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Amine-thioether and amine-pyridine complexes of palladium(II) and the reactivity of the methyl complexes towards CO and allenes

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Abstract

The synthesis and characterization of the complexes $[\text{PdX}_2(\text{L})]$ and $[\text{PdX}(\text{Me})(\text{L})]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} = S\text{-methyl-}D/L\text{-cysteine methyl ester (H[Me]cysMe-}N,S \text{ (a))}, D/L\text{-methionine methyl ester (HmetMe-}N,S \text{ (b))}, 2\text{-[aminomethyl]pyridine (Py}^1\text{-}N,N' \text{ (c))}, 2\text{-[2-aminoethyl]pyridine (Py}^2\text{-}N,N' \text{ (d))}$) have been reported. A single crystal X-ray determination of $[\text{PdCl}(\text{Me})(\text{H[Me]cysMe-}N,S)]$ (**2a**) showed chelate coordination of the NS ligand. The square planar surrounding is completed by the chloride and the methyl group, which is positioned *cis* to the sulfur atom. The crystal structure determination of $[\text{PdCl}(\text{Me})(\text{HmetMe-}N,S)]$ (**2b**) shows an analogous geometry with the HmetMe-NS ligand forming a six-membered chelate ring with palladium. Again the methyl group is *cis* to the sulfur atom. The structure of $[\text{PdCl}(\text{Me})(\text{Py}^2\text{-}N,N')]$ (**2d**) shows the presence of an amine-pyridine ligand also forming a six-membered chelate ring with Pd(II), with the methyl group positioned *cis* to the amine group. The unexpectedly stable methylpalladium complexes reacted with CO to give the corresponding acyl complexes. The structure of $[\text{PdCl}(\text{C}(\text{O})\text{Me})(\text{HmetMe-}N,S)]$ (**5b**) in the solid state shows the presence of a six-membered chelate ring. The acyl group is *cis* to the sulfur atom. The NS and the NN' complexes (**1a–4b**) contain, also in solution, a chelating ligand L as demonstrated by NMR. The complexes $[\text{PdX}(\text{R})(\text{L})]$ ($\text{R} = \text{Me}, \text{C}(\text{O})\text{Me}$; $\text{L} = \text{HmetMe-}N,S$; $\text{H[Me]cysMe-}N,S$) exist in two diastereoisomeric forms which differ by the position of the methyl substituent on the S atom and can be distinguished at low temperatures. The free energy values ($\Delta G^\ddagger$) of the interconversion varies between 49.5 and 62.1 kJ mol⁻¹. Reaction of $[\text{PdX}(\text{R})(\text{L})]$ ($\text{R} = \text{Me}, \text{C}(\text{O})\text{Me}$; $\text{L} = \text{HmetMe-}N,S$; $\text{H[Me]cysMe-}N,S$; $\text{Py}^1\text{-}N,N'$) with allenes afforded $[\text{Pd}(\eta^3\text{-allyl})(\text{L})]\text{Cl}$. This insertion reaction is faster for the NS complexes containing the six-membered rings than for the five-membered NS containing complexes. The kinetics of the allene insertion show a two term rate law, $k_{\text{obs}} = k_1 + k_2[\text{allene}]$, and depend on the nature of both the ligand and the allene substrate; either an allene dependent (k_2 ; for **2a** + 3-methyl-1,2-butadiene, **2b** + 3-methyl-1,2-butadiene and **2b** + 1,2-heptadiene) or an allene independent (k_1 ; for **2b** + 2,4-dimethyl-2,3-pentadiene) pathway is the dominant one.

Keywords: Palladium complexes; Amine sulfur coordination complexes; Insertion reactions; Crystal structures

1. Introduction

The perfectly alternating insertion of CO and alkenes homogeneously catalyzed by Pd(II) complexes [1] has focussed interest on the study of the intimate steps of the catalytic cycle involved, i.e. the CO insertion step in Pd-alkyl

bonds and the scarcely studied alkene insertion steps in Pd-acyl bonds. Recently, insight has been gained from *in situ* studies of catalytic systems by Brookhart et al. [1h] at low temperatures, while we have investigated model systems of the type $[\text{PdX}(\text{R})(\text{L-L})]$ ($\text{R} = \text{alkyl}, \text{C}(\text{O})\text{R}'$; $\text{X} = \text{halide}, \text{O}_3\text{SCF}_3^-, \text{BF}_4^-$), which closely resemble the proposed intermediates [1e,2]. Both Brookhart et al. and our group [2] have designed systems in which stoichiometrically CO and alkenes are coupled alternately and which may be regarded as living systems mimicking the actual copolymerization reaction steps as proposed by Drent [1a] and Sen

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Fig. 1. The H[Me]cysMe, HmetMe, Py¹ and Py² ligands, with numbering scheme.

[1c]. Boersma and co-workers [3] recently discussed similar findings on a semi-living system involving the reaction of a palladium–bipy system with norbornene and CO and solved the crystal structure of [PdI(COC₇H₁₀COC₇H₁₀COMe)–(bipy)] representing an early stage of the growing polymer chain [3a].

In our model systems a number of problems are addressed which deal with the influence of the ligands L–L, the anion Y, the type of R group and last but not least the role of the solvent in these insertion reactions [4]. Although insight into the influence of the various factors is increasing [5], the role of L–L as an ancillary ligand in the coordination sphere of the catalytically active metal site needs more detailed study. This is highlighted by the observation that, whereas PP ligands with large bite angles and flexible backbones enhance the rate of CO and alkene insertion reactions, the use of NN ligands in complexes [PX(R)(NN)] results in many instances in increased reaction rates, although the NN ligands all have small bite angles and even may be very rigid [2a]. These striking differences indicate that different mechanisms are operating for the PP and NN containing catalytic systems.

Considering these results we have extended our ligand L–L' investigations to NS systems of the type [*N*–(thienylidene)-*L*/*D*-methionyl]methyl ester [6], which originated from the *N*–[*N*–(5-methyl-2-thienylmethylidene)-*L*-methionyl]histamine ligand [7]. Here we report the coordination behavior of *D*/*L*-methionine methyl ester (HmetMe-*N,S*), *S*-methyl-*D*/*L*-cysteine methyl ester (H[Me]cysMe-*N,S*), 2-[aminomethyl]pyridine (Py¹-*N,N'*) and 2-[2-aminoethyl]pyridine (Py²-*N,N'*), Fig. 1).

2. Experimental

2.1. Materials

All reactions were carried out in an atmosphere of purified nitrogen, using standard Schlenk techniques. Solvents were dried and distilled prior to use or stored under an inert atmosphere, unless denoted otherwise. Ethyl acetate and triethylamine were of P.A. grade, [PdCl₂(COD)], [PdCl(Me)] (1,5-COD) [8] (COD = cyclo-1,5-octadiene) and 1,2-heptadiene (nBuA) [9] were synthesized by literature procedures. 2-[Methylamine]pyridine (Py¹), 2-[2-ethylamine]pyridine (Py²), 1,2-propadiene, 3-methyl-1,2-butadiene (DMA) and

2,4-dimethyl-2,3-pentadiene (TMA) are commercially available and were used without further purification.

2.2. Instrumentation

¹H and ¹³C{¹H} NMR spectra were recorded on Bruker AMX 300 and AC 100 spectrometers. Chemical shift values are in ppm relative to Me₄Si. Coupling constants are in Herz (Hz). IR spectra were recorded on a Biorad spectrophotometer.

The CO insertion rates were determined using an electronic gasburet, which consists of an Inacom Instruments 5860E/1AB38 mass flow meter (with a range 0.06–9.00 ml min^{–1}) connected to a high pressure glass reaction vessel of 20 ml. In order to avoid CO pressure drop a 300 ml buffer flask was connected. Data points were collected every second. The system was pressurized with 5 bar CO and the gas flow was measured at room temperature.

Allene insertion rates were determined by recording the electronic absorption spectra, at suitable wavelengths, on a Perkin-Elmer lambda 5 UV–Vis spectrophotometer. The experiments were isothermally performed using approximately 1 mM solutions.

Elemental analyses were carried out by Dornis und Kolbe in Germany. Field desorption (FD) mass spectrometry was carried out using a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-MP7000 data system.

Conductivity measurements, during the reaction of **2a**, **2c** and **2b** with DMA, **2b** with TMA and nBuA in CH₂Cl₂, were carried out using a Consort K720 digital conductometer.

2.3. X-ray structure determination

Suitable crystals of **2a**, **2b** and **2d** were mounted on a Lindemann-glass capillary, and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-T diffractometer on a rotating anode (λ = 0.71073 Å, Mo Kα graphite monochromated¹). Accurate unit-cell parameters and an orientation matrix were determined from the setting angles of 25 reflections [10]. The unit-cell parameters were checked for the presence of higher lattice symmetry [11]. Crystal data and details on data collection and refinement are collected in Table 1. Data were corrected for Lp effects and for the observed linear 5% decay of the reference reflections, except for **2d** which showed no decay. An empirical absorption/extinction correction was applied on **2b** and **2d** (DIFABS

Table 1
Crystal data of **2a**, **2b**, **2d** and **5b**

	2a	2b
Formula	$C_8H_{10}NO_2SClPd \cdot 1/2CH_2Cl_2$	$C_8H_{10}NO_2SClPd$
Molecular weight	348.59	320.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
a (Å), b (Å), c (Å)	13.4476(13), 14.626(2), 13.7738(12)	8.783(3), 7.123(2), 9.237(3)
β (°)	114.063(7)	97.04(3)
V (Å ³)	2473.6(4)	573.5(3)
Z	8	2
D_{calc} (g cm ⁻³)	1.872	1.854
μ (cm ⁻¹)	20.8	19.8
T (K)	150	150
Final $R1^a$	0.0338 (5470 $F_o > 4\sigma(F_o)$)	0.0300 (1391 $F_o > 4\sigma(F_o)$)
Final $wR2^b$ [no. of data]	0.0750 [5876]	0.0628 [1425]
	2d	5b
Formula	$C_8H_{11}N_2ClPd$	$C_8H_{10}NO_2SClPd$
Molecular weight	279.08	348.16
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/a$
a (Å), b (Å), c (Å)	10.2417(3), 12.2955(11), 8.5428(6)	8.4339(6), 15.632(2), 10.107(3)
β (°)	114.641(4)	97.14(2)
V (Å ³)	977.81(11)	1322.1(5)
Z	4	4
D_{calc} (g cm ⁻³)	1.896	1.749
μ (cm ⁻¹)	21.0	149.13
T (K)	150	293
Final $R1^a$	0.0211 (1880 $F_o > 4\sigma(F_o)$)	0.068 (2672 $I > 2.5\sigma(I)$)
Final $wR2^b$ [no. of data]	0.0466 [2233]	
Final R_w^c [no. of data]		0.092 [2672]

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

^c $R_w = [\sum [w(|F_o| - |F_c|)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

[12] as implemented in PLATON [13]). Compounds **2a** and **2b** were solved by automated Patterson methods and subsequent difference Fourier techniques (SHELXS86) [14]. **2d** was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92) [15]. Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93) [16]; no observance criterion was applied during refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter amounting to 1.5 or 1.2 times the value of the equivalent isotropic thermal parameter of their carrier atoms, for the methyl hydrogen atoms, and all other hydrogen atoms, respectively. For one of the independent molecules of **2a** a disorder model was refined for the $C^3H_5SC^2H_3$ part of the molecule with one common isotropic displacement parameter for the non-hydrogen atoms, while the hydrogens were refined as described before. Also one of the two independent solvent molecules (CH_2Cl_2) is disordered. The crystal structure contains, in addition to the two-fold screw axis, a pseudo-inversion center, at ($\pm 0.25, 0.320, \pm 0.25$) as indicated by

the MISSY algorithm implemented in the program PLUTON. However since all four crystallographically independent molecules have the same absolute configuration this inversion center can only be approximative. Compounds **2b** and **2d** displayed no disorder. Weights were optimized in the final refinement cycles. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for Crystallography [17]. The unit cell of **2d** can be transformed to orthorhombic but yields an R_{av} of 47%. The metrical orthorhombic symmetry is also not supported by the structure as indicated by the MISSY option as implemented in PLATON [13].

A crystal of **5b** with dimensions $0.03 \times 0.45 \times 1.10$ mm approximately was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $Cu K\alpha$ radiation and ω - 2θ scan. A total of 3012 unique reflections was measured, at room temperature, within the range $-10 \leq h \leq 19$, $0 \leq k \leq 19$, $-12 \leq l \leq 12$, of these 2672 were above the significance level of $2.5\sigma(I)$. The maximum value of $\sin\theta/\lambda$ was $0.63 \text{ \AA}^{-1}$. Two reference reflections ($\bar{1}21, \bar{1}22$) were measured hourly and showed no decrease

during the 36 h collecting time. Unit cell parameters were refined by a least-squares fitting procedure using 23 reflections with $80 < 2\theta < 90^\circ$. Corrections for Lorentz and polarization effects were applied. The structure was solved by direct methods. The hydrogens were calculated. Full-matrix least-squares refinement was performed on F , anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distance to their carrier remained constant at approximately $1.09 \text{ \AA}$, which converged to $R = 0.067$, $R_w = 0.088$, $(\Delta/\sigma)_{\text{max}} = 0.70$. A weighting scheme $w = (2.7 + F_{\text{obs}} + 0.0047 F_{\text{obs}}^2)^{-1}$ was used. An empirical absorption correction [12] was applied, with coefficients in the range 0.57–1.75. The secondary isotropic extinction coefficient [18] refined to $\text{EXT} = 0.08(6)$. A final difference Fourier map revealed a residual electron density between -1.3 and $1.4 \text{ e \AA}^{-3}$, the largest values occurring in the vicinity of the palladium atom. Scattering factors were taken from Cromer and Mann [19]. The anomalous scattering of palladium, chlorine and sulfur was taken into account. All calculations were performed with XTAL [20], unless stated otherwise. The crystal data of **2a**, **2b**, **2d** and **5b** are presented in Table 1; the fractional coordinates are listed in Table 2.

2.4. Synthesis of the ligands

2.4.1. L/D-methionine methyl ester (HmetMe)

Following literature procedures [21], using L-methionine (20.0 g; 0.13 mol), HmetMe was obtained as a yellow oil in 60% yield (HmetMe: $[\alpha]^{20} = -2.43$). *Anal.* Found: C, 43.85; H, 7.69; N, 8.66. Calc. for $\text{C}_6\text{H}_{13}\text{NO}_2\text{S}$: C, 44.15; H, 8.03; N, 8.88%. IR (KBr, cm^{-1}): 1739 (C=O). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K, δ): 15.4 (C^2); 30.2 (C^4); 32.4 (C^3); 53.1 (C^7); 52.8 (C^5); 173.8 (C^6). $^1\text{H}\{^1\text{H}\}$ NMR (KBr, cm^{-1}): 1740 (C=O). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K, δ): 16.5 (C^2); 39.9 (C^3); 52.7 (C^5); 54.3 (C^4); 175.1 (C^6).

2.5. Synthesis of the complexes

2.5.1. $[\text{PdBr}_2(\text{L})]$ ($\text{L} = \text{H}[\text{Me}]_{\text{cysMe-N,S}}$ (**1a**); HmetMe-N,S (**1b**); $\text{Py}^1\text{-N,N'}$ (**1c**); $\text{Py}^2\text{-N,N'}$ (**1d**))

To a stirred suspension of $[\text{PdBr}_2]$ (0.806 g; 3.01 mmol) in CH_2Cl_2 (10 ml) a solution of $\text{H}[\text{Me}]_{\text{cysMe}}$ (0.448 g; 3.01 mmol) in CH_2Cl_2 (15 ml) was added. The mixture was stirred for 18 h at room temperature, after which the solvent was evaporated. The resulting orange sticky solid was washed with Et_2O ($2 \times 10 \text{ ml}$) and subsequently dried, which afforded an air stable solid in 92% yield. $m/z = 415$, $M^+ = 415$ (for $\text{C}_6\text{H}_{11}\text{Br}_2\text{NO}_2\text{S}^{105}\text{Pd}$). *Anal.* Found: C, 15.10; H, 2.80; N, 3.53. Calc. for $\text{C}_6\text{H}_{11}\text{Br}_2\text{NO}_2\text{SPd}$: C, 15.04; H, 2.78; N, 3.51%. IR (KBr, cm^{-1}): 1742 (C=O).

Complexes **1b**, **1c** and **1d** were synthesized in a similar way. **1b**: reacting HmetMe (0.757 g; 2.88 mmol) in CH_2Cl_2 (10 ml) with $[\text{PdBr}_2]$ (0.771 g; 2.88 mmol) afforded the yellow air stable product in quantitative yield. $m/z = 429$, $M^+ = 429$ (for $\text{C}_6\text{H}_{13}\text{Br}_2\text{NO}_2\text{S}^{105}\text{Pd}$). *Anal.* Found: C,

16.65; H, 2.99; N, 3.23. Calc. for $\text{C}_6\text{H}_{13}\text{Br}_2\text{NO}_2\text{SPd}$: C, 16.78; H, 3.05; N, 3.26%. IR (KBr, cm^{-1}): 1736 (C=O). **1c**: $[\text{PdBr}_2]$ (0.545 g; 2.04 mmol) was reacted with Py^1 (0.220 g; 2.04 mmol) in CH_2Cl_2 (10 ml). An air stable yellow complex was obtained in 95% yield. IR (KBr, cm^{-1}): 1617 (C=N). **1d**: Py^2 (0.271 g; 2.22 mmol) reacted with $[\text{PdBr}_2]$ (0.592 g; 2.22 mmol) in CH_2Cl_2 (10 ml) to afford a yellow air stable complex in 95% yield. IR (KBr, cm^{-1}): 1611 (C=N).

Because of the low solubility of the bis bromide complexes $^{13}\text{C}\{^1\text{H}\}$ NMR experiments were not performed.

2.5.2. $[\text{PdCl}(\text{Me})(\text{L})]$ ($\text{L} = \text{H}[\text{Me}]_{\text{cysMe-N,S}}$ (**2a**); HmetMe-N,S (**2b**); $\text{Py}^1\text{-N,N'}$ (**2c**); $\text{Py}^2\text{-N,N'}$ (**2d**))

To a stirred solution of $[\text{PdCl}(\text{Me})(\text{COD})]$ (0.652 g; 2.58 mmol) in CH_2Cl_2 (10 ml) a solution of $\text{H}[\text{Me}]_{\text{cysMe}}$ (0.384 g; 2.58 mmol) in CH_2Cl_2 (10 ml) was added. The mixture was stirred for 3 h at room temperature, after which the solvent was evaporated. The resulting yellow sticky solid was washed with Et_2O ($2 \times 10 \text{ ml}$), in order to remove the COD, and dried. A yellow solid was obtained in 92% yield. Slow diffusion, at room temperature, of Et_2O into a concentrated solution of **2a** in CH_2Cl_2 afforded yellow crystals. *Anal.* Found: C, 23.59; H, 4.64; N, 4.60. Calc. for $\text{C}_6\text{H}_{14}\text{ClNO}_2\text{SPd}$: C, 23.54; H, 4.61; N, 4.58%. IR (CH_2Cl_2 , cm^{-1}): 1746 (C=O). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K, δ): -7.33 (Pd-CH_3) 22.0 (C^2); 43.6 (C^3); 55.8 (C^6); 63.7 (C^4); 171.8 (C^5). Complexes **2b**, **2c** and **2d** were obtained in a similar way. **2b**: $[\text{PdCl}(\text{Me})(\text{COD})]$ (0.286 g; 1.13 mmol) reacted with HmetMe (0.184 g; 1.13 mmol) in CH_2Cl_2 (10 ml) to afford an air stable yellow complex in 95% yield. Yellow crystals were obtained by slow diffusion of Et_2O into a concentrated solution of **2b** in CH_2Cl_2 . *Anal.* Found: C, 26.35; H, 4.97; N, 4.26. Calc. for $\text{C}_7\text{H}_{16}\text{ClNO}_2\text{SPd}$: C, 26.26; H, 5.04; N, 4.38%. IR (CH_2Cl_2 , cm^{-1}): 1735 (C=O). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K, δ): -3.5 (Pd-CH_3) 21.4 (C^2); 34.3 (C^4); 29.7 (C^3); 53.5 (C^7); 54.6 (C^5); 173.5 (C^6). **2c**: starting with $[\text{PdCl}(\text{Me})(\text{COD})]$ (0.169 g; 0.75 mmol) and Py^1 (0.081 g; 0.75 mmol) an off white, air stable solid was obtained in 95% yield. *Anal.* Found: C, 31.74; H, 4.20; N, 10.59. Calc. for $\text{C}_7\text{H}_{11}\text{ClN}_2\text{Pd}$: C, 31.72; H, 4.19; N, 10.57%. IR (KBr, cm^{-1}): 1616 (C=N). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 343 K, δ): 2.2 (Pd-CH_3); 33.5 (C^1); 112.4 (C^4); 118.9 (C^3); 144.3 (C^5); 156.3 (C^6); 164.6 (C^2). **2d**: starting with $[\text{PdCl}(\text{Me})(\text{COD})]$ (0.201 g; 0.89 mmol) and Py^2 (0.109 g; 0.89 mmol) an off white, air stable solid in quantitative yield was isolated. Colorless crystals were obtained by slow diffusion of Et_2O into a concentrated solution of **2d** in CH_3CN . *Anal.* Found: C, 34.41; H, 4.68; N, 10.10. Calc. for $\text{C}_8\text{H}_{13}\text{ClN}_2\text{Pd}$: C, 34.43; H, 4.70; N, 10.04%. IR (KBr, cm^{-1}): 1605 (C=N). $^{13}\text{C}\{^1\text{H}\}$ NMR (90% $\text{CD}_3\text{CN} + 10\%$ DMSO- d_6 , 343 K, δ): -9.9 (Pd-CH_3); 37.8 (C^2); 39.7 (C^1); 122.2 (C^5); 124.4 (C^4); 138.0 (C^6); 151.0 (C^7) 159.7 (C^3).

Table 2

Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for **2a**, **2b**, **2d** and **5b**

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
2a									
Pd(1)	0.25611(4)	0.13564(3)	0.43268(4)	0.0171(1)	Pd(2)	0.47651(4)	0.12321(3)	0.73870(4)	0.0214(1)
Cl(1)	0.33454(13)	0.00288(13)	0.40155(12)	0.0242(4)	Cl(2)	0.36674(14)	0.1008(13)	0.76348(13)	0.0271(5)
S(1)	0.19175(13)	0.26246(12)	0.47803(14)	0.0219(5)	S(2)	0.58786(15)	0.22970(13)	0.71950(14)	0.0265(5)
O(11)	0.0215(5)	0.0068(5)	0.5890(5)	0.046(2)	O(21)	0.6646(5)	−0.0535(4)	0.5670(5)	0.0365(19)
O(12)	0.0498(4)	0.1307(4)	0.6933(4)	0.0393(17)	O(22)	0.6713(4)	0.0689(4)	0.4727(4)	0.0310(17)
N(11)	0.1781(5)	0.0619(4)	0.5186(5)	0.0250(17)	N(2)	0.5319(5)	0.0335(4)	0.6464(4)	0.0212(17)
C(11)	0.3170(6)	0.2096(5)	0.3450(6)	0.029(2)	C(21)	0.4259(7)	0.2151(6)	0.8196(7)	0.034(3)
C(12)	0.1002(6)	0.3211(5)	0.3595(6)	0.034(2)	C(22)	0.5009(6)	0.3026(5)	0.6116(6)	0.034(2)
C(13)	0.0929(5)	0.2101(5)	0.5203(5)	0.0233(17)	C(23)	0.6525(5)	0.1608(5)	0.6523(5)	0.0233(19)
C(14)	0.1454(5)	0.1243(5)	0.5846(5)	0.0220(17)	C(24)	0.5784(5)	0.0865(5)	0.5836(5)	0.0196(17)
C(15)	0.0647(6)	0.0789(5)	0.6217(6)	0.027(2)	C(25)	0.6429(5)	0.0236(5)	0.5413(5)	0.0191(17)
C(16)	−0.0240(8)	0.0958(8)	0.7350(8)	0.056(4)	C(26)	0.7376(7)	0.0173(6)	0.4298(6)	0.036(3)
Pd(3)	0.23559(4)	0.50162(4)	1.05440(4)	0.0211(1)	Pd(4)	−0.03356(5)	0.99703(4)	0.22491(5)	0.0302(2)
Cl(3)	0.15338(15)	0.6315(2)	1.08653(13)	0.0352(6)	Cl(4)	−0.1157(2)	1.1143(2)	0.28117(15)	0.0344(6)
S(3)	0.2980(2)	0.37587(13)	1.00335(15)	0.0264(5)	*S(4)	0.0194(2)	0.8846(2)	1.401(2)	0.0265(4)
O(31)	0.4212(5)	0.6499(4)	0.8533(5)	0.046(2)	*S(4B)	0.0851(6)	0.8987(6)	0.2152(6)	0.0265(4)
O(32)	0.5016(5)	0.5152(5)	0.8554(5)	0.0473(19)	O(41)	0.1538(6)	1.1903(4)	0.0581(5)	0.045(2)
N(3)	0.3112(5)	0.5794(5)	0.9678(5)	0.0249(17)	O(42)	0.2101(5)	1.0620(4)	0.0098(5)	0.0405(17)
C(31)	0.1803(7)	0.4210(7)	1.1431(6)	0.037(3)	N(4)	0.3390(5)	1.0921(5)	0.1530(5)	0.0271(19)
C(32)	0.4175(6)	0.3364(6)	1.1163(6)	0.040(2)	C(41)	−0.0864(8)	0.9003(7)	0.2998(9)	0.050(3)
C(33)	0.3586(6)	0.4298(5)	0.9229(6)	0.032(2)	*C(42A)	0.1411(7)	0.8338(6)	0.2386(7)	0.0265(4)
C(34)	0.3987(5)	0.5269(5)	0.9589(5)	0.0223(17)	*C(42B)	−0.005(2)	0.810(2)	0.139(2)	0.0265(4)
C(35)	0.4416(6)	0.5724(6)	0.8843(6)	0.0286(19)	*C(43A)	0.0764(8)	0.9555(7)	0.0668(8)	0.0265(4)
C(36)	0.5463(8)	0.5525(8)	0.7840(7)	0.051(3)	*C(43B)	0.110(3)	0.954(2)	0.112(3)	0.0265(4)
					C(44)	0.1239(6)	1.0471(5)	0.1289(6)	0.028(2)
					C(45)	0.1634(6)	1.1095(6)	0.0617(6)	0.0294(19)
					C(46)	0.2531(7)	1.1147(8)	−0.0524(6)	0.046(3)
2b									
Pd(1)	0.40214(2)	0.28392(6)	−0.01951(3)	0.0235(1)	Pd(1)	0.14775(2)	0.20504(1)	0.27468(2)	0.0229(1)
Cl(1)	0.58222(11)	0.2995(3)	−0.18376(10)	0.0334(3)	Cl(1)	0.17067(7)	0.02218(5)	0.35592(9)	0.0328(2)
S(1)	0.22377(10)	0.25379(15)	0.13466(12)	0.0297(4)	N(1)	0.1105(2)	0.3620(2)	0.1847(3)	0.0280(6)
O(1)	0.8561(3)	0.2502(7)	0.3372(4)	0.0500(16)	N(1)	0.3525(2)	0.2475(2)	0.4873(3)	0.0253(5)
O(2)	0.7524(3)	0.3955(6)	0.5127(3)	0.0412(10)	C(1)	0.2183(3)	0.4442(2)	0.2800(3)	0.0301(7)
N(1)	0.5947(3)	0.2676(10)	0.1477(4)	0.0299(13)	C(2)	0.2647(3)	0.4338(2)	0.4731(3)	0.0298(7)
C(1)	0.2305(4)	0.2919(14)	−0.1886(5)	0.0389(12)	C(3)	0.3774(2)	0.3486(2)	0.5546(3)	0.0269(7)
C(2)	0.0798(5)	0.4350(9)	0.0982(6)	0.0497(16)	C(4)	0.5047(3)	0.3739(2)	0.6924(4)	0.0363(8)
C(3)	0.3059(4)	0.3383(8)	0.3144(5)	0.0358(14)	C(5)	0.6105(3)	0.2969(2)	0.7616(4)	0.0420(10)
C(4)	0.4629(4)	0.2572(7)	0.3686(5)	0.0316(14)	C(6)	0.5872(3)	0.1948(2)	0.6903(4)	0.0390(10)
C(5)	0.5910(4)	0.3450(6)	0.2941(4)	0.0250(12)	C(7)	0.4566(3)	0.1732(2)	0.5545(3)	0.305(7)
C(6)	0.7478(4)	0.3201(6)	0.3822(4)	0.0262(11)	C(8)	−0.0420(3)	0.1727(2)	0.0779(4)	0.0368(8)
C(7)	0.8957(5)	0.3779(9)	0.6074(5)	0.0407(14)					
5b									
Pd(1)	1.05138(5)	0.61951(3)	0.99810(4)	0.0427(3)					
Cl(1)	0.8554(2)	0.5829(1)	1.1345(2)	0.063(1)					
S(1)	1.2374(2)	0.6713(1)	0.8715(2)	0.0533(9)					
O(1)	0.6232(8)	0.6465(5)	0.6291(7)	0.078(4)					
O(2)	0.7323(7)	0.5623(4)	0.4840(5)	0.063(3)					
O(3)	1.2948(8)	0.5677(4)	1.1933(6)	0.071(4)					
N(1)	0.8632(7)	0.6085(4)	0.8296(6)	0.047(3)					
C(1)	1.198(2)	0.7038(7)	1.245(1)	0.086(7)					
C(2)	1.424(1)	0.6187(8)	0.914(1)	0.084(7)					
C(3)	1.187(1)	0.6255(5)	0.7071(8)	0.057(4)					
C(4)	1.017(1)	0.6492(5)	0.6446(8)	0.056(4)					
C(5)	0.8871(8)	0.5909(4)	0.6924(7)	0.044(3)					
C(6)	0.7322(9)	0.6040(5)	0.5991(7)	0.049(3)					
C(7)	0.589(1)	0.5744(7)	0.3868(8)	0.070(5)					
C(8)	1.204(1)	0.6254(5)	1.1612(8)	0.055(4)					

2.5.3. $[PdBr(Me)[H(Me)cysMe-N,S]]$ (**3a**)

A solution of **2a** (0.191 g; 0.62 mmol) in CH_2Cl_2 (20 ml) was reacted with $[Ag(O_3SCF_3)]$ (0.159 g; 0.62 mmol) for 30 min at room temperature after which the resulting suspension was filtered in order to remove the $AgCl$, after which $NaBr$ (excess) was added. The mixture was stirred for 18 h after which the suspension was filtered and the resulting yellow solution was evaporated. An air stable yellow solid was obtained in 80%. *Anal.* Found: C, 20.52; H, 4.00; N, 3.98. Calc. for $C_6H_{14}BrNO_2SPd$: C, 20.56; H, 4.03; N, 4.00%. IR (KBr, cm^{-1}): 1748 (C=O).

2.5.4. $[PdBr(Me)(L)]$ ($L = HmetMe-N,S$ (**3b**); Py^l-N,N' (**3c**); Py^2-N,N' (**3d**))

Reacting **1b** (0.724 g; 1.77 mmol) with Me_4Sn (0.473 g; 2.65 mmol) in CH_2Cl_2 (15 ml) and CH_3CN (10 ml) for 18 h at room temperature resulted in a brownish solution. Evaporation of the solvent afforded a brown solid which was purified by column chromatography (silica). Using CH_2Cl_2 as the eluent a yellow fraction was isolated. After evaporation of the solvent and drying of the product, the yellow–orange complex **3b** was collected in 60% yield. *Anal.* Found: C, 23.06; H, 4.44; N, 3.78. Calc. for $C_7H_{16}BrNO_2SPd$: C, 23.15; H, 4.43; N, 3.84%. IR (CH_2Cl_2 , cm^{-1}): 1746 (C=O). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 213 K, δ): -5.0 (Pd- CH_3) 21.1, 21.8 (C^2); 28.8, 30.5 (C^4); 33.8, 35.7 (C^3); 54.0 (C^7); 54.5, 55.0 (C^5); 173.8 (C^6). ($CDCl_3$, 233 K, δ): -4.8 (Pd- CH_3) 21.5 (C^2); not observed (C^4); not observed (C^3); 53.8 (C^7); 54.5 (C^5); 174.0 (C^6). ($CDCl_3$, 293 K, δ): -4.5 (Pd- CH_3) 21.4 (C^2); 29.9 (C^4); 34.8 (C^3); 53.5 (C^7); 54.4 (C^5) 174.1 (C^6). **3c** and **3d** were synthesized in a similar way using **1c** and **1d**, respectively. **3c**: IR (KBr, cm^{-1}): 1614 (C=N). **3d**: IR (KBr, cm^{-1}): 1619 (C=N). $^{13}C\{^1H\}$ NMR (CD_3CN , 293 K, δ): not observed (Pd- CH_3); 39.0 (C^1); 40.4 (C^2); 125.0 (C^5); 138.0 (C^4); 139.8 (C^6); 154.4 (C^7); 158.7 (C^3). Elemental analysis of **3c** and **3d** failed, probably due to traces of **1c**.

2.5.5. $[PdI(Me)(L)]$ ($L = H[Me]cysMe-N,S$ (**4a**); $HmetMe-N,S$ (**4b**))

To a solution of **2a** (0.191 g; 0.62 mmol) in CH_2Cl_2 (10 ml) NaI (excess) was added. An immediate color change was observed. After 1 h the suspension was filtered and the residue was washed with H_2O (10 ml). The organic layer was separated and dried on $CaCl_2$. After filtration and subsequent evaporation of the solvent a hygroscopic red solid was obtained in 55% yield. IR (CH_2Cl_2 , cm^{-1}): 1745 (C=O). **4b** was prepared as described for **4a**, starting with **2b** (0.21 g; 0.65 mmol). IR (CH_2Cl_2 , cm^{-1}): 1742 (C=O). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K, δ): 8.56 (Pd- CH_3) 20.5 (C^2); 27.7 (C^4); 30.7 (C^3); 52.7 (C^7); 53.6 (C^5); 172.7 (C^6). Elemental analysis of **4a** and **4b** could not be carried out due to the presence of traces of CH_2Cl_2 , which could not be removed by either washing with Et_2O or drying in vacuo.

2.5.6. $[PdX(COME)(L)]$ ($L = H[Me]cysMe-N,S$; $X = Cl$ (**5a**), Br (**6a**), I (**7a**); $HmetMe-N,S$; $X = Cl$ (**5b**), Br (**6b**), I (**7b**); Py^l-N,N' ; $X = Cl$ (**5c**), Br (**6c**); Py^2-N,N' ; $X = Cl$ (**5d**), Br (**6d**))

Through a yellow solution of **2a** (0.03 g; 0.10 mmol) in $CDCl_3$ (0.5 ml) CO was bubbled for 1 min. A small amount of colloidal palladium was formed and complex **5a** was not isolated. IR (CH_2Cl_2 , cm^{-1}): 1746 (C(O)OMe); 1700 (Pd-C(O)Me).

A pressurizing flask was charged with **2b** (0.06 g; 0.2 mmol) in CH_2Cl_2 (5 ml). The yellow solution was pressurized with CO (5 bar), and the uptake of CO was measured at room temperature. Isolation of **5b** was achieved by filtration over celite and subsequent evaporation of the solvent. Yellow crystals were obtained by slow diffusion of Et_2O into a concentrated solution of **5b**. The crystals were kept in paraffin oil. Elemental analysis could not be carried out owing to slow degradation of the complex. IR (CH_2Cl_2 , cm^{-1}): 1748 (C(O)OMe); 1701 (Pd-C(O)Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K, δ): 21.2 (C^2); 30.2 (C^4); 35.2 (C^3); 38.2 (Pd-C(O)CH₃); 53.4 (C^7); 54.6 (C^5); 173.6 (C^6); 228.3 (Pd-C(O)CH₃).

Compounds **5c**, **5d**, **6a**, **6b**, **6c**, **6d**, **7a**, **7b** were synthesized as described for **5b**. The complexes were not isolated because of the gradual degradation, i.e. small amounts of colloidal palladium were formed on attempted isolation. **5c**: IR (CH_2Cl_2 , cm^{-1}): 1618 (C=N); 1697 (Pd-C(O)Me). **5d**: IR (CH_2Cl_2 , cm^{-1}): 1619 (C=N); 1701 (Pd-C(O)Me). **6a**: IR (CH_2Cl_2 , cm^{-1}): 1748 (C(O)OMe); 1701 (Pd-C(O)Me). **6b**: IR (CH_2Cl_2 , cm^{-1}): 1743 (C(O)OMe); 1700 (Pd-C(O)Me). **6c**: IR (CH_2Cl_2 , cm^{-1}): 1617 (C=N); 1700 (Pd-C(O)Me). **6d**: IR (CH_2Cl_2 , cm^{-1}): 1618 (C=N); 1702 (Pd-C(O)Me). **7a**: IR (CH_2Cl_2 , cm^{-1}): 1747 (C(O)OMe); 1701 (Pd-C(O)Me). **7b**: IR (CH_2Cl_2 , cm^{-1}): 1744 (C(O)OMe); 1699 (Pd-C(O)Me).

2.5.7. $[PdCl\{\eta^3-CH_2C(Me)CH_2\}_2]$ (**8**)

$[PdCl(Me)(COD)]$ (0.387 g; 1.528 mmol) was dissolved in CH_2Cl_2 (10 ml). Allene was bubbled through (2 ml/min) this solution at room temperature which resulted in an almost instant (< 1 min) color change from colorless to yellow. Evaporation of the solvent and subsequent drying of the residue in vacuo afforded a yellow solid in 72% yield. *Anal.* Found: C, 24.40; H, 3.58. Calc. for $C_8H_{14}Cl_2Pd_2$: C, 24.39; H, 3.59%. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.3 ($C^{2'}-CH_3$); 62.4 ($-CH_2-$); 127.5 ($C^{2'}$).

2.5.8. $[PdCl\{\eta^3-CH_2C(Me)C(Me)_2\}_2]$ (**9**)

To a solution of $[PdCl(Me)(COD)]$ (0.183 g; 0.72 mmol) in CH_2Cl_2 (10 ml), DMA (0.051 g; 0.72 mmol) was added. The solution was stirred for 10 min at room temperature, after which the solvent was evaporated, resulting in an air stable yellow solid in 84% yield. *Anal.* Found: C, 31.99; H, 4.93. Calc. for $C_{12}H_{22}Cl_2Pd_2$: C, 32.03; H, 4.93%. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K, δ): 20.9 ($C^{2'}-CH_3$); 24.1 ($anti-CH_3$);

24.7 ($^{\text{syn}}\text{CH}_3$); 58.6 ($-\text{CH}_2$); 89.5 ($-(\text{C}(\text{CH}_3)_2)$); 119.7 ($\text{C}^{2'}$).

2.5.9. $[\text{PdCl}\{\eta^3\text{-C}(\text{Me})_2\text{C}(\text{Me})\text{C}(\text{Me})_2\}]_2$ (**10**)

Synthesized as described for **9**. Reacting the compounds for 10 h at room temperature afforded a yellow solid in 85% yield. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K, δ): 19.3 (C^2-CH_3); 26.7 ($^{\text{anti}}\text{CH}_3$); 28.6 ($^{\text{syn}}\text{CH}_3$); 85.7 ($-(\text{C}(\text{CH}_3)_2)$); 114.4 ($\text{C}^{2'}$). Elemental analysis was not carried out, since the similar complexes **8**, **9** and **11** are analyzed properly.

2.5.10. $[\text{PdCl}\{\eta^3\text{-CH}_2\text{C}(\text{COMe})\text{C}(\text{Me})_2\}]_2$ (**11**)

A solution of $[\text{PdCl}(\text{Me})(\text{COD})]$ (0.154 g; 0.608 mmol) in CH_2Cl_2 (10 ml) was cooled to 223 K and subsequently put under a CO atmosphere (1 bar) for 5 min. 1,1-Dimethylallene (0.083 g; 1.216 mmol) was added which caused a color change from colorless to yellow. Evaporation of the solvent and subsequent drying in vacuo afforded a yellow solid in 65% yield. *Anal.* Found: C, 33.21; H, 4.38. *Calc.* for $\text{C}_{14}\text{H}_{22}\text{O}_2\text{Cl}_2\text{Pd}_2$: C, 33.23; H, 4.39%. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K, δ): 24.6 ($^{\text{anti}}\text{CH}_3$); 25.6 ($^{\text{syn}}\text{CH}_3$); 29.6 ($-(\text{CO})\text{CH}_3$); 56.9 ($-\text{CH}_2$); 92.2 ($-(\text{C}(\text{CH}_3)_2)$); 117.8 ($\text{C}^{2'}$); 199.4 ($-(\text{CO})\text{CH}_3$).

The complexes having the general formula $[\text{Pd}\{\eta^3\text{-allyl}\}(\text{L})][\text{X}]$ were synthesized as yellow hygroscopic solids via two routes, i.e. (A) reaction of $[\text{PdCl}(\text{Me})(\text{L})]$ with allene and (B) reaction of the ligand **L** with a $[\text{PdCl}(\eta^3\text{-allyl})]_2$ complex (Scheme 1).

Elemental analyses of the α -amino ester containing allylpalladium complexes **12a–14b** could not be carried out as a result of the presence of small amounts of allene (Route A) or dimer (Route B) due to the high solubility of the products and starting compounds in apolar solvents like Et_2O and hexane.

2.5.11. $[\text{Pd}\{\eta^3\text{-CH}_2\text{C}(\text{Me})\text{C}(\text{Me})_2\}(\text{H}[\text{Me}]_{\text{cysMe-N,S}})]\text{Cl}$ (**12a**)

Route A. A mixture of **2a** (0.137 g; 0.448 mmol) and 1,1-dimethylallene (0.031 g; 0.448 mmol) in CH_2Cl_2 (10 ml) was stirred for 30 min at room temperature. Evaporation and subsequent drying in vacuo afforded compound **12a** in 75% yield as a hygroscopic yellow solid. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K, δ): 18.1 (C^2-CH_3); 19.8 ($^{\text{anti}}\text{CH}_3$); 20.7 ($^{\text{syn}}\text{CH}_3$); 23.8 (C^3); 39.2 (C^5); 52.4 (C^6); 54.6 (C^4); 65.5 (C^3H_2); 89.0 (C^1H_2); 123.0 (C^2); 172.1 ($\text{C}(\text{O})\text{OCH}_3$). $^3\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 213 K, δ): 20.3^{broad} (C^2-CH_3); 21.0 ($^{\text{anti}}\text{CH}_3$); 22.0 ($^{\text{syn}}\text{CH}_3$); 24.9, 25.0 (C^3); 39.9^{broad} (C^5); 54.2 (C^6); 56.1^{broad} (C^4); 66.9 (C^3H_2); 95.1 (C^1H_2); 125.6, 125.8 ($\text{C}^{2'}$); 172.0, 172.2 (C^5).

Conductivity experiments performed during a reaction of 3-methyl-1,2-butadiene (DMA) and **2a** in CH_2Cl_2 (1283 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at 293 K) showed an increase of conductivity; $\Delta = 2459\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ (293 K). The product showed a specific conductivity (CH_2Cl_2) of $\Delta = 2010\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at 293 K and 4102 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at 343 K.

Complex **12c** $[\text{Pd}\{\eta^3\text{-CH}_2\text{C}(\text{Me})\text{C}(\text{Me})_2\}(\text{Py}^1\text{-N,N'})]\text{-Cl}$ was synthesized as described for **12a**, using a 35 mM solution of **2c** in CDCl_3 . Upon the addition of DMA (1 equiv.) a small amount of colloidal palladium was formed immediately. ^1H (CDCl_3 , 293 K, δ): 8.04 (broad s, 1H, C^6H); 7.47 (broad s, 1H, C^5H); 6.55 (broad s, 1H, C^3H); 6.44 (broad s, 1H, C^4H); 3.62 (broad s, 1H, H^{anti}); 3.12 (broad s, 1H, H^{syn}); 2.84 (broad s, 3H, C^2H_2); 2.05 (broad s, 3H, $^{\text{anti}}\text{CH}_3$); 1.27 (broad s, 3H, $^{\text{syn}}\text{CH}_3$). The product showed a specific conductivity of $\Delta = 3010\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ (CH_2Cl_2 , 293 K).

2.5.12. $[\text{Pd}\{\eta^3\text{-CH}_2\text{C}(\text{Me})\text{C}(\text{Me})_2\}(\text{HmetMe-N,S})]\text{Cl}$ (**12b**)

Route B. To a solution of $[\text{PdCl}\{\eta^3\text{-CH}_2\text{C}(\text{Me})\text{C}(\text{Me})_2\}]_2$ in CH_2Cl_2 (10 ml) a solution of *HmetMe-N,S* (0.146 g; 0.897 mmol) in CH_2Cl_2 (5 ml) was added. The mixture was stirred at room temperature for 18 h after which the solvent was evaporated, resulting in yellow solid **12b** in 86% yield. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K, δ): 20.7 (C^2-CH_3); 22.1 (C^5); 24.9 ($^{\text{anti}}\text{CH}_3$); 25.3 ($^{\text{syn}}\text{CH}_3$); 33.0 (C^4); 33.3 (C^3); 54.3 (C^7); 57.4 (C^3H_2); 59.3 (C^6); 91.0 (C^1H_2); 121.7 ($\text{C}^{2'}$); 174.4 (C^7). Conductivity experiments performed during the reaction of 3-methyl-1,2-butadiene and **2b** in CH_2Cl_2 (1421 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at 293 K) showed an increase of the conductivity; $\Delta = 2530\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ (293 K).

2.5.13. $[\text{Pd}\{\eta^3\text{-CH}_2\text{C}(\text{COMe})\text{C}(\text{Me})_2\}(\text{L})]\text{Cl}$ (**L** = *H[Me]cysMe-N,S* (**13a**); *HmetMe-N,S* (**13b**))

A solution of **2b** (0.092 g; 0.301 mmol) in CH_2Cl_2 (10 ml) was stirred at room temperature under a CO atmosphere (1 bar) for 5 min. DMA (0.020 g; 0.301 mmol) was added and after a color change to yellow, the solution was evaporated and subsequently dried in vacuo affording yellow complex **13b** in 65% yield. Complex **13a** was obtained as described for **13b** in 70% yield. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K, δ): 20.1 (C^2); 29.8 ($\text{C}^{2'}-\text{C}(\text{O})\text{CH}_3$); 24.5 ($^{\text{anti}}\text{CH}_3$); 25.8 ($^{\text{syn}}\text{CH}_3$); 40.2 (C^3); 53.5 (C^6); 56.2 (C^4); 66.3 (C^3H_2); not observed (C^1H_2); not observed ($\text{C}^{2'}$); 171.7 (C^5); 200.6 ($\text{C}^{2'}-\text{C}(\text{O})\text{CH}_3$).

Complexes **14b**, $[\text{Pd}(\text{Me})_2\text{CC}(\text{Me})\text{C}(\text{Me})_2](\text{HmetMe-N,S})[\text{Cl}]$ and **15b**, $[\text{Pd}(\text{H}_2\text{CC}(\text{Me})\text{C}(\text{nBu}))](\text{HmetMe-N,S})[\text{Cl}]$ were synthesized via route A, using **2b** (0.114 g, 0.373 mmol). Conductivity measurements of **14b** (CH_2Cl_2) showed a specific conductivity of $\Delta = 1879$ at 243 K, 2842 at 293 K and 3567 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at 343 K, and for **15b** $\Delta = 1884$ at 243 K, 2942 at 293 K and 3765 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at 343 K.

3. Results

Reaction of ligand **L**, i.e. racemic $\{(\text{S-methyl})\text{-D/L-cysteine}\}$ methyl ester (*H[Me]cysMe* (**a**)); racemic *D/L-methionine* methyl ester (*HmetMe* (**b**)); 2-[amino-

Fig. 2. Numbering of the complexes. a = H[Me]cysMe-*N,S*; b = HmetMe-*N,S*; c = Py²-*N,N'*; d = Py²-*N,N'*.

methyl]pyridine (Py¹ (c)); 2-[2-aminoethyl]pyridine (Py² (d)), respectively with PdBr₂ afforded the 1:1 complexes [PdBr₂(L)] (1), see Fig. 2. The methyl–palladium complexes [PdX(Me)(L)] (X = Cl (2), Br (3), I (4)) were synthesized via various routes. The chloride complex was prepared from [PdCl(Me)(1,5-COD)] and L, which could be converted with an excess of NaI to [PdI(Me)(L)]. [PdBr(Me)(L)] was synthesized from [PdBr₂(L)] and Me₃Sn. The complexes dissolve in polar solvents such as MeCN, CH₂Cl₂, and acetone and can be stored under air for a prolonged period.

3.1. Crystal structures

Single crystal X-ray determinations were carried out for the complexes **2a** (Fig. 3), **2b** (Fig. 6) and **2d** (Fig. 3).

The unit cell of **2a** contains four independent molecules, which all consist of a cysteine ester ligand L which is bidentate bonded to the palladium center via the amine nitrogen (Pd–N = 2.163(7) Å) and the thioether sulfur donor (Pd–S = 2.2407(19) Å). The square-planar coordinated geometry of the palladium atom is further completed by the chlorine atom (Pd–Cl = 2.331(2) Å) and the methyl group (Pd–C11 = 2.026(8) Å). The latter ligand is located *cis* to the sulfur atom, as expected in analogy with corresponding PN palladium complexes where the methyl (or acyl) group is always *cis* to the phosphorus donor atom, being the atom with the highest *trans* influence [2b,22]. The five-membered chelate ring has a λ conformation with an envelope geometry [23], with the methyl ester substituent in an equatorial position and the thioether methyl group in an axial position, analogous to the earlier reported dichloro-(*S*-methyl-*L*-cysteine-*N,S*)palladium(II) complex [24]. The absolute configuration of the sulfur center is *R*, while the stereogenic carbon atom C⁴H of the ligand has an *S* configuration in all four independent molecules in the unit cell. Although four diastereomers, i.e. *RR*, *SS*, *RS* and *SR*, might be present in the solid state, since a racemic mixture of the ligand is used, only one (*SR*) is observed in the crystal lattice. The N–Pd–S bite angle of the NS coordinated cysteine ligand is 86.08(17)°, which is slightly less than the bite angle observed in the dichloro-(*S*-methyl-*L*-cysteine-*N,S*)palladium(II) complex (87.2(3)°) [24].

Complex **2b**, with one independent molecule in the unit cell, has an analogous square planar arrangement around the palladium center, as observed for **2a**, with distances of

Fig. 3. Crystal structures of **2a** [PdCl(Me)[H(Me)cysMe]] (top) and **2d** [PdCl(Me)(Py²)] (bottom). Ortep drawings are drawn with a 50% probability level, hydrogens are omitted for clarity. (This is also true for Fig. 6).

2.149(3) (Pd–N), 2.2528(13) (Pd–S), 2.034(4) (Pd–C) and 2.3246(13) (Pd–Cl) Å. The six-membered chelate ring has a chair conformation with both the methyl ester and the thioether methyl group in equatorial position, as was also observed for dichloro-(*D/L*-methionine-*N,S*)palladium(II) [25]. The NS bite angle is 95.02(10)°, which is slightly less than the bite angle (96.88(37)°) observed in dichloro-(*D/L*-methionine-*N,S*)palladium(II) [25].

The 2-[2-aminoethyl]pyridine (Py²) containing complex **2d** again has a square planar surrounding. Relevant distances are 2.189(2) (Pd–N(py)), 2.053(2) (Pd–NH₂), 2.009(3) (Pd–C) and 2.3358(7) (Pd–Cl) Å. The methyl group is bonded to the palladium center *cis* to the amine moiety, which might indicate that the NH₂ unit has a larger *trans* influence than the pyridine nitrogen donor. The dihedral angle of N2–Pd1–N1–C1 (–0.6(2)°) shows that these atoms all lie in one plane. Since the pyridine group is twisted out of the coordination plane by 26.9° the six-membered ring formed by the chelate bonding of the NN' ligand has a flattened twisted-boat geometry, with an N–Pd–N bite angle of 92.90(9)°. Hydrogen bonds between the NH₂ unit and the chloride ion are observed; the distances (3.426(2) and 3.385(2) Å) and angles (141.1(2) and 153.9(3)°) between the donor and acceptor fall within the normal range [26].

3.2. Structures in solution

The ¹H and ¹³C[¹H] NMR data for the complexes containing the racemic H[Me]cysMe and the HmetMe ligands confirm that, also in solution, these NS ligands are chelate bonded as evidenced by the downfield proton shifts of the S–Me group (Δδ = 0.45–0.67 ppm) and of the proton on the stereogenic carbon atom C⁴H (a), C⁵H (b) (Δδ = 0.06–1.26 ppm) with respect to the values of the free ligands (Table 3).

Table 3

Relevant ^1H NMR data of the complexes **1a–7a**, **1b–7b**, **1c–6c** and **1d–6d**, measured at room temperature

No. [Solvent]	C ² H ₃ (s)	C ⁴ H (m)	C ² H ₃ (s)			Pd–Me (s)	Pd–COMe (s)
H(Me)CysMe	3.68	3.61	2.06				
1a [DMSO]	3.71	4.19	2.64				
2a [CDCl ₃]	3.78	3.88b	2.51b			0.59	
3a [CDCl ₃]	3.81	^a	2.54			0.67	
4a [CDCl ₃]	3.81	3.89	2.53			0.68	
5a [CDCl ₃]	3.79	3.82	2.45				2.60
6a [CDCl ₃]	3.81	^a	2.55				2.18
7a [CDCl ₃]	3.77	3.78	2.42				2.10
No. [Solvent]	C ² H ₃ (s0)	C ⁴ H (m)	C ² H ₃ (s)			Pd–Me (s)	Pd–COMe (s)
HMetMe	3.62	3.53	1.97				
1b [DMSO]	3.72	4.79	2.64				
2b [CDCl ₃]	3.75	3.65	2.45			0.58	
3b [CDCl ₃]	3.76	3.65	2.45			0.60	
4b [CDCl ₃]	3.74	3.59	2.40			0.56	
5b [CDCl ₃]	3.76	3.59	2.41				2.50
6b [CDCl ₃ + CD ₃ CN] (5:1)	3.60	4.20	2.56				2.59
7b [CDCl ₃]	3.79	3.84	2.40				2.54
No. [Solvent]	C ³ H	C ⁴ H	C ⁵ H	C ⁶ H	C ¹ H ₂	Pd–Me (s)	Pd–COMe (s)
Py ¹	6.55dt	6.34d	7.39dt	8.05d	2.89s		
1c [DMSO- <i>d</i> ⁶]	7.57d	7.46t	8.04t	9.05d	3.51b		
2c [CD ₃ CN]	6.66d	6.64t	7.64dt	8.50b	3.31b	0.55s	
3c [DMSO- <i>d</i> ⁶ + CDCl ₃] (3:1)	6.58b	6.58b	7.43b	8.03b	3.34b	0.91b	
5c [CD ₃ CN]	6.60d	6.69t	7.63t	8.27b	2.89s		2.34s
6c [CD ₃ CN]	6.65d	6.74t	7.70t	8.34b	3.01s		2.35s
No. [Solvent]	C ⁴ H	C ⁵ H	C ⁶ H	C ⁷ H	C ¹ H ₂	Pd–Me (s)	Pd–COMe (s)
Py ²	7.10dt	7.06d	7.53dt	8.47d	2.85t		
1d [DMSO- <i>d</i> ⁶]	7.58d	7.46t	8.04t	9.06d	3.29b		
2d [DMSO- <i>d</i> ⁶]	7.38b	7.35b	7.85dt	9.06d	3.05b	0.30s	
3d [DMSO- <i>d</i> ⁶]	7.38b	7.38b	8.17b	9.10b	3.38b	0.67s	
5d [DMSO- <i>d</i> ⁶]	7.34	7.36d	8.01t	9.03d	4.28b		2.05s
6d [DMSO- <i>d</i> ⁶]	7.41t	7.35d	8.13t	9.12d	3.20b		2.19

s, singlet; d, doublet; t, triplet; dt, double triplet; b, broad resonance signal; m, multiplet. The coupling constants of H^3 , H^4 , H^5 and H^6 of the pyridine moiety are approximately $^1J(\text{H}^3-\text{H}^4) = 5.0$ Hz, $^1J(\text{H}^4-\text{H}^5) = 8.4$ Hz, $^1J(\text{H}^5-\text{H}^6) = 4.7$ Hz and of the ethylene-amine bridge $^1J(\text{H}-\text{H}) = 6.6$ Hz.

^a Obscured by the CD_3Me resonance.

Also the $^{13}\text{C}\{^1\text{H}\}$ signals of the S–Me group show downfield shifts ($\Delta\delta = 5.1$ –6.5 ppm) (**2a**, **2b**, **3b** and **4b**; Section 2).

Interestingly, the C^4 and $\text{C}^6\{^1\text{H}\}$ resonances of **2a** have shifted downfield ($\Delta\delta = 9.4$ and 3.1 ppm, respectively), while the analogous signals of **2b**, **3b** and **4b** did not shift to the same extent. In all NS complexes coordination of the carboxylic oxygen atom of the $\text{C}(\text{O})\text{OMe}$ unit does not occur, since the corresponding IR CO absorption (1735 – 1748 cm^{-1}) does not shift notably when compared to the values found for the free ligands (1739 cm^{-1}).

Both the five- and the six-membered NS complexes (**2a**–**4b** and **5b** vide infra) show broad ^1H NMR signals at room temperature. Upon cooling to 213 K the S–Me and the Pd–Me singlets split (Fig. 4) indicating the presence of two diastereoisomers in solution. The ^1H NMR spectra of **2a** at 213 K show a sharp triplet ($^3J(\text{C}^4\text{H}-\text{C}^3\text{H}_2) = 11$ Hz) and a mul-

Fig. 4. ^1H NMR spectra of $[\text{Pd}(\text{Me})(\text{HmetMe})]$ (**4b**) in the S–Me region (2.5–2.0 ppm) and the Pd–Me region (1.0–0.0 ppm), measured in CDCl_3 .

triplet for C^2H in the ratio of 3:1, respectively (Table 3). By using the Karplus relation [27], one may calculate a dihedral angle of -178° for the major component which is in excellent agreement with the dihedral angle of $-178.8(9)^\circ$ found in the solid state for H13–C13–C14–H14, indicating an envelope geometry of the chelate ring with an *S* configuration of C^4 . The minor component clearly has a different dihedral angle which is caused by geometrical changes in the chelate ring [28], and therefore cannot have the five-membered ring with an envelope geometry.

The splitting of the S–Me resonance shows that at lower temperature the sulfur atom has a stable configuration on the NMR time scale and consequently is a stereogenic center. Interconversion at higher temperatures between the two diastereomers probably proceeds via either an inversion of configuration at the sulfur atom ($\Delta G^\ddagger = 50\text{--}62 \text{ kJ mol}^{-1}$) or via a reversible dissociation/association process of the Pd–S bond. It should be noted that both possibilities are intramolecular processes. By using line-shape analysis [29] for **4b** the $\Delta H^\ddagger$ (57.8 kJ mol^{-1}), the $\Delta S^\ddagger$ ($40 \text{ J mol}^{-1} \text{ K}^{-1}$) and the $\Delta G^\ddagger_{243}$ (48.1 kJ mol^{-1}) values could be determined. The positive value for $\Delta S^\ddagger$ is in agreement with the proposed intramolecular character of the aforementioned processes.

The diastereoisomeric ratio in the case of complexes **2a**, **3a** and **4a**, which all have a five-membered chelate ring, are clearly dependent on the nature of the halide anion (Table 4) and changes from 3:1 ($X = \text{Cl}$) to 4.9:1 ($X = \text{I}$). In the case of the complexes **2b**, **3b** and **4b**, which contain six-membered chelate rings, there appears to be a slight decrease in this order, however these differences are small and fall within the experimental error. As it is not possible to assign these complexes as the *SR*, *RS*, *RR* or *SS* diastereoisomeric pairs, these phenomena will not be further discussed. Intuitively it is understandable that in the case of the complexes **2b**, **3b** and **4b**, which contain the more flexible six-membered chelate ring, both the ratios and the $\Delta G^\ddagger$ values will be much less sensitive to the size of the anion than in the complexes with five-membered chelate rings.

Table 4

Free-energy values, $\Delta G^\ddagger$ (kJ mol^{-1}), T_c (K), $\Delta\nu$ (Hz), k (s^{-1}) and the ratio of the two diastereomers for the methyl inversion of **2a–4a** and **2b–5b**

Complex	T_c (K)	$\Delta\nu$ (Hz)	k (s^{-1})	$\Delta G^\ddagger$ (kJ mol^{-1})	Ratio
2a	293	23.4	52	62.1 ± 2.2	3.0:1.0
3a	281	13.7	30	60.7 ± 2.1	4.0:1.0
4a	263	16.0	36	56.3 ± 2.2	4.9:1.0
2b	294	33.0	73	61.5 ± 0.4	1.0:1.0
3b	243	33.0	73	50.0 ± 1.1	0.9:1.0
4b	243	35.4	79	48.0 ± 1.1	0.8:1.0
5b	243	52.5	117	49.5 ± 2.0	1.0:1.0

Measurements were recorded at 300 MHz, using approximately 40 mM solution in CDCl_3 . Inversion barriers were calculated from the coalescence temperature (T_c) and the frequency difference between the coalescing signals in the slow exchange limit ($\Delta\nu$ in Hz) with the formulas $k = \pi\Delta\nu/2$ and $\Delta G^\ddagger = -RT_c \ln[\pi\Delta\nu h/(2kT_c)]$.

In the case of the Py^1 and Py^2 palladium complexes (**1c–6d**) the ligands *L* are bidentate bonded as illustrated by the downfield shift of the $\text{Cl}1_z\text{N}$ moiety ($\delta\Delta = 0.20\text{--}0.62 \text{ ppm}$) and of the H^a pyridine atom ($\delta\Delta = 0.02\text{--}1.02 \text{ ppm}$) with respect to the free ligand values (Table 3). The IR spectra show a shift of the $\text{C}=\text{N}$ moiety ($1605\text{--}1619 \text{ cm}^{-1}$) when compared to the free ligand (approximately 1640 cm^{-1}). All NMR signals are rather broad and temperature dependent. However, ^1H NMR measurements carried out between 213 and 313 K were not very illuminating, since the linewidths of the signals did not change perceptibly.

3.3. Reactivity of the methylpalladium complexes towards CO and allenes

The remarkable stability and the ease of formation of the methylpalladium complexes (**2–4**), containing a coordinated NH_2 substituent, prompted us to study insertion reactions with CO and allenes, which have turned out to be so successful for complexes $[\text{PdX}(\text{Me})(\text{NN})]$ [**2a**, **2c**, **30**, **31**] and $[\text{PdX}(\text{Me})(N\text{--}[(\text{thienylmethylidene})\text{-D/L-methionyl}]\text{-methyl ester-N,S})]$ [**6**].

3.4. Reactions with CO

All methylpalladium complexes reported in this Section reacted very rapidly to give the corresponding acyl complexes which were characterized by NMR and IR and in the case of **5b** (Fig. 5) by a single crystal X-ray determination (Fig. 6).

The square planar complex **5b** shows the characteristic features. The NS ligand is bidentate coordinated and forms with the palladium atom a six-membered ring, which has a chair conformation with the S–Me and the methyl ester substituent both in equatorial positions, analogous to **2b**. The distances are 2.186(6) Å for the Pd–N bond, 2.293(2) Å for the Pd–S bond, 2.351(2) Å for the Pd–Cl bond and 1.966(8) Å for the Pd–acyl bond. Again, we see that the acyl group is *cis* to the sulfur atom, while the Pd–N bond *trans* to the acyl group is slightly lengthened when compared to **2b**, owing to the larger *trans* influence of the acyl group relative to the methyl group. The bite angle of the NS ligand is $94.2(2)^\circ$ in **5b**, which is smaller than for **2b** ($95.02(10)^\circ$), but both are larger than the bite angle of **2a** ($86.08(17)^\circ$) which contains a five-membered chelate ring (see Table 7). Consequently the complementary Cl–Pd–C angle in **2b** and **5b** is smaller than this angle in **2a** and **2d**.

The molecular structures of the acyl complexes (**5a–7b**) in solution are also similar to the structure observed for **5b** in the solid state. Both the S–Me group and the proton on the

Fig. 5. Numbering of the CO inserted complexes.

Fig. 6. Crystal structures of **2b** [PdCl(Me)(HmetMe)] (top) and **5b** [PdCl(C(O)Me)(HmetMe)] (bottom).

stereogenic carbon atom C^4H of ligand **a** (C^5H (**b**)) show downfield shifts of 0.39–0.59 and 0.06–0.67 ppm, respectively, as are also found for the $^{13}C\{^1H\}$ NMR signals of **5b** ($\Delta\delta = 5.8$ and 1.8 ppm, respectively, see Section 2). The 1H NMR of **5b** at 213 K shows the presence of two diastereoisomers in a 1:1 ratio (Table 4) with a $\Delta G^\ddagger$ for interconversion at 243 K which lies in the range of the methylpalladium complexes **2b–4b**. It can be concluded that the substitution of the methyl group by an acyl group appears to have very little influence on the molecular structure, the diastereomeric ratios and the activation energies for interconversion.

Highly remarkable are the very rapid insertion rates of CO into the Pd–Me bond of all complexes, which were measured by electronic gasburet techniques. The formation of the product was monitored by the increase of the absorbance at approximately 1700 cm^{-1} in the IR spectra (Section 2). These rates are among the fastest we have ever measured and are even faster than the insertion rates measured for [PdY(Me)(NN)] (NN = R-DAB, R-Pyca) [32]. All measurements, including blank experiments to determine the rate of diffusion of CO, were carried out in triplicate. The results are reproducible, but since the rates are so close to the time necessary to saturate the solution, approximately 30 s, the data obtained will be discussed only in short and with great scepticism. It appears that the rates, as represented by the half-lives ($21 < \text{half-lives} < 48\text{ s}$), decrease in the order $Cl > Br > I$. In the case of the NS ligands there is no clear dependence on the chelate ring size, but the complexes with six-membered NN' chelate rings appear to react faster than those with the five-membered NN' rings.

In analogy to recently reported insertions of (substituted) allenes into the palladium methyl bond of [PdX(Me)(NN)] [30,31,33] it has been found that the complexes [PdX(Me)(L)] (L = NS) react rapidly and quantitatively to afford η^3 -allylpalladium compounds (Scheme 1). Conductivity experiments showed that the complexes are ionic in solution. The formation of the NS containing allylpalladium complexes were carefully investigated. The insertion of 3-methyl-1,2-butanediene into the Pd–Me bond of **2c** could only be followed by 1H NMR, as reliable kinetic data for this reaction could not be obtained, due to a low solubility of **2c** and the formation of a small amount of colloidal palladium during the insertion reaction.

An alternative and very easy route to the same complexes is to react [PdCl(Me)(1,5-COD)] with the required allene to give [PdCl(η^3 -allyl)]₂ complexes which were then reacted with the proper NS ligand. The chloro-allylpalladium

Scheme 1. Numbering of the η^3 -allyl containing complexes.

Table 5

Relevant ^1H NMR data of the η^3 -allyl containing complexes, 8–15b, measured in CDCl_3 at room temperature

$[\text{PdCl}(\eta^3\text{-allyl})]_2^b$	Y	R^{1anti}	R^{2syn}	R^{3syn}	R^{4anti}			
	2.15s (Me)	2.89s (H)	3.87s (H)	3.87s (H)	2.89s (H)			
	2.03s (Me)	3.14s (H)	3.68s (H)	1.34s (Me)	1.21s (Me)			
	1.95s (Me)	1.46s (Me)	1.62s (Me)	1.62s (Me)	1.46s (Me)			
	2.51s (C(O)Me)	3.31s (H)	4.02s (H)	1.43s (Me)	1.28s (Me)			
$[\text{Pd}(\eta^3\text{-allyl})(\text{NS})]\text{Cl}^c$	Y	R^{1anti}	R^{2syn}	R^{3syn}	R^{4anti}	C^2H_3	$\text{C}^{6/7}\text{H}^d$	$\text{C}^{4/5}\text{H}^d$
	1.94bs (Me)	3.16bs (H)	3.77bs (H)	1.59bs (Me)	1.28b (Me)	2.30bs	3.68s	4.05b
	2.43s (C(O)Me)	3.27s (H)	^a (H)	1.58s (Me)	1.36s (Me)	2.50s	3.73s	4.36b
	2.01s (Me)	3.21bs (H)	3.83bs (H)	1.63s (Me)	1.32s (Me)	2.39s	3.77s	3.92b
	2.42s (C(O)Me)	3.15s (H)	3.74s (H)	1.45s (Me)	1.23s (Me)	2.34bs	3.70s	3.89s
	1.84s (Me)	1.50s (Me)	1.57s (Me)	1.57s (Me)	1.50s (Me)	2.12s	3.71s	4.04s
	1.99s (Me)	^a (H)	3.62s (H)	3.34b (H)	1.20t 0.87m (nBu)	2.24b	3.80s	4.20b

s, singlet; b, broad; bs, broad singlet; m, multiplet; t, triplet.

^a Obscured by the $\text{C}(\text{O})\text{OCH}_3$ resonance.^b For assignment see Refs. [30a] and [36].^c For assignment see Ref. [47].^d For assignment of $\text{C}^{6/7}$ and $\text{C}^{4/5}$ see Fig. 1.

dimer, which is substituted on the central carbon atom, can be synthesized easily and in high yields, as compared to the synthetic routes used thus far [34].

Since the η^3 -allylpalladium complexes lack a proton at the 2-position of the allyl group, resulting in the absence of allylic proton couplings, the easy assignment of the allylic ^1H and $^{13}\text{C}\{^1\text{H}\}$ resonance shifts had to be carried out by analogy with known compounds (Scheme 1, Table 5) [35].

It is clear from the ^1H NMR at room temperature that the NS ligands are chelate bonded ($\Delta\delta \text{S-Me} = 0.15\text{--}0.44 \text{ ppm}$; $\Delta\delta \text{C}^{\text{H}} = 0.36\text{--}0.75 \text{ ppm}$). Accordingly, the existence of at least four isomers per diastereomeric compound, with asymmetric allyl groups, can be expected (Scheme 2). All these stereoisomers are unique since the C^{α} center in both NS ligands, the chelate ring and the sulfur atom are stable stereogenic center elements in the slow exchange limit. In the case of the pentamethyl substituted allyl complex **14b**, if for example both C^{α} and S-Me are *R*, two rotamers are expected (with the central methyl group either up or down). Since the *syn* methyl groups 1 and 4 are magnetically equivalent as are also the *anti* methyl groups 2 and 3, the presence of two diastereoisomers (i.e. rotamers) appears to be confirmed.

The rate of insertion of 3-methyl-1,2-butadiene (DMA), 2,4-dimethyl-2,3-pentadiene (TMA) and 1,2-heptadiene (nBuA) into the Pd-Me bond has been measured for complexes **2a** and **2b** at 292 K (isothermally) in order to investigate the influence of the NS ligand and the type of allene on this process. All reactions were carried out with at least a 7 times higher allene concentration as compared with the concentration of the complex and therefore these conditions correspond to pseudo-first-order conditions. The conversion of the starting complexes was quantitative and in all cases isosbestic points were obtained. All reactions were found to be first order in palladium. The pseudo-first-order rate constants (k_{obs}), when plotted versus the concentration of the allene give straight lines with a non-zero intercept (Fig. 7), indicating that the kinetics follow the typical rate law

Scheme 2. Schematic view of $[\text{Pd}(\eta^3\text{-1,1,2-trimethyl-allyl})(\text{H}[\text{Me}]\text{-cysMe})]\text{Cl}$ (**12a**).

$k_{\text{obs}} = k_1 + k_2[\text{allene}]$. However, in the case of the reaction of **2b** with TMA the slope of the line is very small, indicating that the contribution of the k_2 pathway is negligible. It is further clear that the fastest reactions occur for **2b** with DMA and n-BuA. Much slower rates are found for the reaction of **2b** with TMA and **2a** with DMA.

Nonetheless, all these reactions are slower than the α -diimine containing palladium complexes [31]. In the case of the reaction of **2b** with DMA, the activation parameters have been determined by using the Eyring plot for measurements at 257, 263, 267 and 271 K (Table 6). The large deviations in k_1 make the values of $\Delta H^\ddagger = 95 \pm 50 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 78 \pm 150 \text{ J mol}^{-1} \text{ K}^{-1}$ unreliable and can therefore not be used, while the activation parameters for the allene dependent k_2 pathway ($\Delta H^\ddagger = 9.5 \pm 5 \text{ kJ mol}^{-1}$ and

Fig. 7. Plot of the allene insertion rate, k_{obs} (s^{-1}), vs. the concentration of allene for complex **2b** with DMA, **2b** with nBuA (plot A), **2b** with TMA and **2a** with DMA (plot B), all measured at 293 K. [A] represents the allene concentration. The lines are calculated for the points defined by 7.5, 15, 30, 60 and 120 equivalents. The insertion rates (k_{obs}) were calculated using $\ln\{[A(t) - A(\infty)]/[A(0) - A(\infty)]\} = -kt$. The absorptions $A(0)$, $A(t)$ and $A(\infty)$ were determined at 310 nm for **2b** + DMA, 307 nm for **2b** + TMA; 285 nm for **2a** + DMA and 307 nm for **2b** + nBuA, using 3 ml of an approximately 1 mM $[\text{PdCl}(\text{Me})]\text{(L)}$ solution in CH_2Cl_2 .

Table 6

The k_1 and k_2 values (s^{-1}) obtained at 257, 263, 267 and 271 K, for the reaction of **2b** with DMA

T (K)	k_1 (s^{-1})	k_2 ($M^{-1} s^{-1}$)
257	$1.71 \times 10^{-3} \pm 2.99 \times 10^{-3}$	$1.55 \times 10^{-3} \pm 0.17 \times 10^{-3}$
263 ^a	$-4.04 \times 10^{-4} \pm 1.04 \times 10^{-3}$	$1.65 \times 10^{-3} \pm 0.11 \times 10^{-3}$
267	$1.07 \times 10^{-3} \pm 4.58 \times 10^{-3}$	$1.77 \times 10^{-3} \pm 0.26 \times 10^{-3}$
271	$1.71 \times 10^{-3} \pm 4.02 \times 10^{-3}$	$2.08 \times 10^{-3} \pm 0.23 \times 10^{-3}$

^a The negative value of k_1 clearly indicates the uncertainty and can therefore not be regarded as a quantitative value.

$\Delta S^\ddagger = -197 \pm 30$ J mol⁻¹ K⁻¹) show relatively small deviations.

4. Discussion

The methylpalladium complexes could be prepared in high yields by substitution of 1,5-cyclooctadiene in [PdCl(Me)(1,5-COD)] by ligand L and by reaction of [PdBr₂(L)] with Me₃Sn to afford [PdBr(Me)(L)] directly. Reaction of the methylpalladium complexes with CO gave rapid formation of the corresponding acyl complexes [PdX(C(O)Me)(L)].

4.1. Crystal structures

From a comparison of the S1–C13–C14–N1 dihedral angle (57.9(6)°) of **2a** with the similar angle of the free ligand (72.6°) [36], one may infer that a rotation is needed of the ligand backbone in order to bind the H[Me]cysMe ligand as an NS chelate. The coordination fashion is therefore controlled by the metal and not by the ligand, as is the case for *N*-[*N*-(5-methyl-2-thienylmethylidene)-*L*-methionyl]-histamine [37]. Coordination control by the metal is clearly also the case for other ligands in this study. When considering the HmetMe containing complexes **2b** and **5b** it may be noted that the structures of the complexes and the conformations of the six-membered rings are virtually the same (Fig. 6) with a chair conformation of the ring and the methyl ester and the thiomethyl group positioned equatorially. The five-membered ring of **2a** has an envelope conformation with both substituents in equatorial positions.

It should be noted that in the case of [PdCl₂(meth-*N*,*S*)] [25] and [PtCl(Gly-*L*-met-*N*,*N'*,*S*)] [38] the methyl group on the S atom is in a quasi axial position. All distances between the palladium atom and the surrounding donor atoms (Table 7) are in the normal range [39,40]. The Pd–C bond of the Pd–acyl moiety (1.966(8) Å) of **5b** is in the range found for other neutral and ionic complexes, i.e. [PdCl(C(O)Me)(2,2'-bipyridine)], [PdCl(C(O)Me)(C₅H₄N-2-C(H)=N-*i*Pr)] [2c] and [Pd(C(O)-1-C₁₀H₇)(NN'*N*)]-Otf [41], while again the acyl group is perpendicular to the coordination plane. In the case of **2d** the Pd–N(1) (amine) distance is comparable to those observed for an amine *trans*

Table 7

Selected bond distances (Å), angles (°) and torsion angles (°) of **2a**, **2b**, **2d** and **5b** (e.s.d.s in parentheses)

2a		2b	
Pd–Cl	2.331(2)	Pd–Cl	2.3246(13)
Pd–Cl1	2.026(8)	Pd–Cl	2.034(4)
Pd–S	2.2407(19)	Pd–S	2.2528(13)
Pd–N	2.163(7)	Pd–N	2.149(3)
Cl–Pd–Cl1	90.7(2)	Cl–Pd–Cl	89.83(12)
Cl1–Pd–S	91.2(2)	Cl–Pd–S	88.89(12)
S–Pd–N	86.08(17)	S–Pd–N	95.02(10)
N–Pd–Cl	92.41(17)	N–Pd–Cl	86.17(9)
Pd–S–C13–C14	41.6(4)	Pd–S–C3–C4	–49.7(4)
S–C13–C14–N	–57.9(6)	S–C3–C4–C5	76.0(5)
Pd–N–C14–C13	43.9(7)	C3–C4–C5–N	–78.0(5)
C16–O12–C15–O11	0.6(12)	Pd–N–C5–C4	58.6(6)
		C7–O2–C6–O1	–4.6(7)
2d		5b	
Pd–Cl	2.3358(7)	Pd–Cl	2.351(2)
Pd–C8	2.009(3)	Pd–C8	1.966(8)
Pd–N2	2.189(2)	Pd–S	2.293(2)
Pd–N1	2.053(2)	Pd–N	2.186(6)
Cl–Pd–C8	90.02(7)	Cl–Pd–C8	87.5(3)
C8–Pd–N1	84.77(10)	C8–Pd–S	91.6(3)
N1–Pd–N2	92.90(9)	S–Pd–N	94.2(2)
N2–Pd–Cl	92.30(7)	N–Pd–Cl	86.7(2)
Pd–N2–C3–C2	–3.8(3)	Pd–S–C3–C4	59.1(6)
C1–C2–C3–N2	–52.7(3)	S–C3–C4–C5	–82.8(7)
N1–C1–C2–C3	82.4(3)	C3–C4–C5–N	72.3(8)
Pd–N1–C1–C2	–45.5(3)	Pd–N–C5–C4	–48.7(8)
N2–Pd–N1–C1	–0.6(2)	S–Pd–C8–O3	–86.4(8)
C7–N2–C3–C2	176.4(2)	O1–C6–O2–C7	3(1)
Cl–Pd–N2–C3	–153.15(19)		

to chloride, while the Pd–N2 (pyridyl) distance is shorter than those found for pyridine-imine palladium(II) complexes with a pyridyl *trans* to a methyl group [32].

4.2. The molecular structures in solution

The ¹H and ¹³C{¹H} signals of C^αH, S–Me and Pd–Me indicate that in solution the NS ligand is also chelating. In the case of the Py¹ and Py² containing complexes, the ligands are also chelate bonded, as shown by the ¹H NMR of the H⁶ proton of c (H⁷ of d) of the pyridine group and of the CH₂ unit next to the amine function. Typical for complexes with asymmetric ligands is the observation that the methyl groups are *cis* to the ligand with the highest *trans* influence [42]. Alternatively, one could say that the soft ligands are *cis* to each other as are the hard ligands, thereby balancing the electron push/pull properties of the ligands *trans* to each other.

By means of variable temperature ¹H NMR measurements, in the range 213–313 K, it was possible to determine the free energy values $\Delta G^\ddagger$ associated with the apparent conversion

of the two sets of diastereomers in solution (*RR/SS* and *RS/SR*) of the NS containing complexes. These differ with respect to the position of the methyl group on the S atom and the absolute configuration of the chiral carbon atom (C^4 of **a**, C^5 of **b**). Since the latter is a stable stereogenic center, the conversion of the two isomers involves an inversion of the sulfur center, i.e. *RR* isomerizes to *RS*. As this process is very likely intramolecular, the $\Delta G^\ddagger$ values give an indication of the activation energies, as $\Delta S^\ddagger$ will be small [43]. In the case of the six-membered ring compounds, the activation energies decrease in the order $Cl > Br > I$, which is, however, much less evident for the five-membered ring compounds (Table 4). One might argue that, since the *trans* influence order is $Cl < Br < I$, the Pd–S bond *trans* to I would be weakened most, thereby enhancing an intramolecular Pd–S on/off movement [44] which in any case would proceed faster for six- than for five-membered rings.

4.3. Reactions with CO

The rates of CO insertion reactions with $[PdX(Me)(L)]$, which yielded in all cases the corresponding acyl complexes, are all very high. It has been mentioned that no definite conclusions can be drawn on the basis of the present experiments, as the rates are close to the diffusion rate of CO. The high rates in itself are interesting, since they are higher than observed for analogues PP^3 and NN complexes [32] which were both generally faster than those of PN complexes [2b,6]. These observations highlight that it is very difficult as of yet to understand the role of the ligands.

Since the NS and NN⁺ ligands in this study like PN ligands [2b,45] may be regarded as hemilabile ligands, as they contain both a hard and a soft donor function, one may imagine, as demonstrated for PN ligands in the case of Pt [2b], fairly easy dissociation of one of the donor functions may occur, which is generally the hard one. Such intermediates, with unidentate NN ligands, have also been tentatively proposed to account for the fast insertion observed for complexes $[PdX(Me)(NN)]$ (NN = R-DAB, R-pyca) [32]. Precise kinetic studies of CO insertions are clearly needed, but could in any case not be carried out for the systems at hand owing to lack of proper equipment.

4.4. Reactions with allenes

The η^3 -allylpalladium complexes $[Pd(\eta^3\text{-allyl})(NS)]Cl$ (**12a–15b**, Scheme 1) could be prepared either by reaction of the methyl- or acylpalladium complexes with various allenes, or by the simple bridge breaking reaction of $[PdCl(\eta^3\text{-allyl})]_2$ dimers with the required ligand L (Table 5 and Scheme 1). The latter method appears to be the more efficient one, as $PdCl(Me)$ (1,5-COD) reacts with all allenes used.

According to the 1H NMR and conductivity measurements, the complexes $[Pd(\eta^3\text{-allyl})(NS)]Cl$ contain a chelated NS ligand and are cationic in CH_2Cl_2 [46]. The assignment of the allylic protons of the known dimers **8** and **9** has been

based on literature values [35], while dimers **10** and **11** were assigned by comparison with similar compounds [30a].

For the complex $[Pd(\eta^3\text{-1,1,2,3,3-pentamethyl-allyl})(NS)]Cl$ (**14b**) several isomers are expected, which differ with respect to: (i) the position of the methyl group on the central allylic carbon atom, which can either be pointing up or down with respect to the ligand backbone [46]; (ii) the absolute configuration of C^5 (*R* or *S*); (iii) the configuration of the sulfur atom (*R* or *S*). The first isomerization (up/down) does appear to take place, since the *syn*-methyl groups **1** and **4** are magnetically equivalent as are also the *anti*-methyl groups **2** and **3**, indicating a left/right exchange of the allyl group, which would not be observed when a sulfur inversion takes place.

The observed *syn/syn* and *anti/anti* exchange might occur via a five-coordinate intermediate with the Cl^- temporarily bonded to Pd(II) or via the unidentate NS ligand, as has been unequivocally proven to be the case for $[(\eta^3\text{-allyl})-Pd(NN)]Cl$ complexes by Gogoll et al. [47] and Vrieze and co-workers [30]. Therefore it was a surprise that even at low temperatures (213 K), complexes **12a**, **13a**, **12b**, **13b** and **15b** all showed only one isomeric form in solution, while four structures were expected (Scheme 2). When considering the substituents on the NS ligand it is expected that the NH_2 group will be *trans* to the most substituted end of the η^3 -allyl ligand. However, the possibility that very rapid exchanges between the four possible isomers occur (even at very low temperatures) should not be excluded. Since these exchanges cannot involve $\eta^3\text{-}\eta^1\text{-}\eta^2$ rearrangements, which would render the protons at the unsubstituted side of the allyl group magnetically equivalent, which should easily occur but is not observed, the proposal of one isomer with the NH_2 moiety *trans* seems more likely.

When considering the reaction of allenes with complexes $[PdCl(R)(NS)]$ ($R = Me, C(O)Me$), it is useful to note that extensive kinetic studies have shown that the reactions of alkenes like norbornadiene with $[PdX(C(O)Me)(NN)]$ [30] and allenes with $[PdXR(NN)]$ ($R = Me, C(O)Me$) [30,31] generally have similar features and all follow the two-term rate law: $k_{obs} = k_1 + k_2[A]$ ($A = \text{alkene and allene}$). Also one should realize that the course of insertion reactions of this type is more difficult to interpret than the course of simple substitution reactions of d^8 -metal complexes [48], since the insertion step is preceded by the substitution steps.

First of all, in the case at hand, it is of interest to note that for reactions of **2a** with DMA and of **2b** with TMA the k_1 allene independent pathway appears to be dominant, a situation which has never been encountered before [30,31]. Interesting is also that **2a**, containing a five-membered ring, reacts much slower than the six-membered ring containing complex **2b**. Such behavior has also been observed for diphosphine complexes $[PdX(R)(PP)]$ ($R = Me, C(O)Me$) in their reactions with CO and norbornadiene, where the *dpmp* complex reacted faster than the *dppe* complex [4]. This behavior was rationalized by the notion that greater flexibility of the ring would lower the activation energy for reaching the

necessary five-coordinate transition states, while the larger bite angle would bring the substrates in the transition state close together. However, it should be noted that this was not the case for the analogous $[\text{PdX(R)}(\text{NN})]$ complexes for which fast reactions were obtained for both rigid [2a] and flexible NN ligands [32], with small N–Pd–N bite angles. In these cases it appears that complexes with unidentate NN ligands might play an important role, as was proposed for simple substitution reactions [49].

When comparing the rates as a function of the allene, it is clear that the tetrasubstituted allene (TMA) reacts slower than nBuA and DMA, which both have one substituted side on the allene, thereby facilitating attack of the non-substituted side of the allene at the Pd atom and the insertion step itself. Since the systems discussed here are not very suitable for extensive kinetic investigations, speculations in any depth on the various possible and probable mechanisms will not be made. Let it suffice to say that the k_1 pathway might involve a rate determining solvolysis of Cl^- , with a transition state resembling the initial state (i.e. bond breaking of Pd–Cl is less important than Pd–solvent bond making) [49] followed by a fast substitution (allene) and subsequent insertion step. Another possibility is a rate determining dissociation of either the Pd–N or Pd–S bond followed by fast association of the allene and a migration step. One might also consider a rate determining Pd–Cl dissociation, which, however, is unlikely, since first-order behavior in palladium is observed. The allene dependent k_2 path could involve a rate determining association of the allene or a rate determining insertion step preceeded by rapid association and substitution steps.

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