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1,2-Phenylene diisocyanide for metallotriangles

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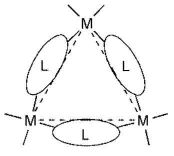
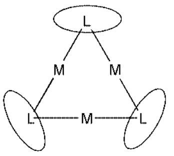
A strain free platinotriangle has been produced using 1,2-phenylene diisocyanide as the ligand determining 60° angles at the vertices, and *trans*-Pt(C_6F_5)$_2$ as the linear link building the sides.

Compared to the number of metallosquares and metallorectangles reported, where the metal occupies either the vertices of the polygon (affording two *cis* coordination positions at 90°), the sides (affording two *trans* coordination positions at 180°), or both, reports on metallotriangles are surprisingly scarce.[1] Moreover, the majority of metallotriangles reported are of class **I**, with metal fragments offering two *cis* coordination positions at 90° occupying the vertices of a distorted equilateral triangle.[2] Curiously there are fewer of the apparently more favorable type **II** structure, where ligands imposing hexagonally based bonds at 60° should yield strain free triangles.

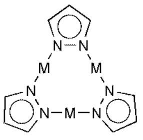


I

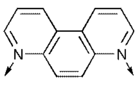


II

A well known family of triangles based on **II**, is that of [M(μ-pz)]$_3$ (pz = pyrazole or substituted pyrazole; M = Au, Ag) compounds **1**, even though the bonding angle determined by the two pz nitrogens in a pentagonal ring is too open (*ca.* 72°).[3] Such triangles have been used to make hexagonal columnar liquid crystals.[4] Some years ago a number of complexes with iminoacyl, [M(CER$_n$=NR′)]$_3$ (M = Au, Ag; ER$_n$ = OR, NR$_2$),[5] or with 2-pyridyl, [Au(C_5H_4N)]$_3$,[6] as bridging groups were reported. These make triangles of the same small size as pyrazolate, and determine M···M distances of 3.3–3.5 Å. For trimeric mercury derivatives with *o*-phenylene, *o*-perfluorophenylene, or 1,2-$C_2B_{10}H_{10}$ at the corners these distances are 3.5–3.7 Å.[7] Only very recently a larger triangle has been reported, in which 4,7-phenanthroline **2** occupies the corners and the dipalladium fragment **3** makes the sides of the triangle.[8]



1



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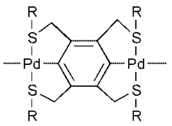
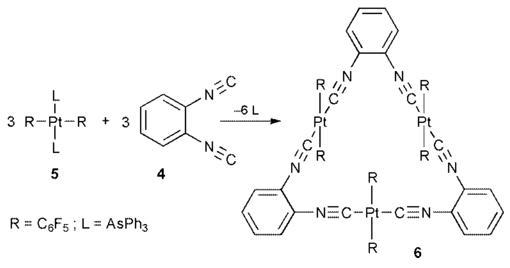


3

Isocyanides are known to bind strongly to many different transition metals. Diisocyanides have been used in the building of coordination polymers, and mixed donors 1,3- and 1,4-cyanoisocyanoarenes have afforded interesting mixed Pd–Cu polymers.[9] So far the only discrete metallapolygon reported involves 1,4-phenylene diisocyanide, making part of a very large tetragold rectangular ring.[10] On the other hand, Takahashi and coworkers have reported the metallosquare [Pd(PEt$_3$)$_2${μ-C_6H_4(C≡C)$_2$}]$_4$, with *o*-diethynylbenzene at the corners. Although the 60° angles determined by the two ethynyl groups are ideal for an equilateral triangle, steric repulsion of the PEt$_3$ ligands forces a strained square instead.[11]

1,2-Phenylene diisocyanide **4** is a neutral ligand geometrically equivalent to the dianionic *o*-diethynylbenzene used by Takahashi and coworkers.[12] We have tested its ability to make metallotriangles by reacting it with *trans*-[Pt(C_6F_5)$_2$(AsPh$_3$)$_2$] **5**.[13] The pentafluorophenyl derivative **5** was chosen because it is quite inert towards isomerization, keeping its *trans* arrangement in substitution reactions. The reaction takes place very easily in CH_2Cl_2 at room temp., leading to the formation of [Pt(C_6F_5)$_2${μ-C_6H_4(NC)$_2$}]$_3$ **6** in high yield (Scheme 1).†



Scheme 1

The molecular structure of **6** is shown in Fig. 1.‡ There is a Pt atom at the center of each side of an equilateral triangle determined by the centers of the aryl rings of the diisocyanide ligands. The non-bonding Pt···Pt distances are *ca.* 5.65 Å. The coordination around the Pt atoms is square planar, with two *trans* isonitriles and two *trans* C_6F_5 groups. It is noteworthy that the metal atom is bonded only to C-donor ligands. The C_6F_5 groups are situated perpendicular to the planar triangle and their planes are more or less coplanar for each Pt(C_6F_5)$_2$ fragment. This can be better seen in Fig. 2, a space filling representation

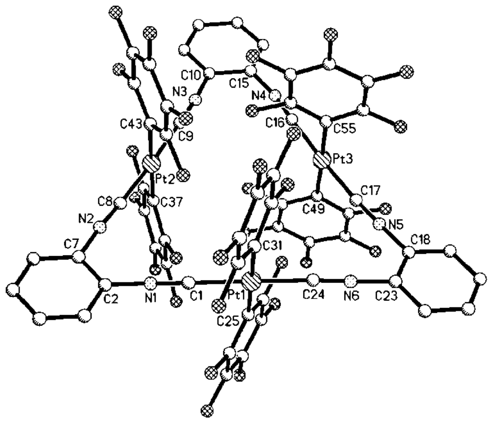


Fig. 1 Molecular structure of **6**. Phenylene hydrogens have been omitted for clarity. Selected distances (Å) and angles (°): Pt(1)–C(1) 1.918(10), Pt(1)–C(24) 1.925(10), Pt(1)–C(25) 2.057(9), Pt(1)–C(31) 2.076(10), C(1)–N(1) 1.170(11), C(2)–N(1) 1.402(11), C(2)–C(7) 1.380(12), C(1)–Pt(1)–C(24) 179.3(4), C(1)–Pt(1)–C(25) 90.9(4), C(1)–Pt(1)–C(31) 88.6(4), C(24)–Pt(1)–C(25) 89.4(4), C(24)–Pt(1)–C(31) 91.0(4), C(25)–Pt(1)–C(31) 178.6(4), Pt(1)–C(1)–N(1) 176.5(8), C(7)–C(2)–N(1) 121.6(8), C(1)–N(1)–C(2) 178.6(9).

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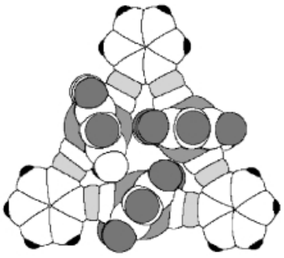

Fig. 2 Space filling structure of **6** viewed perpendicular to the plane of the triangle, showing the orientation of the C_6F_5 rings.

viewed perpendicular to the plane containing the triangle, where the C_6F_5 groups above and below this plane are eclipsing each other almost perfectly. The usual arrangement found for aryl ligands in square planar complexes has the aryl plane perpendicular to the metal coordination plane (torsion angle 90°).[14] In the triangle, this would cause them to clash in the center of the triangle. This is relieved by twisting the pentafluorophenyls about the Pt–C_6F_5 bond (we define twist as 0° for the perpendicular arrangement, thus torsion angle + twist angle = 90°). The average torsion angle around the Pt–C_{ipso} bonds is 54°. The maximum torsion is for C(24)–Pt(1)–C(31)–C_{ortho} = 63°, and the minimum is for C(9)–Pt(2)–C(37)–C_{ortho} = 46°. In addition there is some variation in the torsion angle along the Pt$\cdots C_{ipso}$ (phenylene) vectors. These angles give an idea of how orthogonal are the Pt–C_{ipso} (pentafluorophenyl) bonds to the 'plane' of the triangle. They vary between 103.0° [for C(31)–Pt(1)–C(23)–C(18)] and 77.4° for C(55)–Pt(3)–C(18)–C(23), and their average is close to 90°. van der Waals distances of the order 3.1–3.3 Å are found between the internal F_m or F_o of each ring and the closest carbons of another ring (C_m or C_p for F_m; C_o or C_{ipso} for F_o).[15]

In the C_{3h} symmetry found in the solid state structure, the F atoms inside and outside the triangle, as well as the four H atoms in each phenylene ring, should be diastereotopic (5 F signals and 4 H signals are expected). However only one signal is observed for each type of fluorine (F_o, F_m or F_p) in the ^{19}F NMR spectrum, and the hydrogens display an AA′XX′ pattern. This reveals fast rotation or tilting of the C_6F_5 groups.

A further structural feature worth commenting upon is the Pt–C_6F_5 distances: they range from 2.051 to 2.076 Å (average 2.061 Å), similar to other Pt–C_6F_5 distances and not particularly long. This suggests that the π back donation, which is sometimes invoked as a further source of stability for M–C_6F_5 compared to M–C_6H_5,[16] either is not very important in this case, or is not very much affected by the tilting.

The structural type found for **6** interesting for further elaboration. Both the diisocyanide and the R groups on the Pt can be easily modified to introduce other characteristics. For instance, *p*-substituted fluorinated rings have been used to produce metallomesogens.[17] We are currently pursuing these ideas.

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Notes and references

† To a stirred solution of *trans*-[Pt(C_6F_5)$_2$(AsPh$_3$)$_2$] (156.6 mg, 0.137 mmol) in 40 mL of CH_2Cl_2 was added 1,2-phenylene diisocyanide (17.5 mg, 0.137 mmol) dissolved in 10 mL of CH_2Cl_2. After stirring for 2 h *n*-hexane (20 mL) was added. Upon evaporation, **6** separated as a white solid, which was filtered off, thoroughly washed with *n*-hexane, and dried. Yield: 71 mg (79%). IR: ν(C≡N) 2189 cm^{-1}. δ_H[$(CD_3)_2CO$, room temp., 300 MHz]: 7.83 (m, 6H) and 7.98 (m, 6H), AA′XX′ spin system. δ_F[$(CD_3)_2CO$, ref. $CFCl_3$, room temp., 282 MHz]: −114.3 (m, 12F_o, $^3J_{FPt}$ 284.8 Hz), −161.7 (t, 6F_p, $^3J_{FF}$ 19.9 Hz), −164.1 (m, 12F_m). Crystals for X-ray diffraction were obtained by slow diffusion from THF/hexane.

‡ *Crystal data* for $[Pt\{\mu\text{-}C_6H_4(NC)_2\}]_3\cdot 2THF$ (**6**·2THF): M = 2116.23, triclinic, space group $P\bar{1}$ (no. 2), a = 11.732(2), b = 11.907(2), c = 26.506(3) Å, α = 78.77(1), β = 83.180(1), γ = 65.11(1)°, U = 3291.5(8) Å^3, T = 163(2) K, Z = 2, μ = 6.5 mm^{-1}, 30636 reflections measured, 14436 unique (R_{int} = 0.085), wR_2 = 0.111 (for all 14436 data), R_1 = 0.053 [for 8872 data with $I > 2\sigma(I)$].

CCDC 182/1612. See http://www.rsc.org/suppdata/cc/b0/b001027h/ for crystallographic files in .cif format.

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