COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Diastereoselective formation of a dipalladium(I) complex supported by a bridging tetradentate ligand, and oxidative addition of RS–H across a phosphine-bridged Pd^I–Pd^I bond†

S. Jo Ling Foo, Nathan D. Jones, Brian O. Patrick and Brian R. James*

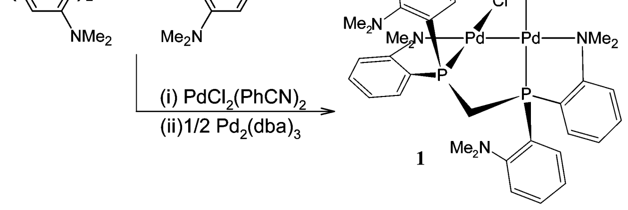
Department of Chemistry, University of British Columbia, Vancouver, B.C, Canada V6T 1Z1.
E-mail: brj@chem.ubc.ca; Fax: +1-604-822-2847; Tel: +1-604-822-6645

Received (in Cambridge, UK) 7th January 2003, Accepted 6th March 2003
First published as an Advance Article on the web 20th March 2003

The ligand $CH_2(P(o\text{-}C_6H_4NMe_2)_2)_2$ (dmapm) gives access to the first example of a dipalladium(I) complex supported by a tetradentate ligand, $Pd_2Cl_2(\mu\text{-}N,P,P,N\text{-dmapm})$, which, unlike the well-known $Pd_2X_2(\mu\text{-dppm})_2$ complexes (X = halide, dppm = bis(diphenylphosphino)methane), reacts with thiols to give addition of RS–H across a phosphine-bridged Pd–Pd bond.

The interactions of organosulfur compounds with transition metal complexes are important in the biological sulfur cycle, and in hydrodesulfurisation catalysis, and are relevant in the potential for H_2 recovery from H_2S.[1] In 1985, we reported the solution reaction of $Pd_2Cl_2(\mu\text{-dppm})_2$ with H_2S that quantitatively gives the “A-frame” bridged-sulfide complex, $Pd_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2$ and H_2.[2] As a continuation of our investigations into these types of reactions,[1–3] we now report the prototype of a new class of Pd^I_2 compounds based on the potentially P_2N_4-hexadentate, but in this instance functionally tetradentate ligand, dmapm,[4] *i.e.*, $Pd_2Cl_2(\mu\text{-}N,P,P,N\text{-dmapm})$ (**1**). Further, reaction of **1** with thiols provides the first example of oxidative addition of RS–H across a phosphine-bridged Pd^I–Pd^I bond.

The conproportionation reaction (Scheme 1) of $PdCl_2(PhCN)_2$, dmapm and $Pd_2(dba)_3$ gives **1** in 76 % isolated yield.[5] (We have also used dmapm in the synthesis of Pd^{II}_2 complexes that are effective catalyst precursors for a Heck reaction[6]). The molecular structure of **1** is shown in Fig. 1.[7] The dmapm ligand adopts a *P,P*-bridging-bis(*P,N*-chelating) coordination mode to give two interpenetrating Pd square planes mutually canted by an unusually large 59.9°. This “T-over-square” structural motif is best exemplified by the Pd^1_2 dimer $[Pd_2(NCMe)_6]^{2+}$, in which the dihedral angle between the planes is 90°,[8] but is significantly less for phosphine-bridged compounds, *e.g.* ~39° for $Pd_2X_2(dppm)_2$, X = Cl, Br.[9] The Pd–Pd bond length in **1** is 2.527(1) Å, the shortest observed for structurally characterised, neutral Pd^I_2 complexes: the shortest Pd^I–Pd^I bond ever observed is 2.500(1) Å found for $[Pd_2(o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3\text{-}o\text{-py})_2]^{2+}$, containing a a *P,O,N*-bridging tridentate ligand.[10] Another rare example of a structurally characterised Pd^I_2 complex supported by a *P,P,P*-bridging tridentate ligand is $[Pd_2(Ph_2PC_2H_4P(Ph)C_2H_4PPh_2)_2]^{2+}$ that has a Pd–Pd length of 2.617(1) Å.[11] To the best of our knowledge, **1** represents the first example of a Pd^I_2 complex supported by a tetradentate ligand, while examples of A-frame Pd^{II}_2 complexes supported by a monoanionic, *P,N,N,P*-tetradentate ligand have recently appeared.[12] In **1**, the Pd–N bonds are trans to, but are not collinear with, the Pd–Pd bond, being bent back (in *syn*-orientation) by ~15 °. In addition, one P–Pd–Pd angle (78.7 °) is smaller than the other (86.99 °), giving rise to unexpected asymmetry in the molecule. This tilting of the Pd–P bonds towards each other is indicative of compressive strain within the PCH_2P backbone of dmapm. Indeed, the “strain-free” P–C–P angle found for isolated dmapm (113.89 °)[4] is considerably larger than that found in **1** (102.85°).



Scheme 1 Synthesis of **1**.

The solution geometry of **1** can be inferred from its NMR spectra to be essentially the same as the solid state geometry. The $^{31}P\{^1H\}$ singlet (220–300 K) at δ −29.9 (from the crystal or bulk powder) indicates 2 chemically equivalent P-atoms, while the NCH_3 groups are manifest as 3 singlets in the ^1H spectrum at δ 3.07, 2.89, and 2.44, with relative integrations of 6 : 6 : 12, corresponding to two diastereotopic sets of methyl groups on the Pd-bound N-atoms, and one set of equivalent methyl groups of the free N-atoms.

The absolute configurations of the P-atoms shown in Fig. 1 are *R,R*. The centrosymmetric space group (*C*2/c) dictates that the *S,S*-diastereomer is also present in equal abundance, and thus **1** is isolated as a racemic mixture; the diastereomeric *meso*-form is absent. Addition of the chiral shift reagent tris(3-heptafluoropropylhydroxymethylene-*d*-camporato)praesodymium(III) gives rise to a $^{31}P\{^1H\}$ spectrum consisting of two closely separated singlets of equal intensity (δ_P −29.31 and −29.34), showing that the singlet observed in the absence of the shift reagent corresponds to a racemic mixture. In addition, a room temperature 2D ^1H EXSY experiment revealed no exchange of free and coordinated NCH_3 groups, showing that **1** is indeed formed diastereoselectively. These results are differ-

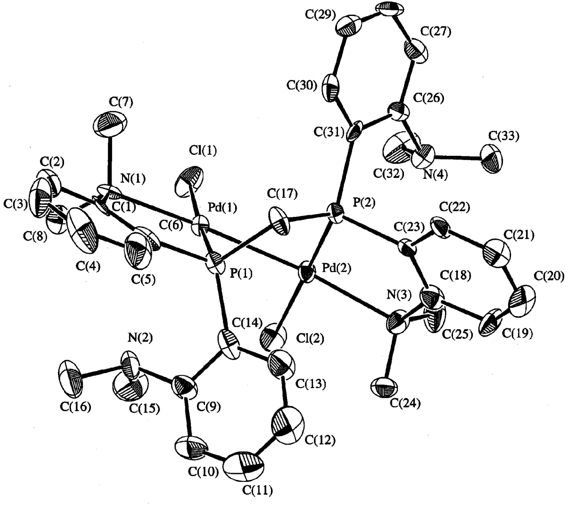
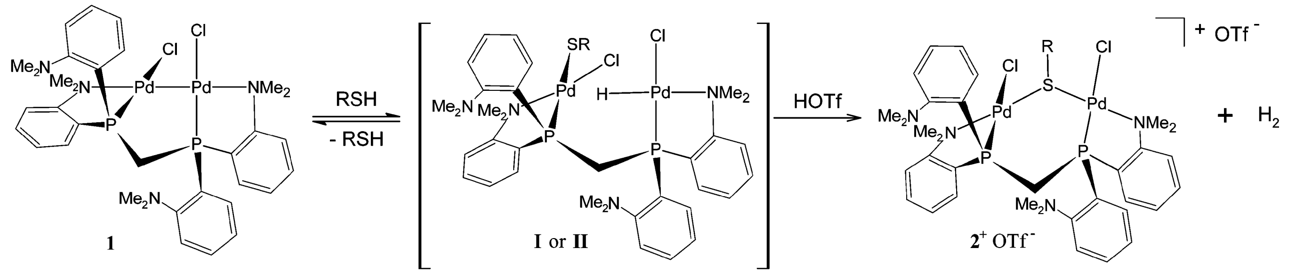


Fig. 1 ORTEP representation of the molecular structure of **1** (*R,R*-diastereomer).

---

† Electronic supplementary information (ESI) available: full synthetic methods and characterisation data for compound **1** and the **2a–2f** salts. See http://www.rsc.org/suppdata/cc/b3/b300177f/

DOI: 10.1039/b300177f



Scheme 2 Proposed mechanism for the reaction of **1** with thiols.

ent from those obtained previously by this group for the $Pd_2Cl_2(\mu\text{-PhPpy}_2)_2$; py = *o*-pyridyl) wherein exchange of free and coordinated N-atoms occurs.[13]

Whereas $PdCl_2(\mu\text{-dppm})_2$ does not react with thiols (RSH), *rac*-**1** reacts with excess RSH in CH_2Cl_2 to form, in 33 and 79% yield, the bridged-thiolate complexes *rac*-$[Pd_2Cl_2(\mu\text{-SR})(\mu\text{-}N,P,P,N\text{-dmapm})][Cl]$; R = Et ($\mathbf{2b}^+Cl^-$), ^{n}Pr ($\mathbf{2c}^+Cl^-$). In the presence of 1 equiv. of added triflic acid (HOTf), the reaction proceeds more reliably to give the corresponding triflate salts of the R = Me ($\mathbf{2a}^+$), Et ($\mathbf{2b}^+$), ^{n}Pr ($\mathbf{2c}^+$), ^{n}Bu ($\mathbf{2d}^+$), Bz ($\mathbf{2e}^+$) and Ph ($\mathbf{2f}^+$) cations in 40–70% yields. *In situ* NMR studies of these reactions revealed the formation of the expected H_2 co-product at δ_H 4.6 (Scheme 2; the H^+ source in the absence of HOTf must come from the RSH or adventitious HCl). The $\mathbf{2}^+$ cations all show a δ_P singlet in the 48–52 ppm region of the $^{31}P\{^1H\}$ spectrum. The molecular structure of the cation of $\mathbf{2c}^+Cl^-$ is shown in Fig. 2, where the Pd–Pd distance is now 3.974 Å.[14]

The reaction between *rac*-**1** and 10 equiv. of PhSH in the absence of added acid was followed by low-temperature NMR spectroscopy in CD_2Cl_2. After 20 min at 223 K, *rac*-**1** had been completely consumed, and the spectrum showed just a pair of doublets, indicative of 2 chemically inequivalent P-atoms, at δ_P 23.2 and 20.3 ($^2J_{PP}$ = 25.2 Hz). The corresponding ^1H NMR spectrum showed the appearance of a hydride doublet at δ_H −17.24 ($^2J_{HP}$ = 16.8 Hz); a $^1H\{^{31}P\}$ measurement confirmed coupling to P by the collapse of this doublet to a singlet. These data are consistent with, but do not uniquely identify, a hydrido-thiolato species such as $[Pd(H)Cl(\mu\text{-dmapm})Pd(SPh)Cl]^+$ (**I** in Scheme 2). At 193 K a second pair of doublets appears in addition to those corresponding to **I**: δ_P 4.0 and 23.0 ($^2J_{PP}$ = 49.6 Hz); a new hydride doublet also appeared at δ_H −9.56 ($^2J_{HP}$ = 15.9 Hz). These data are consistent with the formation of another hydrido-thiolato intermediate (**II**); **I** and **II** are possibly geometrical isomers. An analogous hydrido-mercapto intermediate has been observed in the reaction of H_2S and $Pd_2Br_2(\mu\text{-dppm})_2$,[1] with NMR data similar to those of **I** and **II**. No spectroscopic evidence was found for a putative RSH adduct, and no intermediates were observed in the low temperature reactions of **1** with MeSH, EtSH or ^{n}PrSH. **1** does react with H_2S in CH_2Cl_2 under ambient conditions; the major product generates a singlet at δ_P 48.6 and is probably the μ-S species, but there are side-products as evidenced by several broad δ_P signals in the 25–35 ppm region.

We believe that reaction of **1** with thiols represents the first observation of addition of RS–H across the Pd–Pd bond of a phosphine-bridged Pd^I_2 complex. In related Pd^I_2 reactions, in which a bridging Cp^{-15} or OH^{-16} ligand is ultimately protonated by a thiol and replaced by thiolate, the Pd–Pd bond remains intact in the product, and there was no evidence for hydrido-thiolato intermediates.

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support, and the University of British Columbia for a University Graduate Fellowship (NDJ).

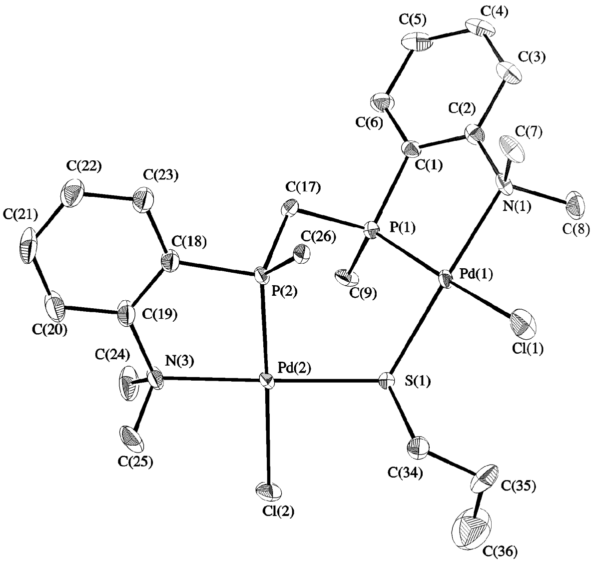


Fig. 2 ORTEP representation of the molecular structure of $\mathbf{2c}^+$ (*R,R*-diastereomer). All but the *ipso* C-atoms of the "dangling" anilinyl rings have been omitted for clarity.

Notes and references

1 B. R. James, *Pure Appl. Chem.*, 1997, **69**, 2213.
2 C.-L. Lee, G. Besenyei, B. R. James, D. A. Nelson and M. A. Lilga, *J. Chem. Soc., Chem. Commun.*, 1985, 1175.
3 T. Y. H. Wong, A. F. Barnabas, D. Sallin and B. R. James, *Inorg. Chem.*, 1995, **34**, 2278 and refs. therein.
4 N. D. Jones, P. H. Meessen, M. B. Smith, S. J. Rettig, B. O. Patrick, U. Losehand and B. R. James, *Can. J. Chem.*, 2002, **80**, 1600.
5 Full synthetic methods and characterisation data for compound **1** and the **2a**–**2f** salts are given in the ESI†.
6 N. D. Jones and B. R. James, *Adv. Synth. Catal.*, 2002, **344**, 1126.
7 Crystal data for **1**·2 $CHCl_3$: $C_{35}H_{44}Cl_8N_4P_2Pd_2$, M = 1079.12, monoclinic, a = 44.988(4), b = 9.984(2), c = 24.531(4) Å, β = 122.73(1)°, V = 9269(3) Å^3, T = 198 K, space group $C2/c$ (no. 15), Z = 8, μ(Mo-K$_\alpha$) = 1.335 mm^{-1}, 29756 reflections measured, 6419 unique (R_{int} = 0.109) which were used in all calculations. $wR2$ = 0.171, $R1$ = 0.060 ($I > 3\sigma(I)$). CCDC 200674. See http://www.rsc.org/suppdata/cc/b3/b300177f/ for crystallographic data in .cif or other electronic format.
8 D. J. Doonan, A. L. Balch, S. Z. Goldberg, R. Eisenberg and S. J. Miller, *J. Am. Chem. Soc.*, 1975, **97**, 1961.
9 G. Besenyei, L. Párkányi, E. Gáes-Baitz and B. R. James, *Inorg. Chim. Acta*, 2002, **327**, 179.
10 K. Tani, S. Nakamura, T. Yamagata and Y. Kataoka, *Inorg. Chem.*, 1993, **32**, 5398.
11 D. L. DuBois, A. Miedaner and R. C. Haltiwanger, *J. Am. Chem. Soc.*, 1991, **113**, 8753.
12 N. Tsukada, O. Tamura and Y. Inoue, *Organometallics*, 2002, **21**, 2521.
13 Y. Xie, C.-L. Lee, Y. Yang, S. J. Rettig and B. R. James, *Can. J. Chem.*, 1992, **70**, 751.
14 Crystal data for $\mathbf{2c}^+Cl^-\cdot H_2O$: $C_{36}H_{51}Cl_3N_4OP_2Pd_2S$, M = 968.99, monoclinic, a = 9.3678(3), b = 17.2299(5), c = 24.7803(9) Å, β = 91.755(2)°, V = 3997.8(2) Å^3, T = 173 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo–K$_\alpha$) = 1.267 mm $^{-1}$, 36546 reflections measured, 9192 unique (R_{int} = 0.048) which were used in all calculations. $wR2$ = 0.070, $R1$ = 0.030 ($I > 2\sigma(I)$). CCDC 200675.
15 H. Werner, H.-J. Kraus and Peter. Thometzek, *Chem. Ber.*, 1982, **115**, 2914.
16 M. A. Jalil, T. Nagai, T. Murahashi and H. Kurosawa, *Organometallics*, 2002, **21**, 3317.