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Imido/nitrene ligands in the complexes of platinum metals [1]

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Abstract

A synthetic search for palladium and platinum complexes with nitrene ligands via reaction of tetranuclear cluster $Pd_4(\mu^2\text{-}CO)_4(\mu^2\text{-}OAc)_4$ with nitrosobenzene and reactions of mononuclear complexes $[MX_4]^{2-}$ (M = Pt, Pd; X = Cl, NO_2) with *o*-phenylenediamine and its *N*-phenyl derivative have been carried out. The complexes obtained, $[Pd(OAc)o\text{-}(PhN)(NO)C_6H_4]_2$, $Pd[o\text{-}(NPh)(N)C_6H_4]_2$, $Pt[o\text{-}(NPh)(N)C_6H_4]_2$, $Pt_2[o\text{-}(NPh)(N)C_6H_4]_4[O_3SCF_3]_2$, and $Pt_2[o\text{-}(NPh)(N)C_6H_4]_4Br_2$, have been structurally characterized by single crystal X-ray diffraction studies. The oxidation of complex $Pt[o\text{-}(NPh)(N)C_6H_4]_2$ by excess AgO_3SCF_3 afforded a heterotricyclic quinoxaline derivative, whose structure has been determined by X-ray analysis. The data obtained suggest that labile nitrene species coordinated to Pd and Pt complexes are possible intermediates in the reactions under study. © 1998 Elsevier Science S.A.

Keywords: Ligands; Nitrene; Clusters

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1. Introduction

Complexes of the platinum group metals, particularly palladium, are known as promising catalysts for the industrially desirable syntheses of aryl isocyanates and carbamates based on nitroarenes [1,2]:

$$ArNO_2 + 3C0 = ArNCO + 2CO_2 \tag{1}$$

$$ArNO_2 + 3C0 + ROH = ArNHCO(O)OR + 2C0_2 \tag{2}$$

Due to the presence of an oxidant (nitroarene) and a reductant (CO) in the reaction system, both low- and high-valent metal compounds could be formed as key reaction intermediates from a starting metal complex or disperse metal, regardless of its initial valence state. Despite numerous works having been published on this topic, the valence

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state, nuclearity, and particularly the nature of ligands in the metal compounds responsible for the catalysis of reactions (1) and (2) are still poorly understood.

Previously [3], the low-valent palladium-561 giant clusters [4,5] have been found to be effective catalyst precursors for both the synthesis of phenylisocyanate from nitrobenzene via reaction (1) and its conjugate reaction, the carbonylation of nitrobenzene coupled with the oxidation of CO to diphenyl carbonate by nitrobenzene

$$PhNO_2 + 3CO + 2PhOH = PhNCO + (PhO)_2CO + CO_2 + H_2O \quad (3)$$

The conjugation of two redox processes within reaction (3) has been suggested as a concerted electron-transfer process, where the metal core of Pd-561 cluster or a similar compound serves as an electron transfer mediator [3].

Although the detailed mechanism of these reactions is still unclear, the loss of two O atoms from the nitrobenzene molecule during its transformation to phenylisocyanate via reactions (1) or (3) can be suggested as a successive elimination of the O atoms to form, at some of the reaction stage, an intermediate nitrene moiety attached to a palladium cluster: $PhN = Pd <$. Similar nitrene intermediates were also suggested for the hydrogen-transfer reduction of nitrobenzene by formic acid in the presence of the giant Pd cluster [6].

Stable nitrene complexes are fairly common for the IV–VI metal groups [7,8] and, to a less extent, for the early VIII group metals and Ru and Os [8–15]. Meanwhile, nitrene derivatives remain rarities in the chemistry of the late VIII group metals. To the best of our knowledge, such compounds are still unknown among complexes of Pd and Pt [7,8]. In this work, we attempted to gain insight into nitrene chemistry of palladium and platinum.

2. Results and discussion

2.1. General approach

Based on the literature data [7–15], the following approaches seem to be the candidates for the syntheses of platinum metal–nitrene complexes: (1) reaction with azo and diazo compounds (e.g., $ArN = NAr$, $Me_3SiN = NSiMe_3$, $ArC(H)N_2$); (2) oxidation of amines (e.g., $ArNH_2$, Me_3SiNHR); (3) reduction of nitroarenes.

In this work, some poly- and mononuclear Pd complexes and mononuclear Pt complexes were examined in reactions with amines, azo and azoxybenzene, phenylhydroxylamine, nitro compounds, and nitrosobenzene as possible ways to synthesise the nitrene complexes. The tetranuclear palladium cluster $Pd_4(\mu^2\text{–CO})_4(\mu^2\text{–OAc})_4$ (I) [16] could

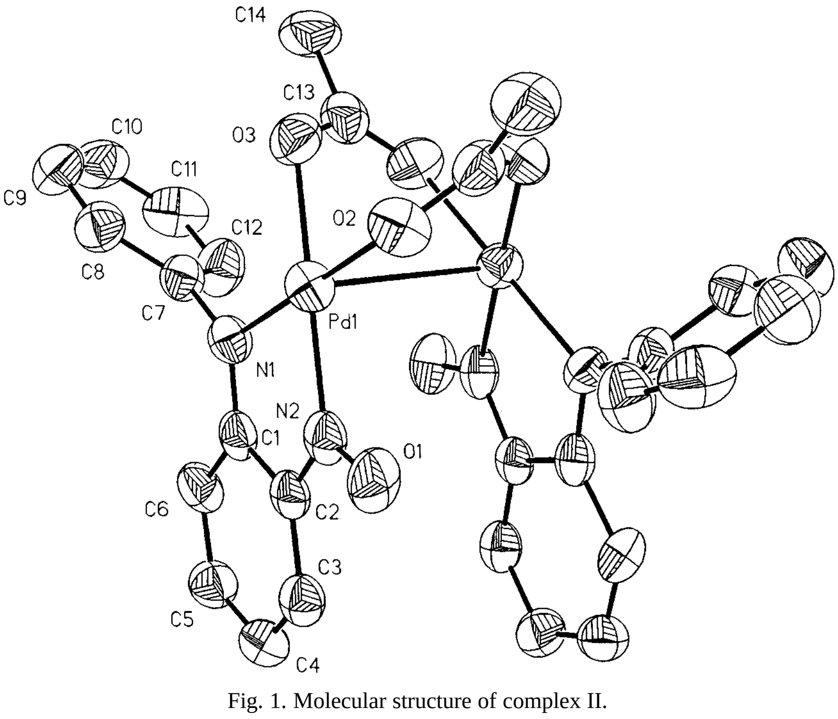


Fig. 1. Molecular structure of complex II.

Table 1
The main geometric parameters for structure II

Bond lengths (Å)			
Pd(1)–Pd(1)	2.840(1)	Pd(1)–N(1)	1.970(9)
Pd(1)–N(2)	1.97(1)	Pd(1)–O(2)	2.072(8)
Pd(1)–O(3)	2.068(8)	N(1)–C(1)	1.31(2)
N(1)–C(7)	1.43(1)	N(2)–O(1)	1.24(1)
N(2)–C(2)	1.37(1)	O(2)–C(13)	1.25(2)
O(3)–C(13)	1.24(2)	C(13)–C(14)	1.50(2)
C(11)–C(15)	1.71(2)		
Bond angles (°):			
Pd(1′)Pd(1)N(1)	103.5(3)	Pd(1′)Pd(1)N(2)	95.8(3)
Pd(1′)Pd(1)O(2)	77.5(2)	Pd(1′)Pd(1)O(3)	81.3(2)
N(1)Pd(1)N(2)	81.8(4)	N(1)Pd(1)O(2)	178.8(4)
N(1)Pd(1)O(3)	92.5(4)	N(2)Pd(1)O(2)	97.5(4)
N(2)Pd(1)O(3)	172.8(4)	O(2)Pd(1)O(3)	88.3(3)
Pd(1)N(1)C(1)	113.7(8)	Pd(1)N(1)C(7)	123.5(7)
C(1)N(1)C(7)	122.3(9)	Pd(1)N(2)O(1)	125.3(7)
Pd(1)N(2)C(2)	113.0(7)	O(1)N(2)C(2)	121.3(9)
Pd(1)O(2)C(13)	123.0(8)	Pd(1)O(3)C(13)	119.1(8)
O(2)C(13)O(3)	127(1)		

act as both an oxidant (in reactions with phenylhydroxylamine and azobenzene) and a reductant (for azoxy, nitro and nitroso compounds) owing to the intermediate oxidation state (+1) of its palladium atoms. Mononuclear Pt, Pd (+2) complexes K_2PtX_4 ($X = Cl$, NO_2) and $K_2Pd(NO_2)_4$ were used as both the metal atom source and oxidants in experiments with 1,2-phenylenediamine and its *N*-phenyl derivative.

Table 2
Main geometric parameters for complex IV

Bond lengths (Å)					
Pt(1)–N(1)	1.954(4)	Pt(1)–N(2)	1.989(6)	Pt(1)–N(1A)	1.954(4)
Pt(1)–N(2A)	1.989(6)	N(1)–C(1)	1.331(9)	N(2)–C(2)	1.368(7)
N(2)–C(7)	1.410(7)	C(1)–C(2)	1.443(8)	C(1)–C(6)	1.391(8)
C(2)–C(3)	1.387(10)	C(3)–C(4)	1.403(8)	C(4)–C(5)	1.407(9)
C(5)–C(6)	1.369(11)	C(7)–C(8)	1.410(10)	C(7)–C(12)	1.389(12)
C(8)–C(9)	1.380(9)	C(9)–C(10)	1.398(14)	C(10)–C(11)	1.416(12)
C(11)–C(12)	1.375(8)	Pt(2)–N(3)	1.949(5)	Pt(2)–N(4)	1.971(6)
Pt(2)–N(3A)	1.949(5)	Pt(2)–N(4A)	1.971(6)	N(3)–C(13)	1.331(9)
N(4)–C(18)	1.366(7)	N(4)–C(19)	1.433(7)	C(13)–C(14)	1.434(8)
C(13)–C(18)	1.437(8)	C(14)–C(15)	1.348(10)	C(15)–C(16)	1.401(9)
C(16)–C(17)	1.380(8)	C(17)–C(18)	1.424(10)	C(19)–C(20)	1.388(10)
C(19)–C(24)	1.381(10)	C(20)–C(21)	1.364(9)	C(21)–C(22)	1.378(11)
C(22)–C(23)	1.391(11)	C(23)–C(24)	1.401(9)		
Bond angles (°)					
N(1)–Pt(1)–N(2)	79.7(2)	N(1)–Pt(1)–N(1A)	180.0(1)		
N(2)–Pt(1)–N(1A)	100.3(2)	N(1)–Pt(1)–N(2A)	100.3(2)		
N(2)–Pt(1)–N(2A)	180.0(1)	N(1A)–Pt(1)–N(2A)	79.7(2)		
Pt(1)–N(1)–C(1)	117.4(4)	Pt(1)–N(2)–C(2)	115.6(4)		
Pt(1)–N(2)–C(7)	123.6(4)	C(2)–N(2)–C(7)	120.8(6)		
N(1)–C(1)–C(2)	114.5(5)	N(1)–C(1)–C(6)	126.7(6)		
C(2)–C(1)–C(6)	118.7(6)	N(2)–C(2)–C(1)	112.8(6)		
N(2)–C(2)–C(3)	126.3(5)	N(2)–C(7)–C(8)	120.5(7)		
N(2)–C(7)–C(12)	120.6(6)	N(3)–Pt(2)–N(4)	80.0(2)		
N(3)–Pt(2)–N(3A)	180.0(1)	N(4)–Pt(2)–N(3A)	100.0(2)		
N(3)–Pt(2)–N(4A)	100.0(2)	N(4)–Pt(2)–N(4A)	180.0(1)		
N(3A)–Pt(2)–N(4A)	80.0(2)	Pt(2)–N(3)–C(13)	117.4(4)		
Pt(2)–N(4)–C(18)	115.2(4)	Pt(2)–N(4)–C(19)	124.7(4)		
C(18)–N(4)–C(19)	120.1(6)	N(3)–C(13)–C(14)	127.4(6)		
N(3)–C(13)–C(18)	113.7(5)	N(4)–C(18)–C(13)	113.6(6)		
N(4)–C(18)–C(17)	126.9(5)	N(4)–C(19)–C(20)	119.9(6)		
N(4)–C(19)–C(24)	119.0(6)				

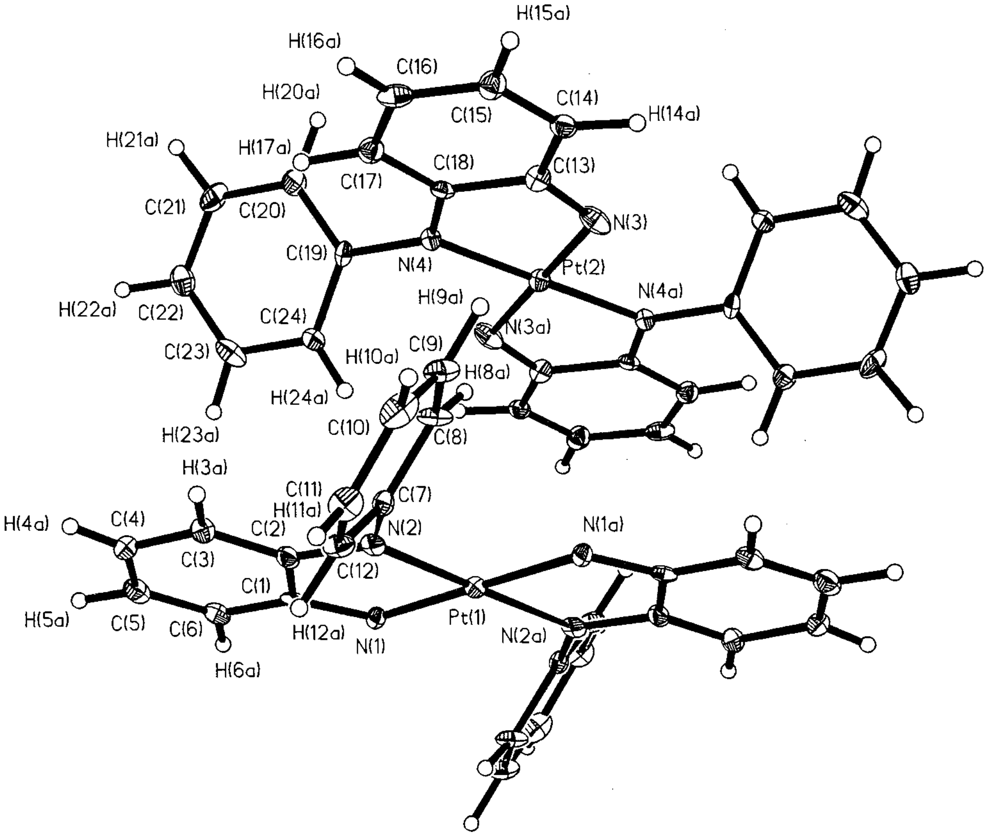


Fig. 2. Two independent molecules of complex IV.

2.2. Reactions of palladium cluster I

2.2.1. Azobenzene

Our experiments showed that cluster I does not react with azobenzene in a benzene solution neither at room temperature nor in boiling benzene [17]. In the last case, only thermal decomposition of cluster I was observed according to the following reactions [18,19]:

$$Pd_4(\mu^2-CO)_4(\mu^2-OAc)_4 \rightarrow Pd + CO_2 + (MeCO)_2.$$

$$Pd_4(\mu^2-CO)_4(\mu^2-OAc)_4 + C_6H_6 \rightarrow Pd + (MeCO)_2 + C_6H_5COOH,$$

no products from the reaction with azobenzene were found.

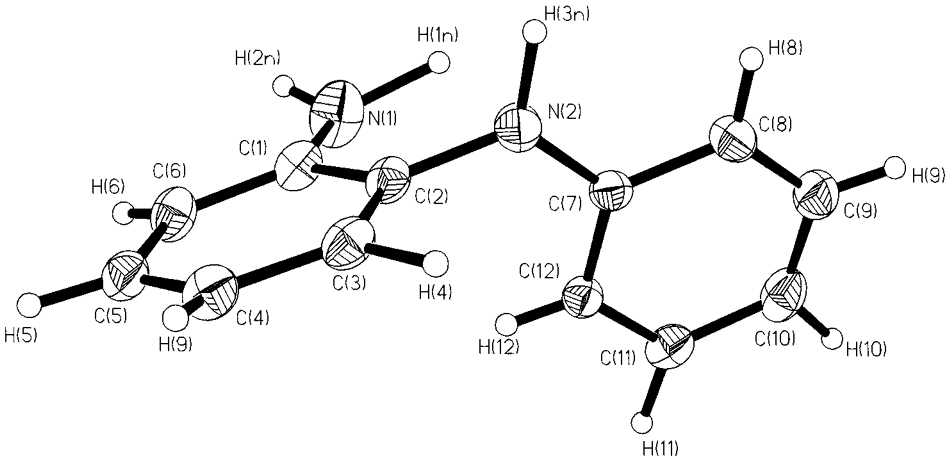


Fig. 3. Molecular structure of initial ligand *N*-phenyl-*o*-phenylenediamine.

2.2.2. Azoxybenzene

Reaction of cluster I with azoxybenzene proceeds slowly at 80°C in toluene. Only CO was observed in the gas phase, whereas neither CO_2 nor any product of the azoxybenzene conversion were found. Under more severe conditions (120°C), azoxybenzene oxidized coordinated CO to CO_2, itself being reduced to azobenzene:

$$Pd_4(\mu^2-CO)_4(\mu^2-OAc)_4 + PhN(O)=NPh \rightarrow Pd + PhN=NPh + CO_2$$

2.2.3. Phenylhydroxylamine

Cluster I readily reacts with phenylhydroxylamine: in benzene and toluene solutions, 50% conversion of I is achieved in 1 h at room temperature to form Pd metal and CO_2 and traces of CO in the gas phase; the liquid products are aniline, azobenzene, and azoxybenzene. No metal complexes but unreacted cluster I were found.

2.2.4. Nitro compounds

Reaction of carbonyl metal clusters with nitroarenes and nitroalkanes is a well-known route to nitrene complexes [10]. Our experiments showed that cluster I does not react with $PhNO_2$ and $MeNO_2$ at 20°C. Neither reduction of the nitro compounds nor other products but the formation of those resulting from the normal thermolysis of I [18] were found even at temperatures up to 80°C.

2.2.5. Nitrosobenzene

In contrast to nitro compounds, nitrosoarenes were found to actively react with cluster I in a toluene or benzene solution at 60°C evolving CO_2.

In the synthetic practice of cluster chemistry, aliphatic tertiary amine oxides are commonly used for removing CO ligands from the coordination sphere of transition metals. The tertiary amines formed coordinate only weakly to low-valent transition metals, and the free coordination vacancy just formed is used for growing the cluster metal skeleton, ligand substitution, etc. [20]. By analogy, in the case of nitrosobenzene, the PhNO molecule could be expected to donate its O atoms to the coordinated CO ligand of I to produce a nitrene ligand:

$$> Pd - CO + PhNO \rightarrow\, > Pd = NPh + CO_2. \tag{4}$$

The supposed nitrene species which could form in reaction (4) is expected to either dimerize to the corresponding azo compound or become attached to the Pd atom forming a nitrene complex.

We found that the product of the reaction between cluster I and nitrosobenzene is an air-stable brown solid, readily soluble in low-polar organic solvents, with empirical formula $PdC_{14}H_{12}O_3N_2$ (complex II): according to IR spectra, complex II does not contain coordinated carbonyl groups. ^1H NMR spectrum displayed acetate group (singlet at $\delta = 1.9$ ppm) and phenyl moiety (characteristic multiplet at $\delta = 6.8$–8.0 ppm) in the composition of complex II. These facts could have been considered as an indication to the oxidation of the coordinated CO ligands by nitrosobenzene without reducing Pd (+1), and the reaction could be tentatively described by the following equation:

$$\begin{aligned} &Pd_4(CO)_4(OAc)_4 + 4PhNO \\ &\quad \rightarrow 4CO_2 + 4[Pd(OAc)(PhN)]. \end{aligned} \tag{5}$$

However, the elemental analysis data of complex II corresponds to a compound containing one acetato group and one nitrosobenzene molecule, along with a nitrene moiety, PhN, per one Pd atom, ‘‘Pd(OAc)(PhN)(PhNO)’’.

Table 3
Main geometric parameters for the molecule of *N*-phenyl-*o*-phenylenediamine

Bond lengths (Å)					
N(1)–C(1)	1.384(5)	N(1)–H(1N)	0.960(52)	N(1)–H(2N)	0.776(46)
N(2)–C(2)	1.419(3)	N(2)–C(7)	1.387(3)	N(2)–H(3N)	0.852(39)
C(1)–C(2)	1.397(4)	C(1)–C(6)	1.395(4)	C(2)–C(3)	1.382(4)
C(3)–C(4)	1.381(4)	C(4)–C(5)	1.374(4)	C(5)–C(6)	1.365(4)
C(7)–C(8)	1.395(4)	C(7)–C(12)	1.390(4)	C(8)–C(9)	1.368(4)
C(9)–C(10)	1.374(5)	C(10)–C(11)	1.374(4)	C(11)–C(12)	1.383(4)
Bond angles (°)					
C(2)–N(2)–C(7)	124.0(2)	N(1)–C(1)–C(2)	120.9(3)		
N(1)–C(1)–C(6)	121.1(3)	C(2)–C(1)–C(6)	117.9(2)		
N(2)–C(2)–C(1)	119.9(2)	N(2)–C(2)–C(3)	120.4(2)		
N(2)–C(7)–C(12)	121.8(2)				

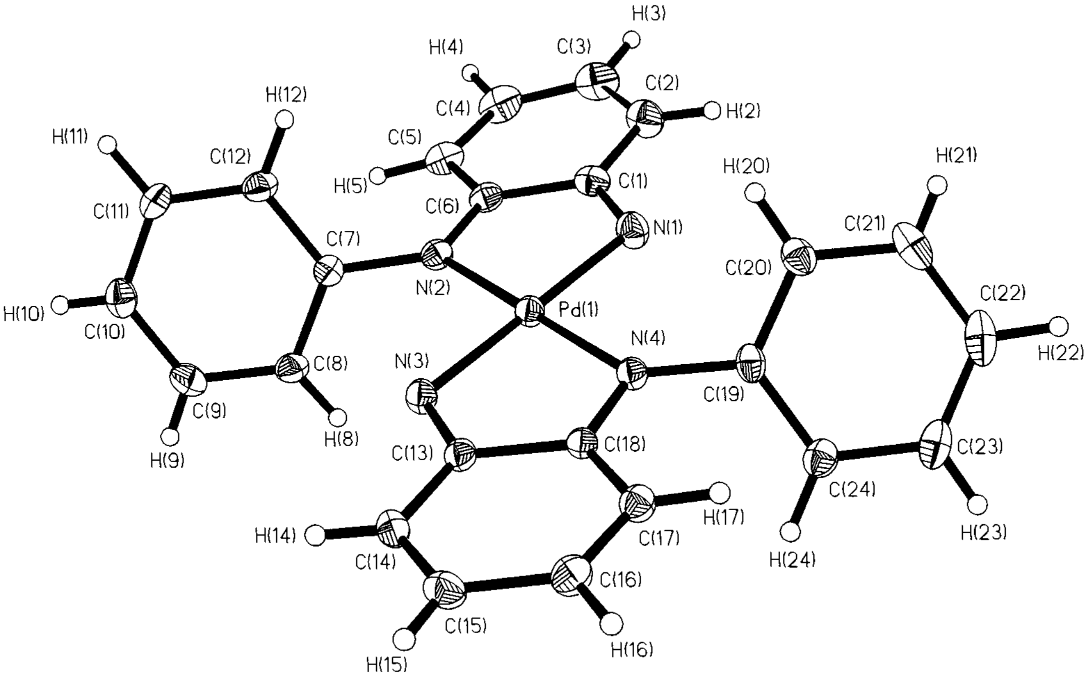
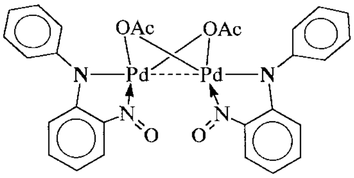


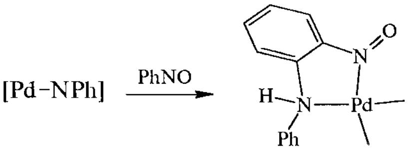
Fig. 4. Molecular structure of complex V.

The single-crystal X-ray structural study of complex II [21] confirmed the complete elimination of the coordinated CO groups from the initial cluster I and the presence of acetato groups in II (Fig. 1, Table 1). However, neither coordinated nitrene nor nitrosobenzene were found in this molecule. Instead, the complex contains a chelating amido ligand, phenyl-*o*-nitrosophenylamide:

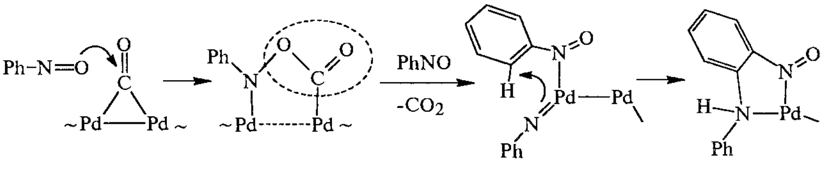


II

The formation of this ligand can be rationalized as the result of insertion of the intermediate nitrene ligand to the C–H bond of the nitrosobenzene molecule



The reaction can be speculated as proceeding via the following scheme



which includes concerted elimination of CO_2 and formation of coordinated nitrene species followed by coordination of another nitrosobenzene molecule; the nitrene ligand then inserts into the C–H bond of the phenyl ring of nitrosobenzene molecule producing an amino complex. Phenyl-*o*-nitrosophenylamine, which could be anticipated as the product of the reaction between the nitrene moiety and nitrosobenzene, undergoes deprotonation to form a coordinated amide.

According to the X-ray data (Fig. 1, Table 1), complex II contains two single-charged anionic ligands, OAc- and phenyl-*o*-nitrosophenylamide, per each palladium atom. It should be emphasized that no protons attached to the O or N atoms of phenyl-*o*-nitrosophenylamide were detected by ^{1}H NMR and X-ray studies. Hence, the metal atoms should be treated as being in the formal oxidation state (+2), although the distance between the two palladium atoms (2.840 Å) suggests some metal–metal interaction, which is not typical of Pd (+2) compounds.

Therefore, palladium (+1) is oxidized to palladium (+2), carbon monoxide is oxidized to carbon dioxide, and the redox transformations of nitrosobenzene lead successively to the elusive nitrene and observable amido ligands.

In addition to complex II, azoxybenzene was found in the reaction products in 10–15% yield based on the CO_2 formed. The formation of azoxybenzene can be considered as a result of the reaction between the intermediate nitrene species and nitrosobenzene:

$$[\mathrm{Pd}=\mathrm{NPh}] + \mathrm{PhNO} \rightarrow \mathrm{PhN(O)NPh} + [\mathrm{Pd}].$$

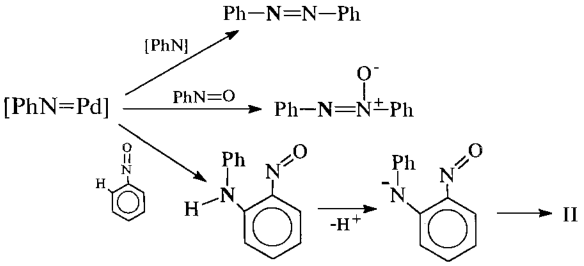
Among the reaction products, small amounts of azobenzene and aniline were also observed. Azobenzene can be

Table 4
Main geometric parameters for the molecule of V

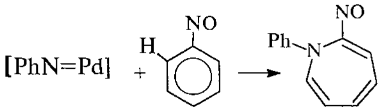
Bond lengths (Å)					
Pd(1)–N(1)	1.970(3)	Pd(1)–N(2)	1.996(3)	Pd(1)–N(3)	1.969(3)
Pd(1)–N(4)	1.995(3)	N(1)–C(1)	1.335(5)	N(2)–C(6)	1.352(4)
N(2)–C(7)	1.426(3)	N(3)–C(13)	1.345(5)	N(4)–C(18)	1.357(4)
N(4)–C(19)	1.422(3)	C(1)–C(2)	1.413(5)	C(1)–C(6)	1.439(4)
Pd(2)–N(5)	1.965(2)	Pd(2)–N(6)	2.005(3)	Pd(2)–N(5A)	1.965(2)
Pd(2)–N(6A)	2.005(3)	N(5)–C(25)	1.336(4)	N(6)–C(30)	1.359(3)
N(6)–C(31)	1.420(4)	C(25)–C(26)	1.411(4)	C(25)–C(30)	1.432(5)
Pd(3)–N(7)	1.993(3)	Pd(3)–N(8)	1.975(3)	Pd(3)–N(7A)	1.993(3)
Pd(3)–N(8A)	1.975(3)	N(7)–C(42)	1.352(4)	N(7)–C(43)	1.422(5)
N(8)–C(37)	1.345(4)	C(37)–C(38)	1.418(4)	C(37)–C(42)	1.439(5)
Bond angles (°)					
N(1)–Pd(1)–N(2)	80.3(1)	N(1)–Pd(1)–N(3)	179.6(1)		
N(2)–Pd(1)–N(3)	100.0(1)	N(1)–Pd(1)–N(4)	99.3(1)		
N(2)–Pd(1)–N(4)	179.1(1)	N(3)–Pd(1)–N(4)	80.4(1)		
Pd(1)–N(1)–C(1)	116.1(2)	Pd(1)–N(2)–C(6)	114.4(2)		
Pd(1)–N(2)–C(7)	126.3(2)	C(6)–N(2)–C(7)	119.3(3)		
Pd(1)–N(3)–C(13)	115.8(2)	Pd(1)–N(4)–C(18)	114.9(2)		
Pd(1)–N(4)–C(19)	123.9(2)	C(18)–N(4)–C(19)	120.7(3)		
N(1)–C(1)–C(2)	126.2(3)	N(1)–C(1)–C(6)	114.4(3)		
N(2)–C(6)–C(1)	114.7(3)	N(2)–C(6)–C(5)	126.3(2)		
C(1)–C(6)–C(5)	119.0(3)	N(2)–C(7)–C(8)	120.5(3)		
N(2)–C(7)–C(12)	119.7(2)	N(3)–C(13)–C(14)	126.2(2)		
N(3)–C(13)–C(18)	114.8(3)	N(4)–C(18)–C(13)	114.1(3)		
N(4)–C(18)–C(17)	127.6(2)	N(4)–C(19)–C(20)	119.8(3)		
N(4)–C(19)–C(24)	121.2(2)	N(5)–Pd(2)–N(6)	79.9(1)		
N(5)–Pd(2)–N(5A)	180.0(1)	N(6)–Pd(2)–N(5A)	100.1(1)		
N(5)–Pd(2)–N(6A)	100.1(1)	N(6)–Pd(2)–N(6A)	180.0(1)		
N(5A)–Pd(2)–N(6A)	79.9(1)	Pd(2)–N(5)–C(25)	116.6(2)		
Pd(2)–N(6)–C(30)	114.5(2)	Pd(2)–N(6)–C(31)	125.3(2)		
C(30)–N(6)–C(31)	120.1(3)	N(5)–C(25)–C(26)	126.6(3)		
N(5)–C(25)–C(30)	114.7(2)	N(6)–C(30)–C(25)	114.3(3)		
N(6)–C(30)–C(29)	127.0(3)	C(25)–C(30)–C(29)	118.5(2)		
N(6)–C(31)–C(32)	119.7(3)	N(6)–C(31)–C(36)	121.5(3)		
N(7)–Pd(3)–N(8)	80.5(1)	N(7)–Pd(3)–N(7A)	180.0(1)		
N(8)–Pd(3)–N(7A)	99.5(1)	N(7)–Pd(3)–N(8A)	99.5(1)		
N(8)–Pd(3)–N(8A)	180.0(1)	N(7A)–Pd(3)–N(8A)	80.5(1)		
Pd(3)–N(7)–C(42)	114.8(2)	Pd(3)–N(7)–C(43)	124.7(2)		
C(42)–N(7)–C(43)	120.4(3)	Pd(3)–N(8)–C(37)	115.2(3)		
N(8)–C(37)–C(38)	125.5(4)	N(8)–C(37)–C(42)	115.2(3)		
N(7)–C(42)–C(37)	114.1(3)	N(7)–C(42)–C(41)	127.8(3)		
N(7)–C(43)–C(44)	120.4(3)	N(7)–C(43)–C(48)	121.2(3)		

considered as the product of coupling of the nitrene ligands, and aniline forms through the reduction of the nitrene ligands.

The formation of the amide ligand and above-mentioned organic compounds (viz., azobenzene, azoxybenzene, and aniline) gives evidence for the participation of a nitrene species [= NPh] as a reaction intermediate:

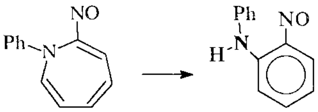


The pathway leading to complex II seems to include the intermediate product of insertion of the nitrogen atom into the aromatic ring, phenylnitrosoazepine:



which is typical of the reactions of free nitrene species.

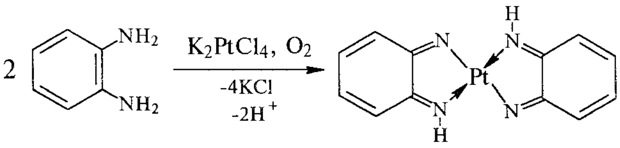
According to data [22], the azepine derivatives are fairly unstable to convert into the corresponding amine.



2.3. Reactions of mononuclear Pt (+2) and Pd (+2) complexes

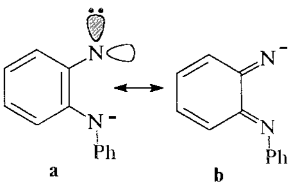
2.3.1. Reaction of [PtCl$_4$]$^{2-}$with o-phenylenediamine

1,2-phenylenediamine is known to be readily oxidized into a quinomide species by alkaline solutions of K$_2$PtCl$_4$ in air, forming the bis-chelate mononuclear complex Pt[(NH)(N)C$_6$H$_4$]$_2$ (III) as the reaction product [23]:



III

Due to the fairly complicated character of this reaction and low solubility of the phenylenediamine-derived complexes, in this work the *N*-phenyl substituted analogue of phenylenediamine was used as a ligand source.



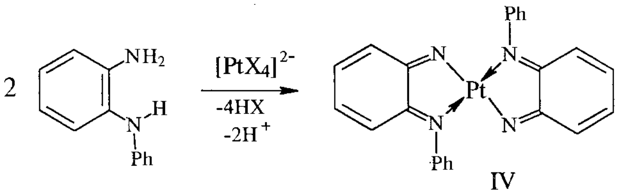
Scheme 1. The nitrene (**a**)/imido (**b**) resonance in description of the ligand structure.

2.3.2. Reaction of $[PdX_4]^{2-}$ and $[PtX_4]^{2-}$ with N-phenyl-o-phenylenediamine

The reaction of $K_2Pt(NO_2)_4$ with *N*-phenyl-*o*-phenylenediamine in a MeCN–H_2O solution was found to form the diamagnetic mononuclear complex $Pt[(NPh)(N)C_6H_4]_2$ (IV). The same complex was obtained via the reaction of K_2PtCl_4 with *N*-phenyl-*o*-phenylenediamine in the presence of LiOH.

According to the X-ray data (Fig. 2, Table 2), the molecule IV contains the Pt(+2) atom in a square-planar environment of four nitrogen atoms. The Pt–N bond lengths (1.954(4)–1.989(6) Å) and angle N–Pt–N (79.7(2)–80.0°) in two independent molecules are averaged and very close to the values observed in III (1.95(2)–1.99(2) Å [23]). However, the N = C bonds of the quinoide ligands in IV (1.331(9)–1.368(7) Å) are somewhat longer than in III (1.31(3) Å) but noticeably shorter than N–Ph (C–N 1.410(7)–1.433(7) Å). It should be noted that the significance of the Pt–N bonds in III and IV from normal values for the Pt(+2) complexes with diamine ligands (2.03–2.07 Å [24,25]), and the redistribution of electron density in the N_2C_2 fragment of the ligand (the C–C distance in IV is equal to 1.443(8)–1.437(8) Å) point to a high delocalization of electrons within the PtN_2C_2 system, including the participation of lone pairs of formally nonequivalent nitrogen atoms.

Since the structural data for the *N*-phenyl-*o*-phenylenediamine molecule were not found in the literature, its structure was determined in this work by a single-crystal X-ray study. The data obtained (Fig. 3, Table 3) allow one to immediately compare the geometries of the initial ligand and those in complexes III and IV. The changes in the ligand geometry (cf. Figs. 2 and 3) attest that the ligand is deprotonated to form *o*-quinoimide anion upon its reaction with the Pt(+2) complexes:



The palladium complex $K_2Pd(NO_2)_4$ reacts with *N*-phenyl-*o*-phenylenediamine in a similar manner as with the platinum (+2) complexes. In the presence of LiOH, diamagnetic complex $Pd[(NPh)(N)C_6H_4]_2$ (V) was obtained. Complex V is more sensitive to protonation and decomposes during column chromatography on silica gel. It was

Table 5
Main geometric parameters for binuclear complex VII

Bond lengths (Å)					
Pt(1)–Pt(1)	3.260(1)	Pt(1)–N(1)	1.962(4)	Pt(1)–N(2)	2.019(5)
Pt(1)–N(3)	1.964(5)	Pt(1)–N(4)	2.024(4)	N(1)–C(1)	1.323(8)
N(2)–C(6)	1.322(7)	N(2)–C(13)	1.453(6)	N(3)–C(7)	1.321(8)
N(4)–C(12)	1.326(8)	N(4)–C(19)	1.456(6)	C(1)–C(2)	1.434(8)
C(1)–C(6)	1.459(7)	C(2)–C(3)	1.344(1 0)	C(3)–C(4)	1.455(8)
C(4)–C(5)	1.334(9)	C(5)–C(6)	1.413(9)	C(7)–C(8)	1.419(9)
C(7)–C(12)	1.464(7)	C(8)–C(9)	1.367(1 0)	C(9)–C(10)	1.439(8)
C(10)–C(11)	1.315(10)	C(11)–C(12)	1.429(9)	C(13)–C(14)	1.368(10)
C(13)–C(18)	1.362(11)	C(14)–C(15)	1.368(7)	C(15)–C(16)	1.365(12)
C(16)–C(17)	1.348(12)	C(17)–C(18)	1.399(8)	C(19)–C(20)	1.381(11)
C(19)–C(24)	1.372(9)	C(21)–C(22)	1.388(8)	C(21)–C(22)	1.357(11)
C(22)–C(23)	1.356(12)	C(23)–C(24)	1.395(7)	S(1)–O(1)	1.344(8)
S(1)–O(2)	1.418(9)	S(1)–O(3)	1.366(5)	S(1)–C(25)	1.736(10)
F(1)–C(25)	1.223(8)	F(2)–C(25)	1.291(13)	F(3)–C(25)	1.315(15)
Bond angles (°)					
N(1)–Pt(1)–N(2)	79.1(2)	N(1)–Pt(1)–N(3)	94.5(2)		
N(2)–Pt(1)–N(3)	171.9(2)	N(1)–Pt(1)–N(4)	172.7(2)		
N(2)–Pt(1)–N(4)	107.0(2)	N(3)–Pt(1)–N(4)	79.1(2)		
Pt(1)–N(1)–C(1)	117.2(3)	Pt(1)–N(2)–C(6)	115.6(3)		
Pt(1)–N(2) C(13)	128.0(4)	C(6)–N(2)–C(13)	116.2(5)		
Pt(1)–N(3)–C(7)	117.4(3)	Pt(1)–N(4)–C(12)	115.5(3)		
Pt(1)–N(4)–C(19)	128.1(4)	C(12)–N(4)–C(19)	116.4(4)		
N(1)–C(1)–C(2)	126.5(5)	N(1)–C(1)–C(6)	114.3(5)		

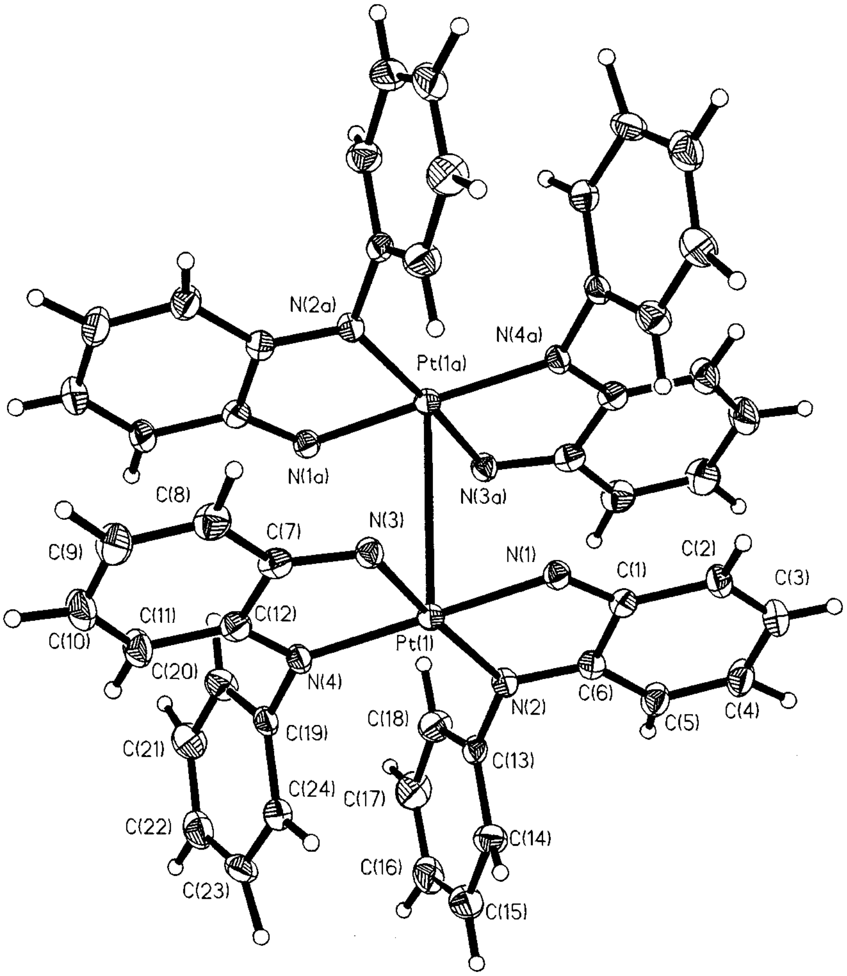


Fig. 5. Dinuclear dication of VII.

separated by extraction with hydrocarbons from the reaction mixture. The X-ray study showed that the geometrical parameters of complex V are very close to those of the platinum analog IV (Fig. 4, Table 4).

Analogously to the Pt atom in IV, the palladium atom in V has a square-planar environment of two *N*-donor ligands in the *o*-quinoide form (Pd–N 1.965(3)–2.005(3) Å, N = C 1.335(5)–1.357(4) Å, N–C(Ph) 1.412(5)–1.426 Å, angle N–Pd–N 79.9(1)–80.5(1)° in three independent molecules). In both complexes IV and V, the Ph substituents formally oriented *trans* and, hence, point toward the metal center due to steric hindrance.

Examination of the ligand geometry in both complexes and that of the free diamine (cf. Figs. 2–4) points unequivocally to the fact that quinoimide structure **b** is much more pronounced than nitrene structure **a** among the two main resonance structures of the ligand (Scheme 1).

Hence, the expected labile nitrene species is stabilized in this case due to the formation of chelate *ortho*-quinoimide structure of the ligand.

2.4. Oxidation of bis-quinonimine Pt complexes by Ag^+

Complex III is known to be readily oxidised by Ag^+ ion under the action of 1 equivalent of AgO_3SCF_3 per Pt atom in the presence of a small amount of acetone (2–5 ml per 1 mmol of reagents) [26]. The reaction results in the

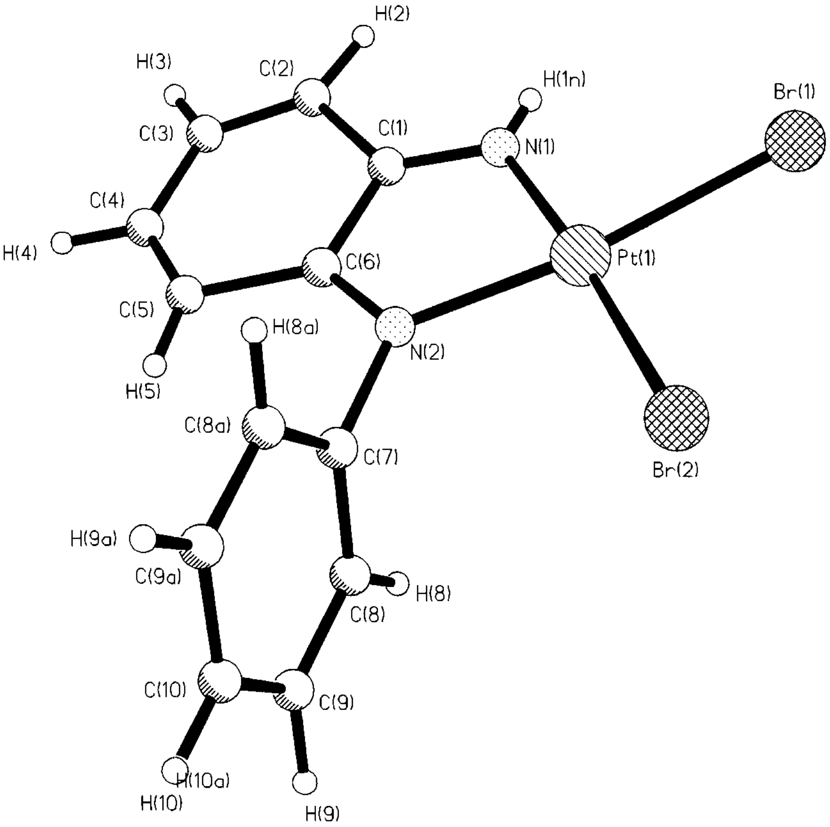
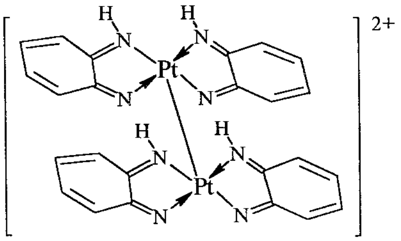


Fig. 6. Molecular structure of complex VIII.

elimination of one electron from the metal orbital to form a dinuclear Pt (+3) (VI) complex with fairly long Pt–Pt bond (3.031 Å) between two metal-bis-chelate moieties [26]:



VI

When the *N*-phenyl derivative (complex IV) was used as a starting compound in the reaction with AgO_3SCF_3, an analogous diamagnetic Pt (+3) cationic complex $\{Pt_2[(NPh)(N)C_6H_4]_4\}[O_3SCF_3]_2$ (VII) was obtained. According to the X-ray data (Fig. 5, Table 5), dication VII has a longer Pt–Pt bond (3.260(1) Å) as compared to that in complex VI.

This effect is apparently caused by nonvalent intramolecular interaction between the bis-chelate fragments of the neighbouring Pt(+3) atoms having an eclipsed conformation. Moreover, the Ph-substituents of the ligands coordinated to each Pt atom are positioned in a *cis*-configuration, in contrast to complex IV which contains nonbonding M–M distance (Pt...Pt 4.8 Å). Such steric constrains lead to slight protruding of the Pt atoms out of the PtN_4 plane (approx. 0.26 Å) and the sliding of the mononuclear bis-chelate fragments at the opposite sides to result in the nonorthogonal angle between the PtN_4 plane and the Pt–Pt bond (angle PtN_4/Pt–Pt 113.2(2)°). The Pt–N bonds in VII vary in length due to the same reason (Pt–N 1.962(4) and 1.964(5) Å; Pt–N(Ph) 2.024(4) Å, angle N–Pt–N(Ph) 79.1(2)°); however, the ligands remain a quinoide structure (C=N 1,321(8) Å and 1.326(8) Å, C–C 1.459(7) and 1.464(7) Å in the PtN_2C_2 cycle).

$CuBr_2$ also reacts with complex IV. The reaction proceeds only in the presence of a small amount of water. The reaction of IV with anhydrous $CuBr_2$ in an acetone solution containing 3–5% of H_2O afforded the diamagnetic

Table 6
Main geometric parameters for complex VIII

Bond lengths (Å)					
Pt(1)–Br(1)	2.414(2)	Pt(1)–Br(2)	2.412(3)	Pt(1)–N(1)	1.901(14)
Pt(1)–N(2)	1.980(15)	N(1)–C(1)	1.249(24)	N(1)–H(1N)	0.674(35)
N(2)–C(6)	1.290(23)	N(2)–C(7)	1.505(21)	C(1)–C(2)	1.540(28)
C(1)–C(6)	1.405(24)	C(2)–C(3)	1.251(28)	C(3)–C(4)	1.359(29)
C(4)–C(5)	1.211(28)	C(5)–C(6)	1.510(26)	C(7)–C(8)	1.383(16)
C(7)–C(8A)	1.383(16)	C(8)–C(9)	1.357(21)	C(9)–C(10)	1.377(18)
C(10)–C(9A)	1.377(18)				
Bond angles (°)					
Br(1)–Pt(1)–Br(2)	91.3(1)	Br(1)–Pt(1)–N(1)	93.1(4)		
Br(2)–Pt(1)–N(1)	175.5(4)	Br(1)–Pt(1)–N(2)	170.5(4)		
Br(2)–Pt(1)–N(2)	98.2(4)	N(1)–Pt(1)–N(2)	77.4(6)		
Pt(1)–N(1)–C(1)	119.1(13)	Pt(1)–N(1)–H(1N)	124.9(29)		
C(1)–N(1)–H(1N)	116.0(31)	Pt(1)–N(2)–C(6)	116.1(11)		
Pt(1)–N(2)–C(7)	125.0(12)	C(6)–N(2)–C(7)	118.9(15)		
N(1)–C(1)–C(2)	128.3(17)	N(1)–C(1)–C(6)	115.2(17)		
N(2)–C(6)–C(1)	112.3(16)	N(2)–C(6)–C(5)	129.7(15)		
N(2)–C(7)–C(8)	118.9(8)	N(2)–C(7)–C(8A)	118.9(8)		

mononuclear Pt (+2) complex $\mathrm{Pt[(NPh)(NH)C_6H_4]Br_2}$ (VIII), which contains the protonated quinoimide ligand. According to the X-ray data (Fig. 6, Table 6), the Pt atom in the molecule of VIII is bound with two bromine (Pt–Br 2.412(3) and 2.414(2) Å; angle Br–Pt–Br 91.3°) and two N atoms of the amido and imido groups (Pt–N(Ph 1.980(15) Å) and Pt–N(H) 1.901(14) Å) of the ligand ((Ph)N=C 1.290(23) Å, (H)N=C 1.249(24) Å, C–C 1.405(24) Å, N–C(Ph) 1.505(21) Å, N–H 0.67(4) Å) which is also in the quinoimide form. The formation of such a ligand, which is unstable as a free molecule, in the reaction with $\mathrm{CuBr_2}$ points to a tendency of the N atom in IV to be attacked by

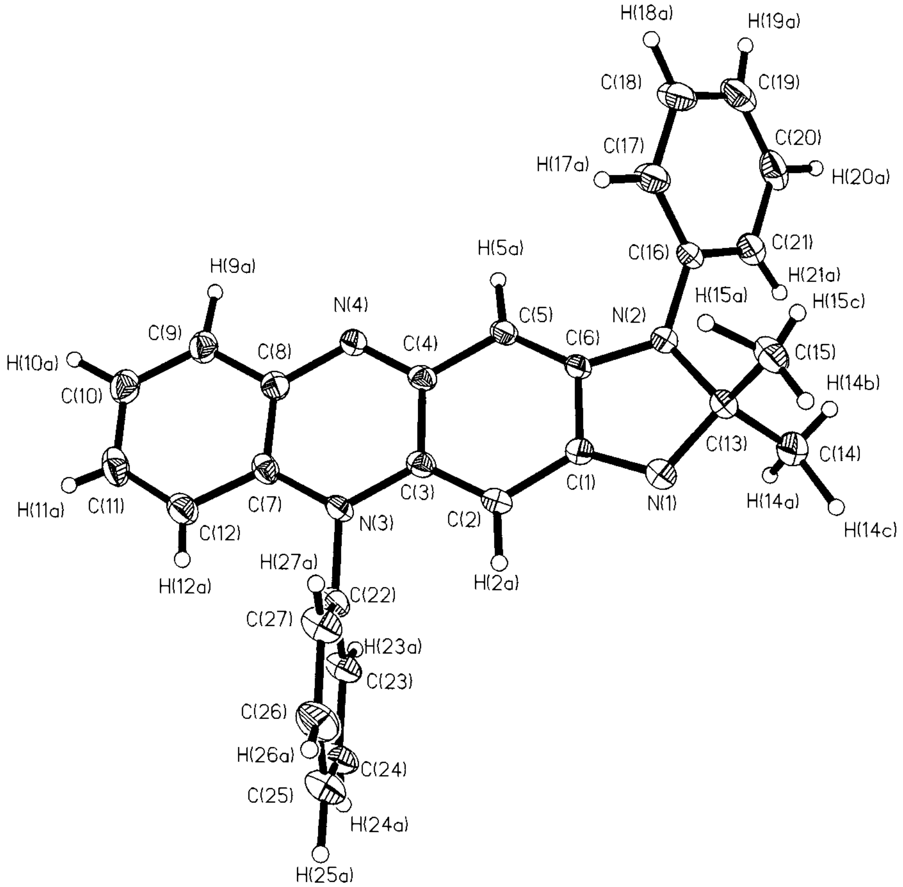
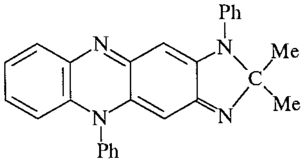


Fig. 7. Molecular structure of compound IX.

the proton of the water molecule activated by the copper atom. In contrast to this, the action of water on complex IV in the absence of copper(+2) does not affect the platinum complex.

An unusual activation of the N atom of the quinoimide ligand was observed on removal of one electron from complex IV. Further oxidation of IV by Ag^+ initiated unexpected transformation of the organic ligands. The reaction of IV with a large excess of AgO_3SCF_3 (5–6 equivalents) in acetone proceeded through the formation of complex VII (TLC monitoring) and eventually produced the heterotricyclic compound of a quinoxaline series (IX)



IX

which is built up of two ligand molecules and the CMe_2 fragment of the acetone molecule. When using VII as the initial reagent in this reaction, a smaller amount of the oxidant (3–4 equivalents of AgO_3SCF_3) is required. The X-ray investigation of IX (Fig. 7, Table 7) showed that the nitrogen atoms of one ligand are connected with two 4- and

Table 7
Main geometric parameters for compound IX

Bond lengths (Å)					
N(1)–C(1)	1.303(6)	N(1)–C(13)	1.453(5)	N(2)–C(6)	1.362(6)
N(2)–C(13)	1.506(6)	N(2)–C(16)	1.424(4)	N(3)–C(3)	1.385(5)
N(3)–C(7)	1.395(6)	N(3)–C(22)	1.447(4)	N(4)–C(4)	1.312(6)
N(4)–C(8)	1.387(5)	C(1)–C(2)	1.434(6)	C(1)–C(6)	1.456(5)
C(2)–C(3)	1.364(7)	C(3)–C(4)	1.471(5)	C(4)–C(5)	1.430(6)
C(5)–C(6)	1.341(7)	C(7)–C(8)	1.410(5)	C(7)–C(12)	1.398(6)
C(8)–C(9)	1.399(7)	C(9)–C(10)	1.372(7)	C(10)–C(11)	1.368(6)
C(11)–C(12)	1.357(8)	C(13)–C(14)	1.526(9)	C(13)–C(15)	1.521(5)
C(16)–C(17)	1.368(7)	C(16)–C(21)	1.383(7)	C(17)–C(18)	1.393(6)
C(18)–C(19)	1.355(9)	C(19)–C(20)	1.349(9)	C(20)–C(21)	1.376(6)
C(22)–C(23)	1.387(6)	C(22)–C(27)	1.344(5)	C(23)–C(24)	1.390(6)
C(24)–C(25)	1.369(6)	C(25)–C(26)	1.381(8)	C(26)–C(27)	1.391(6)

Bond angles (°)			
C(1)–N(1)–C(13)	108.4(3)	C(6)–N(2)–C(13)	109.2(3)
C(6)–N(2)–C(16)	123.7(4)	C(13)–N(2)–C(16)	125.2(4)
C(3)–N(3)–C(7)	121.7(3)	C(3)–N(3)–C(22)	118.4(4)
C(7)–N(3)–C(22)	119.7(3)	C(4)–N(4)–C(8)	118.7(3)
N(1)–C(1)–C(2)	127.6(3)	N(1)–C(1)–C(6)	113.3(4)
C(2)–C(1)–C(6)	119.1(4)	C(1)–C(2)–C(3)	118.4(3)
N(3)–C(3)–C(2)	122.1(3)	N(3)–C(3)–C(4)	115.8(4)
C(2)–C(3)–C(4)	122.1(4)	N(4)–C(4)–C(3)	123.6(4)
N(4)–C(4)–C(5)	118.1(3)	C(3)–C(4)–C(5)	118.3(4)
C(4)–C(5)–C(6)	119.4(3)	N(2)–C(6)–C(1)	105.0(4)
N(2)–C(6)–C(5)	132.4(3)	N(3)–C(7)–C(8)	118.3(4)
N(3)–C(7)–C(12)	123.4(3)	C(8)–C(7)–C(12)	118.3(4)
N(4)–C(8)–C(7)	121.9(4)	N(4)–C(8)–C(9)	119.3(3)
C(7)–C(8)–C(9)	118.9(4)	C(8)–C(9)–C(10)	121.5(4)
C(9)–C(10)–C(11)	118.5(5)	C(10)–C(11)–C(12)	122.3(5)
C(7)–C(12)–C(11)	120.5(4)	N(1)–C(13)–N(2)	103.9(4)
N(1)–C(13)–C(14)	108.4(4)	N(2)–C(13)–C(14)	112.0(3)
N(1)–C(13)–C(15)	109.9(3)	N(2)–C(13)–C(15)	110.8(4)
C(14)–C(13)–C(15)	111.6(5)	N(2)–C(16)–C(17)	119.9(4)
N(2)–C(16)–C(21)	121.1(4)	C(17)–C(16)–C(21)	118.9(3)
C(16)–C(17)–C(18)	120.0(5)	C(17)–C(18)–C(19)	119.9(5)
C(18)–C(19)–C(20)	120.7(4)	C(19)–C(20)–C(21)	120.2(5)
C(16)–C(21)–C(20)	120.3(5)	N(3)–C(22)–C(23)	117.3(3)
N(3)–C(22)–C(27)	121.2(4)	C(23)–C(22)–C(27)	121.5(4)
C(22)–C(23)–C(24)	118.4(3)	C(23)–C(24)–C(25)	120.1(5)
C(24)–C(25)–C(26)	120.8(5)	C(25)–C(26)–C(27)	118.7(4)
C(22)–C(27)–C(26)	120.4(4)		

Table 8
Data collection and processing parameters for investigated compounds

Compound	II	V	*N*-phenyl-*o*-phenylenediamine
Formula	$C_{16}H_{24}N_4O_4Pd_2CH_2Cl_2$	$C_{24}H_{18}N_4Pd$	$C_{12}H_{12}N_2$
Mol. wt.	810.2	468.9	184.3
Color and habit	Brown prism	Black-blue prism	White prism
Space group	$C2/c$	P-1	$P2_1/n$
a (Å)	6.801(4)	12.267(4)	10.818(4)
b (Å)	29.68(2)	12.321(3)	5.864(2)
c (Å)	15.078(9)	14.793(4)	15.721(4)
α (°)	90	82.90(2)	90
β (°)	92.36(5)	76.96(2)	96.09(2)
γ (°)	90	66.69(2)	90
V (Å^3)	3041(3)	1998.9(9)	991.6(5)
Z	4	4[a]	4
ρ_{calcd}(g cm^{-1})	1.770	1.558	1.234
Abs. coefficient (cm^{-1})	14.1	9.46	0.74
Scan type	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
Scan speed	Variable, 2.02–14.65	Variable, 2.02–14.65	Variable, 2.02–14.65
Scan width (°)	1.80	1.60	1.80
2θ range (°)	4–60	2–52	2–56
Unique data	2499	7899	1898
Reflections observed	2119	x6084	1030
Weighting scheme	Unit weights	$w^{-1}=\sigma^2(F)+0.0003F^2$	$w^{-1}=\sigma^2(F)+0.0205F^2$
GOF	0.96	1.80	0.49
R	0.054	0.032	0.058
R_w	0.053	0.042	0.073
Residual extrema in final diff. Map (e Å^{-3})	0.79–0.90	0.61–0.86	0.56–0.04

Compound	IV	VII	VIII
Formula	$C_{24}H_{18}N_4Pt$	$[C_{48}H_{36}N_8Pt_2]2[CF_3O_3S]\ 2C_6H_6$	$C_{12}H_{16}Br_2N_2Pt$
Mol. wt.	557.5	1569.4	543.2
Color and habit	Black-blue prism	Brown prism	Black prism
Space group	P-1	P-1	$P2_1/m$
a (A)	9.668(2)	11.755(2)	10.496(2)
b (A)	10.342(3)	12.035(2)	6.775(2)
c (A)	11.808(2)	12.267(2)	11.291(2)
α (°)	73.83(2)	94.97(3)	90
β (°)	75.81(2)	107.12(3)	91.64(3)
γ (°)	62.60(2)	112.99(3)	90
V (A^3)	997.2(3)	1486.1(9)	802.6(4)
Z	2[b]	1	2
ρ_{calcd}(g cm^{-1})	1.857	1.754	2.248
Abs. coeff. (cm^{-1})	70.5	48.5	137.0
Scan type	$\theta-2\theta$	$\kappa-2\theta$	$\kappa-2\theta$
Scan speed	Variable, 2.02–14.65	Variable, 2.00–29.30	Variable, 2.00–29.30
Scan width (°)	1.60	1.20	1.20
2θ range (°)	3–58	4–54	3–55
Unique data	4884	5822	1662
Reflections observed	3056	4603	1285
Weighting scheme	$w^{-1}=\sigma^2(F)+0.2054F^2$	$w^{-1}=\sigma^2(F)+0.0005F^2$	$w^{-1}=\sigma^2(\mathrm{F})+0.0061F^2$
GOF	0.20	1.16	1.04
R	0.067	0.036	0.063
R_w	0.087	0.055	0.087
Residual extrema in final diff. Map (e Å^{-3})	3.25– 3.63	1.19– 0.67	1.12– 1.15

Compound	IX
Formula	$C_{27}H_{24}N_4$
Mol. Wt	324
Color and habit	Orange prism
Space group	R-3

Table 8 (continued)

Compound	IX
a (Å)	32.118(5)
b (Å)	32.118(5)
c (Å)	11.919(5)
α (°)	
β (°)	
γ (°)	
V (Å^3)	10650(5)
Z	12
ρ_{calcd}(g cm^{-1})	1.130
Abs. coeff. (cm^{-1})	0.7
Scan type	k–2θ
Scan speed	Variable, 2.00–29.30
Scan width (°)	1.20
2θ range (°)	4–55
Unique data	4090
Reflections observed	2024
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0053F^2$
GOF	1.08
R	0.062
R_w	0.087
Residual extrema in final diff. Map (e Å^{-3})	0.46– 0.25

[a] Three independent molecules in unit cell (one in common and two in special positions).

[b] Two independent molecules in special positions of unit cell.

5-positioned carbon atoms of the phenylene ring of the second ligand (N=C 1.312(6) Å, (Ph)N–C 1.385(5) Å). In addition, the N-atoms of the second ligand are attached to the carbon atom of the CMe_2 group derived from acetone (N–C, 1.506(6) Å, (Ph)N–C 1.453(5) Å). In the absence of the oxidant, IV or VII does not react with acetone.

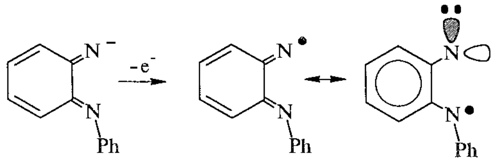
At the first glance, the ligand resonance structure **b** (see Scheme 1) is readily suited to undergoing the Diels-Alder reaction. However, the formation of triheterocyclic compound IX cannot be rationalized within a scheme involving a

Table 9
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^2$) for II

Atom	X	Y	Z	U(eq)[a]
Pd(1)	2910(1)	1212	2451(1)	4.02(2)
N(1)	226(1)	851(3)	1383(6)	4.0(3)
N(2)	260(1)	623(3)	3034(6)	4.0(3)
O(1)	273(1)	555(3)	3844(5)	5.7(3)
C(1)	227(2)	415(4)	1526(7)	4.0(4)
C(2)	247(1)	272(3)	2445(7)	3.6(4)
C(3)	249(1)	−189(4)	2659(7)	4.3(4)
C(4)	231(2)	−512(4)	2023(9)	5.3(4)
C(5)	204(2)	−376(4)	1125(8)	5.1(4)
C(6)	203(2)	66(4)	873(7)	5.0(4)
C(7)	204(2)	1039(4)	508(7)	4.1(3)
C(8)	44(2)	1297(4)	293(8)	5.2(4)
C(9)	23(2)	1489(5)	−54(1)	7.1(6)
C(10)	165(3)	1428(5)	−1141(9)	6.9(5)
C(11)	324(2)	1175(5)	−933(8)	6.6(5)
C(12)	349(2)	980(5)	−105(8)	6.2(5)
O(2)	354(1)	1587(3)	3586(6)	5.4(3)
O(3)	339(1)	1786(3)	1712(5)	5.2(3)
C(13)	492(2)	1818(4)	1305(8)	5.1(4)
C(14)	492(2)	2152(5)	559(9)	6.8(5)
Cl(1)	167(1)	2788(3)	3067(5)	16.7(3)
C(15)	0	2455(8)	1/4	9(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Diels-Alder mechanism. More probably, a reactive species with a nitrene N atom and an N-centered free radical amido group is formed as the result of oxidation of the Pt(+ 3) complex:



Hence, the formation of IX can be speculated as involving an insertion of the nitrene species into the C–H bond of the neighbouring ligand molecule simultaneously with a radical attack of the ArN · Ph species to an aromatic ring of the same ligand.

Table 10
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) U(eq) for IV

Atom	X	Y	Z	$U_{(eq)}$
Pt(1)	0	0	0	24(1)
N(1)	1171(6)	−1849(5)	1035(5)	25(1)
N(2)	−846(6)	604(5)	1577(5)	26(1)
C(1)	901(7)	−1859(6)	2198(6)	25(1)
C(2)	−257(8)	−474(7)	2532(6)	29(1)
C(3)	−698(8)	−338(6)	3718(6)	30(1)
C(4)	14(8)	−1567(7)	4593(6)	33(1)
C(5)	1159(8)	−2904(8)	4255(7)	40(1)
C(6)	1572(8)	−3059(7)	3089(6)	32(1)
C(7)	−1954(7)	2047(6)	1729(5)	25(1)
C(8)	−3458(8)	2647(7)	1381(7)	38(1)
C(9)	−4540(8)	4034(7)	1592(7)	42(1)
C(10)	−4180(9)	4886(7)	2108(7)	53(1)
C(11)	−2653(8)	4288(7)	2425(7)	41(1)
C(12)	−1596(8)	2886(7)	2249(6)	33(1)
Pt(2)	−5000	0	0	29(1)
N(3)	−6501(7)	2078(6)	−255(6)	41(1)
N(4)	−5637(7)	310(6)	1657(5)	32(1)
C(13)	−7225(8)	2689(7)	704(6)	31(1)
C(14)	−8337(7)	4195(7)	736(6)	30(1)
C(15)	−8942(8)	4639(7)	1790(6)	37(1)
C(16)	−8486(8)	3678(7)	2866(7)	38(1)
C(17)	−7367(8)	2235(7)	2889(6)	33(1)
C(18)	−6734(7)	1701(6)	1801(6)	25(1)
C(19)	−5050(8)	−806(7)	2673(5)	28(1)
C(20)	−6051(8)	−1329(7)	3513(6)	36(1)
C(21)	−5486(8)	−2382(7)	4483(7)	44(1)
C(22)	−3923(9)	−2955(7)	4618(7)	46(1)
C(23)	−2889(8)	−2495(7)	3754(7)	47(1)
C(24)	−3470(8)	−1396(7)	2767(6)	35(1)
H(3A)	−1532(14)	565(14)	3950(14)	77(1)
H(4A)	−293(14)	−1597(14)	5358(14)	80(1)
H(5A)	1620(14)	−3731(14)	4947(14)	81(1)
H(6A)	2369(14)	−3885(14)	2846(14)	79(1)
H(8A)	−3700(14)	2087(14)	988(14)	79(1)
H(9A)	−5595(14)	4374(14)	1324(14)	79(1)
H(10A)	−4916(14)	5830(14)	2193(14)	80(1)
H(11A)	−2392(14)	4877(14)	2740(14)	79(1)
H(12A)	−548(14)	2503(14)	2523(14)	79(1)
H(14A)	−8593(14)	4839(14)	−86(14)	78(1)
H(15A)	−9780(14)	5646(14)	1813(14)	79(1)
H(16A)	−8929(14)	4048(14)	3567(14)	78(1)
H(17A)	−6985(14)	1638(14)	3682(14)	77(1)
H(20A)	7184(14)	−936(14)	3417(14)	77(1)
H(21A)	−6201(14)	−2724(14)	5140(14)	79(1)
H(22A)	−3542(14)	−3665(14)	5380(14)	79(1)
H(23A)	−1776(14)	−2919(14)	3776(14)	79(1)
H(24A)	−2749(14)	−1075(14)	2221(14)	79(1)

Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3. Experimental

3.1. General comments

All gases, organic solvents, and reagents were reagent grade. All operations on separation, crystallization and isolation of the final compounds were carried out under dry, oxygen-free argon using standard Schlenk techniques. Tetrahydrofuran was additionally purified by distillation from sodium/benzophenone ketyl in argon atmosphere. Hydrocarbon solvents were dried by refluxing over sodium metal and distilled under argon. Acetonitrile and dichlorometane were purified by double distillation under argon. Thin-layer chromatography (Merck, 5 × 7.5 cm, Kieselgel 60 F_{254}) was used whenever possible to monitor the progress of the reactions under study. Column chromatography was applied to separate the reaction mixtures (Kieselgel 60, Merck, 60–230 mesh ASTM). IR spectra were recorded on a Specord M80 instrument in KBr pellets or in nujol mulls. All NMR measurements were performed on a Bruker 300 instrument in solutions of $CDCl_3$ predried over molecular sieves.

Palladium cluster $Pd_4(\mu^2\text{-}CO)_4(\mu^2\text{-}OAc)_4$ (I) was prepared by the method published in Ref. [16].

3.1.1. Synthesis of $[Pd(OAc)o\text{-}(NPh)(NO)C_6H_4]_2$ (II)

200 mg of cluster I (0.25 mmol, 1 mg-atom Pd), 5 ml of toluene, and a solution of 107 mg (1 mmol) of nitrosobenzene in 5 ml of toluene were placed into a water-jacketed two-neck reaction vessel connected with a gas burette under argon. The system was evacuated, purged with argon, and stirred at 60°C until complete cessation of the CO_2 evolution (3 to 4 h, volumetrical monitoring). The reaction mixture was filtered, and the filtrate was concentrated to ca. 1/4 of the initial volume. Complex II was precipitated by hexane, filtered off, and dried in vacuo; yield: 180 mg (0.16 mmol, 32% based on Pd). For $Pd_2C_{29}H_{26}O_6N_4Cl_2$ calcd. (%): C, 42.96; H, 3.21; N, 6.91. Found (%): C, 42.5; H, 3.5; N, 5.3. Crystals suitable for X-ray diffraction analysis were obtained from a CH_2Cl_2-pentane mixture.

3.1.2. Synthesis of $Pt[o\text{-}(NPh)(N)C_6H_4]_2$ (IV)

To a solution of 200 mg (0.44 mmol) of $K_2Pt(NO_2)_4$ in 70 ml of the MeCN/H_2O (1:1) mixture was added *N*-phenyl-*o*-phenylenediamine (162 mg, 0.88 mmol) at 50°C. The reaction mixture was stirred at 50–80°C until the formation of dark blue solution. After storing the solution for one day at room temperature, TLC (benzene) indicated

Table 11
Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2 ×10^3) U(eq) for *N*-phenyl-*o*-phenylenediamine (L)

Atom	X	Y	Z	$U_{(eq)}$
N(1)	1612(3)	1056(8)	2194(2)	95(1)
N(2)	384(2)	2550(4)	3586(2)	67(1)
C(1)	592(2)	−128(4)	2424(2)	59(1)
C(2)	−3(2)	541(4)	3130(1)	54(1)
C(3)	−996(3)	−716(5)	3361(2)	60(1)
C(4)	−1423(3)	−2614(5)	2900(2)	66(1)
C(5)	−832(3)	−3290(5)	2211(2)	64(1)
C(6)	158(3)	−2080(5)	1981(2)	66(1)
C(7)	1425(2)	2676(4)	4180(1)	52(1)
C(8)	1678(3)	4680(4)	4644(2)	66(1)
C(9)	2715(3)	4845(6)	5219(2)	77(1)
C(10)	3539(3)	3064(6)	5351(2)	74(1)
C(11)	3292(3)	1075(5)	4903(2)	64(1)
C(12)	2249(2)	860(4)	4319(2)	53(1)
H(1N)	1621(37)	2629(91)	2364(26)	121(16)
H(2N)	1784(37)	706(69)	1745(29)	104(14)
H(3N)	−136(34)	3644(70)	3525(24)	101(12)
H(4)	−1406(28)	−264(51)	3870(23)	84(9)
H(5)	−1189(26)	−4600(55)	1867(21)	82(9)
H(6)	523(31)	−2582(62)	1489(23)	97(10)
H(8)	1052(24)	5994(51)	4551(17)	66(7)
H(9)	2885(29)	6115(55)	5560(20)	80(9)
H(9)	−2164(34)	−3342(52)	3040(21)	81(10)
H(10)	4340(32)	3233(55)	5756(23)	93(10)
H(11)	3823(25)	−154(48)	4996(17)	58(7)
H(12)	2050(24)	−512(49)	4050(17)	59(7)

Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 12
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) U(eq) for complex V

Atom	X	Y	Z	$U_{(eq)}$
Pd(1)	7913(1)	6331(1)	−2190(1)	35(1)
N(1)	6565(2)	7074(2)	−2863(2)	49(1)
N(2)	7786(2)	4884(2)	−2553(2)	39(1)
N(3)	9255(2)	5596(2)	−1511(2)	40(1)
N(4)	8049(2)	7783(2)	−1849(2)	36(1)
C(1)	6202(3)	6338(3)	−3190(2)	44(1)
C(2)	5207(3)	6666(3)	−3636(2)	60(1)
C(3)	4971(3)	5816(3)	−3968(2)	67(1)
C(4)	5727(3)	4610(3)	−3901(2)	67(1)
C(5)	6672(3)	4252(3)	−3435(2)	51(1)
C(6)	6912(3)	5104(3)	−3045(2)	42(1)
C(7)	8497(2)	3691(2)	−2324(2)	36(1)
C(8)	9726(3)	3213(3)	−2686(2)	46(1)
C(9)	10 385(3)	2037(3)	−2474(2)	56(1)
C(10)	9843(3)	1344(3)	−1915(2)	53(1)
C(11)	8630(3)	1819(3)	−1542(2)	50(1)
C(12)	7945(3)	2993(3)	−1743(2)	47(1)
C(13)	9587(2)	6349(2)	−1159(2)	36(1)
C(14)	10 518(3)	6032(2)	−640(2)	41(1)
C(15)	10 753(3)	6883(3)	−315(2)	49(1)
C(16)	10 073(3)	8092(3)	−484(2)	48(1)
C(17)	9197(3)	8429(2)	−988(2)	42(1)
C(18)	8921(2)	7581(2)	−1353(2)	34(1)
C(19)	7406(3)	8944(2)	−2185(2)	39(1)
C(20)	6143(3)	9398(3)	−2022(2)	46(1)
C(21)	5515(3)	10 511(3)	−2371(2)	61(1)
C(22)	6113(3)	11 192(3)	−2866(2)	66(1)
C(23)	7363(3)	10 755(3)	−3019(2)	57(1)
C(24)	8015(3)	9637(3)	−2694(2)	45(1)
Pd(2)	1/2	1/2	0	34(1)
N(5)	3920(2)	6195(2)	−748(2)	44(1)
N(6)	5146(2)	6462(2)	327(2)	36(1)
C(25)	3780(2)	7316(2)	−685(2)	39(1)
C(26)	3041(3)	8319(3)	−1142(2)	53(1)
C(27)	2913(3)	9424(3)	−979(3)	56(1)
C(28)	3521(3)	9589(2)	−338(2)	50(1)
C(29)	4272(2)	8645(2)	103(2)	42(1)
C(30)	4453(2)	7480(2)	−75(2)	37(1)
C(31)	5945(2)	6485(2)	878(2)	36(1)
C(32)	5914(3)	5947(2)	1771(2)	42(1)
C(33)	6699(3)	5960(3)	2307(2)	51(1)
C(34)	7507(3)	6509(3)	1987(2)	51(1)
C(35)	7549(2)	7035(2)	1094(2)	45(1)
C(36)	6778(2)	7014(2)	549(2)	39(1)
Pd(3)	0	1/2	−1/2	40(1)
N(7)	−434(2)	6696(2)	−4773(2)	41(1)
N(8)	−1595(2)	5688(2)	−5368(2)	46(1)
C(37)	−2131(3)	6873(3)	−5347(2)	45(1)
C(38)	−3232(3)	7572(3)	−5644(2)	54(1)
C(39)	−3684(3)	8771(3)	−5585(3)	65(1)
C(40)	−3096(3)	9318(3)	−5203(3)	65(1)
C(41)	−2046(3)	8680(3)	−4907(2)	53(1)
C(42)	−1493(3)	7445(3)	−5005(2)	42(1)
C(43)	298(3)	7135(2)	−4428(2)	41(1)
C(44)	666(3)	6692(3)	−3587(2)	45(1)
C(45)	1362(3)	7132(3)	−3243(2)	54(1)
C(46)	1714(3)	7997(3)	−3732(3)	65(1)
C(48)	683(3)	8005(3)	−4928(2)	54(1)
C(47)	1374(3)	8433(3)	−4570(3)	66(1)
H(2)	4787(5)	7466(5)	−3705(5)	62(1)
h(3)	4271(5)	6053(5)	−4230(5)	75(1)
H(4)	5487(5)	3970(5)	−4174(5)	89(1)

Table 12 (continued)

Atom	X	Y	Z	$U_{(eq)}$
H(5)	7213(5)	3405(5)	−3426(5)	59(1)
H(8)	10 034(5)	3663(5)	−3083(5)	49(1)
H(9)	11 104(5)	1758(5)	−2733(5)	46(1)
H(10)	10 239(5)	607(5)	−1827(5)	60(1)
H(11)	8268(5)	1333(5)	−1135(5)	70(1)
H(12)	7121(5)	3350(5)	−1446(5)	70(1)
H(14)	10 930(5)	5257(5)	−520(5)	36(1)
H(15)	11 308(5)	6692(5)	−43(5)	44(1)
H(16)	10 271(5)	8673(5)	−248(5)	53(1)
H(17)	8745(5)	9217(5)	−1111(5)	35(1)
H(20)	5712(5)	8960(5)	−1695(5)	54(1)
H(21)	4804(5)	10 756(5)	−2244(5)	62(1)
H(22)	5648(5)	11 955(5)	−3085(5)	66(1)
H(23)	7764(5)	11 164(5)	−3367(5)	61(1)
H(24)	8871(5)	9338(5)	−2838(5)	37(1)
H(26)	2711(5)	8236(5)	−1506(5)	52(1)
H(27)	2456(5)	10 067(5)	−1292(5)	64(1)
H(28)	3393(5)	10 355(5)	−194(5)	44(1)
H(29)	4660(5)	8764(5)	544(5)	41(1)
H(32)	5339(5)	5556(5)	2003(5)	56(1)
H(33)	6609(5)	5599(5)	2906(5)	67(1)
H(34)	7958(5)	6583(5)	2333(5)	55(1)
H(35)	8076(5)	7408(5)	870(5)	41(1)
H(36)	6863(5)	7311(5)	−87(5)	48(1)
H(38)	−3663(5)	7164(5)	−5843(5)	67(1)
H(39)	−4331(5)	9197(5)	−5830(5)	69(1)
H(40)	−3407(5)	10 126(5)	−5188(5)	70(1)
H(41)	−1782(5)	9084(5)	−4624(5)	94(1)
H(44)	395(5)	6076(5)	−3201(5)	66(1)
H(45)	1530(5)	6899(5)	−2681(5)	73(1)
H(46)	2071(5)	8369(5)	−3507(5)	85(1)
H(47)	1632(5)	8935(5)	−4902(5)	65(1)
H(48)	513(5)	8245(5)	−5549(5)	57(1)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

the absence of free organic ligand and the formation of a dark blue band. It was separated by the use of column chromatography (5 × 30 cm, silica gel, 60–80 ml of benzene). The solution was concentrated to 15–20 ml and after addition of 5–8 ml of hexane or heptane and cooling to 5–10°C gave bronze-black prismatic crystals of $Pt[(NPh)(N)C_6H_4]_2$ (IV) (159 mg, 0.28 mmol, 65%). Anal. Calcd. for $Pt[(NPh)(N)C_6H_4]_2$: C, 51.71; H, 3.23; N, 10.05. Found: C, 51.87; H, 3.44; N, 10.11. IR, ν cm^{-1}: 447s, 497m, 537m, 581vs, 601vs, 631m, 664vs, 708s, 741vs, 751vs, 761vs, 852m, 935m, 1022w, 1072w, 1146m, 1193w, 1123m, 1273m, 1337m, 1460m, 1480m, 1490m, 1547m, 1584m, 1658m, 1671w. Complex IV can be also prepared by reaction of K_2PtCl_4 with the ligand (1:2 mole ratio); however, in this case, the addition of alkali is required and the yield of final product is much lower (maximum 5%)

3.1.3. Synthesis of $Pd[o\text{-}(NPh)(N)C_6H_4]_2$ (V)

To a solution of 250 mg (0.68 mmol) of $K_2Pd(NO_2)_4$ in 70 ml of mixture $MeCN/H_2O$ (1:1) were added *N*-phenyl-*o*-phenylenediamine (250 mg, 1.36 mmol) and LiOH (1 g) at 50°C. The reaction mixture was left to stay for one day at room temperature until the formation of blue-green solution. The solvents were removed to dryness and a solid residue was extracted by boiling hexane (400–600 ml). The blue solution obtained was concentrated to 100 ml and, after cooling to room temperature, afforded black-blue prismatic crystals of $Pd[(NPh)(N)C_6H_4]_2$ (V) (162 mg, 0.35 mmol, 51%). Anal. Calcd. for $Pd[(NPh)(N)C_6H_4]_2$: C, 61.53; H, 3,85; N, 11.96. Found: C, 61.23; H, 3.84; N, 11.82. IR, ν cm^{-1}: 440m, 487m, 530w, 567s, 591s, 631s, 654vs, 706s, 754vs, 761vs, 838m, 918m, 1022w, 1072w, 1146vs, 1183w, 1266m, 1263m, 1337vs, 1383m, 1454s, 1487s, 1514w, 1584w, 1614w, 1654w, 1671w.

3.1.4. Synthesis of $Pt_2[(NPh)(N)C_6H_4]_4[O_3SCF_3]_2$ (VII)

A mixture of 500 mg (0.898 mml) of complex IV and 230 mg (0.895 mmol) of AgO_3SCF_3 with 2–3 ml of acetone was ground in agate mortar at room temperature. To the product prepared, 100 ml of CH_2Cl_2 was added, and the brown solution formed was filtered. After its concentration to 20–30 ml and cooling to −18°C, a brown-green

Table 13
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) U(eq) for VII

Atom	*X*	*Y*	*Z*	$U_{(eq)}$
Pt(1)	8487(1)	9827(1)	−294(1)	37(1)
N(1)	9524(4)	11 635(4)	161(4)	41(1)
N(2)	7948(4)	10 280(4)	−1849(4)	39(1)
N(3)	9009(4)	9601(4)	1315(4)	42(1)
N(4)	7398(4)	7978(4)	−559(4)	41(1)
C(1)	9464(5)	12 244(5)	−685(5)	44(1)
C(2)	10 139(6)	13 559(5)	−552(5)	54(1)
C(3)	9930(6)	14 062(6)	−1485(6)	66(1)
C(4)	9023(7)	13 273(6)	−2634(6)	66(1)
C(5)	8372(6)	12 048(6)	−2790(5)	57(1)
C(6)	8550(5)	11 468(5)	−1841(5)	44(1)
C(7)	8499(5)	8461(6)	1467(5)	47(1)
C(8)	8738(6)	8101(6)	2552(5)	61(1)
C(9)	8080(7)	6893(7)	2587(6)	73(1)
C(10)	7142(7)	6007(6)	1513(6)	72(1)
C(11)	6877(6)	6277(6)	478(5)	60(1)
C(12)	7556(5)	7524(5)	393(5)	47(1)
C(13)	6904(5)	9487(5)	−2943(5)	45(1)
C(14)	5705(6)	9523(6)	−3219(6)	58(1)
C(15)	4698(6)	8817(6)	−4252(6)	74(1)
C(16)	4899(7)	8085(6)	−5017(6)	79(1)
C(17)	6074(7)	8037(6)	−4751(6)	78(1)
C(18)	7105(6)	8741(6)	−3691(6)	64(1)
C(19)	6429(5)	7103(5)	−1651(5)	44(1)
C(20)	6773(6)	6309(6)	−2215(6)	59(1)
C(21)	5836(7)	5437(6)	−3230(6)	70(1)
C(22)	4598(7)	5363(6)	−3643(6)	72(1)
C(23)	4263(6)	6150(6)	−3096(6)	65(1)
C(24)	5186(6)	7049(5)	−2084(5)	54(1)
S(1)	−427(2)	−2981(2)	−3459(2)	64(1)
O(1)	−243(7)	−1815(6)	−3104(8)	191(1)
O(2)	−329(7)	−3476(7)	−2447(6)	163(1)
O(3)	−1426(6)	−3674(7)	−4497(5)	140(1)
F(1)	2100(5)	−2146(7)	−2824(6)	194(1)
F(2)	1135(7)	−2432(9)	−4595(7)	273(1)
F(3)	1025(7)	−3850(8)	−3932(8)	310(1)
C(25)	1052(8)	−2760(9)	−3637(7)	142(1)
C(1B)	3977(9)	8346(9)	180(9)	257(1)
C(2B)	3196(8)	7318(8)	214(8)	143(1)
C(3B)	3479(9)	6883(9)	956(9)	197(1)
C(4B)	4735(9)	7378(9)	1751(9)	188(1)
C(5B)	5707(8)	8505(8)	1916(8)	121(1)
C(6B)	5482(8)	8859(9)	1225(8)	199(1)
H(2)	10 661(10)	14 105(10)	361(10)	50(1)
H(3)	10 322(10)	14 850(10)	−1466(10)	50(1)
H(4)	8934(10)	13 766(10)	−3254(10)	50(1)
H(5)	7929(10)	11 727(10)	−3555(10)	50(1)
H(8)	9425(10)	8691(10)	3329(10)	50(1)
H(9)	8297(10)	6566(10)	3244(10)	50(1)
H(10)	6762(10)	5180(10)	1616(10)	50(1)
H(11)	6225(10)	5651(10)	−222(10)	80(1)
H(14)	5293(10)	9725(10)	−2849(10)	50(1)
H(15)	3877(10)	8836(10)	−4456(10)	80(1)
H(16)	4254(10)	7442(10)	−5818(10)	51(1)
H(17)	6334(10)	7522(10)	−5374(10)	51(1)
H(18)	7965(10)	8703(10)	−3488(10)	80(1)
H(20)	7653(10)	6359(10)	−1904(10)	80(1)
H(21)	6271(10)	4957(10)	−3595(10)	51(1)
H(22)	3937(10)	4734(10)	−4365(10)	81(1)
H(23)	3395(10)	6266(10)	−3402(10)	51(1)
H(24)	4949(10)	7618(10)	−1678(10)	80(1)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

crystalline precipitate was separated, washed with benzene and hexane and dried in vacuo. Yield of $Pt_2[(NPh)(N)C_6H_4]_4[O_3SCF_3]_2$ (VII) is 450 mg (0.319 mmol, 70.9%). Anal.: Calcd. for $Pt_2[(NPh)(N)C_6H_4]_4[O_3SCF_3]_2$: C, 42.49; H, 2,55; N, 7.93. Found: C, 42.55; H, 2.44; N, 7.87. IR, υ cm^{-1}: 440w, 497w, 527m, 561s, 597s, 644vs, 694s, 751s, 831m, 875w, 918w, 999m, 1025s, 1076w, 1159vs, 1230vs, 1260vs, 1286vs, 1367vs, 1447s, 1497s, 1510vs, 1531s, 1561w, 1594m, 1631w, 1671w, 1694w. Single crystals of VII for the X-ray investigation were obtained as a benzene solvate by slow evaporation of a CH_2Cl_2—benzene (5:1) solution caved by the layer of hexane from ampule (7 × 150 mm).

3.1.5. Synthesis of $Pt[(NPh)(NH)C_6H_4]Br_2$ (VIII)

A mixture of 250 mg (0.449 mml) of complex IV and 110 mg (0.5 mmol) of $CuBr_2$ with 2–3 ml of acetone (containing 2–5% of H_2O) was ground in agate mortar at room temperature. To the product prepared, 50 ml of CH_2Cl_2 was added, and the black-red solution was filtered. After the concentration to 20–30 ml and cooling of the solution to −18°C, the black-red needle-shaped crystals were separated, washed with ether and hexane and dried in vacuo. Yield of $Pt[(NPh)(NH)C_6H_4]Br_2$ (VIII) is 210 mg (0.393 mmol, 57.5%). Anal.: Calcd. for $Pt[(NPh)(NH)C_6H_4]Br_2$: C, 26.92; H, 1.87; N, 5.23; Br, 33.64. Found: C, 27.02; H, 1.72; N, 5.47; Br, 33.23. IR, υ cm^{-1}: 472m, 490m, 501w, 594s, 648s, 681w, 698s, 751s, 798s, 825m, 842w, 865w, 895m, 952w, 979w, 1025m, 1072m, 1139w, 1163m, 1189w, 1219w, 1233w, 1266w, 1290w, 1380w, 1400m, 1447m, 1490m, 1531s, 1564w, 1594m, 1624w, 1674w, 1648m. Single crystals suitable for X-ray investigation were prepared by slow evaporation of a CH_2Cl_2 solution of VIII from ampule (15 × 120 mm) at room temperature.

3.1.6. Oxidation of V or VII by AgO_3SCF_3—synthesis of IX

To a solution of complex IV (200 mg, 0.359 mmol) in 20 ml of acetone was added AgO_3SCF_3 (approx. 6 eqiv.) at room temperature until the starting complex IV and intermediately formed VII were consumed (TLC monitoring). Removal of the solvent in vacuo left a brown oilish residue, which was dissolved in CH_2Cl_2 to form a brown-green solution. The solution was chromatographed on silica gel (5 × 35 cm, 50–70 ml of mixture CH_2Cl_2/THF 1:1), and a yellow-orange band ($R_f = 0.4$–0.5) was separated. The orange eluate was concentrated to dryness and oilish brown-red residue was solved in a mixture of benzene and hexane (1:5). The cooling of this solution to -5–-10°C led to the formation of needle-shaped crystals of heterotricyclic compound IX (100 mg, 0.249 mmol, 69.3%). Anal. Calcd for $C_{27}H_{22}N_4$: C, 80.60; H, 5.47; N, 13.93. Found: C, 80.55; H, 5.65; N, 13.65. IR, υ cm^{-1}: 474w, 561w,

Table 14
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) U(eq) for complex VIII

Atom	*X*	*Y*	*Z*	$U_{(eq)}$
Pt(1)	4708(1)	1/4	15 707(1)	40(1)
Br(1)	2965(2)	1/4	14 266(2)	49(1)
Br(2)	3248(3)	1/4	17 320(2)	71(1)
N(1)	5964(12)	1/4	14 527(12)	35(2)
N(2)	6321(15)	1/4	16 659(12)	43(2)
C(1)	7115(19)	1/4	14 840(16)	58(2)
C(2)	8288(20)	1/4	14 051(16)	67(2)
C(3)	9353(18)	1/4	14 577(18)	67(2)
C(4)	9542(17)	1/4	15 773(18)	58(2)
C(5)	8728(19)	1/4	16 512(18)	64(2)
C(6)	7357(16)	1/4	16 070(14)	37(2)
C(7)	6417(17)	1/4	17 992(14)	46(2)
C(8)	6481(18)	4287(21)	18 582(12)	86(2)
C(9)	6601(19)	4278(24)	19 782(14)	107(2)
C(10)	6641(20)	1/4	20 373(16)	89(2)
H(1N)	5839(29)	1/4	13 938(29)	83(3)
H(2)	8006(29)	1/4	13 241(29)	81(3)
H(3)	9933(29)	1/4	14 115(29)	81(3)
H(4)	10 427(29)	1/4	16 036(29)	83(3)
H(5)	8710(29)	1/4	17 336(29)	81(3)
H(8)	6430(29)	5518(30)	18 161(29)	83(3)
H(9)	6612(29)	5544(30)	20 239(29)	86(3)
H(10)	6716(29)	2489(30)	21 233(29)	84(3)

591w, 617w, 634w, 704m, 755s, 768w, 819m, 848w, 1029w, 1076w, 1153w, 1216w, 1250m, 1320m, 1360m, 1400w, 1440w, 1474m, 1497m, 1547m, 1574s, 1601m, 1641s, 2845w, 2864w, 2926m, 2963w, 2987w. Compound IX was prepared by same way using VII as a starting material and 3–4 equivalents of $AgOSCF_3$.

Table 15
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) U(eq) for compound IX

Atom	X	Y	Z	$U_{(eq)}$
N(1)	5382(1)	1718(1)	12 038(3)	60(1)
N(2)	4909(1)	1087(1)	13 251(2)	53(1)
N(3)	5833(1)	746(1)	9790(2)	47(1)
N(4)	5331(1)	20(1)	11 378(2)	46(1)
C(1)	5394(1)	1332(1)	11 755(3)	48(1)
C(2)	5645(1)	1274(1)	10 828(3)	48(1)
C(3)	5617(1)	839(1)	10 686(3)	42(1)
C(4)	5352(1)	438(1)	11 471(3)	42(1)
C(5)	5099(1)	503(1)	12 378(3)	44(1)
C(6)	5119(1)	928(1)	12 504(3)	43(1)
C(7)	5820(1)	308(1)	9678(3)	46(1)
C(8)	5570(1)	−50(1)	10 494(3)	47(1)
C(9)	5567(2)	−486(2)	10 413(3)	57(2)
C(10)	5799(2)	−573(2)	9555(3)	66(2)
C(11)	6036(2)	−221(2)	8769(4)	66(2)
C(12)	6051(2)	208(2)	8813(3)	59(2)
C(13)	5078(2)	1609(2)	13 022(3)	57(2)
C(14)	4662(2)	1692(2)	12 731(4)	77(2)
C(15)	5372(2)	1921(2)	14 001(3)	78(2)
C(16)	4672(1)	835(1)	14 247(3)	49(1)
C(17)	4898(2)	678(2)	14 963(3)	66(2)
C(18)	4666(2)	430(2)	15 935(3)	75(2)
C(19)	4220(2)	350(2)	16 178(4)	77(2)
C(20)	3992(2)	499(2)	15 475(4)	73(2)
C(21)	4213(2)	741(2)	14 505(3)	64(2)
C(22)	6050(1)	1106(1)	8917(3)	49(1)
C(23)	5775(2)	1050(2)	7974(3)	63(2)
C(24)	5978(2)	1386(2)	7115(4)	80(2)
C(25)	6436(2)	1766(2)	7221(4)	87(2)
C(26)	6704(2)	1819(2)	8173(4)	82(2)
C(27)	6502(2)	1476(2)	9017(3)	67(2)
H(2A)	5829(10)	1553(10)	10 311(19)	42(3)
H(5A)	4895(10)	192(10)	12 807(18)	42(3)
H(9A)	5366(13)	−751(13)	10 987(22)	92(3)
H(10A)	5780(10)	−903(11)	9457(20)	57(3)
H(11A)	6187(11)	−286(11)	8318(20)	61(3)
H(12A)	6172(8)	421(8)	8348(17)	23(3)
H(14A)	4479(12)	1516(12)	12 136(22)	80(3)
H(14B)	4516(13)	1655(13)	13 253(23)	87(3)
H(14C)	4806(12)	2082(12)	12 435(22)	76(3)
H(15A)	5699(13)	1858(13)	14 081(23)	91(3)
H(15B)	5516(12)	2269(13)	13 786(22)	87(3)
H(15C)	5212(11)	1831(11)	14 527(20)	58(3)
H(17A)	5226(11)	732(11)	14 779(21)	62(3)
H(18A)	4855(13)	364(13)	16 523(23)	95(3)
H(19A)	4092(12)	185(12)	16 756(21)	71(3)
H(20A)	3692(12)	441(11)	15 655(21)	74(3)
H(21A)	4052(11)	828(11)	14 116(20)	62(3)
H(23A)	5434(10)	782(10)	7908(19)	50(3)
H(24A)	5807(17)	1340(17)	6452(26)	156(3)
H(25A)	6624(12)	2038(13)	6672(22)	88(3)
H(26A)	7043(12)	2137(12)	8220(21)	80(3)
H(27A)	6669(10)	1509(10)	9600(19)	52(3)

Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3.1.7. Crystal structure determinations

The crystals were all mounted in air on glass fibers using 5 min epoxy resin. The unit cells were determined and refined from 24 equivalent reflections with $2\Theta > 22–28°$ and obtained from Syntex P21 (for II), CAD-4 (for VII–IX), and Siemens R3v/m (for IV, V, and *N*-phenyl-*o*-phenylenediamine) four-circle diffractometers at room temperature. Intensity data sets were corrected for the Lorentz and polarization effects. Backgrounds were scanned for 25 of the peak widths on each end of the scan. Three reflections were monitored periodically for each compound as a check for crystal decomposition or movement. No significant variation in these standards was observed, so no correction was applied. Details of crystal parameters, data collection and structure refinement are given in Table 8.

All structures were solved by a direct method to locate the platinum or palladium atoms for II, IV, V, VII, and VIII. For IX at this stage, all nonhydrogen atoms were found. The other atoms in II, IV, V, VII, and VIII were located in the subsequent difference Fourier maps. The DIFABS method [27] was used for the absorption correction of IV, V, VII, and VIII at the stage of the isotropic approximation. An anisotropic refinement was applied to all nonhydrogen atoms, and all hydrogen atoms in the structures were found from the difference Fourier maps and refined in the isotropic approximation (for, IV, V, VII, VIII and the initial ligand). For II, the H atoms were included in calculations as fixed contributions with the constant isotropic temperature factor $u_{iso} = 0.08$ Å^2. The computations were performed using the SHELXTL PLUS program package [28] on a Pentium 100/16 computer. Selected bond lengths and angles for investigated complexes are given in Tables 1–7 and the positional parameters and the equivalent thermal parameters are listed in Tables 9–15. Complete lists of the bond lengths and angles and the tables of thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

4. Conclusion

The results obtained in this work demonstrated that nitrene ligands can be involved into the chemistry of palladium and platinum. Unlike some other VIII group metals (e.g., Fe, Co, Ru, Os), these elements normally form the more labile nitrene complexes, which can further react by inserting the nitrene ligand to the C–H bond of an arene molecule to produce observable products like complex II or polyheterocyclic compound IX. Nevertheless, the data available seem to be encouraging to the search for the stable nitrene complexes of platinum group metals.

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