Metal Complexes of Biologically Important Ligands, CLVI [1]. Metal Complexes of 4-Iodo-L-phenylalanine. Oxidative Addition of 4-Iodo-L-phenylalanine Ester to Palladium(0)

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

4-Iodo-L-phenylalanine gives with the chloro bridged compounds $[(Et_3P)PtCl_2]_2$, $[(Et_3P)PdCl_2]_2$ and $[Cp^*IrCl_2]_2$ the N,O-chelate complexes $(L)(Cl)M[NH_2\text{-}C(H)(CH_2C_6H_4I)CO_2]$ (M = Pt, Pd, Ir; L = PEt_3, Cp^*) (**1** – **3**). Oxidative addition of N-protected 4-iodo-L-phenylalanine methylester to $Pd(dba)_2$ in the presence of 2,2'-bipyridyl or of triphenylphosphine affords the p-phenyl metallated amino acids $(bipy)(I)Pd[C_6H_4CH_2C(H)(NHR)CO_2Me]$ (**4**,**5**) and $(PPh_3)_2(I)Pd[C_6H_4CH_2C(H)(NHR)\ CO_2Me]$ (**6**,**7**). Oxidative addition of the coordinated 4-iodo-L-phenylalaninate in $(Et_3P)(Cl)M[NH_2C(H)(CH_2C_6H_4I)CO_2]$ to $Pd(dba)_2$ was also observed.

Key words: 4-Iodophenylalanine, C-Phenyl-Metallated Amino Acids, Palladium, Platinum, Iridium

Introduction

4-Iodophenylalanine is a very useful [2, 3] compound for the synthesis of various functional phenylalanines, *e.g.* of stannyl, borono or phosphino Phe derivatives and peptides [4] and for the preparation of radiolabelled amino acids and peptides [5].

N,O-Chelate complexes $M(IPheO)_2$ of *p*-iodophenylalaninate with copper(II) [6], cobalt(II), nickel(II) [7] and the structures of $[Cu(bpy)(D,L\text{-}IPheO)]NO_3$ and $[Cu(bpy)(L\text{-}IPheO)]ClO_4$ [8] were reported.

Various strategies have been used to attach organometallic moieties to amino acids and peptides – or *vice versa* – to introduce these biomolecules into organometallic complexes [9]:

• α-amino acids (or their anions) and peptides can be directly bound to a metal atom in organometallic compounds through their functional groups, the amino, N-amide, O-amide [10], O-carboxylate group or the α-carbon atom [11, 12].

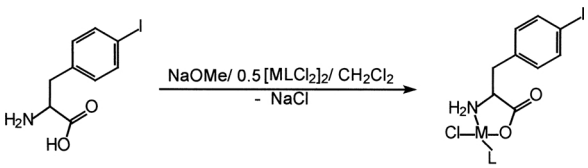
• Organometallic fragments can be attached to functional groups in the side chain of amino acids, *e.g.* the phenyl group as π-donor in Phe [13, 14] or the amino group in lysine.

• In many bioorganometallic complexes the π-coordinated cyclopentadienyl (mostly in ferrocene) or the benzene ring was attached to amino acids and peptides *via* a spacer to the α-carbon atom [15] or to the N-terminus [16] or the C-terminus [17] or the Cp ring was directly bound to the α-C-atom [18]. These complexes include the long known ferrocenylalanine by the pioneering work of Schlögl [15].

In continuation of our studies on organometallic compounds of α-amino acids [1, 9] we report on N,O-chelates of 4-iodo-α-phenylalaninate and on the oxidative addition of 4-iodo-L-phenylalanine derivatives to palladium(0) complexes.

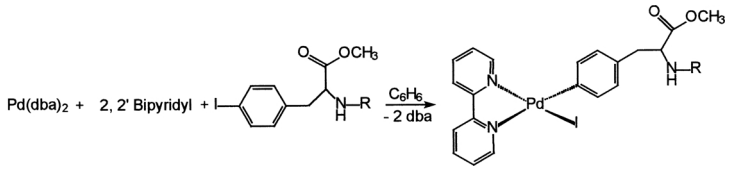
Results and Discussion

The chloro bridged complexes $[MLCl_2]_2$ (M = Pd, Pt, Ir; L = PEt_3, Cp^*) react with 4-iodo-L-phenylala-

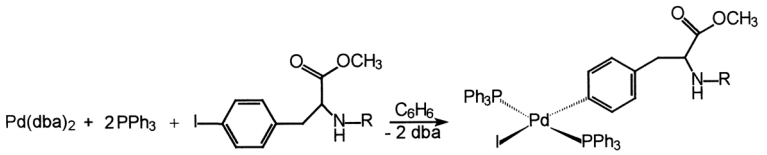


compound	M	L
1	Pt	PEt_3
2	Pd	PEt_3
3	Ir	Cp*

Formula 1.



compound	R
4	$C(O)OC(CH_3)_3$
5	$C(O)C_6H_5$



compound	R
6	$C(O)OC(CH_3)_3$
7	$C(O)C_6H_5$

Formula 2.

ninate to give the N,O-chelates **1**–**3**. The use of chloro bridged complexes was very useful for the synthesis of a large series of organometallic N,O-chelates [9].

The palladium and platinum complexes **1** and **2** are readily soluble in organic solvents (*e.g.* also benzene) whereas **3** is only soluble in dipolar protic solvents *e.g.* dimethylsulfoxide. The IR-spectra of **1**–**3** show the typical absorptions at 3100–3300 cm^{-1} (NH) and at 1640 cm^{-1} (coordinated CO_2). The ^{31}P-NMR spectra show that the planar complexes **1** and **2** are formed as mixtures of *cis/trans*-isomers whereby for **2** one isomer (presumably with the thermodynamically stable *trans*-P-Pt-N structure) [19] is observed in high excess (95/5). For the tetrahedral compound **3** with a chiral Ir atom the ^{1}H and ^{13}C NMR spectra indicate the presence of two diastereomers ($R_{Ir}S_C$, $S_{Ir}S_C$) as it was observed for a series of half sandwich complexes of α-amino acidates [9].

Arylhalides readily undergo oxidative addition reactions with Pd(0) complexes [20].

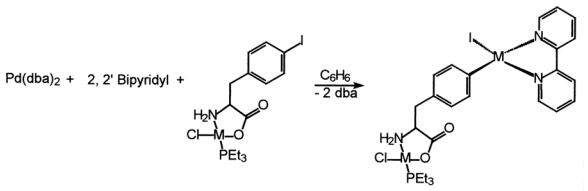
A useful route to aryl-palladium complexes is the reaction of $Pd(dba)_2$ with aryl halides in the presence of N- or P-donors [21]. This reaction has been used by us for the synthesis of α-palladated glycines [12].

The reactions of $Pd(dba)_2$ with N-t-Boc- or N-benzoyl-4-iodo-L-phenylanine methylester in the presence of 2,2'-bipyridyl or of triphenylphosphine give the aryl complexes **4**–**7** in good to excellent yields (60–90%).

The IR spectra of **4**–**7** exhibit the typical carbonyl absorptions at 1741–1746 cm^{-1} (CO_2Me) and at 1660/1715 cm^{-1} (NCO). The ^{1}H and ^{13}C NMR spectra show the expected signals. For the Ph_3P complexes **6** and **7** a highfield shift of the phenylene signal is observed and the *ortho* protons (with regard to Pd) appear as triplets of dublets ($^4J_{PH}$ coupling). The highfield shift of the meta protons can be attributed to the anisotropic cone of the PPh_3 ligands. In the ^{13}C NMR spectrum the *ipso* C atom appears as triplet due to $^2J_{PC}$ coupling, as it was observed for other Pd-aryl complexes [22].

Only one ^{31}P NMR signal is observed for **6** and **7** according to *trans* P-Pd-P structure.

The use of a metal complex fragment as protective group in amino acid derivatives is an interesting strategy. It has been first applied by Kurtz for the protection of the α-amino and carboxyl groups in lysine using Cu(II) chelates [23]. Amine Co(III) complexes [24, 25] and platinum(II) [26] were used as effective protective groups for the NH_2 function in peptide synthesis. *p*-Iodo-L-phenylalanine was prepared from L-*p*-aminophenylalanine by protection of the α-amino and carboxylate group with Cu^{2+} and reactions at the aromatic NH_2 group [3a]. Fischer and Weiß used the pentacarbonyltungsten carbene moiety for the protection of the α-amino group in peptide synthesis [27]. A new example for this method is the reaction of **1** and **2** with $Pd(dba)_2$ in the presence of 2,2'-bipyridyl. The



compound	M
8	Pt
9	Pd

Formula 3.

analyses of products **8** and **9** show that oxidative addition of the aryl-I group to Pd(0) has occured.

In the ^{31}P NMR specta of **8** and of **9** a fourfold set of signals was observed. This finding can be explained under the assumption that 8 isomers are formed in the reaction by Cl/I-exchange and *cis*/*trans* isomerization of the P-M-N moiety. If all isomers are drawn it can be shown that two isomers are equal according to their chemical surrounding of the P nuclei, which results in a fourfold signal set.

Conclusion

It has been shown that the α-amino acid residue can be readily introduced by oxidative addition of 4-iodophenylalanine derivatives to Pd(0). It appears of interest to introduce these stable complexes into peptides. Recently, van Koten *et al.* [28] reported the application of pincer ligands to bind aryl platinum and palladium complexes covalently to amino acids for the labelling of peptides.

Experimental Section

Synthesis of complexes **1** *and* **3**

4-Iodophenylalanine [3b] (146 mg, 0.50 mmol) is dissolved in 10 ml of dichloromethane and NaOMe (0.50 mmol) in methanol is added. The mixture is stirred for 5 min and $[(Et_3P)MCl_2]_2$ [29] (M = Pt, Pd, 0.25 mmol) or $[Cp^*IrCl_2]_2$ [30] (0.25 mmol) are added. Then, the mixture is stirred for 3 h. After addition of a small amount of anhydrous Na_2SO_4 the mixture is stirred for another hour and the precipitate is centrifuged off. The solution is concentrated to 3 ml *in vacuo* and layered with 10 ml of diethylether and 30 ml of *n*-pentane. The product is isolated by centrifugation and dried at 40 °C *in vacuo*.

{(Et$_3$P)PdCl[NH$_2$CH(CH$_2$C$_6$H$_4$-I)CO$_2$]} (**1**)

Yellow powder. Yield 248 mg (90%). M. p. 130 °C (dec.). – IR (KBr): $\nu = 3216$ cm^{-1} m (NH), 1629 s (CO_2). – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.18$ (dt, $^3J_{PH} = 17.5$ Hz, $^3J = 7.6$ Hz, 9H, CH_3, A), 1.19 (dt, $^3J_{PH} = 17.5$ Hz, $^3J = 7.5$ Hz, 9H, CH_3, B), 1.70 – 1.83 (m, 12H, CH_2, A+B), 2.38 – 2.48 (m, 2H, NH'H, A+B), 2.95 – 3.13 (m, 3H, CH'H+NHH', A+B), 3.24 (pd, $^2J = 13.4$ Hz, 2H, CHH'), 3.67 – 3.81 (m, 1H, CH, A), 3.96 – 4.09 (m, 1H, CH,B), 7.02 (d, $^3J = 8.2$ Hz, 4H, C_6H_4, A+B), 7.65 (d, $^3J = 8.2$ Hz, 4H, C_6H_4, A+B). – ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 7.72$ (d, $^2J_{PC} = 3.4$ Hz, CH_3, A), 8.07 (d, $^2J_{PC} = 3.1$ Hz, CH_3, B), 14.57 (d, $^1J_{PC} = 31.2$ Hz, CH_2, A), 15.58 (d, $^1J_{PC} = 33.1$ Hz, CH_2, B), 39.82 (CH_2, A+B), 57.89, 57.93 (CH, A+B), 92.92, 93.02 (*p*-C_6H_4-I, A+B), 131.46, 132.05 (*o*-C_6H_4-I, A+B), 135.45 (*i*-C_6H_4-I, A+B), 138.02, 138.24 (*m*-C_6H_4-I, A+B), 182.05 (CO_2, A+B). – ^{31}P NMR (109.4 MHz, $CDCl_3$): $\delta = 35.05$ (s, A), 37.00 (s, B).

Analysis for $C_{15}H_{24}ClINO_2PPd$ (550.1 g/mol): calcd. C 32.75, H 4.40, N 2.55; found C 32.74, H 4.22, N 2.28.

{(Et$_3$P)PtCl[NH$_2$CH(CH$_2$C$_6$H$_4$-I)CO$_2$]} (**2**)

Colorless powder. Yield 291 mg (91%). M. p. 109 °C (dec.). – IR (KBr): $\nu = 3224$ cm^{-1} m (NH), 1649 s (CO_2). – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.15$ (dt, $^3J_{PH} = 17.1$ Hz, $^3J = 7.7$ Hz, 9H, CH_3), 1.79 (dq, $^2J_{PH} = 10.9$ Hz, $^3J = 7.7$ Hz, 6H, CH_2), 3.09 (dd+m, $^2J = 14.5$ Hz, $^3J = 9.1$ Hz, 2H, CH'H+NH'H), 3.29 (dd, $^2J = 14.5$ Hz, $^3J = 4.2$ Hz, 1H, CHH'), 3.61 – 3.75, 3.80 – 3.92 (m, 2H, CH+NHH'), 7.03 (d, $^3J = 8.4$ Hz, 2H, C_6H_4), 7.66 (d, $^3J = 8.4$ Hz, 2H, C_6H_4). – ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 7.49$ (d, $^2J_{PC} = 4.0$ Hz, CH_3), 13.69 (d, $^1J_{PC} = 38.5$ Hz, CH_2), 39.28 (CH_2), 57.04 (d, $^3J_{PC} = 2.6$ Hz, CH), 93.23 (*p*-C_6H_4-I), 131.36 (*o*-C_6H_4-I), 135.10 (*i*-C_6H_4-I), 138.38 (*m*-C_6H_4-I), 183.62 (d, $^3J_{PC} = 3.4$ Hz, CO_2). – ^{31}P NMR (109.4 MHz, $CDCl_3$): $\delta = 6.36$ (s, $^1J_{PtP} = 3648$ Hz).

Analysis for $C_{15}H_{24}ClINO_2PPt$ (638.8 g/mol): calcd. C 28.20, H 3.79, N 2.19; found C 27.61, H 3.76, N 2.08.

{Cp*IrCl[NH$_2$CH(CH$_2$C$_6$H$_4$-I)CO$_2$]} (**3**)

Yellow powder. Yield 284 mg (87%). M. p. 120 °C (dec.). – IR (KBr): $\nu = 3286$, 3220 cm^{-1} m (NH), 1642 s (CO_2). – ^{1}H NMR (270 MHz, D_6-DMSO): $\delta = 1.54$, 1.55 (s, 30H, CH_3, A+B), 2.66 – 2.75 (m, 2H, CH'H, A+B), 2.95 – 3.08 (m, 2H, CHH', A+B), 3.30 – 3.38 (m, 1H, CH, A), 3.55 – 3.68 (m, 1H, CH, B), 5.05 (pt, $^3J = 8.8$ Hz, 2H, NH'H, A+B), 5.43 – 5.49 (m, 2H, NHH', A+B), 7.08 (d, $^3J = 8.0$ Hz, 4H, C_6H_4, A+B), 7.63 (d, $^3J = 8.0$ Hz, 4H, C_6H_4, A+B). – ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 8.38$, 8.54 (CH_3, A+B), 56.91 (CH, A+B), 82.83, 83.24 (Cp*, A+B), 91.97 (*p*-C_6H_4-I, A+B), 131.77, 131.96 (*o*-C_6H_4-I, A+B), 137.04 (*m*-C_6H_4-I, A+B), 138.92 (*i*-C_6H_4-I, A+B), 180.36, 181.35 (CO_2, A+B).

Analysis for $C_{19}H_{24}ClINO_2Ir$ (652.9 g/mol): calcd. C 34.95, H 3.70, N 2.15; found C 34.67, H 3.64, N 2.13.

Synthesis of complexes **4 – 7**

To a solution of $Pd(dba)_2$ [31] (173 mg, 0.30 mmol) in 10 ml of benzene 2,2'-bipyridyl (47 mg, 0.30 mmol) or PPh_3 (165 mg, 0.63 mmol) and N-Boc-4-iodophenylalanine methylester [32] (122 mg, 0.30 mmol) or N-benzoyl-4-iodophenyl-alanine methylester [32] are added. The mixture is stirred for 1 h at 50 °C (**4**, **5**) and at room temperature (**6**, **7**); a precipitate is centrifuged off and the solvent is removed *in vacuo* from the solution. The residue is washed three times with 5 ml of diethylether each.

*Pd{C_6H_4-CH_2-CH[$NHCO_2C(CH_3)_3$](CO_2Me)}I(bpy) (**4**)*

Orange powder. Yield 118 mg (59%). M. p. 146 °C (dec.). – IR (KBr): $\nu = 3380$ cm^{-1} m (NH), 1742 s (CO_2), 1712 s (CON). – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.40$ (s, 9H, CH_3), 2.93 (dd, $^2J = 13.7$ Hz, $^3J = 6.3$ Hz, 1H, CH'H), 3.00 (dd, $^2J = 13.7$ Hz, $^3J = 5.3$ Hz, 1H, CHH'), 3.68 (s, 3H, CH_3), 4.51 (ddd, $^3J = 5.3$ Hz, $^3J = 6.3$ Hz, $^3J = 8.1$ Hz, 1H, CH), 5.03 (d, $^3J = 8.1$ Hz, 1H, NH), 6.78 – 6.85 (m, 2H, C_6H_4), 7.29 (d, $^3J = 8.5$ Hz, 2H, C_6H_4), 7.33 – 7.62 (m, 5H, bpy), 7.93 – 8.00 (m, 2H, bpy), 9.56 (d, $^3J = 5.3$ Hz, 1H, bpy). – ^{13}C NMR (100.4 MHz, $CDCl_3$): $\delta = 28.28$ (C(**C**H_3)$_3$), 37.96 (CH_2), 52.02 (CH_3), 54.90 (CH), 79.68 (**C**(CH_3)$_3$), 121.78, 122.11, 126.41, 126.56, 128.11, 130.52, 136.31, 138.68, 138.70, 144.37, 150.02, 152.45, 153.51, 155.04, 155.41 (15C, bpy, C_6H_4, NCO), 172.47 (CO_2).

Analysis for $C_{25}H_{28}IN_3O_4Pd$ (667.8 g/mol): calcd. C 44.96, H 4.23, N 6.29; found C 44.56, H 4.16, N 6.22.

*Pd{C_6H_4-CH_2-CH[$NHCOC_6H_5$](CO_2Me)}I(bpy) (**5**)*

Yellow powder. Yield 139 mg (69%). M. p. 137 °C (dec.). – IR (KBr): $\nu = 3428$ cm^{-1} m (NH), 1741 s (CO_2), 1658 s(CON). – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 3.05$ (dd, $^2J = 13.7$ Hz, $^3J = 7.1$ Hz, 1H, CH'H), 3.22 (dd, $^2J = 13.7$ Hz, $^3J = 5.2$ Hz, 1H, CHH'), 3.76 (s, 3H, CH_3), 5.03 (ddd, $^3J = 5.2$ Hz, $^3J = 7.1$ Hz, $^3J = 7.7$ Hz, 1H, CH), 6.57 (d, $^3J = 7.7$ Hz, 1H, NH), 6.83 (d, $^3J = 7.8$ Hz, 2H, C_6H_4), 6.92 (d, $^3J = 7.8$ Hz, 2H, C_6H_4), 7.15 – 7.54 (m, 1H, bpy), 7.29 – 7.53 (m, 8H, bpy, C_6H_5), 7.88 – 8.06 (m, 4H, bpy, C_6H_5), 9.60 (d, $^3J = 5.1$ Hz, 1H, bpy). – ^{13}C NMR (100.4 MHz, $CDCl_3$): $\delta = 37.90$ (CH_2), 52.36 (CH_3), 53.91 (CH), 121.57, 121.89, 126.41, 126.59, 126.95, 128.01, 128.32, 128.60, 130.47, 131.57, 136.36, 136.59, 138.60, 144.72, 150.06, 152.71, 153.63, 155.50, 166.82 (NCO), 172.29 (CO_2).

Analysis for $C_{27}H_{24}IN_3O_3Pd$ (671.8 g/mol): calcd. C 48.27, H 3.60, N 6.25; found C 49.07, H 3.53, N 5.98.

*Pd{C_6H_4-CH_2-CH[$NHCO_2C(CH_3)_3$](CO_2Me)}I(PPh_3)$_2$ (**6**)*

Colorless powder. Yield 279 mg (90%). M. p. 158 °C (dec.). – IR (KBr): $\nu = 3430$ cm^{-1} m (NH), 1746 s (CO_2), 1718 s (CON). – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.43$ (s, 9H, C(CH_3)$_3$), 2.56 (dd, $^2J = 14.2$ Hz, $^3J = 5.6$ Hz, 1H, CH'H), 2.64 (dd, $^2J = 14.2$ Hz, $^3J = 5.9$ Hz, 1H, CHH'), 3.66 (s, 3H, CH_3), 4.31 (ddd, $^3J = 5.6$ Hz, $^3J = 5.9$ Hz, $^3J = 8.4$ Hz, 1H, CH), 4.61 (d, $^3J = 8.4$ Hz, 1H, NH), 5.97 (d, $^3J_{H'H} = 7.8$ Hz, 2H, C_6H_4), 6.54 (td, $^3J_{HH'} = 7.8$ Hz, $^4J_{PH} = 2.1$ Hz, 2H, C_6H_4), 7.20 – 7.54 (m, 30H, PPh_3). – ^{13}C NMR (100.4 MHz, $CDCl_3$): $\delta = 28.34$ (C(**C**H_3)$_3$), 36.47 (CH_2), 51.98 (CH_3), 54.04 (CH), 79.90 (**C**(CH_3)$_3$), 127.73 (t, $^3J = 5.3$ Hz, *p*-PPh_3), 128.77, 129.86, 132.21 (t, $^1J = 23.3$ Hz, *i*-PPh_3), 134.99 (t, $^2J = 6.2$ Hz, *o*-PPh_3), 136.14 (t, $^4J = 4.6$ Hz, *p*-PPh_3), 155.36 (NCO), 157.46 (*i*-C_6H_4), 172.58 (CO_2). – ^{31}P NMR (109.3 MHz, $CDCl_3$): $\delta = 23.38$ (s, PPh_3).

Analysis for $C_{51}H_{50}INO_4P_2Pd$ (1036.2 g/mol): calcd. C 59.11, H 4.86, N 1.35; found C 58.77, H 4.88, N 1.20.

*Pd{C_6H_4-CH_2-CH[$NHCOC_6H_5$](CO_2Me)}I(PPh_3)$_2$ (**7**)*

Colorless powder. Yield 290 mg (93%). M. p. 153 °C (dec.). – IR (KBr): $\nu = 3415$ cm^{-1} m (NH), 1744 s (CO_2), 1662 s(CON). – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 2.74$ (dd, $^2J = 14.0$ Hz, $^3J = 5.5$ Hz, 1H, CH'H), 2.82 (dd, $^2J = 14.0$ Hz, $^3J = 5.7$ Hz, 1H, CHH'), 3.68 (s, 3H, CH_3), 4.82 (ddd, $^3J = 5.5$ Hz, $^3J = 5.7$ Hz, $^3J = 8.0$ Hz, 1H, CH), 6.08 (d, $^3J_{H'H} = 8.1$ Hz, 2H, C_6H_4), 6.24 (d, $^3J = 8.0$ Hz, 1H, NH), 6.61 (td, $^3J_{HH'} = 8.1$ Hz, $^4J_{PH} = 1.9$ Hz, 2H, C_6H_4), 7.09 – 7.63 (m, 35H, PPh_3, C_6H_5). – ^{13}C NMR (100.4 MHz, $CDCl_3$): $\delta = 36.63$ (CH_2), 52.31 (CH_3), 53.45 (CH), 127.03, 127.69 (t, $^3J = 4.9$ Hz, *p*-PPh_3), 128.52, 128.87, 128.97, 129.71, 131.69, 132.08 (t, $^1J = 23.4$ Hz, *i*-PPh_3), 134.01, 134.81 (t, $^2J = 6.3$ Hz, *o*-PPh_3), 136.24 (t, $^4J = 4.8$ Hz, *p*-PPh_3), 156.91 (t, $^2J = 2.2$ Hz, *i*-C_6H_4), 166.91 (NCO), 171,81 (CO_2). – ^{31}P NMR (109.3 MHz, $CDCl_3$): $\delta = 23.12$ (s. PPh_3).

Analysis for $C_{53}H_{46}INO_3P_2Pd$ (1040.2 g/mol): calcd. C 61.19, H 4.46, N 1.35; found C 60.44, H 4.53, N 1.37.

Synthesis of complexes **8** *and* **9**

To a solution of $Pd(dba)_2$ [31] (173 mg, 0.3 mmol) in 10 ml of benzene 2,2'-bipyridyl (47 mg, 0.3 mmol) and complex **1** (165 mg, 0.3 mmol) or complex **2** (192 mg, 0.3 mmol) are added. The solution is stirred for 1 h at 50 °C: a precipitate is centrifuged off and the solvent is removed *in vacuo* from the solution. The residue is extracted with 10 ml of dichloromethane and the extract is concentrated to 3 ml *in vacuo* and layered with 20 ml of *n*-pentane. The resulting precipitate is centrifuged off and washed two times with 10 ml of diethylether each.

*{(Et_3P)PdCl[$NH_2CH(CH_2C_6H_4$-PdI(bpy))CO_2]} (**8**)*

Yellow powder. Yield 180 mg (74%). M. p. 191 °C (dec.). – IR (KBr): $\nu = 3230$ cm^{-1} m (NH), 1627 s (CO_2). – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.95 - 1.18$ (m, 9H, CH_3),

1.58 – 1.92 (m, 6H, CH_2), 2.74 –3 .26 (m, 4H, CH_2, NH_2), 3.54 – 3.71 (m, 2H, CH), 6.75 – 6.98 (m, 2H, C_6H_4), 7.11 – 7.55 (m, 4H, C_6H_4, bpy), 7.78 – 8.19 (m, 5H, bpy), 8.96, 9.37 (s, 1H, bpy). – ^{31}P NMR (109.4 MHz, $CDCl_3$): $\delta = 34.59$ (s, A), 34.70 (s, B), 36.26 (s, C), 36.34 (s, D).

Analysis for $C_{25}H_{32}ClIN_3O_2PPd_2$ (812.7 g/mol): calcd. C 36.95, H 3.97, N 5.17; found C 37.72, H 3.73, N 4.96.

{(Et$_3$P)PtCl[NH$_2$CH(CH$_2$C$_6$H$_4$-PdI(bpy))CO$_2$]} ***(9)***

Yellow powder. Yield 208 mg (77%). M. p. 210 °C (dec.). – IR (KBr): $\nu = 3217$ cm^{-1} m (NH), 1649 s (CO_2). – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.09 - 1.24$ (m, 9H, CH_3), 1.76 – 2.02 (m, 6H, CH_2), 3.01 (dd+m, $^2J = 14.3$ Hz, $^3J = 8.7$ Hz, 2H, CH'H, NH'H), 3.37 (dd+m, $^2J = 14.3$ Hz, $^3J = 3.6$ Hz, 2H, CHH', NHH'), 3.85 – 3.90 (m, 1H, CH), 6.95 – 7.03 (m, 2H, C_6H_4), 7.35 – 7.63 (m, 4H, C_6H_4, bpy), 7.96 – 8.11 (m, 5H, bpy), 9.23, 9.60 (s, 1H, bpy). – ^{31}P NMR (109.4 MHz, $CDCl_3$): $\delta = 5.14$ (s, $^1J_{PtP} = 3498$ Hz, A), 5.23 (s, $^1J_{PtP} = 3498$ Hz, B), 6.38 (s, $^1J_{PtP} = 3649$ Hz, C), 6.46 (s, $^1J_{PtP} = 3649$ Hz, D).

Analysis for $C_{25}H_{32}ClIN_3O_2PPdPt$ (901.4 g/mol): calcd. C 33.31, H 3.58, N 4.66; found C 33.52, H 3.47, N 4.63.

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