Insertion of arylsulfonylnitrene fragments into Pd–Pd bonds. Crystallographic characterization of the novel [$Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}NSO_2C_6H_4NO_2\text{-}2)$] A-frame adduct

Gábor Besenyei,* László Párkányi, Isabella Foch, László I. Simándi† and Alajos Kálmán

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary

The dimeric palladium complex [$Pd_2Cl_2(\mu\text{-dppm})_2$] reacts with arylsulfonyl azides affording novel arylsulfonylnitrene-bridged dinuclear A-frame complexes, [$Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}NSO_2Ar)$].

We have reported earlier that palladium complexes catalyse the carbonylation of sulfonamide derivatives such as salts of *N*-chloroarylsulfonamides, arylsulfonyliodoimines and arylsulfonylselenylimines with CO to the corresponding arylsulfonyl isocyanates.[1] These reactions are of potential interest in the phosgene-free synthesis of arylsulfonylurea type herbicides. Although the mechanisms of these reactions are not known, it is reasonable to assume that arylsulfonylnitrene intermediates may be involved as isocyanate precursors reacting with CO in the coordination sphere of the palladium catalyst. Mononuclear arylsulfonylnitrene complexes have been isolated from reactions of complexes of Mo and W with various sources of the $ArSO_2N$ fragment and obtained *via* oxidation of the coordinated $ArSO_2NH$ moiety.[2,3] The arylsulfonamide ligand has also been observed in complexes of Pt, Ru and Os.[4–6]

To our knowledge no palladium complexes containing the arylsulfonylnitrene ligand have thus far been synthesised and characterised although Lee and Trogler have reported on a palladium complex bearing phenylnitrene ligands that span over two palladium centres.[7] We now report the first examples of dimeric palladium complexes in which the arysulfonylnitrene ligand occupies a bridging position.

We have observed that the dimeric palladium complex [$Pd_2Cl_2(\mu\text{-dppm})_2$] [**1**, dppm = bis(diphenylphosphino)methane] reacts readily with arylsulfonyl azides **2** at room temp. in CH_2Cl_2 [eqn. (1)], affording the novel A-frame type palladium

$$\underset{\mathbf{1}}{[Pd_2Cl_2(\mu\text{-dppm})_2]} + \underset{\mathbf{2}}{ArSO_2N_3} \longrightarrow \underset{\mathbf{3}}{[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}NSO_2Ar)]} + N_2 \quad (1)$$

a Ar = 4-MeC_6H_4
b Ar = Ph
c Ar = 2-$NO_2C_6H_4$
d Ar = 2-Naphthyl

complexes **3** with the $ArSO_2N$ ligand in an apical position. The reaction is accompanied with characteristic changes in the UV–VIS spectrum and the evolution of *ca.* 0.95 mol N_2 per mol Pd complex, as demonstrated by gas volumetric measurements. In a typical experiment the reacting solution contained 0.2 mmol of **1** and 0.3 mmol of **2**, and the expected volume of N_2 was released in *ca.* 2 h. Evaporation and precipitation with MeOH afforded the products in better than 90% yield.

According to X-ray structure analysis, **3c** has an extended boat conformation of the eight-membered Pd–P–C ring (Fig. 1),‡ which is typical for A-frame adducts.[8–11] Remarkably, the coordination geometry of the bridging nitrogen is almost planar [$\Sigma\phi(N)$ = 356.2°; the N atom is located only 0.204 Å above the Pd(1)Pd(2)S plane]. An analogous feature has been observed for the complex [$Ir_2(CO)_2(dppm)_2(\mu\text{-}NPh)$].[12] The short S–N(1) bond distance (1.544 Å) is indicative of d_π–p_π interaction, shifting electron density from the bridging nitrogen to the sulfonyl group. The contribution of resonance structures with negatively charged sulfonyl oxygen atoms is in line with the low values recorded for the $\nu_{as}(SO_2)$ bands (1240–1252 cm^{-1}). Although the S–N(1) bond has a pronounced double bond character, rotation around this axis should be considered feasible.

^1H and ^{31}P NMR chemical shifts and coupling constants of **3a–d**, diagnostic for the dppm ligand in A-frame complexes, fall within a very narrow interval, supporting the close structural similarity of these complexes (Table 1). The observed splitting patterns in the ^1H NMR spectra and the singlets observed for the P nuclei show the equivalence of the diphosphine ligands.[8,9] The nature of the Ar group exerts only a negligible influence on the NMR parameters. We have found that complexes **3** are inert

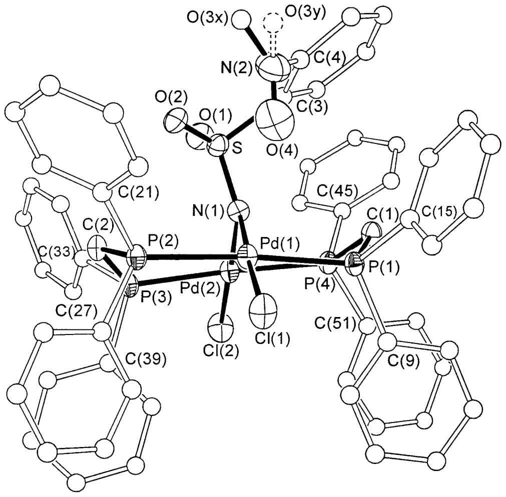

Fig. 1 The molecular structure of [$Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}NSO_2C_6H_4NO_2\text{-}2)$], **3c**. Selected bond distances (Å) and angles (°): Pd(1)–Pd(2) 3.282(1), Pd(1)–N(1) 2.016(4), Pd(2)–N(1) 2.029(4), Pd(1)–Cl(1) 2.316(1), Pd(2)–Cl(2) 2.306(2), S–N(1) 1.544(4), S–O(1) 1.444(4), S–O(2) 1.445(4), O(3x)–N(2) 1.204(3), O(4)–N(2) 1.226(7), Pd(1)–O(4) 3.099(7), S–O(4) 3.324(5); Pd(1)–N(1)–Pd(2) 108.4(2), S–N(1)–Pd(1) 125.7(2), S–N(1)–Pd(2) 122.1(2), N(1)–Pd(1)–Cl(1) 177.1(1), N(1)–Pd(2)–Cl(2) 175.2(1).

Table 1 NMR data of complexes **3a–d**[a]

Complex	δ_H	J_{HH}/Hz	J_{HP}/Hz	δ_P[b]
3a	4.10 (2 H, dq)	12.8	5.9	7.2(s)
	2.57 (2 H, dq)		3.4	
3b	4.01 (2 H, dq)	12.8	5.8	7.1(s)
	2.59 (2 H, dq)		3.4	
3c	4.17 (2 H, dq)	12.9	5.8	6.0(s)
	2.65 (2 H, dq)		3.4	
3d	4.13 (2 H, dq)	12.7	5.9	7.1(s)
	2.53 (2 H, dq)		3.3	

[a] s = Singlet, d = doublet, q = quintet. [b] Relative to 85% H_3PO_4.

toward CO. Exposure of **3a** and **3c** in CH_2Cl_2 to 30 bar CO at 20 °C for 18 h did not afford any products derived from the sulfonylnitrene moieties. This is in agreement with the observation of Ge and Sharp,[13] who demonstrated that CO is inserted into the Rh–N bond of $[Rh_2(CO)_2(dppm)_2(\mu\text{-NR})]$ only if R is not a strongly electron-withdrawing group. Similar factors may be responsible for the lack of reactivity of compounds **3**.

Although arylsulfonylnitrene complexes are probably involved in the carbonylation of sulfonamide derivatives, complexes **3** as model intermediates are too stable for reaction with CO, but very convenient for structural characterisation.

Work is in progress to further explore synthetic routes leading to palladium sulfonylnitrene complexes and their role in catalytic N-carbonylations.

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Footnotes

† E-mail: simandi@cric.chemres.hu

‡ *Crystal data* for **3c**: $C_{56}H_{48}Cl_2N_2O_4P_4Pd_2S\cdot CHCl_3$, orange plate, 0.45 × 0.30 × 0.08 mm, monoclinic, space group $P2_1/n$, a = 12.827(1), b = 19.622(1), c = 23.149(6) Å, β = 98.74(2)°, U = 5758.7(16) Å^3, Z = 4, D_c = 1.582 Mg m^{-3}, μ = 1.051 mm^{-1}. Data were collected at 293 K on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo-Kα radiation. Reflections were collected in the range $2.44 \leqslant \theta \leqslant 29.46°$ and 15935 independent reflections were used in the structure analysis. A semi-empirical (ψ-scan) absorption correction has been applied to the data. The structure was solved by the heavy-atom method and refined against all F^2 data (SHELXL-93)[14] to R_1 = 0.0490 [for 12 251 $F^2 > 2\sigma(F^2)$]; wR_2 = 0.1555 and goodness of fit = 0.978 for all 15 935 F^2, 731 parameters; all non-hydrogen atoms anisotropic except the minor disorder component of O(3) and three Cl atoms of out of nine disordered positions of the solvent. The highest peak of 1.254 e Å^{-3} in the final difference map is located in the vicinity of the Pd(1) atom. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/462.

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