Supplementary material

belonging to the manuscript

"Elucidation of the bonding in Mn(η^2-SiH) complexes by charge density analysis and T_1 NMR measurements: asymmetric oxidative addition and anomeric effects at silicon "

Contents:

S1: Experimental and computational details.

X-ray diffraction.

Data collection. A well faced, white-yellow crystal with the dimensions 0.23 × 0.48 × 0.68 mm was glued inside a 0.01 mm thin-walled capillary and mounted on a Nonius KappaCCD detector system. The sample was cooled with an Oxford Cryostream System to 120 K in 1.5 h with a mean temperature gradient of –2 K/min. Preliminary examination and final data collection were carried out with graphite-monochromated MoK_{α} radiation ($\lambda = 0.71073$ Å) generated from a Nonius FR591 rotating anode running at 50 kV and 60 mA. Intensity data were collected using 1° φ- and ω–scans with a detector-to-sample distance of 40 mm. For the low order data eleven scan sets (2625 frames in total) were collected at a scan angle (Θ) in the range of 0.0 to -17.0° and a scan time between 12 and 150 seconds/frame. For the high order data seven scan sets (1085 frames in total) with a scan time of 200 ($\Theta = -35°$) and 250 ($\Theta = 30°$) seconds/frame were chosen.[1a]

Data reduction. Crystal data for $\mathrm{MeC_5H_4Mn(CO)_2HSiFPh_2}$ at 120 K: $M_r = 392.37$, $a = 16.226(8)$, $b = 7.032(3)$, $c = 20.203(14)$ Å, $\beta = 128.55(3)°$, $V = 1802.8(19)$ Å^3; monoclinic; space group $P2_1/c$; $Z = 4$, $F(000) = 808$, $D_{\mathrm{calc}} = 1.446(2)$ g/cm^3, $\mu = 0.82$ mm^{-1}. The unit cell was determined from 58586 reflection positions. An initial orientation matrix was determined from 10 frames of the first scan set and refined during the integration of the individual scan sets. The intensities were first corrected for beam inhomogeneity and crystal decay by the program "Scalepack" using a tight scale restraint (0.002).[1b]

An absorption correction was then applied [$T_{\mathrm{min}} = 0.767(2)$, $T_{\mathrm{max}} = 0.838(2)$] and symmetry equivalent and multiply measured reflections were averaged with the program "Sortav".[2] After rejection of 689 statistically discrepant reflections and 8548 symmetry forbidden reflections, the internal agreement factor was $R_{\mathrm{int}}(F) = 0.037$ for a total of 177684 reflections yielding 19436 unique reflections. This data set provided 96% of data in $6.4 < 2\Theta < 104.1°$ ($\sin\Theta/\lambda < 1.11$ Å^{-1}).

Multipolar refinements and determination of the deformation density. First, an independent atom model (IAM) refinement was carried out, in which all atoms were treated as spherical.[3] Anisotropic thermal parameters were introduced to describe the thermal motion of all non-hydrogen atoms. Anisotropic thermal parameters for the hydrogen atoms were taken from a neutron diffraction study and fixed.[4] The refinement finally converged at $R_1 = 0.0334$ [$F_o > 4\sigma(F_o)$], $wR_2 = 0.0978$ and $GoF = 1.047$ for 19436 reflections and 226 parameters.

A multipole model was then adopted to describe the deformation of $\rho(\mathbf{r})$ from a spherical distribution. According to a method proposed by Stewart,[5] the electron density $\rho(\mathbf{r})$ in a crystal is described by a sum of aspherical pseudoatoms at the nuclear positions $\{\mathbf{R}_j\}$.

$$\rho(\mathbf{r}) = \sum_j \rho_j(\mathbf{r} - \mathbf{R}_j)$$

Based on the Hansen-Coppens formalism,[6] the pseudoatom density $\rho_j(\mathbf{r} - \mathbf{R}_j)$ is expressed in terms of multipoles ($\mathbf{r}_j = \mathbf{r} - \mathbf{R}_j$):[7]

$$\rho_j(\mathbf{r}_j) = P_c \rho_c(\mathbf{r}_j) + \kappa'^3 P_v \rho_v(\kappa' \mathbf{r}_j) + \sum_{l=0}^{l_{\max}} \sum_{m=-l_{\max}}^{+l_{\max}} \kappa''^3 P_{lm} R_l(\kappa'' \mathbf{r}_j) Y_{lm}(\theta_j, \phi_j)$$

In the refinement of our best model (model 4, see S11), the multipole expansion was truncated at the hexadecapole level ($l_{\max} = 4$) for the Mn and Si atoms, at the octapole level ($l_{\max} = 3$) for the C, F and O atoms. A bond-directed dipole ($l_{\max} = 1$) was also introduced for the hydrogen atoms (two dipoles were allowed to refine for the hydrogen atom in the Mn(η^2-SiH) moiety). Core and spherical valence densities were constructed using Clementi and Roetti Roothaan-Hartree-Fock (RHF)[8a] atomic wave functions expanded over Slater-type basis functions (STO); the radial functions for the deformation densities were single-ζ Slater-type orbitals.[8b] In our final model, both even and odd order multipoles on the Mn atom were allowed to refine assuming a $3d^5$ valence configuration of manganese while adding the 4s electron to the core.[9] The following n_l powers were used for the Slater-type functions: $n_1 = n_2 = n_3 = n_4 = 4$ for the Mn atom, $n_1 = n_2 = 4$, $n_3 = 6$, $n_4 = 8$ for the Si atom, $n_1 = n_2 = 2$, $n_3 = 3$, $n_4 = 4$ for the F, O and C atoms, and $n_1 = 1$ for the H atoms. To reduce the number of multipole population parameters to be refined local C_{3v} symmetry was imposed on the methyl group (C8), and three symmetry planes were introduced (for the two phenyl rings and the cyclopentadienyl ring). A radial scaling (κ') for the spherical density was refined for each atom type, together with a scaling (κ'') of the radial function for the deformation density. The κ'' parameters for the four sets of multipoles ($1 \le l \le 4$) were constrained to have the same values. Also, for the Mn, F and O atoms, the κ' and κ'' parameters for each atom were constrained to be equal. In addition, four sets of kappa values (κ' and κ'') for the four types of chemically different C atoms [C(O), C(Cp), C(Ph) and C(Me)] were refined. During the refinement the H atom positions and their anisotropic thermal parameters were fixed at the values obtained by neutron diffraction

(120 K). The molecule was kept neutral during all refinements.

With the experimental model this procedure refined to the final kappa values (the initial and final ζ values are doubled and given in Bohr^{-1} in square brackets; $\zeta_{\text{final}} = \kappa'' \times \zeta_{\text{initial}}$): $\kappa' = \kappa'' = 1.031(7)$ [7.019/7.234] for Mn, $\kappa' = 0.97(1)$ and $\kappa'' = 1.19(4)$ [3.063/3.651] for Si, $\kappa' = \kappa'' = 0.986(4)$ [5.108/5.038] for F, $\kappa' = \kappa'' = 1.002(5)$ [4.466/4.476] for O, $\kappa' = 0.981(6)$ and $\kappa'' = 0.87(3)$ [3.176/2.756] for C(O), $\kappa' = 0.988(5)$ and $\kappa'' = 0.94(3)$ [3.176/2.995] for C(Cp), $\kappa' = 1.00(1)$ and $\kappa'' = 0.8(1)$ [3.176/2.525] for C(Me), $\kappa' = 0.995(4)$ and $\kappa'' = 0.90(2)$ [3.176/2.858] for C(Ph), $\kappa' = 0.96(4)$ and $\kappa'' = 0.62(8)$ [2.400/1.495] for H [Mn(η^2–SiH)], $\kappa' = 1.16(2)$ and $\kappa'' = 1.41(9)$ [2.400/3.380] for H (Cp, Ph and Me). A correction for the isotropic extinction of Becker & Coppens[10] was tried and found insignificant. The residual electron density map was practically featureless with the maximum and minimum values of 0.30 and –0.24 e/Å^3 (Fourier summation was obtained to a resolution of $\sin\Theta/\lambda < 0.8$ Å^{-1}), respectively. The final agreement factors were $R_1 = 0.0207$, $w_2R_2 = 0.0599$ and $GoF = 0.96$ for 601 parameters with the ratio $N_{\text{ref}}/N_{\text{var}} = 24$. After the last cycle, maximum ratio of the parameter shift over its e.s.d. was 0.006 (kappa for the spherical valence density for the Si pseudoatom).

Hirshfeld's rigid bond test[11a] was applied to the atomic displacement parameters obtained from the refinements. The difference between mean-square amplitudes for all heavy atom bonds except for the Mn–Si and Mn–C(Cp) bonds is within the limit of 1.0×10^{-3} Å^2, proposed by Hirshfeld. However, the difference for the above mentioned Mn-Si and Mn–C(Cp) bonds, due to the different masses of the bonded atoms, is somehow larger, but never exceeds a value of 3.0×10^{-3} Å^2.[11b]

Computational details. All refinements were carried out with the full-matrix least-squares program "XDLSM" of the "XD" suite of programs;[7] the quantity minimized was $\varepsilon = \sum w_1(|F_o| - k\cdot|F_c|)^2$, where k is a scale factor, based on 13961 reflections with $F_o > 3\sigma(F_o)$. Weights were taken as $w_1 = 1/\sigma^2(F_o)$ and $w_2 = 1/\sigma^2(F_o^2)$. For the topological analysis, critical points of the electron density were searched via a Newton Raphson algorithm implemented in "XD". Properties of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ were calculated after transformation of the local axis system into a global system.

DFT calculations using the BPW91 density functional[13] with the 6-311G(d,p) basis set[12] were carried out with the "Gaussian98" program suite.[14] The topological analysis of the theoretical electron densities was carried out with the "AIMPAC" software package.[16]

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S2: Topological analysis and geometrical parameters of $MeC_5H_4Mn(CO)_2HsiFPh_2$.

Unit	Method[a]	Distance [Å]	$\rho(\mathbf{r}_c)$ [e/Å^3]	$\nabla^2\rho(\mathbf{r}_c)$ [e/Å^5]	Ellipticity ε
Mn – Si	Experiment	2.3509(2)	0.51(3)	1.37(5)	9.84
	Theory	2.367	0.50	0.30	2.27
Mn – H	Experiment	1.57	0.75(1)	5.65(1)	0.14
	Theory	1.566	0.76	4.35	0.13
Si – H	Experiment	1.80	0.52(4)	-0.83(6)	0.98
	Theory	1.817	0.53	-1.50	0.69
Mn – C1(O)	Experiment	1.7962(5)	1.00(2)	12.27(3)	0.01
	Theory	1.780	1.05	11.53	0.01
Mn – C2(O)	Experiment	1.7745(5)	1.02(2)	13.96(3)	0.08
	Theory	1.775	1.06	11.36	0.01
Mn – C3(Cp)	Experiment	2.1248(5)	0.480(8)	6.574(8)	34.96
	Theory	2.130	0.51	5.73	2.32
Mn – C4(Cp)	Experiment	2.1418(5)	0.488(8)	6.534(9)	3.86
	Theory	2.142	0.50	5.69	3.29
Mn – C5(Cp)	Theory	2.155	0.48	5.74	3.87
Mn – C6(Cp)	Experiment	2.1264(4)	0.493(7)	6.260(8)	5.02
	Theory	2.148	0.49	5.85	3.77
Mn – C7(Cp)	Theory	2.154	0.50	5.39	2.19
Si – F	Experiment	1.6280(6)	0.86(5)	18.9(1)	0.09
	Theory	1.674	0.74	17.41	0.01
Si – C9(Ph)	Experiment	1.8716(5)	0.92(6)	1.9(1)	0.06
	Theory	1.901	0.79	4.38	0.10
Si – C15(Ph)	Experiment	1.8657(5)	0.81(5)	5.8(1)	0.13
	Theory	1.889	0.81	4.58	0.09
C1=O1	Experiment	1.1466(10)	3.25(5)	-5.9(3)	0.04
	Theory	1.164	3.00	8.09	0.00
C2=O2	Experiment	1.1575(9)	3.22(5)	-17.2(3)	0.05
	Theory	1.166	2.99	7.82	0.00

[a] the experimental values were obtained by multipole refinement of the experimental charge density (model 4, see S1 and S10), the theoretical calculations were performed at the BPW91/6-311G(d,p) level of theory.

Selected angles [deg] for $MeC_5H_4Mn(CO)_2HsiFPh_2$.[a]

Mn – Si – H	Experiment	41.8	C1 – Mn – C2	Experiment	89.6
	Theory	41.4		Theory	87.7
Mn – H – Si	Experiment	88.0	Mn – Si – F	Experiment	107.1
	Theory	88.5		Theory	107.5
Si – Mn – H	Experiment	50.2	Mn – Si – C9(Ph)	Experiment	115.6
	Theory	50.1		Theory	115.6
Si – Mn – C1(O)	Experiment	115.2	Mn – Si – C15(Ph)	Experiment	117.3
	Theory	113.7		Theory	116.8
Si – Mn – C2(O)	Experiment	78.2	C9 – Si – C15	Experiment	109.0
	Theory	78.1		Theory	109.9

[a] the experimental values were obtained by multipole refinement of the experimental charge density (model 4, see S1 and S10), the theoretical calculations were performed at the BPW91/6-311G(d,p) level of theory.

S3a: Fractional atomic coordinates and mean-square atomic displacement parameters for the non-hydrogen atoms.

	Fractional atomic coordinates			Mean-square atomic displacement parameters [Å]					
Atom	x/*a*	*y*/*b*	*z*/*c*	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Mn	0.137680(7)	0.030288(13)	0.459794(5)	0.01396(3)	0.01477(3)	0.01256(3)	-0.00058(3)	0.00718(2)	0.00133(3)
Si	0.23685(1)	0.23507(2)	0.44175(1)	0.01509(5)	0.01474(5)	0.01325(5)	0.00029(3)	0.00817(4)	0.00128(3)
F	0.16019(5)	0.41101(9)	0.38276(4)	0.0219(2)	0.0181(2)	0.0216(2)	0.0041(2)	0.0129(2)	0.0054(2)
O(1)	0.25562(9)	-0.14710(22)	0.62799(6)	0.0330(4)	0.0514(5)	0.0215(3)	-0.0010(4)	0.0095(3)	0.0173(3)
O(2)	0.12500(8)	0.38342(12)	0.53005(5)	0.0398(4)	0.0235(3)	0.0280(3)	0.0013(2)	0.0243(3)	-0.0034(2)
C(1)	0.20949(5)	-0.07871(10)	0.56230(4)	0.0207(2)	0.0285(2)	0.0162(2)	-0.0014(2)	0.0082(2)	0.0070(2)
C(2)	0.13308(4)	0.24600(8)	0.50298(3)	0.0222(2)	0.0195(2)	0.0169(2)	-0.0008(1)	0.0126(1)	-0.0010(1)
C(3)	-0.01635(4)	-0.07964(10)	0.39810(4)	0.0196(2)	0.0282(2)	0.0204(2)	-0.0066(2)	0.0114(2)	0.0000(2)
C(4)	0.04863(6)	-0.22622(9)	0.40344(4)	0.0285(2)	0.0176(2)	0.0228(2)	-0.0051(2)	0.0114(2)	0.0001(1)
C(5)	0.08492(5)	-0.16488(8)	0.35894(4)	0.0250(2)	0.0197(2)	0.0201(2)	0.0013(1)	0.0115(2)	-0.0028(1)
C(6)	0.04216(4)	0.01942(8)	0.32559(3)	0.0179(1)	0.0216(2)	0.0143(1)	0.0003(1)	0.0086(1)	0.0003(1)
C(7)	-0.02150(4)	0.07233(8)	0.34904(3)	0.0150(1)	0.0235(2)	0.0167(1)	0.0002(1)	0.0082(1)	0.0011(1)
C(8)	-0.08608(5)	0.24937(11)	0.32250(4)	0.0219(2)	0.0343(3)	0.0269(2)	0.0097(2)	0.0131(2)	0.0058(2)
C(9)	0.27609(3)	0.13628(7)	0.37898(3)	0.0160(1)	0.0186(1)	0.0145(1)	0.0005(1)	0.0090(1)	0.0009(1)
C(10)	0.34974(4)	-0.01190(8)	0.41222(4)	0.0220(2)	0.0226(2)	0.0220(2)	0.0050(1)	0.0142(2)	0.0030(1)
C(11)	0.38066(5)	-0.08859(10)	0.36713(5)	0.0264(2)	0.0267(2)	0.0316(3)	0.0023(2)	0.0206(2)	-0.0025(2)
C(12)	0.33704(6)	-0.01845(11)	0.28695(5)	0.0272(2)	0.0332(3)	0.0277(2)	-0.0074(2)	0.0203(2)	-0.0105(2)
C(13)	0.26360(5)	0.12815(11)	0.25286(4)	0.0252(2)	0.0379(3)	0.0173(2)	-0.0048(2)	0.0139(2)	-0.0035(2)
C(14)	0.23396(4)	0.20527(9)	0.29877(3)	0.0201(2)	0.0288(2)	0.0149(1)	0.0014(2)	0.0101(1)	0.0027(1)
C(15)	0.35310(4)	0.35461(7)	0.53821(3)	0.0183(1)	0.0189(1)	0.0161(1)	-0.0036(1)	0.0103(1)	-0.0014(1)

C(16)	0.40224(5)	0.50271(8)	0.52789(4)	0.0266(2)	0.0232(2)	0.0202(2)	-0.0083(2)	0.0127(2)	-0.0002(1)
C(17)	0.49076(6)	0.59438(9)	0.59742(5)	0.0292(2)	0.0258(2)	0.0248(2)	-0.0122(2)	0.0142(2)	-0.0035(2)
C(18)	0.53173(5)	0.53914(10)	0.67878(4)	0.0246(2)	0.0291(2)	0.0213(2)	-0.0101(2)	0.0121(2)	-0.0073(2)
C(19)	0.48441(5)	0.39274(11)	0.69054(4)	0.0237(2)	0.0354(3)	0.0166(2)	-0.0095(2)	0.0110(2)	-0.0044(2)
C(20)	0.39600(4)	0.30165(9)	0.62065(3)	0.0213(2)	0.0294(2)	0.0160(2)	-0.0079(2)	0.0105(1)	-0.0015(1)

S3b: Fractional atomic coordinates and mean-square atomic displacement parameters for the hydrogen atoms.

	Fractional atomic coordinates			Mean-square atomic displacement parameters [Å]					
Atom	x/*a*	*y*/*b*	*z*/*c*	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
H(1)	0.25190	0.00570	0.48840	0.0211	0.0342	0.0377	0.0041	0.0166	0.0066
H(3)	-0.05630	-0.08220	0.42580	0.0333	0.0595	0.0339	-0.0116	0.0236	0.0005
H(4)	0.06820	-0.35940	0.43750	0.0597	0.0208	0.0438	-0.0009	0.0272	0.0128
H(5)	0.13800	-0.24270	0.35370	0.0438	0.0379	0.0385	0.0092	0.0247	-0.0054
H(6)	0.05170	0.10330	0.28560	0.0348	0.0378	0.0237	-0.0006	0.0187	0.0033
H(81)	-0.09750	0.29320	0.36800	0.0610	0.0546	0.0515	0.0236	0.0428	0.0104
H(82)	-0.05070	0.36690	0.31420	0.0511	0.0389	0.0599	0.0130	0.0392	0.0169
H(83)	-0.16430	0.22810	0.26250	0.0249	0.0604	0.0462	0.0133	0.0060	0.0023
H(10)	0.38400	-0.07050	0.47450	0.0443	0.0422	0.0356	0.0178	0.0275	0.0153
H(11)	0.43850	-0.20290	0.39400	0.0495	0.0448	0.0609	0.0163	0.0407	0.0063
H(12)	0.36060	-0.07830	0.25120	0.0534	0.0503	0.0453	-0.0023	0.0402	-0.0155
H(13)	0.22900	0.18200	0.19010	0.0520	0.0653	0.0251	0.0051	0.0251	0.0073
H(14)	0.17670	0.32170	0.27140	0.0379	0.0437	0.0288	0.0165	0.0192	0.0105
H(16)	0.37180	0.54530	0.46460	0.0483	0.0469	0.0216	-0.0175	0.0151	0.0057
H(17)	0.52920	0.70870	0.58910	0.0519	0.0482	0.0408	-0.0272	0.0218	0.0008
H(18)	0.60150	0.60950	0.73290	0.0370	0.0450	0.0329	-0.0185	0.0146	-0.0111
H(19)	0.51640	0.34770	0.75370	0.0461	0.0639	0.0194	-0.0163	0.0170	-0.0017
H(20)	0.35990	0.18540	0.63090	0.0435	0.0509	0.0264	-0.0240	0.0171	0.0008

S4: Kappa and multipole parameters for $MeC_5H_4Mn(CO)_2HSiFPh_2$.

Symmetry forbidden multipoles are denoted by an asterisk (*)

Atom	κ'	κ''	P_v	P_{11+}	P_{11-}	P_{10}
Mn	1.031(7)	1.031(7)	4.39(5)	0.00(1)	0.00(1)	-0.01(1)
Si	0.97(1)	1.19(4)	3.8(2)	-0.05(2)	-0.02(2)	-0.10(2)
F	0.986(4)	0.986(4)	7.11(5)	0.005(15)	-0.04(2)	0.01(2)
O(1)	1.002(5)	1.002(5)	5.89(8)	0.02(2)	0.09(3)	-0.02(2)
O(2)	1.002(5)	1.002(5)	5.86(8)	0.04(2)	-0.05(2)	-0.09(2)
C(1)	0.981(6)	0.87(3)	4.39(8)	0.02(2)	0.00(2)	-0.03(3)
C(2)	0.981(6)	0.87(3)	4.49(8)	-0.03(2)	-0.07(2)	0.00(4)
C(3)	0.988(5)	0.94(3)	4.38(7)	0.03(3)	0.00(3)	*
C(4)	0.988(5)	0.94(3)	4.14(7)	-0.05(3)	0.00(3)	*
C(5)	0.988(5)	0.94(3)	4.29(7)	-0.03(3)	0.07(3)	*
C(6)	0.988(5)	0.94(3)	4.11(7)	-0.01(3)	-0.01(3)	*
C(7)	0.988(5)	0.94(3)	4.07(7)	-0.02(3)	0.01(3)	*
C(8)	1.00(1)	0.8(1)	3.9(2)	*	*	-0.02(4)
C(9)	0.995(4)	0.90(2)	4.10(7)	-0.02(3)	-0.03(3)	*
C(10)	0.995(4)	0.90(2)	4.13(7)	0.02(3)	-0.01(3)	*
C(11)	0.995(4)	0.90(2)	4.12(7)	0.00(4)	-0.04(3)	*
C(12)	0.995(4)	0.90(2)	4.07(8)	-0.07(4)	-0.05(3)	*
C(13)	0.995(4)	0.90(2)	4.12(7)	-0.05(3)	0.02(4)	*
C(14)	0.995(4)	0.90(2)	4.23(7)	0.00(3)	0.01(3)	*
C(15)	0.995(4)	0.90(2)	3.98(7)	-0.05(3)	-0.02(3)	*
C(16)	0.995(4)	0.90(2)	4.11(7)	-0.03(3)	-0.07(3)	*
C(17)	0.995(4)	0.90(2)	3.99(7)	0.09(3)	-0.12(3)	*
C(18)	0.995(4)	0.90(2)	4.20(7)	0.07(4)	0.02(3)	*
C(19)	0.995(4)	0.90(2)	4.09(7)	0.02(3)	0.03(3)	*
C(20)	0.995(4)	0.90(2)	4.16(7)	-0.03(3)	0.06(3)	*

Atom	P_{20}	P_{21+}	P_{21-}	P_{22+}	P_{22-}
Mn	-0.16(1)	-0.08(1)	-0.05(1)	-0.05(1)	0.17(1)
Si	-0.01(2)	0.02(2)	0.00(2)	0.05(2)	-0.07(2)
F	-0.05(2)	-0.01(2)	0.01(2)	-0.08(2)	-0.02(2)
O(1)	0.02(3)	-0.04(2)	-0.02(3)	-0.01(3)	0.08(3)
O(2)	0.06(2)	0.04(2)	0.05(2)	0.02(2)	0.03(2)

C(1)	0.53(4)	-0.05(2)	-0.02(3)	0.03(2)	0.04(2)
C(2)	0.52(4)	0.08(2)	0.02(2)	0.03(2)	0.02(2)
C(3)	-0.19(3)	*	*	-0.03(3)	0.10(3)
C(4)	-0.14(3)	*	*	-0.05(3)	0.06(3)
C(5)	-0.20(3)	*	*	-0.05(3)	0.03(3)
C(6)	-0.17(2)	*	*	-0.02(3)	0.06(3)
C(7)	-0.20(2)	*	*	-0.06(3)	0.00(3)
C(8)	-0.04(4)	*	*	*	*
C(9)	-0.21(2)	*	*	0.03(3)	0.02(3)
C(10)	-0.23(3)	*	*	0.04(3)	-0.03(3)
C(11)	-0.21(3)	*	*	0.03(3)	-0.03(3)
C(12)	-0.20(3)	*	*	0.02(4)	0.01(4)
C(13)	-0.20(3)	*	*	0.00(3)	-0.05(3)
C(14)	-0.23(3)	*	*	0.00(3)	-0.03(3)
C(15)	-0.23(3)	*	*	-0.03(3)	0.00(3)
C(16)	-0.21(3)	*	*	0.01(3)	-0.03(3)
C(17)	-0.20(3)	*	*	0.04(3)	0.04(3)
C(18)	-0.29(3)	*	*	0.05(3)	0.03(3)
C(19)	-0.24(3)	*	*	-0.01(3)	-0.02(3)
C(20)	-0.23(3)	*	*	-0.01(3)	0.00(3)

Atom	P_{30}	P_{31+}	P_{31-}	P_{32+}	P_{32-}	P_{33+}	P_{33-}
Mn	0.032(9)	-0.022(9)	-0.012(9)	0.003(9)	-0.004(9)	-0.025(8)	0.047(8)
Si	0.06(3)	-0.27(4)	0.24(4)	0.05(3)	0.02(3)	0.19(3)	0.09(3)
F	0.01(2)	0.01(1)	-0.02(1)	0.00(1)	-0.02(1)	-0.00(1)	-0.01(1)
O(1)	0.00(2)	-0.03(2)	-0.07(2)	-0.01(2)	0.02(2)	-0.07(3)	0.03(3)
O(2)	-0.04(2)	0.01(2)	0.01(2)	-0.07(2)	-0.02(2)	0.06(2)	0.02(2)
C(1)	-0.09(4)	0.00(3)	-0.02(3)	-0.01(3)	0.04(3)	0.01(3)	0.00(3)
C(2)	-0.19(4)	-0.03(3)	-0.03(3)	-0.02(3)	-0.04(3)	0.02(2)	0.00(2)
C(3)	*	0.02(3)	0.02(2)	*	*	0.27(3)	-0.11(3)
C(4)	*	0.05(3)	0.04(3)	*	*	0.22(4)	-0.04(3)
C(5)	*	-0.01(2)	0.00(3)	*	*	0.31(3)	-0.08(3)
C(6)	*	0.06(2)	0.05(2)	*	*	0.24(3)	-0.05(3)
C(7)	*	0.05(2)	0.05(2)	*	*	0.28(3)	-0.11(3)
C(8)	0.15(6)	*	*	*	*	-0.02(3)	*
C(9)	*	-0.02(3)	0.00(3)	*	*	0.23(3)	-0.01(3)
C(10)	*	0.00(3)	0.03(3)	*	*	0.31(3)	0.02(3)

C(11)	*	-0.03(3)	-0.02(3)	*	*	0.30(4)	0.01(4)
C(12)	*	0.00(3)	0.03(3)	*	*	0.29(4)	-0.01(4)
C(13)	*	0.03(3)	0.00(3)	*	*	0.30(4)	0.02(4)
C(14)	*	-0.01(3)	-0.02(3)	*	*	0.33(3)	-0.01(3)
C(15)	*	0.01(3)	-0.03(3)	*	*	0.24(3)	-0.06(3)
C(16)	*	0.06(3)	0.04(3)	*	*	0.28(3)	0.03(3)
C(17)	*	0.01(3)	0.09(3)	*	*	0.28(4)	0.02(3)
C(18)	*	-0.06(3)	0.03(3)	*	*	0.38(4)	0.02(3)
C(19)	*	0.03(3)	0.04(3)	*	*	0.30(3)	0.05(3)
C(20)	*	0.04(3)	0.02(3)	*	*	0.35(3)	0.01(3)

Atom	P_{40}	P_{41+}	P_{41-}	P_{42+}	P_{42-}	P_{43+}	P_{43-}	P_{44+}	P_{44-}
Mn	0.02(1)	0.18(1)	0.20(1)	-0.18(1)	0.22(1)	0.20(1)	0.03(1)	-0.00(1)	-0.11(1)
Si	0.07(4)	-0.03(4)	-0.02(4)	0.07(5)	-0.19(5)	-0.09(4)	0.05(4)	0.00(4)	-0.22(4)

Atom	κ'	κ''	P_v	P_{10}
H(1)	0.96(4)	0.62(8)	1.30(8)	0.20(7)/0.31(8)[a]
H(3)	1.16(2)	1.41(9)	0.84(5)	0.07(2)
H(4)	1.16(2)	1.41(9)	0.82(5)	0.06(2)
H(5)	1.16(2)	1.41(9)	0.85(5)	0.08(2)
H(6)	1.16(2)	1.41(9)	0.80(5)	0.06(2)
H(81)	1.16(2)	1.41(9)	0.96(5)	0.11(2)
H(82)	1.16(2)	1.41(9)	0.94(5)	0.09(2)
H(83)	1.16(2)	1.41(9)	0.95(5)	0.10(2)
H(10)	1.16(2)	1.41(9)	0.85(5)	0.07(2)
H(11)	1.16(2)	1.41(9)	0.90(5)	0.07(2)
H(12)	1.16(2)	1.41(9)	0.79(5)	0.06(2)
H(13)	1.16(2)	1.41(9)	0.90(5)	0.07(2)
H(14)	1.16(2)	1.41(9)	0.91(5)	0.07(2)
H(16)	1.16(2)	1.41(9)	0.80(5)	0.07(2)
H(17)	1.16(2)	1.41(9)	0.84(5)	0.06(2)
H(18)	1.16(2)	1.41(9)	0.80(5)	0.06(2)
H(19)	1.16(2)	1.41(9)	0.80(5)	0.08(2)
H(20)	1.16(2)	1.41(9)	0.82(5)	0.05(2)

[a] Two dipoles oriented in the Mn-Si-H plane were refined for this hydrogen atom.

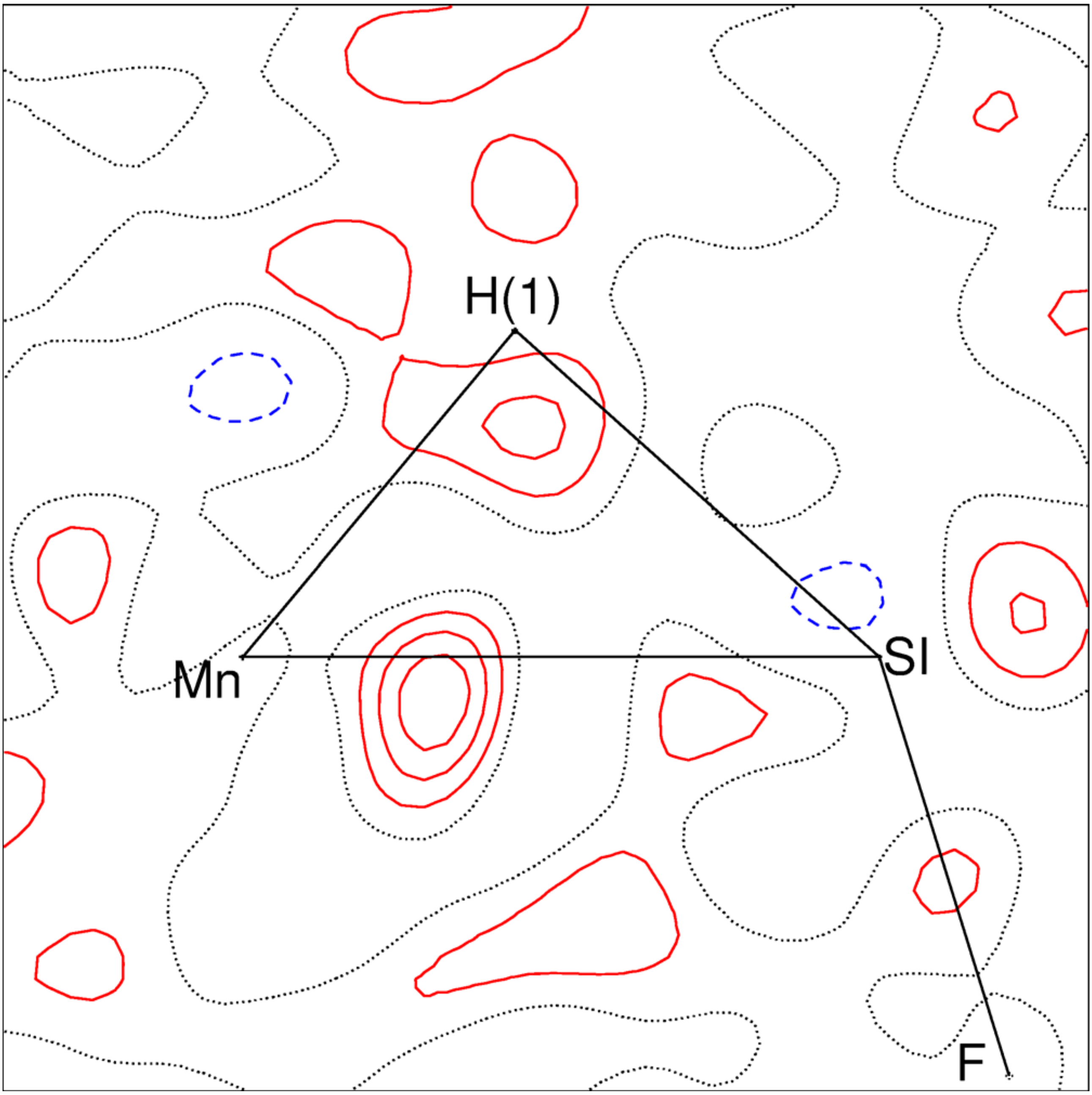
S5: Definition of the local coordinate system for $MeC_5H_4Mn(CO)_2HSiFPh_2$.[a]

Atom	Atom_1	Axis_1	Atom_2	Atom_3	Axis_2
Mn	Si	Y	Mn	H(1)	X
Si	Mn	X	Si	H(1)	Y
F	Si	X	F	Mn	Y
O(1)	C(1)	Z	O(1)	Si	X
O(2)	C(2)	Z	O(2)	Si	X
C(1)	Mn	Z	C(1)	Si	X
C(2)	Mn	Z	C(2)	Si	X
C(3)	C(4)	X	C(3)	C(7)	Y
C(4)	C(5)	X	C(4)	C(3)	Y
C(5)	C(6)	X	C(5)	C(4)	Y
C(6)	C(7)	X	C(6)	C(5)	Y
C(7)	C(3)	X	C(7)	C(6)	Y
C(8)	C(7)	Z	C(8)	C(6)	X
C(9)	C(10)	X	C(9)	C(14)	Y
C(10)	C(11)	X	C(10)	C(9)	Y
C(11)	C(12)	X	C(11)	C(10)	Y
C(12)	C(13)	X	C(12)	C(11)	Y
C(13)	C(14)	X	C(13)	C(12)	Y
C(14)	C(9)	X	C(14)	C(13)	Y
C(15)	C(20)	X	C(15)	C(16)	Y
C(16)	C(15)	X	C(16)	C(17)	Y
C(17)	C(16)	X	C(17)	C(18)	Y
C(18)	C(17)	X	C(18)	C(19)	Y
C(19)	C(18)	X	C(19)	C(20)	Y
C(20)	C(19)	X	C(20)	C(15)	Y
H(1)	Si	X	H(1)	Mn	Y
H(3)	C(3)	X	H(3)	C(7)	Y
H(4)	C(4)	X	H(4)	C(5)	Y
H(5)	C(5)	X	H(5)	C(4)	Y
H(6)	C(6)	X	H(6)	C(7)	Y
H(81)	C(8)	X	H(81)	H(83)	Y
H(82)	C(8)	X	H(82)	H(83)	Y
H(83)	C(8)	X	H(83)	H(82)	Y
H(10)	C(10)	X	H(10)	C(11)	Y
H(11)	C(11)	X	H(11)	C(12)	Y
H(12)	C(12)	X	H(12)	C(11)	Y

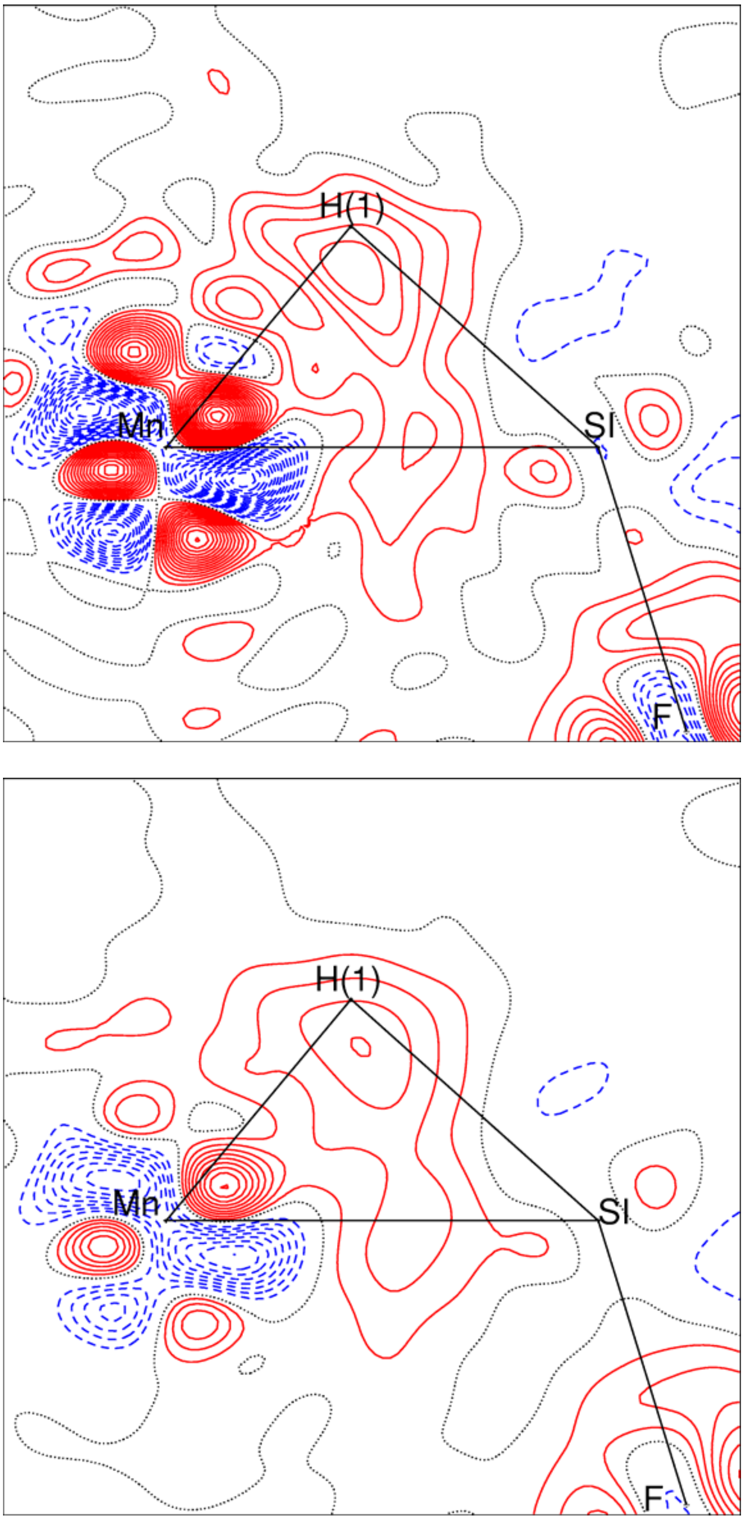
Atom	Atom_1	Axis_1	Atom_2	Atom_3	Axis_2
H(13)	C(13)	X	H(13)	C(12)	Y
H(14)	C(14)	X	H(14)	C(13)	Y
H(16)	C(16)	X	H(16)	C(17)	Y
H(17)	C(17)	X	H(17)	C(18)	Y
H(18)	C(18)	X	H(18)	C(17)	Y
H(19)	C(19)	X	H(19)	C(20)	Y
H(20)	C(20)	X	H(20)	C(19)	Y

[a] The first axis (Axis_1) is given by the internuclear vector from the pseudoatom (Atom) to Atom_1. This together with the second vector from Atom_2 to Atom_3 define the (Axis_1, Axis_2) plane. The third vector is taken perpendicular to this plane. The right-handed local coordinate systems of the pseudoatoms are used throughout.

S6: Residual density map after multipole refinement in the Mn–Si–H plane ($\sin\theta/\lambda \leq 0.8$ Å^{-1}; contour level: ±0.05 eÅ^{-3}; positive, negative and zero contours are marked by solid, dashed and dotted lines, respectively) with $\Delta\rho_{max/min}$ = 0.20/−0.14 eÅ^{-3}

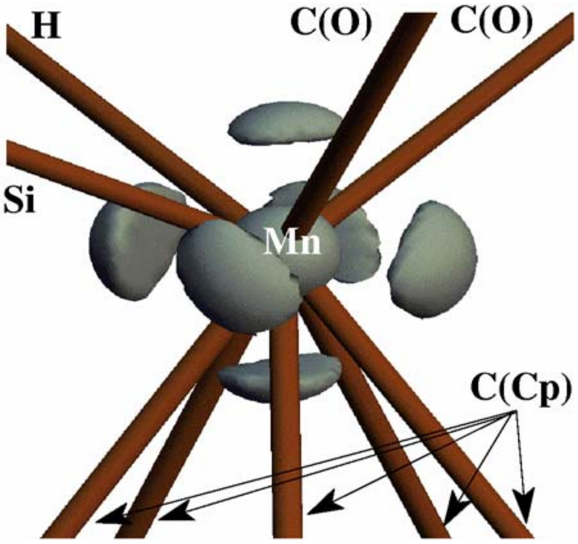


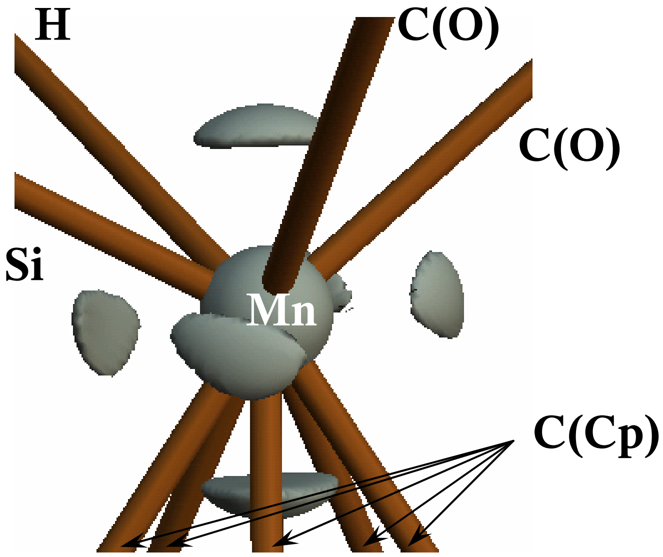
S7: Static (top) and dynamic (bottom) deformation electron density maps ($\Delta\rho = \rho_{mul} - \rho_{IAM}$) in the Mn–Si–H plane (contour level: ±0.05 eÅ^{-3}; positive, negative and zero contours are marked by solid, dashed and dotted lines, respectively).



S8: Isosurface plots of the negative Laplacian of the electron density ($-\nabla^2\rho(r) = 700$ e/A^5)

Top: experimental; bottom: calculated.





S9: Atomic graph of the Mn atom in $MeC_5H_4Mn(CO)_2HSiFPh_2$.

Type	n	*r*, [Å]	$\rho(\mathbf{r}_c)$ [eÅ^{-3}]	$-\nabla^2\rho(\mathbf{r}_c)$ [eÅ^{-5}]

Type	n	r, [Å]	$\rho(\mathbf{r}_c)$ [eÅ^{-3}]	$-\nabla^2\rho(\mathbf{r}_c)$ [eÅ^{-5}]
(3, -3)	6			
Exp		0.330-0.337	20.3-24.3	965-1488
Calc		0.336-0.341	19.5-21.1	742-938
(3, +1)	6			
Exp		0.355-0.365	13.4-16.1	-74-170[a]
Calc		0.358-0.359	15.3-16.0	235-276
(3, -1)	10			
Exp		0.344-0.352	15.6-19.0	247-605
Calc		0.334-0.350	17.4-19.1	480-655

[a] Three critical points of six were located in the region of the *positive* Laplacian.

S10: Topological Parameters at the BCP and RCP from the Multipole Refinements (r in [Å], $\rho(r)$ in [e/Å^3], $\nabla^2\rho(r)$ in [e/Å^5]).

Parameter	Mn–Si	Mn–H	Si–H	Mn–Si–H
		Model 1		
r(A-B)	2.3509(2)	1,5696	1,8063	-
$\rho(r_\mathrm{c})$	0.51(2)	0.77(3)	0.51(2)	0.51(2)
$\nabla^2\rho(r_\mathrm{c})$	0.57(2)	7.08(3)	–0.26(2)	0.40(2)
ε	2.92	0.13	2.62	-
		Model 2		
r(A-B)	2.3509(2)	1.5696	1.8062	-
$\rho(r_\mathrm{c})$	-	0.76(2)	0.52(3)	-
$\nabla^2\rho(r_\mathrm{c})$	-	6.23(3)	–0.85(4)	-
ε	-	0.12	0.34	-
		Model 3		
r(A-B)	2.3509(2)	1.5696	1.8063	-
$\rho(r_\mathrm{c})$	0.52(2)	0.79(3)	-	-
$\nabla^2\rho(r_\mathrm{c})$	0.40(2)	6.63(4)	-	-
ε	2.99	0.16	-	-
		Model 4		
r(A-B)	2.3509(2)	1.5696	1.8063	-
$\rho(r_\mathrm{c})$	0.51(3)	0.75(1)	0.52(4)	0.51(3)
$\nabla^2\rho(r_\mathrm{c})$	1.37(5)	5.65(1)	–0.83(6)	1.32(5)
ε	9.84	0.14	0.98	-

E.s.d in parentheses.

Model 1 - multipoles truncated at the octupole level for all heavy pseudoatoms with all kappas (for the Slater-type functions) fixed;

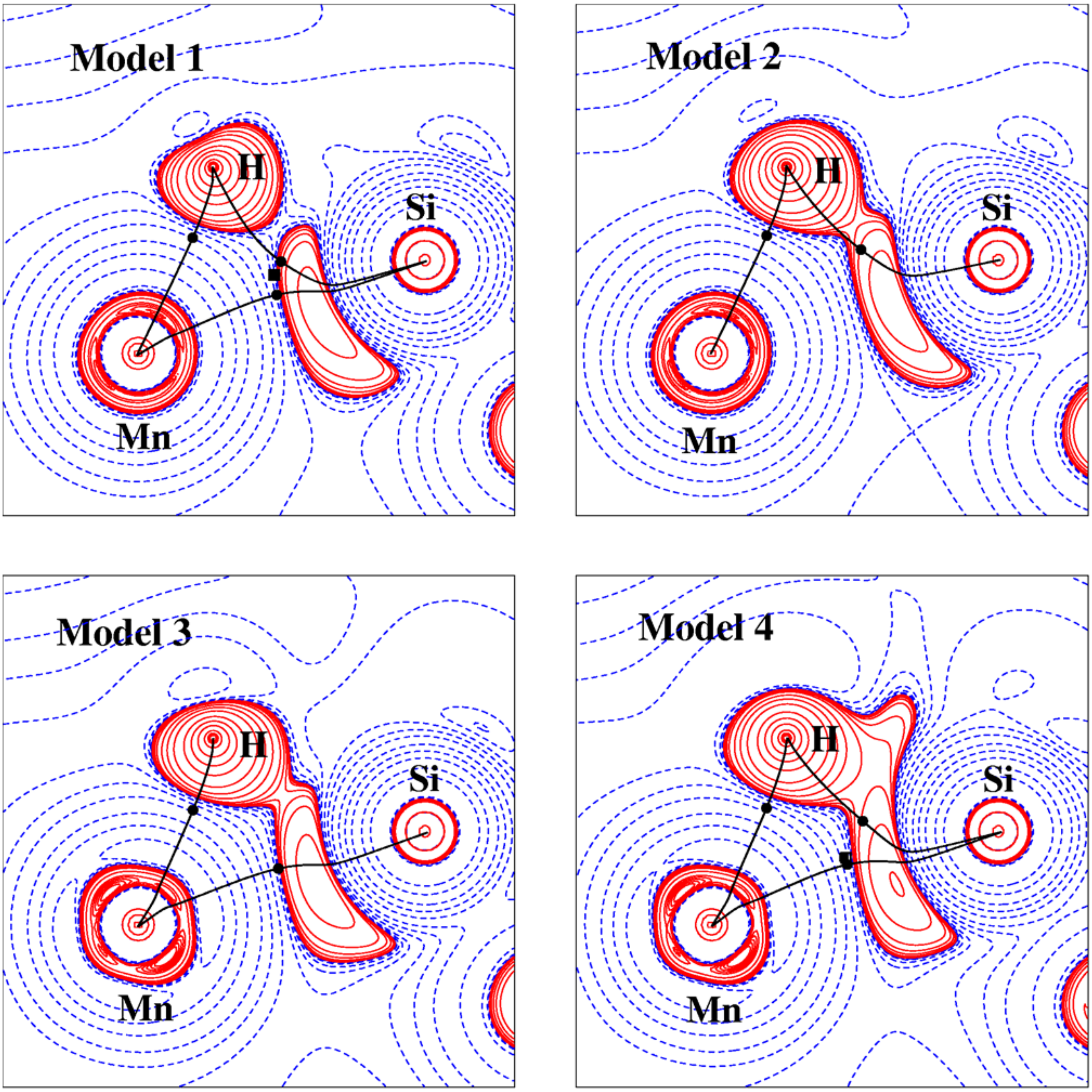
Model 2 - multipoles truncated at the octupole level for all heavy pseudoatoms with all kappas (for the Slater-type functions) refined;

Model 3- multipoles truncated at the hexadecapole level for the Mn and Si pseudoatoms and at the octupole level for the F, O and C pseudoatoms with all kappas (for the Slater-type functions) fixed;

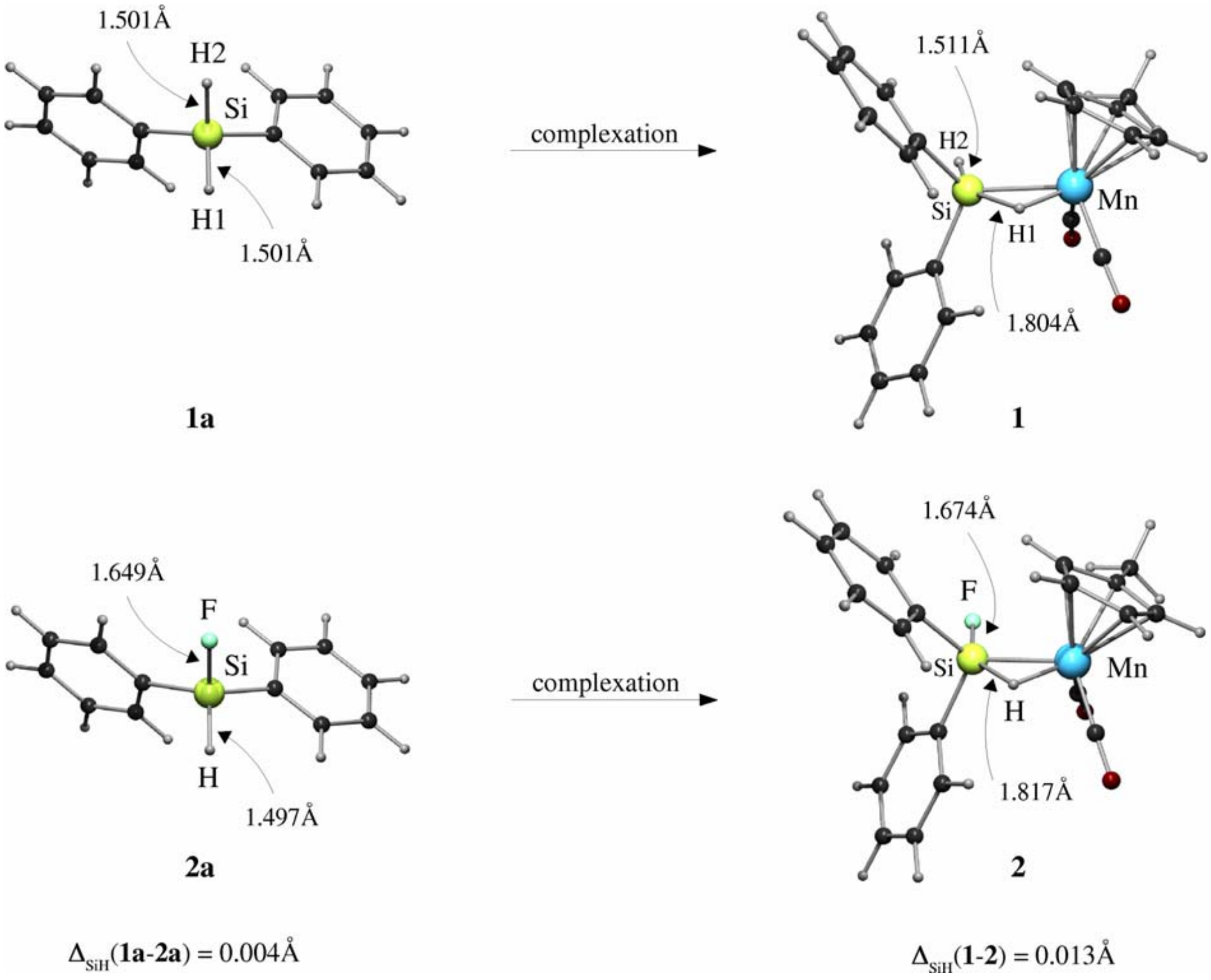
Model 4 - multipoles truncated at the hexadecapole level for the Mn and Si pseudoatoms and at the octupole level for the F, O and C pseudoatoms with all kappas (for the Slater-type functions) refined.

S11: Contour maps of the negative Laplacian of the electron density from the multipole refinements (see Table S14 for details). Positive and negative values are marked by red solid and blue dashed lines, respectively (zero contours are dotted black lines). Contour values are:

0.001, $\pm 2\times 10^{n}$, $\pm 4\times 10^{n}$, $\pm 8\times 10^{n}$ e/Å^{5} , where n = 0, -3, ±2, ±1; additional contour values of 500, 600 and 700 e/Å^{5} are added.



S12: Influence of the substitution pattern at the silicon atom on the Si – H bond distances in 1 and 2 and the corresponding free ligands 1a and 2a



These calculations indicate that the substitution pattern at Silicon in **1** and **2** has a significant influence on the Mn – Si bonding but not on the Si – H bond distances. This is also true for the uncomplexed free ligands. Hence, **1** and **2** present ideal model systems to study the process of partial oxidative addition in η²(Si-H) coordinated Mn (d^6) complexes.