Synthesis of Phosphido-Bridged Phosphinito Platinum(I) Complexes by Reaction of *cis*-$PtCl_2(PHCy_2)_2$ with Oxygenated Bases – Crystal Structure of $[(PCy_2OMe)Pt(\mu\text{-}PCy_2)]_2$(*Pt–Pt*)

Vito Gallo,[a] Mario Latronico,[a,d] Piero Mastrorilli,*[a] Cosimo F. Nobile,[a] Gian P. Suranna,[a] Giuseppe Ciccarella,[b] and Ulli Englert[c]

Keywords: Platinum / Bridging ligands / Phosphinites / Oxygenated bases

Reaction of *cis*-$PtCl_2(PHCy_2)_2$ (**1**) with oxygenated bases leads to phosphido-bridged dinuclear complexes. The product obtained using sodium hydroxide is the asymmetric Pt^I complex $[(Cy_2PH)Pt(\mu\text{-}PCy_2)(\kappa^2P,O\text{-}\mu\text{-}Cy_2PO)Pt(Cy_2PH)]$(*Pt–Pt*) (**2**), which represents a rare example of a complex containing a Pt–Pt–P–O cycle. The reaction products between **1** and NaOR (R = Me, Et) depend on experimental conditions: lack of base results in the formation of *trans*-$[Pt(PHCy_2)Cl(\mu\text{-}PCy_2)]_2$ (**3**) as the main product. Using an excess of base at 50 °C allowed the isolation of the symmetric Pt^I dimers $[(PCy_2OR)Pt(\mu\text{-}PCy_2)]_2$(*Pt–Pt*) (**5**, R = Me; **7**, R = Et) containing two alkyl dicyclohexylphosphinito ligands. The asymmetric compounds $[(PCy_2H)Pt(\mu\text{-}PCy_2)_2Pt(PCy_2OR)]$(*Pt–Pt*) (**4**, R = Me; **8**, R = Et) form after work-up of the reaction of **1** with excess NaOR (8 equiv.) in toluene/methanol at room temperature. Investigations on the mechanism of formation of phosphinito Pt^I complexes (carried out also employing Na-O*t*Bu and NaOPh as oxygenated bases) show that the first two steps of the overall reaction are the metathesis leading to *cis*-$Pt(OR)_2(PHCy_2)_2$ and the subsequent formation of terminal phosphido complexes through ROH elimination. Single crystal X-ray diffraction showed that molecules of **5** are located on crystallographic inversion centres; hence their necessarily planar Pt_2P_2 core contains a Pt–Pt bond.

Introduction

Secondary phosphanes are attractive as ligands for transition metals because they add some peculiar characteristics to the typical σ basicity and π acidity of the trivalent phosphorus compounds because of the presence of the reactive P–H bond: (i) the capability to form polynuclear complexes in which the metal atoms are linked by phosphido bridges; (ii) the possibility to give rise to a metal–hydrogen bond by intramolecular oxidative addition.

Pursuing our studies on platinum complexes with bulky secondary phosphanes such as di-*tert*-butylphosphane[1,2] and dicyclohexylphosphane,[3] we recently became interested in the reactivity of *cis*-$PtCl_2(PHCy_2)_2$ (**1**) with NaOR (R = H, Me, Et, Ph, *t*Bu). The latter compounds, in fact, can act either as nucleophiles and/or as bases, triggering different reaction pathways depending on both the nature of R and the experimental conditions.

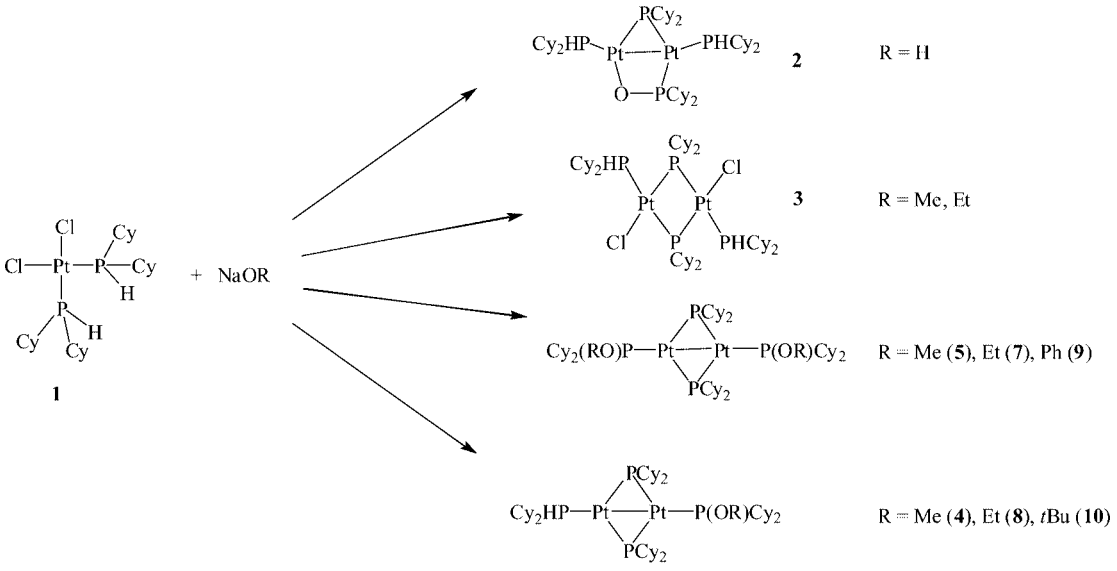
The reaction of alkaline alkoxides with phosphanyl Pt^{II} complexes has been used for the preparation of alkoxo complexes, starting from the corresponding chloro species.[4–8] In some cases the alkoxo complexes are not stable and give rise to redox processes leading to decomposition products,[9] to hydride complexes of platinum(II)[10] or to zerovalent platinum compounds.[11] The reducing ability of alkaline alkoxides towards halide metal complexes has been demonstrated also for Ni[12] and Pd[13] compounds.

Herein we describe the reactivity of *cis*-$PtCl_2(PHCy_2)_2$ (**1**) with sodium hydroxide, alkoxides and phenoxide, which led to phosphido-bridged binuclear platinum compounds, the nature of which depended on both the base and the reaction conditions (Scheme 1).

Results and Discussion

Contrary to *trans*-$PtCl_2(PHtBu_2)_2$, whose reaction with oxygenated bases such as NaOMe,[2] NaOEt[14] or NaOH[15] was ineffective, the reaction of **1** with NaOH in a biphasic CH_2Cl_2/H_2O system proceeded smoothly to form a new dinuclear Pt^I complex whose spectroscopic features and ESI-MS analysis indicate as $[(Cy_2PH)Pt(\mu\text{-}PCy_2)(\kappa^2P,O\text{-}\mu\text{-}$

[a] Dipartimento di Ingegneria delle Acque e di Chimica del Politecnico di Bari,
via Orabona 4, 70125 Bari, Italy
Fax: +39-080-5963611
E-mail: p.mastrorilli@poliba.it
[b] Dipartimento di Ingegneria dell'Innovazione, University of Lecce,
Via Monteroni, 73100 Lecce, Italy
[c] Institut für Anorganische Chemie der RWTH,
Landoltweg 1, 52074 Aachen, Germany
[d] On leave of absence from Dipartimento di Ingegneria e Fisica dell'Ambiente, Università della Basilicata,
viale dell'Ateneo Lucano 10, 85100 Potenza, Italy
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.



Scheme 1.

$Cy_2PO)Pt(Cy_2PH)](Pt–Pt)$ (**2**). The $^{31}P\{^1H\}$ NMR spectrum of **2** (Figure 1) showed 4 mutually coupled doublets of doublets of doublets flanked by ^{195}Pt satellites centred at δ = 134.4, δ = 94.6, δ = 18.5 and δ = 15.9 ppm.

Of these, the latter two can be ascribed to coordinated PCy_2H (comparison with proton-coupled spectrum gave $^1J_{P,H}$ of 310 Hz and 323 Hz respectively) while that at δ = 94.6 is ascribable to a deshielded P–O ligand. The remaining low field signal at δ = 134.4 is flanked by three different sets of satellites and can be attributed to a phosphide involved in a three-membered Pt_2P ring[16,17] bridging two inequivalent Pt atoms. The ^1H NMR spectrum showed, beside cyclohexyl protons, two signals attributable to the hydrogens directly bound to P in coordinated PCy_2H, which were attributed to the proper PCy_2H ligand on the basis of $^1H–^{31}P$ HMQC experiments (Supporting Information, ESI 1). The $^{195}Pt\{^1H\}$ NMR spectrum consisted of two dddd centred at δ = –4798 (Pt^1) and δ = –5205 (Pt^2) (Figure 2).

The characterisation of **2** was completed by IR, elemental and ESI-MS analysis. In particular, the IR spectrum showed two weak bands in the region of P–H stretching (2279 and 2252 cm^{-1}) and bands at 816 and 1024 cm^{-1} ascribable to the P–O stretchings. Eventually, the ESI-MS spectrum showed the signals corresponding to $[M + H]^+$ with an isotope pattern identical to that calculated on the basis of the natural abundances (Figure 3).

Complex **2** is a rare example of an asymmetric monophosphido-bridged Pt^I complex. The spectroscopic data summarised above are consistent either with structure **A**, in which the $P(O)Cy_2$ ligand acts as monodentate (κ-*P* bound to Pt^2), or with structure **B**, in which the $P(O)Cy_2$ acts as bidentate (κ^2-*P,O*) bridging the two Pt atoms (Figure 4).

An equilibrium between the two structures might also be conceived. NMR features can help in discriminating between the two structures. We have previously noticed that binuclear monobridged dicyclohexylphosphane complexes of Pd and Pt such as $[(Cy_2PH)(Cl)Pt(\mu\text{-}PCy_2)Pt(Cy_2PH)_2]$-

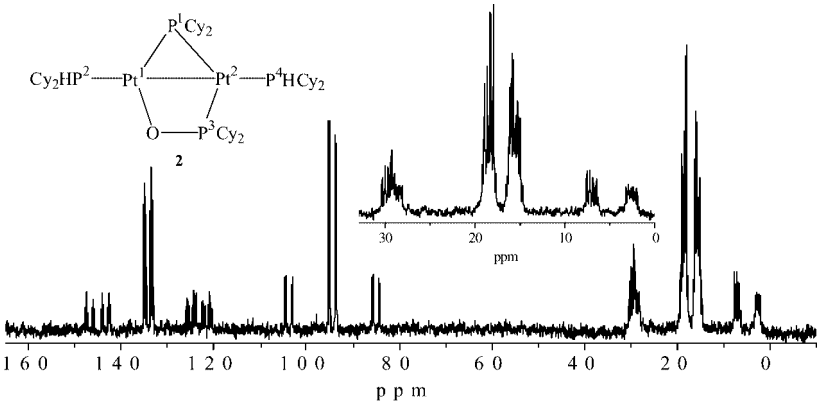


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of **2** (161 MHz, 295 K, C_6D_6).

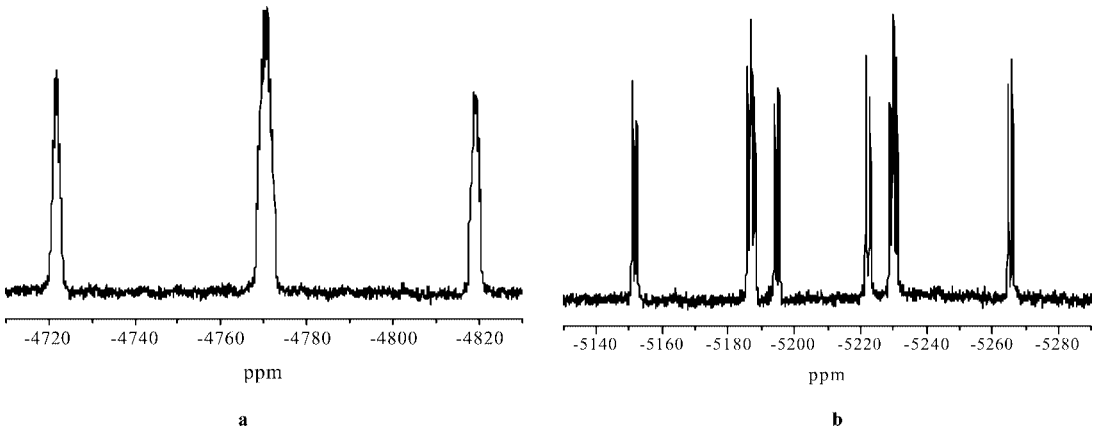


Figure 2. $^{195}Pt\{^1H\}$ NMR spectrum of **2** (295 K, C_6D_6). a: Pt^1; b: Pt^2.

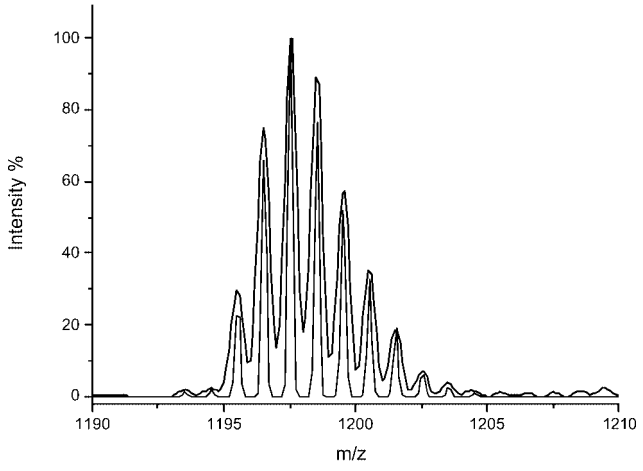


Figure 3. ESI-MS spectrum of **2** (bottom trace: calculated).

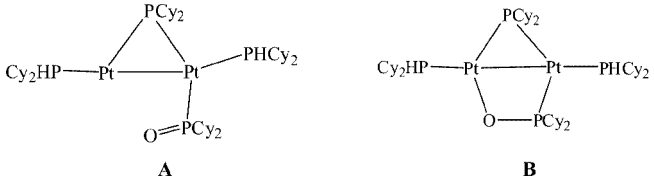


Figure 4. Possible structures of **2**.

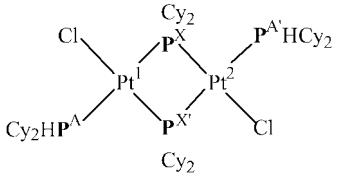
(*Pt–Pt*)[3] or $[(Cy_2PH)(Cl)Pd(\mu\text{-}PCy_2)Pd(Cy_2PH)_2]$-(*Pd–Pd*)[18] (Supporting Information, ESI 2) are characterised by broad $^{31}P\{^1H\}$ NMR signals for all ligands except the bridging PCy_2, a feature that was ascribed to hindered rotation of the $PHCy_2$ ligands about the metal–P bond. The sharp signals found in the $^{31}P\{^1H\}$ NMR of **2** (Figure 1) favour structure **B**, in which both $PHCy_2$ (in particular that bound to Pt^2) have more room to freely rotate around the Pt–P bonds.

The presence of a Pt–P–O–Pt ring in **2** is corroborated by the literature. In fact, XRD analysis of the related Pt^I complex $[Pt(\kappa^2P,O\text{-}\mu\text{-}OPPh_2)(PMePh_2)]_2$ showed that each platinum atom is involved in a four-membered Pt–P–O–Pt ring.[19]

Finally, equilibrium between structures **A** and **B** seems unlikely because the signals found in the $^{195}Pt\{^1H\}$ NMR spectrum recorded at 195 K did not differ significantly from those found at 295 K.

The reaction of **1** with solid sodium methoxide (2 equiv.) in toluene at room temperature gave the symmetric dimer *trans*-$[Pt(PHCy_2)Cl(\mu\text{-}PCy_2)]_2$ (**3**) as the main product (82% yield).[20] Complex **3** was characterised by multinuclear NMR, IR, ESI-MS and elemental analysis. The appearance of an AA′XX′ spin system in the $^{31}P\{^1H\}$ NMR spectrum for the isotopomer not containing ^{195}Pt substantiates the *trans* geometry of the complex. Computer simulation of the spectrum, using as starting chemical shifts and coupling constants those extractable directly from the experimental spectrum,[21] gave the spectroscopic features reported in Table 1 (Supporting Information, ESI 3–4). The values found for $^3J_{P^{A'},Pt^1} = {}^3J_{P^A,Pt^2}$, for $^2J_{P^X,P^{X'}}$ and for $^3J_{P^A,P^X} = {}^3J_{P^{A'},P^{X'}}$ are consistent with a planar geometry of the Pt_2P_2 core.[22]

Table 1. Spectroscopic features for **3** ($CDCl_3$, 295 K).



	P^A	$P^{A'}$	P^X	$P^{X'}$	Pt^1	Pt^2
P^A	15.1	4.2	357.3	9.2	1948	79
$P^{A'}$	4.2	15.1	9.2	357.3	79	1948
P^X	357.3	9.2	–137.9	–150.8	2048	2399
$P^{X'}$	9.2	357.3	–150.8	–137.9	2399	2048
Pt^1	1948	79	2048	2399	–4014	
Pt^2	79	1948	2399	2048		–4014

The analogous palladium(II) complex *trans*-$[Pd(PHCy_2)$-$Cl(\mu\text{-}PCy_2)]_2$ is the reaction product between *cis*-$PdCl_2(PHCy_2)_2$ and 1 equiv. NaOPh and reacts at 50 °C with 1 more equiv. NaOPh to afford the bis(dicyclohexyl)-phenylphosphinito palladium(I) complex $[(PhOPCy_2)Pd(\mu\text{-}PCy_2)]_2$.[23] This reaction is not transferable to our system because **3** was recovered unaltered after 24 h stirring with 2 equiv. NaOMe in toluene at 50 °C (Scheme 2). A possible

explanation for the different reactivity of *trans*-[Pd(PHCy$_2$)Cl(μ-PCy$_2$)]$_2$ and **3** might reside in a different strength of the metal–Cl bond. IR stretching of the Pd–Cl bond (275 cm^{-1}) is in fact 14 cm^{-1} red-shifted with respect to that of the Pt–Cl in **3** (289 cm^{-1}).

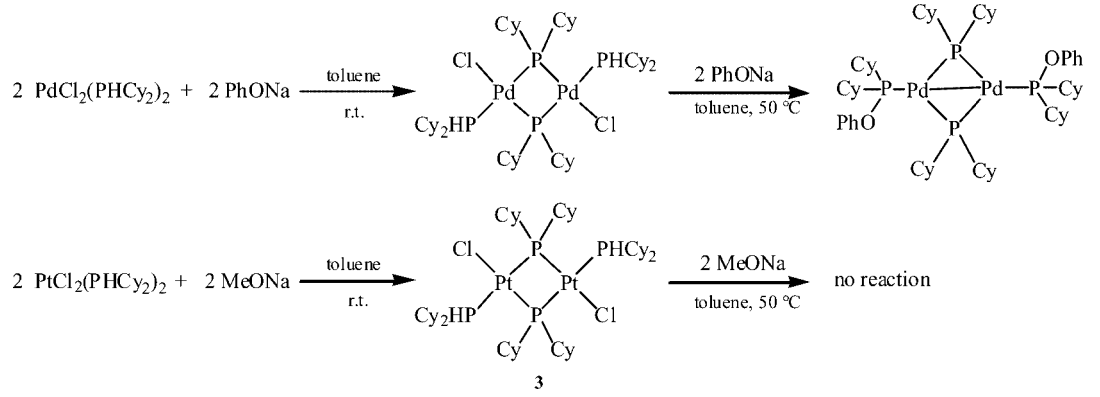
The reaction of **1** with excess NaOMe (5 equiv.) in toluene/methanol at room temperature for 1 day afforded, after work-up, a mixture of products made up of the asymmetric Pt^{I} complex [(PCy$_2$H)Pt(μ-PCy$_2$)$_2$Pt(PCy$_2$OMe)](*Pt–Pt*) (**4**, 60%), the symmetric Pt^{I} dimer [(PCy$_2$OMe)Pt(μ-PCy$_2$)]$_2$-(*Pt–Pt*) (**5**, 35%) and traces of **3** (Scheme 3).

Complex **4** showed in the ^{31}P{^{1}H} NMR spectrum two low field signals and one signal in the region of coordinated PHCy$_2$ (each flanked by ^{195}Pt satellites due to isotopomers containing one or two NMR active Pt atoms). The low field signals are a doublet of doublets centred at δ = 245.7 and a doublet of triplets centred at δ = 173.6. Both signals are due to phosphorus atoms not directly bound to hydrogens (comparison with proton coupled spectra) and are easily assigned, the first to a dicyclohexylphosphido group involved in three-membered rings, and the second, according to ^{1}H NMR and ESI-MS data, to a coordinated PCy$_2$OMe. The remaining signal is a doublet of triplets (further split in the proton-coupled spectrum due to the 318 Hz $^{1}J_{P,H}$) centred at δ = 19.1 ascribed to a coordinated PHCy$_2$. The ^{1}H NMR spectrum showed, beside resonances due to cyclohexyl protons, a doublet at δ = 3.94 [3 H, $^{3}J_{P,H}$ = 13 Hz] ascribable to the methyl group of the coordinated PCy$_2$-OMe and a doublet of multiplets due to the hydrogen directly bound to the phosphorus of the coordinated PCy$_2$H [δ = 6.36, $^{1}J_{P,H}$ = 318 Hz]. The two ^{195}Pt{^{1}H} NMR signals of the atoms directly bound to PHCy$_2$ and PCy$_2$OMe were mutually coupled [$^{1}J_{Pt,Pt}$ = 337 Hz)] and were centred at δ = –5530 and δ = –5570 respectively.

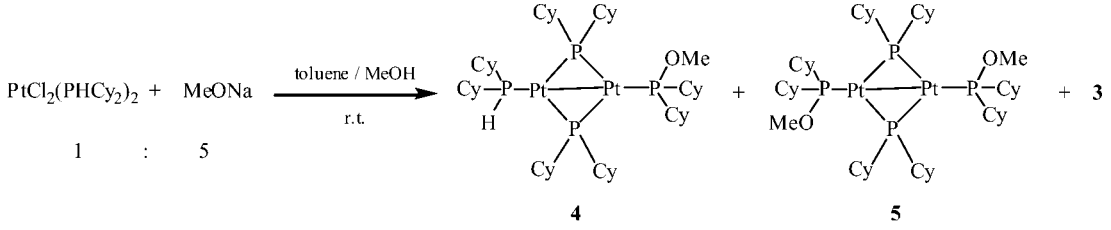
The symmetric dimer **5** showed in the ^{31}P{^{1}H} NMR spectrum the signal of the bridging phosphide at δ = 245.3 and that of the terminal methyl dicyclohexylphosphinite at δ = 171.2. The ^{195}Pt{^{1}H} NMR spectrum consisted of a doublet of triplets centred at δ = –5570 ppm.

Prolonging to 7 days the stirring time of the reaction between **1** and excess NaOMe described above resulted in the synthesis of the dimer **5** as the main product, devoid of the asymmetric complex **4**. This result prompted us to monitor the reaction by ^{31}P{^{1}H} NMR in order to ascertain whether **4** is the precursor of **5**, so as to shed some light on the reaction mechanism. The spectrum recorded after 30 min reaction showed the transformation of **1** into *cis*-Pt(PHCy$_2$)$_2$(OMe)$_2$ (**6**) and traces of **3**. Prolonging the reaction time resulted in the progressive decrease of signals due to **6** with contemporary appearance of signals due to **5**, which became predominant after 2 days.

Complex **6** gave a singlet with ^{195}Pt satellites in the ^{31}P{^{1}H} NMR spectrum [δ = 7.2, $^{1}J_{P,Pt}$ = 3267 Hz], which split into a doublet in the proton-coupled spectrum [$^{1}J_{P,H}$ = 341 Hz)]. The corresponding ^{195}Pt{^{1}H} NMR spectrum consisted in a triplet centred at δ = –4233 [$^{1}J_{P,Pt}$ = 3267 Hz]. Experiments carried out in deuterated solvent allowed assignation of the ^{1}H NMR resonance of the coordinated Cy$_2$P*H* [δ = 3.6, $^{1}J_{H,P}$ = 341 Hz] and OC*H*$_3$ [δ = 3.5, $^{4}J_{H,P}$ = 3.9 Hz; $^{3}J_{H,Pt}$ = 25 Hz]. Complex **6**, which is very soluble in the reaction mixture so as to prevent its precipitation at low temperature, could not be isolated in a pure state because of its fast and irreversible transformation into **4** during solvent removal either by reduced pressure or by bub-



Scheme 2.



Scheme 3.

bling of inert gas. This explains our experimental results: the starting complex **1** reacts with excess methoxide to give **6** (and traces of **3**, which does not further react), which slowly transforms into **5**. If the reaction is stopped when **6** is still present (e.g. 1 day), work-up of the crude results in the formation of a mixture containing **4** (formed mainly during solvent removal) and **5**. Complex **4** could be obtained in a pure state after work-up of the reaction of **1** with excess NaOMe (8 equiv.) in toluene/methanol at room temperature, and **5** could be obtained in 67% yield after 6 h by reacting **1** with excess NaOMe (8 equiv.) in toluene/methanol at 50 °C. Longer reaction times resulted in lower isolated yields because of decomposition of **5** into unidentified products.

Slow evaporation of a toluene solution of **5** deposited yellow-orange crystals suitable for single-crystal X-ray diffraction. The structure of a molecule in the crystal is shown in Figure 5. Significant bond lengths and angles are given in Table 2. The complex crystallises in the monoclinic space group $P2_1/c$. The molecule contains an inversion centre, and therefore the Pt_2P_2 quadrilater with angles of 110.30(4)° and 69.70(4)° is planar for reasons of symmetry; the OCH_3 oxygen atoms also lie in this plane within experimental error. The presence of a Pt–Pt bond is evidenced by an intermetal distance of 2.6307(5) Å, which is comparable with the 2.6127(6) Å and 2.604(1) Å Pt–Pt distances of $[(Pt^tBu_2H)Pt(\mu\text{-}P^tBu_2)_2Pt(CO)]$(*Pt–Pt*)[24] and $[(PPh_3)Pt(\mu\text{-}PPh_2)_2Pt(PPh_3)]$(*Pt–Pt*)[25] respectively. The average Pt–Pt bond length for 66 error-free observations in the CSD[26] amounts to 2.633 Å.

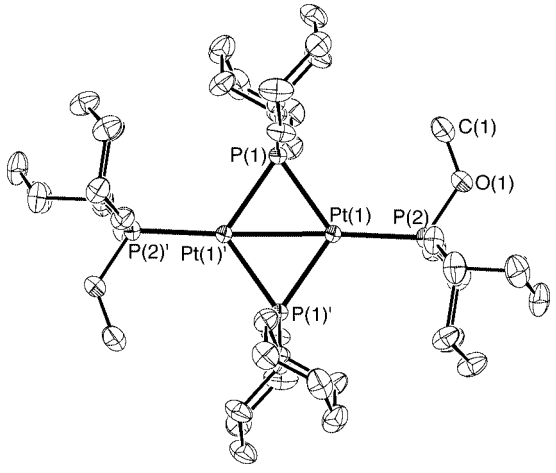


Figure 5. Displacement ellipsoid plot of **5**;[27] ellipsoids are scaled to 30% probability, H atoms have been omitted for clarity.

The Pt–P_μ distances (2.30 Å) are longer than Pt–P_t [2.2150(14) Å]. The external angle P(1)′–Pt(1)–P(2) [122.17(5)°] is smaller than P(1)–Pt(1)–P(2) [127.53(5)°] because of a rather short (2.01 Å) and repulsive H···H contact between a methoxy hydrogen and a H atom of a cyclohexyl substituent bonded to P(1).

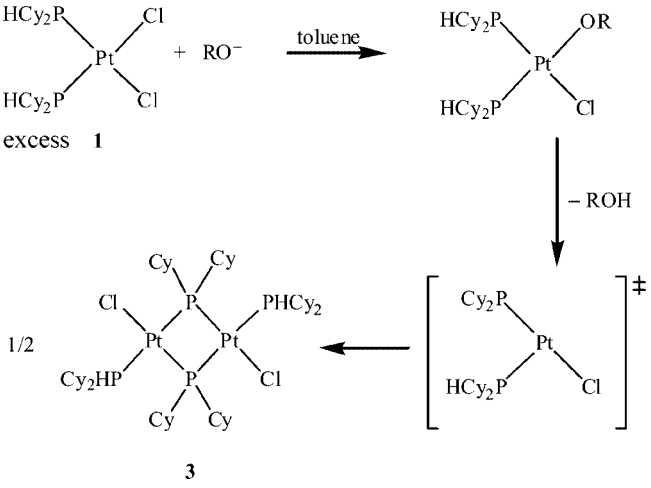
The reactivity shown by **1** towards NaOEt parallels that found for NaOMe: the reaction of **1** with 8 equiv. EtONa at 50 °C in a toluene/ethanol mixture afforded $[(PCy_2OEt)Pt(\mu\text{-}PCy_2)]_2$(*Pt–Pt*) (**7**) in 55% yield after only 2 h. However, because of the higher reactivity shown by EtONa, in this case it was not possible to isolate the asymmetric complex $[(PCy_2H)Pt(\mu\text{-}PCy_2)_2Pt(PCy_2OEt)]$(*Pt–Pt*) (**8**) in a pure state. It was observed in mixture with **7** and characterised in solution by multinuclear NMR spectroscopy.

Table 2. Selected bond lengths [Å] and angles [°] for **5**.

Pt(1)–P(2)	2.2150(14)
Pt(1)–P(1)′	2.2982(15)
Pt(1)–P(1)	2.3058(14)
Pt(1)–Pt(1)′	2.6307(5)
P(2)–O(1)	1.626(4)
C(1)–O(1)	1.365(7)
P(1)–Pt(1)–P(2)	127.53(5)
P(1)′–Pt(1)–P(2)	122.17(5)
Pt(1)′–Pt(1)–P(1)	55.01(4)
Pt(1)′–Pt(1)–P(1)′	55.29(4)
Pt(1)′–Pt(1)–P(2)	177.45(4)

The experimental data presented so far allow some mechanistic considerations to be put forward.

A possible explanation for the selectivity towards **3** of the reaction between **1** and NaOMe (2 equiv.) in toluene could be the accumulation, in these conditions, of the monosubstituted methoxo complex *cis*-$PtCl(OMe)(PHCy_2)_2$, which can dimerise to **3** by loss of methanol (Scheme 4). Such accumulation could derive from the constant lack of methoxide present in the reaction medium, because of its scarce solubility in toluene. Complex *cis*-$PtCl(OMe)(PHCy_2)_2$ could be detected by recording $^{31}P\{^1H\}$ NMR spectra of CD_2Cl_2 solutions of **1**, to which an equimolar amount of NaOMe was added. The solution showed, along with the singlets of residual **1** and **6**, two mutually coupled [$^2J_{P,P}$ = 15 Hz] doublets centred at δ = 17.3 [$^1J_{P,Pt}$ = 3814 Hz] and δ = 8.7 [$^1J_{P,Pt}$ = 2942 Hz] attributable to the P *trans* to Cl and P *trans* to OMe respectively. Analogous results were obtained by using NaOEt instead of NaOMe as limiting reagent. In this case the spectroscopic features of *cis*-$PtCl(OEt)(PHCy_2)_2$ are δ = 16.6 [$^1J_{P,Pt}$ = 3734 Hz, P *trans* to Cl] and δ = 7.4 [$^1J_{P,Pt}$ = 2966 Hz, P *trans* to OEt] [$^2J_{P,P}$ = 18 Hz].



Scheme 4. Proposed mechanism for the formation of **3**.

As to the formation of the alkylphosphinito Pt^{I} dimers observed when the reaction was carried out in the presence of excess NaOR (R = H, Me, Et), a possible mechanism is depicted in Scheme 5.

The initially formed metathesis product *cis*-$Pt(PHCy_2)_2(OR)_2$ can formally lose ROH, giving the terminal phosphido species **a**. The latter can give rise to an intramolecular process involving the metal, the coordinated RO group and the coordinated terminal phosphide, resulting in the phosphinito intermediates **b**. When R is an alkyl group, intramolecular oxidative addition of the P–H bond to Pt followed by hydrogen elimination and dimerisation (path 1) would account for the observed formation of the symmetric dimers $[(PCy_2OR)Pt(\mu\text{-}PCy_2)]_2$(*Pt–Pt*). The sequence of reactions leading from **b** to $[(PCy_2OR)Pt(\mu\text{-}PCy_2)]_2$(*Pt–Pt*) has already been proposed for the synthesis of several analogous systems.[3,18,28]

When R is H, the intramolecular oxidative addition of the P–H bond to Pt is disfavoured by the co-presence in the hypothetically formed $Pt(PCy_2)(H)(PCy_2OH)$ of a strongly basic centre (the terminal phosphide) and an acidic proton ($Cy_2PO\mathit{H}$). Reaction of **a** with **b** (R = H, path 2) can give intermediate **c**, which evolves into the final product **2** after loss of water and ring closure.

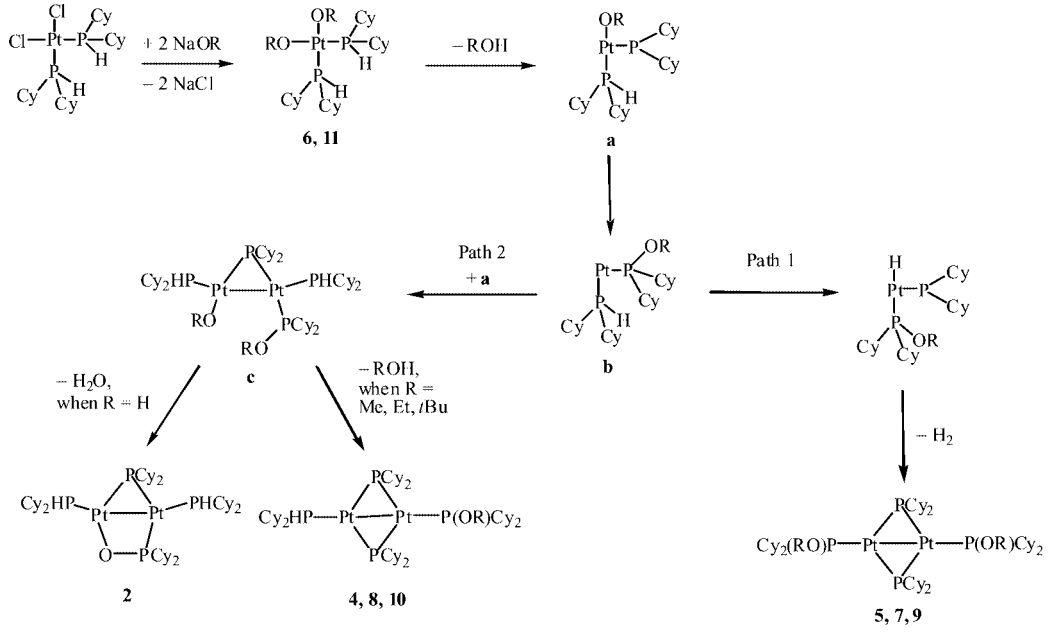
The central point of the suggested mechanism is the metal assisted formation of the P–O bond that leads to the dicyclohexylphosphinito ligands. In the literature, few examples can be found of such a transformation. In particular, the following have been reported: (*i*) $PhOPCy_2$ from $PHCy_2$ and phenoxide ion coordinated to palladium;[23] (*ii*) $MeOPPh_2$ from PPh_2Im (Im = 1-methylimidazole) and methoxide coordinated to ruthenium;[29] (*iii*) 1-phenyl-3*H*-2,1-benzoxaphosphole from *o*-(diphenylphosphanyl)benzyl alkoxide coordinated to platinum;[30] (*iv*) (4-methylphenyl)-dimethylphosphinite from PMe_3 and 4-methylphenoxide coordinated to ruthenium;[31] (*v*) MeOP(Ph)R (R = H, Ph, OMe) from $PPhR^-$ coordinated to osmium and methoxide.[32] In all cases the formation of the P–O bond is explained in terms of intramolecular [intermolecular in case *v*] attack of RO^- on a coordinated phosphide (or phosphane), substantially identical to our proposal for the transformation of **a** into **b**.

Path 2 of Scheme 5 could also explain the formation of the asymmetric complexes $[(PCy_2H)Pt(\mu\text{-}PCy_2)_2Pt(PCy_2OR)]$(*Pt–Pt*), which could be derived from intermediate **c** (R = Me, Et) after loss of alcohol and ring closure. The circumstance that the asymmetric compounds formed only when reaction mixtures containing significant amounts of complexes *cis*-$Pt(PHCy_2)_2(OR)_2$ were evaporated can be explained by the fact that, under reaction conditions, the transformation from **a** to **b** is fast, so that **a** never accumulates in the reaction medium. Putting mixtures containing *cis*-$Pt(PHCy_2)_2(OR)_2$ under vacuum would progressively enhance the amount of **a** in solution, rendering the formation of **c** competitive with Path 1.

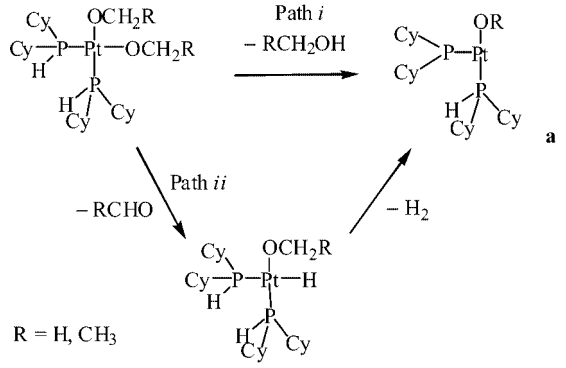
The transformation of *cis*-$Pt(PHCy_2)_2(OR)_2$ into **a** when R is Me or Et deserves comment. It is known that mononuclear dimethoxo Pt^{II} complexes are unstable and give aldehyde, alcohol and traces of CO.[9] In our case, intermediate **a** could form either by alcohol elimination or a dehydrogenative pathway consisting in the formation of Pt hydride with loss of aldehyde and subsequent loss of H_2 (Scheme 6).

In order to ascertain which of the above-mentioned pathways is operative in our system, we have carried out reactions between **1** and phenoxide or *tert*-butoxide, two bases incapable of forming the aldehyde contemplated by path *ii*.

The reaction of **1** with NaOPh (8 equiv.) in toluene at 50 °C for 1 day afforded the symmetrical Pt^{I} dimer $[(PCy_2OPh)Pt(\mu\text{-}PCy_2)]_2$(*Pt–Pt*) (**9**), whereas the asymmetric Pt^{I} complex $[(PCy_2H)Pt(\mu\text{-}PCy_2)_2Pt(PCy_2O\mathit{t}Bu)]$(*Pt–Pt*) (**10**)



Scheme 5. Proposed mechanism for reactions carried out with excess NaOR.



Scheme 6.

was the main product of the reaction of **1** with NaO*t*Bu (8 equiv.) in toluene at 50 °C.

Although the dehydrogenative pathway *ii* of Scheme 6 cannot be conclusively ruled out when NaOMe or NaOEt were the bases, these findings indicate that the loss of alcohol (path *i*) can be responsible (as in the cases of NaOPh or NaO*t*Bu) for the transformation of *cis*-Pt($PHCy_2$)$_2$-$(OR)_2$ into the intermediate Pt($PHCy_2$)(PCy_2)(OR) (**a**).

The diverse behaviour observed passing from NaOPh to NaO*t*Bu can be explained on the basis of the high difference in basicity exhibited by the two oxygenated bases and further supports the mechanism proposed. In fact, according to Scheme 5, the formation of asymmetric monophosphinito dimers is related to the contemporary presence in solution of significant amounts of intermediates **a** and **b**. In the case of NaOPh the formation of **a** is disfavoured because of the low basicity of phenoxide[33] and it is presumable that as soon as it forms it gives **b**, which evolves into **9**. On the contrary, with the very strong base NaO*t*Bu, the loss of *t*BuOH leading to **a** is very fast, so that path 2 of Scheme 5 becomes predominant.

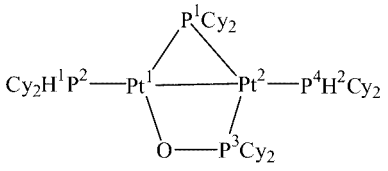
In conclusion, the presence of the relatively weak P–H bonds determines a rich reactivity of **1** with oxygenated bases. Depending on the base and on the experimental conditions it is possible to address the reaction towards the phosphido-bridged Pt^{II} complex **3**, the asymmetric alkyl dicyclohexylphosphinito complexes **4**, **8**, **10** or the bis dicyclohexylphosphinito complexes **5**, **7**, **9**. Using NaOH resulted in the smooth formation of a Pt^{I} complex, showing a rare example of a Pt–P–O–Pt ring.

Experimental Section

General Remarks: All manipulations were carried out under pure dinitrogen, using freshly distilled, thoroughly dehydrated and oxygen-free solvents. All aromatic deuterated solvents were carefully dehydrated (molecular sieves) and deoxygenated (freeze and pump). *cis*-Dichlorobis(dicyclohexylphosphane)platinum(II) (**1**) was prepared as described in ref.[3].

C, H elemental analyses were carried out on a Eurovector CHNS-O Elemental Analyser. Cl elemental analysis was performed by potentiometric titration using a Metrohm DMS Titrino. Melting points were measured with a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded with a Bruker Vector 22 spectrometer. THF (CH_2Cl_2 in the case of **3**) solutions of the complexes were infused with a Cole-Parmer syringe pump. All the ESI-MS spectra were recorded with an Agilent LC/MS SL series instrument adopting the following general conditions: electrospray, positive ions, flow rate 0.200 mL min^{-1}, drying gas flow 4.0 l min^{-1}, nebuliser pressure 25 psi, drying gas temperature 300 °C, capillary voltage 4000 V, mass range 400–1400 *m*/*z*. The isotopic pattern was calculated by the Isotope Pattern Viewer software, downloadable free of charge from the www.surfacespectra.com website. NMR spectra were recorded with a BRUKER Avance 400 spectrometer; frequencies are referenced to Me_4Si (^1H and ^{13}C), 85% H_3PO_4 (^{31}P) and H_2PtCl_6 (^{195}Pt). NMR simulation was performed using the program WINDAISY.

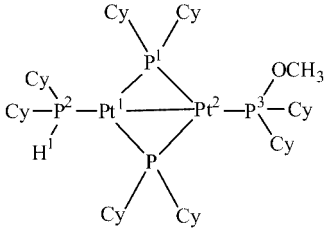
[(Cy_2PH)Pt(μ-PCy_2)(κ^2*P*,*O*-μ-Cy_2PO)Pt(Cy_2PH)](*Pt*–*Pt*) (2): An aqueous solution of NaOH (0.7 mL, 0.90 M) was added to a vigorously stirred colourless CH_2Cl_2 solution (10 mL) of *cis*-[Pt($PHCy_2$)$_2$-Cl_2] (0.203 g, 0.306 mmol) at room temperature. After 3 days the yellow organic phase was separated, washed twice with water and dried on Na_2SO_4. After filtration the solvent was evaporated to dryness under reduced pressure, affording 152 mg of pure **2** as a yellow powder (83%). The complex was air sensitive in solution, very soluble in dichloromethane, toluene and *n*-hexane and scarcely soluble in acetone. $C_{48}H_{90}OP_4Pt_2$ (1197.28): calcd. C 48.15, H 7.58; found C 48.25, H 7.60. LC-MS: exact mass calcd. for $C_{48}H_{90}OP_4Pt_2$: 1196.52 amu; found: 1197.5 [M + H]$^+$. M.p. 135 °C (dec.). IR (KBr): $\tilde{\nu}_{max}$ = 2279 (w, P–H), 2252 (w, P–H), 1024 (s, P=O) cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 295 K): δ = 5.68 [m, $^1J_{H(2),P(4)}$ = 310, $^2J_{H(2),Pt(2)}$ = 53 Hz, H(2)], 4.85 [m, $^1J_{H(1),P(2)}$ = 323, $^2J_{H(1),Pt(1)}$ = 112 Hz, H(1)] ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 295 K): δ = 134.4 [sharp ddd, $^2J_{P(1),P(2)}$ = 48, $^2J_{P(1),P(3)}$ = 229, $^2J_{P(1),P(4)}$ = 54, $^1J_{P(1),Pt(1)}$ = 4091, $^1J_{P(1),Pt(2)}$ = 2985 Hz, P(1)], 94.6 [sharp ddd, $^2J_{P(3),P(1)}$ = 229, $^3J_{P(3),P(2)}$ = 29, $^2J_{P(3),P(4)}$ = 5, $^1J_{P(3),Pt(2)}$ = 3061, $^2J_{P(3),Pt(1)}$ = 42 Hz, P(3)], 18.5 [broad ddd, $^2J_{P(4),P(1)}$ = 54, $^3J_{P(4),P(2)}$ = 112, $^2J_{P(4),P(3)}$ = 5, $^1J_{P(4),Pt(2)}$ = 3682, $^2J_{P(4),Pt(1)}$ = 83 Hz, P(4)], 15.9 [broad ddd, $^2J_{P(2),P(1)}$ = 48, $^3J_{P(2),P(3)}$ = 29, $^3J_{P(2),P(4)}$ = 112, $^1J_{P(2),Pt(1)}$ = 4230, $^2J_{P(2),Pt(2)}$ = 107 Hz, P(2)] ppm. $^{195}Pt\{^1H\}$ NMR (86 MHz, C_6D_6, 295 K): δ = –4798 [dddd, $^1J_{Pt(1),P(1)}$ = 4091, $^1J_{Pt(1),P(2)}$ = 4230, $^2J_{Pt(1),P(3)}$ = 42, $^2J_{Pt(1),P(4)}$ = 83 Hz, Pt(1)], –5205 [dddd, $^1J_{Pt(2),P(1)}$ = 2985, $^2J_{Pt(2),P(2)}$ = 107, $^1J_{Pt(2),P(3)}$ = 3061, $^1J_{Pt(2),P(4)}$ = 3682 Hz, Pt(2)] ppm.



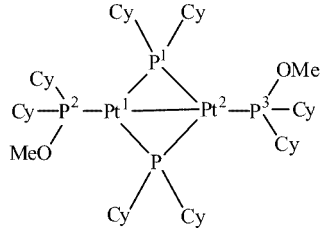
***trans*-Dichlorodi-μ-cyclohexylphosphidobis(dicyclohexylphosphane)-platinum(II) (3):** A suspension of *cis*-[Pt($PHCy_2$)$_2$$Cl_2$] (0.564 g, 0.85 mmol), CH_3ONa (0.092 g, 1.70 mmol) in toluene (20 mL) was vigorously stirred at room temperature (21 °C) for 3 days. The resulting pale yellow suspension was evaporated under reduced pressure. The residue was washed twice with *n*-hexane and the product was extracted with 10 mL CH_2Cl_2. Evaporation of the solvent afforded *trans*-[Pt($PHCy_2$)(PCy_2)Cl]$_2$ as a white powder (0.439 g, 82%). The complex was air stable, very soluble in dichloromethane and chloroform, scarcely soluble in toluene and insoluble in *n*-hexane. $C_{48}H_{90}Cl_2P_4Pt_2$ (1252.18): calcd. C 46.04, H 7.24, Cl 5.66; found C 46.15, H 7.25, Cl 5.68. LC-MS: exact mass calcd. for $C_{48}H_{90}Cl_2P_4Pt_2$: 1250.5 amu; found: 1251.5 [M + H]$^+$. M.p. >300 °C. IR (nujol mull): $\tilde{\nu}_{max}$ = 2337 (m, P–H), 289 (m, Pt–Cl) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 295 K): δ = 3.9 (m, $^1J_{H,P}$ = 322,

$^2J_{H,Pt}$ = 72 Hz, P*H*) ppm. $^{31}P\{^1H\}$ NMR and $^{195}Pt\{^1H\}$ NMR spectroscopic data are reported in Table 1.

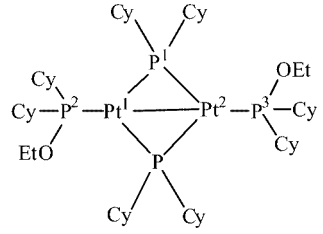
{(Cy$_2$PH)Pt(μ-PCy$_2$)$_2$Pt[Cy$_2$(MeO)P]}(*Pt–Pt*) (4): A solution of CH_3ONa in methanol (1.0 M, 3.2 mL) was added to a vigorously stirred suspension of *cis*-[Pt(PHCy$_2$)$_2$Cl$_2$] (0.262 g, 0.395 mmol) in toluene (10 mL) at room temperature. After 2 h the resulting orange suspension was evaporated under reduced pressure. The product was extracted with 3 × 5 mL hexane and precipitated, as a yellow powder, with acetone (hot/cold). Isolated yield: 0.129 g, 54%. The complex was air sensitive in solution, very soluble in dichloromethane, chloroform, hexane and toluene, scarcely soluble in acetone and methanol. $C_{49}H_{92}OP_4Pt_2$ (1211.31): calcd. C 48.59, H 7.66; found C 48.45, H 7.56. LC-MS: exact mass calcd. for $C_{49}H_{92}OP_4Pt_2$: 1210.54 amu; found: 1211.5 $[M + H]^+$. M.p. 150 °C (dec.). IR (KBr): $\tilde{\nu}_{max}$ = 2234 (w, P–H), 1095 (s), 1020 (s, P–O), 809 (s, P–O) cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 295 K): δ = 6.36 [m, $^1J_{H,P}$ = 318 Hz, H(1)], 3.94 (d, $^3J_{H,P}$ = 13 Hz, POC*H*$_3$) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 295 K): δ = 245.7 [dd, $^2J_{P(1),P(3)}$ = 67, $^2J_{P(1),P(2)}$ = 55, $^1J_{P(1),Pt(1)}$ = 2625, $^1J_{P(1),Pt(2)}$ = 2450 Hz, P(1)], 173.6 [dt, $^3J_{P(3),P(2)}$ = 76, $^2J_{P(3),P(1)}$ = 67, $^1J_{P(3),Pt(2)}$ = 5477 Hz, P(3)], 19.1 [dt, $^3J_{P(2),P(3)}$ = 76, $^2J_{P(2),P(1)}$ = 55, $^1J_{P(2),Pt(1)}$ = 4800, $^2J_{P(2),Pt(2)}$ = 47 Hz, P(2)] ppm. $^{195}Pt\{^1H\}$ NMR (86 MHz, C_6D_6, 295 K): δ = –5530 [dt, $^1J_{Pt(1),P(1)}$ = 2625, $^1J_{Pt(1),P(2)}$ = 4800, $^1J_{Pt(1),Pt(2)}$ = 337 Hz, Pt(1)], –5570 [dtd, $^1J_{Pt(2),P(1)}$ = 2450, $^2J_{Pt(2),P(2)}$ = 47, $^1J_{Pt(2),P(3)}$ = 5477, $^1J_{Pt(2),Pt(1)}$ = 337 Hz, Pt(2)] ppm.



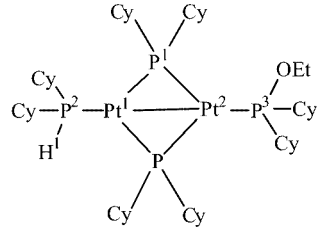
{[Cy$_2$(MeO)P]Pt(μ-PCy$_2$)}$_2$(*Pt–Pt*) (5): A solution of CH_3ONa in methanol (1.0 M, 2.9 mL) was added to a vigorously stirred suspension of *cis*-[Pt(PHCy$_2$)$_2$Cl$_2$] (0.240 g, 0.362 mmol) in toluene (10 mL) at 50 °C. After 6 h the resulting orange suspension was evaporated under reduced pressure. The product was extracted with 3 × 5 mL hexane and precipitated, as a yellow powder, with acetone (hot/cold). Isolated yield: 0.150 g, 67%. The complex was air sensitive in solution, very soluble in dichloromethane, chloroform, hexane and toluene, scarcely soluble in acetone and methanol. $C_{50}H_{94}O_2P_4Pt_2$ (1241.33): calcd. C 48.38, H 7.63; found C 48.48, H 7.65. LC-MS: exact mass calcd. for $C_{50}H_{94}O_2P_4Pt_2$: 1240.55 amu; found: 1241.5 $[M + H]^+$. M.p. 188 °C (dec.). IR (nujol mull): $\tilde{\nu}_{max}$ = 1259 (m, C–O), 1175 (w), 1103 (m), 1054 (m, P–O) cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 295 K): δ = 3.92 (d, $^3J_{H,P}$ = 13 Hz, C*H*$_3$O). $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 295 K): δ = 245.3 [dd, $^2J_{P(1),P(2)}$ = 68, $^1J_{P(1),Pt(1)}$ = 2475 Hz, P(1)], 171.2 [dd, $^2J_{P(2),P(1)}$ = 68, $^3J_{P(2),P(3)}$ = 81, $^1J_{P(2),Pt(1)}$ = 5468, $^2J_{P(2),Pt(2)}$ = 126 Hz, P(2)] ppm. $^{195}Pt\{^1H\}$ NMR (86 MHz, C_6D_6, 295 K): δ = –5570 [dtd, $^1J_{Pt(1),P(1)}$ = 2475, $^1J_{Pt(1),P(2)}$ = 5468, $^2J_{Pt(1),P(3)}$ = 64 Hz, Pt(1)] ppm.



{[Cy$_2$(EtO)P]Pt(μ-PCy$_2$)}$_2$(*Pt–Pt*) (7): A solution of EtONa in dry ethanol (1.0 M, 2.5 mL) was added to a vigorously stirred suspension of *cis*-[Pt(PHCy$_2$)$_2$Cl$_2$] (0.206 g, 0.311 mmol) in toluene (10 mL) at 50 °C. After 2 h the resulting orange suspension was evaporated under reduced pressure. The product was extracted with 3 × 5 mL hexane and precipitated, as a yellow powder, with acetone (hot/cold). Isolated yield: 0.109 g, 55%. The complex was air sensitive in solution, very soluble in dichloromethane, chloroform, hexane and toluene, scarcely soluble in acetone and methanol. $C_{52}H_{98}O_2P_4Pt_2$ (1269.38): calcd. C 49.20, H 7.78; found C 49.12, H 7.75. LC-MS: exact mass calcd. for $C_{52}H_{98}O_2P_4Pt_2$: 1268.58 amu; found: 1269.6 $[M + H]^+$. IR (nujol mull): $\tilde{\nu}_{max}$ = 1263 (m, C–O), 1177 (w), 1102 (m), 1059 (m, P–O), 1001 (m), 849 (m), 818 (w), 749 (m), 525 (m), 462 (m) cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 295 K): δ = 4.39 (m, $^3J_{H,H}$ = 7.1 Hz, CH_3CH_2O) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 295 K): δ = 244.0 [t, $^2J_{P(1),P(2)}$ = 68, $^1J_{P(1),Pt(1)}$ = 2481 Hz, P(1)], 167.3 [t, $^2J_{P(2),P(1)}$ = 68, $^3J_{P(2),P(3)}$ = 77, $^1J_{P(2),Pt(1)}$ = 5451, $^2J_{P(2),Pt(2)}$ = 132 Hz, P(2)] ppm. $^{195}Pt\{^1H\}$ NMR (86 MHz, C_6D_6, 295 K): δ = –5567 [dtd, $^1J_{Pt(1),P(1)}$ = 2481 Hz, $^1J_{Pt(1),P(2)}$ = 5451, $^2J_{Pt(1),P(3)}$ = 132 Hz, Pt(1)] ppm.

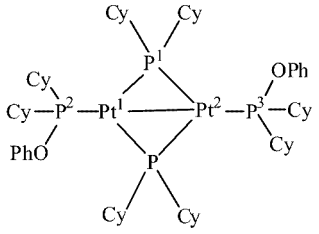


NMR Spectroscopic Features for 8: ^1H NMR (400 MHz, C_6D_6, 295 K): δ = 6.23 [dm, $^1J_{H(1),P(2)}$ = 318 Hz, P(1)], 4.40 (pseudoquintet, $^3J_{H,P}$ = 7, $^3J_{H,H}$ = 7 Hz, POC*H*$_2$CH$_3$), 1.56 (t, $^3J_{H,H}$ = 7 Hz, POCH$_2$C*H*$_3$) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 295 K): δ = 245.4 [dd, $^2J_{P(1),P(3)}$ = 64, $^2J_{P(1),P(2)}$ = 54, $^1J_{P(1),Pt(1)}$ = 2710, $^1J_{P(1),Pt(2)}$ = 2461 Hz, P(1)], 169.5 [dt, $^3J_{P(3),P(2)}$ = 77, $^2J_{P(3),P(1)}$ = 64, $^1J_{P(3),Pt(2)}$ = 5458 Hz, P(3)], 19.5 [dt, $^3J_{P(2),P(3)}$ = 77, $^2J_{P(2),P(1)}$ = 54, $^1J_{P(2),Pt(1)}$ = 4894, $^2J_{P(2),Pt(2)}$ = 54 Hz, P(2)] ppm. $^{195}Pt\{^1H\}$ NMR (86 MHz, C_6D_6, 295 K): δ = –5524 [dt, $^1J_{Pt(1),P(1)}$ = 2710, $^1J_{Pt(1),P(2)}$ = 4894, $^1J_{Pt(1),Pt(2)}$ = 333 Hz, Pt(1)], –5567 [dtd, $^1J_{Pt(2),P(1)}$ = 2461, $^2J_{Pt(2),P(2)}$ = 54, $^1J_{Pt(2),P(3)}$ = 5458, $^1J_{Pt(2),Pt(1)}$ = 337 Hz, Pt(2)] ppm.

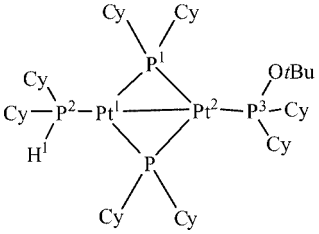


{[Cy$_2$(PhO)P]Pt(μ-PCy$_2$)}$_2$(*Pt–Pt*) (9): Sodium phenoxide (0.285 g, 2.46 mmol) was added to a stirred suspension of *cis*-[Pt(PHCy$_2$)$_2$-Cl$_2$] (0.204 g, 0.308 mmol) in toluene (5 mL). After 24 h stirring at 50 °C the suspension was filtered and the filtrate was concentrated to 3 mL under reduced pressure. The product was obtained, as a yellow solid, by precipitation with acetone (50 mg, 24%). The complex was air sensitive in solution, very soluble in dichloromethane, chloroform, hexane and toluene, scarcely soluble in acetone and methanol. $C_{60}H_{98}O_2P_4Pt_2$ (1365.47): calcd. C 52.78, H 7.23; found C 52.59, H 7.20. LC-MS: exact mass calcd. for $C_{60}H_{98}O_2P_4Pt_2$: 1364.58 amu; found: 1365.6 $[M + H]^+$. IR (KBr): $\tilde{\nu}_{max}$ = 2925 (m), 2848 (m), 1262 (s), 1229 (m), 1100 (vs, P–O), 1021 (vs, P–O), 873

(m), 801 (vs), 678 (w), 518 (w), 501 (w) cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, 295 K): δ = 7.25–7.02 (10 H, Ph), 2.4–0.7 (88 H, Cy) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 295 K) (Supporting Information, ESI 5): δ = 242.7 [t, $^2J_{P(1),P(2)}$ = 71, $^1J_{P(1),Pt(1)}$ = 2469 Hz, P(1)], 163.6 [t, $^2J_{P(2),P(1)}$ = 71, $^3J_{P(2),P(3)}$ = 82, $^1J_{P(2),Pt(1)}$ = 5489, $^2J_{P(2),Pt(2)}$ = 49 Hz, P(2)] ppm. $^{195}Pt\{^1H\}$ NMR (86 MHz, CD_2Cl_2, 295 K): δ = –5524 [dtd, $^1J_{Pt(1),P(1)}$ = 2469, $^1J_{Pt(1),P(2)}$ = 5489, $^2J_{Pt(1),P(3)}$ = 49 Hz, Pt(1)] ppm.



NMR Spectroscopic Features for {(Cy_2PH)Pt(μ-PCy_2)$_2$Pt-[Cy_2(*t*BuO)P]}(*Pt–Pt*) (10): Compound **10** was the main product of reaction of **1** with NaO*t*Bu (8 equiv.) in toluene at 50 °C. ^1H NMR (400 MHz, C_6D_6, 295 K): δ = 6.38 [m, $^1J_{H(1),P(2)}$ = 317 Hz, 2 H, H(1)]; 1.66 (s, 9 H, *t*Bu) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 295 K): δ = 235.8 [dd, $^2J_{P(1),P(3)}$ = 57, $^2J_{P(1),P(2)}$ = 53, $^1J_{P(1),Pt(1)}$ = 2594, $^1J_{P(1),Pt(2)}$ = 2528 Hz, P(1)], 128.7 [dt, $^3J_{P(3),P(2)}$ = 78, $^2J_{P(3),P(1)}$ = 57, $^1J_{P(3),Pt(2)}$ = 5378 Hz, P(3)], 18.4 [dt, $^3J_{P(2),P(3)}$ = 78, $^2J_{P(2),P(1)}$ = 54, $^1J_{P(2),Pt(1)}$ = 4794 Hz, P(2)] ppm. $^{195}Pt\{^1H\}$ NMR (86 MHz, C_6D_6, 295 K): δ = –5492 [dt, $^1J_{Pt(1),P(1)}$ = 2594, $^1J_{Pt(1),P(2)}$ = 4794 Hz, (1)]; –5445 [dt, $^1J_{Pt(2),P(1)}$ = 2528, $^1J_{Pt(2),P(3)}$ = 5378 Hz, Pt(2)] ppm.



***cis*-[Pt($PHCy_2$)$_2$(OPh)$_2$] (11):** Sodium phenoxide (0.116 g, 0.999 mmol) was added to a toluene suspension of *cis*-[Pt($PHCy_2$)$_2$-Cl_2] (0.224 g, 0.338 mmol in 10 mL) and the mixture was stirred at room temperature for 2 h. The resulting suspension was filtered, giving a white solid and a yellow solution. The white solid was washed with water, extracted with CH_2Cl_2 and precipitated with toluene, affording 98 mg (41%) of pure *cis*-[Pt($PHCy_2$)$_2$(Cl)(OPh)] (**12**). The yellow filtrate was evaporated under reduced pressure. The residue was redissolved in 4 mL of dichloromethane and *n*-hexane added , which caused the precipitation of *cis*-[Pt($PHCy_2$)$_2$-(OPh)$_2$] (**11**) as a white solid (0.155 g, 59%). Complex **11** was air stable, very soluble in dichloromethane, toluene, scarcely soluble in hexane. $C_{36}H_{56}O_2P_2Pt$ (777.85): calcd. C 55.59, H 7.26; found C 55.45, H 7.38. M.p. 129–131 °C (dec.). IR (nujol mull): $\tilde{\nu}_{max}$ = 2333 (m, P–H) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 295 K): δ = 3.8 (m, $^1J_{H,P}$ = 367 Hz, P*H*) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 295 K): δ = 5.6 (s, $^1J_{P,Pt}$ = 3389 Hz) ppm. $^{195}Pt\{^1H\}$ NMR (86 MHz, $CDCl_3$, 295 K): δ = –4155 (t, $^1J_{P,Pt}$ = 3389 Hz) ppm.

***cis*-[Pt($PHCy_2$)$_2$(Cl)(OPh)] (12):** $C_{30}H_{51}ClOP_2Pt$ (720.20): calcd. C 50.03, H 7.14, Cl 4.92; found C 50.11, H 7.18, Cl 4.88. M.p. >300 °C (dec.). IR (nujol mull): $\tilde{\nu}_{max}$ = 2330, 2345 (m, P–H), 306 (m, Pt–Cl) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 295 K): δ = 3.83 (m, $^1J_{H,P}$ = 359, $^2J_{H,Pt}$ = 102 Hz, P*H* trans Cl), 3.67 (m, $^1J_{H,P}$ = 352, $^2J_{H,Pt}$ = 91 Hz, P*H* trans OPh) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 295 K): δ = 8.7 (d, $^1J_{P,Pt}$ = 3174, $^2J_{P,P}$ = 14 Hz, P *trans* OPh), 15.2 (d, $^1J_{P,Pt}$ = 3653, $^2J_{P,P}$ = 14 Hz, P *trans* Cl) ppm. $^{195}Pt\{^1H\}$ NMR (86 MHz, $CDCl_3$, 295 K): δ = –4323 (dd, $^1J_{P,Pt}$ = 3174, $^1J_{P,Pt}$ = 3653 Hz) ppm.

X-ray Data Collection, Structure Solution and Refinement of 5:[34] Crystal data, parameters for intensity data collection and convergence results are compiled in Table 3. A yellow platelet of approximate dimensions 0.20 × 0.11 × 0.04 mm was studied at room temperature with a BRUKER-AXS SMART APEX diffractometer. An empirical absorption correction[35] was applied before averaging symmetry-related reflections. The structure was solved by direct methods[36] and refined on F^2.[37]

Table 3. Crystal data and structure refinement for **5**.

Empirical formula	$C_{50}H_{94}O_2P_4Pt_2$
Molecular mass	1241.31
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$ (no. 14)
Unit cell dimensions	
a [Å]	11.1753(13)
b [Å]	21.220(2)
c [Å]	12.2712(14)
β [°]	113.052(2)
V [Å^3]	2677.6(5)
Z	2
$D_{calcd.}$ [Mg m^{-3}]	1.540
Absorption coeff. [mm^{-1}]	5.4
θ Range for data coll. [°]	1.9–28.4
Independent reflections	6689
Observed reflections	4198
Data/parameters	6689/262
Goodness-of-fit on F^2	0.997
R[a] [$I > 2\sigma(I)$]	0.0453
wR_2[b] (all data)	0.0615
Largest diff. peak/hole [e Å^{-3}]	2.55, –1.08 (close to Pt)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Supporting Information: The ^1H-^{31}P HMQC NMR spectrum of **2**, the $^{31}P\{^1H\}$ NMR spectrum of [(Cy_2PH)(Cl)Pt(μ-PCy_2)Pt-(Cy_2PH)$_2$](*Pt–Pt*), the comparison of the experimental $^{31}P\{^1H\}$ NMR spectrum of **3** with that calculated, and the $^{31}P\{^1H\}$ NMR spectrum of **9** are given as supporting information.

Acknowledgments

Italian MIUR (PRIN 2004, project 2004030719_005) is gratefully acknowledged for financial support. We thank Dr. A. Fiore for experimental assistance, Dr. C. Hu for help with the X-ray experiment and Prof. F. P. Fanizzi for helpful discussions.

[1] R. Giannandrea, P. Mastrorilli, C. F. Nobile, M. Palma, F. P. Fanizzi, U. Englert, *Eur. J. Inorg. Chem.* **2000**, 2573–2576.
[2] P. Mastrorilli, M. Palma, C. F. Nobile, F. P. Fanizzi, *J. Chem. Soc., Dalton Trans.* **2000**, 4272–4276.
[3] P. Mastrorilli, C. F. Nobile, F. P. Fanizzi, M. Latronico, C. Hu, U. Englert, *Eur. J. Inorg. Chem.* **2002**, 1210–1218.
[4] R. A. Michelin, M. Napoli, R. Ros, *J. Organomet. Chem.* **1979**, *175*, 239–255.
[5] D. R. Coulson, *J. Am. Chem. Soc.* **1976**, *98*, 3111–3119.
[6] F. Giordano, A. Vitagliano, *Inorg. Chem.* **1981**, *20*, 633–635.
[7] H. E. Bryndza, S. A. Kretchmar, T. H. Tulip, *J. Chem. Soc., Chem. Commun.* **1985**, 977–978.

[8] R. T. Boere, C. J. Willis, *Inorg. Chem.* **1985**, *24*, 1059–1065.
[9] H. E. Bryndza, J. C. Calabrese, M. Marsi, D. C. Roe, W. Tam, J. E. Bercaw, *J. Am. Chem. Soc.* **1986**, *108*, 4805–4813.
[10] D. P. Arnold, M. A. Bennett, *J. Organomet. Chem.* **1980**, *199*, C17–C20.
[11] P. Roffia, G. Gregorio, F. Conti, G. F. Pregaglia, R. Ugo, *J. Mol. Catal.* **1977**, *2*, 191–201.
[12] A. Sacco, P. Mastrorilli, *J. Chem. Soc., Dalton Trans.* **1994**, 2761–2764.
[13] J. Sieler, M. Helms, W. Gaube, A. Svensson, O. Lindqvist, *J. Organomet. Chem.* **1987**, *320*, 129–136.
[14] The reaction was carried out in toluene for 3 h at 50 °C with a NaEtO/Pt molar ratio of 2.
[15] The reaction was carried out in dichloromethane at reflux and the starting material was recovered unaltered after 12 h.
[16] P. E. Garrou, *Chem. Rev.* **1981**, *81*, 229–266.
[17] A. J. Carty, S. A. Maclaughlin, D. Nucciarone, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis* (Eds.: J. G. Verkade, L. D. Quin), VCH Publishers, New York, **1987**, p. 559.
[18] R. Giannandrea, P. Mastrorilli, C. F. Nobile, U. Englert, *J. Chem. Soc., Dalton Trans.* **1997**, 1355–1358.
[19] N. W. Alcock, P. Bergamini, T. M. Gomes-Carniero, R. D. Jackson, J. Nicholls, A. G. Orpen, P. G. Pringle, S. Sostero, O. Traverso, *J. Chem. Soc., Chem. Commun.* **1990**, 980–982.
[20] Complex **4** was obtained in variable amounts also when NaOH, NaOEt or NaOPh were reacted with **1** in toluene with a **1**/base molar ratio of 1/2.
[21] J. B. Brandon, K. R. Dixon, *Can. J. Chem.* **1981**, *59*, 1188–1200.
[22] R. Glaser, D. J. Kountz, R. D. Waid, J. C. Gallucci, D. W. Meek, *J. Am. Chem. Soc.* **1984**, *106*, 6324–6333.
[23] M. Sommovigo, M. Pasquali, P. Leoni, U. Englert, *Inorg. Chem.* **1994**, *33*, 2686–2688.
[24] P. Leoni, G. Chiaradonna, M. Pasquali, F. Marchetti, *Inorg. Chem.* **1999**, *38*, 253–259.
[25] N. J. Taylor, P. C. Chieh, A. J. Carty, *J. Chem. Soc., Chem. Commun.* **1975**, 448–449.
[26] F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *B58*, 380–388.
[27] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2001**.
[28] P. Leoni, M. Sommovigo, M. Pasquali, P. Sabatino, D. Braga, *J. Organomet. Chem.* **1992**, *423*, 263–270.
[29] A. Caballero, F. A. Jalón, B. R. Manzano, G. Espino, M. Pérez-Manrique, A. Mucientes, F. J. Poblete, M. Maestro, *Organometallics* **2004**, *23*, 5694–5706.
[30] P. W. N. M. Van Leeuwen, C. F. Roobeek, A. G. Orpen, *Organometallics* **1990**, *9*, 2179–2181.
[31] J. F. Hartwig, R. G. Bergman, R. A. Andersen, *J. Organomet. Chem.* **1990**, *394*, 417–432.
[32] D. S. Bohle, T. C. Jones, C. E. F. Rickard, W. R. Roper, *Organometallics* **1986**, *5*, 1612–1619.
[33] The scarce basicity of NaOPh can be held responsible for the successful isolation in the state of purity of the phenoxo Pt^{II} complexes *cis*-[$Pt(PHCy_2)_2(OPh)_2$] (**11**) and *cis*-[$Pt(PHCy_2)_2$-(Cl)(OPh)] (**12**), as described in the Exp. Sect.
[34] CCDC-269199 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[35] G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data, University of Göttingen, **1996**.
[36] G. M. Sheldrick *SHELXS97*, program for crystal structure solution, University of Göttingen, **1997**.
[37] G. M. Sheldrick *SHELXL97*, program for crystal structure refinement, University of Göttingen, **1997**.

Received: June 7, 2005
Published Online: September 26, 2005

