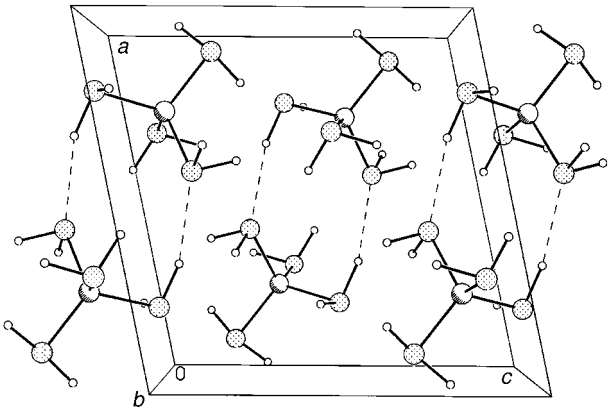


Figure 4. Packing and pair formation of **2** in the crystal.

temperature interval from 8 to 55 K gave no indication of the voluntary formation of a dimer.

Owing to the strongly oxidizing effect of tetravalent germanium, PH_3 and an insoluble yellow solid are formed spontaneously on reaction of $GeCl_4$ with $Li[Al(PH_2)_4]$ in ethylene glycol dimethyl ether at $-45\,^{\circ}C$. After filtration and removal of PH_3, the clear reaction solution contains only tetraphosphanylgermane (**3**) and triphosphanylgermane ($HGe(PH_2)_3$, **6**) in the ratio 1:2.5, as determined by GC-MS. In the EI mass spectrum of **3**, the molecular ion peak is at $m/z = 206$ with a relative intensity of 10% and a correct isotope distribution. The new compounds **2**, **3**, and **6** are indeed thermolabile single-source precursors for CVD processes. They react at the relatively low temperature of 80 °C under cleavage of PH_3 to readily form Si and Ge phosphides. We will report on these elsewhere.

Experimental Section

2: $SiCl_4$ (11.46 g, 67.4 mmol) was added to a solution of $Li[Al(PH_2)_4]$ (0.25 M, 75 mmol) in tetraethylene glycol dimethyl ether (300 mL) at $-30\,^{\circ}C$ over a period of 10 min under continuous stirring. The solution turned orange. The volatile components (PH_3, $HSi(PH_2)_3$, and **2**) were removed under vacuum (10^{-3} Torr) at 20 °C and collected in a cold trap at $-196\,^{\circ}C$. These were then fractionated by condensation in a series of cold traps at -10, -60, and $-196\,^{\circ}C$. Compound **2** was collected in the trap at $-10\,^{\circ}C$, $HSi(PH_2)_3$ at $-60\,^{\circ}C$, and PH_3 at $-196\,^{\circ}C$. Yield: 1.94 g (12.1 mmol, 18%); m.p. $-25\,^{\circ}C$; ^1H NMR (250 MHz, C_6D_6, 25 °C): $\delta =$ 2.04 (dm); ^{31}P NMR (101 MHz, C_6D_6, 25 °C): $\delta = -205.0$ (tm, $^1J(P,H) =$ 185.51, $^2J(P,P) = 14.28$, $^2J(H,H) = 0.37$, $^4J(P,H) = 4.35$ Hz); ^{29}Si NMR (49 MHz, C_6D_6, 25 °C): $\delta = -12.17$ (n of quint, $^1J(Si,P) = 52.5$, $^2J(Si,H) =$ 7.5 Hz); IR (Ar matrix, $-218\,^{\circ}C$): $\tilde{\nu} = 2289$ (vs), 1183 (vs), 840 (w), 721 (m), 633 (m), 566 (w), 478 cm^{-1} (vs); MS (EI): m/z (%): 160 (30) [M^+], 127 (100) [$M^+ - PH_2$], 93 (61) [$SiPH(PH_2)^+$], 61 (17) [$SiPH_2^+$].

3/6: $GeCl_4$ (0.60 g, 2.8 mmol) was added dropwise under stirring to a solution of $Li[Al(PH_2)_4]$ (0.31 M, 3.1 mmol) in ethylene glycol dimethyl ether (10 mL) at $-45\,^{\circ}C$. The release of gas (PH_3) was accompanied by formation of a yellow suspension, which was filtered. According to GC-MS, the clear filtrate contained only **3** and **6** in the ratio 1:2.5. **3**: MS(EI): m/z (%) = 206 (10) [M^+], 173 (100) [$M^+ - PH_2$], 137 (100) [GeP_2H^+], 107 (82) [$GePH^+$], 74 (19) [Ge^+], 67 (19) [$P_2H_3^+$]. **6**: MS(EI): m/z (%): 174 (23) [M^+], 140 (90) [$M^+ - PH_3$], 107 (100) [$M^+ - PH_2PH_3$], 74 (40) [Ge^+].

Received: March 30, 1998 [Z11658IE]
German version: *Angew. Chem.* **1998**, *110*, 2389 – 2391

Keywords: germanium · NMR spectroscopy · phosphorus · silanes · silicon

[1] A. D. Norman, J. *Am. Chem. Soc.* **1968**, *90*, 6556.
[2] M. Baudler, G. Scholz, W. Oehlert, *Z. Naturforsch. B* **1989**, *44*, 627.
[3] A. E. Finholt, C. Helling, V. Imhof, L. Nielsen, E. Jacobsen, *Inorg. Chem.* **1963**, *2*, 504; M. Driess, K. Merz, H. Pritzkow, R. Janoschek, *Angew. Chem.* **1996**, *108*, 2688; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2507.
[4] A. D. Norman, D. C. Wingeleth, *Inorg. Chem.* **1970**, *9*, 98.
[5] The spectrum simulation was carried out with the program Perch, Version 1/96, University of Kuopio (Finland).
[6] A single crystal of **2** was formed in a capillary tube with a diameter of 0.3 mm on a four-circle diffractometer at 242 K by miniaturized zone melting with focused infra-red radiation.[9] **2**: monoclinic, space group $P2_1/c$, $a = 10.659(3)$, $b = 7.137(2)$, $c = 10.832(3)$ Å, $\beta = 101.72(2)^{\circ}$, $V =$ 806.8(4) Å^3, $Z = 4$, $\rho = 1.318$ g cm^{-3}, $\Theta_{max} = 30^{\circ}$; of 2464 measured reflections, 2316 were independent ($R_{merg} = 0.0379$) and 1752 observed ($I > 2\sigma(I)$). The intensities were measured on a Nicolet R3m/V four-circle diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, ω scan, $T =$ 123 K). The structure was solved by direct methods,[10a] and refined with all measured reflections against F^2.[10b] The Si and P atoms were anisotropic, and hydrogen-atom positions were determined from a difference Fourier and refined as riding groups with P–H distances taken from the sum of the covalent radii (1.42 Å) with group isotropic temperature factors. A refinement without imposing certain restrictions led to unreasonably small P–H distances. $R1 = 0.0479$, $wR2 =$ 0.1306 (all data), 50 parameters. Models with higher local symmetry (D_{2d} or S_4) led to significantly higher R values ($R1 > 0.10$). Further details on the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-408423.
[7] GAUSSIAN 94, Revision B.3., M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Oritz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1995**.
[8] Review: W. S. Sheldrick in *The Chemistry of Organic Silicon Compounds* (Eds.: Z. Rappoport, S. Patai), Wiley, New York, **1989**, p. 254.
[9] R. Boese, M. Nussbaumer in *In Situ Crystallisation Techniques in Organic Crystal Chemistry* (Ed.: D. W. Jones), Oxford University Press, Oxford, **1994**, pp. 20 – 37.
[10] a) G. M. Sheldrick, *SHELXS86*, Universität Göttingen, **1986**; b) G. M. Sheldrick, *SHELXL93*, Universität Göttingen, **1993**.

Rate Enhancement of the Radical 1,2-Acyloxy Shift (Surzur – Tanner Rearrangement) by Complexation with Lewis Acids**

Emmanuel Lacôte and Philippe Renaud*

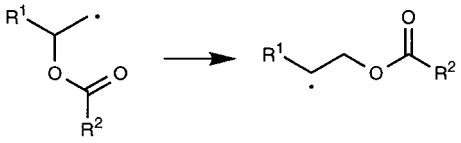
Owing to their mildness and their compatibility with many functional groups, radical reactions have become a very powerful tool for organic synthesis.[1] For instance, unique

[*] Prof. P. Renaud, E. Lacôte
Institut de chimie organique
Université de Fribourg
Pérolles, CH-1700 Fribourg (Switzerland)
Fax: (+41) 263-009-739
E-mail: philippe.renaud@unifr.ch

[**] This work was supported by the fonds national suisse de la recherche scientifique. We thank Prof. H. Zipse for drawing our attention to his calculation results and for helpful suggestions.

  1433-7851/98/3716-2259 $ 17.50+.50/0

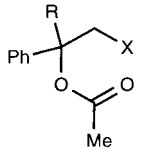
radical rearrangements have found synthetic applications. Among them, the 1,2-acyloxy shift of β-(acyloxy)alkyl radicals (Surzur–Tanner rearrangement, **A** → **B**)) is particularly interesting since it has no equivalent in ionic chemistry.[2] As a



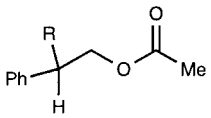
A **B**

consequence, since its discovery by Surzur in 1967[3] and a seminal study by Tanner in 1969,[4] this rearrangement has attracted considerable attention from a mechanistic[5] as well as a synthetic point of view.[6] However, for many β-(acyloxy)alkyl radicals, the rate of rearrangement is too slow for synthetic purposes. Recently, Zipse reported calculations indicating that the rate of the 1,2-acyloxy migration should be enhanced by protic acids.[7] This hypothesis was underlined in a recent review,[2] and Giese has reported that intramolecular protonation of acetate groups may be responsible for the rate acceleration of a closely related fragmentation of α-hydroxy-β-(acetoxy)alkyl radicals.[8] Our experience with Lewis acids in radical reactions[9, 10] led us to investigate their ability to accelerate the rate of the 1,2-acyloxy shift. We report here the first evidence that Lewis acids can efficiently enhance the rate of this rearrangement. This represents, to the best of our knowledge, the first example of a Lewis acid mediated acceleration of a radical rearrangement (with the exception of cyclization reactions).[11]

Our investigation started with the acetate **1**, which has been thoroughly investigated by Beckwith et al.[12] Under standard radical reaction conditions (0.02 M Bu_3SnH, AIBN (azobisisobutyronitrile), refluxing benzene), only the reduced compound **2** could be detected; no rearranged product **3** is observed.[13] Interestingly, in the presence of stoichiometric amounts of Lewis acids such as Et_2AlCl or methylaluminum bis(di-2,6-*tert*-butyl-4-methylphenoxide) (MAD), the migration product **3** was detected. However, the yield was low and poorly reproducible due to Lewis acid induced cationic decomposition of both starting material and products. A reagent less prone to ionization—that is, the secondary benzylic acetate **4**—was chosen next.[14] As anticipated, better yields (up to 76%) were obtained in the presence of Lewis acids, but only the product of direct reduction **5** was observed; no rearranged product **6** was detected.



1 (R = Me, X = Br)
2 (R = Me, X = H)
4 (R = H, X = Br)
5 (R = X = H)



3 (R = Me)
6 (R = H)

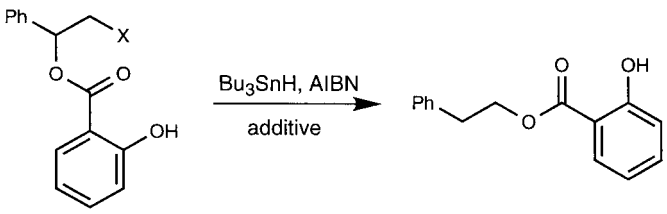
We attribute the inefficiency of the Lewis acids to the presence of only a small amount of complexed radical precursor. To favor the formation of the complex by means of chelation, we decided to use the salicylate **7** instead of the acetate **4** as radical precursor. The results of the radical reactions are reported in Table 1.

Table 1. Radical reduction of **7** with Bu_3SnH in refluxing benzene to provide **8** and **9**. Procedure A: 0.02 M Bu_3SnH; procedure B: Bu_3SnH added over 12 h with a syringe pump.

Entry	Additive[a]	Procedure	Yield [%]	**8**:**9**[b]
1	–	A	88	97:3
2	–	B	78	75:25
3	$MeAl(Op\text{-}Tol)_2$	A	68	62:38
4	$MeAl(Op\text{-}Tol)_2$	B	73	12:88
5	$La(OTf)_3$, NEt_3	A	78	91:9
6	$Yb(OTf)_3$, NEt_3	A	69	95:5
7	$Sc(OTf)_3$, NEt_3	A	75	75:25
8	$Sc(OTf)_3$, DIPA	A	62	76:24
9	$Sc(OTf)_3$, TMEDA	A	66	74:26
10	$Sc(OTf)_3$, quinuclidine	A	86	70:30
11	$Sc(OTf)_3$, 2,6-lutidine	A	71	67:33
12	$Sc(OTf)_3$, 2,6-lutidine	B	76	17:83[c]
13	$Sc(OTf)_3$, 2,6-lutidine (10% cat.)	A	86	98:2
14	$Sc(OTf)_3$, 2,6-lutidine, TEMPO	A	no reaction	–

[a] Tol = tolyl. [b] The ratios were determined by ^1H NMR spectroscopy (360 MHz). [c] 1.0-mmol scale; on a 0.5-mol scale, the ratio was 12:88.

To allow a facile comparison of the additive effects, we used an easily reproducible standard one-pot procedure (A: 0.02 M each Bu_3SnH and **7**). A second procedure (B: 0.02 M **7** and slow addition of Bu_3SnH over 10 h) was used to optimize the



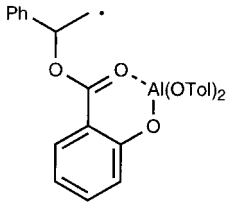
7 (X = Br)
8 (X = H)

9

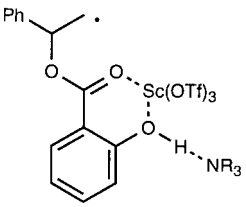
amount of rearranged product **9**. In the absence of Lewis acid, the product of direct reduction **8** was the major product with both procedures (**8**:**9** = 97:3 and 75:25, respectively; entries 1 and 2). Different aluminum Lewis acids were tested, and interesting effects were obtained with methylaluminum bis(4-methylphenoxide). With this additive, the aluminum tris(aryloxide) was formed in situ, as proven by the evolution of methane. With procedure A, the ratio **8**:**9** reached 62:38 (68% yield, entry 3). In contrast, procedure B gave **9** as the major product (**8**:**9** = 12:88, entry 4) without loss of yield. Comparison of entries 1/3 and 2/4 indicates that an approximate 20-fold enhancement in the rate of the rearrangement occurs upon complexation (assuming that the rate of reduction is not influenced by the complexation). Besides aluminum compounds, zinc(II) and magnesium(II) derivatives were investigated; all of them induced a rapid decomposition of the

  1433-7851/98/3716-2260 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **1998**, *37*, No. 16

starting bromide **7**. Trivalent lanthanides[15] which have been applied with success in radical reactions[16] were tested, but only minor effects were noticed (entries 5 and 6). Interestingly, scandium(III) triflate (triflate = trifluoromethanesulfonate (Tf)) was found to be an effective promoter of the rearrangement (entries 7–11). The nature of the coligand proved to be important. Good results were obtained with tertiary amines, but no rate enhancement of the rearrangement was observed with less basic coadditives such as dimethyl sulfoxide (DMSO) and hexamethyl phosphoramide (HMPA). A screening of different amines (entries 7–11; DIPA = diisopropylamine, TMEDA = tetramethylethylenediamine) showed that 2,6-lutidine was the coadditive of choice. By the one-pot procedure, a **8**:**9** ratio of 67:33 (entry 11) was obtained, which is similar to the result observed with methylaluminum bis(4-methylphenoxide) (entry 3). Upon slow addition of Bu_3SnH (procedure B), the major product was the rearranged compound **9** (**8**:**9** = 17:83, entry 12). As expected, stoichiometric amounts of scandium(III) triflate are necessary for the maximum rate enhancement. In the presence of 10 mol% of the Lewis acid, no rate enhancement was perceptible (entry 13). With both scandium(III) triflate and methylaluminum bis(4-methylphenoxide), the presence of a free *ortho*-OH group was necessary for a rate enhancement. Methylation of the phenol fully inhibits the effect of additives.[17] This is in accord with the formation of an aluminum tris(aryloxide) of type **C** or a scandium complex of type **D**. The radical nature of the rearrangement was confirmed by the absence of reaction when 20 mol% of the radical scavenger 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) was used (entry 14).[18]

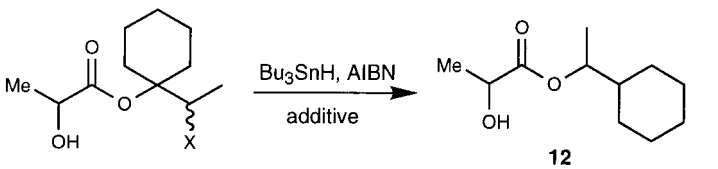


C



D

An even greater increase in the rearrangement rate was observed in the lactate series starting with bromide **10**. In the absence of Lewis acid, the one-pot procedure A furnished exclusively the reduced compound **11** (**11**:**12** ≥ 99:1) in 75% yield. The use of one equivalent of scandium(III) triflate/2,6-lutidine led to preferential formation of the rearranged product **12** (**11**:**12** = 7:93) in 54% yield. This represents an

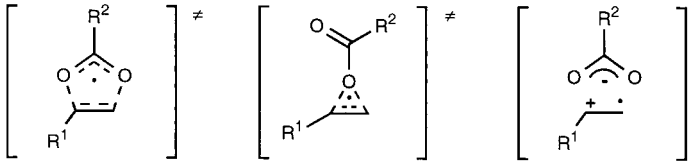


10 (X = Br)
11 (X = H)

no Lewis acid: **11**/**12** ≥99:1
$Sc(OTf)_3$·2,6-lutidine: **11**/**12** 7:93

increase in the reaction rate by three orders of magnitude.[19] Interestingly, under Lewis acidic conditions, it was possible to run the rearrangement at −20 °C (**11**:**12** = 25:75) in 60% yield. This is, to our knowledge, the lowest temperature at which a 1,2-acyloxy shift was observed.[20]

Three mechanisms have been proposed for the acyloxy shift: five-electron five-center shift (**E**), three-electron three-center shift (**F**), and in-cage fragmentation to a carboxylate and an alkene radical cation (**G**).[2] Because of the polarization of the transition states or intermediates **E**–**G**, all three pathways are expected to be favored by complexation with Lewis acids. However, Zipse's recent calculations indicated that the three-center mechanism proceeding via intermediate **F**, which resembles the addition of a carboxylic acid to an olefin radical cation, is favored by protonation of the ester carbonyl group.[7]



E **F** **G**

In conclusion, aluminum and scandium Lewis acid, when used in stoichiometric amounts, can efficiently accelerate the β-(acyloxy)alkyl radical rearrangement. The idea of favoring one mechanism, the three-center shift via **F**, upon complexation is particularly interesting when considering the stereochemical aspect of such rearrangements. Further study of the stereochemical outcome of the reaction, with either chiral substrates or chiral Lewis acids, is under way in our laboratory.

Received: March 2, 1998 [Z11538IE]
German version: *Angew. Chem.* **1998**, *110*, 2369–2371

Keywords: aluminum · Lewis acids · radical reactions · rearrangements · scandium

[1] a) B. Giese, *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*, Pergamon, Oxford, **1988**; b) W. B. Motherwell, D. Crich, *Free Radical Chain Reactions in Organic Synthesis*, Academic Press, London, **1992**; c) D. P. Curran, N. A. Porter, B. Giese, *Stereochemistry of Radical Reactions*, VCH, Weinheim, **1996**.

[2] A. L. J. Beckwith, D. Crich, P. J. Duggan, Q. Yao, *Chem. Rev.* **1997**, *97*, 3273–3312.

[3] J. M. Surzur, P. Teissier, *C. R. Acad. Sci. Fr. Ser. C* **1967**, *264*, 1981–1984.

[4] D. D. Tanner, F. C. P. Law, *J. Am. Chem. Soc.* **1969**, *91*, 7535–7537.

[5] a) L. R. C. Barclay, D. Griller, K. U. Ingold, *J. Am. Chem. Soc.* **1982**, *104*, 4399–4403; b) L. R. C. Barclay, J. Lusztyk, K. U. Ingold, *J. Am. Chem. Soc.* **1984**, *106*, 1793–1796; c) P. Kocovsky, I. Stary, F. Turecek, *Tetrahedron Lett.* **1986**, *27*, 1513–1516; d) H.-G. Korth, R. Sustmann, K. S. Gröninger, M. Leisung, B. Giese, *J. Org. Chem.* **1988**, *53*, 4364–4369; e) A. L. J. Beckwith, P. J. Duggan, *J. Chem. Soc. Perkin Trans. 2* **1992**, 1777–1783; f) A. L. J. Beckwith, P. J. Duggan, *J. Chem. Soc. Perkin Trans. 2* **1993**, 1673–1679; g) D. Crich, F. Filzen, *J. Org. Chem.* **1995**, *60*, 4834–4837; h) A. L. J. Beckwith, P. J. Duggan, *J. Am. Chem. Soc.* **1996**, *118*, 12838–12839; i) H. Zipse, *J. Chem. Soc. Perkin Trans. 2* **1997**, 1797–1800.

[6] a) B. Giese, S. Gilges, K. S. Gröninger, C. Lamberth, T. Witzel, *Liebigs Ann. Chem.* **1988**, 615–617; b) T. Gimisis, G. Ialongo, M. Zamboni, C. Chatgilialoglu, *Tetrahedron Lett.* **1995**, *36*, 6781–6784; c) Y. Itoh, K.

  1433-7851/98/3716-2261 $ 17.50+.50/0

Haraguchi, H. Tanaka, K. Matsumoto, K. T. Nakamura, T. Miyasaka, *Tetrahedron Lett.* **1995**, *36*, 3867 – 3870.
[7] H. Zipse, *J. Am. Chem. Soc.* **1997**, *119*, 1087 – 1093.
[8] S. N. Müller, R. Batra, M. Senn, B. Giese, M. Kisel, O. Shadiro, *J. Am. Chem. Soc.* **1997**, *119*, 2795 – 2803.
[9] a) P. Renaud, P.-A. Carrupt, M. Gerster, K. Schenk, *Tetrahedron Lett.* **1994**, *35*, 1703 – 1706; b) P. Renaud, N. Moufid, L. H. Kuo, D. P. Curran, *J. Org. Chem.* **1994**, *59*, 3547 – 3552; c) P. Renaud, M. Gerster, *J. Am. Chem. Soc.* **1995**, *117*, 6607 – 6608; d) M. Gerster, P. Renaud, *Angew. Chem.* **1996**, *108*, 2523 – 2525; *Angew. Chem. Int. Ed.* **1996**, *35*, 2396 – 2399; e) M. Gerster, L. Audergon, M. Moufid, P. Renaud, *Tetrahedron Lett.* **1996**, *37*, 6335 – 6338; f) A.-R. Fhal, P. Renaud, *Tetrahedron Lett.* **1997**, *38*, 2661 – 2664.
[10] P. Renaud, M. Gerster, *Angew. Chem.* **1998**, *110*, in press; *Angew. Chem. Int. Ed.* **1998**, *37*, in press.
[11] Acceleration of radical cyclizations was recently reported: T. Ooi, Y. Hokke, K. Maruoka, *Angew. Chem.* **1997**, *109*, 1230 – 1231; *Angew. Chem. Int. Ed.* **1997**, *36*, 1181 – 1183. The rate of cyclization of aminyl radicals is also influenced by Lewis acids: C. Hau, O. M. Musa, F. N. Martinez, M. Newcomb, *J. Org. Chem.* **1997**, *62*, 2704 – 2710; for more examples, see reference [10].
[12] A. L. J. Beckwith, C. B. Thomas, *J. Chem. Soc. Perkin Trans. 2* **1973**, 861 – 872.
[13] The product of phenyl migration (neophyl rearrangement) is not observed under these conditions.
[14] Compound **4** was prepared according to the procedure of Beckwith et al.[12] For physical data and elemental analysis, see C. S. Marvel, N. S. Moon, *J. Am. Chem. Soc.* **1940**, *62*, 45 – 49.
[15] S. Kobayashi, *Synlett* **1994**, 689 – 701.
[16] a) M. P. Sibi, C. P. Jasperse, J. Ji, *J. Am. Chem. Soc.* **1995**, *117*, 10779 – 10780; b) M. P. Sibi, J. Ji, *Angew. Chem.* **1996**, *108*, 198 – 200; *Angew. Chem. Int. Ed.* **1996**, *35*, 190 – 192.
[17] In the absence of Lewis acids, the *ortho*-methoxybenzoate rearranged slightly slower (procedure B: the ratio of rearrangement to direct reduction products was 84:16) than the hydroxy-substituted compound **7** (procedure B: the ratio of rearrangement to direct reduction products was 75:25; Table 1, entry 2). This small difference may be attributed to intramolecular protonation.
[18] The hypothesis of an ionic rearrangement followed by a radical reaction was discarded since treatment of **7** with $MeAl(OPh)_2$ or $Sc(OTf)_3$ left the bromide unchanged.
[19] A low diastereoselectivity ($\leq 60\%$ *ds*) was observed.
[20] Most reported 1,2-acyloxy shifts have been conducted at temperatures higher than 60 °C.

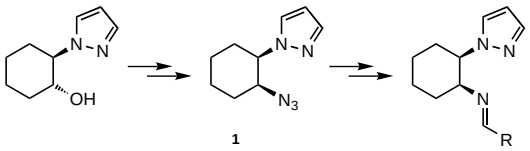
Transition Metal Complexes with Organoazide Ligands: Synthesis, Structural Chemistry, and Reactivity**

Michael Barz, Eberhardt Herdtweck, and Werner R. Thiel*

Organoazides are important starting materials for a multitude of organic reactions,[2] such as in the synthesis of alkylamines from alkyl alcohols or halides ($R{-}X \rightarrow RN_3 \rightarrow R{-}NH_2$) or heterocycles (e.g. [2+3] cycloaddition).[3] The most remarkable aspect in the reactivity of organoazides is the loss of dinitrogen, which can occur thermally, photochemically, or by acid or transition metal catalysis.[4] The highly reactive nitrenes ("R–N") that are generated from the RN_3 fragment, can rearrange to the corresponding imines, insert into C–C bonds, form amines by intra- or intermolecular hydrogen abstraction ("R–N" $\rightarrow R{-}NH_2$), or undergo cycloaddition in the presence of unsaturated substrates (e.g. "R–N" + $C_2H_4 \rightarrow R{-}N(C_2H_4)$).[5]

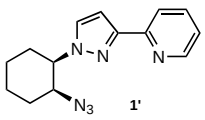
An illustrative example of the stabilization of a "nitrene fragment" at a transition metal center was described by Bergman and Proulx with the reaction of $[Cp_2TaCH_3(PMe_3)]$ with phenylazide, which led to the formation of the tantalum imido complex $[Cp_2TaCH_3(=N{-}C_6H_5)]$.[6] In the intermediate $[Cp_2TaCH_3(N_3{-}C_6H_5)]$, the transition metal center is coordinated by the terminal nitrogen atom (N3) of the azido functionality. This compound was, to our knowledge, the only structurally characterized transition metal complex bearing a RN_3 ligand.[7] This is surprising since many coordination complexes of the azide ion (N_3^-) are known.[8] Here we report the first structurally characterized organoazide complexes, which are coordinated by the alkylated nitrogen atom (N1) to the transition metal center.

For some time we have investigated new chiral chelating ligands for applications in enantioselective catalysis, where the donor centers are linked by 1,2-disubstituted cycloalkanes.[1, 9] The cyclohexaneazide **1** was obtained as a key



1

intermediate during the synthesis of new multidentate imine ligands following this strategy.[9c] Surprisingly, hydrogenation of **1** to the corresponding amine with palladium/charcoal in ethanol proceeds rather slowly, in contrast to the behavior of the analogous pyrazolyl pyridine derivative **1′**.[10] Therefore, investigation of the reactivity of **1** in solution in the presence of transition metal ions like Pd^{II} and Cu^{II}, which are known to be efficient catalysts for the decomposition of organoazides,[4] appeared promising.



1′

Reaction of **1** with $CuCl_2 \cdot 2\,H_2O$ in methanol leads quantitatively to the dinuclear Cu^{II} complex $[\{CuCl_2(\mathbf{1})\}_2]$ (**2**), which is thermally and photochemically (daylight) stable, and crystals suitable for X-ray structure analysis could be obtained by recrystallization from methanol. Reaction of **1** with $[PdCl_2(NCC_6H_5)_2]$ in CH_2Cl_2 gives the Pd^{II} complex $[PdCl_2(\mathbf{1})]$ (**3**) after dissociation of the benzonitrile ligands. In contrast to **2**, **3** is not stable in CH_2Cl_2 and decomposes slowly, even in the absence of light, to yield the amine complex **4**, which is also accessible from the corresponding amine[9c] and $[PdCl_2(NCC_6H_5)_2]$ (Scheme 1).

[*] Priv.-Doz. Dr. W. R. Thiel, Dr. M. Barz, Dr. E. Herdtweck
Anorganisch-chemisches Institut
der Technischen Universität München
Lichtenbergstrasse 4, D-85747 Garching (Germany)
Fax: (+49) 89-28913473
E-mail: thiel@arthur.anorg.chemie.tu-muenchen.de

[**] Ligands with Cycloalkane Backbones, part 7. The authors wish to thank Prof. W. A. Herrmann and the Deutsche Forschungsgemeinschaft for support of this work. Part 6: reference [1]

  1433-7851/98/3716-2262 $ 17.50+.50/0