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A simple and efficient synthesis of bisphosphine platinum(0) complexes with various P–Pt–P angles

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Abstract

Improved syntheses of a series of $[(L)_2Pt(\eta^2\text{-nb})]$ (**4**)–(**8**) (L = PPh_3, 1/2 dpp(*o*-xyl), 1/2 dppb, 1/2 dppbe, 1/2 dppn) complexes are described. Complexes **4**–**8** have been characterized by ^1H, ^{31}P NMR, IR spectroscopy as well as mass spectrometry and elemental analysis. The reaction of $[(dppbe)Pt(Cl_2)]$ with sodium borohydride and tolan was investigated by ^{31}P NMR spectroscopy. The complex $[(dppbe)Pt(\eta^2\text{-tolan})]$ (**11**) has been isolated and characterized. The reactivity of $[(dppn)Pt(\eta^2\text{-nb})]$ with the spirocyclohexyl-1,2,4-trithiolane **12** and the sterically hindered 2,2,4,4-tetramethyl-3-thioxocyclobutanone **13** was tested. The complex $[(dppn)Pt(\eta^2\text{–}\mathbf{13})]$ (**14**) has been isolated and characterized by ^1H, ^{31}P NMR, IR spectroscopy as well as mass spectrometry and elemental analysis. X-ray crystal analyses have been performed on complex **8**, **11** and **14**.

Keywords: Platinum(0) complexes; Olefin complexes; Thioketone complex; Alkyne complex

1. Introduction

$[(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)]$ (**2**) was prepared for the first time by Cook and Jauhal in 1967 [1]. Since this time it has been widely used as starting material: the complex is used for a clean source of the 14 electron metal complex $[(Ph_3P)_2$-Pt(0)] (**3**), which is used to trap unstable molecular species by complexation [2]. The high ligand field stabilization energy results in a high kinetic stability of the formed adducts. The complex fragment with the general formula $(R_3P)_2Pt$ containing the two ^{31}P nucleus and the ^{195}Pt isotope offers the possibility to investigate very easily the products by ^{31}P NMR spectroscopy determining the ^2J(P, P) and ^1J(P, Pt) coupling constants. Also insertion reactions into various bounds especially into sulfur–sulfur bonds have been reported recently [3,4]. The high binding tendency of such complex fragments to sulfur containing species allows the isolation and determination of unstable species [5,6]. The mostly used complex for this experiments is $[(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)]$ (**2**), prepared by the reduction of $[(Ph_3P)_2Pt(II)Cl_2]$ (**1**) with sodium borohydride under an atmosphere of ethene [7] (Scheme 1). Various other reduction agents like sodium amalgam, sodium naphthalene, superhydride, hydrazine have been used successfully for syntheses of analogous derivatives [4,8,9]. Nevertheless sodium borohydride seams to be the best chose for our purposes, it is mild but enough reactive, not highly toxic, nonflammable and moreover, rather cheap.

Here we report on the improved synthesis of $[(Ph_3P)_2Pt(\eta^2\text{-nb})]$ (**4**) (nb = norbornene) [9,10] as well as preparation of complexes $[(L)_2Pt(\eta^2\text{-nb})]$ (**5**)–(**8**) with bisphosphane ligands dppb (1,4-bisdiphenylphosphinobutane), dpp(*o*-xyl) 1,2-bis[(diphenylphospino)methyl]-benzene, dppbe (1,2-bisdiphenylphosphinobenzene) and dppn (1,8-bisdiphenylphosphinonaphthalene).

2. Results and discussion

The displacement of the ethene by norbornene (nb) does not lead to significant changes in the reactivity of the resulting complex **4**. This displacement allows the synthesis

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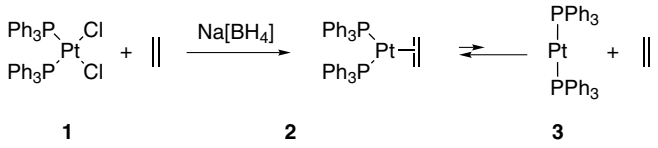
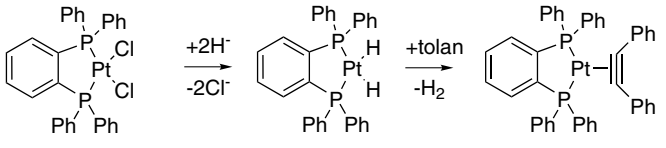


Scheme 1. Synthesis of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**).

of **4** under a standard argon atmosphere. An excess of the olefin is easily achieved by adding the solid nb instead of working under ethene atmosphere. The olefin complexes $[(L)_2Pt(\eta^2\text{-nb})]$ (**4**)–(**8**) are stable in nb containing solution, they are not sensitive against water or bases. The workup can be done by adding water to the reaction mixture followed by extraction with a mixture of THF/diethylether and adding some crystals of nb. Working with nb instead of ethene allows to concentrate the solvent under reduced pressure without decomposition of the complexes. Thus, a better separation from impurities like unreacted $[(Ph_3P)_2Pt(II)Cl_2]$ (**1**) as well as sodium borohydride is possible. The crude products, which are pure enough for further reactions, can be recrystallized from THF/pentane. In the ^{31}P NMR of **4** only one signal with platinum satellites is found at $\delta = 37.5$ with $^1J(P, Pt) = 3550$ Hz, which proves that nb is coordinated exclusive from only one of the two possible sides. In the ^1H NMR spectrum the olefin protons are detected at $\delta = 2.32$ with platinum satellites with a typical $^2J(H, Pt)$ coupling constant of 64 Hz. The latter data agree very well with that reported in the literature [9,10].

As mentioned above, the complex **2** is used as source for 14 electron complex $[(Ph_3P)_2Pt(0)]$ (**3**), which has a linear geometry. A fixation of the P–Pt–P angle by using a bisphosphine ligand leads to a dramatical increase of the reactivity of the resulting 14 electron complex [11,12]. This increase is caused by a decrease of the distance between the HOMO and the LUMO of this complexes. Both orbitals are directed to the binding side of the complex fragment [12]. Keeping these facts in mind a significant change in the reactivity is suspected by displacement of the Ph_3P ligand by bisphosphines with fixed small P–Pt–P angles. Reduction of the platinum(II) complexes $[(L)_2PtCl_2]$ with sodium borohydride in the presents of nb in THF leads to the bisphosphine platinum(0) complexes **5**–**7** (Scheme 2).

The dihydrido complexes $[(L)_2PtH_2]$ can be assumed as intermediate for the reduction [14], in the case of the reduction of complex $[(dppe)PtCl_2]$ (**9**) the formation of such an intermediate was proved by ^{31}P NMR investigations. After reduction in CD_2Cl_2 and decomposition the excess of



Scheme 3. Preparation of tolan complex **11**.

sodium borohydride by washing with water a broad singlet at $\delta = 60.9$ with ^{195}Pt-satellites and $^1J(P, Pt) = 1858$ Hz was observed in the ^{31}P NMR spectrum assignable to the complex $[(dppe)PtH_2]$ (**10**). After adding diphenylacetylene (tolan) complex $[(dppbe)Pt(\eta^2\text{-tolan})]$ (**11**) has been quantitatively formed within 30 min (Scheme 3). Crystals of the slightly red colored complex **11** are yielded by slow diffusion of pentane in a solution of **11** in THF. The result of X-ray structure analysis is presented in Fig. 1. The P–Pt–P angle is 86.56(4)°, the bond lengths are in the same range of those reported for $[(Ph_3P)_2Pt(\eta^2\text{-tolan})]$, the angle C1–C2–C3 with 145.4(3)° is slightly larger than those in $[(Ph_3P)_2Pt(\eta^2\text{-tolan})]$ (140°) [15]. In contrast to the dichloro complexes $[(L)_2PtCl_2]$, the yielded complexes **4**–**8** and **11** are well soluble in CH_2Cl_2, THF or toluene. $[(dppb)Pt(\eta^2\text{-nb})]$ (**5**) and $[(dpp(o\text{-xyl}))Pt(\eta^2\text{-nb})]$ (**6**) are yielded as colorless crystalline compounds whereas [(dppbe)Pt-

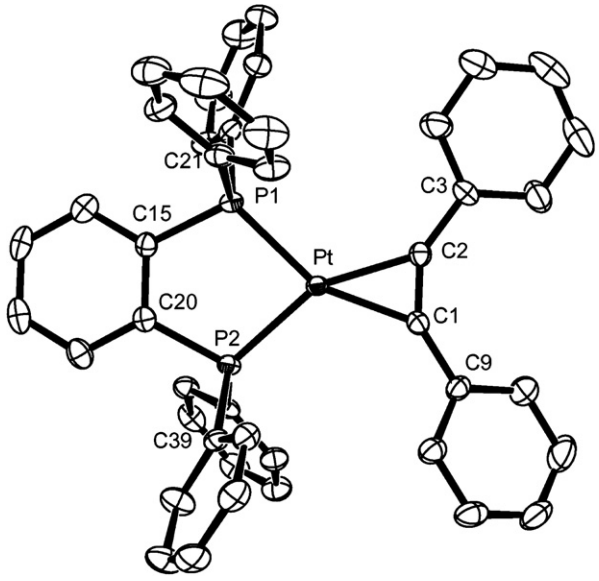
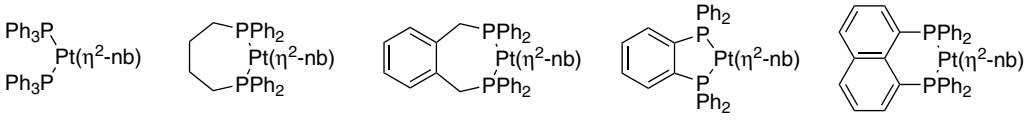


Fig. 1. ORTEP drawing of the molecular structure of complex **11**. Selected bond lengths (Å) and angles (°) : Pt–P(2) 2.2604(10), Pt–P(1) 2.2664(10), Pt–C(1) 2.038(3); Pt–C(6) 2.041(3), C(1)–C(2) 1.301(4), P(2)–Pt–P(1) 86.56(4), C(1)–Pt–C(2) 37.19(12), C(1)–C(2)–C(3) 145.4(3).



Scheme 2. Platinum(0) nb complexes.

(η^2-nb)] (**7**) is a yellow and [(dppn)Pt(η^2-nb)] (**8**) a red colored solid, respectively (see Table 1).

In the series of platinum(0) complexes **5**–**8** there is a trend of the ^1J(P, Pt) coupling constants. The values of this coupling constants decreases with the P–Pt–P bit angle of the phosphine ligand, in the range of 3550 Hz for complex **4** with P–Pt–P of 112°, 3459 Hz for complex **6** with 105° [16] over 3159 Hz for complex **7** with P–Pt–P of round 87° down to 3027 Hz for complex **8**. The small ^1J(P, Pt) coupling constant and the red color of complex **8** suggested a small P–Pt–P angels as found in the red methylene bridged bisphosphine complexes like (dtbpm)Pt(η^2-olefin) with ^1J(P, P) < 3000 Hz and P–Pt–P < 80° [12,13,17].

The result of the X-ray structure analysis for [(dppn)-Pt(η^2-nb)] (**8**) is shown in Fig. 2. The P–Pt–P angle was found to be 88.67(5)° slightly larger then expected from the ^1J(P, Pt) coupling constant. The P–P distance is 3.15 Å, approximately 0.1 Å longer then that reported for the free ligand [18], therefore no additional repulsion energy between the donating atoms has to be surmounted for the coordination of the dppn-ligand to the metal center. The energy, which is necessary for the abstraction of the olefin, increases by decreasing the P–Pt–P angle, therefore the complexes are no efficient source for forming the 14 electron complex fragments [(L)$_2$Pt(0)].

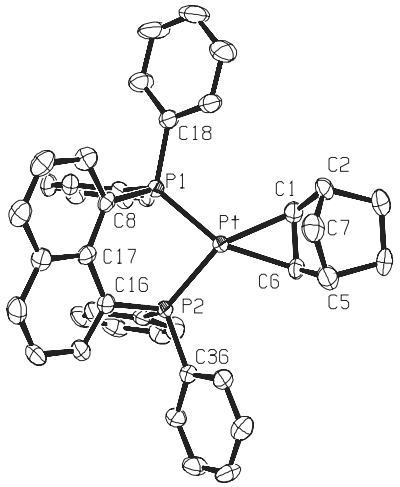
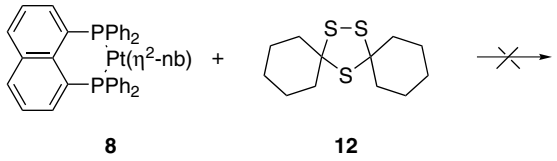


Fig. 2. ORTEP drawing of the molecular structure of complex **8**. Selected bond lengths (Å) and angles (°) : Pt–P(2) 2.2532(14), Pt–P(1) 2.2528(14), Pt–C(1) 2.117(5); Pt–C(6) 2.109(5), C(6)–C(1) 1.469(8), P(2)–Pt–P(1) 88.67(5), C(1)–Pt–C(6) 40.7(2).

In extension of our investigations concerning the reactions of complex **2** with 1,2,4-trithiolanes [5,19], complex **8** was treaded with the spirocyclohexyl-1,2,4-trithiolane **12** in a NMR tube, even after two weeks at room temperature the starting materials were found unreacted side by

Table 1
Crystallographic data for **8**, **11** and **14**

	8	**11**	**14**
Empirical formula	$C_{41}H_{36}P_2Pt \cdot 1.5\ C_4H_8O$	$C_{44}H_{34}P_2Pt$	$C_{42}H_{38}OP_2PtS$
Formula weight (g/mol)	893.88	819.74	847.81
Colour	Red	Orange	Light yellow
Crystal size (mm)	$0.03 \times 0.03 \times 0.02$	$0.04 \times 0.04 \times 0.04$	$0.05 \times 0.05 \times 0.04$
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	11.8301(4)	11.393(2)	13.2547(8)
b (Å)	15.3119(9)	11.505(2)	15.3119(9)
c (Å)	17.0103(9)	14.048(3)	17.0103(9)
α (°)	–	82.34(3)	–
β (°)	92.359(2)	71.74(3)	98.701(4)
γ (°)	–	88.09(3)	–
V (Å^3)	3849.2(2)	1733.0(6)	3412.6(3)
Z	4	2	4
F(000)	1800	812	1688
$\rho_{calcd.}$	1.543	1.571	1.650
μ (Mo Kα) (cm^{-1})	37.66	41.72	43.01
Temperature (°C)	−90	−90	−90
Reflections collected	27139	12175	15140
Absorption correction min/max transmission	Multi-scan 0.8158/0.8755	Multi-scan 0.7515/0.8174	Multi-scan 0.6490/0.7896
Independent reflections (R_{int})	8803 (0.0699)	7852 (0.0250)	7935 (0.0757)
h	−15/14	−14/14	0/17
k	−26/24	−14/14	−20/20
l	−20/20	−18/18	−22/21
Θ range (°)	$2.59 \leqslant \Theta \geqslant 27.50$	$3.08 \leqslant \Theta \geqslant 27.47$	$2.11 \leqslant \Theta \geqslant 27.85$
Completeness to Θ_{max} (%)	99.5	98.9	97.7
Reflections with $F_o > 4\sigma(F_o)$	6250	7084	4622
Number of parameters, restraints	419, 0	424, 0	424, 0
R_1, wR_2 [$F_o > 4\sigma(F_o)$]	0.0437, 0.0934	0.0269, 0.0607	0.0456, 0.0869
R_1, wR_2 (all data)	0.0777, 0.1052	0.0329, 0.0631	0.1028, 0.1051
Goodness-of-fit	1.029	1.026	0.949
Extrema of final difference Fourier synthesis (e/Å^3)	2.259/−2.149	0.877/−1.393	0.961/−2.060



Scheme 4. Attempts for reaction of complex **8** with the 1,2,4-trithiolane derivative **12**.

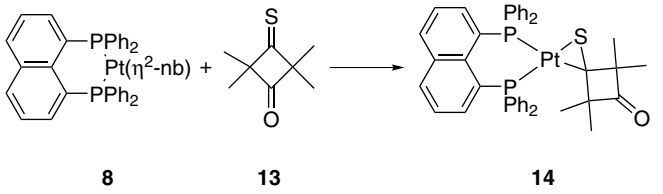
side. The same result was observed after additional heating of this mixture for 3 h at 80 °C (Scheme 4).

This is in contrast to the reaction of the $[(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)]$ (**2**) or $[(Ph_3P)_2Pt(\eta^2\text{-nb})]$ (**4**) with spirocyclohexyl-1,2,4-trithiolane **12** [20] (Scheme 5). The substitution of the nb by another strongly binding olefinic compound is possible via an associative mechanism. The reaction of the sterically hindered 2,2,4,4-tetramethyl-3-thioxocyclobutanon **13** quantitatively leads to a new complex **14** yielded as yellow crystals within two hours at room temperature (Scheme 6).

In the ^{31}P NMR spectrum of **14** an AB spin system was found with $^2J(P, P)$ of 28 Hz and $^1J(P, Pt) = 3972$ Hz and 2472 Hz, respectively. The elemental analysis as well as the found molar peak at $m/z = 847$ confirmed to the formula $C_{42}H_{38}P_2PtS$. The result of the X-ray structure analysis is shown in Fig. 3. The thioketone **13** substituted the nb ligand and is now side on coordinated to the (dppn)Pt complex fragment. The P–Pt–P angle was determined as 87.81(6)° and is comparable with those found in the nb complex **8**. Worth to notice is the high pyramidalization of the thioketone carbon atom. The sum of the angles C2–C1–C4/S1–C1–C2/S1–C1–C4 330° is slightly larger than the sum of the angles in an ideal tetrahedron with 328.5°.

Complex **14** crystallized in the centrosymmetric space group $P2_1/n$ including a racemic mixture of **14**. In the ^1H NMR spectrum only two signals each for two equivalent methyl groups were found, hence the conformation of the complex has to change very fast in terms of the NMR time scale between two diastereoisomers having the platinum atom below and above the plane of the naphthalene rings, respectively.

The above mentioned result indicates that complex **8** shows a significantly reduced reactivity towards 1,2,4-trithiolane **12**, but is still reactive towards the sterically crowded thioketone **13**. This should give us the possibility to trap selectively thiocarbonyl derivatives in the presents of 1,2,4-trithiolanes. This is highly interesting having in mind that 3,3,5,5-teraphenyl-1,2,4-trithiolane splits at



Scheme 6. Preparation of a thioketone complex **14**.

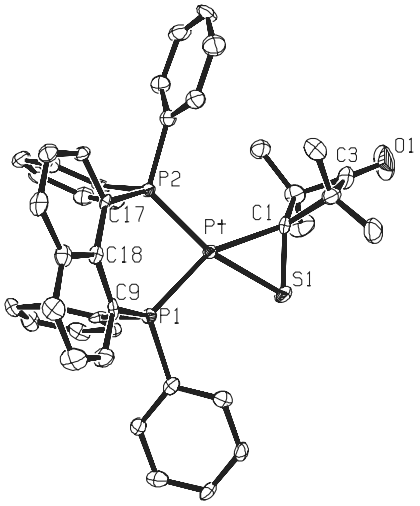


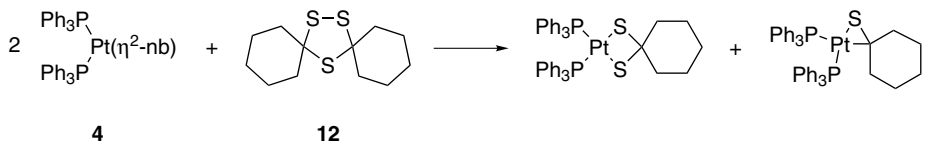
Fig. 3. ORTEP drawing of the molecular structure of complex **14**. Selected bond lengths (Å) and angles (°) : Pt–P(2) 2.2468(15), Pt–P(1) 2.2713(16), Pt–S 2.2784(16), Pt–C(1) 2.134(6), S–C(1) 1.756(7), P(2)–Pt–P(1) 87.81(6), S–Pt–C(1) 46.77(17).

70 °C into the corresponding thioketone and thiosulfine [21], whereas the splitting of alkyl substituted 3,3,5,5-teramethyl-1,2,4-trithiolane is observed at significantly higher temperatures (boiling toluene, 48 h) [22].

In conclusion we succeeded in an improvement of the syntheses of bisphosphine platinum(0) olefin complexes $[(L)_2Pt(\eta^2\text{-olefin})]$. The synthesized complexes especially the complex **7**, **8** and **11**are not very air and moisture sensitive. The reactivity for displacing the olefin by sulfur containing compounds depends on the bisphosphine ligand giving the possibility of tuning the reactivity of such complexes $[(L)_2Pt(\eta^2\text{-nb})]$.

3. Experimental

All reactions were performed under argon, and solvents are of commercial quality. Starting materials **1** [7], other dichlorocomplexes [8,23], **13** [24] and **12** [25] are prepared according to the literature procedure.



Scheme 5. Reaction of complex **4** with **12** [20].

3.1. X-ray measurements

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects and for absorption effects [26,27].

The structures were solved by direct methods (SHELXS [27]) and refined by full-matrix least squares techniques against $|F_o|^2$ (SHELXL-97 [28]). All hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically [28]. XP (SIEMENS Analytical X-ray Instruments Inc.) [28] and Ortep-3 for Windows [29] were used for structure representations.

3.2. Spectroscopic measurements

Melting points were determined with an AXIOLAB microscope with a TMHS 600 heating plate and are uncorrected. ^{1}H (200 MHz), ^{31}P (81 MHz) spectra were determined with or Brucker DPX 200 spectrometers at 25 °C, chemical shifts are referred to the protons of the solvent. All ^{31}P NMR and ^{13}C NMR spectra are proton decoupled. IR spectra were taken with a Perkin–Elmer System 2000 FT-IR spectrometer. Mass spectra were taken with a FINNIGAN MAT SSQ 710 mass spectrometer. Elemental analysis were performed with a LECO CHNS-932.

3.2.1. NMR investigation of synthesis of 11

[(dppbe)Pt(Cl_2)] (**9**) (15 mg, 0.02 mmol) was suspended in a mixture of CD_2Cl_2 (1 mL) and ethanol (0.1 mL). Sodium borohydride (2 mg, 0.05 mmol) was added. After stirring this suspension for 1 h the excess of sodium borohydride was removed by the use of water. The organic layer was separated and ^{31}P NMR spectra was recorded. A broad singlet at $\delta = 60.9$ with ^{195}Pt-satellites and ^1J(P, Pt) = 1858 Hz was observed. After tolan was added to this solution and additional stirring for 30 min, almost quantitatively formation of **11** was observed in ^{31}P NMR spectra.

3.2.2. NMR investigation of reaction of *8* with *12*

In a NMR tube **8** (20 mg, 0.02 mmol) and a excess of **12** (20 mg, 0.075) were dissolved in toluene-d_8 (0.7 mL). After 2 h only signals for **8** were found in the ^{31}P NMR spectra. After storing this probe for 2 weeks at room temperature the same signals were observed. Additional heating this probe at 80 °C for 3 h leaded as well to no significant change of the ^{31}P NMR spectra.

3.3. Synthesis of the [$(L)_2Pt(\eta^2$-nb)] complexes

For the synthesis of the [$(L)_2$Pt(η^2-nb)] complexes **4**–**8** the following procedure was used. Under an argon atmosphere 100–150 mg of the [$(L)_2$Pt(Cl_2)] complex and 250 mg nb were suspended in THF (8 mL) and ethanol (2 mL). Solid sodium borohydride (20 mg) was added and the mixture was stirred at room temperature over night. The reduction is completed when the platinum complex is dissolved in the THF/ethanol solution and only a slight opaqueness (caused by the sodium borohydride) is visible. Adding water (4 mL) and a mixture of ether/THF (for the complexes with small P–Pt–P angle also CH_2Cl_2 can be used) to the reaction mixture resulted in separation of two clear phases. The organic layer was washed with water using a pipette, additional drying of the organic layer is possible by stirring with sodium sulfate for a few minutes. Reducing of solvents to dryness yields the crude products in a yield of 60–80% which are pure enough for further reactions. An additional purification can be achieved by dissolving the crude product in a small volume of nb containing THF. Filtration through celite® (for all complexes except **4** also filtration over a short pad of silica gel is possible) and diffusion of pentane into this solution yields the crystalline compounds of analytical grade.

3.3.1. [$(Ph_3P)_2Pt(\eta^2$-nb)] (*4*)

M.p. 138–143 °C (decomp) (lit.: 140–145 °C [9]). ^{1}H NMR (CD_2Cl_2): δ 7.28 (m, 30H), 2.32 (s with ^{195}Pt-sat., ^2J(H, Pt) = 64.5 Hz, 2H), 2,26 (s, 2H), 1.61-0.73 (m, 5H); 0.18 (d, J(H, H) = 8 Hz). ^{31}P NMR (CD_2Cl_2): δ 37.5 (s with ^{195}Pt-sat., ^1J(P, Pt) = 3550 Hz (lit.: 3550 Hz) [10]). IR (KBr) : ν (cm^{-1}) = 3054(w), 2946(s), 2861(w), 1635(bs), 1479(m), 1434(s), 1095(s), 743(m), 694(s), 517(m). Anal. Calc. for $C_{43}H_{40}P_2Pt$: C, 63.46; H, 4.95. Found: C, 63.53; H, 4.95%.

3.3.2. [(dppb)Pt(η^2-nb)] (*5*)

M.p. 180 °C (decomp). ^{1}H NMR (toluene-d_8): δ 7.55 (m, 8H), 7.00 (m, 12H), 2.68 (m, 3H), 2.51 (s, 2H), 2.28 (m, 4H), 1.60 (m, 4H); 1.28 (m, 4H); 0.41 (d, J(H, H) = 8 Hz, 1H). ^{31}P NMR (toluene-d_8): δ 29.3 (s with ^{195}Pt-sat., ^1J(P, Pt) = 3338 Hz). MS (DEI): $m/z = 619$ (M^+-nb, 100%), 714 (M^+, 3%). Anal. Calc. for $C_{35}H_{38}P_2Pt$: C, 58.74; H, 5.65. Found: C, 58.91; H, 5.35%.

3.3.3. [(dpp(o-xyl))Pt(η^2-nb)] (*6*)

M.p. 158 °C. ^{1}H NMR (toluene-d_8): δ 7.54 (m, 8H), 7.03 (m, 12H), 6.59 (m, 2H), 6.13 (m, 2H), 3.83 (m, 4H, P–CH_2–Ar), 2.67 (s, 2H), 2.42 (s with ^{195}Pt-sat., ^2J(H, Pt) = 62 Hz, 2H), 1.52 (m, 2H), 1.25 (m, 2H), 1.01 (m, 1H), 0.32 (bs, 1H). ^{31}P NMR (toluene-d_8): δ 29.3 (s with ^{195}Pt-sat., ^1J(P, Pt) = 3439 Hz). MS (DEI): $m/z = 66$ (100%), 668 (M^+-nb, 25%), 762 (M^+, 7%). IR (KBr): ν (cm^{-1}) = 3054(w), 2944(s), 2859(w), 1638(bs), 1435(s), 1098(s), 768 (m), 741(s), 695(s), 503(s). Anal. Calc. for $C_{39}H_{38}P_2Pt \cdot 2THF$: C, 62.17; H, 5.99. Found: C, 62.08; H, 6.05%.

3.3.4. [(dppbe)Pt(η^2-nb)] (*7*)

M.p. >250 °C. UV/Vis λ (log(ε)): 304 nm (3.95). ^{1}H NMR (toluene-d_8): δ 7.55 (m, 8H), 6.90 (m, 16H), 3.05 (s with ^{195}Pt-sat., ^2J(H, Pt) = 66 Hz, 2H), 3.02 (s, 2H), 1.75 (m, 2H), 1.01 (m, 2H), 1.42 (m, 2H), 1.2-1.5 (m, 3H),

0.55 (d, J(H, H) = 8 Hz, 1H). ^{31}P NMR (toluene-d_8): δ 58.1 (s with ^{195}Pt-sat., ^{1}J(P, Pt) = 3159 Hz). MS (DEI): m/z = 640 (M^+-nb, 100%), 735 (M^+, 15%). IR (KBr): ν (cm^{-1}) = 3053(w), 2942(s), 2860(w), 1637(bs), 1435(s), 1119(s), 1100(s), 745(m), 694(s), 568(s), 539(m), 523(m), 506(m). Anal. Calc. for $C_{37}H_{34}P_2Pt$: C, 60.41; H, 4.66. Found: C, 60.11; H, 4.69%.

3.3.5. [(dppn)Pt(η^2-nb)] (**8**)

M.p. 156–160 °C. UV/Vis λ (log(ε)): 298 (4.2), 445 nm (2.95). ^{1}H NMR (toluene-d_8): δ 7.51 (m, 2H), 7.41 (m, 2H), 7.30 (m, 8H), 6.88 (m, 12H), 2.97 (s, 2H), 2,83 (s with ^{195}Pt-sat., ^{2}J(H, Pt) = 64 Hz, 2H), 1.77 (m, 2H), 1.59 (m, 1H), 1.42 (m, 2H), 0.61 (d, J(H, H) = 8 Hz, 1H). ^{31}P NMR (toluene-d_8): δ 25.3 (s with ^{195}Pt-sat., ^{1}J(P, Pt) = 3027 Hz). MS (DEI): m/z = 690 (M^+-nb, 100%), 784 (M^+, 40%). IR (KBr): ν (cm^{-1}) = 3052(w), 2942(s), 2858(w), 1630(bs), 1434(s), 1118(s), 1095(s), 771(m), 744(m), 693(s), 529(m), 517(m), 492(m). Anal. Calc. for $C_{41}H_{36}P_2Pt \cdot 1.5THF$: C, 63.15; H, 5.41. Found: C, 62.98; H, 5.38%.

3.4. Synthesis of tolan and thioketone complexes

3.4.1. Synthesis of [(dppbe)Pt(η^2-tolan)] (**11**)

[(dppbe)Pt(Cl_2)] (**9**) (70 mg, 0.1 mmol) was suspended in a mixture of CH_2Cl_2 (5 mL) and ethanol (1 mL). Sodium borohydride (10 mg, 0.26 mmol) was added, the suspension was stirred until an almost clear solution was formed. Water (5 mL) was added to this mixture and the organic layer was separated. To this solution tolan (35 mg, 0.2 mmol) was added. After stirring for 2 h the solution was reduced to dryness, recrystallization of the crude product from THF/pentane yielded **11** (60 mg, 0.07 mmol, 70%) as light orange crystals.

M.p. >235 °C (decomp). ^{1}H NMR (benzene-d_6): δ 7.94 (d, ^{3}J(H, H) = 7.2 Hz, 4H, *o*-H tolan), 7.76 (m, 8H), 7.64 (q, J(H, H) = 3.5 Hz, 2H), 7.11 (dd, ^{3}J(H, H) = 7.4 Hz, ^{3}J(H, H) = 7.2 Hz, 4H, *m*-H tolan), 6.99 (t, ^{3}J(H, H) = 7.4 Hz, 2H, *p*-H tolan), 6.93 (m, 14H). ^{31}P NMR (toluene-d_8): δ 51.7 (s with ^{195}Pt-sat., ^{1}J(P, Pt) = 3102 Hz). MS (DEI): m/z = 641 (M^+-tolan, 100%), 820 (M^+, 20%). Anal. Calc. for $C_{44}H_{34}P_2Pt$: C, 64.47; H, 4.18. Found: C, 64.63; H, 4.10%.

3.4.2. Syntheses of thioketone complex [(dppn)Pt(η^2-13)] (**14**)

Complex **8** (70 mg, 0.08 mmol) and **13** (25 mg, 0.16 mmol) were dissolved in toluene (10 mL). After 30 min almost complete formation of **14** was detected. Reducing the solution to dryness and recrystallization from THF/pentane yielded the **14** (43 mg, 0.05 mmol, 60%) as yellow crystalline solid.

M.p. 263 °C (decomp). ^{1}H NMR ($CDCl_3$): δ 8.05 (m, 2H), 7.79 (m, 1H), 7.48-6.99 (m, 23H), 1.20 (s with ^{195}Pt-sat., ^{4}J(H, Pt) = 5.5 Hz, 6H, CH_3), 0.71 (s, 6H, CH_3). ^{31}P NMR ($CDCl_3$): δ [11.7 (d with ^{195}Pt-sat., ^{1}J(P, Pt) = 3972 Hz) and 9.5 (d with ^{195}Pt-sat., ^{1}J(P, Pt) = 2472 Hz) ^{2}J(P, P) = 28 Hz]. MS (DEI): m/z = 42 (100%), 776 (M^+–Me_2=C=O, 30%), 818 (M^+–(CO), 1.5%), 847 (M^+, 1%). IR (KBr): ν (cm^{-1}) = 1752(s, C=O), 589(m), 524(m), 521(m), 500(m). Anal. Calc. for $C_{42}H_{38}OP_2PtS$: C, 59.50; H, 4.52; S, 3.78. Found: C, 59.11; H, 4.57; S, 3.46%.

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Appendix A. Supplementary material

CCDC 624774, 624775 and 624776 contain the supplementary crystallographic data for **8**, **11** and **14**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.11.051.

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