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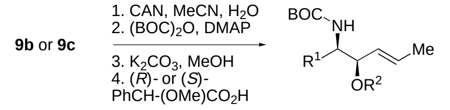

Scheme 8. $R^1 = C_6H_{13}$ or c-C_6H_{11}; R^2 = (*R*)- or (*S*)-PhCH(OMe)CO. CAN = cerium ammonium nitrate, BOC = butoxycarbonyl, DMAP = dimethylaminopyridine.

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Sterically Controlled Pathways in the Reaction of 2,4,6-Tris(isopropyl)benzenesulfonyl Azide and $[Pd_2Cl_2(dppm)_2]$**

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

Organic azides often react with metal complexes with extrusion of N_2, affording imido (nitrene) derivatives.[1] The azide moiety is not necessarily cleaved, however, as illustrated by earlier studies on hydridoosmium and dimeric molybdenum complexes.[2] Several aryl and cyclohexyl azide complexes revealing various modes of coordination have recently been characterized structurally and chemically.[3]

Our previous work on the phosgene-free synthesis of isocyanates has shown that arenesulfonyl azides react with $[Pd_2Cl_2(dppm)_2]$ (**1**, dppm = bis(diphenylphosphanyl)methane), resulting in the formation of arylsulfonylimido A-frame adducts.[4, 5] These novel reactions show good selectivities with most sulfonyl azides, except for the 2-nitro derivative, which gave $[Pd_2Cl_2(dppm)_2(N_3SO_2C_6H_4\text{-}2\text{-}NO_2)]$ as a by-product.[5a] To elucidate the steric effects of azide ligands, we conducted studies with 2,4,6-tris(isopropyl)benzenesulfonyl azide ($TipSO_2N_3$, **2**). The results of these investigations, together with crystallographic data on the parent azide **2**, are presented here.

Reaction of $[Pd_2Cl_2(dppm)_2]$ with **2** affords the azide complex **3** and the nitrene complex **4** in 75 and 25% yield, respectively [Eq. (1); ^1H NMR, see the Experimental Section], involving a very bulky bridging imido ligand. The

$$\begin{gathered}2\,\underset{\mathbf{1}}{[\mathrm{Pd_2Cl_2(dppm)_2}]} + 2\,\underset{\mathbf{2}}{\mathrm{TipSO_2N_3}} \xrightarrow{-\mathrm{N_2}} \\ \underset{\mathbf{3}}{[\mathrm{Pd_2Cl_2(dppm)_2}(\mu,\eta^1\text{-}\mathrm{N_3SO_2Tip})]} + \underset{\mathbf{4}}{[\mathrm{Pd_2Cl_2(dppm)_2}(\mu\text{-}\mathrm{NSO_2Tip})]}\end{gathered} \qquad (1)$$

molecular structures of the complexes formed are shown in Figures 1 and 2. The products are typical A-frame adducts with an extended boat conformation of the $Pd_2P_4C_2$ ring. The Pd–Pd distances are about 0.6 Å longer than in $[Pd_2Br_2(dppm)_2]$, ruling out metal–metal bonding.[6]

The redistribution of valence electrons induced by coordination can be best visualized by comparing bond lengths in free and coordinated sulfonyl azide. Although N3 is disordered in **2** (structure not shown, the numbering corresponds to that of **3**), the short N1–N2 and N2–N3 bonds (1.213(3) and 1.14 Å) indicate multiple bonding, in line with structural data for other sulfonyl azides.[7] Decreased bond orders as a result of complexation are clear from the N2–N3 and N1–N2 distances of 1.248(5) and 1.340(5) Å in **3**. The structural features of **3** are consistent with **2** reacting as a 1,3-dipole ($Ar{-}SO_2{-}N^-{-}N{=}N^+$), producing a zwitterionic structure with the negative charge delocalized on the N1–N2 and N1–S1 bonds. The azide-to-sulfonyl electron transfer shortens the

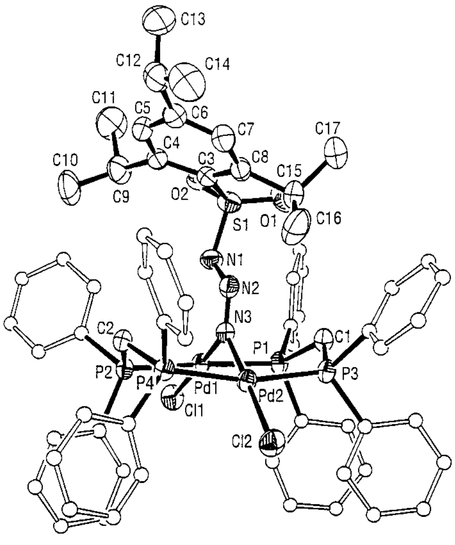

Figure 1. Molecular structure of **3** without hydrogen atoms. Selected interatomic distances [Å] and angles [°]: Pd1···Pd2 3.315(1), Pd1-N3 1.984(4), Pd2-N3 1.972(4), N2-N3 1.248(5), N1-N2 1.340(5), N1-S1 1.627(4), S1-C3 1.808(5), S1-O_{av} 1.437; Pd1-N3-Pd2 113.8(2), Pd1-N3-N2 126.0(3), Pd2-N3-N2 120.2(3), N1-N2-N3 114.7(4); C–H···O close contacts: H9···O2 2.325, C9–H9···O2 114.4, H15···O1 2.205, C15–H15···O1 125.2.

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[*] Dr. G. Besenyei, Prof. L. Párkányi, I. Foch, Prof. L. I. Simándi
Chemical Research Center
Institute of Chemistry
P.O. Box 17, 1525 Budapest (Hungary)
Fax: (+36) 1-325-7554
E-mail: besenyei@cric.chemres.hu

[**] dppm = bis(diphenylphosphanyl)methane. This work was supported by the Hungarian Research Fund (OTKA grant 16213).

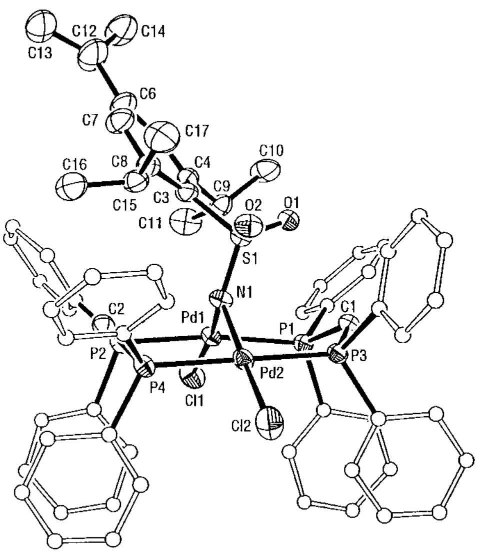

Figure 2. Molecular structure of **4** without hydrogen atoms. Selected interatomic distances [Å] and angles [°]: Pd1 ··· Pd2 3.268(1), Pd1-N1 2.010(2), Pd2-N1 2.039(2), N1-S1 1.579(2), S1-C3 1.810(3), S1-O_{av} 1.451; Pd1-N1-Pd2 107.7(1), Pd1-N1-S1 126.5(1), Pd2-N1-S1 119.3(1); C–H ··· O close contacts: H9 ··· O1 2.334, C9–H9 ··· O1 113.5, H15 ··· O2 2.248, C15–H15 ··· O2 118.2.

N1–S1 distance (**2**: 1.728(2), **3**: 1.627(4) Å) and lengthens the S1–C bond (**2**: 1.773(2), **3**: 1.808(5) Å). Spectroscopic data for **3** and the azide adduct derived from $2\text{-}NO_2C_6H_4SO_2N_3$ suggest that the coordination modes of the azide ligands in these complexes are identical.[5a)]]

Comparison of bonding within the N_3 unit in **3** and in other azide adducts of known structures reveals a variety of metal–azide interactions. The most significant structural discrepancy can be observed with the V and Ta complexes, where the N–N bond close to the metal center is longer than that near the aromatic ring.[3a,b]

^{1}H NMR spectroscopy gives an azide-to-nitrene product ratio (**3**:**4**) of about 3:1. For $2\text{-}NO_2C_6H_4SO_2N_3$, about 15% azide complex was detected, but with other sulfonyl azides only the nitrene complex was observed in the raw reaction mixtures. This implies that the azide and imido adducts have a common intermediate, which, under sterically favorable conditions, collapses to the nitrene complex.[5a] Owing to repulsive interactions of the *ortho* substituents with the phenyl groups, this intermediate may be stabilized by μ,η^1 bridging of the Pd atoms. It seems plausible that the bulkiness of the isopropyl groups leads to the predominant formation of the azide adduct **3**.

The important steric effect of the *o*-isopropyl groups is apparent from the unusual ^{1}H NMR spectrum of **4**. The methylene protons of **4** appear as four separate resonances, in contrast with the doublet/quintet multiplicity observed in other sulfonylimido adducts.[5a] Variable-temperature NMR spectra in $CDBr_3$ show that rotation around the S–N axis is feasible, but the expected coalescence of methylene resonances does not occur up to 125 °C. These spectra clearly indicate that rotation of the isopropyl groups about the C4–C9 and C8–C15 bonds is also hindered. Of the three methyl doublets, the resonance at $\delta = 0.72$ can be attributed to the methyl groups of the *o*-isopropyl groups pointing toward the sulfonyl moiety. The upfield shift of the signals for the other pair of methyl groups to $\delta = 0.21$ can be ascribed to the anisotropic effect of equatorial phenyl moieties. Although the resonances at $\delta = 0.72$ and 0.21 tend to merge upon warming of the sample, the coalescence temperature is again higher than 125 °C. Presumably, steric hindrance by the *o*-isopropyl groups makes an intermediate unfavorable in which both the γ- and α-nitrogen atoms are coordinated, the obvious prerequisite for azide group cleavage. Thus, **3** is the major product from **2**.[2b, 3c, 8]

The sensitivity of **3** to light in both the solid state and in solution requires exclusion of sunlight during manipulations. However, **3** is surprisingly stable in the dark: Its UV/Vis spectrum in CH_2Cl_2 does not change over a period of 22 h at room temperature. Also, **3** remained unchanged overnight when the solution contained five equivalents of 4-nitrobenzenesulfonyl azide, ruling out thermal equilibration with its constituents **1** and **2** (should any free **1** form by thermal dissociation, reaction with $4\text{-}NO_2C_6H_4SO_2N_3$, the most reactive sulfonyl azide studied, would immediately generate the corresponding nitrene complex). Although full conversion of **1** with **2** does occur over a period of about three days, the thermal stability of **3** seems to warrant the conclusion that it is not an intermediate along the reaction path leading to nitrene adduct **4**.

Experimental Section

Reaction of $[Pd_2Cl_2(dppm)_2]$ with **2**: Compounds **1** and **2** were prepared by known procedures.[9, 10] The synthesis and isolation of the azide complex should be carried out under protection from sunlight. A solution of **1** (362 mg, 0.34 mmol) and **2** (290 mg, 0.94 mmol) in CH_2Cl_2 (7 mL) was stirred in a capped Schlenk tube for 4 d at 20–25 °C. Evaporation under vacuum and repeated washing with hexane was followed by column chromatography (Kieselgel 60 F_{254}; CH_2Cl_2/EtOAc 20/1), which resulted in yellow **3** (262 mg) and red **4** (84 mg), the latter being eluted first.

3: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.72$ (d, 12H, $J = 6.7$ Hz; *o,o'*-*i*Pr), 1.30 (d, 6H, $J = 6.9$ Hz; *p*-*i*Pr), 2.46 (dq, 2H, $J_{HH} = 13.4$, $J_{HP} = 3.0$ Hz; CH_2), 2.84 (dq, 2H, $J_{HH} = 13.4$, $J_{HP} = 5.1$ Hz; CH_2), 2.92 (sept, 1H, $J_{HH} = 6.9$ Hz; *p*-*i*Pr), 4.05 (sept, 2H, $J_{HH} = 6.7$ Hz; *o,o'*-*i*Pr), 6.97 (s, 2H; $iPr_3C_6H_2$), 7.0–8.0 (m, 40H; $P\text{–}C_6H_5$); ^{31}P NMR (162 MHz, $CDCl_3$): AA'BB' spectrum; $\delta_A = 12.7$, $\delta_B = 14.6$; FT-IR (KBr): 1289 (ν_{as}, SO_2), 1144 cm^{-1} (ν_s, SO_2); UV/Vis: λ (ε): 330 (24000), 424 nm (5300).

4: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.21$ (d, 6H, $J = 6.9$ Hz; *o,o'*-*i*Pr), 0.72 (d, 6H, $J = 6.3$ Hz; *o,o'*-*i*Pr), 1.15 (d, 6H, $J = 6.9$ Hz; *p*-*i*Pr), 2.43 (brm, 1H; CH_2), 2.71 (brm, 1H; CH_2), 2.75 (sept, 1H, $J = 6.9$ Hz; *p*-*i*Pr), 3.52 (brm, 1H; CH_2), 4.07 (sept, 2H, $J = 6.6$ Hz; *o,o'*-*i*Pr), 5.93 (brm, 1H; CH_2), 6.66 (s, 2H; $iPr_3C_6H_2$), 6.9–8.1 (m, 40H; $P\text{–}C_6H_5$); ^{31}P NMR (162 MHz, $CDCl_3$): poorly resolved AA'BB'-type multiplet centered at $\delta = 6.4$ and 6.8; FT-IR (KBr): 1217 (ν_{as}, SO_2), 1090 cm^{-1} (ν_s, SO_2).

X-ray structure analyses: Enraf-Nonius CAD4 diffractometer, graphite monochromator, $T = 293(2)$ K. Intensity data were corrected for crystal decay for **2** and **3**. All structures were solved by direct methods; hydrogen atoms were placed at calculated positions. An empirical psi-scan absorption correction was applied to the data in all cases. The structures were refined by anisotropic full matrix refinement on F^2 for all non-hydrogen atoms with all unique reflections. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-132472 (**2**), -132473 (**3**), and -132474 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Selected crystal data: **2** ($C_{15}H_{23}N_3O_2S$): $M_r = 309.42$, colorless prism, monoclinic, space group $P2_1/n$, $a = 5.997(1)$, $b = 21.456(2)$, $c = 13.579(1)$ Å, $\beta = 95.88(1)°$, $V = 1738.0(4)$ Å^3, $Z = 4$. **3**

($C_{65}H_{67}Cl_2N_3O_2P_4Pd_2S \cdot CH_2Cl_2$): $M_r = 1446.78$, yellow prism, triclinic, space group $P\bar{1}$, $a = 13.311(2)$, $b = 14.002(1)$, $c = 19.661(3)$ Å, $\alpha = 95.07(1)$, $\beta = 106.45(2)$, $\gamma = 105.35(1)°$, $V = 3335.8(8)$ Å^3, $Z = 2$. **4** ($C_{65}H_{67}Cl_2NO_2P_4Pd_2S \cdot CH_2Cl_2$): $M_r = 1418.76$, red prism, monoclinic, space group $P2_1/c$, $a = 19.037(1)$, $b = 15.689(1)$, $c = 21.576(2)$ Å, $\beta = 97.92(1)°$, $V = 6382.7(8)$ Å^3, $Z = 4$.

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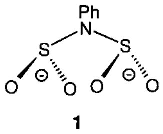
Formation of the Azadisulfite Dianion $[O_2S(\mu\text{-NPh})SO_2]^{2-}$ by Twelvefold Insertion of SO_2 into the Mg–N(Ph) Bonds of $[(thf)MgNPh]_6$**

Justin K. Brask, Tristram Chivers,* and Masood Parvez

The insertion of a sulfur dioxide molecule into a metal–carbon σ bond is a widely studied reaction.[1] For example, SO_2 reacts with organomagnesium reagents to give, upon hydrolysis, sulfinic acids.[1a, 2] The facile insertion of SO_2 into the M–O bonds of the polymeric metal alkoxides $[M(OMe)_2]_n$ (M = Ca, Mg) yields the corresponding methylsulfites.[3] Sulfur dioxide also undergoes insertion into M–NR_2 linkages (e.g., Me_3SnNMe_2).[4] Despite the recent interest in both transition metal[5] and main group imido chemistry,[6–8] the reaction of SO_2 with an "MNR" group has not been reported. Divalent main group imides are normally oligomers, for example the hexagonal prism $[(thf)MgNPh]_6$,[6a] and the outcome of the reaction of these clusters with SO_2 is not readily predictable. Here we describe the generation of the novel azadisulfite anion $[O_2S(\mu\text{-NPh})SO_2]^{2-}$ (**1**) by the reaction of SO_2 with $[(thf)MgNPh]_6$. To our knowledge this is the first report of the double insertion of SO_2 into a single functional group. We also describe the product of the reaction of $[(thf)MgNPh]_6$ with *t*BuNSO, in which the $[(thf)_2MgNPh]_2$ dimer is trapped by cycloaddition with two molecules of *t*BuNSO.



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When SO_2 gas is bubbled into a slurry of $[(thf)MgNPh]_6$[6a] in THF, an immediate reaction occurs to give a yellow solution and, subsequently, a pale yellow precipitate. The product **2** is insoluble in diethyl ether, *n*-hexane, and *n*-pentane, sparingly soluble in THF and toluene, but soluble in benzene. Elemental analyses and $^1H/^{13}C$ NMR spectra of **2** are consistent with the retention of the 1:1 ratio of THF:Ph ligands and the uptake of two SO_2 molecules per MgNPh unit. The X-ray crystal structure analysis[9] of **2** confirmed these conclusions and revealed that a hexameric arrangement is maintained (Figure 1).

$[(thf)Mg\{O_2S(\mu\text{-NPh})SO_2\}]_6$ **2**

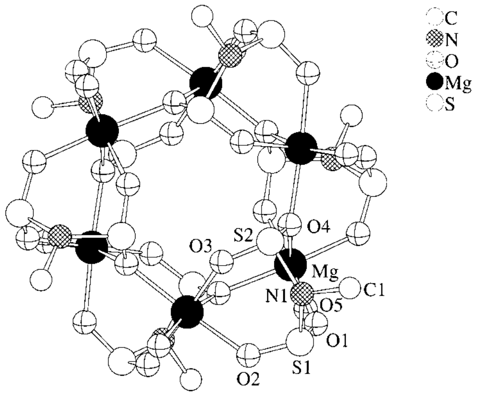

Figure 1. Molecular structure of **2**. For clarity, only the oxygen atoms O5 of the THF molecules and the *ipso*-C atoms of the phenyl groups are shown. Mean values and ranges of bond lengths [Å]: S-O 1.52, 1.479(17)–1.553(16), S-N 1.73, 1.72(2)–1.74(2), Mg-O(λ^2) 2.03, 2.00(2)–2.046(18), Mg-O(λ^3) 2.17, 2.151(18)–2.194(17), Mg-O(THF) 2.068(17).

Complex **2** contains a 48-atom $Mg_6S_{12}N_6O_{24}$ quaternary cluster core with S_6 molecular symmetry. It can be viewed as the result of the insertion of twelve SO_2 molecules into the Mg–NPh bonds of $[(thf)MgNPh]_6$ (Scheme 1), which generates the novel azadisulfite dianion $[O_2S(\mu\text{-NPh})SO_2]^{2-}$ (**1**).[10] Each of these dianions bis-chelates two Mg^{2+} cations, and one oxygen atom exhibits monodentate coordination to a third Mg^{2+} ion. Thus the fundamental building block in the cluster is the adamantane-like $Mg_2S_2O_5N$ unit **3**; each of these units is

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[*] Prof. T. Chivers, J. K. Brask, Dr. M. Parvez
Department of Chemistry
University of Calgary
Calgary, Alberta T2N 1N4 (Canada)
Fax: (+1) 403-289-9488
E-mail: chivers@ucalgary.ca

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