Experimental Section

2: A solution of $[(OC)_5CrNMe_3]$[14] (0.90 g, 3.60 mmol) and **1**[7] (1.19 g, 2.40 mmol) in toluene (100 mL) was irradiated with a high-pressure Hg lamp (Hereaus TQ 150) at $-30\,^{\circ}C$ for 12 h. The reaction mixture was warmed to ambient temperature, and all volatile materials were removed under high vacuum (0.001 Torr). The brown residue was treated with hexane (50 mL) and the resulting slurry was filtered. The small amount of the remaining dark brown residue was washed with hexane (10 mL). The combined filtrates were concentrated under vacuum to 20 mL and stored at $-80\,^{\circ}C$. After 48 h, **2** (0.31 g, 0.85 mmol, 35.5 %) was obtained as light brown crystals. All NMR spectra were recorded in $[D_6]$benzene at 25 °C. ^1H NMR (500 MHz, TMS): $\delta = 0.14$ (s; $SiMe_3$); ^{11}B NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 92.3$; ^{13}C NMR (126 MHz, TMS): $\delta = 2.6$ ($SiMe_3$), 217.6 (CO_{eq}), 218.0 (CO_{ax}); IR (toluene): $\tilde{\nu} = 2064$ (w), 1981 (m), 1942 (vs) cm^{-1} (CO); elemental analysis (%) calcd for $C_{11}H_{18}CrNBO_5Si_2$: C 36.37, H 5.00, N 3.86; found: C 35.47, H 5.10, N 3.72.

3: A solution of $[(\eta^5\text{-}C_5H_5)Re(CO)_3]$ (0.68 g, 2.02 mmol) and **1** (0.50 g, 1.01 mmol) in hexane (100 mL) was irradiated at $-10\,^{\circ}C$ for five days. The reaction mixture was warmed to ambient temperature and all volatile materials were removed under high vacuum (0.001 Torr). The remaining unconverted $[(\eta^5\text{-}C_5H_5)Re(CO)_3]$ was removed by sublimation (50 °C, 0.001 Torr). The brown residue was treated with hexane (40 mL), filtered, and concentrated under vacuum to 15 mL. After storage at $-80\,^{\circ}C$ for 48 h, a mixture of **3** and the unconverted starting material **1** was obtained. This crystalline material was redissolved in hexane (10 mL) and stored at $-80\,^{\circ}C$ for another 48 h. Pure **3** (0.15 g, 0.19 mmol, 18.9 %) was obtained as light yellow crystals. All NMR spectra were recorded in $[D_6]$benzene at 25 °C. ^1H NMR (500 MHz, TMS): $\delta = 0.35$ (s, 18 H; $SiMe_3$), 4.88 (s, 10 H; C_5H_5); ^{11}B NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 100.4$; ^{13}C NMR (126 MHz, TMS): $\delta = 3.7$ ($SiMe_3$), 86.7 (C_5H_5), 203.5 (CO); MS (eV): m/z (%): 785 (22.7) $[M^+]$, 729 (2.9) $[M^+ - 2\,CO]$, 73 (43.3) $[SiMe_3]$.

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[1] a) P. L. Timms, *J. Am. Chem. Soc.* **1967**, *89*, 1629; b) P. L. Timms, *Acc. Chem. Res.* **1973**, *6*, 118, and references therein.

[2] B. Pachaly, R. West, *Angew. Chem.* **1984**, *96*, 444; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 454.

[3] a) S. M. van der Kerk, P. H. M. Budzelaar, A. L. M. van Beijnen, G. J. M. van der Kerk, *Polyhedron* **1984**, *3*, 271, and references therein; b) A. Meller, *Pure Appl. Chem.* **1991**, *63*, 395.

[4] B. G. Ramsey, D. M. Anjo, *J. Am. Chem. Soc.* **1977**, *99*, 3182.

[5] R. Schlögl, B. Wrackmeyer, *Polyhedron* **1985**, *4*, 885.

[6] a) H. Braunschweig, T. Wagner, *Angew. Chem.* **1995**, *107*, 904–905; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 825; b) H. Braunschweig, B. Ganter, *J. Organomet. Chem.* **1997**, *545*, 163; c) H. Braunschweig, M. Müller, *Chem. Ber.* **1997**, *130*, 1295; d) H. Braunschweig, C. Kollann, U. Englert, *Eur. J. Inorg. Chem.* **1998**, 465; e) H. Braunschweig, C. Kollann, K. W. Klinkhammer, *Eur. J. Inorg. Chem.* **1999**, 1523; f) H. Braunschweig, M. Koster, *J. Organomet. Chem.* **1999**, *588*, 231.

[7] H. Braunschweig, C. Kollann, U. Englert, *Angew. Chem.* **1998**, *110*, 3355; *Angew. Chem. Int. Ed.* **1998**, *37*, 3179.

[8] a) M. Shimoi, S. Ikubo, Y. Kawano, *J. Am. Chem. Soc.* **1998**, *120*, 4222; b) A. H. Cowley, V. Lomelí, A. Voigt, *J. Am. Chem. Soc.* **1998**, *120*, 6401; c) G. J. Irvine, C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, *Angew. Chem.* **2000**, *112*, 978; *Angew. Chem. Int. Ed.* **2000**, *39*, 948.

[9] Crystal structure determination of **2**: $C_{11}H_{18}BCrNO_5Si_2$, Siemens P2(1) diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, graphite monochromator); $T = 173(2)$ K, light brown plates, $0.2 \times 0.1 \times 0.05\ mm^3$, triclinic, space group $P\bar{1}$; $a = 9.135(5)$, $b = 9.201(6)$, $c = 12.002(8)$ Å, $\alpha = 109.17(5)$, $\beta = 97.37(5)$, $\gamma = 102.18(4)^{\circ}$, $V = 909.8(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.326\ g\,cm^{-1}$, $\mu(Mo_{K\alpha}) = 7.75\ cm^{-1}$, $F(000) = 376$, 3392 measured reflections ($1.84 < \theta < 25.00^{\circ}$), $\omega - 2\theta$ scans. The empirical absorption correction provided transmission factors between 0.584 and 0.631. The structure was solved by direct methods; 3172 independent reflections, 2024 with $I > 2\sigma(I)$, $R_{int} = 0.05$, 196 variables. All non-hydrogen atoms were refined with anisotropic displacement parameters, all hydrogen atoms were included as riding (C−H = 98 pm, $U_{iso}(H) = 1.3\ U_{iso}(C)$). $R_F = 0.0590$, $wR_{F^2} = 0.0996$ for reflections with $I > 2\sigma(I)$, $w^{-1} = \sigma^2(F_o)$, GOF = 1.026. 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-158000. 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).

[10] R. Boese, P. Paetzold, A. Tapper, *Chem. Ber.* **1987**, *120*, 1295–1298.

[11] A. W. Ehlers, E. J. Baerends, F. M. Bickelhaupt, U. Radius, *Chem. Eur. J.* **1998**, *4*, 210.

[12] a) J. Uddin, C. Boehme, G. Frenking, *Organometallics* **2000**, *19*, 571; b) C. Boehme, J. Uddin, G. Frenking, *Coord. Chem. Rev.* **2000**, *197*, 249.

[13] H. Braunschweig, M. Colling, unpublished results.

[14] W. Strohmeyer, J. F. Guttenberger, H. Blumenthal, G. Albert, *Chem. Ber.* **1966**, *99*, 3419.

The $[(\eta\text{-}C_6H_5Me)NbSn_6Nb(\eta\text{-}C_6H_5Me)]^{2-}$ Ion: A Complex Containing a Metal-Stabilized $Sn_6^{\ 12-}$ Cyclohexane-Like Zintl Ion[**]

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Homoatomic tin Zintl ions isolated from solution include the *nido*-$Sn_9^{\ 4-}$ ion,[1, 2] the *nido*/*closo*-$Sn_9^{\ 3-}$ ion,[3] and the *closo*-$Sn_5^{\ 2-}$ ion.[4] Metal-stabilized Zintl ions include the *closo*-$Sn_6^{\ 2-}$ ion[5] in $[Sn_6\{Cr(CO)_5\}_6]^{2-}$ and *closo*-$Li_2Sn_8^{\ 4-}$.[6] These structures are characterized by electron-deficient boron hydride like cluster bonding described by Wades rules.[7] Related Ge and Pb Zintl ions also adopt *closo*- and *nido*-structures that are occasionally linked to form dimers or polymers.[8, 9] Although the *inter*cluster connections in the linked polyhedra are frequently two-center, two-electron bonds (2c–2e), the *intra*cluster bonding is always electron deficient.

In contrast, the Group 15 polypnictide Zintl ions are characterized by 2c–2e bonds in which structures are directly related to cyclic hydrocarbons.[10, 11] For the polypnictides, conversion of hydrocarbon-like structures into electron-deficient boron hydride like structures can be accomplished by adding verticies to the clusters that do not contribute electrons to cluster bonding. One such transformation involves the conversion of the nortricyclane-like $Sb_7^{\ 3-}$ cluster into the *nido*-$[Sb_7Ni_3(CO)_3]^{3-}$ complex through the addition of Ni(CO) fragments.[12] By comparison, conversion of the boron hydride like Group 14 Zintl ions into cyclic hydro-

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carbon type structures could, in theory, be achieved by adding extra electrons to the clusters. However, reductions of these anionic clusters are not experimentally feasible because of the unrealistically high charges necessary to reach the correct electron count. Alternatively, coordination of a metal fragment that formally donates its valence electrons to intracluster bonding could provide the necessary electrons while keeping the charge in a reasonable range. Herein we report the first such transformation in which a polystannide is converted into an unusual metal-stabilized cyclohexane-like Sn_6^{12-} Zintl ion in the complex $[(\eta\text{-}C_6H_5Me)NbSn_6Nb(\eta\text{-}C_6H_5Me)]^{2-}$.

$Nb(\eta\text{-}C_6H_5Me)_2$[13, 14] reacts with ethylenediamine (en) solutions of K_4Sn_9 in the presence of 2,2,2-cryptand to give low but reproducible yields of $[(\eta\text{-}C_6H_5Me)NbSn_6Nb(\eta\text{-}C_6H_5Me)]^{2-}$ (**1**) as the $[K(2,2,2\text{-crypt})]^+$ salt. The crystalline solid is dark brown, air sensitive, and sparingly soluble or insoluble in most solvents (en, DMF, THF, DMSO, toluene). The salt has been characterized by single-crystal X-ray diffraction, IR and ^{119}Sn NMR spectroscopy, and elemental analysis.

Crystals of $[K(2,2,2\text{-crypt})]_2[(\eta\text{-}C_6H_5Me)NbSn_6Nb(\eta\text{-}C_6H_5Me)]\cdot$en are triclinic, space group $P\bar{1}$, with the anion (**1**) located on the inversion center.[15] The structure of **1** (Figure 1) contains a six-membered ring of tin atoms in a chair cyclohexane conformation. The anion has $\bar{1}$ crystallographic symmetry but virtual D_{3d} point symmetry in solution (ignoring the Me groups). The tin–tin contacts in the ring (2.8348(4)–2.8421(4) Å) are significantly shorter than those in other Zintl ions (e.g. Sn_9^{4-}, $d_{Sn-Sn} = 2.93-3.31$ Å,[1, 2] Sn_5^{2-}, $d_{Sn-Sn} = 2.901$, 3.128 Å)[4] and metallated Zintl ions (e.g. $[Sn_9Cr(CO)_3]^{4-}$, $d_{Sn-Sn} = 2.97-3.31$ Å,[16] $[Sn_6\{Cr(CO)_5\}_6]^{2-}$, $d_{Sn-Sn} = 2.93-2.96$ Å).[5] The Sn_6 ring in **1** ligates to two $(\eta\text{-}C_6H_5Me)Nb$ groups in an η^3, η^3 fashion. In bonding to the tin centers the niobium atoms adopt a familiar three-legged piano stool geometry[17] with Nb–Sn bonds ranging from 2.8433(4)–2.8517(4) Å. These contacts are similar to other Nb–Sn bonds in alkylstannane complexes such as $[\{Nb(Cp)_2(SnMe_3)\}_2(\mu\text{-}O)]$ where Nb–Sn = 2.8619 Å.[18] The η^6 toluene ligands are bound in a slightly asymmetric fashion with Nb–C contacts in the range 2.399(4)–2.446(4) Å [2.42(2) Å (av)]. The Nb–C26 bond is 0.02 Å longer than the others but all are statistically longer than the Nb–C bonds in other structurally characterized $(\eta\text{-}C_6H_5Me)Nb$ containing compounds. For comparison, the Nb–C bonds in the parent compound $[Nb(\eta\text{-}C_6H_5Me)_2]$ average 2.334(5) Å[13] with other$(\eta\text{-}C_6H_5Me)Nb$ compounds having Nb–C bonds in the range 2.305(5)–2.362(5) Å.[13] In contrast, the C–C bonds in the toluene rings average 1.407(5) Å, which is statistically equivalent to those in other compounds.[13] Attempts to monitor the degree of charge transfer into the toluene rings through infrared spectroscopic analysis of the C–C and C–H stretching modes was hindered by the strong, characteristic bands of the $[K(2,2,2\text{-crypt})]^+$ ion.

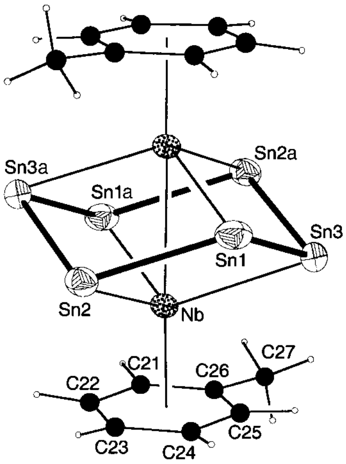

Figure 1. ORTEP plot of **1**. Selected bond lenghts [Å] and angles [°]: Sn1-Sn2 2.8355(4), Sn1-Sn3 2.8348(4), Sn2-Sn3a 2.8421(4), Nb-Sn1a 2.8517(4), Nb-Sn2 2.8433(4), Nb-Sn3 2.8484(4), Nb-Nb 3.0049(6), Nb-C 2.399(4)–2.446(4); Sn2-Nb-Sn1a 107.71(1), Sn1a-Nb-Sn3 108.31(1), Sn3-Nb-Sn2 107.71(1), Sn1-Sn2-Sn3a 109.52(1), Sn3-Sn1-Sn2 108.31(1), Sn1-Sn3-Sn2a 108.22(1). The bold lines emphasize the chair cyclohexane structure of the Sn_6 unit and do not imply relative bond strengths.

The $\{Nb_2Sn_6\}$ core of the structure can also be described as a distorted cube with the two Nb atoms at opposite corners. The cube is compressed along the Nb–Nb diagonal giving rise to a short niobium–niobium distance of 3.0049(6) Å compared with the long tin–tin diagonal of 5.38–5.45 Å. The Nb–Nb separation is consistent with a metal–metal single bond, which allows each Nb center to achieve an 18-electron configuration (see below).

For electron counting purposes, the structure can be viewed as an Sn_6^{12-} Zintl ion which requires fully oxidized Nb^{5+} centers. This formalism is similar to that used for the ME_8^{n-} ions where M = Nb, Mo; E = Sb, As; $n = 2, 3$.[19–21] Experimentally, the ME_8^{n-} ions are prepared by insertion of zero-valent $M(arene)_2$ precursors into polypnictide clusters. For electron counting, however, the structures are conveniently viewed as having fully oxidized metal centers (i.e. Nb^{5+}, Mo^{6+}) with E_8^{8-} rings. While these formalisms do not accurately represent true electronic distributions in the clusters,[22] the S_8 crown-like structures of the E_8 rings are well described by this electron-transfer model. For **1**, the formalism is equally incorrect in describing the actual oxidation states, however, it accurately describes the bonding within the Sn_6 ring. The formal -12 charge is consistent with the cyclohexane-like structure and the short 2c–2e tin–tin bonds. For comparison, the *closo*-Sn_6^{2-} unit in $[Sn_6\{Cr(CO)_5\}_6]^{2-}$ has significantly longer Sn–Sn bonds (2.93–2.96 Å)[5] associated with 3c–2e bonding common to deltahedral clusters. The bond lengths of **1** ($d_{Sn-Sn} = 2.8348(4)-2.8421(4)$ Å) are more akin to those in the cyclic polystannanes[23] with 2c–2e bonds ($d_{Sn-Sn} = 2.77-2.91$ Å) than those of the polyhedral Zintl ion clusters ($d_{Sn-Sn} = 2.90-3.31$ Å). Using the neutral atom formalism, the Nb ions in **1** can be viewed as 18-electron centers, whereby the Sn atoms are two-electron donors and the metal–metal bond is taken into consideration.

The ^{119}Sn NMR spectrum of **1** shows a single resonance signal at $\delta = -149$ with $^1J_{^{119}Sn,^{117}Sn} = 1975$ Hz and $^{2,3}J_{^{119}Sn,^{117}Sn} \approx 630$ Hz. Although the signal is of low resolution, a result of the very limited solubility of the ion, the chemical shift and, more importantly, the $^1J_{^{119}Sn,^{117}Sn}$ coupling constants are also consistent with 2c–2e Sn–Sn interactions.[23] For comparison, the cyclohexastannanes, $(R_2Sn)_6$, show ${}^1J_{^{119}\mathrm{Sn},^{117}\mathrm{Sn}}$ coupling in the range 462–1339 Hz,[23] whereas the electron deficient borane-like Zintl ions display much smaller couplings (e.g *nido*-Sn_9^{4-}, ${}^1J_{^{119}\mathrm{Sn},^{117}\mathrm{Sn}} = 254$ Hz , $[L_2PtSn_9]^{4-}$, ${}^1J_{^{119}\mathrm{Sn},^{117}\mathrm{Sn}} = 79$ Hz).

In the solid state, the stannides show a rich chemistry that spans valence compounds containing discrete Zintl ions, to intermetallic phases characterized by delocalized bonding and metallic behavior.[24] Six-membered rings are found in several of these materials, including Li_5NaSn_4 (puckered 6-rings, chair conformation),[25] $BaSn_5$ (planar 6-rings),[26] and in α-tin itself. Each of these is derived from diamond or graphite related extended structures and does not contain isolated Zintl anions. Other compounds do contain isolated Zintl ions, such as the Sn_2^{6-} ion in $BaMg_2Sn_2$ with an ethane (or dihalogen) like structure and a short Sn–Sn bond of 2.87 Å.[27] The number of tin Zintl ions isolated from solution methods is low and the prospects of preparing new ones are limited by the apparent stability of the $E_9^{3/4-}$ clusters and their derivatives. However, through the use of appropriate transition metal precursors, other metal-stabilized Zintl ions may be accessible through cluster degradation reactions and internal electron transfer.

Experimental Section

Preparation of $[K(2,2,2\text{-crypt})]_2[(\eta\text{-}C_6H_5Me)NbSn_6Nb(\eta\text{-}C_6H_5Me)]\cdot en$. All reactions were performed in a nitrogen atmosphere dry box (Vacuum Atmospheres Company). In vial 1, K_4Sn_9 (50.0 mg, 0.041 mmol) and 2,2,2-crypt (46 mg, 0.12 mmol) were dissolved in en (ca. 3 mL). In vial 2, $Nb(\eta\text{-}C_6H_5Me)_2$ (11.3 mg, 0.041 mmol) was dissolved in toluene (ca. 1 mL) producing a red solution. The content of vial 2 was added to the vial 1 yielding a green-brown solution. The reaction mixture was stirred for 12 h and filtered through tightly packed glass wool in a pipette. Dark brown crystals formed in the reaction vessel after one week. Yield: 12 mg (15 %); NMR analysis of the reaction mixtures showed free toluene (${}^1H$ and ${}^{13}C$ NMR) as the only by-product of the reaction; ${}^{119}Sn$ NMR (186.5 MHz (en/toluene), 25 °C): $\delta = -149$; elemental analysis calcd (%) for $C_{52}H_{96}K_2N_6Nb_2Sn_6O_{12}$: C 31.64, H 4.87, N 4.26 %; found: C 30.53, H 5.00, N 4.33.

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[1] J. D. Corbett, P. A. Edwards, *J. Am. Chem. Soc.* **1977**, *99*, 3313.

[2] R. G. Teller, L. J. Krause, R. C. Haushalter, *Inorg. Chem.* **1983**, *22*, 1809.

[3] S. C. Critchlow, J. D. Corbett, *J. Am. Chem. Soc.* **1983**, *105*, 5715.

[4] M. Somer, W. Carrillo-Cabrera, E.-M. Peters, K. Peters, M. Kaupp, H.-G. von Schnering, *Z. Anorg. Allg. Chem.* **1999**, *625*, 37.

[5] B. Schiemenz, G. Huttner, *Angew. Chem.* **1993**, *105*, 295; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 297.

[6] S. Bobev, S. C. Sevov, *Angew. Chem.* **2000**, *112*, 4274; *Angew. Chem. Int. Ed.* **2000**, *39*, 4108.

[7] K. J. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

[8] C. Downie, Z. J. Tang, A. M. Guloy, *Angew. Chem.* **2000**, *112*, 346; *Angew. Chem. Int. Ed.* **2000**, *39*, 338.

[9] L. Xu, S. C. Sevov, *J. Am. Chem. Soc.* **1999**, *121*, 9245.

[10] H. G. von Schnering in *Rings, Chains, and Macromolecules of Main Group Elements* (Ed.: A. L. Rheingold), Elsevier, Amsterdam, **1977**.

[11] H. G. von Schnering, W. Hönle, *Chem. Rev.* **1988**, *88*, 243.

[12] S. Charles, B. W. Eichhorn, S. G. Bott, *J. Am. Chem. Soc.* **1993**, *115*, 5837.

[13] D. L. Clark, J. C. Gordon, J. T. McFarlan, R. L. Vincent-Hollis, J. G. Watkin, B. D. Zwick, *Inorg. Chem. Acta* **1996**, *244*, 269, and refs therein.

[14] F. G. N. Cloke, M. L. H. Green, D. H. Price, *J. Chem. Soc. Chem. Commun.* **1978**, 431.

[15] Crystal data for $[K(2,2,2\text{-crypt})]_2[(\eta\text{-}C_6H_5Me)NbSn_6Nb(\eta\text{-}C_6H_5Me)]\cdot en$: small dark brown crystal, dimensions $0.268 \times 0.117 \times 0.044$ mm^3, triclinic, space group $P\bar{1}$, $a = 10.8827(3)$, $b = 13.3303(4)$, $c = 13.8264(4)$ Å; $\alpha = 106.794(1)$, $\beta = 112.042(1)$, $\gamma = 90.841(1)^\circ$, $V = 1762.68(9)$ Å^3, $\rho_{calcd} = 1.859$ g cm^{-1}, $3.22^\circ < 2\theta < 55.00^\circ$, $Mo_{K\alpha}$ radiation, $\mu(Mo_{K\alpha}) = 2.575$ mm^{-1}, 8060 unique reflections for 361 parameters. GOF (F^2) = 1.094, $R1 = 0.0283$, $wR2 = 0.0649$ for $I > 2\sigma(I)$ and $R1 = 0.0520$, $wR2 = 0.0799$ for all data. The largest peak in the difference map was 0.832 e Å^{-3}. Measurement performed on a Bruker SMART1000 single crystal CCD-diffractometer operating at 193 K. Data were corrected for absorption (SADABS) and L-P effects and the structure solved and refined (against F^2) using the SHELXTL software package. 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-159171. 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] B. W. Eichhorn, R. C. Haushalter, W. T. Pennington, *J. Am. Chem. Soc.* **1988**, *110*, 8704.

[17] K. M. Smith, R. Poli, P. Legzdins, *Chem. Eur. J.* **1999**, *5*, 1598.

[18] M. L. H. Green, A. K. Hughes, P. Mountford, *J. Chem. Soc. Dalton Trans.* **1991**, 1407.

[19] H. G. von Schnering, J. Wolf, D. Weber, R. Ramirez, T. Meyer, *Angew. Chem.* **1986**, *98*, 372; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 353.

[20] B. W. Eichhorn, S. P. Matamanna, D. R. Gardner, J. C. Fettinger, *J. Am. Chem. Soc.* **1998**, *120*, 9708.

[21] B. Kesanli, B. W. Eichhorn, J. C. Fettinger, B. Scott, unpublished results.

[22] J. Li, K. C. Wu, *Inorg. Chem.* **2000**, *39*, 1538.

[23] L. R. Sita, *Adv. Organomet. Chem.* **1995**, *38*, 189.

[24] T. F. Fässler, S. Hoffmann, *Z. Kristallogr.* **1999**, *214*, 722.

[25] K. Volk, W. Müller, *Z. Naturforsch. B* **1978**, *33*, 593.

[26] T. F. Fässler in *Solid State Chemistry of Inorganic Materials II, Vol. 547* (Eds.: S. M. Kauzlarich, E. M. McCarron III, A. W. Sleight, H.-C. zur Loye), Materials Research Society, Boston, **1999**.

[27] B. Eisenmann, H. Schäfer, *Z. Anorg. Allg. Chem.* **1974**, *403*, 163.

Inversion of Enantioselectivity during the Platinum-Catalyzed Hydrogenation of an Activated Ketone**

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In the past few years there has been a remarkable progress in the enantioselective hydrogenation of α-functionalized (activated) ketones over chirally modified Pt catalysts. This development is reflected by the growing number of reactions in which enantiomeric excesses (*ee*) of 90 % or higher have been achieved. Even more promising is the shift from the early "trial-and-error" strategy to a more rational basis for designing new modifiers and discovering new applications through mechanistic investigations.[1–6] Several mechanistic

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