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Synthesis of Platinum(II) Phoshine Isocyanide Complexes and Study of Their Stability in Isomerization and Ligand Disproportionation Reactions

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Abstract—Phosphine isocyanide complexes *cis*-[$PtCl_2$(CNMes)(P)] with mesitylisocyanide and phoshine ligands were synthesized in yields of 92–98%. The products were characterized by mass spectrometry, IR and ^{1}H NMR, COSY, NOESY, HSQC, and HMBC spectroscopy, and X-ray diffraction analysis. The solid-state and solution structures of the complexes and their stability in isomerization and ligand disproportionation reactions were studied.

Keywords: platinum complexes, isocyanides, phosphines

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Isocyanide ligands in platinum metal complexes (metal oxidation stated 1–3) exhibit strong σ-donor and weak π-acceptor properties [1], due to which such compounds are used to success in crystal engineering [2–5], as catalysts in important organic processes [6–10], and in design of luminescent materials [8, 11–14]. Furthermore, isocyanide complexes serve as precursors in the synthesis of N-heterocyclic [15–20] and acyclic aminocarbene complexes [1, 2, 15, 21–26] (M-NHC and M-ADC, respectively). Of particular interest are mixed-ligand complexes containing, along with the isocyanide ligands, additional auxiliary neutral ligands, such as phosphines: appealing such approach, one can finely adapt the electronic and steric characteristics to target parameters [11, 21, 27]. In particular, Vicenzi et al. [9] proposed a catalytic system including platinum(II) chloride isocyanide phosphine complex for the hydroarylation eaction.

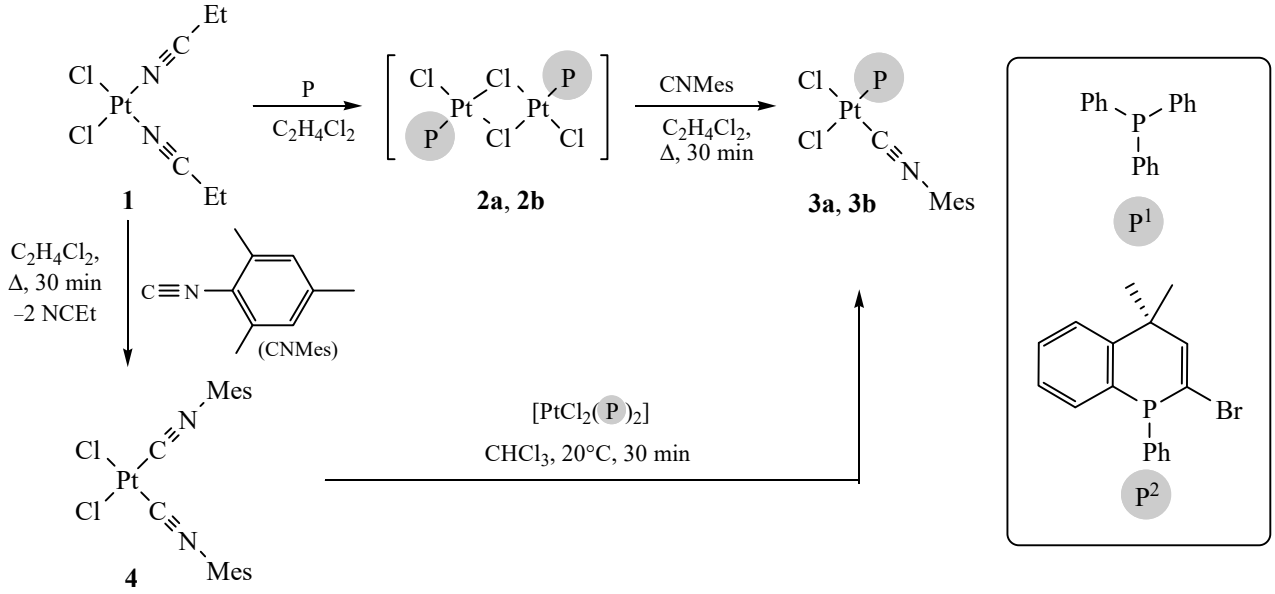
At the same time, compounds like [$PtCl_2$(isocyanide)(phoshine)] have been mentioned in as little as a few works [9, 27–32], and only some of them have reported complete characterization of such compounds, including crystal structure assessment. Analyzing the Cambridge Crystallographic Data Base (CCDC, Version CSD 5.39), we identified two platinum(II) chloride isocyanide phoshine *cis*-[$PtCl_2$(CNR)(PPh_2(CH_2PPh_2–$Fe(CO)_4$)] (R = Cy, CH_2Ts) [33]. The geometry of such complexes in solution (the *cis*- and *trans*-isocyanide complexes differently behave with respect to N-nucleophiles [34]), as well as the possibility of disproportionation into the bisphosphine and bisisocyanide complexes are still to be studied.

In the present communication we report the synthesis of platinum(II) chloride isocyanide phoshine complexes *cis*-[$PtCl_2$(CNMes)(P)] [P = P^1 (**2**), P^2 (**3**)] with the methylisocyanide (CNMes) and phosphine [triphenylphoshie (P^1) and 2-bromo-1,4-dihydro-4,4-dimethyl-1-phenylphosphinoline (P^2)] ligands, their complete structure assessment in solution (correlation NMR spectra: ^{1}H–^{1}H COSY, ^{1}H–^{1}H NOESY, ^{1}H–^{13}C HSQC, and ^{1}H–^{13}C HMBC) and in the solid state (XRD analysis), as well as their stability in the isomerization and ligand disproportionation reactions.

Adding an equimolar amount of phosphine P^1 or P^2 to a solution of *cis*-[$PtCl_2$($NCEt)_2$] in 1,2-dichloroethane forms a poorly soluble chlorine-bridged dimer **2a** or **2b**, which dissolves when isocyanide is added. After the reaction mixture had been refluxed for 30 min, mixed-ligand isocyanide phoshine complexes [$PtCl_2$(CNMes)(P)] [P = P^1 (**3a**), P^2 (**3b**)] were isolated in good yields (92–98%) as single products (Scheme 1).

Complexes **4**, **3a**, and **3b** were isolated as colorless fine crystals and characterized by mass spectrometry and IR and NMR spectroscopy (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{195}Pt, ^{1}H–^{1}H COSY, ^{1}H–^{1}H NOESY, ^{1}H–^{13}C HSQC,

Scheme 1.



P = P^1 (**a**), P^2 (**b**).

and ^1H–^{13}C HMBC). The solid-state structure of the complexes was additionally confirmed by XRD analysis.

The mass spectra of complexes **4**, **3a,** and **3b** contain peaks corresponding to the $[M + Na]^+$ ions and fragment $[M - Cl]^+$ ions. The peak display characteristic isotope distributions, which implies the presence of platinum and chlorine in the ions and is consistent with the proposed structures. The IR spectrum of platinum(II) bismesitylisocyanide complex **4** displays two partially overlapping strong absorption bands peaking in the region of 2200 cm^{-1}, assignable to stretching vibrations of the C≡N bonds and providing evidence showing that complex **4** has a *cis* geometry. At the same time, mixed-ligand isocyanide phosphine complexes **3a** and **3b** give only one ν(C≡N) band peaking in the region of 2190 cm^{-1}.

The ^1H NMR spectra of complexes **4**, **3a**, and **3b** show sets of proton signals of the mesitylisocyanide ligands: two singlets of the *ortho*- and *para*-CH_3 groups in the mesityl rings at 2.10–2.20 ppm, as well as the *meta*-CH singlet at 6.85–7.00 ppm. The two multiplets at 7.40–7.80 ppm in the ^1H NMR spectrum of compound **3a** correspond to triphenylphosphine phenyl protons. The ^1H NMR spectrum of complex **3b** with the 2-bromo-1,4-dihydro-4,4-dimethyl-1-phenylphosphinoline ligandoм has a more complicated pattern. The signals in this spectrum could be assigned by means of ^1H–^1H COSY NMR spectroscopy. In the ^1H–^1H COSY NMR spectrum we could identify two separate spin systems associated with the phenyl and 2-bromo-1,4-dihydro-4,4-dimethylphosphinoline fragments (Fig. 1).

The ^1H–^1H NOESY NMR spectra of complexes **3a** and **3b** allowed us to establish their steric structure in solution. In both cases, the NOESY spectra show cross-peaks between the *ortho*-methyl substituents in the mesityl rings and the CH protons in the phosphine ligands (Fig. 2). The observation of the nuclear Overhauser effect (NOE) between these two ligands suggests their proximate arrangement and, therefore, complexes **3a** and **3b** has a *cis* geometry in solution.

The coordination of isocyanide to platinum shifts the ^{13}C NMR signal of the terminal carbon atom far downfield (the δ_C in CNMes is 166.9 ppm [35], whereas the δ_C for complex **4** is 122.9 ppm), which is characteristic for such isocyanide complexes [36–38]. The $^{31}P\{^1H\}$ NMR spectra of complexes **4**, **3a,** and **3b** display only single signals at –9.1 (**3b**) and 9.3 ppm (**3a**), suggesting that these complexes exist in only one form in solution.

The platinum signal in the ^{195}Pt NMR spectrum of complex **4** is observed at –3755 ppm and has a splitting characteristic for isocyanide complexes on two nuclei ^{14}N in two isocyanideligands ($^2J_{NPt}$ = ~110 Hz). The replacement of one isocyanide ligand in complex **4** by phosphine ligand P^1 or P^2 produces downfield shifting of the platinum signal [–4067 (**3a**)

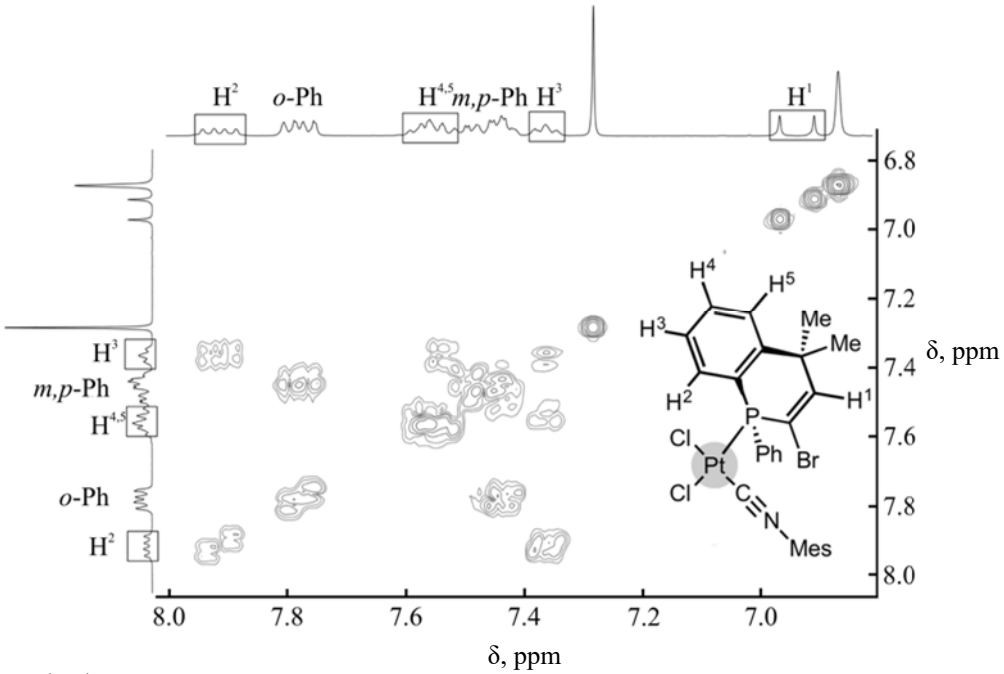


Fig. 1. Fragment $^{1}H–^{1}H$ COSY spectrum of complex **3b** with signal assignment in the 2-bromo-1,4-dihydro-4,4-dimethyl-1-phenylphosphinoline ligand.

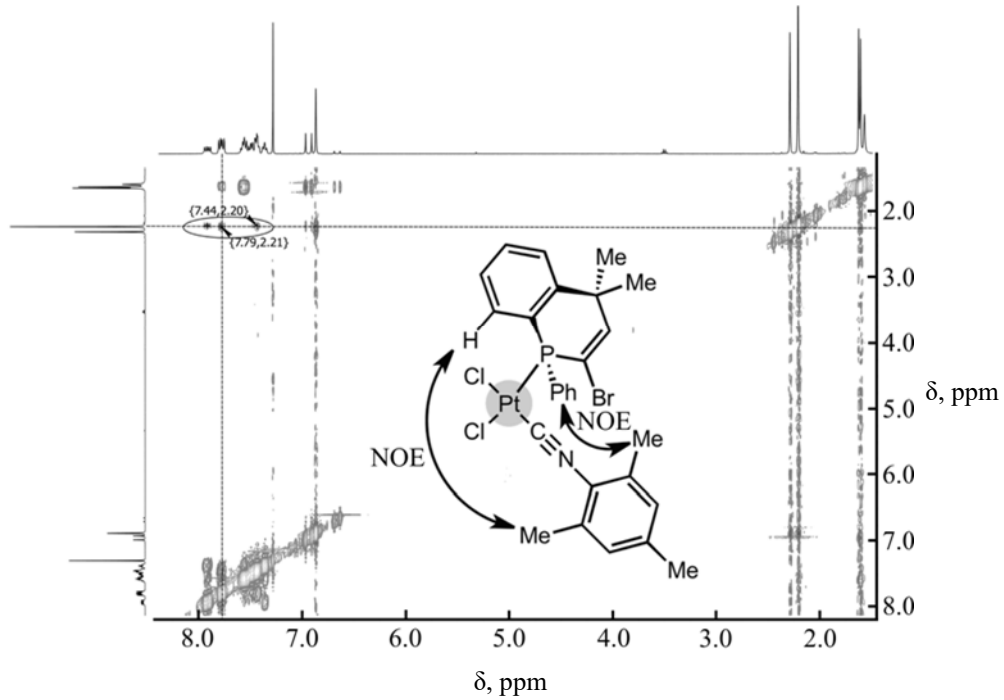


Fig. 2. $^{1}H–^{1}H$ NOESY spectrum of complex **3b** with indicated cross-peaks between protons of the mesitylisocyanide and 2-bromo-1,4-dihydro-4,4-dimethyl-1-phenylphosphinoline ligands.

and –4047 ppm (**3b**)] and additional splitting of the signal due to spin–spin coupling with ^{31}P [$^{1}J_{PPt}$ = 3382 (**3a**) and 3525 Hz (**3b**)].

The solid-state structure of complexes **4**, **3a**, and **3b** was established by XRD analysis (Figs. 3–5). The principal bond lengths and angles in the complexes are listed in the table.

According to the XRD data, the crystal structure of complex **4**·$C_2H_4Cl_2$ comprises the organometallic complexes $C_{20}H_{22}Cl_2N_2Pt$ and $C_2H_4Cl_2$ molecules in a

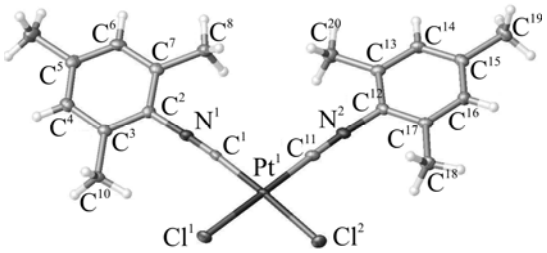


Fig. 3. General view of a molecule of the complex *cis*-$[PtCl_2(CNMes)_2]\cdot C_2H_4Cl_2$ (**4**·$C_2H_4Cl_2$). The solvent molecule is not shown.

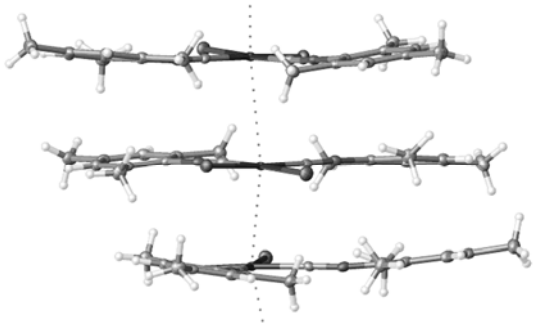


Fig. 4. Metallophilic Pt···Pt contacts in the crystal structures of *cis*-$[PtCl_2(CNMes)_2]\cdot C_2H_4Cl_2$. The solvent molecule is not shown.

1 : 1 ratio. The crystallographically independent part of the structure is represented by two such complexes (the atom numbering in the complexes is the same, but the second one is labeled "A") and two $C_2H_4Cl_2$ molecules. The metal center in the complex has a slightly distorted square-planar structure with the isocyanide groups *cis* to each other (Fig. 3). The C–N–C–Pt fragments are almost linear. The C≡N bond lengths in both isocyanide fragments are similar to those in other isocyanide complexes [1, 36, 39]. Even being cocrystalllized with a molecule of dichloro-ethane, the *cis*-$[PtCl_2(CNMes)_2]$ complex has a crystal packing similar to that of the previously described complex *cis*-$[PdCl_2(CNMes)_2]$ [35]. Like with its palladium analog, the *cis*-$[PtCl_2(CNMes)_2]$ molecules form zigzag chains due to Pt···Pt metallophilic interactions (Fig. 4). Therewith, the distances between the metal centers are alternating [4.0103(4) and 3.3946(4) Å], and the Pt···Pt···Pt angle is 139.448(13)°. A similar packing with short Pt···Pt contacts was reported for isocyanide platinum complexes with other aromatic substituents *cis*-$[PtCl_2(CNR)_2]$ (R = Ph, *p*-Tol, 2,6-$Me_2C_6H_3$, *p*-FC_6H_4, *p*-$CF_3C_6H_4$, *p*-$CH_3OC_6H_4$) [39].

Complexes **3a** and **3b**, both in the solid state and in solution) exist in the *cis* form (Fig. 5). The replacement of the isocyanide by phosphine ligand results in a slight elongation of the platinum–carbon bond and a distortion of the linear shape of the mesitylisocyanide ligand. This is associated with two unidirectional factors: a stronger electron-donor effect of the phosphine ligand compared to isocyanide [40] and a larger steric bulk of phosphine ligands P^1 and P^2 compared to isocyanide. The same reason explains why the Pt–P bonds in **3a** and **3b** are slightly shorter than their bisphosphine precursors **5a** and **5b**. Unlike complex **4**, in complexes **3a** and **3b** no Pt···Pt metallophilic interactions take place.

The fact that the ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{195}Pt\{^1H\}$ spectra of solutions of compounds **3a** and **3b** in $CDCl_3$ contain only single sets of signals suggests the presence of only one isomer in the solution. Using correlation NMR spectroscopy, we found that compounds **3a** and **3b** have *cis* configuration. The *cis* geometry of solid complexes **3a** and **3b** was established by IR spectroscopy and XRD analysis.

Prolong heating of solutions of compounds **2a** and **2b** in $CDCl_3$ (50°C, 20 days) produces no visible changes in the ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra, implying a lack of *cis*/*trans* isomeriza-

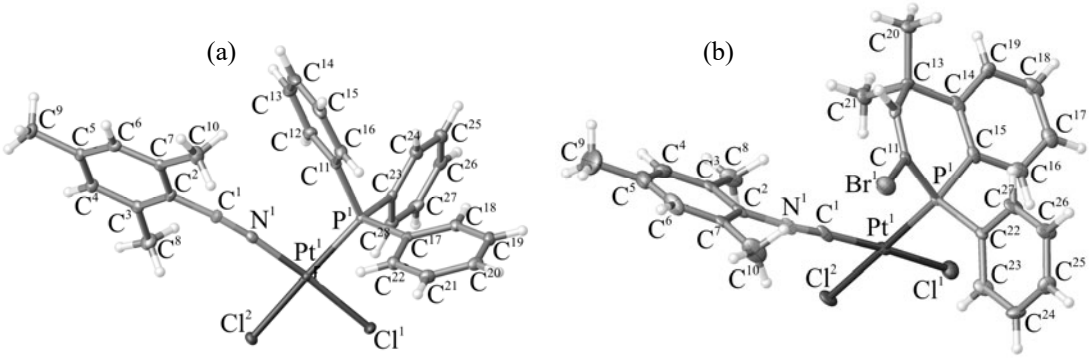


Fig. 5. General view of molecules of complexes (a) **3a** and (b) **3b** in crystal.

Selected bond lengths (Å) and angles (deg) in complexes **2**–**6**

Complex	*d*(Pt–C)	*d*(Pt–P)	*d*(C≡N)	∠Pt–C≡N	∠C≡N–C
2 [41]	–	2.318(1)	–	–	–
3 [42]	–	2.3131(7)	–	–	–
4	1.903(3)	–	1.149(4)	176.4(2)	175.6(2)
	1.925(3)	–	1.141(4)	176.5(3)	175.4(3)
5	1.908(2)	2.2577(7)	1.160(3)	174.8(2)	172.0(3)
6	1.936(1)	2.247(3)	1.333(15)	174.6(10)	165.0(11)

tion characteristic for Pt(II) chloride bisphosphine complexes [42]. Furthermore, such stability suggests a lack of ligand disproportionation, which was previously observed in the platinum(II) chloride isocyanide phosphine complex *cis*-[$PdCl_2$(CNXyl)(PPh_3)] (according to [37], there is an equilibrium between *cis*-[$PdCl_2$(CNXyl)$_2$] and *trans*-[$PdCl_2$(PPh_3)$_2$] in solution).

Thus, to obtain evidence for the thermodynamic nature of mixed-ligand platinum(II) chloride isocyanide phosphine complexes, we synthesized a previously unknown complex *cis*-[$PtCl_2$(CNMes)$_2$] **4** and studied its reaction with bisphosphine complexes *cis*-[$PtCl_2$(P)$_2$]. Note that the modification of the published method [43, 44] of synthesis of bisisocyanide complexes by the replacement of chloroform by 1,2-dichloroethane allowed us to shorten the reaction time to 30 min and synthesize the complex with the preparative yield of 93%. The reaction of equimolar amounts of bisisocyanide complex **4** and the corresponding bisphosphine complex **5a** or **5b** in $CDCl_3$ occurs at room temperature within 30 min to form exclusively complex **3a** or **3b**. Thus, mixed-ligand platinum(II) chloride isocyanide phosphine complexes *cis*-[$PtCl_2$(CNMes)(P)] **3a** and **3b** are resistant to both *cis*/*trans* isomerization and to ligand disproportionation. We found that both in solution and in the solid state, platinum(II) chloride isocyanide phosphine complexes exist exclusively in the *cis* configuration. It was shown that the platinum(II) complexes are resistant to ligand disproportionation and can be synthesized from an equimolar mixture of platinum(II) chloride bisisocyanide and bisphosphine complexes. This differentiated these complexes from analogous palladium(II) complexes with an aromatic isocyanide ligand *cis*-[$PdCl_2$(CNXyl)(PPh_3)], which exist in solution in equilibrium with *cis*-[$PdCl_2$(CNXyl)$_2$] and *trans*-[$PdCl_2$(PPh_3)$_2$] [37].

EXPERIMENTAL

The starting materials and solvents purchased from Aldrich were used as received, except for 1,2-dichloroethane which was distilled over P_2O_5. The mass spectra were measured on a Bruker micrOTOF instrument with electrospray ionization, solvent methanol. The specified *m*/*z* values relate to the most abundant isotopologs. The IR spectra were measured on a Shimadzu FTIR 8400S (4000–400 cm^{-1}) for KBr pellets. The ^1H, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra were obtained on a Bruker Avance II+ spectrometer [400.13 (^1H), 100.61 (^{13}C), 86 MHz (^{195}Pt)] at room temperature, solvent $CDCl_3$.

Complexes *trans*-[$PtCl_2$(P)$_2$] [P^1 = triphenylphosphine (**5a**), P^2 = 2-bromo-1,4-dihydro-4,4-dimethyl-1-phenylphosphinoline (**5b**)] were synthesized by the procedure described in [42].

Synthesis of the complex *cis*-[$PtCl_2$(NCEt)$_2$] (1). To a solution of 1 g of $K_2[PtCl_4]$ in 5 mL of water we added 1 mL of EtCN. The vessel was tightly closed and left to stand at room temperature in sun light-proof conditions. After 7 days, a small hole was made in the lid to let unreacted EtCN to slowly evaporate (≈3 days). Yellow crystals formed and were filtered off, washed with water (50 mL) and Et_2O (2×20 mL), dissolved in CH_2Cl_2 (10 mL), cdried with anhydrous Na_2SO_4, and passed through a bed of silica (1 cm) in a short column, after which the solvent was removed under reduced ressure. Yield 87%. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.44 t (6H, $2CH_3$, ^2J = 7.7), 2.87 q (2H, $2CH_2$, ^2J = 7.6).

Synthesis of the complex *cis*-[$PtCl_2$(CNMes)$_2$] (4). Solid CNMes, 0.77 g (5.32 mmol), was added to a suspension of 1.0 g (2.66 mmol) of $PtCl_2$(NCEt)$_2$ in 50 mL of $C_2H_4Cl_2$. The reaction mixture was refluxed

with stirring for 30 min and then allowed to cooled down to room temperature, the solvent was reduced to 2 mL, and then diluted with Et_2O (10 mL). The precipitate that formed was separated by centrifuging, washed with Et_2O (2×10 mL), and dried in air. Yield 93%. The analytic sample for XRD analysis was prepared by gas diffusion of Et_2O into a solution of the complex in $C_2H_4Cl_2$ at 20°C. IR spectrum, ν, cm^{-1}: 2951, 2918 m (C–H), 2193 s (N≡C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.33 s (6H, CH_3, Mes), 2.43 s (12H, CH_3, Mes), 6.97 s (4H, CH, *m*-Mes). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 18.5 (4C, CH_3), 21.4 (2C, CH_3), 116.6 (2C, CN), 122.9 (2C, C^1), 129.0 (4C, C^3H), 135.7 (4C, C^2), 141.2 (2C, C^4). $^{195}Pt\{^1H\}$ NMR spectrum: δ_{Pt} –3755 ppm. Mass spectrum, *m*/*z*: 579.3802 $[M + Na]^+$ (calculated for $C_{20}H_{22}N_2Cl_2PtNa^+$: 579.3813).

Synthesis of complexes *cis*-[$PtCl_2$(CNMes)P] [P = P^1 (3a), P^2 (3b)]. To a solution of 100 mg (0.27 mmol) $PtCl_2(NCEt)_2$ в 20 mL $C_2H_4Cl_2$ we added in succession 0.27 mmol of phosphine (70 mg of P^1 or 89 mg of P^2) and 39 mg (0.27 mmol) of CNMes, and the reaction mixture was heated under reflux for 0.5 h, and then let to cool down to room temperature, reduced to 2 mL, and diluted with Et_2O (10 mL). The precipitate that formed was separated by centrifugation, washed with Et_2O (2×10 mL), and dried in air.

Complex *cis*-[$PtCl_2$(CNMes)PPh_3] (3b). Yield 98%. IR spectrum, ν, cm^{-1}: 2953, 2920 m (C–H), 2193 s (N≡C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.96 s (6H, CH_3, Mes), 2.24 s (3H, CH_3, Mes), 6.77 s (2H, CH, *m*-Mes), 7.36–7.49 m (9H, CH, *m,p*-Ph), 7.68–7.76 m (6H, CH, *o*-Ph). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm (*J*, Hz): 18.3 (2C, CH_3, Mes), 21.4 (1C, CH_3, Mes), 123.6 (2C, C^1, Mes), 128.6 d (3C, C^1, Ph, $^1J_{CP}$ = 65.9), 128.7 (2C, C^3H, Mes), 128.75 d (6C, C^2H, Ph, $^2J_{CP}$ = 10.8), 131.89 d (3C, C^4H, Ph, $^4J_{CP}$ = 2.8), 134.65 d (6C, C^3H, Ph, $^3J_{CP}$ = 11.8), 135.3 (2C, C^2, Mes), 140.3 (C^4, Mes); the isocyanide carbon signal could not be detected. $^{31}P\{^1H\}$ NMR spectrum: δ_P 9.3 ppm. $^{195}Pt\{^1H\}$ NMR spectrum, δ_{Pt}, ppm (*J*, Hz): –4067 d ($^1J_{PPt}$ = 3382). Mass spectrum, *m*/*z*: 638.1119 $[M - Cl]^+$ (calculated for (3H, CH_3, P^2), 1.60 s (3H, CH_3, P^2), 2.19 s (6H, CH_3, Mes), 2.27 s (3H, CH_3, Mes), 6.85 s (2H, CH, *m*-Mes), 6.92 d (1H, CH, H^1, P^2, $^3J_{PH}$ = 23.3), 7.34 m (1H, CH, H^3, P^2), 7.38–7.48 m (3H, CH, *m,p*-Ph), 7.49–7.58 m (2H, CH, $H^{4,5}$, P^2), 7.71–7.81 m (2H, CH, *o*-Ph, P^2), 7.89 d.d (1H, CH, H^2, P^2, $^3J_{PH}$ = 14.9, $^3J_{HH}$ = 7.6). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 18.6 (2C, CH_3, Mes), 21.4 (1C, CH_3, Mes), 124.0 (2C, C^1, Mes), 32.1 (CH_3, P^2), 31.5 (CH_3, P^2), 43.0 [$C(CH_3)_2$, P^2], 108.8 (P^2), 122.2 (CP, P^2), 126.8 (CH^4, P^2), 127.5 (CH^3, P^2), 128.81 (2C, C^3H, Ph, P^2), 129.0 (2C, C^2H, Mes), 132.2 (C^1P, Ph, P^2), 132.4 (C^4H, Ph, P^2), 134.2 (2C, C^2H, Ph, P^2), 135.0 (CH^2, P^2), 135.8 (2C, C^2, Mes), 140.5 (C^4, Mes), 146.82 (CBr, P^2), 154.4 (CH^1, P^2); the isocyanide carbon signal could not be detected. $^{31}P\{^1H\}$ NMR spectrum: δ_P –9.1 ppm. $^{195}Pt\{^1H\}$ NMR spectrum, δ_{Pt}, ppm (*J*, Hz): –4047 d.t ($^1J_{PPt}$ = 3525, $^2J_{NPt}$ = 105.7). Mass spectrum, *m*/*z*: 706.0358 $[M - Cl]^+$ (calculated for $C_{27}H_{27}BrClNPPt^+$: 706.0358), 765.9940 $[M + Na]^+$ (calculated for $C_{27}H_{27}BrCl_2NPPt\ Na^+$: 765.9961).

X-ray diffraction analysis. The crystal for XRD analysis fixed in a MicroLoop holder was placed into a SuperNova single crystal diffractometer equipped with a CCD-type detector for reflected X-rays and a micro-focus X-ray source. All measurements were performed at 100 K using monochromatized CuK_α radiation. The unit cell parameters were refined by least-squared minimization on no less than 8600 reflexes with 2θ ranging from 7° to 144°. The structures were solved by the Charge Flipping and Intrinsic Phasing methods using Superflip [45, 46] and ShelXT [47], respectively, and refined with ShelXL refinement package [48] incorporated in OLEX2 [49]. In structure **6**, PLATON [50] revealed and included binary twinning along (001)[104] with rotation relative to the second-order axis and the component ratio of 63 : 37. Absorption was included using CrysAlisPro [51] by means of spherical harmonics implemented in the SCALE3 ABSPACK algorithm. Hydrogen atoms were included in the refinement in calculated positions with fixed positional and thermal parameters. The crystal data were deposited at the Cambridge Crystallographic Data center (CCDC 1824479, 1555200, 1836190).

Complex 4. $C_{22}H_{26}Cl_4N_2Pt$, *M* 655.34, monoclinic syngony, space group $P2_1/c$, *a* 16.25605(13), *b* 21.59732(16), *c* 3.89845(12) Å, β 98.3785(8), *V* 4827.49(7) $Å^3$, *Z* 8, d_{calc} 1.803 g/cm^3, μ 15.031 mm^{-1}, 9562 unique reflections with $I > 2\sigma(I)$, $R_1(|F_o| \geq 4\sigma_F)$/$R_1$ (all data) = 0.0273/0.0298, wR_2 ($|F_o| \geq 4\sigma_F$)/wR_2 (all data) = 0.0716/0.0740, *S* 1.062, ρ_{min}/ρ_{max} = 1.52/–1.00 *e*/$Å^3$. CCDC 1555200.

Complex 3a. $C_{29}H_{27}Cl_5NPPt$, *M* 792.82, triclinic syngony, space group $P\bar{1}$, *a* 11.2740(3), *b* 11.2998(2), *c* 13.1126(3) Å, α 85.475(2)°, β 67.315(2)°, γ 76.473(2)°, *V* 1498.36(6) $Å^3$, *Z* 2, d_{calc} 1.757 g/cm^3, μ 13.518 mm^{-1}, 5815 unique reflections with $I > 2\sigma(I)$, R_1 ($|F_o| \geq 4\sigma_F$)/R_1 (all data) = 0.0189/0.0195, wR_2

($|F_o| \geq 4\sigma_F$)/wR_2 (all data) = 0.0451/0.0455, S 1.056, ρ_{min}/ρ_{max} = 0.85/–0.86 e/Å^3. CCDC 1836190.

Complex 3b. $C_{27}H_{27}BrCl_2NPPt$, M 742.36, monoclinic syngony, space group $P2_1/n$, a 8.6554(3), b 9.6211(3), c 31.7247(9) Å, β 93.830(3), V 2635.93(13) Å^3, Z 4, d_{calc} 1.871 g/cm^3, μ 14.291 mm^{-1}, 5159 unique reflections with $I > 2\sigma(I)$, $R_1(|F_o| \geq 4\sigma_F)/R_1$ (all data) = 0.0535/0.0572, wR_2 ($|F_o| \geq 4\sigma_F$)/wR_2 (all data) = 0.1401/0.1418, S 1.170, ρ_{min}/ρ_{max} = 1.62/–1.85 e/Å^3. CCDC 1824479.

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