Experimental Section

A solution of *N*-Pht-*tert*-leucine chloride (1.2 mmol) in CH_2Cl_2 (3 mL) was added at 0°C to a solution of the imine (1 mmol) in CH_2Cl_2 (2 mL). After the mixture was stirred for 30 min at room temperature it was again cooled to 0°C, and the silylketene acetal (1.5 mmol) added. The reaction mixture was stirred and warmed to room temperature over 72 h, then CH_2Cl_2 (10 mL) was added. The solution was then extracted with a 10% $NaHCO_3$ solution (10 mL) and a saturated NaCl solution (10 mL). The organic layer was dried with Na_2SO_4 and the solvent evaporated in vacuo. The products were isolated from the remaining residue by flash chromatography on silica gel with hexane/ethyl acetate mixtures as eluents. For yields and diastereomer ratios see Table 1.

7k: m.p. 146°C; $[\alpha]_D^{22} = -98.5$ ($c = 0.5$ in $CHCl_3$); ^{1}H nmr (500 MHz, $CDCl_3$): $\delta = 0.65$ (s, 3H; CH_3, anisidine), 1.11 (s, 3H; *t*Bu), 1.16 (s, 3H; CH_3), 1.54 (s, 3H; CH_3), 3.60 (s, 3H; OCH_3), 3.67 (s, 3H; OCH_3), 3.95 (s, 3H; OCH_3), 4.34 (s, 1H; αH, *t*Leu), 6.08 (d, $^3J = 8$ Hz, 1H; *o*H, aryl), 6.44 (s, 1H; βH), 6.50 (d, $^3J = 8$ Hz, 2H; *m*H, aryl), 6.71–6.75 (br s, 2H; 3- and 5-H, anisidine), 6.86 (d, $^3J = 8$ Hz, 1H; *o*H, aryl), 7.08 (dd, $^3J_1 = {}^3J_2 = 8$ Hz, 1H; 4-H, anisidine), 7.51 (d, $^3J = 7$ Hz, 1H; *o*H, Pht), 7.61 (ddd, $^3J_1 = {}^3J_2 = 7$ Hz, $^4J = 1$ Hz, 1H, *m*H, Pht), 7.65 (ddd, $^3J_1 = {}^3J_2 = 7$ Hz, $^4J = 1$ Hz, 1H; *m*H, Pht), 7.74 (d, $^3J = 7$ Hz, 1H; *o*H, Pht); ^{13}C nmr (125.8 MHz, $CDCl_3$): $\delta = 17.57$ ($(CH_3)_2C$), 21.34 ($(CH_3)_2C$), 24.40 (CH_3, anisidine), 27.86 (3C, *t*Bu), 37.32 ($(CH_3)_2C$), 50.14 (*t*Bu), 51.69 (OCH_3), 54.69 (OCH_3), 54.92 (OCH_3), 58.41 (β-CH), 65.52 (αCH-*t*Leu), 109.50 (3C, anisidine), 112.27 (*m*-C, aryl), 122.36 (5-C, anisidine), 122.71 (*o*-C, Pht), 122.95 (*o*-C, Pht), 127.11 (1-C, anisidine), 128.29 (6-C, anisidine), 129.12 (*o*-C, aryl), 130.68 (1-C, aryl), 132.29 (C, Pht), 133.53 (*m*-C, Pht), 133.85 (4-C, anisidine), 141.07 (C, Pht), 155.87 (*p*-C, aryl), 158.74 (4-C, anisidine), 166.27 (C(O), *t*Leu), 167.47 (2C, C(O), Pht), 177.21 (CO_2CH_3); HR-MS: calcd for $C_{35}H_{40}N_2O_7$ [M^+] 600.2836; found: 600.2823; elemental analysis calcd for $C_{35}H_{40}N_2O_7$: C 69.98, H 6.71, N 4.66; found: C 69.86, H 6.72, N 4.83.

Received: June 5, 1998
Supplemented version: September 30, 1998 [Z11953IE]
German version: *Angew. Chem.* **1999**, *111*, 166–169

Keywords: amino acids · asymmetric synthesis · chiral auxiliaries · Mannich reaction

[1] a) M. Arend, B. Westermann, N. Risch, *Angew. Chem.* **1998**, *110*, 1096–1122; *Angew. Chem. Int. Ed.* **1998**, *37*, 1044–1070; b) E. F. Kleinmann in *Comprehensive Organic Synthesis, Vol. 2* (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon, Oxford, **1991**, pp. 893–952.

[2] a) S. Krauthäuser, L. A. Christianson, D. R. Powell, S. H. Gellman, *J. Am. Chem. Soc.* **1997**, *119*, 11719–11720; b) D. Seebach, M. Overhand, F. N. M. Kühnle, D. Martioni, L. Oberer, U. Hommel, H. Widmer, *Helv. Chim. Acta* **1996**, *79*, 913–941.

[3] a) D. Enders, D. Ward, J. Arden, G. Raabe, *Angew. Chem.* **1996**, *108*, 1059–1062; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 981–984; b) M. Arend, N. Risch, *Angew. Chem.* **1995**, *107*, 2861–2864; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2861; c) H. Frauenrath, T. Arenz, G. Raabe, M. Zorn, *Angew. Chem.* **1993**, *105*, 74–76; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 83; d) D. A. Evans, F. Urpi, T. C. Somers, J. S. Clark, M. T. Bilodeau, *J. Am. Chem. Soc.* **1990**, *112*, 8215–8216; e) W. Oppolzer, R. Moretti, S. Thomi, *Tetrahedron Lett.* **1989**, *30*, 5603–5606; f) D. Seebach, C. Betschart, M. Schiess, *Helv. Chim Acta* **1984**, *67*, 1593–1597; g) N. Risch, A. Esser, *Liebigs Ann. Chem.* **1992**, *233–237;* h) K. Broadley, S. G. Davies, *Tetrahedron Lett.* **1984**, *25*, 1743–1744; i) W. Oppolzer, P. Schneider, *Helv. Chim. Acta* **1986**, *69*, 1817–1820; j) C. Gennari, I. Venturini, G. Gislon, G. Schimperna, T*etrahedron Lett.* **1987**, *28*, 227–230; k) H. Kunz, W. Pfrengle, *Angew. Chem.* **1989**, *101*, 1041–1042; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1067; l) H. Kunz, D. Schanzenbach, *Angew. Chem.* **1989**, *101*, 1042–1043; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1068; m) H. Waldmann, M. Braun, M. Dräger, *Angew. Chem.* **1990**, *102*, 1445–1447; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1468, n) H. Waldmann, M. Braun, *J. Org. Chem.* **1992**, 57, 4444–4451.

[4] a) E. J. Corey, C. P. Decicco, R. C. Newbold, *Tetrahedron Lett.* **1991**, *32*, 5287–5290; b) K. Ishihara, M. Miyata, K. Hattori, T. Tada, H. Yamamoto, *J. Am. Chem. Soc.* **1994**, *116*, 10520–10524; c) H. Ishitani, M. Ueno, S. Kobayashi, *J. Am. Chem. Soc.* **1997**, *119*, 7153–7154; d) E. Hagiwara, A. Fujii, M. Sodeoka, *J. Am. Chem. Soc.* **1998**, *120*, 2474–2475.

[5] a) J. Sheehan, D. W. Chapman, R. W. Roth, *J. Am. Chem. Soc.* **1952**, *74*, 3822–3825; b) C. R. Mc Arthur, P. M. Worster , A. U. Okon *Synth. Commun.* **1983**, *13*, 311–318.

[6] W. N. Speckamp, H. Hiemstra, *Tetrahedron* **1985**, *41*, 4367–4416.

[7] The crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101780. 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).

[8] H. Waldmann, *Liebigs Ann. Chem.* **1990**, *671–680*, and references therein.

[9] J. O. Osby, M. G. Martin, B. Ganem, *Tetrahedron Lett.* **1984**, *25*, 2093–2096.

[10] W. J. Mc Gahren, J. H. Martin, G. O. Morton, R. T. Hargreaves, R. A. Leese, F. M. Lovell, G. A. Ellestad, E. O'Brien, J. S. E. Holker, *J. Am. Chem. Soc.* **1990**, *102*, 1671–1684.

[11] D. R. Kronenthal, C. Y. Han, M. K. Taylor, *J. Org. Chem.* **1982**, *47*, 2765–2768.

Tetrakis(2,4,6-triisopropylphenyl)diplumbene: A Molecule with a Lead–Lead Double Bond[**]

Martin Stürmann, Wolfgang Saak, Heinrich Marsmann, and Manfred Weidenbruch[*]

Dedicated to Professor Helmut Werner
on the occasion of his 65th birthday

Disilenes, digermenes, and distannenes—compounds with Si=Si, Ge=Ge, and Sn=Sn double bonds—are now well-established molecules, and their properties have been summarized in several review articles.[1, 2] They are usually prepared by the primary generation of the carbene analogues R_2E: (E = Si, Ge, Sn) and subsequent dimerization. Diplumbenes, molecules with a lead–lead double bond, were unknown until now. Furthermore, structurally characterized dialkyl-[3, 4] and diarylplumbylenes (-plumbanediyls)[5, 6] were reported for the first time in the past few years. The latter particles with electron sextets exist both in solution and in the crystal as monomers without noticeable Pb=Pb interactions.

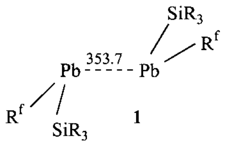
---

[*] Prof. Dr. M. Weidenbruch, Dipl.-Chem. M. Stürmann,
Dipl.-Chem. W. Saak
Fachbereich Chemie der Universität
Carl-von-Ossietzky-Strasse 9–11, D-26111 Oldenburg (Germany)
Fax: (+1) 441-798-3352

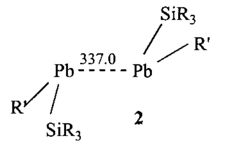
Prof. Dr. H. Marsmann
Fachbereich Chemie der Universität (GH)
Warburger Strasse 100, D-33095 Paderborn (Germany)

[**] Compounds of Germanium, Tin, and Lead. Part 28. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Part 27: M. Weidenbruch, U. Grobecker, W. Saak, E.-M. Peters, K. Peters, *Organometallics* **1998**, *17*, 5206.

A first breakthrough in the field of lead–lead contacts between plumbylene molecules was achieved just recently with the isolation of the heteroleptic plumbylene dimer **1**, which exhibits a Pb–Pb separation of 353.7(1) pm and a *trans* bent angle of the substituents to the Pb–Pb vector of 40.8°.[7] Since intramolecular interactions in **1** between the fluorine atoms of the *ortho*-CF_3 groups and the lead atoms should weaken rather than favor a possible lead–lead bond,[7] we prepared, by the same route, another heteroleptic plumbylene that exists in the solid state as the plumbylene dimer **2**. In comparison to **1**, **2** has a shorter lead–lead separation of 337.0(1) pm and a bending angle of 46.5°.[8] However, the observed lead–lead distances in **2** and especially in **1** are still markedly longer than the value of 295–300 pm calculated for the parent compound $H_2Pb{=}PbH_2$.[7, 9, 10]

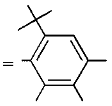


1



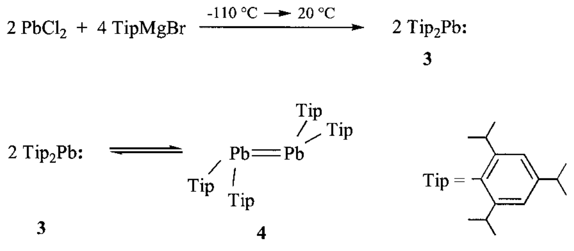
2

SiR$_3$ = Si(SiMe$_3$)$_3$; R^f = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$; R' =



As the choice of substituents seems to be of decisive importance for the formation of a lead–lead double bond, we turned our attention to the 2,4,6-triisopropylphenyl group (Tip), which was previously employed with success not only for the synthesis of the first tetrasilabuta-1,3-diene,[11] but also in the generation of the as yet only distannene that does not dissociate into stannylene molecules in solution.[12] The first attempt to prepare the plumbylene **3** was reported by Okazaki et al. Although these authors were able to demonstrate the existence of this particle in solution up to −40 °C by means of trapping reactions, they were only able to isolate the plumbanes Tip_3PbX (X = Br, I) as solids.[13]

Reaction of the Grignard compound TipMgBr with lead(II) chloride at low temperature furnished a violet solution from which red crystals were isolated by rapid workup (Scheme 1). The product is light- and very air-sensitive and is thermally stable up to 75 °C. Spectral data recorded in the gas phase and in solution supported the presence of the plumbylene **3**, which exists for a short time in solution under strict exclusion of light up to 298 K. However, the absence of a signal in the ^{207}Pb NMR spectra, recorded in the range between $\delta = 0$ and 20000 at 233 and 253 K, as well as the temperature dependence of the ^{13}C NMR signal for the *ipso*-carbon atoms, which exhibits a nonlinear shift to higher field on cooling from 298 ($\delta = 262.4$) to 243 K ($\delta = 236.2$), are suggestive of a possible equilibrium between **3** and the diplumbene **4**.[14]



Scheme 1. Synthesis of **3** and dimerization of **3** to **4**.

An X-ray crystallographic analysis of the red crystals (Figure 1)[15] showed that the diplumbene **4** actually does exist in the solid state. The Pb–Pb bond length of 305.15(3) pm is merely 5 to 10 pm longer than that calculated for $H_2Pb{=}PbH_2$. The folding angles of 43.9° and 51.2° are somewhat smaller than the theoretically calculated values of around 55°.[7, 9, 10] Such deviations, which have also been observed in the distannenes,[2] are possibly due to the replacement of hydrogen atoms in the parent compound by the bulky aryl groups. This may also be the reason for the only moderate torsion of 21.7° about the double bond.

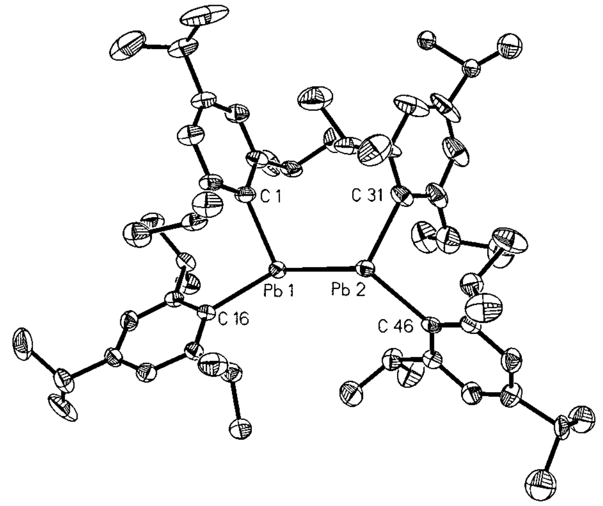


Figure 1. Structure of **4** in the crystal (hydrogen atoms omitted, ellipsoids represent the 50 % probability level). Selected bond lengths [pm] and angles [°]: Pb1–Pb2 305.15(3), Pb1–C1 228.8(5), Pb1–C16 229.3(5), Pb2–C31 230.5(5), Pb2–C46 231.2(5); C1-Pb1-C16 97.8(2), C31-Pb2-C46 102.3(2), C1-Pb1-Pb2 100.5(1), C16-Pb1-Pb2 131.8(2), C31-Pb2-Pb1 99.6(1), C46-Pb2-Pb1 123.5(1).

With the synthesis of compound **4**, homonuclear double bonds between all elements of Group 14 have been realized for the first time. In contrast to C–C double bonds, the bonds between the heavier elements—especially in the case of lead—arise through a double donor–acceptor interaction between the respective doubly occupied 6s orbitals and the empty 6p orbitals of two singlet plumbylene molecules **3** (Figure 2). The low tendency for plumbylenes to undergo dimerization and the weakness of the resultant Pb–Pb double

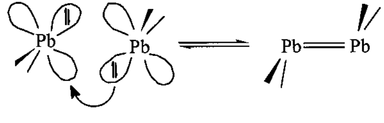


Figure 2. Orbital interactions in the formation of a diplumbene from two singlet plumbylenes.

bond may be due in part to the relativistic contraction of the 6s electron pairs, which are only available for bond formation to a limited extent.[17] Furthermore, this mode of bond formation clearly demonstrates that the lengths of homonuclear double bonds between the heavier elements of Group 14 may well be in the same range as or even larger than the corresponding single bonds.

Experimental Section

At –110 °C solid lead(II) chloride (5.6 g, 20 mmol) was added to a solution of the Grignard reagent TipMgBr, prepared from 1-bromo-2,4,6-triisopropylbenzene (11.44 g, 40.4 mmol) and magnesium (3.0 g, 123 mmol) in THF (100 mL), and the resultant mixture was warmed with vigorous stirring to room temperature within 20 min. The THF solvent was removed by distillation under vacuum, and the residue extracted with *n*-hexane (2 × 50 mL). After separation of the magnesium salts the violet solution was concentrated to a volume of 40 mL and allowed to crystallize at –50 °C. Red crystals (5.8 g, 47 %) of **4** were obtained: m.p. 75 °C (decomp.). Spectroscopic data of **3** in solution: ^{1}H NMR (300 MHz, [D$_8$]toluene, 283 K): $\delta = 1.14$ (d, 24 H, ^3J(H,H) = 6.7 Hz), 1.23 (d, 12 H, ^3J(H,H) = 6.9 Hz, 2.72 (m, 2 H), 2.82 (m, 4 H), 7.68 (s, 4 H); ^{13}C NMR (75 MHz, [D$_8$]toluene, 283 K): $\delta = 24.22$, 24.37, 35.56, 36.28, 128.57, 147.45, 157,45, 255.62 (*ipso*-C, $^1J(^{13}\text{C},^{207}\text{Pb}) = 1100$ Hz at 298 K); MS (CI, isobutane): *m*/*z* (%): 614 (100, M^+); UV/Vis (*n*-hexane): $\lambda_{\max}$ (ε) = 321, 385, 541 nm (960). Elemental analysis of **4** ($C_{60}H_{92}Pb_2$): found (calcd): C 58.57 (58.70), H 7.68 (7.55).

Received: August 26, 1998 [Z12339IE]
German version: *Angew. Chem.* **1999**, *111*, 145–147

Keywords: carbene analogues · lead · main group elements · multiple bonds

---

[1] Reviews of disilenes: R. West, *Angew. Chem.* **1987**, *99*, 1231; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1202; G. Raabe, J. Michl in *The Chemistry of Organic Silicon Compounds, Part 2* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1989**, p. 1015; T. Tsumuraya, S. A. Batcheller, S. Masamune, *Angew. Chem.* **1991**, *103*, 916; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 902; M. Weidenbruch, *Coord. Chem. Rev.* **1994**, *130*, 275; R. Okazaki, R. West in *Multiply Bonded Main Group Metals and Metalloids* (Eds.: R. West, F. G. A. Stone), Academic Press, San Diego, **1996**, p. 232.

[2] Reviews on digermenes and distannenes: K. M. Baines, W. G. Stibbs in *Multiply Bonded Main Group Metals and Metalloids* (Eds.: R. West, F. G. A. Stone), Academic Press, San Diego **1996**, p. 275; M. Driess, H. Grützmacher, *Angew. Chem.* **1996**, *108*, 900; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 827.

[3] $Pb[CH(SiMe_3)_2]_2$: synthesis: P. J. Davidson, M. F. Lappert, *J. Chem. Soc. Chem. Commun.* **1973**, 317; P. J. Davidson, D. H. Harris, M. F. Lappert, *J. Chem. Soc. Dalton Trans.* **1976**, 2268; structure: K. W. Klinkhammer, W. Schwarz, unpublished results. We thank Dr. Klinkhammer for advanced communication.

[4] C. Eaborn, T. Ganicz, P. B. Hitchcock, J. D. Smith, S. E. Sözerli, *Organometallics* **1997**, *16*, 5621.

[5] S. Brooker, J.-K. Buijink, F. T. Edelmann, *Organometallics* **1991**, *10*, 25.

[6] R. S. Simons, L. Pu, M. M. Olmstead, P. P. Power, *Organometallics* **1997**, *16*, 1920.

[7] K. W. Klinkhammer, T. F. Fässler, H. Grützmacher, *Angew. Chem.* **1998**, *110*, 114; *Angew. Chem. Int. Ed.* **1998**, *37*, 124.

[8] M. Stürmann, M. Weidenbruch, K. W. Klinkhammer, F. Lissner, H. Marsmann, *Organometallics* **1998**, *17*, 4425.

[9] G. Trinquier, *J. Am. Chem. Soc.* **1990**, *112*, 2130.

[10] H. Jacobsen, T. Ziegler, *J. Am. Chem. Soc.* **1994**, *116*, 3667.

[11] M. Weidenbruch, S. Willms, W. Saak, G. Henkel, *Angew. Chem.* **1997**, *109*, 2612; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2503.

[12] S. Masamune, L. R. Sita, *J. Am. Chem. Soc.* **1985**, *107*, 6390; A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl, H. Marsmann, *Angew. Chem.* **1991**, *103*, 873 and 978; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 834 and 962; M. Weidenbruch, A. Schäfer, H. Kilian, S. Pohl, W. Saak, H. Marsmann, *Chem. Ber.* **1992**, *125*, 563.

[13] K. Shibata, N. Tokitoh, R. Okazaki, *Tetrahedron Lett.* **1993**, *34*, 1495; N. Tokitoh, N. Kano, K. Shibata, R. Okazaki, *Organometallics* **1995**, *14*, 3121.

[14] Similar observations have been made for the ^{119}Sn signals of the equilibrium $2\,R_2Sn\!: \rightleftharpoons R_2Sn{=}SnR_2$ (R = 2-*t*Bu-4,5,6-Me_3C_6H): M. A. DellaBonna, M. C. Cassani, J. M. Keates, G. A. Lawless, M. F. Lappert, M. Stürmann, M. Weidenbruch, *J. Chem. Soc. Dalton Trans.* **1998**, 1187.

[15] a) Crystal structure analysis of **4**: STOE-IPDS diffractometer, $Mo_{K\alpha}$ radiation, graphite monochromator. The reflections were recorded at 173 K from a shock-cooled crystal with dimensions 1.10 × 0.44 × 0.27 mm^3 under an inert oil to $2\theta_{\max} = 52°$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[16] $C_{60}H_{92}Pb_2$, $M_r = 1227.72$, monoclinic, space group $C2/c$, $Z = 8$, $a = 4755.2(3)$, $b = 1375.24(6)$, $c = 1912.83(9)$ pm, $\beta = 101.155(6)°$, $V = 12273(1) \times 10^6$ pm^3, $\rho_{\text{calcd}} = 1.329$ g cm^{-3}, $\mu = 5.511$ mm^{-1}; of 50232 measured reflections, 11197 were independent and 8498 observed for $I > 2\sigma(I)$. Hydrogen atoms were placed in calculated positions and refined with isotropic temperature factors; all other atoms were refined anisotropically. $R1 = 0.0290$, $wR2 = 0.0729$ (all data) for 553 parameters; max./min. residual electron density 1.070/–0.622 e Å^{-3}. b) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102629. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[16] G. M. Sheldrick, SHELXL-97, Program for crystal structure refinement, Universität Göttingen, Germany, **1997**.

[17] P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563.

[1,3], [3,3], and [3,5] Sigmatropic Rearrangements of Esters Are Pseudopericyclic**

David M. Birney,* Xiaolian Xu, and Sihyun Ham

In 1969 the famous paper by Woodward and Hoffmann describing the conservation of orbital symmetry was published in this journal.[1] All of the well-known rules regarding pericyclic reactions assume that there is a cyclic loop of interacting π orbitals. However, it is possible to have a pericyclic reaction in which this condition is not fulfilled, that is, in which there is *not* cyclic π overlap. The unique characteristics of these "pseudopericyclic" reactions[2] have been described in detail elsewhere;[3] they can be briefly summarized as follows: 1) These reactions have planar transition states, 2) they may have very low barriers if the

---

[*] Dr. D. M. Birney, X. Xu, Dr. S. Ham
Department of Chemistry and Biochemistry
Texas Tech University
Lubbock, TX 79409-1061 (USA)
Fax: (+1) 806-742-1289
E-mail: vddmb@ttu.edu

[**] This work was supported by the Robert A. Welch Foundation.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

1433-7851/99/3801-0189 $ 17.50+.50/0