Aminomethyl and Aminoacetyl Complexes of Palladium(II), Platinum(II), Iron(II) and Rhenium(I) with *N*-Phthaloyl as Amino Protecting Group and Mechanistic Studies on the Palladium-Catalyzed Amidocarbonylation

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Dedicated to Dr. Hachiro Wakamatsu

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New aminomethyl and aminoacetyl complexes with *N*-phthaloyl as the amino protecting group were synthesised by oxidative addition of *N*-phthaloylmethyl or -acetyl halide to carbonylmetallates or to $Pd(PPh_3)_4$ or $[Pt(C_2H_4)(PPh_3)_2]$ to give $[Re\{C(O)CH_2N\text{-phthaloyl}\}(CO)_5]$ (**1**), $[FeCp(CH_2N\text{-phthaloyl})(CO)_2]$ (**2**), $[FeCp\{C(O)CH_2N\text{-phthaloyl}\}(CO)_2]$ (**3**), *trans*-$[PdBr(CH_2N\text{-phthaloyl})(PPh_3)_2]$ (**4**) and *trans*-$[Pd\{C(O)CH_2N\text{-phthaloyl}\}(X)(PPh_3)_2]$ (X = Br, Cl; **5**, **6**). The bis(phosphane) complexes $[Pd(CH_2N\text{-phthaloyl})(X)(R_2PCH_2CH_2PR_2)]$ and $[Pd\{C(O)CH_2N\text{-phthaloyl}\}(X)(R_2PCH_2CH_2PR_2)]$ (X = Cl, Br; R = Ph, C_6H_{11}) **8**–**13** were obtained by ligand exchange from **4**, **5** or **6** with the corresponding bis(phosphanes). Halide abstraction from **4**, **5**, **6**, **10**, **11** or **12** gives the cationic complexes **14** and **15** with formation of a five-membered chelate ring which includes one carbonyl atom of the phthaloyl group. The reaction of **6** with the tridentate ligand $PhP(CH_2CH_2PPh_2)_2$ affords the five-coordinate complex **16** and from $[Pt(C_2H_4)(PPh_3)_2]$ and organic halides the platinum(II) complexes *trans*-$[Pt(CH_2N\text{-phthaloyl})(Cl)(PPh_3)_2]$ (**17**) and $[PtC(O)CH(CH_2Ph)N\text{-phthaloyl}(Cl)(PPh_3)_2]$ (**18**) were isolated. The structures of **2**, **11**, **14**, **15** and **16** were determined by single-crystal X-ray analysis. The mechanism of the palladium-catalysed amidocarbonylation was studied using phthalimide, formaldehyde and CO as a model system which gives *N*-phthaloylglycine in good yield. The proposed elementary steps in the palladium-catalysed amidocarbonylation could be verified by use of the possible intermediates phthaloyl-NCH_2OH and phthaloyl-NCH_2Br as substrates, by oxidative addition of phthaloylmethyl bromide to Pd^0, by insertion of CO into the palladium-carbon-bond of **4** and **8** with formation of **5** or **9**, respectively, and by use of the isolated possible intermediates **4**, **5** and **14** as catalysts. Thus, all crucial steps of the palladium-catalysed amidocarbonylation with the model system phthalimide/formaldehyde/CO have been verified for the first time.

Introduction

Aminomethyl and aminoacyl complexes are possible intermediates in the metal-catalysed amidocarbonylation, i.e. the formation of α-amino acids from aldehydes, amide and carbon monoxide. This three component reaction was discovered by Wakamatsu et al.[1] using octacarbonyldicobalt as a catalyst and was more recently developed into a highly efficient process with palladium catalysts.[2] Here we report on the synthesis of new aminomethyl and aminoacetyl metal complexes with *N*-phthaloyl as the *N*-protecting group,[3] on their role and use as catalysts in amidocarbonylation reactions and on experiments which support the mechanism of the palladium-catalysed amidocarbonylation.

Several η^1- and η^2- (side-on) coordinated aminomethyl complexes are formed from methylene immonium salts $[H_2C{=}NR_2]^+ X^-$ and organometallic compounds.[4] η^1-Aminomethyl complexes of cobaloxime result from the reduced form of bis(dimethylglyoximato)cobalt(II), formaldehyde and aniline.[5] An interesting formation of η^2-$(CHR\text{-}NH_2)$ metal complexes is the photochemical decarboxylation of α-aminocarboxylatocobalt(III) complexes.[6] The insertion of imines into the palladium−acyl bond gives *N*-acyl-aminomethyl chelate complexes, a reaction which may provide a route for the palladium-catalysed formation of polypeptides.[7] Metalated α-amino acid derivatives of

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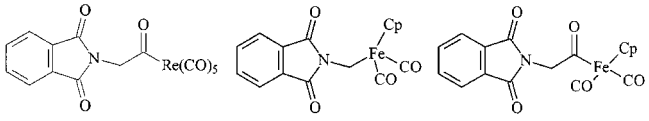
nickel,[8] palladium[7] and manganese[9] of the form L_nM-$C(O)CR_2$-N(*R*)-C(O)R have also been obtained by sequential insertion of carbon monoxide and imine into metal-carbon σ-bonds,[7−9] and recently an interesting palladium-catalysed synthesis of Münchnones (1,3-oxazolium 5-oxides, first isolated by Huisgen et al.[10]) and of α-amino acid derivatives from imines, CO and acyl chloride building blocks has been developed.[11] Its mechanism is similar to that of amidocarbonylation. Rhodium complexes with *N*-protected aminomethyl ligands have been prepared from $[RhCp(CH_2I)(I)(PMe_3)]$ and amides.[12] A general method for the preparation of η^1-aminomethyl and -aminoacetyl complexes with a protected amino group is the reaction of anionic organometallic compounds [Co(dimethylglyoximate)]$^-$ [13] or of metal carbonyls[14,15] with phthaloylmethyl halide, phthaloylglycyl chloride or with mixed anhydrides of *N*-protected α-amino acids.[16,17] The *N*-protected aminomethyl and aminoacetyl metal carbonyls can be interconverted by CO insertion[14,15] or decarbonylation,[14,15,17] respectively, and could be useful for the synthesis of peptides.[14]

Phthalimidomethyl and -acetyl Complexes of Iron and Rhenium Carbonyls

In continuation of our recent work,[14] new examples of metal carbonyls with *N*-protected η^1-aminomethyl and -aminoacetyl ligands (**1**−**3**) were obtained by reactions of the metal carbonyls $[FeCp(CO)_2]^-$ and $[Re(CO)_5]^-$ with phthaloylmethyl chloride and phthaloylacetyl chloride, respectively.



1 **2** **3**

Compounds **1**−**3** show the characteristic M(CO) and MeC=O absorptions in their IR spectra (see Exp. Sect.). The ^1H and ^{13}C NMR spectra of **1**−**3** exhibit the expected signals.

Crystals of **1** suitable for X-ray diffraction were obtained by layering a frozen solution of **2** in CH_2Cl_2 with *n*-pentane. The molecule of **2** (Figure 1) has the classic "piano stool" structure as, for example, in $[FeCp(COCH_3)(CO)(PPh_3)]$.[18] The Fe1−C8 distance [2.042(3) Å] is typical for an iron-carbon σ-bond and of similar length as in $[Co(CH_2$*N*-phthaloyl$)(CO)_4]$ from Marko and co-workers[15] and in $[FeCp(CH_3)(CO)\{Ph_2PN(CH_3)CH(CH_3)Ph\}]$.[19] In the crystal, the Cp rings of different molecules of **1** are arranged in a parallel fashion. Metzler-Nolte et al.[20] have reported the synthesis and structure of $[MoCp(CH_2CH_2$-*N*-phthaloyl$)(CO)_3]$ which is a homologue of the corresponding aminomethyl complex.[14]

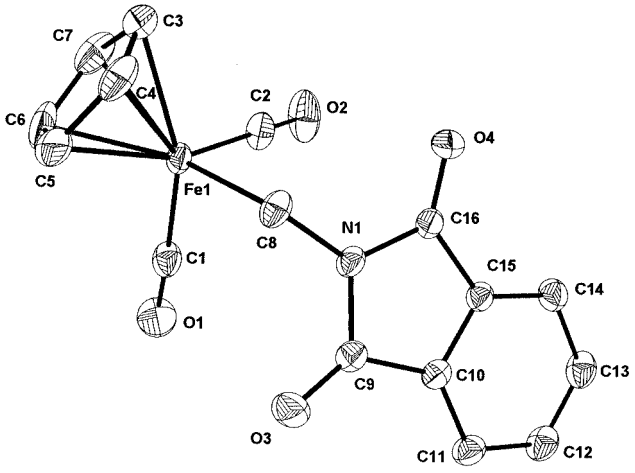


Figure 1. Molecular structure of **2** in the crystal; selected bond lengths (Å) and bond angles (°): Fe(1)−C(1) 1.755(3), O(3)−C(9) 1.204(3), Fe(1)−C(2) 1.750(3), O(4)−C(16) 1.208(3), Fe(1)−C(8) 2.042(3), N(1)−C(8) 1.450(3), O(1)−C(1) 1.144(3), N(1)−C(9) 1.395(3), O(2)−C(2) 1.140(3), N(1)−C(16) 1.391(3); C(2)−Fe(1)−C(1) 93.71(14), O(1)−C(1)−Fe(1) 176.0(3), C(1)−Fe(1)−C(8) 92.77(12), O(2)−C(2)−Fe(1) 177.3(3), C(2)−Fe(1)−C(8) 92.07(12), N(1)−C(8)−Fe(1) 119.7(2), C(16)−N(1)−C(9) 111.4(2), O(3)−C(9)−N(1) 124.9(2), C(16)−N(1)−C(8) 124.1(2), O(4)−C(16)−N(1) 124.6(2), C(9)−N(1)−C(8) 124.2(2)

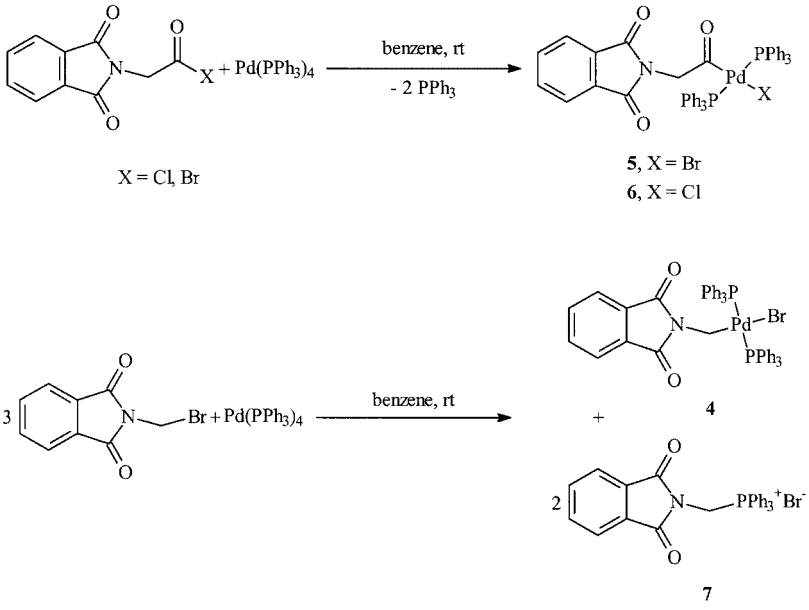
Synthesis of Phthaloylmethyl and -acetyl Complexes of Palladium(II) and Platinum(II)

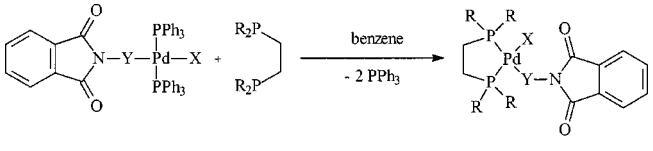
Palladium Complexes

The oxidative addition of organic halides to zero-valent palladium and platinum complexes is a general method for the synthesis of σ-bonded organometallic complexes.[21] This method was successfully applied for the synthesis of the *N*-phthaloylaminomethyl- and -acetylpalladium complexes **4**−**6**, which were prepared from $Pd(PPh_3)_4$ and *N*-phthaloylaminomethyl bromide, *N*-phthaloylaminoacetyl chloride or bromide, respectively. The formation of **4** takes several days (as expected, the methyl bromide is less reactive than the acetyl halides) and here the phosphonium salt **7** is formed as a by-product. A smaller quantity of $Pd(PPh)_4$ than stoichiometrically needed proved to be favourable for good yields of **4**. In a separate experiment it was shown that **7** does not react with $Pd(PPh_3)_4$.

Complexes **4**−**6** decompose slowly in solution. *N*-Phthaloylglycine is formed from **5** and **6** in the presence of moisture. It is interesting to note that complexes **4**−**6** react with the bis(phosphanes) $R_2P(CH_2)_2PR_2$ (R = Ph, C_6H_{11}) to give the complexes **8**−**13**. These reactions proceed by a *trans* → *cis* rearrangement.

In the IR spectra of **4**−**13** the phthaloyl absorptions at 1720 and 1770 cm^{-1} are characteristic. The acetyl carbonyl band of **5**, **6**, **9**, **10**, **12** and **13** is observed between 1660 and 1680 cm^{-1}. In the ^{31}P NMR spectra of **4**−**6** only one signal





	8	9	10	11	12	13
Y	CH_2	$CH_2C(O)$	$CH_2C(O)$	CH_2	$CH_2C(O)$	$CH_2C(O)$
X	Br	Br	Cl	Br	Br	Cl
R	Ph	Ph	Ph	C_6H_{11}	C_6H_{11}	C_6H_{11}

is found, i.e. these complexes are formed as single *trans*-isomers. The X-ray structure determination of **11** (Figure 2) gave bonding parameters which lie in the usual range. Abstraction of halide ions from complexes **4**–**6** and **10**–**12** gives the cationic chelate complexes **14** and **15** in which coordination of one carbonyl oxygen atom of the phthaloyl group takes place.

Interestingly, complexes **14** and **15** are formed from the aminoacetyl complexes **5**, **6**, **11** and **12** by spontaneous decarbonylation, which is probably due to the stability of the formed five-membered chelate ring in **14** and **15** and which should involve alkyl migration.[22] In light of this, the reactions of **5** and **6** to **14** — the *trans* → *cis* isomerisation — can also be understood as being due to an alkyl migration.

The structures of **14** and **15** were confirmed by X-ray diffraction (Figure 3 and 4, respectively). The chelate ring in **14** and **15** has the same structural feature as in the palladium and platinum complexes obtained by oxidative addition of α-bromohippuric acid ester to Pd^0 or Pt^0 and subsequent reaction with $AgBF_4$.[23] An analogous chelate ring is also formed by insertion of imines into the metal–acetyl bond.[7–9] A similar chelate ring is formed from Ni^0 imine complexes and carbon dioxide.[24] The C–Pd–O bite angles in **14** and **15** (82–83°) are very similar to that of the above-mentioned complexes.[7,8,23] The Pd–C bonds in **14** and **15** (2.07–2.08 Å) are longer than that in [Pd{O=C(Ph)NHCHCO$_2$Me}(bipy)]$^+$ [23] which is due to the strong *trans*-influence of the phosphane ligand.

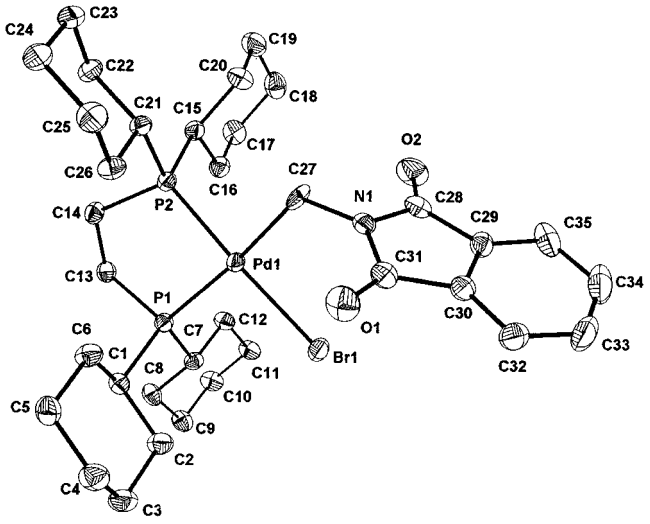
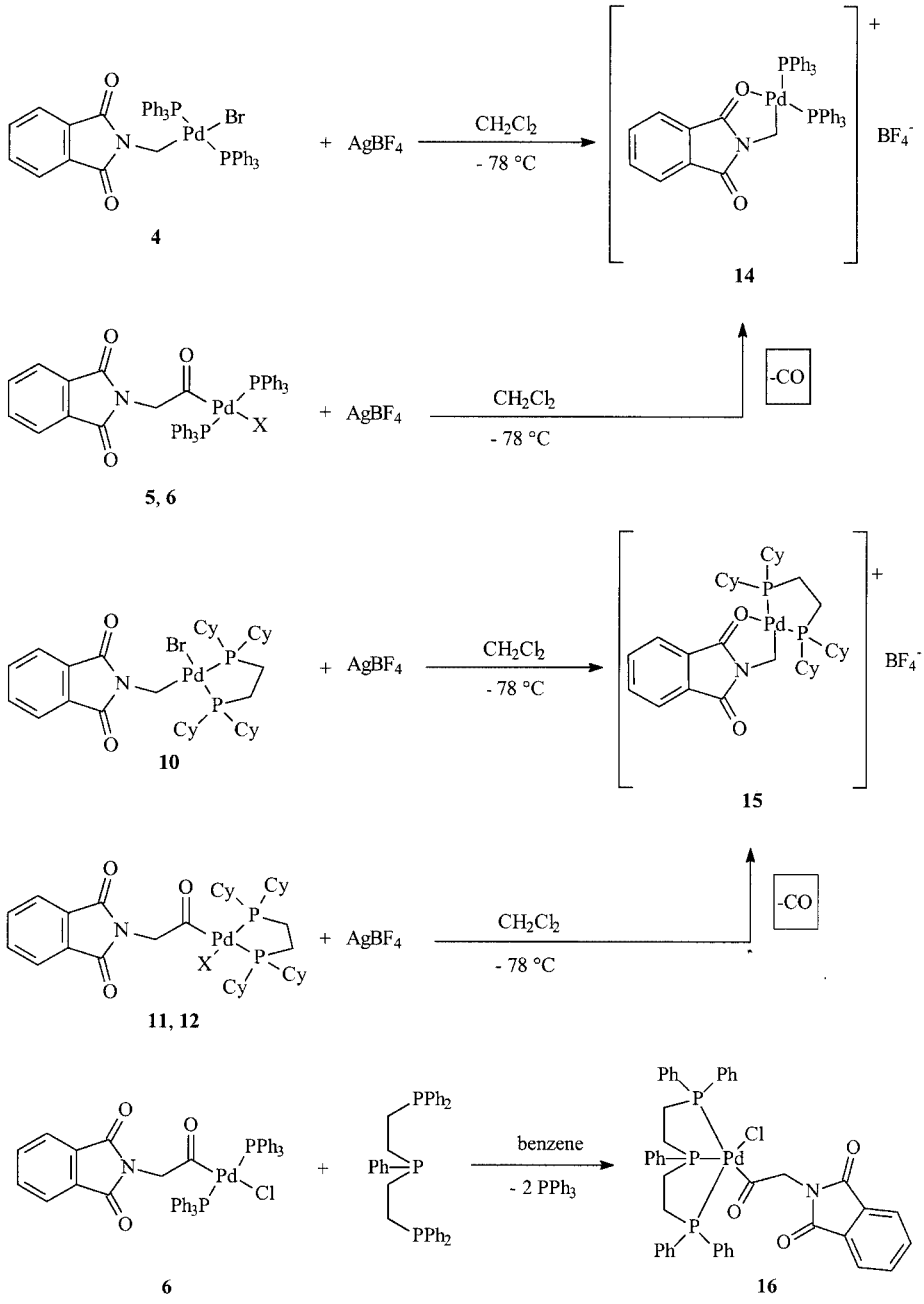


Figure 2. Molecular structure of **11** in the crystal; selected bond lengths (Å) and bond angles (°): Pd(1)–C(27) 2.160(5), N(1)–C(31) 1.402(6), Pd(1)–P(1) 2.3197(13) O(1)–C(31) 1.210(6), Pd(1)–P(2) 2.2324(13) O(2)–C(28) 1.207(6), Pd(1)–Br(1) 2.5068(6), C(28)–C(29) 1.500(7), N(1)–C(27) 1.402(5), C(29)–C(30) 1.365(7), N(1)–C(28) 1.379(6), C(30)–C(31) 1.490(7); C(27)–Pd(1)–P(2) 89.03(12), C(31)–N(1)–C(27) 127.9(5), P(2)–Pd(1)–P(1) 86.66(5), O(1)–C(31)–N(1) 124.8(5), C(27)–Pd(1)–Br(1) 94.32(11), N(1)–C(31)–C(30) 106.3(5), P(1)–Pd(1)–Br(1) 91.25(4), O(1)–C(31)–C(30) 128.9(5), N(1)–C(27)–Pd(1) 115.3(3), O(2)–C(28)–N(1) 124.9(5), C(28)–N(1)–C(27) 121.0(5), N(1)–C(28)–C(29) 106.7(5), C(28)–N(1)–C(31) 110.9(4), O(2)–C(28)–C(29) 128.4(6)

The reaction of **6** with the tridentate ligand $PhP(CH_2CH_2PPh_2)_2$ affords the five-coordinate, 18-electron aminoacetylpalladium complex **16**. The X-ray structure determination (Figure 5) shows the molecule of **16** as a dis-

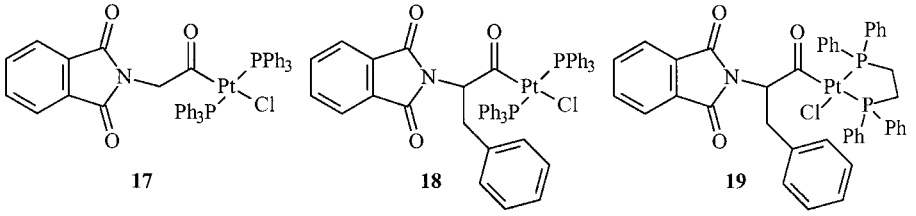


torted trigonal bipyramid with P(1) and P(3) in the axial positions. The P(1), P(3) and Cl(1) atoms lie in a plane (sum of angles 360°). The unusually long Pd−Cl(1) bond (2.69 Å) is remarkable. In the crystal of **16** there are large voids which are occupied by solvent molecules (dichloromethane and *n*-pentane).

Similar five-coordinate palladium and platinum complexes are intermediates in many catalytic reactions,[25] and a series of such complexes with chelate ligands has been isolated and structurally characterised.[25−27]

Platinum Complexes

The platinum complexes **17** and **18** were obtained by oxidative addition of *N*-phthaloylglycyl chloride or *N*-phthaloylphenylalanyl chloride to $[Pt(C_2H_4)(PPh_3)_2]$. The



bis(diphenylphosphanyl)ethane complex **19** was synthesised from **18** by ligand exchange.

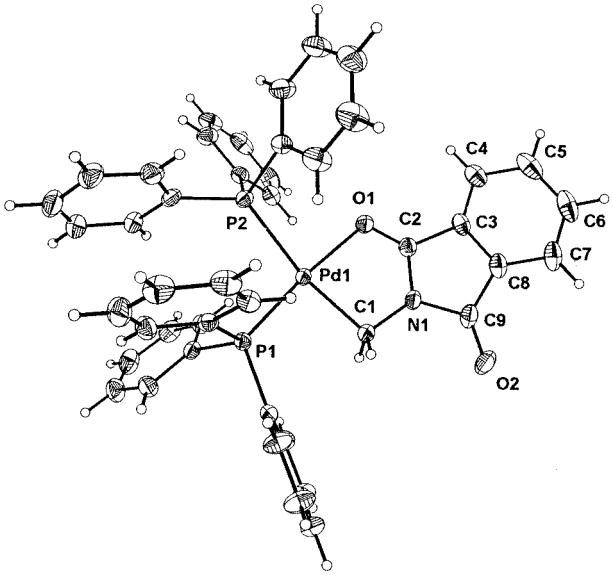


Figure 3. Molecular structure of **14** in the crystal; selected bond lengths (Å) and bond angles (°): Pd(1)−C(1) 2.066(4), N(1)−C(1) 1.454(6), O(2)−C(9) 1.194(6), Pd(1)−P(1) 2.2194(12), N(1)−C(2) 1.341(6), C(2)−C(3) 1.480(6), Pd(1)−P(2) 2.3882(12), N(1)−C(9) 1.429(6), C(8)−C(9) 1.474(8), Pd(1)−O(1) 2.125(3), O(1)−C(2) 1.232(5); C(1)−Pd(1)−O(1) 83.05(15), C(2)−O(1)−Pd(1) 108.0(3), N(1)−C(2)−C(3) 108.9(4), O(1)−Pd(1)−P(2) 87.12(9), C(2)−N(1)−C(9) 111.0(4), O(1)−C(2)−C(3) 127.7(4), C(1)−Pd(1)−P(1) 91.08(13), C(9)−N(1)−C(1) 127.7(4), O(2)−C(9)−C(8) 130.6(5), P(1)−Pd(1)−P(2) 98.50(4), C(2)−N(1)−C(1) 121.0(3), N(1)−C(9)−C(8) 105.0(4), N(1)−C(1)−Pd(1) 103.5(3), O(1)−C(2)−N(1) 123.4(4), O(2)−C(9)−N(1) 124.5(5)

Experiments on the Mechanism of the Palladium-Catalyzed Amidocarbonylation

The proposed mechanism of the palladium-catalysed amidocarbonylation with aldehydes, amides and CO is shown in Scheme 1.[3]

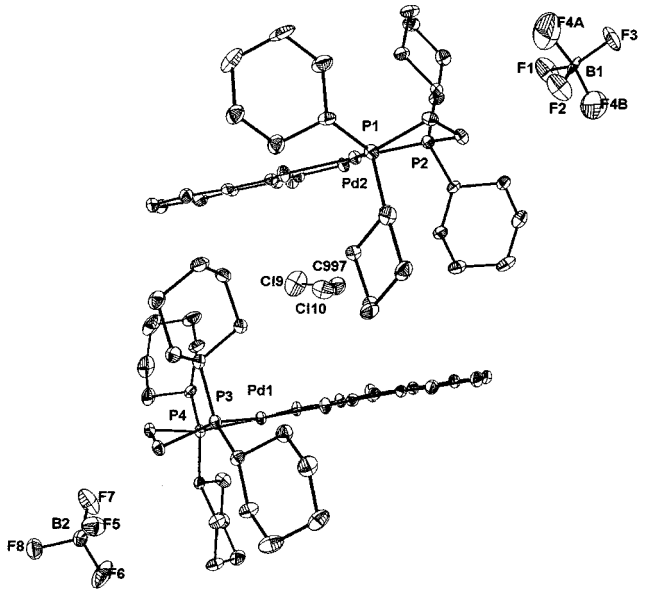
In order to study the elementary steps of the mechanism the palladium-catalysed formation of phthaloylglycine from phthalimide, formaldehyde and CO was chosen as a model system. In the absence of CO and Pd^{2+}, phthalimide reacts with formaldehyde to give *N*-(hydroxymethyl)phthalimide.[13] The chosen reactants seemed to be favourable because phthalimide cannot form an oxazolone ring as side-product and the aldehyde does not carry β-hydrogen atoms. Hence, β-hydride elimination is not possible and a satisfying yield of 55% of the glycine derivative was achieved at 120 °C and 60 bar CO using 0.25 mol % $PdBr_2$ and 0.5 mol % PPh_3 as catalyst in the presence of 35 mol % LiBr and 1 mol % H_2SO_4. The yield strongly decreases at lower temperature (Table 1).

The following results confirm the previously proposed mechanism:[2]

1) With (hydroxymethyl)phthalimide or (bromomethyl)phthalimide as substrate the same yield of phthaloylglycine (55%) is obtained as with phthalimide and paraformaldehyde (Table 1). In many experiments[2] the temperature of 120 °C proved to be favourable. Experiments 3 and 4 in Table 2 demonstrate the need for halide and acid as cocatalysts.

2) Oxidative addition of the organic halide to Pd^0 was verified by the isolation of complex **4** from the reaction of (bromomethyl)phthalimide and $Pd(PPh_3)_4$.

3) The insertion of carbon monoxide into the aminoalkyl−palladium bond (which may occur via alkyl



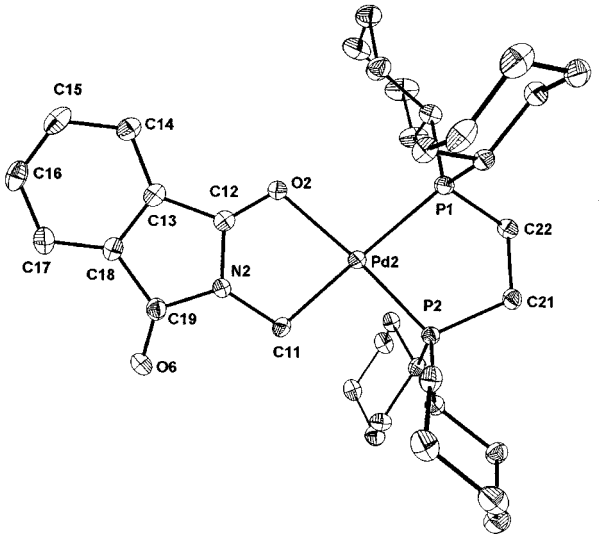


Figure 4. Molecular structure of **15** in the crystal; selected bond lengths (Å) and bond angles (°): Pd(2)−C(11) 2.083(4), N(2)−C(11) 1.464(5), O(6)−C(19) 1.202(5), Pd(2)−P(1) 2.3193(11) N(2)−C(12) 1.364(5), C(12)−C(13) 1.473(5), Pd(2)−P(2) 2.2203(10) N(2)−C(19) 1.403(5), C(18)−C(19) 1.488(6), Pd(2)−O(2) 2.148(3), O(2)−C(12) 1.238(5); C(11)−Pd(2)−O(2) 82.71(12), C(12)−O(2)−Pd(2) 109.4(3), N(2)−C(12)−C(13) 107.6(4), O(2)−Pd(2)−P(1) 98.49(7), C(12)−N(2)−C(19) 111.0(3), O(2)−C(12)−C(13) 129.7(4), C(11)−Pd(2)−P(2) 92.66(11), C(19)−N(2)−C(11) 127.7(3), O(6)−C(19)−C(18) 129.7(4), P(1)−Pd(2)−P(2) 86.12(4), C(12)−N(2)−C(11) 121.1(3), N(2)−C(19)−C(18) 105.9(4), N(2)−C(11)−Pd(2) 104.2(2), O(2)−C(12)−N(2) 122.6(4), O(6)−C(19)−N(2) 124.4(4)

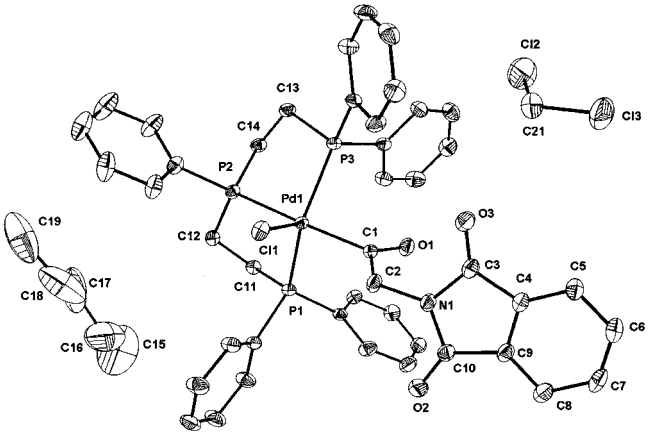
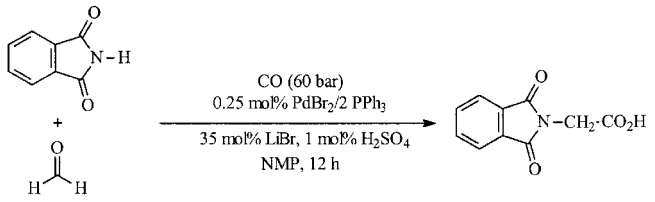


Figure 5. Molecular structure of **16** in the crystal; selected bond lengths (Å) and bond angles (°): Pd(1)−C(1) 2.035(2), Pd(1)−Cl(1) 2.6855(6), C(3)−N(1) 1.399(3), Pd(1)−P(1) 2.3133(6), C(1)−C(2) 1.540(3), N(1)−C(10) 1.379(3), Pd(1)−P(2) 2.3381(6), O(1)−C(1) 1.195(3), O(2)−C(10) 1.214(3), Pd(1)−P(3) 2.3297(6), C(2)−N(1) 1.454(3), O(3)−C(3) 1.195(3); P(1)−Pd(1)−P(2) 85.20(2), C(1)−Pd(1)−P(3) 91.67(6), C(2)−C(1)−Pd(1) 115.07(15) P(1)−Pd(1)−P(3) 137.67(2) P(1)−Pd(1)−Cl(1) 114.10(2) N(1)−C(2)−C(1) 112.64(19) P(3)−Pd(1)−P(2) 85.30(2), P(2)−Pd(1)−Cl(1) 97.626(19) C(10)−N(1)−C(2) 124.8(2), C(1)−Pd(1)−P(1) 89.82(7), P(3)−Pd(1)−Cl(1) 108.02 (2) C(10)−N(1)−C(3) 111.9(2), C(1)−Pd(1)−Cl(1) 93.61(7), O(1)−C(1)−Pd(1) 125.99(17) C(3)−N(1)−C(2) 122-.8(2) C(1)−Pd(1)−P(2) 168.76(7) O(1)−C(1)−C(2) 118.9(2)

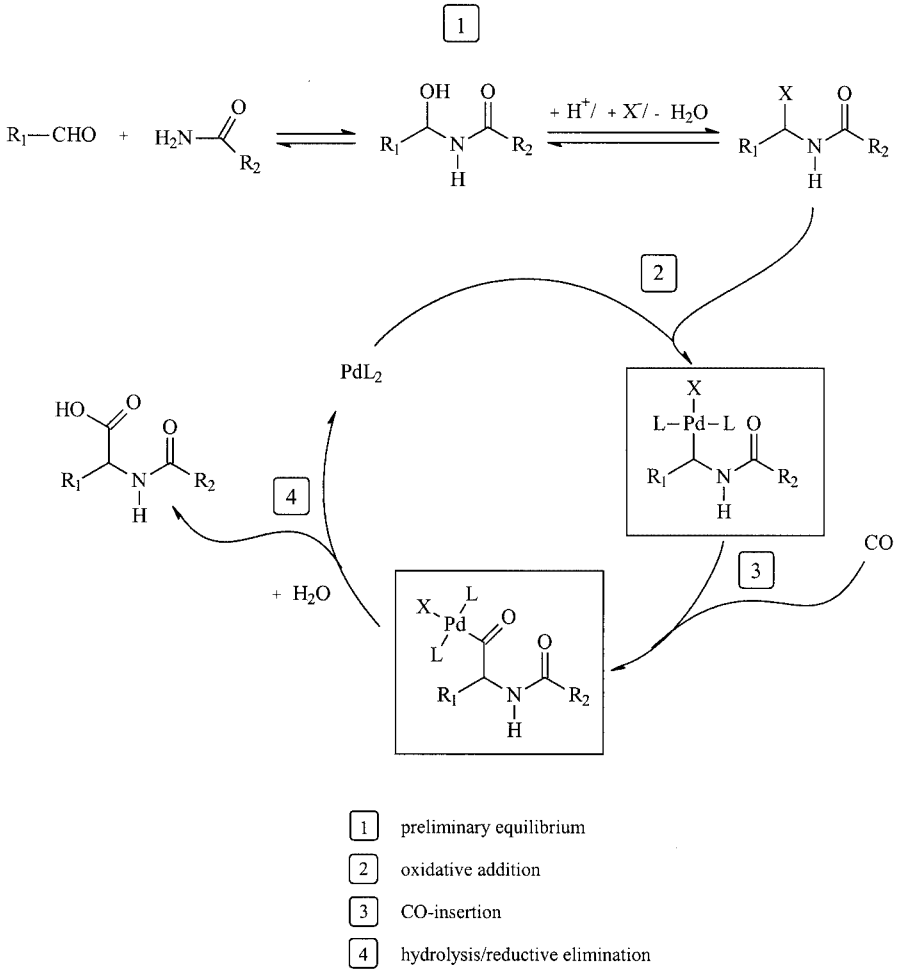
Table 1. Palladium-catalysed amidocarbonylation with the model system phthalimide/formaldehyde



Exp.	Temperature (°C)	Yield (%)[a]
1	80	–
2	100	20
3	120	55

[a] Isolated yield.

migration[22]) has been realized with the alkyl complexes **4** and **8** in CD_2Cl_2 solutions. The reaction was followed by ^{31}P NMR spectroscopy in a high pressure NMR tube. With **4** at 60 °C and 50 bar CO after 180 min the signal (δ = 19.7 ppm) of the acetyl complex **6** was detected (besides



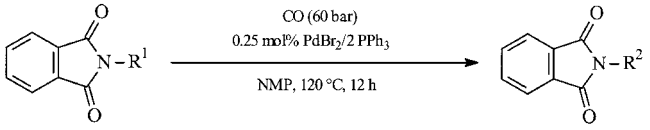
Scheme 1

that of **7** at δ = 21.9 ppm). Similarly, with **8** at 50 bar CO and 130 °C after 1 h two ^{31}P NMR doublets were observed (with low intensity) which correspond to **9**. Obviously the CO insertion is more difficult with **8**, which has a bis(phosphane) chelate ligand.

The reverse decarbonylation reaction has been observed in CH_2Cl_2 solution of **12** where, after 1−2 days at 20 °C, the ^{31}P NMR signals of **11** appeared. Also, the spontaneous decarbonylation of **5**, **6**, **11** and **12** when treated with Ag^+ should be mentioned here.

4) The final step of the catalytic cycle — the hydrolysis of the acetylpalladium complex and formation of palladium(0) and phthaloylglycine — is supported by the observation that *N*-phthaloylglycine and palladium black are formed from solutions of **5** and **6** in CH_2Cl_2 in contact with air. It is remarkable that in entry 6 (Table 2) without addition of water phthaloylglycine was not formed from phthaloylmethyl bromide. Addition of methanol (entry 7, Table 2) gave *N*-phthaloylglycine (20%) and *N*-(methoxy)methylphthalimide (65%) as products.

Table 2. Use of intermediates in the model system phthalimide/formaldehyde



Exp.	R^1	Addition [equiv.]	H_2SO_4 [equiv.]	LiBr [equiv.]	Product yield [%][a] R^2	
1	H	CH_2O [1.0]	0.001	0.35	$-CH_2CO_2H$	55
2	$-CH_2OH$	−	0.01	0.35	$-CH_2CO_2H$	57
3	$-CH_2OH$	−	−	0.35	$-CH_2CO_2H$	10
4	$-CH_2OH$	−	0.01	−	−	
5	$-CH_2Br$	H_2O [1.0]	0.01	−	$-CH_2CO_2H$	48
6	$-CH_2Br$	−	0.01	−	−	
7	$-CH_2Br$	MeOH [1.0]	0.01	−	$-CH_2CO_2Me$ + $-CH_2OMe$	20 65
8	$-CH_2OMe$	−	0.01	−	−	
9	$-CH_2OMe$	−	0.01	0.35	−	

[a] Isolated yield.

5) Finally, the complexes **4**, **5** and **14**, which are possible intermediates in the amidocarbonylation, were used as catalysts for the reaction of phthalimide with paraformaldehyde. Under standard conditions (0.25 mol % complex, 120 °C, 60 bar CO, in NMP, 12 h) *N*-phthaloylglycine was obtained in yields of 48, 45 or 51% which corresponds to the activity of the normal catalyst $PdBr_2{\cdot}2PPh_3$.

In summary, all critical steps of the palladium-catalysed amidocarbonylation (Scheme 1) have been fully established for the model system phthalimide/formaldehyde/CO.

Experimental Section

The complexes $Pd(PPh_3)_4$,[28] $[Pt(C_2H_4)(PPh_3)_2]$[29] *N*-phthaloylglycyl chloride, *N*-phthaloylglycyl bromide[30] and *N*-phthaloylphenylalanyl chloride[31] were prepared according to the literature. The other starting materials were used as purchased.

Pentacarbonyl(*N*-phthaloylaminoacetyl)rhenium(I) (1): Dirheniumdecacarbonyl (700 mg, 1.1 mmol) was added to a mixture of 20.1 g of Na/Hg (6.63 mmol Na) and 25 mL of THF while stirring and cooling to −78 °C. After 1 h, the mixture was allowed to warm up to room temperature and was stirred for 2 h. The dark-red solution was removed with a syringe and added slowly to a solution of 380 mg of *N*-phthaloylglycyl chloride in 15 mL of THF at −78 °C. After 2 h of stirring at room temperature, the suspension was filtered and the filtrate was concentrated in vacuo. The resulting residue was washed several times with water, dried in vacuo and crystallised from CH_2Cl_2/*n*-pentane to give 735 mg of the colourless product (84% yield). ^1H NMR (270 MHz, 25 °C, $CDCl_3$): δ = 7.85−7.60 (m, 4 H, C_6H_4), 4.46 (s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, 25 °C, $CDCl_3$): δ = 246.3 [ReC(O)R], 181.9 [$Re(CO)_5$], 180.7 [$Re(CO)_5$], 167.9 (CON), 134.0, 132.3, 123.4 (C_6H_4), 69.4 (CH_2) ppm. IR (Nujol): $\tilde{\nu}$ = 2141 m, 2066 s, 2039, 2012 s, 1774 w, 1713 s, 1619 s cm^{-1}. $C_{15}H_6NO_8Re$ (514.4): calcd. C 35.02, H 1.18, N 2.72; found C 34.57, H 1.26, N 2.69.

Dicarbonyl(cyclopentadienyl)(*N*-phthaloylaminomethyl)iron(II) (2): Na/Hg (10.24 g, 3.3 mmol Na) was treated with a solution of bis(dicarbonylcyclopentadienyliron) (400 mg, 1.1 mmol) in 20 mL of THF at −78 °C. While stirring, the mixture was allowed to warm up to room temperature. After 3 h, the solution was removed with a syringe and added slowly to a solution of bromomethylphthalimide (456 mg, 1.9 mmol) in 15 mL of THF at −78 °C. The resulting dark red solution was stirred for 2 h at −78 °C and 3 h at room temperature. The colourless precipitate was separated by centrifugation. The dark red solution was concentrated in vacuo and the residue was crystallised from a CH_2Cl_2/*n*-pentane mixture. One of the resulting yellow crystals was selected for X-ray analysis. The rest of the product was dried in vacuo. Yield: 423 mg (66%). ^1H NMR (270 MHz, 25 °C, $CDCl_3$): δ = 7.80−7.20 (m, 4 H, C_6H_4), 4.94 (s, 5 H, C_5H_5), 3.99 (s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, 25 °C, $CDCl_3$): δ = 215.8 [$Fe(CO)_2$], 168.7 (CON), 133.7, 133.4, 122.7, (C_6H_4), 85.4 (C_5H_5), 11.2 ($FeCH_2$) ppm. IR (Nujol): $\tilde{\nu}$ = 2002 s, 1960 s, 1770 m, 1708 s cm^{-1}. $C_{16}H_{11}FeNO_4$ (337.1): calcd. C 57.01, H 3.29, N 4.15; found C 56.83, H 3.24, N 4.14.

Dicarbonyl(cyclopentadienyl)(*N*-phthaloylaminoacetyl)iron(II) (3): Na/Hg (3.66 g, 1.1 mmol Na) was treated with a solution of bis(dicarbonylcyclopentadienyliron) (140 mg, 0.4 mmol) in 15 mL of THF at −78 °C. While stirring, the mixture was allowed to warm up to room temperature. After 3 h, the solution was removed with a syringe and added slowly to a solution of *N*-phthaloylaminoacetyl chloride (180 mg, 0.8 mmol) in 15 mL of THF at −78 °C. The resulting dark solution was stirred for 1 h at −78 °C and 1 h at room temperature. The colourless precipitate was separated by centrifugation. The dark red solution was concentrated in vacuo and the residue was crystallised from a CH_2Cl_2/*n*-pentane mixture to afford 222 mg of yellow crystals (76% yield). ^1H NMR (270 MHz, 25 °C, $CDCl_3$): δ = 7.80−7.50 (m, 4 H, C_6H_4), 4.94 (s, 5 H, C_5H_5), 4.56 (s, 2 H, CH_2) ppm. IR (Nujol): $\tilde{\nu}$ = 2016 s, 1963 s, 1773 w, 1708 s, 1665 s cm^{-1}. $C_{17}H_{11}FeNO_5$ (365.1): calcd. C 55.92, H 3.04, N 3.84; found C 55.52, H 3.10, N 3.96.

***trans*-Bromo(*N*-phthaloylaminomethyl)bis(triphenylphosphane)-palladium(II) (4):** (Bromomethyl)phthalimide (200 mg, 0.83 mmol) was dissolved in 30 mL of benzene and $Pd(PPh_3)_4$ (960 mg, 0.83 mmol) was added at room temperature. After stirring for 2 days the resulting precipitate was separated by centrifugation, and

washed with a small amount of benzene and pentane. The by-product **7** was extracted from the residue with methanol. The remaining solid was dissolved in CH_2Cl_2 and precipitated with pentane. The yellow product was washed with a small amount of benzene and dried in vacuo. Yield: 178 mg (73%). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ = 7.84−7.30 (m, 34 H, C_6H_4, PPh_3), 2.71 (br., 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, 25 °C, CD_2Cl_2): δ = 169.2 (CON), 135.0, 133.1, 131.3, 130.2, 128.3, 128.0, 121.9 (C_6H_4, PPh_3), 54.0 (CH_2) ppm. $^{31}P\{^1H\}$ NMR (109.4 MHz, 25 °C, CD_2Cl_2): δ = 26.8 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3057 w, 1771 w, 1699 s, 1436 s cm^{-1}. $C_{45}H_{36}BrNO_2P_2Pd{\cdot}0.25CH_2Cl_2$ (892.3): calcd. C 60.94, H 4.12, N 1.57; found C 60.91, H 3.92, N 1.47.

***trans*-Bromo(*N*-phthaloylaminoacetyl)bis(triphenylphosphane)palladium(II) (5):** *N*-Phthaloylglycyl bromide (220 mg, 0.77 mmol) was dissolved in 30 mL of benzene and $Pd(PPh_3)_4$ (1202 mg, 0.77 mmol) was added at room temperature. After stirring for 1 h the resulting precipitate was separated by centrifugation, washed with benzene and diethyl ether and dried in vacuo to give 592 mg of the yellow product (76% yield). ^1H NMR (270 MHz, 25 °C, CD_2Cl_2): δ = 7.88−7.25 (m, 34 H, C_6H_4, PPh_3), 4.03 (s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, 25 °C, CD_2Cl_2): δ = 228.8 [PdC(O)R], 166.8 (CON), 135.1, 134.0, 131.8, 130.5, 128.3, 123.2 (C_6H_4, PPh_3), 39.8 (CH_2) ppm. $^{31}P\{^1H\}$ NMR (109.4 MHz, 25 °C, CD_2Cl_2): δ = 19.8 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3054 w, 1772 w, 1719 s, 1684 s, 1436 s cm^{-1}. $C_{46}H_{36}BrNO_3P_2Pd$ (899.1): calcd. C 61.45, H 4.04, N 1.56; found C 61.57, H 4.15, N 1.56.

***trans*-Chloro(*N*-phthaloylaminoacetyl)bis(triphenylphosphane)palladium(II) (6):** *N*-Phthaloylglycyl chloride (132 mg, 0.57 mmol) was dissolved in 20 mL of benzene and $Pd(PPh_3)_4$ (890 mg, 0.57 mmol) was added at room temperature. After stirring for 1 h the resulting precipitate was separated by centrifugation, washed with benzene and diethyl ether and dried in vacuo. The colourless product was obtained in 81% yield (487 mg). ^1H NMR (270 MHz, 25 °C, CD_2Cl_2): δ = 7.72−7.36 (m, 34 H, C_6H_4, PPh_3), 3.96 (s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, 25 °C, CD_2Cl_2): δ = 210.4 [PdC(O)R], 166.6 (CON), 134.8, 133.8, 131.7, 131.0, 130.4, 128.2, 123.0 (C_6H_4, PPh_3), 21.9 (CH_2) ppm. $^{31}P\{^1H\}$ NMR (109.4 MHz, 25 °C, CD_2Cl_2): δ = 20.30 (s) ppm. IR (KBr): $\tilde{\nu}$ = 1770 w, 1716 s, 1660 s, 1437 s cm^{-1}. $C_{46}H_{36}ClNO_3P_2Pd$ (854.6): calcd. C 64.65, H 4.25, N 1.64; found C 64.69, H 4.30, N 1.65.

***N*-Phthaloylaminomethyltriphenylphosphonium Bromide (7):** This compound was obtained as by-product with **4**. Compound **7** was also prepared from bromomethylphthalimide and triphenylphosphane in benzene. ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ = 7.72−7.36 (m, 34 H, C_6H_4, PPh_3), 3.96 (s, 2 H, CH_2) ppm. $^{13}C\{H\}$ NMR (100.5 MHz, 25 °C, CD_2Cl_2): δ = 166.5 (CON), 135.8 (d, $^4J_{P,C}$ = 3 Hz, PPh_3), 135.1 (C_6H_4), 134.5 (d, $^2J_{P,C}$ = 10.0 Hz, PPh_3), 131.0 (C_6H_4), 130.4 (d, $^3J_{P,C}$ = 12.5 Hz, PPh_3), 123.9 (C_6H_4), 116.3 (d, $^1J_{P,C}$ = 84.6 Hz, PPh_3), 35.9 (d, $^1J_{P,C}$ = 57.3 Hz, PCH_2) ppm. $^{31}P\{^1H\}$ NMR (109.4 MHz, 25 °C, CD_2Cl_2): δ = 20.3 (s) ppm. $C_{27}H_{21}BrNO_2P$ (502.3): calcd. C 63.72, H 4.40, N 2.79, Br 15.89; found C 64.56, H 4.21, N 2.67, Br 15.91. The found analyses are from the by-product of **4**.

***cis*-Bromo[1,2-bis(diphenylphosphanyl)ethane](*N*-phthaloylaminomethyl)palladium(II) (8):** *trans*-Bromo(*N*-phthaloylaminomethyl)bis(triphenylphosphane)palladium(II) (**4**; 500 mg, 0.57 mmol) and bis(diphenylphosphanyl)ethane (230 mg, 0.57 mmol) were stirred in 20 mL of benzene for 2 h. The precipitate was separated by centrifugation, washed with benzene and diethyl ether and dried in vacuo to give 318 mg of the yellow product (75% yield). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ = 7.85−7.25 (m, 24 H, C_6H_4, PPh_2), 3.36 (4t, $^3J_{P,H}$ = 6.8 Hz, 2 H, CH_2), 2.41 (m, 2 H, P-CH_2), 2.06 (m, 2 H, P-CH_2) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, 25 °C, CD_2Cl_2): δ = 167.0 (CON), 135.1, 134.0, 131.6, 131.2, 130.6, 128.0, 122.8 (C_6H_4, PPh_2), 49.5 (CH_2); 21.1 (P-CH_2), 19.6 (P-CH_2) ppm. $^{31}P\{^1H\}$ NMR (109.4 MHz, 25 °C, CD_2Cl_2): δ = 58.80 (d, $^2J_{P,P}$ = 32 Hz, 1 P), 36.81 (d, $^2J_{P,P}$ = 32 Hz, 1 P) ppm. IR (KBr): $\tilde{\nu}$ = 3051 w, 2937 w, 1773 w, 1695 s, 1442 s cm^{-1}. $C_{35}H_{30}BrNO_2P_2Pd$ (744.9): calcd. C 56.44, H 4.06, N 1.88; found C 56.80, H 4.15, N 1.86.

***cis*-Bromo[1,2-bis(diphenylphosphanyl)ethane](*N*-phthaloylaminoacetyl)palladium(II) (9):** *trans*-Bromo(*N*-phthaloylaminoacetyl)bis(triphenylphosphane)palladium(II) (**5**; 180 mg, 0.23 mmol) and bis(diphenylphosphanyl)ethane (108 mg, 0.27 mmol) were stirred in 15 mL of benzene for 2 h at room temperature. The precipitate was separated by centrifugation, washed with benzene and diethyl ether and dried in vacuo to give 158 mg of the pale yellow product (89% yield). ^1H NMR (270 MHz, 25 °C, CD_2Cl_2): δ = 7.90−7.10 (m, 24 H, C_6H_4, PPh_2), 4.61 (s, CH_2), 2.42 (m, 2 H, CH_2CH_2), 2.19 (m, 2 H, CH_2CH_2) ppm. $^{31}P\{^1H\}$ NMR (109.5 MHz, 25 °C, CD_2Cl_2): δ = 42.47 (d, $^2J_{P,P}$ = 43 Hz, 1 P), 27.58 (d, $^2J_{P,P}$ = 43 Hz, 1 P). IR (Nujol): $\tilde{\nu}$ = 1771, 1715, 1672, 1435 cm^{-1}. $C_{36}H_{30}BrNO_3P_2Pd$ (772.9): calcd. C 55.94, H 3.91, N 1.88, Br, 10.34; found C 55.82, H 3.52, N 1.78, Br 10.18.

***cis*-Chloro[1,2-diphenylphosphanyl)ethane](*N*-phthaloylaminoacetyl)palladium(II) (10):** Complex **6** (163 mg, 0.19 mmol) and 1,2-bis(diphenylphosphanyl)ethane (80 mg, 0.20 mmol) in 25 mL of benzene were stirred at room temperature. After 30 min a clear solution was obtained and after 2 h a yellow precipitate appeared which was centrifuged off and washed several times with benzene and *n*-pentane. Pale yellow powder. Yield: 109 mg (79%). ^1H NMR (400 MHz, 25 °C, Cd_2Cl_2): δ = 7.87−7.20 (m, 24 H, PPh_2, C_6H_4), 4.64 (s, 2 H, CH_2), 2.47 (m, 2 H, CH_2CH_2), 2.18 (m, 2 H, CH_2CH_2) ppm. $^{31}P\{H\}$ NMR (109.4 MHz, 25 °C, CD_2Cl_2): δ = 44.88 (d, $^2J_{P,P}$ = 41 Hz, 1 P), 28.5 (d, $^2J_{P,P}$ = 41 Hz, 1 P) ppm. IR (Nujol): $\tilde{\nu}$ = 1770, 1716, 1670, 1437 cm^{-1}. $C_{36}H_{30}ClNO_3P_2Pd$ (728.5): calcd. C 59.36, H 4.15, N 1.92; found C 59.53, H 4.50, N 2.01.

***cis*-Bromo[1,2-bis(dicyclohexylphosphanyl)ethane](*N*-phthaloylaminomethyl)palladium(II) (11):** *trans*-Bromo(*N*-phthaloylaminomethyl)bis(triphenylphosphane)palladium(II) (**4**; 167 mg, 0.19 mmol) and bis(dicyclohexylphosphanyl)ethane (81 mg, 0.19 mmol) were stirred in 25 mL of benzene for 2 h at room temperature. The precipitate was separated by centrifugation, washed with benzene and diethyl ether and crystallised from CH_2Cl_2/pentane. One of the resulting yellow crystals was selected for X-ray analysis. The rest were dried in vacuo to afford 102 mg of product (70% yield). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ = 7.70−7.40 (m, 4 H, C_6H_4), 3.46 (pseudo-t, $^3J_{P,H}$ = 6.1 Hz, 2 H), 2.40−1.00 (m, 48 H, C_6H_{11}, CH_2CH_2) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, 25 °C, CD_2Cl_2): δ = 168.7 (CON), 133.7, 132.5, 128.3, 121.8 (C_6H_4), ca. 53.7 (CH_2), 35.8−26.0 (C_6H_{11}), 25.3 (dd, $^1J_{P,C}$ = 27.6, $^2J_{P,C}$ = 21.5 Hz, CH_2), 20.2 (dd, $^1J_{P,C}$ = 19.8, $^2J_{P,C}$ = 19.4 Hz, CH_2) ppm. $^{31}P\{^1H\}$ NMR (109.4 MHz, 25 °C, CD_2Cl_2): δ = 74.02 (d, $^2J_{P,P}$ = 18 Hz, 1 P), 66.34 (d, $^2J_{P,P}$ = 18 Hz, 1 P) ppm. IR (Nujol): $\tilde{\nu}$ = 1770 w, 1701 s, 1417 s. $C_{35}H_{54}BrNO_2P_2Pd$ (769.1): calcd. C 54.66, H 7.08, N 1.82; found C 55.00, H 6.69, N 1.81.

***cis*-Bromo[1,2-bis(dicyclohexylphosphanyl)ethane](*N*-phthaloylaminoacetyl)palladium(II) (12):** *trans*-Bromo(*N*-phthaloylaminoacetyl)bis(triphenylphosphane)palladium(II) (**5**; 152 mg, 0.17 mmol) and bis(dicyclohexylphosphanyl)ethane (72 mg, 0.17 mmol) were stirred in 20 mL of benzene for 2 h at room temperature. The pre-

cipitate was separated by centrifugation, washed with benzene and diethyl ether and dried in vacuo to give 103 mg of the yellow product (88% yield). ^{1}H NMR (270 MHz, 25 °C, CD_2Cl_2): δ = 7.83−7.65 (m, 4 H, C_6H_4), 4.99 (s, 2 H, CH_2), 2.20−1.20 (m, 48 H, C_6H_{11}, CH_2CH_2) ppm. ^{13}C NMR (100.5 MHz, 25 °C, CD_2Cl_2): δ = 206.4 [PdC(O)R], 167.7 (CON), 133.7, 132.5, 123.0 (C_6H_4), 35.0−26.0 (C_6H_{11}), 30.6 (CH_2), 24.5 (dd, $^1J_{P,C}$ = 21.5 Hz, $^2J_{P,C}$ = 27.6 Hz, CH_2CH_2), 19.4 (dd, $^1J_{P,C}$ = 10.4 Hz, $^2J_{P,C}$ = 14.8 Hz, CH_2CH_2) ppm. ^{31}P{^{1}H} NMR (109.4 MHz, 25 °C, CD_2Cl_2): δ = 67.05 (d, $^2J_{P,P}$ = 34 Hz, 1 P), 54.68 (d, $^3J_{P,P}$ = 34 Hz, 1 P) ppm. $C_{36}H_{54}BrNO_3P_2Pd$ (797.1): calcd. C 54.25, H 6.83, N 1.76, Br 10.02; found C 53.94, H 6.92, N 1.66, Br 9.87.

***cis*-Chloro[1,2-bis(diphenylphosphanyl)ethane](*N*-phthaloylaminoacetyl)palladium(II) (13):** Compound **6** (180 mg, 0.21 mmol) and bis(diphenylphosphanyl)ethane (90 mg, 0.21 mmol) were stirred in 30 mL of benzene. After 1 h a clear solution was obtained from which, after 2−3 h, a yellow precipitate appeared. The solid was centrifuged off and washed several times with benzene and *n*-pentane, and dried in vacuo. Yellow powder. Yield: 136 mg (86%). ^{1}H NMR (270 MHz, 25 °C, CD_2Cl_2): δ = 7.85−7.65 (m, 4 H, C_6H_4), 5.04 (s, 2 H, CH_2), 2.25−1.20 (m, 48 H, C_6H_{11}, CH_2CH_2) ppm. ^{31}P{H} NMR (109.4 MHz, 25 °C, CD_2Cl_2): δ = 69.43 (d, $^2J_{P,P}$ = 31 Hz, 1 P), 54.68 (d; $^3J_{P,P}$ = 31 Hz, 1 P). IR (Nujol): $\tilde{\nu}$ = 1767 w, 1714 s, 1677 m, 1436 m cm^{-1}. $C_{36}H_{54}ClNO_3P_2Pd{\cdot}0.25CH_2Cl_2$ (773.9): calcd. C 56.26, H 7.10, N 1.81; found C 56.63, H 7.04, N 1.43.

Complex 14: A solution of **6** (50 mg, 0.06 mmol) in 15 mL of dichloromethane was treated with $AgBF_4$ (12 mg, 0.06 mmol) at −78 °C. The mixture was allowed to warm up to room temperature and was stirred for 4 h. The colourless solid was separated by centrifugation and the yellow solution was concentrated and layered with *n*-pentane. Yellow crystals suitable for X-ray diffraction were obtained. Yield: 38 mg (72%). Complex **14** was also obtained from **4** or **5** using the same procedure. ^{1}H NMR (270 MHz, 25 °C, CD_2Cl_2): δ = 7.80−7.15 (m, 40 H, C_6H_4, PPh_3), 3.22 (pseudo-t, $^3J_{P,H}$ = 2 Hz, 2 H, CH_2) ppm. ^{31}P{H} NMR (109.4 MHz, 25 °C, CD_2Cl_2): δ = 36.42 (br., 1 P), 18.77 (br., 1 P) ppm. IR (Nujol): $\tilde{\nu}$ = 1777 w, 1711 m, 1635 s, 1439 s cm^{-1}. $C_{45}H_{36}BF_4NO_3Pd{\cdot}0.25CH_2Cl_2$ (899.2): calcd. C 60.44, H 4.06, N 1.56; found C 60.44, H 4.23, N 1.53.

Complex 15: A solution of **12** (127 mg, 0.18 mmol) in 20 mL of CH_2Cl_2 was cooled to −78 °C, treated with $AgBF_4$ (35 mg, 0.18 mmol) and stirred for 1 h. Then, the mixture was warmed up to room temperature and was stirred for another 1 h. The solid was separated by centrifugation, the yellow solution was concentrated and the oily residue was stirred in pentane for 12 h, whereby a pale yellow powder was formed, which was centrifuged off and dried in vacuo. The solid was dissolved in CH_2Cl_2 and filtered through celite. The clear, yellow solution was cooled with liquid nitrogen and layered with *n*-pentane. After 2 days pale yellow crystals were obtained which were suitable for X-ray crystallography. Pale yellow powder, 74 mg (53%). Complex **15** was also prepared from **11** or **13**, using the same procedure. ^{1}H NMR (270 MHz, 25 °C, CD_2Cl_2): δ = 7.90−7.70 (m, 4 H, C_6H_4), 3.43 (pseudo-t, $^3J_{P,H}$ = 6.4 Hz, 2 H, CH_3), 2.20−1.20 (m, 48 H, C_6H_{11}, CH_2CH_2) ppm. ^{31}P{^{1}H} NMR (109.4 MHz, 25 °C, CD_2Cl_2): δ = 83.37 (d, $^2J_{P,P}$ = 15 Hz, 1 P), 71.36 (d, $^2J_{P,P}$ = 15 Hz, 1 P) ppm. IR (Nujol): $\tilde{\nu}$ = 1775, 1725, 1636 cm^{-1}. $C_{36}H_{54}BF_4NO_3P_2Pd{\cdot}0.25CH_2Cl_2$ (797.2): calcd. C 53.11, H 6.89, N 1.76; found C 53.39, H 6.77, N 1.59.

[Bis(2-diphenylphosphanylethyl)phenylphosphane]chloro(*N*-phthaloylaminoacetyl)palladium(II) (16): Bis(diphenylphosphanylethyl)phenylphosphane (120 mg, 0.22 mmol) was added to a solution of **6** (130 mg, 0.15 mmol) in 25 mL of benzene and stirred for 3 h. The yellow precipitate was centrifuged off, washed several times with benzene and *n*-pentane and dried in vacuo. The pale yellow powder was dissolved in dichloromethane. The solution was filtered through celite and layered with *n*-pentane. After some days pale yellow crystals were formed which were suitable for X-ray diffraction. Yield 66%. ^{1}H NMR (270 MHz, 25 °C, CD_2Cl_2): δ = 8.00−7.00 (m, 29 H, C_6H_4, PPh_2, PPh), 4.34 (s, 2 H, CH_2), 3.50−2.10 (m, 8 H, $PCH_2CH_2PCH_2CH_2P$) ppm. ^{31}P{^{1}H} NMR (109.4 MHz, 25 °C, CD_2C_2): δ = 80.0 (t, $^2J_{P,P}$ = 36.8 Hz, 1 P, PPh), 35.5 (d, $^2J_{P,P}$ = 36.7 Hz, 2 P, -PPh_2) ppm. IR (Nujol): $\tilde{\nu}$ = 1769 w, 1714 s, 1699 w, 1663 m cm^{-1}. $C_{44}H_{39}ClNO_3P_3Pd$ (864.6): calcd. C 61.13, H 4.55, N 1.62; found C 61.31, H 5.29, N 1.14.

***trans*-Chloro(*N*-phthaloylaminoacetyl)bis(triphenylphosphane)platinum(II) (17):** (η^2-Ethene)bis(triphenylphosphane)platinum(0) (126 mg, 0.17 mmol) was dissolved in 20 mL of benzene and *N*-phthaloylglycyl chloride (67 mg, 0.30 mmol) was added to the yellow solution at room temperature. After stirring for 1 h the resulting precipitate was separated by centrifugation, washed with benzene and diethyl ether and dried in vacuo to give 175 mg of colourless product (93% yield). ^{1}H NMR (270 MHz, 25 °C, $CDCl_3$): δ = 7.50−6.80 (m, 34 H, C_6H_4, PPh_3), 3.30 (s, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, 25 °C, CD_2Cl_2): δ = 210.2 [PtC(O)R], 166.9 (CON), 135.0, 133.4, 132.1, 130.5, 130.1, 128.2, 122.9 (C_6H_4, PPh_3), 59.0 (CH_2) ppm. ^{31}P{^{1}H} NMR (109.4 MHz, 25 °C, CD_2Cl_2): δ = 35.8 (sat), 20.6 (s), 5.3 (sat) ppm; $^1J_{P,Pt}$ = 3330 Hz. IR (KBr): $\tilde{\nu}$ = 1772 w, 1717 s, 1658 s, 1435 s cm^{-1}. $C_{46}H_{36}ClNO_3P_2Pt$ (959.7): calcd. C 58.60, H 3.85, N 1.49; found C 58.60, H 3.87, N 1.41.

***trans*-Chloro(*N*-phthaloylphenylalanyl)bis(triphenylphosphane)platinum(II) (18):** (η^2-Ethene)bis(triphenylphosphane)platinum(0) (340 mg, 0.5 mmol) was dissolved in 25 mL of benzene and *N*-phthaloylphenylalanyl chloride (67 mg, 0.30 mmol) was added to the yellow solution at room temperature. After stirring for 12 h the resulting precipitate was separated by centrifugation, washed with benzene and diethyl ether and dried in vacuo to afford 377 mg of an almost colourless product (73% yield). ^{1}H NMR (270 MHz, 25 °C, $CDCl_3$): δ = 7.90−7.05 (m, 34 H, C_6H_4, PPh_3), 6.87 (m, 3 H, *p*-C_6H_4), 6.50 (m, 2 H, C_6H_4), 3.84 (dd, $^3J_{H,H}$ = 4.1 Hz, $^2J_{H,H}$ = 12.3 Hz, 1 H, CH), 3.02 (dd, $^2J_{H,H}$ = 14.1 Hz, $^3J_{H,H}$ = 4.1 Hz, 1 H, CH_2), 2.74 (dd, $^2J_{H,H}$ = 14.3, $^3J_{H,H}$ = 12.1 Hz, 1 H, CH_2) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, 25 °C, $CDCl_3$): δ = 213.6 [PtC(O)R], 171.4 (CON), 138.0, 135.3, 133.7, 131.6, 130.6, 128.6, 128.0, 126.0, 123.4, 123.1 (C_6H_4, Ph, PPh_3), 60.5 (CH), 41.1 (CH_2) ppm. ^{31}P{^{1}H} NMR (109.4 MHz, 25 °C, $CDCl_3$): δ = 37.4 (sat), 21.8 (s), 6.3 (sat, $^1J_{P,Pt}$ = 3399 Hz), 37.0 (sat), 21.6 (s), 6.1 (sat, $^1J_{P,Pt}$ = 3385 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1776 w, 1714 s, 1654 s, 1438 s cm^{-1}. $C_{53}H_{42}ClNO_3P_2Pt$ (1033.4): calcd. C 61.60, H 4.10, N 1.36; found C 61.21, H 4.06, N 1.23.

***cis*-Chlorobis[1,2(diphenylphosphanyl)ethane](*N*-phthaloylphenylalanyl)platinum(II) (19):** Complex **18** (220 mg, 0.21 mmol) and bis(diphenylphosphanylethane) (84 mg, 0.21 mmol) were stirred in 20 mL of benzene at room temperature. After 1 h a clear yellow solution was obtained. After 1 day stirring the solution was concentrated to 5 mL and diethyl ether was added. The resulting precipitate was centrifuged off, washed several times with diethyl ether and then with pentane and dried in vacuo. Colourless powder. Yield 131 mg (69%). ^{1}H NMR (270 MHz, 25 °C, $CDCl_3$): δ = 8.20−6.80 (m, 29 H, PPh_2, C_6H_5, C_6H_4), 5.07 (m, 1 H, CH), 3.91 (dd, $^2J_{H,H}$ = 14.1 Hz, $^3J_{H,H}$ = 3.3 Hz, CH_2), 2.94 (dd, $^2J_{H,H}$ = 14.1 Hz, $^3J_{H,H}$ = 13.0 Hz, CH_2), 2.30−1.80 (m, 4 H, CH_2CH_2)

Table 3. Crystallographic data for **2**, **11**, **14**, **15** and **16**

	2	**11**	**14**	**15**	**16**
Formula	$C_{16}H_{11}FeNO_4$	$C_{35}H_{54}BrNO_2P_2Pd$	$C_{45}H_{36}BF_4NO_2P_2Pd$	$C_{71}H_{110}B_2Cl_2F_8N_2O_4P_4Pd_2$	$C_{50}H_{53}Cl_3NO_3P_3Pd$
M_r	337.11	769.04	877.90	1636.81	1021.59
Crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	8.2954(8)	11.8160(10)	10.518(3)	11.4737(13)	17.3883(10)
b (Å)	9.7015(11)	19.938(4)	12.860(2)	16.723(2)	15.7147(9)
c (Å)	17.635(2)	15.5380(10)	15.348(4)	21.594(3)	18.4968(10)
α (°)	90	90	97.19	109.956(2)	90
β (°)	92.108(9)	107.64	92.90	93.573(2)	106.3910(1)
γ (°)	90	90	105.80	103.714(2)	90
V (Å^3)	1418.2(3)	3488.4(8)	1974.0(8)	3736.6(8)	4848.9(5)
Z	4	4	2	2	4
$\rho_{calcd.}$ (g·cm^{-3})	1.579	1.464	1.477	1.455	1.399
μ (mm^{-1}]	1.080	1.800	0.610	0.706	0.689
Crystal size (mm)	0.47 × 0.40 × 0.13	0.38 × 0.25 × 0.25	0.40 × 0.35 × 0.30	0.30 × 0.20 × 0.20	0.35 × 0.30 × 0.25
2θ range (°)	2.31−24.97	3.82−50.00	3.96−50.32	2.04−58.72	2.84−58.62
Index range	$0 \le h \le 9$	$-14 \le h \le 1$	$0 \le h \le 12$	$-15 \le h \le 11$	$-22 \le h \le 22$
	$-11 \le k \le 0$	$-23 \le k \le 1$	$-14 \le k \le 14$	$-20 \le k \le 20$	$-20 \le k \le 20$
	$-20 \le l \le 20$	$-17 \le l \le 18$	$-14 \le l \le 14$	$-26 \le l \le 26$	$-23 \le l \le 23$
Collected reflns.	2678	7505	6333	22301	27917
Independent reflns.	2493	61118	5963	11720	9343
R_{int} (%)	0.0075	0.0357	0.0193	0.0344	0.0243
Max./min. transmissions	0.9999/0.8133	1.000/0.825		1.0000/0.8232	1.0000/0.8991
Parameters	688	1592	892	1700	2104
$R1/wR2$ [$F > 4\sigma(F)$]	0.0402/0.0791	0.0463/0.0927	0.0446/0.1165	0.0386/0.0927	0.0295/0.0776
GoF	1.093	1.024	1.032	0.935	0.986
Largest diff. peak and hole [e·Å^{-3}]	0.259/−0.206	0.821/0.514	0.653/−0.783	0.556/−0.582	0.529/−0.469

ppm. $^{31}P\{^1H\}$ NMR (109.5 MHz, 25 °C, CD_2Cl_2): δ = 42.91 (d, sat), 35.89 (d, 1 P), 28.85 (d, sat), $^1J_{P,Pt}$ = 4233.9 Hz; 51.89 (d, sat), 32.54 (d, 1 P), 13.17 (d, sat) ppm; $^1J_{P,Pt}$ = 1539.0, $^2J_{P,P}$ = 5.9 Hz. $C_{43}H_{36}ClNO_3P_2Pt$ (907.2): calcd. C 56.93, H 4.00, N 1.54; found C 56.46, H 4.06, N 1.26.

X-ray Structure Determination: The data in Table 3 were collected on an Enraf Nonius CAD 4 diffractometer (**2**), a Siemens P4 diffractometer (for **11**, **14**) or a Siemens P4 diffractometer with a SMART area detector (for **15**, **16**). CCDC-153852 (**2**), -226832 (**11**), -226831 (**14**), -226833 (**15**) and -226834 (**16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Amidocarbonylation Experiments

The general procedure is described in ref.[2]

1. *N*-Phthaloylglycine: Phthalimide (3.68 g, 25 mmol), paraformaldehyde (0.76 g, 25 mmol), $PdBr_2$ (16.7 mg, 0.0625 mmol) and PPh_3 (33 mg, 0.125 mg, 0.5 mol %) in 25 mL of *N*-methylpyrrolidine were reacted at 120 °C under 60 bar CO in a 300 mL high-pressure reactor for 12 h. The product was recrystallised from water/2-propanol. Isolated yield: 2.82 g (55%); m.p. 193 °C. ^1H NMR (400 MHz, 25 °C, [D$_6$]DMSO): δ = 13.0 (br. s, 1 H, COO*H*), 7.85−7.97 (m, 4 H, *H*-aromat.), 4.32 (s, 2 H, *H*-2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 25 °C, [D$_6$]DMSO): δ = 169.0 (*C*OOH), 167.4 (C-4), 134.9 (*C*-4′), 131.5 (*C*-6), 123.5 (*C*-5), 39.8 (*C*-2) ppm. IR (KBr): $\tilde{\nu}$ = 2985 m, 2936 w, 1773 s, 1724 s, 1416 s, 1247 s cm^{-1}. MS (CI, 70 eV): *m*/*z* = 206 [M + H$^+$], 188 [M + H$^+$ − H_2O], 160 [M$^+$ − CO_2H], 133, 103.

2. Reaction of *N*-(bromomethyl)phthalimide with Methanol and Carbon Monoxide: *N*-(Bromomethyl)phthalimide (1.48 g, 20 mmol), methanol (1 mL, 25 mmol) in 25 mL of NMP, $PdBr_2$ (13.5 mg, 0.05 mol, 0.25 mol %) and PPh_3 (27 mg, 0.1 mmol, 0.5 mol %) were reacted at 120 °C under 60 bar CO for 12 h. The volatile components were removed in vacuo and the residue was taken up in a saturated aqueous solution of $NaHCO_3$, which was then extracted twice with ethyl acetate. The combined organic phases were dried over $MgSO_4$ and the solvent was removed in vacuo. A sample of 1.0 g of the product (3.5 g) was purified by chromatography on silica (100 g, elution with hexane/ethyl acetate, 7:3).

Methyl *N*-Phthaloylglycinate: R_f = 0.28; isolated yield 0.25 g (20%). ^1H NMR (400 MHz, 25 °C, [D$_6$]DMSO): δ = 7.90−8.05 (m, 4 H, *H*-aromat.), 4.50 (s, 2 H, *H*-2), 3.72 (s, 3 H, OC*H*$_3$) ppm. $^{13}C\{1H\}$ NMR (100 MHz, 25 °C, [D$_6$]DMSO): δ = 168.1 (*C*OOH), 167.1 (*C*-4), 134.9 (*C*-4′), 131.4 (*C*-6), 123.5 (*C*-5), 52.5 (O*C*H$_3$), 38.8 (*C*-2) ppm. IR (KBr): $\tilde{\nu}$ = 3475 w, 2977 w, 1774 m, 1751 s, 1727 s, 1423 s, 1399 m, 1374 m, 1224 s cm^{-1}. MS (CI, 70 eV): *m*/*z* = 219 [M$^+$], 188 [M + H$^+$ − CH_3OH], 160 [M$^+$ − CO_2CH_3], 133, 104, 76.

***N*-(Methoxymethyl)phthalimide:** R_f = 0.5; isolated yield 0.70 g (65%). ^1H NMR (400 MHz, 25 °C, [D$_6$]DMSO): δ = 7.88−7.93 (m, 4 H, *H*-aromat.), 4.95 (s, 2 H, *H*-2), 3.28 (s, 3 H, OC*H*$_3$) ppm. $^{13}C\{1H\}$ NMR (100 MHz, 25 °C, [D$_6$]DMSO): δ = 167.8 (*C*-4), 134.9 (*C*-4′), 131.4 (*C*-6), 123.6 (*C*-5), 68.4 (*C*-2), 52.5 (O*C*H$_3$) ppm. MS (CI, 70 eV): *m*/*z* = 191 [M$^+$], 160, 133, 104, 76.

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[1] H. Wakamatsu, J. Uda, N. Yamakami, *J. Chem. Soc., Chem. Commun.* **1971**, *1540*; DEB **1971**, 2115 985 (*Chem. Abstr.* **1972**, *76*, 25 585); H. Wakamatsu, *Kagaku* **1989**, *44*, 448.

[2] M. Beller, M. Eckert, *Angew. Chem.* **2000**, *112*, 1026−1044; *Angew. Chem. Int. Ed.* **2000**, *39*, 1010−1027; M. Beller, M. Eckert, F. Vollmüller, S. Bogdanovic, H. Geissler, *Angew. Chem.* **1997**, *109*, 1534−1536; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1494−1496; M. Beller, M. Eckert, F. Vollmüller, *J. Mol. Cat.* **1998**, *135*, 23−33; D. Gördes, H. Neumann, A. Jacobi von Wangelis, C. Fischer, K. Drauz, H.-P. Krimmer, *Adv. Synth. Catal.* **2003**, *345*, 510−516; M. Beller, W. A. Moradi, M. Eckert, H. Neumann, *Tetrahedron Lett.* **1999**, *40*, 4523−4526.

[3] Ch. Easton, C. A. Hutton, *Synlett* **1998**, 457. It is of interest that H. Wakamatsu, the pioneer in organometallic amino acid chemistry, in his bachelor thesis used phthaloylamino acid for the synthezis of phthaloyl peptide esters: K. Yamashita, H. Wakamatsu, Y. Sahashi, *J. Agr. Chem. Soc., Jpn.* **1953**, *27*, 649−652.

[4] E. W. Abel, R. J. Rowley, *J. Chem. Soc., Dalton Trans.* **1975**, 1096−1099; C. W. Fong, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* **1975**, 1100−1104; M. Matsumoto, K. Nakatsu, K. Tani, A. Nakamura, S. Otsuka, *J. Am. Chem. Soc.* **1974**, *96*, 6777−6778; S. S. Crawford, G. Firestein, H. D. Kaesz, *J. Organomet. Chem.* **1975**, *91*, C57−C60; D. J. Sepelak, C. G. Pierpont, E. K. Barefield, J. T. Budz, C. A. Poffenberger, *J. Am. Chem. Soc.* **1976**, *98*, 6178−6185.

[5] G. N. Schrauzer, R. J. Windgassen, *Nature* **1967**, *214*, 492; G. L. Blackmer, T. M. Vickrey, J. N. Marx, *J. Organomet. Chem.* **1974**, *72*, 261−267.

[6] A. L. Poznyak, V. I. Pavlovski, *Angew. Chem.* **1988**, *100*, 812−819; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 789−795; *Z. Anorg. Allg. Chem.* **1982**, *485*, 225−233; A. L. Poznyak, V. I. Pavloski, E. B. Chuklanova, T. N. Polynova, M. A. Porai-Koshits, *Monatsheft Chem.* **1982**, *113*, 561−564; E. Natarajan, P. Natarajan, *Inorg. Chem.* **1992**, *31*, 1215−1220; R. M. Hartshorn, S. G. Telfer, *Dalton* **1999**, 3565−3571; R. M. Hartshorn, S. G. Telfer, *J. Chem. Soc., Dalton Trans.* **2000**, 2801−2808; S. Das, G. R. A. Johnson, N. B. Nazhat, R. Saadalla-Nazhat, *J. Chem. Soc., Faraday Trans. I* **1984**, *80*, 2759−2766; D. M. Tonei, L.-J. Baker, P. J. Brothers, G. R. Clark, D. C. Ware, *Chem. Commun.* **1998**, 2593−2594 and references cited therein.

[7] R. D. Dghaym, K. J. Yaccato, B. A. Arndtsen, *Organometallics* **1998**, *17*, 4−6; S. Kacker, J. S. Kim, A. Sen, *Angew. Chem.* **1998**, *110*, 1335−1337; *Angew. Chem. Int. Ed.* **1998**, *37*, 1251−1253; L. Cavallo, *J. Am. Chem. Soc.* **1999**, *121*, 4238−4241; R. D. Dghaym, R. Dhawan, B. A. Arndtsen, *Angew. Chem.* **2001**, *113*, 3328−3330; *Angew. Chem. Int. Ed.* **2001**, *40*, 3228−3230.

[8] J. L. Davis, B. A. Arndtsen, *Organometallics* **2000**, *19*, 4657−4659.

[9] D. Lafrance, J. L. Davis, R. Dhawan, B. A. Arndtsen, *Organometallics* **2001**, *20*, 1128−1136.

[10] R. Huisgen, H. Gotthardt, H. O. Bayer, F. C. Schaefer, *Angew. Chem.* **1964**, *76*, 185−186; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 136−137; H. O. Bayer, R. Huisgen, R. Knorr, F. C. Schaefer, *Chem. Ber.* **1970**, *103*, 2581−2597; E. Funke, R. Huisgen, *Chem. Ber.* **1971**, *104*, 3222−3228.

[11] R. Dhawan, R. D. Dghaym, B. A. Arndtsen, *J. Am. Chem. Soc.* **2003**, *125*, 1474−1475.

[12] M. Steinmetz, H. Werner, *J. Organomet. Chem.* **1989**, *369*, 309−319.

[13] G. L. Blackmer, Ch.-W. Tsai, *J. Organomet. Chem.* **1978**, *155*, C17−C20.

[14] W. Beck, W. Petri, *J. Organomet. Chem.* **1977**, *127*, C40; W. Petri, W. Beck, *Chem. Ber.* **1984**, *117*, 3265−3269.

[15] I. Nagy-Gergely, G. Szalontai, F. Ungváry, L. Markó, M. Moret, A. Sironi, C. Zucchi, A. Sisak, C. M. Tschoerner, A. Martinelli, A. Sorkau, G. Pályi, *Organometallics* **1997**, *16*, 2740−2742.

[16] R. W. Hungate, F. Miller, M. S. Goodman, *Tetrahedron Lett.* **1988**, *29*, 4273−4276.

[17] C. Amiens, G. Balavoine, F. Guibé, *J. Organomet. Chem.* **1993**, *443*, 207−219.

[18] I. Bernal, H. Brunner, M. Muschiol, *Inorg. Chim. Acta* **1988**, *142*, 235−242; R. E. Marsh, *Inorg. Chim. Acta* **1989**, *157*, 1−2; H. Y. Liu, L. L. Koh, K. Eriks, W. P. Giering, A. Prock, *Acta Crystallogr. Sect.* **1990**, *C 46*, 51−54.

[19] H. Brunner, B. Hammer, I. Bernal, M. Draux, *Organometallics* **1983**, *2*, 1595−1603; s. auch: S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton, M. Whittaker, *J. Am. Chem. Soc.* **1987**, *109*, 5711−5719.

[20] A. Hess, O. Brosch, T. Weyhermüller, N. Metzler-Nolte, *J. Organomet. Chem.* **1999**, *589*, 75−84.

[21] A. J. Canty, G. K. Anderson, in *Comprehensive Organometallic Chemistry II* (Eds.: R. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press. **1995**, *9*, 233, 433.

[22] F. Calderazzo, *Angew. Chem.* **1977**, *89*, 365−317; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 299−310; B. A. Markies, D. Kruis, M. H. P. Prietveld, K. A. N. Verkerk, J. Boersma, H. Kooijam, M. T. Lakin, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1995**, *117*, 5263−5274 and references cited therein; K. Frankcombe, K. Cavell, R. Knott, B. Yates, *Chem. Commun.* **1996**, 781−782; A. J. Canty, in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), *Pergamon*, Pr*ess* **1995**, *9*, 255−256.

[23] B. Kayser, C. Missling, J. Knizek, H. Nöth, W. Beck, *Eur. J. Inorg. Chem.* **1998**, 375−379.

[24] D. Walther, *Z. Chem.* **1989**, *29*, 146.

[25] L. Maresca, G. Natile, *Comments Inorg. Chem.* **1993**, *14*, 349−366; M. E. Cucciolito, A. Panunzi, F. Ruffo, V. G. Albano, M. Monari, *Organometallics* **1999**, *18*, 3482−3489; V. G. Albano, G. Natile, A. Panunzi, *Coord. Chem. Rev.* **1994**, *133*, 67−114; V. G. Albano, M. Monari, I. Orabona, Panunzi, G. Roviello, F. Ruffo, *Organometallics* **2003**, *22*, 1223−1230.

[26] See, for example: R. Garrone, A. M. Romano, R. Santi, R. Millini, *Organometallics* **1998**, *17*, 4519−4522 and references cited therein.

[27] S. Aizawa, T. Iida, S. Funahashi, *Inorg. Chem.* **1996**, *35*, 5163−5167.

[28] D. R. Coulson, *Inorg. Synth. XIII*, 121.

[29] U. Nagel, *Chem. Ber.* **1982**, *115*, 1998−1999.

[30] S. Gabriel, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 2647−2650.

[31] R. Pfaehler, *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 1700−1702.

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