Palladium Complexes with the Tridentate Dianionic Ligand Pyridine-2,6-dicarboxylate, dipic. Crystal Structure of $[Pd(dipic)(PBu_3)]_2$

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The reactions of $[Pd(acac)_2]$ or $[Pd(OAc)_2]_3$ with pyridine-2,6-dicarboxylic acid (H_2dipic) in acetonitrile afford [Pd(dipic)(NCMe)] in high yield. This complex has been used as starting material in the preparation of a variety of neutral an anionic complexes. The dipicolinate anion behaves as a tridentate ligand in all cases, but two modes of coordination are found, depending on the ligand: as a pincer ligand O,N,O-bonded to the same palladium, giving mononuclear complexes, and as an O,N-chelate N,O′-bridging ligand in dinuclear complexes. An X-ray determination of the structure of a dimer, $[Pd(dipic)(PBu_3)]_2$ (monoclinic, space group $P2_1/n$, $a = 18.144(4)$ Å, $b = 13.191(2)$ Å, $c = 19.571(3)$ Å, $\beta = 113.45(2)°$, $Z = 4$, $R = 0.050$, $R_w = 0.054$) shows that the ligand is coordinated to one palladium in a η^2-N,O chelate fashion and one oxygen atom of the other carboxylate group makes a bridge to the other palladium atom, in a novel bonding mode for the dipic ligand.

Introduction

This exploration of palladium dipicolinate complexes has been motivated by our interest in palladium chemistry and in metal-containing liquid crystals.[1] The rigid tridentate coordination of this flat chelate ligand (Figure 1a), found for many bivalent or trivalent transition metals,[2,3] can provide a metal containing rigid core which, conveniently modified, should eventually produce palladium-containing liquid crystals with a net dipolar moment along the Pd−N bond. Moreover, it has been reported that K[Pt(dipic)Cl] forms gel in water, what already suggests that the anisotropic shape of the molecule indeed induces uncommon physical properties.[2] It is not difficult to envisage the potentiality of tuning of these molecular designs for materials, not only as liquid crystals but also in the field of nonlinear optics.

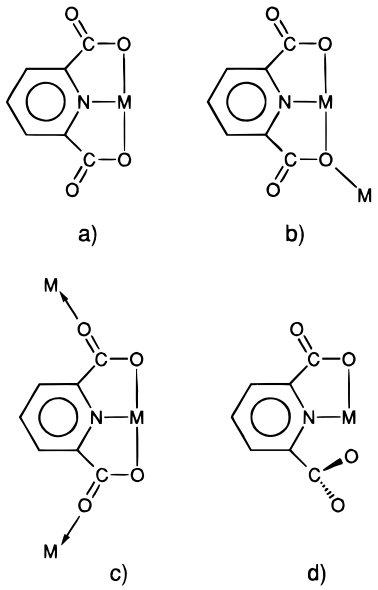

Figure 1. Coordination modes for the dipicolinate dianion.

There are however a few examples of other coordination modes of this ligand such as bridging of two metals atoms (Figure 1b),[4] polymerization of chelate complexes by coordination of the carbonyl atom (structural assignments based only upon electronic and infrared spectral data, Figure 1c),[5] and bidentate N−O coordination (Figure 1d).[2,3k,6] For this reason

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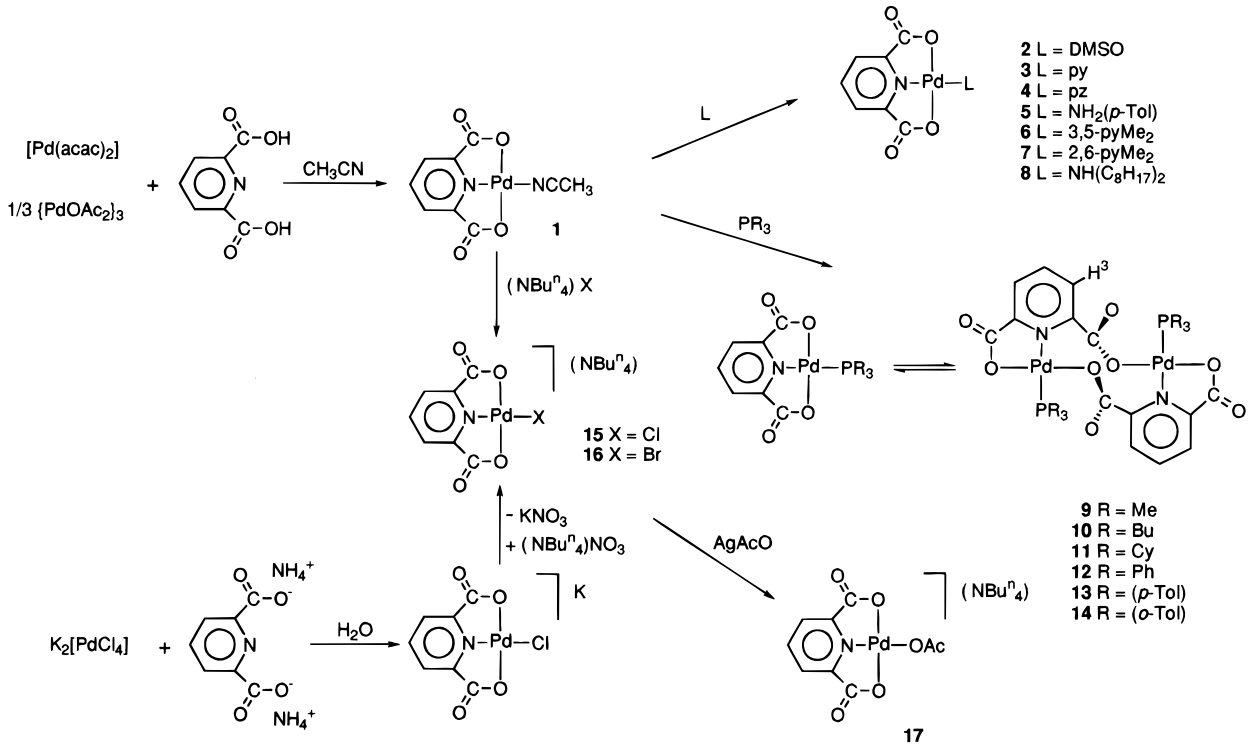
Scheme 1



it seemed convenient to explore first the coordination behavior on Pd with the simple and easily available unmodified dipic ligand prior to attempting modifications on the ligand, sometimes difficult to achieve, in order to introduce the desired physical properties.

We have previously reported palladium complexes containing the sulfur analog dinegative anion of 2,6-bis(thiocarboxylic) acid (H_2pdtc).[7] The tridentate ligand dipic incorporates harder donor atoms (*N*,*O*,*O*) than pdtc (*N*,*S*,*S*). The differences in the coordination behavior of the two ligands, including a new bonding mode for the dipicolinic ligand, are reported and discussed here.

Results and Discussion

The syntheses and structures of the new complexes are summarized in Scheme 1.

Neutral dipic Complexes. [Pd(dipic)($NCCH_3$)] (**1**) has been synthesized in very good yield by reacting a palladium salt of a weak acid ([Pd(acac)$_2$] or [Pd($AcO)_2]_3$) with dipicolinic acid ($pK_{a1} = 2.83$, $pK_{a2} = 3.66$),[8] in acetonitrile.

The pale yellow complex **1**, which contains the four coordination positions of the palladium atom bonded to hard donor atoms, is insoluble in common organic solvents. The elemental analysis (see Experimental Section) reveals a 1:1:1 (Pd, dipic, NCMe) stoichiometry. The most prominent features of its IR spectrum are a broad intense band at ca. 1688 cm^{-1}, which is assigned to the ν(CO) vibrations of the coordinated $-CO_2^-$ groups, and two absorptions at 2334 and 2306 cm^{-1} in the ν(C≡N) region (ν(C≡N), $\delta(CH_3) + \nu$(C−C)) which are similar to those of free NCMe (2254, 2290 cm^{-1}).[9] The ^{1}H NMR spectrum could only be obtained in deuterated DMSO, revealing the displacement of acetonitrile (the spectrum contains a resonance at 2.06 ppm corresponding to free NCMe). This has been further confirmed by the isolation of the DMSO complex **2**, which has been characterized by analytical and spectroscopic methods. Its IR spectrum in Nujol shows a strong absorption at 910 cm^{-1} for the S=O stretching mode, with O-coordination of the DMSO ligand.[10a] It is interesting to note that the hard dipic ligand induces the palladium atom to select the hard donor atom of the DMSO ligand. The ^{1}H NMR spectra of **1** and **2** in DMSO solution are identical, and consist of two sets of signals of two different products. The major isomer (ca. 83%) shows the symmetric pattern expected for the pyridine protons in the structure depicted in Scheme 1. The minor isomer (ca. 17%) exhibits three distinct pyridinic proton signals showing the nonequivalence of the three pyridinic hydrogens, which requires an asymmetric bonding mode for the chelating dipic ligand. Although a detailed assignment of the structure is precluded by the absence of other data, the results found for the phosphine complexes **9**−**14** (*vide infra*) point to a dimeric nature of this minor isomer, but we cannot be sure whether the DMSO is still O-coordinated.[10b]

A general synthetic route to neutral derivatives is shown in Scheme 1. N- and P-donor ligands also displace easily the weakly coordinated acetonitrile to give the corresponding neutral complexes [Pd(dipic)L], **3**−**13**, in high yield.

(a) N-Donor Ligands. The insolubility of the complexes with pyridine (**3**), pyrazine (**4**), or *p*-toluidine (**5**), precluded the acquisition of informative ^{1}H NMR spectra; therefore, these complexes have been characterized only by IR and elemental analysis. In order to obtain more soluble compounds with N-donors, the acetonitrile was replaced by 3,5-lutidine, 2,6-lutidine or di-*n*-octylamine, to afford compounds **6**, **7**, and **8**. The ^{1}H NMR spectra of **6**−**8** in $CDCl_3$ show AB_2 spin systems which are in agreement with the mononuclear structure shown in Scheme 1. The compound with dioctylamine (**8**) is soluble

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enough in benzene, where it exhibits an AX_2 spin system for the pyridinic protons with notable displacement of the signals with respect to the $CDCl_3$ solution, suggesting strong interactions between the pyridyl ligand and the solvent.

(b) P-Donor Ligands. In contrast to the simple spectra observed for complexes with N-donor ligands and for the related complex [Pd(pdtc)PPh_3],[7] the ^{1}H NMR spectrum of the trimethylphosphine derivative **9** in $CDCl_3$ solution shows three inequivalent pyridinic hydrogens: One triplet at 8.11 ppm ($^3J_{HH}$ = 7.8 Hz) assigned to H^4; and two doublets of triplets at 7.99 and 7.66 ppm ($^4J_{HH} \approx {}^5J_{HP} \approx 1.5$ Hz) for H^3 and H^5. This spectrum reveals an asymmetric bonding mode for the dipic ligand and is similar to the spectra reported for complexes *trans*-$[M(dipic)_2]^{2-}$ (M = Pd, Pt) containing dipic as a bidentate *N,O* ligand.[3k,6,12] The $^{31}P\{^1H\}$ NMR spectrum of **9** in $CDCl_3$ solution exhibits a single resonance at δ = 6.1 ppm.

These data, together with the results of molecular weight measurements (680 in $CHCl_3$), strongly suggest the dinuclear structure proposed for **9** in Scheme 1, which is actually found by X-ray diffaction for the related complex **10** (see below). The dipic ligand is coordinated to one palladium in a η^2-N,O chelate fashion, and the second carboxylic group serves as a bridge to the other palladium atom, in an asymmetric bonding mode previously unknown for the dipic ligand. It is remarkable, however, that the difference of bonding between the two carboxylate groups is not reflected in the IR spectra of the phosphine complexes which, in the region of $\nu_{asym}(COO^-)$, are similar to those recorded for the monomeric complexes **3**−**8**. Thus the infrared spectra are useless in this case for elucidation of the stereochemistry.

The reaction of **1** with PBu_3 or PCy_3 afford compounds **10** and **11**, respectively. Their ^{1}H NMR spectra in $CDCl_3$ show the coexistence in solution of the dinuclear (still very dominant, virtually exclusive for **10** and a majority for **11**) and the monomeric isomers. This dimer−monomer equilibrium is somewhat influenced by the solvent and the ^{1}H NMR in actone or benzene spectra exhibit a higher dimer−monomer ratio.

With triarylphosphines the solubility of the corresponding complexes are decreased. Nevertheless, the complexes **12**−**14** are soluble enough in $CDCl_3$, where their ^{31}P NMR spectra exhibit two signals suggesting again a dimer−monomer mixture. Their ^{1}H NMR spectra are complex and show an overlap of resonances in the aromatic region, yet the signals corresponding to the monomer and the dimer can be recognized for the pyridinic protons. The signals of the AB_2 spin system attributable to the mononuclear compound (minor component) are distinctly observed. For the dimer, H^5 is observed as doublet of triplets at low field; H^3 appears as a broad signal at a rather high field (δ 6.2−6.8 ppm), due to anisotropic shielding by the phenyl rings of the phosphine; finally H^4 is overlapped by signals of the aryl protons of the phosphines, but its presence in the range 7.4−7.7 ppm can be deduced from integration and by COSY experiments.

Further evidence for a solution equilibrium is obtained from variable-temperature ^{1}H or ^{31}P NMR studies, where a change of the monomer/dimer ratio with temperature is observed. Upon increase of the temperature to 315 K, the resonances of the monomer increase in intensity, while those of the dimer decrease. The opposite behavior is observed with decreasing temperature. These data are consistent with an equilibrium between dimer and monomer where the monomers are entropically favored, as found recently for palladium complexes with 2-pyridinethiolate.[11] The thermodynamic parameters determined by ^{1}H NMR for the equilibrium dimer ⇌ 2 monomer for **13** are ΔH = 27 ± 2 kJ mol^{-1} and ΔS = 48 ± 5 J K^{-1} mol^{-1} (from the changing ratios of the integrated intensities of the pyridinic protons, over the range 265−315 K, for a solution of 0.007 mmol of **13** in 0.5 mL of $CDCl_3$).

The values of the equilibrium constants (K = [monomer]^2/[dimer], in mol L^{-1}) determined for the different neutral complexes by NMR integration are as follows: 0 (only dimer is observed) for complex **9**; very small for complex **10**; ca. 5.5 × 10^{-3} for complexes **11**−**13**; 2.5 × 10^{-2} for **14**; and infinite (only monomer observed) for complexes **6**−**8**. These values suggest that the monomer is favored by the ligands with the lower *trans* influence or with the higher steric requirement. Thus, all the N-donor ligands give only monomer, whereas phosphines tend to give mainly dimer. Alkylphosphines give almost exclusively dimer except for the bulky PCy_3 (cone angle 170°),[12] and arylphosphines show the highest proportion of monomer for the bulkiest P(*o*-Tol)$_3$ (cone angle 194°).[12]

This behavior can be understood considering the fact that the pincer structure of the ligand adopted in the monomers is quite strained and imposes short N−Pd distances (more compatible with L ligands with low *trans* influence), and low O−Pd−O angles (more favored by bulky L ligands.

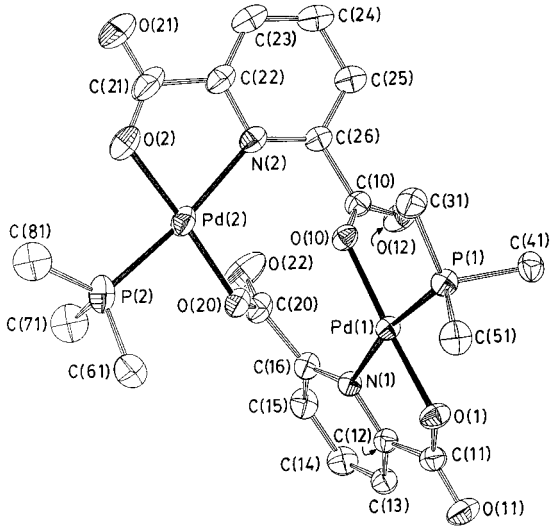

Figure 2. View of the structure of [Pd(dipic)(PBu_3)]$_2$ **10** showing the atom numbering scheme; only the first carbons of the PBu_3 are drawn for clarity.

Table 1. Crystallographic Data for [Pd(dipic)(PBu_3)]$_2$ (**10**)

formula	$C_{38}H_{60}N_2O_8P_2Pd_2$	Z	4
fw	947.65	T, K	293
cryst system	monoclinic	ρ_{calc}, g cm^{-3}	1.47
space group	$P2_1/n$ (No. 14)	F(000)	1952
a, Å	18.114(4)	λ(Mo Kα), Å	0.710 73 (graphite
b, Å	13.191(2)		monochromator)
c, Å	19.571(3)	μ, cm^{-1}	9.47
β, deg	113.45(2)	cryst size,	0.2 × 0.16 × 0.13;
V, Å^3	4290(1)	mm; color	yellow

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = [\Sigma(w(|F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{1/2}$.

Structure of [Pd(dipic)PBu_3]$_2$ (10). The X-ray structure and numbering scheme for complex **10** are shown in Figure 2. Positional and thermal parameters for the relevant atoms are given in Table 1, and selected bond lengths and angles in Table 2. The X-ray determination confirms the structure proposed on the basis of spectroscopic data. The molecule is a dimer in which each dipic ligand is coordinated to one palladium in a chelate manner through one carboxylate oxygen atom and the pyridyl nitrogen, while the other carboxylate group, twisted out

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Pd(dipic)(PBu_3)]_2$ (**10**)

Pd(1)−P(1)	2.234(2)	Pd(1)−N(1)	2.140(5)
Pd(1)−O(1)	2.000(5)	Pd(1)−O(10)	2.000(5)
Pd(2)−N(2)	2.139(6)	Pd(2)−O(2)	1.990(6)
Pd(2)−O(20)	2.020(5)	Pd(2)−P(2)	2.219(3)
N(1)−C(12)	1.361(8)	N(1)−C(16)	1.351(9)
O(1)−C(11)	1.299(9)	O(10)−C(10)	1.282(9)
N(2)−C(22)	1.364(9)	N(2)−C(26)	1.349(9)
O(2)−C(21)	1.27(1)	O(20)−C(20)	1.292(9)
C(10)−O(12)	1.223(9)	C(10)−C(26)	1.52(1)
C(12)−C(11)	1.51(1)	C(16)−C(20)	1.49(1)
C(11)−O(11)	1.213(8)	O(21)−C(21)	1.24(1)
C(20)−O(22)	1.20(1)	C(21)−C(22)	1.54(1)
N(1)−Pd(1)−P(1)	169.8(2)	O(1)−Pd(1)−P(1)	89.8(2)
O(1)−Pd(1)−N(1)	81.0(2)	O(10)−Pd(1)−P(1)	87.8(2)
O(10)−Pd(1)−N(1)	101.4(2)	O(10)−Pd(1)−O(1)	177.4(2)
O(2)−Pd(2)−N(2)	81.2(3)	O(20)−Pd(2)−N(2)	102.6(2)
O(20)−Pd(2)−O(2)	176.0(3)	P(2)−Pd(2)−N(2)	171.7(2)
P(2)−Pd(2)−O(2)	90.8(2)	P(2)−Pd(2)−O(20)	85.4(2)
C(31)−P(1)−Pd(1)	114.9(3)	C(41)−P(1)−Pd(1)	109.5(3)
C(41)−P(1)−C(31)	106.2(4)	C(51)−P(1)−Pd(1)	115.7(3)
C(51)−P(1)−C(31)	107.8(4)	C(51)−P(1)−C(41)	101.5(4)
C(12)−N(1)−Pd(1)	108.3(4)	C(16)−N(1)−Pd(1)	131.9(5)
C(16)−N(1)−C(12)	118.2(6)	C(11)−O(1)−Pd(1)	115.7(4)
C(10)−O(10)−Pd(1)	119.1(4)	C(22)−N(2)−Pd(2)	109.7(5)
C(26)−N(2)−Pd(2)	132.8(5)	C(26)−N(2)−C(22)	117.0(7)
C(21)−O(2)−Pd(2)	115.9(6)	C(20)−O(20)−Pd(2)	118.5(5)
O(12)−C(10)−O(10)	127.4(7)	C(26)−C(10)−O(10)	112.9(6)
C(26)−C(10)−O(12)	119.4(7)	C(20)−C(16)−N(1)	119.8(6)
C(12)−C(11)−O(1)	116.0(6)	O(11)−C(11)−O(1)	124.8(7)
O(11)−C(11)−C(12)	119.2(7)	C(16)−C(20)−O(20)	112.6(7)
O(22)−C(20)−O(20)	126.0(8)	O(22)−C(20)−C(16)	121.3(8)
O(21)−C(21)−O(2)	125(1)	C(22)−C(21)−O(2)	118.3(8)
C(22)−C(21)−O(21)	117(1)	C(21)−C(22)−N(2)	113.3(8)
C(10)−C(26)−N(2)	117.8(7)		

of the pyridine plane, is bonded to the second palladium atom of the dimer. The two bridges are arranged in a complementary head-to-tail manner. The resulting coordination around each palladium is distorted square planar with the remaining fourth coordination site filled by the phosphorus atom of the tributylphosphine.

In related complexes the pyridine ring and the chelating carboxylate are nearly coplanar with the coordination plane.[2,3k,13] However, in **10** the pyridine ring is twisted by 20.0(2)° (for that on Pd(1)), or 12.2(2)° (for that on Pd(2)), with respect to the coordination planes. The deviation from coplanarity of the chelated carboxylate groups with respect to the pyridine ring is reflected in the torsion angles O(1)−(11)−C(12)−N(1) = −3(1)°, and O(2)−C(21)−C(22)−N(2) = −7(1)°. The bridging carboxylate groups are rotated with respect to the pyridine ring by 36.4(4) and 42.1(4)°. The C−O distances and angles for the chelate and bridged carboxylate groups are very similar since both carboxylates are coordinated. The dipic ligands are oriented in such a way that their aromatic rings are very nearly perpendicular to one another (dihedral angle 84.4(2)°), whereas the dihedral angle between the coordination planes of the two palladium atoms is 69.76(8)°.

The phosphine seems to exert a marked influence on the *trans* Pd−N distances (2.140(5) and 2.139(6) Å). They are noticeably longer than the distances found in $[Pd(pdtc)Br]^-$ (2.034(8) Å)[7] or in dipicolinate complexes of platinum (1.88−2.03 Å)[2] and are similar to those found in the series of dimers $[Pd(\mu\text{-}\eta^2\text{-pyS-}N,S)Cl(PR_3)]_2$ (PR_3 = PMe_3, PMe_2Ph, and $PMePh_2$),[14] all of them having the PR_3 ligand in position *trans* to the N atom, which are in the range of 2.124(6)−2.137(9) Å.

The tendency of the dipicolinate complexes to dimerization is absent in the related complex $[Pd(pdtc)PPh_3]$, as determined by ^{1}H NMR spectroscopy.[7] A plausible explanation for this different behavior is suggested by the structural features of both families. For $[Pd(pdtc)Br]^-$ the chelating cycle is relatively free of strain (N−Pd−S = 86.44(6)°), whereas for **10** the chelating carboxylate groups have a smaller bite angle (N(1)−Pd(1)−O(1) = 81.0(2)°; N(2)−Pd(2)−O(2) = 81.2(3)°). This is related to the shorter C−O distance (1.299(9) and 1.27(1) Å) compared to the C−S distance (1.711(9) Å, as well as by the longer Pd−N distance in **10**. Consequently the chelating cycles in the dipicolinate derivatives are more strained and have a higher tendency to relieve this strain by forming dimers (with only one strained cycle per palladium) rather than monomers (with two strained cycles per palladium), specially when the ancillary ligand induces a long Pd−N bond.

Ionic Dipic Complexes. A fast reaction takes place when $[NBu^n_4]Br$ is added to a suspension of **1** in acetone with formation of $[NBu^n_4][Pd(dipic)Br]$ (**16**). Alternatively $[NBu^n_4][Pd(dipic)Cl]$ (**15**) was made by reaction of K_2PdCl_4 with $(NH_4)_2$dipic in water, followed by cation exchange with $[NBu^n_4]Cl$, in a procedure similar to that reported by Zhou and Kostic for the platinum complex $[NBu^n_4][Pt(dipic)Cl]$.[2] Using this alternative method, the formation of a gellike substance was observed for K[Pd(dipic)Cl] in water, as reported for the platinum complex, although their behavior was not further studied. These $[NBu^n_4]^+$ salts are soluble in polar organic solvents. The ^{1}H NMR spectra of the yellow solutions of **15** and **16** in $CDCl_3$ show AX_2 systems for the pyridinic protons in agreement with a mononuclear structure.

The reaction of **15** with AgAcO in acetone produces a yellow solution from which, after filtration to eliminate the precipitate AgCl, yellow crystals of **17** were isolated. The IR spectrum of this compound affords little structural information since it exhibits overlapped absorptions in the carboxylate stretching region. The acetato group is formulated as monodentate ligand on the basis of the observation of an AX_2 pattern for the pyridinic protons in the ^{1}H NMR spectrum.

Other attempts to obtain complexes that had been easily prepared for the homologous dptc series failed in the dipic derivatives. Thus, several attempts at obtaining cyano complexes by treating halide complexes **15** or **16** with AgCN, or the acetonitrile derivative **1** with $[NBu^n_4]CN$, gave mixtures of compounds containing terminal (ν(CN) 2141 cm^{-1}) and bridging (ν(CN) 2181 cm^{-1}) cyanide ligands, which could not be separated as pure samples.

Conclusions

The dipicolinate anion behaves as a tridentate ligand toward palladium, but its coordination as a pincer ligand produces a somewhat strained situation. For this reason some monomeric complexes show a tendency to dimerization in what is a novel coordination mode for this ligand, with relief of strain. These cases look not propitious to produce palladium liquid crystals.

The strain in the coordination of dipic as pincer ligand for Pd seems to arise mainly from the short C−O distances, compared to the longer Pd−S distances in the related pdtc derivatives (pdtc is very stable as pincer ligand). Consequently the use of modified dipic or pdtc ligands in order to produce metal-containing liquid crystals where these ligands act as tridentate pincers should be oriented along two possible lines: (i) O,N,O-pincers might be used for the smaller (first row) transition metals where the shorter M-N distances will reduce the strain in the cycle or with ancillary ligands which favor monomeric species. (ii) S,N,S-pincers should be used preferably

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for heavier transition metals. Research along these lines with adequately modified dipic and pdtc ligands is underway.

Experimental Section

Literature methods were used to prepare $[Pd(acac)_2]$,[15] $[Pd(OAc)_2]_3$,[16] and $(NH_4)_2$dipic.[2] Instrumentation was described previously.[7] All the compounds gave satisfactory elemental analyses (Table S9, Supporting Information). Only representative NMR data are given here. A complete listing of NMR data is available as Supporting Information (Table S10).

Preparation of [Pd(dipic)(NCCH$_3$)] (1). Method a. Palladium acetate (0.5 g, 2.23 mmol) and pyridine-2,6-dicarboxylic acid (0.372 g, 2.23 mmol) were stirred at room temperature in acetonitrile (10 mL) for 6 h. A pale yellow precipitate of **1** was formed which was collected on a frit, washed with acetone (3 × 3 mL) and air-dried. Yield: 0.668 g (96%). IR (Nujol, cm^{-1}): ν(CO) 1688, ν(MeCN)) 2334, 2306.

Method b. $[Pd(acac)_2]$ (1.00 g, 3.28 mmol), and pyridine-2,6-dicarboxylic acid (0.5485 g, 3.28 mmol) were stirred in acetonitrile (10 mL) for 24 h. The precipitate was collected on a frit, washed with chloroform (3 × 5 mL) and acetone (3 × 5 mL) and air-dried. Yield: 0.872 g (85%).

Preparation of [Pd(dipic)(DMSO)] (2). Complex **1** (0.1 g, 0.32 mmol) was dissolved in 5 mL of hot DMSO. When the solution was clear, the solvent was removed in vacuo. The resulting oily residue was triturated in chloroform to give a solid which was collected on a frit and air-dried. Yield: 0.102 g (91%). IR (Nujol, cm^{-1}): ν(C═O) 1660; ν(S═O) 910. ^{1}H NMR (DMSO-d_6): monomer δ 8.33 (t, 1, J_{HH} = 7.8 Hz, H^4), 7.82 (d, 2, J_{HH} = 7.8 Hz, H^{3,5}); dimer 8.32 (t, 2, J_{HH} = 7.8 Hz, H^4), 7.92, 7.51 (dd, 2, 2, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.3 Hz, H^3, H^5).

Preparation of [Pd(dipic)py] (3). To a suspension of **1** (0.1 g, 0.32 mmol) in acetone was added pyridine (0.028 mL, 0.35 mmol), and the mixture was stirred overnight. The new pale yellow precipitate was collected on a frit, washed with acetone (3 × 3 mL), and dried in vacuo. Yield: 0.162 g (86%). IR (Nujol, cm^{-1}): ν(C═O) 1667.

Compounds **4**−**14** were made similarly, for complexes **6**−**8** a solution was obtained, and the solvent was removed in a rotatory evaporator. The residue was washed in ether and recrystallized in chloroform/diethyl ether to yield yellow crystals, which were filtered and washed with diethyl ether.

6. Yield: 86%. IR (Nujol, cm^{-1}): ν(C═O) 1667. ^{1}H NMR ($CDCl_3$): δ 8.21, 7.93 (AB_2 spin system, J_{HH} = 7.8 Hz, H^4, H^{3,5} dipic), 8.10 (s, 2, H^{2,6} py), 7.57 (s, 1, H^4 py), 2.36 (s, 6, Me).

11. Yield: 83%. IR (Nujol, cm^{-1}): ν(C═O) 1674. ^{1}H NMR ($CDCl_3$): dimer δ 7.97 (t, 2, J_{HH} = 7.8 Hz, H^4 dipic), 8.14, 7.82 (dt, 2, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH} \approx {}^5J_{HP} \approx$ 1.4 Hz, H^3, H^5 dipic), 2.2−1.1 (m, 66, C_6H_{11}); monomer: 8.21, 8.02 (AB_2 spin system, H^4, H^{3,5} dipic). $K_{25°C}$ = 5.1 × 10^{-3} mol L^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$): dimer 44.7 s; monomer 41.1 s.

13. Yield: 94%. IR (Nujol, cm^{-1}): ν(C═O) 1676. ^{1}H NMR ($CDCl_3$): dimer, δ 7.95 (dt, 2, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH} \approx {}^5J_{HP} \approx$ 1.4 Hz, H^5 dipic), 7.60 (t, 2, J_{HH} = 7.8 Hz, H^4 dipic), 6.24 (b, 2, H^3 dipic), 7.7−7.1 (m, C_6H_4), 2.32 (s, 18, Me); monomer, δ 8.21, 8.02 (AB_2 spin system, J_{HH} = 7.8 Hz, H^4, H^{3,5} dipic), 2.39 (s, 9, Me). $K_{25°C}$ = 5.5 × 10^{-3} mol L^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$): dimer 22.2 s, monomer 19.4 s.

Preparation of [NBu$^n_4$][Pd(dipic)Cl] (15). To a solution of $K_2[PdCl_4]$ obtained by mixing in water (20 mL) $PdCl_2$ (0.5 g, 2.82 mmol) and KCl (0.42 g, 5.64 mmol) was added $(NH_4)_2$dipic (0.57 mmol, 2.84 mmol), and the solution was stirred for 4 h at 75 °C. Then a solution of (Bu$^n_4$N)NO_3 (prepared by mixing concentrated solutions of $AgNO_3$ (0.575 g, 3.38 mmol) and (Bu$^n_4$N)Br (1.091 g, 3.38 mmol) in water) was added. A yellow precipitate was formed which was filtered, washed with cold water, and dried in vacuo. The solid was recrystallized from dichloromethane−diethyl ether. Yield: 1.212 g (78%). IR (Nujol, cm^{-1}): ν(C═O) 1663, ν(Pd−Cl) 315. ^{1}H NMR ($CDCl_3$): δ 8.11 (t, 1, J_{HH} = 7.7 Hz, H^4 dipic), 7.81 (d, 2, J_{HH} = 7.7 Hz, H^{3,5} dipic), 3.28 (m, 8, NCH_2), 1.69 (m, 8, NCH$_2$CH_2), 1.48 (m, 8, CH_2-CH$_3$), 1.02 (t, 12, −CH_3).

Preparation of [NBu$^n_4$][Pd(dipic)Br] (16). Complex **1** (0.1 g, 0.32 mmol) and (Bu$^n_4$N)Br (0.103 g, 0.32 mmol) were stirred in acetone (10 mL). After 10 min a solution had been formed which was filtered through Celite and concentrated *in vacuo* to *ca*. 5 mL. Addition of diethyl ether produced orange crystals of **16**. Yield: 0.159 g (84%). IR (Nujol, cm^{-1}): ν(C═O) 1665, ν(Pd−Br) 258. ^{1}H NMR ($CDCl_3$): δ 8.11 (t, 1, J_{HH} = 7.7 Hz, H^4 dipic), 7.82 (d, 2, J_{HH} = 7.7 Hz, H^{3,5} dipic), 3.28 (m, 8, NCH_2), 1.69 (m, 8, NCH$_2$CH_2), 1.48 (m, 8, CH_2-CH$_3$), 1.02 (t, 12, −CH_3).

Preparation of [NBu$^n_4$][Pd(dipic)(OAc)] (17). Silver acetate (0.073 g, 0.437 mmol) and **15** (0.2 g, 0.364 mmol) in acetone (20 mL) were stirred in the dark overnight. The AgCl precipitate was filtered off, and the yellow solution was concentrated. Addition of diethyl ether gave orange crystals which were recrystallized from acetone−diethyl ether by cooling at −20 °C. Yield: 0.18 g (86%). IR (Nujol, cm^{-1}): ν(C═O) 1660, 1638. ^{1}H NMR ($CDCl_3$): δ 8.05 (t, 1, J_{HH} = 7.7 Hz, H^4 dipic), 7.73 (d, 2, J_{HH} = 7.7 Hz, H^{3,5} dipic), 3.28 (m, 8, NCH_2), 1.99 (s, 3, CH_3CO$_2^-$), 1.69 (m, 8, NCH$_2$CH_2), 1.48 (m, 8, CH_2CH$_3$), 1.02 (t, 12, −CH_3).

X-ray Structure of [Pd(dipic)(PBu$_3$)]$_2$. Crystals suitable for X-ray determination were grown by slow diffusion of hexane into a concentrated solution of **10** in CH_2Cl_2. Relevant crystallographic details are given in Table 1. Unit cell parameters were determined from the least-squares refinement of a set of 25 centered reflections. Three reflections were measured every 1 h as orientation and intensity control. Significant decay was not observed. Heavy atoms were located from a Patterson synthesis, and the remaining non-hydrogen atoms by DIRDIF.[17] Full-matrix least-squares refinements were made with SHELX76.[18] After isotropic refinement, an absorption correction was applied with DIFABS.[19] The carbon atoms of two butyl groups [C(71) to C(74), and C(81) to C(84)] of one of the PBu_3 ligands showed some degree of thermal disorder which, despite repeated attempts, could not be modeled satisfactorily. Therefore, the two butyl groups were refined as rigid groups, affixed to the same phosphorus atom, P(2), with individual isotropic temperature factors. The remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically positioned (except for the carbon atoms involved in the disorder), and were given a common isotropic temperature factor which was refined. Torsion angles and least-squares planes were calculated with PARST.[20] The drawing was made with PLATON.[21]

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Supporting Information Available: Tables of atomic coordinates (Table S1), anisotropic thermal parameters for non-hydrogen atoms (Table S2), atomic parameters for hydrogen atoms (Table S3), bond distances (Table S4) and angles (Table S5), torsion angles (Table S6), least-squares planes (Table S7), crystallographic details including text with experimental details (Table S8), microanalyses, yield, and IR data (Table S9), and NMR data (Table S10) (15 pages). Ordering information is given on any current masthead page.

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