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Synthesis and characterization of chelate and bridging triazenide complexes of palladium and platinum. Stereoselective oxidative addition of chlorine or iodine to [NBu$_4$][Pt(C$_6$F$_5$)$_2$(η^2-PhNNNPh)]

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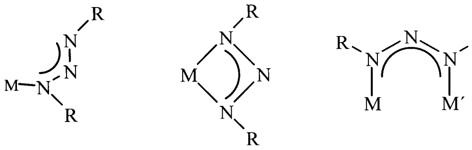
The triazenide complexes *cis*-[M(C$_6$F$_5$)$_2$(η^2-ArNNNAr)]$^-$ (M = Pd, Pt; Ar = C$_6$H$_5$, C$_6$H$_4$Me-*p*), *anti*-[{Pd(C$_6$F$_5$)(L)(μ-PhNNNPh)}$_2$] [L = PPh$_3$, *t*-BuNC, PhCN, tht (tht = SC$_4$H$_8$, tetrahydrothiophene)] and *anti*-[{Pd(C$_6$F$_5$)(Br)(μ-PhNNNPh)}$_2$]$^{2-}$ have been prepared by treatment of the corresponding precursors [{M(C$_6$F$_5$)$_2$(μ-OH)}$_2$]$^{2-}$ (M = Pd, Pt), [{Pd(C$_6$F$_5$)(L)(μ-X)}$_2$] (X = OH or Cl) and [{Pd(C$_6$F$_5$)(Br)(μ-Br)}$_2$]$^{2-}$ with either ArN=NNHAr or ArNNNAr$^-$. The stereoselective oxidation of *cis*-[Pt(C$_6$F$_5$)$_2$(PhNNNPh)]$^-$ with PhICl$_2$ or I$_2$ leads to the synthesis of the corresponding mononuclear platinum(IV) complex *cis,trans*-[Pt(C$_6$F$_5$)$_2$(PhNNNPh)(X)$_2$]$^-$ (X = Cl or I). The crystal structures of *cis*-[Pd(C$_6$F$_5$)$_2$(η^2-PhNNNPh)]$^-$, *anti*-[{Pd(C$_6$F$_5$)(*t*-BuNC)(μ-PhNNNPh)}$_2$] and *cis,trans*-[Pt(C$_6$F$_5$)$_2$(η^2-PhNNNPh)(Cl)$_2$]$^-$ have been established by X-ray diffraction. The Pd ··· Pd distance bridged by the rigid triazenido ligands in *anti*-[{Pd(C$_6$F$_5$)(*t*-BuNC)(μ-PhNNNPh)}$_2$] is 2.9907(8) Å where a boat conformation of the central 'Pd$_2$N$_6$' eight-membered ring is observed. The [Pt(C$_6$F$_5$)$_2$(η^2-PhNNNPh)(Cl)$_2$]$^-$ anion shows an octahedral arrangement around the platinum atom, involving two *trans*-chloro ligands, two *cis*-C$_6$F$_5$ groups and a chelating triazenide.

Introduction

The study of transition metal complexes containing 1,3-diaryltriazenide [RN=N–NR]$^-$ ligands has increased greatly in the past few years, because of their potential reactivity in relation to their several modes of coordination.[1] This anion is a "small bite" three-atom donor ligand that can act as a monodentate group (a), a chelating ligand (b) (generating highly strained, four-membered rings) or a bridging ligand between two metal centres (c) (see Scheme 1).[2,3] Complexes containing bridging triazenido groups can exhibit unusually strong M–M interactions with a formal bond order of zero.[4,5] The chelating bonding mode is less common for this ligand, and the unique example known in palladium chemistry is the recently reported [Pd(mesityl)(η^2-PhNNNPh)(PPh$_3$)],[6] but to the best of our knowledge (Cambridge Structural Database, CSD) no crystal structure of any chelated triazenido complex of palladium or platinum is available so far.



(a) (b) (c)

Scheme 1

Here, we describe the synthesis and characterization of new chelate and bridging triazenido palladium(II) and platinum(II) complexes, including the first crystal structure of a mononuclear chelate triazenide palladium complex, together with the crystal structure of a dimeric palladium derivative. The stereoselective oxidation of a monomeric triazenido platinum(II) complex with either phenyliodonium dichloride (PhICl$_2$), a reagent used to deliver chlorine stoichiometrically, or I$_2$ affording novel dichloro or diiodo triazenido platinum(IV) complexes is also reported. The dichloro chelate triazenido platinum(IV) complex has been characterized by X-ray diffraction.

Results and discussion

Monomeric complexes [NBu$_4$][Pd(C$_6$F$_5$)$_2$(η^2-ArNNNAr)]

The di-μ-hydroxo complexes [NBu$_4$]$_2$[{M(C$_6$F$_5$)$_2$(μ-OH)}$_2$] (M = Pd,[7] Pt[8]) react with 1,3-diaryltriazenes ArN=NNHAr to yield the corresponding monomeric triazenido complexes [M(C$_6$F$_5$)$_2$(η^2-ArNNNAr)]$^-$ **1**–**4** (Scheme 2) with the concomitant liberation of H$_2$O. Complexes **1**–**4** have been characterized on the basis of partial elemental analyses and spectroscopic data (IR, ^{1}H and ^{19}F-{^{1}H} NMR). The IR spectra of complexes **1**–**4** show the characteristic absorptions of the C$_6$F$_5$ group[9] at 1630, 1490, 1450, 1050, 950 and a split band at *ca.* 800 cm^{-1}, derived from the so-called X-sensitive mode in C$_6$F$_5$-halogen molecules, which is characteristic of the *cis*-M(C$_6$F$_5$)$_2$ fragment[10] and behaves like a ν(M–C) band.[11] The IR spectra also show a very strong band at 1250–1270 cm^{-1} which is indicative of the triazenide acting as a chelating ligand.[6] Measurements of the molar conductivity in acetone indicate that compounds **1**–**4** behave as 1 : 1 electrolytes[12] in accordance with the formulae given. Mass spectra (FAB$^-$) of complexes **1**, **3** and **4** clearly support the proposed formulae showing the peaks corresponding to [M(C$_6$F$_5$)$_2$(ArNNNAr)]$^-$, with coincident experimental and calculated isotopic distributions. The ^{1}H NMR spectra of **1**–**4** show the resonances of the ArNNNAr ligand as well as the

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Table 1 Selected bond lengths (Å) and bond angles (°) for complex **1**

Pd–C(1)	1.994(5)	Pd–N(3)	2.117(4)
Pd–C(11)	2.006(5)	N(1)–N(2)	1.306(7)
Pd–N(1)	2.095(4)	N(2)–N(3)	1.308(7)
C(1)–Pd–C(11)	85.2(2)	N(2)–N(1)–Pd	97.7(3)
C(1)–Pd–N(1)	105.6(2)	N(2)–N(3)–Pd	96.6(3)
C(11)–Pd–N(3)	109.8(2)	N(1)–N(2)–N(3)	106.2(4)
N(1)–Pd–N(3)	59.5(2)		

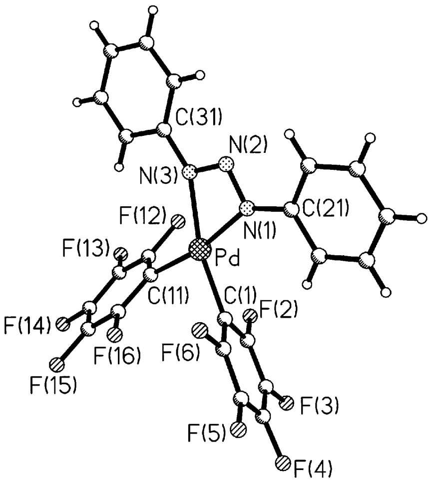
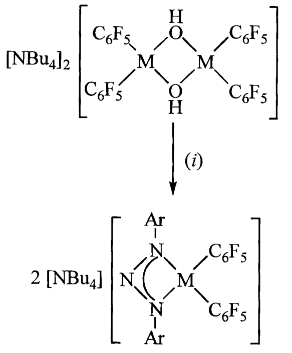


Fig. 1 Crystal structure of the anion of **1** showing the atom numbering scheme.



1	M = Pd	Ar = C_6H_5
2	M = Pd	Ar = *p*-MeC_6H_4
3	M = Pt	Ar = C_6H_5
4	M = Pt	Ar = *p*-MeC_6H_4

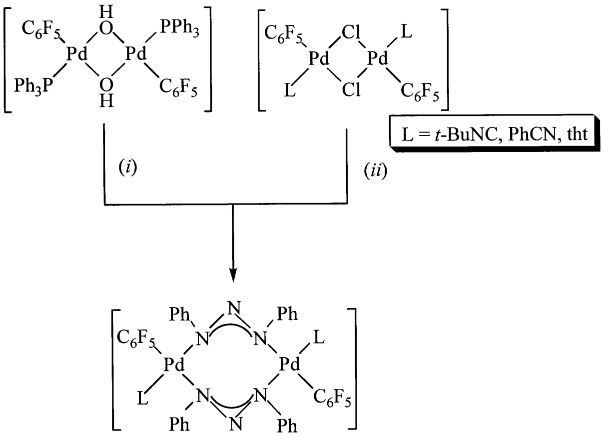
Scheme 2 (*i*) 2ArN=NNHAr.

signals assigned to the protons of the NBu_4 group. The ^{19}F NMR patterns are consistent with the presence of two equivalent C_6F_5 groups, *i.e.*, three sharp resonances with the intensity ratio $2(F_o)$: $1(F_p)$: $2(F_m)$, indicating freely rotating pentafluorophenyl rings around the C–M bond. As expected, the *ortho*-F signals of complexes **2** and **4** are flanked by the satellites due to coupling to ^{195}Pt.

The crystal structure of **1** has been determined by X-ray diffraction studies (see Fig. 1 and Tables 1 and 5). So far as we are aware this is the first chelate triazenide palladium species to be structurally characterized.[13] The structure shows the palladium atom bonded to a chelated PhNNNPh ligand and two C_6F_5 groups. The palladium centre geometry is square planar with all Pd, N(1), N(3), C(1) and C(11) atoms lying on a plane (mean deviation 0.015 Å). A strong distortion around the palladium atom due to the very small bite of the PhNNNPh ligand [N(1)–Pd–N(3) 59.5(2)°] have been found. The Pd–N(1)–N(2)–N(3) four-membered ring is coplanar to the palladium centre and one of the phenyl rings [C(31)–C(36)] (mean deviation 0.014 Å). The other phenyl ring [C(21)–C(26)] and the C_6F_5 groups [C(1)–C(6) and C(11)–C(16)] present dihedral angles of 7.6, 67.1 and 57.6° to the palladium plane, respectively. The Pd–N(1) and Pd–N(3) bond lengths [2.095(4) and 2.117(4) Å, respectively] are approximately the same. Furthermore, similar N(1)–N(2) and N(2)–N(3) bond lengths have been found [1.306(7) and 1.308(7) Å, respectively], indicating that the ligand chelates in a chemically equivalent environment and there is extensive π delocalization over the entire ring. This feature is common to other related compounds, such as $[Os_3(CO)_{11}Cl(\eta^2-C_6F_5NNNC_6F_5)]$.[14] The N(1)–N(2)–N(3) angle of 106.2(4)° is close to that observed in $[Os_3(CO)_{11}Cl(\eta^2-C_6F_5NNNC_6F_5)]$,[14] and differs considerably from the values found in $[Ru_3(\mu-H)(CO)_{10}(\mu-C_6F_5NNNC_6F_5)]$,[14] and other complexes where the triazenide bridges two metals centres (mean value 116°). This fact emphasizes the strained nature of the Pd–N(1)–N(2)–N(3) four-membered ring.

Dimeric complexes $[\{Pd(C_6F_5)(L)(\mu-PhNNNPh)\}_2]$ and $[NBu_4]_2[\{Pd(C_6F_5)(Br)(\mu-PhNNNPh)\}_2]$

In acetone solution, the palladium hydroxo-complex[15] $[\{Pd(C_6F_5)(PPh_3)(\mu-OH)\}_2]$ reacts with two equivalents of 1,3-diphenyltriazene, PhN=NNHPh, to give the di-μ-triazenide complex *anti*-$[\{Pd(C_6F_5)(PPh_3)(\mu-PhNNNPh)\}_2]$ **5**. The analogous triazenide-bridged palladium complexes $[\{Pd(C_6F_5)(L)(\mu-PhNNNPh)\}_2]$ **6**–**8** and the related $[NBu_4]_2[\{Pd(C_6F_5)(Br)(\mu-PhNNNPh)\}_2]$ **9** have been prepared by reaction in acetone or methanol of the halogeno-complexes $[\{Pd(C_6F_5)(L)(\mu-Cl)\}_2]$ [L = *t*-BuNC,[16] PhCN,[17] tht (tetrahydrothiophene)[18]] or $[NBu_4]_2[\{Pd(C_6F_5)(Br)(\mu-Br)\}_2]$[19] with $[NBu_4]OH$ and PhN=NNHPh in the molar ratio 1 : 2 : 2, as shown in Schemes 3 and 4.



5	L = PPh_3
6	L = *t*-BuNC
7	L = PhCN
8	L = tht

Scheme 3 (*i*) 2PhN=NNHPh; (*ii*) 2PhN=NNHPh/$2OH^-$.

The new complexes **5**–**9** have been characterized by partial elemental analysis and spectroscopic data. Mass spectra (FAB^+) of complexes **6** and **8** support the dinuclear nature of these complexes showing the peaks corresponding to $[\{Pd(C_6F_5)(L)(PhNNNPh)\}_2]$, with coincident experimental and calculated isotopic distributions. Complex **9** behaves in acetone as a 1 : 2 electrolyte,[12] in accordance with the formula given. Complexes **5**–**9** give the characteristic infrared absorptions of the C_6F_5 group[9] at 1630, 1490, 1450, 1050, 950 cm^{-1} as well as a band at *ca.* 785 cm^{-1} for the so-called X-sensitive mode[11] and

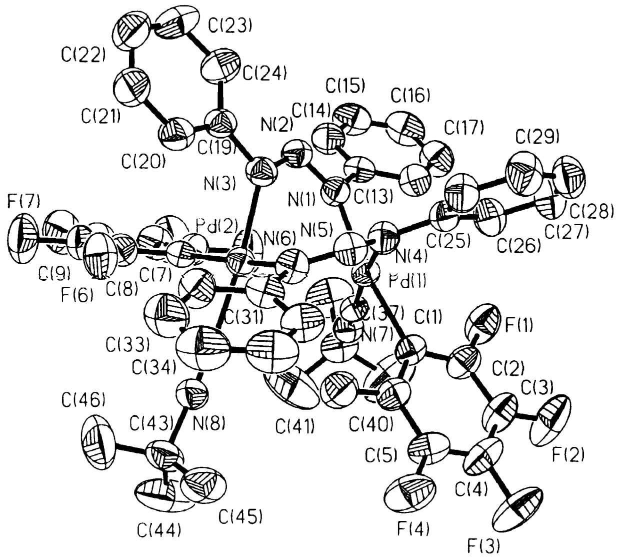
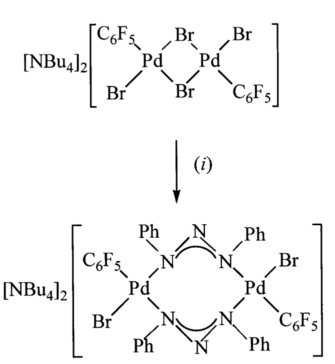


Fig. 2 ORTEP[35] diagram of **6**. Thermal ellipsoids are at 50% probability.



9

Scheme 4 (*i*) 2PhN=NNHPh/2OH$^-$.

a strong band at 1350–1375 cm^{-1} corresponding to a bridging triazenide ligand.[6] IR spectra of **6** and **7** show also an absorption at *ca.* 2230 cm^{-1} which is assigned to ν(C≡N) of the *t*-BuNC group (for **6**)[20,21] and to ν(C≡N) of the PhCN ligand (for **7**). Although compounds **5**–**9** could exist either as *anti* and/or *syn* isomers, the NMR data showed that they exist as a unique isomer in solution. Thus, the ^{19}F NMR spectra of **5**–**7** and **9** exhibit three resonances with relative intensities of 2 : 1 : 2 (2F$_o$: 1F$_p$: 2F$_m$) corresponding to only one type of pentafluorophenyl ring. No isomerization process was observed when a solution of **6** was kept in solution in CDCl$_3$ for a prolonged period. An *anti* structure of **6** was revealed by X-ray diffraction.

The ^{19}F NMR spectrum of compound **8** at room temperature shows the presence of two resonances for the *ortho*-fluorine atoms together with a resonance for the *para*-fluorine atom which suggests the rotation around the Pd–C bond is hindered. The ^{1}H NMR spectrum of **6** shows one singlet for the neutral ligand *t*-BuNC at δ 1.17. No noticeable change was observed in the ^{1}H NMR spectrum of **6** when it was recorded in the temperature range −50 to +50 °C indicating rigidity of the triazenido-bridge complex.

Suitable crystals of complex **6** were grown from dichloromethane–hexane. The structure of **6** is shown in Fig. 2 with selected bond lengths and angles in Table 2. The geometry around each palladium atom is approximately square planar. The bridging PhNNNPh ligands are *cis* with respect to each other, whereas the ancillary *t*-BuNC and C$_6$F$_5$ ligands are *trans* related. The ligand coordination planes at each palladium are tilted at an angle of 42.5° to one another and are somewhat staggered [hence C(37)–Pd(1)···Pd(2)–C(42) torsion angle is 64.8°]. The Pd$_2$(μ-NNN) fragments are not planar, the palladium atoms being on different sides of the plane defined by the nitrogen atoms, as in other triazenido complexes.[22] The phenyl rings, except the C19^C24 ring, are rotated with respect to the plane of their bonded triazenido groups. The Pd(1)–N(1) bond distance (*trans* to the C$_6$F$_5$ group) is longer than the Pd(1)–N(4) bond (*trans* to the *t*-BuNC ligand). The Pd···Pd distance bridged by the rigid triazenido ligands in *anti*-[{Pd(C$_6$F$_5$)(*t*-BuNC)(μ-PhNNNPh)}$_2$] is 2.9907(8) Å, which lies within the distances reported for binuclear complexes containing three-atom bridging ligands.[4] The related platinum complex [{PtCl(PEt$_3$)(μ-PhNNNPh)}$_2$], in which the Pt···Pt distance is 2.9302(8) Å, exhibits Pt–Pt coupling between two metal centres in the ^{195}Pt NMR spectrum.[4] The face to face juxtaposition of two square planar d^8 metal centres is expected to result in antibonding interactions between the metal centres on the basis of qualitative molecular orbital theory. However, the frequent occurrence of short contacts in such units has caused much debate regarding the possible ways by which these metal–metal interactions could become favourable.[23] Recent work in this area has suggested several factors which make the metal–metal interaction in these systems less antibonding.[24,25]

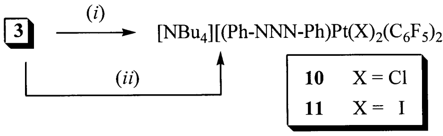
Table 2 Selected bond lengths (Å) and bond angles (°) for complex **6**

Pd(1)–C(37)	1.929(5)	Pd(2)–N(3)	2.068(4)
Pd(1)–C(1)	2.026(5)	Pd(2)–N(6)	2.090(4)
Pd(1)–N(4)	2.073(4)	N(1)–N(2)	1.302(4)
Pd(1)–N(1)	2.098(4)	N(2)–N(3)	1.308(5)
Pd(1)···Pd(2)	2.9907(8)	N(4)–N(5)	1.314(6)
Pd(2)– C(42)	1.932(5)	N(5)–N(6)	1.302(5)
Pd(2)–C(7)	2.030(5)		
C(37)–Pd(1)–C(1)	86.6(2)	C(42)–Pd(2)–N(3)	173.9(2)
C(37)–Pd(1)–N(4)	175.1(2)	C(7)–Pd(2)–N(3)	88.4(2)
C(1)–Pd(1)–N(4)	88.5(2)	C(42)–Pd(2)–N(6)	92.1(2)
C(37)–Pd(1)–N(1)	92.7(2)	C(7)–Pd(2)–N(6)	168.9(2)
C(1)–Pd(1)–N(1)	169.4(2)	N(3)–Pd(2)–N(6)	92.3(2)
N(4)–Pd(1)–N(1)	92.2(2)	N(1)–N(2)–N(3)	117.0(4)
C(42)–Pd(2)–C(7)	86.4(2)	N(41)–N(5)–N(6)	117.2(4)

The different structural behaviour of the triazenide as a chelating (complexes **1**–**4**) or bridging (complexes **5**–**9**) ligand could be attributed to the identity of the ancillary ligands. For instance, the higher *trans* influence of the pentafluorophenyl ligand compared to the bromide ligand[26] should favour the formation of the dimeric complex **9**.

Monomeric platinum(IV) complexes [NBu$_4$][Pt(C$_6$F$_5$)$_2$-(PhNNNPh)(X)$_2$]

Treatment of dichloromethane solutions of **3** at room temperature with the stoichiometrically required amount of the mild chlorine-transfer agent phenyliodonium dichloride (PhICl$_2$) or I$_2$ leads to the synthesis of the corresponding [NBu$_4$] salts of the mononuclear platinum(IV) complex *cis,trans*-[Pt(C$_6$F$_5$)$_2$-(PhNNNPh)(X)$_2$]$^-$ (X = Cl **10** or I **11**; see Scheme 5). Both complexes are isolated as air-stable solids in high yields and behave as 1 : 1 electrolytes in acetone solution. Similar oxidation attempts carried out on the palladium complexes **1** and **6** led to the starting materials. Mass spectra (FAB$^-$) of complexes **10** and **11** clearly support the proposed formulae showing the peaks corresponding to [M(C$_6$F$_5$)$_2$(ArNNNAr)(X)$_2$]$^-$. Their IR



Scheme 5 (*i*) PhICl$_2$ for **10**. (*ii*) I$_2$ for **11**.

Table 3 IR data (cm^{-1}) relevant to pentafluorophenyl groups of the monomeric platinum compounds

Complex	X-Sensitive[a]	ν(C–C)	ν(C–F)
3	808, 796	1498	958
4	806, 796	1502	956
10	800, 792	1508	970
11	796, 788	1508	968

[a] See ref. 11.

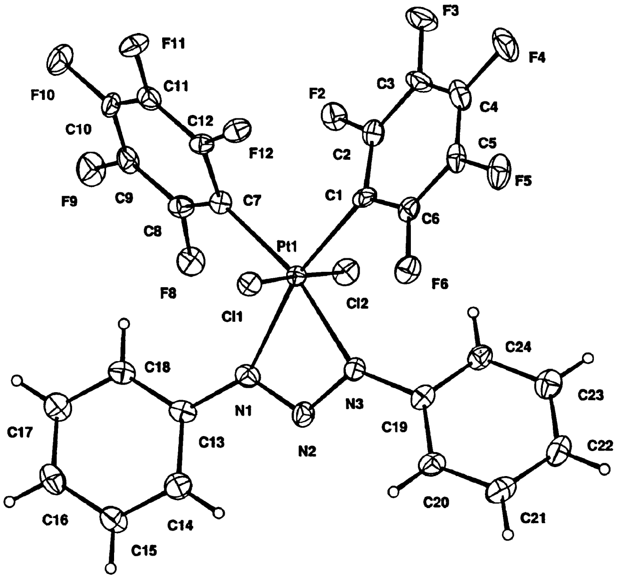
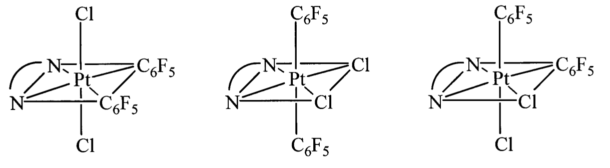


Fig. 3 ORTEP diagram of the anion of **10**. Thermal ellipsoids are at 50% probability.

spectra show a noticeable shift of both ν(C–C) and the ν(C–F) vibrational modes toward higher frequencies (Table 3), in accord with the increased oxidation state of the metal centre.[27,28] On the other hand, a strong absorption is observed at 344 cm^{-1} corresponding to ν(Pt–Cl).

The ^{19}F NMR spectra of **10** and **11** in CDCl$_3$ solution show only one type of C$_6$F$_5$ group at room temperature, which means that a single diastereomer of the three possible ones (Scheme 6) is present, which means that the oxidative addition proceeds stereoselectively, and that the presence of isomer (c) must be ruled out (two non-equivalent C$_6$F$_5$ groups should be observed in the spectra, one *trans* to Cl and one *trans* to N); however, the synthesis and characterization of a related (c) isomer [Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)(Br)$_2$]$^-$ has been recently reported.[27] As expected the magnitude of the ^{195}Pt–F coupling constants are smaller than those usually found for Pt(II) complexes.[27]



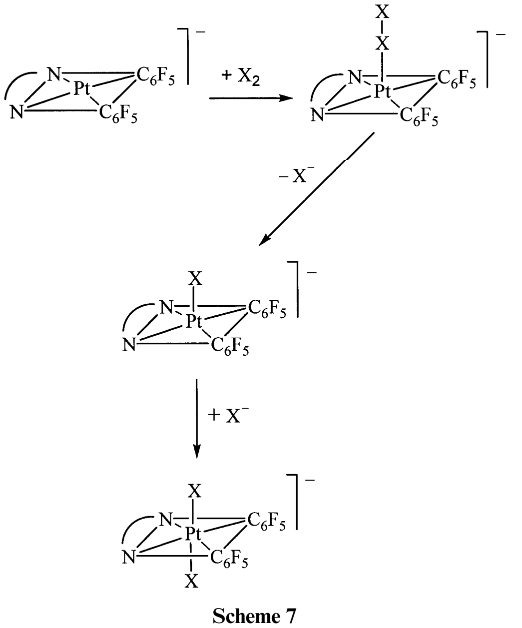
Scheme 6

Since the analysis of all available spectroscopic data did not allow us to distinguish between isomers (a) and (b), the structure of **10** was determined by X-ray diffraction methods. This is the first chelate triazenide platinum species to be structurally characterized. The structure is shown in Fig. 3 with selected bond lengths and angles in Table 4. The anion **10** shows an octahedral arrangement around the platinum atom, involving two *trans* chloro ligands [177.73(6)°], two *cis*-C$_6$F$_5$ groups [91.1(3)°] and a chelating triazenide [N(3)–Pt–N(1) = 60.0(2)°] (similar to that found in **1**). Thus, the complex is obtained as isomer (a), similar to the established structure of the neutral complex *cis,trans*-[Pt(C$_6$F$_5$)$_2$(en)(O$_2$C^{n}Pr)$_2$] (en = ethylenediamine).[28] The platinum–chlorine distances are a bit shorter than those previously observed for a chlorine atom *trans* to a chlorine atom in the related dianionic complex *cis*-[Pt(C$_6$F$_5$)$_2$Cl$_4$]$^{2-}$.[29] The Pt–C(1) and Pt–C(7) distances are similar to those previously observed for *cis,trans*-[Pt(C$_6$F$_5$)$_2$(en)(O$_2$C^{n}Pr)$_2$].[28] The chelating PhNNNPh ligand forms a Pt–N(1)–N(2)–N(3) four-membered ring which is almost coplanar [largest deviation from the plane for N(2), 0.015 Å]. The N–N–N angle of 106.2(5)° is close to that of **1**. The Pt–N(1) and Pt–N(3) distances are somewhat different, the C13^C18 and C19^C24 rings are rotated by 8.9° and 30.6° respectively with respect to the PtN$_3$ chelate ring. The two C$_6$F$_5$ rings are rotated by 57.2° with respect to each other.

Table 4 Selected bond lengths (Å) and bond angles (°) for complex **10**

Pt(1)–C(7)	2.039(6)	Pt(1)–Cl(1)	2.3151(17)
Pt(1)–C(1)	2.041(7)	Pt(1)–Cl(2)	2.3279(17)
Pt(1)–N(1)	2.136(5)	N(1)–N(2)	1.325(7)
Pt(1)–N(3)	2.107(5)	N(2)–N(3)	1.327(7)
C(7)–Pt(1)–C(1)	91.1(3)	N(3)–Pt(1)–Cl(1)	91.28(16)
C(7)–Pt(1)–N(3)	165.2(2)	N(1)–Pt(1)–Cl(1)	84.90(16)
C(1)–Pt(1)–N(3)	103.7(2)	C(7)–Pt(1)–Cl(2)	93.09(18)
C(7)–Pt(1)–N(1)	105.3(2)	C(1)–Pt(1)–Cl(2)	88.63(18)
C(1)–Pt(1)–N(3)	109.8(2)	N(3)–Pt(1)–Cl(2)	86.44(16)
C(1)–Pt(1)–N(1)	163.2(2)	N(1)–Pt(1)–Cl(2)	94.00(16)
N(3)–Pt(1)–N(1)	60.0(2)	Cl(1)–Pt(1)–Cl(2)	177.73(6)
C(7)–Pt(1)–Cl(1)	89.12(18)	N(1)–N(2)–N(3)	106.2(5)
C(1)–Pt(1)–Cl(1)	91.85(19)		

The most widely accepted mechanism in oxidative addition reactions of halogens on square-planar platinum(II) complexes (Scheme 7) is that originally formulated by Skinner and Jones in 1969.[30] The first step involves a linear adduct between the metal complex and the halogen molecule formed by donation of electron density from the metal to the X$_2$ molecule. The anionic nature of the Pt centre in **10** and **11** should reasonably enhance its donor ability, thus favouring the start of the process.[31] The second step assumes the release of an X$^-$ ion, yielding a five-coordinate platinum(IV) intermediate, whose vacant coordination site can be occupied by either a (donor) solvent molecule or another X$^-$ ion. The whole process should therefore result in a *trans* addition of the halogen.



Scheme 7

Experimental

Instrumental measurements

C, H, and N analyses were performed with a Carlo Erba model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance at a heating rate of 5 °C min^{-1} and the solid samples under nitrogen flow (100 mL min^{-1}). Molar conductivities were measured in acetone solution ($c \approx 5 \times 10^{-4}$ mol L^{-1}) with a Crison 525 conductimeter. The NMR spectra were recorded on a Bruker AC 200E or Varian Unity 300 spectrometer, using $SiMe_4$ and $CFCl_3$ as the standard, respectively. In the ^{1}H NMR spectra of the ionic compounds, the signal of the NBu_4^+ cation has been omitted. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. Mass spectra were recorded on a Fisons V.G. Autospec spectrometer using the standard Cs$^+$ ion FAB (acceleration voltage 35 kV) and nitrobenzyl alcohol as matrix.

Materials

The starting complexes $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (M = Pd,[7] Pt[8]), $[\{Pd(C_6F_5)(L)(\mu\text{-}X)\}_2]$ (X = OH, Cl; L = PPh$_3$,[15] *t*-BuNC,[16] PhCN,[17] tht (tetrahydrothiophene)),[18] $[NBu_4]_2[\{Pd(C_6F_5)(Br)(\mu\text{-}Br)\}_2]$,[19] ArN=NNHAr[32] and PhICl$_2$[33] were prepared by procedures described elsewhere. Solvents were dried by the usual methods.

Preparation of complexes $[NBu_4][Pd(C_6F_5)_2(ArNNNAr)]$ (Ar = C_6H_5 1 and C_6H_4Me-*p* 2). To a solution of ArN=NNHAr (0.114 mmol) in methanol (10 cm^3) was added $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (0.1 g, 0.071 mmol). After stirring at room temperature for 5 min an orange solid was collected by filtration and air-dried.

1: Yield 86%. (Found: C, 54.4; H, 5.2; N, 6.3. $C_{40}H_{46}N_4F_{10}Pd$ requires C, 54.6; H, 5.3; N, 6.4%). Mp: 205 °C dec. Λ_M/S cm^2 mol^{-1} 101. IR (Nujol, cm^{-1}) 796, 782 (Pd–C$_6$F$_5$). ^{1}H NMR (CDCl$_3$) δ 7.10 (m, 4H$_m$), 6.90 (m, 4H$_o$ + 2H$_p$). ^{19}F NMR (CDCl$_3$) δ −115.5 (d, 4F$_o$, J_{om} = 23.4 Hz), −162.5 (t, 2F$_p$, J_{mp} = 20.3 Hz), −164.9 (m, 4F$_m$). Mass spectrum (FAB$^-$): *m*/*z* 636 (M).

2: Yield 75%. (Found: C, 55.8; H, 5.6; N, 6.2. $C_{42}H_{50}N_4F_{10}Pd$ requires C, 55.6; H, 5.6; N, 6.2%). Mp: 214 °C dec. Λ_M/S cm^2 mol^{-1} 104. IR (Nujol, cm^{-1}) 794, 784 (Pd–C$_6$F$_5$). ^{1}H NMR (CDCl$_3$) δ 6.89 (d, 4H$_m$, *J* = 8.4 Hz), 6.75 (d, 4H$_o$, *J* = 8.4 Hz), 2.21 (s, 6H, CH$_3$). ^{19}F NMR (CDCl$_3$) δ −115.4 (d, 4F$_o$, J_{om} = 23.4 Hz), −162.7 (t, 2F$_p$, J_{mp} = 20.3 Hz), −165.0 (m, 4F$_m$). Mass spectrum (FAB$^-$): *m*/*z* 440 (M − ArNNNAr).

Preparation of complexes $[NBu_4][Pt(C_6F_5)_2(ArNNNAr)]$ (Ar = C_6H_5 3 and C_6H_4Me-*p* 4). To a solution of ArN=NNHAr (0.127 mmol) in methanol (10 cm^3) was added $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (0.1 g, 0.063 mmol). The solution was stirred under reflux for 1 h. Solvent was partially evaporated under reduced pressure and an orange solid was collected by filtration and air-dried.

3: Yield 56%. (Found: C, 49.9; H, 4.6; N, 5.5. $C_{40}H_{46}N_4F_{10}Pt$ requires C, 49.6; H, 4.8; N, 5.8%). Mp: 228 °C dec. Λ_M/S cm^2 mol^{-1} 94. IR (Nujol, cm^{-1}) 808, 796 (Pt–C$_6$F$_5$). ^{1}H NMR (CDCl$_3$) δ 7.12 (m, 4H$_m$), 6.90 (m, 4H$_o$ + 2H$_p$). ^{19}F NMR (CDCl$_3$) δ −118.8 (d, 4F$_o$, J_{om} = 21.4 Hz, J_{PtF_o} = 463.6), −164.2 (t, 2F$_p$, J_{mp} = 20.3 Hz), −166.1 (m, 4F$_m$). Mass spectrum (FAB$^-$): *m*/*z* 726 (M).

4: Yield 49%. (Found: C, 50.3; H, 4.9; N, 5.4. $C_{42}H_{50}N_4F_{10}Pt$ requires C, 50.7; H, 5.1; N, 5.6%). Mp: 230 °C dec. Λ_M/S cm^2 mol^{-1} 90. IR (Nujol, cm^{-1}) 806, 796 (Pt–C$_6$F$_5$). ^{1}H NMR (CDCl$_3$) δ 6.90 (d, 4H$_m$, *J* = 8.4 Hz), 6.84 (d, 4H$_o$, *J* = 8.4 Hz), 2.23 (s, 6H, CH$_3$). ^{19}F NMR (CDCl$_3$) δ −118.7 (d, 4F$_o$, J_{om} = 22.6 Hz, J_{PtF_o} = 472), −164.4 (t, 2F$_p$, J_{mp} = 20.3 Hz), −166.1 (m, 4F$_m$). Mass spectrum (FAB$^-$): *m*/*z* 754 (M).

Preparation of complex $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-}PhNNNPh)\}_2]$ 5. To a solution of PhN=NNHPh (71 mg, 0.362 mmol) in acetone (10 cm^3) was added $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-}OH)\}_2]$ (0.2 g, 0.181 mmol). The solution was stirred for 30 min and then solvent was removed under reduced pressure and the residue was treated with hexane. The orange solid was filtered off and air-dried. Yield 60%. (Found: C, 59.2; H, 3.7; N, 5.6. $C_{72}H_{50}N_6F_{10}P_2Pd_2$ requires C, 59.1; H, 3.4; N, 5.7%). Mp: 149 °C dec. IR (Nujol, cm^{-1}) 798 (Pd–C$_6$F$_5$). ^{1}H NMR (CDCl$_3$) δ 7.68–6.44 (m, 20H). ^{19}F NMR (CDCl$_3$) δ −117.8 (m, 4F$_o$), −160.1 (t, 2F$_p$, J_{mp} = 20.3 Hz), −162.5 (m, 4F$_m$). ^{31}P NMR (CDCl$_3$) δ 28.5 (s). Mass spectrum (FAB$^+$): *m*/*z* 905 (M − 2PhNNNPh − C$_6$F$_5$)$^+$.

Preparation of complex $[\{Pd(C_6F_5)(t\text{-}BuNC)(\mu\text{-}PhNNNPh)\}_2]$ 6. To a solution of PhN=NNHPh (50 mg, 0.255 mmol) in methanol (10 cm^3) was added 20% [NBu$_4$]OH (aq) (0.33 cm^3, 0.255 mmol). To the resulting solution was added $[\{Pd(C_6F_5)(t\text{-}BuNC)(\mu\text{-}Cl)\}_2]$ (100 mg, 0.128 mmol). After stirring at room temperature for 5 min an orange solid was collected by filtration and air-dried. Yield 78%. (Found: C, 49.7; H, 3.2; N, 9.8. $C_{46}H_{38}N_8F_{10}Pd_2$ requires C, 50.0; H, 3.5; N, 10.1%). Mp: 184 °C dec. IR (Nujol, cm^{-1}) 2230 *ν*(CN), 788 (Pd–C$_6$F$_5$). ^{1}H NMR (CDCl$_3$) δ 7.89 (d, 4H$_o$, *J* = 7.6 Hz), 7.40 (d, 4H$_o$, *J* = 7.7 Hz), 7.33–6.88 (m, 8H$_m$ + 4H$_p$), 1.17 (s, 18H, *t*-BuNC). ^{19}F NMR (CDCl$_3$) δ −112.7 (d, 4F$_o$, J_{om} = 22.6 Hz), −160.1 (t, 2F$_p$, J_{mp} = 20.3 Hz), −163.9 (m, 4F$_m$). Mass spectrum (FAB$^+$): *m*/*z* 1104 (M)$^+$

Preparation of complex $[\{Pd(C_6F_5)(PhCN)(\mu\text{-}PhNNNPh)\}_2]$ 7. To a solution of PhN=NNHPh (48 mg, 0.242 mmol) in acetone (10 cm^3) was added 20% [NBu$_4$]OH (aq) (0.32 cm^3, 0.242 mmol). To the resulting solution was added $[\{Pd(C_6F_5)(PhCN)(\mu\text{-}Cl)\}_2]$ (0.1 g, 0.121 mmol). After stirring at room temperature for 5 min a yellow solid was collected by filtration and air-dried. Yield 68%. (Found: C, 52.7; H, 2.4; N, 10.1. $C_{50}H_{30}N_8F_{10}Pd_2$ requires C, 52.4; H, 2.6; N, 9.8%). Mp: 187 °C dec. IR (Nujol, cm^{-1}) 2228 *ν*(CN), 780 (Pd–C$_6$F$_5$). ^{1}H NMR (CDCl$_3$) δ 7.85 (d, 4H$_o$, *J* = 7.7 Hz), 7.40 (d, 4H$_o$, *J* = 7.8 Hz), 7.35–6.87 (m, 10H PhCN + 8H$_m$ + 4H$_p$). ^{19}F NMR (CDCl$_3$) δ −112.7 (d, 4F$_o$, J_{om} = 22.6 Hz), −160.1 (t, 2F$_p$, J_{mp} = 20.3), −163.9 (m, 4F$_m$).

Preparation of complex $[\{Pd(C_6F_5)(tht)(\mu\text{-}PhNNNPh)\}_2]$ 8. To a solution of PhN=NNHPh (49 mg, 0.25 mmol) in methanol (10 cm^3) was added 20% [NBu$_4$]OH (aq) (0.33 cm^3, 0.25 mmol). To the resulting solution was added $[\{Pd(C_6F_5)(tht)(\mu\text{-}Cl)\}_2]$ (0.1 g, 0.125 mmol). After stirring at room temperature for 5 min a red solid was collected by filtration and air-dried. Yield 68%. (Found: C, 47.3; H, 3.4; N, 7.5; S, 5.5. $C_{44}H_{36}N_6F_{10}Pd_2S_2$ requires C, 47.4; H, 3.3; N, 7.5; S, 5.8%). Mp: 156 °C dec. IR (Nujol, cm^{-1}) 784 (Pd–C$_6$F$_5$). ^{1}H NMR (CDCl$_3$) δ 8.03 (d, 4H$_o$, *J* = 7.6 Hz), 7.33–6.88 (m, 8H$_m$ + 4H$_p$), 7.00 (d, 4H$_o$, *J* = 7.7 Hz), 2.65 (m, 4H, α-CH$_2$, tht), 1.72 (m, 4H, β-CH$_2$, tht). ^{19}F NMR (CDCl$_3$) δ −115.7 (br, 2F$_o$), −118.2 (br, 2F$_o$), −159.7 (t, 2F$_p$, J_{mp} = 20.3 Hz), −163.1 (m, 4F$_m$). Mass spectrum (FAB$^+$): *m*/*z* 920 (M)$^+$.

Preparation of complex $[NBu_4]_2[\{Pd(C_6F_5)(Br)(\mu\text{-}PhNNNPh)\}_2]$ 9. To a solution of PhN=NNHPh (29.2 mg, 0.148 mmol) in methanol (10 cm^3) was added 20% [NBu$_4$]OH (aq) (0.19 cm^3, 0.148 mmol). To the resulting solution was added $[NBu_4]_2[\{Pd(C_6F_5)(Br)(\mu\text{-}Br)\}_2]$ (100 mg, 0.074 mmol). After stirring at room temperature for 5 min an orange solid was collected by filtration and air-dried. Yield 75%. (Found: C, 51.4; H, 5.8; N, 7.0. $C_{68}H_{92}N_8Br_2F_{10}Pd_2$ requires C, 51.6; H, 5.9; N, 7.1%). Mp: 184 °C dec. Λ_M/S cm^2 mol^{-1} 180. IR (Nujol, cm^{-1}) 794 (Pd–C$_6$F$_5$). ^{1}H NMR (CDCl$_3$) δ 7.48 (d, 4H$_o$, *J* = 7.7 Hz), 7.11–6.91 (m, 8H$_m$ + 4H$_p$), 6.69 (d, 4H$_o$, *J* = 7.7 Hz). ^{19}F NMR (CDCl$_3$) δ −118.1 (d, 4F$_o$, J_{om} = 28.8 Hz), −161.9 (t, 2F$_p$,

Table 5 Crystal structure determination details

	1	6	10
Formula	$C_{40}H_{46}F_{10}N_4Pd$	$C_{46}H_{38}F_{10}N_8Pd_2$	$C_{40}H_{46}Cl_2F_{10}N_4Pt$
FW	879.21	1105.64	1038.80
Crystal system	Monoclinic	Monoclinic	Monoclinic
a/Å	13.274(1)	13.610(3)	12.546(1)
b/Å	20.613(1)	18.834(4)	22.555(2)
c/Å	14.939(1)	18.215(4)	15.608(1)
β/°	100.16(1)	100.24(3)	111.31(1)
Unit cell volume/Å^3	4023.5(5)	4595(2)	4114.7(6)
T/K	173(2)	293(2)	293(2)
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
Z	4	4	4
μ/mm^{-1}	0.541	0.866	3.620
Reflections collected	8689	7228	8958
Independent reflections	4530	5819	7192
R_{int}	0.0580	0.0257	0.0487
R_1 [$I > 2\sigma(I)$]	0.0507	0.0339	0.0375
wR_2 (all data)	0.1351	0.0825	0.0933

J_{mp} = 19.5 Hz), −164.7 (m, 4F$_m$). Mass spectrum (FAB$^-$): m/z 1021 (M − Br), 904 (M − PhNNNPh).

Preparation of complex [NBu$_4$][Pt(C$_6$F$_5$)$_2$(PhNNNPh)(Cl)$_2$] 10. To a solution of complex **3** (150 mg, 0.155 mmol) in dichloromethane (10 cm^3) was added PhICl$_2$ (42.6 mg, 0.155 mmol). The solution was stirred for 15 min and then solvent was removed under reduced pressure and the residue was treated with isopropanol. The yellow solid was filtered off and air-dried. Yield 50%. (Found: C, 46.1; H, 4.3; N, 5.3. $C_{40}H_{46}N_4Cl_2F_{10}Pt$ requires C, 46.3; H, 4.5; N, 5.4%). Mp: 170 °C dec. Λ_M/S cm^2 mol^{-1} 110. IR (Nujol, cm^{-1}) 344 ν(Pt–Cl), 800, 792 (Pt–C$_6$F$_5$). ^{1}H NMR (CDCl$_3$) δ 7.10 (m, 10H). ^{19}F NMR (CDCl$_3$) δ −116.8 (d, 2F$_o$, J_{om} = 26.8 Hz, J_{PtF_o} = 94.2), −119.9 (d, 2F$_o$, J_{om} = 23.4 Hz, J_{PtF_o} = 91.9), −160.7 (t, 2F$_p$, J_{mp} = 20.3), −164.2 (m, 2F$_m$), −165.5 (m, 2F$_m$). Mass spectrum (FAB$^-$): m/z 796 (M).

Preparation of complex [NBu$_4$][Pt(C$_6$F$_5$)$_2$(PhNNNPh)(I)$_2$] 11. To a solution of complex **3** (0.1 g, 0.103 mmol) in dichloromethane (10 cm^3) was added I$_2$ (26 mg, 0.103 mmol). The solution was stirred for 15 min and then solvent was removed under reduced pressure and the residue was treated with isopropanol. The yellow solid was filtered off and air-dried. Yield 50%. (Found: C, 39.4; H, 3.8; N, 4.6. $C_{40}H_{46}N_4F_{10}I_2Pt$ requires C, 39.3; H, 3.8; N, 4.6%). Mp: 149 °C dec. Λ_M/S cm^2 mol^{-1} 111. IR (Nujol, cm^{-1}) 796, 788 (Pt–C$_6$F$_5$). ^{1}H NMR (CDCl$_3$) δ 7.10 (m, 10H). ^{19}F NMR (CDCl$_3$) δ −103.4 (d, 2F$_o$, J_{om} = 26.8 Hz, J_{PtF_o} = 138.6), −109.5 (d, 2F$_o$, J_{om} = 23.4 Hz, J_{PtF_o} = 132.1), −161.4 (t, 2F$_p$, J_{mp} = 20.3), −164.7 (m, 2F$_m$), −165.5 (m, 2F$_m$). Mass spectrum (FAB$^-$): m/z 978 (M − 1).

X-Ray structure determination

Single crystals of **1**, **6** and **10** suitable for diffraction studies were grown from dichloromethane–hexane, mounted on a glass fibre and transferred to the diffractometer [Siemens P4 (compounds **6** and **10**) with LT2 low temperature attachment (compound **1**)]. Details of data collection and refinement are given in Table 5. Unit cell parameters were determined from a least-squares fit of 60 (**1**), 32 (**6**) and 25 (**10**) accurately centred reflections (9 < 2θ < 25°). Reflections were collected using ω scans and empirical ψ-scan absorption correction was made. The structures were solved by the heavy atom method (**1** and **6**) or by direct methods (**10**) and refined anisotropically on F^2 [SHELX-97 (**1** and **10**) and SHELX-93 (**6**) programs].[34]

CCDC reference numbers 165253–165255.

See http://www.rsc.org/suppdata/dt/b1/b102944b/ for crystallographic data in CIF or other electronic format.

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