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Supporting Information

for

"Valence Shell Charge Concentrations and the Dewar-Chatt-Duncanson Model"

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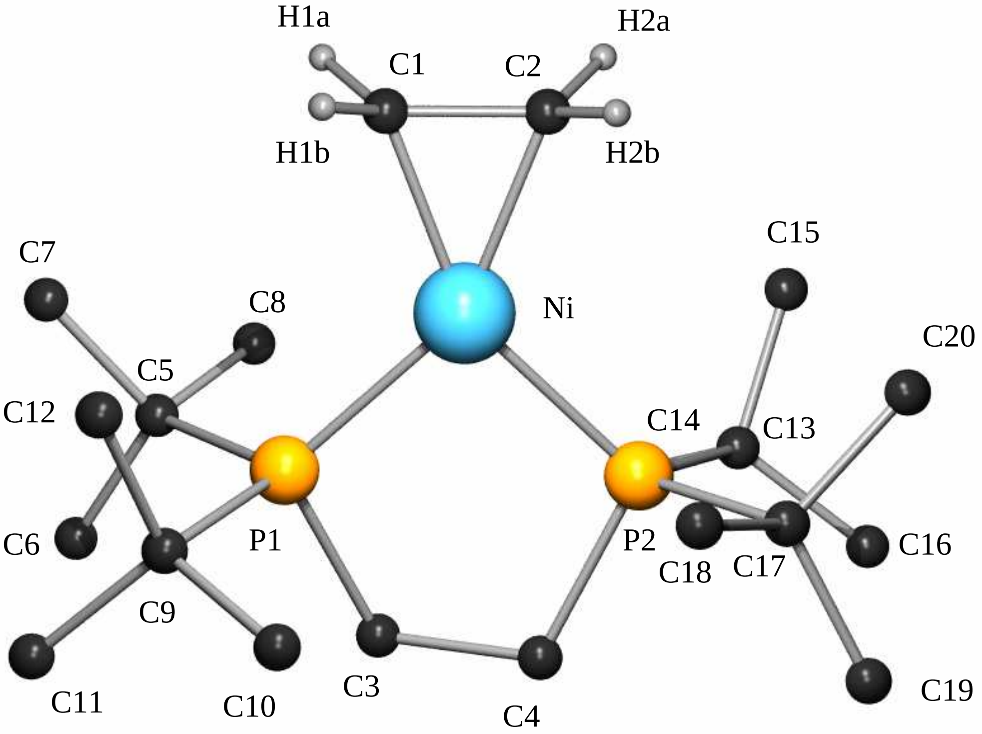
Contents:

S1: Molecular drawing and labeling scheme of 1.



S2: Charge Density Study of [(C_2H_4)Ni{(Me_3C)P(CH_2)$_2$P(CMe_3)}] 1.

Data Collection. A well faced, yellow crystal of **1** with the dimensions 0.64 x 0.56 x 0.46 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 110 K in 2.5 h with a mean temperature gradient of -1 K/min. Preliminary examination and final data collection were carried out with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) generated from a Nonius FR 591 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 three φ -scan sets (540 frames in total) at a scan angle (Θ) of 0.0, 10.0 and -17.0° with a scan time of 15, 30 and 80 seconds/frame, respectively, and seven ω -scan sets (699 frames in total; Θ = -17.0 - 16.3°) with a scan time of 15 and 80 seconds/frame were collected. For the high order data five ω-scan sets (625 frames in total; Θ = -40.3 and 40.0°) with a scan time of 160 seconds/frame were collected in addition to ten ω -scan sets (778 frames in total; Θ = 30.2°) with the same scan time.[1a]

Data Reduction. Crystal data for **1** at 110 K: M_r = 405.20, a = 8.1610(1) Å, b = 19.7390(1) Å, c = 14.5160(1) Å, β = 104.8640(4)°, V = 2260.13(2) Å^3; monoclinic; space group $P2_1/n$; Z = 4; F(000) = 888; D_{calc} = 1.191 g/cm^3; μ = 0.999 mm^{-1}. The unit cell was determined from 65900 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 programm "Scalepack" using a tight scale restraint (0.001).[1b]

An absorption correction was then applied (T_{min} = 0.605, T_{max} = 0.654) and symmetry equivalent and multiply measured reflections were averaged with the program "Sortav".[2] After rejection of 4313 statistically discrepant reflections, the internal agreement factor was $R_{int}(F)$ = 0.0365 for a total of 262409 reflections yielding 31967 unique reflections. This data set provided 99.7% of data in 4.1 < 2Θ < 115.8° (sinΘ/λ < 1.192 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. Anisotropic thermal parameters were introduced to describe the thermal motion of all non-hydrogen atoms. All hydrogen atoms were found in the difference map calculated from the model containing all non-hydrogen atoms. Isotropic temperature parameters for the hydrogen atoms were derived from the parent carbon atom ($U_H = 1.5U_{C,sp^3}$, $U_H = 1.2U_{C,sp^2}$). The refinement finally converged at $R_1 = 0.0379$, $wR_2 = 0.0585$ and $GooF = 0.938$ for 18930 reflections ($\sin\Theta/\lambda < 1.00$ Å^{-1}) and 340 parameters.[3] 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,[4] the electron density $\rho(\mathbf{r})$ in a crystal is described by a sum of aspherical pseudoatoms at the nuclear positions $\{\mathbf{R}_j\}$.

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

Based on the Hansen-Coppens formalism,[5] the pseudoatom density $\rho_j(\mathbf{r} - \mathbf{R}_j)$ is expressed in terms of multipoles:[6]

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

In the refinement of our best model the multipole expansion was truncated at the octapole level ($l_{\max} = 3$) for the phosphorus and carbon atoms, except for C1 and C2, which were treated, together with the nickel atom with additional hexadecapoles ($l = 4$). A bond-directed dipole ($l = 1$) was introduced for the hydrogen atoms. Core and spherical valence densities were constructed using Su and Coppens Hartree-Fock (HF)[7] atomic wave functions expanded over Slater-type basis functions. The radial functions for the valence deformation densities were of single Slater-type.

During the refinement the hydrogen positions [$r(C_{sp^2}\text{-H}) = 1.094$, $r(C_{sp^3}\text{-H}) = 1.100$ Å] and their isotropic thermal parameters (values derived from the IAM refinement) were fixed. To reduce the number of independently populated multipole parameters, the carbon atoms of the *tert*-butyl group C5 - C8 were assumed to be chemically equivalent (*chemically constrained model*) with the corresponding carbons of the other three *tert*-butyl groups (C9 - C12, C13 - C16 and C17 - C20, respectively). Furthermore, the hydrogen atoms of (*i*) the methyl group, (*ii*) the hydrogen atoms of the CH_2CH_2 unit (H3a, H3b, H4a, H4b) and (*iii*) the olefinic hydrogens (H1a, H1b, H2a and H2b) were set equal, respectively. In addition, local C_3 pseudo symmetry was imposed on the methyl group carbon atoms (C6, C7, C8, C10, C11, C12, C14, C15, C16, C18, C19, C20). The nickel atom was assumed to lie on a 2-fold axis in order to render the P1,P2 and C3, C4 atoms, respectively, chemically equal (see Figure S1).

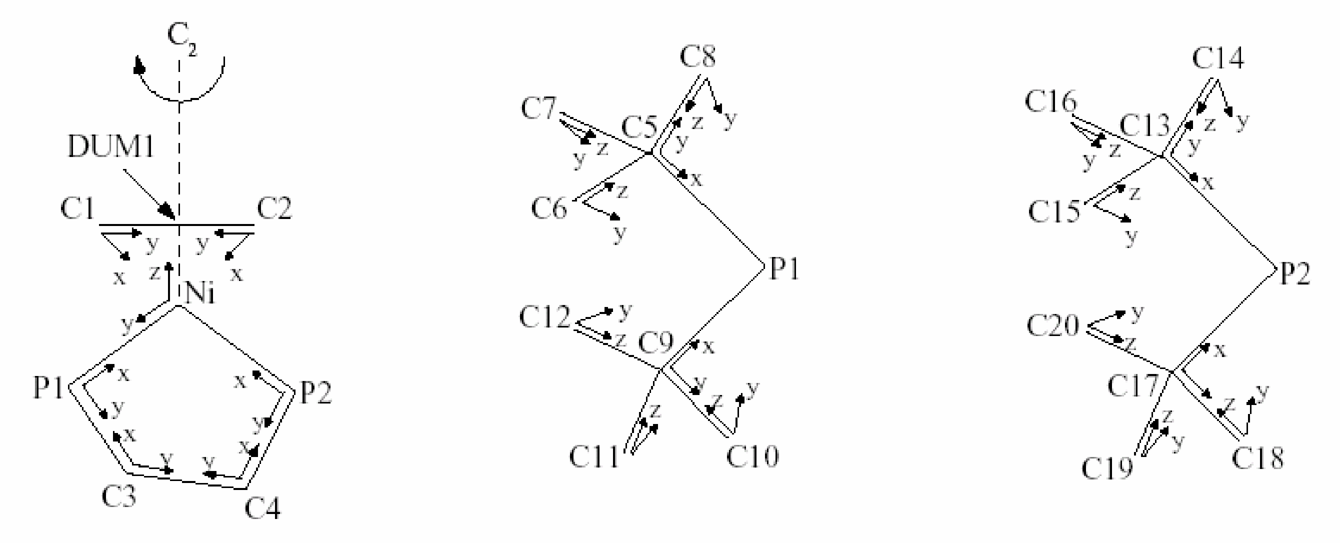


Figure S1. Local Coordinate Systems for **1** before normalization (r. h.: right hand setting; l. h.: left hand setting). The local coordinate systems are defined by two vectors $\vec{v}_1$ and $\vec{v}_2$. The third vetor is taken to be perpendicular to the plane spanned by $\vec{v}_1$ and $\vec{v}_2$. Finally an orthonormal triplet (e_{ax1}, e_{ax2}, e_{ax3}) is formed (right handed if not specified otherwise), with: $e_{\text{ax1}} = \frac{\vec{v}_1}{|\vec{v}_1|}$; $e_{\text{ax2}} = \frac{\vec{v}_3 \times \vec{v}_1}{|\vec{v}_3 \times \vec{v}_1|}$; $e_{\text{ax3}} = \frac{\vec{v}_3}{|\vec{v}_3|}$.

Definition of $\vec{v}_1$ and $\vec{v}_2$:

Ni [z axis: Ni → DUM1; y axis: Ni→ P1; r. h.], P1 [x axis: P1→ Ni; y axis: P1→ C(3); r. h.], P2 [x axis: P2→ Ni; y axis: P2→ C4; r. h.], C1 [x axis: C1→ Ni; y axis: C1→ C2; r. h.], C2 [x axis: C2→ Ni; y axis: C2→ C1; r. h.], C3 [x axis: C3→ P1; y axis: C3→ C4; r. h.], C4 [x axis: C4→ P2; y axis: C4→ C3; r. h.]. For Ni the z-axis is oriented along the pseudo 2-fold axis.

C5 [x axis: C5→ P1; y axis: C5→ C8; r. h.], C6 [z axis: C6→ C5; y axis: C6→ P1; r. h.], C7 [z axis: C7→ C5; y axis: C7→ P1; r. h.], C8 [z axis: C8→ C5; y axis: C8→ P1; r. h.], C9 [x axis: C9→ P1; y axis: C9→ C10; l. h.], C10 [z axis: C10→ C9; y axis: C10→ P1; l. h.], C11 [z axis: C11→ C9; y axis: C11→ P1; l. h.], C12 [z axis: C12→ C9; y axis: C12→ P1; l. h.], C13 [x axis: C13→ P2; y axis: C13→ C14; r. h.], C14 [z axis: C14→ C13; y axis: C14→ P2; r. h.], C15 [z axis: C15→ C13; y axis: C15→ P2; r. h.], C16 [z axis: C16→ C13; y axis: C16→ P2; r. h.], C17 [x axis: C17→ P2; y axis: C17→ C18; l. h.], C18 [z axis: C18→ C17; y axis: C18→ P2; l. h.], C19 [z axis: C19→C17; y axis: C19→ P2; l. h.], C20 [z axis: C20→ C17; y axis: C20→ P2; l. h.]. For the carbon atoms C6, C7, C8, C10, C11, C12, C14, C15, C16, C18, C19 and C20 the z-axes are oriented along the pseudo 3-fold axes.

A radial scaling parameter (κ') to adjust the spherical density was refined for each type of heavy atom present in **1**, while in the case of the H atoms κ' was kept fixed (1.20). In addition, for chemically non-equivalent atoms, except for the methyl group carbons, different κ' factors were used

(9 in total). In addition a radial scaling parameter (κ") was refined in the case of the Ni atom and one κ" parameter was adopted for the two P atoms using all data. The κ' and κ" values were then fixed for the final refinement using data up to $\sin\Theta/\lambda < 1.0$ Å^{-1}. The molecule was kept neutral during all refinements.

The final agreement factors were $R_1 = 0.0174$, $wR = 0.0205$ and $GooF = 0.7392$ for 15032 reflections ($F_o > 2\sigma(F_o)$; $\sin\Theta/\lambda < 1.00$ Å^{-1}) and 317 parameters ($N_{ref}/N_{var} = 47$); see S3 and S4 for final multipole population parameters and fractional atomic coordinates.

S3a: Fractional atomic coordinates and mean-square atomic displacement parameter for the non-hydrogen atoms of 1.

	Fractional atomic coordinates			$U_{eq}{}^{a}$
Atom	x/*a*	*y*/*b*	*z*/*c*	[Å²]
Ni	0.392324(6)	0.131743(3)	0.759493(5)	0.0103(1)
C(1)	0.275107(58)	0.196873(23)	0.823410(31)	0.0191(1)
C(2)	0.346563(59)	0.143017(25)	0.885533(29)	0.0196(1)
P(1)	0.379407(11)	0.161735(4)	0.614305(6)	0.0110(1)
P(2)	0.533311(11)	0.040047(4)	0.749966(6)	0.0104(1)
C(3)	0.518384(51)	0.101064(19)	0.570755(26)	0.0143(1)
C(4)	0.533335(51)	0.031991(19)	0.621863(26)	0.0139(1)
C(5)	0.476183(52)	0.246324(19)	0.596553(29)	0.0166(1)
C(6)	0.525649(62)	0.256275(23)	0.502194(35)	0.0243(1)
C(7)	0.355260(63)	0.303087(21)	0.609224(35)	0.0235(1)
C(8)	0.638683(61)	0.252543(22)	0.678063(36)	0.0242(1)
C(9)	0.165886(50)	0.153801(21)	0.524373(27)	0.0172(1)
C(10)	0.120016(60)	0.078169(25)	0.518657(35)	0.0270(1)
C(11)	0.158228(63)	0.178693(27)	0.423456(31)	0.0261(1)
C(12)	0.029729(55)	0.190239(26)	0.562114(34)	0.0245(1)
C(13)	0.766236(46)	0.038216(20)	0.816025(28)	0.0159(1)
C(14)	0.857553(54)	0.089221(26)	0.766792(37)	0.0259(1)
C(15)	0.784967(57)	0.063559(28)	0.918244(33)	0.0263(1)
C(16)	0.856123(52)	-0.030177(24)	0.819301(34)	0.0225(1)
C(17)	0.432825(47)	-0.042726(18)	0.772923(25)	0.0142(1)
C(18)	0.241527(53)	-0.034445(21)	0.729689(32)	0.0205(1)
C(19)	0.488522(59)	-0.106615(20)	0.728633(33)	0.0219(1)
C(20)	0.460920(59)	-0.052166(23)	0.880671(30)	0.0226(1)

[a] U_{eq} = 1/3 of the trace of the orthogonalized U Tensor.

	Mean-square atomic displacement parameters [Å^2]					
Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Ni	0.01092(2)	0.01070(2)	0.00971(2)	0.00003(2)	0.00345(2)	-0.00134(2)
C(1)	0.02090(16)	0.01856(15)	0.01943(15)	0.00318(13)	0.00824(13)	-0.00390(12)
C(2)	0.02186(16)	0.02534(18)	0.01295(13)	0.00236(14)	0.00679(12)	-0.00120(12)
P(1)	0.01297(3)	0.00971(3)	0.01072(3)	0.00062(2)	0.00380(2)	0.00031(2)
P(2)	0.01099(3)	0.01048(3)	0.01006(3)	0.00043(2)	0.00305(2)	0.00003(2)
C(3)	0.01951(14)	0.01283(12)	0.01261(12)	0.00239(11)	0.00760(11)	0.00063(10)
C(4)	0.01932(14)	0.01164(12)	0.01224(12)	0.00217(10)	0.00631(11)	-0.00074(9)
C(5)	0.01950(14)	0.01126(12)	0.02041(14)	-0.00028(10)	0.00792(12)	0.00180(10)
C(6)	0.02976(20)	0.02114(17)	0.02672(18)	0.00108(14)	0.01565(16)	0.00811(14)
C(7)	0.02978(19)	0.01171(13)	0.03204(20)	0.00357(13)	0.01349(16)	0.00174(13)
C(8)	0.02359(17)	0.01697(15)	0.03001(19)	-0.00677(13)	0.00316(15)	-0.00096(13)
C(9)	0.01665(13)	0.01748(14)	0.01539(13)	0.00094(11)	0.00016(11)	0.00234(11)
C(10)	0.02337(18)	0.02025(17)	0.02970(20)	-0.00436(14)	-0.00709(15)	0.00060(14)
C(11)	0.02836(19)	0.03193(21)	0.01504(14)	0.00463(16)	0.00017(13)	0.00520(14)
C(12)	0.01588(14)	0.02984(20)	0.02733(18)	0.00428(14)	0.00465(13)	0.00405(15)
C(13)	0.01179(12)	0.01735(14)	0.01749(13)	0.00054(10)	0.00189(10)	0.00150(11)
C(14)	0.01477(14)	0.02622(19)	0.03478(21)	-0.00389(13)	0.00307(14)	0.00981(16)
C(15)	0.01977(16)	0.03547(23)	0.01953(16)	-0.00049(15)	-0.00236(12)	-0.00701(15)
C(16)	0.01658(14)	0.02170(17)	0.02883(19)	0.00621(12)	0.00501(13)	0.00467(14)
C(17)	0.01561(12)	0.01284(12)	0.01405(12)	-0.00121(10)	0.00391(10)	0.00153(9)
C(18)	0.01500(14)	0.01999(15)	0.02555(17)	-0.00367(11)	0.00365(12)	0.00225(13)
C(19)	0.02795(18)	0.01218(13)	0.02649(17)	0.00051(12)	0.00880(15)	-0.00036(12)
C(20)	0.02797(18)	0.02487(17)	0.01517(14)	-0.00574(14)	0.00579(13)	0.00507(12)

S3b: Fractional atomic coordinates and isotropic mean-square atomic displacement parameter for the hydrogen atoms of 1.

	Fractional atomic coordinates			
Atom	x/*a*	*y*/*b*	*z*/*c*	U_{iso} [Å²]
H(3a)	0.472690	0.093750	0.493450	0.0170
H(3b)	0.643460	0.125460	0.585240	0.0170
H(4a)	0.644000	0.002730	0.614530	0.0160
H(4b)	0.421790	0.000970	0.589070	0.0160
H(6a)	0.415800	0.259900	0.439790	0.0360
H(6b)	0.606530	0.215310	0.487200	0.0360
H(6c)	0.600380	0.302930	0.506490	0.0360
H(7a)	0.421790	0.351640	0.610970	0.0350
H(7b)	0.312580	0.295940	0.674460	0.0350
H(7c)	0.243310	0.306650	0.548210	0.0350
H(8a)	0.684650	0.304910	0.680160	0.0360
H(8b)	0.738290	0.217780	0.668660	0.0360
H(8c)	0.614430	0.240320	0.747380	0.0360
H(10a)	-0.010520	0.072590	0.474860	0.0400
H(10b)	0.130140	0.057290	0.590220	0.0400
H(10c)	0.206440	0.049160	0.486610	0.0400
H(11a)	0.263930	0.157350	0.398720	0.0390
H(11b)	0.165290	0.234400	0.422150	0.0390
H(11c)	0.037400	0.161790	0.376560	0.0390
H(12a)	0.051080	0.245260	0.570210	0.0360
H(12b)	0.034160	0.170090	0.633380	0.0360
H(12c)	-0.095450	0.181530	0.513190	0.0360
H(14a)	0.989510	0.093340	0.808890	0.0380
H(14b)	0.797460	0.139560	0.760560	0.0380
H(14c)	0.856910	0.071840	0.694680	0.0380
H(15a)	0.727210	0.029680	0.961090	0.0390
H(15b)	0.728470	0.114340	0.915480	0.0390
H(15c)	0.920900	0.068530	0.953210	0.0390
H(16a)	0.990710	-0.021030	0.853630	0.0340
H(16b)	0.843850	-0.050870	0.747360	0.0340
H(16c)	0.806380	-0.068310	0.860100	0.0340
H(18a)	0.213090	-0.032800	0.651550	0.0300
H(18b)	0.196130	0.012900	0.754600	0.0300
H(18c)	0.174160	-0.077850	0.749890	0.0300
H(19a)	0.415090	-0.149480	0.744840	0.0330

S3b: Fractional atomic coordinates and isotropic mean-square atomic displacement parameter for the hydrogen atoms of 1. (*cont.*).

H(19b)	0.625220	-0.117470	0.751420	0.0330
H(19c)	0.463450	-0.101870	0.650680	0.0330
H(20a)	0.425050	-0.006780	0.914830	0.0340
H(20b)	0.592450	-0.064610	0.918580	0.0340
H(20c)	0.378170	-0.093530	0.892050	0.0340
H(1a)	0.333360	0.247110	0.832540	0.0230
H(1b)	0.138150	0.199110	0.793350	0.0230
H(2a)	0.265570	0.102820	0.900940	0.0230
H(2b)	0.459920	0.153130	0.942710	0.0230

S4: Kappa and multipole poopulation parameter of 1.

Symmetry forbidden multipoles are denoted by an asterisk (*)

Atom	κ'	κ''	P_v	P_{11+}	P_{11-}	P_{10}
Ni	1.011[c]	1.078[c]	7.774(14)	*	*	0.035(7)
P(1)[a]	0.936[c]	1.00[d]	5.641(31)	0.189(15)	-0.127(15)	0.023(16)
C(1)[a]	0.947[c]	0.885[c]	4.745(24)	-0.008(10)	-0.082(10)	0.002(14)
C(3)[a]	0.978[c]	1.00[d]	4.413(22)	-0.007(9)	-0.097(8)	-0.005(8)
C(5)[b]	1.025[c]	1.00[d]	3.649(14)	0.022(6)	-0.011(6)	-0.004(5)
C(6)[b]	0.961[c]	1.00[d]	4.637(15)	*	*	-0.059(6)
C(7)[b]	0.961[c]	1.00[d]	4.589(14)	*	*	-0.048(6)
C(8)[b]	0.961[c]	1.00[d]	4.620(14)	*	*	-0.047(7)

[a] The multipole population coefficients of P(2), C(2) and C(4) were set equal to the corresponding coefficients of P(1), C(1) and C(3), respectively (chemically constrained model).

[b] The multipole population coefficients of C(9), C(10), C(11), C(12)/ C(13), C(14), C(15), C(16)/ C(17), C(18), C(19), C(20) were set equal to the corresponding coefficients of C(5), C(6), C(7), C(8), respectively (chemically constrained model).

[c] Values for κ' and κ'' were refined using all data and then fixed in the final refinements.

[d] Fixed values.

Atom	P_{20}	P_{21+}	P_{21-}	P_{22+}	P_{22-}
Ni	-0.232(21)	*	*	0.315(19)	-0.132(22)
P(1) [a]	-0.060(15)	0.033(13)	0.050(13)	0.250(14)	-0.026(14)
C(1) [a]	0.029(11)	-0.019(11)	-0.002(16)	-0.039(9)	0.109(9)
C(3) [a]	0.011(9)	-0.009(8)	-0.016(8)	0.035(7)	0.024(7)
C(5)[b]	-0.017(6)	0.015(5)	0.016(6)	0.002(6)	-0.011(6)
C(6) [b]	0.017(6)	*	*	*	*
C(7)[b]	-0.013(7)	*	*	*	*
C(8) [b]	0.000(7)	*	*	*	*

[a] The multipole population coefficients of P(2), C(2) and C(4) were set equal to the corresponding coefficients of P(1), C(1) and C(3), respectively (chemically constrained model).

[b] The multipole population coefficients of C(9), C(10), C(11), C(12)/ C(13), C(14), C(15), C(16)/ C(17), C(18), C(19), C(20) were set equal to the corresponding coefficients of C(5), C(6), C(7), C(8), respectively (chemically constrained model).

Atom	P_{30}	P_{31+}	P_{31-}	P_{32+}	P_{32-}	P_{33+}	P_{33-}
Ni	0.001(7)	*	*	0.003(6)	-0.003(6)	*	*
P(1)[a]	-0.012(16)	-0.316(16)	-0.258(15)	0.032(14)	0.006(14)	0.186(15)	-0.117(14)
C(1)[a]	0.004(14)	-0.214(11)	-0.273(11)	-0.028(15)	0.014(15)	0.022(9)	-0.139(10)
C(3)[a]	0.044(10)	-0.110(9)	-0.165(9)	-0.028(9)	-0.021(9)	0.164(8)	-0.049(8)
C(5)[b]	-0.006(6)	-0.128(6)	-0.153(7)	-0.004(6)	0.012(6)	0.133(6)	-0.074(6)
C(6)[b]	0.281(7)	*	*	*	*	0.006(7)	0.137(7)
C(7)[b]	0.267(7)	*	*	*	*	-0.001(7)	0.136(7)
C(8)[b]	0.256(8)	*	*	*	*	0.004(7)	0.152(7)

[a] The multipole population coefficients of P(2), C(2) and C(4) were set equal to the corresponding coefficients of P(1), C(1) and C(3), respectively (chemically constrained model).

[b] The multipole population coefficients of C(9), C(10), C(11), C(12)/ C(13), C(14), C(15), C(16)/ C(17), C(18), C(19), C(20) were set equal to the corresponding coefficients of C(5), C(6), C(7), C(8), respectively (chemically constrained model).

Atom	P_{40}	P_{41+}	P_{41-}	P_{42+}	P_{42-}
Ni	0.100(12)	*	*	0.137(11)	0.003(11)
P(1)[a]	-	-	-	-	-
C(1)[a]	0.016(14)	0.030(14)	0.011(17)	0.036(12)	0.077(14)
C(3)[a]	-	-	-	-	-
C(5)[b]	-	-	-	-	-
C(6)[b]	-	-	-	-	-
C(7)[b]	-	-	-	-	-
C(8)[b]	-	-	-	-	-

[a] The multipole population coefficients of P(2), C(2) and C(4) were set equal to the corresponding coefficients of P(1), C(1) and C(3), respectively (chemically constrained model).

[b] The multipole population coefficients of C(9), C(10), C(11), C(12)/ C(13), C(14), C(15), C(16)/ C(17), C(18), C(19), C(20) were set equal to the corresponding coefficients of C(5), C(6), C(7), C(8), respectively (chemically constrained model).

Atom	P_{43+}	P_{43-}	P_{44+}	P_{44+}
Ni	*	*	0.006(11)	-0.008(11)
P(1)[a]	-0.008(17)	-0.015(17)	0.012(12)	-0.068(12)
C(1)[a]	-0.008(17)	-0.015(17)	0.012(12)	-0.068(12)
C(3)[a]	-	-	-	-
C(5)[b]	-	-	-	-
C(6)[b]	-	-	-	-
C(7)[b]	-	-	-	-
C(8)[b]	-	-	-	-

[a] The multipole population coefficients of P(2), C(2) and C(4) were set equal to the corresponding coefficients of P(1), C(1) and C(3), respectively (chemically constrained model).

[b] The multipole population coefficients of C(9), C(10), C(11), C(12)/ C(13), C(14), C(15), C(16)/ C(17), C(18), C(19), C(20) were set equal to the corresponding coefficients of C(5), C(6), C(7), C(8), respectively (chemically constrained model).

	H(3a)[a]	H(6a)[a]	H(1a)[a]
κ'	1.20[b]	1.20[b]	1.20[b]
κ''	1.00[b]	1.00[b]	1.00[b]
P_v	0.785(8)	0.801(3)	0.665(11)
P_{10}	0.072(6)	0.088(3)	0.046(7)

[a] The multipole population coefficients of all methyl group hydrogens were set equal to H(6a), for H(3b), H(4a), H(4b) equal to H(3a) and for H(1b), H(2a), H(2b) equal to H(1a) (chemically constrained model).

[b] Fixed values.

S5: Residual density maps after multipole refinement for 1.

The residual electron density map was practically featureless with the maximum and minimum values of 0.10 and -0.32 e/Å^3 (sinΘ/λ < 0.8 Å^{-1}), respectively (see also Figure S2 for details). Hirshfeld's rigid bond test[8] was applied to the atomic displacement parameters obtained from the refinements. The difference between mean-square amplitudes never exceeds the limit of $1.0 \cdot 10^{-3}$ Å^2, proposed by Hirshfeld.

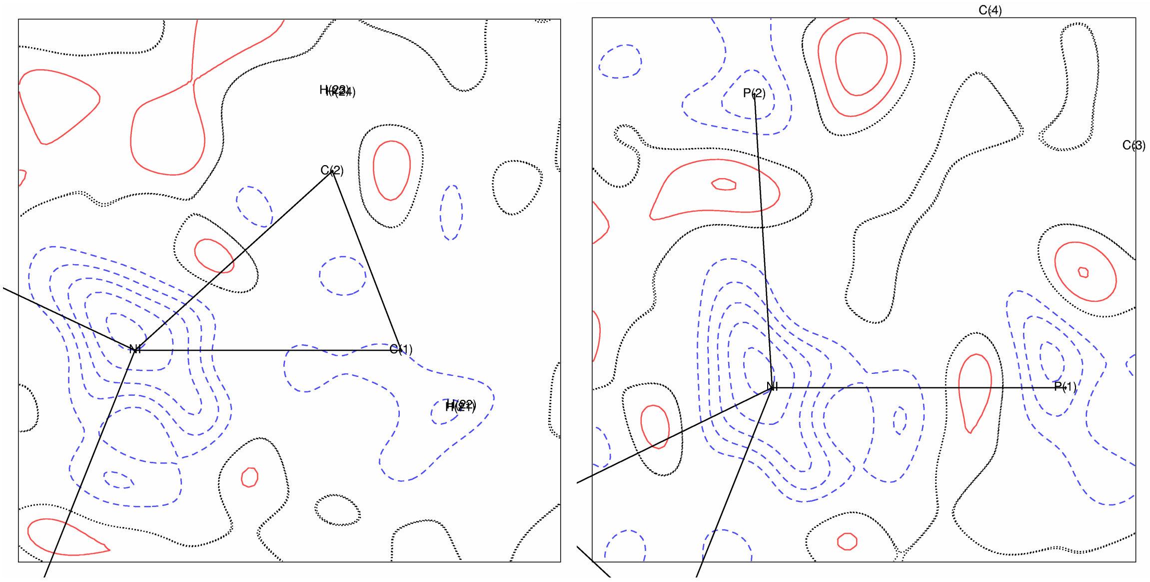


Figure S2. Residual Density Maps of **1** (data cut-off at sinΘ/λ = 0.8 Å^{-1}; contour level = 0.05 eÅ^{-3}). (a) Ni,C1,C2 plane; (b) Ni,P1,P2 plane.

Computational Details. All refinements were carried out with the full-matrix least-squares program "XDLSM" of the "XD" suite of programs;[6] the quantity minimized was $\varepsilon = \Sigma w_1(|F_o| - k \cdot |F_c|)^2$, where k is a scale factor, based on 15038 reflections with $F_o > 3\sigma(F_o)$. Weights were taken as $w_1 = 1/\sigma^2(F_o)$ and $w_2 = 1/\sigma^2(F_o{}^2)$. Convergence was assumed when a maximal shift/esd < 10^{-11} was achieved. 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 $\nabla^2(\mathbf{r})$ were calculated after transformation of the local axis system into a global system. DFT calculations using the B3LYP density functional[9] and a standard basis set of triple-ζ quality plus polarisation[10a-c] (6-311G(d)) were carried out with the "Gaussian03" program suite (release B.03).[11] The topological analysis of the theoretical electron densities was carried out with the "AIMPAC" software package.[12] A comparison between topological and geometrical parameters (experiment vs. theory) is given in S6.

S6: Topological analysis of the charge density and geometrical parameter of 1.

Unit	Method[a]	Distance [Å]	$\rho(\mathbf{r}_c)$ [e/Å^3]	$\nabla^2\rho(\mathbf{r}_c)$ [e/Å^5]	Ellipticity ε
C1 – C2	Experiment	1.4189(6)	2.107	-20.875	0.25
	Theory	1.4221	1.918	-16.547	0.27
Ni – C1	Experiment	1.9708(4)	0.671	8.393	1.03
	Theory	1.9623	0.723	5.934	0.87
Ni – C2	Experiment	1.9715(4)	0.670	8.392	1.05
	Theory	1.9623	0.723	5.934	0.87
Ni – P1	Experiment	2.1655(1)	0.717	2.877	0.09
	Theory	2.2095	0.608	4.386	0.05
Ni – P2	Experiment	2.1680(1)	0.714	2.917	0.09
	Theory	2.2095	0.608	4.386	0.05
P1 – C3	Experiment	1.8675(4)	0.875	1.310	0.08
	Theory	1.8901	1.010	-6.277	0.10
P2 – C4	Experiment	1.8665(4)	0.876	1.377	0.08
	Theory	1.8901	1.010	-6.277	0.10
C3-C4	Experiment	1.5419(6)	1.485	-7.925	0.03
	Theory	1.5447	1.547	-11.238	0.01

[a] The experimental values were obtained by multipole refinement of the experimental charge density, the theoretical calculations were performed at the B3LYP/6-311G(d) level of theory.

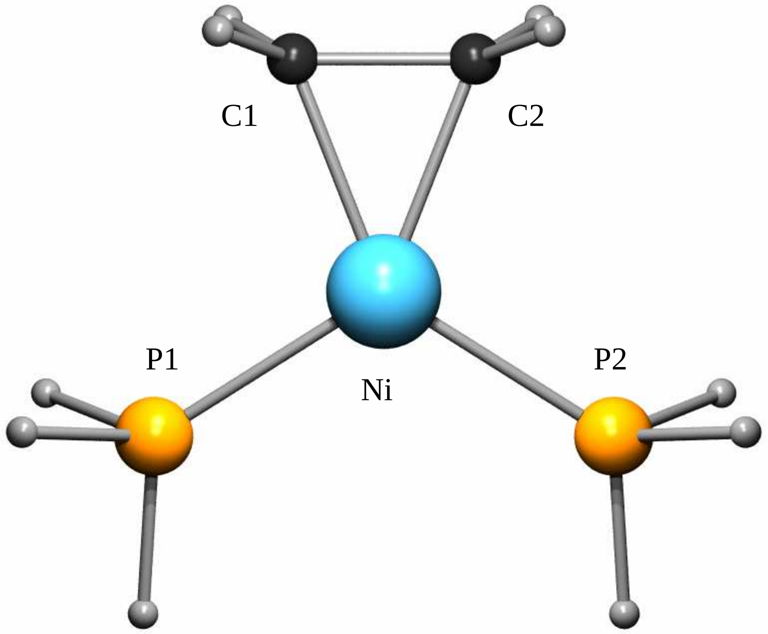
S7a: Topological analysis of the charge density and geometrical parameter of models 1a, 2 and 3.

Unit[a]	Model[b]	Distance [Å]	$\rho(\mathbf{r}_c)$ [e/Å^3]	$\nabla^2\rho(\mathbf{r}_c)$ [e/Å^5]	Ellipticity ε
C1 – C2	**1a**	1.4177	1.939	-16.940	0.27
	2	1.4515	1.810	-14.528	0.26
	3	1.4510	1.962	-18.030	0.32
Ni – C1	**1a**	1.9544	0.736	6.074	0.97
	2	1.8948	0.837	6.624	0.50
	3	1.8445	0.975	8.092	0.24
Ni – P1	**1a**	2.1390	0.680	4.583	0.04
Ni – N1	**2**	2.0439	0.520	9.593	0.10
Ni – N1	**3**	2.0298	0.546	9.679	0.15
N1 – C3	**2**	1.4807	1.739	-15.270	0.04
N1 – C3	**3**	1.4848	1.722	-14.974	0.04
C3-C4	**2**	1.5277	1.665	-13.640	0.06
	3	1.5284	1.663	-13.601	0.05

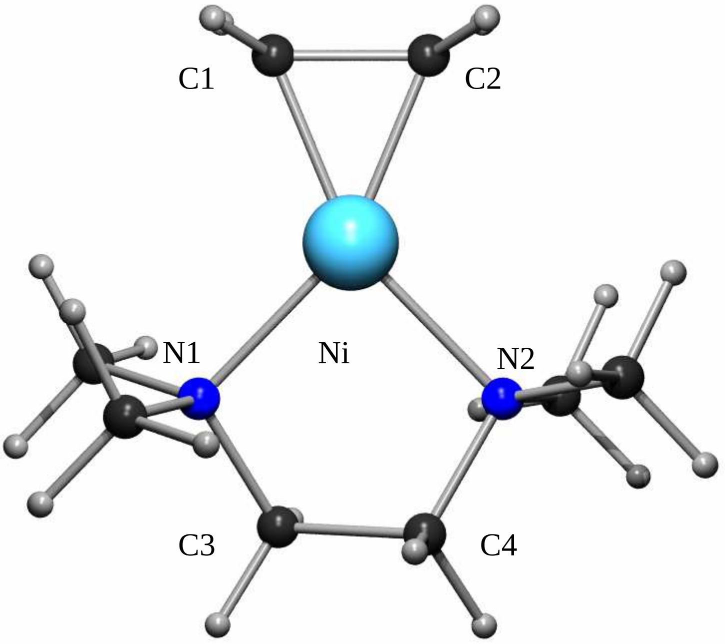
[a] Labels according to S7b.

[b] Calculations were performed at the B3LYP/6-311G(d) level of theory with symmetry restrained for 1a, 2 and 3 to C_{2v}, C_2 and C_2, respectively.

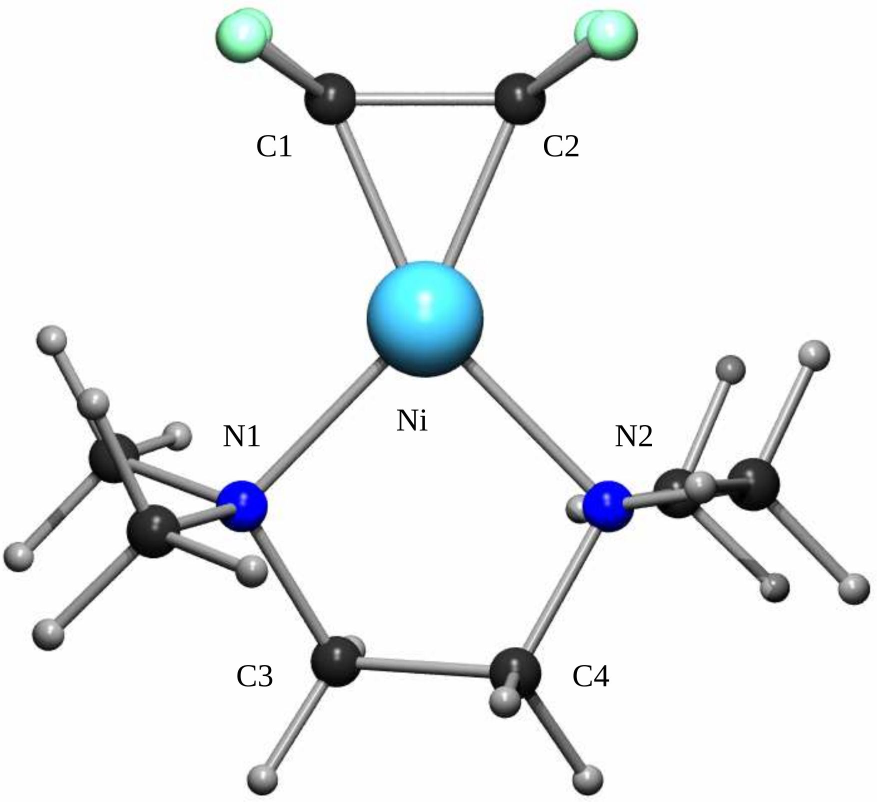
S7b: Ball and Stick Representation of models 1a, 2 and 3.



[Ni(η^2-C_2H_4)(PH_3)$_2$] 1



[Ni(η^2-C_2H_4)TMEDA] 2



[Ni(η^2-C_2F_4)TMEDA] 3

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