Inorg. Chem. **1999,** *38,* 3944−3946

Reaction of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ with Arenesulfonyl Azides. Kinetics and Mechanism of Formation of Arenesulfonylimido-Bridged A-Frame Adducts

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Received August 7, 1998

Introduction

Organic azides represent an important source of the RN: moiety and are used in transition metal chemistry for the preparation of metal imido complexes.[1−3] The reaction of a metal−metal bond with an organic azide usually affords complexes with a bridging imido group.[4] Recently, interest has been increasing in the mechanism of reactions between aromatic azides and metal complexes.[5−8]

In our earlier work aimed at the phosgene-free synthesis of arenesulfonylureas, we have found that *N*-chloroarenesulfonamidates can be catalytically carbonylated with CO to arenesulfonyl isocyanates in the presence of palladium(II) complexes.[9−11] These isocyanates are precursors of arenesulfonylureas, representatives of a family of low dose herbicides widely used in plant protection. The mechanism of the N-carbonylation reaction is not known, but palladium sulfonylnitrene complexes may be implicated as possible intermediates.

In a study to elucidate their chemistry, we reacted the dimeric Pd(I) complex $[Pd_2Cl_2(\mu\text{-dppm})_2]$ (**1**), where dppm is bis(diphenylphosphino)methane, with arenesulfonyl azides (**2**). The observed reaction 1 was accompanied with the evolution of N_2, affording a series of novel arenesulfonylnitrene-bridged dinuclear A-frame complexes, $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-NSO}_2Ar)]$ (**3**).[12]

$$\underset{(\mathbf{1})}{[Pd_2Cl_2(\mu\text{-dppm})_2]} + \underset{(\mathbf{2})}{ArSO_2N_3} \rightarrow \underset{(\mathbf{3})}{[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-NSO}_2Ar)]} + N_2 \quad (1)$$

$Ar = (\mathbf{a})\ 4\text{-}CH_3OC_6H_4;\ (\mathbf{b})\ 4\text{-}CH_3C_6H_4;\ (\mathbf{c})\ C_6H_5;$
$(\mathbf{d})\ 4\text{-}FC_6H_4;\ (\mathbf{e})\ 2\text{-}NO_2C_6H_4;\ (\mathbf{f})\ 4\text{-}AcC_6H_4;\ (\mathbf{g})\ 4\text{-}NO_2C_6H_4$

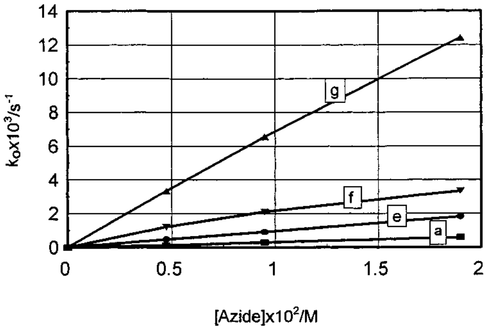

Figure 1. Dependence of the pseudo-first-order rate constant k_o on the $ArSO_2N_3$ concentration. Ar = 4-$MeOC_6H_4$ (**a**), 2-$NO_2C_6H_4$ (**e**), 4-AcC_6H_4 (**f**), 4-$NO_2C_6H_4$ (**g**). Solvent CH_2Cl_2, *T* = 25 °C, $[Pd_2Cl_2(\mu\text{-dppm})_2] = 4.75 \times 10^{-4}$ M.

The scarcity of mechanistic information on the reactions of arenesulfonyl azides with metal complexes prompted us to carry out a kinetic study of reaction 1, which takes place at measurable rates at room temperature with all seven azides.

Experimental Section

$[Pd_2Cl_2(\mu\text{-dppm})_2]$ was synthesized by a known method.[13] Arenesulfonyl azides were prepared by reacting the corresponding arenesulfonyl chlorides with sodium azide in aqueous ethanol.[14] Imido-bridged (nitrene) complexes $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-NSO}_2Ar)]$ (Ar = 4-$CH_3OC_6H_4$, 4-$CH_3C_6H_4$, C_6H_5, 4-FC_6H_4, 2-$NO_2C_6H_4$, 4-AcC_6H_4, 4-$NO_2C_6H_4$) were prepared and analyzed as described previously.[12]

UV−vis spectra were recorded as a function of time on a Hewlett-Packard 8452A diode-array spectrophotometer equipped with a thermostated cell compartment. The kinetics were monitored at selected wavelengths using the sets of spectra obtained.

Results and Discussion

The reaction of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ (**1**) in CH_2Cl_2 with arenesulfonyl azides **2a**−**g** was monitored by UV−vis spectroscopy. The typical time evolution of the spectra is shown in the Supporting Information (S2) for the reaction of **1** with a 40-fold excess of tosyl azide (**2b**) at 25 °C. The appearance of sharp, well-defined isosbestic points indicates a single reaction involving the absorbing species. The spectra of the starting Pd dimer **1** and the product nitrene complexes **3a**−**g** are available from independent measurements. The reaction of **1** with the other six arenesulfonyl azides gave analogous spectral changes, with very close similarity between the spectra of the product nitrene complexes. Tosyl and phenylsulfonyl azide (**2b** and **2c**) do not absorb above 300 nm, but the 2- and 4-nitro derivatives (**2e** and **2g**) contribute to the absorbance up to about 400 nm. To avoid excessive absorbance and still have readily measurable rates, certain limitations were imposed on the sulfonyl azide concentrations used in the kinetic runs.

The spectrophotometric measurements gave no indication of any detectable intermediate in the reaction. Solutions of **3** prepared by dissolving the solid product in CH_2Cl_2 are stable.

Kinetic runs were carried out at 330, 360, and 418 nm in CH_2Cl_2 under pseudo-first-order conditions, using a 10-fold or greater excess of the arenesulfonyl azides over **1**. The absor-

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10.1021/ic980937p CCC: $18.00

Table 1. Temperature Dependence of Rate Constant k (in M^{-1} s^{-1}) for the Reaction of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ with Various Arenesulfonyl Azides $ArSO_2N_3$[a]

	Ar						
t/°C	4-$MeOC_6H_4$	4-MeC_6H_4	C_6H_5	4-FC_6H_4	2-$NO_2C_6H_4$	4-AcC_6H_4	4-$NO_2C_6H_4$
35	0.0398						
30	0.0366	0.033	0.0517	0.118	0.123	0.199	
25	0.0289	0.0283	0.0370	0.085	0.096	0.176	0.656
20	0.0183	0.0201		0.061		0.135	0.509
15	0.0140	0.0161	0.0258	0.044	0.058	0.104	0.406
10	0.00948	0.0119		0.032		0.0853	0.281
5		0.0102	0.0162		0.034		0.229
0	0.00702	0.0078	0.0111	0.021	0.0023	0.0445	0.205

[a] Each value is the average of at least six runs reproducible to within ±4%. Individual kinetic measurements were carried out at 3 wavelengths, under pseudo-first-order conditions using various reactant concentrations.

Table 2. Activation Parameters from the Eyring Plot of Rate Constant k (Eq 2) for Reaction 1 (Estimated Errors: $\Delta H^{\ddagger}$, ±2 kJ mol^{-1}; $\Delta S^{\ddagger}$, ±4 J mol^{-1} K^{-1})

2	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1} (25 °C)
4-$CH_3OC_6H_4SO_2N_3$	37.3	−150	82.1
4-$CH_3C_6H_4SO_2N_3$	31.6	−169	82.1
$C_6H_5SO_2N_3$	32.0	−164	81.0
4-$FC_6H_4SO_2N_3$	38.2	−138	79.0
2-$NO_2C_6H_4SO_2N_3$	35.1	−147	78.9
4-$AcC_6H_4SO_2N_3$	32.4	−152	77.5
4-$NO_2C_6H_4SO_2N_3$	31.3	−143	74.0

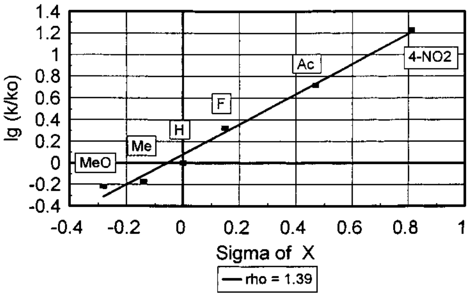


Figure 2. Hammett plot of the relative rate constant for reactions (**1**).

bance vs time curves showed excellent first-order behavior, as demonstrated by the log($A - A_\infty$) or log($A_\infty - A$) vs time plots or Guggenheim plots. The latter were used in slower runs where A_∞ could not be determined with sufficient accuracy. After preliminary tests by plotting all of the A vs time curves were evaluated by fitting with a single-exponential function, and the observed first-order rate constants (k_o) from that source were used as primary data. The value of k_o was independent of the concentration of the Pd dimer for all of the seven systems studied.

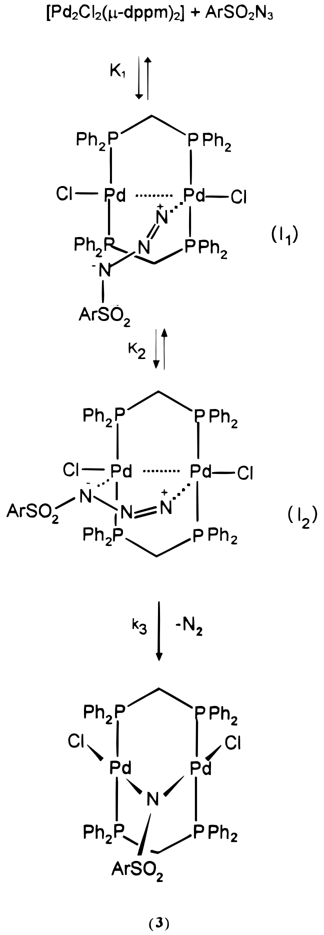
The pseudo-first-order rate constant (k_o) for each azide is proportional to the arenesulfonyl azide concentration (Figure 1 and Supporting Information, S3). Consequently, the rate law is of the form given by eq 2. The reproducibility of k was better

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

than ±3% for each azide, measured at three wavelengths and various reactant concentrations. At 0−15 °C the scatter of k was ±4%.

The temperature dependence of the second-order rate constant k was studied in the interval of 0−30 °C under pseudo-first-order conditions. The second-order rate constants are listed in Table 1 for the different azides. The activation parameters were

Scheme 1



determined from the Eyring plots (Supporting Information, S4) and are listed in Table 2 together with the rate constants at 25 °C.

At a given temperature rate constant k increases with increasing electron-withdrawing power of the aromatic substituent (4-CH_3O < 4-CH_3 < 4-H < 4-F < 2-NO_2 < 4-Ac < 4-NO_2). At 25 °C a factor of about 25 is found upon going from the 4-methoxy to the 4-nitro derivative. The 2-NO_2 derivative is 6 times less reactive than the 4-NO_2 compound, which is apparently due to steric hindrance. The relative reactivities of the 4-substituted benzenesulfonyl azides **2a−d, f, g** obey the Hammett relationship shown in Figure 2. The σ values for the 4-substituents were taken from ref 19. From the

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slope of the straight line a reaction constant of $\rho = 1.39$ has been obtained, suggesting the electrophilic attack of the arenesulfonyl azide on the Pd dimer. The observed kinetic behavior and the activation parameters are consistent with an associative bimolecular mechanism involving a transition state with a relatively small extent of bond-breaking (small $\Delta H^{\ddagger}$) but extensive ordering of the reactants and solvent molecules (large negative $\Delta S^{\ddagger}$). Since the reaction takes place with extrusion of a N_2 molecule from the azide, complex formation between the azide and Pd complex **1** would probably be required before the rate-determining step. A concerted process seems to be unlikely due to the low enthalpies of activation. The lack of detectable complex formation between the reactants still permits preequilibria, producing reactive intermediate(s) in very low concentration. This would be consistent with the high degree of ordering indicated by the large negative activation entropies.

The observed reactivity pattern and activation parameters resemble those reported by Collman et al. for the reaction of organic azides with mononuclear rhodium and iridium halocarbonyl complexes, affording N_2 complexes.[15]

Similarly large negative $\Delta S^{\ddagger}$ values have been reported by James *et al.*[16] for the reaction of **1** with CO, affording A-frame CO adducts. A different picture emerged for the analogous reactions of the corresponding Pt dimer,[17] where positive $\Delta S^{\ddagger}$ pointed to a dissociative process.

The reaction mechanism shown in Scheme 1 accommodates both electrophilic attack by the arenesulfonyl azide and the large negative $\Delta S^{\ddagger}$.

Scheme 1 involves consecutive preequilibria producing intermediates $\mathbf{I_1}$ and $\mathbf{I_2}$, followed by rate-determining expulsion of the N_2 molecule. Accordingly, the observed rate constant of eq 2 can be given as $k = K_1K_2k_3$. In $\mathbf{I_1}$ the azide is terminally bonded to one of the Pd atoms. Cyclic intermediate $\mathbf{I_2}$ is likely to form, by analogy to [2+3] dipolar cycloadditions between organic 1,3-dipolar reagents and dipolarophiles.[18] The large negative entropies of activation are probably associated with the preequilibrium complexation (K_1K_2) in which the highly ordered $\mathbf{I_2}$ is generated. Dinitrogen expulsion directly from $\mathbf{I_1}$ is unlikely since it requires the formation of the free nitrene, which would then have to encounter **1** to produce imido complex **3**. This kind of bond breaking is too energy-demanding to be consistent with the observed low activation enthalpies. The high selectivity of product formation also excludes the involvement of free nitrene.

According to a recent report,[6] PhN_3 adds across a heterobinuclear bond between Zr and Ir in a Cp complex through a μ-phenyl azide intermediate, which can be thermally converted to a bridging imido complex with N_2 extrusion (between 75 and 105 °C, $\Delta H^{\ddagger} = 122$ kJ mol^{-1}).

This suggests that intermediate $\mathbf{I_1}$ may in principle transform to both an arenesulfonyl azide and a nitrene (imido)-bridged complex. Apparently, there are special conditions that permit the formation and detection of an arenesulfonyl azide-bridged Pd dimer. Work is in progress to explore this possibility.

Acknowledgment. This work was supported by the Hungarian Science Foundation (OTKA Grant T16213).

Supporting Information Available: Table of NMR data of compounds **3a**, **3d**, and **3f** and figures showing the time evolution of the UV–vis spectra; dependence of the pseudo-first-order rate constant on the arenesulfonyl azide concentration; typical Eyring plots.

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