Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


# Single-component conductors based on closed-shell Ni and Pt bis(dithiolene) complexes: metallization under high pressure

*Hadi Hachem, HengBo Cui, Takao Tsumuraya, Reizo Kato,* Olivier Jeannin, Marc Fourmigué*, Dominique Lorcy**

*Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France*
*Condensed Molecular Materials Laboratory, RIKEN, Wako-shi, Saitama 351-0198, Japan*
*Priority organization for Innovation and excellence, Kumamoto University, Kumamoto 860-8555, Japan*

## Supplementary Information

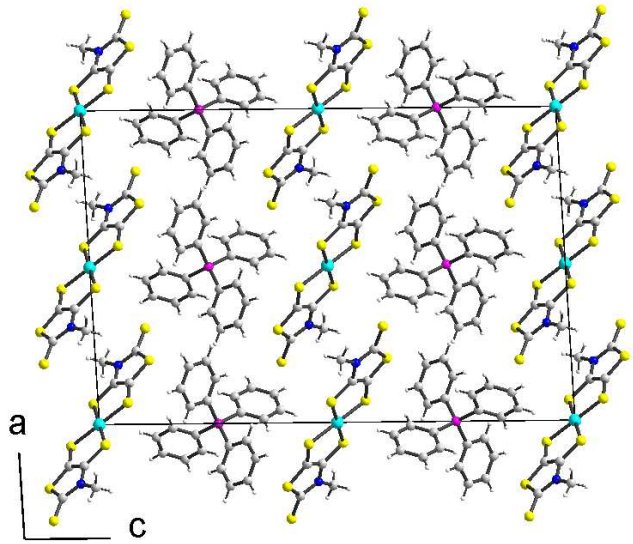


**Figure S1**. Projection view along *b* of the unit cell of the non-solvated salt $[Ph_4P][Ni(Me\text{-}thiazdt)_2]$.

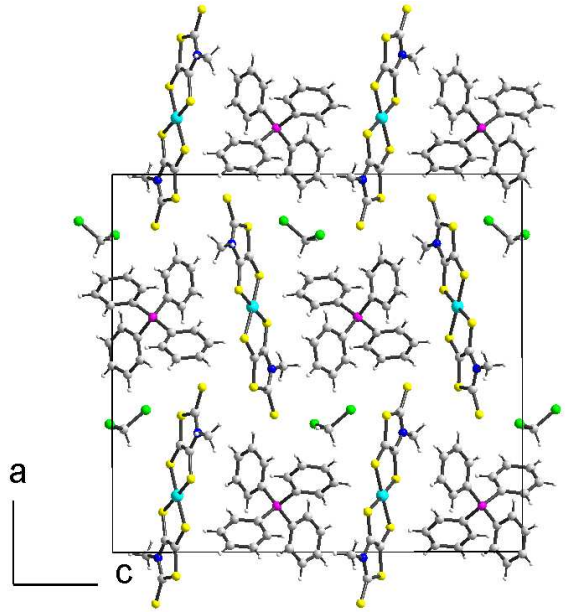


**Figure S2**. Projection view along *b* of the unit cell of the $CH_2Cl_2$-solvated salt $[Ph_4P][Ni(Me\text{-}thiazdt)_2]$.

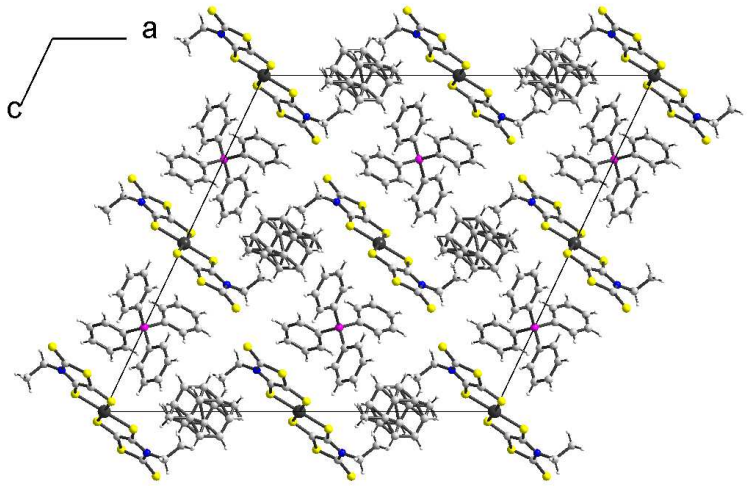


**Figure S3**. Projection view along *b* of the unit cell of the toluene-solvated salt $[Ph_4P][Pt(Et\text{-}thiazdt)_2]\bullet[toluene]$.

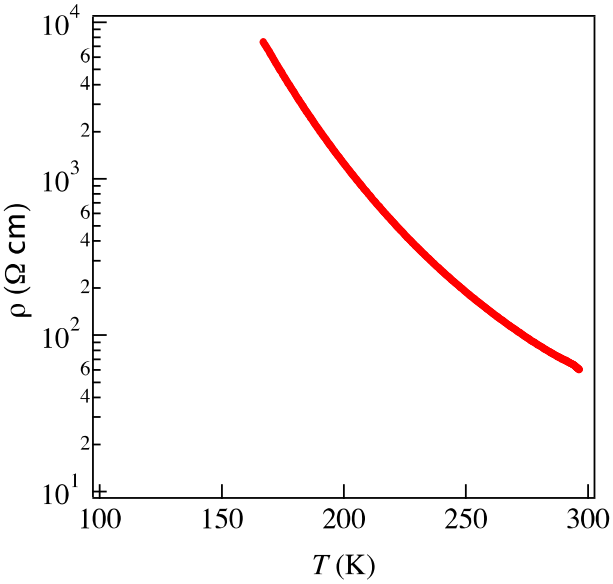


**Figure S4**. Temperature dependence of the resistivity of **PtMe** at ambient pressure.

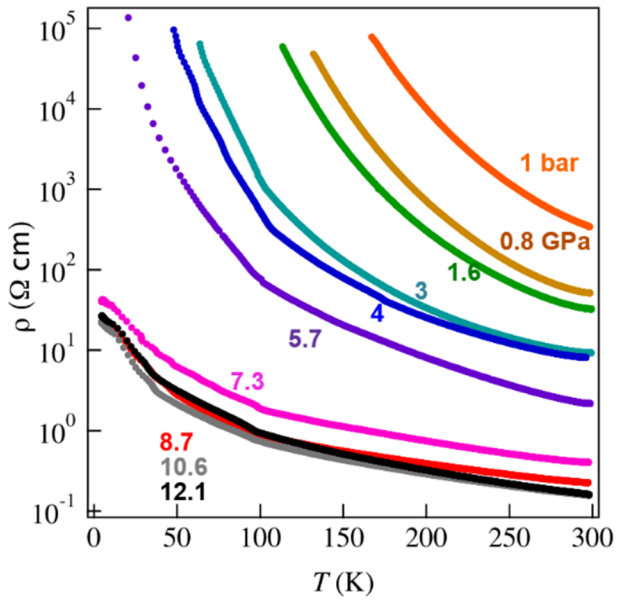


**Figure S5**. Temperature dependence of the resistivity of **PtEt** at different pressures between 1 bar and 12.1 GPa

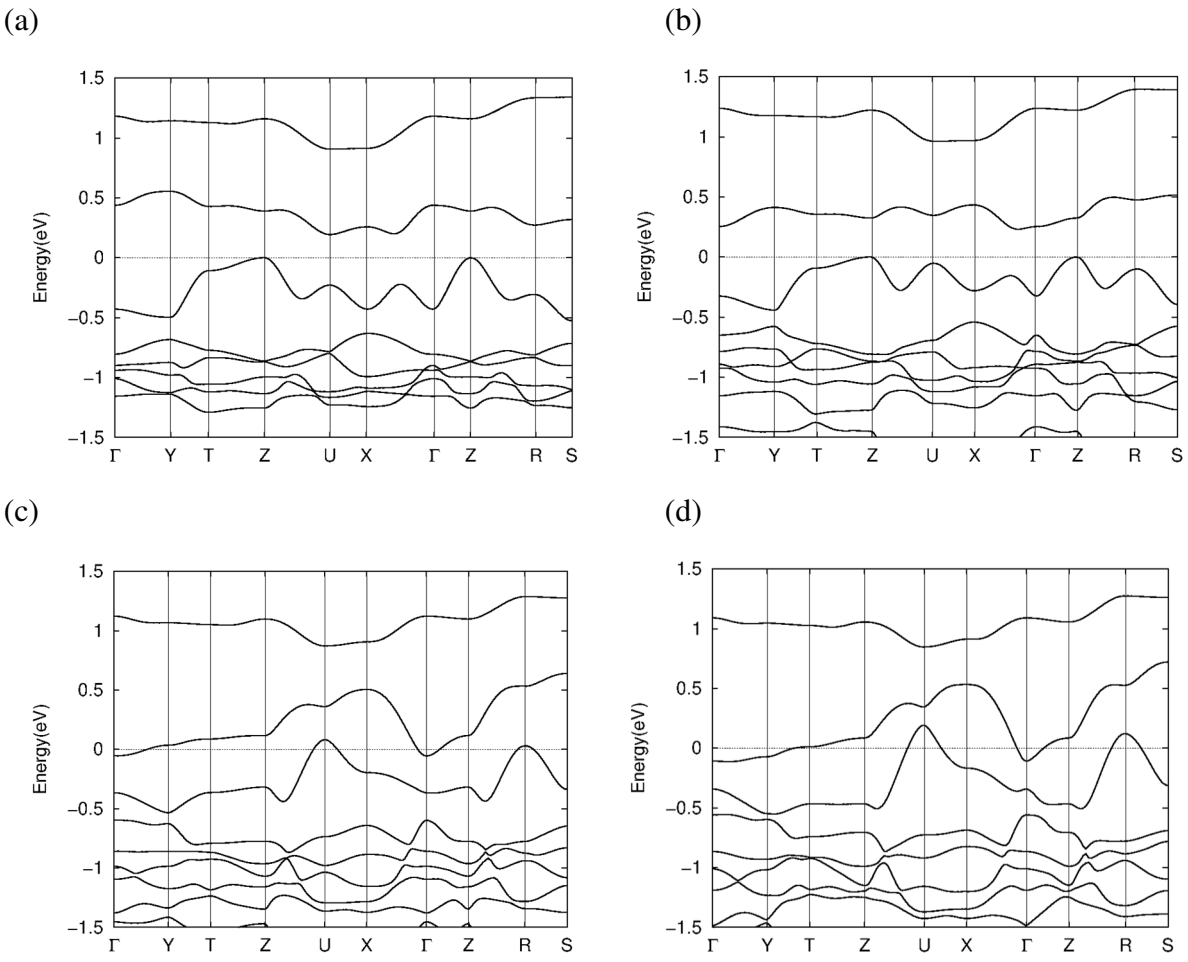


**Figure S6**. Calculated band structures of *tricl*-**NiEt** at (a) 2 GPa, (b) 4 GPa, (c) 6 GPa and (d) 8 GPa. The dotted lines at Energy = 0 eV in (a) and (b) represents the top of the valence bands and those in (c) and (d) are the Fermi energy.

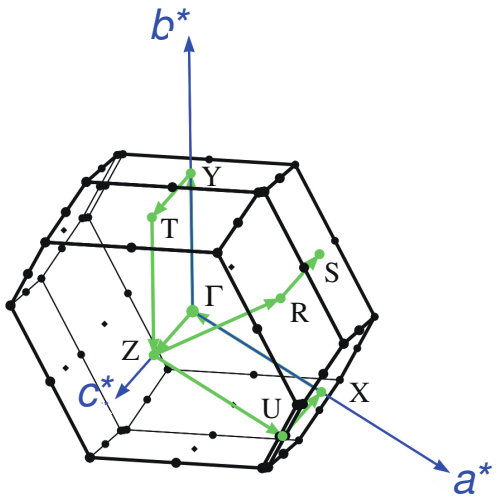


**Figure S7**. The first Brillouin zone of the optimized structure of *tricl*-**NiEt** at 6 GPa. *a**, *b**, and *c** are reciprocal lattice vectors.

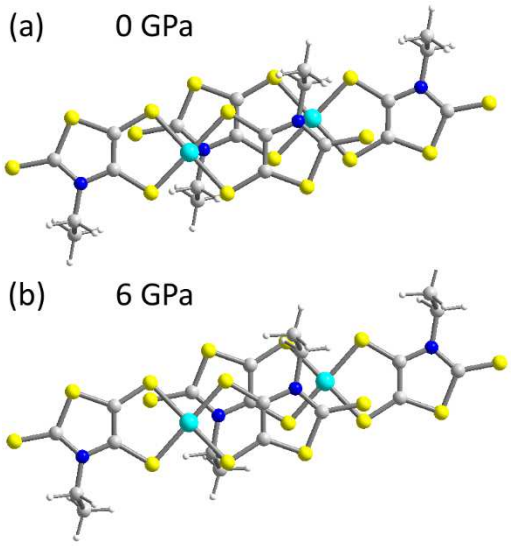


**Figure S8**. Overlap between [Ni(Et-thiazdt)$_2$] complexes in *tricl*-**NiEt** in calculated structures at (a) 0 GPa and (b) 6 GPa.

**Table S1**. Optimized crystallographic coordinates of *tricl*-**NiEt** at 0 GPa (cif format)

```
data_VESTA_phase_1_0GPa
_pd_phase_name                         'XCrySDen XSF file'
_cell_length_a                       6.06054
_cell_length_b                       7.63661
_cell_length_c                       10.46549
_cell_angle_alpha                    75.04736
_cell_angle_beta                     83.02126
_cell_angle_gamma                    62.17379
_symmetry_space_group_name_H-M       'P 1'
_symmetry_Int_Tables_number          1

loop_
_symmetry_equiv_pos_as_xyz
  'x, y, z'

loop_
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_B_iso_or_equiv
  _atom_site_type_symbol
  C1      1.0   0.273157    0.339217    0.346876    Biso  1.000000 C
  C2      1.0   -0.273157   -0.339217   -0.346876   Biso  1.000000 C
  C3      1.0   0.105142    -0.453819   0.326672    Biso  1.000000 C
  C4      1.0   -0.105142   0.453819    -0.326672   Biso  1.000000 C
  C5      1.0   -0.092018   0.449410    0.201031    Biso  1.000000 C
  C6      1.0   0.092018    -0.449410   -0.201031   Biso  1.000000 C
  C7      1.0   0.290897    0.186013    -0.211535   Biso  1.000000 C
  C8      1.0   -0.290897   -0.186013   0.211535    Biso  1.000000 C
  C9      1.0   0.216063    0.065401    -0.090533   Biso  1.000000 C
  C10     1.0   -0.216063   -0.065401   0.090533    Biso  1.000000 C
  H1      1.0   0.320587    0.121279    -0.298573   Biso  1.000000 H
  H2      1.0   -0.320587   -0.121279   0.298573    Biso  1.000000 H
  H3      1.0   0.461020    0.194357    -0.194527   Biso  1.000000 H
  H4      1.0   -0.461020   -0.194357   0.194527    Biso  1.000000 H
  H5      1.0   0.180360    0.136490    -0.006160   Biso  1.000000 H
  H6      1.0   -0.180360   -0.136490   0.006160    Biso  1.000000 H
  H7      1.0   0.364684    -0.092140   -0.064203   Biso  1.000000 H
  H8      1.0   -0.364684   0.092140    0.064203    Biso  1.000000 H
  H9      1.0   0.045564    0.060062    -0.110366   Biso  1.000000 H
  H10     1.0   -0.045564   -0.060062   0.110366    Biso  1.000000 H
  N1      1.0   0.095117    0.396994    -0.248284   Biso  1.000000 N
  N2      1.0   -0.095117   -0.396994   0.248284    Biso  1.000000 N
  Ni3     1.0   0.500000    0.500000    0.500000    Biso  1.000000 Ni
  S1      1.0   0.467315    -0.238869   -0.440091   Biso  1.000000 S
  S2      1.0   -0.467315   0.238869    0.440091    Biso  1.000000 S
  S3      1.0   0.154184    -0.295850   0.395773    Biso  1.000000 S
  S4      1.0   -0.154184   0.295850    -0.395773   Biso  1.000000 S
  S5      1.0   0.171166    0.220482    0.264286    Biso  1.000000 S
  S6      1.0   -0.171166   -0.220482   -0.264286   Biso  1.000000 S
  S7      1.0   -0.296547   0.467216    0.101872    Biso  1.000000 S
  S8      1.0   0.296547    -0.467216   -0.101872   Biso  1.000000 S
```

**Table S2**. Optimized crystallographic coordinates of *tricl*-**NiEt** at 2 GPa (cif format)

```
data_VESTA_phase_1_2GPa
_pd_phase_name                         'XCrySDen XSF file'
_cell_length_a                         6.14483
_cell_length_b                         7.41449
_cell_length_c                         9.64117
_cell_angle_alpha                      73.33695
_cell_angle_beta                       81.39041
_cell_angle_gamma                      61.07145
_symmetry_space_group_name_H-M         'P 1'
_symmetry_Int_Tables_number            1

loop_
_symmetry_equiv_pos_as_xyz
   'x, y, z'

loop_
   _atom_site_label
   _atom_site_occupancy
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_B_iso_or_equiv
   _atom_site_type_symbol
   C1        1.0     0.280755     0.330855     0.342962     Biso  1.000000 C
   C2        1.0    -0.280755    -0.330855    -0.342962     Biso  1.000000 C
   C3        1.0     0.107231    -0.454351     0.322103     Biso  1.000000 C
   C4        1.0    -0.107231     0.454351    -0.322103     Biso  1.000000 C
   C5        1.0    -0.085933     0.442090     0.194481     Biso  1.000000 C
   C6        1.0     0.085933    -0.442090    -0.194481     Biso  1.000000 C
   C7        1.0     0.301157     0.181327    -0.209291     Biso  1.000000 C
   C8        1.0    -0.301157    -0.181327     0.209291     Biso  1.000000 C
   C9        1.0     0.240385     0.039339    -0.080351     Biso  1.000000 C
   C10       1.0    -0.240385    -0.039339     0.080351     Biso  1.000000 C
   H1        1.0     0.335529     0.122951    -0.307486     Biso  1.000000 H
   H2        1.0    -0.335529    -0.122951     0.307486     Biso  1.000000 H
   H3        1.0     0.463229     0.196804    -0.191313     Biso  1.000000 H
   H4        1.0    -0.463229    -0.196804     0.191313     Biso  1.000000 H
   H5        1.0     0.188625     0.108492     0.013695     Biso  1.000000 H
   H6        1.0    -0.188625    -0.108492    -0.013695     Biso  1.000000 H
   H7        1.0     0.400805    -0.119911    -0.052806     Biso  1.000000 H
   H8        1.0    -0.400805     0.119911     0.052806     Biso  1.000000 H
   H9        1.0     0.085021     0.020808    -0.105147     Biso  1.000000 H
   H10       1.0    -0.085021    -0.020808     0.105147     Biso  1.000000 H
   N1        1.0     0.094853     0.397610    -0.243283     Biso  1.000000 N
   N2        1.0    -0.094853    -0.397610     0.243283     Biso  1.000000 N
   Ni3       1.0     0.500000     0.500000     0.500000     Biso  1.000000 Ni
   S1        1.0     0.454914    -0.228700    -0.435470     Biso  1.000000 S
   S2        1.0    -0.454914     0.228700     0.435470     Biso  1.000000 S
   S3        1.0     0.150995    -0.287939     0.391613     Biso  1.000000 S
   S4        1.0    -0.150995     0.287939    -0.391613     Biso  1.000000 S
   S5        1.0     0.179978     0.205218     0.261553     Biso  1.000000 S
   S6        1.0    -0.179978    -0.205218    -0.261553     Biso  1.000000 S
   S7        1.0    -0.288679     0.458580     0.091437     Biso  1.000000 S
   S8        1.0     0.288679    -0.458580    -0.091437     Biso  1.000000 S
```

**Table S3**. Optimized crystallographic coordinates of *tricl*-**NiEt** at 4 GPa (cif format)

```
data_VESTA_phase_1_4GPa
_pd_phase_name                         'XCrySDen XSF file'
_cell_length_a                         6.34157
_cell_length_b                         7.37139
_cell_length_c                         8.92956
_cell_angle_alpha                      72.86463
_cell_angle_beta                       80.41441
_cell_angle_gamma                      59.40762
_symmetry_space_group_name_H-M         'P 1'
_symmetry_Int_Tables_number            1

loop_
_symmetry_equiv_pos_as_xyz
  'x, y, z'

loop_
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_B_iso_or_equiv
  _atom_site_type_symbol
  C1      1.0   0.283301    0.329981    0.341101    Biso  1.000000 C
  C2      1.0   -0.283301   -0.329981   -0.341101   Biso  1.000000 C
  C3      1.0   0.109931    -0.450202   0.318738    Biso  1.000000 C
  C4      1.0   -0.109931   0.450202    -0.318738   Biso  1.000000 C
  C5      1.0   -0.082798   0.442224    0.193032    Biso  1.000000 C
  C6      1.0   0.082798    -0.442224   -0.193032   Biso  1.000000 C
  C7      1.0   0.300805    0.172918    -0.207970   Biso  1.000000 C
  C8      1.0   -0.300805   -0.172918   0.207970    Biso  1.000000 C
  C9      1.0   0.248450    0.019203    -0.074566   Biso  1.000000 C
  C10     1.0   -0.248450   -0.019203   0.074566    Biso  1.000000 C
  H1      1.0   0.339516    0.119318    -0.316991   Biso  1.000000 H
  H2      1.0   -0.339516   -0.119318   0.316991    Biso  1.000000 H
  H3      1.0   0.455075    0.188865    -0.185821   Biso  1.000000 H
  H4      1.0   -0.455075   -0.188865   0.185821    Biso  1.000000 H
  H5      1.0   0.185055    0.083663    0.030106    Biso  1.000000 H
  H6      1.0   -0.185055   -0.083663   -0.030106   Biso  1.000000 H
  H7      1.0   0.414446    -0.140147   -0.046445   Biso  1.000000 H
  H8      1.0   -0.414446   0.140147    0.046445    Biso  1.000000 H
  H9      1.0   0.108066    -0.006197   -0.106763   Biso  1.000000 H
  H10     1.0   -0.108066   0.006197    0.106763    Biso  1.000000 H
  N1      1.0   0.092651    0.392956    -0.240821   Biso  1.000000 N
  N2      1.0   -0.092651   -0.392956   0.240821    Biso  1.000000 N
  Ni3     1.0   0.500000    0.500000    0.500000    Biso  1.000000 Ni
  S1      1.0   0.448944    -0.226110   -0.428921   Biso  1.000000 S
  S2      1.0   -0.448944   0.226110    0.428921    Biso  1.000000 S
  S3      1.0   0.155393    -0.279089   0.384913    Biso  1.000000 S
  S4      1.0   -0.155393   0.279089    -0.384913   Biso  1.000000 S
  S5      1.0   0.181015    0.200206    0.264320    Biso  1.000000 S
  S6      1.0   -0.181015   -0.200206   -0.264320   Biso  1.000000 S
  S7      1.0   -0.284557   0.456320    0.089404    Biso  1.000000 S
  S8      1.0   0.284557    -0.456320   -0.089404   Biso  1.000000 S
```

**Table S4**. Optimized crystallographic coordinates of *tricl*-**NiEt** at 6 GPa (cif format)

```
data_VESTA_phase_1_6GPa
_pd_phase_name                         'XCrySDen XSF file'
_cell_length_a                         6.58132
_cell_length_b                         7.41023
_cell_length_c                         8.24348
_cell_angle_alpha                      72.80923
_cell_angle_beta                       79.97575
_cell_angle_gamma                      57.58493
_symmetry_space_group_name_H-M         'P 1'
_symmetry_Int_Tables_number            1

loop_
_symmetry_equiv_pos_as_xyz
  'x, y, z'

loop_
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_B_iso_or_equiv
  _atom_site_type_symbol
  C1      1.0   0.286161    0.331292    0.337769    Biso  1.000000 C
  C2      1.0   -0.286161   -0.331292   -0.337769   Biso  1.000000 C
  C3      1.0   0.111903    -0.445803   0.314852    Biso  1.000000 C
  C4      1.0   -0.111903   0.445803    -0.314852   Biso  1.000000 C
  C5      1.0   -0.079549   0.443088    0.191914    Biso  1.000000 C
  C6      1.0   0.079549    -0.443088   -0.191914   Biso  1.000000 C
  C7      1.0   0.297702    0.165395    -0.202989   Biso  1.000000 C
  C8      1.0   -0.297702   -0.165395   0.202989    Biso  1.000000 C
  C9      1.0   0.244648    0.004091    -0.072988   Biso  1.000000 C
  C10     1.0   -0.244648   -0.004091   0.072988    Biso  1.000000 C
  H1      1.0   0.348975    0.118000    -0.324854   Biso  1.000000 H
  H2      1.0   -0.348975   -0.118000   0.324854    Biso  1.000000 H
  H3      1.0   0.441441    0.177812    -0.166593   Biso  1.000000 H
  H4      1.0   -0.441441   -0.177812   0.166593    Biso  1.000000 H
  H5      1.0   0.166506    0.059948    0.043739    Biso  1.000000 H
  H6      1.0   -0.166506   -0.059948   -0.043739   Biso  1.000000 H
  H7      1.0   0.410837    -0.157043   -0.042055   Biso  1.000000 H
  H8      1.0   -0.410837   0.157043    0.042055    Biso  1.000000 H
  H9      1.0   0.119447    -0.020030   -0.122151   Biso  1.000000 H
  H10     1.0   -0.119447   0.020030    0.122151    Biso  1.000000 H
  N1      1.0   0.090146    0.388542    -0.237576   Biso  1.000000 N
  N2      1.0   -0.090146   -0.388542   0.237576    Biso  1.000000 N
  Ni3     1.0   0.500000    0.500000    0.500000    Biso  1.000000 Ni
  S1      1.0   0.444496    -0.226077   -0.420655   Biso  1.000000 S
  S2      1.0   -0.444496   0.226077    0.420655    Biso  1.000000 S
  S3      1.0   0.157708    -0.272666   0.379484    Biso  1.000000 S
  S4      1.0   -0.157708   0.272666    -0.379484   Biso  1.000000 S
  S5      1.0   0.185318    0.199070    0.263992    Biso  1.000000 S
  S6      1.0   -0.185318   -0.199070   -0.263992   Biso  1.000000 S
  S7      1.0   -0.283680   0.453464    0.092890    Biso  1.000000 S
  S8      1.0   0.283680    -0.453464   -0.092890   Biso  1.000000 S
```

**Table S5**. Optimized crystallographic coordinates of *tricl*-**NiEt** at 8 GPa (cif format)

```
data_VESTA_phase_1_8GPa
_pd_phase_name                         'XCrySDen XSF file'
_cell_length_a                         6.64945
_cell_length_b                         7.40209
_cell_length_c                         7.90404
_cell_angle_alpha                      72.96861
_cell_angle_beta                       79.64172
_cell_angle_gamma                      56.70513
_symmetry_space_group_name_H-M         'P 1'
_symmetry_Int_Tables_number            1

loop_
_symmetry_equiv_pos_as_xyz
  'x, y, z'

loop_
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_B_iso_or_equiv
  _atom_site_type_symbol
  C1        1.0    0.287061     0.330881     0.335539     Biso  1.000000 C
  C2        1.0   -0.287061    -0.330881    -0.335539     Biso  1.000000 C
  C3        1.0    0.111600    -0.443690     0.312124     Biso  1.000000 C
  C4        1.0   -0.111600     0.443690    -0.312124     Biso  1.000000 C
  C5        1.0   -0.079417     0.442881     0.190116     Biso  1.000000 C
  C6        1.0    0.079417    -0.442881    -0.190116     Biso  1.000000 C
  C7        1.0    0.298393     0.160922    -0.196962     Biso  1.000000 C
  C8        1.0   -0.298393    -0.160922     0.196962     Biso  1.000000 C
  C9        1.0    0.241847    -0.002407    -0.071666     Biso  1.000000 C
  C10       1.0   -0.241847     0.002407     0.071666     Biso  1.000000 C
  H1        1.0    0.360275     0.114956    -0.325044     Biso  1.000000 H
  H2        1.0   -0.360275    -0.114956     0.325044     Biso  1.000000 H
  H3        1.0    0.436075     0.171578    -0.150159     Biso  1.000000 H
  H4        1.0   -0.436075    -0.171578     0.150159     Biso  1.000000 H
  H5        1.0    0.153133     0.050083     0.050341     Biso  1.000000 H
  H6        1.0   -0.153133    -0.050083    -0.050341     Biso  1.000000 H
  H7        1.0    0.407892    -0.165562    -0.038004     Biso  1.000000 H
  H8        1.0   -0.407892     0.165562     0.038004     Biso  1.000000 H
  H9        1.0    0.125119    -0.025022    -0.132701     Biso  1.000000 H
  H10       1.0   -0.125119     0.025022     0.132701     Biso  1.000000 H
  N1        1.0    0.090580     0.386263    -0.234568     Biso  1.000000 N
  N2        1.0   -0.090580    -0.386263     0.234568     Biso  1.000000 N
  Ni3       1.0    0.500000     0.500000     0.500000     Biso  1.000000 Ni
  S1        1.0    0.443281    -0.223910    -0.418626     Biso  1.000000 S
  S2        1.0   -0.443281     0.223910     0.418626     Biso  1.000000 S
  S3        1.0    0.157177    -0.269498     0.377206     Biso  1.000000 S
  S4        1.0   -0.157177     0.269498    -0.377206     Biso  1.000000 S
  S5        1.0    0.187343     0.197330     0.261881     Biso  1.000000 S
  S6        1.0   -0.187343    -0.197330    -0.261881     Biso  1.000000 S
  S7        1.0   -0.286244     0.452058     0.094510     Biso  1.000000 S
  S8        1.0    0.286244    -0.452058    -0.094510     Biso  1.000000 S
```