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Synthesis and characterization of *cis*-bis[(*p*-tolylsulfonyl)methyl]palladium(II) complexes

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Abstract

$(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ ($R \equiv p\text{-}CH_3C_6H_4SO_2CH_2$) (**1**) has been prepared by reaction of LiR with $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br_4]$. Treatment of **1** with $AgClO_4$ in MeCN leads to the formation of $[PdR_2(NCMe)_2]$ (**2**). Complexes **1** and **2** are sources of complexes containing the *cis*-PdR_2 moiety *via* (a) bridge splitting reactions; (b) bridge splitting and Br^- displacement; (c) MeCN displacement; or (d) metathesis with Tl(acac). A variety of anionic and neutral palladium complexes: $(NBu_4)[PdBrR_2L]$ ($L \equiv CN^tBu$, $PMePh_2$, PPh_3 or 4-Mepy); $(NBu_4)_2[PdR_2(CN)_2]$; $(NBu_4)[PdR_2(acac)]$; $(NBu_4)_2[Pd_2Br_2R_4(\mu\text{-dppm})]$; and $[PdR_2L_2]$ ($L \equiv$ NCMe, CN^tBu, $PMePh_2$, PPh_3 or 4-Mepy; $L_2 \equiv$ 1,5-COD, bipy, 4,4′-Me_2bipy, dppe or dppm) has been obtained and characterized. NMR studies reveal equilibria between some of these species, and some steric hindrance to the rotation of the bulky R groups.

1. Introduction

A number of (arylsulfonyl)alkyl metal complexes have been described in the last few years (metal = Ni [1] or W [2]). The Ni complexes were studied in order to throw some light on the mechanism of the various reactions of α-sulfonyl carbanions promoted by transition metal salts [3,4]. Previously two palladium complexes with the ligand (phenylsulfonyl)methyl had been synthesized and characterized [5], and reported to be significantly stable.

In the course of our work we became interested in stable systems containing Pd-C(sp^3) bonds and the precedents cited above directed our attention to the (arylsulfonyl)methyl system. Rather than preparing particular complexes we decided to approach the synthesis of general stable precursors from which specific complexes could be easily obtainable, a goal successfully developed for C_6X_5 (X ≡ F or Cl) [6] and, more recently, Me [7,8] derivatives. In order to obtain more informative ^1H NMR spectra, we chose the *p*-$CH_3C_6H_4SO_2CH_2$ group.

In this paper we report the development of a general synthetic route to complexes containing the moiety *cis*-PdR_2 ($R \equiv p\text{-}CH_3C_6H_4SO_2CH_2$) that prove to be among the most stable Pd–C(sp^3) systems prepared.

2. Results and discussion

2.1. Synthesis of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ and $[PdR_2(NCMe)_2]$

Treatment of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br_4]$ with LiR ($R \equiv p\text{-}CH_3C_6H_4SO_2CH_2$) (molar ratio 1:5) in tetrahydrofuran affords the yellow air-stable complex $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (**1**) in reasonable yield (75%). This compound behaves as a 2:1 electrolyte in acetone solution and gives satisfactory elemental analyses. Treatment of **1** with $AgClO_4$ (molar ratio 1:2) in NCMe produces $[PdR_2(NCMe)_2]$ (**2**) together with AgBr and $(NBu_4)ClO_4$. AgBr can be easily eliminated by filtration, but the difficulties met in the separation of **2** from $(NBu_4)ClO_4$ (see Experimental section (3)) lower the yield in **2** to 65%.

The reactions of these complexes with several monodentate and bidentate donors are summarized in Scheme 1.

2.2. Reactions with bidentate donors

When strongly coordinating neutral chelating ligands are used, the monomeric complex $[PdR_2(L\text{–}L)]$ (**3–5**) (L–L ≡ 2,2′-bipyridine, bipy, **3**, 4,4′-dimethyl-

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2,2′-bipyridine, Me_2bipy, **4**, or 1,2-bis(diphenylphosphino)-ethane, dppe, **5**) is produced from either **1** or **2**, regardless of the solvent and the L–L:Pd ratio used. Thus, if an L–L:Pd ratio of 1:2 is used, half of the starting material is recovered unchanged and the ligand does not coordinate as exobidentate. Moreover, the presence of Br^- in solution does not lead to the formation of $(NBu_4)_2[PdBr_2R_2]$ and the dinuclear complex **1** is formed upon crystallization even in the presence of an excess of $(NBu_4)Br$.

The anionic dimer is therefore the most convenient precursor for $[PdR_2(L–L)]$ complexes with strong ligands. The advantages of $[PdR_2(NCMe)_2]$ (**2**) become apparent when less strongly coordinating ligands are used. Thus on reaction with 1,5-cyclooctadiene (COD), **2** is converted into $[PdR_2(COD)]$ (**6**) in high yield, whereas with **1** as starting material an equilibrium is established ($K_{(1)} = 4.7\ (\pm 0.5) \times 10^{-4}$ mol L^{-1} by ^1H NMR spectroscopy).

$$(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4] + 2COD \rightleftharpoons 2[PdR_2(COD)] + 2(NBu_4)Br \quad (1)$$

The reaction of **2** and bis(diphenylphosphino)-methane (dppm) yields $[PdR_2(dppm)]$ (**7**) regardless of the solvent and the dppm:Pd ratio used. However when **1** is treated with dppm (dppm:Pd = 1:2) in acetone $(NBu_4)_2[Pd_2Br_2R_4(\mu\text{-dppm})]$ (**8**) is formed. Subsequent addition of dppm to make an overall dppm:Pd ratio of 1:1 leads to the formation of $[PdR_2(dppm)]$ (**7**). In $CHCl_3$ the reaction follows the same path but **8** is always contaminated with some unreacted binuclear complex and some $[PdR_2(dppm)]$ (**7**).

Complex **1** also reacts with Tl(acac) in dichloromethane to give $(NBu_4)[PdR_2(acac)]$ (**9**), in which the acetylacetonate acts as a chelating ligand.

TABLE 1. Yields, conductivities, microanalytical and IR spectral data

Complex	Yield (%)	Microanalyses [a]			IR (cm^{-1}) [b] or Λ_M ($ohm^{-1}\ cm^2\ mol^{-1}$) [c]
		C	H	N	
1 $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$	75	49.89 (50.10)	7.01 (7.09)	1.75 (1.83)	$\Lambda_M = 153$
2 *cis*-$[PdR_2(NCMe)_2]$	65	44.85 (45.59)	4.58 (4.59)	4.89 (5.32)	NCMe 2288, 2316
3 $[PdR_2(bipy)]$	95	52.01 (51.96)	4.30 (4.36)	4.56 (4.66)	
4 $[PdR_2(Me_2bipy)]$	80	53.29 (53.46)	5.11 (4.80)	4.44 (4.45)	
5 $[PdR_2(dppe)]$	75	59.29 (59.82)	5.25 (5.02)		
6 $[PdR_2(COD)]$	85	52.00 (52.12)	5.59 (5.47)		
7 $[PdR_2(dppm)]$	75	59.00 (59.39)	4.77 (4.86)		
8 *cis,cis*-$(NBu_4)_2[Pd_2Br_2R_4(\mu\text{-dppm})]$	90	55.56 (55.71)	7.16 (6.83)	1.48 (1.46)	$\Lambda_M = 223$
9 $(NBu_4)[PdR_2(acac)]$	70	56.14 (56.51)	7.95 (7.82)	1.65 (1.78)	$\Lambda_M = 125$
10 *cis*-$[PdR_2(CN^tBu)_2]$	75	51.01 (51.10)	6.10 (5.94)	4.37 (4.58)	CN^tBu 2200, 2217
11 *cis*-$[PdR_2(PMePh_2)_2]$	80	59.35 (59.68)	5.33 (5.25)		
12 *cis*-$[PdR_2(PPh_3)_2]$	78	64.18 (64.43)	5.03 (4.99)		
13 *cis*-$[PdR_2(4\text{-}Mepy)_2]$	86	52.67 (53.29)	5.06 (5.11)	4.23 (4.44)	
16 *cis*-$(NBu_4)[PdBrR_2(PPh_3)] \cdot Me_2CO$	90	58.82 (58.53)	7.14 (6.95)	1.23 (1.29)	$\Lambda_M = 103$
18 *cis*-$(NBu_4)_2[PdR_2(CN)_2]$	83	60.88 (61.17)	9.08 (9.24)	5.47 (5.71)	CN^-, 2104, 2113 $\Lambda_M = 180$

[a] Calculated figures in parentheses.
[b] Nujol mull.
[c] In 5×10^{-4} M acetone solutions.

2.3. Reactions with monodentate ligands

Neutral monodentate ligands L (L ≡ CN^{t}Bu, $PMePh_2$, PPh_3 or 4-Mepy) easily displace acetonitrile from **2** (L:Pd = 2:1) to give the corresponding neutral mononuclear compounds $[PdR_2L_2]$ (**10–13**) in high yield.

$$1/2(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4] + L \rightleftharpoons (NBu_4)[PdBrR_2L] \quad (2)$$

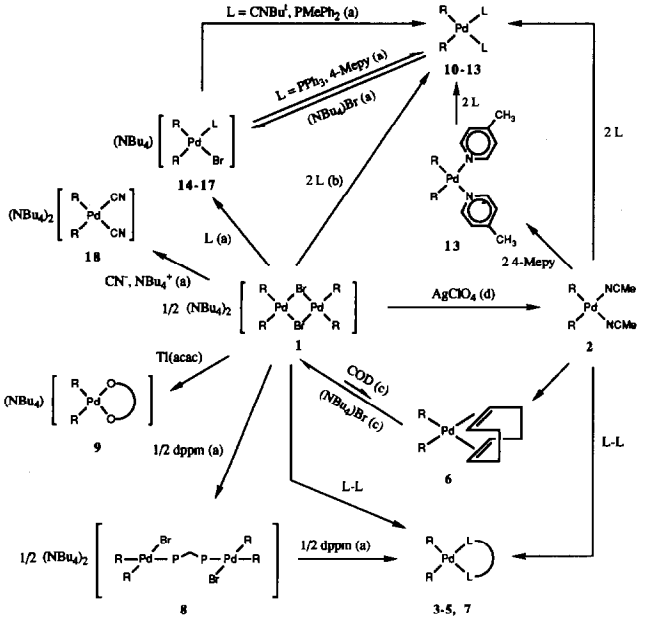
$$(NBu_4)[PdBrR_2L] + L \rightleftharpoons [PdR_2L_2] + (NBu_4)Br \quad (3)$$

The reactions starting with the anionic dimer $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (**1**) seem more complicated. The addition of L should proceed with bridge splitting of the dimer (eqn. (2)) and eventual Br^- displacement (eqn. (3)), and these equilibria can be strongly influenced by solvation and solubility effects. ^1H and $^{31}P\{^1H\}$ NMR spectroscopy show that the reactions in L:Pd ratio of 1:1 in acetone mainly produce $(NBu_4)[PdBrR_2L]$ (**14–17**), along with very small amounts of starting material and $[PdR_2L_2]$. Hence equilibrium (2) is strongly displaced to the right. Notwithstanding, a pure solid could be obtained only for $(NBu_4)[PdBrR_2(PPh_3)]$ (**16**), which crystallizes with a molecule of acetone. Addition of a second mole of L (overall L:Pd ratio of 2:1) does not drive equilibrium (3) completely to the right with L = 4-Mepy or PPh_3; in these two cases significant concentrations of both $(NBu_4)[PdBrR_2L]$ and $[PdR_2L_2]$ are detected in the spectra. However, pure $[PdR_2L_2]$ (**10–13**) complexes are isolated in high yield if the reaction is carried out in ethanol. Complexes **12** and **13**, when dissolved in acetone in the presence of $(NBu_4)Br$, re-establish equi-

TABLE 2. NMR data for $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (**1**) and its derivatives [a]

Complex	p-$CH_3C_6H_4SO_2CH_2$(^{1}H NMR)				Ligand (^{1}H NMR)	Ligand (^{31}P NMR)
	CH_3	CH_2	$H_A(C_6H_4)$ [b]	$H_B(C_6H_4)$ [b]		
1 [c]	2.36s	3.23s	7.18d	7.76d		
2	2.38s	2.93s	7.25d	7.79d	Me: 2.18s	
3	2.44s	3.18s	7.31d [d,e]	7.90d [e]	H_3: 8.24d; H_4: 7.94 m[e]; H_5: 7.43m [d]; H_6: 8.65d ($J(H_5\text{–}H_6)$ = 4.5; $J(H_3\text{–}H_4)$ = 7.5)	
4	2.43s	3.10s	7.29d	7.88d	Me: 2.43s; H_3: 8.03s; H_5: 7.19 [d]; H_6: 8.49d ($J(H_5\text{–}H_6)$ = 5.5)	
5	2.31s	3.40m [f]	7.07d	$H_b + H_{Ph}$:	7.35–7.95; CH_2: 1.80–2.70	48.6s
6	2.41s	3.39s	7.28d	7.80d	CH: 6.13br; CH_2: 2.64br	
7	2.34s	3.18m [f]	7.13d	$H_B + H_{Ph}$:	7.26–7.85; CH_2: 4.01t [8.5]	−27.0s
8 [g]	2.28s 2.39s	2.80m 2.96m	$H_A + H_B + H_{Ph}$:		6.90–8.00; CH_2: 4.01t [9]	17.7s
9 [g]	2.34s	3.04s	7.15d	7.89d	H(acac): 5.0s; Me(acac): 1.68s	
10	2.38s	2.80s	7.22d	7.76d	^{t}Bu: 1.58s	
11	2.33s	3.14s	7.11d	$H_B + H_{Ph}$:	7.20–7.60; Me: 1.76d [N = 7.5] [h]	7.2s
12	2.29s	3.49br	$H_A + H_B + H_{Ph}$:		6.90–7.90	25.7s
13	2.35s [i]	3.01s	7.20d	7.75d	Me: 2.32s [i], $H_{2,6}$: 8.70m; $H_{3,5}$: 7.10m	
14 [j,k]	2.34s 2.37s	2.89s 3.40s	7.21d 7.29d	7.72d 7.82d	^{t}Bu: 1.48s	
15 [j,k]	2.30s 2.40s	3.04d [9] 3.55d [9]	$H_A + H_B + H_{Ph}$:		7.00–7.90; Me: 2.10d [8]	8.8s
16 [j,k]	2.29s 2.39s	3.13d [9] 3.80d [9]	$H_A + H_B + H_{Ph}$:		7.00–7.90; Me_2CO: 2.08s	23.7s
17 [j,k]	2.34s 2.34s	3.08s 3.44s	7.22d 7.22d	7.73d 7.87d	Me: 2.34s: $H_{2,6}$: 8.76m; $H_{3,5}$: 7.12m	
18 [g]	2.35s	3.03s	7.16d	7.81d		

[a] $CDCl_3$ solutions, unless otherwise indicated; J(H–H)/Hz values are in parentheses and J(P–H)/Hz in square brackets.
[b] $(AB)_2$ spin system with $J(H_A\text{–}H_B)$ = 8 Hz unless otherwise indicated.
[c] NBu_4^+: 3.40–3.80 (N–CH_2), 1.20–2.20 (CH_2CH_2), 0.80–1.10 (CH_3).
[d] Signals partially overlap with solvent peak.
[e] Partially overlapped signals.
[f] $X_2AA'X_2'$ spin system.
[g] NBu_4^+: 3.10–3.50 (N–CH_2), 1.10–2.00 (CH_2CH_2), 0.80–1.10 (CH_3).
[h] $X_3AA'X_3'$ spin system, $N = J(A\text{–}X) + J(A\text{–}X')$.
[i] Assignments supported by NOE experiments.
[j] NBu_4^+: 3.25–3.60 (N–CH_2), 1.10–1.95 (CH_2CH_2), 0.75–1.05 (CH_3).
[k] In $(CD_3)_2CO$.



Scheme 1. (a) Acetone; (b) ethanol; (c) chloroform; (d) acetonitrile. L ≡ CN^tBu, $PMePh_2$, PPh_3 or 4-Mepy; L–L ≡ bipy, Me_2bipy, dppe or dppm.

librium (3). The equilibrium constant was estimated for **16** by $^{31}P\{^1H\}$ NMR spectroscopy ($K_{(3)} = 0.63 \pm 0.03$). ^{31}P or ^1H NMR spectra in $CDCl_3$ show that in this solvent equilibrium (3) is completely displaced to the right even for 4-Mepy or PPh_3, thus showing the influence of the solvent on these reactions.

Finally, treatment of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (**1**) with $(NBu_4)Br$ and an excess of KCN in acetone gives $(NBu_4)_2[PdR_2(CN)_2]$ (**18**).

2.4. Characterization and structure of the complexes

Elemental analyses, IR spectral data and conductivities are listed in Table 1, and ^1H and $^{31}P\{^1H\}$ NMR data are summarized in Table 2. All the IR spectra of the (*p*-tolylsulfonyl)methyl derivatives show very strong absorptions due to the symmetric and antisymmetric stretching modes of the SO_2 group [9] at *ca.* 1280 and 1130 cm^{-1}. A medium intensity absorption at *ca.* 880 cm^{-1} is also observed when NBu_4^+ is present.

The $CH_3C_6H_4SO_2CH_2$ moieties give rise in the ^1H NMR spectra to singlets for the CH_2 and CH_3 groups in the R ligand when no phosphorus donors are present; their aromatic protons exhibit the expected pattern for a *p*-tolyl group (AA'BB' spin system, observed as an AB pattern). Resonances due to the ligands and to the NBu_4^+ group (if present) are also detected in the spectra, with the appropriate intensities. A *cis* geometry is assigned to all the $[PdR_2LL']^{n-}$ ($n = 0$, 1 or 2) complexes as discussed below.

The ^1H NMR spectrum of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (**1**) (Table 2) is as expected for a symmetric structure where the four R groups are equivalent, and their *cis* arrangement is obviously a necessity from their dinuclear structure. The *cis* arrangement is also imposed in the case of chelating ligands (complexes **3–6** and **9**). For complex **7** the chemical shifts correspond to dppm acting as a chelating ligand [10], from which a *cis* arrangement necessarily follows.

The two inequivalent R groups in $[PdBrR_2L]^-$ (**14–17**) and in $[Pd_2Br_2R_4(\mu\text{-dppm})]^{2-}$ (**8**) give rise to two sets of signals in their ^1H NMR spectra; this supports a *cis* geometry for these anionic complexes. Consistent with previous reports [8], the downfield CH_2 signal is assigned to the group *cis* to the halide. A curious feature of complexes **15** and **16** is that $^3J(^{31}P\text{–}^1H)$ for each inequivalent CH_2 groups is the same (9 Hz), even when the phosphine is *cis* to one of the R groups and *trans* to the other; a HETCOR NMR ($^1H\text{–}^{13}C$) experiment on **15** revealed that $^2J(^{13}C\text{–}^{31}P)$ values are, however, very different (119.3 and 5.2 Hz) and support the assignment of the downfield doublet (showing the bigger $^{13}C\text{–}^{31}P$ coupling) to the methylene *trans* to the phosphine. It is also worth noting (Fig. 1) that the heights of the two CH_2 signals for **16** at room temperature are similar at 80 MHz but very different at 300 MHz, the one assigned to the group *cis* to the phosphine being smaller. This broadening suggests that there is a hindered rotation of R around the Pd–R bond that affects the R group closer to the bulkier phosphine more severely; the two hydrogens of the corresponding methylene group are approaching coalescence at room temperature at 300 MHz, and should become diastereotopic at lower temperatures. This phenomenon was further studied for *cis*-$[PdR_2(PR'_3)_2]$ (see below).

Proving a *cis* or *trans* geometry for the complexes $[PdR_2L_2]^{n-}$ ($n = 0$ or 2; L = monodentate ligand) is more difficult since in both geometries the two R groups are chemically equivalent and this reduces the value of NMR information. The *cis* geometry of $[PdR_2(NCMe)_2]$ (**2**), $[PdR_2(CN^tBu)_2]$ (**10**), and $(NBu_4)_2[Pd_2R_2(CN)_2]$ (**18**) can be assigned on the basis of their IR spectra which show two bands in the ν(CN) region (C_{2v}, $A_1 + B_2$). However, the IR spectrum in the ν(CN) region of $[PdR_2(NCMe)_2]$ (**2**) is similar to that of free NCMe (2254 cm^{-1}, ν(CN); 2290 cm^{-1}, $\delta(CH_3) + \nu(C\text{–}C)$) [11], showing two absorptions at 2316 and 2288 cm^{-1}; in other words, one might also expect two bands for a *trans* complex (and four for a *cis* complex) and the IR evidence for **2** is not conclusive, although the fact that **2** is precursor of a wide range of complexes containing the moiety *cis*-PdR_2 favours a *cis* geometry.

The *cis* geometry of $[PdR_2(PMePh_2)_2]$ (**11**) is based on its ^1H NMR spectrum, which shows a virtually coupled doublet centred at 1.76 ppm (X part of an $X_3AA'X'_3$ spin system with $N = J(A-X) + J(A-X') =$ 7.5 Hz) in the methyl phosphine region, characteristic of bis(phosphine) complexes where the $^2J(P-P')$ is small [12].

The geometry of square-planar complexes containing two PPh_3 ligands is usually based on the observation (*cis*) or absence (*trans*) of an IR absorption in *ca.* 550 cm^{-1} [13]. However, the presence of a strong absorption at 548 cm^{-1} due to the R groups in $[PdR_2(PPh_3)_2]$ (**12**) precludes the use of this criterion. A proof of the *cis* geometry of **12** comes from its low-temperature ^1H spectrum. As we commented for **16**, a noteworthy feature of the ambient-temperature ^1H NMR spectra of $[PdR_2L_2]$ (L = $PMePh_2$, **11**; PPh_3, **12**) in $CDCl_3$ at 80 MHz is the broad CH_2 resonances, so pronounced in **12** that they can hardly be detected (Fig. 2). This broadening is greater than is expected for the X part of an $X_2AA'X'_2$ spectrum. When the temperature is reduced these resonances split into two new broad resonances (Fig. 3), which are assigned to diastereotopic hydrogen atoms on the CH_2 groups, as confirmed by shift correlation COSY experiments. Restriction of rotation will produce diastereotopic geminal hydrogens only in the *cis* isomer, thus providing a proof of structure assignment in **11** and **12**. The resonance shown by the CH_2 group in **11** (L = $PMePh_2$) coalesces at a lower temperature than that of **12** (L = PPh_3), as expected for a bulkier ligand such as PPh_3 compared to $PMePh_2$. The calculated activation energies for rotation are 11.9 and 13.1 kcal mol^{-1} respectively, according to the Eyring equation [14]. Neither **10** (L ≡ CN^tBu) nor **13** (L = 4-Mepy) with smaller ligands showed temperature-dependence in their spectra.

Finally, unequivocal assignment of the geometry of **13** cannot be made from the IR or NMR spectra. However, since it reacts with L (L = CN^tBu, $PMePh_2$ or PPh_3) to give the corresponding derivatives *cis*-$[PdR_2L_2]$ it seems reasonable also to assign it a *cis* structure.

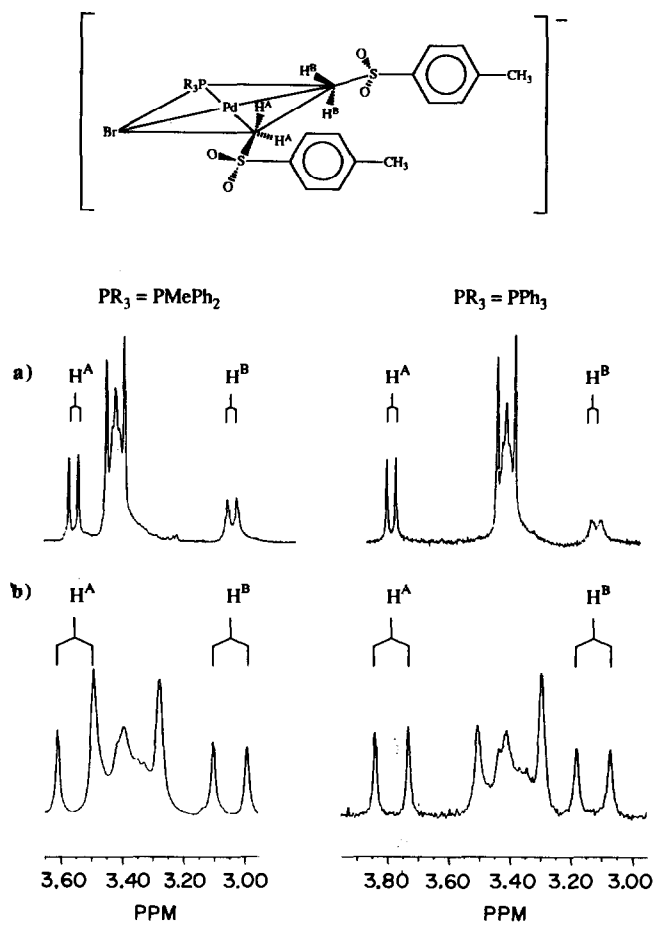


Fig. 1. ^1H NMR spectra ($(CD_3)_2CO$, 300 K) of *cis*-(NBu_4)-$[PdBrR(PR_3)_2]$ (PR_3 = $PMePh_2$ or PPh_3) in the CH_2SO_2 region at (a) 299.95 MHz and (b) 80.13 MHz.

3. Experimental details

Carbon, hydrogen and nitrogen analyses were carried out on a Perkin-Elmer 240 microanalyser. Conductivities were measured with a Crison 522 conductimeter. IR spectra were recorded (in the range 4000–200 cm^{-1}) on a Perkin-Elmer 833 spectrophotometer using Nujol mulls between polyethylene sheets; ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-80 or a Varian UNITY 300 instrument. Chemical shifts are in δ, parts per million (ppm) downfield referred to Me_4Si for ^1H, and to H_3PO_4 (85%, external) for ^{31}P.

Literature methods were used to prepare $(NBu_4)_2$-$[Pd_2(\mu\text{-}Br)_2Br_4]$ [15] and $p\text{-}CH_3C_6H_4SO_2CH_3$ [16].

3.1. Preparation of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (1)

n-Butyllithium (7.7 ml of 1.6 M solution in hexane, 12.32 mmol) was added dropwise to a stirred solution of $p\text{-}CH_3C_6H_4SO_2CH_3$ (RH) (2.1 g, 12.34 mmol) in dry THF (70 ml) at −78°C under dinitrogen. The mixture was allowed to warm to room temperature and stirred for a further 3 h. The suspension formed was cooled to −40°C and $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br_4]$ (2.9 g, 2.46 mmol) was added. The mixture was allowed to warm to room temperature then stirred for 30 min, during which time the suspended solid gradually dissolved to give a red-brown solution. After removal of any remaining carbanion by treatment with 0.5 ml of water, the solution was dried under vacuum and the

residue was extracted with dichloromethane (3 × 20 ml). The filtrates were combined and the resulting solution was dried over magnesium sulphate, filtered and evaporated to dryness. The oily residue was stirred with isopropanol (20 ml) to give a yellow solid, which was recrystallized from dichloromethane–diethyl ether, at a yield of 75%.

3.2. Preparation of cis-[$PdR_2(NCMe)_2$] (2)

To a solution of $AgClO_4$ (0.135 g, 0.65 mmol) in NCMe (10 ml) was added $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (0.5 g, 0.325 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. The oily residue was redissolved in ethanol (2 ml); on addition of diethyl ether (30 ml) a white solid, mainly $(NBu_4)ClO_4$, precipitated. The solid was removed by filtration and the solution evaporated to dryness. Addition of diethyl ether (30 ml) and NCMe (1 ml) to the residue and stirring gave **2** in 65% yield as a white solid which was collected, washed with diethyl ether and dried under vacuum. The purification process must be repeated if **2** is still contaminated with $(NBu_4)ClO_4$.

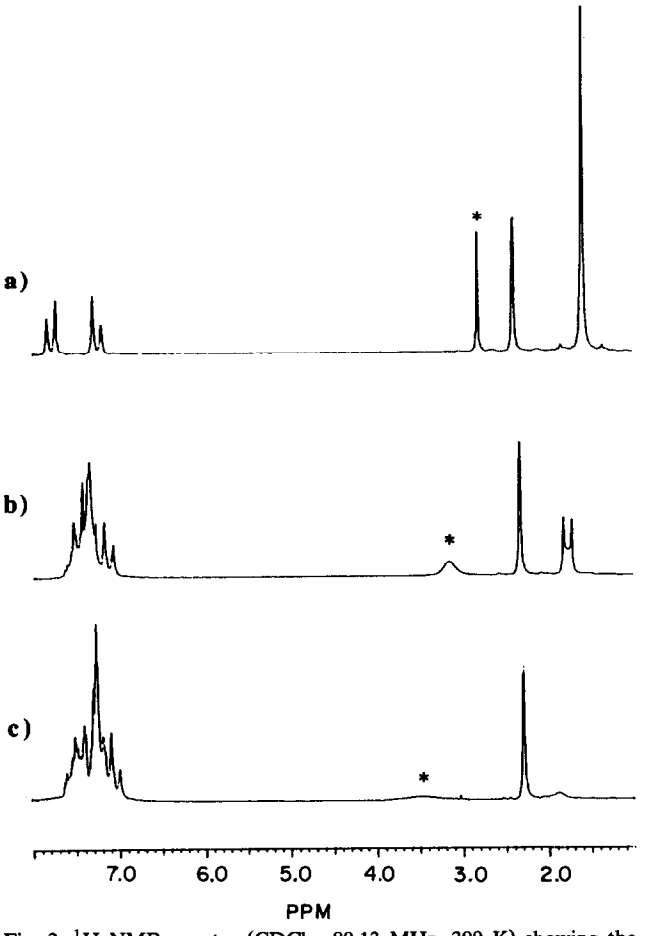


Fig. 2. ^1H NMR spectra ($CDCl_3$, 80.13 MHz, 300 K) showing the different broadening of the CH_2 resonances (*) for: (b) *cis*-$[PdR_2(PMePh_2)_2]$; and (c) *cis*-$[PdR_2(PPh_3)_2]$. The spectrum of *cis*-$[PdR_2(CN^tBu)_2]$ (a) is given for comparison.

3.3. Preparation of $(NBu_4)_2[Pd_2Br_2R_4(\mu\text{-dppm})]$ (8)

Addition of dppm (0.051 g, 0.13 mmol) to a suspension of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (0.2 g, 0.13 mmol) in acetone (30 ml) instantaneously gave a pale yellow solution which was filtered through kieselguhr, and the solvent was evaporated under vacuum. The oily residue was stirred with cold diethyl ether (10 ml) to give a white solid in 90% yield.

3.4. Preparation of $(NBu_4)[PdR_2(acac)]$ (9)

A mixture of Tl(acac) (0.122 g, 0.40 mmol) and $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (0.308 g, 0.20 mmol) in dichloromethane (30 ml) was stirred for 1 h. The insoluble TlBr was filtered off and the resulting solution was evaporated to dryness. The oily residue was triturated with hexane (10 ml) to give a white solid, which was recrystallized from ethanol–diethyl ether, in yield of 70%.

3.5. Preparation of $[PdR_2L_2]$

3.5.1. From $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (1): $[PdR_2(4\text{-}Mepy)_2]$ (13)

To a yellow suspension of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (0.20 g, 0.13 mmol) in ethanol (15 ml) was added 4-Mepy (51 μl, 0.52 mmol). The mixture was stirred for 5 h, and the resulting white precipitate was filtered off, washed with ethanol (3 ml) and air-dried. The solid was recrystallized from dichloromethane–diethyl ether to give **13** in 86% yield.

3.5.2. From $[PdR_2(NCMe)_2]$ (2): $[PdR_2(COD)]$ (6)

To a solution of $[PdR_2(NCMe)_2]$ (0.16 g, 0.30 mmol) in chloroform (30 ml) was added COD (41 μl, 0.33 mmol). The solution was stirred for 10 min and then evaporated to dryness. The resulting solid was washed with hexane–diethyl ether (1:1; 10 ml), filtered and air-dried. Complex **6** was isolated in 85% yield.

3.5.3. From $[PdR_2(4\text{-}Mepy)_2]$ (13): $[PdR_2(PMePh_2)_2]$ (11)

To a solution of $[PdR_2(4\text{-}Mepy)_2]$ (0.10 g, 0.16 mmol) in acetone (40 ml) was added $PMePh_2$ (59 μl, 0.32 mmol). After 1 h stirring the solution was vacuum evaporated. The oily residue was stirred with cold diethyl ether (10 ml) to give a white solid, which was recrystallized from dichloromethane–diethyl ether in yield 80%.

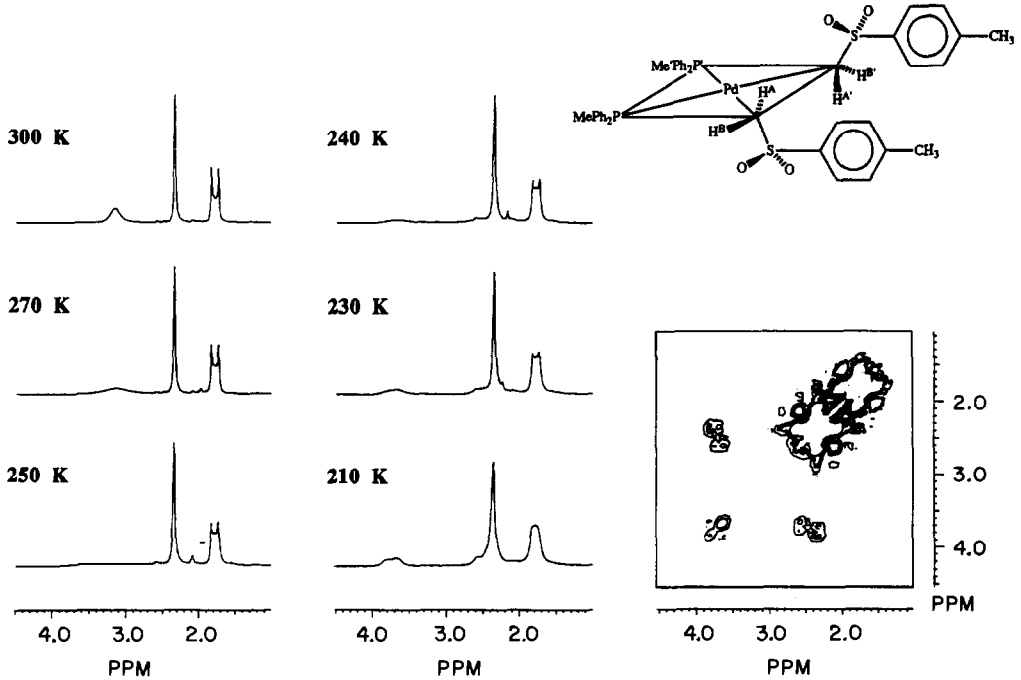


Fig. 3. Variable-temperature ^1H NMR spectra and two-dimensional COSY spectrum at 215 K ($CDCl_3$, 80.13 MHz) of *cis*-$[PdR_2(PMePh_2)_2]$.

3.6. Preparation of $(NBu_4)[PdBrR_2L]$: $(NBu_4)[PdBrR_2(PPh_3)] \cdot Me_2CO$ (16)

A solution of PPh_3 (0.106 g, 0.40 mmol) in acetone (10 ml) was added dropwise to a stirred suspension of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (0.31 g, 0.20 mmol) in the same solvent (20 ml). The mixture was stirred for 2 h, filtered and taken to dryness under vacuum. The oily residue was triturated with cold acetone (2 ml) whereupon a white solid precipitated. The solid was filtered off, washed with cold acetone (2 ml) and air-dried. Complex **16** crystallizes with a molecule of acetone and was isolated in 80% yield.

Complexes **14**, **15** and **17** were prepared similarly, but the addition of hexane was necessary to precipitate them. They were isolated in high yield but pure samples could not be obtained.

3.7. Preparation of $(NBu_4)_2[PdR_2(CN)_2]$ (18)

A mixture of KCN (0.034 g, 0.52 mmol), $(NBu_4)Br$ (0.084 g, 0.26 mmol) and $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (0.2 g, 0.13 mmol) in acetone (40 ml) was stirred for 1 h. The acetone was evaporated to dryness and water (20 ml) was added to the residue. The complex was extracted from the aqueous mixture with dichloromethane (40 ml). The organic layer was separated, dried with $MgSO_4$ and concentrated by evaporation to give a colourless oil, which was stirred with cold diethyl ether (10 ml) to give a white solid in 83% yield.

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