# A *triangulo*-Triplatinum Cluster with no Bridging Atom: The Structure of $[Pt_3(2,6\text{-}Me_2C_6H_3NC)_2(\mu\text{-}Ph_2PCH_2PPh_2)_3]^{2+}$

**Arleen M. Bradford,**[a] **Nicholas C. Payne,***[a] **Richard J. Puddephatt,***[a] **Dong-Sheng Yang and Todd B. Marder**[b]

[a] *Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7*
[b] *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

The complex cation $[Pt_3(2,6\text{-}Me_2C_6H_3NC)_2(\mu\text{-dppm})_3]^{2+}$, dppm = $Ph_2PCH_2PPh_2$, characterized by X-ray structure analysis, is the first triplatinum cluster which contains no single-atom bridging ligand; it completes a series of clusters based on the equatorial $[Pt_3(\mu\text{-dppm})_3$ unit in which two axial ligands, L, are present and in which structures with $Pt_3(\mu_3\text{-L})_2$, $Pt_3(\mu_3\text{-L})(L)$ and $Pt_3(L)_2$ units are very close in energy.

---

All reported *triangulo*-triplatinum cluster complexes possess one or more one-atom bridging ligand.[1] These bridging ligands may be equatorial $\mu_2$-ligands {*e.g.* $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$, $[Pt_3(\mu\text{-}SO_2)_2(PR_3)_3(CNR)_2]$, $[Pt_3(\mu\text{-}CNR)_3(CNR)_3]$ and related compounds}[1,2] or axial $\mu_3$-ligands {*e.g.* $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$, dppm = $Ph_2PCH_2PPh_2$}[3] or $\mu_2$-ligands {*e.g.* $[Pt_3(\mu\text{-}CO)(\mu\text{-dppm})_4]^{2+}$, dmpm = $Me_2PCH_2PMe_2$},[4] and the need for such bridging ligands has been rationalized by EHMO calculations.[5] The cluster electron count in the above compounds can vary from 42–46 electrons.[1–5] Triplatinum clusters with the 44 electron count and no one-atom bridge are known but they have an open linear or A-frame structure in the complexes $Pt_3(XyNC)_6(PPh_3)_2]^{2+}$, Xy = 2,6-$Me_2C_6H_3$, **1**,[6,7] or $[Pt_3(XyNC)_4(\mu\text{-dppm})_2]^{2+}$, **2**,[7] respectively. This paper reports a new 44 electron $Pt_3$ cluster, which is the first *triangulo*-$Pt_3$ cluster with no one-atom bridging group and whose structure poses an interesting theoretical puzzle. The new chemistry is shown in Scheme 1,† R = Xy, and the

---

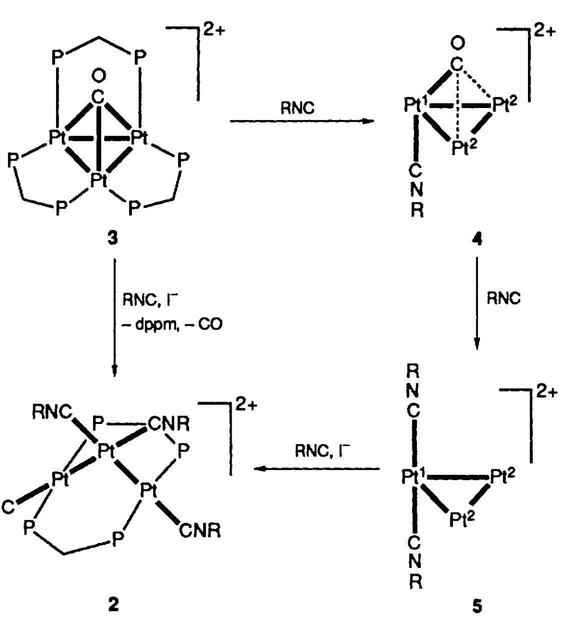
† New complexes were characterized by elemental analysis and multinuclear NMR studies. The structure of **4**, R = cyclohexyl, as **4** $(PF_6)_2$ was determined crystallographically and, in agreement with the spectroscopic data, indicates the presence of a semi-bridging CO; however, partial disorder involving the CO and RNC ligands precluded detailed determination of their geometries. The identity of **2**, as **2** $(PF_6)_2$, was also confirmed crystallographically in agreement with ref. 7. Complex **4**, R = Xy, gives ν (CO) = 1793 $cm^{-1}$, ν (C≡N) = 2165 $cm^{-1}$, $^1J(Pt^1CO)$ = 1200 Hz, $^1J(Pt^2CO)$ = 400 Hz, indicating a semi-bridging CO is present.

structure of $[Pt_3(CNXy)_2(\mu\text{-dppm})_3][PF_6]_2$, **5**, is shown in Fig. 1.‡

The striking features of the structure of **5** are as follows: (i), Both isocyanide ligands are bound in a terminal fashion to Pt(1) with Pt(1)–C(9) = 1.93(2) Å and Pt(1)–C(19) = 1.97(2) Å. Distances of C(9) and C(19) from Pt(2) and Pt(3) range from 2.84(2)–3.26(2) Å, clearly too long for a significant bonding interaction. The ν(C≡N) value of 2122 $cm^{-1}$ in the solid or in solution also confirms the presence of only terminal XyNC ligands. (ii), The distances Pt(1)–Pt(2) = 2.653(1), Pt(1)–Pt(3) = 2.647(1), Pt(2)–Pt(3) = 2.582(1) Å are all typical of Pt–Pt single bonds.[1–7]

Thus, addition of two RNC ligands to **3** [mean Pt–Pt 2.634(1) Å] has resulted in a lengthening of bonds to Pt(1) (9 and 13σ) and a significant shortening of Pt(2)–Pt(3) by 38σ. There is, therefore, no evidence for opening of Pt–Pt bonds to give a complex analogous to **1** or **2** and related compounds.[6–8]§

Thus, complex **5** is the first *triangulo*-triplatinum complex without a single-atom bridging ligand, and the first triplatinum cluster to contain an approximately octahedral platinum centre.[1] Why do the isocyanide ligands not bridge? At this stage, we have no simple answer. EHMO calculations¶ on the model compound $[Pt_3(CNH)_2(\mu\text{-}H_2PCH_2PH_2)_3]^{2+}$ suggest that the structure with two $\mu_3$-HNC ligands should be more stable than structure **5** (Fig. 2), but indicate that the HOMO is $B_1$, in the bridged structure but $A_1$ in the terminal structure and that the HOMO–LUMO gap is greatest for an intermediate structure (Fig. 2). Presumably, a trade-off between these factors determines the ground-state geometry. Nevertheless, experimental results show very clearly that the isocyanide ligands are terminal and it is relevant to note that **5** is isolobal to the complex $[Pt_2(CO)\{P(OPh)_3\}_3Fe(CO)_4]$, in which the formally $d^8$ octahedral fragment $[PtL_2(XyNC)_2]^{2+}$ in **5** is replaced by the $d^8$ $[Fe(CO)_4]$ fragment.[9] The structure of **5** completes the series containing $Pt_3(\mu_3\text{-}L)_2$, L = $SnF_3(\mu_3\text{-}L)L]^{2+}$, L = CO; $[Pt_3L_2]^{2+}$, L = XyNC, **5**. The fluxionality of such complexes, including **4** and **5**, shows that interconversion between these structural types is facile and mimics the mobility of ligands on a Pt(111) surface. The fluxionality of **4** and **5** is most easily observed by their $^{31}P$ NMR spectra, each



Scheme 1

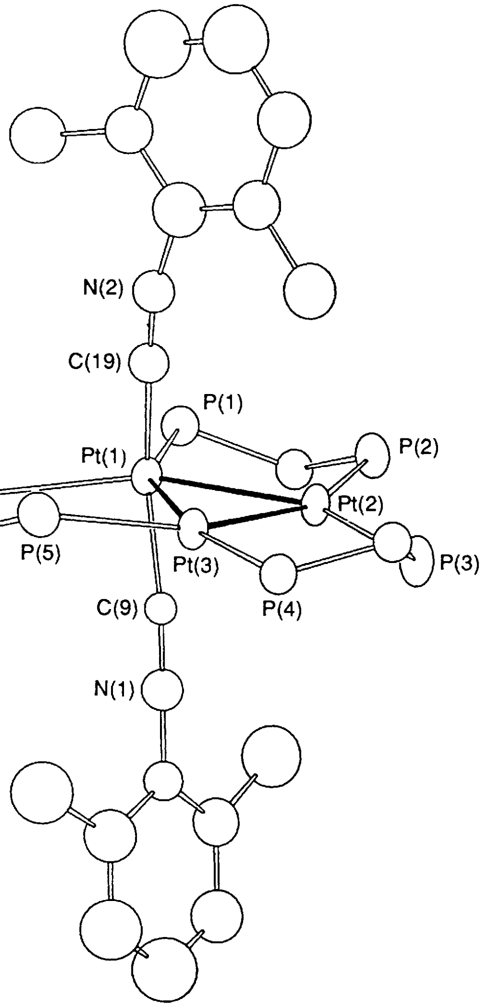


**Fig. 1** A view of the structure of **5**. Selected parameters are: Pt(1)–C(9) = 1.93(2), Pt(1)–C(19) = 1.97(2) Å, C(9)–Pt(1)–C(19) = 150(1)°

---

‡ *Crystal data* for **5**: $C_{93}H_{84}F_{12}N_2P_8Pt_3\cdot C_3H_6O$; $M_r$ = 2348.8, monoclinic, space group $P2_1$ (No. 4), $a$ = 17.639(2), $b$ = 19.704(3), $c$ = 14.544(1) Å, β = 101.99(1)°, $U$ = 4945(2) $Å^3$, $Z$ = 2, Mo-Kα radiation, λ = 0.71073 Å, 8531 unique data, full-matrix least-squares refinement, phenyl rings refined as rigid groups, $R_1$ = 0.0713, $R_2$ = 0.0783. Atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Although distances for bridged metal–metal bonds can be deceptive, the μ-dppm ligands present in **5** do not constrain the Pt atoms to remain in bonding distance (see **2** for example) and so the conclusion that Pt–Pt bonding is not weakened in **5** relative to **3** is justified.

¶ Molecular orbital calculations of the extended Hückel type: R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397; R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **36**, 2179; *J. Chem. Phys.*, 1962, **37**, 2872; all calculations were carried out using ICONS, with fragment MO analysis: A. Rossi, J. Howell, D. Wallace, K. Haraki and R. Hoffmann. Program ICON8, *QCPE No. 517*, 1986, **6**, 100. Hückel constant = 1.75, and Weighted $H_{ij}$ (modified Helmholz–Wolfsberg formula) were used throughout: J. H. Ammeter, H.-B. Burgi, J. C. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 3686. Parameters for the calculations were taken from R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 7240. The shorter Pt–C bond was maintained at 2.02 Å as the angle θ = ∠C–Pt¹–C varied from 80° to 180°, and the HNC ligands were kept linear and perpendicular to the $Pt_3$ plane.

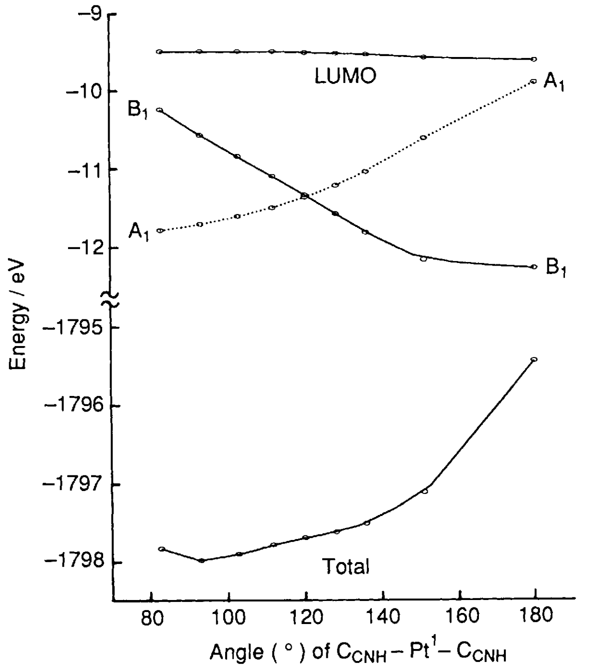


**Fig. 2** The calculated total energy and energies of the HOMOs and LUMO of $[Pt_3(C{\equiv}NH)_2(\mu\text{-}H_2PCH_2PH_2)_3]^{2+}$ as a function of the angle C–Pt1–C. The symmetry labels refer to $C_{2v}$ point group. The orbital $B_1$ has $p_zd_\pi$ character at the Pt centres and has PtC $\sigma^*$ character in the bridged structure, whereas $A_1$ has $p_\sigma d_\sigma$ character at the Pt centres and has $Pt^1$–C $\sigma^*$ character in the terminal structure

of which shows three resonance signals at low temperature but only a broad resonance at room temperature or above and appears to be unique for isocyanide ligands.

We thank the NSERC (Canada) for financial support, and Drs Lj. Manojlovic-Muir and K. W. Muir for most helpful advice.

*Received, 30th April 1990; Com. 0/01914C*

## References

1 D. M. P. Mingos and R. W. M. Wardle, *Transition Met. Chem. (Weinheim Ger.)*, 1985, **10**, 441; N. K. Eremko, E. G. Mednikov and S. S. Kurasov, *Russ. Chem. Rev.*, 1985, **54**, 394.
2 D. M. P. Mingos, I. D. Williams and M. J. Watson, *J. Chem. Soc., Dalton Trans.*, 1988, 1509.
3 G. Ferguson, B. R. Lloyd and R. J. Puddephatt, *Organometallics*, 1986, **5**, 344.
4 S. S. M. Ling, N. Hadj-Bagheri, Lj. Manojlović-Muir, K. W. Muir and R. J. Puddephatt, *Inorg. Chem.*, 1987, **26**, 231.
5 D. G. Evans and D. M. P. Mingos, *J. Organomet. Chem.*, 1982, **240**, 34; C. Mealli, *J. Am. Chem. Soc.*, 1988, **352**, 397.
6 C. E. Briant, D. I. Gilmour and D. M. P. Mingos, *J. Organomet. Chem.*, 1986, **308**, 381.
7 Y. Yamamoto, K. Takahashi and H. Yamazaki, *J. Am. Chem. Soc.*, 1986, **108**, 2458.
8 R. Bender, P. Braunstein, A. Tiripicchio and M. T. Camellini, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 861.
9 A. Dedieu and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 2074.