ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 587 (1999) 165–175

Journal of Organo metallic Chemistry

Synthesis of palladium and platinum complexes containing the multidentate ligands $PPh_2CH_2(^tBu)$=N–N=C(R)Q (R = H, Me; Q = 2-pyridine, 2-thiophene, *o*-BrC_6H_4). Crystal structure of [PtMe{$PPh_2CHC(^tBu)$NNCMe(2-py)-κ^3N,N',P}] and [PdBr{$PPh_2CH_2C(^tBu)$=N–N=CHC_6H_4}-κ^3C,N,P]

Chunghun Lee [a], Youngjin Kang [a], Sang Ook Kang [a,1], Jaejung Ko [a,*], Jung Whan Yoo [a], Moon Hwan Cho [b]

[a] *Department of Chemistry, Korea University, Chochiwon, Chungnam 339-700, South Korea*
[b] *Department of Chemistry, Kangwon National University, Chuncheon 200-701, South Korea*

Received 9 February 1999; received in revised form 20 May 1999

Abstract

The reaction of $PPh_2CH_2C(^tBu)$=NN=CMe(NC_5H_4) (**1**) with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] gave the six-membered metallacycle [$PtMe_2${$PPh_2CHC(^tBu)$NNCMe(2-py)-κ^2N,P}] (**4**) which was converted into [PtMe{$PPh_2CHC(^tBu)$NNCMe(2-py)-κ^3N,N',P}] (**5**) at elevated temperature. Treatment of the methyl platinum complex **5** with an excess of MeI gave [$PtMe_2I${$PPh_2CHC(^tBu)$NNCMe(2-py)-κ^3N,N',P}]. A similar reaction of $PtMe_2$(cod) with [$PPh_2CH_2C(^tBu)$=NN=C(HSC_4H_3)] (**2**) also afforded $PtMe_2${$PPh_2CH_2C(^tBu)$NNC(H)SC_4H_3-κ^2N,P} (**7**). The prolonged heating of **7** led to decomposition rather than the cycloplatination product. The treatment of **2** with $PtCl_2$(cod) in the presence of NEt_3 gave the deprotonated platinum(II) complex [Pt{PPh_2CH=$C(^tBu)$N–N=C(H)SC_4H_3-κ^2N,P}$_2$] (**8**) containing an ene-hydrazone backbone. The cyclopalladated metallacycle [PdBr{$PPh_2CH_2C(^tBu)$=N–N=CHC_6H_4}-κ^3C,N,P] (**9**) has been prepared by the oxidative addition of the *o*-halo-substituted phosphino hydrazone derived from $PPh_2CH_2C(^tBu)$=N–N=C(H)(*o*-BrC_6H_4) (**3**) to $Pd_2(dba)_3$. These new complexes have been characterized by ^1H-, ^{13}C-, and ^{31}P-NMR, and elemental analyses. The molecular structures of **4**, **5** and **9** have been determined by a single-crystal X-ray diffraction study. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Phosphino hydrazone; Palladium; Platinum; Crystal structure; Cyclization

---

1. Introduction

In recent years, cyclometalated compounds with multidentate ligands have been extensively studied because of their potential utility in organic synthesis [1], and a number of their synthetic approaches have been investigated [2]. Among these, the palladium and platinum complexes with multidentate ligands are especially interesting because of their catalytic activity [3]. It has recently been found that P–N ligands, in particular, are suitable ligands for palladium or platinum-catalyzed cross-coupling reactions [4] and allylic alkylation [5]. Moreover, there is an increasing interest in the palladium(II) and platinum(II) complexes with terdentate ligands such as PNN [6], PNC [7], SNC [8], and PNP [9].

Recently, Shaw and co-workers have described the synthesis of the phosphino hydrazone *Z*-$Ph_2PCH_2C(^tBu)$=NNH_2 (**L**) [10] and its extensive chemistry [11]. Compound **L** easily undergoes condensation with aldehydes and ketones to give azines. We reasoned that the condensation of 2-acetylpyridine or 2-thiophenecarbaldehyde with **L** ought to give a new ligand that can coordinate to the palladium or platinum as a terdentate ligand. This proved to be the case. These ligands attracted our attention because they contain the two tautomeric forms such as an azine↔ene-hydrazone, i.e. a 1,3-proton shift and the intrinsic flexibility

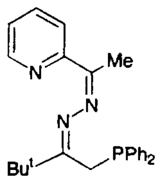
---

* Corresponding author. Fax: + 82-415-8675396.

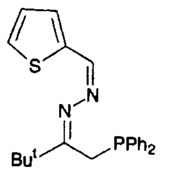
[1] Also corresponding author.

PII: S0022-328X(99)00290-9

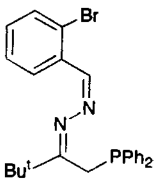
of the ligands facilitates the adaptation of the bite angles between the metal and the donor atoms. In addition, we are interested in conducting a systematic study of the use of terdentate ligands obtained by replacing the pyridine moiety with 2-bromobenzene. As part of our continuing studies on the synthetic utility and understanding of the uncommon coordination geometry of multidentate ligands [12], we attempted to synthesize a variety of palladium and platinum complexes. We now report the synthesis, reactivity, and characterization of the palladium and platinum complexes of the multidentate ligand and the single-crystal X-ray structures of three such compounds.



1



2



3

2. Results and discussion

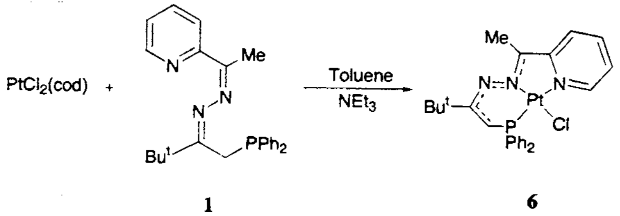
2.1. Synthesis and characterization of the ligands

The phosphino-N-acetylpyridine hydrazone PPh$_2$-CH$_2$C(^{t}Bu)=NN=CMe(NC$_5$H$_4$) (**1**) was prepared by the condensation of hydrazone phosphine PPh$_2$CH$_2$C-(^{t}Bu)=NNH$_2$ with 2-acetylpyridine in hot methanol. The azine ligands PPh$_2$CH$_2$C(^{t}Bu)=NN=CHQ (Q = 2-thiophenecarboxaldehyde **2**; 2-bromobenzaldehyde **3**) were similarly prepared. Ligands **1**–**3** were characterized by ^{1}H-, ^{13}C- and ^{31}P-NMR, IR and elemental analysis. The ^{31}P{^{1}H}-NMR spectrum of **1** showed a singlet at δ -10.78, which is in agreement with similar diarylphosphine ligands. The resonance of the methylene carbon appears as a doublet with coupling ^2J(PC) = 26.1 Hz in the ^{13}C-NMR spectrum. We suggest that ligands **1**–**3** have the *anti* configuration around the C=N bond as do the several complexes derived from them.

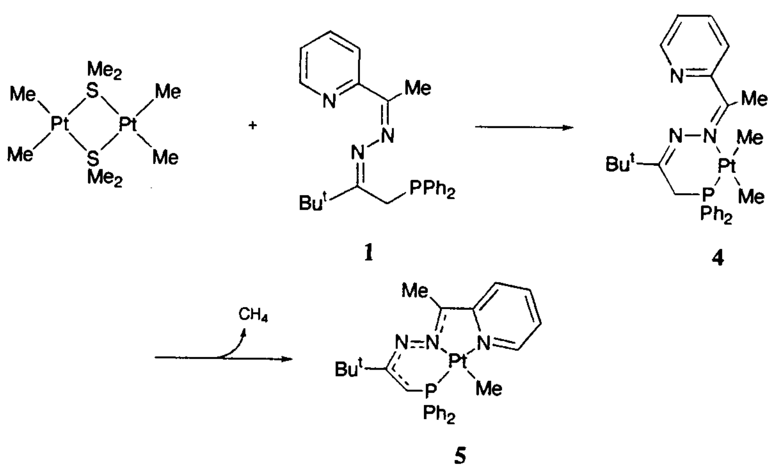
2.2. Synthesis and characterization of complexes from the ligand **1**

The reaction of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] with ligand **1** in toluene afforded a greenish–yellow solid **4** which showed the common pattern for a 'PtMe$_2$' *cis* arrangement with the corresponding loss of SMe$_2$. The product **4** was also prepared by the reaction of PtMe$_2$(cod) and ligand **1** in high yield. However, the product could not be isolated in pure form, since a further reaction occurred to give the cyclization product even at room temperature (r.t.). When the reaction was carried out at elevated temperature, it gave rise to the nitrogen coordination product PtMe{PPh$_2$CHC(^{t}Bu)NNCMe(2-py)-κ^3*N*,*N*′,*P*} (**5**) (Scheme 1).

These reactions are expected to proceed by ligand substitution to give the corresponding dimethyl(PN)-platinum(II) complex followed by elimination of methane from Pt–Me and an N–H bond formed by the involvement of an azine↔ene-hydrazone tautomerism. The isostructural complex, PtCl{PPh$_2$CHC(^{t}Bu)-NNCMe(2-py)-κ^3*N*,*N*′,*P*} (**6**) has been synthesized from the reaction of PtCl$_2$(cod) with **1** in toluene (Eq. (1)).



(1)



Scheme 1.

Compounds **4**–**6** were characterized by ^{1}H-, ^{13}C- and ^{31}P-NMR, mass spectrometry and elemental analysis. The structures of **4** and **5** were determined by single-crystal X-ray diffraction. The NMR spectroscopic data for **4** and **5** are consistent with the solid-state structure as determined by X-ray crystallography. In the ^{1}H-NMR spectrum of **4**, the resonances of the methyl groups bound to platinum gave rise to two signals at δ 0.62 and -0.06 with ^2J(PtH) values in the range 70–90 Hz, as reported for analogous compounds [13]. The coupling constant values with $^2J(\mathrm{PtH}) = 90.4$ and $^2J(\mathrm{PtH}) = 69.6$ Hz are assigned to the methylplatinum *trans* to the imine and phosphorus, respectively, since phosphorus has the stronger *trans* influence. These are typical values for methylplatinum(II) complexes [14]. The presence of two Pt–CH_3 bonds was further proved by the observation of two resonances in the ^{13}C-NMR spectrum at 7.62 and 1.22 ppm, which couple with ^{31}P and ^{195}Pt. The methylene CH_2P protons gave two peaks at δ 3.55 and 2.51 with $^2J(\mathrm{PH}) = 2.1$ and $^3J(\mathrm{PtH}) = 21.6$ Hz, demonstrating that the methylene protons are diastereotopic. The complex showed a single resonance in its ^{31}P{^{1}H}-NMR spectrum with satellites due to platinum-195, and the large value of ^1J(PtP) of 3773 Hz is consistent with a phosphorus *trans* to a methyl group [15]. Complex **4** slowly decomposed in solution to give **5**, together with methane. This is an example of the well-known cyclometallation reaction [16]. This could involve an azine↔ene-hydrazone tautomerism, i.e. a 1,3-proton shift. The equilibrium between the azine↔ene forms of organic molecules, containing the $CH_2C{=}N{-}N$ fragment, is well-known [17], and it has been shown that the presence of a metal fragment and a specific organic fragment may shift the equilibrium by imposing coordination to the metal center. In the ^{1}H-NMR data for complex **5**, the single platinum-methyl resonance, coupled with ^{195}Pt, appears at δ 0.67 with $^2J(\mathrm{PtH}) = 68.2$ Hz. Compared to the complex **4**, the coupling constant ^2J(PtH) is smaller. However, this value is still within the range expected for a platinum(II) complex [18], and the difference may be attributed to the geometric changes during *ortho* metalation. The methine CH=C proton gave a peak at δ 4.23 ppm with $^4J(\mathrm{PtH}) = 39.2$ Hz. Additionally, ^{195}Pt couplings are present in the ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectra of the platinum compound **5**; the large Pt–P coupling constant of 3786 Hz, and Pt–C coupling constant of 786 Hz on the methyl group of **5** indicate that the methyl resides *cis* with respect to the phosphorus. Although all the spectra of **4** and **5** are consistent with the proposed formulation, the bonding mode and configuration of **4** and **5** are still unclear. Accordingly, the monomeric nature for **4** and **5** were confirmed through a single-crystal X-ray diffraction analysis.

2.3. Description of the molecular structures of 4 and 5

Suitable crystals of **4** and **5** were grown in toluene–hexane solution. Details of the X-ray data collection and structure refinement for complexes **4** and **5** are presented in Table 1. The molecular structure and atom-numbering schemes for **4** and **5** are given in Fig. 1 and Fig. 2, respectively. Selected bond distances and angles are given in Table 2. The crystal structure of **4** consists of discrete molecules separated by van der Waals distances. The platinum atom of **4** is in a slightly distorted square-planar environment coordinated to phosphorus, two carbons, and iminic nitrogen atom. The iminic nitrogen and the phosphorus adopt a *cis* arrangement. The ligand–platinum distances are close to other platinum complexes containing six-membered phosphino–imino chelates [15]. The Pt–C(30) distance of 2.061(10) Å is relatively short, probably due to the better π-accepting capacity of the *trans*-situated imino nitrogen N9.

Several points are noteworthy regarding the structure in **4**. The pyridyl group of the ligand in **4** is rotated away from the phosphorus atom giving an *anti* configuration. The six-membered ring chelate of the PN ligand causes a twisted conformation of the ligand. In particular, the methylene group is puckered, resulting in the diastereotopic behavior in the ^{1}H-NMR of **4**. The molecular structure of **5** comprises the expected square planar arrangement of the three donor atoms of PNN and the methyl ligand around the platinum atom. The bond angles between Pt and two neighboring donor atoms lie in the range 85.16(19)–95.3(3)°, the smallest angles corresponding to the terdentate ligand. The ligand–palladium distances are close to those of other palladium complexes containing five- and six-membered phosphino-imino chelates [9c]. The most striking features of **5** are the configurations around the C=N bonds. The 'ene' carbons, C(12) and C(17), are separated by 1.38(2) Å, consistent with a C=C double bond. The imine N(11)–C(12) distance (1.36(2) Å) is slightly longer than that of **4**. A significant change in bond length is observed for the N(11)–N(10) distance (1.33(2) Å), consistent with an N=N double bond. The bond lengths of the ligand indicate that **5** exists in the azine↔ene-hydrazone tautomerism, leading to the delocalization through five atoms, C(17)–C(12)–N(11)–N(10)–C(8).

2.4. Oxidative addition to PtMe{$PPh_2CHC(^tBu)$-NNCMe(2-Py)-κ^3N,N',P}

The addition of iodomethane to a solution of **5** in CH_2Cl_2 at 50–60°C led to the immediate formation of a dimethylplatinum(IV) complex $PtMe_2I$\{PPh_2CHC-(^{t}Bu)NNCMe(2-py)-κ^3N,N',P\} (**10**) (Eq. (2)). Oxidative addition of the alkyl halides to platinum(II) substrates

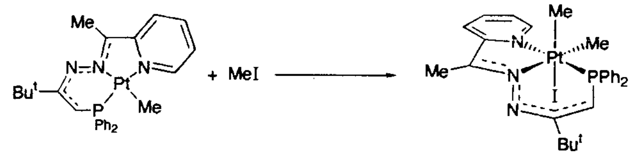
Table 1
Crystallographic data for **4**, **5** and **9**

Formula	$C_{27}H_{34}N_3PPt$	$C_{26}H_{30}N_3PPt$	$C_{25}H_{26}BrN_2PPd$
Formula weight	626.6	610.6	571.8
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P1$	$P2_1/c$
a (Å)	11.693(7)	8.808	11.990(7)
b (Å)	15.661(19)	9.867	13.132(9)
c (Å)	14.613(6)	16.145	19.349(11)
α (°)		103.50	
β (°)	93.018(4)	96.69	97.605(5)
γ (°)		112.96	
V (Å^3)	2672.0(4)	1221.9	3020.0(3)
Z	4	2	4
F(000)	1240	600	1332
D_{calc} (g cm^{-3})	1.558	1.660	1.454
Absorption coefficient (mm^{-1})	5.329	5.825	2.013
Crystal dimensions (mm)	0.3 × 0.2 × 0.2	0.4 × 0.2 × 0.4	0.2 × 0.2 × 0.3
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Data set (hkl)	−14:14, 0:19, 0:18	−10:10, −11:11, 0:19	0:14, 0:16, −23:23
θ Range (°)	1.91–25.97	1.33–25.97	1.71–25.97
T (K)	293	293	293
No. of data collected	5559	4950	6237
No. of unique reflections	5238	4770	5909
No. of parameters refined	289	280	320
Goodness-of-fit	0.853	0.564	0.910
R [a]	0.036	0.073	0.057
R_w [b]	0.103	0.164	0.114

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $R_w = \Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/[\sigma^2(F_c)+0.001(F_o)^2]$.

is well documented and experimental evidence points to a *trans* stereochemistry in the resulting platinum compounds [19].



5 **10**

(2)

Compound **10** was characterized by NMR spectroscopy and elemental analysis. The complex **10** gave two PtMe resonances in the ^{1}H-NMR spectrum. The coupling constant ^2J(PtH) was 65 Hz for the PtMe group *trans* with the iodide and 62 Hz for the PtMe group *trans* to the imine nitrogen. As reported for analogous compounds [20], the methyl *trans* to the iodide appears at higher fields as compared with the methyl groups *trans* to the nitrogen atoms and has a somewhat higher value of ^2J(PtH) due to the low *trans* influence of the iodide [13]. Our results are consistent with previous observations. The reduced coupling constants ^2J(PtH) for **10** compared to **5** are typical of platinum(IV) compared to platinum(II) [21]. Two resonances in the ^{13}C-NMR spectrum appear at δ 3.6 and −0.9 ppm with platinum satellites (J(PtC) = ca. 730–780 Hz). The small value of ^1J(Pt–P) (1692 Hz) in the ^{31}P{^{1}H}-NMR spectrum is also typical for platinum(IV) [22].

*2.5. Synthesis and characterization of complexes from the ligand **2***

The six-membered metallacycle PtMe$_2${PPh$_2$CH$_2$C(^{t}Bu)=N–N=C(H)SC$_4$H$_3$-κ^2*N*,*P*} (**7**) was prepared by the reaction of PtMe$_2$(cod) with **2** in toluene (Scheme

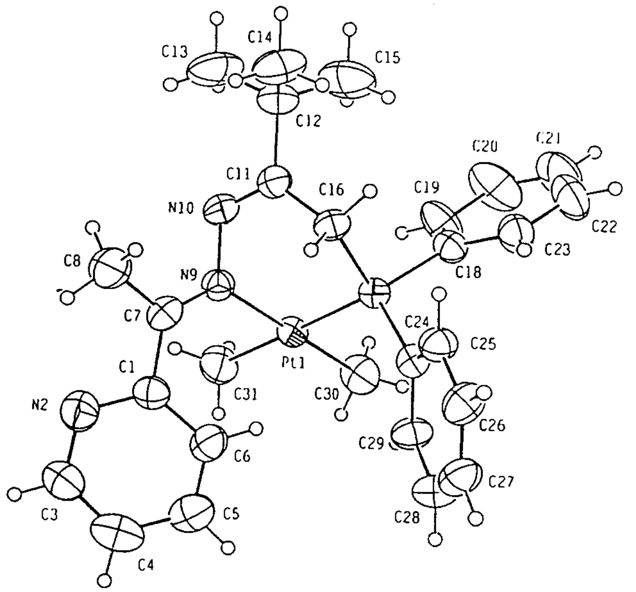


Fig. 1. Molecular structure of PtMe$_2${PPh$_2$CH$_2$C(^{t}Bu)=N–N=CMe(2-py)-κ^2*N*,*P*} (**4**). The thermal ellipsoids are drawn at the 30% level.

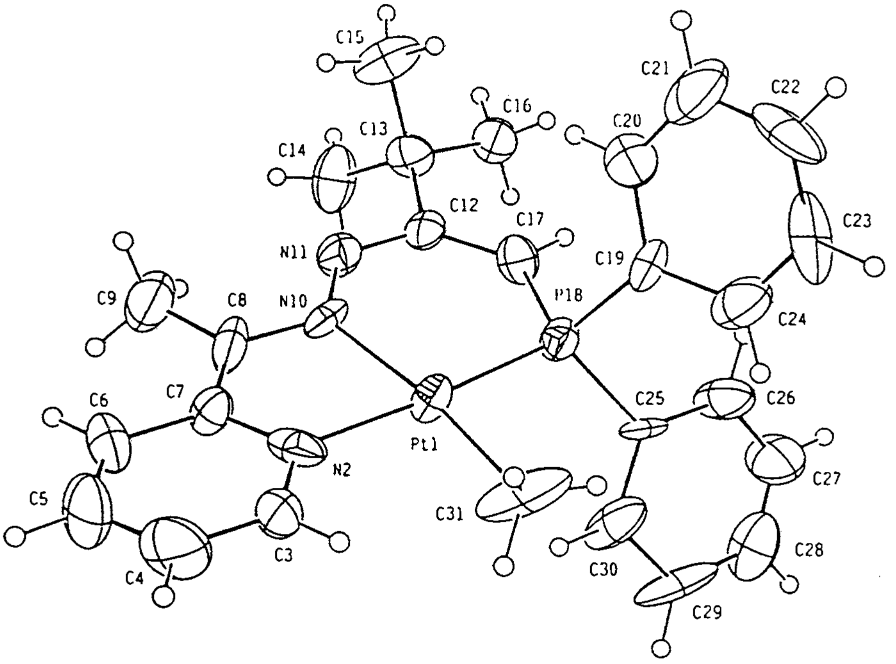


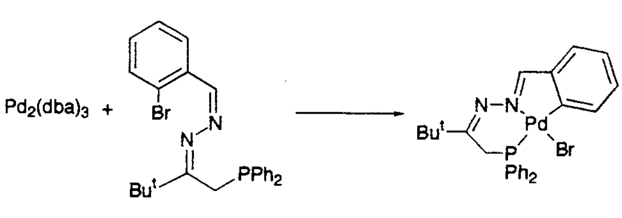
Fig. 2. Molecular structure of $PtMe\{PPh_2CH\overset{\cdots}{-}C(^tBu)\overset{\cdots}{-}N\overset{\cdots}{-}N\overset{\cdots}{-}CMe(2\text{-}py)\text{-}\kappa^3N,\acute{N},P\}$ (**5**). The thermal ellipsoids are drawn at the 30% level.

2). The compound **7** is a yellow solid which was characterized by ^1H-, ^{13}C- and ^{31}P-NMR spectra and elemental analysis. In the ^1H-NMR spectrum, the resonance of the methyl group bound to platinum appears as two doublets at δ 0.71 and 0.57 due to coupling with the phosphorus atom and coupling constant values ($^2J(PtH)$ = ca. 70–90 Hz) are characteristic for a platinum(II) compound with the methyl *trans* to N and P. The resonance due to the iminic proton is also coupled with $^{195}Pt(^3J(PtH)$ = ca. 41 Hz), thus showing the coordination of the ligand to platinum through the nitrogen. The methylene resonance appears as an AB quartet. The ^{13}C-NMR spectrum of **7** showed two separated doublet resonances for the two $Pt–CH_3$ groups. The value of δ 24.3 for the chemical shift of the methylene carbon is as expected in a six-membered chelate ring, whereas in a five-membered chelate ring, a higher value of δ ca. 40 is found [15]. The $^{31}P\{^1H\}$-NMR spectrum of **7** consisted of a singlet at δ 31.6 with satellites due to $^{195}Pt[J(PtP) = 2144$ Hz].

Treatment of the ligand **2** with $PtCl_2(cod)$ in hot toluene in the presence of triethylamine gave the neutral deprotonated platinum(II) complex **8** in 75% yield. The initial indication of the mononuclear formulation for **8** stemmed from the observation of a parent ion in the mass spectrum at m/z 929. In the ^1H-NMR spectrum, the PCH proton appeared as a doublet at δ 4.17 with a satellite due to coupling to $^{195}Pt(^3J(PtH) = 48.2$ Hz) and with $^2J(PH) = 8.8$ Hz. The values are comparable to those observed for the deprotonated six-membered metal complexes [23]. The $^{13}C\{^1H\}$-NMR spectrum shows a doublet at δ 79.1 with $^1J(PC) = 48.8$ Hz, typical of an enamine carbon in a six-membered ring. This resonance is shifted almost 55 ppm downfield as compared with the methylene carbon of **7**. The observation of a CH carbon at δ 178 coupled with the phosphorus atom is also consistent with the neutral structure for **8**.

2.6. Synthesis and characterization of complexes from ligand 3

The metallacycle $[PdBr\{PPh_2CH_2C(^tBu){=}N{-}N{=}CH(C_6H_4)\text{-}\kappa^3C,N,P\}]$ (**9**) was prepared by the reaction of $Pd_2(dba)_3$(dba = dibenzylideneacetone) with the potentially terdentate P,N,C ligand $PPh_2CH_2C(^tBu){=}N{-}N{=}CH(C_6H_4Br)$ (**3**) by oxidative addition of one of the *ortho* C–Br bonds in toluene (Eq. (3)).



3 **9**

(3)

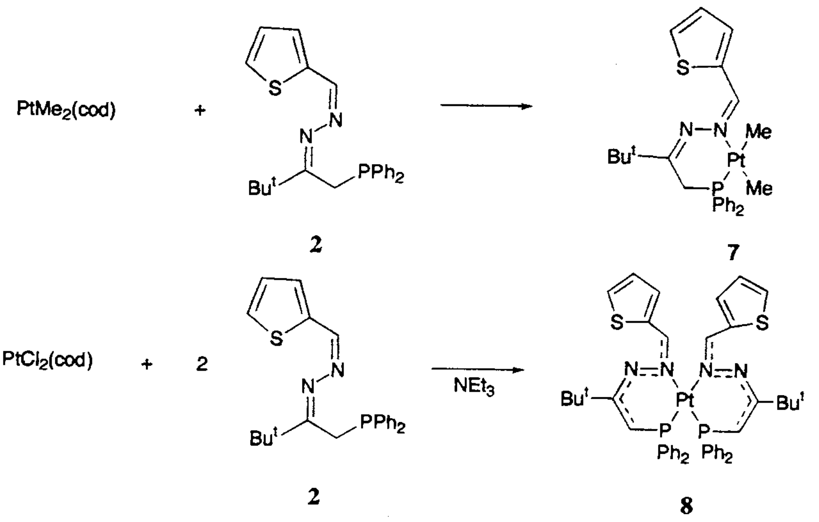
The resulting yellow product **9** was isolated as a moderately air-sensitive, crystalline solid in high yield. This compound is readily soluble in benzene, toluene, and THF. Compound **9** was characterized by its ^1H-, ^{13}C- and ^{31}P-NMR spectra, elemental analysis and the crystal structure determination of **9**. The mass spectra of the compounds were also recorded. The iminic proton resonance was present at δ 8.70 with $^4J(PH) = 2.8$ Hz, and its coupling constant with phosphorus shows a coordination of the nitrogen atom to the palladium. The methylene group gives rise to one signal in the ^{1}H-NMR spectrum (δ 3.07). The ^{13}C data are also consistent with the assigned structure. In particular, the low value of δ 21.2 for the methylene carbon is in agreement with the observed low value of δ 24.0 for the six-membered [Mo(CO)$_4$(PPh$_2$CH$_2$C(^{t}Bu)=NNMe$_2$)] complex [24]. This value is comparable to those of **6**. In the IR spectrum of **9**, the peaks at 1615 and 1574 cm^{-1} are assigned to the stretching mode of ν(C=N). Although all the spectra are consistent with the proposed formulation, the bonding mode in **9** is still unclear. Accordingly, the nature of the metal center for **9** was confirmed through a single-crystal X-ray diffraction analysis.

2.7. Description of the molecular structure of **9**

A crystal of **9** suitable for an X-ray diffraction study was grown from hexane at −15°C. A summary of the data collection and crystallographic parameters for **9** is given in Table 1. The relevant bond lengths and angles are shown in Table 2. The crystal structure is composed of discrete molecules separated by van der Waals distances. The molecular structure of **9** is given in Fig. 2. The molecule contains one PdC$_3$N five-membered ring and one PdN$_2$C$_2$P six-membered ring. The palladium

Table 2
Selected bond lengths (Å) and bond angles (°) for **4**, **5** and **9**

Bond lengths					
Compound ***4***					
Pt(1)–C(30)	2.061(10)	Pt(1)–C(31)	2.088(10)	Pt(1)–N(9)	2.123(7)
Pt(1)–P(17)	2.249(2)	C(7)–N(9)	1.293(11)	N(9)–N(10)	1.413(9)
N(10)–C(11)	1.269(11)	C(11)–C(16)	1.498(11)	C(16)–P(17)	1.876(7)
Compound ***5***					
Pt(1)–N(2)	2.053(17)	Pt(1)–C(31)	2.10(2)	Pt(1)–N(10)	2.127(14)
Pt(1)–P(18)	2.175(5)	N(2)–C(7)	1.37(2)	C(7)–C(8)	1.37(3)
C(8)–N(10)	1.36(2)	N(10)–N(11)	1.33(2)	N(11)–C(12)	1.36(2)
C(12)–C(17)	1.38(2)	C(17)–P(18)	1.78(2)		
Compound ***9***					
Pd(1)–C(1)	2.044(8)	Pd(1)–N(1)	2.054(6)	Pd(1)–P	2.318(2)
Pd(1)–Br	2.424(11)	P–C(13)	1.835(8)	N(1)–C(7)	1.298(10)
N(1)–N(2)	1.402(9)	N(2)–C(8)	1.276(10)	C(1)–C(6)	1.391(11)
C(6)–C(7)	1.449(11)	C(8)–C(13)	1.510(11)		
Bond angles					
Compound ***4***					
C(30)–Pt(1)–C(31)	86.7(4)	C(30)–Pt(1)–N(9)	179.3(4)		
C(31)–Pt(1)–N(9)	92.9(3)	C(30)–Pt(1)–P(17)	95.3(3)		
N(9)–Pt(1)–P(17)	85.16(19)	C(7)–N(9)–Pt(1)	130.5(6)		
N(10)–N(9)–Pt(1)	114.2(5)	C(11)–N(10)–N(9)	116.0(7)		
N(10)–C(11)–C(16)	124.7(7)	C(11)–N(10)–N(9)	111.7(5)		
C(24)–P(17)–C(16)	101.0(3)	C(18)–P(17)–Pt(1)	119.0(3)		
C(16)–P(17)–Pt(1)	109.1(3)				
Compound ***5***					
N(2)–Pt(1)–C(31)	91.7(9)	N(2)–Pt(1)–N(10)	79.9(7)		
C(31)–Pt(1)–N(10)	171.4(9)	N(2)–Pt(1)–P(18)	174.3(6)		
C(31)–Pt(1)–P(18)	94.0(7)	N(10)–Pt(1)–P(18)	94.4(5)		
N(2)–C(7)–C(8)	117.9(17)	N(10)–C(8)–C(7)	119.4(18)		
N(11)–N(10)–C(8)	119.8(16)	N(11)–N(10)–Pt(1)	130.5(12)		
C(8)–N(10)–Pt(1)	109.8(13)	N(10)–N(11)–C(12)	124.6(16)		
N(11)–C(12)–C(17)	131.9(19)				
Compound ***9***					
C(1)–Pd(1)–N(1)	81.3(3)	C(1)–Pd(1)–P	169.6(2)		
N(1)–Pd(1)–P	89.88(18)	C(1)–Pd(1)–Br	93.1(2)		
N(1)–Pd(1)–Br	170.07(18)	P–Pd(1)–Br	96.42(6)		
C(13)–P–Pd(1)	103.4(3)	C(7)–N(1)–N(2)	110.8(6)		
C(7)–N(1)–Pd(1)	113.4(5)	N(2)–N(1)–Pd(1)	134.7(5)		
C(8)–N(2)–N(1)	120.2(7)	C(6)–C(1)–Pd(1)	111.3(6)		
C(1)–C(6)–C(7)	116.0(7)	N(1)–C(7)–C(6)	117.9(8)		
N(2)–C(8)–C(13)	126.0(7)				



Scheme 2.

atom is in a slightly distorted square-planar environment, coordinated to carbon, bromine, nitrogen, and the phosphorus atoms. The metallacycle is approximately planar; the largest deviation from the mean plane determined by the five atoms is 0.0135 Å for N(1). The angles between adjacent atoms in the coordination sphere lie in the range 96.42(6) (P–Pd–Br) to 81.3(3)° (C(1)–Pd–N(1)), the smallest angles corresponding to the terdentate ligand. The distances between the palladium and the coordinated atoms are well within the range of values obtained for other analogous compounds [25].

3. Conclusions

We have shown that the potentially terdentate ligands **1**, **2**, and **3** can coordinate to palladium and platinum in bi- and terdentate coordination modes. The reaction of **1** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ or $PtMe_2(cod)$ gave the unstable six-membered metallacycle $[PtMe_2\{PPh_2CH_2C(^{t}Bu){=}NN{=}CMe(2\text{-}py)\text{-}\kappa^2P,N\}]$ which was slowly converted into the cyclization product $[PtMe\{PPh_2CHC(C^{t}Bu)NNCMe(2\text{-}py)\text{-}\kappa^3N,N',P\}]$ (**5**). Accordingly, **1** stabilizes a series of organoplatinum complexes with a strong tendency to terdentate coordination. Oxidative addition of methyl iodide to **5** led to the immediate formation of a Pt(IV) complex. However, carbonylation of **5** under 23 bar of CO at r.t. proceeds very slowly. The six-membered metallacycle $PtMe_2\{PPh_2CHC(^{t}Bu)NNC(H)SC_4H_3\text{-}\kappa^2N,P\}$ (**7**) was prepared by the reaction of $PtMe_2(cod)$ with **2**. The prolonged heating **7** led to decomposition rather than the cycloplatination product with a PNS coordination fashion. Therefore, bidentate coordination is preferred in the platinum compound with the ligand **2**. The five- and six-membered palladacycle $[PdBr\{PPh_2\text{-}CH_2C(^{t}Bu){=}N\text{–}N{=}CHC_6H_4\text{-}\kappa^3C,N,P\}]$ was prepared by the reaction of $Pd_2(dba)_3$ with the potentially terdentate PNC ligand $PPh_2CH_2C(^{t}Bu){=}N\text{–}N{=}CH(o\text{-}BrC_6H_4)$ by oxidative addition of the *ortho* C–Br bond. However, the reaction of $Ni(cod)_2$ or $Pt(cod)_2$ led to intractable products. The stability and isolation of the palladium complex **9** may have catalytic applications. We are currently in the process of using this complex to synthesize allylic alkylation reactions.

4. Experimental

4.1. General procedures

All manipulations were performed under a dry, oxygen-free, dinitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmosphere HE-493 dry box. Toluene and hexane were freshly distilled over sodium benzophenone prior to use. All ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on a Gemini 200 spectrometer operating at 200.1, 50.3, and 80.9 MHz, respectively. Chemical shifts were referenced relative to either TMS (^{1}H) or benzene-d_6 (^{1}H, δ 7.156; ^{13}C{^{1}H}, δ 128.00), while ^{31}P-NMR spectra were referenced relative to 85% phosphoric acid. IR spectra were recorded on a Biorad FTS-165 spectrometer. Mass spectra were recorded on a high-resolution VG 70-VSEG instrument and elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer. The ligand $Z\text{-}Ph_2PCH_2C(^{t}Bu){=}NNH_2$ was prepared according to the literature method. $[Me_2PtSMe_2]_2$ [26] and $Pt(cod)_2$ [27] were prepared by published methods. K_2PtCl_4, $MeC(O)^{t}Bu$, and $Pd_2(dba)_3$ were used as received from Strem Chemicals.

4.1.1. *$PPh_2CH_2C(^tBu){=}N{-}N{=}C(Me)NC_5H_4$* (***1***)

A mixture of phosphino hydrazone **L** (1.0 g, 3.35 mmol) and 2-acetylpyridine (0.375 ml, 3.35 mmol) was refluxed in benzene (10 ml) for 1.5 h. The solution was evaporated to dryness under reduced pressure. The solids were washed with cold methanol. The crude solid was crystallized by dissolving in methanol and placing a layer of hexane above it in a Schlenk tube, and white crystals were obtained in 52% yield. M.p. 68–70°C. ^1H-NMR ($CDCl_3$): δ 8.62 (d, 1H, $J_{HH} = 3.48$ Hz, NC_5H_4), 7.82 (d, 1H, $J_{HH} = 5.44$ Hz, NC_5H_4), 7.58–7.05 (m, 12H, *pyridyl* and *phenyl* groups), 3.10 (d, 2H, $J_{H-P} = 3.60$ Hz, CH_2), 2.22 (s, 3H, CH_3), 1.22 (s, 9H, CMe_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 168.55 (s, 1C, $C{=}N$), 155.52 (s, 1C, $C{=}N$), 146.17, 139.11, 136.77, 135.62, 133.05, 131.16, 128.53, 123.44, 121.08, 38.87 (s, 1C, CMe_3), 29.25 (s, 3C, CMe), 28.42 (d, 1C, $J(PC) = 26.1$ Hz, CH_2), 13.77 (s, 1C, CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −10.78. IR (KBr pellet, cm^{-1}): 1652 (ν(C=N)), 1616 (ν(C=N)).

4.1.2. *$PPh_2CH_2C(^tBu){=}N{-}N{=}C(H)SC_4H_3$* (***2***)

A mixture of phosphino hydrazone **L** (0.67 g, 2.25 mmol) and 2-thiophenecarbaldehyde (0.22 ml, 2.25 mmol) was refluxed in benzene (5 ml) for 3 h. The solvents were removed in vacuo. The yellow powders were washed with cold MeOH. Recrystallization from a solution of MeOH layered by hexane produced crystals in 55% yield. M.p. 82–84°C. ^1H-NMR ($CDCl_3$): δ 8.20 (s, 1H, CH), 7.58–6.95 (m, 13H, *Ph* and SC_4H_3), 3.58 (d, 2H, $J(PH) = 2.64$ Hz, CH_2), 1.24 (s, 9H, CMe_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 175.71 (s, 1C, $C{=}N$), 155.78 (s, 1C, $C{=}N$), 151.31, 140.02, 139.04, 133.36, 132.95, 130.95, 129.05, 128.66, 127.23, 38.52 (s, 1C, CMe_3), 29.33 (d, 1C, $J(PC) = 31.2$ Hz, CH_2), 28.74 (s, 3C, CMe_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −8.16. IR (KBr pellet, cm^{-1}): 1606.9 (ν(C=N)).

4.1.3. *$PPh_2CH_2C(^tBu){=}N{-}N{=}C(H)Q$ (Q = 2-bromobenzyl)* (***3***)

Compound **3** was prepared according to the same method used for **2**, except that 2-bromobenzaldehyde was used instead of 2-acetylpyridine. Yield: 54%. M.p. 88–90°C. ^1H-NMR ($CDCl_3$): δ 8.36 (s, 1H, CH), 7.65–7.04 (m, 14H, *Ph* and NC_5H_4), 3.51 (d, 2H, $J(PH) = 2.4$ Hz, CH_2), 1.27 (s, 9H, CMe_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 175.92 (s, 1C, $C{=}N$), 155.74 (s, 1C, $C{=}N$), 139.05, 138.71, 133.16, 132.90, 132.76, 131.25, 128.69, 127.10, 125.17, 38.72 (s, 1C, CMe_3), 29.14 (s, 3C, CMe_3), 28.66 (d, 1C, $J(PC) = 22.6$ Hz). IR (KBr pellet, cm^{-1}): 1607.2 (ν(C=N)).

4.1.4. *$PtMe_2\{PPh_2CH_2C(^tBu){=}N{-}N{=}CMe(2\text{-}py)\text{-}\kappa^2N,P\}$* (***4***)

Method (*i*). To a stirred toluene (10 ml) solution of $[PtMe_2(\mu\text{-}SMe_2)]_2$ (0.100 g, 0.174 mmol) was added a toluene solution of $PPh_2CH_2C(^tBu){=}N{-}N{=}CMe(py)$ (**2**) (0.140 g, 0.348 mmol) dropwise at −20°C. The solution was warmed to r.t., and the solution was stirred for 1 h. The solvent was removed in vacuo. The resulting residue was recrystallized by dissolving in toluene (6 ml) and placing a layer of hexane, and greenish–yellow crystals were obtained in 35% yield.

Method (*ii*). Compound **4** was also prepared according to Method (i), except that $PtMe_2(cod)$ was used instead of $[PtMe_2(\mu\text{-}SMe_2)]_2$ in 80% yield. M.p. 159–161°C. ^1H-NMR (C_6D_6): δ 8.68 (d, 1H, $J(HH) = 7.6$ Hz, CH), 7.57 (d, 1H, $J(HH) = 3.2$ Hz, CH), 7.92–7.24 (m, 12H, *Ph* and *pyridyl*), 3.55 (dd, 1H, $^2J(PH) = 2.1$, $^3J(PtH) = 21.6$ Hz, CH_2P), 2.51 (dd, 1H, $^2J(PH) = 2.1$, $^3J(PtH) = 21.6$ Hz, CH_2P), 2.30 (s, 3H, CH_3), 0.88 (s, 9H, ^{t}Bu), 0.62 (d, 3H, $^3J(PH) = 7.6$, $^2J(PtH) = 90.4$ Hz, $Pt{-}CH_3$), −0.06 (d, 3H, $^3J(PH) = 8.1$, $^2J(PtH) = 69.6$ Hz, $Pt{-}CH_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 181.64 (s, 1C, $C{=}N$), 170.10 (s, 1C, $C{=}N$), 148.37, 135.05, 134.76, 132.81, 132.01, 131.78, 130.80, 130.07, 128.78, 128.60, 128.22, 128.01, 30.50 (s, 1C, CMe_3), 27.51 (s, 3C, CMe_3), 24.99 (d, 1C, $^1J(PC) = 8.48$ Hz, CH_2) 7.62 (d, 1C, $^2J(PC) = 16.8$, $^1J(PtC) = 778$ Hz, $Pt{-}CH_3$), 1.22 (d, 1C, $^2J(PC) = 11.7$, $^1J(PtC) = 748$ Hz, $Pt{-}CH_3$). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −1.31 (d, $J(PtP) = 3772.7$ Hz). IR (KBr pellet, cm^{-1}): 1604, 1587 (ν(C=N)). MS (EI): *m*/*z* 626 [M^+]. Anal. Calc. for $C_{27}H_{34}N_3PPt$: C, 51.71; H, 5.43. Found: C, 51.22; H, 5.21%.

4.1.5. *$PtMe\{PPh_2CH\underline{\cdots}C(^tBu)\underline{\cdots}N\underline{\cdots}N\underline{\cdots}CMe(2\text{-}py)\text{-}\kappa^3N,N',P\}$* (***5***)

$PPh_2CH_2C(^tBu){=}N{-}N{=}CMe(py)$ (**2**) (0.140 g, 0.348 mmol) was added to a solution of $[PtMe_2(\mu\text{-}SMe_2)]_2$ (0.100 g, 0.174 mmol) in 10 ml of toluene, and this mixture was heated at 55°C for 2 h. The solvent and the liberated SMe_2 were removed under vacuum, and the resulting oily blue solid was washed with pentane to give a blue solid. The crude solid was recrystallized by dissolving in toluene and placing a layer of hexane above it, and deep blue crystals were obtained in 45% yield. M.p. 132–136°C (dec.). ^1H-NMR (C_6D_6): δ 7.82–6.86 (m, 14H, *Ph* and *pyridyl*), 4.23 (d, 1H, $^2J(HP) = 2.4$, $^3J(HPt) = 39.2$ Hz, CH), 2.17 (s, 3H, CH_3), 1.26 (s, 9H, ^{t}Bu), 0.67 (d, 3H, $^3J(HP) = 3.1$, $^2J(HPt) = 49.6$ Hz, CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 182.4 (d, 1C, $^2J(PC) = 18.8$ Hz, $C{=}N$), 158.2 (s, 1C, $^2J(PtC) = 35.6$ Hz, $C{=}N$), 144.5, 142.8, 138.8, 136.7, 133.00, 132.8, 129.8, 128.2, 121.4, 77.4 (d, 1C, $^1J(PC) = 51.2$ Hz, CHP), 38.8 (s, 1C, CMe_3), 30.5 (s, 3C, CMe_3), 22.6 (s, 1C, CH_3), −0.68 (d, 1C, $^2J(PC) = 12.8$, $^1J(PtC) = 786$ Hz, $Pt{-}CH_3$). $^{31}P\{^1H\}$-NMR (C_6D_6): δ −1.31 (d, $J(PtP) = 3786.1$ Hz). IR (KBr pellet, cm^{-1}): 1593 (ν(C=N)). MS (EI): *m*/*z* 611 [M^+]. Anal. Calc. for $C_{26}H_{30}N_3PPt$: C, 51.11; H, 4.91. Found: C, 50.84; H, 4.82%.

4.1.6. Oxidative addition reaction

To a stirred solution of **5** (0.035 g, 0.057 mmol) in dichloromethane (5 ml) was added MeI (0.15 ml). The solution was heated to 50–60°C. After 4 h the violet solution was evaporated to dryness. The product was extracted with toluene (6 ml). The volume was reduced to ca. 3 ml and the product layered with hexane (4 ml) and the violet product was filtered. The product was dried in vacuo, yielding 35 mg of a violet product (82%). M.p. 143°C (dec.). ^{1}H-NMR (CDCl$_3$): δ 8.08–7.17 (m, 14H, *Ph* and *Py*), 4.28 (d, 1H, ^{2}J(HP) = 4.8, ^{3}J(HPt) = 30.8 Hz, C*H*), 2.54 (s, 3H, C*H*$_3$), 1.48 (d, 3H, ^{3}J(HP) = 1.5, ^{2}J(PtH = 61.53 Hz, C*H*$_3$), 1.36 (s, 9H, ^{t}Bu), 0.58 (d, 3H, ^{3}J(HP) = 3.4, ^{2}J(HPt) = 64.84 Hz, C*H*$_3$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 183.9 (d, 1C, ^{2}J(PC) = 16.6 Hz, *C*=N), 160.3 (s, 1C, ^{2}J(PtC) = 33.8 Hz, *C*=N), 148.6, 145.3, 142.2, 137.2, 134.7, 133.6, 129.2, 128.6, 123.2, 76.8 (d, 1C, ^{1}J(PC) = 48.4 Hz, *C*HP), 39.4 (s, 1C, *C*Me$_3$), 29.2 (s, 3C, C*Me*$_3$), 23.4 (s, 1C, *C*H$_3$), 3.6 (d, 1C, ^{2}J(PC) = 11.6, ^{1}J(PtC) = 734 Hz, Pt–*C*H$_3$), −0.9 (d, 1C, ^{2}J(PC) = 12.2, ^{1}J(PtC) = 778 Hz, Pt–*C*H$_3$). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ −12.84 (d, J(PtP) = 1691.8 Hz). Anal. Calc. for C$_{27}$H$_{33}$IN$_3$PPt: C, 43.06; H, 4.39. Found: C, 43.46; H, 4.51%.

4.1.7. *PtCl{PPh$_2$CH$\overset{\cdots}{-}$C(^{t}Bu)$\overset{\cdots}{-}$N$\overset{\cdots}{-}$N$\overset{\cdots}{-}$CMe(2-py)-κ^{3}N,N′,P}* (**6**)

PPh$_2$CH$_2$C(^{t}Bu)=N–N=CMe(py) (**2**) (0.1 g, 0.25 mmol) and PtCl$_2$(cod) (0.093 g, 0.25 mmol) were put into a 100 ml Schlenk flask. This flask was evacuated and refilled with dinitrogen before 10 ml of toluene and 0.2 ml of NEt$_3$ were added to the flask via syringe with stirring. The mixture was refluxed for 3 h, and the solvent was removed in vacuo. The resulting blue solid was extracted with toluene and filtered through a 2 cm filter of Celite, and the toluene was removed under vacuum. Recrystallization from a solution of toluene layered with hexane gave rise to deep blue crystals in 68% yield. M.p. 156–158°C. ^{1}H-NMR (CDCl$_3$): δ 8.92 (d, 1H, J(HH) = 6.8 Hz, C*H*), 7.84–7.12 (m, 13H, *Ph* and *py*), 3.99 (d, 1H, J(PH) = 4.4, J(PtH) = 11.4 Hz, C*H*P), 2.26 (s, 3H, J(PtH) = 9.6 Hz, C–C*H*$_3$), 1.27 (s, 9H, ^{t}Bu). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 184.8 (d, 1C, ^{2}J(PC) = 18.2 Hz, *C*–N), 161.6 (s, 1C, ^{2}J(PtC) = 37.1 Hz, *C*=N), 147.3, 144.6, 139.6, 138.2, 133.3, 133.1, 130.3, 128.3, 118.9, 79.2 (d, 1C, ^{1}J(PC) = 54.2 Hz, *C*HP), 38.4 (s, 1C, *C*Me$_3$), 30.35 (s, 3C, C*Me*$_3$), 19.3 (s, 1C, C*C*H$_3$). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ −9.22 (d, J(PtP) = 3668.7 Hz). IR (KBr pellet, cm^{-1}): 1592 (ν(C=N)). Anal. Calc. for C$_{25}$H$_{27}$ClN$_3$PPt: C, 47.61; H, 4.28. Found: C, 47.33; H, 4.12%.

4.1.8. *PtMe$_2${PPh$_2$CH$_2$C(^{t}Bu)=N–N=C(H)SC$_4$H$_3$-κ^{2}N,P}* (**7**)

A 100 ml Schlenk tube was charged with 0.07 g (0.178 mmol) of **2**, 0.067 g (0.195 mmol) of PtMe$_2$(cod), and 10 ml of toluene. The reaction mixture was stirred at r.t. for 1 h. The volume was reduced to ca. 4 ml and the solution was layered with hexane (4 ml). The yellow product was filtered and dried in vacuo, yielding 94 mg of a yellow product (85%). M.p. 202–204°C. ^{1}H-NMR (CDCl$_3$): δ 8.66 (d, 1H, ^{4}J(PH) = 2.2 Hz, ^{3}J(PtH) = 40.8 Hz, C*H*), 7.83–6.94 (m, 13H, *Ph* and *thiophene*), 3.44 (dd, 1H, ^{2}J(PH) = 2.2 Hz, ^{3}J(PtH) = 23.8 Hz, C*H*$_2$P), 2.49 (dd, 1H, ^{2}J(PH) = 1.6 Hz, ^{3}J(PtH) = 22.4 Hz, C*H*$_2$P), 0.86 (s, 9H, ^{t}Bu), 0.71 (d, 3H, ^{3}J(PH) = 7.4 Hz, ^{2}J(PtH) = 91.2 Hz, Pt–C*H*$_3$), 0.57 (d, 3H, ^{3}J(PH) = 7.6 Hz, ^{2}J(PtH) = 70.2 Hz, Pt–C*H*$_3$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 178.4 (s, 1C, *C*=N), 174.3 (s, 1C, *C*=N), 147.1, 134.9, 134.7, 132.2, 131.9, 130.7, 129.8, 128.5, 128.2, 126.4, 38.9 (s, 1C, *C*Me$_3$). 27.3 (s, 3C, C*Me*$_3$), 24.3 (d, 1C, ^{1}J(PC) = 8.9 Hz, *C*H$_2$), 7.9 (d, 1C, ^{2}J(PC) = 14.4 Hz, ^{1}J(PtC) = 788 Hz, Pt–*C*H$_3$), −0.8 (d, 1C, ^{2}J(PC) = 10.8 Hz, ^{1}J(PtC) = 754 Hz, Pt–*C*H$_3$). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ 31.6 (s, J(PtP) = 2143.7 Hz). IR (KBr pellet, cm^{-1}): 1602, 1585 (ν(C=N)). Anal. Calc. for C$_{25}$H$_{31}$N$_2$PSPt: C, 48.48; H, 5.01. Found: C, 48.73; H, 5.26%.

4.1.9. *Pt{PPh$_2$CH=C(^{t}Bu)-N–N=C(H)SC$_4$H$_3$-κ^{2}N,P}$_2$* (***8***)

A 100 ml Schlenk tube was charged with 0.2 g (0.51 mmol) of PPh$_2$CH$_2$C(^{t}Bu)=N–N=C(H)SC$_4$H$_3$, 0.19 g (0.51 mmol) of PtCl$_2$(cod), and 15 ml of toluene. The reaction mixture was stirred at r.t. for 0.5 h, and 0.17 ml of NEt$_3$ was added. This mixture was heated at 60°C for 2 h. The white precipitate was removed by filtration, and the solvent was removed by vacuum. The purification was achieved by preparative TLC using a solvent mixture of CH$_2$Cl$_2$ and diethyl ether (20:1). An analytical sample of the new compound was obtained by recrystallization from a 2:1 mixture of CH$_2$Cl$_2$ and hexane in 75% yield. M.p. 156–158°C. ^{1}H-NMR (CDCl$_3$): δ 8.20 (s, 1H, C*H*), 7.62–6.64 (m, 13H, *Ph* and *thiophene*), 4.17 (d, 1H, ^{2}J(PH) = 8.8 Hz, ^{3}J(PtH) = 48.2 Hz, C*H*P), 1.44 (s, 9H, ^{t}Bu). ^{13}C{^{1}H}-NMR (CDCl$_3$): 178.4 (d, 1C, ^{2}J(PC) = 6.4 Hz, *C*–N), 154.7 (s, 1C, *C*=N), 144.3; 132.8, 132.7, 132.4, 130.4, 129.7, 128.8, 127.9, 126.5, 123.7, 123.0, 79.1 (d, 1C, ^{1}J(PC) = 48.8 Hz, CHP), 37.7 (s, 1C, *C*Me$_3$), 30.9 (s, 3C, C*Me*$_3$). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ 22.5 (d, J(PtP) = 3155.2 Hz). IR (KBr pellet, cm^{-1}): 1570 (ν(C=N)). MS (EI): m/z 929 [M^{+}]. Anal. Calc. for C$_{42}$H$_{48}$N$_4$P$_2$S$_2$Pt: C, 54.25; H, 5.17. Found: C, 54.03; H, 5.02%.

4.1.10. *PdBr{PPh$_2$CH$_2$C(^{t}Bu)=N–N=CH(C$_6$H$_4$)-κ^{3}C,N,P}* (**9**)

To a solution of Pd$_2$(dba)$_3$ (0.197 g, 0.22 mmol) in CH$_2$Cl$_2$ (5 ml) was added a solution of PPh$_2$CH$_2$-C(^{t}Bu)=N–N=CH(C$_6$H$_4$Br) (**3**) (0.2 g, 0.43 mmol) in CH$_2$Cl$_2$ (5 ml) with stirring. The mixture was

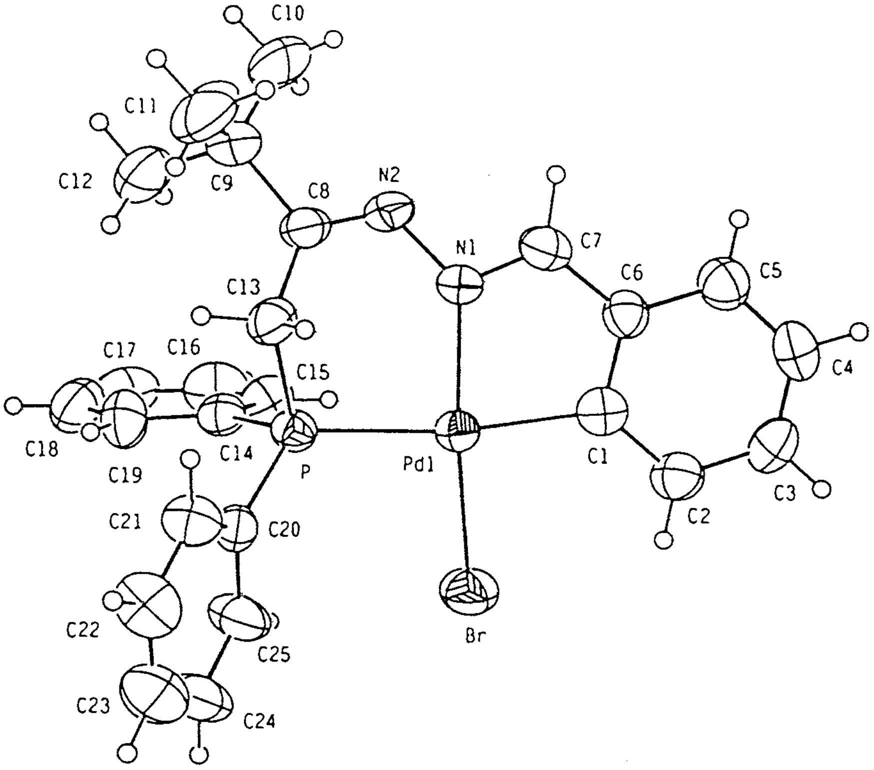


Fig. 3. Molecular structure of PdBr{PPh$_2$CH$_2$C(^{t}Bu)=N–N=CH(C$_6$H$_4$)-κ^3*C*,*N*,*P*} (**9**). The thermal ellipsoids are drawn at the 30% level.

refluxed for 1 h, and the solvent was removed in vacuum. The yellow residue was extracted with hexane (15 ml). The solution was reduced to small volume and after cooling to −15°C overnight, yellow microcrystals were obtained in 42% yield. M.p. 108–110°C. ^{1}H-NMR (CDCl$_3$): δ 8.70 (d, 1H, ^4J(PH) = 2.8 Hz, C*H*), 7.82–7.02 (m, 14H, *Ph*), 3.07 (d, 2H, *J*(PH) = 10.2 Hz, C*H*$_2$P), 0.85 (s, 9H, ^{t}Bu). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 179.1 (d, 1C, ^2J(PC) = 4.15 Hz, *C*=N), 171.2 (s, 1C, *C*=N), 142.4, 136.2, 133.9, 132.3, 131.2, 130.2, 129.5, 128.9, 128.7, 125.6, 40.7 (s, 1C, *C*Me$_3$), 27.3 (s, 3C, C*Me*$_3$), 21.2 (d, 1C, ^1J(PC) = 13.7 Hz, *C*H$_2$P). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ 18.13. IR (KBr pellet, cm^{-1}): 1615, 1574 (ν(C=N)). Anal. Calc. for C$_{25}$H$_{26}$N$_2$PBrPd: C, 52.52; H, 4.58. Found: C, 52.21; H, 4.42%.

4.2. X-ray crystallography

Details of the crystal data and a summary of intensity data collection parameters for **4**, **5**, and **9** are given in Table 1. The crystals of **4** and **5** were grown from a toluene–hexane solution at −15°C. The crystal of **9** was grown from hexane solutions stored at −20°C. The crystals of **4**, **5**, and **9** were mounted in thin-wall glass capillaries and sealed under argon. The data sets **4**, **5**, and **9** were collected on an Enraf CAD4 automated diffractometer. Mo–K$_\alpha$ radiation (λ = 0.7107 Å) was used for all structures. Each structure was solved by the application of direct methods using the SHELXL-86 program and least-squares refinement using SHELXL-93. Non-hydrogen atoms of **4**, **5**, and **9** were anisotropically refined, and hydrogen atoms were isotropically refined. The hydrogen atoms were included as constant contributions to the structure factors. Selected bond distances and angles for **4**, **5**, and **9** are given in Table 2. The molecular structure of compounds **4**, **5**, and **9** are given in Figs. 1–3, respectively.

5. Supplementary material

Tables of bond distances and angles, atomic coordinates, fractional coordinates for hydrogen atom, thermal parameters, and X-ray data for **4**, **5**, and **9** (24 pages) are available. Ordering information is given on any current masthead page.

Acknowledgements

We appreciate the financial support of the Basic Science Research Institute Program, Ministry of Education 1998, Project no. 3426.

References

[1] (a) I. Omae, Chem. Rev. 79 (1979) 287. (b) I. Omae, Coord. Chem. Rev. 83 (1988) 137.

[2] (a) J. Albert, A. Gonzalez, J. Granell, R. Moragas, C. Puerta, P. Valerga, Organometallics 16 (1977) 3775. (b) G. van Koten, Pure Appl. Chem. 61 (1989) 1681. (c) P.L. Alsters, P.F. Engel, M.P. Hogerheide, M. Copijn, A.L. Spek, G. van Koten, Organometallics 12 (1993) 1831. (d) C. Chan, D.M.P. Mingos, A.J.P. White, D.J. Williams, J. Chem. Soc. Chem. Commun. (1996) 81. (e) H. Kraatz, D. Milstein, J. Organomet. Chem. 488 (1995) 223.

[3] (a) P. Wehman, L. Borst, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Chem. Soc. Chem. Commun. (1996) 217 (b) R. van Asselt, C.J. Elsevier, Organometallics 11 (1992) 1999. (c) P. Wehman, G.C. Dol, E.R. Moorman, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Fraanje, K. Goubitz, Organometallics 13 (1994) 4856.

[4] B. Jedlicka, C. Kratky, W. Weissensteiner, M.J. Widhalm, Chem. Soc. Chem. Commun. (1993) 1329

[5] (a) B.M. Trost, T.R. Verhoeven, J. Am. Chem. Soc. 100 (1978) 3435. (b) P. von Matt, A. Pfaltz, Angew. Chem. Int. Ed. Engl. 32 (1993) 566. (c) J. Sprinz, G. Helmchen, Tetrahedron Lett. 34 (1993) 1769. (d) J. Sprinz, M. Kiefer, G. Helmchen, M. Reggelin, G. Huttner, O. Walter, L. Zsolnai, Tetrahedron Lett. 35 (1994) 1523.

[6] (a) R.E. Rulke, V.E. Kaasjager, P. Wehman, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, J. Fraanje, K. Goubitz, A.L. Spek, Organometallics 15 (1996) 3022. (b) P. Wehman, R.E. Rulke, V.E. Kaasjager, C.J. Elsevier, H. Kooijman, A.L. Spek, K. Vrieze, R.W.N.M. van Leeuwen, J. Chem. Soc. Chem. Commun. (1995) 331. (c) T.B. Rauchfuss, P.A. Tucker, Inorg. Chem. 19 (1980) 3306.

[7] (a) D. Hedden, D.M. Roundhill, W.C. Fultz, A.L. Rheingold, Organometallics 5 (1986) 336. (b) D. Hedden, D.M. Roundhill, Inorg. Chem. 24 (1985) 4152.

[8] (a) C.R. Sinha, D. Bandyopadhyay, A. Chakravorty, J. Chem. Soc. Chem. Commun. (1988) 468. (b) T. Kawamoto, L. Nagasaw, H. Kuma, Y. Kushi, Inorg. Chem. 35 (1996) 2427. (c) S. Chattopadhyay, C. Sinha, P. Basu, A. Chakravorty, Organometallics 10 (1991) 1135. (d) A.K. Mahapatra, D. Bandyopadhyay, P. Bandyopadhyay, A. Chakravorty, Inorg. Chem. 25 (1986) 2214

[9] (a) S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1992) 1469. (b) S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1993) 3653. (c) S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1994) 3311.

[10] K.K. Hii, S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1992) 2361.

[11] (a) S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1991) 1183. (b) S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1994) 713. (c) S.D. Perera, B.L. Shaw, J. Chem. Soc. Chem. Commun. (1994) 1201. (d) S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1992) 999. (e) S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Organomet. Chem. 428 (1992) 59.

[12] (a) D. You, S.O. Kang, J. Ko, M. Choi, Bull. Kor. Chem. Soc. 18 (1997) 305. (b) C. Paek, S.O. Kang, J. Ko, P.J. Carroll, Organometallics 16 (1997) 2110. (c) C. Paek, S.O. Kang, J. Ko, P.J. Carroll, Organometallics 16 (1997) 1503.

[13] (a) M. Crespo, Polyhedron 15 (1996) 1981. (b) P.K. Monaghan, R.J. Puddephatt, Organometallics 4 (1985) 1406. (c) C.R. Baar, H.A. Jenkins, J.J. Bittal, G.P.A. Yap, R.J. Puddephatt, G. Ferguson, A.J. Lough, J. Chem. Soc. Chem. Commun. (1989) 1297.

[14] J.D. Ruddick, B.L. Shaw, J. Chem. Soc. A (1969) 2801.

[15] K.K. Hii, S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1994) 103.

[16] (a) A.D. Ryabov, Chem. Rev. 90 (1990) 403. (b) J.Y. Saillard, R. Hoffmann, J. Am. Chem. Soc. 106 (1984) 2006.

[17] S.D. Perera, B.L. Shaw, J. Chem. Soc. Chem. Commun. (1995) 865.

[18] (a) C.M. Anderson, M. Crespo, M.C. Jennings, A.J. Lough, G. Ferguson, R.J. Puddephatt, Organometallics 10 (1991) 2672. (b) C.M. Anderson, M. Crespo, G. Ferguson, A.J. Lough, R.J. Puddephatt, Organometallics 11 (1992) 1177.

[19] (a) J.D. Scott, R.J. Puddephatt, Organometallics 5 (1986) 1538. (b) M. Crespo, R.J. Puddephatt, Organometallics 6 (1987) 2548.

[20] D. Lopez, M. Crespo, M. Font-Bardia, X. Solans, Organometallics 16 (1997) 1233.

[21] (a) J.D. Scott, R.J. Puddephatt, Organometallics 2 (1983) 1643. (b) C.M. Anderson, R.J. Puddephatt, G. Ferguson, A.J. Lough, J. Chem. Soc. Chem. Commun. (1989) 1297.

[22] J.D. Kennedy, W. McFarlane, R.J. Puddephatt, P.J. Thompson, J. Chem. Soc. Dalton Trans. (1976) 874.

[23] S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1993) 3653.

[24] S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Organomet. Chem. 428 (1992) 59.

[25] (a) A.M. Aarif, F. Esfevan, A. Garcia-Bernabe, P. Lahuerta, M. Sanau, M.A. Vbeda, Inorg. Chem. 36 (1997) 6472. (b) H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer, R. Weiss, J. Am. Chem. Soc. 103 (1980) 1047. (c) C. King, D.M. Roundhill, F.R. Fronczek, Inorg. Chem. 26 (1987) 4288.

[26] J.D. Scott, R.J. Puddephatt, Organometallics 2 (1983) 1643.

[27] J.L. Spencer, Inorg. Synth. XIX (1979) 213.