Supporting Information

Open-Ended Metallodithiolene Complexes with the 1,2,4,5-Tetrakis(diphenylphosphino)benzene (tpbz) Ligand: Modular Building Elements for the Synthesis of Multimetal Complexes

by

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Procedures for Crystal Growth, Collection and Processing of Diffraction Data, and Solving and Refining of Structures.

All crystals used in X-ray diffraction data collections were obtained by the vial-in-a-vial vapor diffusion technique. The following solvent pairs identify specific combinations successfully employed as solvent/diffusing vapor for crystal growth: [Cl₂Ni(tpbz)]·Et₂O (orange plates): CH₂Cl₂/Et₂O; [(NC)₂C₂S₂]Ni(tpbz)·2(CHCl₃) (orange blocks): CHCl₃/MeOH; [(Me₂C₂S₂)]Ni(tpbz)·2(CH₂Cl₂) (light brown-green columns): CH₂Cl₂/Et₂O; [(Me₂C₂S₂)Pt(tpbz)]: 2(CH₂Cl₂) (yellow plates): CH₂Cl₂/Et₂O; [(Ph₂C₂S₂)Ni(tpbz)] (clear yellow blocks): CH₂Cl₂/Et₂O; [(Ph₂C₂S₂)Pd(tpbz)] (pale orange columns): CH₂Cl₂/Et₂O or ClCH₂CH₂Cl/Et₂O; [(Ph₂C₂S₂)Pt(tpbz)] (yellow columns): CH₂Cl₂/n-pentane; [(Ph₂C₂S₂)₂PtIV(η²-tpbz)]: 2ClCH₂CH₂Cl (dark blue blocks): ClCH₂CH₂Cl/Et₂O or ClCH₂CH₂Cl/n-pentane; [(MeO-p-C₆H₄)₂C₂S₂]Ni(tpbz)] (clear yellow blocks): chlorobenzene/hexanes or chlorobenzene/BuOMe; [(Ph₂C₂S₂)Pt(tpbz)Ni(S₂C₂Me₂)]: 2½(ClCH₂CH₂Cl) (orange plates): ClCH₂CH₂Cl/BuOMe or ClCH₂CH₂Cl/hexanes; [(Ph₂C₂S₂)Ni(tpbzO₂)₂]·CH₂Cl₂ (orange plates): CH₂Cl₂/Et₂O; [(Me₂C₂S₂)Pt(tpbzO₂)]: 2CH₂Cl₂ (orange plates): CH₂Cl₂/Et₂O; [(Me₂C₂S₂)Ni(tpbzS₂)] (yellow needles): CH₂Cl₂/Et₂O or CH₂Cl₂/n-pentane; [Ni(dppbO₂)₃][I₃]₂ (orange-red plates): CH₂Cl₂/Et₂O for both triclinic and monoclinic polymorphs.

All crystals were coated with paratone oil and mounted on the end of a nylon loop attached to the end of the goniometer. Data were obtained at a temperature of 100, 150 or 158 K that was maintained by a cold nitrogen stream supplied under the control of an Oxford Cryostream 800 attachment. The data collection instrument was either a Bruker D8 Venture Photon 100 instrument, the radiation source for which was a Cu Incoatec I microfocus source generating X-rays with λ = 1.54178 nm, a Bruker Smart APEX II CCD diffractometer equipped with a Mo fine-focus sealed tube providing radiation at λ = 0.71073 nm, or a Bruker D8 Quest Photon 3 diffractometer that similarly operated with the Mo Kα 0.71073 nm light source.

The data sets obtained with the D8 Venture were hemispheres of data comprised from the following assemblies of ω-scan frames and frame times: [(Ph₂C₂S₂)Ni(tpbz)]: 10 sets of 326 or 330 frames at 10 or 20 sec/frame; [(MeO-p-C₆H₄)₂C₂S₂]Ni(tpbz)]: 7 sets of 368 or 371 frames at 40 or 20 sec/frame. The data sets that were collected with the APEX II diffractometer implemented one of the following programmed routines: (1) Three sets of 363 frames in ω (0.5°/scan) with φ held constant at 0, 120, and then 240°; (2) Three sets of 606 frames in ω (0.3°/scan) with φ held
constant at 0, 120, and then 240º; (3) Three sets of 400 frames in ω (0.5º/scan), collected at φ = 0.00, 90.00 and 180.00º and two sets of 800 frames in φ (0.45º/scan) collected with ω constant at -30.00 and 210.00º. The data collection program and frame time used for these data sets were as follows: [(Me2C2S2)Ni(tpbz)]·2(CH2Cl2): Routine 3, 60 sec; [(Me2C2S2)Pt(tpbz)]·2(CH2Cl2): Routine 2, 30 sec; [(Ph2C2S2)Pd(tpbz)]: Routine 1, 40 sec; [(Ph2C2S2)Pt(tpbz)]: Routine 1, 80 sec; [(Ph2C2S2)2Pt(tpbz)]:2(ClCH2CH2Cl): Routine 3, 60 sec; [(Me2C2S2)Ni(tpbzS2)]: Routine 2, 90 sec; triclinic [Ni(dppbO2)3][I3]: Routine 2, 60 sec; [Cl2Ni(tpbz)]·Et2O: Routine 2, 50 sec; [((NC)2C2S2)Ni(tpbz)]·2(CHCl3): Routine 3: 25 sec. The data sets gathered with the D8 Quest Photon 3 ([(Ph2C2S2)Pt(tpbz)Ni(S2C2Me2)]·2½(ClCH2CH2Cl), [(Ph2C2S2)Ni(tpbzO2)·CH2Cl2, [(Me2C2S2)2Pt(tpbzO2)], and monoclinic [Ni(dppbO2)3][I3]) were comprised of sets of frames, each of 0.5º width in either ω or φ, whose number and scan parameters were determined by the “Strategy” routine in APEX3.

All data were collected under control of either the Bruker SMART,1 APEX22a-2f or APEX32g software packages. Raw data were reduced to F² values using the SAINT+3 or SAINT4 software, and a global refinement of unit cell parameters was performed using ~3,660–9,990 selected reflections from the full data set. For [(Ph2C2S2)Pt(tpbz)Ni(S2C2Me2)]·2½(ClCH2CH2Cl), analysis of 1675 reflections having I/σ(I) > 20 and chosen from the full data set with CELL_NOW showed the crystal to belong to the triclinic system and to be twinned by a 180º rotation about c*. The raw data were processed using the multi-component version of SAINT under control of the two-component orientation file generated by CELL_NOW; and an absorption correction was applied using the TWINABS routine.6 All other data sets were corrected for absorption on the basis of multiple measurements of symmetry equivalent reflections or by numerical methods with the use of SADABS,7 as described by Krause et al.8 All structure solutions were obtained by direct methods using SHELXM,9 SHELXS10 or SHELXT,11 while refinements were accomplished by full-matrix least-squares procedures using SHELXL.12 Both the SHELXS and SHELXL programs are incorporated into the SHELXTL13 and APEX2/APEX32 software suites.

All structure refinements were routine except as noted: (1) In the structure of [(Me2C2S2)Ni(tpbzS2)] (JPD184), one terminal sulfido ligand was disordered between two positions and was modeled as an 88:12 distribution between the two sites; (2) For [((MeO-p-C6H4)2C2S2)Ni(tpbz)] (JPD950), one phenyl group was disordered between two positions and refined with isotropic thermal parameters as a best-fit distribution between the two sites; (3) For
[(Ph₂C₂S₂)₂PtIV(η²-tpbz)]·2CICH₂CH₂Cl (JPD736), minor disorder for one phenyl group of the tpbz ligand and one Cl atom of the interstitial solvent was observed and similarly treated with split atom models. (4) In the structure of [(Ph₂C₂S₂)Ni(tpbzO₂)]·(CH₂Cl₂), residual density attributed to partially occupied/disordered solvent CH₂Cl₂ sites was removed with PLATON SQUEEZE\textsuperscript{14} (Spek, 2015). Furthermore, five reflections determined to be partially or wholly obscured by the beamstop were omitted from the final refinement. (5) The structure of [(Ph₂C₂S₂)Pt(tpbz)Ni(S₂C₂Me₂)]·2.5(CICH₂CH₂Cl) was refined as a two-component twin, and the disordered interstitial CICH₂CH₂Cl molecules were refined with constraints approximating ideal geometries. (6) The monoclinic polymorph of [Ni(dppbO₂)₃][I₃] showed one triiodide ion (I₁···I₃) to be disordered over two closely neighboring sites in a 0.703(4)/0.297(4) ratio. The two components of the disorder were refined as rigid rods. Additionally, a small peak appearing to be a partially occupied lattice water site was removed with PLATON SQUEEZE\textsuperscript{14}. Seven reflections partially or totally obscured by the beamstop were omitted from the final refinement. In all the structures, hydrogen atoms were added in calculated positions and included as riding contributions with isotropic displacement parameters 1.2-1.5 times those of the carbon atoms to which they were attached. Thermal ellipsoid images have been created with the use of XP, which also is part of the SHELXTL package. All structures were checked for overlooked symmetry and other errors by the checkCIF service provided by the International Union of Crystallography.\textsuperscript{15} Final unit cell data and refinement statistics are collected in Tables S1-S4.

Computational Details

The density functional theory (DFT) calculations were carried out at the supercomputing facility at Tulane University, using the GAUSSIAN-09 package.\textsuperscript{16} Geometry optimizations of structures were carried out with no symmetry restrictions beginning with the coordinates of the molecules from X-ray crystallographic data. The geometries were optimized at the Becke, 3-Parameter, Lee-Yang-Parr (B3LYP) level of theory\textsuperscript{17} with typical basis sets. Frequency calculations were done to confirm the validity of optimized structures. For the transition metals (nickel, palladium and platinum), a double-ζ (DZ) basis set with an effective electron core potential (LANL2DZ ECP) was implemented.\textsuperscript{18} The 6-31G (d,p) basis set was chosen for the light main group elements (C and N), whereas the triple-ζ (TZVP) was used for the heavier elements (S and P), and a Gaussian split valence (SV) basis set\textsuperscript{19} was used for the hydrogen atoms. The molecular
orbital (MOs) plots were created using the Chemcraft program package (http://www.chemcraftprog.com).

References

1) SMART, Version 5.625, Bruker-AXS, Madison, Wisconsin, 2000.
2) (a) APEX2, Version 2008.6-1, Bruker-AXS, Madison, Wisconsin, 2008. (b) APEX2, Version 2009.1-0, Bruker-AXS, Madison, Wisconsin, 2009. (c) APEX2, Version 2009.9-0, Bruker-AXS, Madison, Wisconsin, 2009. (d) APEX2, Version 2009.11-0, Bruker-AXS, Madison, Wisconsin, 2009. (e) APEX2, Bruker-AXS, Inc., Madison, Wisconsin, USA, 2014. (f) APEX2, Bruker-AXS, Inc., Madison, Wisconsin, USA, 2015. (g) APEX3, Bruker-AXS, Inc., Madison, Wisconsin, USA, 2016. (h) APEX3, Bruker-AXS, LLC, Madison, Wisconsin, USA, 2020.
3) SAINT+, Bruker-AXS, Version 7.03, Madison, Wisconsin, 2004.
4) (a) SAINT, Version 7.60A, Bruker AXS, Inc., Madison, Wisconsin, 2008. (b) SAINT, Version 7.68A, Bruker AXS, Inc., Madison, Wisconsin, 2009. (c) SAINT, Bruker AXS, Inc., Madison, Wisconsin, 2014. (d) SAINT, Bruker AXS, Inc., Madison, Wisconsin, 2015. (e) SAINT, Bruker AXS, LLC, Madison, Wisconsin, 2020.
5) Sheldrick, G. M. CELL_NOW, University of Göttingen, Göttingen, Germany, 2008.
6) Sheldrick, G. M. TWINABS, University of Göttingen, Göttingen, Germany, 2009.
7) (a) Sheldrick, G. M. SADABS, Version 2.05, Universität Göttingen, Göttingen, Germany, 2002. (b) Sheldrick, G. M. SADABS, Version 2007/4, Universität Göttingen, Göttingen, Germany, 2007. (c) Sheldrick, G. M. SADABS, Version 2008/2, Universität Göttingen, Göttingen, Germany, 2008. (d) SADABS, Bruker AXS, Inc., Madison, Wisconsin, 2014. (e) SADABS, Bruker AXS, Inc., Madison, Wisconsin, 2015. (f) SADABS, Bruker AXS, Inc., Madison, Wisconsin, 2016.
8) Krause, L.; Herbst-Irmer, R.; Sheldrick, G.M.; Stalke; D. Comparison of Silver and Molybdenum Microfocus X-ray Sources for Single-Crystal Structure Determination. J. Appl. Cryst. 2015, 48, 3-10.
9) Sheldrick, G. M. SHELXM, Version 2004/1, University of Göttingen, Göttingen, Germany, 2004.
10) (a) Sheldrick, G. M. SHELXS-97, University of Göttingen, Göttingen, Germany, 1997. (b) Sheldrick, G. M. SHELXS-97, University of Göttingen, Göttingen, Germany, 2008. (c) Sheldrick, G. M. A Short History of SHELX. Acta Crystallogr., Sect. A: Foundations Adv. 2008, 64, 112-122.
11) (a) SHELXT, Bruker AXS, Inc., Madison, Wisconsin, 2014. (b) Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. Acta Crystallogr., Sect. A: Foundations Adv. 2015, 71, 3-8.
12) (a) Sheldrick, G. M. SHELXL-97, University of Göttingen, Göttingen, Germany, 1997. (b) Sheldrick, G. M. SHELXL-97, University of Göttingen, Göttingen, Germany, 2008. (c) Sheldrick, G. M. A Short History of SHELX. Acta Crystallogr., Sect. A 2008, 64, 112-122. (d) Sheldrick, G. M. SHELXL-2014. University of Göttingen, Göttingen, Germany, 2014. (e) Sheldrick, G. M. SHELXL-2014/7. University of Göttingen, Göttingen, Germany, 2015. (f) Sheldrick, G. M.
SHELXL. University of Göttingen, Göttingen, Germany, 2015. (g) Sheldrick, G. M. SHELXL-2018/1 University of Göttingen, Göttingen, Germany, 2018.

(13) (a) SHELXTL, Version 6.10, Bruker-AXS, Madison, Wisconsin, 2000. (b) SHELXTL, Version 2008/4, Bruker-AXS, Madison, Wisconsin, 2008. (c) SHELXTL, Bruker-AXS, Madison, Wisconsin, 2014. (d) SHELXTL, Bruker-AXS, Madison, Wisconsin, 2015. (e) SHELXTL, Bruker-AXS, Madison, Wisconsin, 2016.

(14) Spek, A.L. PLATON SQUEEZE: A Tool for the Calculation of the Disordered Solvent Contribution to the Calculated Structure Factors. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 9-18.

(15) See http://checkcif.iucr.org/

(16) Gaussian 09, Revision A. 02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(17) (a) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. J. Chem. Phys. 1993, 98, 5648-5652. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density Phys. Rev. B 1988, 37, 785-789.

(18) https://bse.pnl.gov/bse/portal. (Accessed Mach 4, 2021).

(19) Schäfer, A.; Horn, H.; Ahlrichs, R. Fully Optimized Contracted Gaussian Basis Sets for Atoms Li to Kr. J. Chem. Phys. 1992, 97, 2571-2577.

(20) Chemcraft, Version 1.8 (build 445); http://chemcraftprog.com (accessed March 4, 2021).
Table S1. Unit Cell and Refinement Data for Compounds 1, 4, 5 and 7.

| compound   | [Cl2Ni(tpbz)] | [(mnt)Ni(tpbz)] | [(mnt)Ni(tpbz)] | [(mnt)Pt(tpbz)] |
|------------|---------------|-----------------|-----------------|----------------|
| compound # | JPD412        | JPD267          | JPD751          | JPD150         |
| structure #| Et2O          | 2CHCl3         | 2CH2Cl2        | 2CH2Cl2        |
| solvent/cocrystallite formula | C₅₈H₇₂Cl₅NiOP₄ | C₆₀H₴₄Cl₂Ni₂P₂S₂ | C₆₀H₵₂Cl₅NiP₄S₂ | C₆₀H₵₂Cl₄P₄PtS₂ |
| fw, g/mol  | 1018.49       | 1252.38        | 1161.52        | 1297.91        |
| temperature, K | 100           | 100            | 100            | 100            |
| wavelength, Å | 0.71073       | 0.71073        | 0.71073        | 0.71073        |
| 20 range, deg. | 2.34 – 55.70 | 4.22 – 56.74   | 3.24 – 60.44   | 3.22 – 56.56   |
| crystal system | orthorhombic | orthorhombic    | monoclinic     | monoclinic     |
| a, Å       | 34.703(3)     | 13.510(3)      | 15.7180(18)    | 21.157(5)      |
| b, Å       | 9.2939(9)     | 16.403(3)      | 15.836(4)      | 15.836(4)      |
| c, Å       | 15.5064(14)   | 25.380(5)      | 16.713(18)     | 16.576(4)      |
| dOH, deg.  | 90            | 90             | 90             | 90             |
| dOD, deg.  | 90            | 90             | 100.039(2)     | 99.604(4)      |
| Z           | 4             | 4              | 4              | 4              |
| volume, Å³ | 5001.2(8)     | 5624.2(19)     | 5489.6(11)     | 5476(2)        |
| density, g/cm³ | 1.353         | 1.479          | 1.405          | 1.574          |
| µ, mm⁻¹    | 0.664         | 0.860          | 0.780          | 2.991          |
| crystal size | 0.02 x 0.12 x 0.32 | 0.09 x 0.14 x 0.17 | 0.04 x 0.09 x 0.47 | 0.05 x 0.15 x 0.24 |
| color, habit | orange plate  | orange block   | brwn-grn column | yellow plate   |
| limiting indices, h | -44 < h < 45  | -17 < h < 18   | -29 < h < 29   | -28 < h < 27   |
| limiting indices, k | -12 < k < 12  | -21 < k < 21   | -22 < k < 22   | -20 < k < 20   |
| limiting indices, l | -20 < l < 19  | -33 < l < 33   | -23 < l < 23   | -21 < l < 21   |
| reflections collected | 40918         | 100119         | 52873          | 24025          |
| independent data | 11569         | 14060          | 7799           | 6526           |
| restraints  | 1             | 0              | 0              | 0              |
| parameters refined | 597           | 676            | 322            | 322            |
| GooF       | 1.090         | 1.048          | 1.105          | 1.035          |
| R1, eR2    | 0.0574, 0.1259 | 0.0413, 0.1087 | 0.0450, 0.1434 | 0.0308, 0.0750 |
| R1, eR2    | 0.0725, 0.1327 | 0.0481, 0.1141 | 0.0590, 0.1468 | 0.0360, 0.0776 |
| largest diff. peak, eÅ⁻³ | 0.734         | 0.650          | 2.930          | 1.601          |
| largest diff. hole, eÅ⁻³ | -0.755        | -1.153         | -0.572         | -0.790         |
| abs structure parameter | 0.013(15) | -0.012(11) | - | - |

*GooF = \(\frac{\sum w(F_o^2 - F_c^2)^2}{(n-p)}\), where \(n\) is the number of reflections and \(p\) is the total number of parameters refined; *R1 = \(\frac{\sum |F_o| - |F_c|}{\sum |F_o|}\); *R indices for data cut off at 1 > 2σ(I); *wR2 = \(\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}\); *w = 1/\(\sigma^2(F_o^2) + (xP)^2 + yP^2\), where \(P = [2F_o^2 + Max(F_o^2,0)]/3; *R indices for data.
### Table S2. Unit Cell and Refinement Data for Compounds 8, 9, 11, and 10.

| compound | structure # | solvent/cocrystallite | formula | fw, g/mol | temperature, K | wavelength, Å | 20 range, deg. | crystal system | space group | a, Å | b, Å | c, Å | α, deg. | β, deg. | γ, deg. | volume, Å³ | density, g/cm³ | color, habit | limiting indices, h | limiting indices, k | limiting indices, l | reflections collected | independent data | restraints | parameters refined | R1, wR² | wR² | largest diff. peak, e Å⁻³ | largest diff. hole, e Å⁻³ | abs structure parameter |
|----------|-------------|-----------------------|---------|-----------|---------------|---------------|----------------|---------------|-------------|--------|--------|--------|---------|---------|---------|----------|----------------|----------------|----------------|----------------|-----------------|----------------|----------------|----------------|----------------|----------------|
| **8**    | JP659       | none                  | C₆₀H₅₂Ni₃P₂S₂ | 1115.80   | 1.54178       | 6.84 – 148.77 | monoclinic     | C2/c         | 21.951(4)  | 16.7831(3) | 16.4070(3) | 90      | 112.864(1) | 90     | 5569.75(18) | 1.331       | yellow block | -27 ≤ h ≤ 27 | -20 ≤ k ≤ 20 | -20 ≤ l ≤ 20 | 35518            | 5650           | 339         | 339               | 0.0340, 0.0918 | 0.0408, 0.1122 | 0.0362, 0.0836 | 0.492           | -0.199                | -               | 1063         |
| **9**    | JP757       | none                  | C₆₀H₅₂P₄PdS₂ | 1163.49   | 0.71073       | 3.14 – 58.44 | monoclinic     | C2/c         | 21.7574(15)| 16.9716(12)| 16.2670(11)| 90      | 112.666(1) | 90     | 5542.87(7)  | 1.394       | pale orange column | -29 ≤ h ≤ 28 | -23 ≤ k ≤ 23 | -22 ≤ l ≤ 22 | 26293             | 7084           | 339         | 339               | 0.0376, 0.0952 | 0.0558, 0.1179 | 0.0487, 0.0870 | 1.247           | -0.457                | -               | 1074         |
| **11**   | JP798       | none                  | C₆₀H₅₂P₄PtS₂ | 1252.18   | 0.71073       | 3.14 – 57.39 | monoclinic     | C2/c         | 21.7804(15)| 16.9661(12)| 16.2774(12)| 90      | 112.727(1) | 90     | 5547.9(7)   | 1.499       | yellow column     | -29 ≤ h ≤ 28 | -22 ≤ k ≤ 22 | -21 ≤ l ≤ 21 | 26168             | 7003           | 339         | 339               | 0.0433, 0.1044 | 0.0555, 0.1177 | 0.0487, 0.0870 | 1.883           | -0.995                | -               | 9063         |
| **10**   | JP736       | 2(CIC₃H₃CHCl)         | C₆₀H₅₀Cl₃P₃PtS₄ | 1692.43   | 0.71073       | 3.03 – 59.72 | triclinic     | P-1          | 13.9324(12)| 14.0989(12)| 21.2092(18)| 89.716(1)     | 13.9324(12)| 21.2092(18)| 3955.7(6)  | 1.421        | dark blue block | -19 ≤ h ≤ 19 | -19 ≤ k ≤ 19 | -29 ≤ l ≤ 29 | 77174             | 21625          | 2           | 2                 | 0.0433, 0.1044 | 0.0554, 0.1180 | 0.0487, 0.0870 | 3.844           | -2.215                | -               | 8482         |

aGoof = \[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum n(w(F_o^2)^2)(n-p)^2}\], where n = number of reflections and p is the total number of parameters refined; bR1 = \[\sum ||F_o|| - ||F_c||/\sum ||F_o||\] R indices for data cut off at 1 > 2σ(I); c\(wR2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}\) \(w = 1/\sigma^2(F_o^2) + (xP)^2 + yP^2\), where P = \[\sum F_o^2 + \sum F_c^2\]/3; dR indices for all data.
| Compound | Compounds 12, 15, and 16 Unit Cell and Refinement Data | Compound | Compounds 12, 15, and 16 Unit Cell and Refinement Data | Compound | Compounds 12, 15, and 16 Unit Cell and Refinement Data |
|----------|------------------------------------------------------|----------|------------------------------------------------------|----------|------------------------------------------------------|
| Compound | ((adt)Ni(tpbz)) | ([ppt)Pt(tpbz)Ni(mdt)] | ([ppt)Ni(tpbzO)] | Structure # | JPD950 | JPD1139 | JPD1132 |
| Solvent | none | 2½(CICCH2CH2Cl) | C2H2ClNiP4PtS4 | Formula | C70H56NiO2P4S2 | 1676.48 | CH2Cl2 | C69H54Cl2NiO2P4S2 |
| Molecule | 1175.85 | 150 | 150 | Temperature, K | 150 | 150 | 150 |
| Wavelength, Å | 1.54178 | 0.71073 | 0.71073 | Solvent | none | 2½(ClCH2CH2Cl) | CH2Cl2 |
| Crystal System | monoclinic | triclinic | triclinic | Crystal System | monoclinic | triclinic | triclinic |
| Space Group | P21/n | P-1 | P-1 | Space Group | P21/n | P-1 | P-1 |
| a, Å | 12.0422(4) | 12.5374(6) | 13.4505(18) | a, Å | 12.0422(4) | 12.5374(6) | 13.4505(18) |
| b, Å | 38.5014(13) | 12.5692(6) | 16.597(2) | b, Å | 38.5014(13) | 12.5692(6) | 16.597(2) |
| c, Å | 14.0003(6) | 24.7673(13) | 16.653(2) | c, Å | 14.0003(6) | 24.7673(13) | 16.653(2) |
| α, deg. | 90 | 92.953(2) | 64.068(4) | α, deg. | 90 | 92.953(2) | 64.068(4) |
| β, deg. | 112.798(2) | 91.560(2) | 70.817(4) | β, deg. | 112.798(2) | 91.560(2) | 70.817(4) |
| γ, deg. | 90 | 108.166(2) | 72.092(4) | γ, deg. | 90 | 108.166(2) | 72.092(4) |
| Volume, Å3 | 5984.0(4) | 3699.6(3) | 3098.4(7) | Volume, Å3 | 5984.0(4) | 3699.6(3) | 3098.4(7) |
| Density, g/cm3 | 1.305 | 1.505 | 1.321 | Density, g/cm3 | 1.305 | 1.505 | 1.321 |
| μ, mm−1 | 2.484 | 2.565 | 0.615 | μ, mm−1 | 2.484 | 2.565 | 0.615 |
| Color, Habit | yellow-grn plate | orange plate | orange plate | Color, Habit | yellow-grn plate | orange plate | orange plate |
| Limiting Indices, h | -14 < h < 14 | -19 < h < 19 | -19 < h < 19 | Limiting Indices, h | -14 < h < 14 | -19 < h < 19 | -19 < h < 19 |
| Limiting Indices, k | -44 < k < 46 | -19 < k < 19 | -23 < k < 23 | Limiting Indices, k | -44 < k < 46 | -19 < k < 19 | -23 < k < 23 |
| Limiting Indices, l | -16 < l < 14 | 0 < l < 38 | -23 < l < 23 | Limiting Indices, l | -16 < l < 14 | 0 < l < 38 | -23 < l < 23 |
| Reflections Collected | 51648 | 32993 | 144627 | Reflections Collected | 51648 | 32993 | 144627 |
| Independent Data | 11399 | 32993 | 19027 | Independent Data | 11399 | 32993 | 19027 |
| Parameters Refined | 703 | 856 | 728 | Parameters Refined | 703 | 856 | 728 |
| GooF2 | 1.039 | 1.277 | 1.044 | GooF2 | 1.039 | 1.277 | 1.044 |
| R1, wR2 | 0.0479, 0.1008 | 0.0751, 0.1691 | 0.0488, 0.1165 | R1, wR2 | 0.0479, 0.1008 | 0.0751, 0.1691 | 0.0488, 0.1165 |
| R1, wR2 | 0.0699, 0.1106 | 0.0827, 0.1717 | 0.0878, 0.1350 | R1, wR2 | 0.0699, 0.1106 | 0.0827, 0.1717 | 0.0878, 0.1350 |
| Largest Diff. Peak, eÅ3 | 0.830 | 2.720 | 0.802 | Largest Diff. Peak, eÅ3 | 0.830 | 2.720 | 0.802 |
| Largest Diff. Hole, eÅ3 | -0.388 | -6.777 | -0.915 | Largest Diff. Hole, eÅ3 | -0.388 | -6.777 | -0.915 |
| Abs Structure Parameter | - | - | - | Abs Structure Parameter | - | - | - |

Notes:
1. GooF2 = Σ(w(Fo2 – Fc2)/|Fo2|)²/(n – p)², where n = number of reflections and p is the total number of parameters refined;
2. R1 = Σ(|Fo2| – |Fc2|)/Σ|Fo2|;
3. R indices for data cut off at I > 2σ(I);
4. wR2 = Σ(w(Fo2 – Fc2)²)/Σ(w(Fo2)²); w = 1/[σ(Fo2)² + (xP)² + yP], where P = [2Fo2 + Max(Fo2)²]/3;
5. R indices for all data.
Table S4. Unit Cell and Refinement Data for Compounds 17, 18 and [19][I].

| compound | ([mtd]Pt(tpbzO)_3) | ([mtd]Ni(tpbzS)_2) | ([dppbO)_2]Ni[I]_2 | ([dppbO)_2]Ni[I]_2 |
|----------|-----------------|-----------------|-------------------|-------------------|
| compound # | JPD1146 | JPD184 | JPD334 | JPD1118 |
| structure # | none | none | none | none |
| solvent | C_{53}H_{40}O_2P_4P_4S_2 | C_{53}H_{40}NiP_4S_2 | C_{90}H_{72}O_6NiO_6P_6 | C_{90}H_{72}O_6NiO_6P_6 |
| fw, g/mol | 1160.05 | 1055.79 | 2255.41 | 2255.40 |
| temperature, K | 150 | 100 | 100 | 150 |
| wavelength, Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| 2θ range, deg. | 4.18 – 66.45 | 0.05 | 2.46 – 49.52 | 12.02 | 3.12 – 54.00 | 1.82 | 3.628 – 46.660 |
| crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | P2_1/c | P2_1/c | P-1 | P2_1/c |
| a, Å | 17.0751(11) | 9.3284(12) | 13.0484(12) | 15.0552(10) |
| b, Å | 16.0625(10) | 30.3864(4) | 13.3478(12) | 26.0258(18) |
| c, Å | 20.5241(13) | 19.858(3) | 26.880(3) | 22.6547(15) |
| α, deg. | 90 | 90 | 102.137(1) | 90 |
| β, deg. | 108.283(2) | 98.487(2) | 92.504(1) | 101.217(2) |
| γ, deg. | 90 | 90 | 106.961(1) | 90 |
| volume, Å³ | 5345.0(6) | 5567.1(13) | 4350.1(7) | 8707.1(10) |
| Z | 4 | 4 | 2 | 4 |
| density, g/cm³ | 1.442 | 1.260 | 1.722 | 1.721 |
| μ, mm⁻¹ | 2.864 | 0.649 | 2.514 | 2.512 |
| crystal size | 0.21 x 0.21 x 0.26 | 0.03 x 0.03 x 0.18 | 0.02 x 0.13 x 0.21 | 0.05 x 0.06 x 0.28 |
| color, habit | dark orange column | yellow needle | orange plate | orange-red plate |
| limiting indices, h | -26 ≤ h ≤ 26 | -10 ≤ h ≤ 10 | -16 ≤ h ≤ 16 | -15 ≤ h ≤ 16 |
| limiting indices, k | -24 ≤ k ≤ 24 | -35 ≤ k ≤ 35 | -17 ≤ k ≤ 17 | -28 ≤ k ≤ 28 |
| limiting indices, l | -31 ≤ l ≤ 31 | -23 ≤ l ≤ 23 | -34 ≤ l ≤ 34 | -25 ≤ l ≤ 25 |
| reflections collected | 403235 | 39326 | 37066 | 153572 |
| independent data | 20472 | 9510 | 18761 | 12505 |
| restraints | 0 | 1 | 0 | 36 |
| parameters refined | 606 | 610 | 985 | 989 |
| Goof/ | 1.081 | 0.964 | 0.945 | 1.023 |
| R1, % | 0.0239, 0.0594 | 0.0898, 0.1686 | 0.0427, 0.0931 | 0.0505, 0.1241 |
| wR2, % | 0.0314, 0.0641 | 0.1753, 0.2007 | 0.0707, 0.1017 | 0.0794, 0.1403 |
| largest diff. peak, e Å⁻³ | 2.242 | 0.873 | 1.226 | 2.552 |
| largest diff. hole, e Å⁻³ | -0.781 | -0.405 | -1.590 | -1.094 |

*Goof = [Σw(Fo² - Fc²)|²/(n-p)]¹/², where n = number of reflections and p is the total number of parameters refined; R1 = Σ||Fo|| - |Fc||/Σ|Fo||; R1 is for data cut off at 1 > 2σ(I); wR2 = (Σ[w(Fo² - Fc²)]²)/Σ[w(Fo²)]²; w = 1/[σ²(Fo²) + (apF)² + bP²], where P = [2F² + Max(Fo²,0)]/3; R1 is for all data.

Table S5. Selected bond lengths (Å) and angles (deg.) for the two polymorphs of [(dppbO)_2]Ni[I]. Chemically identical values are averaged.a

| bond | Nickel | Monoclinic |
|------|--------|----------|
| Ni–O | 2.061[1] | 2.060[2] |
| P–O | 1.495[1] | 1.493[2] |
| P–C | 1.823[2] | 1.828[3] |
| O–Ni–Otrans | 173.26[7] | 173.65[10] |
| O–Ni–Ocis, intra-ligand | 85.86[7] | 86.47[10] |
| O–Ni–Ocis, inter-ligand | 91.47[4] | 91.28[6] |
| θ | 58.7 | 55.6 |

*aUncertainties are propagated according to Taylor, J. R. An Introduction to Error Analysis; 2nd ed.; University Science Books: Sausalito, CA, 1997, pp 73-77. cCarbon atom of central C4H4 arene ring. cFold angle between NiO2 plane and P2_1/c mean plane of central arene ring.
Figure S1. Full atom labeling for [(tpbz)NiCl$_2$]. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.
Figure S2. Full atom labeling for \[\{(\text{NC})_2\text{C}_2\text{S}_2\text{Ni}(\eta^2-\text{tpbz})\}\]. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.

Figure S3. Atom labeling for interstitial CHCl$_3$ in \[\{(\text{NC})_2\text{C}_2\text{S}_2\text{Ni}(\eta^2-\text{tpbz})\}\cdot2(\text{CHCl}_3)\]. The thermal ellipsoid plot is drawn at the 50% level.
Figure S4. Full atom labeling for [(Me$_2$C$_2$S$_2$)Ni(η$_2$-tpbz)]. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.

Figure S5. Thermal ellipsoid plot of [(Me$_2$C$_2$S$_2$)Ni(η$_2$-tpbz)] at the 50% level with interstitial CH$_2$Cl$_2$ molecule shown.
Figure S6. Full atom labeling for [(Me₂C₂S₂)Pt(η²-tpbz)]. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.
Figure S7. Atom labeling for interstitial CH$_2$Cl$_2$ in [(Me$_2$C$_2$S$_2$)Pt(η$^2$-tpbz)]·2(CH$_2$Cl$_2$). The thermal ellipsoid plot is drawn at the 50% level. The second CH$_2$Cl$_2$ molecule is symmetry-related to that which is shown.
**Figure S8.** Full atom labeling for \([\text{Ph}_2\text{C}_2\text{S}_2]\text{Ni(}\eta^2\text{-tpbz})]. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.

**Figure S9.** Full atom labeling for \([\text{Ph}_2\text{C}_2\text{S}_2]\text{Pd(}\eta^2\text{-tpbz})]. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.
**Figure S10.** Full atom labeling for [(Ph₂C₂S₂)Pt(η²-tpbz)]. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.
Figure S11. Full atom labeling for [(Ph₂C₂S₂)₂Pt(η²-tpbz)]. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.

Figure S12. Full atom labeling for the interstitial ClCH₂CH₂Cl molecules in [(Ph₂C₂S₂)₂Pt(η²-tpbz)]·2(ClCH₂CH₂Cl). The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity. Chlorine atom Cl₄ is disordered over two positions and refined with a split atom model.
Figure S13. Full atom labeling for [(CH₃O-p-C₆H₄)₂C₂S₂]Ni(η²-tpbz)]. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity. For the phenyl ring defined by C47-C52, one position of two over which it is disordered is shown.

Figure S14. Full atom labeling for [(CH₃O-p-C₆H₄)₂C₂S₂]Ni(η²-tpbz)]. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity. For the phenyl ring defined by C47-C52, the second position of two over which it is disordered is shown.
Figure S15. Full atom labeling for \([\text{Ph}_2\text{C}_2\text{S}_2]\text{Pt(tpbz)}\text{Ni(S}_2\text{C}_2\text{Me}_2)]\). The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.

Figure S16. Full atom labeling for the interstitial solvent in \([\text{Ph}_2\text{C}_2\text{S}_2]\text{Pt(tpbz)}\text{Ni(S}_2\text{C}_2\text{Me}_2)]\cdot2\frac{1}{2}(\text{ClCH}_2\text{CH}_2\text{Cl})\). The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity. The atoms of these solvent molecules have been handled with a mixture of anisotropic and isotropic refinement owing to the positional disorder that they show.
Figure S17. Full atom labeling for [(Me₂C₂S₂)Pt(η²-tpbzO₂)]. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.
Figure S18. Full atom labeling for \([\text{Ph}_2\text{C}_2\text{S}_2]\text{Ni}(\eta^2-\text{tpbzO}_2)\]. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.

Figure S19. Atom labeling for interstitial \(\text{CH}_2\text{Cl}_2\) in \([\text{Ph}_2\text{C}_2\text{S}_2]\text{Ni}(\eta^2-\text{tpbzO}_2)\cdot\text{CH}_2\text{Cl}_2\). The thermal ellipsoid plot is drawn at the 50% level. Chlorine atom 1 and carbon atom 69 are disordered over two positions and consequently refined using a split atom model.
Figure S20. Full atom labeling for [(Me₂C₂S₂)Ni(η²-tpbzS₂)]. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.
Figure S21. Full atom labeling for [Ni(dpdpbO$_2$)$_3$]$^{2+}$ in [Ni(dpdpbO$_2$)$_3$][I$_3$]$_2$ (triclinic polymorph). The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.
Figure S22. Partial atom labeling for [Ni(dppbO$_2$)$_3$][I$_3$]$_2$ (triclinic polymorph) with counteranions shown. One full I$_3^-$ anion and two half I$_3^-$ anions are paired with the dication. The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.
Figure S23. Full atom labeling for $[\text{Ni(dppbO}_2\text{)}_3]^{2+}$ in $[\text{Ni(dppbO}_2\text{)}_3][\text{I}_3]_2$ (monoclinic polymorph). The thermal ellipsoid plot is drawn at the 50% level, and all H atoms are omitted for clarity.
Figure S24. $^1$H NMR spectrum of $[\text{Cl}_2\text{Ni(tpbz)}]$ in CD$_2$Cl$_2$. Signals not corresponding to [Cl$_2$Ni(tpbz)] are marked with “x”.

Figure S25. $^{31}$P NMR spectrum of $[\text{Cl}_2\text{Ni(tpbz)}]$ in CD$_2$Cl$_2$. 
**Figure S26.** $^1$H NMR spectrum of [Cl$_2$Pd(tpbz)] in DMSO-d$_6$. Signals not corresponding to [Cl$_2$Pd(tpbz)] are marked with “x”.

**Figure S27.** $^{31}$P NMR spectrum of [Cl$_2$Pd(tpbz)] in DMSO-d$_6$. 
Figure S28. $^1$H NMR spectrum of [Cl$_2$Pt(tpbz)] in DMSO-d$_6$. Signals not corresponding to [Cl$_2$Pt(tpbz)] are marked with “x”.

Figure S29. $^{31}$P NMR spectrum of [Cl$_2$Pt(tpbz)] in DMSO-d$_6$. 
Figure S30. $^1$H NMR spectrum (CDCl$_3$) of [(mnt)Ni(tpbz)].

Figure S31. Close-up of the aromatic region of the $^1$H NMR spectrum (CDCl$_3$) of [(mnt)Ni(tpbz)].
**Figure S32.** $^{31}$P NMR spectrum (CDCl$_3$) of [(mnt)Ni(tpbz)].

**Figure S33.** IR spectrum (KBr disk) of [(mnt)Ni(tpbz)].
**Figure S34.** MALDI mass spectrum (positive ion mode) of [(mnt)Ni(tpbz)].
**Figure S35.** Cyclic voltammogram of [(mnt)Ni(tpbz)] in CH$_2$Cl$_2$. The working electrode was Pt disk, the scan speed 100 mV/sec, and the supporting electrolyte ["Bu$_4$][PF$_6$].

**Figure S36.** Differential pulse voltammogram of [(mnt)Ni(tpbz)] in CH$_2$Cl$_2$. The working electrode was Pt disk, the scan speed 100 mV/sec, and the supporting electrolyte ["Bu$_4$][PF$_6$].
Figure S37. $^1$H NMR spectrum (CDCl$_3$) of [(mdt)Ni(tpbz)]. Signals not belonging to [(mdt)Ni(tpbz)] are designated with "x".

Figure S38. Close-up $^1$H NMR spectrum (CDCl$_3$) of [(mdt)Ni(tpbz)].
Figure S39. $^{31}$P NMR spectrum (CDCl$_3$) of [(mdt)Ni(tpbz)].

Figure S40. UV-vis absorption spectrum (CH$_2$Cl$_2$) of [(mdt)Ni(tpbz)].
**Figure S41.** ESI mass spectrum (positive ion mode) of [(mdt)Ni(tpbz)].

**Figure S42.** Cyclic voltammogram of [(mdt)Ni(tpbz)] in CH$_2$Cl$_2$. The working electrode was glassy carbon, the scan speed 100 mV/sec, and the supporting electrolyte ["Bu$_4$][PF$_6$].
Figure S43. Differential pulse voltammogram (oxidizing direction) of [(mdt)Ni(tpbz)] in CH₂Cl₂. The working electrode was glassy carbon, and the supporting electrolyte was ["Bu₄][PF₆].

Figure S44. Differential pulse voltammogram (reducing direction) of [(mdt)Ni(tpbz)] in CH₂Cl₂. The working electrode was glassy carbon, and the supporting electrolyte was ["Bu₄][PF₆].
Figure S45. $^1$H NMR spectrum (CDCl$_3$) of [(mdt)Pd(tpbz)].

Figure S46. $^{31}$P NMR spectrum (CDCl$_3$) of [(mdt)Pd(tpbz)].
Figure S47. UV-vis spectrum (CH$_2$Cl$_2$) of [(Me$_2$C$_2$S$_2$)Pd(tpbz)].

Figure S48. ESI mass spectrum (positive ion mode) of [(Me$_2$C$_2$S$_2$)Pd(tpbz)].
**Figure S49.** $^1$H NMR spectrum (CDCl$_3$) of [(Me$_2$C$_2$S$_2$)Pt(tpbz)].

**Figure S50.** $^{31}$P NMR spectrum (CDCl$_3$) of [(Me$_2$C$_2$S$_2$)Pt(tpbz)].
Figure S51. ESI mass spectrum (positive ion mode) of [(Me$_2$C$_2$S$_2$)Pt(tpbz)].

Figure S52. ESI mass spectrum (positive ion mode) of [(Me$_2$C$_2$S$_2$)Pt(tpbz)].
Figure S53. $^1$H NMR spectrum (CDCl$_3$) of [(Ph$_2$C$_2$S$_2$)Ni(tpbz)].

Figure S54. Close-up of the aromatic region of the $^1$H NMR spectrum (CDCl$_3$) of [(Ph$_2$C$_2$S$_2$)Ni(tpbz)].
Figure S55. $^{31}$P NMR spectrum (CDCl$_3$) of [(Ph$_2$C$_2$S)$_2$Ni(tpbz)].
Figure S56. ESI mass spectrum (positive ion mode) of [(Ph$_2$C$_2$S)$_2$Ni(tpbz)].
Figure S57. Cyclic voltammogram of [(Ph$_2$C$_2$S$_2$)Ni(tpbz)] in CH$_2$Cl$_2$ with ["Bu$_4$N][PF$_6$] supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The scan rate was 100 mV/s.

Figure S58. Cyclic voltammogram of [(Ph$_2$C$_2$S$_2$)Ni(tpbz)] in CH$_2$Cl$_2$ with ["Bu$_4$N][PF$_6$] supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The scan rate was 100 mV/s.
Figure S59. Differential pulse voltammogram of [(Ph₂C₂S₂)Ni(tpbz)] in CH₂Cl₂ with ["Bu₄N][PF₆] supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The pulse amplitude was 50 mV.
Figure S60. Elemental analysis of [(Ph₂C₂S₂)Ni(tpbz)] from Midwest Microlab, LLC. The form is reproduced with the permission of Midwest Microlab.
Figure S61. $^1$H NMR spectrum (CDCl$_3$) of [(Ph$_2$C$_2$S$_2$)Pd(tpbz)].

Figure S62. $^{31}$P NMR spectrum (CDCl$_3$) of [(Ph$_2$C$_2$S$_2$)Pd(tpbz)].
Figure S63. ESI mass spectrum (positive ion mode) of [(Ph₂C₂S₂)Pd(tpbz)].
Figure S64. Cyclic voltammogram of [(Ph$_2$C$_2$S$_2$)Pd(tpbz)] in CH$_2$Cl$_2$ with [$^n$Bu$_4$N][PF$_6$] supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The scan rate was 100 mV/s.

Figure S65. Differential pulse voltammogram of [(Ph$_2$C$_2$S$_2$)Ni(tpbz)] in CH$_2$Cl$_2$ with [$^n$Bu$_4$N][PF$_6$] supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The pulse amplitude was 50 mV.
Figure S66. Elemental analysis of [(Ph₂C₂S₂)Pd(tpbz)] from Galbraith Laboratories, Inc. The form is reproduced with the permission of Galbraith Laboratories.
Figure S67. $^{31}$P NMR spectrum (CDCl$_3$) of [(Ph$_2$C$_2$S)$_2$Pd(tpbz)].

Figure S68. ESI mass spectrum (positive ion mode) of [(Ph$_2$C$_2$S)$_2$Pt(tpbz)].
Figure S69. Cyclic voltammogram of [(Ph₂C₂S₂)Pt(tpbz)] in CH₂Cl₂ with ["Bu₄N][PF₆] supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The scan rate was 100 mV/s.

Figure S70. Differential pulse voltammogram of [(Ph₂C₂S₂)Pt(tpbz)] in CH₂Cl₂ with ["Bu₄N][PF₆] supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The pulse amplitude was 50 mV.
Figure S71. Elemental analysis of [(Ph₂C₂S₂)Pt(tpbz)] from Galbraith Laboratories, Inc. The form is reproduced with the permission of Galbraith Laboratories.
Figure S72. $^1$H NMR spectrum (CD$_2$Cl$_2$) of [(Ph$_2$C$_2$S$_2$)$_2$Pd(tpbz)].

Figure S73. $^{31}$P NMR spectrum (CD$_2$Cl$_2$) of [(Ph$_2$C$_2$S$_2$)$_2$Pd(tpbz)].
Figure S74. ESI mass spectrum (positive ion mode) of [(Ph₂C₂S₂)₂Pt(tpbz)].

Figure S75. CV of [(Ph₂C₂S₂)₂Pt(tpbz)] in CH₂Cl₂ with ["Bu₄N][PF₆] supporting electrolyte, Pt disk working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The scan rate was 100 mV/s.
Figure S76. $^1$H NMR spectrum of [(MeO-p-C$_6$H$_4$)$_2$C$_2$S$_2$]Ni(tpbz)] in CDCl$_3$.

Figure S77. $^{31}$P NMR spectrum of [(MeO-p-C$_6$H$_4$)$_2$C$_2$S$_2$]Ni(tpbz)] in CDCl$_3$. 
Figure S78. ESI mass spectrum (positive ion mode) of $[([\text{MeO-}p-\text{C}_6\text{H}_4])_2\text{C}_2\text{S}_2\text{Ni}(\text{tpbz})]$.

Figure S79. Cyclic voltammogram of $[((\text{MeO-}p-\text{C}_6\text{H}_4))_2\text{C}_2\text{S}_2\text{Ni}(\text{tpbz})]$ in CH$_2$Cl$_2$ with $[\text{Bu}_4\text{N}][\text{PF}_6]$ supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The scan rate was 100 mV/s.
Figure S80. Differential pulse voltammogram, moving in the direction of positive potential, of \[((\text{CH}_3\text{O})_p\text{C}_6\text{H}_4\text{C}_2\text{S}_2)\text{Ni(tpbz)}\] in CH\(_2\)Cl\(_2\) with [\text{nBu}_4\text{N}][\text{PF}_6]\] supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The pulse amplitude was 50 mV.

Figure S81. Differential pulse voltammogram, moving in the direction of negative potential, of \[((\text{CH}_3\text{O})_p\text{C}_6\text{H}_4\text{C}_2\text{S}_2)\text{Ni(tpbz)}\] in CH\(_2\)Cl\(_2\) with [\text{nBu}_4\text{N}][\text{PF}_6]\] supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The pulse amplitude was 50 mV.
**Figure S82.** Elemental analysis of [((MeO-p-C₆H₄)₂C₂S₂)Ni(tpbz)] from Kolbe Microanalytical Laboratory. The form is reproduced with the permission of Kolbe Microanalytical Laboratory.

| Sample Name | % C  | % H  | % N  | % P  | % S  | Argon | V2 |
|-------------|------|------|------|------|------|-------|----|
| JPD 175 - b | 71.29| 4.86 | 10.41| 5.51 |      | x     | >  |
|             |      |      |      |      |      |       | x  |

Kind regards

Patrick Springer

Anal. Calcd for [((MeO-p-C₆H₄)₂C₂S₂)Ni(tpbz)], [C₇₀H₆₈NiO₃P₂S₄]: C, 71.50; H, 4.80; P, 10.54; S, 5.45.
Figure S83. $^1$H NMR spectrum of $[((\text{MeO-}p\text{-C}_6\text{H}_4)\text{C}_2\text{S}_2)\text{Pd(tpbz)\}}$ in CDCl$_3$.

Figure S84. $^{31}$P NMR spectrum of $[((\text{MeO-}p\text{-C}_6\text{H}_4)\text{C}_2\text{S}_2)\text{Pd(tpbz)\}}$ in CDCl$_3$. 
Figure S85. UV-vis spectrum (CH₂Cl₂) of [(MeO-p-C₆H₄)₂C₂S₂]Pd(tpbz)].

Figure S86. ESI mass spectrum (positive ion mode) of [(MeO-p-C₆H₄)₂C₂S₂]Pd(tpbz)].
Figure S87. Cyclic voltammogram of [((CH$_3$O-p-C$_6$H$_4$)$_2$C$_2$S$_2$)Pd(tpbz)] in CH$_2$Cl$_2$ with ["Bu$_4$N][PF$_6$] supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The scan rate was 100 mV/s.
Figure S88. Differential pulse voltammogram, moving in the direction of positive potential, of \([\text{[(CH}_3\text{O}-p\text{-C}_6\text{H}_4)\text{C}_2\text{S}_2)\text{Pd(tpbz)}]}\) in \(\text{CH}_2\text{Cl}_2\) with \([\text{"Bu}_4\text{N}][\text{PF}_6]\) supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The pulse amplitude was 50 mV.

Figure S89. Differential pulse voltammogram, moving in the direction of negative potential, of \([\text{[(CH}_3\text{O}-p\text{-C}_6\text{H}_4)\text{C}_2\text{S}_2)\text{Pd(tpbz)}]}\) in \(\text{CH}_2\text{Cl}_2\) with \([\text{"Bu}_4\text{N}][\text{PF}_6]\) supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The pulse amplitude was 50 mV.
Figure S90. $^1$H NMR spectrum of [(MeO-$p$-C$_6$H$_4$)$_2$C$_2$S$_2$]Pt(tpbz)] in CDCl$_3$.

Figure S91. $^{31}$P NMR spectrum of [(MeO-$p$-C$_6$H$_4$)$_2$C$_2$S$_2$]Pt(tpbz)] in CDCl$_3$. 
Figure S92. UV-vis spectrum (CH$_2$Cl$_2$) of [((MeO-p-C$_6$H$_4$)$_2$C$_2$S$_2$)Pt(tpbz)].

Figure S93. ESI mass spectrum (positive ion mode) of [((MeO-p-C$_6$H$_4$)$_2$C$_2$S$_2$)Pt(tpbz)].
Figure S94. Cyclic voltammogram of [(CH₃O-p-C₆H₄)₂C₂S₂)Pt(tpbz)] in CH₂Cl₂ with [⁷Bu₄N][PF₆] supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The scan rate was 100 mV/s.

Figure S95. Differential pulse voltammogram, moving in the direction of positive potential, of [(CH₃O-p-C₆H₄)₂C₂S₂)Pt(tpbz)] in CH₂Cl₂ with [⁷Bu₄N][PF₆] supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The pulse amplitude was 50 mV.
Figure S96. $^1$H NMR spectrum of [(pdt)Pt(tpbz)Ni(mdt)] in CDCl$_3$.

Figure S97. $^{31}$P NMR spectrum of [(pdt)Pt(tpbz)Ni(mdt)] in CDCl$_3$. 
Figure S98. UV-vis spectrum in CH₂Cl₂ of [(Ph₂C₂S₂)Pt(tpbz)Ni(S₂C₂Me₂)].

Figure S99. Mass spectrum (ESI, positive ion mode) of [(Ph₂C₂S₂)Pt(tpbz)Ni(S₂C₂Me₂)].
Figure S100. Cyclic voltammogram of [(Ph₂C₂S₂)Pt(tpbz)Ni(S₂C₂Me₂)] in CH₂Cl₂ with [⁷Bu₄N][PF₆] supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The scan rate was 100 mV/s.
Figure S101. $^1$H NMR spectrum (CDCl$_3$) of [(Ph$_2$C$_2$S)$_2$Ni(tpbzO$_2$)].

Figure S102. $^{31}$P NMR spectrum (CDCl$_3$) of [(Ph$_2$C$_2$S)$_2$Ni(tpbzO$_2$)].
Figure S103. UV-vis spectrum (CH₂Cl₂) of [(Ph₂C₂S₂)Ni(tpbzO₂)].

Figure S104. Mass spectrum (ESI, positive ion mode) of [(Ph₂C₂S₂)Ni(tpbzO₂)].
Figure S105. Cyclic voltammogram of \([\text{Ph}_2\text{C}_2\text{S}_2]\text{Ni(tpbzO}_2\text{)}\) in CH\(_2\text{Cl}_2\) with \([^6\text{Bu}_4\text{N}]\text{PF}_6\) supporting electrolyte, glassy carbon working electrode, Pt wire counter electrode and AgCl/Ag reference electrode. The scan rate was 100 mV/s.
Figure S106. $^1$H NMR spectrum (CDCl$_3$) of [((CH$_3$)$_2$C$_2$S)$_2$Pt(tpbzO$_2$)].

Figure S107. $^{31}$P NMR spectrum (CDCl$_3$) of [((CH$_3$)$_2$C$_2$S)$_2$Pt(tpbzO$_2$)].
Figure S108. Mass spectrum (ESI, positive ion mode) of [(Me₂C₃S₂)Pt(tpbzO₂)].
Figure S109. $^1$H NMR spectrum (CDCl$_3$) of $[[\text{C}_8\text{H}_{14}]_2\text{S}_2]\text{Ni(tpbS}_2$.

Figure S110. $^{31}$P NMR spectrum (CDCl$_3$) of $[[\text{C}_8\text{H}_{14}]_2\text{S}_2]\text{Ni(tpbS}_2$. 
**Figure S111.** UV-vis spectrum (CH$_2$Cl$_2$) of [(Me$_2$C$_2$S$_2$)Ni(tpbzS$_2$)].

**Figure S112.** Mass spectrum (ESI, positive ion mode) of [(Me$_2$C$_2$S$_2$)Ni(tpbzS$_2$)].
**Figure S113.** Elemental analysis of [(Me₂C₂S₂)Ni(tpbzS₂)] from Galbraith Laboratories, Inc. The form is reproduced with the permission of Galbraith Laboratories.
Figure S114. UV-vis spectrum (CH$_2$Cl$_2$) of [Ni(dppbO$_2$)$_3$][I$_3$].

Figure S115. Mass spectrum (ESI, positive ion mode) of [Ni(dppbO$_2$)$_3$]$^{2+}$. 

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Figure S116. Molecular orbital energy level diagram illustrating the frontier MOs for [(pdt)Ni(tpbz)]. Images are presented at the 0.03 contour level.
**Table S6.** Atomic Coordinates for Optimized [(pdt)Pt(tpbz)Ni(mdt)].

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | X     | Y     | Z     |
|---------------|---------------|-------------|-------------------------|-------|-------|-------|
| 1             | 78            | 0           |                         | 3.232403 | 0.004368 | 0.196555 |
| 2             | 28            | 0           |                         | -5.639882 | -0.002076 | 0.084196 |
| 3             | 16            | 0           |                         | 4.890738  | -1.620118 | -0.202738 |
| 4             | 16            | 0           |                         | 4.901464  | 1.624287  | -0.181603 |
| 5             | 16            | 0           |                         | -7.143396 | 1.555500  | 0.486837  |
| 6             | 16            | 0           |                         | -7.150263 | -1.55337  | 0.477940  |
| 7             | 15            | 0           |                         | 1.573089  | -1.566811 | 0.622692  |
| 8             | 15            | 0           |                         | 1.570967  | 1.575478  | 0.617154  |
| 9             | 15            | 0           |                         | -4.070032 | 1.536363  | -0.401172 |
| 10            | 15           | 0           |                         | -4.067756 | -1.541147 | -0.392166 |
| 11            | 6            | 0           |                         | 7.589531  | -1.530392 | -0.643226 |
| 12            | 6            | 0           |                         | 7.613052  | -2.581740 | -1.576699 |
| 13            | 1            | 0           |                         | 6.736779  | -2.755777 | -2.20317  |
| 14            | 6            | 0           |                         | 8.740351  | -3.390254 | -1.716559 |
| 15            | 1            | 0           |                         | 8.738215  | -4.196285 | -2.453868 |
| 16            | 6            | 0           |                         | 9.867246  | -3.171365 | -0.922964 |
| 17            | 1            | 0           |                         | 10.749742 | -3.805367 | -1.031925 |
| 18            | 6            | 0           |                         | 9.854234  | -2.137340 | 0.014923  |
| 19            | 1            | 0           |                         | 10.727037 | -1.961406 | 0.647712  |
| 20            | 6            | 0           |                         | 8.728000  | -1.329089 | 0.156726  |
| 21            | 1            | 0           |                         | 8.721201  | -0.529688 | 0.897626  |
| 22            | 6            | 0           |                         | 6.379189  | -0.679820 | -0.475239 |
| 23            | 6            | 0           |                         | 6.380549  | 0.677736  | -0.483504 |
| 24            | 6            | 0           |                         | 7.558513  | 1.522630  | -0.823215 |
| 25            | 6            | 0           |                         | 8.282393  | 1.305445  | -2.00845  |
| 26            | 1            | 0           |                         | 7.979572  | 0.497278  | -2.674411 |
| 27            | 6            | 0           |                         | 9.371203  | 2.109202  | -2.340232 |
| 28            | 1            | 0           |                         | 9.918172  | 1.920983  | -3.266817 |
| 29            | 6            | 0           |                         | 9.57796   | 3.154814  | -1.499761 |
| 30            | 1            | 0           |                         | 10.610187 | 3.785495  | -1.761183 |
| 31            | 6            | 0           |                         | 9.042347  | 3.389552  | -0.324866 |
| 32            | 1            | 0           |                         | 9.335151  | 4.204687  | 0.340786  |
| 33            | 6            | 0           |                         | 7.953081  | 2.585330  | 0.008500  |
| 34            | 1            | 0           |                         | 7.400339  | 2.771836  | 0.929972  |
| 35            | 6            | 0           |                         | 1.462487  | -3.055592 | -0.451374 |
| 36            | 6            | 0           |                         | 1.840367  | -2.930034 | -1.797820 |
| 37            | 1            | 0           |                         | 2.242056  | -1.982672 | -2.159040 |
| 38            | 6            | 0           |                         | 1.729096  | -4.020032 | -2.660205 |
| 39            | 1            | 0           |                         | 2.031633  | -3.915146 | -3.703623 |
| 40            | 6            | 0           |                         | 1.254407  | -5.244854 | -2.186590 |
| 41            | 1            | 0           |                         | 1.177574  | -6.095533 | -2.861434 |
| 42            | 6            | 0           |                         | 0.891713  | -5.378925 | -0.845951 |
| 43            | 1            | 0           |                         | 0.531361  | -6.337461 | -0.467867 |
| 44            | 6            | 0           |                         | 0.994624  | -4.290390 | 0.021539  |
| 45            | 1            | 0           |                         | 0.715496  | -4.408027 | 1.068610  |
| 46            | 6            | 0           |                         | 1.521517  | -2.192831 | 2.354311  |
Table S6 Continued. Atomic Coordinates for Optimized [(pdt)Pt(tpbz)Ni(mdt)].

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 47            | 6             | 0           | 0.327144    | -2.44176    | 3.046910    |
| 48            | 1             | 0           | -0.638841   | -2.255163   | 2.578958    |
| 49            | 6             | 0           | 0.363458    | -2.936748   | 4.352051    |
| 50            | 1             | 0           | -0.572273   | -3.126230   | 4.881328    |
| 51            | 6             | 0           | 1.587087    | -3.184347   | 4.975230    |
| 52            | 1             | 0           | 1.612090    | -3.567738   | 5.997120    |
| 53            | 6             | 0           | 2.778064    | -2.934136   | 4.291597    |
| 54            | 1             | 0           | 3.738711    | -3.120160   | 4.774991    |
| 55            | 6             | 0           | 2.750515    | -2.434752   | 2.989987    |
| 56            | 1             | 0           | 3.682955    | -2.224317   | 2.463170    |
| 57            | 6             | 0           | 1.461018    | 3.066379    | -0.454148   |
| 58            | 6             | 0           | 0.967355    | 4.293034    | 0.014396    |
| 59            | 1             | 0           | 0.665917    | 4.403062    | 1.056137    |
| 60            | 6             | 0           | 0.868332    | 5.384017    | -0.850271   |
| 61            | 1             | 0           | 0.487620    | 6.336035    | -0.475642   |
| 62            | 6             | 0           | 1.261605    | 5.261012    | -2.183425   |
| 63            | 1             | 0           | 1.188776    | 6.118022    | -2.855746   |
| 64            | 6             | 0           | 1.762244    | 4.044865    | -2.652209   |
| 65            | 1             | 0           | 2.089608    | 3.948992    | -3.68893    |
| 66            | 6             | 0           | 1.868863    | 2.952121    | -1.792649   |
| 67            | 1             | 0           | 2.291309    | 2.012166    | -2.149259   |
| 68            | 6             | 0           | 1.515533    | 2.199620    | 2.349889    |
| 69            | 6             | 0           | 2.742844    | 2.437777    | 2.990026    |
| 70            | 1             | 0           | 3.676192    | 2.224820    | 2.465744    |
| 71            | 6             | 0           | 2.767471    | 2.935210    | 4.292141    |
| 72            | 1             | 0           | 3.726852    | 3.117784    | 4.779707    |
| 73            | 6             | 0           | 1.574965    | 3.187658    | 4.972541    |
| 74            | 1             | 0           | 1.597618    | 3.569596    | 5.995022    |
| 75            | 6             | 0           | 0.352857    | 2.943755    | 4.345049    |
| 76            | 1             | 0           | -0.584132   | 3.134651    | 4.871576    |
| 77            | 6             | 0           | 0.319677    | 2.452723    | 3.039213    |
| 78            | 1             | 0           | -0.645249   | 2.265976    | 2.568155    |
| 79            | 6             | 0           | -0.046184   | -0.700864   | 0.352107    |
| 80            | 6             | 0           | -0.046984   | 0.706609    | 0.347664    |
| 81            | 6             | 0           | -1.240375   | 1.395068    | 0.100881    |
| 82            | 1             | 0           | -1.241754   | 2.485251    | 0.093888    |
| 83            | 6             | 0           | -2.433334   | 0.703120    | -0.136555   |
| 84            | 6             | 0           | -2.432530   | -0.703775   | -0.131810   |
| 85            | 6             | 0           | -1.238622   | -1.392509   | 0.109998    |
| 86            | 1             | 0           | -1.238470   | -2.482730   | 0.109920    |
| 87            | 6             | 0           | -4.065650   | 2.059426    | -2.168518   |
| 88            | 6             | 0           | 2.891673    | 2.351214    | -2.894297   |
| 89            | 6             | 0           | -1.913060   | 2.199338    | -2.427760   |
| 90            | 6             | 0           | 2.965681    | 2.716662    | -4.228513   |
| 91            | 6             | 0           | -2.046370   | 2.911451    | -4.784071   |
| 92            | 6             | 0           | -4.206979   | 2.865913    | -4.848987   |
Table S6 Continued. Atomic Coordinates for Optimized [(pdt)Pt(tpbz)Ni(mdt)].

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
|               |               |             | X          | Y          | Z          |
| 93            | 1             | 0           | -4.260963  | 3.178150  | -5.893757  |
| 94            | 6             | 0           | -5.377055  | 2.608666  | -4.133242  |
| 95            | 1             | 0           | -6.350557  | 2.717704  | -4.614634  |
| 96            | 6             | 0           | -5.311553  | 2.201460  | -2.800883  |
| 97            | 1             | 0           | -6.225209  | 1.989096  | -2.242424  |
| 98            | 6             | 0           | -3.924515  | 3.082865  | 0.585636   |
| 99            | 6             | 0           | -4.235269  | 3.021214  | 1.953733   |
| 100           | 1             | 0           | -4.614652  | 2.092210  | 2.380551   |
| 101           | 6             | 0           | -4.089408  | 4.151605  | 2.756863   |
| 102           | 1             | 0           | -4.340031  | 4.095497  | 3.817695   |
| 103           | 6             | 0           | -3.648682  | 5.355087  | 2.20179    |
| 104           | 1             | 0           | -3.544642  | 6.241442  | 2.830948   |
| 105           | 6             | 0           | -3.55572   | 5.426521  | 0.839997   |
| 106           | 1             | 0           | -3.022777  | 6.367870  | 0.398633   |
| 107           | 6             | 0           | -3.492556  | 4.296413  | 0.031784   |
| 108           | 1             | 0           | -3.266237  | 4.364799  | -1.032262  |
| 109           | 6             | 0           | -4.059792  | -2.076727 | -2.155911  |
| 110           | 6             | 0           | -2.884167  | -2.333540 | -2.878643  |
| 111           | 1             | 0           | -1.906403  | -2.210458 | -2.412249  |
| 112           | 6             | 0           | -2.955274  | -2.745436 | -4.209828  |
| 113           | 1             | 0           | -2.034584  | -2.940935 | -4.762856  |
| 114           | 6             | 0           | -4.195304  | -2.904253 | -4.830409  |
| 115           | 1             | 0           | -4.247050  | -3.224655 | -5.872819  |
| 116           | 6             | 0           | -5.367044  | -2.646014 | -4.117742  |
| 117           | 1             | 0           | -6.339656  | -2.762440 | -4.599210  |
| 118           | 6             | 0           | -5.304474  | -2.228332 | -2.788491  |
| 119           | 1             | 0           | -6.219633  | -2.015128 | -2.232777  |
| 120           | 6             | 0           | -3.921805  | -3.080653 | 0.605440   |
| 121           | 6             | 0           | -4.241957  | -3.011561 | 1.970971   |
| 122           | 1             | 0           | -4.628616  | -2.081576 | 2.389038   |
| 123           | 6             | 0           | -4.096142  | -4.136013 | 2.782427   |
| 124           | 1             | 0           | -4.354026  | -4.074168 | 3.841194   |
| 125           | 6             | 0           | -3.646132  | -5.340964 | 2.238553   |
| 126           | 1             | 0           | -3.542120  | -6.222720 | 2.873759   |
| 127           | 6             | 0           | -3.343630  | -5.419901 | 0.878831   |
| 128           | 1             | 0           | -3.003428  | -6.362521 | 0.445906   |
| 129           | 6             | 0           | -3.480522  | -4.295770 | 0.062366   |
| 130           | 1             | 0           | -3.247017  | -4.370129 | -0.999748  |
| 131           | 6             | 0           | -9.844807  | 1.579070  | 1.035042   |
| 132           | 1             | 0           | -10.762792 | 1.011245  | 1.249381   |
| 133           | 1             | 0           | -10.044932 | 2.227085  | 0.162661   |
| 134           | 1             | 0           | -9.654780  | 2.249469  | 1.892491   |
| 135           | 6             | 0           | -8.664654  | 0.676346  | 0.781978   |
| 136           | 6             | 0           | -8.667486  | -0.671186 | 0.778674   |
| 137           | 6             | 0           | -9.851316  | -1.570101 | 1.028104   |
| 138           | 1             | 0           | -9.663036  | -2.245991 | 1.881615   |
Table S6 Continued. Atomic Coordinates for Optimized [(pdt)Pt(tpbz)Ni(mdt)].

| Center Number | Atomic Number | Atomic Type | X           | Y           | Z           |
|---------------|---------------|-------------|-------------|-------------|-------------|
| 139           | 1             | 0           | -10.055389  | -2.212472   | 0.152471    |
| 140           | 1             | 0           | -10.766534  | -0.999470   | 1.246780    |
Table S7. Atomic Coordinates for Optimized [(pdt)Ni(tpbz)].

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               | X           | Y           | Z           |
| 1             | 28            | -2.350486   | 0.045313   | 0.144352   |
| 2             | 16            | -3.850573   | -1.546188  | -0.102497  |
| 3             | 15            | -0.738110   | 1.613401   | 0.386474   |
| 4             | 15            | 4.854019    | 1.578207   | -0.905455  |
| 5             | 6             | -5.404174   | -0.707782  | -0.325439  |
| 6             | 6             | -0.628609   | 2.305665   | 2.091245   |
| 7             | 6             | -1.832671   | 2.576314   | 2.762263   |
| 8             | 1             | -2.783228   | 2.356920   | 2.272132   |
| 9             | 6             | -1.813400   | 3.116865   | 4.047671   |
| 10            | 1             | -2.756005   | 3.323953   | 4.557673   |
| 11            | 6             | -0.599075   | 3.382122   | 4.682404   |
| 12            | 1             | -0.587137   | 3.798324   | 5.691744   |
| 13            | 6             | 0.600875    | 3.107354   | 4.025465   |
| 14            | 1             | 1.554710    | 3.307953   | 4.517546   |
| 15            | 6             | 0.588631    | 2.571920   | 2.736764   |
| 16            | 1             | 1.534796    | 2.360774   | 2.237550   |
| 17            | 6             | 0.876341    | 0.757073   | 0.102139   |
| 18            | 6             | 2.066269    | 1.419305   | -0.227926  |
| 19            | 1             | 2.062330    | 2.505088   | -0.323560  |
| 20            | 6             | 3.261084    | 0.718965   | -0.445702  |
| 21            | 6             | 5.719196    | 1.676621   | 0.729042   |
| 22            | 6             | 5.104713    | 1.473521   | 1.974228   |
| 23            | 1             | 4.038512    | 1.247918   | 2.025705   |
| 24            | 6             | 5.846684    | 1.547894   | 3.155044   |
| 25            | 1             | 5.352465    | 1.384658   | 4.115283   |
| 26            | 6             | 7.211982    | 1.832756   | 3.110869   |
| 27            | 1             | 7.790673    | 1.890710   | 4.034865   |
| 28            | 6             | 7.834908    | 2.036928   | 1.878486   |
| 29            | 1             | 8.904171    | 2.253431   | 1.833929   |
| 30            | 6             | 7.096478    | 1.950248   | 0.698852   |
| 31            | 1             | 7.596386    | 2.091066   | -0.262110  |
| 32            | 6             | 4.307519    | 3.326535   | -1.181229  |
| 33            | 6             | 4.342448    | 4.336246   | -0.206800  |
| 34            | 1             | 4.663267    | 4.102043   | 0.808822   |
| 35            | 6             | 3.979406    | 5.645817   | -0.527136  |
| 36            | 1             | 4.019257    | 6.420461   | 0.241731   |
| 37            | 6             | 3.568595    | 5.965610   | -1.821597  |
| 38            | 1             | 3.286987    | 6.990688   | -2.070499  |
| 39            | 6             | 3.527299    | 4.970072   | -2.799719  |
| 40            | 1             | 3.210326    | 5.212454   | -3.815848  |
| 41            | 6             | 3.905507    | 3.666027   | -2.484837  |
| 42            | 1             | 3.894261    | 2.898734   | -3.262708  |
| 43            | 16            | -3.912671   | 1.561800   | -0.195916  |
| 44            | 15            | -0.734974   | -1.460883  | 0.602816   |
| 45            | 15            | 4.834299    | -1.633991  | -0.694162  |
| 46            | 6             | -5.426381   | 0.648456   | -0.396353  |
Table S7 Continued. Atomic Coordinates for Optimized [(pdt)Ni(tpbz)].

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 47            | 6             | 0           | -0.640668   | -1.920097   | 2.383087    |
| 48            | 6             | 0           | 0.569491    | -2.159483   | 3.053131    |
| 49            | 1             | 0           | 1.520769    | -2.070948   | 2.527471    |
| 50            | 6             | 0           | 0.567058    | -2.513401   | 4.402738    |
| 51            | 1             | 0           | 1.514524    | -2.696900   | 4.913396    |
| 52            | 6             | 0           | -0.638630   | -2.631675   | 5.095902    |
| 53            | 1             | 0           | -0.636834   | -2.907156   | 6.152468    |
| 54            | 6             | 0           | -1.844767   | -2.391730   | 4.436404    |
| 55            | 1             | 0           | -2.791258   | -2.477749   | 4.973161    |
| 56            | 6             | 0           | -1.850089   | -2.032659   | 3.068600    |
| 57            | 1             | 0           | -2.792745   | -1.836446   | 2.574157    |
| 58            | 6             | 0           | 0.875413    | -0.644294   | 0.210703    |
| 59            | 6             | 0           | 2.059928    | -1.350459   | -0.030377   |
| 60            | 1             | 0           | 2.049858    | -2.439109   | 0.025660    |
| 61            | 6             | 0           | 3.250851    | -0.696760   | -0.370420   |
| 62            | 6             | 0           | 4.497077    | -3.230766   | 0.182225    |
| 63            | 6             | 0           | 4.066801    | -4.411930   | -0.439407   |
| 64            | 1             | 0           | 3.866196    | -4.422373   | -1.511088   |
| 65            | 6             | 0           | 3.889002    | -5.582018   | 0.303245    |
| 66            | 1             | 0           | 3.554451    | -6.492246   | -0.198736   |
| 67            | 6             | 0           | 4.133332    | -5.589836   | 1.676233    |
| 68            | 1             | 0           | 3.994054    | -6.505514   | 2.254252    |
| 69            | 6             | 0           | 4.567335    | -4.420897   | 2.306567    |
| 70            | 1             | 0           | 4.772567    | -4.420569   | 3.379178    |
| 71            | 6             | 0           | 4.758477    | -3.256529   | 1.564415    |
| 72            | 1             | 0           | 5.122549    | -2.353626   | 2.061354    |
| 73            | 6             | 0           | 4.667863    | -2.071654   | -2.484976   |
| 74            | 6             | 0           | 3.451363    | -2.197988   | -3.174369   |
| 75            | 6             | 0           | 5.864438    | -2.270969   | -3.193073   |
| 76            | 6             | 0           | 3.434821    | -2.522948   | -4.531500   |
| 77            | 6             | 0           | 5.847147    | -2.604115   | -4.547488   |
| 78            | 6             | 0           | 4.631196    | -2.728828   | -5.220473   |
| 79            | 1             | 0           | 2.505955    | -2.042625   | -2.653035   |
| 80            | 1             | 0           | 6.819915    | -2.156975   | -2.676473   |
| 81            | 1             | 0           | 2.479619    | -2.615867   | -5.052417   |
| 82            | 1             | 0           | 6.787678    | -2.756875   | -5.080639   |
| 83            | 1             | 0           | 4.615443    | -2.981291   | -6.282635   |
| 84            | 6             | 0           | -0.663603   | -3.041954   | -0.330650   |
| 85            | 6             | 0           | -0.232825   | -4.244888   | 0.245751    |
| 86            | 6             | 0           | -1.033983   | -3.022843   | -1.685425   |
| 87            | 6             | 0           | -0.158023   | -5.405995   | -0.525785   |
| 88            | 6             | 0           | -0.951218   | -4.183673   | -2.452428   |
| 89            | 6             | 0           | -0.513052   | -5.377000   | -1.874382   |
| 90            | 1             | 0           | 0.045196    | -4.280618   | 1.299239    |
| 91            | 1             | 0           | -1.408672   | -2.100011   | -2.129996   |
| 92            | 1             | 0           | 0.177718    | -6.337206   | -0.065802   |
Table S7 Continued. Atomic Coordinates for Optimized [(pdt)Ni(tpbz)].

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 93            | 1             | 0           | -1.246616   | -4.158640   | -3.502932   |
| 94            | 1             | 0           | -0.457387   | -6.287361   | -2.474554   |
| 95            | 6             | 0           | -0.709965   | 3.064978    | -0.737338   |
| 96            | 6             | 0           | -1.186100   | 2.894810    | -2.047110   |
| 97            | 6             | 0           | -0.234589   | 4.322023    | -0.336935   |
| 98            | 6             | 0           | -1.166630   | 3.960752    | -2.944714   |
| 99            | 6             | 0           | -0.223375   | 5.387297    | -1.238064   |
| 100           | 6             | 0           | -0.687087   | 5.208159    | -2.541583   |
| 101           | 1             | 0           | -1.596698   | 1.931705    | -2.351702   |
| 102           | 1             | 0           | 0.122387    | 4.475330    | 0.681849    |
| 103           | 1             | 0           | -1.545355   | 3.819083    | -3.958422   |
| 104           | 1             | 0           | 0.147775    | 6.361728    | -0.916102   |
| 105           | 1             | 0           | -0.683602   | 6.045221    | -3.242630   |
| 106           | 6             | 0           | -6.614363   | 1.478982    | -0.722815   |
| 107           | 6             | 0           | -7.421422   | 1.178581    | -1.835142   |
| 108           | 6             | 0           | -6.940343   | 2.612492    | 0.043200    |
| 109           | 6             | 0           | -8.521758   | 1.970397    | -2.156645   |
| 110           | 6             | 0           | -8.041513   | 3.404245    | -0.279967   |
| 111           | 6             | 0           | -8.838961   | 3.086823    | -1.380343   |
| 112           | 1             | 0           | -7.173315   | 0.315520    | -2.452820   |
| 113           | 1             | 0           | -6.322344   | 2.864614    | 0.905639    |
| 114           | 1             | 0           | -9.132620   | 1.717009    | -3.026110   |
| 115           | 1             | 0           | -8.278588   | 4.275739    | 0.334638    |
| 116           | 1             | 0           | -9.700506   | 3.708105    | -1.634392   |
| 117           | 6             | 0           | -6.591731   | -1.598539   | -0.377544   |
| 118           | 6             | 0           | -7.720459   | -1.345445   | 0.422999    |
| 119           | 6             | 0           | -6.605023   | -2.742950   | -1.195454   |
| 120           | 6             | 0           | -8.825411   | -2.193566   | 0.392451    |
| 121           | 6             | 0           | -7.710892   | -3.591348   | -1.223520   |
| 122           | 6             | 0           | -8.827723   | -3.320748   | -0.431538   |
| 123           | 1             | 0           | -7.721523   | -0.474030   | 1.077649    |
| 124           | 1             | 0           | -5.736646   | -2.958736   | -1.818953   |
| 125           | 1             | 0           | -9.689574   | -1.975658   | 1.024187    |
| 126           | 1             | 0           | -7.699916   | -4.470453   | -1.872020   |
| 127           | 1             | 0           | -9.693340   | -3.986349   | -0.452917   |