**Lois Isabella**

# A $[Pd_2Cl_2(\mu\text{-dppm})_2]$ komplex reakciója arénszulfonil-azidokkal. Szerkezeti és kinetikai vizsgálatok

Budapesti Műszaki és Gazdaságtudományi Egyetem,
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Doktori munkám kiindulópontjául az MTA Kémiai Kutatóközpont Kémiai Intézetének Koordinációs Kémiai Osztályán végzett alapkutatások szolgáltak. Célkitűzésünk az volt, hogy palládium-nitrénkomplexeket állítsunk elő, és vizsgáljuk szerkezetüket illetve reaktivitásukat. Kutatómunkánk során egy új reakciót figyeltünk meg, miszerint aromás szulfonil-azidok a $[Pd_2Cl_2(\mu\text{-dppm})_2]$ dimerrel nitrénkomplexeket eredményeznek. Az új vegyületeket spektroszkópiai (IR, NMR) és röntgendiffrakciós módszerekkel jellemeztük. A reakció kinetikai vizsgálata során azt találtuk, hogy az átalakulás elsőrendű mindkét reaktánsra nézve. A sebességi állandók hőmérsékletfüggéséből meghatároztuk a reakció aktiválási paramétereit. Kimutattuk, hogy összefüggés van a tanulmányozott arénszulfonil-azidok egyes szerkezeti jellemzői és reakciókészsége között. Megfigyeltük, hogy *orto*-szubsztituált aromás szulfonil-azidok esetében a reakcióban melléktermékként azidkomplexek keletkeznek. Az izolált azidkomplexekről kimutattuk, hogy azok nem intermedierjei az ugyanabból a szulfonil-azidból származtatható nitrénkomplexeknek. Szerkezeti és kinetikai vizsgálataink alapján javaslatot tettünk a reakció mechanizmusára. Doktori értekezésemet a Budapesti Műszaki és Gazdaságtudományi Egyetem Szervetlen Kémia Tanszékén védtem meg.

Ezúton fejezem ki köszönetemet témavezetőimnek, Dr. Simándi Lászlónak és Dr. Besenyei Gábornak munkám irányításáért és áldozatkész oktató-nevelő munkájukért.

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# Reaction of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ with arenesulfonyl azides. Structural and kinetic studies

Ph.D. thesis

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## Introduction

Organic azides can interact with metal complexes in many different ways. In most cases, as witnessed by numerous reports on this subject, cleavage of the azide moiety takes place. This kind of transformation typically results in the formation of imido (nitrene) complexes with concomitant production of dinitrogen and has been observed with a variety of transition metal complexes. Coordination compounds in which unfragmented azide molecules are bound to metal centres were implicated earlier only in mechanistic considerations. Recently, however, a series of papers have been published, demonstrating that organic azides can actually be stabilized in the coordination sphere of metal ions. Some of these compounds have been identified as intermediates decomposing to the respective imido adducts.

Palladium, and complexes of group 10 metals in general, show only a very week tendency to form nitrene complexes. On the contrary, palladium has remarkable activities in reactions allowing to form C-N bonds, *e.g.* in catalytic carbonylation of nitroarenes to aryl isocyanates. Our interest in nitrene complexes of palladium was initiated by the earlier observations demonstrating that the catalytic carbonylation of certain arenesulfonamide derivatives offers new phosgene-free routes for the industrially important arenesulfonyl isocyanates. It was postulated that palladium nitrene complexes might be involved in these catalytic transformations.

In the course of searching for viable routes to arenesulfonylimido complexes of palladium, we observed that the interaction of palladium dimer **1** with arenesulfonyl azides **2** results in the formation of imido adducts $[Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2Ar)]$, **3** (dppm stands for bis(diphenylphosphino)-methane, Ar designates an aryl group).

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

Tha aim of this work was to give a detailed description of reaction (1) including structural characterization of the products formed and to disclose the kinetics and mechanism of the reaction of arenesulfonyl azides with the dimer $[Pd_2Cl_2(\mu\text{–}dppm)_2]$.

## Experimental and analytical methods

Palladium dimer **1** and the sulfonyl azides were prepared by established procedures. Solvents were of analytical grade and used without further purification. NMR spectra were recorded at 20°C on a Varian Unity Inova spectrometer at 400 MHz ($^1H$), 101 MHz ($^{13}C$) and 162 MHz ($^{31}P$). IR spectra were obtained on a Nicolet 205 FTIR spectrometer on KBr pellets or on $CCl_4$ solutions. UV-Vis spectra were taken on a HP 8453 diode array spectrophotometer using $CH_2Cl_2$ as solvent. The kinetics were monitored at selected wavelengths at 330, 360 and 418 nm. MS-FAB analyses were carried out on a VG ZAB2-SEQ tandem mass spectrometer. For elemental analyses, vacuum dried samples were used (ethanol reflux, *ca.* 0.1 Torr). The determination of the unit cell parameters and intensity data collections were performed on an Enraf-Nonius CAD4 diffractometer.

## Experimental results and discussion

### Synthetic and structural studies

Reaction of the palladium complex $[Pd_2Cl_2(dppm)_2]$, **1**, with arenesulfonyl azides, **2**, results in the formation of novel A-frame adducts $[Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2Ar)]$, **3**. 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 (Ar = **a** - 4-$NO_2C_6H_4$, **b** - 4-$AcC_6H_4$, **c** - 4-$FC_6H_4$, **d** - $C_6H_5$, , **e** - 4-$CH_3C_6H_4$, **f** - 4-$CH_3OC_6H_4$, **g** - 2-naphthyl, **h** - 2-$NO_2C_6H_4$, **i** - ferrocenyl and **j** - 2,4,6-*i*-$Pr_3C_6H_2$). The $^1$H NMR spectra are consistent with the apical position of the arenesulfonylimido moiety by showing the expected doublet/quintet splitting pattern of the methylene hydrogens. 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.

The structural details of the nitrene complexes were determined by crystallographic studies carried out on single crystals of **3g**-**3i**. The molecular structure of **3i** is shown in Fig. 1. As expected, these complexes adopt boat conformations with methylene atoms bent toward the imido ligands occupying the apical position. The short S–N bond distance is a common structural feature of the crystallographically characterized complexes ($d_{S-N}$ = **3g** - 1.541(3) Å; **3h** - 1.556(4) Å; **3i** - 1.565(3) Å and are indicative of extensive $d_\pi$-$p_\pi$ interaction between the sulfur and nitrogen atoms. In solution, however, free rotation about the S–N axis is manifested by the single sharp resonances observed in the $^{31}$P NMR spectra, supporting the equivalence of the four P-nuclei.

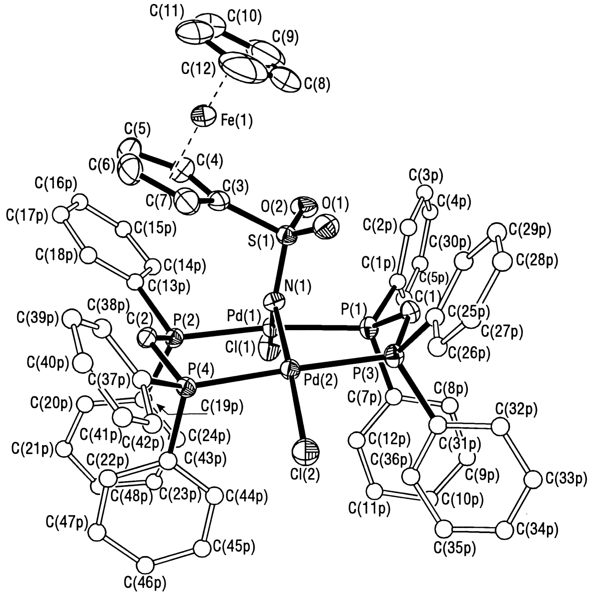

Fig. 1: The molecular structure of $[Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2Fc)]$, **3i**

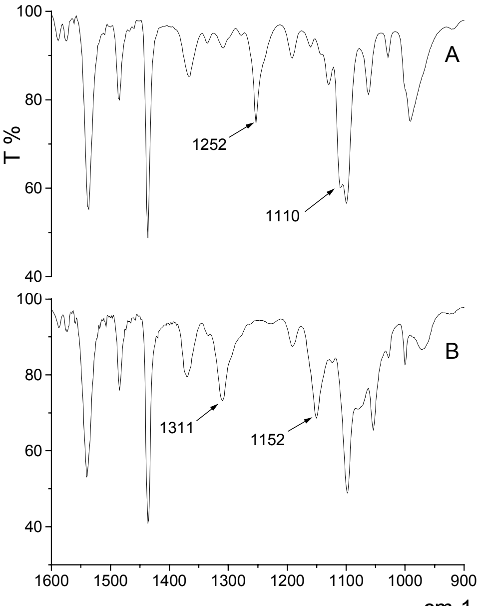

Fig. 2: The IR spectrum of **3h** (**A**) and a 85:15 mixture of **4h** and **3h** (**B**)

Although reaction (1) shows selectivities better than 95 % for most of the sulfonyl azides ($^1$H NMR), we observed a by-product with 2-nitrobenzenesulfonyl azide, which formed in 10-15 %. Our attempts to isolate the by-product in pure form have not been successful, but studies carried out on enriched samples did allow to take an insight into the chemical nature of this constituent.

Curve **A** in Figure 2 shows the IR spectrum of an analytically pure sample of the nitrene complex $[Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2C_6H_4NO_2\text{-}2)]$, **3h**, while curve **B** was recorded on a sample containing the unknown component and **3h** in a molar ratio of *ca* 85:15. Spectra in Figure 2 clearly show that not only the nitrene complex **3h**, but also the by-product contains a sulfonyl group. In the former case, it was characterised by the $\nu$as,$SO_2$ and $\nu$s,$SO_2$ 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. Other peaks did not vary on going from the pure nitrene complex to the mixture containing the unknown component. These observations allow to conclude that the by-product is also a derivative of the palladium dimer and the sulfonyl azide, and both the nitrene complex **3h** and the unknown component exhibit the same basic structural features. An important fact is that the enriched sample has a higher nitrogen content than the nitrene adduct. 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 $[Pd_2Cl_2(dppm)_2(2\text{-}NO_2C_6H_4SO_2N_3)]$, **4h**. The ligation of an unfragmented azide molecule received further support from the observation that irradiation of the solutions of the enriched samples by visible light resulted in the formation of free sulfonyl azide **2h** and **1**. This experiment unequivocally proves that the by-product is an azide complex and its formulation as $[Pd_2Cl_2(dppm)_2(2\text{-}NO_2C_6H_4SO_2N_3)]$ is correct. Experiments with the sterically more hindered 2,4,6-tris(isopropyl)benzenesulfonyl azide, $TipSO_2N_3$, have led to the isolable azide complex $[Pd_2Cl_2(dppm)_2(\mu\text{–}N_3SO_2Tip)]$ whose molecular structure was established crystallographically (see Fig. 3).

## Kinetic and mechanistic studies

The reaction of $[Pd_2Cl_2(dppm)_2]$, **1**, in $CH_2Cl_2$ with arenesulfonyl azides was monitored by UV-vis spectroscopy. Kinetic runs were carried out under pseudo-first-order conditions, using a 10-fold or greater excess of the azide over **1**. The absorbance *vs* time curves showed excellent first-order behaviour, as demonstrated by the log($A$–$A_\infty$) or log($A_\infty$–$A$) vs time plots or Guggenheim plots. Based on the linear dependence of the first-order rate constants ($k_o$) on the concentration of the azide and the dimer, respectively, the rate law is of the form shown by eq (2).

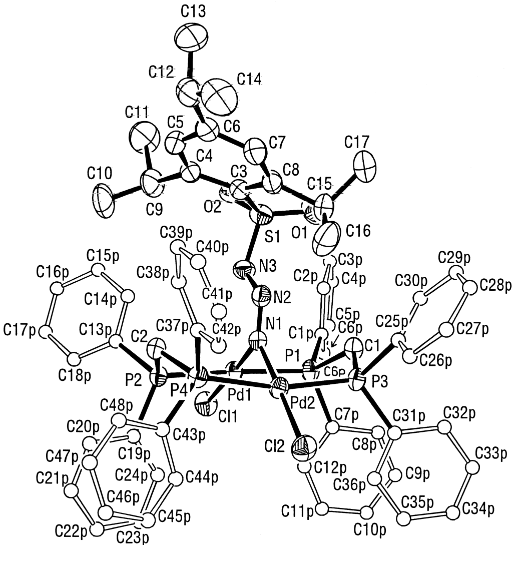

Fig. 3: The molecular structure of $[Pd_2Cl_2(dppm)_2(\mu\text{–}N_3SO_2Tip)]$, **4j**

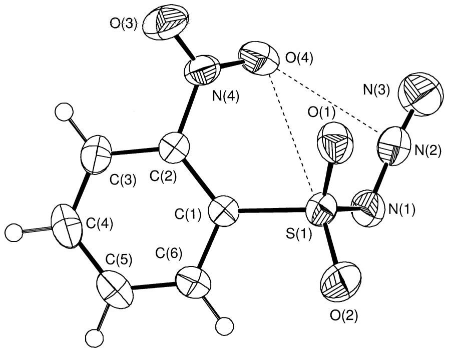

Fig. 4: The molecular structure of 2-nitrobenzenesulfonyl azide, **2h**

$$\text{rate} = k_o[Pd_2Cl_2(dppm)_2] = k[Pd_2Cl_2(dppm)_2][ArSO_2N_3] \quad (2)$$

The temperature dependence of the second-order rate constants was studied in the interval 0-30°C and activation parameters were determined from the Eyring plots (see Table 1). The observed kinetic behaviour and the activation parameters are in line with an associative bimolecular mechanism involving a transition state with relatively small extent of bond-breaking (small $\Delta H^{\ddagger}$) but extensive ordering of the reactants and solvent molecules (large negative $\Delta S^{\ddagger}$).

At a given temperature, the rate constant $k$ increases with increasing electron-withdrawing power of the aromatic substituent. In order to find a relationship between the kinetic behaviour and the structural parameters of the azides, the molecular structures of **2a**, **2b** and **2f** have been determined crystallographically. A comparison of the N–N bond lengths did not reveal, however, any changes that could be ascribed to the electronic nature of the aromatic substituents. The insensitivity of the N–N distances to the electron-withdrawing power of the *para*-substituents was due to the fact that the bond orders of the nitrogen-nitrogen bonds are *ca* 1.5 and 2.5 and, consequently, small alterations of these bond orders induce only changes of the bond lengths that fall into the range of standard deviation of crystallographic data. IR spectroscopy proved to be an indispensable tool for tracing the structural changes induced by the various substituents on the aryl moiety. As is shown by Table 1, both the second-order rate constants and the $\nu_{as}(N_3)$ frequencies increase with increasing electron-withdrawing power (with growing values of Hammett`s σ constants), which demonstrates a clear relationship of the kinetic and structural data. It seems worth mentioning that seemingly negligible structural changes (small Δν values) affect the reactivity of the azides remarkably.

Spectroscopic and kinetic investigations with 2-nitrobenzenesulfonyl azide, **2h**, seem to contradict the conclusions made in conjunction with the *para*-substituted reagents. The $\nu_{as}(N_3)$ band of the most reactive azide (**2a**) shows up at 2131,2 $cm^{-1}$, while the same vibration of **2h** appears at 2147,7 $cm^{-1}$. This remarkably high value is not accompanied, however, with an increased reactivity of **2h** toward **1**, as could be expected from an extrapolation of the spectroscopic and kinetic data. Instead, as demonstrated by our studies, $k(2\text{-}NO_2)$ is about 7 times smaller than $k(4\text{-}NO_2)$.

Table 1: The dependence of the activation parameters, rate constants and the position of the $\nu as,N_3$ band on the electron withdrawing power of X in $4\text{–}XC_6H_4SO_2N_3$

| X | $\Delta H^{\ddagger}$ (kJ $mol^{-1}$) | $\Delta S^{\ddagger}$ (J $mol^{-1}K^{-1}$) | $\Delta G^{\ddagger}$ (kJ $mol^{-1}$) | $k$ at 15°C ($M^{-1}s^{-1}$) | $\nu_{as}(N_3)$ ($cm^{-1}$) | $\sigma_p$ |
|---|---|---|---|---|---|---|
| $NO_2$ | 31.3 | −143 | 74.0 | 0.406 | 2131.2 | 0.81 |
| $CH_3C(O)$ | 32.4 | −152 | 77.5 | 0.104 | 2128.1 | 0,47 |
| F | 38.2 | −138 | 79.0 | 0.044 | 2127.3 | 0.15 |
| H | 32.0 | −164 | 81.0 | 0.026 | 2126.9 | 0 |
| $CH_3$ | 31.6 | −169 | 82.1 | 0.016 | 2125.0 | −0,14 |
| $CH_3O$ | 37.3 | −150 | 82.1 | 0.014 | 2123.8 | −0.28 |

Crystallographic data collected for 2-nitrobenzenesulfonyl azide show that **2h** has extraordinary structural properties that turn it into a rather exceptional example. Steric interactions between the nitro and sulfonyl groups do not allow a coplanar arrangement of the former with the aryl ring. Twisting of the nitro group around the C(2)-N(4) bond (see Fig. 4) opens a route for interactions not available for a nitro group in *para*-position. The O(4) atom carrying partial negative charge seems to be involved in electrostatic attraction with the S(1) and N(2) atoms, both representing the positive ends of their own dipoles. The pronounced shortening of the N-N bonds, that is also reflected by the outstandingly high frequency of the $\nu_{as}(N_3)$ band, is thus ascribed to interactions of the participating sulfonyl, nitro and azide moieties. In the case of **2h,** these combined effects make the azide group more electrophilic than in any other sulfonyl azide studied here. The coincidence of solution (IR) and solid phase structural data allows to conclude that the arrangement of the interacting groups is energetically favourable and the interaction observed in the solid state does not vanish in solution.

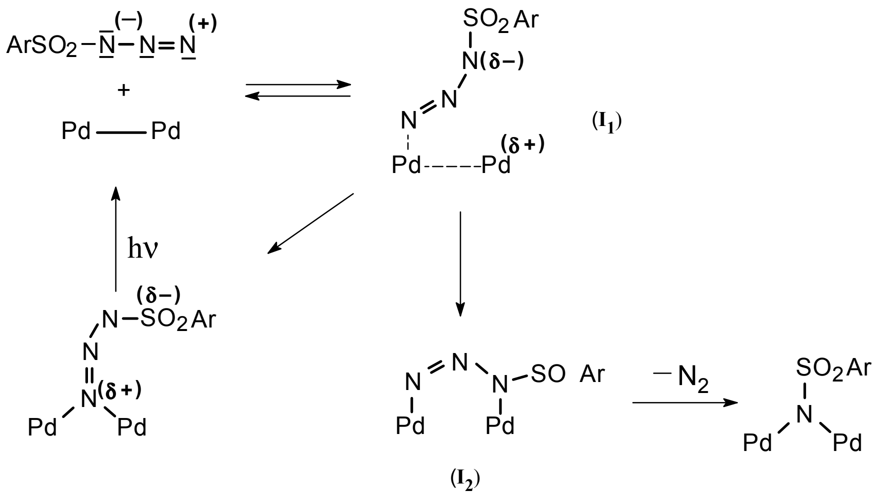

Fig. 5: Mechanistic scheme of the interaction of arenesulfonyl azides with $[Pd_2Cl_2(\mu\text{–}dppm)_2]$ (Pd — Pd stands for **1**)

Although we ascribe most of the structural peculiarities of **2h** to the interactions of the nitro group with the sulfonyl and azide moieties, its decreased reactivity requires further explanation. According to our mechanistic considerations, the formation of the nitrene adduct is preceded by the generation of an azide complex in which both the $\alpha$ and the $\gamma$ nitrogens are coordinated (**I$_2$**) (see Fig. 5). It seems plausible to suppose that a substituent in *ortho*-position brings about additional disadvantageous interactions with the phenyl groups of the dppm ligands and decreases the reaction rate leading to the nitrene complex. The importance of steric effects in the interaction of arenesulfonyl azides with **1** has been documented in the case of 2,4,6-tris(isopropyl) benzene-sulfonyl azide. This compound has proved to be a reagent with which the azide complex **4j** rather than nitrene adduct **3j** is formed as major product.

## Summary

The reaction of the dimeric complex, $[Pd_2Cl_2(\mu\text{–}dppm)_2]$, with arenesulfonyl azides, $ArSO_2N_3$, has proved to be a convenient route for the preparation of nitrene complexes of palladium. The new complexes have been characterized by spectroscopic and crystallographic methods. Kinetic investigations support a mechanism involving a transition state with small extent of bond breaking but extensive ordering of the participating molecules. The structural changes induced by the *para*-substituents on the aryl moiety are reflected by the magnitude of the rate constants. *Ortho*-substituents change the chemoselectivity of the reaction and result in the formation of isolable complexes incorporating coordinated arenesulfonyl azide molecules.

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