Synthesis and X-ray Structures of [$Os_3Pt(CO)_9(\mu_4$-η^2-C≡CPh)(η^1-C≡CPh)(L)] (L = 4,4′-Dimethyl-2,2′-bipyridine, 4,4′-bis(*tert*-butyl)-2,2′-bipyridine): New Heterometallic Clusters with a μ_4-η^2- and an η^1-Acetylide Group on a Spiked-Triangular Metal Core

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Treatment of [$Os_3(CO)_{10}(NCMe)_2$] with platinum bis(alkynyl) complexes *cis*-[Pt(C≡CPh)$_2$(L)] [L = 4,4′-dimethyl-2,2′-bipyridine (Me_2bipy), 4,4′-bis(*tert*-butyl)-2,2′-bipyridine (*t*Bu_2bipy)] at room temperature readily affords the novel, spiked-triangular heterometallic cluster complexes [$Os_3Pt(CO)_9(\mu_4$-η^2-C≡CPh)(η^1-C≡CPh)(L)] (L = Me_2bipy **1**, *t*Bu_2bipy **2**) in moderate yields. X-ray analysis of both complexes reveals that one alkynyl moiety is coordinated to the metal atoms in a μ_4-η^2(||) mode, accompanied by a concomitant transfer of an η^1-C≡CPh group from the platinum centre to the osmium atom to give a metal framework with an osmium atom apically bonded to an Os_2Pt triangle.

Introduction

There is continuing interest in transition metal σ-alkynyl complexes and polymers stemming from their possible applications in materials science.[1,2] Within this field, rigid-rod polymers based on metals linked by alkynyl groups in a *trans*-configuration have proved particularly fruitful, and a number of new materials with novel electronic properties have been prepared, the nature of which depends on the metals, the ancillary ligands and the spacer units.[3−10] Likewise, *cis*-platinum bis(alkynyl) complexes have recently been exploited as novel precursors for the synthesis of a series of homo- or heterobimetallic complexes in which the second metal is linked to the bis(alkynyl) molecule by coordination to the alkynyl C≡C triple bonds.[11−16] The use of alkynyl platinum species as alkynylating agents is also known.[15] These bimetallic complexes have been shown to exhibit a range of interesting chemical and physical properties.[17] In an effort to extend this chemistry to other multimetallic systems, we have studied the reactions of some *cis*-[Pt(C≡CPh)$_2$(diimine)] complexes with [$Os_3(CO)_{10}(NCMe)_2$]. To our surprise, we have discovered that this leads to new heterometallic complexes formed by transformations involving η^1-acetylide transfer, opening of the Os_3 triangle and formation of two Pt−Os bonds. We describe herein the characterization of two new compounds [$Os_3Pt(CO)_9(\mu_4$-η^2-C≡CPh)(η^1-C≡CPh)(L)] [L = 4,4′-dimethyl-2,2′-bipyridine (Me_2bipy), 4,4′-bis(*tert*-butyl)-2,2′-bipyridine (*t*Bu_2bipy)] showing two distinct bonding modes for the alkynyl fragment.

Results and Discussion

The mixed-metal cluster compounds [$Os_3Pt(CO)_9(\mu_4$-η^2-C≡CPh)(η^1-C≡CPh)(L)] (L = Me_2bipy **1**, *t*Bu_2bipy **2**) were readily prepared by the room temperature reactions of the molecular tweezers *cis*-[Pt(C≡CPh)$_2$(L)] with one molar equivalent of [$Os_3(CO)_{10}(NCMe)_2$] in CH_2Cl_2 (Scheme 1). Complexes **1** and **2** were isolated by preparative TLC as stable red solids in moderate yields and characterized by satisfactory IR and NMR spectroscopy and FAB mass spectrometry. X-ray crystallography established the full details of their molecular structures and the coordination modes of the alkynyl moiety.

Crystals of **1** and **2** were grown from hexane/CH_2Cl_2 at room temperature. Complex **1** crystallized in an asymmetric unit possessing two crystallographically independent molecules. Perspective drawings of **1** and **2** are depicted in Figure 1 and 2, respectively. The structural features of both **1** and **2** are very similar and they will not be discussed separately. The molecular structures of **1** and **2** reveal that the Os_3 triangle has opened out with Os−Os−Os angles of 112.31(2) and 111.41(3)° in **1** and **2**, respectively. This is accompanied by the formation of two Pt−Os bonds. Three carbonyl groups are bound to each osmium atom. The metal core of **1** and **2** consists of an essentially isosceles Os_2Pt triangle, with a third osmium atom, Os(2), apically bonded to Os(1) to give an "out-of-plane" spiked-triangular metal framework. The Pt centre adopts a pseudo square planar geometry. Although there are several known examples of Os_3Pt clusters containing a closed Os_3 triangle with a spiked Pt atom,[18,19] complexes comprising an open triangular cluster of three osmium atoms with a Pt(diimine) moiety spanning one of the two Os−Os bonds are very rare. To the best of our knowledge, structurally characterized examples of such a metal core have only been encountered in [$Os_3Pt(CO)_{11-n}(L)_n(\mu_3$-S$)_2$] (*n* = 1, 2; L = PPh_3, PMe_2Ph) with phosphane ligands on the Pt atom.[20,21] The Pt−Os distances range from 2.6397(6) to 2.6770(6) Å in **1** and **2**, and are somewhat shorter than those in previously reported Os_3Pt clusters {2.712(1) Å in [$Os_3Pt(\mu$-H)(μ_4-η^2-C≡CPh)$(CO)_{10}(PCy_3)$],[18] 2.714(1)−2.811(1) Å in

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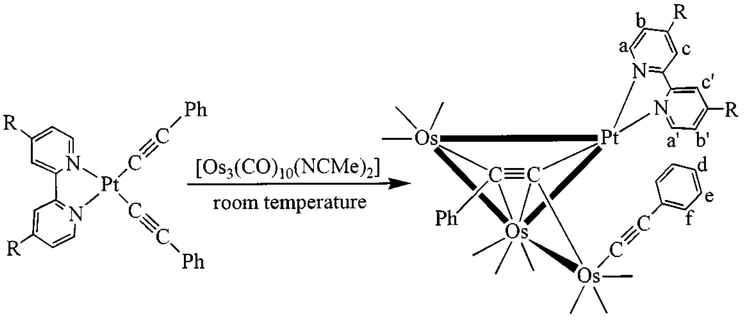
1434−1948/01/0303−0623 $ 17.50+.50/0



R = Me **1**, *t*Bu **2**

Scheme 1. Synthesis of complexes **1** and **2**

$[\mathrm{Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(COD)}]$,[22] 2.764(1) Å in $[\mathrm{Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}}]$,[19] 2.789(1)-2.936(1) Å in $[\mathrm{Os_3Pt(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2}]$[20]}. The spiked Os(1)−Os(2) edge [2.8909(6) Å in **1**, 2.914(1) Å in **2**] is notably longer than the other Os(1)−Os(3) bond [2.8032(7) Å in **1**, 2.810(1) Å in **2**] in both cases. The Pt−N bond [2.148(7)−2.174(7) Å] is also lengthened after coordination to the cluster motif relative to those observed in other *cis*-platinum bis(alkynyl) diimine complexes [2.04−2.07 Å],[13,14] probably due to the electron-withdrawing nature of the $\mathrm{Os_3}$ fragment.

Another remarkable feature in the formation of **1** and **2** is the activation of a phenylacetylide unit in the starting platinum complex and its facile transfer from the platinum centre to the spiked osmium atom, resulting in a terminal alkynyl group on the Os(2) atom. The −C≡CPh group is σ-bonded to Os(2) in an η^1 mode with the C≡C bond length [average 1.21(2) Å] and Os(2)−C−C bond angle [average 175(1)°] typical of a metal−acetylide bond. The presence of an η^1-acetylide ligand is a relatively rare phenomenon in osmium cluster chemistry, although terminal acetylides are common in mononuclear osmium complexes.[23−25] A similar feature is only found in the homometallic $[\mathrm{Os_3(CO)_6(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)(\eta^1\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)_2(NH_2Et)_2}]$[26] and the heterometallic $[\mathrm{(\eta^5\text{-}C_5Me_5)W(O)(\mu\text{-}O)Os_3(\eta^1\text{-}C{\equiv}CPh)(CO)_{11}}]$[27] complexes.

The remaining Pt-alkynyl unit is coordinated to the $\mathrm{Os_3}$ chain with a μ_4-η^2(‖)-C≡CPh moiety (Figure 3), in a manner similar to $[\mathrm{CpWOs_3(CO)_{11}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)}]$ involving an alkynyl transfer and formation of two W−Os bonds.[28] The

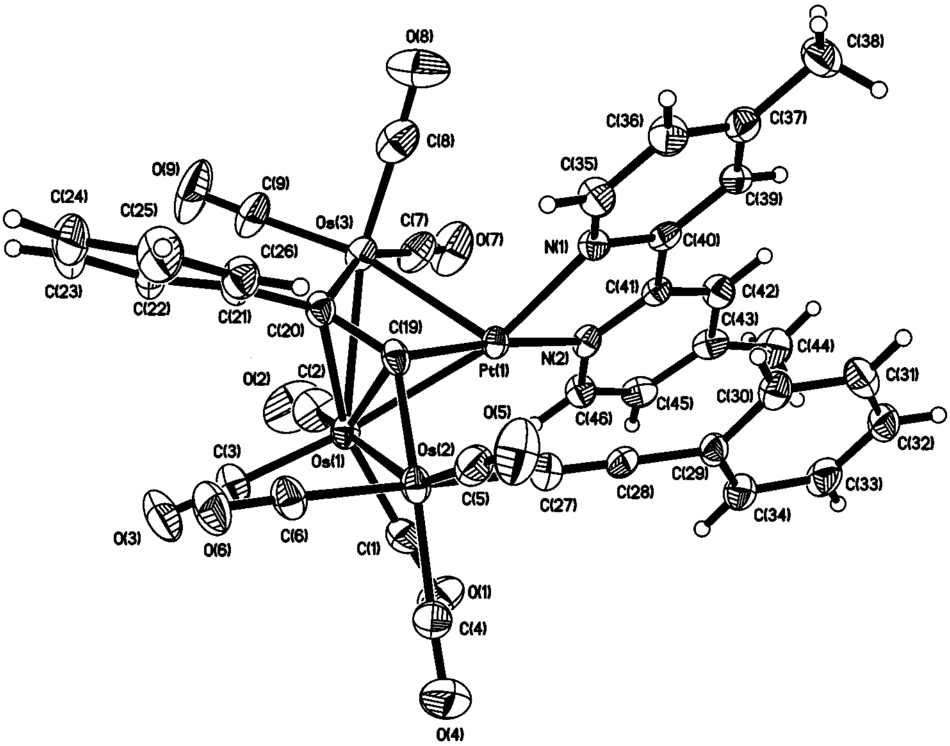


Figure 1. Molecular structure of **1**; important bond lengths (Å) and angles (°): Pt(1)−Os(1) 2.6732(6), Pt(1)−Os(3) 2.6397(6), Os(1)−Os(2) 2.8909(6), Os(1)−Os(3) 2.8032(7), Pt(1)−C(19) 2.011(9), Os(1)−C(19) 2.169(9), Os(1)−C(20) 2.30(1), Os(2)−C(19) 2.06(1), Os(3)−C(20) 2.16(1), Os(2)−C(27) 2.08(1), C(19)−C(20) 1.37(1), C(27)−C(28) 1.21(1); Os(1)−Pt(1)−Os(3) 63.69(2), Pt(1)−Os(1)−Os(3) 57.58(2), Pt(1)−Os(3)−Os(1) 58.74(2), Pt(1)−Os(1)−Os(2) 71.58(1), Os(2)−Os(1)−Os(3) 112.42(2), Pt(1)−C(19)−C(20) 112.1(7), Os(3)−C(20)−C(19) 103.5(6), C(19)−Os(1)−C(20) 35.6(4), Os(2)−C(27)−C(28) 174.0(9)

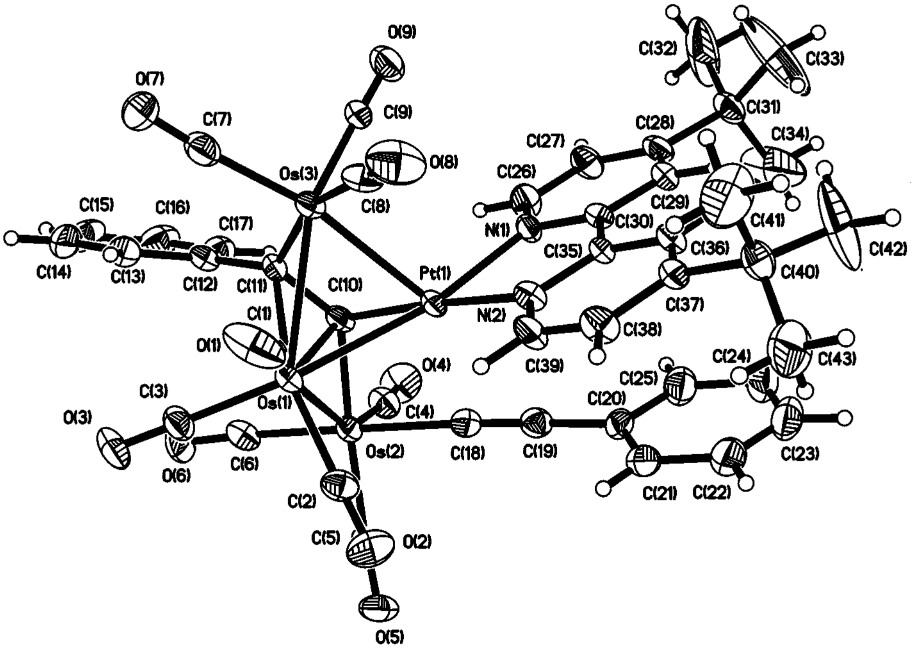


Figure 2. Molecular structure of **2**; important bond lengths (Å) and angles (°): Pt(1)−Os(1) 2.6604(8), Pt(1)−Os(3) 2.6500(9), Os(1)−Os(2) 2.914(1), Os(1)−Os(3) 2.810(1), Pt(1)−C(10) 2.018(9), Os(1)−C(10) 2.196(9), Os(1)−C(11) 2.326(9), Os(2)−C(10) 2.04(1), Os(3)−C(11) 2.075(9), Os(2)−C(18) 2.10(1), C(10)−C(11) 1.42(1), C(18)−C(19) 1.21(2); Os(1)−Pt(1)−Os(3) 63.90(3), Pt(1)−Os(1)−Os(3) 57.87(2), Pt(1)−Os(3)−Os(1) 58.23(3), Pt(1)−Os(1)−Os(2) 71.95(3), Os(2)−Os(1)−Os(3) 111.41(3), Pt(1)−C(10)−C(11) 109.1(6), Os(3)−C(11)−C(10) 105.9(6), C(10)−Os(1)−C(11) 36.4(3), Os(2)−C(18)−C(19) 176(1)

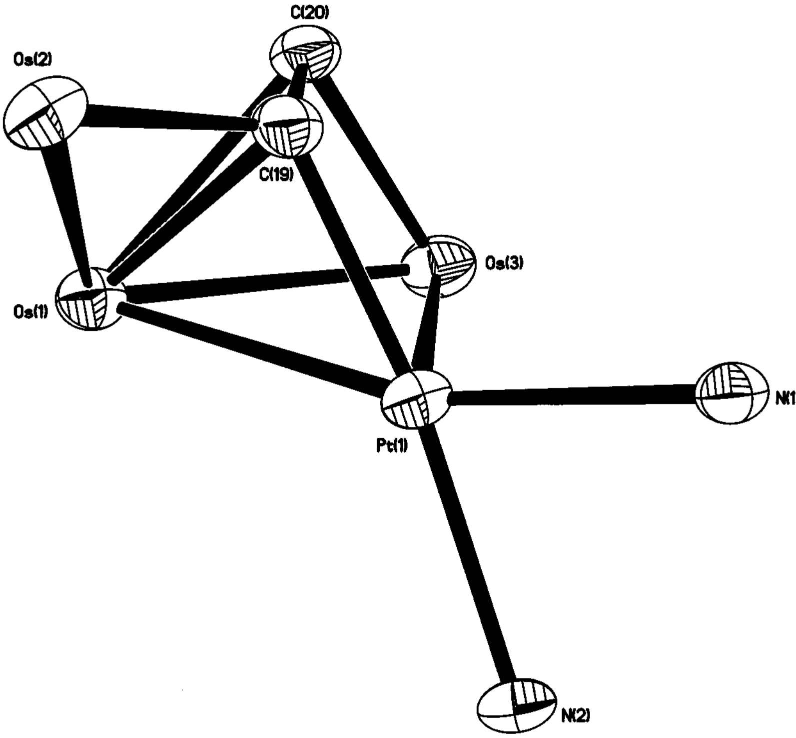


Figure 3. A perspective view of **1** showing the metal core and alkynyl coordination

vectors Pt(1)−Os(3) and C(19)−C(20) in **1** as well as Pt(1)−Os(3) and C(10)−C(11) in **2** are nearly parallel. Although μ_4-η^2(⊥) bonding modes have been documented for acetylides in spiked tetrametallic systems such as [$Os_3Pt(\mu$-H)(μ_4-η^2-C≡CPh)$(CO)_{10}(PCy_3)$],[18] [(η^5-C_5H_5)$FeRuCo_2(CO)_9(\mu$-CO)(μ_4-η^2-C≡CPh)],[29] [(η^5-$C_5H_5)_2Ni_2Fe_2(CO)_5(\mu$-$PPh_2$)($\mu_4$-$\eta^2$-C≡CPh)][30] and [$Ru_3Pt(\mu$-H){$\mu_4$-$\eta^2$-C≡C(*t*Bu)}$(CO)_9$(COD)],[31] clusters with a μ_4-η^2(||)-C≡CPh group are, to the best of our knowledge, not common. The C(19)−C(20)−Os(3)−Pt(1) mean plane makes a dihedral angle of 57.2° with the triangular Os_2Pt plane in **1** [58.2° in **2**]. Formally, the μ_4-η^2-C≡CPh ligand forms a π bond with Os(1) and three separate σ bonds to Os(2), Os(3) and Pt(1) in each case. Assuming that the μ_4-η^2-C≡CPh and η^1-C≡CPh moieties act as a five- and one-electron donor, respectively, each of the complexes **1** and **2** has 62 cluster valence electrons (CVE) which is consistent with a 16-electron Pt centre. This apparent low CVE count is commonly observed in clusters containing Pt atoms.[32]

Experimental Section

Preparation of [$Os_3Pt(CO)_9$(μ_4-η^2-C≡CPh)(η^1-C≡CPh)(Me_2bipy)] (1): A CH_2Cl_2 solution of [$Os_3(CO)_{10}(NCMe)_2$] (0.050 g, 0.054 mmol) was stirred at room temperature with *cis*-[Pt(C≡CPh)$_2$(Me_2bipy)][14,33] (0.031 g, 0.054 mmol) under nitrogen. After 30 min. the solvent was evaporated under vacuum, and the crude product was purified by preparative TLC, eluting with *n*-hexane/CH_2Cl_2 (3:2, v/v) to afford an orange band (R_f = 0.30) which was identified as complex **1** (0.023 g, 30%). − IR (CH_2Cl_2): ν(CO) = 2084 w, 2065 w, 2048 vs, 2012 s, 1998 m, 1973 m and 1960 sh cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 2.33 (s, 3 H, Me), 2.49 (s, 3 H, Me), 6.08 (d, J = 7.3 Hz, 2 H, H_f), 6.58 (t, J = 7.3 Hz, 2 H, H_e), 6.79 (t, J = 7.3 Hz, 1 H, H_d), 7.16−7.49 (m, 9 H, H_b, $H_{b'}$, H_c, $H_{c'}$ and Ph), 8.67 (d, J = 6.8 Hz, 1 H, H_a or $H_{a'}$), 8.85 (d, J = 5.4 Hz, 1 H, H_a or $H_{a'}$). − FAB MS: m/z = 1404 [M^+]. − $C_{37}H_{22}N_2O_9Os_3Pt$ (1404.27): calcd. C 31.51, H 1.57, N 1.99; found C 31.40, H 1.45, N 1.78.

Preparation of [$Os_3Pt(CO)_9$(μ_4-η^2-C≡CPh)(η^1-C≡CPh)(tBu$_2$bipy)] (2): A mixture of [$Os_3(CO)_{10}(NCMe)_2$] (0.050 g, 0.054 mmol) and [Pt(C≡CPh)$_2$(tBu$_2$bipy)] (0.036 g, 0.054 mmol) was stirred at room temperature under nitrogen for 30 min. The resulting orange-red solution was evaporated to dryness and the residue was subjected to TLC with *n*-hexane/CH_2Cl_2 (3:2, v/v) as eluent to give complex **2** as an orange band (R_f = 0.50) in 28% yield (0.022 g). − IR (CH_2Cl_2): ν(CO) = 2083 w, 2064 w, 2048 vs, 2011 s, 1998 m, 1972 m and 1958 sh cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.30 (s, 9 H, *t*Bu), 1.43 (s, 9 H, *t*Bu), 6.02 (d, J = 7.6 Hz, 2 H, H_f), 6.53 (t, J = 7.6 Hz, 2 H, H_e), 6.78 (t, J = 7.6 Hz, 1 H, H_d), 7.18−7.60 (m, 9 H, H_b, $H_{b'}$, H_c, $H_{c'}$ and Ph), 8.74 (d, J = 5.4 Hz, 1 H, H_a or $H_{a'}$), 8.91 (d, J = 5.7 Hz, 1 H, H_a or $H_{a'}$). − FAB MS: m/z = 1488 [M^+]. − $C_{43}H_{34}N_2O_9Os_3Pt$ (1488.43): calcd. C 34.70, H 2.30, N 1.88; found C 34.49, H 2.20, N 1.75.

Crystallographic Data for 1·CH_2Cl_2: $C_{38}H_{24}Cl_2N_2O_9Os_3Pt$, M = 1489.18, triclinic, space group P1(bar), a = 9.317(1), b = 17.843(2), c = 25.672(3) Å, α = 73.857(2), β = 87.260(2), γ = 86.020(2)°, U = 4087.8(8) Å^3, Z = 4, T = 293 K, μ(Mo-K_α) = 128.91 cm^{-1}, 24218 reflections measured, 17554 unique, R(int) = 0.0370, final $R1$ = 0.0408, w$R2$ = 0.0894 (based on F^2) for 17554 [$I > 2\sigma(I)$] observed reflections.

Crystallographic Data for 2·CH_2Cl_2: $C_{44}H_{36}Cl_2N_2O_9Os_3Pt$, M = 1573.34, triclinic, space group P1(bar), a = 11.420(2), b = 13.972(3), c = 16.438(3) Å, α = 111.92(3), β = 101.84(3), γ = 90.69(3)°, U = 2370.1(8) Å^3, Z = 2, T = 293 K, μ(Mo-K_α) = 111.23 cm^{-1}, 13770 reflections measured, 10007 unique, R(int) = 0.0484, final $R1$ = 0.0553, w$R2$ = 0.1639 (based on F^2) for 10007 [$I > 2\sigma(I)$] observed reflections.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-151605 (**1**) and CCDC-151606 (**2**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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