

Electronic Supplementary Information

On the Structural Diversity of [K(18-Crown-6)EPh₃] (E = C, Si, Ge, Sn, Pb) Complexes: Synthesis, Crystal Structures and NOESY NMR Study

Christian Kleeberg*

Institut für Anorganische und Analytische Chemie,
Technische Universität Carolo-Wilhelmina zu Braunschweig,
Hagenring 30, 38106 Braunschweig, Germany.

* Author E-mail Address: ch.kleeberg@tu-braunschweig.de

Contents

1. Thermal decomposition of ((<i>i</i> PrN) ₂ C ₂ H ₄)B–PbPh ₃ (4c)	S2
2. ¹ H- ¹ H NOESY NMR spectra of 6a-d	S3
3. Variable temperature ¹ H NMR spectra of [K(18-C-6)CPh ₃] (6a).....	S7
4. Reaction of <i>in situ</i> prepared 6a , 6c-d with BnBr to Ph ₃ E–CH ₂ Ph.....	S8
References.....	S10

1. Thermal decomposition of $((iPrN)_2C_2H_4)B-PbPh_3$ (**4c**)

Under an atmosphere of nitrogen a small amount of **4c** was placed in a melting point capillary and flame sealed. The capillary was heated to 114° – 115° C until formation of a black material. Some of the black material was attached to a glass rod by means of perfluoroether oil (in the presence of air) and a powder diffraction pattern was recorded using an Oxford Diffraction Nova A instrument, using mirror-focused $CuK\alpha$ radiation at nominally 100 K. The data were reduced employing the CrysAlisPro software.^{S1} A Rietveld fitting was performed using the structure of elemental lead as starting structure.^{S3} The refined parameters were: unit cell parameters, phase scale factor, background coefficients. A polynomial background function was employed to account for the amorphous scattering of the oil and glass (Fig. S1).^{S2} The final crystallographic and Rietveld refinement data are listed below:

Cell setting and space group	:	cubic, $Fm\bar{3}m$ (no. 225)
$a = b = c / \text{\AA}$:	4.951(2)
R_{wp} / R_p	:	3.59% / 2.47%

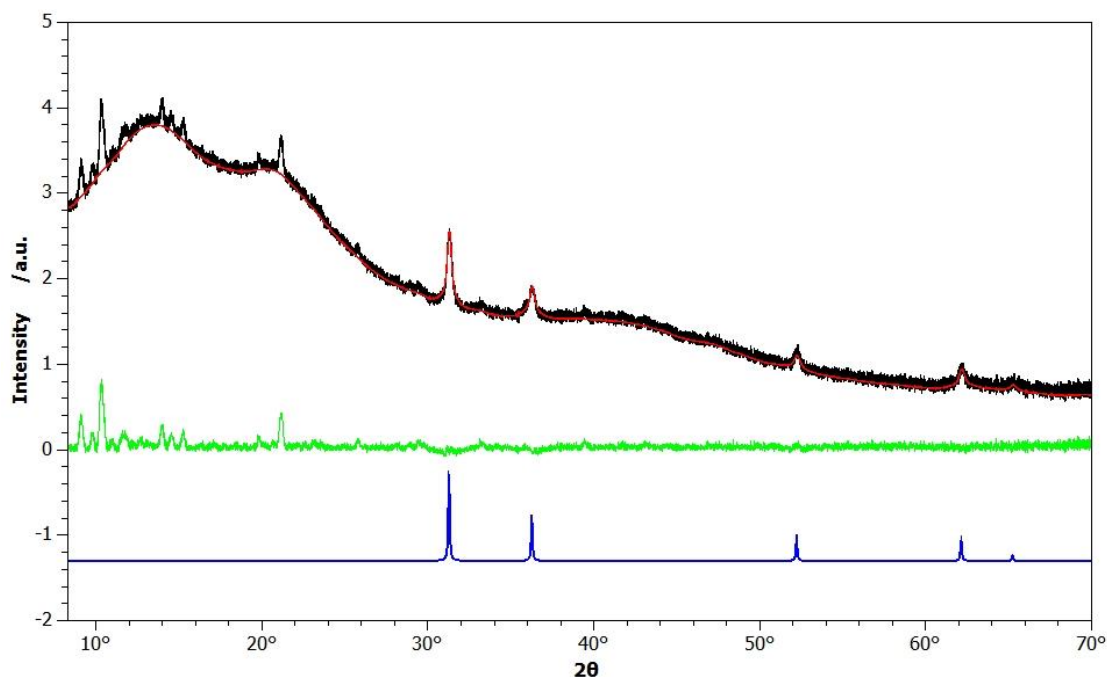


Fig. S1: X-ray powder diffraction pattern ($\lambda = 1.54184 \text{ \AA}$) of the decomposition mixture of **4c**. black: measured data, red: result of Rietveld refinement, green: difference, blue: calculated powder pattern of Pb from literature data (intensity and zero-point are arbitrary)^{S3}.

The diffraction pattern gives evidence that one of the decomposition products of **4c** is elemental lead. However, additional reflections below $2\theta = 30^\circ$ are observed indicating the presence of so far unidentified additional crystalline material. Note that none of the lead oxides PbO , PbO_2 and Pb_3O_4 account for these reflections.

2. ^1H - ^1H NOESY NMR spectra of **6a-d**

In a nitrogen filled glovebox a sample of the respective compound was dissolved in dried and degassed THF- d_8 at a concentration of 40–46 $\mu\text{mol/ml}$, the solution was filtered, filled into an NMR tube and flame sealed.

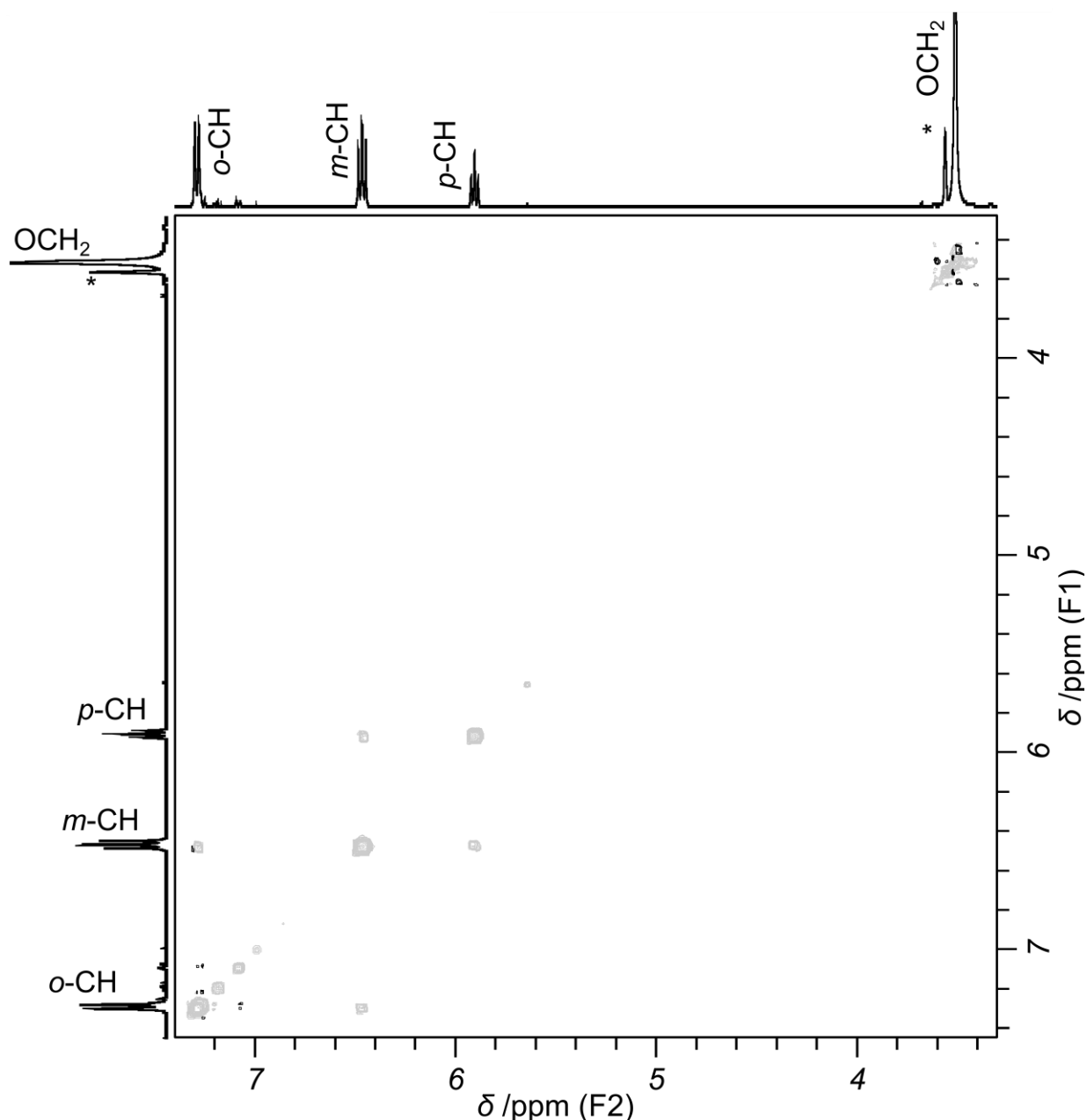


Fig. S2: ^1H - ^1H -NOESY NMR spectrum of **6a** in THF- d_8 at $-70\text{ }^\circ\text{C}$. * residual THF signal.

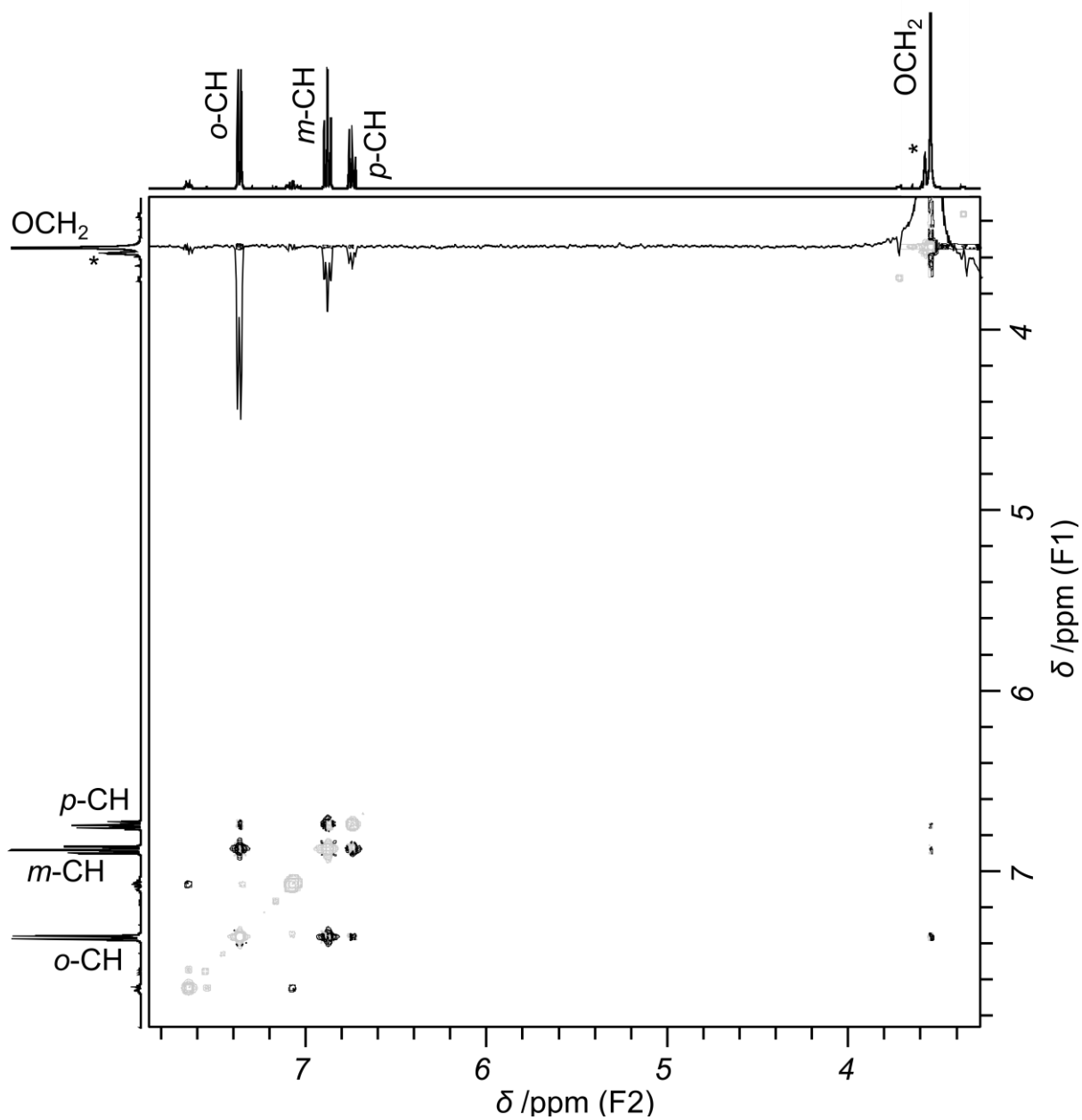


Fig. S3: ^1H - ^1H -NOESY NMR spectrum of **6b** in THF-d_8 at rt.
Inset: Trace of the NOESY spectrum at the shift of the OCH_2 signal. * residual THF signal.

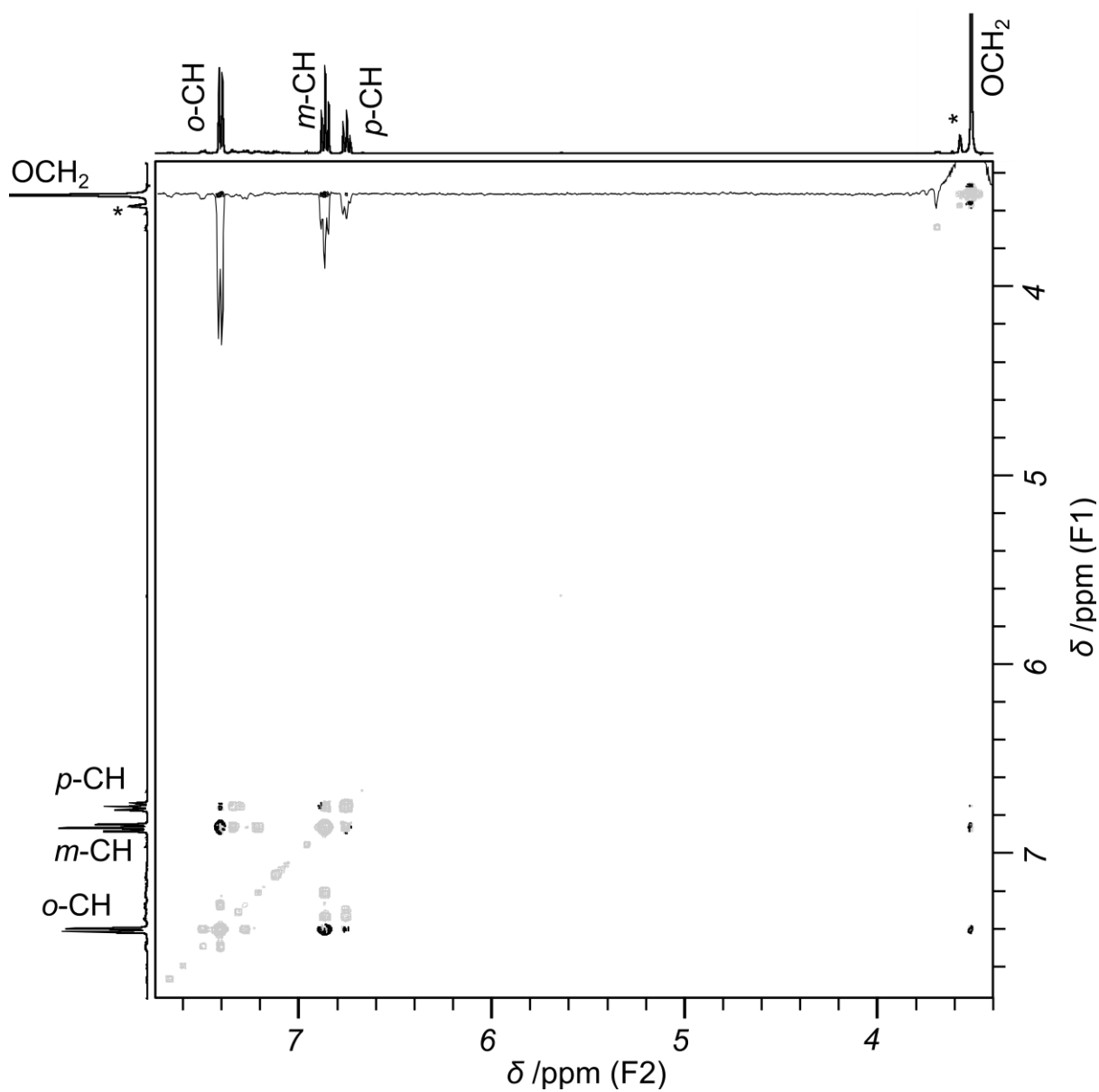


Fig. S4: ^1H - ^1H -NOESY NMR spectrum of **6c** in THF-d_8 at rt.
Inset: Trace of the NOESY spectrum at the shift of the OCH_2 signal. * residual THF signal.

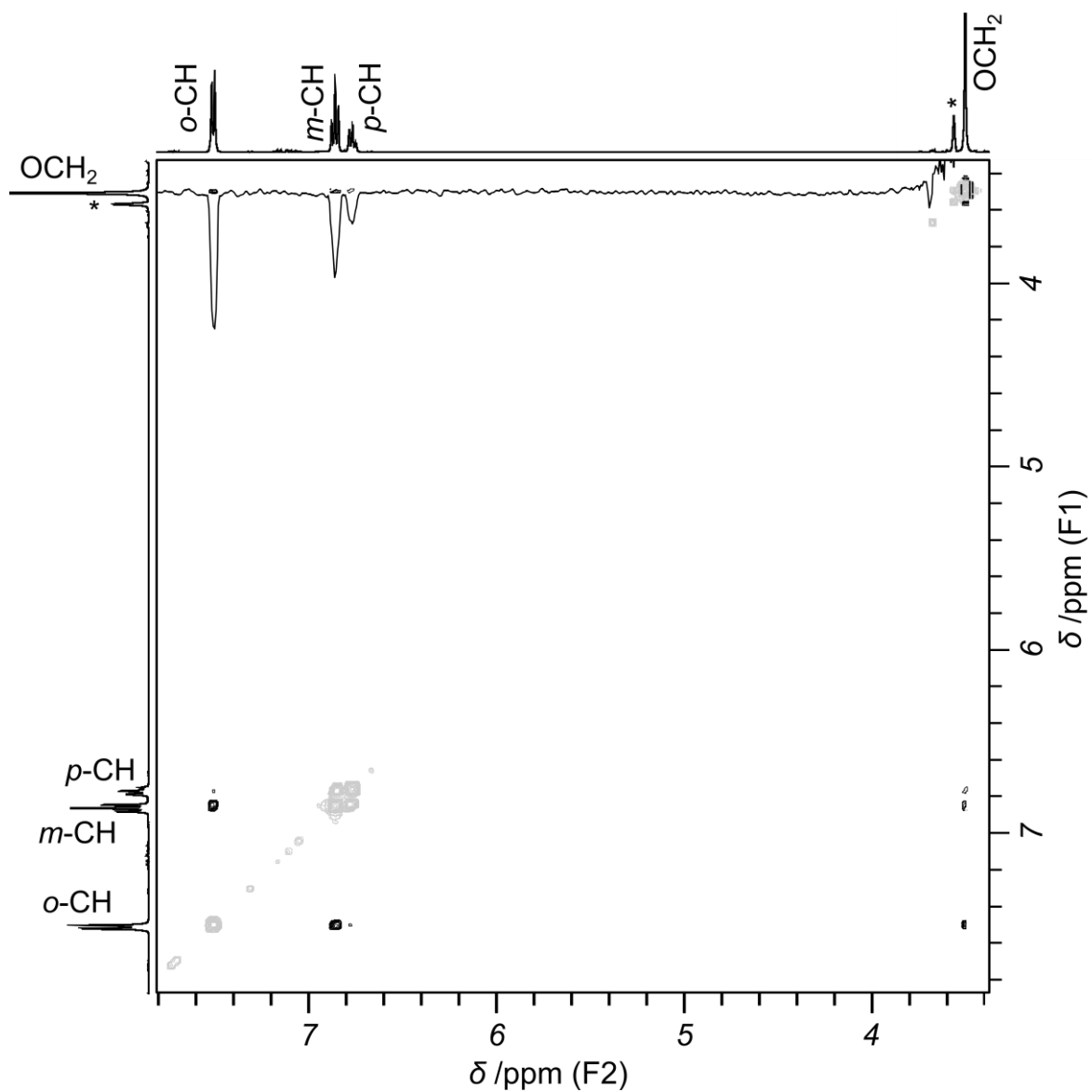


Fig. S5: ^1H - ^1H -NOESY NMR spectrum of **6d** in THF-d_8 at rt.
Inset: Trace of the NOESY spectrum at the shift of the OCH₂ signal. * residual THF signal.

3. Variable temperature ^1H NMR spectra of $[\text{K}(18\text{-C-6})\text{CPh}_3]$ (**6a**)

The sample was prepared as described in paragraph 2.

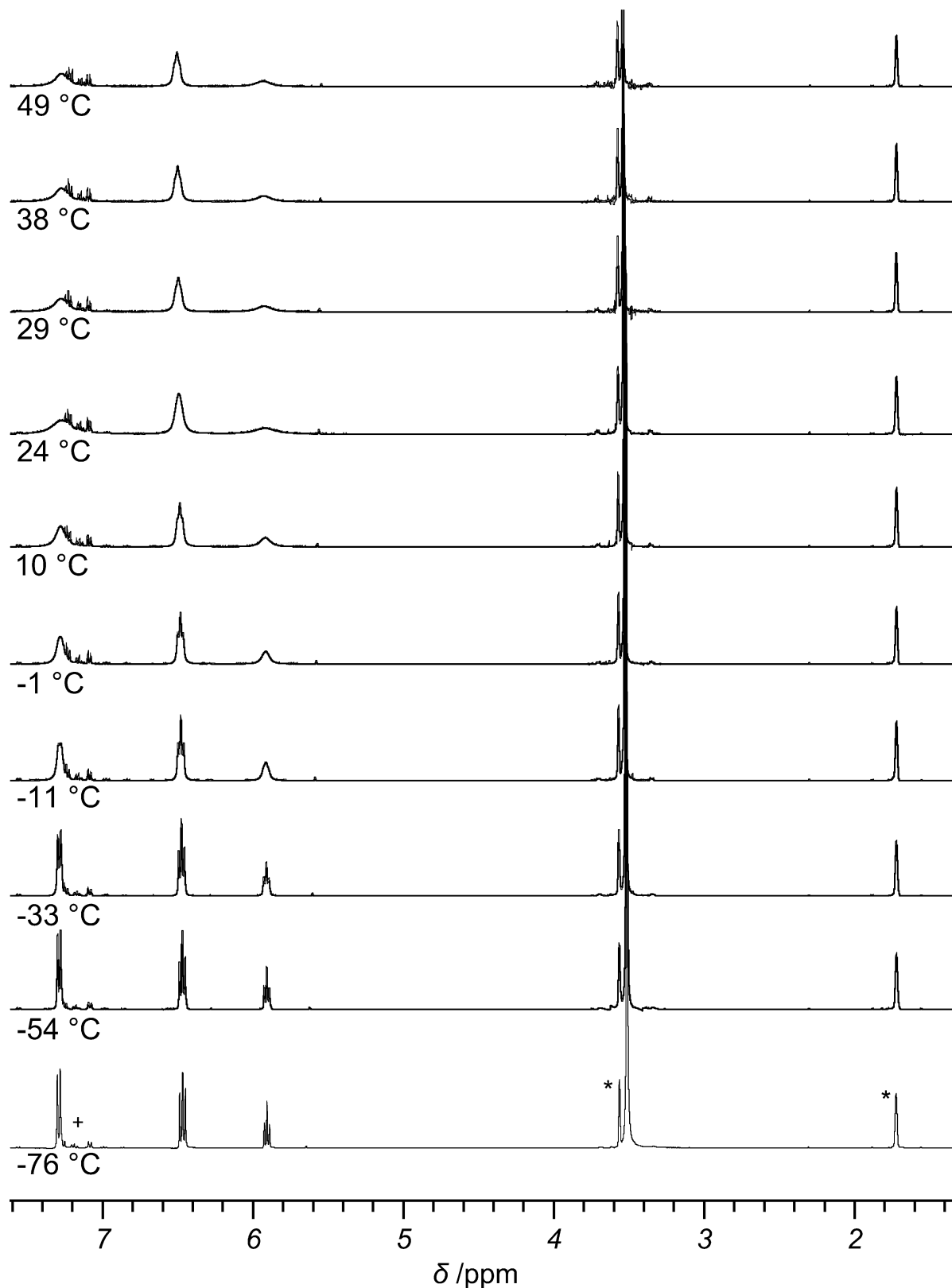


Fig. S6: Variable temperature ^1H NMR spectra of **6a** in THF-d_8 .
+ Impurity. * Residual THF signal.

4. Reaction of *in situ* prepared **6a,c-d** with BnBr to Ph₃E–CH₂Ph

Ph₃C–CH₂Ph:^{S4a} Under an atmosphere of nitrogen **5** (110 mg, 289 μmol, 1 eq) and **3a** (107 mg, 289 μmol, 1 eq) were mixed in dry THF (6 ml). After 5 min benzyl bromide (100 μl, 144 mg, 842 μmol, 2.9 eq) was added and the mixture stirred for 1 h at rt. After removal of the solvent *in vacuo* the residue was extracted with diethyl ether (10 ml) and filtered through a plug of silica gel (∅ 3 cm x 5 cm, *n*-pentane) to give the title compound as colourless crystals (81 mg, 242 μmol, 84%) after evaporation of the solvent.

¹H NMR (300 MHz, CDCl₃): δ = 7.28 – 7.07 (m, 15 H, CH_{Ar}), 7.06 – 6.99 (m, 1 H, CH_{Ar}), 6.97 – 6.91 (m, 2 H, CH_{Ar}), 6.64 – 6.58 (m, 2 H, CH_{Ar}), 3.91 (s, 2 H, CH₂).

¹³C NMR (75 MHz, CDCl₃): δ = 146.7 (*ipso*-C_{CPh₃}), 138.6 (*ipso*-C_{Bn}), 131.2 (*o*-CH_{Bn}), 129.9 (*o*-CH_{CPh₃}), 127.7 (*m*-CH_{CPh₃}), 127.4 (*m*-CH_{Bn}), 126.1 (*p*-CH_{Bn}), 126.0 (*p*-CH_{CPh₃}), 58.7 (CPh₃), 46.4 (CH₂Ph).

Ph₃GeCH₂Ph:^{S4b} Under an atmosphere of nitrogen **5** (62 mg, 165 μmol, 1 eq) and **3b** (70 mg, 162 μmol, 1 eq) were mixed in dry THF (5 ml). After 5 min benzyl bromide (83 mg, 485 μmol, 3.0 eq) was added and the mixture stirred for 2 h at rt. After removal of the solvent *in vacuo* the residue was extracted with diethyl ether (3 ml) and filtered through a plug of silica gel (∅ 1 cm x 5 cm, *n*-pentane) to give the title compound in 90% purity (34 mg, 76 μmol, 47%).

¹H NMR (300 MHz, CDCl₃): δ = 7.48 – 6.80 (m, 20 H, CH_{Ar}), 2.99 (s, 2 H, CH₂).

¹³C NMR (75 MHz, CDCl₃): δ = 139.1, 136.4, 135.3, 129.1, 128.9, 128.3, 128.2, 124.6, 23.7 (CH₂).

Ph₃Sn-CH₂Ph:^{S4c} Under an atmosphere of nitrogen **5** (60 mg, 130 μmol, 1 eq) and **4b** (50 mg, 130 μmol, 1 eq) were mixed in dry toluene (8 ml). After 5 min benzyl bromide (50 μl, 72 mg, 421 μmol, 3.2 eq) was added and the mixture stirred for 1 h at rt. After removal of the solvent *in vacuo* the residue was extracted with diethyl ether (10 ml) and purified by chromatography on silica gel (Ø 1 cm x 15 cm, *n*-pentane; *R_f* = 0.1, *n*-pentane, silica gel) to give the title compound as colourless crystals (26 mg, 70 μmol, 57%) after evaporation of the solvent.

¹H NMR (300 MHz, CDCl₃): δ = 7.44 – 7.37 (m, 9 H, CH_{Ar}), 7.36 – 7.28 (m, 6 H, CH_{Ar}), 7.10 – 7.01 (m, 3 H, CH_{Ar}), 6.88 – 6.82 (m, 2 H, CH_{Ar}), 2.93 (s, 2 H, CH₂).

¹³C NMR (75 MHz, CDCl₃): δ = 138.2 (*ipso*-C_{Bn}), 136.1 (*o/m*-CH_{Ph₃Si}), 134.2 (*ipso*-CH_{Ph₃Si}), 129.6 (*p*-CH_{Ph₃Si}), 129.3 (*o/m*-CH_{Bn}), 128.1 (*o/m*-CH_{Bn}), 127.9 (*p*-CH_{Ph₃Si}), 124.5 (*p*-CH_{Bn}), 23.6 (CH₂).

References:

- S1 Agilent Technologies, *CrysAlisPro*, Version 1.171.35.11, 2011.
- S2 B. A. Hunter, *Rietica for Windows*, Version 1.7.7, 1997.
- S3 R. W. G. Wyckhoff, *Crystal Structures*, 1963, **1**, 7–83.
- S4 (a) M. I. Watkins and G. A. Olah, *J. Am. Chem. Soc.*, 1981, **103**, 6566-6575; (b) S. Kiyooka, T. Shibuya, F. Shiota and R. Fujiyama, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 1361-1363; (c) C. Eaborn, A. R. Hancock and W. A. Stańczyk, *J. Organomet. Chem.*, 1981, **218**, 147-154.