Supplementary information

Table S1. Crystal data, data collection, and structure refinement parameters for **1**.

Complex	**1**
Formula	$C_{28}H_{28}ClN_2PPt$
Molecular weight	724.93
Crystal dimension, mm	0.26×0.18× 0.10
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	10.0799(4)
b, Å	9.1672(4)
c, Å	30.428(1)
α, deg.	90
β, deg.	93.080(1)
γ, deg.	90
V, Å^3	2807.6(2)
Z	4
d_{calc}, g cm^{-3}	1.715
θ_{max}, deg.	28.0
μ, cm^{-1}	53.60
Transmission, T_{min}/T_{max}	0.411/0.616
No. unique refls (R_{int})	6724 (0.0264)
No. obs. refls ($I>2\sigma(I)$)	5559
R_1 (on *F* for obs. refls)[a]	0.0363
wR_2 (on F^2 for all refls)[b]	0.0681
GOF	1.079

[a] $R_1 = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$

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

Preparation of Q[$PtCl_3(NCNMe_2)$] (Q = Me_4N, Et_4N). QCl (0.025 mmol) was added to a solution of [$PtCl_2(NCNR_2)_2$] (81 mg, 0.02 mmol) in $MeNO_2$ (0.5 mL) and the reaction mixture was refluxed. After 7 min it was cooled to RT and the complex formed was precipitated with toluene (ca. 10 mL). In each case, the precipitate was washed with Et_2O (two 2 mL-portions). Yields were 79 mg, 89% (Q = Me_4N), 68 mg, 68% (Q = Et_4N).

(NMe_4)[$PtCl_3(NCNMe_2)$] (**5**). Anal. Calcd for $C_{28}H_{28}N_2Cl_3PPt$: C, 20.31; H, 4.47; N, 9.62%. Found: C, 20.80; H, 4.95; N, 9.27%. HRESI$^-$-MS, *m/z*: 370.9265 [$PtCl_3(NCNMe_2)]^-$ [370.9196 calcd.]. IR spectrum in KBr, selected bands, cm^{-1}: 2293 s *ν*(C≡N). ^{1}H NMR in $(CD_3)_2CO$, *δ*: 2.97 (s, 6*H*, $NCNCH_3$), 3.48 (s, 12*H*, NCH_3). $^{13}C\{^1H\}$ NMR was not recorded because of the poor solubility of **5** in the most common deuterated solvents.

(NEt_4)[$PtCl_3(NCNMe_2)$] (**6**). Anal. Calcd for $C_{11}H_{26}N_3Cl_3Pt$: C, 26.33; H, 5.22; N, 8.37%. Found: C, 26.83; H, 5.38; N, 8.42%. HRESI$^+$-MS, *m/z*: 130.1604 $[NEt_4]^+$ [130.1596 calcd.]. HRESI$^-$-MS, *m/z*: 370.9260 $[PtCl_3(NCNMe_2)]^-$ [370.9196 calcd.]. IR spectrum in KBr, selected bands, cm^{-1}: 2297 s *ν*(C≡N). ^{1}H NMR in CD_2Cl_2, *δ*: 1.43 (t, $^3J_{HH}$ 7.5 Hz, 12*H*, CH_3 from Et), 2.98 (s, 5.4*H*, NCH_3), 3.51 (q, $^3J_{HH}$ 7.5 Hz, 8*H*, NCH_2). $^{13}C\{^1H\}$ NMR in CD_2Cl_2, *δ*: 8.1 (CH_3 from Et), 40.2 (NCH_3), 53.3 (NCH_2); the NCN carbon was not detected.

(Et_4N)[$PtCl_3${N(CH_2Ph)=C(H)Ph}] (**15**). Anal. Calcd for $C_{22}H_{33}N_2Cl_3Pt$: C, 42.14; H, 5.31; N, 4.47%. Found: C, 42.55; H, 4.85; N, 4.26%. HRESI$^+$-MS, *m/z*: 130.1584 $[NEt_4]^+$ [130.1596 calcd.]. HRESI$^-$-MS, *m/z*: 495.9759 [$PtCl_3${N(CH_2Ph)=CHPh}]$^-$ [495.9713 calcd.]. ^{1}H NMR in $CDCl_3$, *δ*: 1.38 (t, $^3J_{HH}$ 7.5 Hz, 12*H*, CH_3 from Et), 5.33 and 5.41 (E and Z signals could not be discriminated by ^{1}H,^{1}H-NOESY NMR method, E/Z ratio = 1:1, s+s, br, 2*H*, NCH_2), 7.29–7.72 (m, 10*H*, Ph), 9.31 and 9.32 (s+s, 1*H*, N=CH).

Due to a low solubility of **5** in the most common organic solvents, compound **14** was only detected by NMR experiment and was not isolated from the reaction mixture.

Identification of the products of nucleophilic addition of $HON(CH_2Ph)_2$ to uncoordinated NCR (R = NMe_2, **20**; R = Ph, **21**; R = CH_2Ph, **22**; NEt_2, **23**; NC_5H_{10}, **24**; NC_4H_8O, **25**). **$NHC(NMe_2)ON(CH_2Ph)_2$** (**20**). ESI$^+$-MS, *m/z*: 266 $[M - OH]^+$ [266 calcd.], 306 $[M + Na]^+$ [306 calcd.]. ^{1}H NMR in C_6D_6, *δ*: 2.43 (s, 6*H*,

NMe), 3.67 (s, 4*H*, NCH_2). **$NHC(Ph)ON(CH_2Ph)_2$** (**21**). ESI^+-MS, *m/z*: 339 $[M + Na]^+$ [339 calcd.]. ^1H NMR in C_6D_6, δ: 4.59 (s, 4*H*, NCH_2), 8,36 and 8,39 (s+s, 1*H*, NH). **$NHC(CH_2Ph)ON(CH_2Ph)_2$** (**22**). ESI^+-MS, *m/z*: 331 $[M + H]^+$ [331 calcd.], 353 $[M + Na]^+$ [353 calcd.]. ^1H NMR in C_6D_6, δ: 3.23 (s, 2*H*, CCH_2), 4.70 (s, 4*H*, NCH_2), 8.39 (s, 1*H*, NH).

$NHC(NEt_2)ON(CH_2Ph)_2$ (**23**). ESI^+-MS, *m/z*: 312 $[M + H]^+$ [312 calcd.], 334 $[M + Na]^+$ [334 calcd.]. ^1H NMR in C_6D_6, δ: 0.89 (t, $^3J_{HH}$ 7.1 Hz, 6*H*, Me), 2.96 (q, $^3J_{HH}$ 7.1 Hz, 4*H*, CH_2 from Et), 4.70 (s, 4*H*, $ONCH_2$), 4.99 (s, br, 1*H*, NH), 6.9–7.9 (2m, 20*H*, Ph).

$NHC(NC_5H_{10})ON(CH_2Ph)_2$ (**24**). ESI^+-MS, *m/z*: 324 $[M + H]^+$ [324 calcd.], 346 $[M + Na]^+$ [346 calcd.]. ^1H NMR in C_6D_6, δ: 2.43 (s, 6*H*, NMe), 3.67 (s, 4*H*, NCH_2). δ: 1.18–1.26 (m, 6*H*, β-CH_2 and γ-CH_2), 3.00–3.08 (m, 4*H*, α-CH_2), 3.85 (s, 4*H*, $ONCH_2$), 4.61 (s, br, 1*H*, NH), 7.10–7.50 and 7.83–7.89 (2m, 20*H*, Ph).

$NHC(NC_4H_8O)ON(CH_2Ph)_2$ (**25**). ESI^+-MS, *m/z*: 326 $[M + H]^+$ [326 calcd.], 348 $[M + Na]^+$ [348 calcd.]. ^1H NMR in C_6D_6, δ: δ: 2.41 (t, $^3J_{HH}$ 4.8 Hz, 4*H*, NCH_2 from NC_4H_8O), 3.04 (t, $^3J_{HH}$ 4.8 Hz, 4*H*, OCH_2), 3.87 (s, 4*H*, $ONCH_2$), 4.74 (s, br, 1*H*, NH), 7.15–7.50 and 7.84–7.90 (2m, 20*H*, Ph).