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Arylsulfonylnitrene and arenesulfonyl azide complexes of palladium

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Reaction of $[Pd_2Cl_2(dppm)_2]$ **1** with arenesulfonyl azides RSO_2N_3 in CH_2Cl_2 at ambient temperature resulted in the formation of dimeric palladium complexes with bridging arylsulfonylnitrene ligands $[Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2R)]$ **2** (R = phenyl **a**, 4-methylphenyl **b**, 4-nitrophenyl **c**, 2-nitrophenyl **d**, 2-naphthyl **e** or ferrocenyl **f**). According to their NMR spectra, complexes **2a–2f** are typical A-frame adducts, which has been verified by single crystal X-ray diffraction studies on **2d**–**2f**. The short N(1)–S(1) distances [1.541(3)–1.565(3) Å] reflect the double bond character of these bonds and indicate a d_π–p_π interaction of the sulfur atom and the imido nitrogen atom. With 2-nitrobenzenesulfonyl azide a by-product was observed in a yield of 10–15%. Based on spectroscopic properties (^1H and ^{31}P NMR, IR) and elemental analysis, this compound contains a bridging arenesulfonyl azide ligand, $[Pd_2Cl_2(dppm)_2(\mu\text{-}2\text{-}O_2NC_6H_4SO_2N_3)]$ **3d**. Irradiation with light of $\lambda > 455$ nm caused selective dissociation of **3d** into **1** and $2\text{-}O_2NC_6H_4SO_2N_3$. The azide complex **3d** is *not* an intermediate in the formation of the corresponding nitrene complex **2d**.

Introduction

Chemically reactive species, such as carbenes and nitrenes, can often be stabilised as ligands in metal complexes.[1] The stability of nitrene complexes is especially apparent with high-valent transition metals, where multiple bonding is facilitated also by the strong π-donor properties of the imido (nitrene) ligand. The isolation of stable nitrene complexes of certain transition metals under a given set of conditions may indicate that reactive nitrene intermediates are possibly involved in catalytic reactions occurring under similar conditions. This may be a useful tool in elucidating the mechanisms of some complex reactions. Mechanistic considerations and the search for new synthetic strategies are the major factors that have contributed to the exceptional growth of research activity associated with transition metal imido complexes.

In the course of our studies on the chemical properties of palladium complexes depicted by the general formula of $[Pd_2Cl_2(P\text{–}P)_2]$ [where P–P denotes bis(diphenylphosphino)methane, dppm, or 1,1-bis(diphenylphosphino)ethane, dppmMe] we have observed that the palladium dimers $[Pd_2Cl_2(dppm)_2]$, $[Pd_2Cl_2(dppm)(dppmMe)]$ and *syn*-$[Pd_2Cl_2(dppmMe)_2]$ can preserve the short-lived sulfur monoxide and selenium monoxide in their co-ordination spheres.[2] Earlier, we prepared a series of these complexes and characterised them by spectroscopic methods. The structure of the $[Pd_2Cl_2(dppm)_2(\mu\text{-}SO)]$ adduct has been determined by X-ray crystallography. Later, we became interested in palladium-stabilised nitrene complexes. This interest was initiated by our observations showing that the catalytic carbonylation of certain arenesulfonamide derivatives offers new phosgene-free routes for the industrially important arenesulfonyl isocyanates.[3] We supposed palladium nitrene complexes to be intermediates in these catalytic transformations. This turned our attention toward the synthesis, structural and chemical properties of palladium complexes containing co-ordinated arylsulfonylnitrene ligands. The search for a suitable synthetic route to these complexes revealed that the interaction of the dimeric complex $[Pd_2Cl_2(dppm)_2]$ with arenesulfonyl azides results in the formation of dinuclear, sulfonylnitrene bridged adducts $[Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2R)]$ (R = aryl).[4]

Owing to their theoretical interest and potential synthetic utility, the chemistry of nitrene complexes is well explored. The literature data accumulated over the past decades have been reviewed from various aspects.[1,5–7] While metal centres with empty d orbitals can effectively stabilise imido ligands, nitrene complexes of metals belonging to Group 10 (VIII) are rare,[1d,8] and we are not aware of any palladium sulfonylnitrene complexes other than those described in our preliminary report.[4] Complexes with arylsulfonylnitrene moieties ligated to mononuclear centres of Ru, W and Mo have been described, however.[9–11]

In this paper we report the synthesis and structural characterisation of a series of novel $[Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2R)]$ A-frame derivatives, including the results of single crystal X-ray diffraction studies of complexes where R = 2-nitrophenyl, 2-naphthyl or ferrocenyl. Spectroscopic evidence will also be presented supporting the formation of an arenesulfonyl azide complex, $[Pd_2Cl_2(dppm)_2(\mu\text{-}N_3SO_2C_6H_4NO_2\text{-}2)]$, as a by-product in the reaction of $[Pd_2Cl_2(dppm)_2]$ with 2-nitrobenzenesulfonyl azide.

Results and discussion

Reaction of the palladium complex $[Pd_2Cl_2(dppm)_2]$ **1** with arenesulfonyl azides, RSO_2N_3 results in the formation of novel A-frame adducts $[Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2R)]$ **2**. The reaction takes place smoothly in CH_2Cl_2 at ambient temperature and is accompanied with evolution of stoichiometric amounts of nitrogen gas, as determined by volumetric experiments [eqn. (1)] (R = C_6H_5 **a**, $4\text{-}CH_3C_6H_4$ **b**, $4\text{-}O_2NC_6H_4$ **c**, $2\text{-}O_2NC_6H_4$ **d**, 2-naphthyl **e** or ferrocenyl **f**).

$$\underset{\mathbf{1}}{[Pd_2Cl_2(dppm)_2]} + RSO_2N_3 \longrightarrow \underset{\mathbf{2}}{[Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2R)]} + N_2 \quad (1)$$

The ^1H NMR spectra are consistent with the apical position of the arylsulfonylimido moiety by showing the expected doublet/quintet splitting pattern of the methylene hydrogen atoms (see Table 1). The chemical shift values and the magnitude of the *J*(HH) and *J*(HP) coupling constants are similar to those observed in related spin systems.[12]

The novelty of dimetallic arylsulfonylnitrene complexes prompted us to carry out detailed structural investigations. The

Table 1 The NMR spectroscopic data of compounds **2a**–**2f** and **3d**[a]

Complex	R	δ_H	J_{HH}/Hz	J_{HP}/Hz	δ_P
2a	Phenyl	4.01 (2 H, dq)	12.8	5.8	7.1 (s)
		2.58 (2 H, dq)	12.8	3.4	
2b	4-Methylphenyl[b]	4.10 (2 H, dq)	12.8	5.9	7.2 (s)
		2.57 (2 H, dq)	12.8	3.4	
		2.22 (3 H, s)			
2c	4-Nitrophenyl	3.89 (2 H, dq)	12.8	5.8	6.5 (s)
		2.66 (2 H, dq)	12.8	3.5	
2d	2-Nitrophenyl	4.17 (2 H, dq)	12.9	5.8	6.0 (s)
		2.65 (2 H, dq)	12.9	3.3	
2e	2-Naphthyl	4.13 (2 H, dq)	12.7	5.9	7.1 (s)
		2.53 (2 H, dq)	12.7	3.4	
2f	Ferrocenyl	4.27 (2 H, dq)	12.5	6.2	7.6 (s)
		4.08 (2 H, m)			
		4.04 (5 H, s)			
		3.71 (2 H, m)			
		2.53 (2 H, dq)	12.5	3.3	
3d	2-Nitrophenyl	2.93 (2 H, dq)	13.6	5.1	13.5[c]
		2.56 (2 H, dq)	13.6	3.1	15.0

[a] Spectra were recorded in $CDCl_3$ and referenced to internal TMS or external 85% H_3PO_4, respectively; d = doublet, q = quintet, m = multiplet, s = singlet. [b] ^{13}C NMR: δ 21.4 (CH_3Ph) and 24.5 (CH_2). [c] AA′BB′ system.

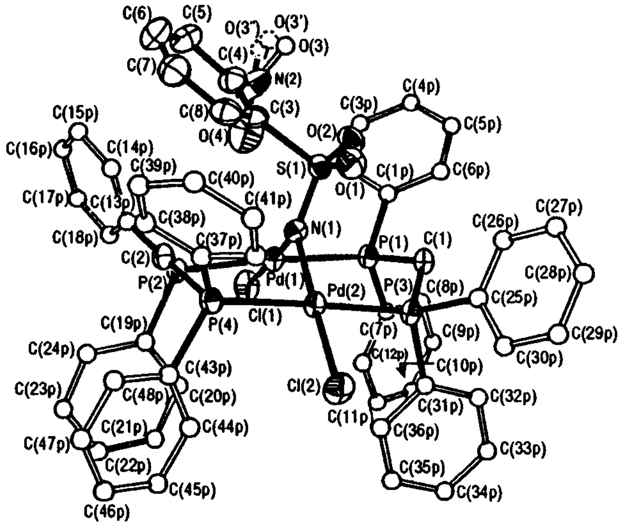


Fig. 1 Molecular structure of $[Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2C_6H_4NO_2\text{-}2)]$ **2d**.

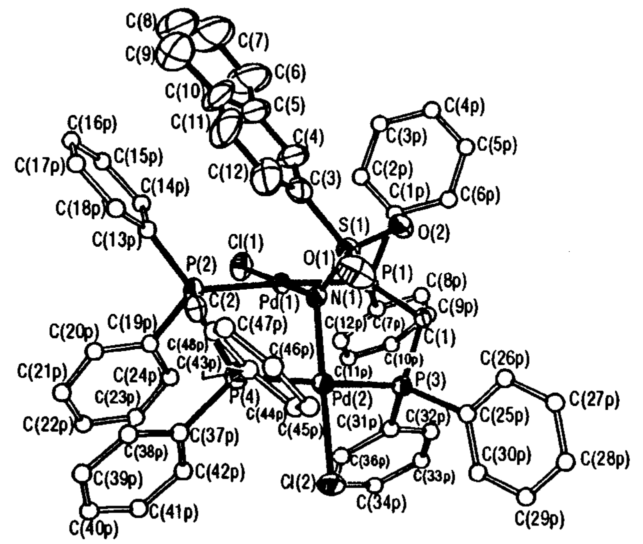


Fig. 2 Molecular structure of complex **2e**, molecule 2.

geometrical arrangement deduced from the spectroscopic features of the complexes has been confirmed by single crystal X-ray diffraction studies in the case of **2d**–**2f**. Selected bond lengths and angles are presented in Table 2.

Figs. 1–3 show typical A-frame structures in which the diphosphine ligands are arranged in *trans-trans* positions. The *N*-arylsulfonyl moieties occupy the apical sites and the methylene carbon atoms are bent toward the bridging nitrogen atom, forming thereby the well known "boat" conformation. An overview of the structural data reveals the close structural similarity of **2d**–**2f**. The Pd(1) ··· Pd(2) distances vary between 3.231 and 3.350 Å, excluding any bonding metal–metal interaction {*cf.* the Pd–Pd distance is only 2.699(5) Å in the related $[Pd_2Br_2(dppm)_2]$ complex[13]}. The Pd–N bond lengths are in the range of 2.007(4) and 2.029(3) Å. To our knowledge, there is only one crystallographically characterised palladium complex with a bridging nitrene unit,[8] in which the respective distances lie between 2.009 and 2.071 Å. The Pd–N bond lengths in **2d**–**2f** are in line with the single bond character of the palladium–nitrogen interaction as a metal–nitrogen single bond is expected to be in the region of 1.9–2.15.[14] In contrast, with other metals the imido nitrogen atom tends to form an additional d_π–p_π bond with the metal centres, and bond orders of higher than one are common.[1d]

The bond lengths and angles around the palladium centres do not differ significantly from the corresponding data of other $[Pd_2Cl_2(dppm)_2(\mu\text{-}X)]$ derivatives[15] and reflect a slightly distorted square planar geometry around the metal ions.

The short S(1)–N(1) bond distance [1.541(3)–1.565(3) Å] is a further common feature of the structures **2d**–**2f**. The sum of covalent radii of sulfur and nitrogen atoms is 1.70 Å therefore the S–N bonds [and, as indicated by the similar values of $\nu(SO_2)$ stretching bands, in **2a**–**2c** as well, see Table 3] should be regarded as having strong double bond character. This structural feature suggests an extensive d_π–p_π interaction between the bridging imido nitrogen atom and the sulfur atom. The sum of angles around the nitrogen atoms in **2d**–**2f**, which approaches 360°, gives further evidence for this additional bond formation. The shift of electron density toward the sulfonyl group is also reflected by the position of the $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$ bands, showing a shift of 60–80 cm^{-1} to lower wavenumbers, as compared with the same bands recorded for sulfonamides.

A planar trigonal symmetry about the bridging nitrogen atom has been observed in the structurally characterised $[Rh_2(CO)_2(dppm)_2(\mu\text{-}NC_6H_4NO_2\text{-}4)]$[16] and $[Ir_2(CO)_2(dppm)_2(\mu\text{-}NC_6H_4CH_3\text{-}4)]$[17] A-frame adducts. An analysis of the crystallographic data published on $[Pd_3(PEt_3)_3(\mu\text{-}NPh)_2(\mu\text{-}NHPh)]$ reveals, however, that none of the nitrogen atoms seem to follow this behaviour.[8]

Table 2 Selected bond lengths (Å) and angles (°) of complexes **2d**–**2f**

		2e		
	2d	molecule 1	molecule 2	**2f**
Pd(1)···Pd(2)	3.281(1)	3.288(1)	3.231(1)	3.350(1)
Pd(1)–N(1)	2.019(3)	2.016(4)	2.007(4)	2.010(2)
Pd(2)–N(1)	2.029(3)	2.013(4)	2.019(4)	2.010(2)
Pd(1)–Cl(1)	2.316(1)	2.330(1)	2.342(2)	2.328(1)
Pd(2)–Cl(2)	2.306(1)	2.328(1)	2.318(2)	2.334(1)
N(1)–S(1)	1.541(3)	1.556(4)	1.562(4)	1.565(3)
S(1)–O(1)	1.444(3)	1.434(4)	1.422(4)	1.436(2)
S(1)–O(2)	1.446(3)	1.445(4)	1.450(4)	1.442(2)
S(1)–C(3)	1.801(4)	1.759(6)	1.790(7)	1.762(3)
Pd(1)–P(1)	2.327(1)	2.323(1)	2.336(2)	2.315(1)
Pd(1)–P(2)	2.333(1)	2.357(1)	2.331(2)	2.315(1)
Pd(2)–P(3)	2.330(1)	2.318(1)	2.313(2)	2.333(1)
Pd(2)–P(4)	2.316(1)	2.312(2)	2.324(2)	2.326(1)
Pd(1)–N(1)–Pd(2)	108.3(2)	109.4(2)	106.8(2)	112.8(1)
Pd(1)–N(1)–S(1)	125.7(2)	125.5(2)	125.0(2)	118.5(1)
Pd(2)–N(1)–S(1)	122.3(2)	123.8(2)	124.2(2)	124.7(1)
C(3)–S(1)–N(1)	108.2(2)	105.7(2)	108.3(2)	107.5(2)
O(1)–S(1)–O(2)	115.0(2)	114.5(3)	116.2(3)	116.2(2)
Cl(1)–Pd(1)–N(1)	177.1(1)	177.5(1)	175.5(1)	174.1(1)
Cl(2)–Pd(2)–N(1)	175.1(1)	177.2(1)	179.1(1)	177.1(1)
P(1)–Pd(1)–P(2)	174.4(1)	174.4(1)	174.1(1)	171.6(1)
P(3)–Pd(2)–P(4)	175.1(1)	175.5(1)	177.3(1)	173.6(1)
Pd(2)–N(1)–S(1)–O(2)	126.6(2)	101.3(3)	121.5(3)	145.9(2)
Pd(2)–N(1)–S(1)–O(1)	−6.4(3)	−29.6(4)	−10.4(4)	15.0(2)
P(1)–Pd(1)–Pd(2)–P(4)	175.7(1)	169.8(1)	172.7(1)	−169.4(1)
P(3)–Pd(1)–Pd(2)–P(2)	168.3(1)	169.5(1)	172.7(1)	−178.8(1)
O(4)–N(2)–C(4)–C(3)	57.8(7)			

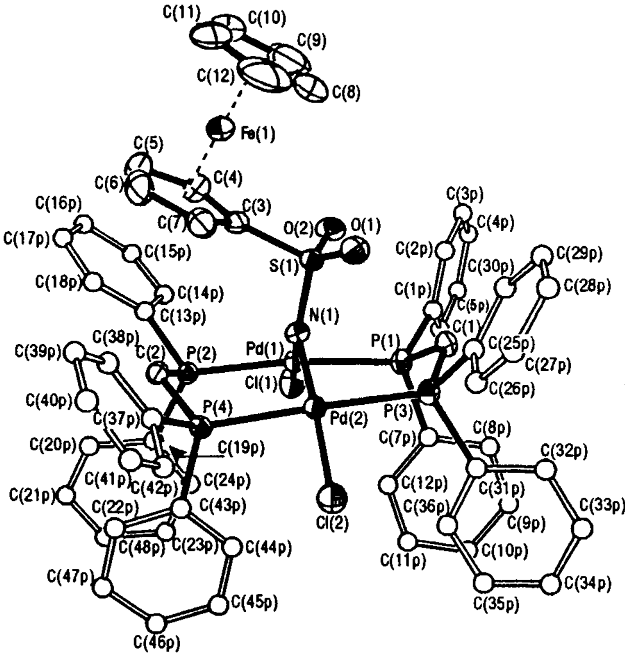


Fig. 3 Molecular structure of $[Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2R)]$ **2f** (R = ferrocenyl).

To our knowledge, structurally characterised derivatives of ferrocenesulfonamide are rare. A comparison of the C(Cp)–S and S–N bond lengths in **2f** with the respective data of ferrocenesulfonamide and the sulfonylurea $RSO_2NHC(O)NHBu$ (R = ferrocenyl)[18] reveals that electron donating properties of the substituents on the nitrogen atom bring about changes of opposite directions in these distances. This observation is in conformity with the conclusions drawn upon a statistical analysis of derivatives containing the CSO_2N fragment.[19]

Interestingly, the disposition of the ferrocenesulfonyl unit is the most symmetrical among the three arylsulfonyl moieties. This is reflected by the almost equal O(1)···P(3) and O(2)···P(1) distances (3.267 and 3.409 Å) and also by the Pd(2)–N(1)–S(1)–O torsion angles (see Table 2). The central arrangement of the ferrocenyl moiety is apparently due to the lack of any asymmetric substitution on the Cp ring. The other two aryl groups are unsymmetrically substituted with respect to the S(1)–C(3) bonds and this results in twisted orientations of the arylsulfonyl moieties to achieve minimum steric interactions.

When the aryl group is naphthyl there are two independent molecules in the asymmetric unit. Molecule 1 is different from 2 in that the naphthyl group is rotated by 180° about the S(1)–C(3) axis. The different orientation of the naphthyl moiety is accompanied by other small structural changes like twisting about the N(1)–S(1) bond and modifications in the Pd(1)··· Pd(2) distance and Pd(1)–N(1)–Pd(2) angle.

Sharp and co-workers[16] have observed that an imido/amido equilibrium is established readily with $[Rh_2(CO)_2(dppm)_2(\mu\text{-}NR)]$ complexes. The ratio of these two components depends on the nature of R, and only the imido form could be detected when R was the electron-withdrawing substituent $4\text{-}O_2NC_6H_4$. In agreement with these findings, our complexes do not exhibit any sign of imido/amido tautomerism and the ^1H NMR spectra show a doublet/quintet splitting pattern for the methylene hydrogen atoms, whose integration is always correct for two protons in both resonances. Additional proof for the lack of interaction of the bridging nitrogen atom with the methylene group of dppm ligands comes from the C(1)–P and C(2)–P bond lengths [1.811(6)–1.845(4) Å], which are *ca.* 0.1 Å longer than those observed in P–CH–P bridges.

A further analogy with the rhodium compounds is that complexes **2b** and **2d**, when subjected to carbonylation, did not show any tendency for CO insertion and no isocyanate formation was observed. Our original aim was to study the carbonylation of palladium nitrene complexes to shed light on the mechanistic details of two-step oxidative carbonylation reactions.[3]

Although reaction (1) shows selectivities better than 95% for most of the sulfonyl azides (^1H NMR), we observed a by-product with 2-nitrobenzenesulfonyl azide, which formed in 10–15%. Efforts to isolate and identify this compound have caused an unexpected turn in our research.

If the raw product obtained from complex **1** and $2\text{-}O_2NC_6H_4SO_2N_3$ (*via* evaporation of the reaction mixture to dryness) was analysed by ^1H NMR spectroscopy resonances of weak intensity were observed at δ 2.56 and 2.93. The ^{31}P NMR spectrum was also indicative of the presence of a by-product having non-equivalent phosphorus nuclei. While purification of the raw reaction mixture to obtain the pure nitrene adduct could be accomplished easily, the by-product proved to be elusive and our first attempts to isolate and characterise it were unsuccessful. By taking advantage of the better solubility of the nitrene complex, we enriched the samples to have the unknown component as a major constituent. A series of the IR spectra illustrates the spectral changes occurring during this operation (Fig. 4).

We have been unable to obtain crystals of the unknown component suitable for X-ray diffraction studies, therefore its characterisation is based on NMR and IR spectroscopy and elemental analysis.

Spectra in Fig. 4 clearly show that not only the nitrene complex **2d** but also the by-product contains a sulfonyl group. In the former case it was characterised by the $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$ stretching vibrations at 1252 and 1110 cm^{-1}, while bands at 1311 and 1152 cm^{-1} were assigned to the same vibrations of the unknown component. The shift of $\nu(SO_2)$ bands to lower wavelengths indicates that conjugation of the sulfonyl group to its substituents is by far not as extensive as that in the nitrene complex. Other peaks at 1536, 1484, 1435, 1356 and 1098

Table 3 The UV–VIS and IR data of complexes **2a**–**2f** and **3d**

	UV–VIS		IR (KBr, cm^{-1})			
Compound	λ/nm	$\varepsilon/M^{-1}\ cm^{-1}$	$\nu_{asym}(NO_2)$	$\nu_{sym}(NO_2)$	$\nu_{asym}(SO_2)$	$\nu_{sym}(SO_2)$
2a	262 (sh)	41600			1242	1106[a]
	329	19300				
2b	262 (sh)	42200			1241	1105[a]
	329	19100				
2c	262 (sh)	43400	1524	1346	1249	1107[a]
	331	21300				
2d	271 (sh)	35400	1536	1365	1252	1110 (sh)
	331	18700				
2e	265 (sh)	44500			1245	1106 (sh)
	328	19900			1233	
2f	262 (sh)	44700			1241	1098[a]
	328	19300				
3d	329[b]	26400	1540	1369	1311	1152
	417[b]	5200				

[a] Owing to overlap with other vibrations, assignments of $\nu_{sym}(SO_2)$ bands were done by a deconvolution of the 1260–1050 cm^{-1} region. [b] Obtained after subtracting contribution of complex **2d**, as determined from the ^1H NMR spectcrum of a mixture of **3d** and **2d**.

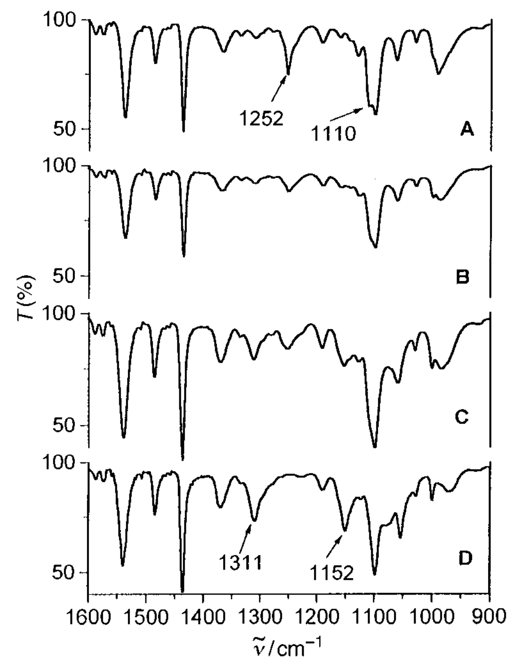


Fig. 4 The IR spectra of complex **2d** (**A**), and mixtures of **2d** and **3d**: **B**, 13% (raw reaction product); **C**, 38% and **D**, 85% of **3d**.

cm^{-1} did not vary on going from the pure nitrene complex (top spectrum) to the mixtures containing the unknown component. These observations allow us to conclude that the by-product is also a derivative of the palladium dimer and the sulfonyl azide, and both the nitrene complex **2d** and the unknown component exhibit the same basic structural features.

An important fact is that the increasing percentage of the unknown component in the sample was accompanied with an increasing nitrogen content (see Experimental section). A good agreement between the experimental and calculated elemental analysis data was found when the unknown component in the mixtures was assumed to be the azide complex $[Pd_2Cl_2(dppm)_2(2\text{-}O_2NC_6H_4SO_2N_3)]$ **3d**.

The ^1H NMR spectrum of the by-product clearly shows the presence of two doublets of quintets, which can readily be attributed to non-equivalent methylene hydrogen atoms. The difference of the chemical shifts of the methylene protons is remarkably less than that in the spectra of the nitrene complexes but the values of the *J*(HH) and *J*(HP) coupling constants, which are more informative with respect to the structural relationship, emphasise the structural similarities of the azide and nitrene adducts. Unexpectedly, the ^{31}P NMR spectrum reflects the non-equivalence of the phosphorus nuclei, which form an AA′BB′ spin system. In $M_2(P\text{–}P)_2L_n$ complexes, the non-equivalence of the phosphorus nuclei is typically attained in two ways: (i) the phosphorus atoms of a diphosphine ligand are equivalent but different from those of the other diphosphine, or (ii) the *trans* phosphorus atoms are equivalent but the P nuclei of the bridging ligands are magnetically different. The former case results in *J*(HP) couplings of 10–15 Hz and the methylene hydrogen atoms appear as doublets of triplets.[2] In the latter version the methylene hydrogen atoms are coupled not only to the adjacent but to the remote P atoms as well thereby keeping the quintet splitting pattern.[20,21] As for the structure of **3d**, it can be concluded that the magnetic inequivalence of the P nuclei is induced by the azide ligand that is supposed to have a fixed orientation similar to that of the diazonium ligand in the related platinum dimer.[20] The NMR spectral data of **3d** unambiguously demonstrate that this complex has a typical A-frame structure and the position of the apical azide ligand is asymmetric with respect to the phosphorus nuclei attached to the same metal centre.

Although azido complexes of transition metals are common, complexes containing a co-ordinated organic azide are rare[22–24] and, to our knowledge, no complexes ligating an arenesulfonyl azide ligand have previously been reported. Therefore, our aim was to acquire further evidence to support our conclusion.

Although mass spectroscopy with fast atom bombardment ionisation proved to be a convenient way of characterising sulfonylnitrene complexes, we have not been able to detect the molecular ion of the proposed azide complex. Instead, it was the nitrene adduct that was observed in MS measurements (M^+, *m*/*z* 1252). The appearance of this peak was not surprising as we know that the sample analysed did indeed contain some (≈15%) nitrene complex (see Experimental section). The lack of the molecular ion corresponding to the azide complex can be explained by assuming that this compound decomposes to the nitrene adduct during the procedure of sample preparation or, alternatively, nitrogen is lost (and perhaps other fragmentation processes occur) upon ionisation of the sample. The MS spectrum of **3d**, however, does provide some information with respect to the azide adduct by displaying an ion cluster around *m*/*z* 1094, completely absent in the MS spectrum of **2d**. We ascribed this group of ions to the fragment $[Pd_2Cl_2(dppm)_2N_3]^+$. The experimental and simulated distribution of peak intensities showed good agreement. The appearance of the fragment at *m*/*z* 1094 coincides with the behaviour of 2-nitrobenzenesulfonyl azide under conditions of the MS experiments. Spectra recorded by using both EI and FAB techniques showed that bond breaking between the sulfonyl and the azide groups is the major route of fragmentation, because the peak at *m*/*z* 186 was more intense than that at *m*/*z* 228 in both spectra.

In order to obtain further evidence that the by-product is an azide complex, we made attempts at transforming **3d** to the nitrene adduct. When searching for the right conditions for this reaction, we found absorption bands of the free palladium dimer $[Pd_2Cl_2(dppm)_2]$ in the UV–VIS spectrum of a solution of the enriched mixture. Evaporation of an aliquot of this solution to dryness and analysis of the solid residue by IR spectroscopy revealed the presence of free 2-nitrobenzenesulfonyl azide [$\nu_{asym}(N_3)$ 2145 cm^{-1}]. This observation unequivocally shows that the by-product is an azide complex and its formulation as $[Pd_2Cl_2(dppm)_2(2\text{-}O_2NC_6H_4SO_2N_3)]$ is correct.

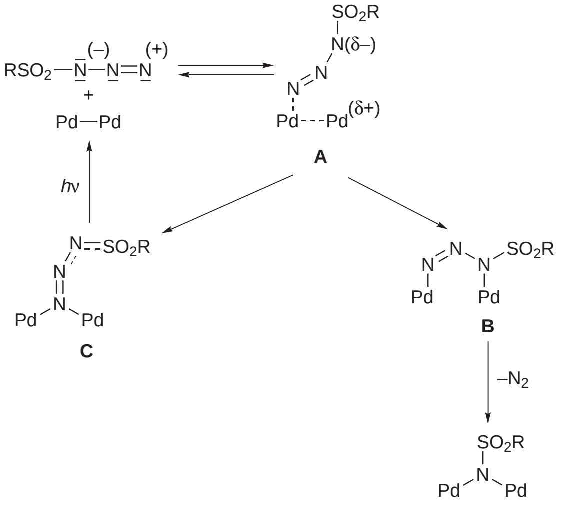
Further examination of this remarkable reaction of complex **3d** has revealed that the dissociation of the azide complex is a photolytic process. A solution of **3d** in CH_2Cl_2 did not show any detectable change in the UV–VIS spectrum for 22 h at ambient temperature, if it was kept in the dark. Irradiation of the solution by sunlight or by the filtered light ($\lambda > 455$ nm) of a xenon lamp resulted in the rapid decomposition of the azide complex to $[Pd_2Cl_2(dppm)_2]$ and $2\text{-}O_2NC_6H_4SO_2N_3$. The products of photolysis were identified by ^1H NMR, UV–VIS and IR spectroscopy and TLC. If the photolysis was accomplished in the presence of $4\text{-}CH_3C_6H_4SO_2N_3$ or $4\text{-}O_2NC_6H_4SO_2N_3$, the respective nitrene complexes **2b** and **2c** could be readily recognised in the ^1H NMR spectra. The details of the experiments are described in the Experimental section.

The ^1H NMR spectrum of a photolysed sample of complex **3d** is consistent with the presence of **1**, **2d** and **3d** in a ratio of 45 : 33 : 22. Detection of **3d** does not necessarily mean, however, that the decomposition of the photolysed sample was not complete. A comparison of the results obtained under varying conditions allows to conclude that **3d** in this sample is not a residue of the original complex but a product of a secondary reaction of **1** and $2\text{-}O_2NC_6H_4SO_2N_3$ obtained photolytically. Complex **3d** may be formed during the evaporation of the solvent dichloromethane, and also during sample preparation and NMR analysis. This is shown by the experiments carried out in the presence of a 10 molar excess of $4\text{-}CH_3C_6H_4SO_2N_3$ or a 5 molar excess of $4\text{-}O_2NC_6H_4SO_2N_3$. In these cases no **3d** could be observed in the photolysed samples because the free added azides trapped **1**, thereby preventing the reaction between the primary photolytic decomposition products **1** and $2\text{-}O_2NC_6H_4SO_2N_3$. Following an identical reasoning, we may conclude that the increased proportion of the nitrene complex **2d** should also be attributed to a secondary reaction of **1** and $2\text{-}O_2NC_6H_4SO_2N_3$ and not a direct transformation of **3d** to **2d**. This conclusion may be deduced from the observation that photolysis of **3d** in the presence of $4\text{-}O_2NC_6H_4SO_2N_3$ results in the predominant formation of **2c** and leads to only a negligible, if any, increase of the percentage of **2d**, as shown by a comparison of the composition of the starting mixture (15% **2d**) with that of the photolysed product (18% **2d**). The nitrene complex **2d** is, however, the major constituent of the reaction mixture if a photolysed solution of **3d** is allowed to stand for 2 d.

Although the azide complex **3d** can be converted into the nitrene adduct **2d** this is not a straightforward process but is preceded by the photolytic decomposition of **3d** to its constituents **1** and $2\text{-}O_2NC_6H_4SO_2N_3$. The chemical behaviour of **3d** is consistent with the conclusion that the azide complex is not an intermediate but a product of a side reaction. Conversion of **3d** into **2d** represents a pathway which is mechanistically different from those described for related transformations.[22–24]

The ability of organic azides to react with double and triple bonds with the formation of *N*-heterocycles is well known from organic chemistry.[25] The analogous interaction of a triple bonded molybdenum dimer with organic azides has been studied as an organometallic model reaction of (2+3) cycloaddition.[26] Although conversion of the organic azide into both nitrene and azide ligands was equally detected, formation of the expected five-membered dimetallatriazene ring could not be observed.

Reaction (1) can also be considered as an example of cycloaddition across a palladium–palladium bond (Scheme 1).



Scheme 1 Pd—Pd represents **1**; R is the same as in **a**–**f**; in **C**, R denotes 2-nitrophenyl.

Organic azides are known to have amphiphilic character, but in this reaction they will certainly behave as electrophiles with respect to the Pd–Pd bond. As a 1,3-dipole, the sulfonyl azide carries a positive charge on the remote nitrogen atom in one of its major resonance forms. It seems likely that the sulfonyl azide approaches the reactive part of the dimer with the rod-like azide group to minimise steric interactions. The electrophilic azide group can cause polarisation of the Pd–Pd bond, resulting in the formation of an ionic intermediate **A**, which may rearrange to **B** or, in sterically controlled cases, to **C**. Such steric hindrance may emerge when an *ortho* substituent is present on the aryl group. We believe that the formation of complex **3d** is due to the presence of the *ortho* substituent on the phenyl ring in $2\text{-}O_2NC_6H_4SO_2N_3$. Species **B** is the intermediate from which nitrogen can be extruded with ease, resulting in the formation of a nitrene adduct, as has been demonstrated in organic reactions[25] and also postulated with organometallic reagents.[24,26] The structure type of species **C** is stable in the case of dimetallic complexes and is thought to be the right description of **3d** as well. Spectroscopic features of **3d** are in line with this proposal.

Photodissociation of complex **3d** is likely to occur through an intermediate different from **B**. Therefore, formation of **2d** does not necessarily take place during decomposition to **1** and $2\text{-}O_2NC_6H_4SO_2N_3$. We know of only one light-driven dissociation among $[Pd_2Cl_2(dppm)_2(\mu\text{-}X)]$ type adducts, *viz.* for X representing co-ordinated acetylenes.[27] In our case, however, breaking of the Pd–N bonds can be accomplished by irradiation with photons of much lower energy.

Work on the synthesis and characterisation of complexes with sterically more demanding substituents on the aryl group is in progress in our laboratory.

Experimental

Palladium dimer **1** and the sulfonyl azides were prepared by established procedures.[28,29] Solvents were of analytical grade used without further purification.

The NMR spectra were recorded at 30 °C on a Varian Unity Inova spectrometer at 400 (^1H), 101 (^{13}C) and 162 MHz (^{31}P). Chemical shifts are reported in ppm units and are referenced to TMS and 85% H_3PO_4. The IR spectra were obtained on a

Table 4 Crystal data, data collection and refinement parameters for complexes **2d**–**2f**

	2d	**2e**	**2f**
Empirical formula	$C_{56}H_{48}Cl_2N_2O_4P_4Pd_2S\cdot CHCl_3$	$C_{60}H_{51}Cl_2NO_2P_4Pd_2S\cdot 0.5CHCl_3$	$C_{60}H_{53}Cl_2FeNO_2P_4Pd_2S\cdot C_3H_6O$
Formula weight	1371.97	1344.02	1373.60
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	*Pbca*
a/Å	12.827(1)	21.714(4)	12.414(2)
b/Å	19.622(1)	14.489(3)	22.267(2)
c/Å	23.149(6)	38.342(7)	44.002(5)
β/°	98.74(2)	90.39(1)	
V/Å^3	5758.7(16)	12063(4)	12163(3)
Z	4	8	8
D_c/Mg m^{-3}	1.582	1.480	1.500
μ/mm^{-1}	1.051	0.937	1.093
F(000)	2760	5427	5568
Crystal colour	Yellow	Yellow	Yellow
Crystal description	Block	Block	Block
Crystal size/mm	0.45 × 0.30 × 0.08	0.30 × 0.20 × 0.18	0.50 × 0.40 × 0.18
Maximum and minimum transmission	1.0000 and 0.8451	1.0000 and 0.9759	1.000 and 0.903
Reflections collected	15932	25644	18026
Independent reflections	15932 [R(int) = 0.0182]	25644	17628 [R(int) = 0.0095]
Reflections $>2\sigma(I)$	7997	10598	8915
Data/restraints/parameters	15932/88/760	25644/1703/1407	17628/154/696
Goodness of fit on F^2	0.909	0.813	0.843
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0471, 0.1046	0.0469, 0.0915	0.0401, 0.0859
(all data)	0.1618, 0.12010	0.1604, 0.1092	0.1215, 0.0984
Largest difference peak and hole/e Å^{-3}	1.199 and −1.012	0.816 and −0.937	0.795 and −1.039

Nicolet 205 FTIR spectrometer in KBr pellets, UV–VIS spectra on a HP 8453 diode array spectrophotometer using CH_2Cl_2 as solvent. The FABMS analyses were carried out on a VG ZAB2-SEQ tandem mass spectrometer on samples prepared in a 3-nitrobenzyl alcohol or thioglycerol matrix. Elemental analyses were performed on vacuum dried samples (ethanol reflux, *ca.* 0.1 Torr).

Crystal structure determinations of complexes 2d–2f

The determination of the unit cell parameters and intensity data collections were performed on an Enraf-Nonius CAD4 diffractometer at 293(2) K with Mo-Kα radiation (λ 0.71073 Å). Crystal data and refinement details are listed in Table 4.

Unit cell parameters were determined by least-squares of the setting angles of 25 reflections in the θ ranges 15.49–15.92 (**2d**), 12.43–12.95 (**2e**) and 11.25–11.97° (**2f**). The ω–2θ scan method was used for the data collection for **2d** and ω scans were applied for **2e** and **2f**. The structures were solved by direct methods using the SHELXS 97[30] (**2d**, **2f**) and the SIR 92[31] (**2e**) program and subsequent difference syntheses. The SHELXL 97[32] program was used for anisotropic full-matrix least-squares refinement on F^2. Hydrogen atoms were included in structure factor calculations but not refined. Their isotropic displacement parameters were approximated from the U(eq) value of the atom to which they were bonded [U(H) = 1.3U(eq)].

High displacement parameters observed for the C14p–C18p and the C43p–C48p phenyl rings in complex **2f** may indicate disorder, but no attempt was made to resolve the splitting of the atomic positions. Neutral atomic scattering factors and anomalous scattering factors were taken from ref. 33.

CCDC reference number 186/1258.

See http://www.rsc.org/suppdata/dt/1999/293/ for crystallographic files in .cif format.

Preparation of nitrene complexes [$Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2R)$] 2a–2f

To a solution of 0.21 g (0.2 mmol) of complex **1** in 4 cm^3 of CH_2Cl_2 0.4 mmol of RSO_2N_3 was added in 1 cm^3 of CH_2Cl_2 in one portion. The solution was stirred at ambient temperature (*ca.* 20 °C) until all the palladium dimer was consumed (1–2 h). The reaction can be monitored by TLC (dichloromethane–ethyl acetate 20 : 1). When the reaction was complete, the solvent was reduced to half volume and the product precipitated with methanol. The microcrystalline solid was collected on a glass filter and washed several times with methanol and diethyl ether to remove the excess of sulfonyl azide. Dissolution of the product in CH_2Cl_2 and reprecipitation with methanol gave azide-free samples with isolated yields better than 75% (Found: C, 55.21; H, 3.97; N, 1.20; S, 2.35. $C_{56}H_{49}Cl_2NO_2P_4Pd_2S$ **2a** requires C, 55.69; H, 4.09; N, 1.16; S, 2.66. Found: C, 55.78; H, 4.08; N, 1.20; S, 2.59%; $[M + H]^+$, m/z 1222. $C_{57}H_{51}Cl_2NO_2P_4Pd_2S$ **2b** requires C, 56.04; H, 4.21; N, 1.15; S, 2.62%; M, m/z 1221. Found: C, 53.31; H, 3.81; N, 2.31; S, 2.55. $C_{56}H_{48}Cl_2N_2O_4P_4Pd_2S$ **2c** requires C, 53.69; H, 3.86; N, 2.24; S, 2.56. Found: C, 53.55; H, 3.86; N, 2.27; S, 2.20%. M^+, m/z 1252. $C_{56}H_{48}Cl_2N_2O_4P_4Pd_2S$ **2d** requires C, 53.69; H, 3.86; N, 2.24; S, 2.56. Found: C, 57.02; H, 4.02; N, 1.16; S, 2.35. $C_{60}H_{51}Cl_2NO_2P_4Pd_2S$ **2e** requires C, 57.30; H, 4.09; N, 1.11; S, 2.55. Found: C, 54.30; H, 3.98; N, 1.13; S, 2.28. $C_{60}H_{53}Cl_2FeNO_2P_4Pd_2S$ **2f** requires C, 54.78; H, 4.06; N, 1.06; S, 2.44%).

Isolation of the azide complex [$Pd_2Cl_2(dppm)_2(2\text{-}O_2NC_6H_4SO_2\text{-}N_3)$] 3d

The complex [$Pd_2Cl_2(dppm)_2$] (1.05 g, 1.0 mmol) in 12 cm^3 of CH_2Cl_2 was allowed to react with 0.5 g (2.2 mmol) of 2-nitrobenzenesulfonyl azide, added in 2 cm^3 of CH_2Cl_2 in one portion. A Schlenk tube with the reaction mixture was attached to a bubbler to release the nitrogen evolved and was covered with an aluminium foil to protect the solution from light. When the palladium dimer could not be detected by TLC (in *ca.* 2–3 h) two thirds of the solvent was removed under vacuum and the product precipitated with methanol. The yellow crystals were collected on a glass filter and the nitrene complex removed by fractional dissolution. This procedure was carried out by adding acetone in 5 cm^3 portions, which were removed from the solid by suction after a few minutes of stirring the slurry on the filter with a spatula. The change of the ratio of the nitrene and azide complex could be monitored by TLC (chloroform–acetone 30 : 1) or by IR spectroscopy. An intermediate stage of this process is shown in Fig. 4, spectrum **C**. Integration of the ^{1}H NMR spectrum gave an azide content of 38%. This ratio of **2d** and **3d** requires a nitrogen content of 3.06%, in good agreement with the experimentally found value of 3.02%. When the concentration of the azide complex reached *ca.* 60% the remaining solid was dissolved in $CHCl_3$, filtered through a Celite layer, concentrated and reprecipitated with methanol. Two or three fractions were collected, from which the first one (80–100 mg) generally contained more than 80% of azide complex. It is advisable to protect solutions of **3d** from sunlight during manipulations. Spectrum **D** in Fig. 4 was recorded on a sample with 85% azide complex (Found: C, 52.07; H, 3.79; N, 4.11; S, 2.11. A 85 : 15 mixture of **3d** and **2d** requires C, 52.72; H, 3.79; N, 4.06; S, 2.50%).

Photolysis of complex 3d

A 400 W xenon lamp was used as a light source, which was filtered with a 420 nm filter at the exit of the beam. A 455 nm filter was applied to cover the height of the Schlenk tube filled with the solution of the azide complex. The distance between the lamp and the reaction mixture was 50 cm. The solution was magnetically stirred and the decomposition was monitored by UV–VIS spectroscopy. Physical measurements and reactions were carried out with samples containing about 85% of the azide complex **3d** (Fig. 4, spectrum **D**).

The azide complex (11.0 mg) was dissolved in 18.0 cm^3 of CH_2Cl_2 and irradiated as described above. UV–VIS spectra showed a strong decrease at 330 nm, while bands at 360 and 418 nm increased in intensity. After 40 min of irradiation the solution was cooled to *ca.* -10 °C and evaporated to dryness using an oil pump and a liquid nitrogen trap. The solid residue was dissolved quantitatively in $CDCl_3$ and the ^{1}H NMR spectrum recorded. Three palladium complexes could be identified, the main component being the palladium dimer **1** (45%), accompanied with **2d** (33%) and **3d** (22%) (based on integration of the ^{1}H NMR spectra).

Photolysis of complex 3d in the presence of 4-nitrobenzenesulfonyl azide

The photolysis was carried out in the same way as described above, but in the presence of 5 molar equivalents of the azide. The UV–VIS spectra did not show the formation of **1**, which is attributable to the fast reaction of $[Pd_2Cl_2(dppm)_2]$ with the azide. After the photolysis was stopped the reaction mixture was stirred for 25 min. The ^{1}H NMR spectrum was consistent with the presence of two A-frame adducts, **2c** (82%) and **2d** (18%). No azide complex could be observed in the ^{1}H NMR spectrum. If the photolysis was carried out in the presence of 10 molar equivalents of 4-$CH_3C_6H_4SO_2N_3$, nitrene complexes **2b** and **2d** were observed in a ratio of 3 : 2.

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