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Inorganica Chimica Acta 235 (1995) 327–338

Inorganica Chimica Acta

Stabilization and reaction behaviour of a terminal phosphido unit on a mononuclear Pt(II) centre. Synthesis and X-ray structure of a cationic diphenylphosphine complex $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(PHPh_2)][OSO_2CF_3]$ and a diphenylphosphido-bridged Pt(II)/Pd(II) complex $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\mu\text{-}PPh_2)Pd(C_6H_4CH_2NMe_2\text{-}2)(H_2O)][BF_4]\cdot CH_2Cl_2$ ☆

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Received 3 November 1994; revised 30 January 1995

Abstract

Reaction of diphenylphosphine with the complexes $[Pt(NCN)(H_2O)]X$ ($NCN = C_6H_3(CH_2NMe_2)_2$-2,6; $X = BF_4$ (**1a**), OSO_2CF_3 (**1b**)) leads to substitution of the H_2O ligand to afford the ionic Pt(II) complexes $[Pt(NCN)(PHPh_2)]X$ ($X = BF_4$ (**2a**), OSO_2CF_3 (**2b**)). The X-ray structure of the square-planar diphenylphosphine complex **2b** is described; triclinic, space group $P\bar{1}$, $a = 12.168(1)$, $b = 12.407(1)$, $c = 18.676$ (1) Å, $\alpha = 90.78(1)$, $\beta = 104.55(1)$, $\gamma = 94.18(1)°$, $Z = 4$, $R = 0.038$. Deprotonation of the $PHPh_2$ ligand of **2** with n-BuLi affords the unprecedented, neutral, mononuclear, Pt(II) terminal phosphido complex $[Pt(NCN)(PPh_2)]$ (**3**), the characterization of which in solution by $^{31}P\{^1H\}$ and ^1H NMR is described. Complex **3** reacts with the complex cations of $[Pt(NCN)(H_2O)][BF_4]$ and $[Pd\{C_6H_4CH_2NMe_2\text{-}2\text{-}C,N\}(N{\equiv}CMe)_2][BF_4]$ to afford the new, ionic, dinuclear phosphido-bridged complexes $[\{Pt(NCN)\}_2(\mu\text{-}PPh_2)][BF_4]$ (**4**) and $[Pt(NCN)(\mu\text{-}PPh_2)Pd(C_6H_4CH_2NMe_2\text{-}2)(H_2O)][BF_4]$ (**5**), respectively. The X-ray crystal structure of the heterobimetallic complex $\mathbf{5}\cdot CH_2Cl_2$ is reported: monoclinic, space group $P2_1/n$, $a = 14.476(1)$, $b = 14.452(1)$, $c = 18.209(2)$ Å, $\beta = 94.12(1)°$, $Z = 4$, $R = 0.049$. The reaction of MeI with **3** gives, rather than Pt(IV) oxidative addition products, the new Pt(II) *trans*-bis(methyldiphenylphosphine) complex $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}C\}(I)(PMePh_2)_2]$ (**6**) and known $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N'\}(I)]$. The chemical behaviour and NMR data of the phosphido complex **3** are consistent with this complex being formulated as a kind of tertiary phosphine, PPh_2R, in which R is an organometallic moiety {Pt(NCN)} bonded through platinum to phosphorus.

Keywords: Crystal structures; Platinum complexes; Palladium complexes; Dinuclear complexes; Diphenylphosphine complexes; Diphenylphosphido-bridged complexes

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1. Introduction

The potentially terdentate, monoanionic, aryldiamine ligands $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (NCN) and $[C_6H_4\text{-}(CH_2N(Me)CH_2CH_2NMe_2)\text{-}2]^-$ (CNN) can be used to prepare a wide variety of cyclometallated complexes in which two five-membered chelate rings bring the two N-donor atoms into either *trans* or *cis* positions, respectively, see Fig. 1. The most important aspect of this type of fixed ligand arrangement, particularly with NCN, is the unique organometallic chemistry that it generates, and we have been able to prepare nickel, palladium and platinum complexes with interesting

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☆ Dedicated to Professor Ugo Croatto in memory of his great contributions to coordination and organometallic chemistry.

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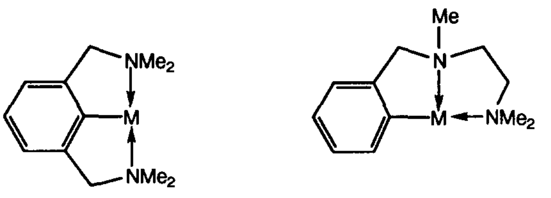
SSDI 0020-1693(95)04484-Q



NCN complex CNN complex

Fig. 1. Schematic drawings of NCN and CNN d^8 transition metal complexes.

chemistry and unusual interactions or oxidation states [1].

Many metals bind the phosphido anion (PR_2^-) either terminally or in a bridging mode [2], though palladium and platinum chemistry has, as far as we know, not yet provided an isolated example of a mononuclear species with a terminally bound phosphido ligand. We became interested in discovering whether the unique steric and electronic properties of the NCN ligand could be used to stabilize such an interaction and so provide a species with mutually *trans*-positioned covalent M–C(aryl) and M–PR_2 bonds. Since trialkyl- and triarylphosphines should displace the weakly coordinated H_2O ligand from the Pt(II) centre in $[Pt(NCN)(H_2O)]X$ ($X=BF_4$ [3], OSO_2CF_3 [4]) we have taken the reaction of the ionic triflate species with $PHPh_2$ as a first step towards this goal. Based on literature precedents [5], the coordinated phosphine in $[Pt(NCN)(PHPh_2)]^+$ could then be deprotonated with a base. The present paper presents the successful application of this strategy to afford the first mononuclear platinum η^1-phosphido complex $[Pt(NCN)(PPh_2)]$, and its reactivity towards a number of electrophiles is described.

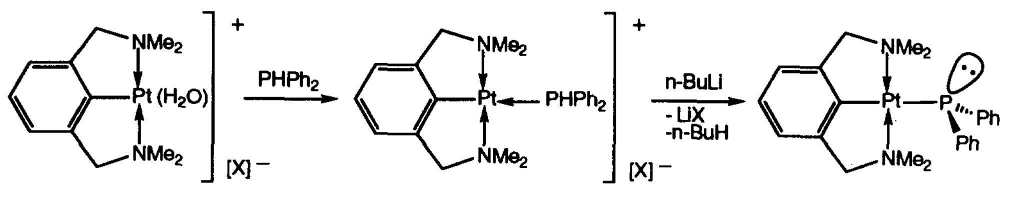
2. Results

2.1. Synthesis and characterization of ionic diphenylphosphine complexes

In a ligand substitution reaction diphenylphosphine, $PHPh_2$, reacts with known $[Pt(NCN)(H_2O)]X$ ($X=BF_4$ (**1a**) [3]; OSO_2CF_3 (**1b**) [4]) to replace the O-bonded H_2O ligand and so affords, quantitatively, the corresponding ionic complexes $[Pt(NCN)(PHPh_2)]X$ ($X=BF_4$ (**2a**), OSO_2CF_3 (**2b**)); Scheme 1. The new diphenylphosphine complexes **2a**,**b** are isolated in high yield as air-stable white solids and, compatible with their ionic character, they are soluble in polar solvents such as CH_2Cl_2 and acetone, but are insoluble in diethyl ether, benzene and hexane. The tetrafluoroborate complex **2a** after recrystallization is isolated as a solvate complex **2a**$\cdot 0.5CH_2Cl_2$. Complexes **2a** and **2b** have been characterized both spectroscopically and by elemental microanalysis. The cation of **2** in acetone-d_6 affords a $^{31}P\{H\}$ NMR singlet resonance at δ 5.2 ppm (downfield of free $PHPh_2$ at $\delta=-40$ ppm) with distinctive platinum satellites ($^1J(^{195}Pt,^{31}P)=2028$ Hz). In the ^1H NMR (acetone-d_6) spectrum of **2a** and **2b** the characteristic signal for the P–H proton is found at 6.89 and 6.96 ppm, respectively, with a large one-bond coupling to phosphorus of 354 Hz; for the triflate complex **2b** it was possible to resolve the platinum satellites for this proton ($^2J(^{195}Pt,H)=4$ Hz). We have also completed a single crystal X-ray diffraction study of the triflate complex **2b**; in the literature there are only two studies on compounds containing the Pt–P–H unit [6] and in neither of these was the P–H proton located.

2.2. Description of the crystal and molecular structure of 2b

The asymmetric part of the triclinic unit cell of **2b** contains two similar but crystallographically independent $[Pt(NCN)(PHPh_2)]^+$ complex cations and two non-coordinated triflate anions. Some relevant bond lengths and angles related to the molecular structure of the cations are presented in Table 1, and an ORTEP drawing of one of these cations (molecule 1) of **2b**, Fig. 2, shows it to be based on a square-planar four-coordinate Pt(II) centre. The terdentate, *N*,*C*,*N'* bonding of the NCN ligand includes a normal pseudo *trans* N–Pt–N arrangement and the fourth coordination site *trans* to C_{ipso} of the aryl ring is occupied by the datively P-bonded $PHPh_2$ ligand. In both molecule 1 and molecule 2 the phosphorus atom has a tetrahedral geometry and the P–H bond does not lie in the metal coordination plane (defined by Pt, N, N, P, C(*ipso*)). This latter aspect is clearly illustrated by Newman projections along the P–Pt bond shown in Fig. 3. The principal difference between the structures of the two crystallographically



X = BF_4, **1a**; OSO_2CF_3, **1b** X = BF_4, **2a**; OSO_2CF_3, **2b** **3**

Scheme 1. Syntheses of diphenylphosphine complexes **2** and diphenylphosphido complex **3**.

Table 1
Selected interatomic distances (Å) and interbond angles (°) for **2b** [a]

	Molecule 1	Molecule 2 [b]
Distances (Å)		
Pt(1)–P(1)	2.3458(19)	2.360(2)
Pt(1)–N(101)	2.102(6)	2.119(6)
Pt(1)–N(102)	2.106(6)	2.127(7)
Pt(1)–C(101)	1.990(7)	1.961(7)
P(1)–C(113)	1.838(9)	1.821(9)
P(1)–C(119)	1.833(8)	1.829(8)
N(101)–C(107)	1.534(9)	1.400(12)
N(101)–C(108)	1.501(10)	1.416(19)
N(101)–C(109)	1.486(9)	1.399(16)
N(102)–C(110)	1.518(9)	1.526(13)
N(102)–C(111)	1.492(10)	1.483(15)
N(102)–C(112)	1.493(9)	1.477(14)
C(101)–C(102)	1.402(11)	1.366(11)
C(101)–C(106)	1.365(11)	1.377(11)
C(102)–C(103)	1.388(11)	1.375(14)
C(102)–C(110)	1.486(10)	1.489(13)
C(103)–C(104)	1.401(14)	1.377(15)
C(104)–C(105)	1.363(12)	1.369(15)
C(105)–C(106)	1.392(11)	1.369(13)
C(106)–C(107)	1.497(11)	1.481(14)
Angles (°)		
P(1)–Pt(1)–N(101)	102.99(18)	97.9(2)
P(1)–Pt(1)–N(102)	96.75(18)	101.6(2)
P(1)–Pt(1)–C(101)	176.8(2)	176.8(2)
N(101)–Pt(1)–N(102)	160.0(2)	159.9(3)
N(101)–Pt(1)–C(101)	80.2(3)	80.1(3)
N(102)–Pt(1)–C(101)	80.0(3)	80.6(3)
Pt(1)–P(1)–C(113)	112.5(3)	114.4(3)
Pt(1)–P(1)–C(119)	120.8(3)	121.5(3)
C(113)–P(1)–C(119)	106.6(4)	105.5(4)
Pt(1)–N(101)–C(107)	107.6(4)	111.4(6)
Pt(1)–N(101)–C(108)	116.0(5)	111.5(8)
Pt(1)–N(101)–C(109)	109.9(4)	110.5(7)
C(107)–N(101)–C(108)	106.2(5)	102.8(11)
C(107)–N(101)–C(109)	107.1(6)	106.8(10)
C(108)–N(101)–C(109)	109.4(6)	113.5(10)
Pt(1)–N(102)–C(110)	107.9(4)	106.9(6)
Pt(1)–N(102)–C(111)	118.8(5)	105.7(5)
Pt(1)–N(102)–C(112)	107.0(4)	114.8(7)
C(110)–N(102)–C(111)	106.5(5)	110.1(8)
C(110)–N(102)–C(112)	107.8(6)	108.0(7)
C(111)–N(102)–C(112)	108.5(6)	111.2(9)
Pt(1)–C(101)–C(102)	116.5(6)	120.3(6)
Pt(1)–C(101)–C(106)	118.8(6)	119.3(6)
C(101)–C(102)–C(110)	115.0(6)	112.8(8)
C(103)–C(102)–C(110)	128.0(7)	127.7(8)
C(101)–C(106)–C(107)	113.6(7)	113.0(8)
N(101)–C(107)–C(106)	109.2(6)	115.6(8)
N(102)–C(110)–C(102)	108.7(6)	111.3(7)

[a] Atom numbering scheme is that of molecule 1.

[b] In this molecule there is some unresolved ring puckering disorder in the PtCCCN chelate rings and geometrical data associated with these rings, in particular those involving N(2), are less accurate than those of molecule 1.

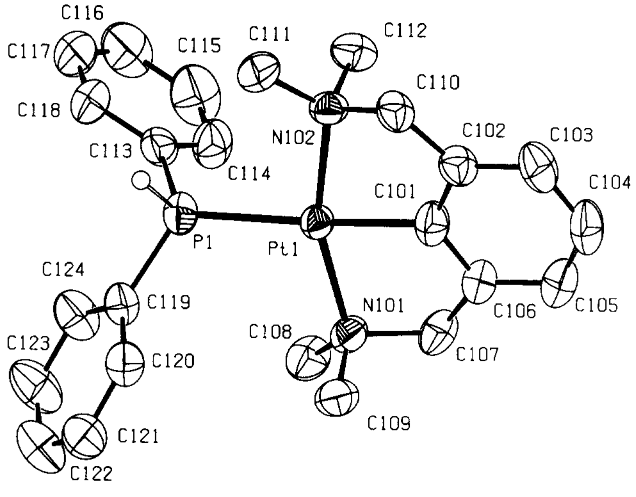


Fig. 2. ORTEP plot (50% probability level) of one complex monocation [Pt(NCN)(PHPh$_2$)]$^+$ of **2b**. H atoms, except H(2), are not shown for clarity.

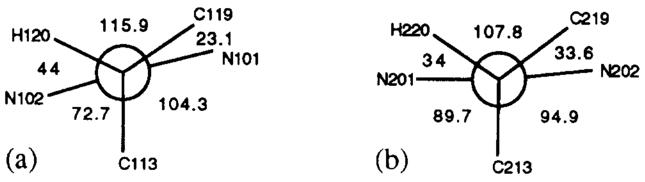


Fig. 3. Newman projections along the P→Pt axis with corresponding dihedral angles (°) of (a) molecule 1 and (b) molecule 2 of the cation of **2b**.

independent complex cations lies in the puckering of the five-membered PtNCCC chelate rings which have the Pt–C bond in common. Molecule 1 features an NCN ligand with twofold axial symmetry about the Pt–C bond, whereas molecule 2 which has some unresolved puckering disorder exhibits an NCN ligand with approximate mirror symmetry perpendicular to the metal coordination plane. It is interesting to note that this latter conformation is the one usually found for square pyramidal species such as [Ni(NCN)X$_2$] [7] and [Pt(NCN)X(η^1-Z)] (Z = I$_2$ [8], SO$_2$ [9]) rather than square-planar species [M(NCN)X] [1,10]. In the cation of **2b** the Pt–P distance of 2.353(2) Å (av.) exceeds significantly the corresponding Pt to secondary phosphine bond length in either of the neutral complexes [Pt$_2$Cl$_4$(μ-Bu^{t}HPCH$_2$CH$_2$PHBu$^t_2$)] (2.229(2) and 2.228(2) Å) [6] or [PtCl(μ-PPh$_2$)(PPh$_2$)]$_2$ (2.313(3) Å) [6].

2.3. Synthesis of the neutral phosphido complex 3

Our strategy to obtain a neutral phosphido platinum complex was based on the removal of the diphenylphosphine P–H proton of **2**, and we tried unsuccessfully various bases like NEt$_3$ and Na$_2$CO$_3$ for this purpose. However, when a colourless solution of **2a** or **2b** in Et$_2$O is reacted with n-butyllithium at −40 °C there is a distinct colour change to yellow and from this reaction mixture the desired phosphido product [Pt(NCN)(PPh$_2$)] (**3**) can be isolated as a bright yellow solid (see Scheme 1). This crude product, still containing lithium salts, proved to be extremely air-sensitive, particularly in solution, and attempts to purify it by recrystallization inevitably led to decomposition. However, extracting the crude material with toluene, filtration and evaporation of the solvent afforded [Pt(NCN)(PPh_2)] (**3**) that was pure enough for spectroscopic and further synthetic studies; recrystallization of **3** to provide analytically pure samples has still not been achieved. Solutions of **3** under a nitrogen atmosphere at 20 °C show ~50% decomposition after three days, though solid **3** can be stored under a nitrogen atmosphere at −20 °C for many days without showing significant decomposition.

The ^1H NMR spectrum of **3** shows all the signals one anticipates for the postulated structure. Compared to the $[Pt(NCN)(PHPh_2)]^+$ cation, this spectrum shows a high field shift for the CH_2 and NCH_3 groups and more significantly no P–H resonance. The $^{31}P\{H\}$ NMR spectrum of **3** has a resonance at $\delta = 0.11$ ppm with platinum satellites ($^1J(^{195}Pt,P) = 1305$ Hz). This chemical shift is close to that of free triphenylphosphine (−5 ppm) and is consistent with **3** being formulated as an unusual kind of tertiary phosphine PPh_2R in which R is an organometallic moiety {Pt(NCN)} bonded through platinum to phosphorus, see Scheme 1. Further characterization of **3** includes MS data (see Section 5); its identification as a phosphido species, with a lone pair of electrons on the phosphorus atom (as in tertiary phosphines) also comes from the products obtained when it is reacted with electrophiles (vide infra).

2.4. *Reactions of 3 with organometallic electrophiles*

Reactions of **3** with the ionic platinum complex [Pt(NCN)(H_2O)][BF_4] [3] and the palladium complex [Pd($C_6H_4CH_2NMe_2$-2)(N≡CMe)$_2$][BF_4] [12] in toluene both demonstrate the nucleophilic character of its pyramidal phosphorus centre. In the former reaction a dinuclear diphenylphosphido-bridged complex [(NCN)-Pt(μ-PPh_2)Pt(NCN)][BF_4] (**4**) is obtained as a white solid in 94% yield. As expected for an ionic species, **4** is soluble in polar solvents such as acetone (these solutions are air-sensitive) but it is not soluble in either diethyl ether or hexane. The presence of a BF_4^- counter-anion is shown in its IR spectrum by the ν(B–F) vibrations that afford a strong broad absorption at 1050 cm^{-1}. The ^1H NMR (acetone-d_6) spectrum measured at room temperature affords signals and integrals consistent with the proposed dinuclear formulation; there are complex resonance patterns in the aromatic region and there are somewhat broad, multiple resonances for the CH_2 and NMe_2 protons at δ ~4.2 and ~2.9 ppm, respectively. The ^1H NMR spectrum of **4** is temperature dependent and at −50 °C, although the appearance of the CH_2 resonances is not altered greatly, many aryl resonances are sharper and there are now clearly four different singlet NMe resonances the ^{195}Pt satellites of which are not fully resolved. These data show that complex **4** is a fluxional molecule in solution and that the preferred low temperature conformation is asymmetric. In the $^{31}P\{H\}$ NMR spectrum of **4** at −20 °C the phosphorus atom of the single PPh_2 unit, bridging between the two platinum centres, resonates at 8.73 ppm as a quintuplet in a 1:8:18:8:1 pattern ratio ($^1J(^{195}Pt,P) = 1508$ Hz); these data indicate a phosphorus centre bridging symmetrically between two {Pt(NCN)} units.

In a similar way the reaction of **3** with [Pd($C_6H_4CH_2NMe_2$-2-*C*,*N*)(N≡CMe)$_2$][BF_4] afforded a yellow solid which was expected to be [Pt(NCN)(μ-PPh_2)Pd($C_6H_4CH_2NMe_2$-2-*C*,*N*)(N≡CMe)][BF_4]. However, detailed characterization of the recrystallized material (including ^1H and $^{31}P\{^1H\}$ NMR, elemental microanalysis and an X-ray crystal structure) showed the isolated product to be the closely related aqua species [Pt(NCN)(μ-PPh_2)Pd($C_6H_4CH_2NMe_2$-2-*C*,*N*)(H_2O)][BF_4] (**5**), obtained as its dichloromethane solvate, i.e. **5**·CH_2Cl_2. The expected acetonitrile adduct is probably formed in the initial reaction but it would appear to be hygroscopic and, through reaction with adventitious water present in the polar solvents used for work-up and recrystallization, is converted to **5**.

2.5. *Description of the molecular structure of 5·CH_2Cl_2*

The crystal structure of **5**·CH_2Cl_2 comprises 4 molecules of the complex cation, 4 tetrafluoroborate anions and 4 molecules of CH_2Cl_2 in the monoclinic unit cell. There are no chemically significant intermolecular interactions except for a single hydrogen bond between the coordinated water molecule of each cation with a nearby tetrafluoroborate anion; (O···F = 2.644(11) Å). Some relevant bond lengths and interbond angles related to the molecular structure of the cation are presented in Table 2. An ORTEP drawing of the cation of **5**, Fig. 4, shows the square-planar four-coordinate Pt(II) and Pd(II) centres linked by a single diphenylphosphido unit. The Pt(II) coordination sphere is completed by a terdentate, *N*,*C*,*N'*-bonded NCN ligand with the P-donor atom of the PPh_2 bridge positioned *trans* to C_{ipso} of the aryl ring. At the Pd(II) centre the corresponding Pd–P bond is supplemented by a *C*,*N*-chelating $C_6H_4CH_2NMe_2$-2 ligand and an η^1 O-bonded water molecule so arranged that the O-donor atom is *trans* to C_{ipso} of the aryl ring. The overall shape of the cation is determined by the pyramidal configuration of the phosphorus centre of the PPh_2 bridge and the skewed orientation of the two metal coordination planes with respect to each other (angle between planes = 71.1(2)°). The structure of the heterometallic cation of **5** shows no exceptional features as regards the chelate ligand bonding modes and compared to the starting material **2b** the Pt–C and Pt–N bond distances are very similar.

Table 2
Selected interatomic distances (Å) and interbond angles (°) for $5 \cdot CH_2Cl_2$

Distances (Å)			
Pt–P	2.4386(18)	N(3)–C(33)	1.477(12)
Pt–N(1)	2.129(6)	C(1)–C(2)	1.363(11)
Pt–N(2)	2.133(7)	C(1)–C(6)	1.388(11)
Pt–C(1)	1.983(7)	C(2)–C(3)	1.395(12)
Pd–P	2.2929(19)	C(2)–C(10)	1.472(13)
Pd–O	2.214(6)	C(3)–C(4)	1.369(16)
Pd–N(3)	2.165(7)	C(4)–C(5)	1.361(16)
Pd–C(25)	1.979(9)	C(5)–C(6)	1.415(13)
P–C(13)	1.838(7)	C(6)–C(7)	1.489(11)
P–C(19)	1.815(7)	C(13)–C(14)	1.377(11)
N(1)–C(7)	1.516(11)	C(25)–C(26)	1.380(12)
N(1)–C(8)	1.483(11)	C(25)–C(30)	1.427(11)
N(1)–C(9)	1.507(11)	C(26)–C(27)	1.398(12)
N(2)–C(10)	1.514(12)	C(27)–C(28)	1.349(14)
N(2)–C(11)	1.482(11)	C(28)–C(29)	1.356(15)
N(2)–C(12)	1.484(11)	C(29)–C(30)	1.371(14)
N(3)–C(31)	1.521(13)	C(30)–C(31)	1.498(14)
N(3)–C(32)	1.471(13)		
Angles (°)			
P–Pt–N(1)	103.80(18)	Pt–N(2)–C(10)	107.1(5)
P–Pt–N(2)	96.4(2)	Pt–N(2)–C(11)	118.1(5)
P–Pt–C(1)	174.5(2)	Pt–N(2)–C(12)	106.9(5)
N(1)–Pt–N(2)	159.8(3)	C(10)–N(2)–C(11)	108.8(7)
N(1)–Pt–C(1)	80.2(3)	C(10)–N(2)–C(12)	108.2(7)
N(2)–Pt–C(1)	79.7(3)	C(11)–N(2)–C(12)	107.4(7)
P–Pd–O	89.41(16)	Pd–N(3)–C(31)	102.7(5)
P–Pd–N(3)	178.3(2)	Pd–N(3)–C(32)	114.7(6)
P–Pd–C(25)	97.8(2)	Pd–N(3)–C(33)	110.6(6)
O–Pd–N(3)	89.9(2)	C(31)–N(3)–C(32)	108.4(8)
O–Pd–C(25)	171.8(3)	C(31)–N(3)–C(33)	109.7(7)
N(3)–Pd–C(25)	83.0(3)	C(32)–N(3)–C(33)	110.4(8)
Pt–P–Pd	110.12(7)	Pt–C(1)–C(2)	119.6(6)
Pt–P–C(13)	103.5(2)	Pt–C(1)–C(6)	117.8(5)
Pt–P–C(19)	115.4(2)	C(1)–C(2)–C(10)	113.4(7)
Pd–P–C(13)	117.2(2)	C(1)–C(6)–C(7)	116.0(7)
Pd–P–C(19)	106.3(2)	N(1)–C(7)–C(6)	109.4(6)
C(13)–P–C(19)	104.5(3)	N(2)–C(10)–C(2)	111.7(8)
Pt–N(1)–C(7)	109.4(4)	P–C(19)–C(20)	124.0(6)
Pt–N(1)–C(8)	108.1(5)	P–C(19)–C(24)	117.1(6)
Pt–N(1)–C(9)	116.3(5)	Pd–C(25)–C(26)	131.2(6)
C(7)–N(1)–C(8)	109.5(6)	Pd–C(25)–C(30)	111.9(6)
C(7)–N(1)–C(9)	105.1(6)	N(3)–C(31)–C(30)	107.4(8)
C(8)–N(1)–C(9)	108.3(6)		

The Pt–P distance of 2.4386(18) Å in **5** is however significantly longer than in **2b** (2.353(2) Å, av.).

2.6. Reaction of 3 with MeI

Further evidence supporting our proposal of **3** as a phosphido complex is found in the nature of the products one obtains when this complex is reacted in solution with excess MeI. Removal of the solvent from the reaction mixture affords a pale cream solid identified by ^1H and $^{31}P\{H\}$ NMR spectroscopy as a 1:1 mixture of known [Pt^{II}(NCN-*N*,*C*,*N*′)(I)] [3], and a new complex **6** identified as *trans*-[Pt(NCN-*C*)(I)(PMePh$_2$)$_2$]. The latter has not been separated from [Pt(NCN)(I)] but can be unambiguously identified by its characteristic spectroscopic data. In **6** a square-planar Pt(II) centre is coordinated by two mutually *trans* diphenylmethylphosphines (Scheme 2) and the NCN ligand is a monodentate C-bonded ligand with the Pt–C(*ipso*) σ-bond positioned *trans* to the iodide atom. The CH_2NMe_2 arms of NCN are not coordinated as is evidenced in the ^1H NMR spectrum of the mixture by a singlet for the NMe protons at $\delta = 2.02$ ppm without platinum satellites. However, there are platinum satellites on the NCN methylene protons ($J(^{195}Pt,H) = 10$ Hz) and the small value of the coupling constant is consistent with a four-bond coupling path between Pt and CH_2 that runs through C(*ipso*) and the aryl ring. The newly formed PMe groups in the $PMePh_2$ ligands of **6** are coupled to both phosphorus atoms and, due to the large value of ^2J(P(Pt)P), resonate in the ^1H NMR spectrum as an apparent triplet at $\delta = 1.54$ ppm with platinum satellites ($^3J(^{195}Pt,H) = 36$ Hz). The probable mechanism for the formation of [Pt^{II}(NCN-*N*,*C*,*N*′)(I)] and *trans*-[Pt(NCN-*C*)(I)(PMePh$_2$)$_2$] (**6**) is discussed below.

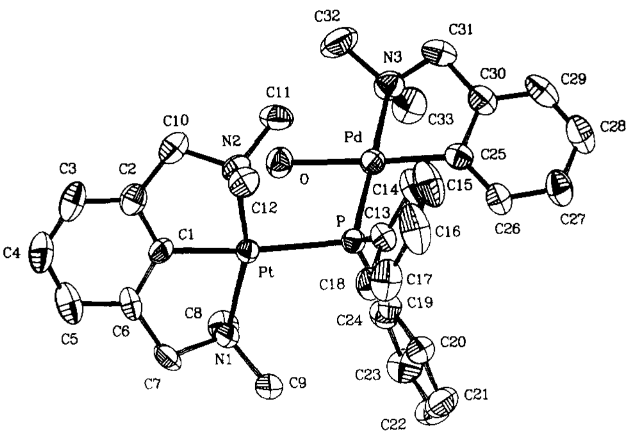
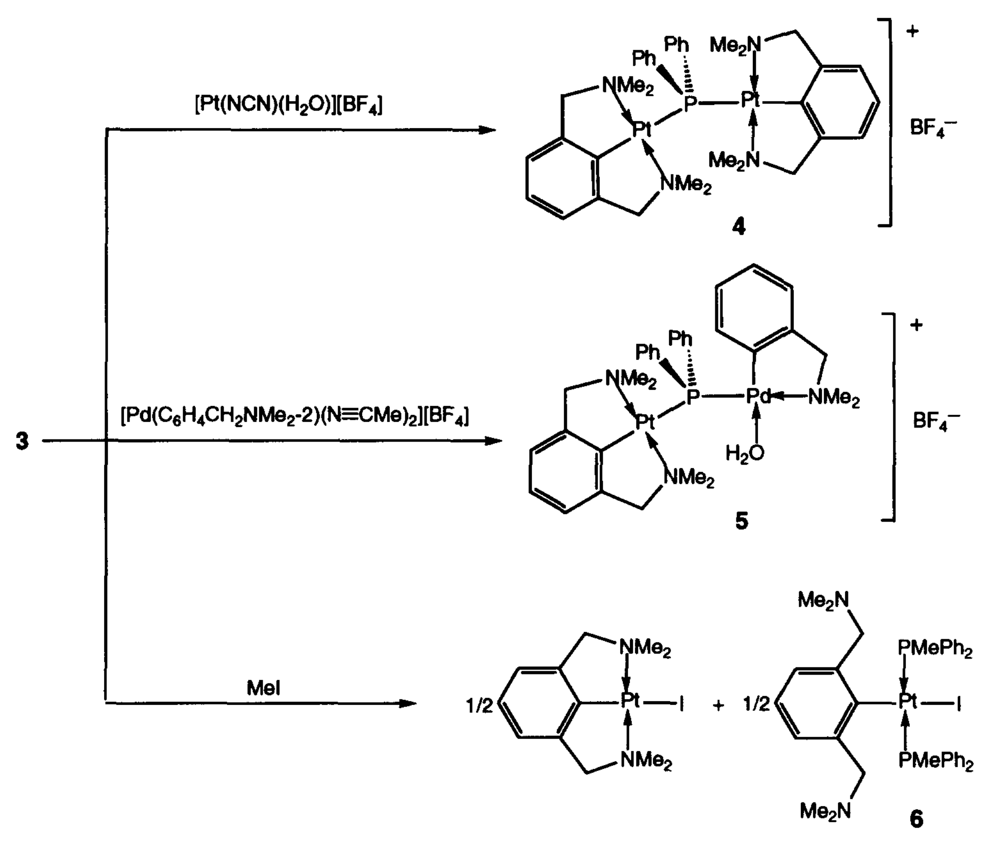


Fig. 4. ORTEP plot (50% probability level) of the complex monocation [Pt(NCN)(μ-PPh$_2$)Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(H$_2$O)]$^+$ of **5**. H atoms are not shown for clarity.

3. Discussion

Our preparation of the neutral phosphido complex [Pt(NCN)(PPh$_2$)] (**3**) by a deprotonation reaction of cationic diphenylphosphine complexes **2a** or **2b** with n-BuLi as base has direct parallels to synthetic methods successfully used by other groups to prepare phosphido complexes of several transition metals including Os [5a–d], Ru [5d] and W [5e]. Complex **3** is a member of the distinctive class of mononuclear metal phosphido species that contain a three-coordinate P(III) centre which has a transition metal as one of their substituents [11]. Such complexes have geometries characterized by a pyramidal phosphorus centre having an uncoordinated lone pair, a long M–P bond and a small (≤114°) M–P–R



Scheme 2. Reactions of diphenyphosphido complex 3 with electrophiles.

angle; in this case the PR_2 ligand is a formal one-electron donor and the phosphorus centre should be nucleophilic, Fig. 5(a) [13]. An alternative bonding mode of a PR_2 ligand is one in which there is a trigonal planar phosphorus geometry, a short M–P bond and a large (~130°) M–P–R bond angle, Fig. 5(b); in this case the M-to-P bond has double bond character and the ligand is a phosphenium cation that has electrophilic properties [13]. For our Pt(II) chemistry with a d^8 metal centre the formation of an $M{=}PR_2$ unit would require Pt–N bond dissociation as the suitable metal orbital for $d\pi$–$p\pi$ interactions is, a priori, not available. Several studies have shown that an M–PR_2 unit can be the source of rich chemistry including a very high reactivity towards electrophiles [14] and in some cases to nucleophiles also [15]. Besides this interest in reactivity there is also continuing theoretical interest in the influence of the metal centre on the pyramidal inversion in M–PR_2 systems [13]. Our present results show that 3, from both NMR parameters and from chemical reactions is, with little doubt, a phosphido complex with a phosphorus centre having nucleophilic character and in this complex monodentate coordination of a PPh_2^- to platinum has been stabilized by terdentate coordination of the NCN ligand. The unexpectedly high air-sensitivity of 3 may be a consequence of the combination of the lone pair on phosphorus and the adjacent filled dz^2 orbital on platinum, both of which can act as nucleophiles, and this 'double lone-pair' reactivity is being studied further.

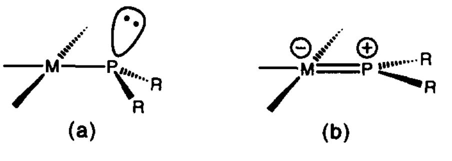


Fig. 5. Schematic drawings of (a) phosphido and (b) phosphenium transition metal complexes.

The formation of the dinuclear complexes 4 and 5 (with bridging diphenylphosphido units) by reaction of complex 3 with a cationic organometallic species clearly illustrates that the terminal phosphido complex has a phosphorus lone pair that is available for coordination. The ^{31}P NMR chemical shifts of 4 and 5 (8.73 and 42.6 ppm, respectively) and the large difference between them are fully consistent with phosphine lone-pair donation (from 3) to Pt(II) and Pd(II) ions; there is a fairly general rule that for analogous transition metal complexes δP values are found at increasingly higher field as one descends a triad [16]. Bridging phosphido units in neutral complexes are not unusual in platinum and palladium chemistry [17] and include di- and trinuclear species [17a–c] and larger clusters such as $[Pt(PPh_2)_2]_n$ (n = 6–10) [17d]. However, cationic platinum metal phosphido species [18] are much rarer and it is into this category that complexes 4 and 5 fall. Due to the unusual asymmetric nature of complex **5** and the presence of an unsupported phosphido bridge useful comparisons of the geometrical data for this species with those in the literature are necessarily limited. However, as regards the bridging phosphido unit in the cation of **5** one sees that the Pt–P distance (2.4386(18) Å) is significantly longer than those in either $[(PPh_3)PhPt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]^+$ (2.247(7) and 2.162(8) Å) [18d] or $[Pt_3(PPh_3)_3(\mu\text{-}H)(\mu\text{-}PPh_2)_2]^+$ (2.312(3), 2.299(3), 2.220(3) and 2.212(3) Å) [18e] and that the Pd–P distance (2.2929(19) Å) compares favourably with those in $[Pd_3(\mu\text{-}Cl)(\mu\text{-}PPh_2)(PPh_3)_3]^+$ (2.204(6), 2.27(4), 2.28(2) and 2.203(6) Å) [18f] and $[Pd_2(\mu\text{-}PPh_2)_2\{\mu\text{-}(Pr^i)_2PCH_2CH_2P(Pr^i)_2\}(PPh_3)_2]^+$ (2.239 and 2.184 Å) [18g]. One aspect of both **4** and **5** that is worth emphasizing is that the two metal centres are linked by a single diphenylphosphido bridge, and hereby they show their close relationship to a number of other NCN complexes of general formula $[(NCN)M(\mu\text{-}X)M'(NCN)]Z$ that contain either an unsupported halide or hydride bridge; examples include $[(NCN)Pd(\mu\text{-}Cl)Pd(NCN)][BF_4]$ and $[(NCN)Pt(\mu\text{-}H)\text{-}Pt(NCN)][BF_4]$ [19,20]. The presence of an unsupported bridge generally seems to lead to solution fluxionality and the temperature dependent ^1H NMR data for **5** are in this sense not unexpected. For **5**, the $^{31}P\{H\}$ NMR data are consistent with a heterobimetallic system and the most likely fluxional process is rotation of the {(NCN)Pt} units around the Pt–P axes. Fluxionality due to dissociation occurring slowly on the NMR time-scale could produce mononuclear phospido species and this could be the underlying cause of the air-sensitivity of this complex in solution.

Although the formation of complex **6** and [Pt(NCN)(I)] from the reaction of **3** with MeI was used to further illustrate the nucleophilicity of the phosphorus centre in the latter complex, it is worth mentioning here that the mechanism by which **6** arises is by no means clear cut. On the one hand, one could anticipate the first step to be direct electrophilic attack of Me^+ at the phosphorus atom leading to an intermediate ionic species $[Pt(NCN)(PMePh_2)]I$ in which a methyldiphenylphosphine ligand coordinates to the metal centre; a similar result has been reported by Malisch et al. [14d]. On the other hand, we know that MeI also reacts with $[Pt(NCN)(H_2O)]^+$, presumably by attack on the Pt dz^2 orbital to form a Pt(IV) intermediate, followed by a 1,2 sigmatropic shift of the Me group to the aryl skeleton, to afford a Wheland intermediate type of complex [3,4]; this reversible process has been studied theoretically by Hoffmann and co-workers [21]. In the case of **3** initial attack at Pt followed by transfer of the Me group to P (a 1,2 shift across the Pt–P bond) could also be a possible route to the intermediate ionic species $[Pt(NCN)(PMePh_2)]^+$. From this species intermolecular ligand exchange rearrangements and direct interaction of the metal atom and the halogen lead to a 1:1 mixture of [Pt(NCN)(I)] and **6** in which two $PMePh_2$ ligands have replaced both coordinated nitrogens of the NCN chelate. Here, as in many other reactions of cationic $[Pt(NCN)(L)]^+$ with halide-containing reagents, the thermodynamic stability of the halide complex [Pt(NCN)X] appears to be an important driving force.

4. Conclusions

The distinctive electronic and steric properties of the terdentate ligand system NCN have again led to a new area of chemistry, in this case related to stabilization of a terminal Pt–PPh_2 unit, with potential for the preparation of mixed metal complexes. Current studies are directed to discovering whether related ligands such as $[C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)\text{-}2]^-$ (CNN) [22] and potentially pentadentate ligands $[C_6H_3(CH_2N(Me)CH_2CH_2NMe_2)_2\text{-}2,6]^-$ (NNCNN) [23] will exhibit such a rich chemistry as NCN [1]. Certainly it is clear that our concept and application of the small organometallic cavity based on aryldiamine ligands (forming an M–C σ-bond) has considerable potential in areas like homogeneous catalysis, where studies of unusual interactions, stabilized intermediates and uncommon oxidation states are particularly relevant.

5. Experimental

5.1. General

All reactions were performed under dry nitrogen using standard Schlenk techniques. All solvents were distilled from the usual drying agents prior to use. The ionic complexes $[Pd(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)(N{\equiv}C\text{-}Me)_2][BF_4]$ [12] and $[Pt(NCN)(H_2O)][BF_4]$ (**1a**) [3] were prepared according to literature procedures; $[Pt(NCN)(H_2O)][OSO_2CF_3]$ (**1b**) was prepared in an analogous method to that used for **1a** starting from [Pt(NCN)Cl] and $AgOSO_2CF_3$ [4]. ^1H and $^{31}P\{^1H\}$ NMR were recorded at 200.13 and 81.02 MHz, respectively, on a Bruker AC 200 spectrometer; chemical shifts (δ) are referenced to TMS (0.0 ppm) and 85% H_3PO_4 (0.0 ppm), respectively. IR spectra were recorded on Perkin-Elmer 283 spectrophotometer. Mass spectra were obtained with a Kratos MS80 massspectrometer. Elemental microanalyses were performed by the analytical department of the Institute of Applied Chemistry, TNO, Zeist, Netherlands and Dornis und Kolbe, Mikroanalytisches Laboratorium, Mühlheim a/d Ruhr, Germany.

5.2. *Synthesis of [Pt(NCN)($PHPh_2$)]X (X = BF_4 (2a), OSO2CF_3 (2b))*

To a solution of [Pt(NCN)(H_2O)]X (X = BF_4, OSO_2CF_3) (0.61 mmol) in acetone (5 ml) was added $PHPh_2$ (100 μl, 0.61 mmol) at room temperature. A white solid deposited within 2 min. After stirring for 10 min, Et_2O (15–20 ml) was added slowly to further precipitate the white product. The solvent was removed by decantation and the remaining solid was washed with Et_2O (15 ml) leading to [Pt(NCN)($PHPh_2$)]X (**2a**) (0.37 g, 92%) or **2b** (0.39 g, 90%). Crystalline materials can be obtained from Et_2O-layered CH_2Cl_2 solutions.

2a: *Anal.* Calc. for $C_{24}H_{30}BF_4N_2PPt \cdot 0.5CH_2Cl_2$: C, 41.93; H, 4.45; N, 3.99; P, 4.41. Found: C, 41.72; H, 4.42; N, 3.99; P, 4.37%. IR (KBr, cm^{-1}): 2320 w ν(PH), 1050 s br ν(BF). ^1H NMR (acetone-d_6), δ: 2.97 (s, *J*(PtH) = 43, NCH_3), 4.40 (s, *J*(PtH) = 50, NCH_2), 7.1 (m, aryl of NCN); 6.86 (d, *J*(PH) = 353, *J*(PtH) not observed, PH). $^{31}P\{H\}$ NMR (acetone-d_6), δ: 5.21 (*J*(PPt) = 2028).

2b: *Anal.* Calc. for $C_{25}H_{30}F_3N_2O_3PPtS$: C, 41.61; H, 4.19; N, 3.88; P, 4.29. Found: C, 41.66; H, 4.20; N, 3.84; P, 4.39%. IR (KBr, cm^{-1}): 2315 ν(PH), 1265, 1140, 1025 (s) ν(SO). ^1H NMR (acetone-d_6), δ: 2.95 (s, *J*(PtH) = 43, NCH_3), 4.39 (s, *J*(PtH) = 50, NCH_2), 7.1 (AB_2 multiplet, aryl of NCN); 6.89 (d, *J*(PH) = 354, *J*(PtH) = 4, PH) 7.6 and 7.9 (m, Ph). ^{13}C NMR (acetone-d_6), δ: 55.8 (*J*(PtC) = 13, *J*(PC) = 2.5, NCH_3), 80.3 (*J*(PtC) = 47, *J*(PC) = 5.2, NCH_2), 162.5 (*J*(PC) = 95, *J*(PtC) not observed, C1 of NCN), 146 (*J*(PC) = 2, *J*(PtC) = 64, C2 of NCN), 120.6 (*J*(PC) = 5, *J*(PtC) = 20, C3 of NCN), 127.5 (C4 of NCN), 127.7 (*J*(PC) = 43, *J*(PtC) not observed, C1 of Ph), 130.5 (*J*(PC) = 10, *J*(PtC) < 1, C3 of Ph), 132.3 (*J*(PC) = 3, C4 of Ph), 135.1 (*J*(PC) = 12, *J*(PtC) = 10, C2 of Ph). $^{31}P\{H\}$ NMR (acetone-d_6), δ: 5.2 (*J*(PPt) = 2028).

Table 3
Crystal data and details of the structure determination for **2b** and **5**$\cdot CH_2Cl_2$

	2b	**5**$\cdot CH_2Cl_2$
Crystal data		
Formula	$C_{24}H_{30}N_2PPt \cdot CF_3SO_3$	$C_{33}H_{43}N_3OPPdPt \cdot BF_4 \cdot CH_2Cl_2$
Molecular weight	721.63	1001.93
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	12.168(1)	14.476(1)
b (Å)	12.407(1)	14.452(1)
c (Å)	18.676(1)	18.209(2)
α (°)	90.78(1)	
ß (°)	104.55(1)	94.12(1)
γ (°)	94.18(1)	
V ($Å^3$)	2720.3(4)	3799.7(6)
Z	4	4
D_{calc} (g cm^{-3})	1.762	1.7513(3)
F(000), electrons	1416	1968
μ (cm^{-1})	53.9	129.5
Crystal size (mm)	0.20 × 0.25 × 0.75	0.28 × 0.28 × 0.08
Data collection and refinement		
Temperature (K)	295	295
θ_{min}, θ_{max} (°)	1.13, 25.00	2.43, 74.98
Radiation (Å)	Mo Kα (Zr-filtered), 0.71073	Cu Kα (Ni-filtered), 1.54178
Scan type	$\omega/2\theta$	$\omega/2\theta$
Δω (°)	0.55 + 0.35tan θ	0.92 + 0.15tan θ
Horizontal and vertical aperture (mm)	3.0, 4.0	3.0, 6.0
Reference reflections	0 −4 −1, 0 −4 1	2 4 −2, 4 2 0, −2 4 2
Data set	*h* −13:14; *k* −14:14; *l* −22:0	*h* −18:18; *k* −18:0; *l* 0:22
Total data	9871	8543
Total unique data	9567	7864
Observed data	7412 ($I > 2.5\sigma(I)$)	6260 ($I > 2.5\sigma(I)$)
DIFABS correction range		0.699–1.455
No. refined parameters	345	452
Weighting scheme	$w = 1.0/\sigma^2(F)$	$w = 1.0/\sigma^2(F)$
Final *R*, *wR*, *S*	0.038, 0.037, 2.76	0.049, 0.062, 3.13
$(\Delta/\sigma)_{av}$ in final cycle	0.01	0.045
Min. and max. residual density (e $Å^{-3}$)	−1.90, 1.40 (near Pt)	−2.93, 1.64 (near Pt, Pd)

Table 4

Fractional coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for **2b**

Atom	x	y	z	U_{eq} [a] ($Å^2$)
Molecule 1				
Pt(1)	0.09688(2)	0.15001(2)	0.11820(2)	0.0354(1)
P(1)	0.06737(18)	0.33004(15)	0.08710(12)	0.0453(7)
N(101)	0.2752(5)	0.1520(5)	0.1540(3)	0.046(2)
N(102)	-0.0762(5)	0.0939(5)	0.0970(3)	0.040(2)
C(101)	0.1125(7)	-0.0046(6)	0.1428(4)	0.049(3)
C(102)	0.0152(6)	-0.0758(6)	0.1166(4)	0.046(3)
C(103)	0.0256(8)	-0.1841(6)	0.1325(5)	0.059(3)
C(104)	0.1324(8)	-0.2155(6)	0.1706(5)	0.064(3)
C(105)	0.2257(7)	-0.1443(6)	0.1946(4)	0.058(3)
C(106)	0.2164(6)	-0.0351(6)	0.1802(4)	0.044(3)
C(107)	0.3036(6)	0.0579(6)	0.2062(4)	0.054(3)
C(108)	0.3354(6)	0.2520(6)	0.1965(5)	0.056(3)
C(109)	0.3236(6)	0.1319(7)	0.0899(4)	0.053(3)
C(110)	-0.0868(6)	-0.0249(5)	0.0737(4)	0.045(3)
C(111)	-0.1611(6)	0.1472(6)	0.0393(5)	0.056(3)
C(112)	-0.1091(7)	0.1020(7)	0.1686(4)	0.054(3)
C(113)	0.0172(7)	0.4046(6)	0.1569(5)	0.049(3)
C(114)	0.0583(7)	0.3820(6)	0.2307(5)	0.060(3)
C(115)	0.0224(9)	0.4395(7)	0.2823(6)	0.083(4)
C(116)	-0.0521(9)	0.5179(7)	0.2613(7)	0.087(5)
C(117)	-0.0910(9)	0.5395(7)	0.1885(7)	0.084(5)
C(118)	-0.0582(7)	0.4840(6)	0.1358(5)	0.064(3)
C(119)	0.1797(6)	0.4185(6)	0.0636(4)	0.044(3)
C(120)	0.2303(7)	0.3835(6)	0.0111(4)	0.051(3)
C(121)	0.3202(7)	0.4456(7)	-0.0060(5)	0.062(3)
C(122)	0.3579(8)	0.5428(7)	0.0309(5)	0.075(4)
C(123)	0.3061(8)	0.5793(7)	0.0821(5)	0.075(4)
C(124)	0.2180(7)	0.5179(6)	0.0999(5)	0.063(3)
Molecule 2				
Pt(2)	0.69854(3)	0.25769(2)	0.41649(2)	0.0459(1)
P(2)	0.74302(19)	0.20898(17)	0.54162(12)	0.0531(8)
N(201)	0.7033(6)	0.1030(5)	0.3683(4)	0.060(3)
N(202)	0.6663(8)	0.4229(5)	0.4255(5)	0.083(4)
C(201)	0.6690(6)	0.2942(6)	0.3119(4)	0.052(3)
C(202)	0.6583(7)	0.3991(7)	0.2917(5)	0.061(3)
C(203)	0.6352(8)	0.4253(8)	0.2184(6)	0.079(4)
C(204)	0.6233(8)	0.3432(9)	0.1660(5)	0.079(4)
C(205)	0.6371(7)	0.2383(8)	0.1860(5)	0.069(4)
C(206)	0.6590(7)	0.2130(7)	0.2591(5)	0.062(3)
C(207)	0.6710(14)	0.1045(9)	0.2909(5)	0.156(8)
C(208)	0.6208(16)	0.0273(11)	0.3845(10)	0.309(15)
C(209)	0.8139(11)	0.0695(12)	0.3880(8)	0.261(10)
C(210)	0.6856(9)	0.4769(7)	0.3563(5)	0.081(4)
C(211)	0.5447(9)	0.4224(8)	0.4262(7)	0.107(6)
C(212)	0.7404(12)	0.4832(8)	0.4907(6)	0.138(7)
C(213)	0.8947(7)	0.2190(6)	0.5868(4)	0.053(3)
C(214)	0.9356(8)	0.1804(7)	0.6558(5)	0.064(3)
C(215)	1.0506(9)	0.1857(7)	0.6870(5)	0.071(4)
C(216)	1.1269(8)	0.2264(7)	0.6496(6)	0.075(4)
C(217)	1.0873(9)	0.2640(8)	0.5800(6)	0.079(4)
C(218)	0.9700(8)	0.2598(7)	0.5482(5)	0.066(4)
C(219)	0.6750(7)	0.2679(6)	0.6082(4)	0.052(3)
C(220)	0.7309(7)	0.3526(7)	0.6559(5)	0.063(3)
C(221)	0.6731(10)	0.3963(8)	0.7033(5)	0.080(4)
C(222)	0.5681(10)	0.3546(10)	0.7072(6)	0.091(5)
C(223)	0.5149(9)	0.2719(10)	0.6607(7)	0.091(5)
C(224)	0.5685(8)	0.2286(7)	0.6103(6)	0.074(4)

(continued)

Table 4 (*continued*)

Triflate anion 1				
S(1)	0.6408(2)	0.79558(17)	0.15203(14)	0.0610(8)
F(11)	0.5028(6)	0.8101(6)	0.0233(4)	0.140(3)
F(12)	0.5751(6)	0.9593(5)	0.0735(4)	0.148(4)
F(13)	0.4448(6)	0.8734(6)	0.1085(5)	0.156(4)
O(11)	0.5828(6)	0.6940(5)	0.1580(4)	0.098(3)
O(12)	0.7301(5)	0.7901(6)	0.1171(4)	0.105(3)
O(13)	0.6639(8)	0.8639(6)	0.2157(4)	0.148(4)
C(1)	0.5352(9)	0.8644(9)	0.0872(6)	0.078(4)
Triflate anion 2				
S(2)	0.2892(3)	0.1947(3)	0.42012(18)	0.0953(12)
F(21)	0.0766(7)	0.2237(7)	0.3932(5)	0.157(4)
F(22)	0.1149(7)	0.1083(7)	0.3242(4)	0.164(4)
F(23)	0.1145(6)	0.0757(5)	0.4351(4)	0.123(3)
O(21)	0.3001(9)	0.2722(8)	0.3672(5)	0.181(6)
O(22)	0.3472(8)	0.1010(9)	0.4139(7)	0.187(6)
O(23)	0.3050(7)	0.2372(6)	0.4930(4)	0.119(4)
C(2)	0.1502(9)	0.1479(9)	0.3908(6)	0.083(5)

[a] U_{eq} = 1/3 of the trace of the orthogonalized U.

5.3. *Synthesis of [Pt(NCN)(PPh$_2$)] (3)*

A solution of n-butyllithium (0.031 g, 0.48 mmol) in hexane was added dropwise to a stirred suspension of [Pt(NCN)(PHPh$_2$)][BF$_4$] (**2a**) (0.32 g, 0.48 mmol) in Et_2O (30 ml) held at −40 °C by a dry-ice/acetone bath. The mixture was stirred further while the temperature of the mixture was slowly raised over ~45 min to 0 °C. The bright yellow suspension thus obtained was then cooled down to −50 °C. Subsequently cold hexane (30 ml at −50 °C) was added to the reaction mixture resulting in the precipitation of a yellow solid which was isolated by centrifugation from the mother liquor and washed with cold hexane (20 ml). This afforded complex **3** (0.25 g, 90%) contaminated with $LiBF_4$ as an air-sensitive bright yellow solid. Extraction of this solid with toluene (25 °C) and filtration to remove $LiBF_4$ afforded a yellow solution of complex **3**, pure enough for further chemical reactions. Attempts at recrystallization inevitably led to product degradation.

^{1}H NMR (C_6D_6), δ: 2.52 (s, 12H, J(PtH) = 43, NCH_3), 3.35 (s, 4H, J(PtH) = 48, NCH_2), 7.1 (m, 9H, aryl), 8.24 (m, 4H, aryl o-H of PPh_2). ^{31}P NMR (toluene-d$_8$, 254 K), δ: 0.1 (J(PPt) = 1305). Mass spectrum: m/e 571 $(M+H)^+$, 587 $(M+O+H)^+$.

5.4. *Reaction of 3 with [Pt(NCN)(H$_2$O)][BF$_4$]; synthesis of [Pt(NCN)$_2$(μ-PPh$_2$)][BF$_4$] (4)*

[Pt(NCN)(H$_2$O)][BF$_4$] (0.12 g, 0.24 mmol) was added to a stirred solution of **3** (0.14 g, 0.24 mmol) in toluene (20 ml) at −20 °C. The mixture was allowed to warm up slowly and a white solid began to deposit from the reaction mixture. After 2 h, the white material was filtered off and washed with toluene (15 ml) and pentane (15 ml) affording crude **4**; yield 0.24 g (94%). NMR spectra showed small amounts of mononuclear impurities. After recrystallization from a CH_2Cl_2/diethyl ether mixture at −20 °C the complex was obtained analytically pure as the solvate complex **4**·0.5CH$_2$Cl$_2$.

Anal. Calc. for $C_{36}H_{48}BF_4N_4PPt_2 \cdot 0.5CH_2Cl_2$: C, 40.32; H, 4.54, N, 5.15. Found: C, 39.92; H, 4.59, N, 5.11.%. IR (KBr, cm^{-1}): 1050 br s ν(BF). ^{1}H NMR (acetone-d$_6$), δ: 2.70–3.03 (m, 24H, NCH_3), 3.93–4.42 (m, 8H, CH_2N), 6.80–7.05 (m, 6H, aryl of NCN), 7.43–8.37 (m, 10H, aryl of PPh_2). ^{31}P{H} NMR (acetone-d$_6$), δ: 8.73 (1:8:18:8:1 pentet, J(PPt) = 1508).

5.5. *Reaction of 3 with [Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(N≡CMe)$_2$][BF$_4$]; synthesis of [Pt(NCN)(μ-PPh$_2$)Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(H$_2$O)][BF$_4$] (5)*

To a stirred, bright yellow, solution of **3** (0.11 g, 0.19 mmol) in toluene (20 ml) at −50 °C was added [Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(N≡CMe)$_2$][BF$_4$] (0.082 g, 0.20 mmol). As the temperature of the reaction mixture was slowly raised over 1 h to room temperature the colour of the mixture became paler. At room temperature a small amount of excess [Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(N≡CMe)$_2$][BF$_4$] was filtered off to afford a clear, pale yellow solution which was evaporated to dryness in vacuo. The residual solid was washed with pentane (2×15 ml) to afford a beige solid. Recrystallization of this solid from a CH_2Cl_2/pentane mixture at −20 °C afforded the solvate complex **5**·CH$_2$Cl$_2$ as rhombic crystals suitable for X-ray crystallography; yield 0.06 g (30%). *Anal.* Calc. for $C_{33}H_{43}BF_4N_3OPPdPt \cdot CH_2Cl_2$: C, 40.76; H, 4.53; N, 4.19. Found: C, 39.97; H, 4.50; N, 4.08%. ^{1}H NMR (CD_2Cl_2 + drop of acetone-d$_6$ for solubility) δ: 2.50 (s, H_2O), 2.54 (s, 3H, (Pd)NCH$_3$), 2.55 (s, 3H, (Pd)NCH$_3$), 2.71 (s, 12H, J(PtH) = 42.5, NCH_3 of NCN), 3.89 (s, 2H, (Pd)NCH$_2$), 4.06 (s, 4H,

Table 5
Final atomic coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for $5 \cdot CH_2Cl_2$

Atom	x	y	z	U_{eq} [a] (Å^2)
Pt	0.61368(2)	0.74377(2)	0.35562(2)	0.0371(1)
Pd	0.50617(4)	0.50783(4)	0.29414(3)	0.0436(2)
P	0.57720(12)	0.63797(12)	0.25330(10)	0.0389(5)
O	0.5570(4)	0.5430(4)	0.4083(3)	0.0563(19)
N(1)	0.7611(4)	0.7469(4)	0.3655(4)	0.0453(17)
N(2)	0.4739(5)	0.7756(5)	0.3758(4)	0.0496(19)
N(3)	0.4364(5)	0.3875(5)	0.3343(4)	0.059(3)
C(1)	0.6339(5)	0.8237(5)	0.4438(4)	0.045(2)
C(2)	0.5606(6)	0.8474(5)	0.4829(5)	0.055(3)
C(3)	0.5761(8)	0.9068(6)	0.5429(5)	0.071(4)
C(4)	0.6634(8)	0.9382(7)	0.5633(6)	0.076(4)
C(5)	0.7362(8)	0.9147(6)	0.5238(6)	0.073(3)
C(6)	0.7227(6)	0.8571(5)	0.4611(4)	0.051(3)
C(7)	0.7935(5)	0.8315(6)	0.4093(5)	0.058(3)
C(8)	0.7942(6)	0.6621(6)	0.4050(5)	0.057(3)
C(9)	0.8084(6)	0.7531(6)	0.2946(5)	0.057(3)
C(10)	0.4733(7)	0.8025(6)	0.4561(5)	0.062(3)
C(11)	0.4025(6)	0.7036(6)	0.3595(6)	0.063(3)
C(12)	0.4470(6)	0.8579(5)	0.3304(5)	0.055(3)
C(13)	0.5105(5)	0.7100(5)	0.1853(4)	0.049(3)
C(14)	0.4199(6)	0.6908(6)	0.1620(5)	0.063(3)
C(15)	0.3697(8)	0.7544(7)	0.1170(7)	0.090(4)
C(16)	0.4092(9)	0.8346(7)	0.0953(6)	0.092(5)
C(17)	0.5006(8)	0.8539(6)	0.1166(5)	0.075(4)
C(18)	0.5514(7)	0.7924(6)	0.1621(5)	0.058(3)
C(19)	0.6757(5)	0.5981(5)	0.2057(4)	0.044(2)
C(20)	0.7024(6)	0.6363(6)	0.1395(5)	0.056(3)
C(21)	0.7847(7)	0.6070(7)	0.1114(6)	0.074(4)
C(22)	0.8391(7)	0.5398(7)	0.1472(6)	0.077(4)
C(23)	0.8107(7)	0.5006(6)	0.2102(6)	0.071(3)
C(24)	0.7295(6)	0.5278(5)	0.2393(5)	0.054(3)
C(25)	0.4613(5)	0.4578(5)	0.1969(5)	0.048(3)
C(26)	0.4930(6)	0.4700(5)	0.1279(4)	0.054(3)
C(27)	0.4594(7)	0.4173(6)	0.0674(5)	0.065(3)
C(28)	0.3927(8)	0.3534(7)	0.0745(6)	0.078(4)
C(29)	0.3581(7)	0.3423(7)	0.1412(6)	0.074(4)
C(30)	0.3913(6)	0.3893(6)	0.2030(5)	0.060(3)
C(31)	0.3553(7)	0.3751(7)	0.2773(6)	0.076(4)
C(32)	0.3995(9)	0.3995(8)	0.4069(6)	0.090(5)
C(33)	0.4973(8)	0.3055(6)	0.3344(6)	0.076(4)
Cl(1)	0.4848(3)	0.0875(3)	0.2053(4)	0.173(3)
Cl(2)	0.2953(3)	0.0933(3)	0.2310(3)	0.1462(19)
C(34)	0.3763(9)	0.0801(11)	0.1681(8)	0.125(7)
F(1)	0.2304(7)	0.6822(6)	0.4982(5)	0.157(4)
F(2)	0.2469(7)	0.6016(7)	0.6039(5)	0.160(5)
F(3)	0.3480(7)	0.5910(6)	0.5223(5)	0.152(4)
F(4)	0.2152(9)	0.5314(7)	0.4996(6)	0.202(7)
B(1)	0.2528(10)	0.6047(10)	0.5317(8)	0.082(5)

[a] U_{eq} = 1/3 of the trace of the orthogonalized U.

J(PtH) = 51, NCH_2 of NCN), 6.7–8.0 (m, 17H, aryl). ^{31}P NMR (acetone-d_6, −35 °C) δ: 42.6 br (J(PtP) = 1880). IR (KBr, cm^{-1}): 1050 br s ν(BF).

5.6. *Reaction of 3 with methyl iodide; synthesis of [Pt(NCN)(I)(PMePh$_2$)$_2$] (6)*

To a stirred bright yellow solution of [Pt(NCN)(PPh$_2$)] (**3**) (0.14 g, 0.25 mmol) in toluene (30 ml) methyl iodide (0.07 g, 0.49 mmol) was added dropwise at −50 °C whereupon the colour immediately became paler. The temperature was raised slowly over 90 min to room temperature and the solvent then pumped off in vacuo. The solid residue was then extracted with a minimum of CH_2Cl_2. Addition of a pentane layer to this extract afforded a cream solid precipitate which was isolated by filtration and washed further with pentane. This solid was characterized spectroscopically as a 1:1 mixture of **6** and known [Pt(NCN)(I)].

6: ^{1}H NMR (CD_2Cl_2), δ: 1.54 (t, 6H, $^{(4+2)}J$(PH) = 7, ^3J(PtH) = 36, PCH_3), 2.02 (s 12H, NCH_3), 3.46 (s, 4H, ^4J(PtH) = 10, NCH_2), 6.8–7.7 (m, aryl). ^{31}P{H} NMR (CD_2Cl_2), δ: 0.7 (J(PPt) = 2917).

5.7. *X-ray data collection, structure determination and refinement of 2b and 5·CH$_2$Cl$_2$*

X-ray data for **2b** and **5** were collected on an Enraf-Nonius CAD4 diffractometer for crystals mounted on top of a glass fibre. Unit cell parameters were derived from SET4 setting angles [24] of 25 reflections in the range $12 < \theta < 18°$ and $14 < \theta < 20°$ for **2b** and $5 \cdot CH_2Cl_2$, respectively, and checked for higher lattice symmetry [25]. Intensity data for **2b** were corrected for Lp and for linear decay (9%) of the intensity control reflections during 130 h of X-ray exposure time, but an absorption correction was deemed unnecessary for this needle-shaped crystal. Intensity data for **5** were corrected for Lp, for a linear decay (16.2%) of the intensity control reflections during 130 h of X-ray exposure time, and for absorption using the DIFABS method [26]. The structural solutions for **2b** (using Patterson techniques) and for $5 \cdot CH_2Cl_2$ (using direct methods to reveal the Pd and Pt positions) were found with SHELXS86 [27] and subsequent difference Fourier analyses, with SHELX76 [28] being used for full matrix least-squares refinement on F. Hydrogen atoms were introduced at calculated positions (C–H = 0.98 Å), except those on the P atom in **2b** and on the water O atom in $5 \cdot CH_2Cl_2$ which were located from difference Fourier maps. All non-hydrogen atoms were refined with anisotropic thermal motion parameters. H atoms were taken into account in the refinement riding on their carrier atoms except for P–H of **2b** for which the positional parameters were refined as well; the H atoms of **2b** were refined with five common isotropic thermal parameters, those of **5** were refined with one common isotropic thermal parameter. Neutral atom scattering factors were taken from Cromer and Mann [29] and corrected for anomalous dispersion [30]. All calculations (SHELXS86, SHELX76 and PLATON [31] (geometrical calculations and drawings)) were done on a MicroVAX II cluster.

Crystal data and numerical details of the data collection and structure refinement of **2b** and **5** are given in Table 3. Final refined atomic coordinates and equivalent isotropic thermal parameters are listed in Tables 4 (**2b**) and 5 (**5**·CH_2Cl_2). Selected structural data (bond distances, interbond angles and dihedral angles) for **2b** and **5**·CH_2Cl_2 are found in Tables 1 and 2, respectively.

6. Supplementary material

Complete tables of fractional coordinates of all atoms, bond distances and angles, anisotropic thermal parameters, and observed and calculated structure factors for **2b** and **5**·CH_2Cl_2 may be obtained from author A.L.S.

Acknowledgements

The X-ray data collection of **2b** and **5**·CH_2Cl_2 was kindly done by A.J.M. Duisenburg. This work was supported in part (A.L.S. and W.J.J.S.) by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for Scientific Research (N.W.O.).

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