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Unprecedented nitrosyl-bridged double-A-frame triplatinum complexes, $[Pt_3(\mu\text{-triphosphine})_2(\mu\text{-NO})_2(RNC)_2](BF_4)_4$

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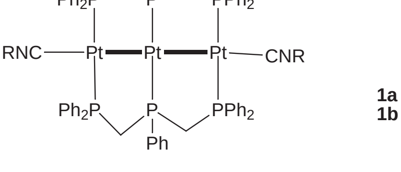
Reaction of linear triplatinum complexes, *linear*-$[Pt_3(\mu\text{-dpmp})_2(RNC)_2](PF_6)_2$ 1, with an excess of [NO][BF$_4$] afforded an unprecedented nitrosyl-bridged double-A-frame triplatinum complexes, $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-NO})_2(RNC)_2](BF_4)_4$ [2a: R = 2,6-xylyl; 2b: R = 2,4,6-mesityl, dpmp = bis(diphenylphosphinomethyl)phenylphosphine], which were characterized by X-ray crystallographic analysis and extended Hückel MO calculations.

Metal–metal bonded small-size transition-metal clusters have attracted increasing attention, since they could be minimal models for the surface of heterogeneous catalysts and have the potential to promote new homogeneous reactions which are not established by mononuclear centers.[1] We have recently reported a new strategic synthetic route to homo- and hetero-trimetallic clusters with Pt_2M cluster cores by using a tridentate phosphine ligand, bis(diphenylphosphinomethyl)phenylphosphine (dpmp).[2–5] In particular, we have demonstrated the synthesis and characterization of linearly ordered, side-by-side triplatinum complex, *linear*-$[Pt_3(\mu\text{-dpmp})_2(RNC)_2](PF_6)_2$ [**1a**: R = xylyl (Xyl)], which could be regarded as an indispensably important expansion of the well known chemistry on dppm-bridged diplatinum complexes, where dppm = bis(diphenylphosphino)methane. Complex **1a** was also shown to react with H$^+$, electron-deficient alkynes, and *p*-nitrophenyl isocyanide, affording asymmetrical A-frame triplatinum clusters bridged by hydride and the organic molecules, where only one Pt–Pt bond breaking took place even treated with an excess amount of reagents.[6] In the present report, we have examined the reaction of **1** [R = Xyl, mesityl (Mes)] with [NO][BF$_4$] and have successfully isolated and characterized unprecedented nitrosyl-bridged double-A-frame triplantinum complexes, $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-NO})_2(RNC)_2](BF_4)_4$. The reaction involves a novel, simultaneous three-center oxidative addition on linearly ordered triplatinum core supported by the tridentate phosphine ligands.



1a R = Xyl
1b R = Mes

Reaction of **1a** with an excess of [NO][BF$_4$] yielded pale green crystals formulated as $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-NO})_2(XylNC)_2](BF_4)_4$ **2a** (yield 66%).† Similar reaction of **1b** also gave $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-NO})_2(MesNC)_2](BF_4)_4$ **2b** in 68% yield. The IR spectra of **2** indicated the presence of terminal isocyanide ligands at 2206 (**2a**), 2205 cm^{-1} (**2b**) and nitrosyl units at 1514 (**2a**), 1513 cm^{-1} (**2b**), the latter corresponding to the values for N–O triple bond rather than double bond. The detailed structure of **2a** was determined by an X-ray crystallographic analysis and an ORTEP plot for the complex cation is illustrated in Fig. 1.‡ The complex cation has a crystallographically imposed inversion center on the central platinum (Pt2) and consists of three platinum atoms linearly supported by two dpmp ligands. The Pt–Pt separation of 3.0962(4) Å, indicating the absence of a Pt–Pt bond, is shorter than those for the A-frame diplatinum complexes with dppm ligands, *e.g.* $[Pt_2Cl_2(\mu\text{-NO})(\mu\text{-dppm})_2]BPh_4$ **3a** (3.246 Å),[7a] $[Pt_2Cl_2(\mu\text{-NO})(\mu\text{-dppm})_2]BF_4$ **3b** (3.186 Å),[7b] $[Pt_2Cl_2(\mu\text{-CH}_2)(\mu\text{-dppm})_2]$ (3.151 Å),[8] and is comparable to that of $[Pt_2Cl_2(\mu\text{-CS}_2)(\mu\text{-dppm})_2]$ (3.094 Å).[9] Two nitrosyl groups are inserted into the two Pt–Pt bonds of **2a** with an almost symmetrical manner, Pt1–N1 2.020(6) Å, Pt2–N1 2.019(6) Å, Pt1–N1–Pt2 100.1(3)°, Pt1–N1–O1 125.9(6)°, Pt2–N1–O1 133.2(6)°, resulted in a double-A-frame trimetallic structure. This is the first structurally characterized example of nitrosyl-bridged double-A-frame trinuclear clusters on the basis of analysis of the Cambridge Crystallographic Structure Database. The N–O bond lengths is 1.09(1) Å,§ which corresponds to values for a neutral N–O triple bond rather than an N–O double bond,[10] and is in accord with the IR data. This nitrosyl-bridging structure is quite different from that of **3** which involves an NO$^-$ unit with an N–O bond length of 1.20(2) Å.[7,8] From the X-ray crystal structure, the present reaction can be regarded as a novel three-center oxidative addition proceeding on a linear triplatinum center, which involves an apparent two electron transfer from the triplatinum core to two NO$^+$ ions.

Structurally characterized nitrosyl-bridged diplatinum complexes are extremely rare, with the two complexes **3** being the sole example, probably owing to the low-lying LUMO and small HOMO–LUMO gap as Hoffmann predicted theoretically on the basis of extended Hückel MO calculations.[11] In order to elucidate the electronic structure of **2**, we have carried out EHMO calculations on a model compound [Pt$_3$(μ-

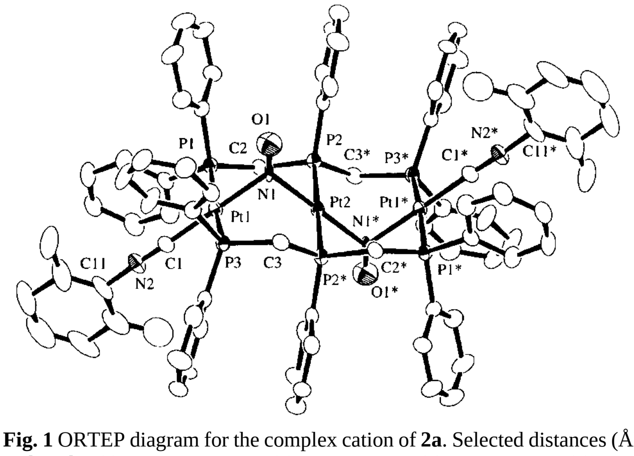


Fig. 1 ORTEP diagram for the complex cation of **2a**. Selected distances (Å) and angles (°): Pt1···Pt2 3.0962(4), Pt1–P1 2.358(2), Pt1–P3 2.343(2), Pt1–N1 2.020(6), Pt1–C1 1.923(8), Pt2–P2 2.321(2), Pt2–N1 2.019(6), O1–N1 1.09(1), N2–C1 1.14(1); N1–Pt1–C1 176.1(2), N1–Pt2–N1* 180.0, Pt1–N1–Pt2 100.1(3), Pt1–N1–O1 125.9(6), Pt2–N1–O1 133.2(6), Pt1–C1–N2 175.7(7).

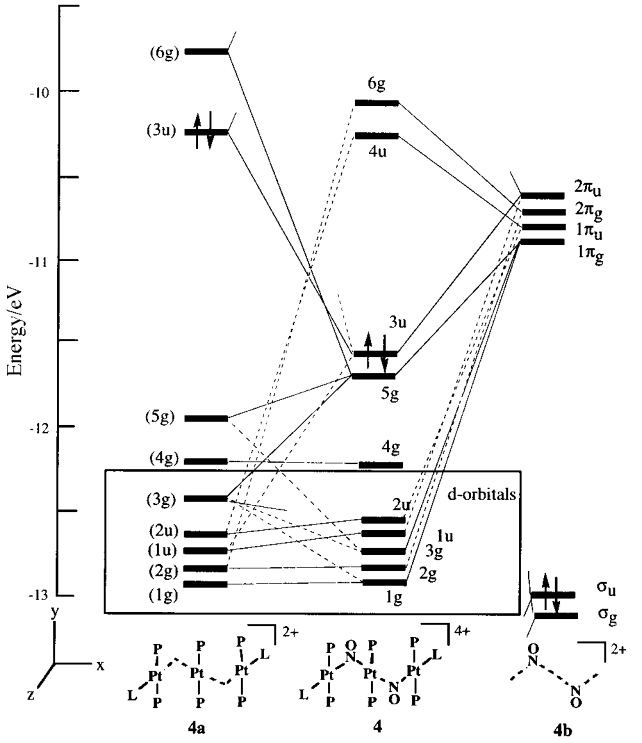


Fig. 2 MO interaction diagram for $[Pt_3(\mu\text{-}NO)_2(PH_3)_6(CNH)_2]^{4+}$ **4** (C_i), in terms of the fragments $[Pt_3(PH_3)_6(CNH)_2]^{2+}$ **4a** and $[NO)_2]^{2+}$ **4b**; P = PH_3, L = CNH.

$NO)_2(PH_3)_6(CNH)_2]^{4+}$ **4** (C_i), the ideal coordinates being derived from simplification of the crystal structure of **2a**.[12–15] An interaction diagram for **4** in terms of the fragments $[Pt_3(PH_3)_6(CNH)_2]^{2+}$ **4a** and $[(NO)_2]^{2+}$ **4b** is shown in Fig. 2.[16] The triplatinum system of **1** has a Pt–Pt σ-bonding orbital (HOMO) and σ-antibonding orbital (LUMO) at higher and lower energy levels, respectively, than the corresponding σ_{Pt-Pt} and σ^*_{Pt-Pt} orbitals of the diplatinum model.[2] The decrease of the σ–σ* energy gap causes the HOMO (3u) and LUMO (6g) of **4a** to match well with the low-laying π* orbitals of **4b** ($2\pi_u$ and $1\pi_g$), generating two significant bonding interactions, 3u (−11.61 eV) and 5g (−11.62 eV) orbitals of **4**. These two bonding orbitals should be responsible for partial electron transfer from the Pt_3^{2+} core to the two bridging NO^+ groups and stabilize the double-A-frame structure. There is no bonding overlap between the central and terminal Pt atoms as expected from the crystal structure. When CO groups are used instead of NO^+, the high-lying π* orbitals of CO groups do not match with the σ and σ* orbitals of the Pt_3^{2+} core and the corresponding 3u (−10.62 eV) and 5g (−11.34 eV) orbitals are destabilized at higher energy levels, consistent with our failure to obtain $[Pt_3(\mu\text{-}dpmp)_2(\mu\text{-}CO)_2(RNC)_2]^{2+}$ from the reaction of **1** with CO.

The present results could provide useful information in relation to metal-surface mimetic chemistry or fine organometallic cluster chemistry. We are now attempting to explore the reactivity of complex **2**, involving transformation of bridging NO groups to nitrogen-containing organic compounds.

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Notes and references

† To a 20 ml dichloromethane solution containing 100 mg of *linear*-$[Pt_3(\mu\text{-}dpmp)_2(XylNC)_2](PF_6)_2$ was added 27 mg of $[NO][BF_4]$. The reaction solution was stirred at room temp. for 3 h during which it changed from orange to pale green. The solution was concentrated to *ca.* 3 ml and was kept in a refrigerator to afford block-shaped plae green crystals of $[Pt_3(\mu\text{-}dpmp)_2(\mu\text{-}NO)_2(XylNC)_2](BF_4)_4{\cdot}CH_2Cl_2$ (**2a**$\cdot CH_2Cl_2$) in 66% yield. Anal. Calc. for $C_{83}H_{78}O_2N_4P_6B_4F_{16}Cl_2Pt_3$: C, 42.51; H, 3.83; N, 1.84. Found: C, 42.37; H, 3.34; N, 2.38%. A similar procedure using *linear*-$[Pt_3(\mu\text{-}dpmp)_2(MesNC)_2](PF_6)_2$ **1b** (43 mg) afforded pale green crystals of $[Pt_3(\mu\text{-}dpmp)_2(\mu\text{-}NO)_2(MesNC)_2](BF_4)_4{\cdot}2CH_2Cl_2$ (**2b**$\cdot 2CH_2Cl_2$) in 68% yield. Anal. Calc. for $C_{86}H_{84}O_2N_4P_6B_4F_{16}Cl_4Pt_3$: C, 41.89; H, 3.43; N, 2.27. Found: C, 42.02; H, 3.45; N, 1.80%. Complex **1b** was prepared by the reaction of **1a** with MesNC and was characterized by X-ray crystallography, which will be reported elsewhere.

‡ *Crystal data*: **2a**$\cdot CH_2Cl_2{\cdot}3H_2O$ ($C_{83}H_{84}N_4O_5P_6B_4F_{16}Cl_2Pt_3$, M_r = 2406.83, T = −116 °C, monoclinic, space group $P2_1/c$, a = 12.873(4), b = 29.350(6), c = 14.826(4) Å, β = 110.49(3)°, V = 5246(2) Å^3, Z = 2. A pale green block-shaped crystal was fixed on the top of a glass fiber with Paraton N oil. 9211 reflections ($4 < 2\theta < 50°$) were measured on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation. The structure was solved by direct methods using the program SIR92 and was refined to R = 0.058, R_w = 0.072, and GOF = 2.53 for 6842 independent reflections with $I > 3\sigma(I)$. CCDC 182/1201. See http://www.rsc.org/suppdata/cc/1999/745/ for crystallographic files in .cif format.

§ It should be noted that the Pt–N and N–O bond lengths derived from the X-ray crystallography might involve relatively large errors on the basis of flat (N1) and large (O1) thermal motions of the NO unit, the former seemingly resulting from the influence of highly scattering Pt Atoms.

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