Exploring the Reactivity towards Acidic Protic Ligands of the Di-μ-hydroxo Complex $[NBu_4]_2[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2]$: A Convenient Precursor in the Preparation of New Palladacyclopentadiene Complexes

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The dinuclear hydroxo complex $[NBu_4]_2[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2]$ (**I**) reacts in a 1:2 molar ratio with a wide variety of protic electrophiles H(L) bearing different sets of donor atoms (L = O^O, N^S or O^N) to give the mononuclear anionic palladium(II) derivatives with the general formula $[Pd\{C_4(COOMe)_4\}(L)]^-$ [O^O = salycilaldehydate (sal) (**1**), acetohydroxamate (ahx) (**2**) and benzohydroxamate (bhx) (**3**); N^S = 2-pyridinthiolate (spy) (**4**), 2-pyrimidinthiolate (spym) (**5**), 3-methyl-2-imidazolin-thiolate (meimt) (**6**) and 2-aminothiophenolate (2-atp) (**7**); O^N = *N*-phenylsalycilaldiminate (*N*-phsal) (**8**), *N*-*p*-chlorophenylsalycilaldiminate (*N*-clsal) (**9**), *N*-*p*-tolylsalycilaldiminate (*N*-tolsal) (**10**), 2-aminophenolate (2-atp) (**11**), 2-pyrrole-carboxaldeydate (2-pcal) (**12**), 8-hydroxiquinolinate (oxin) (**13**), picolinate (2-pic) (**14**)]. Structural characterisation by X-ray diffraction of complexes **5**, **8** and **13** confirmed the proposed formula. Dinuclear complexes $[NBu_4]_2$ $[Pd\{C_4(COOMe)_4\}(\mu\text{-az})]_2$ (az = pyrazolate (pz) (**15**), triazolate (tz) (**16**) and 3,5-dimethylpyrazolate (3,5-Me_2pz) (**17**) were obtained when treating **I** with azoles in the same molar ratio, and also treating the hydroxo complex with chloranilic acid (chl) (**18**) and squarate (sq) (**19**) in 1:1 proportion to yield compounds $[NBu_4]_2[Pd\{C_4(COOMe)_4\}\{(\mu\text{-O–O})\}]$ with the ligands acting as *bis*-bidentate ones. A related process takes place when (**I**) reacts with ammonium *O*,*O*′-dialkyldithiophosphates in acetone under mild conditions and complexes $[NBu_4][Pd\{C_4(COOMe)_4\}\{S(S)P(OR)_2\}]$ (R = Me (**20**), Et (**21**), *i*Pr (**22**)) are obtained. Deprotonation of secondary amines Et_2NH, Pr_2NH, piperidine or morpholine by (**I**) in the presence of carbon disulfide leads to the corresponding dithiocarbamate complexes $[Pd\{C_4(COOMe)_4\}(S_2CNR_2)]$ **23**–**26**. (**I**) also promotes the nucleophilic addition of water to pyridine-2-carbonitrile and a mononuclear complex **27** containing the pyridine-2-carboxamidate ligand is formed. Its structure has been determined by a single-crystal diffraction study. The new complexes were fully characterised by analytical and spectroscopic techniques (FAB-MS, IR; ^1H, ^{13}C and ^{31}P-NMR).

Introduction

The chemistry of metallacycles has received growing interest during the last few years, as a result of their involvement in catalytic processes and their applications in organic synthesis.[1] The cycloaddition of two unsaturated fragments to a metal unit is one of the most useful methods of metallacycle synthesis, since it gives access to relatively complex structures starting from small unsaturated molecules.[1a] In particular, the oxidative cycloaddition of acetylenic esters such as dimethylacetylenedicarboxylate (dmad) to Ni, Pd and Pt has received attention in the past,[2,3] in part because of its involvement in different oligomerization and co-oligomerization catalytic reactions,[4] and also because of the interesting behaviour as precursors in organometallic chemistry of the compounds formed. Specifically, the polymeric palladacyclopentadiene complex [1,2,3,4-tetrakis(methoxycarbonyl)-1,3-butadiene-1,4-diyl]palladium(II) (TCPC) $[Pd(C_4(COOMe)_4)]_n$, obtained in the reaction of dmad with $Pd(dba)_2$ (dba = dibenzylidenacetone) reacts with a wide range of donor ligands to give soluble discrete molecules,[2,3,5,6] although to date, just a few crystal structures of such palladacyclopentadiene compounds are known.[7,8] Other interesting features recently studied are their use as catalysts in several types of reactions. Thus, intramolecular carbametalation and [2 + 2 + 2] cycloaddition,[9] enyne metathesis accompanied by skeletal rearrangement,[10,11] co-cyclotrimerization of various alkynes[5], and hydrostannation of cyclopropenes,[12] have employed TCPC amongst other derivatives as the catalyst. In this sense, in the frame of our collaboration with Fairlamb and co-workers, we have reported the first application of mononuclear palladacyclopentadiene complexes containing

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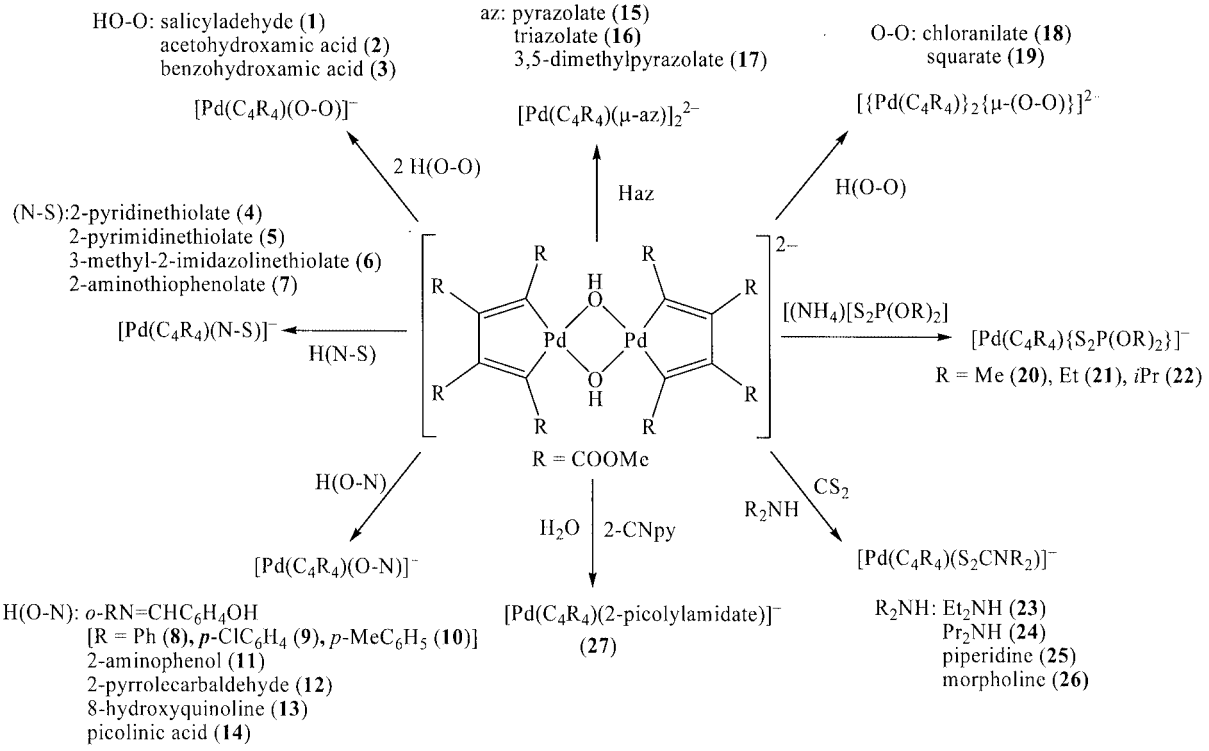
imidato ligands as catalysts in standard Stille cross-coupling reactions,[13]stating that yields and reaction times are dependent on the presence and type of these ligands. The exceptional catalytic properties of related dinuclear derivatives are currently under investigation, and suggest potential applications of compounds presented here.

On the other hand, in addition to their interest related to applied fields such antitumour activity of Pt^{II} complexes or catalytic processes,[14] the synthetic value of palladium(II) and platinum(II) di-μ-hydroxo complexes is a subject of growing study. For example, Sharp[15,16] and later others[17] have employed several such complexes as precursors in the preparation of scarce oxo and imido derivatives that are also relevant to C–O and C–N bond forming reactions in catalytic processes.[14] The reactivity towards protic substrates of dinuclear compounds $[Pd(\mu\text{-}OH)L^n]_2$ (L^n = orthometallated imine-based ligands) provides a general route to obtain dinuclear complexes with double and mixed bridges that have shown liquid crystal behaviour.[18] In this sense, during the last few years we have also been developing the usefulness of binuclear hydroxo complexes of palladium in the preparation of an extensive selection of new compounds, by means of a simple acid-base reaction.[19] Our more recent contribution to the area has been the synthesis of the dinuclear complex $[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2][NBu_4]_2$ and its use in the preparation of new palladacyclopentadiene derivatives that, as mentioned above, have shown interesting catalytic properties.[13] We expand in this paper on the reactivity of this complex towards several protic electrophiles and describe other related reactions, like that against amines in the presence of carbon disulfide or the addition of water experienced by pyridine-2-carbonitrile when $[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2][NBu_4]_2$ is present in the reaction.

Results and Discussion

The palladacyclopentadiene complex $[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2]^{2-}$ (**I**) was conveniently prepared by reaction of the polymeric complex $[Pd\{C_4(COOMe)_4\}]_n$ with NBu_4OH in water.[13] Its reactivity was easily followed by the disappearance of both an IR stretching vibration at 3600 cm^{-1} and a high-field shielded ^1H NMR resonance at δ = –0.85 ppm. The reactions explored in this paper are displayed in Scheme 1 and specific conditions followed for each of them are collected in the experimental section.

The hydroxo complex reacts with weak protic acids H(L) to give mono- or binuclear species depending on whether the deprotonated acid $(L)^-$ is *exo*- or *endo*-bidentate. These reactions can be viewed as an initial proton abstraction by (**I**) that provides $(L)^-$ and the metal substrate, subsequently trapped by the anion to form the new complexes. The protonation at the nucleophilic oxygen atom of the bridging OH should give an initial *aqua* complex that experiences H_2O replacement by the *endo*- or *exo*-bidentated $(L)^-$ leading to the formation of $[Pd\{C_4(COOMe)_4\}(L)]^-$ (**1**–**14**) or $[Pd\{C_4(COOMe)_4\}(\mu\text{-}L)]_2^{2-}$ (**15**–**17**) respectively. Similarly, the use of ligands able to coordinate in a *bis*-bidentate mode reacting with the precursor (**I**) in a 1:1 molar ratio allows the obtention of complexes **18** and **19**. The considerable nucleophilicity of the bridging OH groups of **I** makes it also



Scheme 1. Reactivity of the hydroxo complex $[NBu_4]_2[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2]$ (**I**).

reactive towards ammonium *O,O′*-dialkyldithiophosphates, yielding complexes **20**–**22** with the concomitant release of NH_3 and H_2O. The preparation of the dithiocarbamate complexes **23**–**26** should involve a first step of amine deprotonation, followed by nucleophilic attack of R_2N^- to carbon disulfide to form the dithiocarbamate anion. On the other hand, the activation of nitriles with respect to attack by nucleophiles in the coordination sphere of metal ions has attracted considerable interest.[20] We have described the attack of OH^- and MeO^- on benzonitrile coordinated to Pt^{II}[21] and the use of the hydroxo complex $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ in the formation of complexes containing amidate ligands,[22] and now we employ a similar reaction between **I** and pyridine-2-carbonitrile in acetone/water to prepare complex **27**.

The new palladium complexes are air-stable and their IR spectra show two very strong bands [ν(CO)] around 1700 cm^{-1} characteristic of the carboxylate groups,[2] in some cases partly overlapped by those absorptions attributed to the incoming deprotonated ligands (see Exp. Section). The ^{1}H-NMR spectra show the corresponding signals of these ligands, and as a common feature the characteristic chemical shifts of the methoxycarbonyl groups, which act as a preliminary probe for the compounds geometry, i.e., symmetric complexes show two signals and asymmetric show four resonances, in accordance with previous results.[7,8]

The proposed nuclearity of the new complexes is also confirmed by FAB mass spectrometry and the negative FAB-MS data of the complexes with the *m/z* values for the observed fragments are collected in the experimental section. The abundance of the signals around the parent ion are consistent in all cases with the natural isotopic abundances. This technique has special relevance conferring the mononuclearity of complexes with heterocyclic-2 thiolate ligands **4**–**7**, as NMR spectroscopic data would be compatible with either mononuclear complexes with the ligands acting in a chelating mode or dinuclear complexes with bridging ligands. This extent has been further proved by X-ray diffraction analysis of compound **5** whose structure and selected bond lengths and angles are shown in Figure 1 and Table 1. The Pd–N and Pd–S distances are slightly longer than the ones found for related Pd^{II} complexes with this ligand[23] and the N(1)–Pd–S(1) angle is considerably smaller than 90°, in agreement with previously reported data for four-membered N,S-chelate rings.[24,25]

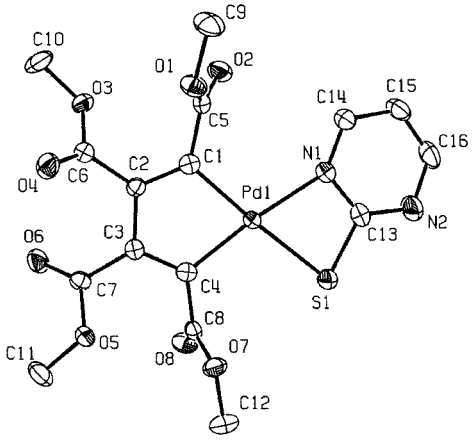


Figure 1. ORTEP diagram of anion complex **5** with the atom numbering Scheme; thermal spheres are drawn at the 50% probability level.

The mononuclear nature of complexes **8** and **13** that contain chelating ON donor ligands has also been confirmed by single-crystal X-ray analysis. The ORTEP diagrams of the two anions are shown in Figure 2 and Figure 3, while the relevant bond lengths and angles are reported in

Table 1. Selected bond lengths [Å] and angles [°] for complexes **5**, **8**, **13**, **20** and **27**.

	5	**8**	**13**	**20**	**27**
Pd(1)–C(1)	2.023(3)	2.007(3)	2.019(2)	2.05(3)	2.036(7)
Pd(1)–C(4)	1.986(3)	2.002(3)	1.981(2)	2.00(2)	1.741(6)
Pd(1)–N(1)	2.114(3)	2.111(2)	2.122(2)		1.882(5)
Pd(1)–N(2)					2.040(5)
Pd(1)–S(1)	2.3734(8)			2.406(8)	
Pd(1)–S(2)				2.396(7)	
Pd(1)–O(9)		2.0636(19)	2.0689(17)		
C(4)–Pd(1)–C(1)	79.29(12)	79.46(11)	79.30(9)	79.9(4)	79.6(3)
C(4)–Pd(1)–N(1)	172.48(11)	178.80(10)	171.32(9)		172.4(3)
C(4)–Pd(1)–N(2)					96.9(3)
C(1)–Pd(1)–N(1)	107.37(11)	101.51(10)	106.33(9)		107.1(2)
C(1)–Pd(1)–N(2)					176.4(2)
C(4)–Pd(1)–O(9)		90.83(10)	94.00(8)		
C(1)–Pd(1)–O(9)		167.91(9)	172.73(8)		
C(4)–Pd(1)–S(1)	103.85(8)			177.8(7)	
C(1)–Pd(1)–S(1)	176.77(9)			99.6(8)	
C(4)–Pd(1)–S(2)				97.0(7)	
C(1)–Pd(1)–S(2)				176.5(7)	
N(1)–Pd(1)–N(2)					76.5(2)
N(1)–Pd(1)–S(1)	69.45(7)				
O(9)–Pd(1)–N(1)		88.12(8)	80.66(7)		
S(1)–Pd(1)–S(2)				83.53(10)	

Table 1. The torsion angles of the six-membered ring chelate in (**8**) suggest for it a distorted sofa conformation.[26]

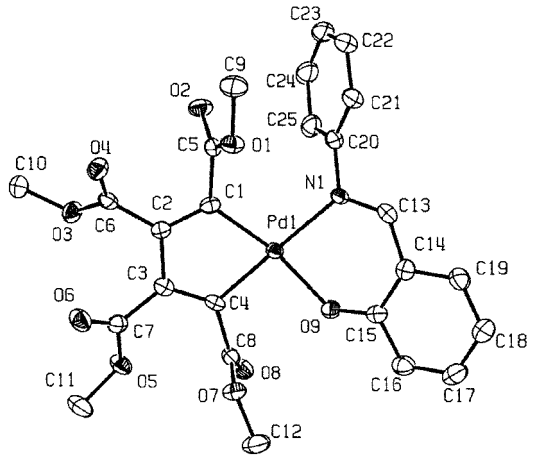


Figure 2. X-ray crystal structure of **8**. Thermal ellipsoids are drawn at 50% probability. Hydrogens omitted for clarity.

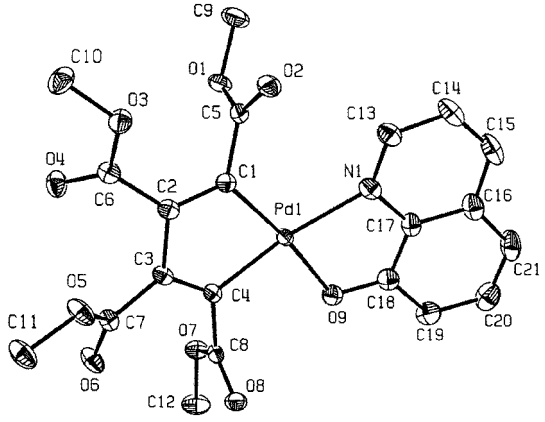


Figure 3. An ORTEP representation of **13**.

The structure of the dimethyldithiophosphate complex **20** has been established and is shown in Figure 4. The Pd–S distances are slightly longer than those found in related complexes (Table 1).[27] It can be inferred from this Table that the Pd–C bond lengths in complexes **5**, **8**, **13**, **21** are

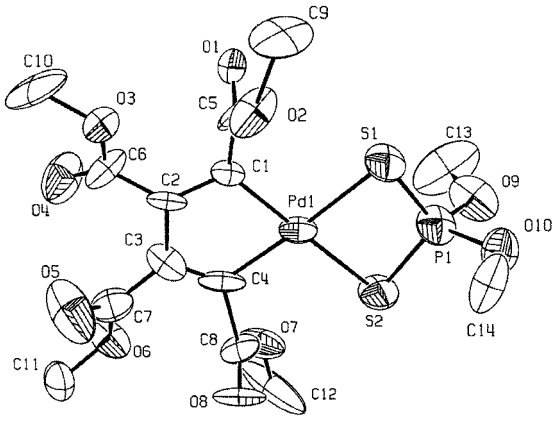


Figure 4. ORTEP diagram of **20**; thermal ellipsoids are drawn at the 50% probability level.

all similar with values of ca. 2 Å, with independence of the donor atom placed in *trans*- to the metallacyclic carbon. However, the distance Pd(1)–C(4) in complex **27** *trans*- to the pyridinic nitrogen is comparatively shorter. In this structure (Figure 5) is also found a short Pd(1)–N(1) distance if compared with the analogous one in complex **5** with the 2-pyrimidinthiolate ligand described above.

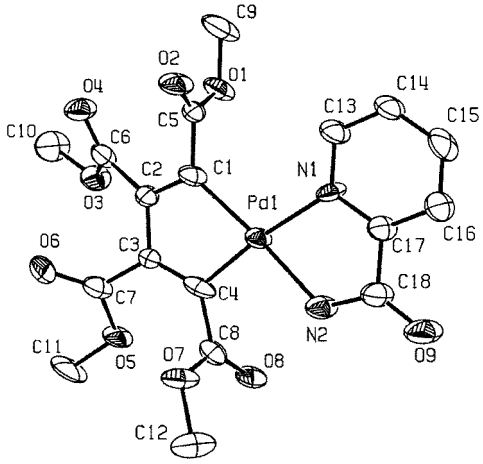


Figure 5. Structure of the $[Pd\{C_4(COOMe)_4\}(2\text{-}HNCOpy)]^-$ anion in the single crystal structure of **27**. All hydrogen atoms have been omitted for clarity.

The five new structures may be described as nearly planar, and their deviation from the planar coordination has been quantified by the $N_1{*}C_1C_4Pd_1$ and $E{**}C_4C_1Pd_1$ improper torsion angles (see Table 2).[28]

Table 2. Distortion parameters from square-planar coordination.

Improper torsion angles [°]	**5**	**8**	**13**	**20**	**27**
N(1)[a] C(1)–C(4)–Pd(1)	2.19	–0.47	4.17	–1.55	–2.14
E[b] C(4)–C(1)–Pd(1)	–0.53	5.19	1.98	–1.19	–0.60

[a] Except **20** (S1). [b] E = S(1) **5**; O(9) **8**, **13**; S(2) **20** and N(2) **27**.

Experimental Section

General Remarks for Synthesis: C,H,N,S analyses were carried out with a Carlo–Erba model 1108 microanalyser. IR spectra were recorded with a Perkin–Elmer spectrophotometer 16F PC FT-IR, using Nujol mulls between polyethylene sheets. NMR spectroscopic data were recorded on Bruker Avance 200, 300 and 400 spectrometers. Mass spectrometric analyses were performed with a Fisons VG Autospec double-focusing spectrometer, operated in the negative mode. Ions were produced by fast atom bombardment (FAB) with a beam of 25-keV Cs atoms. The mass spectrometer was operated with an accelerating voltage of 8 kV and a resolution of at least 1000. The hydroxo complex precursor $[NBu_4]_2[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2]$ was prepared by a published method.[13] Reagents were purchased from commercial sources and used directly unless otherwise stated in the text.

Preparations

Complexes $[NBu_4][Pd[C_4(COOMe)_4\}(O–O)]$ [O–O: Salycilaldehydate (sal) (1), Acetohydroxamate (ahx) (2) and Benzohydroxamate (bhx) (3)]: These mononuclear complexes were obtained according

to the following general method. To an acetone solution (10 mL) of hydroxo complex (0.07 g, 0.054 mmol) the stoichiometric amount of H(O–O) (molar ratio 1:2) was added. The solution was stirred at room temperature for 30 min and the solvent was partly evaporated under reduced pressure. The addition of diethyl ether caused the formation of yellow-orange solids, which were filtered off, washed with diethyl ether and air-dried. The compounds were recrystallised from dichloromethane/diethyl ether.

[NBu$_4$][Pd(C$_4${COOMe}$_4$)(sal)] (1): Yield 0.072 g (88%), m.p. 153 °C (dec.). $C_{35}H_{53}NO_{10}Pd$ (754.2): calcd. C 55.7, H 7.1, N 1.9; found C 55.5, H 7.0, N 2.0. IR (Nujol) $\tilde{\nu}$ = 1692 (vs), 1612 (vs), 1596 (vs), 1556 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.60 (s, 6 H, COOMe), 3.75 (s, 3 H, COOMe), 3.80 (s, 3 H, COOMe), 6.39 (m, 1 H, aromatic), 6.64 (d, 1 H, aromatic, J = 8.8 Hz), 7.17–7.27 (m, 2 H, aromatics), 9.06 (s, 1 H, CH=O) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 50.9 (COO*Me*), 51.0 (COO*Me*), 51.2 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 512 [Pd{C_4(COOMe)$_4$}(sal)]$^-$ + 1.

[NBu$_4$][Pd(C$_4${COOMe}$_4$)(ahx)] (2): Yield 0.068 g (89%), m.p. 180 °C (dec.). $C_{30}H_{52}N_2O_{10}Pd$ (707.2): calcd. C 50.9, H 7.4, N 4.0; found C 50.6, H 7.3, N 4.0. IR (Nujol) $\tilde{\nu}$ = 3155 (m) (ν NH), 1726 (vs), 1709 (vs), 1688 (vs), 1592 (vs) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.92 (s, 3 H, Me), 3.58 (s, 6 H, COOMe), 3.65 (s, 3 H, COOMe), 3.74 (s, 3 H, COOMe), 10.42 (br., 1 H, NH) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 16.7 (Me), 50.7 (COO*Me*), 50.8 (COO*Me*), 51.0 (COO*Me*), 51.1 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 463 [Pd{C_4(COOMe)$_4$}(ahx)]$^-$ – 1; 448 [Pd{C_4(COOMe)$_4$}(O–NH–CO)]$^-$ – 1.

[NBu$_4$][Pd(C$_4${COOMe}$_4$)(bhx)] (3): Yield 0.063 g (76%), m.p. 203 °C (dec.). $C_{35}H_{54}N_2O_{10}Pd$ (769.2): calcd. C 54.6, H 7.1, N 3.6; found C 54.8, H 7.3, N 3.8. IR (Nujol) $\tilde{\nu}$ = 3268 (s) cm^{-1} (ν NH), 1698 (vs), 1682 (vs), 1596 (vs), 1572 (vs) cm^{-1}. ^{1}H NMR (200 MHz, CD_3CN): δ = 3.55 (s, 6 H, COOMe), 3.61 (s, 3 H, COOMe), 3.71 (s, 3 H, COOMe), 7.38–7.49 (m, 3 H, aromatics), 7.66–7.69 (m, 2 H, aromatics), 10.38 (br., 1 H, NH) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 50.1 (COO*Me*), 50.2 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 526 [Pd{C_4(COOMe)$_4$}(bhx)]$^-$.

Complexes [NBu$_4$][Pd{C$_4$(COOMe)$_4$}(N–S)] [N–S: 2-Pyridinthiolate (spy) (4), 2-Pyrimidinthiolate (spym) (5) 3-Methyl-2-imidazolinthiolate (meimt) (6) and 2-Aminothiophenolate (2-atp) (7)]: The complexes were obtained by treating [NBu$_4$]$_2$[Pd$_2${C$_4$(COOMe)$_4$}$_2$(μ-OH)$_2$] (0.100 g, 0.077 mmol) with the corresponding heterocyclic-2-thione or 2-aminothiophenol (molar ratio 1:2) in acetone (10 mL). The solution was stirred at room temperature for 30 min and then concentrated under reduced pressure until half volume. Slow addition of diethyl ether caused the formation of yellow complexes, which were filtered off, washed with diethyl ether and air-dried. The compounds were recrystallised from dichloromethane/diethyl ether.

[NBu$_4$][Pd{C$_4$(COOMe)$_4$}(spy)] (4): Yield 0.086 g (75%), m.p. 131 °C (dec.). $C_{33}H_{52}N_2O_8PdS$ (743.26): calcd. C 53.3, H 7.0, N 3.8, S 4.3; found C 53.2, H 7.0, N 3.7, S 4.4. IR (Nujol) $\tilde{\nu}$ = 1716 (vs), 1694 (vs), 1594 (s), 1578 (s) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.62 (s, 3 H, COOMe), 3.64 (s, 3 H, COOMe), 3.68 (s, 3 H, COOMe), 3.77 (s, 3 H, COOMe), 6.61 (m, 1 H, spy), 6.79 (m, 1 H, spy), 7.23 (m, 1 H, spy), 7.79 (m, 1 H, spy) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 51.0 (COO*Me*), 51.3 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 500 [Pd{C_4(COOMe)$_4$}(spy)]$^-$.

[NBu$_4$][Pd{C$_4$(COOMe)$_4$}(spym)] (5): Yield 0.082 g (72%), m.p. 130 °C (dec.). $C_{32}H_{51}N_3O_8PdS$ (744.25): calcd. C 51.6, H 6.9, N 5.6, S 4.3; found C 51.4, H 6.8, N 5.6, S 4.2. IR (Nujol) $\tilde{\nu}$ = 1712 (vs), 1698 (vs), 1570 (s), 1554 (s) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.61 (s, 3 H, COOMe), 3.63 (s, 3 H, COOMe), 3.67 (s, 3 H, COOMe), 3.72 (s, 3 H, COOMe), 6.61 (m, 1 H, spym), 8.01 (dd, 1 H, spym, J^3 = 5.0, J^4 = 2.5 Hz), 8.24 (dd, 1 H, spym, J^3 = 5.0, J^4 = 2.5 Hz) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 51.0 (COO*Me*), 51.2 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 501 [Pd{C_4(COOMe)$_4$}(spym)]$^-$.

[NBu$_4$][Pd{C$_4$(COOMe)$_4$}(meimt)] (6): Yield 0.087 g (76%), m.p. 135 °C. $C_{32}H_{53}N_3O_8PdS$ (746.26): calcd. C 51.5, H 7.2, N 5.6, S 4.3; found C 51.2, H 7.3, N 5.9, S 4.2. IR (Nujol) $\tilde{\nu}$ = 1694 (vs), 1532 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.09 (s, 3 H, Me), 3.41 (s, 3 H, COOMe), 3.42 (s, 3 H, COOMe), 3.47 (s, 3 H, COOMe), 3.63 (s, 3 H, COOMe), 6.21 (d, 1 H, meimt, J = 1.4 Hz), 6.36 (d, 1 H, meimt, J = 1.4 Hz) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 34.3 (meimt), 48.0 (COO*Me*), 49.1 (COO*Me*), 49.2 (COO*Me*), 49.3 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 501 [Pd{C_4(COOMe)$_4$}(meimt)]$^-$.

[NBu$_4$][Pd{C$_4$(COOMe)$_4$}(2-atp)] (7): Yield 0.087 g (75%), m.p. 145 °C (dec.). $C_{34}H_{54}N_2O_8PdS$ (757.29): calcd. C 53.9, H 7.2, N 3.7, S 4.2; found C 54.1, H 7.5, N 3.8, S 4.4. IR (Nujol) $\tilde{\nu}$ = 3292 (m), 3252 (m), 1674 (s), 1592 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.60 (s, 3 H, COOMe), 3.69 (s, 3 H, COOMe), 3.72 (s, 3 H, COOMe), 3.77 (s, 3 H, COOMe), 4.64 (s, 2 H, NH_2), 6.70 (m, 1 H, 2-atp), 6.89 (m, 1 H, 2-atp), 6.97 (m, 1 H, 2-atp), 7.42 (m, 1 H, 2-atp) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 50.8 (COO*Me*), 50.9 (COO*Me*), 51.0 (COO*Me*), 51.1 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 514 [Pd{C_4(COOMe)$_4$}(2-atp)]$^-$.

Complexes [NBu$_4$][Pd{C$_4$(COOMe)$_4$}(N–O)] [H(N–O): *N*-Phenylsalycilaldimine (*N*-phsal) (8), *N*-*p*-Chlorophenylsalycilaldimine (*N*-clsal) (9), *N*-*p*-Tolylsalycilaldimine (*N*-tolsal) (10), 2-Aminophenol (2-ap) (11), 2-Pyrrolecarboxaldeyde (2-pcal) (12), 8-Hydroxiquinoline (oxin) (13), Picolinic Acid (2-pic) (14): The complexes were obtained by treating [NBu$_4$]$_2$[Pd$_2${C$_4$(COOMe)$_4$}$_2$(μ-OH)$_2$] (0.100 g, 0.077 mmol) with the corresponding protic ligand (HO–N) (molar ratio 1:2) in acetone (10 mL). The solution was stirred at room temperature for 30 min and then concentrated under reduced pressure until ca. one fifth of the initial volume. Slow addition of diethyl ether caused the formation of yellow complexes, which were filtered off, washed with diethyl ether and air-dried. The compounds were recrystallised from dichloromethane/diethyl ether.

[NBu$_4$][Pd{C$_4$(COOMe)$_4$}(*N*-phsal)] (8): Yield 0.106 g (83%), m.p. 175 °C (dec.). $C_{41}H_{58}N_2O_9Pd$ (829.33): calcd. C 59.4, H 7.0, N 3.4; found C 59.2, H 7.2, N 3.7. IR (Nujol) $\tilde{\nu}$ = 1700 (vs), 1686 (vs), 1606 (s), 1586 (s), 1530 (s) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.84 (s, 3 H, COOMe), 3.56 (s, 3 H, COOMe), 3.59 (s, 3 H, COOMe), 3.90 (s, 3 H, COOMe), 6.40 (m, 1 H, *N*-phsal), 6.77 (d, 1 H, *N*-phsal, J = 8.4 Hz), 7.08 (m, 1 H, *N*-phsal), 7.15 (m, 2 H, *N*-phsal), 7.32 (m, 4 H, *N*-phsal), 7.94 (s, 1 H, CH=N) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 50.7 (COO*Me*), 50.9 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 586 [Pd{C_4(COOMe)$_4$}(*N*-phsal)]$^-$.

[NBu$_4$][Pd{C$_4$(COOMe)$_4$}(*N*-clsal)] (9): Yield 0.105 g (80%), m.p. 160 °C (dec.). $C_{41}H_{57}ClN_2O_9Pd$ (863.77): calcd. C 57.0, H 6.6, N 3.2; found C 57.3, H 6.9, N 3.0. IR (Nujol) $\tilde{\nu}$ = 1688 (vs), 1606 (s), 1572 (s), 1526 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.00 (s, 3 H, COOMe), 3.63 (s, 3 H, COOMe), 3.64 (s, 3 H, COOMe), 3.95 (s, 3 H, COOMe), 6.46 (m, 1 H, *N*-clsal), 6.82 (d, 1 H, *N*-clsal, J = 8.5 Hz), 7.25 (m, 6 H, *N*-clsal), 7.95 (s, 1 H, CH=N) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 50.5 (COO*Me*), 50.8 (COO*Me*), 50.9 (COO*Me*), 51.0 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 622 [Pd{C_4(COOMe)$_4$}(*N*-clsal)]$^-$.

[NBu_4][Pd{C_4(COOMe)$_4$}(*N*-tolsal)] (10): Yield 0.097 g (75%), m.p. 136 °C (dec.). $C_{42}H_{60}N_2O_9Pd$ (843.35): calcd. C 59.8, H 7.2, N 3.3; found C 59.9, H 7.4, N 3.4. IR (Nujol) $\tilde{\nu}$ = 1702 (vs), 1686 (s), 1600 (s), 1586 (s), 1530 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3 H, Me), 2.86 (s, 3 H, COOMe), 3.57 (s, 3 H, COOMe), 3.59 (s, 3 H, COOMe), 3.90 (s, 3 H, COOMe), 6.40 (m, 1 H, *N*-tolsal), 6.76 (d, 1 H, *N*-tolsal, *J* = 8.4 Hz), 7.16 (m, 6 H, *N*-tolsal), 7.93 (s, 1 H, CH=N) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 20.8 (Me), 50.5 (COO*Me*), 50.9 (COO*Me*), 51.0 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 600 [Pd{C_4(COOMe)$_4$}(*N*-tolsal)]$^-$.

[NBu_4][Pd{C_4(COOMe)$_4$}(2-ap)] (11): Yield 0.102 g (90%), m.p. 165 °C (dec.). $C_{34}H_{54}N_2O_9Pd$ (741.22): calcd. C 55.1, H 7.3, N 3.8; found C 55.3, H 7.5, N 3.6. IR (Nujol) $\tilde{\nu}$ = 3310 (m), 3260 (m), 1688 (s), 1598 (s), 1538 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.61 (s, 3 H, COOMe), 3.67 (s, 3 H, COOMe), 3.68 (s, 3 H, COOMe), 3.82 (s, 3 H, COOMe), 4.18 (s, 2 H, NH_2), 6.25 (m, 1 H, 2-ap), 6.60 (d, 1 H, 2-ap, *J* = 7.8 Hz), 6.87 (m, 2 H, 2-ap) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 51.1 (COO*Me*), 51.2 (COO*Me*), 51.3 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 499 [Pd{C_4(COOMe)$_4$}(2-ap)]$^-$.

[NBu_4][Pd{C_4(COOMe)$_4$}(2-pcal)] (12): Yield 0.075 g (67%), m.p. 155 °C (dec.). $C_{33}H_{52}N_2O_9Pd$ (727.19): calcd. C 54.5, H 7.2, N 3.8; found C 54.7, H 7.3, N 4.0. IR (Nujol) $\tilde{\nu}$ = 1694 (vs), 1564 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.63 (s, 3 H, COOMe), 3.64 (s, 3 H, COOMe), 3.78 (s, 3 H, COOMe), 3.80 (s, 3 H, COOMe), 6.24 (d, 1 H, 2-pcal, *J* = 4.0 Hz), 6.96 (d, 1 H, 2-pcal, *J* = 4.0 Hz), 7.05 (m, 1 H, 2-pcal), 8.53 (s, 1 H, CHO) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 50.9 (COO*Me*), 51.0 (COO*Me*), 51.2 (COO*Me*), 51.3 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 484 [Pd{C_4(COOMe)$_4$}(2-pcal)]$^-$.

[NBu_4][Pd{C_4(COOMe)$_4$}(oxin)] (13): Yield 0.091 g (76%), m.p. 205 °C (dec.). $C_{37}H_{54}N_2O_9Pd$ (777.25): calcd. C 57.2, H 7.0, N 3.6; found C 57.3, H 7.2, N 3.6. IR (Nujol) $\tilde{\nu}$ = 1708 (vs), 1694 (vs), 1570 (s), 1498 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.64 (s, 3 H, COOMe), 3.65 (s, 3 H, COOMe), 3.81 (s, 3 H, COOMe), 3.86 (s, 3 H, COOMe), 6.77 (d, 1 H, oxin, *J* = 7.8 Hz), 6.84 (d, 1 H, oxin, *J* = 7.0 Hz), 7.31 (m, 2 H, oxin), 8.10 (d, 1 H, oxin, *J* = 8.4 Hz), 8.33 (m, 1 H, oxin) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 50.9 (COO*Me*), 51.1 (COO*Me*), 51.2 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 534 [Pd{C_4(COOMe)$_4$}(oxin)]$^-$.

[NBu_4][Pd{C_4(COOMe)$_4$}(2-pic)] (14): Yield 0.087 g (5%), m.p. 130 °C (dec.). $C_{34}H_{52}N_2O_{10}Pd$ (755.20): calcd. C 54.1, H 6.9, N 3.7; found C 54.1, H 7.1, N 3.9. IR (Nujol) $\tilde{\nu}$ = 1698 (vs), 1644 (vs), 1600 (vs) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.62 (s, 3 H, COOMe), 3.65 (s, 3 H, COOMe), 3.77 (s, 3 H, COOMe), 3.80 (s, 3 H, COOMe), 7.44 (m, 1 H, 2-pic), 7.89 (m, 1 H, 2-pic), 8.15 (d, 1 H, 2-pic, *J* = 7.2 Hz), 8.35 (d, 1 H, 2-pic, *J* = 4.7 Hz) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 50.9 (COO*Me*), 51.0 (COO*Me*), 51.1 (COO*Me*), 51.4 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 512 [Pd{C_4(COOMe)$_4$}(2-pic)]$^-$.

Complexes [NBu_4]$_2$[Pd_2{C_4(COOMe)$_4$}$_2$(μ-az)] [az = Pyrazolate (pz) (15), Triazolate (tz) (16) and 3,5-Dimethylpyrazolate (3,5-Me_2pz) (17)]: These dinuclear complexes were obtained according to the following general method. To a solution of hydroxo complex (0.07 g, 0.054 mmol) in dichloromethane (10 mL) was added the corresponding azolate (molar ratio 1:2). The solution was stirred at room temperature for 20 min and then concentrated under reduced pressure until about one fifth of the initial volume. Slow addition of diethyl ether caused the formation of yellow complexes, which were filtered off, washed with diethyl ether and air-dried. The compounds were recrystallised from dichloromethane/diethyl ether.

[NBu_4]$_2$[Pd(C_4{COOMe}$_4$)(μ-pz)]$_2$ (15): Yield 0.051 g (68%), m.p. 160 °C (dec.). $C_{62}H_{102}N_6O_{16}Pd_2$ (1400.34): calcd. C 53.2, H 7.3, N 6.0; found C 53.4, H 7.5, N 6.3. IR (Nujol) $\tilde{\nu}$ = 1688 (vs), 1616 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.37 (s, 12 H, COOMe), 3.58 (s, 12 H, COOMe), 5.89 (m, 2 H, pz), 7.26 (m, 4 H, pz) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 50.6 (COO*Me*), 50.7 (COO*Me*), 101.3 (pz), 137.3 (pz) ppm. FAB-MS (negative mode): *m*/*z* (%) = 1158 [(NBu_4)Pd_2{C_4(COOMe)$_4$}$_2$(μ-pz)$_2$]$^-$, 917 [Pd_2{C_4(COOMe)$_4$}$_2$(μ-pz)$_2$]$^-$ + 1, 849 [Pd_2{C_4(COOMe)$_4$}$_2$(μ-pz)]$^-$.

[NBu_4]$_2$[Pd(C_4{COOMe}$_4$)(μ-tz)]$_2$ (16): Yield 0.055 g (72%), m.p. 167 °C (dec.). $C_{60}H_{100}N_8O_{16}Pd_2$ (1402.3): calcd. C 51.4, H 7.2, N 8.0; found C 51.6, H 7.2, N 8.3. IR (Nujol) $\tilde{\nu}$ = 1692 (vs), 1552 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.40 (s, 12 H, COOMe), 3.59 (s, 12 H, COOMe), 7.73 (m, 4 H, tz) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 50.5 (COO*Me*), 50.7 (COO*Me*), 150.0 (tz) ppm. FAB-MS (negative mode): *m*/*z* (%) = 1160 [(NBu_4)-Pd_2{C_4(COOMe)$_4$}$_2$(μ-tz)$_2$]$^-$, 919 [Pd_2{C_4(COOMe)$_4$}$_2$(μ-tz)$_2$]$^-$ + 1, 851 [Pd_2{C_4(COOMe)$_4$}$_2$(μ-tz)]$^-$.

[NBu_4]$_2$[Pd(C_4{COOMe}$_4$)(μ-3,5-Me_2pz)]$_2$ (17): Yield 0.053 g (67%), m.p. 167 °C (dec.). $C_{66}H_{110}N_6O_{16}Pd_2$ (1456.45): calcd. C 54.4, H 7.6, N 5.8; found C 54.5, H 7.7, N 6.0. IR (Nujol) $\tilde{\nu}$ = 1698 (vs), 1642 (s), 1546 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.18 (s, 12 H, 3,5-Me_2pz) 3.37 (s, 12 H, COOMe), 3.57 (s, 12 H, COOMe), 5.34 (s, 2 H, 3,5-Me_2pz) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 14.1 (3,5-Me_2pz), 50.4 (COO*Me*), 50.5 (COO*Me*), 100.4 (3,5-Me_2pz), 146.6 (3,5-Me_2pz) ppm. FAB-MS (negative mode): *m*/*z* (%) = 1214 [(NBu_4)Pd_2{C_4(COOMe)$_4$}$_2$(μ-3,5-Me_2pz)$_2$]$^-$, 973 [Pd_2{C_4(COOMe)$_4$}$_2$(μ-3,5-Me_2pz)$_2$]$^-$ + 1, 877 [Pd_2-{C_4(COOMe)$_4$}$_2$(μ-3,5-Me_2pz)]$^-$.

Complexes [NBu_4]$_2$[Pd_2{C_4(COOMe)$_4$}$_2$(μ-O–O)] [O–O = Chloranilate (chl) (18) and Squarate (sq) (19)]: These dinuclear complexes were obtained according to the following general method. To an acetone solution (10 mL) of hydroxo complex (0.07 g, 0.054 mmol) the stoichiometric amount of H(O–O) (molar ratio 1:1) was added. The solution was stirred at room temperature for 30 min and the solvent was partly evaporated under reduced pressure. The addition of diethyl ether caused the formation of yellow-orange solids, which were filtered off, washed with diethyl ether and air-dried. The compounds were recrystallised from dichloromethane/diethyl ether.

[NBu_4]$_2$[Pd_2(C_4{COOMe}$_4$)$_2$(μ-chl)] (18): Yield 0.057 g (72%), m.p. 215 °C (dec.). $C_{62}H_{96}Cl_2N_2O_{20}Pd_2$ (1473.2): calcd. C 50.5, H 6.6, N 1.9; found C 50.6, H 6.9, N 2.2. IR (Nujol) $\tilde{\nu}$ = 1703 (vs), 1504 (vs) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.63 (s, 12 H, COOMe), 3.76 (s, 12 H, COOMe) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 51.1 (COO*Me*), 51.2 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 1230 [(NBu_4)Pd_2{C_4(COOMe)$_4$}$_2$(μ-chl)]$^-$.

[NBu_4]$_2$[Pd_2(C_4{COOMe}$_4$)$_2$(μ-sq)] (19): Yield 0.060 g (81%), m.p. 150 °C (dec.). C60H96N2O20Pd2 (1378.2): calcd. C 52.3, H 7.0, N 2.0; found C 52.4, H 7.2, N 2.2. IR (Nujol) $\tilde{\nu}$ = 1736 (vs), 1704 (vs), 1556 (vs), 1494 s cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.65 (s, 12 H, COOMe), 3.71 (s, 12 H, COOMe) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 51.2 (COO*Me*), 51.6 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 1138 [(NBu_4)Pd_2{C_4(COOMe)$_4$}$_2$(μ-sq)]$^-$ +2; 895 [Pd_2{C_4(COOMe)$_4$}$_2$(μ-sq)]$^-$ + 1; 502 [Pd{C_4(COOMe)$_4$}-(sq)]$^-$.

Complexes [NBu_4][Pd{C_4(COOMe)$_4$}{S_2P(OR)$_2$}] [R: Me (20), Et (21), *i*Pr (22)]: To a solution of the precursor [NBu_4]$_2$[Pd_2-{C_4(COOMe)$_4$}$_2$(μ-OH)$_2$] (0.100 g, 0.077 mmol) in dichloromethane (10 mL) was added the corresponding ammonium dialkyldithiophosphate (molar ratio 1:2). The solution was refluxed for 30 min and then concentrated under reduced pressure until ca. one

fifth of the initial volume. Slow addition of diethyl ether caused the formation of yellow complexes, which were filtered off, washed with diethyl ether and air-dried. The compounds were recrystallised from dichloromethane/diethyl ether.

[NBu$_4$][Pd{C$_4$(COOMe)$_4$}{S$_2$P(OMe)$_2$}] (20): Yield 0.099 g (82%), m.p. 140 °C (dec.). $C_{30}H_{54}NO_{10}PPdS_2$ (790.27): calcd. C 45.6, H 6.9, N 1.8, S 8.1; found C 45.7, H 7.1, N 1.9, S 8.3. IR (Nujol) $\tilde{\nu}$ = 1698 (vs), 1022 (vs), 654 (vs) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.61 (s, 6 H, COOMe), 3.69 (s, 6 H, COOMe), 3.70 (d, 6 H, Me, J_{PH} = 14.6 Hz) ppm. ^{31}P NMR (200 MHz, $CDCl_3$): δ = 109.3 (s, 1P) ppm. FAB-MS (negative mode): *m*/*z* (%) = 547 [Pd{C$_4$(COOMe)$_4$}{S$_2$P(OMe)$_2$}]$^-$.

[NBu$_4$][Pd{C$_4$(COOMe)$_4$}{S$_2$P(OEt)$_2$}] (21): Yield 0.101 g (80%), m.p. 128 °C (dec.). $C_{32}H_{58}NO_{10}PPdS_2$ (818.33): calcd. C 47.0, H 7.1, N 1.7, S 7.8; found C 47.1, H 7.4, N 2.0, S 8.1. IR (Nujol) $\tilde{\nu}$ = 1692 (vs), 1012 (vs), 652 (vs) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.30 (t, 6 H, Et), 3.61 (s, 6 H, COOMe), 3.69 (s, 6 H, COOMe), 4.10 (m, 4 H, Et) ppm. ^{31}P NMR (200 MHz, $CDCl_3$): δ = 104.5 (s, 1P) ppm. FAB-MS (negative mode): *m*/*z* (%) = 575 [Pd{C$_4$(COOMe)$_4$}{S$_2$P(OEt)$_2$}]$^-$.

[NBu$_4$][Pd{C$_4$(COOMe)$_4$}{S$_2$P(O*i*Pr)$_2$}] (22): Yield 0.079 g (61%), m.p. 143 °C (dec.). $C_{34}H_{62}NO_{10}PPdS_2$ (846.38): calcd. C 48.2, H 7.4, N 1.6, S 7.6; found C 48.4, H 7.5, N 1.9, S 7.9. IR (Nujol) $\tilde{\nu}$ = 1692 (vs), 1011 (vs), 645 (vs) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.60 (d, 12 H, *i*Pr, *J* = 6.2), 3.61 (s, 6 H, COOMe), 3.69 (s, 6 H, COOMe), 4.74 (m, 2 H, *i*Pr) ppm. ^{31}P NMR (200 MHz, $CDCl_3$): δ = 101.1 (s, 1P) ppm. FAB-MS (negative mode): *m*/*z* (%) = 603 [Pd{C$_4$(COOMe)$_4$}{S$_2$P(O*i*Pr)$_2$}]$^-$.

Complexes [NBu$_4$][Pd{C$_4$(COOMe)$_4$}(S$_2$CNR$_2$)] [R$_2$NH: Et$_2$NH (23), Pr$_2$ (24), Piperidine (25), Morpholine (26)]: In separate experiments, to a solution of complex [NBu$_4$]$_2$[Pd$_2${C$_4$(COOMe)$_4$}$_2$(μ-OH)$_2$] (0.100 g, 0.077 mmol) in acetone (10 mL) was added the corresponding amine (molar ratio 1:2) and a slight excess of carbon disulfide. The solution was refluxed for 30 min and then concentrated under reduced pressure until ca. one fifth of the initial volume. Slow addition of diethyl ether caused the formation of yellow complexes, which were filtered off, washed with diethyl ether and air-dried. The compounds were recrystallised from dichloromethane/diethyl ether.

[NBu$_4$][Pd{C$_4$(COOMe)$_4$}(S$_2$CNEt$_2$)] (23): Yield 0.082 g (69%), m.p. 132 °C (dec.). $C_{33}H_{58}N_2O_8PdS_2$ (781.37): calcd. C 50.7, H 7.5, N 3.6, S 8.2; found C 50.9, H 7.7, N 3.7, S 8.4. IR (Nujol) $\tilde{\nu}$ = 1724 (vs), 1706 (vs), 1505 (vs) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.19 (t, 6 H, Et), 3.60 (s, 6 H, COOMe), 3.67 (s, 6 H, COOMe), 3.74 (q, 4 H, Et) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 12.4 (Et), 43.9 (Et), 50.8 (COO*Me*), 50.9 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 539 [Pd{C$_4$(COOMe)$_4$}(S$_2$CNEt$_2$)]$^-$ + 1.

[NBu$_4$][Pd{C$_4$(COOMe)$_4$}(S$_2$CNPr$_2$)] (24): Yield 0.086 g (69%), m.p. 182 °C (dec.). $C_{35}H_{62}N_2O_8PdS_2$ (809.43): calcd. C 51.9, H 7.7, N 3.5, S 7.9; found C 51.9, H 7.8, N 3.6, S 8.1. IR (Nujol) $\tilde{\nu}$ = 1694 (vs), 1504 (vs) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, 6 H, Pr), 1.64 (m, 4 H, Pr), 3.62 (m, 10 H, Pr + COOMe), 3.69 (s, 6 H, COOMe) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 11.1 (Pr), 20.5 (Et), 50.8 (COO*Me*), 50.9 (COO*Me*), 51.1 (Pr) ppm. FAB-MS (negative mode): *m*/*z* (%) = 566 [Pd{C$_4$(COOMe)$_4$}-(S$_2$CNPr$_2$)]$^-$.

[NBu$_4$][Pd{C$_4$(COOMe)$_4$}(S$_2$CNC$_5$H$_{10}$)] (25): Yield 0.094 g (77%), m.p. 165 °C (dec.). $C_{34}H_{58}N_2O_8PdS_2$ (809.43): calcd. C 51.5, H 7.4, N 3.5, S 8.1; found C 51.7, H 7.4, N 3.7, S 8.0. IR (Nujol) $\tilde{\nu}$ = 1694 (vs), 1500 (vs) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.65 (m, 6 H, S$_2$CNC$_5$H$_{10}$), 3.45 (s, 6 H, COOMe), 3.49 (s, 6 H, COOMe), 3.85 (t, 4 H, S$_2$CNC$_5$H$_{10}$) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 15.2 (S$_2$CNC$_5$H$_{10}$), 16.5 (S$_2$CNC$_5$H$_{10}$), 38.6 (S$_2$CNC$_5$H$_{10}$), 50.5 (COO*Me*), 50.7 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 551 [Pd{C$_4$(COOMe)$_4$}(S$_2$CNC$_5$H$_{10}$)]$^-$ + 1.

[NBu$_4$][Pd{C$_4$(COOMe)$_4$}(S$_2$CNC$_4$H$_8$O)] (26): Yield 0.099 g (82%), m.p. 186 °C (dec.). $C_{33}H_{56}N_2O_9PdS_2$ (795.36): calcd. C 49.8, H 7.1, N 3.5, S 8.1; found C 50.1, H 7.3, N 3.6, S 8.3. IR (Nujol) $\tilde{\nu}$ = 1694 (vs), 1499 (vs) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.62 (s, 6 H, COOMe), 3.68 (m, 10 H, S$_2$CNC$_4$H$_8$O + COOMe), 4.00 (t, 4 H, S$_2$CNC$_4$H$_8$O) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 47.2 (S$_2$CNC$_4$H$_8$O), 50.9 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 552 [Pd{C$_4$(COOMe)$_4$}(S$_2$CNC$_4$H$_8$O)]$^-$.

Hydration of pyridine-2-carbonitrile: Complex [NBu$_4$][Pd-{C$_4$(COOMe)$_4$}(2-HNCOpy)] (27): To a solution of [NBu$_4$]$_2$-[Pd$_2${C$_4$(COOMe)$_4$}$_2$(μ-OH)$_2$] (0.100 g, 0.077 mmol) in acetone/H$_2$O (10:0.5 mL) was added pyridine-2-carbonitrile (0.018 g, 0.154 mmol). The resultant clear solution was stirred for 30 min at room temperature and then concentrated under reduced pressure until ca. one fifth of the initial volume. Slow addition of diethyl ether caused the formation of yellow complexes, which were filtered

Table 3. Crystal data and structure refinement for compounds **5**, **8**, **13**, **20** and **27**.

	5	**8**	**13**	**20**	**27**
Formula	$C_{32}H_{51}N_3O_8PdS$	$C_{41}H_{58}N_2O_9Pd$	$C_{37}H_{54}N_2O_9Pd$	$C_{30}H_{54}NO_{10}PPdS_2$	$C_{34}H_{53}N_3O_9Pd$
Molecular mass	744.22	829.29	777.22	790.23	754.19
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P21/n$	$P2_1/c$	Cc	$Pcab$
a [Å]	10.3174(6)	9.6870(10)	10.8804(6)	8.9363(7)	20.002(2)
b [Å]	20.4166(16)	11.3580(10)	9.1196(5)	22.938(2)	17.359(3)
c [Å]	17.3615(19)	36.978(2)	38.995(2)	18.9201(17)	21.299(2)
β [°]	100.486(9)	91.78	95.3460(10)	102.281(6)	90
V [Å^3]	3596.1(5)	4066.5(6)	3852.4(4)	3789.4(6)	7395.3(16)
Z	4	4	4	4	8
T [K]	173(2)	173(2)	100(2)	173(2)	173(2)
Reflections collected	7028	9782	23503	3566	7553
μ [mm^{-1}]	0.624	0.511	0.535	0.692	0.556
Independent reflections	6324	7155	8645	2495	6504
Final $R1$	0.0328	0.0335	0.0405	0.0631	0.0633
$wR2$ [$I > 2\sigma(I)$]	0.0770	0.0768	0.0838	0.1676	0.1603
R indices (all data)	$R1$ = 0.0488	$R1$ = 0.0482	$R1$ = 0.0451	$R1$ = 0.0937	$R1$ = 0.1103
	$wR2$ = 0.0823	$wR2$ = 0.0814	$wR2$ = 0.0859	$wR2$ = 0.1916	$wR2$ = 0.1767

off, washed with diethyl ether and air-dried. The compounds were recrystallised from acetone/diethyl ether.

Complex [NBu_4][Pd{C_4(COOMe)$_4$}(2-HNCOpy)] (27): Yield 0.091 g (78%), m.p. 123 °C. $C_{34}H_{53}N_3O_9Pd$ (754.22): calcd. C 54.1, H 7.1, N 5.6; found C 54.2, H 7.4, N 5.8. IR (Nujol) $\tilde{\nu}$ = 3352 (vs), 1698 (vs), 1630 (vs), 1596 (vs), 1586 (vs), 1566 (vs) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.63 (s, 6 H, COOMe), 3.76 (s, 3 H, COOMe), 3.78 (s, 3 H, COOMe), 5.24 (br., 1 H, NH), 7.37 (m, 1 H, 2-HNCOpy), 7.87 (m, 1 H, 2-pic), 8.08 (m, 1 H, 2-HNCOpy), 8.38 (m, 1 H, 2-HNCOpy) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 50.9 (COO*Me*), 51.0 (COO*Me*), 51.1 (COO*Me*), 51.3 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* (%) = 511 [Pd{C_4(COOMe)$_4$}(2-HNCOpy)]$^-$.

X-ray Structure Analysis: Suitable crystals of **5**, **8**, **13**, **20** and **27** were grown from dichloromethane/ether liquid diffusion. The crystals were mounted onto the tip of a glass fibre, and the data collection was performed with a Siemens P4 diffractometer for **5**, **8**, **20** and **27**, the scan mode was θ-2θ. Data collection for **13** was performed with a Bruker Smart CCD diffractometer with a nominal crystal to detector distance of 4.5 cm. Diffraction data were collected with a ω scan run. A total of 1371 frames were collected at 0.3° intervals and 10°s per frame. The diffraction frames were integrated using the SAINT package[29] and corrected for absorption with SADABS.[30] The structures were solved by direct methods SHELXS-97[31] and refined by full-matrix least-squares SHELXL-97[31] (Table 3). Hydrogen atoms were included using a riding model. CCDC-258720 (for **5**) -258721 (for **8**), -258722 (for **13**), -258723 (for **20**) and -258724 (for **27**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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