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Journal of Organometallic Chemistry 490 (1995) 35–43

Journal of Organometallic Chemistry

Metal complexes of biologically important ligands: synthesis of amino acidato complexes of Pd^{II} containing a *C,N*-cyclometallated group as an ancillary ligand

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Received 21 June 1994

Abstract

New amino acidato complexes of Pd^{II} of stoichiometry [Pd(C–N)(Aa)] (C–N = *C,N*-cyclometallated ligand, Aa = *N,O*-amino acidato ligand) have been obtained by reaction of [Pd(C–N)(acac)] (C–N = *N,N*-dimethylbenzylamine-C^2,*N* (dmba) (**1**) or *N,N*-dimethyl(*S*-α-phenylethyl)amine-C^2,*N* (*S*-dmphea) (**2**)) with glycine, chiral amino acids (alanine, phenylalanine and valine), and amino acid derivatives (*N*-acetylglycine and *N*-acetyl-α,β-dehydroalanine) in MeOH. The compounds are characterized by IR, ^{1}H and ^{13}C NMR. The geometry of these complexes has been unambiguously determined by NOE difference experiments and NOESY measurements.

Keywords: Palladium; Cyclometallated; Amino acid complexes

1. Introduction

The chemistry of palladium(II) complexes containing amino acidato ligands has undergone fast growth in recent years [1,2]. This interest began with the discovery of Rosenberg et al. that certain Group 10 metal complexes (mainly Pt complexes) exhibit carcinostatic activity [3]. This was the starting point of systematic and extensive research work in this area, which included not only the chemical behaviour of this kind of complex, but pharmaceutical and biological properties too.

These properties are related closely to the stereochemistry of the compounds, and it is clear from the active complexes discovered that *cis* displaceable ligands are necessary, and therefore the "carrier" ligand(s) should occupy *cis* coordination sites in a four-coordinate planar complex. Bidentate ligands remove the possibility of *cis* complex isomerizing into the thermodynamically more stable *trans* configuration, and an amino acid anion seems to be a good choice. Some Pd^{II} complexes with nitrogen or oxygen donors also exhibit potential antitumour activity [4].

In the course of our research into the chemistry of *C,N*-cyclometallated derivatives [5], we have tried to synthesise new amino acidato complexes of Pd^{II} containing a *C,N*-cyclometallated group as ancillary ligand. The cyclometallated groups choosen were dmba (*N,N*-dimethylbenzylamine-C^2,*N*) and *S*-dmphea (*N,N*-dimethyl(*S*-α-phenylethyl)-amine-C^2,*N*), the last one acting as a source of chirality. Chiral *C,N*-cyclopalladated groups can be useful for the resolution of racemic mixtures and the assignment of the absolute configuration of optically active ligands [6]. Moreover, the use of a chiral ancillary ligand provides the possibility of exploring the diastereoselectivity (or not) of the synthetic process.

2. Results and discussion

As we have previously described [7], the acetylacetonate is easily displaced from the Pd(acac-*O,O'*) complexes in reactions with substrates containing acidic H atoms. For this reason, we have chosen complexes of

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SSDI 0022-328X(94)05204-2

stoichiometry [Pd(C–N)(acac)] (**1**), (**2**) as starting materials in reactions with amino acids.

Acetylacetonate complexes [Pd(dmba)(acac)] (**1**) and [Pd(*S*-dmphea)(acac)] (**2**) were obtained by treatment of the corresponding chlorine-bridged derivatives with the stoichiometric amount of Tl(acac) in dichlorometh-

Table 1
^{1}H NMR data (δ, ppm; J, Hz) for complexes (**1**)–(**15**)

Complex	Resonances for the C–N group	Resonances for the amino acidate or acac groups
(**1**) [a]	7.3 (m, 1H), 7.0 (m, 2H), 6.9 (m, 1H) (C_6H_4), 2.89 (s, 2H, CH_2N), 2.81 (s, 6H, NMe_2)	5.30 (s, 1H, CH-acac), 2.00, 1.93 (2s, 6H, CH_3-acac)
(**2**) [a]	7.3 (m, 1H), 7.0 (m, 2H), 6.8 (m, 1H) (C_6H_4), 3.90 (q, 1H, CH, $^3J_{H-H}$ = 6.6 Hz), 2.88, 2.62 (2s, 6H, NMe_2), 1.49 (d, 3H, CH_3)	5.30 (s, 1H, CH-acac), 2.00, 1.93 (2s, 6H, CH_3-acac)
(**3**) [b]	6.9 (m, 2H), 6.8 (m, 2H) (C_6H_4), 3.9 (s, 2H, CH_2N), 2.7 (s, 6H, NMe_2)	4.64 (t, 2H, NH_2, $^3J_{H-H}$ = 6.6 Hz), 3.17 (t, 2H, CH_2)
(**4**) [b]	7.0–6.7 (m, 4H, C_6H_4), 3.86 (AB system, not resolved, 2H, CH_2N), 2.69 (s, 6H, NMe_2)	4.87 (m, 1H, NH), 4.33 (m, 1H, NH), 3.25 (q, 1H, CH, $^3J_{H-H}$ = 6.6 Hz), 1.27 (d, 3H, CH_3)
(**5**) [b]	6.88 (m, 2H), 6.75 (m, 2H) (C_6H_4) 3.85, 3.75 (AB system, 2H, CH_2N, $^2J_{H-H}$ = 15.0 Hz), 2.63, 2.53 (2s, 6H, NMe_2)	7.35–7.10 (m, 5H, Ph), 4.90 (m, 1H, NH), 4.00 (m, 1H, NH), 3.45 (m, 1H, CH), 3.15, 2.95 (AB system no resolved, 2H, CH_2)
(**6**) [a]	6.95 (m, 3H), 6.71 (d, 1H, $^3J_{H-H}$ = 7.2 Hz) (C_6H_4), 3.78 (s, 2H, CH_2N), 2.81, 2.78 (2s, 6H, NMe_2)	3.84 (m, 1H, NH), 3.45 (m, 1H, C*H*^{i}Pr), 2.50 (m, 2H, NH + C*H*Me_2), 1.13, 1.10 (2d, 6H, CH*Me*$_2$, $^3J_{H-H}$ = 6.90 Hz)
(**7**) [a]	7.00–6.82 (m, 5H, C_6H_4 + NH), 3.57, 3.09 (AB system, 2H, CH_2N, $^2J_{H-H}$ = 13.7 Hz), 2.75, 2.04 (2s, 6H, NMe_2)	4.19, 4.04 (AB system [c], 2H, CH_2, $^2J_{Ha-Hb}$ = 17.85 Hz, $^3J_{Ha-NH}$ = 6.30 Hz, $^3J_{Hb-NH}$ = 4.95 Hz), 2.07 (s, 3H, $C(O)CH_3$)
(**8**) [a]	7.00–6.80 (m, 4H, C_6H_4), 3.58, 3.12 (AB system, 2H, CH_2N $^2J_{H-H}$ = 13.9 Hz), 2.84, 1.99 (2s, 6H, NMe_2)	8.06 (s, 1H, NH), 6.37 (s, 1H, $=CH_2$), 5.87 (s, 1H, $=CH_2$) 2.11 (s, 3H, $C(O)CH_3$)
(**9**) [a]	7.00–6.90 (m, 2H), 6.80 (d, 1H, $^3J_{H-H}$ = 6.6 Hz), 6.74 (d, 1H, $^3J_{H-H}$ = 7.2 Hz) (C_6H_4), 3.86 (q, 1H, CH, $^3J_{H-H}$ = 6.6 Hz), 2.84, 2.60 (2s, 6H, NMe_2), 1.41 (d, 3H, CH_3)	3.80 (m, 1H, NH), 3.67 (m, 1H, NH), 3.66, 3.64 (AB system, no resolved, 2H, CH_2)
(**10a**) [a]	6.98 (t, 1H, $^3J_{H-H}$ = 7.2 Hz), 6.91 (t, 1H, $^3J_{H-H}$ = 7.2 Hz), 6.82 (d, 1H), 6.72 (d, 1H) (C_6H_4), 3.81 (q, 1H, CH, $^3J_{H-H}$ = 6.6 Hz), 2.82, 2.62 (2s, 6H, NMe_2), 1.43 (d, 3H, CH_3)	4.10 (m, 1H, NH), 3.72 (q, 1H, CH, $^3J_{H-H}$ = 6.6 Hz), 2.78 (m, 1H, NH) 1.58 (d, 3H, CH_3)
(**10a, 10b**) [a]	6.99 (t, 2H, $^3J_{H-H}$ = 7.2 Hz), 6.91 (t, 2H, $^3J_{H-H}$ = 7.2 Hz), 6.84 (d, 1H), 6.83 (d, 1H), 6.72 (d, 1H), 6.71 (d, 1H) (C_6H_4) 3.86 (q, 1H, CH, *R*-isomer, $^3J_{H-H}$ = 6.6 Hz), 3.83 (q, 1H, CH, *S*-isomer, $^3J_{H-H}$ = 6.6 Hz), 2.88, 2.63 (2s, 6H, NMe_2, *R*-isomer), 2.83, 2.62 (2s, 6H, NMe_2, *S*-isomer), 1.46 (d, 3H, CH_3, *R*-isomer), 1.42 (d, 3H, CH_3, *S*-isomer)	4.18 (m, 1H, NH, *S*-isomer), 4.00 (m, 1H, NH, *R*-isomer), 3.73 (q, 2H, CH), 2.76 (m, 1H, NH, *S*-isomer), 2.68 (m, 1H, NH, *R*-isomer), 1.59 (d, 3H, CH_3), 1.57 (d, 3H, CH_3)
(**11a**) [a]	6.98 (t, 1H, $^3J_{H-H}$ = 7.2 Hz), 6.86 (t, 1H, $^3J_{H-H}$ = 7.2 Hz), 6.76 (d, 1H), 6.49 (d, 1H) (C_6H_4), 3.66 (q, 1H, CH, $^3J_{H-H}$ = 6.6 Hz), 2.72, 2.56 (2s, 6H, NMe_2), 1.28 (d, 3H, CH_3)	7.30–7.20 (m, 5H, Ph), 3.97 (m, 1H, NH), 3.80 (m, 1H, CH), 3.50, 3.27 (AB system [c], 2H, CH_2, $^2J_{Ha-Hb}$ = 14.10 Hz, $^3J_{Ha-NH}$ = 3.60 Hz, $^3J_{Hb-NH}$ = 10.50 Hz), 2.51 (m, 1H, NH).
(**11a, 11b**) [a]	6.98 (m, 2H), 6.82 (m, 4H), 6.50 (d, 2H, $^3J_{H-H}$ = 6.6 Hz), 3.73 (m, 2H, CH), 2.83, 2.59 (2s, 6H, NMe_2, *R*-isomer) 2.76, 2.58 (2s, 6H, NMe_2, *S*-isomer), 1.42 (d, 3H, CH_3, *R*-isomer, $^3J_{H-H}$ = 6.6 Hz), 1.35 (d, 3H, CH_3, *S*-isomer, $^3J_{H-H}$ = 6.6 Hz)	7.30–7.20 (m, 10H, Ph), 4.04 (m, 1H, NH, *S*-isomer), 3.84 (m, 3H, NH, *R*-isomer + CH), 3.47, 3.25 (2m, 4H, CH_2, 2 AB overlapped systems), 2.66 (m, 1H, NH, *R*-isomer), 2.49 (m, 1H, NH, *R*-isomer)
(**12a**) [a]	7.00 (t, 1H, $^3J_{H-H}$ = 7.2 Hz), 6.92 (t, 1H, $^3J_{H-H}$ = 7.2 Hz), 6.81 (d, 1H), 6.72 (d, 1H) (C_6H_4), 3.73 (q, 1H, CH, $^3J_{H-H}$ = 6.6 Hz), 2.80, 2.60 (2s, 6H, NMe_2), 1.38 (d, 3H, CH_3)	3.50 (m, 2H, NH + C*H*^{i}Pr), 2.47 (m, 2H, NH + C*H*Me_2), 1.15 (d, 3H, CH*Me*$_2$, $^3J_{H-H}$ = 7.2 Hz), 1.13 (d, CH*Me*$_2$, 3H, $^3J_{H-H}$ = 7.2 Hz)
(**12a, 12b**) [a]	6.99 (m, 2H), 6.91 (m, 2H), 6.84 (m, 2H), 6.71 (m, 2H) 3.97 (m, 1H, CH, *R*-isomer), 3.79 (m, 1H, CH, *S*-isomer) 2.88 (s, 3H, NMe_2, *R*-isomer), 2.83 (s, 3H, NMe_2, *S*-isomer) 2.62 (s, 6H, NMe_2, *R* + *S*-isomers), 1.44 (d, 6H, CH_3, *R* + *S*-isomers)	4.03 (m, 1H, NH, *S*-isomer), 3.77 (m, 1H, NH, *R*-isomer), 3.49 (m, 2H, C*H*^{i}Pr), 2.47 (m, 4H, NH + C*H*Me_2, *R* + *S* isomers), 1.12 (d, 6H, CH*Me*$_2$, *R* + *S*-isomers, $^3J_{H-H}$ = 6.6 Hz), 1.10 (d, CH*Me*$_2$, 6H, *R* + *S*-isomers, $^3J_{H-H}$ = 6.6 Hz)
(**13**) [a]	6.99–6.90 (m, 3H), 6.62 (d, 1H, $^3J_{H-H}$ = 6.9 Hz) (C_6H_4) 3.63 (q, 1H, CH, $^3J_{H-H}$ = 6.3 Hz), 2.55, 2.09 (2s, 6H, NMe_2) 1.05 (d, 3H, CH_3)	7.09 (s, 1H, NH), 4.19, 4.07 (AB system [c], 2H, CH_2, $^2J_{Ha-Hb}$ = 18.0 Hz, $^3J_{Ha-NH}$ = 5.0 Hz, $^3J_{Hb-NH}$ = 5.0 Hz), 2.05 (s, 3H, $COCH_3$)
(**14**) [a]	7.00–6.90 (m, 3H), 6.63 (d, 1H, $^3J_{H-H}$ = 6.3 Hz) (C_6H_4) 3.66 (q, 1H, CH, $^3J_{H-H}$ = 6.3 Hz), 2.63, 2.06 (2s, 6H, NMe_2) 1.05 (d, 3H, CH_3)	8.07 (s, 1H, NH), 6.36 (s, 1H, $=CH_2$), 5.87 (s, 1H, $=CH_2$), 2.11 (s, 3H, $COCH_3$)
(**15**) [a]	7.21 (s, 1H), 6.84 (s, 3H) (C_6H_4), 3.44 (s, 2H, CH_2N), 2.37 (s, 6H, NMe_2)	3.65 (s, broad, 4H, CH_2 + NH_2) 1.54 (s, br, 6H, $P(CH_2CH_3)_3$), 1.05 (s, br, 9H, $P(CH_2CH_3)_3$)

[a] In $CDCl_3$; [b] In DMSO-d_6; [c] AB part of an ABX system.

Table 2
$^{13}C\{^1H\}$ NMR data (δ, ppm; J, Hz) for complexes (1)–(15)

Complex	Resonances for the C–N group	Resonances for the amino acidate or acac groups
(1) [a]	146.91, 145.70, 130.62, 124.60, 124.12, 120.79 (C_6H_4) 73.79 (CH_2N), 51.75 (NMe_2)	188.09, 186.22 (CO–acac), 99.98 (CH–acac), 28.12, 27.14 (CH_3–acac)
(2) [a]	152.2, 146.2, 130.5, 124.7, 124.1, 121.4 (C_6H_4), 75.1 (CH), 51.2, 45.6 (NMe_2), 17.5 (CH_3)	188.1, 186.3 (CO–acac), 100.0 (CH–acac), 28.2, 27.5 (CH_3–acac)
(3) [b]	148.44, 145.73, 132.46, 124.13, 123.51, 121.44 (C_6H_4) 71.32 (CH_2N), 51.14 (NMe_2)	177.95 (CO_2^-), 47.65 (CH_2)
(4) [b]	148.50, 146.10, 133.06, 124.04, 123.43, 121.39 (C_6H_4) 71.33 (CH_2N), 51.01 (NMe_2)[c]	179.54 (CO_2^-), 54.45 (CH), 20.28 (CH_3)
(5) [b]	148.30, 146.20, 133.66, 124.02, 123.36, 121.31 (C_6H_4) 71.29 (CH_2N), 51.01 (NMe_2)[c]	179.54 (CO_2^-), 138.05, 127.98, 127.57, 126.12 (Ph), 59.84 (CH), 41.15 (CH_2)
(6) [a]	148.32, 144.54, 131.43, 125.91, 124.58, 122.11 (C_6H_4) 72.37 (CH_2N), 51.90, 51.77 (NMe_2)	179.52 (CO_2^-), 64.93 (CH^iPr), 31.29 ($CHMe_2$), 19.53, 17.52 ($CHMe_2$)
(7) [a]	146.86, 142.72, 131.56, 125.05, 124.80, 121.19 (C_6H_4) 72.23 (CH_2N), 52.70, 51.49 (NMe_2)	178.57 (CO_2^-), 170.26 (CO), 43.89 (CH_2), 23.21 (CH_3)
(8) [a]	146.86, 142.81, 131.67, 125.10, 124.94, 121.45 (C_6H_4) 72.25 (CH_2N), 52.94, 51.46 (NMe_2)	171.11, 168.57 (CO_2^- + CO), 134.78 (C=), 106.34 (=CH_2), 24.84 (CH_3)
(9) [a]	152.9, 144.9, 131.8, 125.4, 124.4, 122.5 (C_6H_4), 73.8 (CH), 50.8, 45.4 (NMe_2), 16.2 (CH_3)	179.6 (CO_2^-), 48.4 (CH_2)
(10a) [a]	153.16, 144.85, 131.93, 125.31, 124.40, 122.48 (C_6H_4), 73.89 (CH), 50.93, 45.45 (NMe_2), 16.84 (CH_3)	181.41 (CO_2^-), 55.42 (CH), 21.27 (CH_3)
(10a, 10b) [a]	153.22, 152.92, 145.16, 144.88, 131.91, 131.80, 125.57 125.34, 125.30, 124.40, 122.46 (2 C_6H_4), 73.93, 73.75 (2 CH) 50.98, 50.62, 45.52, 45.23 (2 NMe_2), 17.14, 15.82 (2 CH_3)	181.31, 181.24 (2 CO_2^-), 55.41 (2 CH), 21.33, 21.26 (2 CH_3)
(11a) [a]	152.96, 145.00, 131.53, 125.34, 124.54, 122.70 (C_6H_4), 73.32 (CH), 50.17, 45.06 (NMe_2), 14.96 (CH_3)	179.37 (CO_2^-), 136.75, 129.42, 129.16, 127.39 (Ph), 61.04 (CH), 40.61 (CH_2)
(11a, 11b) [a]	153.21, 153.05, 144.87, 144.65, 131.59, 131.45, 125.32, 125.28, 124.50, 124.46, 122.63, 122.57 (2 C_6H_4), 73.96, 73.57 (2 CH), 50.93, 50.45, 45.49, 45.25 (2 NMe_2), 16.80, 15.76 (2 CH_3)	179.62, 179.47 (2 CO_2^-), 136.89, 136.75, 129.44, 129.14, 129.09, 127.37, 127.26 (2 Ph), 60.98, 60.89 (2 CH), 40.60, 40.40 (2 CH_2)
(12a) [a]	153.31, 145.18, 131.30, 125.33, 124.52, 122.63 (C_6H_4), 73.87 (CH), 50.85, 45.54 (NMe_2), 16.56 (CH_3)	179.30 (CO_2^-), 64.93 (CH^iPr), 31.31 ($CHMe_2$), 19.60, 17.59, ($CHMe_2$)
(12a, 12b) [a]	153.27, 152.96, 145.26, 145.02, 131.48, 131.36, 125.23, 124.34, 122.51, 122.41 (2 C_6H_4), 73.89 (2 CH), 50.96, 50.79, 45.59, 45.25 (2 NMe_2), 17.16, 16.03 (2 CH_3)	179.79, 179.66 (2 CO_2^-), 64.75 (2 CH^iPr), 31.27 (2 $CHMe_2$), 19.47, 19.44, 17.65, 17.48 (2 $CHMe_2$)
(13) [a]	150.63, 144.48, 131.23, 125.64, 124.86, 122.26 (C_6H_4) 72.73 (CH), 48.22, 45.38 (NMe_2), 10.55 (CH_3)	178.58 (CO_2^-), 170.18 (CO), 43.88 (CH_2), 23.17 (CH_3)
(14) [a]	150.66, 144.73, 131.19, 125.26, 124.92, 122.35 (C_6H_4) 72.31 (CH), 48.11, 45.53 (NMe_2), 10.34 (CH_3)	170.88, 168.65 (CO_2^- + CO), 134.84 (=C), 106.24 (=CH_2), 24.86 (CH_3)
(15) [a]	149.89 (d, $^2J_{C-P}$ = 9.1 Hz), 142.86, 136.12 (d, $^3J_{C-P}$ = 6.0 Hz) 129.16, 126.02 (d, $^3J_{C-P}$ = 2.0 Hz), 122.85 (C_6H_4), 69.41 (CH_2N), 45.69 (NMe_2)	181.32 (d, CO_2^-, $^3J_{C-P}$ = 2.5 Hz), 46.12 (CH_2) Phosphinic carbon atoms: 14.94 (d, $^1J_{C-P}$ = 28.7 Hz, $P(CH_2CH_3)_3$) 7.84 (d, $^2J_{C-P}$ = 1.5 Hz, $P(CH_2CH_3)_3$)

[a] In $CDCl_3$; [b] In DMSO-d_6; [c] Solvent resonance obscures the other NMe_2 resonance.

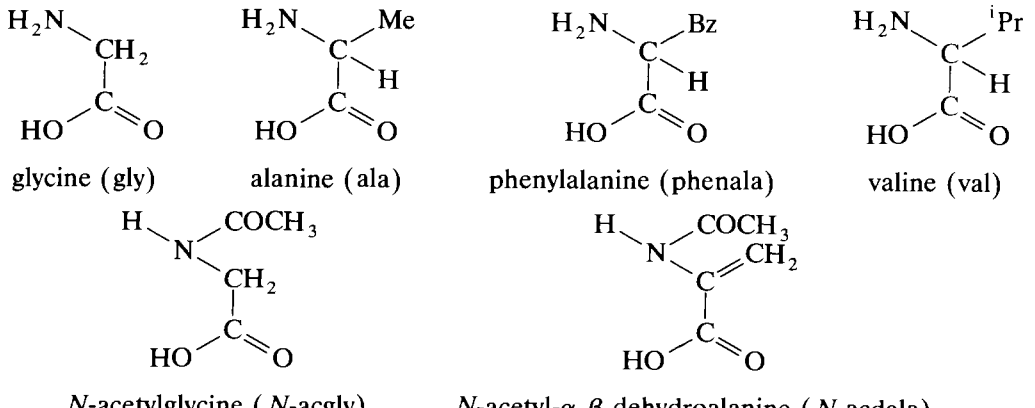
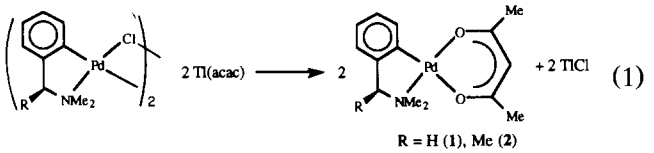


Fig. 1.

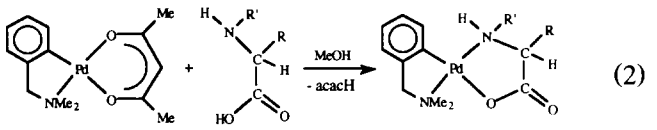
ane at room temperature, by a slight modification of the previously described procedure [8], as is represented in Eq. 1:



(1)

These products have satisfactory elemental analysis, and they are characterized by their IR and NMR (^{1}H and ^{13}C{^{1}H}) data (see Tables 1 and 2 and Experimental Section).

The acetylacetonate ligand can be easily displaced from the Pd complexes (**1**) and (**2**) by aminoacidate ligands. Thus, complex (**1**) reacts with the amino acids represented in Fig. 1 (in the case of alanine, phenylalanine and valine the *R,S*-racemic mixtures were used) giving the corresponding amino acidato complexes [Pd(dmba)(Aa)] (**3**)–(**8**) as schematized in Eq. 2.



(2)

R′ = H	R = H (**3**)
	R = Me (**4**)
	R = Bz (**5**)
	R = ^{i}Pr (**6**)
R′ = $COCH_3$	R = H (**7**)
R′ = $COCH_3$	C(R)H = C=CH_2 (**8**)

The reactions were carried out in refluxing MeOH, except for complex (**8**), for which the reaction was performed in MeOH at room temperature. From the methanolic solutions, complexes (**3**)–(**8**) readily crystallize pure as air-stable white solids after solvent evaporation and Et_2O addition to the concentrated solutions. Complexes (**3**) and (**4**) have been obtained previously, although by a different synthetic procedure [1c].

In the IR spectra of the complexes (**3**)–(**8**) vibrations associated with the COOH group of the free amino acid have disappeared, and the corresponding absorptions for all the expected functional groups in the molecule are present: Absorptions in the 3500–3000 cm^{-1} region show the presence of NH_2 or NH groups [9,10]; in the 1700–1500 cm^{-1} zone we observe strong absorptions because of the carboxylato group [9,11,12] and in the 900–750 cm^{-1} region characteristic absorptions of the *C,N*-cyclometallated groups were observed [5].

The analysis of the ^{1}H NMR spectra (see Table 1) of complexes (**3**)–(**8**) gave more structural information. The data are consistent with the proposed structure in Eq. 2; the palladium atom is in a square planar environment, surrounded by a *C,N*-chelating ligand and an amino acidate coordinated through the N-atom of the NHR group and one oxygen of the carboxylate. The *trans-N-N* geometry is proposed, by analogy with the similar complexes [Pd(dmba)(PPh_2–CH_2–C(O)OC_2H_5)] and [Pd(dmba)(PPh_2–CH_2–C(O)O)] [13] and was confirmed later by NOE difference experiments and ^{1}H-^{1}H NOESY measurements.

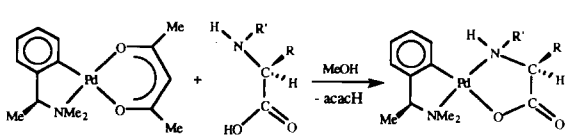
For complex (**3**), the existence of a symmetry plane coincident with the molecular plane is reflected in the chemical equivalence of the two H atoms of the NH_2 group, as well as for the H atoms of the CH_2 groups and for the Me groups of the NMe_2 unit. For complexes (**4**)–(**6**) the presence of a chiral carbon atom in the amino acidato group causes the loss of the symmetry plane, and this is clearly reflected in its ^{1}H NMR spectra. Resonances corresponding to the H atoms of the NH_2 group are split, as well as the H atoms of the CH_2 (dmba), which now appear as an AB system, and the Me groups of the NMe_2 unit (two singlets).

The splitting of the NH_2 resonances (in particular, the upfield shifting of one resonance) in complexes (**4**)–(**6**) ($\Delta\delta = \delta(H)_{NH}$ at low field—$\delta(H)_{NH}$ at high field; $\Delta\delta = 0$ (**3**), $\Delta\delta = 0.54$ ppm (**4**), $\Delta\delta = 0.90$ ppm (**5**) and $\Delta\delta = 1.34$ ppm (**6**)) is notable. This splitting becomes higher as the R-substituent (see Eq. 2) becomes longer.

The ^{1}H NMR spectrum of [Pd(dmba)(*N*-acgly)] (**7**) is also consistent with the proposed structure, and reflects the chirality of the N atom of the coordinated acetylglycinate. Both CH_2 groups (dmba and amino acidate ligand) appeared as AB systems and two anisochronous resonances were observed for the NMe_2 unity. A similar situation was found for complex [Pd(dmba)(*N*-acdala)] (**8**) as a result of the chirality of the coordinated N atom. The diastereotopicity of the NMe_2 unit observed in (**4**)–(**8**) also means that the pyramidal inversion at N is blocked.

The ^{13}C{^{1}H} NMR spectra of complexes (**3**)–(**8**) (see Table 2) show the presence of all the expected carbon atoms, and confirm the proposed structures.

Subsequently we carried out reactions between the starting compound [Pd(*S*-dmphea)(acac-O,O′)] (**2**) and the amino acids showed in Fig. 1 (glycine, *S*-alanine, *S*-phenylalanine, *S*-valine, *N*-acetylglycine and *N*-acetyl-α,β-dehydroalanine) in 1:1 molar ratio to give the corresponding amino acidato complexes [Pd(*S*-dmphea)(Aa)] as in Eq. 3.



(3)

R′ = H R = H (**9**)
R = Me (**10a**)
R = Bz (**11a**)
R = ^{i}Pr (**12a**)
R′ = $COCH_3$ R = H (**13**)
R′ = $COCH_3$ C(R)H = $C{=}CH_2$ (**14**)

All the reactions were carried out in refluxing MeOH, except for that yielding complex (**14**), for which the reaction was performed in MeOH at room temperature. After evaporation of the solvent, the crude residue was treated with CH_2Cl_2 in order to remove the unreacted amino acid. Further evaporation of the CH_2Cl_2 and treatment of the residue with Et_2O afforded the corresponding pure amino acidato complexes as white solids.

The IR spectra of these complexes again showed the absence of vibrations associated with the COOH group in the free amino acid and the presence of the absorptions corresponding to all expected functional groups. The IR spectra were very similar to those described for complexes (**3**)–(**8**) and can be analyzed in the same terms (see above).

As discussed for complexes (**3**)–(**8**), analysis of the ^{1}H NMR spectra provided more structural information. For complex [Pd(*S*-dmphea)(gly)] (**9**) the absence of symmetry elements is clearly reflected by the observation of two different resonances for the two diastereotopic H atoms of the NH_2, as well as for the two H atoms of the CH_2 group and for the two Me groups of the NMe_2 unit.

To obtain more structural information, some NOE difference experiences and two-dimensional ^{1}H ^{1}H-NOESY measurements for mixing times of 400 ms were performed on compounds (**9**) and (**12a**), ^{1}H ^{1}H-NOESY spectra were obtained. The NOE interactions allowed us to confirm the *trans* N–N geometry proposed for these compounds, as well as the unambiguous assignment of all resonances in the spectra.

For both compounds, key features of the assignments were that there is a strong NOE interaction from $H_{o'}$ to the C*–H and C*–Me_1 resonances, which allowed the unambiguous assignment of the signals because of the two ortho protons H_o and $H_{o'}$ at about 6.70 ppm and 6.80 ppm respectively, and that selective irradiation of the H_o signal in both complexes produced a clear NOE enhancement of the signal(s) because of the NH_2 group, confirming the proximity of these nuclei, only possible for a *trans* N-N geometry of the complexes. Moreover, the strong interaction at the C*–Me_1 resonance with the isopropyl group of the aminoacidate in (**12a**) provides additional confirmation of the *trans* N-N geometry of the complexes, as this NOE interaction clearly indicates that both groups are on the same side of the molecule. Unambiguous assignment of all resonances was made on the basis of the following features: in both compounds the resonance at 2.60 ppm because of one methyl group of the NMe_2 unit showed a strong NOE interaction with the resonance because of the methyl of the C*(Me)(H) group and a weaker one with the proton resonance of the same group, which indicates that the perturbed methyl group (Me_2) is eclipsed by Me_1; finally, the methyl resonance at about 2.80 ppm resulting from the other methyl group of the NMe_2 unit showed a strong NOE interaction with the resonance resulting from the proton of the C*(Me)(H) group, and a weaker one with the methyl resonance of the same group, showing that the perturbed methyl group (Me_3) is eclipsed by this CH group. The most informative enhancements are

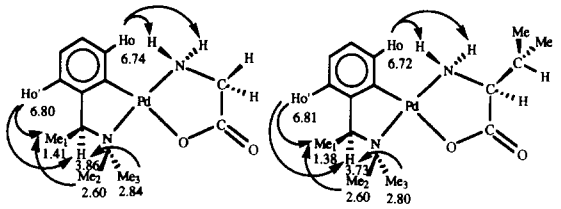


Fig. 2.

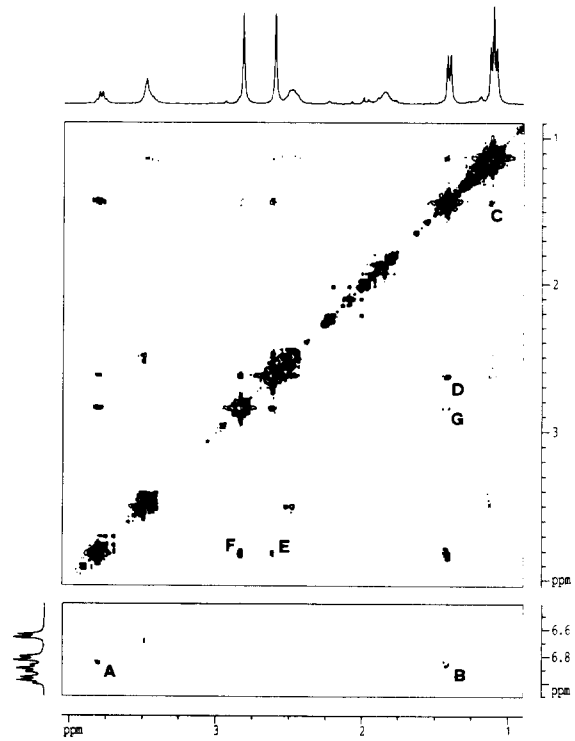


Fig. 3. NOESY experiment performed on compound (**12a**) at a measuring frequency of 300.13 MHz. The mixing time was 400 ms and the data were acquired into a 512×1024 matrix and then transformed into 1024×1024 points using a sine window in each dimension. NOE correlations referred in the text are as follows. A $H_{o'}$–C*H, B $H_{o'}$–Me_1, C Me_1-isopropyl group, D Me_1–Me_2, E C*H–Me_2, F C*H–Me_3, G Me_1–Me_3.

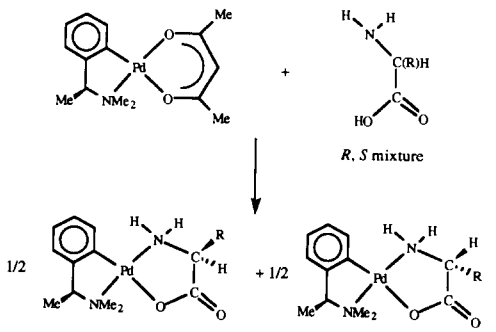
summarized in Fig. 2, and Fig. 3 shows the ^{1}H-^{1}H NOESY of compound (**12a**).

The similarity in the pattern of the ^{1}H NMR spectra of all complexes [Pd(*S*-dmphea)(Aa)] (**10a**)–(**12a**) for these signals allowed us to extrapolate these assignments to the rest of compounds.

The ^{1}H NMR spectrum of [Pd(*S*-dmphea)(*N*-acgly)] (**13**) at room temperature showed resonances corresponding to the presence of a single product, and a similar behaviour was observed for [Pd(*S*-dmphea)(*N*-acdala)] (**14**). The spectra do not show any change when the temperature is lowered, and even at −80°C, the same set of resonances is observed. We thought that the observation of only a set of signals could be explained through the equilibrium represented in the Fig. 4, which involves the fast pyramidal inversion at the N atom of the amino acid.

The ^{13}C{^{1}H} NMR spectra of these complexes (**9**), (**10a**), (**11a**), (**12a**), (**13**) and (**14**) show the resonances for all the expected carbon atoms in the molecule, and confirm the proposed structure.

Next we tried diastereoselective synthesis of [Pd(*S*-dmphea)(Aa)] because a complex with a chiral ancillary ligand such as [Pd(*S*-dmphea)(acac)] (**2**) can promote a stereoselective reaction. We therefore tried reactions between [Pd(*S*-dmphea)(acac)] (**2**) and the *R*,*S*-racemic mixtures of the amino acids alanine, phenylalanine, and valine. The reactions were carried out in MeOH at 0°C, room temperature, and in refluxing MeOH, and using an excess of the amino acid (Pd complex : amino acid = 1 : 2). The isolation of the products was carried out using a similar work-up to that described above for the *S*-amino acid derivatives, and the new complexes were characterized by the usual methods. The performed reactions are summarised in Eq. 4.



(4)

R = Me (**10a**) (*S*,*S*) R = Me (**10b**) (*S*,*R*)
R = Bz (**11a**) (*S*,*S*) R = Bz (**11b**) (*S*,*R*)
R = ^{i}Pr (**12a**) (*S*,*S*) R = ^{i}Pr (**12b**) (*S*,*R*)

Unfortunately, in all cases the product obtained was a 1 : 1 mixture of both diastereoisomers, as deduced from the ^{1}H NMR spectra, showing that the reactions were not diastereoselective. The assignment of the

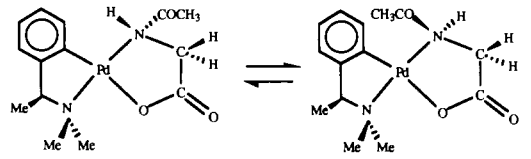
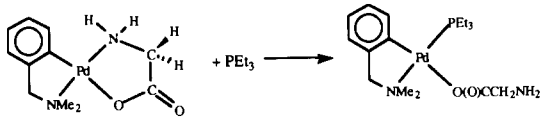


Fig. 4.

resonances to the (*S*,*R*) or (*S*,*S*) isomers was carried out by comparison with the pure (*S*,*S*) forms. Small variations have been detected for the (*S*,*S*) isomer in the mixture when compared with the pure (*S*,*S*) products. In some cases, the overlapping of signals precludes unambiguous assignments.

Finally, we studied the reactivity of [Pd(dmba)(gly)] (**3**) towards phosphines because this provides an additional support to the *trans* N-N geometry of starting complexes. Compound (**3**) reacts with an equimolecular amount of PEt_3 in CH_2Cl_2 giving, after evaporation of the solvent and *n*-hexane addition, complex [Pd(dmba)(*O*-gly)(PEt_3)] (**15**), as shown in Eq. 5.

Complex (**15**) showed the required elemental analysis and the expected IR absorptions corresponding to the coordinated groups. Its ^{31}P{^{1}H} NMR spectrum shows a single resonance at 26.00 ppm, in keeping with the presence of PEt_3, and showing the presence of a single product. In this case, the ^{1}H NMR spectrum does not provide sufficient structural information, but the ^{13}C{^{1}H} NMR spectrum is really informative. The small value measured for $^2J_{Cipso(dmba)-P} = 9.0$ Hz [14] implies that the cyclometallated phenyl of the dmba and the PEt_3 are *cis*, as proposed in Eq. 5. The doublet structure of the carbonyl resonance confirms the η^1–O coordination of the glycinate.



(5)

(**15**)

These results are consistent with the established structure of the starting complex (and for all the complexes [Pd(C–N)(Aa)]) and show that displacement of the coordinated NH_2 is easier than that of the carboxylate group, confirming that the reaction takes place with retention of the palladium stereochemistry.

A study of these complexes as catalysts in cyclopropanation of alkenes with diazoalkanes is currently under way.

3. Experimental details

Solvents were dried and distilled prior to use by the standard methods. IR spectra (4000–200 cm^{-1}) were

recorded on a Perkin-Elmer 883 IR Spectrophotometer in Nujol mulls between polyethylene plates. ^1H NMR spectra were recorded on a Varian Unity-300 and on a Bruker ARX-300 spectrometers at 300.13 MHz in $CDCl_3$ or DMSO-d_6 using the solvent signal as internal standard. $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Unity 300 spectrometer at 75.47 MHz in $CDCl_3$ or DMSO-d_6 using the solvent signal as internal standard. $^{31}P\{^1H\}$ NMR spectra were recorded at 121.47 MHz in $CDCl_3$ and externally referenced to H_3PO_4 (85%). Elemental analysis were carried out on a Perkin-Elmer 240-B microanalyser. Optical rotations were measured at the sodium-D line (589 nm) on solutions in a 1-dm cell at 20°C with a Perkin-Elmer Model 241 C polarimeter. The amine *S*-α-$C_6H_5CH(Me)NMe_2$ was prepared according to literature methods [15]. The starting compounds [{Pd(μ-Cl)($C_6H_4CH_2NMe_2$-2)}$_2$] and [{Pd(μ-Cl)(*S*-α-$C_6H_4CH(Me)NMe_2$-2)}$_2$] were prepared according to published methods [16].

3.1. Synthesis of acetylacetonato complexes (1) and (2)

Complexes (**1**) and (**2**) were synthesized according to the method described in Ref. [8] with slight modifications.

Complex (**1**): to a solution of 1.645 g (3.00 mmol) of [{Pd(μ-Cl)($C_6H_4CH_2NMe_2$-2)}$_2$] in 35 ml of CH_2Cl_2, was added Tl(acac) (1.821 g, 6.00 mmol). The resulting suspension was stirred for 30 min. at room temperature and then filtered. The obtained pale-yellow solution was evaporated to dryness, and the residue was stirred with 30 ml of cold hexane, giving (**1**) as a pale-yellow solid. Yield: 1.875 g (92%). Anal. Calc. for $C_{14}H_{19}NO_2Pd$: C, 49.49; H, 5.63; N, 4.12. Found: C, 49.19; H, 5.55; N, 4.39%. IR (cm^{-1}): 1589, 1516 (C=O, acac), 865, 852, 746 (dmba), 793 (*Π*(C–H), acac).

Complex (**2**) was obtained similarly: [(Pd(μ-Cl)(*S*-α-$C_6H_4CH(Me)NMe_2$-2)}$_2$] (1.740 g, 3.00 mmol) reacts with Tl(acac) (1.821 g, 6.00 mmol) to give 1.958 g (92% yield) of (**2**) as a pale-yellow solid. Anal. Calc. for $C_{15}H_{21}NO_2Pd$: C, 50.93; H, 5.98; N, 3.96. Found: C, 51.50; H, 6.54; N, 3.96%. IR (cm^{-1}): 1590, 1573, 1514 (C=O, acac), 938, 760, 755 (*S*-dmphea), 796 (*Π*(C–H), acac).

3.2. Synthesis of complexes of stoichiometry

[Pd(dmba)(Aa)] (Aa = aminoacidate) (**3**)–(**7**). These complexes were prepared through the same procedure. As a general method, we describe here the synthesis of [Pd(dmba)(gly)] (**3**). To a solution of 0.170 g (0.5 mmol) of [Pd(dmba)(acac)] (**1**) in 25 ml of MeOH, was added glycine (0.037 g, 0.5 mmol). The resulting solution was heated under reflux for 30 min, becoming colourless. After cooling, the solution was reduced in vacuo to 2 ml. The addition of Et_2O (30 ml) and subsequent stirring gave (**3**) as a white solid. Yield: 0.134 g (85%). Anal. Calc. for $C_{11}H_{16}N_2O_2Pd$: C, 41.98; H, 5.12; N, 8.90. Found: C, 41.39; H, 5.09; N, 8.77%. IR (cm^{-1}): 3312, 3226 (NH_2), 1642, 1599, 1581 (carboxylate), 867, 852, 744 (dmba).

3.2.1. [Pd(dmba)(ala)] (4)

0.170 g (0.5 mmol) of (**1**) reacted with 0.044 g (0.5 mmol) of alanine to give 0.142 g (87% yield) of (**4**) as a white solid. Anal. Calc. for $C_{12}H_{18}N_2O_2Pd$: C, 43.85; H, 5.52; N, 8.52. Found: C, 43.78; H, 5.50; N, 8.70%. IR (cm^{-1}): 3287, 3274 (NH_2), 1629, 1593, 1579 (carboxylate), 865, 847, 738 (dmba).

3.2.2. [Pd(dmba)(phenala)] (5)

0.170 g (0.5 mmol) of (**1**) reacted with 0.082 g (0.5 mmol) of phenylalanine to give 0.147 g (73% yield) of (**5**) as a white solid. The complex crystallizes as [Pd(dmba)(phenala)] · H_2O. Anal. Calc. for $C_{18}H_{24}N_2O_3Pd$: C, 51.13; H, 5.72; N, 6.62. Found: C, 51.80; H, 5.72; N, 6.98%. IR (cm^{-1}): 3205 (broad, NH_2), 1617, 1578 (carboxylate), 850, 822 (dmba).

3.2.3. [Pd(dmba)(val)] (6)

0.170 g (0.5 mmol) of (**1**) reacted with 0.058 g (0.5 mmol) of valine to give 0.160 g (90% yield) of (**6**) as a white solid. The complex crystallizes as [Pd(dmba)(val)] · H_2O. Anal. Calc. for $C_{14}H_{24}N_2O_3Pd$: C, 44.87; H, 6.45; N, 7.47. Found: C, 44.24; H, 6.12; N, 7.34%. IR (cm^{-1}): 3238, 3153 (NH_2), 1617 (carboxylate), 868, 852, 737 (dmba).

3.2.4. [Pd(dmba)(N-acgly)] (7)

0.170 g (0.5 mmol) of (**1**) reacted with 0.058 g (0.5 mmol) of *N*-acetylglycine to give 0.125 g (70% yield) of (**7**) as pale-yellow solid. The complex crystallizes as [Pd(dmba)(*N*-acgly)] · H_2O. Anal. Calc. for $C_{13}H_{20}N_2O_4Pd$: C, 41.67; H, 5.38; N, 7.47. Found: C, 41.28; H, 5.27; N, 7.98%. IR (cm^{-1}): 3356 (NH), 1722 (acetyl), 1665, 1602 (carboxylate), 871, 850, 745 (dmba).

3.2.5. [Pd(dmba)(N-acdala)] (8)

To a solution of 1.018 g (3.00 mmol) of (**1**) in 100 ml of MeOH, was added *N*-acetyl-α,β-dehydroalanine (0.774 g, 6.00 mmol) and the resulting solution was stirred at room temperature for 30 min (less amino acid decreases the yield; a higher temperature, as in refluxing MeOH, promotes the decomposition of the product). At this point, the colour of the solution was deep yellow. From this solution, the solvent was removed to dryness and the residue extracted with 10 ml of CH_2Cl_2. After filtration of the unreacted amino acid, the extract was evaporated to 2 ml and cold Et_2O (15 ml) was added, giving (**8**) as a deep yellow solid. Yield: 0.91 g (82%). Anal. Calc. for $C_{14}H_{18}N_2O_3Pd$: C, 45.60;

H, 4.92; N, 7.60. Found: C, 45.43; H, 5.15; N, 7.14%. IR (cm^{-1}): 3402, 3313 (NH), 1675 (acetyl), 1578 (carboxylate), 847, 816, 748 (dmba).

3.3. Synthesis of complexes of stoichiometry [Pd(S-dmphea)(Aa)] (9)–(14)

3.3.1. [Pd(S-dmphea)(gly)] (9)

To a solution of 0.177 g (0.5 mmol) of [Pd(*S*-dmphea)(acac)] (**2**) in 25 ml of MeOH, was added glycine (0.037 g, 0.5 mmol) and the resulting solution was heated under reflux for 30 min, changing from pale-yellow to colourless. The solution, was evaporated to dryness and the residue extracted with 10 ml of CH_2Cl_2. After filtration of the unreacted amino acid, the CH_2Cl_2 solution was concentrated to 2 ml and the residue treated with 15 ml of Et_2O, giving (**9**) as a white solid. Yield: 0.136 g (83%). Analysis, Calc. for $C_{12}H_{18}N_2O_2Pd$: C, 43.85; H, 5.52; N, 8.52. Found: C, 43.36; H, 5.46; N, 9.36%. $[\alpha]_D$ +13.4° (c 0.030, methanol). IR (cm^{-1}): 3314, 3205 (NH_2), 1621, 1598, 1578 (carboxylate), 753, 740 (*S*-dmphea).

3.3.2. [Pd(S-dmphea)(S,R-ala)] (10a), (10b)

The mixture of both diastereoisomers is obtained following a procedure similar to that described for complex (**9**). 0.177 g (0.5 mmol) of (**2**) reacted with 0.089 g (1.0 mmol) of *S,R*-alanine to give 0.153 g (90% yield) of a 1:1 mixture of the complexes (**10a**) and (**10b**).

3.3.2.1. Complex [Pd(S-dmphea)(S-ala)] (10a). 0.177 g (0.5 mmol) of (**2**) reacted with 0.045 g (0.5 mmol) of *S*-alanine to give 0.153 g (90% yield) of (**10a**) as a white solid. The complex crystallizes as [Pd(*S*-dmphea)(*S*-ala)]·H_2O. Analytical and IR data are given for complex (**10a**). Anal. Calc. for $C_{13}H_{22}N_2O_3Pd$: C, 43.27; H, 6.14; N, 7.77. Found: C, 43.46; H, 5.83; N, 7.86%. $[\alpha]_D$ +13.2° (c 0.027, methanol), IR (cm^{-1}) 3241, 3155 (NH_2), 1641, 1579 (carboxylate), 843, 805, 780, 735 (*S*-dmphea).

3.3.3. [Pd(S-dmphea)(S,R-phenala)] (11a), (11b)

A mixture of both diastereoisomers is obtained: 0.177 g (0.5 mmol) of (**2**) reacted with 0.165 g (1.0 mmol) of *S,R*-phenylalanine to give 0.196 g (94% yield) of a 1:1 mixture of (**11a**) and (**11b**). The complex [Pd(*S*-dmphea)(*S*-phenala)] (**11a**) can be synthesized pure using the same work-up: 0.177 g (0.5 mmol) of (**2**) reacted with 0.082 g (0.5 mmol) of *S*-phenylalanine to give 0.183 g (88% yield) of (**11a**) as a white solid. The complex crystallizes as [Pd(*S*-dmphea)(*S*-phenala)]·$1/2H_2O$. Analytical and IR data are given for complex (**11a**). Anal. Calc. for $C_{19}H_{25}N_2O_{2.5}Pd$: C, 53.34; H, 5.89; N, 6.55. Found: C, 53.54; H, 6.05; N, 6.52%. $[\alpha]_D$ +37.5° (c 0.023, methanol). IR (cm^{-1}): 3225, 3130 (NH_2), 1628, 1579 (carboxylate), 822, 806, 779, 740 (*S*-dmphea).

3.3.4. [Pd(S-dmphea)(S,R-val)] (12a), (12b)

A mixture of both diastereoisomers is obtained: 0.177 g (0.5 mmol) of (**2**) reacted with 0.117 g (1.0 mmol) of *S,R*-valine to give 0.148 g (80% yield) of a 1:1 mixture of (**12a**) and (**12b**). The complex [Pd(*S*-dmphea)(*S*-val)] (**12a**) can be synthesized pure using the same work-up: 0.177 g (0.5 mmol) of (**2**) reacted with 0.059 g (0.5 mmol) of *S*-valine to give 0.145 g (79% yield) of (**12a**) as a white solid. Analytical and IR data are given for complex (**12a**). Anal. Calc. for $C_{15}H_{24}N_2O_2Pd$: C, 48.60; H, 6.48; N, 7.56. Found: C, 48.45; H, 6.42; N, 7.35%. $[\alpha]_D$ +20.5° (c 0.027, methanol). IR (cm^{-1}): 3230, broad (NH_2), 1612, 1578 (carboxylate), 778 (S-dmphea).

3.3.5. [Pd(S-dmphea)(N-acgly)] (13)

To a solution of 0.177 g (0.5 mmol) of (**2**) in 25 ml of MeOH was added *N*-acetylglycine (0.177 g, 1.0 mmol). The reaction mixture was heated under reflux for 30 min, but did not show an appreciable change of colour. After cooling, the solvent was evaporated to dryness and the residue extracted with 10 ml of CH_2Cl_2. The unreacted amino acid was filtered off, and the resulting solution was concentrated to 2 ml. The oily residue was stirred with Et_2O (15 ml), giving (**13**) as a pale-yellow solid. Yield: 0.074 g (40%). Anal. Calc. for $C_{14}H_{20}N_2O_3Pd$: C, 45.35; H, 5.40; N, 7.56. Found: C, 45.22; H, 5.70; N, 8.21%. $[\alpha]_D$ +10.0° (c 0.027, methanol). IR (cm^{-1}): 3354 (NH), 1681 (acetyl), 1607, 1577 (carboxylate), 813, 777, 748 (*S*-dmphea).

3.3.6. [Pd(S-dmphea)(N-acdala)] (14)

To a solution of 0.354 g (1.0 mmol) of (**2**) in 25 ml of MeOH was added *N*-acetyl-α,β-dehydroalanine (0.129 g, 1.0 mmol). The reaction mixture was stirred at room temperature for 30 min and a deep-yellow colour developed. From this deep-yellow solution the solvent was evaporated to dryness and the residue extracted with 10 ml of CH_2Cl_2. The unreacted amino acid was filtered off and the resulting solution was concentrated to 2 ml. Addition of cold Et_2O (15 ml) to the extract and stirring gave complex (**14**) as a yellow solid. Yield: 0.155 g (41%). Anal. Calc. for $C_{15}H_{20}N_2O_3Pd$: C, 47.07; H, 5.23; N, 7.32. Found: C, 46.71; H, 5.64; N, 6.84%. $[\alpha]_D$ +40.0° (c 0.026, methanol). IR (cm^{-1}): 3310 (NH), 1694 (acetyl), 1601, 1576 (carboxylate), 816, 804, 777 (*S*-dmphea).

3.4. [Pd(dmba)(O-gly)(PEt_3)] (15)

A suspension of 0.102 g (0.30 mmol) of [Pd(dmba)(gly)] (**3**) in 20 ml of CH_2Cl_2 was treated with PEt_3 (44.3 μl, 0.30 mmol). The initial white suspension became clear in 10 min (small amounts of undissolved

product were removed by filtration). The solvent was then removed under reduced pressure, and the oily residue was treated with 15 ml of hexane with vigorous stirring, giving **(15)** as a white solid. The yield was 0.074 g (57%). Anal. Calc. for $C_{17}H_{31}N_2O_2PPd$: C, 47.16; H, 7.16; N, 6.47. Found: C, 47.02; H, 7.05; N, 6.85%. IR (cm^{-1}): 3188, 3050 (NH_2), 1631, 1575, (carboxylate), 867, 846, 771, 748 (dmba).

Acknowledgements

Financial support from D.G.I.C.Y.T. (Spain) (Projects PB92-0364 and PB91-0696). E.P.U. thanks D.G.A. for a grant. We thank Prof. J. Fornies for invaluable logistical support.

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