Metal Complexes of Biologically Important Ligands, CVIII [◇]

Metal Complexes of Alkyne-Bridged α-Amino Acids☆

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The palladium-mediated coupling of *p*-ethynylphenylalanine (*p*-epa) with different halogenated benzenes yielded alkyne-bridged α-amino acids. A series of cationic mono- to hexanuclear $(Ph_3P)_2Pt$ complexes with the anions of *p*-ethynylphenylalanine and alkynyl- or benzene-bridged di-, tri-, tetra- and hexa-ethynyl phenylalanines as N,O-chelate ligands was prepared. *N*-*t*-Boc-*p*-ethynylphenylalanine methyl ester was metal-substituted to give complexes of the types $Ph_3PAu\text{-}C{\equiv}C\text{–}R$ and $(Et_3P)_2Pt(C{\equiv}CR)_2$. The benzene-bridged di-, tri-, tetra- and hexa-*p*-ethynylphenylalanine methyl esters form Schiff bases with ferrocene aldehyde and a tripodal ligand was obtained from $Ph_2PCH_2CH_2CH_2NH_2$ and the benzene-bridged triethynylphenyl-alanine. The structure of $(Ph_3P)_2Pt[NH_2C(H)(CH_2C_6H_4C{\equiv}CH)CO_2]^+\ BF_4^-$ was determined by X-ray diffraction.

Non-proteinogenic amino acids influence the biological properties of peptides and are useful for the synthesis of peptidomimetics[3]. The synthesis of unnatural amino acids is based either on electrophilic[4] or nucleophilic[5] equivalents. A valuable building block for the derivatization of phenylalanines has been developed by Schwabacher et al.[6]. *p*-Iodophenylalanine was used as starting material to build, under palladium catalysis, amino acids which are bridged by a heteroatom[6] or the iodo substituent was replaced by sulfur-containing fragments or trimethyltin[7]. The palladium-mediated coupling of terminal acetylides with *p*-iodophenylalanine afforded fluorescent marker molecules[8a], which find growing attention in organometallic chemistry[8b-e]. Undheim et al. and Savi et al. reported the Pd-catalyzed synthesis of a series of α,α′-hydrocarbon bis(α-amino acids), including α,α′-alkynyl-bridged bis(glycines) and of alkyne−bridged oxazolidines[9].

By means of the Heck[10], especially the Sonogashira reaction[11], we were able to synthesize various acetylide-bridged phenylalanines[12a]. *p*-Ethynylphenylalanine was proven to be a potent inhibitor of the enzyme tryptophan-hydroxylase[13]; therefore structural details of this compound appear of interest. The bis-, tris-, tetra- and hexapodal[12b] amino acids should be useful starting compounds in peptide chemistry, for the synthesis of organic as well as metallo-dendrimers[14], and for linearly-bridged metal complexes with unusual optical or electrical properties[15]. The scope of organometallic complexes of α-amino acids and peptides has been recently reviewed[16].

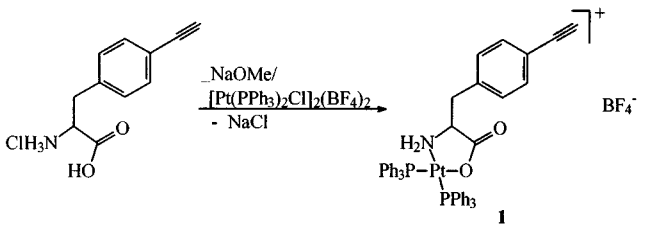
In this paper we wish to present the coordination chemistry of the new amino acid derivatives.

[◇] For part CVII see ref.[1].

Results and Discussion

Chloro-bridged metal complexes have proven to be ideal starting materials for the synthesis of N,O-α-aminocarboxylate metal compounds[16]. We have chosen the chloro-bridged complexes $[(Ph_3P)_2Pt(\mu\text{-}Cl)_2Pt(PPh_3)_2]^{2+}$, $(Et_3P)(Cl)Pd(\mu\text{-}Cl)Pd(Cl)(PEt_3)$ and $Cp^*(Cl)Rh(\mu\text{-}Cl)_2Rh(Cl)Cp^*$ from which N,O-chelates with natural α-amino acids have been obtained in our group.[16][17][18][19]

The reaction of the chloro-bridged cationic complex $\{[(Ph_3P)_2Pt(\mu\text{-}Cl)]_2\}\{BF_4\}_2$ with the anion of *p*-ethynylphenylalanine yielded the cationic N,O-chelate **1**.



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Suitable crystals for structure determination by X-ray diffraction of **1** were obtained by liquid-liquid diffusion of diethyl ether into an methanolic solution of **1** at room temperature. By this means the structure of the new non-proteinogenic amino acid *p*-ethynylphenylalanine (*p*-epa)[12a] has been established. The Pt−ligand atom distances are close to those of similar complexes, e.g. $(n\text{Bu}_3P)(Cl)Pt(O_2CCH_2N{=}C(H)NMe_2)$[20a], (dppe)Pt[N(COMe)$CH_2$-$CO_2$][20b] and $(Ph_3P(Cl)Pt(NH_2CMe_2CO_2)$[20c].
The bond angle C11−C10−C7 is not exactly linear.

The analogous reactions of bis-, tris-, tetra- and hexa-ethynylphenylalanine derivatives gave the cationic complexes **2**−**7**.

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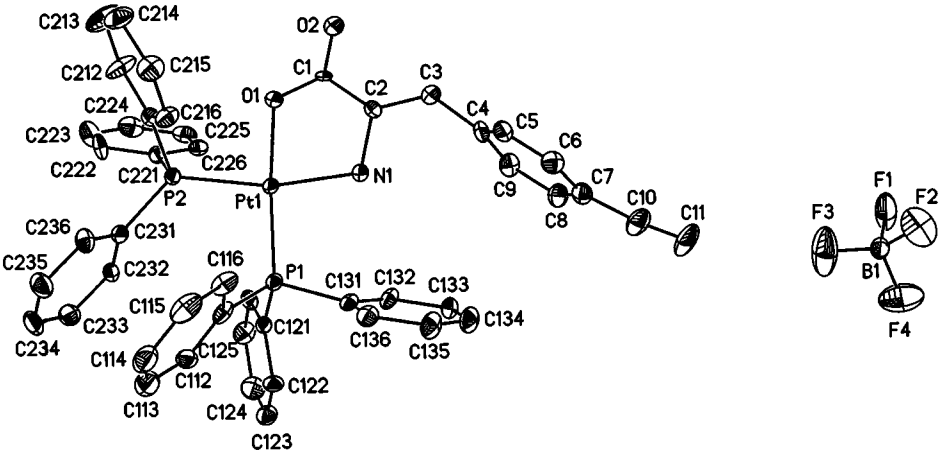
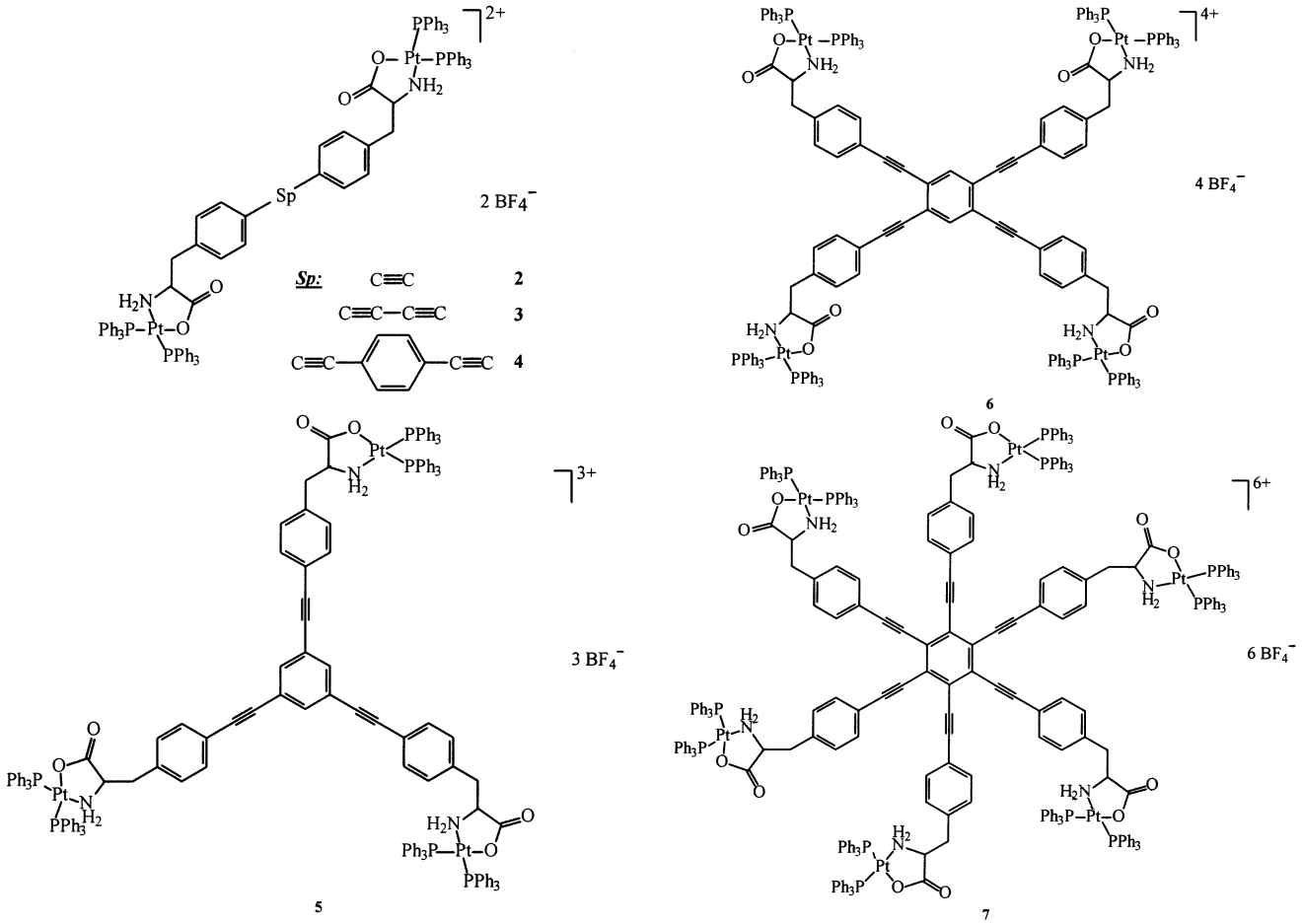
Figure 1. Structure of complex **1**[a]

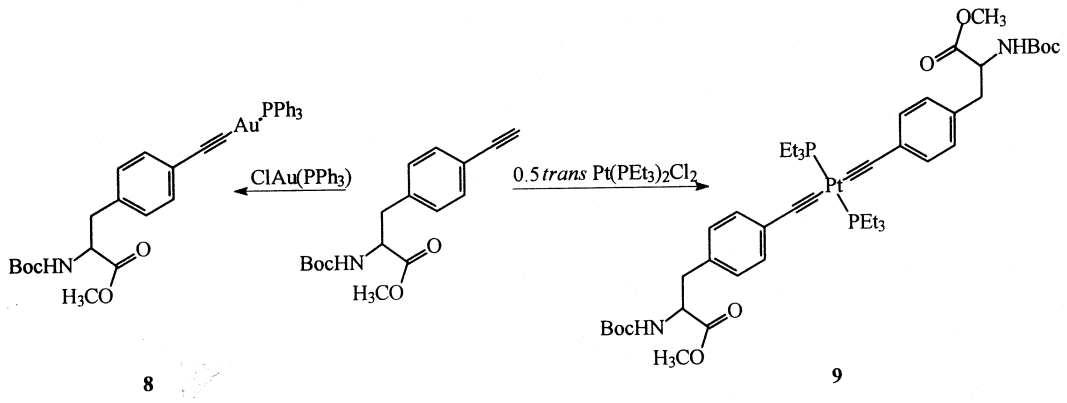


[a] Selected bond lengths [pm] and angles [°]: Pt−P1 225.3 (2), Pt−P2 225.8 (2), Pt−N1 209.5 (8), Pt−O1 207.1 (7), C10−C11 117.2 (17); N1−Pt−P2 165.9 (2), N1−Pt−P1 95.0 (2), O1−Pt−N1 81.0 (3), O1−Pt−P2 85.18 (19), C7−C10−C11 173.1 (16).

The IR spectra of the compounds **2**−**7** exhibit characteristic absorptions for η^2-coordinated α-amino carboxylates at $\nu \approx 1675\ cm^{-1}$ next to the ν(C≡C) vibrations at $\nu \approx 2205\ cm^{-1}$. The high symmetry of **2**−**7** is manifested in the ^{1}H- and ^{13}C-NMR spectra. Only one set of signals is observed. The ^{31}P-NMR spectra show a set of double doublets due to the different ligands *trans* to the P atoms with corresponding platinum satellites (^{195}Pt- ^{31}P coupling).

Terminal acetylide functions in organic molecules have successfully been used to build metal acetylide complexes which are also of interest for nonlinear optics. On the other hand the metal atom of bis(acetylide) complexes can func-



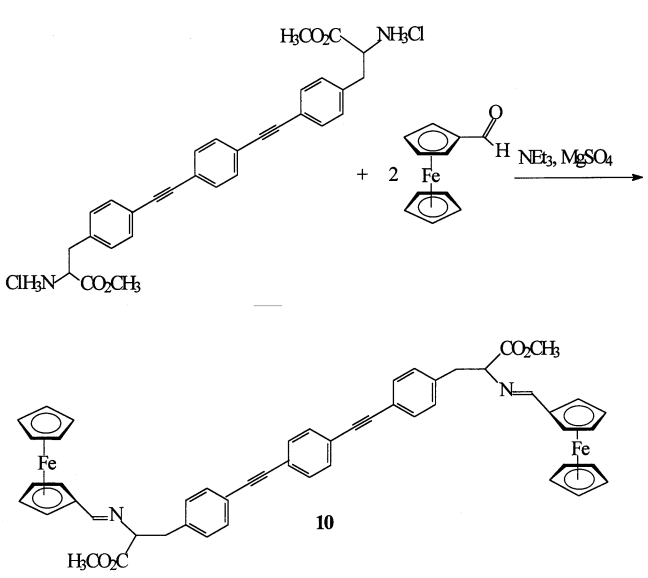


8 **9**

tion as a linker and support the conjugation of biological molecules[21]. Following known procedures[22] *p*-epa was treated with Ph_3PAuCl and *trans*-$(Ph_3P)_2PtCl_2$ to yield the compounds **8** and **9**.

Complexes **8** and **9** were characterized by IR-, ^1H-, ^{13}C- and ^{31}P-NMR spectroscopy. For **9** the characteristic $\nu(C{\equiv}C)$ absorption is found at 2103 cm^{-1}. The other spectroscopic data could be compared to similar known compounds[22].

Ferrocenyl Schiff base complexes of amino acids find application as lipophilic and chromophoric groups for masking of peptide bonds[23a]. Also interactions of the redoxac-



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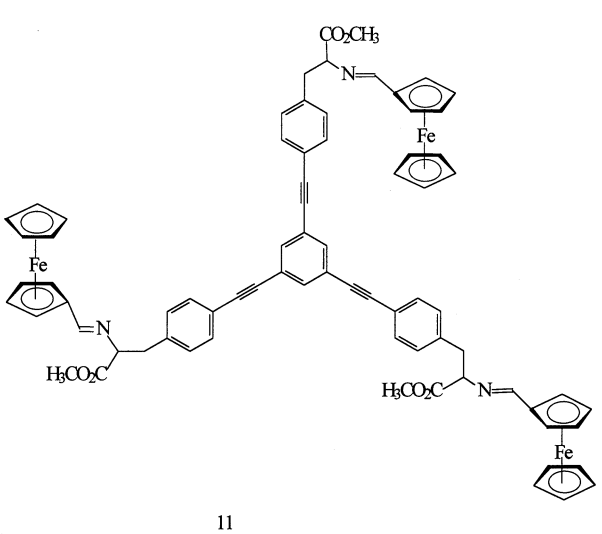

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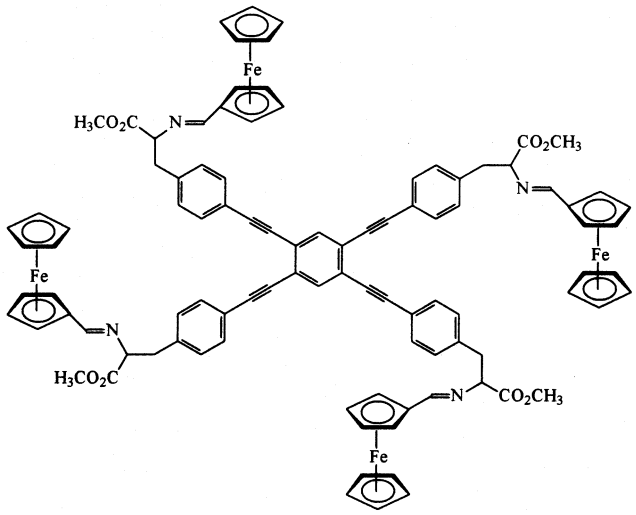

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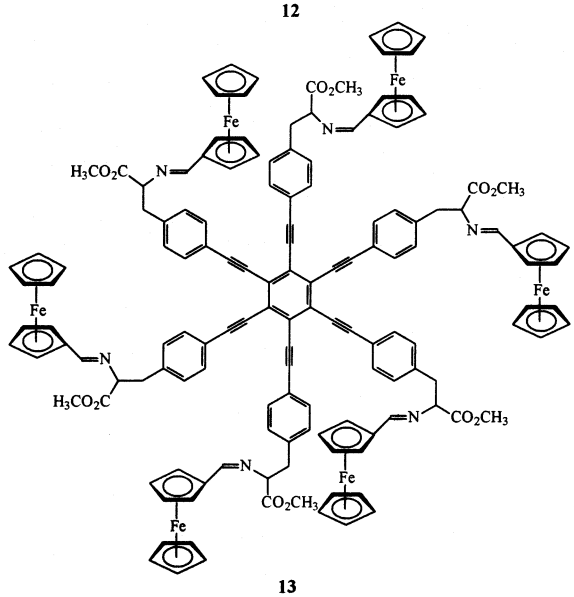

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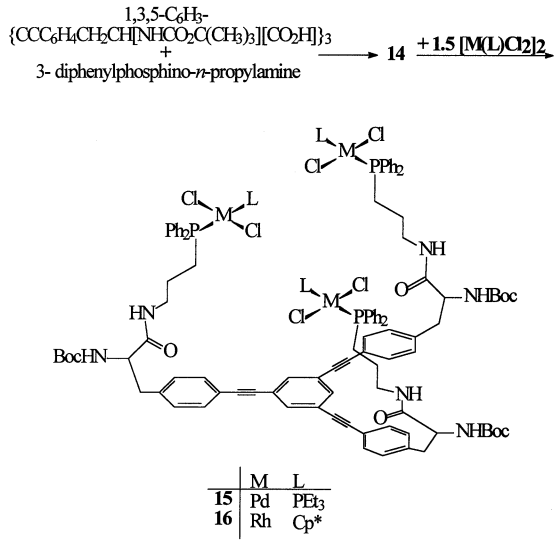
tive ferrocenyl unit and redoxactive enzymes are objects of investigations[23b]. The condensation between ferrocenecarbaldehyde and the corresponding phenylalanine esters afforded the orange Schiff base complexes **10**−**13**. For recent examples of star-shaped metal complexes derived from 1,3,5-triethynylbenzene as in **5** and **11** see ref.[24].

The successful formation of the Schiff base is proven by the intense ν(C=N) IR absorption band at 1636 cm^{-1} and by the imine proton signal (δ ≈ 7.90) in the ^{1}H-NMR spectrum. The ^{1}H-NMR signal of the H atom at α-C was not observed. A correlated ^{1}H/^{1}H-NMR experiment showed that the α-proton has the same chemical shift as the OCH_3 group of the methyl ester.

Using common methods of peptide chemistry the tripodal tris amino acid was derivatized and treated with 3-diphenylphosphanyl-*n*-propylamine to give the tripodal phosphane ligand **14** which may function as a tridentate chelate ligand. The reaction of **14** with 0.5 equivalents of $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) gave no defined compound, probably because the phosphane groups are not pre-organized. On the other hand the reactions of **14** with 1,5 equivalents of $[(Et_3P)PdCl(\mu\text{-}Cl)]_2$ or [Cp* $RhCl(\mu\text{-}Cl)]_2$ (Cp* = pentamethylcyclopentadienyl) yielded the three core complexes **15** and **16**.



The ^{31}P-NMR spectrum of **15** shows several signal sets due to *cis* and *trans* isomers with the most intensive one having a coupling constant of 538 Hz. This coupling constant is typical for *trans*-situated phosphanes[25]. In contrast, compound **16** is formed as one isomer with a doublet in the ^{31}P-NMR spectrum due to the $^1J_{Rh\text{-}P}$ coupling of 143 Hz.

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Experimental Section

General: All reactions were carried out in dry solvents under argon. − NMR: Jeol GSX 270 (^{1}H 270.0; ^{13}C 67.9; ^{31}P 109.3 MHz). Tetramethylsilane as internal standard; H_3PO_4 (85%) as external standard. − IR: 5ZDX FT-IR. − $ClAu(PPh_3)$[26], *trans*-$Pt(PEt_3)_2Cl_2$ [27a], $\{[(Ph_3P)_2Pt(\mu\text{-}Cl)]_2\}\{BF_4\}_2$ [28], $[(Et_3P)PdCl(\mu\text{-}Cl)]_2$ [27b], [Cp* $RhCl(\mu\text{-}Cl)]_2$ [29], 3-diphenylphosphanyl-*n*-propylamine[30] and the acetylide-substituted phenylalanines were prepared according to literature procedures[12]. Formylferrocene was purchased from Fluka and stored in the dark under argon.

{(Ph$_3$P)$_2$Pt[(NH$_2$)(O$_2$C)CHCH$_2$C$_6$H$_4$C≡CH]}BF$_4$ (**1**): To a solution of 34 mg (0.15 mmol) of *p*-ethynylphenylalanine hydrochloride in 10 ml of methanol was added 0.30 mmol of NaOMe and the mixture was stirred for 5 min. at room temperature. After addition of a solution of 120 mg (0.075mmol) of $\{[(Ph_3P)_2Pt(\mu\text{-}Cl)]_2\}\{BF_4\}_2$ in 10 ml of dichloromethane, the mixture was stirred for additional 3 h. The volatiles were evaporated, the residue was washed two times with 5 ml of water and dried at 50°C in vacuo. The resulting powder was finally recrystallized several times from dichloromethane/diethyl ether. Yield 121 mg (81%), colorless powder, m.p. 250°C (decomp.). − IR (KBr): ṽ = 3295 cm^{-1} m (NH_2), 1654 s (CO_2), 1084 s (BF_4). − ^{1}H NMR ($CDCl_3$): δ = 2.85 (dd, ^2J = 14.6 Hz, ^3J = 3.4 Hz, 1 H, CH′H), 3.13 (dd, ^2J = 14.6 Hz, ^3J = 7.5 Hz, 1 H, CHH′), 3.16 (s, 1 H, CH), 3.19−3.30 (m, 1 H, CH), 3.98−4.12 (m, 2 H, NH_2), 6.95 (d, ^3J = 8.1 Hz, 2 H, C_6H_4), 7.15−7.50 (m, 32 H, C_6H_4, PPh_3). − ^{13}C NMR ($CDCl_3$): δ = 38.90 (CH_2), 56.58 (CH), 77.76 (C≡CH), 83.41 (*C*≡CH), 120.85, 125.33 (d, ^1J = 84.1 Hz, *i*-PPh_3), 126.38 (d, ^1J = 83.5 Hz, *i*-PPh_3), 128.61 (d, ^3J = 11.4 Hz, *m*-PPh_3), 129.17 (d, ^3J = 11.5 Hz, *m*-PPh_3), 129.60, 131.66 (d, ^4J = 2.3 Hz, *p*-PPh_3), 132.21 (d, ^4J = 2.2 Hz, *p*-PPh_3), 132.66, 133.91 (d, ^2J = 10.8 Hz, *o*-PPh_3), 134.59 (d, ^2J = 10.6 Hz, *o*-PPh_3), 136.91, 182.94 (CO_2). − ^{31}P NMR ($CDCl_3$): δ = 7.70 (d, ^2J = 24.3 Hz, ^1J = 3586 Hz), 8.54 (d, ^2J = 24.3 Hz, ^1J = 3484 Hz). − $C_{47}H_{40}BF_4NO_2P_2Pt$ (994.7): calcd. C 56.75, H 4.05, N 1.41; found C 56.80, H 4.05, N 1.15.

{(Ph$_3$P)$_2$Pt[(NH$_2$)(CO$_2$)CHCH$_2$C$_6$H$_4$C≡CC$_6$H$_4$CH$_2$CH(CO$_2$)(NH$_2$)]Pt(PPh$_3$)$_2$}{BF$_4$}$_2$ (**2**): The reaction was carried out as described for **1** with 43 mg (0.10 mmol) of the ligand of **2** as dihydrochloride, 0.40 mmol of NaOMe, 160 mg (0.10 mmol) of $\{[(Ph_3P)_2Pt(\mu\text{-}Cl)]_2\}\{BF_4\}_2$ for 16 h. Yield 178 mg (91%), colorless powder, m.p. 220°C (decomp.). − IR (KBr): ṽ = 3303 cm^{-1} m (NH_2), 1676 s (CO_2), 1084 s (BF_4). − ^{1}H NMR ($CDCl_3$+CD_3OD): δ = 2.99 (dd, ^2J = 14.9 Hz, ^3J = 4.9 Hz, 2 H, CH′H), 3.11 (dd, ^2J = 14.9 Hz, ^3J = 7.6 Hz, 2 H, CHH′), 3.97−4.08 (m, 2 H, CH), 6.99 (d, ^3J = 8.3 Hz, 4 H, C_6H_4), 7.10−7.47 (m, 64 H, C_6H_4, PPh_3). − ^{13}C NMR ($CDCl_3$+CD_3OD): δ = 38.69 (CH_2), 56.48 (CH), 89.33 (C≡C), 121.75, 124.94 (d, ^1J = 77.0 Hz, *i*-PPh_3), 125.85 (d, ^1J = 74.9 Hz, *i*-PPh_3), 128.40 (d, ^3J = 11.4 Hz, *m*-PPh_3), 128.97 (d, ^3J = 11.3 Hz, *m*-PPh_3), 129.26, 131.64, 132.01 (*p*-PPh_3), 132.17 (*p*-PPh_3), 133.53 (d, ^2J = 10.3 Hz, *o*-PPh_3), 134.21 (d, ^2J = 10.5 Hz, *o*-PPh_3), 135.94, 183.71 (CO_2). − ^{31}P NMR ($CDCl_3$+CD_3OD): δ = 7.54 (d, ^2J = 24.1 Hz, ^1J = 3610 Hz), 8.29 (d, ^2J = 24.1 Hz, ^1J = 3466 Hz). − $C_{92}H_{78}B_2F_8N_2O_4P_4Pt_2$ (1963.3): calcd. C 56.28, H 4.01, N 1.43; found C 55.72, H 4.08, N 1.34.

{(Ph$_3$P)$_2$Pt[(NH$_2$)(CO$_2$)CHCH$_2$C$_6$H$_4$C≡CC≡CC$_6$H$_4$CH$_2$CH(CO$_2$)(NH$_2$)]Pt(PPh$_3$)$_2$}{BF$_4$}$_2$ (**3**): The reaction was carried out as described for **1** with 45 mg (0.10 mmol) of the ligand of **3** as dihydrochloride, 0.40 mmol of NaOMe, 160 mg (0.10 mmol) of $\{[(Ph_3P)_2Pt(\mu\text{-}Cl)]_2\}\{BF_4\}_2$ for 16 h. Yield 184 mg (93%), colorless powder, m.p. 235°C (decomp.). − IR (KBr): ṽ = 3303, 3223 cm^{-1} m (NH_2), 1679 s (CO_2), 1084 s (BF_4). − ^{1}H NMR

($CDCl_3$+CD_3OD): δ = 2.90−3.04 (m, 4 H, CH_2), 3.95−4.03 (m, 2 H, CH), 6.97 (d, ^3J = 7.8 Hz, 4 H, C_6H_4), 7.16−7.46 (m, 64 H, C_6H_4, PPh_3). − ^{13}C NMR ($CDCl_3$+CD_3OD): δ = 38.86 (CH_2), 56.66 (CH), 74.22, 81.34 (C≡C), 120.28, 125.05 (d, ^1J = 79.8 Hz, *i*-PPh_3), 126.03 (d, ^1J = 78.1 Hz, *i*-PPh_3), 128.53 (d, ^3J = 11.4 Hz, *m*-PPh_3), 129.09 (d, ^3J = 11.2 Hz, *m*-PPh_3), 129.44, 131.74 (*p*-PPh_3), 132.25 (*p*-PPh_3), 132.96, 133.65 (d, ^2J = 11.1 Hz, *o*-PPh_3), 134.38 (d, ^2J = 10.3 Hz, *o*-PPh_3), 137.34, 183.43 (d, ^3J = 5.2 Hz, CO_2). − ^{31}P NMR ($CDCl_3$+CD_3OD): δ = 7.43 (d, ^2J = 24.4 Hz, ^1J = 3506 Hz), 8.47 (d, ^2J = 24.4 Hz, ^1J = 3445 Hz). − $C_{94}H_{78}B_2F_8N_2O_4P_4Pt_2 \times CH_2Cl_2$ (2072.3): calcd. C 55.06, H 3.89, N 1.35; found C 54.60, H 3.92, N 1.30.

{1,4-C_6H_4[C≡$CC_6H_4CH_2CH(CO_2)(NH_2)$ $Pt(PPh_3)_2]_2$}-{BF_4}$_2$ (**4**): The reaction was carried out as described for **1** with 53 mg (0.10 mmol) of the ligand of **4** as dihydrochloride, 0.40 mmol of NaOMe, 160 mg (0.10 mmol) of {[$(Ph_3P)_2Pt(\mu\text{-}Cl)]_2$}{$BF_4$}$_2$ for 16 h. Yield 184 mg (89%), colorless powder, m.p. 260°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3299, 3223 cm^{-1} m (NH_2), 2213 (C≡C), 1666 s (CO_2), 1084 s (BF_4). − ^{1}H NMR ($CDCl_3$): δ = 2.89 (dd, ^2J = 13.6 Hz, ^3J = 4.3 Hz, 2 H, CH′H), 3.13 (dd, ^2J = 13.6 Hz, ^3J = 7.2 Hz, 2 H, CHH′), 3.32−3.47 (m, 2 H, CH), 3.98−4.19 (m, 4 H, NH_2), 7.01 (d, ^3J = 8.3 Hz, 4 H, C_6H_4), 7.12−7.49 (m, 64 H, C_6H_4, PPh_3), 7.59 (s, 4 H, C_6H_4). − ^{13}C NMR ($CDCl_3$): δ = 38.70 (CH_2), 56.50 (CH), 89.50, 90.75 (C≡C), 121.81, 122.88, 125.01 (d, ^1J = 78.9 Hz, *i*-PPh_3), 125.90 (d, ^1J = 76.4 Hz, *i*-PPh_3), 128.49 (d, ^3J = 11.2 Hz, *m*-PPh_3), 129.05 (d, ^3J = 11.1 Hz, *m*-PPh_3), 129.28, 131.44, 131.71, 132.08 (*p*-PPh_3), 132.26 (*p*-PPh_3), 133.57 (d, ^2J = 10.6 Hz, *o*-PPh_3), 134.27 (d, ^2J = 10.8 Hz, *o*-PPh_3), 135.97, 183.75 (d, ^3J = 4.0 Hz, CO_2). − ^{31}P NMR ($CDCl_3$): δ = 7.71 (d, ^2J = 24.2 Hz, ^1J = 3595 Hz), 8.55 (d, ^2J = 24.2 Hz, ^1J = 3446 Hz). − $C_{100}H_{82}B_2F_8N_2O_4P_4Pt_2 \times 1/2\ CH_2Cl_2$ (2105.9): calcd. C 57.48, H 3.98, N 1.33; found C 57.29, H 4.23, N 1.25.

{1,3,5-C_6H_3[C≡$CC_6H_4CH_2CH(CO_2)(NH_2)$ $Pt(PPh_3)_2]_3$}-{BF_4}$_3$ (**5**): The reaction was carried out as described for **1** with 75 mg (0.10 mmol) of the ligand of **5** as trihydrochloride, 0.60 mmol of NaOMe, 240 mg (0.15 mmol) of {[$(Ph_3P)_2Pt(\mu\text{-}Cl)]_2$}{$BF_4$}$_2$ for 16 h. Yield 256 mg (84%), colorless powder, m.p. 270°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3300, 3225 cm^{-1} m (NH_2), 2208 (C≡C), 1674 s (CO_2), 1085 s (BF_4). − ^{1}H NMR ($CDCl_3$+CD_3OD): δ = 2.89−3.15 (m, 6 H, CH_2), 4.03 (pt, ^3J = 6.4 Hz, 3 H, CH), 6.98 (d, ^3J = 8.0 Hz, 6 H, C_6H_4), 7.10−7.46 (m, 96 H, C_6H_4, PPh_3), 7.69 (s, 3 H, C_6H_3). − ^{13}C NMR ($CDCl_3$+CD_3OD): δ = 38.73 (CH_2), 56.58 (CH), 87.95, 90.17 (C≡C), 121.27, 123.87, 124.99 (d, ^1J = 79.0 Hz, *i*-PPh_3), 125.95 (d, ^1J = 77.4 Hz, *i*-PPh_3), 128.45 (d, ^3J = 11.3 Hz, *m*-PPh_3), 129.02 (d, ^3J = 11.4 Hz, *m*-PPh_3), 131.67 (*p*-PPh_3), 132.11 (*p*-PPh_3), 132.18, 133.89 (d, ^2J = 10.6 Hz, *o*-PPh_3), 133.89, 134.25 (d, ^2J = 10.6 Hz, *o*-PPh_3), 136.41, 183.56 (CO_2). − ^{31}P NMR ($CDCl_3$+CD_3OD): δ = 7.56 (d, ^2J = 24.0 Hz, ^1J = 3623 Hz), 8.53 (d, ^2J = 24.0 Hz, ^1J = 3440 Hz). − $C_{147}H_{120}B_3F_{12}N_3O_6P_6Pt_3 \times CH_2Cl_2$ (3141.1): calcd. C 56.59, H 3.91, N 1.34; found C 56.49, H 4.00, N 1.17.

{1,2,4,5-C_6H_2[C≡$CC_6H_4CH_2CH(CO_2)(NH_2)$ $Pt(PPh_3)_2]_4$}-{BF_4}$_4$ (**6**): The reaction was carried out as described for **1** with 73 mg (0.075 mmol) of the ligand of **6** as tetrahydrochloride, 0.60 mmol of NaOMe, 240 mg (0.15 mmol) of {[$(Ph_3P)_2Pt(\mu\text{-}Cl)]_2$}{$BF_4$}$_2$ for 16 h. Yield 261 mg (86%), brown powder, m.p. 276°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3299, 3225 cm^{-1} m (NH_2), 2198 (C≡C), 1674 s (CO_2), 1084 s (BF_4). − ^{1}H NMR ($CDCl_3$+CD_3OD): δ = 2.82 (dd, ^2J = 14.1 Hz, ^3J = 11.2 Hz, 4 H, CH′H), 3.08−3.20 (m, 4 H, CHH′), 4.03−4.17 (m, 4 H, CH), 6.99 (d, ^3J = 7.7 Hz, 8 H, C_6H_4), 7.09−7.45 (m, 128 H, C_6H_4, PPh_3), 7.76 (s, 2 H, C_6H_2). − ^{13}C NMR ($CDCl_3$+CD_3OD): δ = 39.04 (CH_2), 56.68 (CH), 87.74, 95.49 (C≡C), 121.05, 125.05 (d, ^1J = 89.7 Hz, *i*-PPh_3), 125.25, 126.03 (d, ^1J = 88.9 Hz, *i*-PPh_3), 128.38 (d, ^3J = 11.6 Hz, *m*-PPh_3), 128.89 (d, ^3J = 10.9 Hz, *m*-PPh_3), 129.23, 131.57 (*p*-PPh_3), 131.95, 132.04 (*p*-PPh_3), 133.56 (d, ^2J = 10.6 Hz, *o*-PPh_3), 134.02, 134.33 (d, ^2J = 10.5 Hz, *o*-PPh_3), 136.89, 183.46 (CO_2). − ^{31}P NMR ($CDCl_3$+CD_3OD): δ = 7.40 (d, ^2J = 23.9 Hz, ^1J = 3622 Hz), 8.47 (d, ^2J = 23.9 Hz, ^1J = 3440 Hz). − $C_{194}H_{158}B_4F_{16}N_4O_8P_8Pt_4 \times CH_2Cl_2$ (4133.7): calcd. C 56.65, H 3.90, N 1.35; found C 56.10, H 3.99, N 1.15.

{1,2,3,4,5,6-C_6[C≡$CC_6H_4CH_2CH(CO_2)(NH_2)$ $Pt(PPh_3)_2]_6$}-{BF_4}$_6$ (**7**): The reaction was carried out as described for **1** with 71 mg (0.05 mmol) of the ligand of **7** as hexahydrochloride, 0.60 mmol of NaOMe, 240 mg (0.15 mmol) of {[$(Ph_3P)_2Pt(\mu\text{-}Cl)]_2$}{$BF_4$}$_2$ for 16 h. Yield 244 mg (81%), brown powder, m.p. 300°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3304, 3231 cm^{-1} m (NH_2), 2198 (C≡C), 1675 s (CO_2), 1084 s (BF_4). − ^{1}H NMR ($CDCl_3$+CD_3OD): δ = 2.82 (pt, *J* = 11.9 Hz, 6 H, CH′H), 3.19 (pt, *J* = 10.7 Hz, 6 H, CHH′), 4.29 (pt, ^3J = 14.7 Hz, 6 H, CH), 7.09−7.51 (m, 204 H, C_6H_4, PPh_3). − ^{13}C NMR ($CDCl_3$+CD_3OD): δ = 39.18 (CH_2), 56.47 (CH), 87.23, 99.70 (C≡C), 120.92, 125.32 (d, ^1J = 110.8 Hz, *i*-PPh_3), 126.29 (d, ^1J = 108.1 Hz, *i*-PPh_3), 127.82, 128.56 (d, ^3J = 10.7 Hz, *m*-PPh_3), 129.02 (d, ^3J = 12.8 Hz, *m*-PPh_3), 129.72, 131.59 (*p*-PPh_3), 132.12 (*p*-PPh_3), 132.18, 133.74 (d, ^2J = 10.0 Hz, *o*-PPh_3), 134.61 (d, ^2J = 8.9 Hz, *o*-PPh_3), 137.63, 183.14 (CO_2). − ^{31}P NMR ($CDCl_3$+CD_3OD): δ = 7.32 (d, ^2J = 23.6 Hz, ^1J = 3623 Hz), 8.79 (d, ^2J = 23.6 Hz, ^1J = 3477 Hz). − $C_{288}H_{234}B_6F_{24}N_6O_{12}P_{12}Pt_6 \times 2\ CH_2Cl_2$ (6203.9): calcd. C 56.14, H 3.86, N 1.35; found C 55.53, H 4.09, N 1.18.

General Procedure for the Preparation of the σ-Acetylide Metal Complexes **8** *and* **9**: To a solution of 99 mg (0.20 mmol) of $ClAu(PPh_3)$ or 100 mg (0.20 mmol) of *trans*-$Pt(PEt_3)_2Cl_2$ in 10 ml of diethylamine were added 67 mg (0.22 mmol) or 133 mg (0.44 mmol) of *N*-*t*-Boc-4-ethynyl-L-phenylalanine methyl ester and a catalytic amount of CuI. The solutions were stirred at room temp. for 3 h in the dark and the volatiles were evaporated. The residues were each extracted with a mixture of dichloromethane/diethyl ether (1/3; 5 ml) and the solvent was evaporated. The resulting precipitates were washed with pentane (2 × 10 ml) and dried in vacuo.

$(PPh_3)Au${C≡$CC_6H_4CH_2CH[NHCO_2C(CH_3)_3](CO_2Me)$} (**8**): Yield 131 mg (86%), colorless powder, m.p. 99°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3439 cm^{-1} (NH), 1743 m, 1713 s (CO_2, CON). − ^{1}H NMR ($CDCl_3$): δ = 1.39 (s, 9 H, CH_3), 2.93−3.09 (m, 2 H, CH_2), 3.65 (s, 3 H, CH_3), 4.53 (pq, ^3J = 6.1 Hz, 1 H, CH), 4.92 (d, ^3J = 8.4 Hz, 1 H, NH), 6.99 (d, ^3J = 8.1 Hz, 2 H, C_6H_4), 7.39−7.56 (m, 17 H, PPh_3, C_6H_4). − ^{13}C NMR ($CDCl_3$): δ = 28.36 [$C(CH_3)_3$], 38.32 (CH_2), 52.55 (CH_3), 54.39 (CH), 79.94 [$C(CH_3)_3$], 83.35, 105.09 (C≡C), 123.62, 128.99, 129.21 (d, ^3J = 11.4 Hz, *m*-PPh_3), 131.67, 131.80 (d, ^1J = 8.9 Hz, *i*-PPh_3), 132.57, 134.35 (d, ^2J = 13.7 Hz, *o*-PPh_3), 134.70 (24 C, C_6H_4, PPh_3), 155.14 (CON), 172.40 (CO_2). − ^{31}P NMR ($CDCl_3$): δ = 42.84. − $C_{35}H_{35}NO_4PAu \times 1/2\ CH_2Cl_2$ (804.1): calcd. C 53.02, H 4.51, N 1.74; found C 52.54, H 4.13, N 1.46.

trans-$(PEt_3)_2Pt${C≡$CC_6H_4CH_2CH[NHCO_2C(CH_3)_3](CO_2Me)$}$_2$ (**9**): Yield 182 mg (88%), yellow powder, m.p. 135°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3443 cm^{-1} (NH), 2102 s (C≡C), 1745 m, 1715 s (CO_2, CON). − ^{1}H NMR ($CDCl_3$): δ = 1.46 (dt, ^3J = 8.3 Hz, ^3J = 7.8 Hz, 18 H, CH_3), 1.35 (s, 18 H, CH_3), 2.10 (tq, ^2J = 7.4 Hz, ^3J = 7.8 Hz, 12 H, CH_2), 2.88−3.02 (m, 4 H, CH_2), 3.65 (s, 6 H, CH_3), 4.48 (pq, ^3J = 7.2 Hz, 2 H, CH), 4.87 (d, ^3J = 8.3 Hz, 2 H, NH), 6.89 (d, ^3J = 8.0 Hz, 4 H, C_6H_4), 7.13 (d, ^3J = 8.0 Hz, 4 H, C_6H_4). − ^{13}C NMR ($CDCl_3$): δ = 8.22 (t, ^2J = 12.2

Hz, CH_3), 16.16 (t, ^1J = 17.9 Hz, CH_2), 28.18 [C(CH_3)$_3$], 37.95 (CH_2), 52.15 (CH_3), 54.23 (CH), 79.87 [C(CH_3)$_3$], 109.00, 128.99, 131.09, 132.62 (12 C, C_6H_4), 155.23 (CON), 172.55 (CO_2). − ^{31}P NMR ($CDCl_3$): δ = 11.50 (^1J = 2371 Hz). − $C_{46}H_{70}N_2O_8P_2Pt$ (1036.1): calcd. C 53.33, H 6.81, N 2.70; found C 52.71, H 6.67, N 2.69.

1,4-C_6H_4[-C≡C$C_6H_4CH_2CH(CO_2CH_3)(N=C$-Fc)] (**10**): To a solution of 112 mg (0.20 mmol) of the ligand of **4** as dihydrochloride dimethyl ester in 20 ml of dichloromethane were added 61.8 µl (0.44 mmol) of triethylamine. The solution was stirred at room temperature for 15 min, 96 mg (0.44 mmol) of ferrocenealdehyde and 150 mg of $MgSO_4$ were added and stirring was continued for 24 h in the dark. The precipitate was separated by centrifugation, the volatiles were evaporated from the supernatant solution, and the residue was extracted with a mixture of diethyl ether/tetrahydrofuran (3/1; 2 × 15 ml). The solvent was evaporated, the resulting precipitate was washed with pentane (3 × 10 ml) and dried in vacuo. Yield 138 mg (79%), orange powder, m.p. 108°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2216 cm^{-1} w (C≡C), 1737 s (CO_2), 1635 s (C=N). − ^{1}H NMR ($CDCl_3$): δ = 3.16 (dd, ^2J = 14.1 Hz, ^3J = 8.8 Hz, 2 H, CH′H), 3.34 (dd, ^2J = 14.1 Hz, ^3J = 5.1 Hz, 2 H, CHH′), 3.73 (s, 6 H, CH_3), 4.02 (s, 12 H, CH, C_5H_5), 4.36 (s, 4 H, C_5H_5), 4.60 (s, 2 H, C_5H_5), 4.65 (s, 2 H, C_5H_5), 7.19 (d, ^3J = 8.1 Hz, 4 H, C_6H_4), 7.42 (d, ^3J = 8.1 Hz, 4 H, C_6H_4), 7.47 (s, 4 H, C_6H_4), 7.93 (s, 2 H, CH). − ^{13}C NMR ($CDCl_3$): δ = 39.30 (CH_2), 52.08 (CH_3), 68.70, 68.92, 69.09, 70.79 (C_5H_5), 74.72 (CH), 79.34 (C_5H_5), 88.99, 91.04 (C≡C), 121.21, 123.06, 129.66, 131.45, 137.87, 138.55 (18 C, C_6H_4), 164.71 (C=N), 171.81 (CO_2). − $C_{52}H_{44}N_2O_4Fe_2$ (872.6): calcd. C 71.57, H 5.08, N 3.21; found C 71.57, H 5.22, N 3.84.

1,3,5-C_6H_3[-C≡C-C_6H_4-CH_2-$CH(CO_2CH_3)(N=C$-Fc)] (**11**): The reaction was carried out as described for **10** with 70 mg (0.10 mmol) of the ligand of **5** as trihydrochloride trimethyl ester, 45.7 µl (0.33 mmol) of triethylamine and 70 mg (0.33 mmol) of ferrocenealdehyde. Yield 107 mg (84%), orange powder, m.p. 123°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2211 cm^{-1} w (C≡C), 1740 s (CO_2), 1636 s (C=N). − ^{1}H NMR ($CDCl_3$): δ = 3.15 (dd, ^2J = 14.0 Hz, ^3J = 9.0 Hz, 3 H, CH′H), 3.34 (dd, ^2J = 14.0 Hz, ^3J = 4.6 Hz, 3 H, CHH′), 3.73 (s, 9 H, CH_3), 4.05 (s, 18 H, CH, C_5H_5), 4.36 (s, 6 H, C_5H_5), 4.58 (s, 3 H, C_5H_5), 4.63 (s, 3 H, C_5H_5), 7.20 (d, ^3J = 8.1 Hz, 6 H, C_6H_4), 7.41 (d, ^3J = 8.1 Hz, 6 H, C_6H_4), 7.52 (s, 3 H, C_6H_3), 7.93 (s, 3 H, CH). − ^{13}C NMR ($CDCl_3$): δ = 39.30 (CH_2), 52.30 (CH_3), 68.68, 68.92, 69.10, 70.74, 70.79 (C_5H_5), 74.76 (CH), 79.39 (C_5H_5), 87.70, 90.32 (C≡C), 120.96, 123.93, 129.65, 131.66, 133.83, 138.69 (24 C, C_6H_4, C_6H_3), 164.69 (C=N), 171.82 (CO_2). − $C_{75}H_{63}N_3O_6Fe_3$ × 1/2 CH_2Cl_2 (1312.3): calcd. C 69.09, H 4.92, N 3.20; found C 68.98, H 4.60, N 3.23.

1,2,4,5-C_6H_2[-C≡C-C_6H_4-CH_2-$CH(CO_2CH_3)(N=C$-Fc)] (**12**): The reaction was carried out as described for **10** with 51 mg (0.05 mmol) of the ligand of **6** as tetrahydrochloride tetramethyl ester, 30.5 µl (0.22 mmol) of triethylamine and 47 mg (0.22 mmol) of ferrocenealdehyde. Yield 67 mg (80%), orange powder, m.p. 132°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2204 cm^{-1} w (C≡C), 1739 s (CO_2), 1636 s (C=N). − ^{1}H NMR ($CDCl_3$): δ = 3.06−3.22 (m, 4 H, CH′H), 3.27−3.38 (m, 4 H, CHH′), 3.72 (s, 12 H, CH_3), 4.04 (s, 24 H, CH, C_5H_5), 4.34 (s, 8 H, C_5H_5), 4.57 (s, 4 H, C_5H_5), 4.64 (s, 4 H, C_5H_5), 7.11−7.23 (m, 8 H, C_6H_4), 7.39−7.48 (m, 8 H, C_6H_4), 7.62 (s, 2 H, C_6H_2), 7.92 (s, 4 H, CH). − ^{13}C NMR ($CDCl_3$): δ = 39.41 (CH_2), 52.42 (CH_3), 68.81, 68.91, 69.15, 70.85, 70.88 (C_5H_5), 74.65 (CH), 79.32 (C_5H_5), 87.54, 95.32 (C≡C), 121.20, 125.13, 129.80, 131.77, 134.90, 138.91 (30 C, C_6H_4, C_6H_2), 164.83 (C=N), 171.87 (CO_2). − $C_{98}H_{82}N_4O_8Fe_4$ × CH_2Cl_2 (1752.1): calcd. C 67.86, H 4.83, N 3.20; found C 67.00, H 4.73, N 3.30.

1,2,3,4,5,6-C_6[-C≡C-C_6H_4-CH_2-$CH(CO_2CH_3)(N=C$-Fc)] (**13**): The reaction was carried out as described for **10** with 75 mg (0.05 mmol) of the ligand of **7** as hexahydrochloride hexamethyl ester, 45.7 µl (0.33 mmol) of triethylamine and 70 mg (0.33 mmol) of ferrocenealdehyde. Yield 96 mg (78%), orange powder, m.p. 131°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2206 cm^{-1} w (C≡C), 1739 s (CO_2), 1636 s (C=N). − ^{1}H NMR ($CDCl_3$): δ = 3.15 (dd, ^2J = 13.6 Hz, ^3J = 9.2 Hz, 6 H, CH′H), 3.36 (dd, ^2J = 13.6 Hz, ^3J = 5.2 Hz, 6 H, CHH′), 3.75 (s, 18 H, CH_3), 4.06 (s, 36 H, CH, C_5H_5), 4.37 (s, 12 H, C_5H_5), 4.58 (s, 6 H, C_5H_5), 4.68 (s, 6 H, C_5H_5), 7.16 (d, ^3J = 8.2 Hz, 12 H, C_6H_4), 7.44 (d, ^3J = 8.2 Hz, 12 H, C_6H_4), 7.95 (s, 6 H, CH). − ^{13}C NMR ($CDCl_3$): δ = 39.34 (CH_2), 52.33 (CH_3), 68.75, 68.96, 69.15, 70.84 (C_5H_5), 74.65 (CH), 79.30 (C_5H_5), 87.23, 99.13 (C≡C), 121.25, 127.22, 129.74, 131.73, 139.05 (42 C, C_6H_4, C_6), 164.73 (C=N), 171.78 (CO_2). − $C_{144}H_{120}N_6O_{12}Fe_6$ × 2 CH_2Cl_2 (2631.3): calcd. C 66.63, H 4.75, N 3.19; found C 66.23, H 4.89, N 3.14.

1,3,5-C_6H_3{C≡C$C_6H_4CH_2CH$[$NHCO_2C(CH_3)_3$][CO_2-$(CH_2)_3PPh_2$]}$_3$ (**14**): To a solution of 94 mg (0.10 mmol) of the ligand of **5** as *N*-Boc-protected triacid in 5 ml of tetrahydrofuran was added a solution of 98 mg (0.40 mmol) of 3-diphenylphosphanyl-*n*-propylamine in 5 ml of tetrahydrofuran and 38.0 µl (0.30 mmol) of *N*-ethylmorpholine. The solution was cooled to 0°C and 81 mg (0.60 mmol) of 1-hydroxybenzotriazole and 96 mg (0.50 mmol) of 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride were added. After stirring for 24 h, evaporation of the solvent gave a colorless residue from which the product was isolated by flash chromatography (silica gel, 30 cm, CH_2Cl_2/methanol 30:1). Yield 123 mg (76%), colorless powder, m.p. 185°C. − IR (KBr): $\tilde{\nu}$ = 3322 cm^{-1} m (NH), 2211 w (C≡C), 1706 s, 1684 s, 1651 s (CO_2, CON). − ^{1}H NMR ($CDCl_3$): δ = 1.37 (s, 27 H, CH_3), 1.46−1.60 (m, 6 H, CH_2), 1.93 (pt, ^3J = 7.9 Hz, 6 H, CH_2), 3.03 (pd, ^3J = 5.3 Hz, 6 H, CH′H, CH_2), 3.24 (dd, ^2J = 13.1 Hz , ^3J = 7.0 Hz, 6 H, CHH′, CH_2), 4.23 (pq, ^3J = 7.2 Hz, 3 H, CH), 5.00 (m, 3 H, NH), 5.79 (t, ^3J = 6.2 Hz, 3 H, NH), 7.16 (d, ^3J = 8.1 Hz, 6 H, C_6H_4), 7.26−7.42 (m, 36 H, C_6H_4, PPh_2), 7.58 (s, 3 H, C_6H_3). − ^{13}C NMR ($CDCl_3$): δ = 24.97 (d, ^2J = 10.4 Hz, CH_2), 25.74 (d, ^1J = 18.4 Hz, CH_2), 28.16 [C(CH_3)$_3$], 38.53 (CH_2), 40.33 (d, ^3J = 14.9 Hz, CH_2), 55.73 (CH), 80.28 [C(CH_3)$_3$], 87.99, 90.27 (C≡C), 121.42, 124.02, 128.50, 128.69 (d, ^3J = 10.3 Hz, *m*-PPh_2), 129.52, 131.99, 132.79 (d, ^2J = 18.5 Hz, *o*-PPh_2), 134.00, 137.65, 138.30 (d, ^1J = 13.9 Hz, *i*-PPh_2, 60 C, C_6H_4, C_6H_3, PPh_2), 155.42, 171.01 (CON). − ^{31}P NMR ($CDCl_3$): δ = −16.14. − $C_{99}H_{105}N_6O_9P_3$ × 2 H_2O(1654.9): calcd. C 71.98, H 6.65, N 5.08; found C 71.77, H 6.26, N 4.77.

General Procedure for the Preparation of the Complexes **15** *and* **16**: To a solution of 81 mg (0.05 mmol) of ligand **14** in 10 ml of dichloromethane were added 45 mg of [(Et_3P)PdCl(µ-Cl)]$_2$ or 46 mg of [Cp*RhCl(µ-Cl)]$_2$ (0.075 mmol each). The solutions were stirred at room temp. for 16 h, concentrated in vacuo and the residues were washed with 10 ml of diethyl ether and 30 ml of pentane.

1,3,5-C_6H_3{C≡C$C_6H_4CH_2CH$[$NHCO_2C(CH_3)_3$][CO_2-$(CH_2)_3PPh_2$]$Pd(PEt_3)(Cl)_2$}$_3$ (**15**): Yield 123 mg (98%), yellow powder, m.p. 183°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3428 cm^{-1} m (NH), 2213 (C≡C), 1713, 1677 s (CON), 354, 329 w (Pd−Cl). − ^{1}H NMR ($CDCl_3$): δ = 0.93 (dt, $^3J_{PH}$ = 17.8 Hz, $^3J_{HH}$ = 7.7 Hz, 27 H, CH_3, B), 1.16 (dt, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.5 Hz, 27 H, CH_3, A), 1.37 (s, 18 H, CH_3, A+B), 1.51−1.65 (m, 6 H, CH_2, A+B), 1.81−1.95 (m, 18 H, CH_2, A+B), 2.14−2.32 (m, 6 H, CH_2, A+B), 2.89−3.41 (m, 12 H, CH_2, A+B), 4.25−4.40 (m, 3 H, CH, A+B), 5.09 (d, ^3J = 6.8 Hz, 3 H, NH, A+B), 6.52 (t, ^3J = 5.0 Hz, 3 H, NH, A+B), 7.19 (d, ^3J = 8.2 Hz, 4 H, C_6H_4), 7.29−7.84 (m,

39 H, C_6H_4, C_6H_3, PPh_2). – ^{13}C NMR ($CDCl_3$): δ = 8.23, 8.60 (d, ^2J = 1.5 Hz; 3.2 Hz, CH_3, A+B), 14.33 (dd, ^1J = 25.7 Hz, ^3J = 3.1 Hz, CH_2, A), 16.70 (d, ^1J = 30.4 Hz, CH_2, B), 21.99 (d, ^1J = 27.8 Hz, CH_2, A+B), 24.00 (CH_2, A+B), 28.26 [$C(CH_3)_3$, A+B], 39.20 (CH_2, A+B), 39.74 (d, ^2J = 14.4 Hz, CH_2, A+B), 55.64 (CH, A+B), 79.83 [$C(CH_3)_3$, A+B], 87.77, 90.55 (C≡C, A+B), 121.07, 124.02, 128.39–133.69 (m, 6 C, C_6H_4, C_6H_3, PPh_2, A+B), 133.95, 137.93, 155.12 (CON, A+B), 170.93 (CON, A+B). – ^{31}P NMR ($CDCl_3$): δ = 11.37 (d, $^2J_{trans}$ = 538 Hz), 14.85 (d, $^2J_{cis}$ = 234 Hz), 25.09 (d, $^2J_{trans}$ = 538 Hz), 30.15 (d, $^2J_{cis}$ = 234 Hz). – $C_{117}H_{150}Cl_6N_6O_9P_6Pd_3$ (2502.3): calcd. C 56.16, H 6.04, N 3.36; found C 56.51, H 5.95, N 3.34.

1,3,5-C_6H_3{*C*≡*CC*$_6$*H*$_4$*CH*$_2$*CH*[*NHCO*$_2$*C*(*CH*$_3$)$_3$][*CO*$_2$-(*CH*$_2$)$_3$*PPh*$_2$]*Rh*(*Cp**)(*Cl*)$_2$}$_3$ (**16**): Yield 123 mg (97%), orange powder, m.p. 209°C (decomp.). – IR (KBr): $\tilde{\nu}$ = 3341 cm^{-1} m (NH), 2213 (C≡C), 1713, 1674 s (CON). – ^1H NMR ($CDCl_3$): δ = 1.29 (s, 18 H, CH_3), 1.31 (s, 15 H, CH_3), 1.42–1.58 (m, 6 H, CH_2), 2.47–3.19 (m, 18 H, CH_2), 4.29 (pq, ^3J = 6.7 Hz, CH), 5.13–5.37 (m, 3 H, NH), 6.24–6.46 (m, 3 H, NH), 7.18 (d, ^3J = 7.6 Hz, 6 H, C_6H_4), 7.32 (d, ^3J = 7.6 Hz, 6 H, C_6H_4), 7.38–7.52 (m, 18 H, PPh_2), 7.58 (s, 3 H, C_6H_3), 7.69–7.86 (m, 12 H, PPh_2). – ^{13}C NMR ($CDCl_3$): δ = 8.62 (Cp^*), 23.48 (CH_2), 26.74 (d, ^1J = 28.7 Hz, CH_2), 28.20 [$C(CH_3)_3$], 38.68 (CH_2), 39.86 (d, ^2J = 13.4 Hz, CH_2), 55.34 (CH), 79.57 [$C(CH_3)_3$], 87.51, 90.69 (C≡C), 98.69 (dd, J_{PC} = 6.7 Hz, J_{RhC} = 2.4 Hz, cp^*), 120.72, 124.11, 128.35 (dd, J_{PC} = 9.8 Hz, J_{RhC} = 3.9 Hz, PPh_2), 129.62, 130.89 (d, J_{PC} = 12.3 Hz, PPh_2), 131.53, 133.28 (d, J_{PC} = 9.6 Hz, PPh_2), 133.67, 133.92 (d, J_{PC} = 9.0 Hz, PPh_2), 138.38, 155.19 (CON,), 170.01 (CON). – ^{31}P NMR ($CDCl_3$): δ = 27.34 (d, J_{RhP} = 143 Hz). – $C_{129}H_{150}Cl_6N_6O_9P_3Rh_3 \times CH_2Cl_2$ (2627.9): calcd. C 59.42, H 5.83, N 3.19; found C 59.59, H 6.08, N 3.10.

X-ray-Structural Determination of **1**: $C_{47}H_{40}BF_4NO_2P_2Pt$, MW = 994.64, crystal size 0.15 × 0.15 × 0.1mm^3. The slightly yellow prism was covered with perfluoropolyether oil, mounted on a glass fiber and centered at 183(2) K. All reflections in the range 2 θ = 13.7–49.4° (index ranges $-33 < h < 33$, $-33 < k < 33$, $-10 < l < 17$) were measured by using a Siemens P4 diffractometer equipped with a CCD area detector. Hexagonal, space group *R*3, a = 28.708(5), b = 28.708(5), c = 14.458(3) Å, V = 10320(4) Å^3, Z = 9, d(calcd.) = 1.440 Mg/m^3, = 3.182 mm^{-1}, F(000) = 4446, independent reflections 6091 [R(int) = 0.0534], 5890 observed with $I > 4\,\sigma(I)$; at semiempirical absorption correction, max./min. transmission 0.972/0.698. The structure was solved by the heavy-atom method, and the non-hydrogen atoms were refined anisotropically. H atoms in calculated positions were included – the final refinement against F^2 using a riding model (SHELX93 programs). 523 variables, $R1$ = 0.0408, $wR2$ = 0.1015, largest residual peak: 2.624 e/Å^3 close to Pt.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102301. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

☆ Dedicated to Professor *Meinhart Zenk* on the occasion of his 65th birthday.

[1] Part 107: K. Sünkel, W. Hoffmüller, W. Beck, *Z. Naturforsch.*, in press.

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