

# Cyclic dimerization of tetracyanoethylene promoted on linear triplatinum centres leading to novel nitrene-bridged Pt<sub>3</sub> complexes†

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Reactions of linear triplatinum complexes, *linear*-[Pt<sub>3</sub>( $\mu$ -dpmp)<sub>2</sub>(RNC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (**1**), with excess tetracyanoethylene (tcne) afford the novel nitrene-bridged asymmetrical A-frame triplatinum complexes, [Pt<sub>3</sub>( $\mu$ -dpmp)<sub>2</sub>( $\mu$ -C<sub>12</sub>N<sub>8</sub>)(RNC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (**2a**; R = 2,6-xylyl; **2b**; R = 2,4,6-mesityl, dpmp = bis(diphenylphosphinomethyl)phenylphosphine), in which two tcne molecules are coupled to form a (heptacyanocyclopent-1-enyl)nitrene moiety.

Studies on organic reactions promoted by multinuclear metal centres are directly implicated in the development of industrial heterogeneous catalysts and could lead to metal-surface mimetic chemistry.<sup>1</sup> Multimetallic systems have the potential to organize different types of reaction processes in synergetic fashion into new homogeneous reactions which are not established by mononuclear metal centres. Recently, we have reported the linearly ordered, side-by-side triplatinum complex, *linear*-[Pt<sub>3</sub>( $\mu$ -dpmp)<sub>2</sub>(RNC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> **1a** (R = xylyl (Xyl)), which reacted with H<sup>+</sup>, NO<sup>+</sup>, electron-deficient alkynes and *p*-nitrophenyl isocyanide, affording asymmetrical and double A-frame triplatinum clusters through their oxidative insertion into the Pt–Pt single bonds.<sup>2,3</sup> Here, we have examined reactions of **1** (R = Xyl, mesityl (Mes)) with a strongly electron-deficient olefin, tetracyanoethylene (tcne), and have successfully isolated and characterized the novel, nitrene-bridged triplatinum complexes, [Pt<sub>3</sub>( $\mu$ -dpmp)<sub>2</sub>( $\mu$ -C<sub>12</sub>N<sub>8</sub>)(RNC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, in which two tcne molecules are coupled to form a (heptacyanocyclopent-1-enyl)nitrene moiety.

Complex **1a** readily reacts with excess of tetracyanoethylene (tcne) to afford pale green crystals formulated as [Pt<sub>3</sub>( $\mu$ -dpmp)<sub>2</sub>( $\mu$ -C<sub>12</sub>N<sub>8</sub>)(XylNC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> **2a** in high yield.† Similar reaction of **1b** also gave [Pt<sub>3</sub>( $\mu$ -dpmp)<sub>2</sub>( $\mu$ -C<sub>12</sub>N<sub>8</sub>)(MesNC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> **2b** in 38% yield. The IR and <sup>1</sup>H NMR spectra of **2** indicated the presence of two terminal isocyanide ligands, and the <sup>31</sup>P{<sup>1</sup>H} NMR spectra exhibited three multiplets with <sup>195</sup>Pt satellite peaks in a 1 : 1 : 1 ratio. The detailed structure of **2a** was determined by X-ray crystallographic analysis and an ORTEP plot for the complex cation is illustrated in Fig. 1.§ The complex cation involves an asymmetrical triplatinum core supported by two dpmp ligands. The Pt(1)–Pt(2) distance of 2.6446(8) Å corresponds to a Pt–Pt single bond, and the Pt(2)–Pt(3) separation of 3.2150(8) Å is indicative of the absence of a Pt–Pt bond. The two tcne molecules are coupled to form a (heptacyanocyclopent-1-enyl)nitrene moiety which is inserted into one of the Pt–Pt bonds of **1a** (Scheme 1). Structurally characterized nitrene-bridged platinum and palladium complexes are extremely rare<sup>4</sup> in spite of their importance as metal-surface nitrene intermediates in the metal-catalyzed reduction of NO and nitro compounds and, to our knowledge, this is the first example of a trinuclear platinum complex with a nitrene-bridging ligand. The N(11) atom rather asymmetrically bridges Pt(2) and Pt(3) and adopts a planar sp<sup>2</sup> geometry with the sum of the bond angles being 359.9°. The Pt<sub>2</sub>N plane is almost co-

planar with the [C(11)C(12)] olefin unit and the relatively short N(11)–C(11) bond length indicates that the electron density on the N atom is delocalized through a p<sub>π</sub>–p<sub>π</sub> interaction between the nitrene and olefin units as shown in Scheme 1. The C(11)–C(12) bond length is longer than that of a usual C–C double bond. A similar tendency was observed in [Ir<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -dpmp)<sub>2</sub>( $\mu$ -NPh)]<sup>5</sup> and [Rh<sub>2</sub>(CO)<sub>2</sub>(dpmp)<sub>2</sub>( $\mu$ -N(*p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>))]<sup>6</sup> (dpmp = bis(diphenylphosphino)methane). The heptacyanocyclopent-1-enyl moiety adopts an envelop conformation with the C(14) atom in the apex site and the C(13), C(14) and C(15) atoms having sp<sup>3</sup> tetrahedral configuration. The present type of tcne cyclic dimerization is very rare; the only related compound reported is *N*-(heptacyanocyclopent-1-enyl)triphenylphosphoranimine which was formed by reaction of tcne with triphenylphosphine.<sup>7</sup>

The cyclic dimerization of tcne did not proceed by the dpmp-bridged diplatinum complex, [Pt<sub>2</sub>( $\mu$ -dpmp)<sub>2</sub>(XylNC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>,<sup>8</sup> although it proceeded rapidly with the triplatinum complex **1a**; the reaction was monitored by electronic absorption spectral change with an isosbestic point at 345 nm. The reaction with excess of tcne (>10 equiv.) proceeded with a first order dependency on the starting complex **1a** with the pseudo-first order rate constant of 4.0 × 10<sup>−3</sup> s<sup>−1</sup>. Whereas no stable intermediate was observed, the tcne adduct **A** might be formed at the initial step by analogy with the reaction of **1a** with electron-deficient alkynes (Scheme 1).<sup>3</sup> The strong *trans* influence of the Pt–Pt bond may cause the zwitterionic Pt–C bond breaking (**B**), together with the nucleophilic attack of the

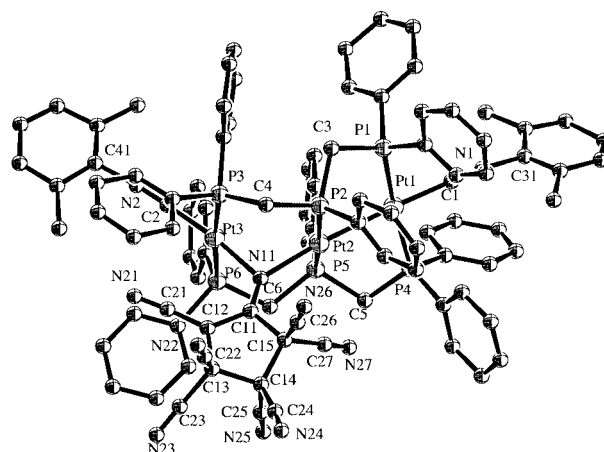
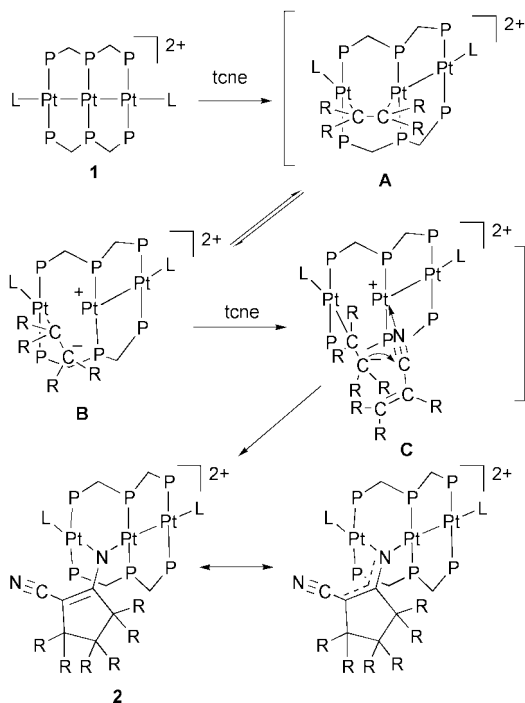


Fig. 1 ORTEP diagram for the complex cation of **2a**. Selected distances (Å) and angles (°): Pt(1)–Pt(2) 2.6446(8), Pt(2)–Pt(3) 3.2150(8), Pt(1)–P(1) 2.312(5), Pt(1)–P(4) 2.328(5), Pt(1)–C(1) 2.01(2), Pt(2)–P(2) 2.263(4), Pt(2)–P(5) 2.277(4), Pt(3)–P(3) 2.341(4), Pt(3)–P(6) 2.349(4), Pt(3)–C(2) 1.90(2), Pt(2)–N(11) 2.18(1), Pt(3)–N(11) 2.05(1), N(11)–C(11) 1.26(2), C(11)–C(12) 1.46(2), C(11)–C(15) 1.54(2), C(12)–C(13) 1.54(3), C(13)–C(14) 1.60(3), C(14)–C(15) 1.57(3); Pt(2)–Pt(1)–C(1) 177.8(6), Pt(1)–Pt(2)–N(11) 175.1(4), N(11)–Pt(3)–C(2) 173.0(6), Pt(2)–N(11)–Pt(3) 98.9(6), Pt(2)–N(11)–C(11) 138(1), Pt(3)–N(11)–C(11) 123(1), N(11)–C(11)–C(12) 129(2), N(11)–C(11)–C(15) 123(2), C(12)–C(11)–C(15) 108(1), C(11)–C(12)–C(13) 110(1), C(11)–C(12)–C(21) 127(2), C(13)–C(12)–C(21) 123(2).

† Electronic supplementary information (ESI) available: further structural and experimental data for **2a**·2(CH<sub>3</sub>)<sub>2</sub>CO. See <http://www.rsc.org/suppdata/cc/b1/b1018051/>



Scheme 1 L = XylNC (a), MesNC (b); R = CN.

carbanion on the electron-deficient nitrile carbon of the second tcne molecule (C) – this was inferred as a key step for the coupling. A detailed study on the reaction mechanism is now in progress.

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## Notes and references

‡ To 20 mL of dichloromethane solution containing 71 mg of linear-[Pt<sub>3</sub>(μ-dpmp)<sub>2</sub>(XylNC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> was added 37 mg of tcne (0.29 mmol). The reaction solution was stirred at room temperature for 1 h, and the color of the solution immediately changed from orange to pale green. The solvent was removed under reduced pressure and the residue was washed with benzene and diethyl ether; it was then extracted with 20 mL of dichloromethane. The solution was concentrated to ca. 10 mL and was kept in a refrigerator after the addition of a small amount of Et<sub>2</sub>O to afford block-shaped pale green crystals of [Pt<sub>3</sub>(μ-dpmp)<sub>2</sub>(μ-C<sub>12</sub>N<sub>8</sub>)(XylNC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> **2a** in 86% yield. Anal. Calc. for C<sub>94</sub>H<sub>76</sub>N<sub>10</sub>P<sub>8</sub>F<sub>12</sub>Pt<sub>3</sub>: C, 46.91; H, 3.18; N, 5.82. Found: C, 46.67; H, 3.30; N, 5.54%. IR (Nujol/cm<sup>-1</sup>): 2189, 2168 (XylN≡C), 1571 (C=C), 840 (PF<sub>6</sub>). UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>/nm (log ε) 404 (3.22). <sup>1</sup>H NMR (C<sub>2</sub>Cl<sub>2</sub>): δ 1.34, 1.98 (s, *o*-Me, 6H), 2.9–5.5 (m, CH<sub>2</sub>, 8H), 6.1–8.8 (m, Ar, 56H). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ -5.7 (m, 1P, <sup>1</sup>J<sub>PP</sub> 2450 Hz), 0.2 (m, 1P, <sup>1</sup>J<sub>PP</sub>

2906 Hz), 6.1 (m, 1P, <sup>1</sup>J<sub>PP</sub> 2556 Hz). Recrystallization of **2a** from an acetone-diethyl ether mixed solvent yielded block-shaped crystals of **2a**·(CH<sub>3</sub>)<sub>2</sub>CO which were suitable for X-ray crystallography.

A similar procedure using linear-[Pt<sub>3</sub>(μ-dpmp)<sub>2</sub>(MesNC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> **1b** (62 mg) afforded pale green crystals of [Pt<sub>3</sub>(μ-dpmp)<sub>2</sub>(μ-C<sub>12</sub>N<sub>8</sub>)(MesNC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (**2b**·CH<sub>2</sub>Cl<sub>2</sub>) in 38% yield. Anal. Calc. for C<sub>97</sub>H<sub>82</sub>N<sub>10</sub>P<sub>8</sub>F<sub>12</sub>Pt<sub>3</sub>: C, 46.24; H, 3.28; N, 5.56. Found: C, 46.48; H, 3.08; N, 5.70%. Complex **1b** was prepared by the reaction of **1a** with MesNC and was characterized by X-ray crystallography, which will be reported elsewhere. IR (Nujol/cm<sup>-1</sup>): 2186, 2169 (MesN≡C), 1573 (C=C), 838 (PF<sub>6</sub>). UV-Vis (in CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>/nm (log ε) 391 (3.37). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.28, 1.90 (s, *o*-Me, 6H), 2.06, 2.20 (s, *p*-Me, 3H), 3.4–5.2 (m, CH<sub>2</sub>, 8H), 6.2–8.6 (m, Ar, 54H). <sup>31</sup>P{<sup>1</sup>H} NMR (in CD<sub>2</sub>Cl<sub>2</sub>): δ -7.3 (m, 1P, <sup>1</sup>J<sub>PP</sub> 2514 Hz), -1.6 (m, 1P, <sup>1</sup>J<sub>PP</sub> 2926 Hz), 4.2 (m, 1P, <sup>1</sup>J<sub>PP</sub> 2571 Hz). § Crystal data for **2a**·(CH<sub>3</sub>)<sub>2</sub>CO: C<sub>97</sub>H<sub>82</sub>N<sub>10</sub>OP<sub>8</sub>F<sub>12</sub>Pt<sub>3</sub>, *M* = 2464.82, *T* = -118 °C, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 13.872(4), *b* = 53.155(12), *c* = 15.130(4) Å, β = 97.90(2)°, *V* = 11 050(4) Å<sup>3</sup>, *Z* = 4. A pale yellow, block-shaped crystal was fixed on the top of a glass fiber with Paratone N oil. 14381 reflections (4 < 2θ < 45°) were measured on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation. The structure was solved by Patterson methods using the program DIRDIF94 and was refined with SHELXL-93 to *R*<sub>1</sub> = 0.068 for 10081 independent reflections with *I* > 2σ(*I*) and *wR*<sub>2</sub> = 0.227 for all data.

CCDC 160684. See <http://www.rsc.org/suppdata/cc/b1/b1018051/> for crystallographic data in .cif or other electronic format.

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