Synthesis of Phosphido-Bridged Phosphinito Platinum(I) Complexes by Reaction of *cis*-PtCl₂(PHCy₂)₂ with Oxygenated Bases – Crystal Structure of [(PCy₂OMe)Pt(µ-PCy₂)]₂(Pt-Pt)

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Reaction of *cis*-PtCl₂(PHCy₂)₂ (1) with oxygenated bases leads to phosphido-bridged dinuclear complexes. The product obtained using sodium hydroxide is the asymmetric Pt^I complex [(Cy₂PH)Pt(μ -PCy₂)($\kappa^2 P$,O- μ -Cy₂PO)Pt(Cy₂PH)](*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(PHCy₂)Cl(μ -PCy₂)]₂ (3) as the main product. Using an excess of base at 50 °C allowed the isolation of the symmetric Pt^I dimers [(PCy₂OR)Pt(μ -PCy₂)]₂(*Pt*–*Pt*) (5, R = Me; 7, R = Et) containing two alkyl dicyclohexylphosphinito ligands. The asymmetric compounds [(PCy₂H)Pt(μ -PCy₂)₂Pt(PCy₂OR)](*Pt*–*Pt*) (4, R =

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*-PtCl₂(PHCy₂)₂ (1) with NaOR (R = H, Me, Et, Ph, *t*Bu). The latter compounds, in fact,

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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 Pt¹ complexes (carried out also employing Na-OtBu and NaOPh as oxygenated bases) show that the first two steps of the overall reaction are the metathesis leading to *cis*-Pt(OR)₂(PHCy₂)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 Pt₂P₂ core contains a Pt–Pt bond. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

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 zero-valent 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-PtCl₂(PHCy₂)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*-PtCl₂(PH*t*Bu₂)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 CH₂Cl₂/H₂O system proceeded smoothly to form a new dinuclear Pt^I complex whose spectroscopic features and ESI-MS analysis indicate as $[(Cy_2PH)Pt(\mu-PCy_2)(\kappa^2 P, O-\mu-$

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Scheme 1.

Cy₂PO)Pt(Cy₂PH)](*Pt–Pt*) (2). The ³¹P{¹H} NMR spectrum of 2 (Figure 1) showed 4 mutually coupled doublets of doublets of doublets flanked by ¹⁹⁵Pt satellites centred at $\delta = 134.4$, $\delta = 94.6$, $\delta = 18.5$ and $\delta = 15.9$ ppm.

Of these, the latter two can be ascribed to coordinated PCy₂H (comparison with proton-coupled spectrum gave ${}^{1}J_{P,H}$ of 310 Hz and 323 Hz respectively) while that at $\delta =$ 94.6 is ascribable to a deshielded P–O ligand. The remaining low field signal at $\delta = 134.4$ is flanked by three different sets of satellites and can be attributed to a phosphide involved in a three-membered Pt₂P 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 PCy₂H, which were attributed to the proper PCy₂H ligand on the basis of ¹H–³¹P HMQC experiments (Supporting Information, ESI 1). The ¹⁹⁵Pt{¹H} NMR spectrum consisted of two dddd centred at $\delta = -4798$ (Pt¹) and $\delta = -5205$ (Pt²) (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)Cy₂ ligand acts as monodentate (κ -*P* bound to Pt²), or with structure **B**, in which the P(O)Cy₂ 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 $[(Cy_2PH)(Cl)Pt(\mu-PCy_2)Pt(Cy_2PH)_2]$ -



Figure 1. ³¹P{¹H} NMR spectrum of **2** (161 MHz, 295 K, C₆D₆).



Figure 2. ¹⁹⁵Pt{¹H} NMR spectrum of 2 (295 K, C_6D_6). a: Pt¹; b: Pt².



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



Figure 4. Possible structures of 2.

 $(Pt-Pt)^{[3]}$ $[(Cy_2PH)(Cl)Pd(\mu-PCy_2)Pd(Cy_2PH)_2]$ or (Pd-Pd)^[18] (Supporting Information, ESI 2) are characterised by broad $^{31}P\{^1H\}$ NMR signals for all ligands except the bridging PCy₂, a feature that was ascribed to hindered rotation of the PHCy₂ ligands about the metal-P bond. The sharp signals found in the ${}^{31}P{}^{1}H$ NMR of 2 (Figure 1) favour structure **B**, in which both $PHCy_2$ (in particular that bound to Pt²) 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 $[Pt(\kappa^2 P, O-\mu-OPPh_2)(PMePh_2)]_2$ 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 ¹⁹⁵Pt{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(PHCy₂)Cl(μ -PCy₂)]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 ³¹P{¹H} NMR spectrum for the isotopomer not containing ¹⁹⁵Pt 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 ${}^{3}J_{P^{A'},Pt^{1}} = {}^{3}J_{P^{A},Pt^{2}}$, for ${}^{2}J_{P^{X},P^{X'}}$ and for ${}^{3}J_{P^{A},P^{X}} =$ ${}^{3}J_{\mathbf{P}^{\mathbf{A}'},\mathbf{P}^{\mathbf{X}'}}$ are consistent with a planar geometry of the $\mathrm{Pt}_{2}\mathrm{P}_{2}$ core.[22]

Table 1. Spectroscopic features for 3 (CDCl₃, 295 K).



	Cy ₂					
	$\mathbf{P}^{\mathbf{A}}$	$\mathbf{P}^{\mathbf{A}'}$	$\mathbf{P}^{\mathbf{X}}$	$\mathbf{P}^{\mathbf{X}'}$	$\mathbf{P}\mathbf{t}^1$	Pt ²
PA	15.1	4.2	357.3	9.2	1948	79
$\mathbf{P}^{\mathbf{A}'}$	4.2	15.1	9.2	357.3	79	1948
$\mathbf{P}^{\mathbf{X}}$	357.3	9.2	-137.9	-150.8	2048	2399
$\mathbf{P}^{\mathbf{X}'}$	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(PHCy₂)- $Cl(\mu-PCy_2)]_2$ is the reaction product between *cis*-PdCl₂(PHCy₂)₂ and 1 equiv. NaOPh and reacts at 50 °C with 1 more equiv. NaOPh to afford the bis(dicyclohexyl)phenylphosphinito palladium(I) complex [(PhOPCy₂)Pd(µ-PCy₂)]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

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explanation for the different reactivity of *trans*-[Pd-(PHCy₂)Cl(μ -PCy₂)]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 [(PCy₂H)Pt(μ -PCy₂)₂Pt(PCy₂OMe)](*Pt*-*Pt*) (**4**, 60%), the symmetric Pt^I dimer [(PCy₂OMe)Pt(μ -PCy₂)]₂-(*Pt*-*Pt*) (**5**, 35%) and traces of **3** (Scheme 3).

Complex 4 showed in the ³¹P{¹H} NMR spectrum two low field signals and one signal in the region of coordinated PHCy₂ (each flanked by ¹⁹⁵Pt satellites due to isotopomers containing one or two NMR active Pt atoms). The low field signals are a doublet of doublets centred at $\delta = 245.7$ and a doublet of triplets centred at $\delta = 173.6$. 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 ¹H NMR and ESI-MS data, to a coordinated PCy₂OMe. The remaining signal is a doublet of triplets (further split in the proton-coupled spectrum due to the 318 Hz ${}^{1}J_{\rm PH}$) centred at δ = 19.1 ascribed to a coordinated PHCy₂. The ¹H 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 PCy2-OMe and a doublet of multiplets due to the hydrogen directly bound to the phosphorus of the coordinated PCy₂H $[\delta = 6.36, {}^{1}J_{P,H} = 318 \text{ Hz}]$. The two ${}^{195}\text{Pt}\{{}^{1}\text{H}\}$ NMR signals of the atoms directly bound to PHCy2 and PCy2OMe were mutually coupled $[{}^{1}J_{\text{Pt,Pt}} = 337 \text{ Hz})]$ and were centred at $\delta = -5530$ and $\delta = -5570$ respectively.

The symmetric dimer **5** showed in the ³¹P{¹H} NMR spectrum the signal of the bridging phosphide at $\delta = 245.3$ and that of the terminal methyl dicyclohexylphosphinite at $\delta = 171.2$. The ¹⁹⁵Pt{¹H} NMR spectrum consisted of a doublet of triplets centred at $\delta = -5570$ 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 ³¹P{¹H} 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(PHCy₂)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 ¹⁹⁵Pt satellites in the ³¹P{¹H} NMR spectrum [$\delta = 7.2$, ¹*J*_{P,Pt} = 3267 Hz], which split into a doublet in the proton-coupled spectrum [¹*J*_{P,H} = 341 Hz)]. The corresponding ¹⁹⁵Pt{¹H} NMR spectrum consisted in a triplet centred at $\delta = -4233$ [¹*J*_{P,Pt} = 3267 Hz]. Experiments carried out in deuterated solvent allowed assignation of the ¹H NMR resonance of the coordinated Cy₂PH [$\delta = 3.6$, ¹*J*_{H,P} = 341 Hz] and OCH₃ [$\delta = 3.5$, 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 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 $110.30(4)^\circ$ and $69.70(4)^{\circ}$ is planar for reasons of symmetry; the OCH₃ 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 $[(PtBu_2H)Pt(\mu-PtBu_2)_2Pt(CO)](Pt-Pt)^{[24]}$ and $[(PPh_3)Pt(\mu-Pt)^{[24]}]$ PPh₂)₂Pt(PPh₃)](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)-

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

2.2150(14)
2.2982(15)
2.3058(14)
2.6307(5)
1.626(4)
1.365(7)
127.53(5)
122.17(5)
55.01(4)
55.29(4)
177.45(4)

Pt(μ -PCy₂)]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 [(PCy₂H)Pt(μ -PCy₂)₂Pt(PCy₂OEt)](*Pt*-*Pt*) (8) in a pure state. It was observed in mixture with 7 and characterised in solution by multinuclear NMR spectroscopy.

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)(PHCy₂)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(O-Me)(PHCy₂)₂ could be detected by recording ${}^{31}P{}^{1}H$ NMR spectra of CD₂Cl₂ 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 $[^{2}J_{P,P} = 15 \text{ Hz}]$ doublets centred at $\delta = 17.3 [^{1}J_{P,Pt}]$ = 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 Na-OMe as limiting reagent. In this case the spectroscopic features of *cis*-PtCl(OEt)(PHCy₂)₂ are $\delta = 16.6 [^{1}J_{P,Pt} =$ 3734 Hz, P *trans* to Cl] and δ = 7.4 [¹J_{P,Pt} = 2966 Hz, P *trans* to OEt] $[^2J_{P,P} = 18 \text{ Hz}].$



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(PHCy₂)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 [(PCy₂OR)Pt(μ -PCy₂)]₂(*Pt*-*Pt*). The sequence of reactions leading from **b** to [(PCy₂OR)Pt(μ -PCy₂)]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(PCy₂)(H)(PCy₂OH) of a strongly basic centre (the terminal phosphide) and an acidic proton (Cy₂POH). Reaction of **a** with **b** ($\mathbf{R} = \mathbf{H}$, 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*) PhOPCy₂ from PHCy₂ and phenoxide ion coordinated to palladium;^[23] (*ii*) MeOPPh₂ from PPh₂Im (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 PMe₃ 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 asymmetric complexes $[(PCy_2H)Pt(\mu - PCy_2)_2Pt$ the (PCy₂OR)](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(PHCy₂)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(PHCy₂)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(PHCy₂)₂(OR)₂ into **a** when R is Me or Et deserves comment. It is known that monouclear 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 H₂ (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 [(PCy₂-OPh)Pt(μ -PCy₂)]₂(*Pt*-*Pt*) (**9**), whereas the asymmetric Pt^I complex [(PCy₂H)Pt(μ -PCy₂)₂Pt(PCy₂OtBu)](*Pt*-*Pt*) (**10**)



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





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 Na-OPh or NaO*t*Bu) for the transformation of *cis*-Pt(PHCy₂)₂-(OR)₂ into the intermediate Pt(PHCy₂)(PCy₂)(OR) (**a**).

The diverse behaviour observed passing from NaOPh to NaOtBu 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 NaOtBu, 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^{II} 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

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spectrometer. THF (CH₂Cl₂ 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 mLmin⁻¹, drying gas flow 4.0 lmin⁻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 Me₄Si (¹H and ¹³C), 85% H₃PO₄ (³¹P) and H₂PtCl₆ (¹⁹⁵Pt). NMR simulation was performed using the program WINDAISY.

 $[(Cy_2PH)Pt(\mu-PCy_2)(\kappa^2 P, O-\mu-Cy_2PO)Pt(Cy_2PH)](Pt-Pt)$ (2): An aqueous solution of NaOH (0.7 mL, 0.90 M) was added to a vigorously stirred colourless CH2Cl2 solution (10 mL) of cis-[Pt(PHCy2)2-Cl₂] (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 Na₂SO₄. 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. C₄₈H₉₀OP₄Pt₂ (1197.28): calcd. C 48.15, H 7.58; found C 48.25, H 7.60. LC-MS: exact mass calcd. for C48H90OP4Pt2: 1196.52 amu; found: 1197.5 [M + H]+. M.p. 135 °C (dec.). IR (KBr): \tilde{v}_{max} = 2279 (w, P–H), 2252 (w, P–H), 1024 (s, P=O) cm⁻¹. ¹H NMR (400 MHz, C₆D₆, 295 K): δ = 5.68 [m, ${}^{1}J_{H(2),P(4)} = 310, {}^{2}J_{H(2),Pt(2)} = 53 \text{ Hz}, \text{ H}(2)], 4.85 \text{ [m, } {}^{1}J_{H(1),P(2)} =$ 323, ${}^{2}J_{H(1),Pt(1)} = 112 \text{ Hz}$, H(1)] ppm. ${}^{31}P{}^{1}H{}$ NMR (161 MHz, C_6D_6 , 295 K): $\delta = 134.4$ [sharp ddd, ${}^2J_{P(1),P(2)} = 48$, ${}^2J_{P(1),P(3)} = 229$, ${}^{2}J_{P(1),P(4)} = 54, {}^{1}J_{P(1),Pt(1)} = 4091, {}^{1}J_{P(1),Pt(2)} = 2985 \text{ Hz}, P(1)], 94.6$ [sharp ddd, ${}^{2}J_{P(3),P(1)} = 229, {}^{3}J_{P(3),P(2)} = 29, {}^{2}J_{P(3),P(4)} = 5, {}^{1}J_{P(3),Pt(2)}$ = 3061, ${}^{2}J_{P(3),Pt(1)}$ = 42 Hz, P(3)], 18.5 [broad ddd, ${}^{2}J_{P(4),P(1)}$ = 54, ${}^{3}J_{P(4),P(2)} = 112, {}^{2}J_{P(4),P(3)} = 5, {}^{1}J_{P(4),Pt(2)} = 3682, {}^{2}J_{P(4),Pt(1)} = 83 \text{ Hz},$ P(4)], 15.9 [broad ddd, ${}^{2}J_{P(2),P(1)} = 48$, ${}^{3}J_{P(2),P(3)} = 29$, ${}^{3}J_{P(2),P(4)} = 112$, ${}^{1}J_{P(2),P(1)} = 4230$, ${}^{2}J_{P(2),P(2)} = 107$ Hz, P(2)] ppm. ${}^{195}Pt\{^{1}H\}$ NMR (86 MHz, C₆D₆, 295 K): $\delta = -4798$ [dddd, ¹J_{Pt(1),P(1)} = 4091, ${}^{1}J_{Pt(1),P(2)} = 4230, {}^{2}J_{Pt(1),P(3)} = 42, {}^{2}J_{Pt(1),P(4)} = 83 \text{ Hz}, Pt(1)], -5205$ [ddd, ${}^{1}J_{Pt(2),P(1)} = 2985, {}^{2}J_{Pt(2),P(2)} = 107, {}^{1}J_{Pt(2),P(3)} = 3061,$ ${}^{1}J_{\text{Pt}(2),\text{P}(4)} = 3682 \text{ Hz}, \text{Pt}(2)$] ppm.



trans-Dichlorodi- μ -cyclohexylphosphidobis(dicyclohexylphosphane)platinum(II) (3): A suspension of *cis*-[Pt(PHCy₂)₂Cl₂] (0.564 g, 0.85 mmol), CH₃ONa (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 CH₂Cl₂. Evaporation of the solvent afforded *trans*-[Pt(PHCy₂)(PCy₂)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. C₄₈H₉₀Cl₂P₄Pt₂ (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 C₄₈H₉₀Cl₂P₄Pt₂: 1250.5 amu; found: 1251.5 [M + H]⁺. M.p. >300 °C. IR (nujol mull): $\tilde{v}_{max} = 2337$ (m, P–H), 289 (m, Pt–Cl) cm⁻¹. ¹H NMR (400 MHz, CDCl₃, 295 K): $\delta = 3.9$ (m, ¹J_{H,P} = 322,

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

{(Cy₂PH)Pt(µ-PCy₂)₂Pt[Cy₂(MeO)P]}(Pt-Pt) (4): A solution of CH₃ONa in methanol (1.0 M, 3.2 mL) was added to a vigorously stirred suspension of cis-[Pt(PHCy₂)₂Cl₂] (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. C49H92OP4Pt2 (1211.31): calcd. C 48.59, H 7.66; found C 48.45, H 7.56. LC-MS: exact mass calcd. for C₄₉H₉₂OP₄Pt₂: 1210.54 amu; found: 1211.5 [M + H]⁺. M.p. 150 °C (dec.). IR (KBr): $\tilde{v}_{max} = 2234$ (w, P–H), 1095 (s), 1020 (s, P–O), 809 (s, P–O) cm⁻¹. ¹H NMR (400 MHz, C₆D₆, 295 K): $\delta = 6.36$ $[m, {}^{1}J_{H,P} = 318 \text{ Hz}, \text{ H}(1)], 3.94 \text{ (d, } {}^{3}J_{H,P} = 13 \text{ Hz}, \text{ POC}H_3) \text{ ppm.}$ ³¹P{¹H} NMR (161 MHz, C₆D₆, 295 K): δ = 245.7 [dd, ²J_{P(1),P(3)} = 67, ${}^{2}J_{P(1),P(2)}$ = 55, ${}^{1}J_{P(1),Pt(1)}$ = 2625, ${}^{1}J_{P(1),Pt(2)}$ = 2450 Hz, P(1)], 173.6 [dt, ${}^{3}J_{P(3),P(2)} = 76$, ${}^{2}J_{P(3),P(1)} = 67$, ${}^{1}J_{P(3),Pt(2)} = 5477$ Hz, P(3)], 19.1 [dt, ${}^{3}J_{P(2),P(3)} = 76$, ${}^{2}J_{P(2),P(1)} = 55$, ${}^{1}J_{P(2),Pt(1)} = 4800$, ${}^{2}J_{P(2),Pt(2)}$ = 47 Hz, P(2)] ppm. ¹⁹⁵Pt{¹H} NMR (86 MHz, C₆D₆, 295 K): δ = $-5530 [dt, {}^{1}J_{Pt(1),P(1)} = 2625, {}^{1}J_{Pt(1),P(2)} = 4800, {}^{1}J_{Pt(1),Pt(2)} =$ 337 Hz, Pt(1)], -5570 [dtd, ${}^{1}J_{Pt(2),P(1)} = 2450$, ${}^{2}J_{Pt(2),P(2)} = 47$, ${}^{1}J_{Pt(2),P(3)} = 5477, {}^{1}J_{Pt(2),Pt(1)} = 337 \text{ Hz}, Pt(2)] \text{ ppm.}$



 $\{ [Cy_2(MeO)P]Pt(\mu-PCy_2) \}_2(Pt-Pt)$ (5): A solution of CH₃ONa in methanol (1.0 M, 2.9 mL) was added to a vigorously stirred suspension of cis-[Pt(PHCy₂)₂Cl₂] (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. C₅₀H₉₄O₂P₄Pt₂ (1241.33): calcd. C 48.38, H 7.63; found C 48.48, H 7.65. LC-MS: exact mass calcd. for C₅₀H₉₄O₂P₄Pt₂: 1240.55 amu; found: 1241.5 [M + H]⁺. M.p. 188 °C (dec.). IR (nujol mull): \tilde{v}_{max} = 1259 (m, C–O), 1175 (w), 1103 (m), 1054 (m, P–O) cm⁻¹. ¹H NMR (400 MHz, C₆D₆, 295 K): δ = 3.92 (d, ³J_{H,P} = 13 Hz, CH₃O). ³¹P{¹H} NMR (161 MHz, C₆D₆, 295 K): δ = 245.3 [dd, ${}^{2}J_{P(1),P(2)} = 68$, ${}^{1}J_{P(1),Pt(1)} = 2475$ Hz, P(1)], 171.2 [dd, ${}^{2}J_{P(2),P(1)} =$ 68, ${}^{3}J_{P(2),P(3)} = 81$, ${}^{1}J_{P(2),Pt(1)} = 5468$, ${}^{2}J_{P(2),Pt(2)} = 126$ Hz, P(2)] ppm. ¹⁹⁵Pt{¹H} NMR (86 MHz, C₆D₆, 295 K): $\delta = -5570$ [dtd, ¹J_{Pt(1),P(1)} = 2475, ${}^{1}J_{Pt(1),P(2)}$ = 5468, ${}^{2}J_{Pt(1),P(3)}$ = 64 Hz, Pt(1)] ppm.



 $\{ [Cy_2(EtO)P]Pt(\mu - PCy_2) \}_2(Pt - Pt)$ (7): A solution of EtONa in dry ethanol (1.0 M, 2.5 mL) was added to a vigorously stirred suspension of cis-[Pt(PHCy₂)₂Cl₂] (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. C₅₂H₉₈O₂P₄Pt₂ (1269.38): calcd. C 49.20, H 7.78; found C 49.12, H 7.75. LC-MS: exact mass calcd. for C₅₂H₉₈O₂P₄Pt₂: 1268.58 amu; found: 1269.6 [M + H]⁺. IR (nujol mull): $\tilde{v}_{max} = 1263$ (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, C₆D₆, 295 K): $\delta = 4.39$ (m, ${}^{3}J_{H,H} = 7.1$ Hz, CH₃CH₂O) ppm. ${}^{31}P{}^{1}H{}$ NMR (161 MHz, C₆D₆, 295 K): δ = 244.0 [t, ²J_{P(1),P(2)} = 68, ¹J_{P(1),Pt(1)} = 2481 Hz, P(1)], 167.3 [t, ${}^{2}J_{P(2),P(1)} = 68$, ${}^{3}J_{P(2),P(3)} = 77$, ${}^{1}J_{P(2),P(1)} =$ 5451, ${}^{2}J_{P(2),Pt(2)} = 132 \text{ Hz}, P(2)] \text{ ppm. } {}^{195}\text{Pt}{}^{1}\text{H} \text{ NMR } (86 \text{ MHz},$ C_6D_6 , 295 K): $\delta = -5567$ [dtd, ${}^1J_{Pt(1),P(1)} = 2481$ Hz, ${}^1J_{Pt(1),P(2)} =$ 5451, ${}^{2}J_{\text{Pt}(1),\text{P}(3)} = 132 \text{ Hz}, \text{Pt}(1)$] ppm.



NMR Spectroscopic Features for 8: ¹H NMR (400 MHz, C₆D₆, 295 K): $\delta = 6.23$ [dm, ¹J_{H(1),P(2)} = 318 Hz, P(1)], 4.40 (pseudoquintet, ³J_{H,P} = 7, ³J_{H,H} = 7 Hz, POCH₂CH₃), 1.56 (t, ³J_{H,H} = 7 Hz, POCH₂CH₃) ppm. ³¹P{¹H} NMR (161 MHz, C₆D₆, 295 K): $\delta = 245.4$ [dd, ²J_{P(1),P(3)} = 64, ²J_{P(1),P(2)} = 54, ¹J_{P(1),P(1)} = 2710, ¹J_{P(1),P(2)} = 2461 Hz, P(1)], 169.5 [dt, ³J_{P(3),P(2)} = 77, ²J_{P(3),P(1)} = 64, ¹J_{P(3),P(1)} = 4894, ²J_{P(2),P(2)} = 54 Hz, P(2)] ppm. ¹⁹⁵Pt{¹H} NMR (86 MHz, C₆D₆, 295 K): $\delta = -5524$ [dt, ¹J_{P(1),P(1)} = 2710, ¹J_{P(1),P(2)} = 4894, ¹J_{P(1),P(2)} = 333 Hz, P(1)], -5567 [dtd, ¹J_{P(2),P(1)} = 2461, ²J_{P(2),P(2)} = 54, ¹J_{P(2),P(3)} = 5458, ¹J_{P(2),P(1)} = 337 Hz, P(2)] ppm.



{[Cy₂(PhO)P]Pt(μ -PCy₂)}₂(*Pt*-*Pt*) (9): Sodium phenoxide (0.285 g, 2.46 mmol) was added to a stirred suspension of *cis*-[Pt(PHCy₂)₂-Cl₂] (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. C₆₀H₉₈O₂P₄Pt₂ (1365.47): calcd. C 52.78, H 7.23; found C 52.59, H 7.20. LC-MS: exact mass calcd. for C₆₀H₉₈O₂P₄Pt₂: 1364.58 amu; found: 1365.6 [M + H]⁺. IR (KBr): $\tilde{v}_{max} = 2925$ (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, CD₂Cl₂, 295 K): δ = 7.25–7.02 (10 H, Ph), 2.4–0.7 (88 H, Cy) ppm. ³¹P{¹H} NMR (161 MHz, C₆D₆, 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. ¹⁹⁵Pt{¹H} NMR (86 MHz, CD₂Cl₂, 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 {(Cy₂PH)Pt(μ-PCy₂)₂Pt-[Cy₂(*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, C₆D₆, 295 K): $\delta = 6.38$ [m, ¹J_{H(1),P(2)} = 317 Hz, 2 H, H(1)]; 1.66 (s, 9 H, *t*Bu) ppm. ³¹P{¹H} NMR (161 MHz, C₆D₆, 295 K): $\delta = 235.8$ [dd, ²J_{P(1),P(3)} = 57, ²J_{P(1),P(2)} = 53, ¹J_{P(1),P(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. ¹⁹⁵Pt{¹H} NMR (86 MHz, C₆D₆, 295 K): $\delta = -5492$ [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(PHCy₂)₂(OPh)₂] (11): Sodium phenoxide (0.116 g, 0.999 mmol) was added to a toluene suspension of cis-[Pt(PHCy2)2-Cl₂] (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 CH2Cl2 and precipitated with toluene, affording 98 mg (41%) of pure cis-[Pt(PHCy₂)₂(Cl)(OPh)] (12). The yellow filtrate was evaporated under reduced pressure. The residue was redissolved in 4 mL of dichloromethane and nhexane added, which caused the precipitation of cis-[Pt(PHCy₂)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. C36H56O2P2Pt (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): $\tilde{v}_{max} = 2333$ (m, P–H) cm⁻¹. ¹H NMR (400 MHz, CDCl₃, 295 K): δ = 3.8 (m, ${}^{1}J_{H,P}$ = 367 Hz, PH) ppm. ${}^{31}P{}^{1}H$ NMR (161 MHz, CDCl₃, 295 K): $\delta = 5.6$ (s, ${}^{1}J_{P,Pt} = 3389$ Hz) ppm. ${}^{195}Pt{}^{1}H$ NMR (86 MHz, CDCl₃, 295 K): δ = -4155 (t, ¹J_{P.Pt} = 3389 Hz) ppm.

cis-[Pt(PHCy₂)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): $\tilde{v}_{max} = 2330$, 2345 (m, P–H), 306 (m, Pt–Cl) cm⁻¹. ¹H NMR (400 MHz, CDCl₃, 295 K): $\delta = 3.83$ (m, ¹J_{H,P} = 359, ²J_{H,Pt} = 102 Hz, PH trans Cl), 3.67 (m, ¹J_{H,P} = 352,

 ${}^{2}J_{\text{H,Pt}} = 91 \text{ Hz}, \text{ PH trans OPh) ppm. }{}^{31}\text{P}{}^{1}\text{H} \text{ NMR (161 MHz, CDCl_3, 295 K): } \delta = 8.7 \text{ (d, }{}^{1}J_{\text{P,Pt}} = 3174, \, {}^{2}J_{\text{P,P}} = 14 \text{ Hz}, \text{ P trans OPh}, 15.2 \text{ (d, }{}^{1}J_{\text{P,Pt}} = 3653, \, {}^{2}J_{\text{P,P}} = 14 \text{ Hz}, \text{ P trans Cl} \text{ ppm.}$ ${}^{195}\text{Pt}{}^{1}\text{H} \text{ NMR (86 MHz, CDCl_3, 295 K): } \delta = -4323 \text{ (dd, }{}^{1}J_{\text{P,Pt}} = 3174, \, {}^{1}J_{\text{P,Pt}} = 3653 \text{ Hz} \text{ ppm.}$

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 $0.20 \times 0.11 \times 0.04$ 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				
<i>a</i> [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			
$D_{\text{calcd.}} [\text{Mg}\text{m}^{-3}]$	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 [eÅ ⁻³]	2.55, -1.08 (close to Pt)			
[a] $R = \sum F_{o} - F_{c} / \sum F_{o} $. [b] $wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}$.				

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

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