fresh zeolites undoped with aminopropylsilyl groups did not develop the characteristic purple color.

Independently, a piece of thin glass (18 × 18 mm^2) was treated with [3-(2,3-epoxypropoxy)propyl]trimethoxysilane (2 mM) in toluene (10 mL, 110 °C, 1 h) under argon to assemble a layer of 3-(2,3-epoxypropoxy)propylsilyl groups on the glass surface (see Scheme 1 B). The presence of surface-bound terminal epoxy groups attached on the glass was confirmed by pale-red coloration of the surface when treated with an aminated azo dye (Fat Brown RR) at 110 °C in toluene.[14] The UV/Vis spectrum of the glass showed a broad band with the absorption maximum at ≈440 nm. Undoped glasses gave negligible intensities in the ≈440 nm region.

The coated glass plate was inserted into a suspension of 3-aminopropylsilyl-coated zeolite powders in toluene (0.1 g, 10 mL) and the mixture was refluxed (> 1 h) under argon (see Scheme 1 C). The zeolite-coated opaque glass was then removed from the reaction mixture and washed extensively with toluene. The zeolite-coated glass was subsequently sonicated in toluene for 20 s to remove physisorbed zeolite crystals on the chemically bound first layer.

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[1] a) S. Feng, T. Bein, *Nature* **1994**, *368*, 834–836; b) S. Feng, T. Bein, *Science* **1994**, *265*, 1839–1841.

[2] a) A. Gouzinis, M. Tsapatsis, *Chem. Mater.* **1998**, *10*, 2497–2504; b) L. C. Boudreau, J. A. Kuck, M. Tsapatsis, *J. Membr. Sci.* **1999**, *152*, 41–59, and references therein.

[3] S. Mintova, J. Hedlund, B. Schoeman, V. Valtchev, J. Sterte, *Chem. Commun.* **1997**, 15–16.

[4] a) G. Clet, J. C. Jansen, H. van Bekkum, *Chem. Mater.* **1999**, *11*, 1696–1702; b) N. van der Puil, F. M. Dautzenberg, H. van Bekkum, J. C. Jansen, *Microporous Mesoporous Mater.* **1999**, *27*, 95–106, and references therein.

[5] a) T. Munoz, Jr., K. J. Balkus, Jr., *Chem. Mater.* **1998**, *10*, 4114–4122; b) T. Munoz, Jr., K. J. Balkus, Jr., *J. Am. Chem. Soc.* **1999**, *121*, 139–146.

[6] a) Y. Yan, T. Bein, *J. Am. Chem. Soc.* **1995**, *117*, 9990–9994; b) Y. Yan, T. Bein, *J. Phys. Chem.* **1992**, *96*, 9387–9393; c) T. Bein, *Chem. Mater.* **1996**, *8*, 1636–1653.

[7] Z. Li, C. Lai, T. E. Mallouk, *Inorg. Chem.* **1989**, *28*, 178–182.

[8] a) G. A. Ozin, A. Kuperman, A. Stein, *Angew. Chem. Adv. Mater.* **1989**, *101*, 373-390; *Angew. Chem. Int Ed. Engl. Adv. Mater.* **1989**, *28*, 359–376; *Adv. Mater.* **1989**, *1*, 69–86; b) G. A. Ozin, *Adv. Mater.* **1992**, *4*, 612–650.

[9] G. D. Stucky, J. E. MacDougall, *Science* **1990**, *247*, 669–678.

[10] a) J. Caro, G. Finger, J. Kornatowski, *Adv. Mater.* **1992**, *4*, 273–276; b) J. Caro, M. Noack, J. Richter-Mendau, F. Marlow, D. Petersohn, M. Griepentrog, J. Kornatowski, *J. Phys. Chem.* **1993**, *97*, 13685–13690; c) M. Noack, P. Kölsch, D. Venzke, P. Toussaint, J. Caro, *Microporous Mater.* **1994**, *3*, 201–206; d) P. Kölsch, D. Venzke, M. Noack, E. Lieske, P. Toussaint, J. Caro, *Stud. Surf. Sci. Catal.* **1994**, *84*, 1075–1082.

[11] C. Plog, W. Maunz, P. Kurzwei, E. Obermeir, C. Scheibe, *Sens. Actuators* **1995**, *24–25*, 403–406.

[12] Due to this low intensity, this reflection is usually not observed even from the corresponding powder diffraction patterns as noticed in the inset. See: M. M. J. Treacy, J. B. Higgins, R. von Ballmoos, *Collection of Simulated XRD Powder Patterns for Zeolites, 3rd ed.*, International Zeolite Association, Zürich, **1996**, pp. 500–503.

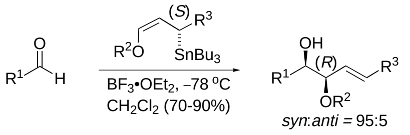
[13] a) S. Sheng, J. J. Kraft, S. M. Schuster, *Anal. Biochem.* **1993**, *211*, 242–249; b) P. J. Lamothe, P. G. McCormic, *Anal. Chem.* **1973**, *45*, 1906–1911.

[14] J. D. Godfrey, Jr., E. M. Gordon, D. J. Von Langen, *Tetrahedron Lett.* **1987**, *28*, 1603–1606.

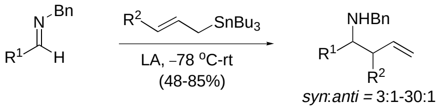
Addition of Enantioenriched γ-Oxygenated Allylic Stannanes to *N*-Acyl Iminium Intermediates: A New Synthesis of *syn*-Amino Alcohol Derivatives**

James A. Marshall,* Kevin Gill, and Boris M. Seletsky

Some years ago we discovered a facile route to monoprotected *syn*-1,2-diol derivatives through BF_3-promoted addition of enantioenriched γ-oxygenated allylic stannanes to aldehydes (Scheme 1).[1] We had hoped to extend these additions to imines, along the lines reported by Keck and Enholm (Scheme 2),[2] but were unsuccessful in these attempts. No detectable β-amino ether adducts were formed, even at room temperature. We attributed these failures to the lower reactivity of oxygenated allylic stannanes relative to their nonoxygenated allyl and crotyl counterparts.[3]



Scheme 1. A facile route to monoprotected *syn*-1,2-diol derivatives. R^1 = alkyl, alkenyl; R^2 = methoxymethyl (MOM), tributylsilyl (TBS), benzyloxymethyl (BOM); R^3 = alkyl.



Scheme 2. Addition of allylic stannanes to imines. R^1 = *c*-C_6H_{11}, Ph, *s*Bu, *i*Pr; R^2 = H, Me; Lewis acid LA = $BF_3 \cdot OEt_2$, $TiCl_4$. Bn = benzyl, rt = room temperature.

A report by Yamamoto and Schmid, describing the addition of a γ-OMOM allylic stannane to several *N*-acyliminium intermediates from Hiemstra and Speckamp[4] (Scheme 3), prompted our examination of this alternative route to β-amino alcohol derivatives.[5] In fact, addition of the racemic (*Z*)-γ-oxygenated allylic stannanes **2a** and **2b**[1] to the *N*-acyliminium precursor **1**, derived from isovaleraldehyde,[5] proceeded in high yield to afford the desired adducts (Table 1). Unfortunately, a mixture of *syn* and *anti* isomers **3** and **4** was obtained from these additions.

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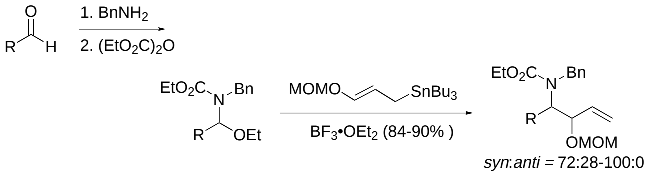
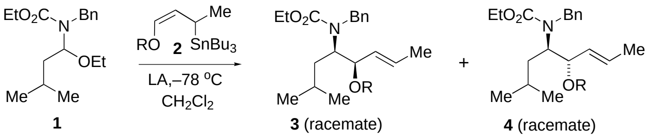


Scheme 3. Addition of γ-OMOM allylic stannanes to *N*-acyliminium intermediates. R = *i*Pr, *i*Bu.

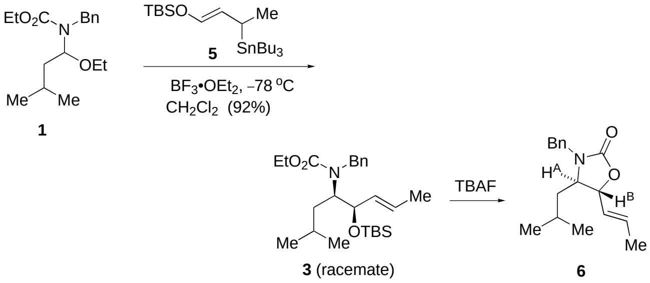
Table 1. Additions of racemic allylic stannanes **2** to **1**, the *N*-benzyl-*N*-carbethoxyiminium salt of isovaleraldehyde.



R	LA	Yield [%][a]	**3**:**4**
TBS (**2a**)	BF$_3$·OEt$_2$	72	86:14
MOM (**2b**)	BF$_3$·OEt$_2$	72	84:16
MOM (**2b**)	BF$_3$·OEt$_2$	92[b]	84:16
MOM (**2b**)	TiCl$_4$	82	86:14

[a] Yield of **3** and **4**. [b] Lewis acid added to premixed stannane and carbamate.

Interestingly, the racemic (*E*)-γ-OTBS allylic stannane **5** afforded only the *syn* adduct **3** when treated with the ethoxy carbamate **1** (Scheme 4).[6] The relative stereochemistry of this adduct is assigned by analogy with related additions to aldehydes and in consideration of the coupling constant ($J_{A,B}$ = 5.9 Hz)[7] of the indicated *trans*-oxazolidinone protons of **6**,[5] into which **3** is readily converted. While this result was encouraging, it failed to meet our needs for a route to enantioenriched amino alcohol adducts, as we have not yet been able to devise a synthesis of enantioenriched (*E*)-γ-oxygenated allylic stannanes such as **5**.

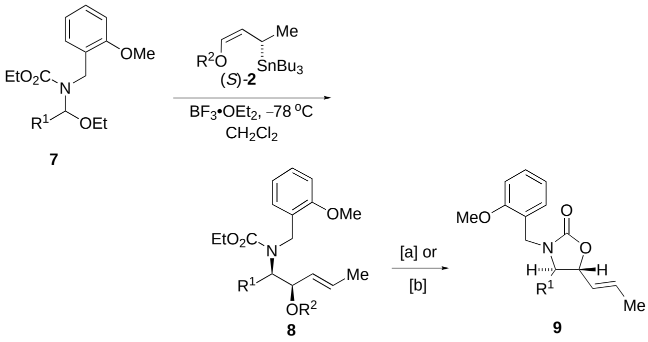


Scheme 4. Reaction of (*E*)-γ-OTBS allylic stannane **5** with ethoxy carbamate **1**. For product **6**, $J_{A,B}$ = 5.9 Hz. TBAF = tetrabutylammonium fluoride.

We next examined additions of the racemic (*Z*)-γ-OTBS allylic stannane **2a** to the ethoxy carbamate derived from isovaleraldehyde and (*R*)-α-phenethylamine in the hopes of effecting a kinetic resolution by using a twofold excess of the stannane.[8] The result was a nearly 1:1 mixture of the diastereomeric *syn* adducts and a modest 8% enantioenrichment of the recovered stannane, favoring the *R* enantiomer (*R*)-**2a**. Interestingly, the *syn*:*anti* ratio of the diastereomeric adducts was found to be 98:2, as opposed to 86:14 previously observed with the benzyl analogue **1** of the *N*-α-phenethyl carbamate. Thus it appeared that branching at the benzylic center caused a marked improvement in the diastereoselectivity of the addition.

Supposing that this improvement was the consequence of increased bulk or restricted rotation of the *N*-benzylic group in the *N*-acyliminium intermediate, we examined the *o*-methoxybenzyl derivative **7a** and the enantioenriched (*S*)-γ-silyloxy allylic stannane **2a** (Table 2, entry 1). The results were quite promising: the *syn* adduct **8aa** predominated over the *anti* adduct by over 95:5. The relative stereochemistry of the *syn* adduct was confirmed through its one-step conversion into the *trans*-oxazolidinone **9a**.[5] The OMOM adduct **8ab** afforded the identical oxazolidinone (entry 2) by a two-step procedure involving sequential treatment with aqueous acid followed by base. The absolute configuration of the adducts was initially assigned by analogy to the well-studied additions of stannanes **2a** and **2b** to aldehydes.[1]

Table 2. Additions of enantioenriched allylic stannanes (*R*)-**2a** and **2b** to *N*-acyliminium salts.

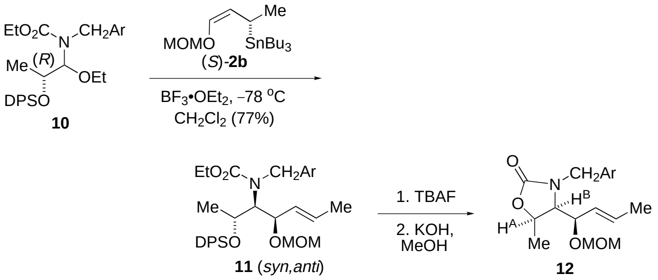


Entry	R¹	R²	Yield [%] **8**	Yield [%] **9**
1	*i*Bu (**7a**)	TBS (**2a**)	90 (**8aa**)	91 (**9a**)
2	*i*Bu (**7a**)	MOM (**2b**)	91 (**8ab**)	88 (**9a**)
3	C$_6$H$_{13}$ (**7b**)	TBS (**2a**)	71[c] (**8ba**)	93 (**9b**)
4	C$_6$H$_{13}$ (**7b**)	MOM (**2b**)	66 (**8bb**)	82 (**9b**)
5	*c*-C$_6$H$_{11}$ (**7c**)	TBS (**2a**)	67[d] (**8ca**)	94 (**9c**)
6	*c*-C$_6$H$_{11}$ (**7c**)	MOM (**2b**)	78 (**8cb**)	72 (**9c**)
7	2-furyl (**7d**)	TBS (**2a**)	73 (**8da**)	94 (**9d**)
8	2-furyl (**7d**)	MOM (**2b**)	65 (**8db**)	decomp.

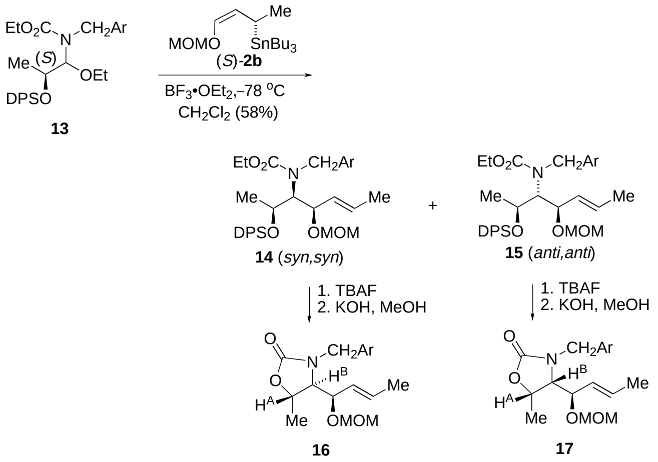
[a] For R² = TBS: TBAF, THF. [b] For R² = MOM: 1. HCl, H$_2$O, THF, 2. KOH, THF, MeOH. [c] R² = H. [d] A mixture was used: 42% of R² = H and 25% of R² = TBS.

Additions to the *N*-acyliminium intermediates from carbamates **7b**–**7d** were equally selective (entries 3–8). The diastereomeric *anti* adducts made up less than 5% of the product, based on GC analysis. This analysis also revealed that the *ee* value of adduct **9a** was over 95%. We were unable to separate the enantiomers of adducts **9b**–**9d** by this technique or by HPLC on several columns. However, we were able to determine *ee* values (>95%) of adducts **9b** and **9c** through removal of the *N*-*o*-methoxybenzyl groups with ceric ammonium nitrate[9] and conversion of the derived oxazolidinones to the *N*-*tert*-butoxycarbonyl (BOC) amino alcohols by addition of (BOC)$_2$O and cleavage of the resulting *N*-BOC oxazolidinones with aqueous K$_2$CO$_3$.[10] The *N*-BOC alcohols obtained through this sequence were analyzed as their *O*-methyl mandelic esters.[11] The ^{1}H NMR spectra of the *R* and *S* derivatives confirmed both the *ee* values (>95%) and the assigned absolute configuration of these compounds.

The matching/mismatching characteristics of the addition were examined with the OMOM allylic stannane (*S*)-**2b**[12] and the *N*-(*o*-methoxybenzyl)carbamates **10** and **13** derived from the DPS ether derivatives of (*R*)- and (*S*)-lactic aldehyde (Schemes 5 and 6; DPS = Si*t*BuPh$_2$).[13] As expected from analogous additions to aldehydes,[1] the *R*/*S* combination is the matched pairing and affords the *syn*,*anti* adduct **11** as the exclusive product (Scheme 5). The *S*/*S* combination led to a 60:40 mixture of the *syn*,*syn* and *anti*,*anti* adducts **14** and **15** (Scheme 6). The relative stereochemistry of these adducts was confirmed through ^{1}H NMR analysis of the derived oxazolidinones **12**, **16**, and **17**. The observed diastereoselectivity is consistent with a preferred antiperiplanar acyclic transition state (Scheme 7).

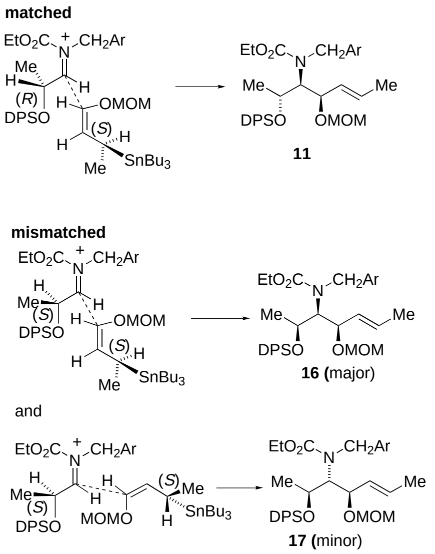


Scheme 5. Reaction of **2b** with **10**. For product **12**, $J_{A,B} = 7.2$ Hz. Ar = *o*-MeOC$_6$H$_4$.



Scheme 6. Reaction of **2b** with **13**. Adducts **14** and **15** are formed as a 60:40 mixture. For product **16**, $J_{A,B} = 3.6$ Hz. For product **17**, $J_{A,B} = 7.5$ Hz. Ar = *o*-MeOC$_6$H$_4$.

The present findings extend the utility of nonracemic γ-oxygenated allylic stannanes to the preparation of enantioenriched *syn*-β-amino alcohol derivatives.[14] These products are potential precursors of α-amino-β-hydroxy acids, β-amino-α-hydroxy acids, amino and aza sugars, and related natural products of biological interest.[15] The reason for the unprecedented enhanced diastereoselectivity of the *o*-methoxybenzyl derivatives is at present obscure. Neither steric nor electronic factors offer likely explanations, as reactions with the *o*-methyl- or *p*-methoxybenzyl analogues of **7** both gave approximately 80:20 mixtures of *syn* and *anti* adducts. The issue is a complex one and may depend upon *E*/*Z* preferences of the intermediate acyliminium ion.[4] It is also possible that internal hydrogen bonding between the *o*-methoxy oxygen atom and the acidic acyliminiun hydrogen atom gives rise to a rotationally restricted transition state.[16] Further studies with other nucleophilic reagents and *ortho*-substituted benzylic imines are clearly warranted. However, mechanistic rationale aside, the influence of *ortho*-methoxy substitution on diastereoselectivity is unexpected and of significant practical import to the success of the present methodology. It is worth noting that although other routes to enantioenriched β-amino alcohols are known,[17] few proceed with simultaneous creation of a carbon–carbon bond and two contiguous stereogenic centers.[18,19]



Scheme 7. Possible transition states for matched and mismatched pairing of allylic stannane (*S*)-**2a** and the Speckamp iminium intermediates from ODPS-protected lactic aldehyde.

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[1] J. A. Marshall, *Chem. Rev.* **1996**, *97*, 31–47; J. A. Marshall, G. P. Luke, *J. Org. Chem.* **1991**, *56*, 483–485; J. A. Marshall, G. S. Welmaker, *J. Org. Chem.* **1992**, *57*, 7158–7163.

[2] G. E. Keck, E. J. Enholm, *J. Org. Chem.* **1985**, *50*, 146–147.

[3] J. A. Marshall, J. A. Jablonowski, G. S. Welmaker, *J. Org. Chem.* **1996**, *61*, 2904–2907.

[4] H. Hiemstra, W. N. Speckamp, in *Comprehensive Organic Synthesis*, *Vol. 2* (Ed.: B. M. Trost), Pergamon, Oxford, **1991**, pp. 1047–1082.

[5] Y. Yamamoto, M. Schmid, *J. Chem. Soc. Chem. Commun.* **1989**, 1310–1312.

[6] (*E*)-γ-Silyloxy allylic stannanes afford markedly higher *syn*:*anti* ratios of adducts compared to their *Z* isomers in additions to aldehydes: J. A. Marshall, G. S. Welmaker, *J. Org. Chem.* **1992**, *57*, 7158–7163; J. A. Marshall, J. A. Jablonowski, L. M. Elliott, *J. Org. Chem.* **1995**, *60*, 2662–2663.

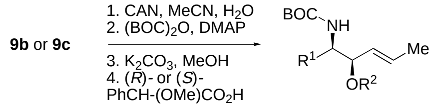
[7] The corresponding *cis*-oxazolidinone derived from the *anti* adduct **4** showed a coupling of 8.0 Hz for these two protons.

[8] Imines of enantioenriched α-phenethylamine afford enantioeniched homoallylic amines upon addition of achiral allylic titanium and boron reagents. These additions proceed by a cyclic transition state: Y. Gao,

F. Sato, *J. Org. Chem.* **1995**, *60*, 8136–8137; K. Watanabe, K. Ito, S. Itsuno, *Tetrahedron*: *Asymmetry* **1995**, *6*, 1531–1534.

[9] H. Kotsuki, T. Araki, A. Miyazaki, M. Iwasaki, P. K. Datta, *Organic Lett.* **1999**, *1*, 499–502

[10]



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.

[11] B. M. Trost, J. L. Belletire, S. Godleski, P. G. McDougal, J. M. Balkovec, J. J. Baldwin, M. E. Christy, G. S. Ponticello, S. L. Varga, J. D. Springer, *J. Org. Chem.* **1986**, *51*, 2370–2374.

[12] J. A. Marshall, A. W. Garofalo, K. W. Hinkle, *Org. Synth.*, in press.

[13] S. K. Massad, L. D. Hawkins, D. C. Baker, *J. Org. Chem.* **1983**, *48*, 5180–5182; S. H. Montgomery, M. C. Pirrung, C. H. Heathcock, *Carbohydr. Res.* ***1990***, *202*, 13–32.

[14] For a recent new approach to the *anti* isomers, see N. A. Petasis, I. A. Zavialov, *J. Am. Chem. Soc.* **1998**, *120*, 11798–11799; review: D. J. Ager, I. Parkash, D. R. Schaad, *Chem. Rev.* **1996**, *96*, 835–875.

[15] For aditional transformations of oxazolidinones related to **9**, see S. Kano, Y. Yuasa, T. Yokomatsu, S. Shibuya, *J. Org. Chem.* **1988**, *53*, 3865–3868.

[16] E. J. Corey, J. J. Rohde, *Tetrahedron Lett.* **1997**, *38*, 37–40.

[17] R. Bloch, *Chem. Rev.* **1998**, *98*, 1407–1438.

[18] S. Kobayashi, H. Ishitani, M. Ueno, *J. Am. Chem. Soc.* **1998**, *120*, 431–432. Both *syn* and *anti* adducts could be prepared but the additions were most effective with aromatic aldehydes.

[19] M. Horikawa, J. Bush-Petersen, E. J. Corey, *Tetrahedron Lett.* **1999**, *40*, 3843–3846. Mixtures of *syn* and *anti* adducts were formed, with *syn* being favored.

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

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

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

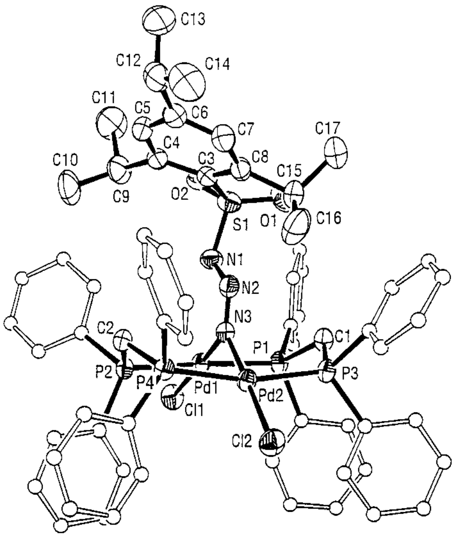


Figure 1. Molecular structure of **3** without hydrogen atoms. Selected interatomic distances [Å] and angles [°]: Pd1 ⋯ Pd2 3.315(1), Pd1-N3 1.984(4), Pd2-N3 1.972(4), N2-N3 1.248(5), N1-N2 1.340(5), N1-S1 1.627(4), S1-C3 1.808(5), S1-O_{av} 1.437; Pd1-N3-Pd2 113.8(2), Pd1-N3-N2 126.0(3), Pd2-N3-N2 120.2(3), 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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