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Metal complexes of biologically important ligands, LXXXVII [1] α-Amino carboxylate complexes of palladium(II), iridium(III) and ruthenium(II) from chloro-bridged ortho-metallated metal compounds and $[(OC)_3Ru(Cl)(\mu\text{-}Cl)]_2$

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Abstract

The chloro-bridged ortho-metallated compounds $[(L)Pd(\mu\text{-}Cl)]_2$ (HL = 2-benzylpyridine, 2-phenylpyridine, azobenzene) and $[(L)_2Ir(\mu\text{-}Cl)]_2$ (LH = 2-phenylpyridine) react with α-amino carboxylates to give the N,O-chelate complexes $(L)Pd\text{–}NH_2C(H)(R)CO_2$ and $(L)_2Ir\text{–}NH_2C(H)(R)CO_2$. The chloro-bridged carbonyl complex $[(OC)_3Ru(Cl)(\mu\text{-}Cl)]_2$ and prolinate afford the N,O-chelate $(Cl)(OC)_3Ru$(prolinate). From the osmium complex $[(OC)_3Os(Cl)(\mu\text{-}Cl)]_2$ and *N,N*-dimethylglycine methylester the ionic compound $[HN(Me_2)CH_2CO_2Et]^+(Os(CO)_3Cl_3)^-$ (**25**) was obtained. The structures of [2-(2-pyridylmethyl)phenyl-C^1,N]Pd(prolinate)], [(2-pyridylphenyl-C^1,N)$_2$Ir(prolinate)] and of **25** were determined by X-ray diffraction.

Keywords: Palladium; Iridium; Ruthenium; Biologically-important ligands; α-Amino carboxylates

1. Introduction

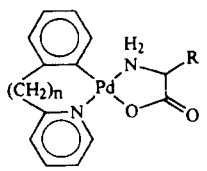
Chloro-bridged ortho-metallated compounds and chloro-bridged metal carbonyls have proven to be useful starting compounds for many reactions [2].

Cleavage of chloro bridges from μ-dichloro-bis[2-(2-dimethylaminomethyl)phenyl-C^1,N]dipalladium and substitution of chloride by α-aminoacidates gave a series of N,O-chelate complexes $(C_6H_4CH_2NMe_2)Pd(NH_2C(H)CRCO_2)$ [3–5]. In continuation of our work on organometallic complexes of α-amino acids and their derivatives, we now report on the synthesis and characterization of N,O-α-amino acidato compounds which were prepared from the ortho-metallated complexes $[(L)Pd(\mu\text{-}Cl)]_2$ (LH = 2-benzylpyridine [6], 2-phenylpyridine [7], azo-benzene [8]) and from $[L_2Ir(\mu\text{-}Cl)]_2$ (LH = 2-phenylpyridine) [9]. The latter fluorescent iridium(III) complex is a powerful photoreducing agent [10].

We also studied the reaction of the chloro-bridged carbonyl complexes $[(OC)_3M(Cl)(\mu\text{-}Cl)]_2$ (M = Ru [11], Os [12]) with α-aminocarboxylates and glycine ester. Metalcarbonyl fragments can be used as markers for peptides [13] and other biomolecules [14]. The reactions of $[(OC)_3Ru(Cl)(\mu\text{-}Cl)]_2$ with nucleobases have been studied [15].

2. Results and discussion

The reactions of the chloro-bridged palladium(II) and iridium(III) complexes with sodium salts of glyOH, L-alaOH, D-valOH, D-leuOH, L-pheOH and L-proOH in methanol gave the complexes **1–21**



1 - 10

Complex	*n*	α-amino acid
1	1	glycine
2	1	L-alanine
3	1	D-valine

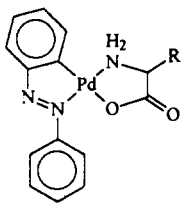
* Corresponding author.

[1] For part 86 see Ref. [1]. Dedicated to Professor Marvin Rausch on the occasion of his 65th birthday.

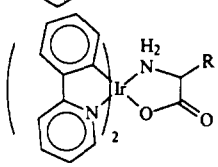
[2] X-ray structural determination.

PII S0022-328X(96)06166-9

4	1	D-leucine
5	1	L-proline
6	0	glycine
7	0	L-alanine
8	0	D-valine
9	0	D-leucine
10	0	L-proline



11	glycine
12	L-alanine
13	D-valine
14	D-leucine
15	L-proline

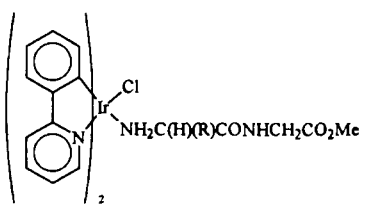


16-21

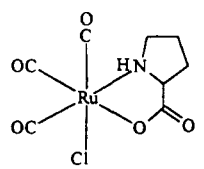
16	glycine
17	L-alanine
18	L-valine
19	D-leucine
20	L-proline
21	L-phenylalanine

The dipeptide esters glyglyOMe, alaglyOMe afforded with $[(2\text{-phenylpyridine-}C^2,N)_2Ir(\mu\text{-}Cl)]_2$ the complexes **22**, **23**.

$(OC)_3Ru(Cl)(\mu\text{-}Cl)_2$ and $[(OC)_3Os(\mu\text{-}Cl)]_2$ gave with sodium amino acidates a mixture of products. The prolinate complex **24** could be separated.



22: R = H
23: R = Me



24

$[HNMe_2CH_2CO_2Et]^+[(OC)_3OsCl_3]^-$

25

For all the complexes **1–21** the trans O–metal–C(Ph) arrangement has to be assumed. This geometry was confirmed by X-ray structural determination of **5**, **15** [16], **20** and was also found for α-aminocarboxylato palladium(II) complexes of 2-(2-dimethylaminomethyl)-phenyl [3–5] and may be due to the strong *trans* influence of the C-donor [17].

From the reaction of *N,N*-dimethylglycine methylester with $[(OC)_3Os(Cl)(\mu\text{-}Cl)]_2$ the ionic complex $[HNMe_2CH_2CO_2Et]^+[(OC)_3OsCl_3]^-$ (**25**) was obtained in low yield. The origin of HCl for the formation of **25** remains unclear (partial hydrolysis of the chloro Os complex?). The complex $Cs[(OC)_3OsCl_3]$ has been previously reported [18].

The IR spectra of **1–21** and **24** show the $\nu_{as}CO_2$ absorption at 1610–1640 cm^{-1} which is characteristic for N,O-chelates. The three intensive νCO bands of **24** and **25** point to the fac configuration [19].

The ^1H NMR spectra of **1**, **2** and **4** show dynamic behaviour in solution which is due to inversion of the six membered chelate ring which was first observed by Fuchita and coworkers [20]. The CH_2 group of **4** appears as singlet (δ 4.29) at room temperature and shows an AB spin system below −30°C. The coalescence temperature for **4** is about −25°C.

The complexes **16–23** are chiral. By coordination of the non-chiral glycinate in **16** the two pyridyl-phenyl ligands become non-equivalent and complicated multiplets are observed in the range δ 6–9 (ppy) and 3.2 (CH_2) in the ^1H NMR spectra.

The formation of diastereoisomers of **17–20** (ca. 1 : 1) can be detected by the doubling of the ^1H NMR signals of characteristic groups (e.g. for α-C–CH_3 of **17**, CH(CH_3)$_2$ for **18**). The ^{13}C NMR spectrum of the chiral complex **16** shows 22 signals for the two ppy-ligands and one signal for α-C. The diastereoisomers of the complexes **17–21** show the doubling of all ^{13}C NMR signals (amino acid and ppy-ligands). For the prolinate complex **20** only one set of ^1H NMR and ^{13}C NMR signals was observed; i.e. one diastereoisomer was separated.

The UV–vis absorptions of the educt $[(2\text{-pyridylphenyl-}C^1N)_2Ir(\mu\text{-}Cl)]_2$ [9,21] and of the complexes **16–22** are very similar. Characteristic are the strong metal to ligand charge transfer bands at 350–450 nm.

The complexes **16–22** show strong fluorescence at ca. 515 nm in DMSO or CH_2Cl_2 solution on exposure to UV light even at room temperature, and **18–21** also on exposure to day light (see Experimental part). This fluorescence may be useful for the marking of peptides.

2.1. Structures of 5, 20 and 25 in the crystals (Figs. 1–3, Tables 1–5)

Colourless crystals of **5** were obtained by cooling a saturated methanol solution. The coordination around the palladium atom is planar (sum of angles 360°). Of the two possible geometric isomers, the O–Pd–C structure is found (Fig. 1). The five membered chelate ring and the proline heterocycle are cis connected, an arrangement which has been observed in other prolinate chelate complexes [23]. The Pd–O bond length (209.4 pm) is (through the strong influence of the C donor) longer than in bis(prolinate)palladium [24]. The six membered chelate ring has a boat form [20].

Crystals of **20** were obtained from a saturated CH_2Cl_2 solution to which pentane was added dropwise. The cell of **20** contains two independent molecules which have the same configuration at the metal atom. The two N donors are trans configurated, which give the structure

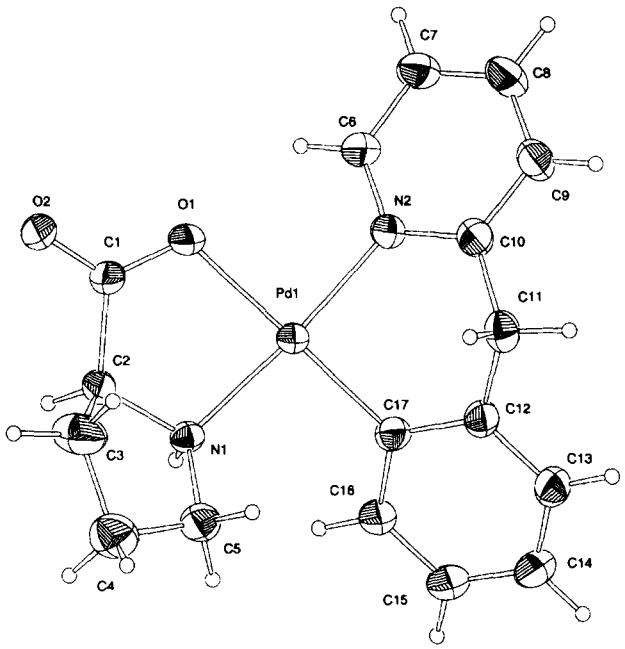


Fig. 1. Molecular structure of **5** in the crystal.

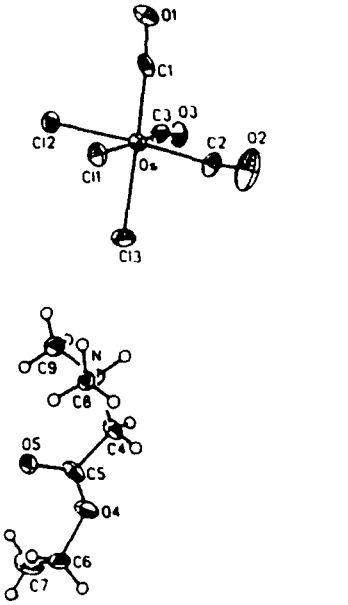


Fig. 3. Molecular structure of **25** in the crystal.

shown in Fig. 2. The chiral N atom of prolinate has the S configuration as found in **5** and other prolinate complexes [23]. The Ir–C and Ir–N bond lengths are similar to those in other ortho-metallated rhodium and iridium complexes [25].

Crystals of **25** were formed from diethyl ether–hexane. The anion $[(OC)_3OsCl_3]^-$ shows the fac form (Fig. 3).

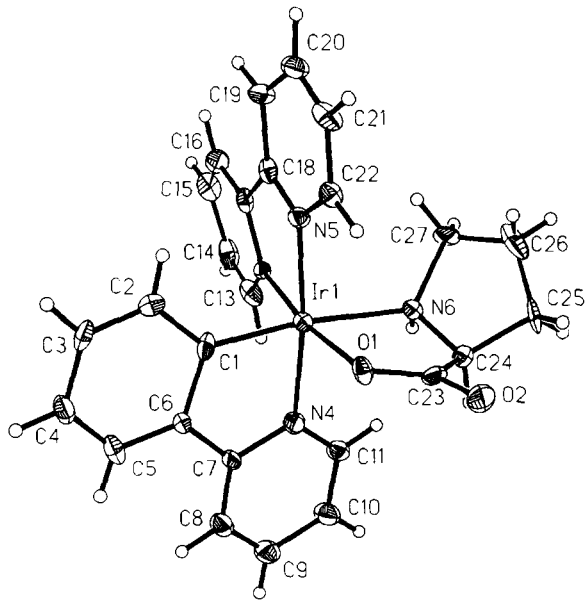


Fig. 2. Molecular structure of **20** in the crystal.

3. Experimental

The reactions were carried out with Schlenk tubes and under N_2 atmosphere. The starting materials were prepared as described previously [6–8,11,12]. IR: Nicolet 520 FT, Perkin–Elmer 841. NMR: Jeol FX 90Q, Jeol GSX 270, Jeol EX 400 with TMS or solvent as standards. UV–vis: Kontron UVIKON 810 with UNICON 21. Fluorescence: Perkin–Elmer FS 3000. The emmission was measured by irradiation into the maximum of absorption. Elemental analyses: Heraeus VT.

3.1. Synthesis of 1–10

To the α-amino acid (0.4 mmol) in methanol (3 ml) 0.4 mmol of NaOMe in methanol are added dropwise. The mixture is gently heated until most of the amino acid is dissolved. Then $[Pd(C_6H_4CH_2C_5H_4N)(\mu\text{-Cl})]_2$ (124 mg, 0.2 mmol) or $[Pd(C_6H_4\text{–}C_5N_4N)(\mu\text{-Cl})]_2$ (118 mg, 0.2 mmol) and methanol (4 ml) are added. After stirring for 14–18 h the precipitate is centrifuged off. For an improved yield of **1** the precipitate may be extracted with methanol. From the combined solutions the methanol is removed in vacuo and the residue is washed twice with 4 ml of water and dried for 9 h at 60°C in vacuo.

The complexes are soluble in DMF, DMSO or methanol.

1. White powder; yield 94 mg (67%); m.p. > 220°C. IR (KBr, cm^{-1}): 3249 m, 3125 m (NH), 1609 vs (CO_2), 1574 s (C=C, C=N, NH_2), 1382 m (CO). ^1H NMR (400 MHz, CD_3OD–d^6-DMSO): δ = 8.73 d, 7.90 ψt, 7.63 d, 7.32 ψt, 7.10 dd, 7.06 dd, 6.92 ψt, 6.86 ψt

Table 1
Selected bond distances (pm) and angles (deg) of **5**, **20** and **25**

5							
Pd–O1	209.1(4)	Pd–N2	202.3(4)	Pd–N1	205.9(4)	Pd–C17	198.1(5)
O1–Pd–N1	82.7(1)	N1–Pd–C17	96.4(2)	C10–C11–C12	113.5(4)		
O1–Pd–N2	92.1(1)	N2–Pd–C17	88.8(2)	C11–C12–C17	120.7(4)		
O1–Pd–C17	178.9(2)	Pd–N2–C10	123.9(3)	Pd–C17–C12	119.4(4)		
N1–Pd–N2	174.6(2)	N2–C10–C11	116.6(4)				
20							
Ir1–C12	197(2)	Ir1–N5	204.0(9)	Ir1–O1	214.7(11)		
O1–C23	129(2)	N5–C22	135(2)	C7–C7	144(2)		
C23–C24	154(2)	Ir1–C1	195.8(11)	Ir1–N4	205.8(8)		
Ir1–N6	218.4(8)	N6–C24	151(2)	C21–C22	140(2)		
N5–Ir1–N4	173.1(4)	C27–N6–Ir1	120.8(7)	N5–Ir1–N6	92.8(3)		
C24–N6–Ir1	108.8(8)						
25							
Os–Cl1	239.1(8)	Os–Cl2	246.0(8)	Os–Cl3	240.2(4)		
Os–C1	189(1)	Os–C2	199(3)	Os–C3	185(3)		
N–C4	148(1)	N–C8	145(3)	N–C9	155(4)		
C4–C5	150(2)	C5–O5	123(2)	C5–O4	135(2)		
O4–C6	159(2)	C6–C7	147(3)				
C4–N–C9	116(2)	C4–N–C8	111(2)	C8–N–C9	112(2)		
C4–C5–O4	108(1)	C4–C5–O5	125(2)	O4–C5–O5	120(3)		
C5–O4–C6	107(2)	O4–C6–C7	95(2)				

Table 2
Crystallographic data for **5**, **20** and **25** [22]

	5	**20**	**25**
Formula	$C_{17}H_{18}N_2O_2Pd$	$C_{27}H_{24}N_3O_2Ir \cdot 2H_2O$	$C_9H_{14}Cl_3NO_5Os$
Fw (g mol^{-1})	388.73	650.76	512.8
Crystal size (mm^3)	0.23 × 0.23 × 0.23	0.45 × 0.30 × 0.20	0.15 × 0.2 × 0.7
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12_1$ (No. 19)	$P2_1$	$Pna2_1$
a (pm)	822.3(2)	1032.2(3)	641.5(3)
b (pm)	999.4(3)	1786.4(5)	2444(1)
c (pm)	1928.3(6)	1300.5(6)	1024.0(4)
β (°)		90.24(3)	
V (nm^3)	1.5847	2.398	1.605
Z	4	4	4
ρ calc. (g cm^{-3})	1.63	1.75	2.12
Diffractometer	E.N.CAD4	Synthex R3	
Temperature (°C)	23	20	20
μ(Mo K α) (mm^{-1})	1.162	5.602	8.3
	ω scan		
2θ range (°)	4–46	3–46	4–55
No. reflections collected	2493	6970	2225
No. unique data	2185	3495	1932
No. observed reflections ($I > 2\sigma(I)$)	2169	3259	1478
Absorption correction	empirical	semi-empirical	empirical
Min./max.			
Transmission	0.96/0.99	0.083/0.148	0.074/0.110
Program	SHELXL93	SHELXL93	SHELXTL PLUS
Parameters refined			
(non-H atoms)	200	631	171
R (%)	2.86($R1$)/7.04($wR2$)	3.04($R1$)/5.06($wR2$)	3.25(R)/3.72(R_w)
FLACK parameter	−0.03(5)	0.004(10)	
Residual electron density (e × 10^{-6} pm^{-3})	+0.285/−0.271	0.802/−1.256	0.53/−1.70
Extinction coefficient	0.0215(11)		

Table 3
Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **5**

Atom	x	y	z	U_{eq}
Pd(1)	2264(1)	1338(1)	3463(1)	38(1)
O(1)	1042(5)	2352(4)	2669(2)	57(1)
O(2)	−1236(5)	2331(4)	2064(2)	68(1)
N(1)	396(5)	−9(4)	3340(2)	38(1)
N(2)	4042(5)	2739(4)	3498(2)	45(1)
C(1)	−311(7)	1837(5)	2487(3)	47(1)
C(2)	−824(7)	534(5)	2830(3)	48(1)
C(3)	−2362(7)	679(7)	3266(4)	87(2)
C(4)	−2265(8)	−443(7)	3782(4)	79(2)
C(5)	−521(7)	−451(6)	3960(3)	57(1)
C(6)	4566(8)	3238(6)	2891(3)	57(2)
C(7)	5736(8)	4223(6)	2854(3)	67(2)
C(8)	6369(7)	4713(6)	3458(4)	75(2)
C(9)	5843(8)	4218(6)	4082(3)	63(2)
C(10)	4689(7)	3207(5)	4092(3)	49(1)
C(11)	4095(7)	2590(6)	4752(3)	53(1)
C(12)	4125(6)	1088(5)	4753(2)	46(1)
C(13)	4879(7)	422(6)	5299(3)	57(1)
C(14)	4908(8)	−961(7)	5325(3)	69(2)
C(15)	4213(8)	−1672(6)	4798(3)	66(2)
C(16)	3447(7)	−1032(5)	4255(3)	53(1)
C(17)	3382(6)	365(5)	4222(3)	45(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(1H each, CH_{ar}), 4.30 (s, 2H, $PhCH_2$), 3.50 (s, 2H, αCH_2). ^{13}C NMR (100.5 MHz, CD_3OD–d^6-DMSO): $\delta = 181.92$ (CO_2), 159.97 (Pd–C), 152.66, 143.16 (q), 140.16, 138.57 (q), 135.02, 127.14, 125.85, 125.37, 124.92, 123.33 (CH_{ar}), 48.92 (αC). Anal. Found: C, 47.92; H, 4.21; N, 7.99. $C_{14}H_{14}N_2O_2Pd$ (348.7). Calc.: C, 48.21; H, 4.05; N, 8.03%.

2. White microcrystalline powder; yield 97 mg (67%), dec. > 170°C. The residue was extracted with 4 ml of DMF. The DMF was removed in vacuo and the product was washed with water. IR (KBr, cm^{-1}): 3260 m, 3227 m, 3114 m (NH), 1622 vs (CO_2), 1597 s, 1574 s (C=C, C=N, NH_2), 1387 m (CO). ^1H NMR (400 MHz, CD_3OD): $\delta = 8.71$ d, 7.79 ψt, 7.51 d, 7.18 t, 7.09 d, 7.03 d, 6.91 t, 6.86 ψt (1H each, CH_{ar}), 4.25 (s, 2H, $PhCH_2$), 3.63 (q, 1H, αH, $^3J = 7.0$ Hz), 1.51 (d, 3H, $CHCH_3$, $^3J = 7.0$ Hz). ^{13}C NMR (100.5 MHz, CD_3OD): $\delta = 184.82$ (CO_2), 160.54 (Pd–C), 152.98, 143.03 (q), 140.26, 138.88 (q), 135.39, 127.28, 126.15, 125.45, 125.23, 123.46 (CH_{ar}), 56.90 (αC), 20.76 ($CHCH_3$). Anal. Found: C, 48.95; H, 4.77; N, 7.64. $C_{15}H_{16}N_2O_2Pd \cdot 1/4H_2O$ (367.2). Calc.: C, 49.05; H, 4.50; N, 7.63%.

3. White powder; yield 42 mg (27%); dec. > 160°C. The mixture was reacted only for 4 h. Elemental palladium was formed. IR (KBr, cm^{-1}): 3335 w, 3219 w, 3111 w (NH), 1620 vs, br (CO_2), 1608 s, 1574 s (C=C, C=N, NH_2), 1372 m (CO). ^1H NMR (400 MHz, CD_3OD): $\delta = 8.71$ d, 7.80 ψt, 7.52 d, 7.18 t, 7.15 dd, 7.03 dd, 6.91 ψt, 6.87 ψt (1H each, CH_{ar}), $\delta_A = 4.30$, $\delta_B = 4.21$ ($PhCH_2$, J(A,B) = 14.6 Hz), 3.49 (d, αH, $^3J = 3.9$ Hz), 2.35–2.30 (m, 1H, $CH(CH_3)_2$), 1.20 d, 1.14 d (je 3H, $CH(CH_3)_2$). ^{13}C NMR (100.5 MHz, CD_3OD): $\delta = 183.41$ (CO_2), 160.61 (Pd–C), 153.08, 143.23 (q), 140.30, 138.91 (q), 135.27, 127.31, 126.24, 125.49, 125.29, 123.49 (CH_{ar}), 66.34 (αC), 32.94 ($CH(CH_3)_2$), 19.49/18.38 ($CH(CH_3)_2$). Anal. Found: C, 50.99; H, 5.45; N, 7.02. $C_{17}H_{20}N_2O_2Pd \cdot 1/2H_2O$ (399.8). Calc.: C, 51.06; H, 5.29; N, 7.01%.

4. White powder; yield 108 mg (67%); dec. > 200°C. IR (KBr, cm^{-1}): 3225 m, 3153 m, 3111 m (NH), 1615 vs, br(CO_2), 1574 s (C=C, C=N, NH_2), 1376 m (CO). ^1H NMR (400 MHz, CD_3OD): $\delta = 8.72$ dd, 7.82 ψt, 7.53 d, 7.21 ψt, 7.10 dd, 7.03 dd, 6.91 ψt, 6.86 ψt (1H each, CH_{ar}), 4.27 (s, 2H, $PhCH_2$), 3.60–3.55 (m, 1H, αH), 1.94–1.74 (m, 3H, ($CH_2CH(CH_3)_2$)), 1.00 d, 0.96 d ($CH(CH_3)_2$, $^3J = 6.2$ Hz). ^{13}C NMR (100.5 MHz, d^6-DMSO): $\delta = 179.43$ (CO_2), 158.49 (Pd–C), 151.51, 143.99, 139.23, 137.61, 135.05, 125.90, 124.53, 124.44, 123.41, 122.55 (CH_{ar}), 57.78 (αC), 47.68 ($PhCH_2$), 43.63 ($CH_2CH(CH_3)_2$), 23.74 ($CH_2CH(CH_3)_2$), 23.02/21.91 ($CH_2CH(CH_3)_2$). Anal. Found: C, 52.95; H, 5.88; N, 7.02. $C_{18}H_{22}N_2O_2Pd \cdot 1/8H_2O$ (407.0). Calc.: C, 53.10; H, 5.51; N, 6.87%.

5. White powder; yield 124 mg (80%); dec. > 200°C. IR (KBr, cm^{-1}): 3170 br (NH), 1640 vs, br (CO_2), 1605 s, 1574 s (C=C, C=N), 1385 m (CO). ^1H NMR (400 MHz, CD_3OD, 40°C): $\delta = 8.66$ d, 7.80 t, 7.53 d, 7.32 d, 7.19 t, 7.04 d, 6.92 t, 6.91 t (1H each, CH_{ar}), $\delta_A = 4.48$, $\delta_B = 4.07$ ($PhCH_2$, J(A,B) = 14.6 Hz), 4.06–4.02 (m, 1H, αH), 3.06–3.01 (m, 2H, δCH_2), 2.26–2.02 (m, 2H, βCH_2), 1.93–1.63 (m, 2H, γCH_2). ^{13}C NMR (100.5 MHz, CD_3OD): $\delta = 184.31$ (CO_2), 160.79 (Pd–C), 153.10, 144.59, 140.28, 138.82, 135.48, 127.29, 126.19, 125.39, 125.31, 123.40 (CH_{ar}), 66.92 (αC), 53.73 (δC), 31.39 (βC), 26.26 (γC). Anal. Found: C, 52.06; H, 4.81; N, 7.25. $C_{17}H_{18}N_2O_2Pd$ (388.6). Calc.: C, 52.51; H, 4.64; N, 7.21%.

6. White powder; yield 127 mg (95%); m.p. > 220°C. IR (KBr, cm^{-1}): 3282 m, 3252 m, 3121 m (NH), 1617 s (CO_2), 1606 s, 1580 s (C=C, C=N), 1380 m (CO). ^1H NMR (400 MHz, CD_3OD): $\delta = 8.47$ d, 7.94 t, 7.82 d, 7.54 d, 7.24 t, 7.10 t, 7.04 t, 6.91 d (1H each, ppy), 3.50 (s, 2H, αH). ^{13}C NMR (100.5 MHz, CD_3OD): $\delta = 185.70$ (CO_2), 166.20 (Pd–C), 152.05 (q), 150.82, 147.19 (q), 140.82, 133.84, 130.23, 125.84, 124.85, 123.80, 119.94 (ppy), 49.84 (αC). Anal. Found: C, 46.96; H, 4.03; N, 8.46. $C_{13}H_{12}N_2O_2Pd$ (334.7). Calc.: C, 46.66; H, 3.61; N, 8.37%.

7. Light yellow powder; yield 90 mg (65%); m.p. > 220°C. The residue was extracted with 4 ml of DMF. After removal of DMF in vacuo the product was washed with water. IR (KBr, cm^{-1}): 3229 m, 3123 m (NH), 1620 vs (CO_2), 1604 s, 1579 s (C=C, C=N), 1385 s (CO). ^1H NMR (400 MHz, CD_3OD): $\delta = 8.42$ d, 7.89 ψt, 7.77 d, 7.50 d, 7.20 ψt (1H each, ppy), 7.18–6.98

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **20**

Atom	x	y	z	U_{eq}
Ir(2)	2161(5)	−1934(2)	9299(4)	34(14)
Ir(1)	2838(5)	−4953(2)	4298(4)	34(14)
O(1)	4353(9)	−5108(4)	3192(7)	43(2)
O(2)	4759(13)	−5444(6)	1563(9)	69(3)
O(3)	617(10)	−1778(4)	8174(7)	46(3)
O(4)	214(11)	−1452(5)	6568(8)	61(3)
O(5)	6825(16)	5670(6)	2931(11)	94(5)
O(6)	1767(17)	2440(8)	2077(12)	103(5)
N(1)	1862(11)	−869(5)	9842(8)	40(3)
N(2)	2412(10)	−3037(5)	8956(8)	37(3)
N(3)	3254(12)	−1562(6)	7957(9)	45(3)
N(4)	3137(11)	−6024(4)	4829(8)	43(3)
N(5)	2557(11)	−3851(5)	3951(8)	37(3)
N(6)	1709(13)	−5330(5)	2972(8)	46(3)
C(1)	3998(16)	−4720(5)	5450(10)	45(4)
C(2)	4515(14)	−4016(6)	5830(11)	45(4)
C(3)	5357(15)	−3986(7)	6603(10)	52(4)
C(4)	5844(17)	−4616(7)	7085(11)	56(5)
C(5)	5409(16)	−5287(7)	6784(11)	53(4)
C(6)	4529(15)	−5383(6)	6005(10)	41(4)
C(7)	3976(14)	−6083(6)	5671(10)	37(3)
C(8)	4283(16)	−6767(6)	6064(12)	55(4)
C(9)	3699(19)	−7400(7)	5725(12)	63(5)
C(10)	2816(18)	−7333(6)	4911(14)	67(7)
C(11)	2543(15)	−6640(7)	4506(11)	45(4)
C(12)	1323(13)	−4730(5)	5156(9)	28(3)
C(13)	509(18)	−5216(8)	5735(13)	56(5)
C(14)	−516(18)	−4984(9)	6253(11)	64(5)
C(15)	−832(15)	−4200(8)	6314(11)	56(4)
C(16)	−107(17)	−3735(8)	5784(13)	54(4)
C(17)	923(14)	−3988(7)	5196(9)	42(3)
C(18)	1654(14)	−3511(7)	4460(10)	39(4)
C(19)	1359(17)	−2738(7)	4285(12)	54(5)
C(20)	2025(18)	−2383(7)	3498(13)	55(5)
C(21)	2955(16)	−2737(7)	2997(12)	54(4)
C(22)	3210(15)	−3491(6)	3206(10)	43(3)
C(23)	4019(16)	−5379(6)	2309(12)	44(4)
C(24)	2617(15)	−5667(6)	2192(11)	45(4)
C(25)	2018(17)	−5498(8)	1152(10)	63(5)
C(26)	1268(27)	−4849(13)	1311(14)	123(9)
C(27)	860(15)	−4784(7)	2365(11)	55(4)
C(28)	3729(14)	−2149(6)	10143(10)	40(4)
C(29)	4475(15)	−1667(7)	10725(10)	48(4)
C(30)	5590(16)	−1899(8)	11235(12)	67(5)
C(31)	5841(16)	−2663(7)	11317(11)	56(4)
C(32)	5111(18)	−3174(7)	10720(14)	65(5)
C(33)	4057(13)	−2927(6)	10173(10)	40(3)
C(34)	3349(14)	−3401(6)	9471(10)	37(3)
C(35)	3585(16)	−4133(6)	9264(11)	51(4)
C(36)	2936(17)	−4515(7)	8489(11)	59(4)
C(37)	2023(16)	−4113(6)	7953(12)	51(4)
C(38)	1762(17)	−3417(6)	8185(12)	57(5)
C(39)	969(15)	−2168(7)	10475(10)	44(4)
C(40)	476(17)	−2860(8)	10775(12)	53(5)
C(41)	−409(16)	−2899(8)	11567(11)	51(4)
C(42)	−890(17)	−2288(8)	12082(12)	60(4)
C(43)	−398(15)	−1613(8)	11777(10)	44(4)
C(44)	473(17)	−1518(7)	10960(12)	47(4)
C(45)	975(13)	−833(6)	10644(9)	33(3)
C(46)	670(13)	−131(6)	11064(10)	41(3)
C(47)	1234(17)	519(8)	10713(11)	52(4)
C(48)	2092(17)	477(7)	9911(14)	62(5)
C(49)	2390(17)	−239(7)	9493(12)	51(4)
C(50)	992(17)	−1522(6)	7273(11)	48(4)
C(51)	2332(15)	−1244(6)	7176(10)	45(4)
C(52)	2928(17)	−1403(8)	6146(13)	59(4)
C(53)	3500(24)	−2120(9)	6294(12)	93(7)
C(54)	4106(17)	−2103(8)	7354(12)	65(4)
O(8)	7534(22)	5721(11)	3775(18)	167(8)
O(7)	2386(25)	2413(9)	1118(18)	151(9)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(m, 3H, ppy), 3.67 (q, 1H, αH, $^3J = 7.3$ Hz), 1.53 (d, 3H, CHCH_3, $^3J = 7.3$ Hz). ^{13}C NMR (100.5 MHz, CD_3OD): $\delta = 184.47$ (CO_2), 165.97 (Pd–C), 152.67 (q), 150.55, 147.13 (q), 140.58, 134.29, 130.08, 125.64, 124.76, 123.61, 119.80 (ppy), 56.38 (αC), 20.63 (CHCH_3). Anal. Found: C, 47.69; H, 4.35; N, 8.08. $C_{14}H_{14}N_2O_2Pd$ (348.7). Calc.: C, 48.22; H, 4.05; N, 8.03%.

8. Light yellow powder; yield 146 mg (97%); m.p. 220°C. The residue was extracted with 4 ml of DMF. After removal of DMF the product was washed with 4 ml of water. IR (KBr, cm^{-1}): 3221 m, 3128 m (NH), 1624 vs, br (CO_2), 1605 s, 1579 s (C=C, C=N), 1372 s (CO). ^{1}H NMR (400 MHz, CD_3OD): $\delta = 8.35$ d, 7.76 ψt, 7.61 d, 7.40 d (1H each, ppy), 7.07–6.98 (m, 4H, ppy), 3.47 (d, 1H, αH, $^3J = 4.4$ Hz), 2.36–2.32 (m, 1H, CH(CH$_3$)$_2$), 1.18/1.11 (d each, 6H, CH(CH_3)$_2$). ^{13}C NMR (100.5 MHz, CD_3OD): $\delta = 183.55$ (CO_2), 165.89 (Pd–C), 152.86 (q), 150.61, 147.06 (q), 140.46, 134.20, 130.03, 125.63, 124.73, 123.50, 119.73 (ppy), 65.94 (αC), 33.00 (CH(CH$_3$)$_2$), 19.36/18.14 (CH(CH_3)$_2$). Anal. Found: C, 49.81; H, 4.93; N, 7.28. $C_{16}H_{18}N_2O_2$-Pd · 1/2H_2O. Calc.: C, 49.82; H, 4.95; N, 7.25%.

9. Light yellow powder; yield 115 mg (74%); dec. > 180°C. IR (KBr, cm^{-1}): 3221 m, 3113 m (NH), 1624 vs (CO_2), 1605 s, 1580 s (C=C, C=N), 1378 s (CO). ^{1}H NMR (400 MHz, CD_3OD): $\delta = 8.36$ d, 7.78 t, 7.63 d, 7.40 d (1 H each, ppy), 7.06–6.98 (m, 4H, ppy), 3.61–3.59 (m, 1H, αH), 1.90–1.85 (m, 2H, CH_2), 1.79–1.74 (m, 1H, CH$_2$CH(CH$_3$)$_2$), 1.01/0.99 (je d, 6H, CH(CH_3)$_2$). ^{13}C NMR (100.5 MHz, CD_3OD): $\delta = 184.75$ (CO_2), 165.85 (Pd–C), 152.84 (q), 150.59, 147.08 (q), 140.46, 134.21, 130.03, 125.59, 124.73, 123.53, 119.72 (ppy), 59.03 (αC), 44.92 (CH_2), 25.67 (CH(CH$_3$)$_2$), 23.49/22.37 (CH(CH_3)$_2$). Anal. Found: C, 51.16; H, 5.35; N, 7.05. $C_{17}H_{20}N_2O_2Pd$ · 1/2H_2O (399.8). Calc.: C, 51.07; H, 5.29; N, 7.01%.

10. Colourless powder; yield 54 mg (36%). IR (KBr, cm^{-1}): 3169 m, br (NH), 1620 vs (CO_2), 1604 s, 1580 s (C=C, C=N), 1369 s (CO). ^{1}H NMR (400 MHz, CD_3OD): $\delta = 8.40$ d, 7.85 ψt, 7.72 d, 7.48 dd (1H each, ppy), 7.17–7.04 (m, 4H, ppy), 4.09–4.05 (m, 1H, αH), 3.46–3.19 (m, 2H, δH), 2.25–2.07 (m, 2H, βH), 1.93–1.70 (m, 2H, γH). ^{13}C NMR (100.5 MHz, CD_3OD): $\delta = 184.37$ (CO_2), 166.10 (Pd–C), 153.18

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **25**

Atom	x	y	z	U_{eq}
Os	395(1)	1311(1)	0	49(1)
Cl(1)	−1229(15)	752(3)	1624(8)	62(2)
Cl(2)	−1375(15)	771(3)	−1697(8)	63(2)
Cl(3)	3226(6)	669(2)	47(15)	79(1)
N	7332(13)	−341(3)	−59(20)	51(3)
C(1)	−1946(25)	1778(4)	121(36)	56(6)
O(1)	−3371(17)	2058(4)	−117(45)	102(5)
C(2)	2060(45)	1726(11)	1307(29)	64(8)
O(2)	2586(59)	1935(13)	2024(28)	169(14)
C(3)	1561(38)	1697(10)	−1371(27)	55(6)
O(3)	2651(27)	1955(6)	−2212(19)	75(5)
C(4)	9560(17)	−502(4)	2(34)	55(3)
C(5)	9894(19)	−1110(5)	97(79)	65(4)
O(4)	11906(15)	−1211(4)	−200(38)	87(6)
O(5)	8549(15)	−1456(4)	−129(42)	97(5)
C(6)	12451(29)	−1792(7)	411(18)	81(7)
C(7)	12896(40)	−2056(9)	−846(29)	129(11)
C(8)	6224(47)	−513(10)	1106(26)	50(7)
C(9)	6152(62)	−494(15)	−1335(35)	81(11)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(q), 150.60, 147.13 (q), 140.69, 134.86, 130.34, 125.78, 124.84, 123.60, 119.88 (ppy), 66.38 (αC), 53.44 (δC), 31.21 (βC), 26.33 (γC). Anal. Found: C, 51.07; H, 4.75; N, 7.58. $C_{16}H_{16}N_2O_2Pd$ (374.7). Calc.: C, 51.28; H, 4.30; N, 7.48%.

3.2. Synthesis of 11–15

To the amino acid (0.4 mmol) in methanol (3 ml) 0.4 mmol of NaOMe in methanol are added dropwise. The mixture is gently heated until most of the amino acid is dissolved. Then $[Pd(C_6H_4N{=}NPh)(\mu\text{-}Cl)]_2$ (0.2 mmol, 129 mg) and methanol (2 ml) are added. The orange-red suspension is stirred for 3 h (compound **11**), 4 h (compound **12**) and for 15 h (compound **13–15**). The yellow precipates of **11–13** are filtered off, washed with small amounts of methanol and dried in vacuo. For the isolation of **14** and **15** the solvent is removed in vacuo from the yellow solutions and the residue is titrurated with dichloromethane (8 ml). After centrifugation from the clear solutions in CH_2Cl_2 the solvent is removed in vacuo. **11–13** are only soluble in CH_3OH–DMSO; **14** and **15** are soluble in CH_2Cl_2.

11. Yellow powder, 140 mg (97%); m.p. > 220°C. IR (KBr, cm^{-1}): 3294 m, 3236 m, 3126 m (NH), 1620 (CO_2), 1588 s, 1573 s (C=C, NH_2), 1380 (CO). ^1H NMR (400 MHz, CD_3OD–d^6-DMSO): $\delta = 8.20$ (dd, 2H, Ph), 8.01 (dd, 1H, Ph), 7.60–7.53 (m, 3H, Ph), 7.52–7.14 (m, 3H, Ph), 3.27 (s, 2H, αH). ^{13}C NMR (100.5 MHz, CD_3OD–d^6-DMSO): 178.76 (CO_2), 163.30 (Pd–C), 155.03 (q), 151.17 (q), 133.49, 132.03, 131.81, 129.93, 129.17, 125.99, 123.75 (Ph), 46.55 (αC). Anal. Found: C, 46.39; H, 3.57; N, 11.69. $C_{14}H_{13}N_3O_2Pd$ (361.7). Calc.: C, 46.49; H, 3.62; N, 11.62%.

12. Yellow powder; yield 132 mg (88%); m.p. > 220°C. IR (KBr, cm^{-1}): 3276 m, 3223 m (NH), 1629 vs (CO_2), 1605 sh, 1590 s (C=C, NH_2), 1396 s, 1383 s (CO). ^1H NMR (400 MHz, CD_3OD–d^6-DMSO): $\delta =$ 8.19 dd, 8.00 dd, 7.86 dd (1H, Ph), 7.57–7.49 (m, 4H, Ph), 7.31–7.23 (m, 2H, Ph), 3.41 (q, 1H αH, $^3J = 7.3$ Hz), 1.35 (d, 3H, $CHCH_3$, $^3J = 7.3$ Hz). Anal. Found: C, 48.00; H, 4.01; N, 11.26. $C_{15}H_{15}N_3O_2Pd$ (375.1). Calc.: C, 47.95; H, 4.02; N, 11.18%.

13. Yellow powder; yield 148 mg (92%); m.p. 220°C (dec.). IR (KBr, cm^{-1}): 3229 m, 3130 m (NH_2), 1625 vs (CO_2), 1608 sh, 1574 s. ^1H NMR (400 MHz, CD_3OD): $\delta = 8.22$–8.16 (m, 2H, Ph), 8.00–7.96 (m, 1H, Ph), 7.55–7.47 (m, 3H, Ph), 7.34–7.19 (m, 3H, Ph), 3.45 (d, 1H, αH, $^3J = 4.1$ Hz), 2.36–2.27 (m, 1H, $CH(CH_3)_2$), 1.19/1.09 (d, 6H, $CH(CH_3)_2$, $^3J = 7.0$ Hz). ^{13}C NMR (100.5 MHz, CD_3OD): $\delta = 183.73$ (CO_2), 165.38 (Pd–C), 155.37 (q), 153.00 (q), 134.37, 132.92, 132.71, 130.95, 130.15, 127.12, 124.88 (Ph), 64.87 (αC), 32.88 ($CH(CH_3)_2$), 19.19 ($CH(CH_3)_2$). Anal. Found: C, 50.37; H, 4.64; N, 10.42. $C_{17}H_{19}N_3O_2Pd$ (403.8). Calc.: C, 50.57; H, 4.74; N, 10.41%.

14. Yellow powder; yield 156 mg (94%); m.p. 220°C (dec.). IR (KBr, cm^{-1}): 3216 m, 3103 m (NH_2), 1626 vs, br (CO_2), 1575s (C=C, NH_2), 1379 s (CO). ^1H NMR (400 MHz, CD_3OD–CD_2Cl_2): $\delta = 8.08$–8.06 (m, 2H, Ph), 7.85 (d, 1H, Ph), 7.43–7.35 (m, 3H, Ph), 7.19 (t, 1H, Ph), 7.08 (t, 1H, Ph), 7.02 (d, 1H, Ph), 3.52–3.49 (m, 1H, αH), 1.87–1.78 (m, 1H, CH_2), 1.70–1.61 (m, 1H, $CH(CH_3)_2$), 0.95/0.93 (d, 6H, $CH(CH_3)_2$, $^3J =$ 6.1 Hz). ^{13}C NMR (CD_3OD–CD_2Cl_2): $\delta = 184.15$ (CO_2), 164.74 (Pd–C), 154.95 (q), 152.35 (q), 133.56, 132.50, 132.26, 130.69, 129.69, 126.70, 124.57 (Ph), 57.74 (αC), 44.37 (CH_2), 25.40 ($CH(CH_3)_2$), 23.24/22.14 ($CH(CH_3)_2$). Anal. Found: C, 49.75; H, 4.69; N, 9.52. $C_{18}H_{21}N_3O_2Pd \cdot 1/4CH_2Cl_2$ (439.1). Calc.: C, 49.91; H, 4.94; N, 9.56%.

15. Orange powder; yield 160 mg (ca. 100%); m.p. 210°C (dec.). Compound **15** was recrystallized several times from CH_2Cl_2–hexane. IR (KBr, cm^{-1}): 3216 m, 3176 br (NH), 1623 (CO_2), 1575 (C=C, NH_2), 1378 s (CO). ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 8.19$–8.17 (m, 2H, Ph), 7.99 (d, 1H, Ph), 7.52–7.31 (m, 3H, Ph), 7.30–7.19 (m, 3H, Ph), 4.51 (m, 1H, NH?), 4.12–4.07 (m, 1H, αH), 3.60–3.26 (m, 2H, δH), 2.31–2.13 (m, 2H, βH), 1.97–1.75 (m, 2H, γH). ^{13}C NMR (100.5 MHz, CD_2Cl_2): $\delta = 179.98$ (CO_2), 164.26 (Pd–C), 155.44 (q), 151.78 (q), 132.95, 131.98, 131.80, 130.27, 129.09, 126.07, 124.05 (Ph), 64.86 (αC), 52.62 (δC), 29.84 (βC), 25.23 (γC). Anal. Found: C, 49.69; H, 4.16; N, 10.31. $C_{17}H_{17}N_3O_2Pd \cdot 1/2H_2O$ (410.8). Calc.: C, 49.71; H, 4.42; N, 10.23%.

3.3. Synthesis of 16–23

To the α-amino acid or its ester hydrochloride (0.3 mmol) in methanol (3 ml) the equimolar amount of NaOMe in methanol is added and warmed gently. To this solution a suspension of $[Ir(ppy)_2Cl]_2$ (160 mg, 0.15 mmol) in methanol (30 ml) is added and the mixture is stirred for 14–18 h at 20°C. From the clear, yellow solution the solvent is removed in vacuo and the residue is dissolved in dichloromethane. Sometimes methanol was added to give complete dissolution.

NaCl is centrifuged off and the solution is concentrated and pentane is slowly added. The complexes are soluble in DMF and DMSO, less in methanol–CH_2Cl_2 and almost insoluble in diethyl ether or pentane.

16. Fine, yellow rod-like crystals; yield 75 mg (41%); m.p. > 250°C. IR (KBr, cm^{-1}): 3301 m, 3260 m, 3163 m (NH_2), 1619 vs (CO_2), 1605 vs, 1582 vs (C=C, C=N). Fluorescence (λ, nm, CH_2Cl_2): 514. ^1H NMR (400 MHz, d^6-DMSO): δ = 9.06 (d, 1H), 8.66 (d, 1H), 8.16 (t, 2H), 7.96–7.91 (m, 2H), 7.69 (d, 2H), 7.45 (t, 1H), 7.38 (t, 1H), 6.76 (t, 1H), 6.74 (t, 1H), 6.60 (t, 1H), 6.59 (t, 1H), 6.22 (d, 1H), 5.96 (d, 1H) (ppy), 4.86–4.82 (m, 1H, N*H*), 4.24–4.17 (m, 1H, N*H*), 3.35–3.16 (m, 2H, α*H*). ^{13}C NMR (100.5 MHz, d^6-DMSO): δ = 181.37 (*C*O_2), 168.58/167.82 (Ir–*C*), 153.20, 150.41, 147.74, 147.52, 144.81, 144.44, 137.54, 137.48, 132.33, 131.65, 128.54(2), 124.09, 123.86, 122.60, 122.31, 120.28, 119.67, 118.93, 118.85 (ppy), 44.02 (α*C*). Anal. Found: C, 47.60; H, 3.69; N, 7.02. $C_{24}H_{20}IrN_3O_2 \cdot 1.75H_2O$ (606.2). Calc.: C, 47.55; H, 3.91, N, 6.93%.

17. Recrystalization from hot methanol gave small, yellow, irridescent crystals; yield 63 mg (35%); m.p. > 250°C. IR (KBr, cm^{-1}): 3262 m, 3156 m (NH_2), 1625 vs (CO_2), 1606 vs, 1583 s (C=C, C=N). ^1H NMR (270 MHz, CD_3OD): δ = 9.00 (d, 1H), 8.93 (d, 1H), 8.73–8.65 (m, 2H), 8.06 (t, 4H), 7.94–7.86 (m, 4H), 7.65–7.61 (m, 4H), 7.39–7.29 (m, 4H), 6.81–6.74 (m, 4H), 6.64–6.58 (m, 4H), 6.31–7.61 (m, 4H), 7.39–7.29 (m, 4H), 6.81–6.74 (m, 4H), 6.64–6.58 (m, 4H), 6.31–6.21 (m, 2H), 6.05 (d, 2H) (ppy), 3.95–3.79 (m, 2H, C*H*CH_3), 1.45/1.34 (je d, je 3H, CHC*H*$_3$). Anal. Found: C, 50.06; H, 4.23; N, 6.65. $C_{25}H_{22}IrN_3O_2 \cdot 0.75H_2O$ (602.2). Calc.: C, 49.85; H, 3.92; N, 6.97%.

18. Small, yellow orange rods; yield 155 mg (80%); m.p. > 250°C. IR (KBr, cm^{-1}): 3314 m, 3246 m (NH_2), 1621 vs (CO_2), 1605 vs, 1582 (C=C, C=N). UV–Vis (λ_{max}, nm (log ε), 10^{-4}–10^{-5} *m*, CH_2Cl_2): 263 (5.1), 351 (0.8), 403 (0.5), 450 (0.4). Fluorescence (λ, nm, CH_2Cl_2): 516. ^1H NMR (270 MHz, d^6-DMSO): 9.12 (t, 2H), 8.61 (d, 1H), 8.51 (d, 1H), 8.15 (t, 4H), 7.91 (t, 4H), 7.73–7.66 (m, 4H), 7.41–7.31 (m, 4H), 6.79–6.72 (m, 4H), 6.59 (t, 4H), 6.30 (d, 1H), 6.27 (d each, 1H), 5.93 (t, 2H) (ppy), 3.33–3.22 (br, 2H, α*H*), 2.29–2.24 (m, 2H, C*H*$(CH_3)_2$), 0.89/0.88/0.87/0.64 (d, 12H, $CH(CH_3)_2$, ^3J = 7.0 Hz). ^{13}C NMR (68 MHz, d^6-DMSO): δ = 181.40 (*C*O_2), 168.54/168.48/168.39/168.17 (Ir–*C*), further 33 signals in the range 153.21–118.59 (ppy), 59.77/59.69 (α*C*), 31.10/30.79 (*C*H$(CH_3)_2$), 18.91/18.88/16.44/16.13 (CH-(*C*$H_3)_2$). Anal. Found: C, 49.98; H, 4.23; N, 6.38. $C_{27}H_{26}IrN_3O_2 \cdot 1.75H_2O$ (648.2). Calc.: C, 50.03; H, 4.58; N, 6.47%.

19. Yellow needles; yield 106 mg (55%); m.p. 240°C (dec.). IR (KBr, cm^{-1}): 3294 m, 3248 m, 3159 m (NH_2), 1617 (CO_2), 1604 vs, 1582 (C=C, C=N). Fluorescence (λ, nm, CH_2Cl_2): 514. ^1H NMR (270 MHz, d^6-DMSO): δ = 9.01 (d, 1H), 8.94 (d, 1H), 8.54 (d, 1H), 8.48 (d, 1H), 8.09–8.03 (m, 4H), 7.90–7.86 (m, 4H), 7.63–7.60 (m, 4H), 7.36–7.33 (m, 4H), 6.77–6.71 (m, 4H), 6.58–6.53 (m, 4H), 6.19 (t, 2H), 5.91–5.88 (m, 2H) (ppy), 5.24 (br, 1H, N*H*), 4.55 (br, 1H, N*H*), 3.43–3.07 (br, 4H, NH_2 and α*H*?), 1.80–1.22 (m, 6H, C*H*$_2$C*H*$(CH_3)_2$), 0.83/0.81/0.75/0.71 (d each, 12 H, $CH(CH_3)_2$, ^3J = 6.2 Hz). ^{13}C NMR (68 MHz, d^6-DMSO): δ = 183.19/182.52 (*C*O_2), 168.64/168.55/168.37/168.06 (Ir–*C*), further 28 signals in the range 153.72–118.69 (ppy), 52.83/52.48 (α*C*), 44.64/44.36 (*C*H_2), 23.73/23.60 (*C*H$(CH_3)_2$), 23.55/23.43/21.11/21.06 (CH(*C*$H_3)_2$). Anal. Found: C, 51.63; H, 4.59; N, 6.47. $C_{28}H_{28}IrN_3O_2 \cdot H_2O$ (648.8). Calc.: C, 51.84; H, 4.66; N, 6.48%.

20. Yellow crystals; yield 57 mg (29%); m.p. > 250°C. IR (KBr, cm^{-1}): 3189 m (NH), 1611 vs (CO_2), 1605 vs, 1582 (C=C, C=N). UV–Vis (λ_{max}, nm, (log ε), 10^{-4}–10^{-5} *m*, CH_2Cl_2): 260 (4.1), 356 (0.7), 405 (0.4), 450 (0.4). Fluorescence (λ, nm, CH_2Cl_2): 512. ^1H NMR (270 MHz, d^6-DMSO): δ = 9.07 (d, 1H), 8.68 (dd, 1H), 8.18 (t, 2H), 7.79 (ψt, 2H), 7.76–7.40 (m, 4H), 6.81–6.57 (m, 4H), 6.31 (dd, 1H), 5.90 (dd, 1H) (ppy), 4.11–4.09 (m), 3.81–3.78 (m, 2H, α*H* and N*H*?), 2.20–1.33 (m, C*H*$_2$). ^{13}C NMR (68 MHz, d^6-DMSO): 182.41 (*C*O_2), 168.55/167.67 (Ir–*C*), 152.31, 149.95, 147.68, 147.56, 144.59, 144.11, 137.89, 137.68, 132.51, 131.75, 128.79, 128.57, 124.34, 124.00, 122.72, 122.53, 120.45, 119.88, 119.14, 119.03 (ppy), 61.29 (α*C*), 47.68 (δ*C*), 30.45 (β*C*), 25.86 γ*C*). Anal. Found: C, 50.18; H, 4.33; N, 6.45. $C_{27}H_{24}IrN_3O_2 \cdot 2H_2O$ (650.8). Calc.: C, 49.83; H, 4.34; N, 6.46%.

21. Orange crystals; yield 70 mg (34%); m.p. > 240°C. IR (KBr, cm^{-1}): 3301 m, 3282 m, 3256 m (NH_2), 1619 vs (CO_2), 1605 vs; 1582 vs (C=C, C=N). ^{13}C NMR (100.5 MHz, d^6-DMSO): δ = 181.18/180.69 (*C*O_2), 168.49/168.40/168.27/167.35 (Ir–*C*), 43 further signals in the range 152.85–118.71 (Ph and ppy), 55.63/55.49 (α*C*), 48.57 (*C*H_2). Anal. Found: C, 54.28; H, 4.05; N, 6.02. $C_{31}H_{26}IrN_3O_2 \cdot 1.25H_2O$ (687.3). Calc.: C, 54.16; H, 4.18; N, 6.10%.

22. Yellow powder; yield 183 mg (88%); m.p. 180°C (dec.). IR (KBr, cm^{-1}): 3309 m, 3256 m (NH), 1743 s (CO_2Me), 1679 s (CONH), 1606 s, 1582 s (C=C,

C=N), 240 m (IrCl, polyethylene). Anal. Found: C, 46.75; H, 3.80; N, 7.88. $C_{27}H_{26}ClIrN_4O_3 \cdot 0.75H_2O$ (695.7). Calc.: C, 46.61; H, 3.97; N, 8.06%.

23. Yellow powder; yield 190 mg (87%); m.p. 145°C (dec.). IR (KBr, cm^{-1}): 3303 m, 3256 m (NH), 1750 vs (CO_2Me), 1675 s, 1654 s (CONH), 1606 s, 1581 s (C=C, C=N), 237 m (IrCl, polyethylene). Anal. Found: C, 45.78; H, 4.07; N, 7.21. $C_{28}H_{28}ClIrN_4O_3 \cdot 2H_2O$ (732.3). Calc.: C, 45.93; H, 4.40; N, 7.65%.

24. To a solution of L-proline (85.5 mg, 0.74 mmol) in methanol (3 ml) the equimolar amount of NaOMe in methanol and $[Ru(CO)_3Cl_2]_2$ (190 mg, 0.37 mmol) are added. The light yellow solution is stirred for 3 h at room temperature and the solvent is removed in vacuo. The residue is extracted four times with dried THF and NaCl is centrifuged off. From the combined THF solutions the solvent is removed in vacuo and the yellow powder is dried for 6 h at 70°C. Yield 243 mg (98%); m.p. 85°C (dec.). IR (KBr, cm^{-1}): 3150 br (NH), 2136 vs, 2051 vs, 1974 vs (CO), 1634 vs (CO_2), 321 m (in polyethylene, RuCl). Anal. Found: C, 30.11; H, 3.17; N, 4.01. $C_8H_8ClNO_3Ru \cdot 1/5THF$ (349.1). Calc.: C, 30.27; H, 2.76; N, 4.00%.

25. $[(OC)_3OsCl_2]_2$ (35 mg, 0.10 mmol) and *N*,*N*-dimethylglycine methylester (28 μl, 0.20 mmol) are stirred for 3 days in dried (Al_2O_3) THF (3ml). The solution is concentrated in vacuo and the residue is triturated with diethyl ether (10 ml) for 12 h. The precipitate is centrifuged off and extracted twice with diethyl ether (5 ml). The combined Et_2O solutions are concentrated to 5 ml and hexane is added. After some days colourless crystals are obtained which are stable in air. Crystals for the X-ray diffraction were isolated from a solution of $[(OC)_3OsCl_2]_2$ (0.20 mmol) and $Me_2NCH_2CO_2Et$ (0.20 mmol) in CH_2Cl_2 (5 ml) which was stirred for some minutes. After addition of hexane (5 ml) the solution was left in air. IR (nujol, cm^{-1}): 3084 m, 3059 m (NH); 3119 s, 2035 vs, 2000 vs, 1980 sh (CO); 1745 s (CO_2Et), 331 m, 295 s (OsCl). ^1H NMR (270 MHz, $CDCl_3$–CD_3OD (5%)): $\delta = 4.27$ (q, $J = 6.8$ Hz, 2H, OCH_2), 3.93 (s, 2H, NCH_2), 2.99 (s, 6H, NMe_2), 2.27 (br, 1H, NH), 1.32 (t, $J = 6.8$ Hz, 3H, OCH_2CH_3). Anal. Found: C, 20.79; H, 2.73; N, 2.77. $C_9H_{14}Cl_3NO_5Os$ (512.8). Calc.: C, 21.08; H, 2.75; N, 2.73%.

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