The first mononuclear triazatrimethylenemethane metal complex, [Pt{NPhC(NPh)NPh}(cod)] (cod = cycloocta-1,5-diene)

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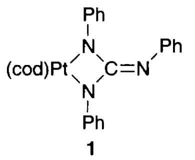
The first example of a mononuclear complex containing the triazatrimethylenemethane ligand is prepared by the silver(I) oxide-mediated reaction of [PtCl$_2$(cod)] with *N,N′,N″*riphenylguanidine; the single-crystal X-ray structure shows that the ligand bonds in an η^2 fashion, forming an essentially planar four-membered PtNCN metallacycle.

In recent years there has been significant interest in the chemistry of complexes containing trimethylenemethane (TMM) ligands.[1] Heteroatom-substituted TMM derivatives have also attracted attention, and examples include complexes containing oxygen,[2,3] sulfur,[4] silicon[5] and nitrogen[6] heteroatoms. Complexes of other hetero-TMM ligands, formally derived from urea-[7] and thiourea-dianions[8] have also been reported. In a recent communication,[9] the synthesis and X-ray structure of the lithium salt of the triazatrimethylenemethane dianion [C(NPh)$_3$]$^{2-}$ was reported, and it was considered that this dianion could be used for the synthesis of metal derivatives of this ligand. The reaction of dianionic reagents with metal-halide complexes offers a general synthetic route into TMM and related complexes.[3,10] Here we report the first example of a monomeric transition-metal complex containing the triazatrimethylenemethane ligand, synthesised using very mild reaction conditions.

Reaction of [PtCl$_2$(cod)] (cod = cycloocta-1,5-diene)[11] with 1 equiv. of *N,N′,N″*-triphenylguanidine, PhNHC(NPh)NHPh, in refluxing dichloromethane in the presence of excess silver(I) oxide gave, after work-up, the triazatrimethylenemethane complex **1**, as a yellow, air-stable, crystalline solid, in 94% yield.† This one-step reaction can be carried out in undried solvents, in air, thereby allowing access to triazatrimethylenemethane complexes without requiring the separate preparation of the presumably air-sensitive dianion [C(NPh)$_3$]$^{2-}$. Silver(I) oxide has been previously used in related syntheses of a range of metal–carbon, –nitrogen, –oxygen and –sulfur-containing complexes, with the reagent acting as both a halide-abstracting reagent and a base.[14]

Only one example of a guanidine dianion coordinated to a transition-metal centre has been reported previously, this being the diiron complex **2** formed by reaction of dicyclohexylcarbodiimide and Fe(CO)$_5$.[15]



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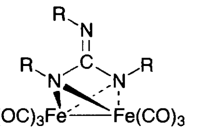
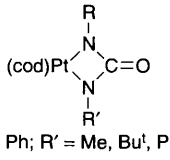


2; R = C$_6$H$_{11}$ or Pr^i



3; R = Ph; R′ = Me, Bu^t, Ph, Ad
R = Me; R′ = C(O)Me

In order to assess the bonding of the ligand to the platinum centre in the mononuclear complex **1**, a single-crystal X-ray structure determination was carried out.‡ The molecular structure (Fig. 1) shows the complex to contain an η^2-triazatrimethylenemethane (guanidine dianion) ligand, bonded *via* two of the nitrogen atoms, forming a Pt–N–C–N four-membered metallacycle. This is essentially planar, with no atom deviating from the least-squares plane by more than 0.05(1) Å [for N(2)]. The C(1)–N(3) bond distance, 1.30(1) Å, is significantly shorter than the C(1)–N(1) and C(1)–N(2) bond distances [both 1.40(1) Å]. By comparison, the average C–N bond distance in the dianion Li$_2$[C(NPh)$_3$] is 1.36(1) Å,[9] indicating the presence of localised double [C(1)–N(3)] and single [C(1)–N(1) and C(1)–N(2)] bonds in **1**. The difference in the Pt–N(1) and Pt–N(2) bond distances, 2.034(8) and 2.002(7) Å respectively, can be attributed to steric interactions between the phenyl substituents on N(1) and N(3). The orientation of the imino phenyl substituent presumably precludes fully symmetrical binding of the ligand to the platinum. The phenyl substituents are tipped out of the metallcyclic plane, with C(11), C(21) and C(31) respectively 0.84(1) Å above, 0.62(1) Å below, and 0.34(1) Å below the metallacyclic plane as depicted in

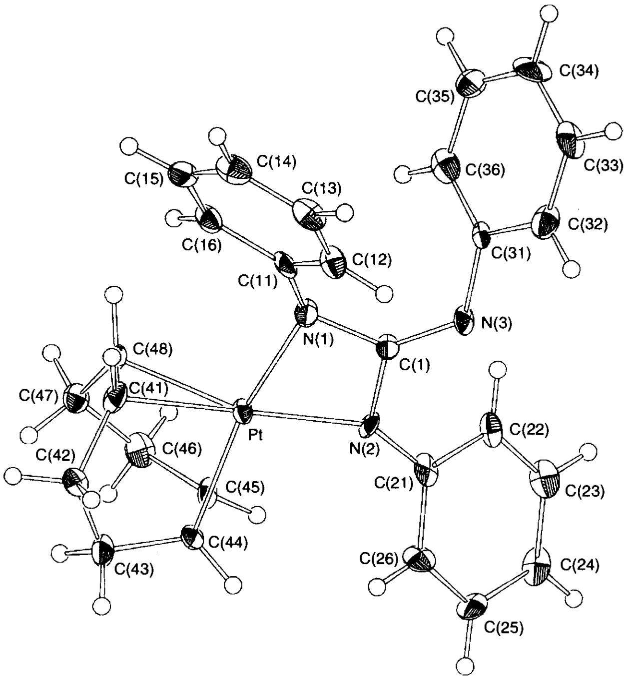


Fig. 1 Molecular structure of [Pt{NPhC(NPh)NPh}(cod)] **1**, with atom numbering scheme. Selected bond lengths (Å) and angles (°): Pt–N(1) 2.034(8), Pt–N(2) 2.002(7), N(1)–C(1) 1.40(1), N(2)–C(1) 1.40(1), N(3)–C(1) 1.30(1), N(3)–C(31) 1.41(1), Pt–C(41) 2.173(9), Pt–C(48) 2.183(9), Pt–C(44) 2.188(9), Pt–C(45) 2.155(9), N(1)–Pt–N(2) 65.9(3), Pt–N(1)–C(1) 94.7(5), Pt–N(2)–C(1) 96.0(5), N(1)–C(1)–N(2) 103.3(7), N(1)–C(1)–N(3) 133.0(8), N(2)–C(1)–N(3) 123.7(8).

1. Complex **1** overall bears a strong resemblance to formally isoelectronic carbonato complexes, such as $[\mathrm{Pt(CO_3)(PPh_3)_2}]$, which also contains an essentially planar four-membered ring system.[18]

Other derivatives such as $[\mathrm{Pt\{NPhC(NPh)NPh\}(PPh_3)_2}]$ can also be synthesised *via* the silver(I) oxide method. In addition, the presence of the labile cod ligand in **1** potentially allows access to analogues containing a wide range of ancillary donor ligands.

Preliminary studies show that the synthetic method employed for the synthesis of **1** can be extended to the synthesis of related metallacyclic complexes. Thus, reaction of $[\mathrm{PtCl_2(cod)}]$ with a range of ureas, mediated by silver(I) oxide, affords the ureylene complexes[7] **3**, which can also be formulated as metal complexes of the oxadiazatrimethylenemethane dianionic ligand $[\mathrm{RNC(O)NR'}]^{2-}$. The complex $[\mathrm{Pt\{NPhC(O)NAd\}(cod)}]$ (Ad = 1-adamantyl) has been characterised by a single-crystal X-ray structure and full details of these investigations will be reported in due course.

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Footnotes

† Complex **1** has been fully characterised by ^{1}H and ^{13}C{^{1}H} NMR and IR spectroscopies, and by elemental analysis. The positive-ion electrospray mass spectrum of **1** in MeCN–H_2O yields a major ion for $[\mathbf{1} + \mathrm{H}]^+$ at *m/z* 589, with excellent agreement between the observed and calculated[12] isotope distribution patterns. The C=N nitrogen of **1** is likely to be the most basic centre in the molecule,[13] and thus protonation is likely to occur at this site.

‡ Yellow rectangular blocks were obtained on crystallisation by vapour diffusion of diethyl ether into a saturated dichloromethane solution of **1** at 4 °C. Accurate cell parameters and intensity data were collected on a Nicolet R3 diffractometer, using a crystal of dimensions 0.80 × 0.24 × 0.22 mm, and Mo-Kα radiation ($\lambda = 0.71073$ Å). *Crystal data.* $\mathrm{C_{27}H_{27}N_3Pt\cdot 0.5\,Et_2O}$, $M = 625.67$, monoclinic, space group $P2_1/c$ with $a = 9.862(1)$, $b = 14.497(3)$, $c = 17.436(3)$ Å, $\beta = 103.02(1)°$, $U = 2428.7(6)$ Å^3, $D_c = 1.711$ g cm^{-3}, $Z = 4$, μ(Mo-Kα) = 5.80 mm^{-1}, $F(000) = 1236$. A total of 4291 reflections in the range $2 < \theta < 25°$ were collected at 130(2) K, of which 4270 were unique. These were subsequently corrected for Lorentz and polarisation effects, and for linear absorption by a ψ scan method ($T_{\mathrm{max,\,min}} = 0.49, 0.18$). The structure was solved by Patterson interpretation (SHELXS-86[16]) and developed routinely. A penultimate difference map revealed electron density which was attributed to a disordered diethyl ether molecule lying across an inversion centre in the lattice. In the final cycle of full-matrix least-squares refinement based on F^2 using SHELXL-93,[17] all non-hydrogen atoms were assigned anisotropic temperature factors, with all hydrogens in calculated positions. The refinement converged with $R_1 = 0.0456$ for 3197 data with $I \geqslant 2\sigma(I)$, 0.0612 for all data; $wR_2 = 0.1147$, and GOF = 0.933. The largest parameter shift was 0.4σ (for the disordered diethyl ether solvent molecule) in the final cycle, and in the final difference map the largest features were +2.58 and −1.97 e Å^{-3} near the platinum atom. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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