Proton NMR Data

Proton NMR data (δ in ppm) in acetone-d_6 for indole-3-acetamide: N(1)H 10.32 br s; C(2)H 7.28 s; C(4)H 7.59 d; C(5)H 7.01 t; C(6)H 7.08 t; C(7)H 7.38 d; C(8)H 3.60 s; amide NH_2 6.63 br s and 6.30 br s. For *N*-(3-indolylacetyl)-L-alanine: N(1)H 10.10 br s; C(2)H 7.40 s; C(4)H 7.60 d; C(5)H 7.02 t; C(6)H 7.10 t; C(7)H 7.48 d; C(8)H 3.66 s; amide NH 7.22 br s; CH 4.52 q; CH_3 1.45 d. For *N*-(3-indolylacetyl)-L-phenylalanine: N(1)H 10.15 br s; C(2)H 7.27 s; C(4)H 7.47 d; C(5)H 7.03 t; C(6)H 7.18 t; C(7)H 7.34 d; C(8)H 3.80 s; amide NH 7.35 br s; CH 4.82 m; CH_2 3.14 m; phenyl 7.40 m and 7.10 m. For *N*-(3-indolylacetyl)-L-valine: N(1)H 10.15 br s; C(2)H 7.50 s; C(4)H 7.60 d; C(5)H 7.03 t; C(6)H 7.15 t; C(7)H 7.45 d; C(8)H 3.93 s and 3.91 s; amide NH 7.20 br s; CH 4.46 d; CH 2.10; CH_3 0.94 m. For *N*-(3-indolylacetyl)-L-leucine: N(1)H 10.13 br s; C(2)H 7.50 s; C(4)H 7.58 d; C(5)H 7.03 t; C(6)H 7.14 t; C(7)H 7.44 d; C(8)H 3.89 s and 3.88 s; amide NH 7.30 br s; CH 4.55 m; CH 1.70 m; CH_2 1.60 m; CH_3 0.89 br t. For *N*-(3-indolylacetyl)-L-isoleucine: N(1)H 10.15 br s; C(2)H 7.50 s; C(4)H 7.59 d; C(5)H 7.03 t; C(6)H 7.15 t; C(7)H 7.45 d; C(8)H 3.89 s and 3.88 s; amide NH 7.15 br s; CH 4.49 d; CH 1.80 m; CH_2 1.40 m; CH_3 0.80 m. For *N*-(3-indolylacetyl)-L-aspartic acid: N(1)H 10.15 br s; C(2)H 7.50 s; C(4)H 7.59 d; C(5)H 7.03 t; C(6)H 7.14 t; C(7)H 7.43 d; C(8)H 3.87 s; amide NH 7.50 br s; CH 4.88 m; CH_2 2.91 m. Proton NMR data (δ in ppm) in acetone-d_6 for indole-3-acetic acid: N(1)H 10.32 br s; C(2)H 7.30 s; C(4)H 7.58 d; C(5)H 7.01 t; C(6)H 7.09 t; C(7)H 7.39 d; C(8)H 3.73 s. For indole-3-propionic acid: N(1)H 10.32 br s; C(2)H 7.13 s; C(4)H 7.55 d; C(5)H 6.98 t; C(6)H 7.07 t; C(7)H 7.36 d; C(8)H 3.02 t; CH_2 2.66 t. For indole-3-acetic acid ethyl ester: N(1)H 10.32 br s; C(2)H 7.27 s; C(4)H 7.54 d; C(5)H 7.00 t; C(6)H 7.08 t; C(7)H 7.38 d; C(8)H 3.71 s; CH_2 4.08 q; CH_3 1.16 t. For tryptophol: N(1)H 9.95 br s; C(2)H 7.15 s; C(4)H 7.55 d; C(5)H 6.98 t; C(6)H 7.07 t; C(7)H 7.35 d; C(8)H 3.80 m; CH_2 2.98 t. Carbon-13 chemical shifts (in ppm) in acetone-d_6 for indole-3-acetamide: C(2) 124.5; C(3) 110.0; C(4a) 128.2; C(4) 119.5; C(5) 119.5; C(6) 122.0; C(7) 112.0; C(7a) 137.3; C(8) 33.5; C=O 174.0. For *N*-(3-indolylacetyl)-L-alanine: C(2) 124.8; C(3) 109.5; C(4a) 128.3; C(4) 119.5; C(5) 119.6; C(6) 122.0; C(7) 112.0; C(7a) 137.5; C(8) 33.5; C=O 172.0; CH 58.0; CH_3 18.0; COOH 174.1

Table S1. Proton Chemical Shifts (ppm) for the Products of the Reactions in Eq 3, of Various Indole Derivatives with *cis*-$[Pt(en)(sol)_2]^{2+}$ Complex. Atoms are numbered as in **1**.

indole derivative	structure	N(1)H	C(2)H	C(4)H	C(5)H	C(6)H	C(7)H	$C(8)H_2$	amide-NH	other
indole-3-acetamide	**3**	10.80 br	8.55 s	8.12 d	7.44 t	7.37 t	7.58 d	4.70 d, 3.52 d	9.15 s, 8.90 s	-
N-(3-indolylacetyl)-L-alanine	**6**	11.12 br, 11.05 br	8.58 s, 8.38 s	8.15 d, 8.11 d	7.45 t	7.37 t	7.57 d	3.60 d, 3.55 d, 4.72 d, 4.62 d	9.65 br, 9.85 br	4.60 q, 1.50 d, 1.48 d,
N-(3-indolylacetyl)-L-leucine	**6**	11.12 br, 11.06 br	8.50 s, 8.38 s	8.14 d, 8.10 d	7.45 t	7.38 t	7.59 d	4.78 d, 4.66 d, 3.64 d, 3.59 d	9.92 br, 9.70 br	4.60 m, 0.92 m, 1.65 m, 1.60 m
N-(3-indolylacetyl)-L-isoleucine	**6**	11.11 br, 11.08 br	8.50 s, 8.43 s	8.13 br dd,	7.45 t	7.37 t	7.58 d	4.80 d, 4.67 d, 3.70 d, 3.65 d	9.75 br, 9.53 br	4.62 d, 4.58 d, 1.40 m, 1.10 m, 0.80 m
N-(3-indolylacetyl)-L-valine	**6**	11.10 br, 11.05 br	8.50 s, 8.44 s	8.13 br dd	7.45 t	7.37 t	7.61 d	4.81 d, 4.68 d, 3.72 d, 3.65 d	9.75 br, 9.50 br	4.58 d, 4.54 d, 2.10 m, 0.99 m
N-(3-indolylacetyl)-L-phenylalanine	**6**	11.1 br	8.42 s, 7.80 s	8.08 d, 8.06 d	7.42 t	7.38 t	7.56 d	4.65 d, 4.60 d, 3.62 d, 3.52 d	9.90 br, 9.80 br	4.94 m, 3.32 m, 3.12 m, 7.18 m, 7.15 m
N-(3-indolylacetyl)-DL-aspartic acid	**6**	11.10 br	8.50 s, 8.47 s	8.16 d, 8.11 d	7.47 t	7.38 t	7.59 d	4.73 d, 4.69 d, 3.70 d, 3.66 d	9.90 br, 9.60 br	4.97 m, 3.30 m

Table S2. Carbon-13 Chemical Shifts (ppm) for the Products of the Reactions in Eq 3, of Various Indole Derivatives with *cis*-$[Pt(en)(sol)_2]^{2+}$ Complex. Atoms are numbered as in **1**.

indole derivative	structure	C(2)	C(3)	C(4a)	C(4)	C(5)	C(6)	C(7)	C(7a)	C(8)	C=O	CH	CH_3	COOH
indole-3-acetamide	**3**	119.0	72.0	133.0	122.5	129.0	123.5	114.5	141.0	35.0	192.0	-	-	-
N-(3-indolylacetyl)-L-alanine	**6**	120.0, 118.0	71.5	132.0	122 br	128.5	123.5	114.0	140.0	37.0 34.0	188	50.0	16.0, 18.0	173.0

Table S3. Temperature Dependence of ^{195}Pt Chemical Shifts

complex	$\Delta\delta$, ppm/K
$K_2[PtCl_4]$[a]	0.97 ± 0.02
cis-$[Pt(en)(sol)_2](ClO_4)_2$[b]	1.2 ± 0.2
cis-$[Pt(en)(indole\text{-}3\text{-}acetamide)](ClO_4)_2$[b]	0.29 ± 0.10

[a] In a 1.0 M solution of NaCl in D_2O.

[b] In acetone-d_6.

Table S4. Platinum-195 Chemical Shifts[a] at 296 K

complex	δ, ppm
$K_2[PtCl_4]$	-1628
$Pt(acac)_2$	-408
$[Pt(en)(O^3\text{-}HAsc)_2]$[b]	-1780
$[Pt(en)(O^2,O^3\text{-}Asc)]$[b]	-1712
$[Pt(en)(C^2,O^5\text{-}Asc)]$[b]	-2634
$[Pt(en)(C^2\text{-}HAsc)(O^3\text{-}HAsc)]$[b]	-2663
$[Pt(NH_2CH_2C(O)NR)_2]$[c]	-2483
cis-$[Pt(en)(sol)_2](ClO_4)_2$[d]	-1890
cis-$[Pt(en)(\text{indole-3-acetamide})](ClO_4)_2$ **(3)**[d]	-2332
cis-$[Pt(en)(N\text{-(3-indolylacetyl)-L-alanine})](ClO_4)_2$ **(6)**[d]	-2340

[a] External reference was a saturated solution of $K_2[PtCl_4]$ in a 1.0 M solution of NaCl in D_2O.

[b] Ascorbate complexes, from ref. 52.

[c] From ref. 53. Coordinated atoms are highlighted.

[d] In acetone-d_6.

Table S5. Molecular Masses and the Observed Molecular Peaks in Electrospray Mass Spectra of the Products of the Reaction between *cis*-$[Pt(en)(sol)_2]^{2+}$ or *cis*-$[Pd(dtco)(sol)_2]^{2+}$and Indole-3-acetamide or Its Amino-Acid Derivatives

product	structure	mass	m/z
cis-[Pt(en)(indole-3-acetamide)]$^{2+}$	**3**	429.3	429.0
cis-[Pt(en)(*N*-(3-indolylacetyl)-L-alanine)]$^{2+}$	**6**	501.4	500.4
cis-[Pt(en)(*N*-(3-indolylacetyl)-L-valine)]$^{2+}$	**6**	529.4	528.3
cis-[Pt(en)(*N*-(3-indolylacetyl)-L-leucine)]$^{2+}$	**6**	543.5	542.5
cis-[Pt(en)(*N*-(3-indolylacetyl)-L-isoleucine)]$^{2+}$	**6**	543.5	542.5
cis-[Pt(en)(*N*-(3-indolylacetyl)-DL-aspartic acid)]$^{2+}$	**6**	545.4	544.4
cis-[Pt(en)(*N*-(3-indolylacetyl)-L-phenylalanine)]$^{2+}$	**6**	577.4	576.4
cis-[Pd(dtco)(indole-3-acetamide)]$^{2+}$	**3**[a]	428.8	427.3

[a] Bidentate ligand is dtco.

Table S6. Proton Chemical Shifts (ppm) for the Three Products of Indole-3-acetamide Coordination to the Three Palladium(II) Complexes.[a] Atoms are numbered as in **1**

complex	N(1)H	C(2)H	C(4)H	C(5)H	C(6)H	C(7)H	$C(8)H_2$	Amide-NH
cis-$[Pd(en)(sol)_2]^{2+}$	11.50 br	9.05 br	8.15 d	7.48 t	7.38 t	7.58 d	4.75 br, 3.55 br	9.07 s, 8.63 s
cis-$[Pd(dtco)(sol)_2]^{2+}$	12.01 br	8.73 s	8.11 d	7.51 t	7.39 t	7.76 d	4.30 s, 3.35 br	9.06 br, 9.55 br
cis-$[Pd(Me_4en)(sol)_2]^{2+}$	10.40 br	7.40 s	7.56 d	7.12 t	7.05 t	7.45 d	4.0 br	9.15 s, 9.05s, 8.88 s, 8.68 s

[a] In acetone-d_6 at 296 K.

Table S7. Carbon-13 Chemical Shifts (ppm) for the Three Products of Indole-3-acetamide Coordination to the Three Palladium(II) Complexes.[a] Atoms are numbered as in **1**

complex	C(2)	C(3)	C(4a)	C(4)	C(5)	C(6)	C(7)	C(7a)	C(8)	C=O
cis-$[Pd(en)(sol)_2]^{2+}$	120.2	69.0 br	132.0	123.4	127.0	123.5	117.0	140.0	34.5	188.0
cis-$[Pd(dtco)(sol)_2]^{2+}$	120.1	69.8	131.5	121.2	129.0	123.5	117.0	140.7	35.0	187.0
cis-$[Pd(Me_4en)(sol)_2]^{2+}$	124.5	107.5	128.0	119.0	120.5	121.9	117.5	137.5	33.5	184.0 183.0

[a] In acetone-d_6 at 296 K

 9

Figure Captions

Figure S1. Dependence on the gradient strength of absolute integrated intensities of the ^{1}H NMR resonances of indole-3-acetamide (●) and of complex **3** (■)in acetone-d_6 at 271 K.

Figure S2. ^{1}H-^{13}C HMQC spectrum of complex **3**. The solvent was acetone-d_6, the temperature was 296 K, and the concentration of **3** was 0.10 M.

Figure S3. Diastereomers RS (**6a**) and SS (**6b**) of $[Pt(en)(N\text{-}(3\text{-indolylacetyl})\text{-L-alanine})]^{2+}$ complex. The structures was calculated by molecular mechanics (CHARMM) and optimized by quantum-mechanics (density-functional theory, program package ADF). Hydrogen atoms are omitted for clarity.

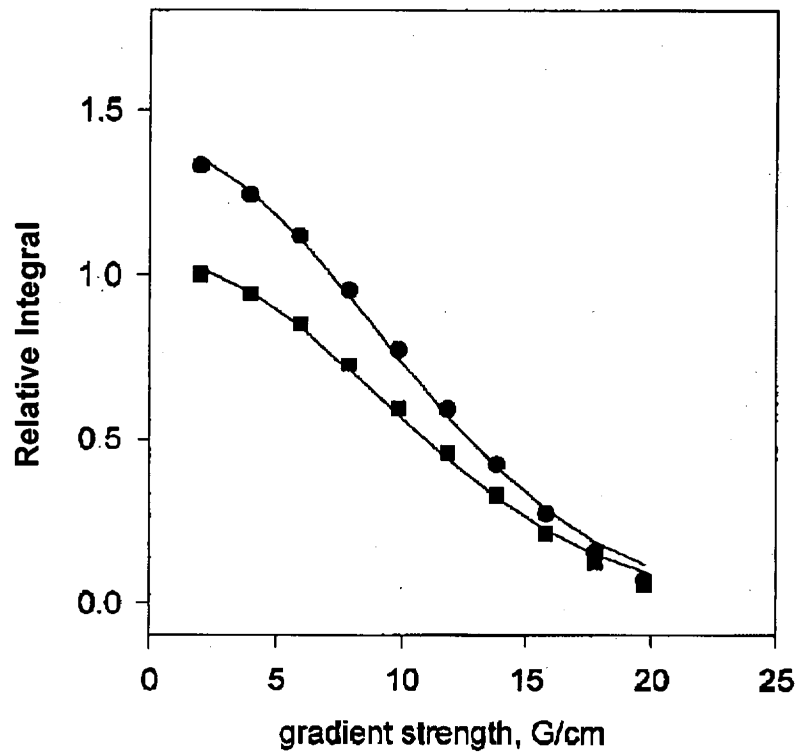


Figure S1. Dependence on the gradient strength of absolute integrated intensities of the ^1H NMR resonances of indole-3-acetamide (●) and of complex **3** (■)in acetone-d_6 at 271 K.

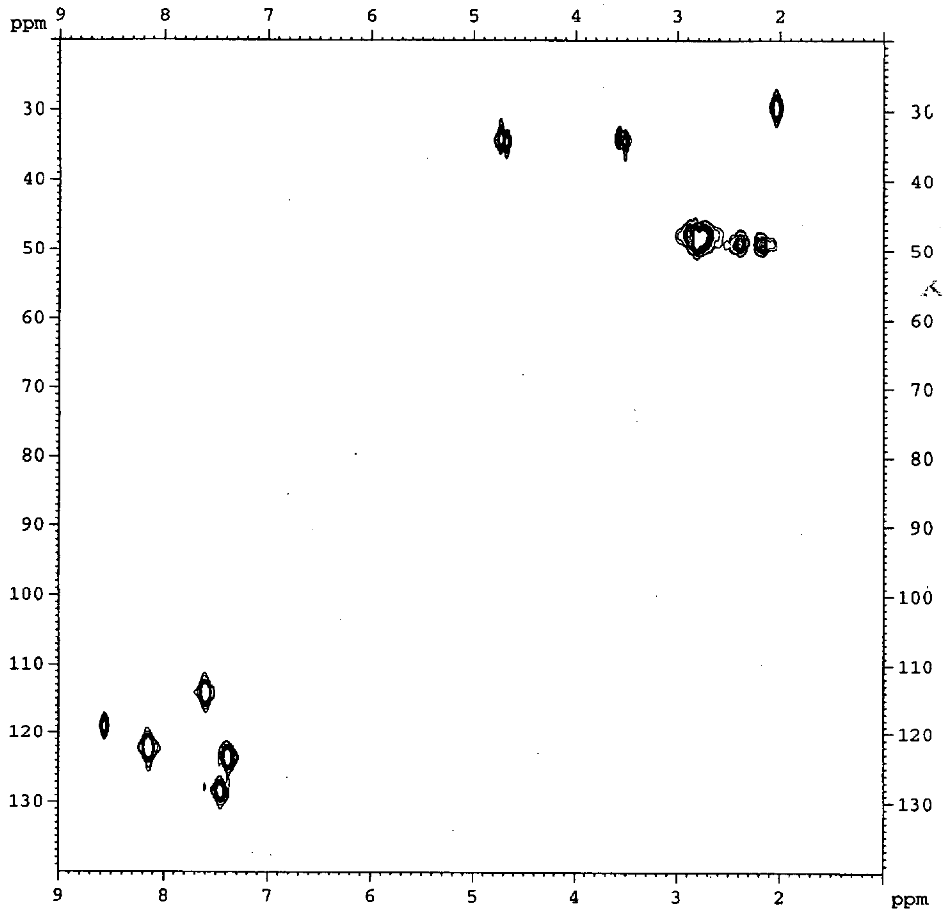
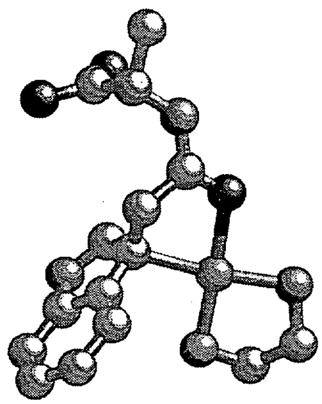
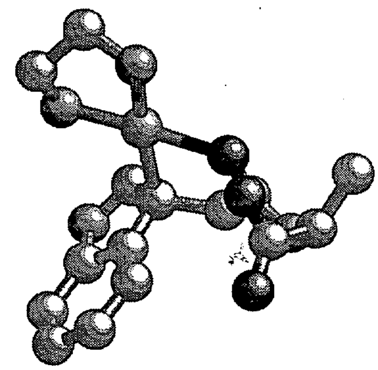


Figure S2. ^1H-^{13}C HMQC spectrum of complex **3**. The solvent was acetone-d_6, the temperature was 296 K, and the concentration of **3** was 0.10 M.

 12



6a



6b

Figure S3. Diastereomers RS (**6a**) and SS (**6b**) of [Pt(en)(*N*-(3-indolylacetyl)-L-alanine)]$^{2+}$ complex. The structures was calculated by molecular mechanics (CHARMM) and optimized by quantum-mechanics (density-functional theory, program package ADF). Hydrogen atoms are omitted for clarity.

Alternative mechanism that involves the equilibrium between two forms of indole-3-acetamide, followed by the coordination of *cis*-[Pt(en)(sol)$_2$]$^{2+}$ to one of these forms

$$\mathrm{I_1} \underset{}{\overset{K}{\rightleftharpoons}} \mathrm{I_2} \xrightarrow[\mathrm{Pt(en)(sol)_2}^{2+}]{k_2} \mathbf{3}$$

$K = k_1/k_{-1}$

Under steady-state approximation, eq S1, the initial rate of the product formation is given in eq S2. If I_2 reacts with the platinum(II) complex more rapidly than it returns to I_1, as stated in eq S3, eq S2 reduces to eq S4:

$$k_{-1} + k_2[\mathrm{Pt(en)(sol)_2}^{2+}] >> k_1 \qquad \text{(S1)}$$

$$d[3]/dt = (k_1k_2[\mathrm{I_1}][\mathrm{Pt(en)(sol)_2}^{2+}])/(k_{-1} + k_2[\mathrm{Pt(en)(sol)_2}^{2+}]) \qquad \text{(S2)}$$

$$k_{-1} << k_2[\mathrm{Pt(en)(sol)_2}^{2+}] \qquad \text{(S3)}$$

$$d[3]/dt = k_1[\mathrm{I_1}] \qquad \text{(S4)}$$

Because the concentration of the platinum(II) complex does not figure in eq S4, the simple expression agrees with the evidence in Figure 3.