticity is lifted. In all known mononuclear complexes of tmbp this ligand is perfectly planar, with C–C bond lengths in the rings between 1.38 and 1.41 Å, thus displaying a high degree of aromaticity.[4,5] In contrast, the C–C bond lengths of **1** range from 1.33(2) Å, typical for isolated C=C bonds, to 1.47(2) Å (length of a single C–C bond ≈ 1.53 Å). Importantly, the inter-ring C–C bond length in **1** is rather short [1.41(2) Å] when compared to the characteristic values for the nonreduced uncoordinated ligand (1.49 Å, average of two isomers)[7] and for mononuclear complexes of tmbp (ca. 1.47 Å).[4,5] Also the C–P bonds are rather long [1.77(2)–1.80(2) Å] compared to the C–P bond lengths of "aromatic" tmbp (1.71–1.74 Å).[4,5] These data point to partial reduction of the tmbp ligand by electron transfer from the triosmium core, causing cleavage

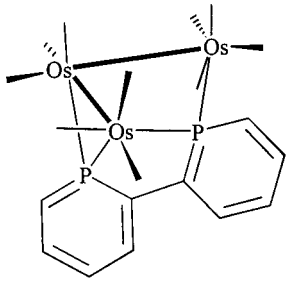

Figure 1. Schematic molecular structure of cluster **1**

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of the Os–Os bond.[8] Another remarkable feature is the enormous difference between the two Os–P–Os bridge angles: 75.2(1)° [P(2)] spanning the intact Os(1)–Os(3) bond, but 110.0(1)° [P(1)] spanning the nonbonded Os(1) and Os(2) centres.

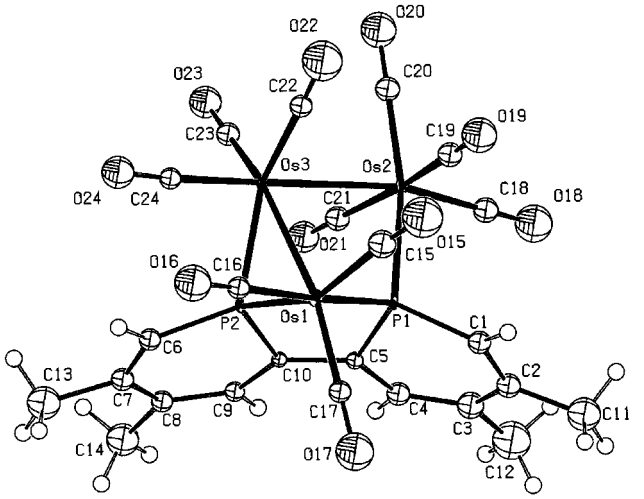

Figure 2. X-ray crystal structure of cluster **1**; selected bond lengths (Å) and angles (°) with standard deviations in parentheses: Os(1)–Os(3) 2.8856(9), Os(2)–Os(3) 2.9567(9), Os(1)–P(1) 2.395(4), Os(2)–P(1) 2.441(4), Os(1)–P(2) 2.351(3), Os(3)–P(2) 2.376(4), P(1)–C(1) 1.77(2), P(1)–C(5) 1.80(2), C(1)–C(2) 1.37(2), C(2)–C(3) 1.46(3), C(3)–C(4) 1.38(2), C(4)–C(5) 1.39(2), P(2)–C(6) 1.78(2), P(2)–C(10) 1.80(1), C(6)–C(7) 1.33(2), C(7)–C(8) 1.47(2), C(8)–C(9) 1.37(2), C(9)–C(10) 1.44(2), C(5)–C(10) 1.41(2); Os(1)–Os(3)–Os(2) 85.93(2), Os(1)–P(1)–Os(2) 110.9(1), Os(1)–P(2)–Os(3) 75.2(1), P(1)–Os(1)–P(2) 75.1(1), C(1)–P(1)–C(5) 100.1(6), C(6)–P(2)–C(10) 101.6(7)

The very different environments of both phosphorus atoms are reflected in their ^{31}P NMR chemical shifts (δ = 26.2 and –146.2). Both values significantly deviate from the strongly positive ^{31}P chemical shifts for "aromatic tmbp" complexes (δ = 178–250).[4,5] The loss of aromaticity is also reflected in the shift of the proton signals to smaller ppm values (ca. 1.5 ppm) compared to those of the noncoordinated tmbp ligand.

Cluster **1** is deep-purple coloured due to a broad absorption band at 540 nm. The corresponding electronic transition exhibits negligible solvatochromism,[9] in contrast to the lowest-energy electronic transition of $[Os_3(CO)_{10}(bpy)]$, which possesses a dominant metal(core)-to-ligand charge transfer character.[1,10] The involved frontier orbitals of **1** probably have a dominant contribution from the tmbp ligand.[8] This may explain the observed inherent photostability of **1**, as no specific metal–ligand or metal–metal bonds are significantly weakened upon visible excitation.[11]

The different electronic structure with regard to that of $[Os_3(CO)_{10}(bpy)]$ is also indicated by the electrochemical behaviour of **1** which, in the first instance, was studied by cyclic voltammetry. At room temperature and at v = 20 mV/s the reduction of **1** is a chemically irreversible two-electron process ($E_{p,c}$ = –1.73 V *vs.* Fc/Fc$^+$), resulting in loss of CO. At v = 100 V/s the reduction becomes a chemically reversible one-electron process ($E_{1/2}$ = –1.74 V *vs.* Fc/Fc$^+$). The reduction potential is more negative than would be expected for a dominantly tmbp-localized reduction of isomeric $[Os_3(CO)_{10}(\sigma P,\sigma P'\text{-tmbp})]$ with a molecular and electronic structure resembling that of $[Os_3(CO)_{10}(\alpha\text{-diimine})]$.[12] On the other hand, the higher stability of the radical anion **1**$^{-\bullet}$ does not correspond to the reduction being localized significantly on the cluster core.[3] We assume that the higher LUMO energy of **1** reflects the partial negative charge on the tmbp ligand, as deduced from the crystallographic data.

A detailed (spectro)electrochemical and quantum chemical investigation of **1** is currently being carried out.[8]

Experimental Section

General: UV/Vis: Varian Cary 4E. – IR: Bio-Rad FTS 60A – NMR: Bruker AMX 300. – MS (FAB): JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-MP 7000 data system. – Elemental analyses were performed at H. Kolbe Mikroanalytisches Laboratorium in Mülheim an der Ruhr.

$[Os_3(CO)_{10}(tmbp)]$ (1): $[Os_3(CO)_{10}(MeCN)_2]$[12] (190 mg) and tmbp (45 mg, 0.9 equiv.) were dissolved in freshly distilled THF (50 mL) under an atmosphere of dry N_2. The yellow solution quickly turned red and finally deep purple. After 1.5 h the solvent was evaporated in vacuo, and the crude purple product was purified by column chromatography over silica, eluting with hexane/dichloromethane (20:1). Single crystals suitable for a crystal structure determination were grown from hexane at 293 K.

1: IR (hexane): ν(CO) = 2104 m, 2057 s, 2036 m, 2025 sh, 2022 vs, 2007 w, 1991 m, 1976 m, 1959 w, 1952 w cm^{-1} – ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ = 1.90 (s, Me), 2.04 (s, Me), 2.15 (s, Me), 2.20 (s, Me), 6.36 (d, $^2J(P_a–H)$ = 32.1 Hz, 1 H), 6.39 (d, $^2J(P_b–H)$ = 28.5 Hz, 1 H), 6.75 (d, $^3J(P_a–H)$ = 17.4 Hz, 1 H), 6.93 (d, $^3J(P_b–H)$ = 19.2 Hz, 1 H). – ^{31}P{H} NMR (300 MHz, 293 K, $CDCl_3$): δ = –146.2 (d, P_a), 26.2 (d, P_b), $J(P_a–P_b)$ = 108 Hz. – UV/Vis (*n*-hexane): λ = 340 sh, 436 sh, 540 nm. – $C_{24}H_{16}O_{10}Os_3P_2$ (1097): calcd. C 26.28, H 1.47, P 5.65; found C 26.39, H 1.54, P 5.74. – MS (FAB): *m/z* = 1097 [M$^+$].

X-ray Structure of 1: $C_{24}H_{16}O_{10}Os_3P_2$, M = 1097, monoclinic, space group $P2_1/a$, a = 9.8115(8), b = 16.359(1), c = 18.276(1) Å, β = 98.693(6)°, U = 2899.7(3) Å^3, Z = 4, D_x = 2.51 gcm^{-3}, λ(Cu-K_α) = 1.5418 Å, μ(Cu-K_α) = 257.9 cm^{-1}, T = 253 K, F(000) = 1992, 5954 unique reflections measured, final R = 0.060 for 5264 observed reflections. During the measurement the two reference reflections that were measured hourly showed an increase in intensity which could not be explained. This may be the reason why only the heavy atoms (Os and P) could be refined anisotropically. The results of the structure refinement with respect to the geometry of the molecule were, however, satisfactory.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136584. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk).

Cyclic Voltammetry: Cyclic voltammograms of **1** in freshly distilled THF (with 0.1 M Bu_4NPF_6 as electrolyte) were recorded under argon in a gas-tight single-compartment cell equipped with a Pt-disk

working microelectrode (r = 0.4 mm), a Pt-gauze auxiliary electrode and an Ag-coil pseudoreference electrode. Potential control was achieved with a PAR Model 283 potentiostat.

Photochemistry: Continuous-wave irradiation was performed with a Spectra Physics 2025 argon-ion laser. Nanosecond time-resolved UV/Vis experiments were carried out with 7 ns pulses (fwhm) of a 532 nm line obtained by frequency doubling of the 1064 nm fundamental of a Spectra Physics GCR-3 Nd:YAG laser. Details of the data collection system have been described elsewhere.[2]

Acknowledgments

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[9] UV/Vis absorption maxima of the lowest-energy electronic transition of **1** in different solvents: 540 (hexane), 556 ($\varepsilon = 3.6 \times 10^3$ $M^{-1}cm^{-1}$, THF), 553 (acetonitrile), 559 (pyridine) nm.
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[11] Cluster **1** is photostable upon continuous irradiation in CCl_4, THF, acetonitrile or pyridine at room temperature (λ_{irr} = 514.5 nm). No UV/Vis transient was observed even on a nanosecond time scale [λ_{irr} = 532 nm, τ(laser pulse) = 7 ns].
[12] The electrode potentials for the one-electron reduction of uncoordinated tmbp and 4,4′-dimethyl-2,2′-bipyridine (dmb) in DMF are $E_{1/2}$ = –1.85 V and –2.16 V *vs.* SCE, respectively.[7] In contrast, for the clusters **1** and $[Os_3(CO)_{10}(\sigma N,\sigma N'\text{-dmb})]$[14] in THF the values are closer, *viz.* $E_{1/2}$ = –1.70 V (208 K) and –1.89 V (213 K) *vs.* $Fc/Fc^{+\cdot}$ respectively.
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