Polymer [Pd(CH_2SO_2C_6H_4Me)_2]_n, Precursor to Remarkably Stable Pd Organometallics

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A polymer [Pd(CH_2SO_2C_6H_4Me)_2]_n is obtained by thermalolysis of cis-[Pd(CH_2SO_2C_6H_4Me)_2(NCMe)_2] to release the MeCN ligands. The corresponding coordination sites are then occupied by weak Pd–O bonds, easier to break than the previous Pd–N bonds. This allows to produce from the polymer cis complexes containing ligands weaker than NCMe, such as acetone or water. The complexes cis-[Pd(CH_2SO_2C_6H_4Me)_2(OH)_2], cis-[Pd(CH_2SO_2C_6H_4Me)_2(OH)], cis-[Pd(CH_2SO_2C_6H_4Me)_2(OH)(OH)], cis-[Pd(CH_2SO_2C_6H_4Me)_2(OH)_2], cis-[Pd(CH_2SO_2C_6H_4Me)_2(OH)(OH)]_2, and cyclic dimers [Pd(CH_2SO_2C_6H_4Me)_2(OH)]_2 with bridging methylsulphone groups are formed. The Pd-PPh_3OH, 1:1:1 reaction of the polymer produces cis-[Pd(CH_2SO_2C_6H_4Me)_2(PPh_3)(OH)], which isomerizes to trans-[Pd(CH_2SO_2C_6H_4Me)_2(PPh_3)(OH)]_2, with water O-coordinated to Pd and making hydrogen bonds to the two SO_2 groups as seen in its X-ray structure. A similar role is played by NH_2 in the structures of trans-[Pd(CH_2SO_2C_6H_4Me)_2(PPh_3)(NH_2)]_2 and the dimer μ[N(NH_2)trans-[Pd(CH_2SO_2C_6H_4Me)_2(PPh_3)]], in addition to these interesting intramolecular hydrogen bonding properties provided by the SO_2 groups, the structural and ^1H NMR data available suggest that the CH_2SO_2C_6H_4Me group is an interesting kind of alkyl strongly σ donor, with high trans influence, and forming very stable Pd complexes extraordinarily reluctant to reductive elimination and to hydrolysis by water at room temperature.

Introduction

Palladium-mediated or catalysed cross-coupling reactions, used to form C–C and C–heteroatom bonds, are today among the most powerful transformations of organic synthesis. Over the last decades, our group has made some relevant mechanistic contributions in this field using Pd–C(sp^3) systems based in fluoroaryl palladium complexes, which are relatively stable and offer easy monitoring of the reactions by ^19F NMR. We are now interested in highly stable Pd–C(sp^3) systems. In this respect, Pd–CF_3 compounds are an important area of study in the last years. Pd catalysed Ar–CF_3 bond formation is interesting for fluorination of organic molecules, but reductive elimination from Pd complexes containing Pd–CF_3 bonds is extremely difficult. Other interesting Pd–C(sp^3) systems are methyl derivatives, fairly stable compared to many other alkyls that are prone to undergo β-H elimination. The thermal stability of these methyl derivatives depends on the ancillary ligands, but is not very high. Some time ago we reported the preparation of the (arylsulfonyl)alkyl-palladium complexes (NBu_3)_2[Pd(μ-Br)_2R_4] and cis-[PdR_3(NCMe)_2] (R = CH_2SO_2C_6H_4Me) and their use as general sources of complexes containing a cis-Pd(CH_2SO_2C_6H_4Me)_2 moiety. Anionic ((NBu_3)_2[PdBrR_1], (NBu_3)_2[PdR_2(CN)], (NBu_3)_2[PdR_2(acac)], (NBu_3)_2[PdBrR_2(μ-dppm)]), and neutral ([PdR_3]) complexes (L = monodentate ligand; L_2 = bidentate ligand) were synthesized and characterized. A few complexes with this special type of alkyl, namely [PdR_3(COD)], [PdR_2(COD)] (R = CH_2SO_2C_6H_4Me), and [Pd(μ(CHPh)_2SO_2L)]_2, had been reported before, and Fiorani et al. later reported in the preparation of trans-[PdClR(PPh_3)]_2 by treatment of cis-[PdClR(PPh_3)]_2 with K[18-crown-6](R). As expected for a late transition metal, the (arylsulfonyl)alkyl groups in all these complexes prefer to coordinate to palladium through the carbon atom in a ɑ-alkyl fashion while the oxygen atoms of the sulfonyl group do not coordinate. The opposite preference is generally found for alkali metals, which bind to the highly electronegative oxygen atoms.

In this paper we are recovering the topic because the few Pd arylsulfonylalkyl complexes reported so far have shown a considerable inertness of the Pd–C(sp^3) bond. Compared to CF_3 derivatives, the arylsulfonylalkyl complexes are prepared much more easily and we see them as a convenient study model to look for methods to induce difficult couplings, complementary to the inert CF_3 or to the more reactive Me group. Its inertness could be also useful in the field of materials, where reactivity is a property to be avoided. The Pd–CH_2SO_2C_6H_4Me bond is, for instance, more inert than the Pd–CF_3 bond (which has a reputation of inertness) towards olefin insertion: [PdX(CH_2SO_2C_6H_4Me)(COD)] is reluctant to insertion, while...
[Pd(X(C₆F₅))(COD)] gives the allyl product of C₆F₅ insertion into a double bond of COD.¹¹ Comparing CH₂SO₂C₆H₄Me with Me, the formation of ethane from [PdMe₂L₂] (L = phosphine) is very fast,³ in conditions where the similar arylsulfonfonylalkyl complexes reported by us are perfectly stable.⁴ This inertness of the Pd–C bond is further encountered here in its resistance to hydrolysis by water or other weakly acidic molecules. Moreover, the oxygen atoms of sulfones are very weak donors for Pd, and the coordination chemistry reported for them is very scarce,¹²⁻¹³ but in this paper we are examining new unusual aspects of the participation of the sulfone oxygen atoms in palladium complexes. The synthesis of the homoleptic polymer [Pd(CH₂SO₂C₆H₄Me)₂]ₙ provides a structure with bridging CH₂SO₂C₆H₄Me groups, which is a general precursor to any of the complexes reported previously by other methods.⁴ The controlled reactivity of this polymer uncovers an unexpected and highly interesting intramolecular structural interplay of first order (O or N coordination) and second order (H···O=S=O hydrogen bonding) interactions when OH₂ or RNH₂ molecules are used as ligands.

**Results and discussion**

1. **Synthesis and characterization of [Pd(CH₂SO₂C₆H₄Me)₂]ₙ**

Complex cis-[Pd(CH₂SO₂C₆H₄Me)₂(NCMe)₂] (1) has shown to be excellent precursor to other Pd complexes with stronger ligands, by displacing the weak acetonitrile ligands.⁴ In general, complexes [PdR₂L₂] (R = conventional aryl or alkyl) require strongly coordinating ligands (e.g. phosphines) for their stabilization, and they undergo easy reductive elimination if the ligands are weak. In view of the unusual thermal stability of complex 1 with a weak ligand MeCN, we decided to submit it to a thermal study. The thermogravimetric analysis of 1 (at 5 °C/min) revealed that two MeCN molecules per Pd atom were quickly eliminated at 134 °C. Alternatively, heating in an oven the white complex 1 at 80 °C up to constant weight (about 1 day) produced the complete elimination of MeCN. In both cases, contrary to complexes with conventional alkyls or aryls, the loss of ligand does not lead to reductive elimination and formation of black Pd, but to formation of a red solid (2) of composition [Pd(CH₂SO₂C₆H₄Me)₂]ₙ.

Only few complexes with stoichiometry [PdR₂]ₙ have been reported previously: the dicyclopalladated cis-[Pd[(=C(=O)-C₆H₄NO₂=O)]₄],¹⁴ the tetranuclear [Pd(CH₅SPH₂)₄]ₙ and [Pd(CH₅CN)₄]ₙ.⁵ Proposed to have a chain structure.¹⁶ In all these complexes the apparent coordination deficiency of the Pd atom is compensated by participation of the heteroatoms O, S or N in coordination, yielding monomeric, oligomeric or polymeric structures. Similarly, in [Pd(CH₄SO₂C₆H₄Me)₂]ₙ a polymeric structure should be formed to achieve 4-coordination for Pd.

Solubility tests show that, in effect, 2 is insoluble in solvents such as dry CDC₁₃ or dry CD₃CN, (the case of moist solvents is discussed later). This insolubility suggests a polymeric structure with the apparent coordinative deficiency of Pd atoms being compensated by involvement of the oxygen atoms of SO₂ in bonding to Pd. This is supported by the changes observed in the ν(S=O) stretching absorptions comparing 1 and 2. For 1, where the O atoms are not involved in bonding, two bands are observed at 1135 and 1274 cm⁻¹. In 2 these bands are shifted to lower wavelengths (1116 and 1257 cm⁻¹), reflecting a decrease of S=O bond order when some electron density of the double bond is polarized towards the oxygen atom upon lone pair donation to Pd. Similar wavenumber shifts have been reported comparing MeSO₂Ph (1148 and 1285 cm⁻¹) with LiCH₄SO₂Ph (1113 and 1211 cm⁻¹), in this case attributed to the formation of Li–O bonds.¹⁷

In the absence of crystals suitable for X-ray diffraction studies, the exact structure of the polymer could not be ascertained, but there are good reasons to propose that the mutual arrangement of the two R groups is cis. First of all, there is a very high thermodynamic tendency in Pd¹ for the ligands with high trans influence (the two R groups) to avoid mutually trans arrangement.¹⁸ This preference was systematically observed for R = CH₅SO₂C₆H₄Me in all the [Pd(CH₅SO₂C₆H₄Me)₂] compounds reported previously,⁴ and is proposed also for the polymer, where the O-donor SO₂ groups have very low trans influence: the arrangement thermodynamically expected is a trans disposition of the R and O ligands. The reactivity discussed later is also consistent with this proposal in most cases. And the exceptions can be explained.

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**Fig. 1** Thermogravimetry diagram of cis-[Pd(CH₂SO₂C₆H₄Me)₂(NCMe)₂] (1).
The S=O···Pd links giving rise to the polymer can produce head/head or head/tail arrangements, both compatible with the cis arrangement of the two Pd–C bonds, and can also have different tacticity around the S atoms (Chart 1). The polymer isolated looks very homogeneous but, beyond that, we do not have any data to favour one structure over another. The polymer [Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_3$]$_n$ can also be prepared from (NBu$_4$)[Pd($μ$-Br)$_2$(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$]$_n$ by reaction with AgNO$_3$ in Me$_2$CO/MeCN (8/1 mixture), filtration of AgBr, and evaporation of the solution to dryness. Slow addition of water leaves a residue, which is repeatedly washed with water to remove any remaining NBu$_4$NO$_3$. This residue is a mixture of Pd complexes stabilized only by MeCN or water, which are lost upon prolonged heating at 100 °C (about 3 days) affording 2 in high yield.

2. Special reactivity of [Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_3$]$_n$

Polymer 2 is a general precursor to all the cis complexes that in our previous paper were synthesized from cis-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_3$(NCMe)$_2$] (1), but 2 is an even better precursor because the Pd–O=S bonds are weaker than the Pd-NCMe bonds. As a matter of fact, complex 1 can be obtained from 2 + 2MeCN. Also, complex (NBu$_4$)[Pd($μ$-Br)$_2$(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$] (the other previous general precursor) can be obtained from 2 + (NBu$_4$)Br. Beyond that, polymer 2 allows for the study of some interesting reactions with other weak ligands such as acetone and water, which would not replace acetonitrile. Whereas cationic aquocomplexes of Pd are not infrequent, neutral aquocomplexes [PdR$_2$(OH)$_2$] are particularly scarce due to the soft-acid character of Pd and the hard-base character of water.

2.a Water complexes

The red polymer 2 is soluble in (CD$_3$)$_2$CO producing a pale yellow solution. At 293 K this solution displays $^1$H NMR signals of C$_6$H$_4$ (two pseudodoublets, AA’XX’ spin system), CH$_2$ (broad signal), and CH$_3$ (sharp singlet), as well as a broad signal due to water contained in the (CD$_3$)$_2$CO solvent (Fig. 2a).

The low temperature $^1$H NMR spectrum of 2 at 188 K (Fig. 2b) shows the presence of several compounds, which are participating in fast exchange processes producing the broad signals observed at room temperature: cis-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_3$OH$_2$]$_2$ (3) ($δ$(OH$_2$) = 5.93 ppm, $δ$(CH$_3$) = 2.81 ppm), cis-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$(OC)(CD$_3$)$_2$)$_2$ (4) ($δ$(CH$_3$) = 2.77 ppm), cis-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$(OH$_2$)(OC)(CD$_3$)$_2$] (5) ($δ$(OH$_2$) = 6.03 ppm, $δ$(CH$_3$) = 2.90, 2.71 ppm), and free water ($δ$(OH$_2$) = 3.81 ppm). The low field chemical shifts of coordinated water correspond to their higher acidity compared to free water.

The polymer can also be dissolved in moist CDCl$_3$ or moist CD$_2$Cl$_2$, producing yellow solutions. At variance with the (CD$_3$)$_2$CO case, since these solvents are non coordinating, water is the only ligand available to split the polymer. The low temperature $^1$H NMR spectra of these solutions suggest the presence of two new water complexes in solution. According to the NMR integrals both complexes have the same stoichiometric formula [Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_3$(OH)$_2$]$_n$ with a Pd:OH$_2$ 1:1 ratio. With this stoichiometry, and keeping the cis arrangement of the two R groups, the cyclic dimers 6 and 7 (Scheme 1), which differ in the tectivity of the S atoms in the cycle, are the smaller and more plausible structures that achieve 4-coordination for Pd. The S atoms having one coordinated and one uncoordinated O atom are chiral, and 6 and 7 are R,S and R,R diastereomers. Single crystals of these complexes could not be obtained but the proposed structures are supported by the fact that the diastereotopism observed for the H atoms of the methylene groups requires SO$_2$ groups where one oxygen atom is coordinated to Pd and the other is not. Dimer 6 accounts for the observation in the $^1$H NMR spectra and COSY experiments of eight equal intensity H atoms (4 non equivalent CH$_3$ groups with diastereotropic H atoms). On the other hand dimer 7, which possesses a C$_2$ symmetry axis, fits well with the observation of only four equal intensity H atoms (2 non equivalent CH$_2$ groups with diastereotropic H atoms).

Scheme 1 suggests that the end of the hydration reaction of the polymer should be cis-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_3$(OH)$_2$]$_2$ (3). This is observed upon addition of a large excess of OH$_2$(OH$_2$:Pd = 20:1) to a suspension of 2 in Et$_2$O. Solutions of 3 in CDCl$_3$ or CD$_2$Cl$_2$ give the same $^1$H NMR spectra obtained for the solutions of 2 in the same moist solvents, showing that the mixture 6+7+OH$_2$ is thermodynamically preferred to 3 in these conditions. This spontaneous oligomerization with water extrusion is a further support for the structures proposed for 6 and 7. Complexes 3, 6, and 7 quickly lose water out of the solution and eventually regenerate the polymer.
The observation that fragmentation of the polymer upon addition of only one water ligand per Pd atom gave rise to well defined structures suggested us to try this 1:1 ratio in reactions with a more conventional ligand (PPh₃). This was a fortunate decision that eventually led to very interesting results. Addition of PPh₃ (1:1 molar ratio) to a solution of 2 in CHCl₃ yielded a very uneven mixture of two complexes (8, 2%), and (9, 98%) from which complex 9 can be crystallized. Their ¹H NMR spectra in CDCl₃ allowed to assign 8 as cis-[Pd(CH₃SO₂C₆H₄Me)₂(OH)₂(PPh₃)] and 9 as trans-[Pd(CH₃SO₂C₆H₄Me)₂(OH)₂(PPh₃)] (9, 98%). This mixture of 8 and 9 can also be obtained from any other combination of reagents that fixes the appropriate Pd:PPh₃ 1:1 ratio of components. For instance, by 1:1 reaction in wet chloroform of 2 and cis-[Pd(CH₃SO₂C₆H₄Me)₂(PPh₃)] (10).⁴

A low temperature variable study of this addition of PPh₃ to a yellow solution of 2 in wet CDCl₃ at −60 °C (1:1 molar ratio) reveals the sequence shown in Scheme 2. At low temperature complex 10 is formed, producing partial discoloration of the initial yellow solution, while half of the palladium remains unreacted (in the form of hydrated forms of the polymer). Letting the solution to warm up, these are the only products observed for a long temperature range, but at 0 °C a rearrangement reaction starts, accompanied of almost complete discoloration, forming 8, which more slowly isomerizes to 9. Eventually the 8/9 ratio reaches 2/98, which is the thermodynamic equilibrium (Scheme 2).

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\begin{align*}
1/\text{n cis-[PdR₃]ₙ} + \text{PPh₃} + \text{OH}_₂ & \xrightleftharpoons[0 °C]{-60 °C \text{CDCl₃}} 1/2 \text{cis-[PdR₂(PPh₃)₂] (10)} \\
+ 1/2n \text{cis-[PdR₂(OH)₂]ₙ (6 or 7)} & \rightarrow \text{trans-[PdR₂(PPh₃)(OH₂)]} \\
& \xrightarrow{\text{room T}} \text{cis-[PdR₂(PPh₃)(OH₂)]} \\
\end{align*}
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Scheme 2 Stepwise formation of the aquo complex 9.

The formation of a complex with geometrical trans preference, 9, by rearrangement of two precursors with clear cis preference, 2 and 10, catches the eye and is somewhat surprising and unexpected, considering that the reluctance for the two CH₃SO₂C₆H₄Me groups to be trans to each other had been so far the dominant feature. The reason for this was understood when the crystal structure of 9 was determined by X-ray crystallography. The structure shows a fairly regular square planar coordination for the Pd atom, with the two CH₃SO₂C₆H₄Me occupying trans positions as expected. Since the SO₂ groups are oriented by the methylene group away from the Pd and are lying above and below the coordination plane, this is relatively free of hindrance and the bond angles do not need to be very distorted from 90° (Fig. 3).²¹ Relevant bond distances and angles are given in Fig. 3. The most salient features of the structure are: i) the two CH₃SO₂C₆H₄Me groups are trans; and ii) the water molecule, trans to PPh₃, makes intramolecular hydrogen bonds to the sulfone groups, connecting each water hydrogen atom to one oxygen atom of each SO₂ unit. These two very uncommon features are probably working together in a synergism that stabilizes this structure.

None of the hydrogen atoms involved in hydrogen bonding was located in the Fourier map but their positions were calculated with a riding model. After imposing a O–H distance of 0.938 Å (a value that has been observed by neutron diffraction),²² the calculated hydrogen bond distances and angles are HSA···O₂ = 2.163 Å; O₅-HSA···O₂ = 124.36°; and HSB···O₄ = 1.825 Å; O₅-HSB···O₄ = 142.63°. The two S atoms of the sulfone group lie, respectively, above and below the coordination plane. Although the H–O–H angle is not symmetrically arranged relative to the coordination plane, one oxygen atom of each SO₂ group is roughly oriented towards the water molecule, allowing for the formation of the two hydrogen bonds. These values of the H–O lengths correspond to hydrogen bonds of moderate strength.²³ However, the intramolecular cooperation of two hydrogen bond of the same OH₂ molecule must reinforce the bonding effect, which is able to compensate the electronically unfavourable contribution of the trans arrangement of the two CH₃SO₂C₆H₄Me groups in this complex. As a matter of fact, in contrast with the easy loss of water from cis-[Pd(CH₃SO₂C₆H₄Me)₂(OH₂)]ₙ, which occurs when trying to obtain in the solid state these complexes observed in solution, the water ligand in 9 is firmly coordinated. The highly stabilizing hydrogen bond interaction is not in contradiction with a high lability of the system, typical of H-bonding systems even for strong bonds, under some
conditions. In fact this water molecule is very labile in CDCl₃ solution and it exchanges quickly with the free water present in the solvent.

For a better qualitative estimation of steric requirements and trans influence of the CH₃SO₂C₆H₄Me group and its influence in formation of cis and trans isomers, the X-ray structure of cis-[Pd(CH₃SO₂C₆H₄Me₂)(PPh₃)₂] (10) was studied, and is shown in Fig. 4. The structure confirms the cis geometry that has been assigned to this complex. It shows a fairly regular square planar coordination for Pd, with the SO₂ groups above and below the coordination plane. In that disposition these groups minimize steric hindrance with the other ligands and with each other. The C1-Pd1-C2 is only 87.1(3)°, compared to 95.69(7)° defined by the P1-Pd1-P2 bulkier PPh₃ ligands.

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Pd1-P1 = 90.2(2).
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Fig. 4 Molecular structure of 10 from X-ray crystallography. The thermal ellipsoids are set at a 50% probability level. Selected bond lengths [Å] and bond angles [°]: Pd1-P1 = 2.3355(19), Pd1-P2 = 2.351(2), Pd1-C1 = 2.097(8), Pd1-C2 = 2.117(7), C1-Pd1-C2 = 87.1(3), P1-Pd1-P2 = 95.69(7), C2-Pd1-P2 = 87.3(2), C1-Pd1-P1 = 90.2(2).

The comparison of bond lengths in the two structures as a possible indication of trans influence and electron donating ability is somewhat puzzling. In general trans influence of hydride and C-ligands is the highest, followed by phosphines. The Pd–C distances found for the two mutually trans CH₃SO₂C₆H₄Me groups in complex 9 (2.093(3) and 2.121(3) Å) are almost identical to those found in complex 10 (2.097(8) and 2.117(7) Å) where these groups are trans to PPh₃. Should this be interpreted as a sign of identical trans influence on the Pd–CH₃SO₂C₆H₄Me bond length of PPh₃ and CH₃SO₂C₆H₄Me? Or, in other words, should it be concluded that PPh₃ and CH₃SO₂C₆H₄Me exert very similar structural trans influences? On the contrary, the Pd–P distances are very different in complex 9 (2.2084(7) Å, trans to OH₂) or in complex 10 (2.3355(19) Å and 2.351(2) Å, trans to CH₃SO₂C₆H₄Me). The large Pd–P bond length difference reflects the fact that OH₂ is among the ligands with lowest trans influence. It also suggests that the relationship between bond length to the influenced ligand and trans influence of the influencing is not simple.

Ligands with the highest trans influences are typically strong σ donors that polarize the electron density of the trans bond towards that donor atom, elongating and weakening that bond. Based in this model, the consequence is that the conflict between trans effects of two ligands will have a marked bond length consequence on the weaker σ donor ligand, but the effect on the stronger σ donor can be very minor. With this model the bond length data observed are compatible with a trans influence sequence CH₃SO₂C₆H₄Me > PPh₃. This interpretation seems to be supported by the observation of a chemical shift difference of the CH₃ groups in the trans complex 9 compared to any other cis complex. In the ¹H NMR spectrum of cis-[Pd(CH₃SO₂C₆H₄Me₂)(OH₂)(PPh₃)] (8) the two inequivalent CH₃ groups give rise to two doublets (at 2.78 and 3.04 ppm) with very close ¹J(CH₃–P–H) coupling constants (8.5 and 7.8 Hz). In the ¹H NMR spectrum of cis-[Pd(CH₃SO₂C₆H₄Me₂)(PPh₃)₂] (10) the CH₃ group appears as a broad signal at 3.49 ppm. In contrast, the equivalent CH₃ groups in trans-[Pd(CH₃SO₂C₆H₄Me₂)(OH₂)(PPh₃)] (9) appear as a much more shielded doublet at 1.96 ppm, with ¹J(CH₃–P–H) = 3.0 Hz. This clear difference in shielding reflects the stronger electronic polarization of the H₃C–Pd bond towards Pd (and through it to the bond and the donor atom in trans position) when the ligand in front is a weaker σ donor.

2.4 Ammonia and other N–H hydrogen donor complexes

The decisive role of water in the constitution of complex 9 suggests immediately other molecules that could play and perhaps reinforce the role of water as O-ligand towards Pd and “chelate” H-donor towards the oxygen atoms of two SO₂ groups cis to the water ligand. In effect, the NH₃ complex trans-[Pd(CH₃SO₂C₆H₄Me₂)(NH₃)(PPh₃)] (11), equivalent to 9, can be obtained by treatment of 9 with NH₃, or by a variation of the procedure to the one shown in Scheme 2 for the water complex. The later consists of the rearrangement of cis-[Pd(CH₃SO₂C₆H₄Me₂)(PPh₃)₂] (10) and cis-[Pd(CH₃SO₂C₆H₄Me₂)(NH₃)(PPh₃)] (12). Complex 12 was obtained from polymer 2 and NH₃, and was isolated and fully characterized. The only practical difference with the preparation of the water complex was that the fast formation of cis-[Pd(CH₃SO₂C₆H₄Me₂)(NH₃)(PPh₃)] (13) was observed first, which then isomerized slowly (several days) to trans-[Pd(CH₃SO₂C₆H₄Me₂)(NH₃)(PPh₃)] (Scheme 3).

Single crystals of 11 could be obtained and its X-ray diffraction structure was solved and is shown in Figure 5, along with relevant bond distances and angles. It confirms a square planar coordination for Pd, just slightly distorted. The two CH₃SO₂C₆H₄Me groups are trans, and the ammonia molecule, trans to PPh₃, makes intramolecular hydrogen bonds to the sulfone groups, connecting two of the NH₃ hydrogen atoms each to one oxygen atom of each SO₂ unit, and the remaining hydrogen atom makes an intermolecular hydrogen bond with the SO₂ unit of a neighbouring molecule. There is a reciprocal interaction from the neighbouring molecule, and these intermolecular interactions define dimers in the solid state structure. The two SO₂ groups are located at opposite sides of the coordination plane.

Fig. 4 Molecular structure of 10 from X-ray crystallography. The thermal ellipsoids are set at a 50% probability level. Selected bond lengths [Å] and bond angles [°]: Pd1-P1 = 2.3355(19), Pd1-P2 = 2.351(2), Pd1-C1 = 2.097(8), Pd1-C2 = 2.117(7), C1-Pd1-C2 = 87.1(3), P1-Pd1-P2 = 95.69(7), C2-Pd1-P2 = 87.3(2), C1-Pd1-P1 = 90.2(2).
As for the water complex, the NH₃ hydrogen atom positions were calculated with a riding model. After imposing a N–H distance of 1.030 Å (a value that has been observed by neutron diffraction), the calculated hydrogen bond distances and angles are H₁B···O₄ = 2.030 Å; N₁-H₁B···O₄ = 127.30°; H₁C···O₂ = 1.963 Å; N₁-H₁C···O₂ = 146.95°; and H₁A···O₁# = 2.158 Å; N₁-H₁A···O₁# = 160.99°. All these values of the H···N lengths, intra- and intermolecular, correspond to hydrogen bonds of moderate strength.

A closely related complex was obtained using hydrazine in Pd:N₂H₄ 2:1 ratio. The X-ray diffraction structure of the corresponding complex, and relevant distances and angles are given in Figure 6. The structure reveals two Pd atoms equivalent by an S₂ axis, connected by a bridging hydrazine ligand. The two coordination planes are arranged almost parallel, at the distance imposed by the Pd-N-N-Pd kink.

In this interesting dimeric structure the hydrogen bonding interactions show interesting differences with the previous structures. They are intramolecular as the majority of the interactions already discussed, but the two H atoms on one N atom interact with the O atoms of the CH₃SO₂C₆H₄Me groups of the other Pd atom, and not to the CH₃SO₂C₆H₄Me groups on the Pd atom coordinated with that N atom. This produces two effects: i) the hydrazine creates a double bridging connection of the two Pd centres, one through the Pd-N-N-Pd bond interactions, and another through the Pd-N-H···O-S-CH₂-Pd hydrogen bond interactions; and ii) in order to make that system of hydrogen bonding interactions possible, the two SO₂ groups at each Pd are both oriented above the same face of the coordination plane, that one closer to the other coordination plane of the dimer. Note that in the mononuclear molecules discussed before the two SO₂ groups were oriented one above and the other below the coordination plane.

The N₂H₄ hydrogen atom positions were calculated with a riding model, and a N–H distance of 1.030 Å was imposed (a value that has been observed by neutron diffraction). The resulting calculated hydrogen bond distances and angles are H₁B···O₄# = 1.959 Å; N₁-H₁B···O₄# = 155.65°; and H₁A···O₂# = 1.926 Å; N₁-H₁A···O₂# = 153.26°. These values of the H···N lengths correspond to hydrogen bonds of moderate strength. A related reinforced coordination of water, NH₃ as ligand for Pd.

2.4 Structural comparison with other molecular systems

The ability of the methylsulfonyl Pd complexes to incorporate one molecule of OH₂ or NH₂R per Pd has not been exhausted in the previous experiments. It is obvious that, looking to the automatism of the sequential steps that build the complexes...
from their precursors as in an industrial assembly line, changing the PPh₃ ligand by others or using other NH₃R ligands might allow for the successful syntheses of many related complexes. In this respect, Kickham and Loeb reported the synthesis of palladium metalloreceptors for water, ammonia, amines, hydrazine, and the hydrazinium ion.⁹,²⁶,²⁷ For this purpose they designed [Pd(L)(CH₃CN)]⁺ cationic complexes (L = 5,8,11-trioxo-2,14-dithia-15-m-cyclophane) or 5,8,11,14,17-pentaaza-2,20-dithia-21-m-cyclophane) as metalloreceptors to coordinate the substrate molecule by O or N σ donation to the Pd center (displacing MeCN) while simultaneously interacting with the peripheral crown ether oxygen atoms via hydrogen bonding. The authors described the structure of their complex with NH₃ saying that the metal-bound NH₃ substrate is “nested” into the partial crown created by the polyether chain of the macrocycle. In this case the main driving force attracting the molecule to the preformed nest is the strong bond formed by the hard heteroatom (O or N) base with the acidic Pd cation. Using that nesting image we could say in the case of the complexes 9, 11, and 14 reported here the “bird” is attracted to a nest much less comfortable initially, because the acidic site it offers is softer (neutral complex) and the Pd–O or Pd–N bonds will be weaker. However, it is the bird who will heavily rearrange the nest to its own convenience, to make cooperative hydrogen bonding with two SO₂ groups instead of one, by producing cis-trans isomerization against the electronic preferences (trans influence of the ligands) in Pd. Obviously the tight cooperative hydrogen bonding interactions in 9, 11, and 14 are more structurally decisive than in the metalloreceptors above.

3. Stability of CH₂SO₂CH₂Me Pd complexes

Finally, it is worth commenting briefly on the notable stability in different circumstances of all the CH₂SO₂CH₂Me Pd complexes. Concerning hydrolysis, alkyl complexes undergo fast hydrolysis with water to release alkane, whereas CH₂SO₂CH₂Me complexes are compatible with water in the solvent or as ligand, as shown in the previous sections. They require acidic conditions with HX to undergo hydrolysis to CH₂SO₂CH₂Me and [PdX(CH₂SO₂CH₂Me)L₂]⁺ or, under more stringent conditions, [PdX₂L]⁺. As for reductive elimination, cis dialkyl Pd complexes with common weak monodentate ligands couple fast or very fast to the corresponding alkyl–alkyl, whereas the cis CH₂SO₂CH₂Me complexes reported here are very reluctant to couple. In fact they do not couple when heated to 134 °C to produce the polymer. These properties make the Pd(CH₂SO₂CH₂Me systems potentially interesting in many fields, from catalysis to materials.

Conclusions

In this work the inertness of the Pd–CH₂SO₂CH₂Me bond has let us synthesize by thermolysis a homoleptic Pd polymer that is a very general precursor to almost any Pd complex with this group, as well as some uncommon water and acetone complexes, including unusual water, ammonia, and hydrazine complexes where the coordinated OH, or NH₃R (R = H, NH₃) ligand brings about cis to trans isomerization to establish double hydrogen bridging to two SO₂ groups. As for the inertness of the Pd–C bond observed in this family of compounds, CH₂SO₂CH₂Me is a highly donor alkyl type group that produces Pd complexes with unusual resistance to reductive elimination and hydrolysis. In this respect it reminds the stability of fluorinated aryls, and that of mesityl or fluoromesityl derivatives, and seems superior to perfluorinated aryls. Consequently it should be a good model for studies of reactions on challenging inert groups. The group is also interesting for application in the field of metal-containing materials demanding thermal stability of the complexes used in the device (e.g. thermotropic liquid crystals).

Acknowledgements

We gratefully acknowledge financial support of the Spanish MINECO (DGI, grants CTQ2014-52796-P and CTQ2016-80913-P), and the Junta de Castilla y León (grant VA256U13; UIC 176).

Notes and references


9 In this respect we have experienced in the experimental study of alkyl coupling using the Negishi reaction (a-e) or bimetallic Pd/Au alkyl transmetalations (f, g): (a) E. Gloria, J. M.

10 For instance, in the field of thermotropic liquid crystals conventional alkylcomplexes are excluded due to their thermal lability.


18 This behavior has been referred to as antisymbiotic effect (a), or as transphobia (b): (a) R. G. Pearson, Inorg. Chem., 1973, 12, 712; (b) J. Vicente, J. A. Abad, A. D. Frankland and M. C. Ramírez de Arellano, Chem. Eur. J., 1999, 5, 3066.


21 A different case is the rotation around the Pd–C bond, to which the SO₂ group imposes severe restriction (see reference 4).


23 Hydrogen bonding distance ranges proposed in the literature: strong, 1.2–1.5 Å; moderate, 1.5–2.2 Å; weak, 2.2–3.2 Å. G. A. Jeffrey, An Introduction to Hydrogen Bonding, Oxford University Press, 1997.

24 Note that in this electronic polarization along the C–Pd–L axis the ligand with higher trans influence (the C atom in our case) develops some positive partial charge, making a stronger bond to Pd, and the L atom recovers electron density, weakening the interaction with Pd and eventually facilitating the dissociation of L.

25 Y. Han and H. V. Huynh, Dalton Trans., 2009, 2201.
Supporting Information

Polymer [Pd(CH₂SO₂C₆H₄Me)₂]ₙ, Precursor to Remarkably Stable Pd Organometallics.

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1. General methods
All reactions were performed in air unless otherwise stated. If necessary, solvents were dried using a solvent purification system SPS PS-MD-5 or distilled from appropriate drying agents under nitrogen, prior to use. Reagents and solvents used were of commercially available reagent quality.

$^1$H, $^{31}$P{$^1$H} and $^{13}$C{$^1$H} NMR spectra were recorded with Bruker AV-400 and/or Varian Inova 500-MR instruments. Chemical shifts (in δ units, parts per million) were referenced to the residual solvent signal ($^1$H and $^{13}$C{$^1$H}), and to 85% H$_3$PO$_4$ ($^{31}$P{$^1$H}). Elemental analysis for carbon, hydrogen and nitrogen was performed on a Perkin Elmer 2400 CHN elemental analyser. Infrared spectra were recorded with a Perkin-Elmer FTIR 1720 X spectrophotometer with samples prepared as Nujol mulls. Thermogravimetric analyses were made with Perkin-Elmer TGA-7 analyser under nitrogen at a heating rate of 5 °C/min.

2. Synthesis and characterization of the products

2.1. [Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$]$_n$ (2)

Complex 1 (500 mg, 0.95 mmol) was heated in an oven at 80 °C up to constant weight (about 1 day) to give the stoichiometric amount of polymer 2.

To a suspension of AgNO$_3$ (474 mg, 2.79 mmol) in a mixture (40 mL) of acetone and acetonitrile (8:1) was added (NBu$_4$)$_2$[Pd$_2$(µ-Br)$_2$(CH$_2$SO$_2$C$_6$H$_4$Me)$_4$] (2.14 g, 1.39 mmol). The mixture was stirred in the dark for 30 min. The insoluble AgBr was filtered off and the resulting solution was evaporated to dryness. Water (20 mL) was added carefully to the oily residue to give a white solid, which was filtered, washed with water ($3 \times 20$ mL) and dried under vacuum. The resulting solid was heated in an oven at 100 °C up to constant weight (about 3 days) to give polymer 2. Yield: 88%. Analysis calculated for C$_{16}$H$_{18}$O$_4$PdS$_2$: C, 43.20; H, 4.08. Found: C, 42.93; H, 4.05. $^1$H NMR (400.14 MHz, wet CDCl$_3$, 204 K) 6 δ = 2.17 (d, $J_{HH} = 10.7$ Hz, 1H, CH$_2$), 2.33–2.47 (12H, CH$_3$), 2.64 (d, $J_{HH} = 12.0$ Hz, 1H, CH$_2$), 2.82 (d, $J_{HH} = 10.2$ Hz, 1H, CH$_2$), 2.96 (d, $J_{HH} = 12.0$ Hz, 1H, CH$_2$), 3.12 (d, $J_{HH} = 10.7$ Hz, 1H, CH$_2$), 3.22 (d, $J_{HH} = 10.2$ Hz, 1H, CH$_2$), 3.45 (m, 2H, CH$_2$), 4.99 (s, 2H, H$_2$O), 5.69 (s, 2H, H$_2$O), 7.20–7.40 (m, 8H, H$_A$ of C$_6$H$_4$), 7.60–7.90 (m, 8H, H$_X$ of C$_6$H$_4$). 7 δ = 2.33–2.47 (12H, CH$_3$), 2.76 (d, $J_{HH}$...
= 10.2 Hz, 2H, CH$_2$), 2.98 (d, $J_{HH} = 10.2$ Hz, 2H, CH$_2$), 3.20–3.36 (m, 4H, CH$_2$), 5.31 (br, 4H, H$_2$O), 7.20–7.40 (m, 8H, H$_A$ of C$_6$H$_4$), 7.60–7.90 (m, 8H, H$_X$ of C$_6$H$_4$).

2.2. cis-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$(OH)$_2$] (3)

To a red suspension of 2 (150 mg, 0.34 mmol) in diethyl ether (20 mL) was added water (123 µL, 6.83 mmol). The mixture was stirred for 30 min, and the resulting white precipitate was filtered off, washed with diethyl ether (3 mL) and dried under vacuum. Yield: 90%. Analysis calculated for C$_{16}$H$_{22}$O$_6$PdS$_2$: C, 39.96; H, 4.61. Found: C, 39.93; H, 4.51.

2.3. trans-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$(OH)$_2$](PPh$_3$)] (9)

To a solution of 10 (114 mg, 0.12 mmol) in wet chloroform (20 mL) was added polymer 2 (52 mg, 0.12 mmol). After 30 min stirring the solution was vacuum evaporated. The residue was treated with diethyl ether (10 mL) to give a white solid, which was collected, washed with diethyl ether and dried under vacuum. Yield: 86% (8 + 9). Analysis calculated for C$_{34}$H$_{35}$O$_4$PPdS$_2$: C, 56.31; H, 4.86. Found: C, 55.91; H, 4.94. Pure 9 was isolated by crystallization of the white solid in chloroform-hexane. $^1$H NMR (400.14 MHz, CDCl$_3$, 293 K) $\delta = 1.96$ (d, $J_{HP} = 3.0$ Hz, 4H, CH$_2$), 2.35 (s, 6H, CH$_3$), 7.17 (m, 4H, H$_A$ of C$_6$H$_4$), 7.36–7.50 (m, 9H, Ph), 7.52 (m, 4H, H$_X$ of C$_6$H$_4$), 7.64 (m, 6H, Ph). $^1$H NMR (400.14 MHz, CDCl$_3$, 204 K) $\delta = 1.88$ (br, 4H, CH$_2$), 2.34 (s, 6H, CH$_3$), 6.95 (br, 2H, H$_2$O), 7.19 (m, 4H, H$_A$ of C$_6$H$_4$), 7.37–7.55 (m, 13H, Ph + H$_X$ of C$_6$H$_4$), 7.64 (m, 6H, Ph). $^{31}$P{$^1$H} NMR (161.98 MHz, CDCl$_3$, 204 K) $\delta = 42.00$ (s, 1P). $^{13}$C{$^1$H} NMR (100.62 MHz, CDCl$_3$, 293 K) $\delta = 21.4$, 44.4 (d, $J_{CP} = 7.8$ Hz), 126.3, 128.5 (d, $J_{CP} = 11.3$ Hz), 129.2, 129.8 (d, $J_{CP} = 56.3$ Hz), 131.0 (d, $J_{CP} = 2.6$ Hz), 134.5 (d, $J_{CP} = 11.3$ Hz), 142.2, 142.8.

2.4. trans-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$(NH$_3$)(PPh$_3$)] (11)

To a suspension of 9 (145 mg, 0.20 mmol) in diethyl ether (20 mL) was bubbled ammonia for 20 s. The mixture was stirred for 5 min, and the resulting white precipitate was filtered off, washed with diethyl ether (3 mL) and dried under vacuum. Yield: 90%. Analysis calculated for C$_{34}$H$_{36}$NO$_4$PPdS$_2$: C, 56.39; H, 5.01; N, 1.93. Found: C, 56.12;
H, 4.90; N, 1.88. $^1$H NMR (400.14 MHz, CDCl$_3$, 293 K) $\delta = 2.02$ (d, $J_{HP} = 4.4$ Hz, 4H, CH$_2$), 2.31 (s, 6H, CH$_3$), 3.68 (s, 3H, NH$_3$), 7.09 (m, 4H, H$_A$ of C$_6$H$_4$), 7.33 (m, 4H, H$_X$ of C$_6$H$_4$), 7.38–7.50 (m, 9H, Ph), 7.74 (m, 6H, Ph).

$^{13}$P { $^1$H} NMR (161.98 MHz, CDCl$_3$, 293 K) $\delta = 38.96$ (s, 1P).

$^{13}$C { $^1$H} NMR (100.62 MHz, CDCl$_3$, 293 K) $\delta = 21.3, 43.1$ (d, $J_{CP} = 8.1$ Hz), 125.8, 128.4 (d, $J_{CP} = 10.7$ Hz), 129.1, 130.5 (d, $J_{CP} = 51.0$ Hz), 130.6 (d, $J_{CP} = 2.4$ Hz), 134.9 (d, $J_{CP} = 11.4$ Hz), 141.6, 143.8.

2.5. cis-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$(NH$_3$)$_2$] (12)

To a red suspension of 2 (150 mg, 0.34 mmol) in diethyl ether (20 mL) was bubbled ammonia for 2 min. The mixture was stirred for 10 min, and the resulting white precipitate was filtered off, washed with diethyl ether (3 mL) and dried under vacuum. Yield: 90%. Analysis calculated for C$_{16}$H$_{24}$N$_2$O$_4$PdS$_2$: C, 40.13; H, 5.05; N, 5.85. Found: C, 40.25; H, 4.85; N, 5.87.

$^1$H NMR (400.14 MHz, CDCl$_3$, 293 K) $\delta = 2.38$ (s, 6H, CH$_3$), 2.60 (s, 4H, CH$_2$), 2.73 (s, 6H, NH$_3$), 7.23 (m, 4H, H$_A$ of C$_6$H$_4$), 7.73 (m, 4H, H$_X$ of C$_6$H$_4$).

$^{13}$C { $^1$H} NMR (100.62 MHz, CDCl$_3$, 293 K) $\delta = 21.4, 34.7, 126.2, 129.4, 142.2, 142.3.

2.6. cis-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$(NH$_3$)(PPh$_3$)] (13)

A mixture of 10 (116.3 mg, 0.12 mmol) and 12 (57.5 mg, 0.12 mmol) was dissolved in chloroform (20 mL). After 10 min stirring the solution was vacuum evaporated. The residue was treated with diethyl ether (10 mL) to give a white solid, which was collected, washed with diethyl ether and dried under vacuum. Yield: 87%. Analysis calculated for C$_{34}$H$_{36}$NO$_4$PPdS$_2$: C, 56.39; H, 5.01; N, 1.93. Found: C, 56.05; H, 4.89; N, 1.92.

$^1$H NMR (400.14 MHz, CDCl$_3$, 293 K) $\delta = 2.14$ (s, 3H, NH$_3$), 2.31 (s, 3H, CH$_3$), 2.40 (s, 3H, CH$_3$), 2.77 (d, $J_{HP} = 8.7$ Hz, 2H, CH$_2$), 3.15 (d, $J_{HP} = 7.9$ Hz, 2H, CH$_2$), 7.04 (m, 2H, H$_A$ of C$_6$H$_4$), 7.16 (m, 2H, H$_X$ of C$_6$H$_4$), 7.26 (m, 2H, H$_A$ of C$_6$H$_4$), 7.42–7.54 (m, 9H, Ph), 7.76 (m, 6H, Ph), 7.82 (m, 2H, H$_X$ of C$_6$H$_4$).

$^{31}$P { $^1$H} NMR (161.98 MHz, CDCl$_3$, 293 K) $\delta = 25.32$ (s, 1P). $^{13}$C { $^1$H} NMR (100.62 MHz, CDCl$_3$, 293 K) $\delta = 21.3, 21.4, 36.9$ (d, $J_{CP} = 6.6$ Hz), 42.46 (d, $J_{CP} = 103.4$ Hz), 126.2, 126.3, 128.8, 129.0 (d, $J_{CP} = 9.8$ Hz), 129.3, 130.5 (d, $J_{CP} = 37.2$ Hz), 130.7 (d, $J_{CP} = 1.6$ Hz), 134.7 (d, $J_{CP} = 12.4$ Hz), 141.5, 141.8, 142.4, 143.6 (d, $J_{CP} = 5.2$ Hz).
2.7. \((\mu-N_2H_4)(\text{trans-}[\text{Pd}(\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{Me})_2(\text{PPh}_3)]_2) (14)\)

To a suspension of 9 (148 mg, 0.20 mmol) in diethyl ether (20 mL) was added hydrazine monohydrate (5.0 µL, 0.10 mmol). The mixture was stirred for 20 min, and the resulting white precipitate was filtered off, washed with diethyl ether (3 mL) and dried under vacuum. Yield: 81%. Analysis calculated for C\(_{68}\)H\(_{70}\)N\(_2\)O\(_8\)P\(_2\)Pd\(_2\)S\(_4\): C, 56.47; H, 4.88; N, 1.94. Found: C, 56.07; H, 4.78; N, 1.90. \(^1\)H NMR (400.14 MHz, CDCl\(_3\), 293 K) \(\delta = 2.31\) (s, 12H, CH\(_3\)), 2.36 (d, \(J_{HP} = 3.5\) Hz, 8H, CH\(_2\)), 7.04 (m, 8H, H\(_A\) of C\(_6\)H\(_4\)), 7.33–7.50 (m, 26H, Ph + H\(_X\) of C\(_6\)H\(_4\)), 7.65 (m, 12H, Ph), 7.81 (s, 4H, N\(_2\)H\(_4\)). \(^{31}\)P\(\{^1\)H\}\) NMR (161.98 MHz, CDCl\(_3\), 293 K) \(\delta = 38.97\) (s, 1P). \(^{13}\)C\(\{^1\)H\}\) NMR (125.67 MHz, CDCl\(_3\), 293 K) \(\delta = 21.4, 42.5\) (d, \(J_{CP} = 8.0\) Hz), 126.4, 128.4 (d, \(J_{CP} = 10.8\) Hz), 129.1, 130.0 (d, \(J_{CP} = 51.4\) Hz), 130.6, 134.9 (d, \(J_{CP} = 11.6\) Hz), 141.5, 143.2.
3. NMR figures

**Fig. S1:** $^1$H NMR and COSY (400.14 MHz, 204 K) of [Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$]$_n$ (2) in wet CDCl$_3$. 
Fig. S2: $^1$H NMR (400.14 MHz, 204 K), $^{31}$P{$^1$H} NMR (161.98 MHz, 204 K) and $^{13}$C{$^1$H} NMR (100.62 MHz, 293 K) of trans-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$(OH$_2$)(PPh$_3$)] (9) in CDCl$_3$
Fig. S3: $^1$H NMR (400.14 MHz, 293 K), $^{31}$P$[^1$H$]$ NMR (161.98 MHz, 293 K) and $^{13}$C$[^1$H$]$ NMR (100.62 MHz, 293 K) of trans-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$(NH$_3$)(PPh$_3$)] (11) in CDCl$_3$. 
Fig. S4: $^1$H NMR (400.14 MHz, 293 K) and $^{13}$C{$^1$H} NMR (100.62 MHz, 293 K) of cis-[$\text{Pd(CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{Me})_2(\text{NH}_3)_2]$ (12) in CDCl$_3$. 

![NMR spectra image]
Fig. S5: $^1$H NMR (400.14 MHz, 293 K), $^{31}$P{$^1$H} NMR (161.98 MHz, 293 K) and $^{13}$C{$^1$H} NMR (100.62 MHz, 293 K) of cis-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$(NH$_3$)(PPh$_3$)] $^{13}$ (13) in CDCl$_3$
Fig. S6: $^1$H NMR (400.14 MHz, 293 K), $^{31}$P{$^1$H} NMR (161.98 MHz, 293 K) and $^{13}$C{$^1$H} NMR (125.67 MHz, 293 K) of (μ-N$_2$H$_4$(trans-[Pd(CH$_2$SO$_2$C$_6$H$_4$Me)$_2$(PPh$_3$)])$_2$) (14) in CDCl$_3$. 
4. X-ray structure determinations

Single crystals of 9 (slow diffusion of hexane into a chloroform solution), 10-2CHCl₃ (evaporation of a chloroform-cyclohexane solution), 11 (slow diffusion of hexane into a chloroform solution) and 14·3CH₂Cl₂ (evaporation of a dichloromethane-hexane solution) suitable for X-ray diffraction studies were obtained as indicated. Diffraction data were collected by using an Oxford Diffraction Supernova diffractometer, equipped with an Atlas CCD area detector and a four-circle kappa goniometer. For the data collection Mo microfocus source with multilayer optics were used at 298.15 and 150.00 K respectively. Using OLEX2,¹ the structure was solved with the SHELXT² structure solution program using direct methods and refined with the SHELXL³ refinement package using least squares minimization. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at idealized positions and refined by using the riding model. Crystal data and particular details are given in Table S1.

CCDC-1529832 (for 9), CCDC-1529833 (for 10-2CHCl₃), CCDC-1533563 (for 11) and CCDC-1533564 (14·3CH₂Cl₂) contain the supplementary crystallographic data for the structures reported in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
### Table S1. Crystal data and structure refinement for 9, 10·2CHCl₃, 11 and 14·3CH₂Cl₂

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<tr>
<td><strong>Index ranges</strong></td>
<td>-14 ≤ h ≤ 14, -13 ≤ k ≤ 16, -17 ≤ l ≤ 16</td>
<td>-19 ≤ h ≤ 14, -25 ≤ k ≤ 25, -18 ≤ l ≤ 27</td>
<td>-13 ≤ h ≤ 14, -13 ≤ k ≤ 16, -18 ≤ l ≤ 16</td>
<td>-19 ≤ h ≤ 19, -24 ≤ k ≤ 24, -20 ≤ l ≤ 14</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>13251</td>
<td>22914</td>
<td>14204</td>
<td>20462</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.055</td>
<td>1.059</td>
<td>1.031</td>
<td>1.060</td>
</tr>
<tr>
<td><strong>Final R indexes [I&gt;=2σ (I)]</strong></td>
<td>R₁ = 0.0401, wR₂ = 0.0699</td>
<td>R₁ = 0.1018, wR₂ = 0.2286</td>
<td>R₁ = 0.0449, wR₂ = 0.0772</td>
<td>R₁ = 0.0361, wR₂ = 0.0709</td>
</tr>
<tr>
<td><strong>Final R indexes [all data]</strong></td>
<td>R₁ = 0.0623, wR₂ = 0.0799</td>
<td>R₁ = 0.01596, wR₂ = 0.2675</td>
<td>R₁ = 0.0763, wR₂ = 0.0898</td>
<td>R₁ = 0.0514, wR₂ = 0.0795</td>
</tr>
<tr>
<td><strong>Largest diff. peak/hole / e Å⁻³</strong></td>
<td>0.45/-0.46</td>
<td>1.71/-1.36</td>
<td>0.47/-0.46</td>
<td>1.71/-1.06</td>
</tr>
</tbody>
</table>

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