Supporting Information

Unusual Selectivity of a (pincer)Ni-hydride Reacting with CO_2

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Computational Details

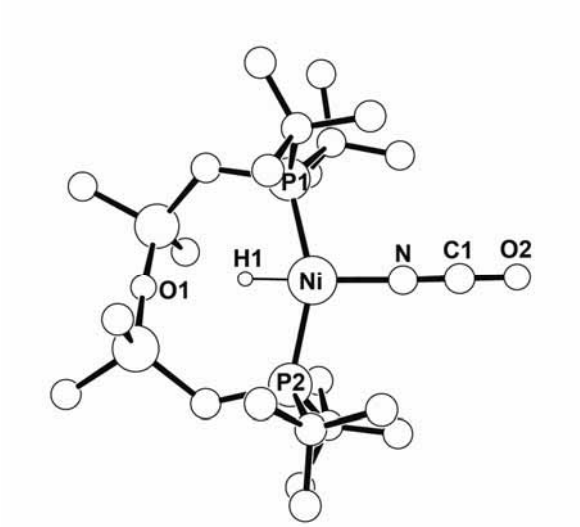
All calculations were carried out using Density Functional Theory as implemented in the Jaguar 6.0 suite[1] of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP[2-5] functional and the 6-31G** basis set with no symmetry restrictions. Transition metals were represented using the Los Alamos LACVP basis[6,7]. The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry using Dunning's correlation-consistent triple-ζ basis set[8] cc-pVTZ(-f) that includes a double set of polarization functions. For all transition metals, we used a modified version of LACVP, designated as LACV3P, in which the exponents were decontracted to match the effective core potential with the triple-ζ quality basis.

The models used in this study consist of up to ~80 atoms, which represent the non-truncated substrates that were also used in the related experimental work.

References

1. Jaguar, version 6.0, *Schrödinger, L.L.C, New York, NY, 2005*.
2. Becke, A. D., *Phys. Rev. A* **1988,** *38*, 3098.
3. Becke, A. D., *J. Chem. Phys.* **1993,** *98*, 5648.
4. Lee, C. T.; Yang, W. T.; Parr, R. G., *1988* **Phys. Rev. B,** *37*, 785.
5. Vosko, S. H.; Wilk, L.; Nusair, M., *Can. J. Phys.* **1980,** *58*, 1200.
6. Hay, P. J.; Wadt, W. R., *J. Chem. Phys.* **1985,** *82*, 270.
7. Wadt, W. R.; Hay, P. J., *J. Chem. Phys.* **1985,** *82*, 284.
8. Dunning, T. H., *J. Chem. Phys.* **1989,** *90*, 1007.

S1. (POP)Ni(NCO).

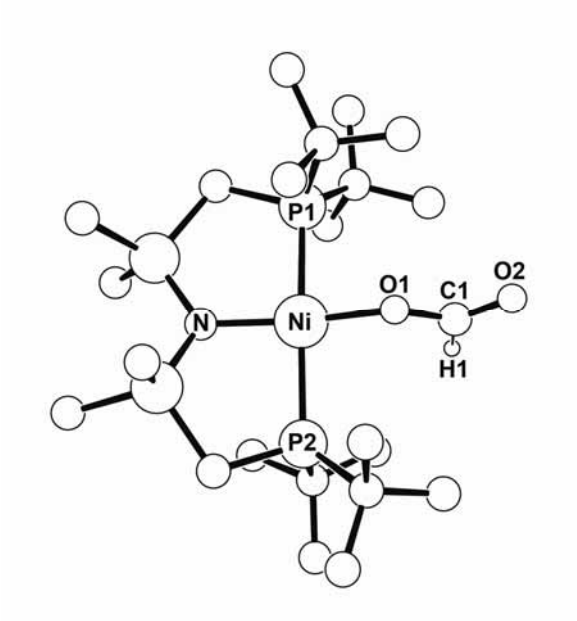


3 (0.0 kcal/mol)

Select bond lengths (Å) and bond angles (°).

Ni-P1	2.269
Ni-P2	2.270
Ni-H1	1.426
Ni-N	1.921
Ni-O1	3.759
P1-Ni-P2	154.2
N-Ni-H1	173.8
Ni-N-C1	174.1
O1-Ni-H1	17.4

S2. (PNP)Ni(OCOH).

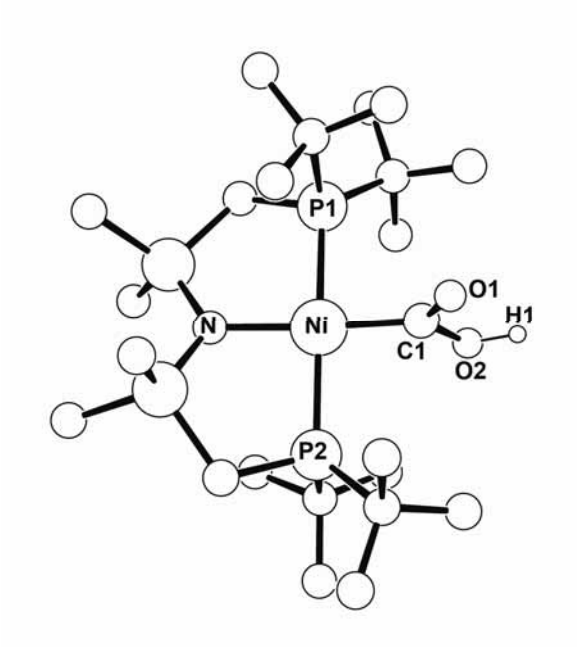


2 (+19.1 kcal/mol)

Select bond lengths (Å) and bond angles (°).

Ni-P1	2.357
Ni-P2	2.346
Ni-N	1.941
Ni-O1	1.888
P1-Ni-P2	170.5
N-Ni-O1	163.8
Ni-O1-C1	135.2

S3. (PNP)Ni(COOH)



1 (+21.4 kcal/mol)

Select bond lengths (Å) and bond angles (°).

Ni-P1	2.331
Ni-P2	2.336
Ni-N	1.994
Ni-C1	1.886
P1-Ni-P2	173.3
N-Ni-O1	171.4
Ni-C1-O1	123.9
Ni-C1-O2	118.6

4. Optimized Structures.

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Ni	15.790938795	2.170573748	18.127257070
P	16.638535451	0.389696659	19.250537633
P	14.429642996	3.968444980	17.876062777
Si	15.380343730	1.673618062	22.089661147
Si	12.749787247	3.031226454	20.642421956
O	14.003386577	2.302567552	21.430834793
C	16.575487275	3.088513471	22.433815394
H	16.071436462	3.826957189	23.068883161
H	16.892447961	3.594134089	21.518062004
H	17.473304666	2.757976765	22.967206586
C	14.907455278	0.869611320	23.731445884
H	14.471384809	1.608794904	24.412932703
H	15.777813159	0.430757588	24.233319516
H	14.167749120	0.073341731	23.591881634
C	16.017596619	0.232941261	21.008492630
H	16.726645741	-0.360203580	21.601229364
H	15.119381461	-0.394865237	20.938684333
C	16.010318348	-1.264506380	18.480237421
C	18.550367268	0.400802584	19.418968542
C	11.778613691	4.043977870	21.907063572
H	12.398080226	4.825071087	22.362274256
H	11.412135980	3.400909707	22.715184399
H	10.908371557	4.533180329	21.453567520
C	11.637842696	1.664233538	19.978371121
H	12.144554553	1.037644088	19.239237607
H	10.717680667	2.046813426	19.524100663
H	11.347112070	1.022203662	20.818248502
C	13.394090356	4.325052468	19.391040723
H	12.552143955	4.977328897	19.123475543
H	14.040076867	4.941641434	20.030881057
C	15.535911071	5.536430272	17.743084164
C	14.826360126	6.868436333	18.058467503
H	15.562339051	7.681076112	18.011625035
H	14.394168552	6.884258736	19.063363790
H	14.034255819	7.106349473	17.346807934
C	13.136809867	3.915952972	16.455378907
C	16.115378176	-2.490149445	19.410181338
C	16.737934217	-1.568757918	17.157269099
C	14.518320794	-1.017782206	18.157024999
C	19.143654508	-0.902793433	19.985485512
C	18.903154924	1.557139536	20.376218148
C	19.188664231	0.713094459	18.050022089
C	12.423869845	5.259219284	16.206987657
C	12.084910233	2.866783318	16.873792966
C	13.789458653	3.427667364	15.146062388
C	16.673941009	5.333499464	18.770146597
C	16.167837915	5.597267826	16.338619519
H	19.993597210	1.674286739	20.409461496
H	18.562578572	1.369840096	21.397440941
H	18.476757501	2.506596906	20.038976578
H	20.218354330	-0.762558840	20.159719989
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H	18.697094415	-1.189262952	20.943600979
H	20.266612679	0.866531705	18.188872820
H	18.760317935	1.613423804	17.604362771
H	19.061011052	-0.097781012	17.331710954
H	15.704987853	-3.362441437	18.885746524
H	15.541554511	-2.373788324	20.333719154
H	17.145921585	-2.728794056	19.680603915
H	16.218170774	-2.390027827	16.647671649
H	17.769992577	-1.893475660	17.317546088
H	16.736078712	-0.702838173	16.493101484
H	14.085694536	-1.927985765	17.722394349
H	14.405569563	-0.205325261	17.433701444
H	13.931207668	-0.771557047	19.049282068
H	17.358506290	6.189809712	18.722230347
H	17.244469155	4.424626181	18.555557900
H	16.304294535	5.265829365	19.798759711
H	16.976803245	6.338551381	16.339480691
H	15.447652309	5.907091801	15.576415876
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H	11.601319460	5.099396607	15.497788438
H	13.090588956	6.002051281	15.761938310
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H	13.004422306	3.308250258	14.388322339
H	14.292014087	2.469359841	15.285131733
H	14.523608692	4.131002578	14.748799563
H	11.377988802	2.721696181	16.047690154
H	11.508095032	3.179101821	17.747796832
H	12.543027519	1.896593736	17.089501233
N	16.435851326	1.859345318	16.344491035
C	16.925851050	1.748719419	15.257393879
O	17.416043708	1.634597412	14.165118621
H	15.431548542	2.497947015	19.468078097

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Ni	4.088691762	-4.924073134	-7.136091710
P	5.374892595	-6.282826502	-8.551480335
P	2.671806035	-3.389551863	-6.043118495
Si	7.070919313	-3.849389190	-7.742958723
Si	5.575275006	-2.837735917	-5.354355033
C	1.764009334	-6.683661160	-7.637546695
N	5.588473162	-3.725889798	-6.848454258
C	7.399833509	-2.352490484	-8.865536508
H	7.532779257	-1.432567154	-8.286044445
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C	6.956040924	-5.379535792	-8.875445612
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H	3.083639369	-7.577017319	-11.371862376
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H	6.705212528	-6.692264785	-5.970294296
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H	7.685433671	-1.414015772	-5.475962099
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H	0.422188805	-2.112557336	-4.241004267
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C	1.897736675	-2.216420128	-7.349697804
C	3.068707306	-1.486011511	-8.045499307
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C	1.160738998	-3.047512418	-8.418742209
H	0.772149385	-2.376334391	-9.195161723
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O	2.852812778	-6.345514049	-7.008257994
O	1.205651517	-7.767629164	-7.539940432
H	1.339254962	-5.895415278	-8.296240767

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Ni	4.026336755	-4.921999042	-7.168787620
P	5.301515390	-6.320949004	-8.528415712
P	2.711846099	-3.365120762	-6.027136564
Si	7.012911909	-3.849226672	-7.807679631
Si	5.659281290	-3.006608894	-5.249293098
O	1.630890415	-5.893226002	-8.303641713
N	5.638273727	-3.818671534	-6.770321345
C	7.281168379	-2.261062111	-8.821289172
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H	6.387501619	-2.005461546	-9.402678275
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H	3.545291368	-6.038085671	-11.859211443
H	4.594799765	-4.900305342	-11.018130184
H	3.064228985	-5.406517315	-10.274353777
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C	7.570740437	-8.014973774	-7.921546930
H	7.957407038	-8.851741561	-7.325982814
H	8.230260257	-7.161156049	-7.746329351
H	7.651839934	-8.300038988	-8.975051829
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H	5.076812894	-7.165054197	-5.657653110
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C	5.308726795	-9.040165707	-7.560193305
H	5.424597200	-9.548919061	-8.520479327
H	5.689510495	-9.721564740	-6.788652816
H	6.591200338	-6.284530237	-5.891612170
H	4.247158085	-8.876656330	-7.361251179
C	6.708694380	-1.417258291	-5.184806070
H	7.778028748	-1.605948426	-5.328700486
H	6.597781542	-0.933709259	-4.206166597
H	6.396081154	-0.694984592	-5.947472526
C	6.221914933	-4.089392853	-3.789877014
H	7.253359074	-4.437298814	-3.920016927
H	5.589142960	-4.979184301	-3.689577373
H	6.178361364	-3.537826549	-2.841810425
C	3.857054649	-2.496407506	-4.860765402
H	3.616799896	-2.803503634	-3.839414458

H	3.710465036	-1.412106853	-4.904213829
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C	1.836881287	-5.115354603	-4.061116626
H	1.066581168	-5.466612884	-3.362740860
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H	-0.677580692	-4.844253854	-4.972193117
H	0.277423307	-5.099299493	-6.438507158
H	-0.478265528	-3.529817826	-6.131206784
C	0.832444083	-2.833118552	-3.862736808
H	0.082151477	-3.270209797	-3.191763742
H	0.373142201	-1.969339365	-4.345206524
H	1.652716366	-2.473948022	-3.236454882
C	2.143145502	-2.001000606	-7.257357907
C	3.419997126	-1.329421668	-7.808109245
H	3.139956140	-0.658315423	-8.629955319
H	4.135043620	-2.064871888	-8.182496146
H	3.929553237	-0.724466982	-7.052128302
C	1.397737429	-2.648250238	-8.440963208
H	1.126631205	-1.866036269	-9.161899804
H	0.479487909	-3.154357136	-8.135908257
H	2.021499908	-3.384468395	-8.951701632
C	1.254357033	-0.917385341	-6.619420199
H	1.113868153	-0.102721965	-7.341738033
H	1.704006962	-0.480835675	-5.721790358
H	0.261223354	-1.293972592	-6.361221019
C	2.597939382	-6.140439537	-7.345865552
O	2.475854525	-7.153004320	-6.667479962
H	1.006863502	-6.643435708	-8.242519592

Experimental

General Considerations. All manipulations were performed using standard Schlenk techniques or in an argon-filled glovebox unless otherwise noted. Pentane and THF were purified using an Innovative Technologies solvent purification system Pure Solv 400-6-MD. Benzene D-6 was dried under Ph_2CO/Na, vacuum transferred and stored in the glovebox under argon. CO_2 was used as received from commercial vendors. $[(^tBu_2PCH_2SiMe_2)_2N]NiH$ and (PNP)NiCl were prepared following the published synthesis.[1] NMR chemical shifts are reported in ppm relative to protio impurities in the deutero solvents. Coupling constants are given in Hz. ^{31}P NMR spectra are referenced to external standards of H_3PO_4. NMR spectra were recorded with a Varian Unity INOVA instrument (400 MHz ^1H; 162 MHz ^{31}P). Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. Mass spectra were acquired on a MAT-95-XP spectrometer (Thermo Electron Corp, Bremen, Germany). "PNP" is $N(SiMe_2CH_2PBu_2^t)_2$.

$[(^tBu_2PCH_2SiMe_2)_2NH]NiH(BAr^f_4)$

A solution of 20 mg (0.039 mmol) of (PNP)NiCl and 35 mg (0.039 mmol) of $NaB[3,5-(CF_3)_2C_6H_3]_4$ in 0.5 mL CD_2Cl_2 was agitated end-over-end for 1 h. The solution was freeze-pump-thaw degassed and 760 mmHg of H_2 was added on a vacuum line. In time of mixing the solution had changed color from red to yellow. NMR analysis showed complete conversion into the new $(PNHP)NiH(BAr^f_4)$. **^1H NMR (CD_2Cl_2):** 7.76 (br.s, Ar-o, 8 H), 7.59 (br.s, Ar-p, 4 H), 1.33 (t, J_{P-H}, 7.0 Hz, ^{t}Bu, 18H), 1.32 (t, J_{P-H}, 7.0 Hz, ^{t}Bu, 18H), 1.23-1.26 (m, CH_2, 4H), 0.48 (s, SiMe, 6H), 0.39 (s, SiMe, 6H), –22.06 (t, J_{P-H}, 66.1 Hz, Ni-H, 1H). The N-H proton was not located. **$^{31}P\{^1H\}$ NMR (CD_2Cl_2):** 63.2 . **^{19}F NMR (CD_2Cl_2):** –63.2 (s).

[(^{t}Bu$_2$PCH$_2$SiMe$_2$)$_2$N]NiH

a) **From (PNHP)NiHOTf and Et$_3$N in D$_8$THF.** 15 mg (0.023mmol) of {[(^{t}Bu$_2$PCH$_2$SiMe$_2$)$_2$NH]NiH(OTf)} was dissolved in 0.5ml of deuterated THF. To this solution a 10-fold excess (3.2μL) of Et$_3$N was added. The NMR of the resulting yellow solution showed 90% conversion to (PNP)NiH. **^{1}H NMR (D$_8$THF):** 1.30 (t, J_{P-H}, 6.3 Hz, ^{t}Bu, 36H), 0.95 (t, J_{P-H}, 6.6 Hz, CH$_2$, 4H), 0.61 (s,SiMe, 12H), -21.30 (t, J_{P-H}, 66 Hz, NiH, 1H). **^{31}P{^{1}H} NMR (D$_8$THF):** 73.2 .

b) **From [(PNHP)Ni(H)]BAr$^{f}_4$ and LiN^{i}Pr$_2$ in THF.** A solution of (PNHP)NiH(BAr$^{f}_4$) in CD_2Cl_2 obtained from 20 mg of (PNP)NiCl, 35 mg of NaB[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$ and 1 atm H_2 (as above) was dried in vacuum and dissolved in 3 mL of THF. 4.2 mg (0.039 mmol) of LiN^{i}Pr$_2$ was added. After 10 minutes of stirring all volatiles were removed in vacuum. The residue was extract with 2 x 10 mL of pentane and filtered through the glass filter. Pentane was removed in vacuum to give yellow solid. NMR analysis showed complete conversion into (PNP)Ni-H. **^{1}H NMR (C$_6$D$_6$):** 1.23 (t, J_{P-H}, 6.4 Hz, ^{t}Bu, 36H), 0.82 (t, J_{P-H}, 4.8 Hz, CH$_2$, 4H), 0.40 (s, SiMe, 12H), –21.19 (t, J_{P-H}, 68 Hz, NiH, 1H). **^{31}P{^{1}H} NMR (C$_6$D$_6$):** 73.8 .

Reaction of (PNP)NiH with CO$_2$. 16.2 mg (0.032 mmol) of (PNP)NiH was dissolved in 0.5mL of benzene in a J-Young NMR tube leaving a yellow solution. The solution was freeze-pump-thawed once followed by the addition of one atmosphere of CO_2 to the frozen solution. The solution was thawed to room temperature and shaken vigorously. After four days of end-over-end agitation, full conversion of the starting material to the new single product, (POP)Ni(H)(NCO), was observed. From a pentane solution, crystals were grown at –40 °C suitable for X-ray diffraction analysis. **^{1}H NMR (25 °C C$_6$D$_6$):** 1.26 (t, J_{P-H}, 6.6, ^{t}Bu, 36 H), 0.62 (m, CH$_2$, 4 H), 0.18 (s, SiMe, 12 H), –25.52 (t, J_{P-H}, 78.1, NiH, 1H). **^{31}P{^{1}H} NMR (25 °C C$_6$D$_6$):** 41.6. **MS (CI) THF:** 509.2423 $C_{22}H_{53}P_2Si_2NiO$ $[M–NCO]^+$**;** the loss of the cyanate ligand in forming a positive ion speaks for "NCO" connectivity in the molecule, and thus against the molecule as still containing two C=O bonds (i.e. not containing intact CO_2). **IR (KBr):** 2224 cm^{-1} (N=C=O). This molecule is decomposed within minutes by CH_2Cl_2, with color change to orange and production of diverse products, including paramagnetic species.

1. Ingleson, Michael J.; Fullmer, Benjamin C.; Buschhorn, Drew T.; Fan, Hongjun; Huffman, John C.; Caulton, Kenneth G., Inorg. Chem., **2008**, *47*(2), 407-409.

Crystal Structure Determination. An orange crystal (approximate dimensions 0.21 × 0.13 × 0.13 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX II Kappa Duo diffractometer equipped with an APEX II detector at 150(2) K.

Data collection

The data collection was carried out using Mo K_α radiation (graphite monochromator) with a frame time of 30 seconds and a detector distance of 5.0 cm. A collection strategy was calculated and complete data to a resolution of 0.77 Å with a redundancy of 4 were collected. Four major sections of frames were collected with 0.50º ω and ϕ scans. Data to a resolution of 0.77 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 9978 strong reflections from the actual data collection after integration (SAINT).[1] The intensity data were corrected for absorption (SADABS).[2]

Structure solution and refinement

The space group P2(1)/c was determined based on intensity statistics and systematic absences. The structure was solved using SIR-2004[3] and refined with SHELXL-97.[4] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters, with the exception of H1ni, which was found in the difference map and only its thermal parameter was refined. The final full matrix least squares refinement converged to R1 = 0.0243 and wR2 = 0.0671 (F^2, all data). The remaining electron density is minuscule and located on bonds.

1 SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.

2 An empirical correction for absorption anisotropy.
R. Blessing, *Acta Cryst*. A51, 33 - 38 (1995).

3 Sir2004, A Program for Automatic Solution and Refinement of Crystal Structures.
M. C. Burla, R. Caliandro, M. Carnalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Sagna. Vers. 1.0 (2004).

4 A short history of *SHELX*.
G. M. Sheldrick, *Acta Cryst*. A64, 112 - 122 (2008).