Electronic Supplementary Information

Diamidocarbene-derived palladium and nickel–sulfur clusters

Minji Lee,[ab†] Hyunju Noh[ab†] and Youngsuk Kim*[abc]

[a] Department of Chemistry, Pusan National University, Busan, Republic of Korea
[b] Institute for Future Earth, Pusan National University, Busan, Republic of Korea
[c] Chemistry Institute for Functional Materials, Pusan National University, Busan,
Republic of Korea

*E-mail: youngsuk.kim@pusan.ac.kr

Table of contents

Materials and Methods

1. General methods

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere. All air- and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen.

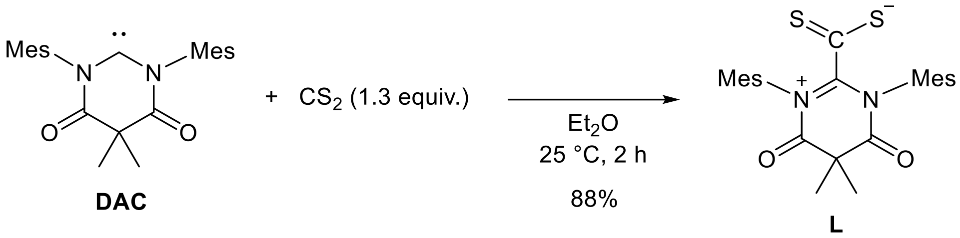
All NMR spectra were recorded using a Bruker Ascend^{TM} 400 MHz spectrometer. Chemical shifts were referenced to the residual solvent peaks.[1] Mass spectrometry (MS) spectra were acquired using a Shimadzu LCMS-2050 single quadrupole mass spectrometer, equipped with a dual ion source combining electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI). High-resolution mass spectrometry (HRMS) spectra were obtained on a SCIEX ZenoTOF 7600 mass spectrometer, fitted with an electrospray ionization (ESI) source. Elemental analyses were conducted at the GIST Advanced Institute of Instrumental Analysis, using a Thermo Fisher Scientific FlashSmart elemental analyzer.

2. Reagents

Diamidocarbene (DAC) was synthesized according to a reference.[2] Carbon disulfide (CS_2), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$), bis(cyclooctadiene)nickel(0) ($Ni(cod)_2$) and all other chemicals were purchased from commercial sources and used as received unless otherwise specified. 3Å molecular sieves were activated at 240 °C under a dynamic vacuum overnight prior to use. Anhydrous solvents were purchased from commercial sources and stored over activated 3Å molecular sieves. Chloroform-d_1 ($CDCl_3$), Acetonitrile-d_3 (CD_3CN) and Benzene-d_6 (C_6D_6) were dried using activated 3Å molecular sieves.

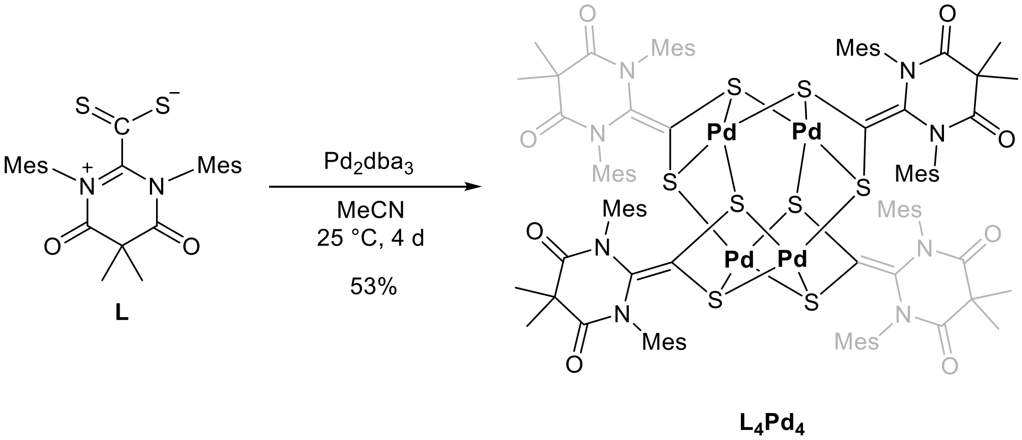
Experimental Details

Synthesis of DAC–CS$_2$ (L)



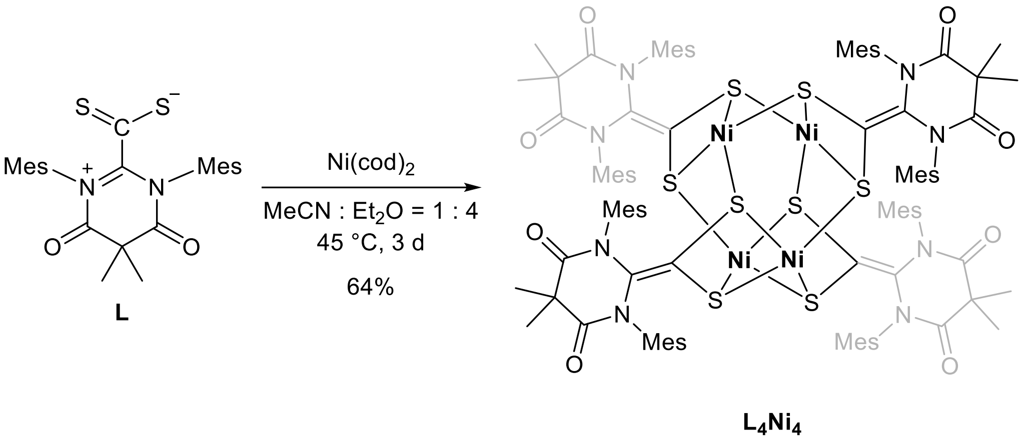
In a N$_2$ atmosphere glovebox, DAC (50.0 mg, 0.13 mmol) was placed in a 4 mL vial and subsequently dry diethyl ether (1.0 mL) was added to the vial. The solution was stirred at 25 °C, and carbon disulfide (CS$_2$, 10.4 μL, 0.17 mmol) was added. The reaction mixture was stirred for 2 hours. Reddish-brown precipitates were formed during the reaction. All volatiles in the reaction mixture were removed *in vacuo*, and the resulting solid was washed with dry diethyl ether (1 × 2 mL) to afford 52.6 mg of the product (88%). Single crystals suitable for X-ray crystallography were obtained from the slow diffusion of pentane into a dichloromethane solution. MS (ESI + APCI): m/z calculated for [$C_{25}H_{29}N_2O_2S_2$ $(M + H)^+$] 453.2, found 453.2. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.84 (s, 4H), 2.34 (s, 12H), 2.23 (s, 6H), 1.92 (s, 8H) ppm. ^{1}H NMR (CD$_3$CN, 400 MHz) δ 6.91(s, 4H), 2.36 (s, 12H), 2.26 (s, 6H), 1.91(s, 6H) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) δ 228.7, 171.7, 140.8, 136.0, 130.0, 129.4, 51.3, 24.0, 21.1, 19.1 ppm. See **Figure S1** for signal assignments.

Synthesis of L$_4$Pd$_4$



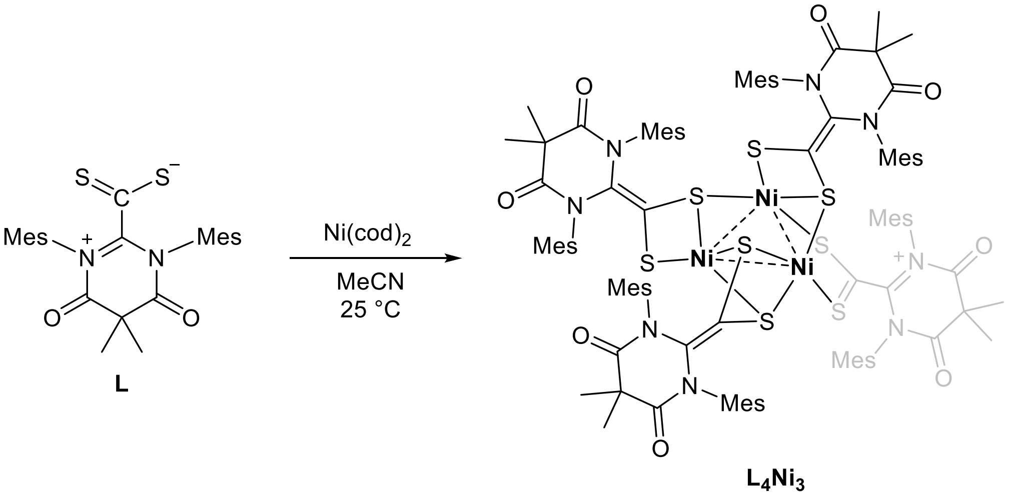
In a N$_2$ atmosphere glovebox, **L** (10.0 mg, 0.022 mmol) and Pd$_2$dba$_3$ (10.3 mg, 0.011 mmol) were placed in a 4 mL vial, followed by the addition of dry acetonitrile (0.5 mL). The reaction mixture was allowed to stand overnight. After 4 days, black crystals appeared, which were then washed with dry acetonitrile and dried *in vacuo* to yield the product as an air-sensitive solid (6.6 mg, 53%). Single crystals suitable for X-ray crystallography were obtained from an acetonitrile/ether solution. HRMS (ESI): m/z calculated for [$C_{100}H_{112}N_8O_8Pd_4S_8$ $(M)^+$] 2235.2568, found 2235.2553. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.11(s, 4H), 6.92(s, 4H), 6.81(s, 4H), 6.70(s, 4H), 2.42(s, 12H), 2.31(s, 12H), 2.30(s, 12H), 2.18(s, 12H), 2.13(s, 12H), 2.01(s, 12H), 1.74(s, 12H), 1.53(s, 12H) ppm. ^{1}H NMR (CD$_3$CN, 400 MHz) δ 7.19(s, 1H), 6.98(s, 1H), 6.90(s, 1H), 6.76(s, 1H), 2.44(s, 3H), 2.33(s, 3H), 2.28(s, 3H), 2.16(s, 3H), 2.12(s, 3H), 2.01(s, 3H), 1.71(s, 3H), 1.42(s, 3H) ppm. ^{1}H NMR (C$_6$D$_6$, 400 MHz) δ 6.88(s, 4H), 6.84(s, 4H), 6.82(s, 4H), 6.63(s, 4H), 2.30(s, 12H), 2.27(s, 12H), 2.26(s, 12H), 2.25(s, 12H), 2.16(s, 12H), 2.09(s, 12H), 1.77(s, 12H), 1.59(s, 12H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.1, 169.0, 139.7, 139.2, 138.8, 137.7, 137.5, 135.7, 133.7, 132.5, 131.7, 130.4, 129.7, 129.5, 129.3, 103.8, 77.2, 47.8, 26.9, 22.1, 21.4, 21.3, 20.3, 20.0, 19.7, 19.4 ppm. See **Figure S2** for signal assignments.

Synthesis of L_4Ni_4



In a N_2 atmosphere glove box, **L** (15.0 mg, 0.033 mmol) and $Ni(cod)_2$ (6.8 mg, 0.025 mmol) were placed in a 4 mL vial. Subsequently, a dry acetonitrile : diethyl ether (1:4) solution (2.5 mL) was added to the vial. The reaction mixture was heated at 45 °C for 1 hour and then filtered through a thin pad of Celite to remove any insoluble material. The resulting filtrate was further heated at 45 °C for 3 days. After 3 days, small brown crystals appeared, which were collected and dried *in vacuo*, yielding the product as an air-sensitive solid (8.1 mg, 64%). Single crystals suitable for X-ray crystallography were obtained from an acetonitrile/diethyl ether solution. Anal. Calcd for $C_{100}H_{112}Ni_4N_8O_8S_8$: C, 58.72; H 5.52; N, 5.48. Found: C, 58.44; H 5.52; N, 5.93. ^{1}H NMR (CD_3CN, 400MHz) δ 7.27 (s, 4H), 7.18 (s, 4H), 7.05 (s, 4H), 6.73 (s, 4H), 2.43 (s, 12H), 2.42 (s, 12H), 2.17 (s, 24H), 2.10 (s, 12H), 1.949 (s, 12H), 1.69 (s, 12H), 1.39 (s, 12H) ppm. $^{13}C\{^{1}H\}$ NMR (CD_3CN, 100 MHz) δ 169.7, 169.5, 140.5, 140.4, 139.3, 138.6, 138.4, 137.1, 134.1, 133.5, 133.3, 131.2, 130.4, 130.3, 130.0, 96.0, 48.4, 27.2, 22.9, 21.7, 21.5, 20.5, 20.4, 20.2, 19.7 ppm. See **Figure S3** for signal assignments.

Synthesis of L_4Ni_3



L_4Ni_3
(a few crystals)

In a N_2 atmosphere glove box, **L** (10.0 mg, 0.022 mmol) and $Ni(cod)_2$ (3.04 mg, 0.011 mmol) were placed in a 4 mL vial, and subsequently dry acetonitrile (0.6 mL) was added to the vial. The reaction mixture was shaken for 1 minute and then filtered to a thin pad of Celite to remove any insoluble material. The resulting filtrate was concentrated *in vacuo* to half its volume. Recrystallization by layering dry ether over the concentrated filtrate resulted in the formation of brown block-shaped crystals of the product along with other byproducts, preventing the isolation of pure product on any preparative scale.

NMR

General information

All NMR spectra were recorded using a Bruker Ascend^{TM} 400 MHz spectrometer. Chemical shifts were referenced to the residual solvent peaks.[1]

NMR spectra

^{1}H, ^{13}C NMR spectra of L

(A)

(B)

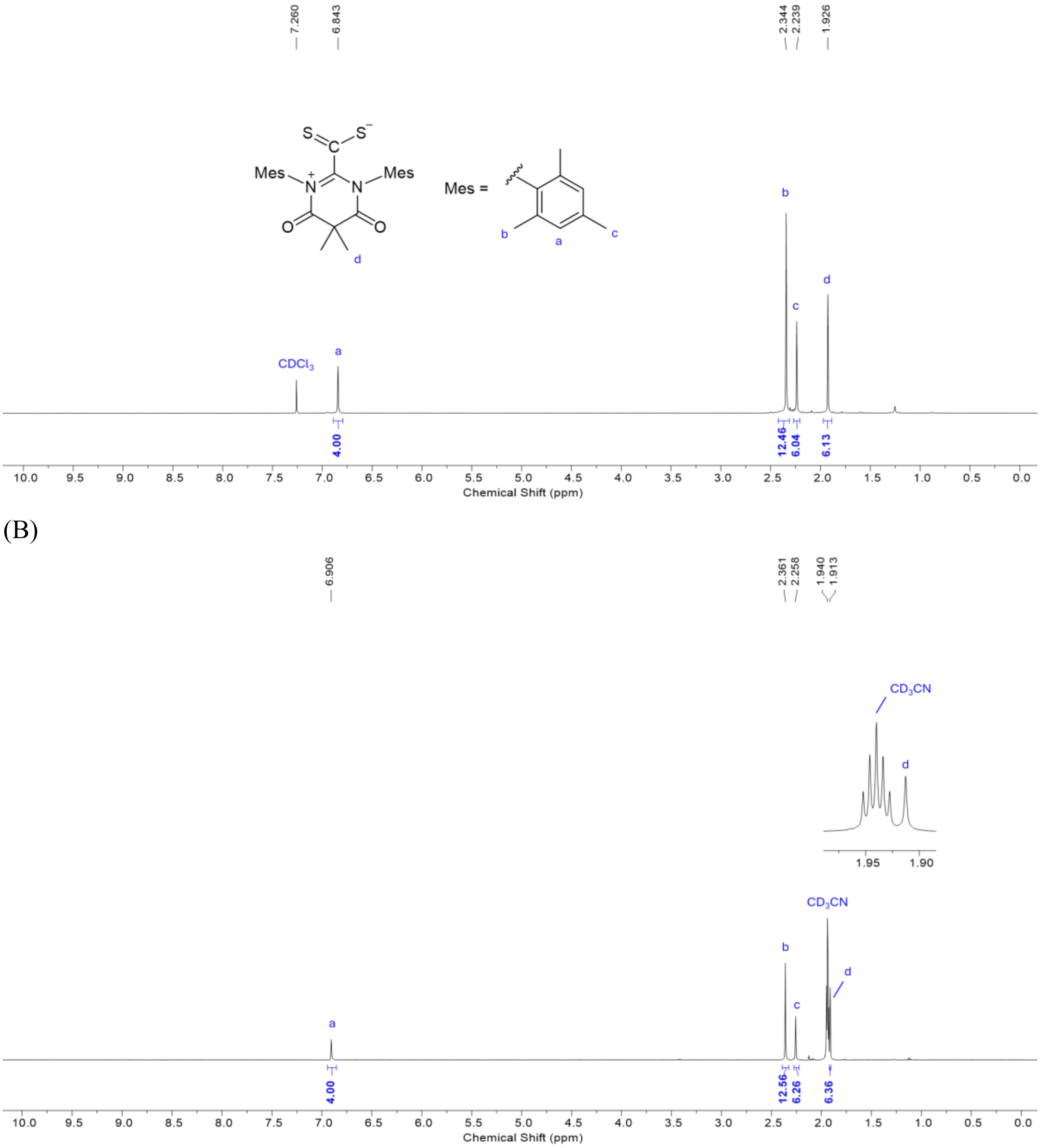


Figure S1. (A) ^{1}H NMR spectrum in $CDCl_3$ and (B) CD_3CN, and (C) proton decoupled ^{13}C NMR spectrum and assignment of the signals for **L** (* not detected).

(C)

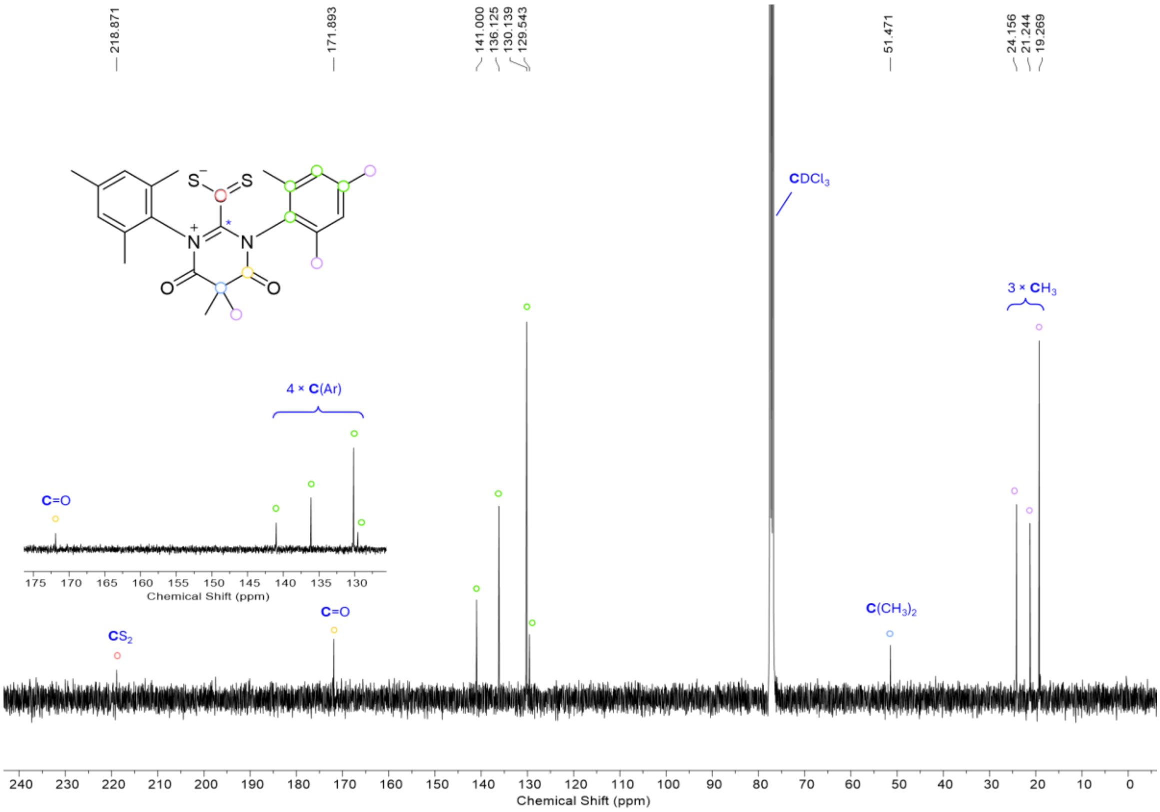


Figure S1 (continued). (A) ^{1}H NMR spectrum in $CDCl_3$ and (B) CD_3CN, and (C) proton decoupled ^{13}C NMR spectrum and assignment of the signals for **L** (* not detected).

^{1}H, ^{13}C NMR spectra of L$_4$Pd$_4$

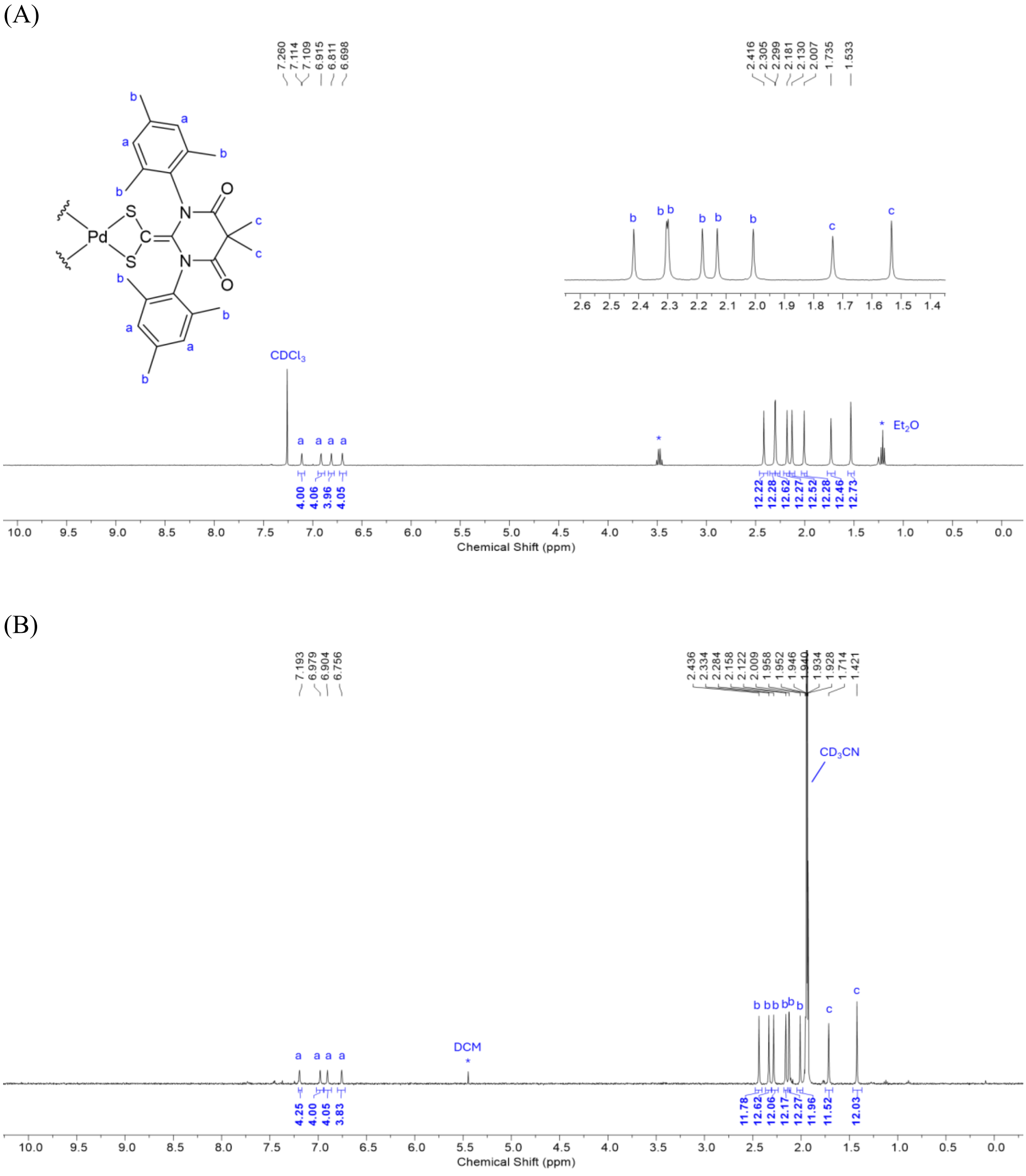


Figure S2. (A) ^{1}H NMR spectrum in CDCl$_3$, (B) CD$_3$CN, (C) C$_6$D$_6$, and (D) proton decoupled ^{13}C NMR spectrum and assignment of the signals for **L$_4$Pd$_4$**.

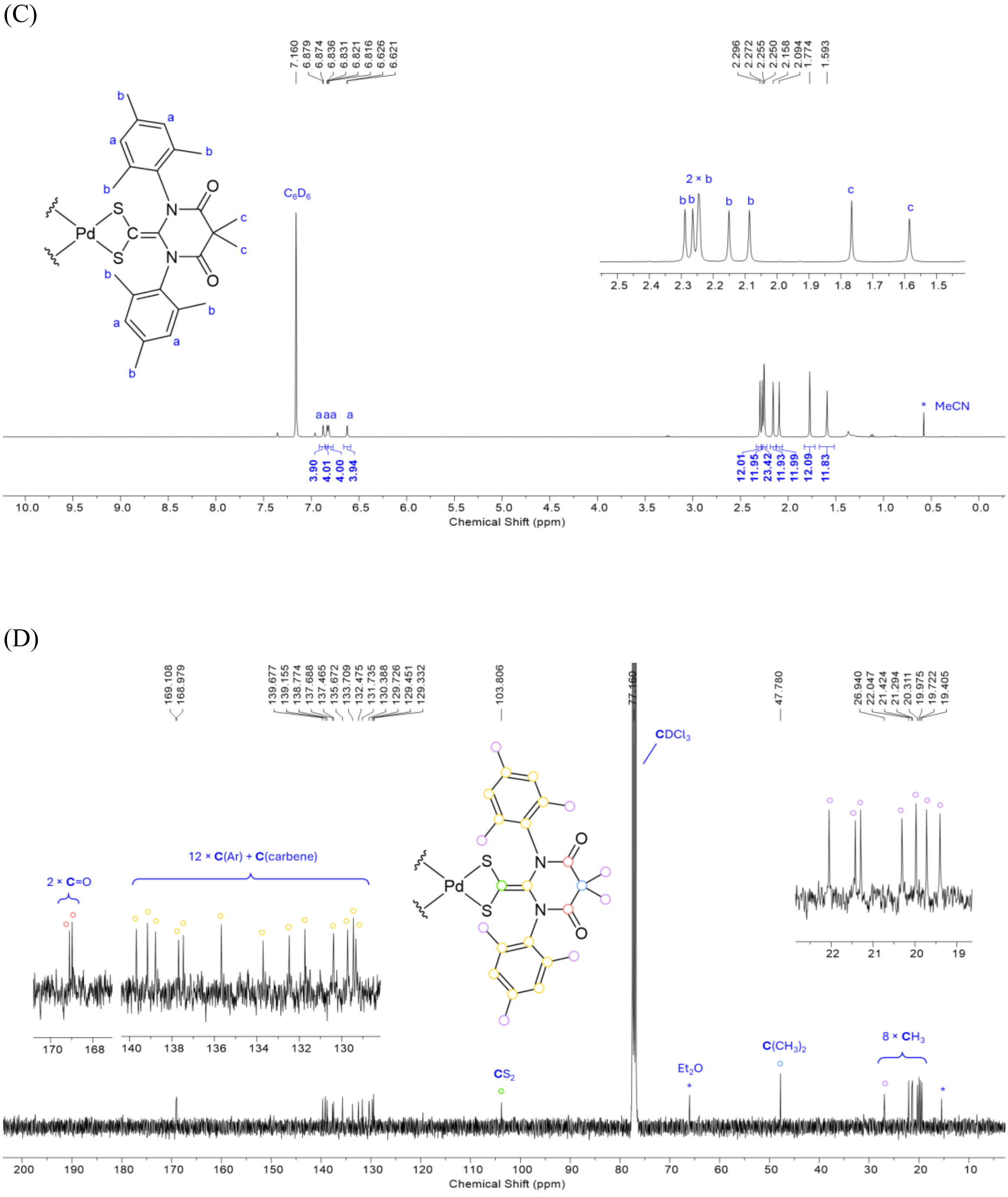


Figure S2 (continued). (A) ^{1}H NMR spectrum in $CDCl_3$, (B) CD_3CN, (C) C_6D_6, and (D) proton decoupled ^{13}C NMR spectrum and assignment of the signals for **L_4Pd_4**.

^{1}H, ^{13}C NMR spectra of L$_4$Ni$_4$

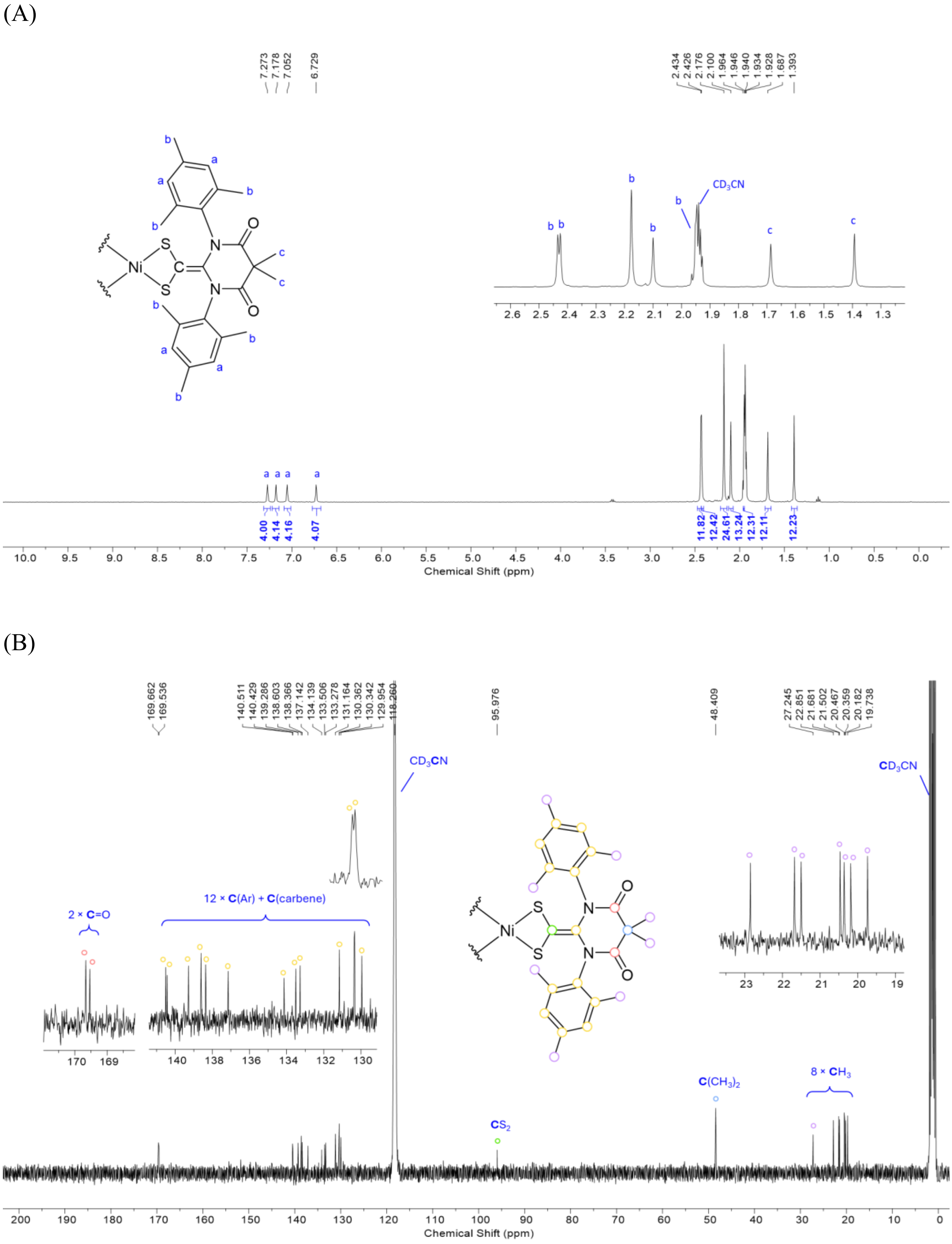


Figure S3. (A) ^{1}H NMR spectrum and (B) proton decoupled ^{13}C NMR spectrum and assignment of the signals for **L$_4$Ni$_4$**.

To confirm that the **L_4Pd_4** and **L_4Ni_4** clusters remain intact and do not dissociate into ligands in solution, we measured the NMR spectra of a mixture containing the cluster and free ligand.

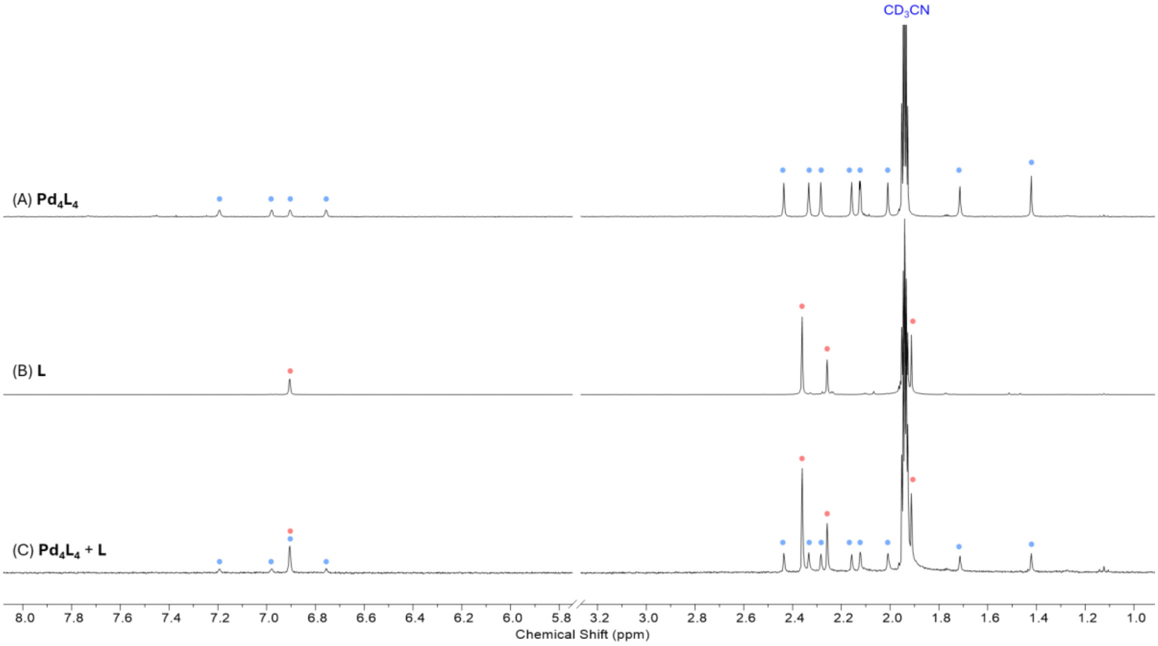


Figure S4. ^{1}H NMR spectrum of (A) **L_4Pd_4** (blue circle), (B) **L** (red circle), and (C) mixture of **L_4Pd_4** and **L**.

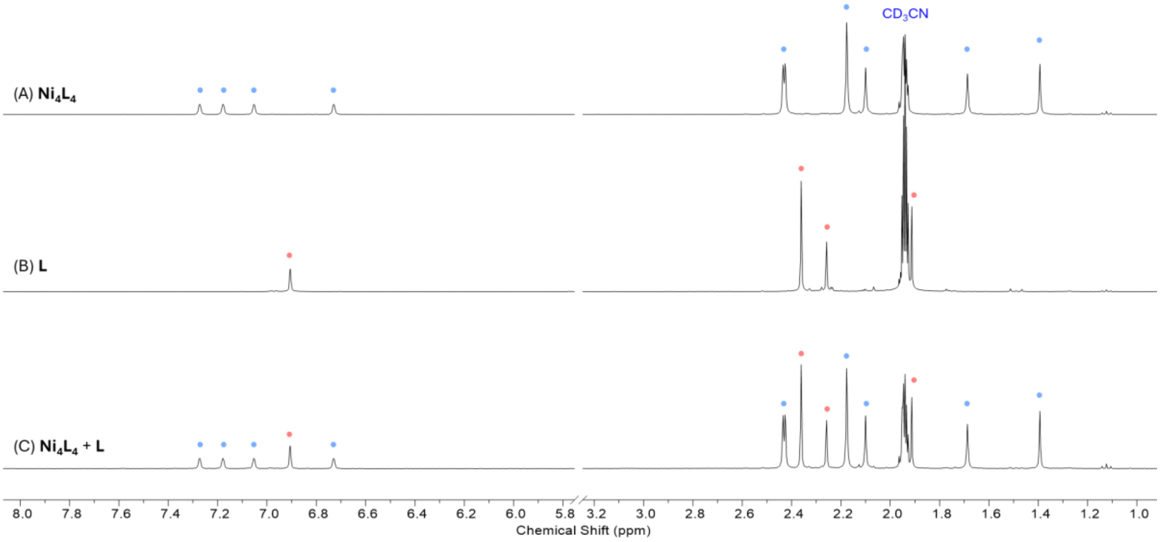


Figure S5. ^{1}H NMR spectrum of (A) **L_4Ni_4**, (B) **L**, and (C) mixture of **L_4Ni_4** and **L**.

X-ray Crystallography

CCDC 2381957–2381960 contains the supplementary crystallographic data for **L**, **L_4Pd_4**, **L_4Ni_4**, and **L_4Ni_3**, respectively. These data can be obtained free of charge *via* https://www.ccdc.cam.ac.uk/

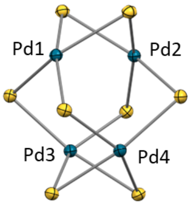
General information

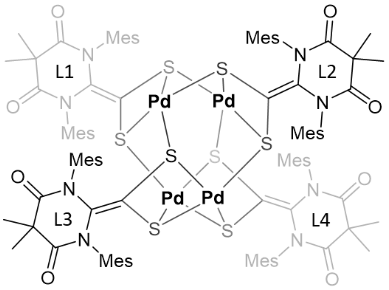
A suitable crystal was coated with immersion oil and the diffraction data was measured with a Mo Kα radiation source on a Bruker D8 Venture diffractometer. Using Olex2,[3] The structure was solved by ShelXT[4] using intrinsic phasing and refined by ShelXL[5] using least squares minimization. All the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added to their geometrically ideal positions.

Crystal data and structure refinements

	L	**L_4Pd_4**	**L_4Ni_4**	**L_4Ni_3**
Empirical formula	$C_{25}H_{28}N_2O_2S_2$	$C_{102}H_{115}N_9O_8Pd_4S_8$	$C_{102}H_{115}N_9Ni_4O_8S_8$	$C_{106.75}H_{125.53}N_{9.68}Ni_3O_{8.85}S_8$
Formula weight	452.61	2277.10	2086.34	2118.48
Temperature/K	100	150	150	150
Crystal system	orthorhombic	triclinic	triclinic	triclinic
Space group	$Pca2_1$	P-1	P-1	P-1
a/Å	31.023(5)	15.1195(5)	15.1288(8)	14.1896(15)
b/Å	8.7121(14)	15.5620(5)	15.5209(8)	16.1897(18)
c/Å	17.796(3)	21.9749(7)	21.5815(12)	25.073(2)
α/°	90	89.1590(10)	89.171(2)	89.342(4)
β/°	90	83.5970(10)	84.225(2)	89.718(4)
γ/°	90	76.3130(10)	76.607(2)	66.280(4)
Volume/$Å^3$	4809.7(13)	4991.9(3)	4904.6(5)	5272.9(10)
Z	8	2	2	2
$\rho_{calc}g/cm^3$	1.250	1.515	1.413	1.334
μ/mm^{-1}	0.245	0.937	0.988	0.749
F(000)	1920.0	2332.0	2188.0	2233.0
Crystal size/mm^3	0.1 × 0.1 × 0.1	0.1 × 0.08 × 0.08	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.676 to 50.054	4.83 to 50.7	4.636 to 50.7	3.632 to 50.376
Index ranges	$-36 \leq h \leq 35$, $-9 \leq k \leq 10$, $-21 \leq l \leq 21$	$-18 \leq h \leq 18$, $-18 \leq k \leq 18$, $-26 \leq l \leq 26$	$-18 \leq h \leq 18$, $-18 \leq k \leq 18$, $-25 \leq l \leq 25$	$-16 \leq h \leq 16$, $-19 \leq k \leq 19$, $-30 \leq l \leq 30$
Reflections collected	27140	288654	299389	217573
Independent reflections	8467 [R_{int} = 0.1415, R_{sigma} = 0.1364]	18271 [R_{int} = 0.0845, R_{sigma} = 0.0289]	17932 [R_{int} = 0.2189, R_{sigma} = 0.0620]	18939 [R_{int} = 0.1328, R_{sigma} = 0.0590]
Data/restraints/parameters	8467/1/575	18271/74/1240	17932/44/1201	18939/95/1278
Goodness-of-fit on F^2	1.020	1.076	1.011	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0753, wR_2 = 0.1641	R_1 = 0.0248, wR_2 = 0.0547	R_1 = 0.0333, wR_2 = 0.0839	R_1 = 0.0887, wR_2 = 0.2396
Final R indexes [all data]	R_1 = 0.1063, wR_2 = 0.1916	R_1 = 0.0322, wR_2 = 0.0603	R_1 = 0.0517, wR_2 = 0.0916	R_1 = 0.1185, wR_2 = 0.2797
Largest diff. peak/hole / e $Å^{-3}$	0.60/-0.35	0.57/-0.47	1.77/-1.20	1.45/-1.65
Flack parameter	0.00(11)	-	-	-

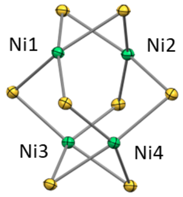
Structural data

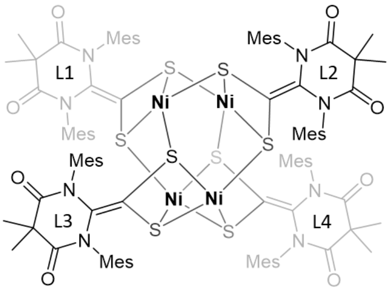




Pd–Pd (Å)				Σ(∠S– Pd –S) (°)[a]		C_{DAC}–C_{CS_2} (Å)		NCCS torsion angle (°)	
Short Pd–Pd		Long Pd–Pd							
Pd(1)–Pd(2)	2.6522(6)	Pd(1)–Pd(3)	3.2977(5)	Pd(1)	354.61(5)	L1	1.361(4)	L1	10.7(4)
Pd(3)–Pd(4)	2.6526(5)	Pd(1)–Pd(4)	3.2845(4)	Pd(2)	354.27(5)	L2	1.359(4)	L2	10.1(4)
		Pd(2)–Pd(3)	3.2899(5)	Pd(3)	354.33(5)	L3	1.361(3)	L3	10.1(4)
		Pd(2)–Pd(4)	3.3064(4)	Pd(4)	354.23(5)	L4	1.361(3)	L4	9.3(4)

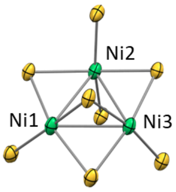
Table S1. Selected bond lengths (Å) and angles (°) for **L_4Pd_4**. *a*. Uncertainties for the sum of angles are given as the root sum of the squares of the individual estimated standard deviations.

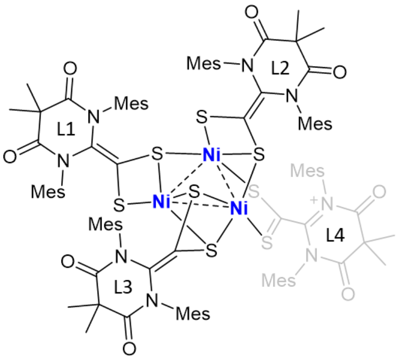




Ni–Ni (Å)				Σ(∠S– Ni –S) (°)[a]		C_{DAC}–C_{CS_2} (Å)		NCCS torsion angle (°)	
Short Ni–Ni		Long Ni–Ni							
Ni(1)–Ni(2)	2.4214(6)	Ni(1)–Ni(3)	3.0907(4)	Ni(1)	355.63(6)	L1	1.357(4)	L1	8.0(4)
Ni(3)–Ni(4)	2.4156(5)	Ni(1)–Ni(4)	3.0925(5)	Ni(2)	355.67(6)	L2	1.357(4)	L2	8.4(4)
		Ni(2)–Ni(3)	3.0836(4)	Ni(3)	355.60(6)	L3	1.358(4)	L3	8.4(4)
		Ni(2)–Ni(4)	3.1027(5)	Ni(4)	355.93(6)	L4	1.359(4)	L4	8.2(4)

Table S2. Selected bond lengths (Å) and angles (°) for **L_4Ni_4**. *a*. Uncertainties for the sum of angles are given as the root sum of the squares of the individual estimated standard deviations.





Ni–Ni (Å)		Σ(∠S– Ni –S) (°)[a]		C_{DAC}–C_{CS_2} (Å)		NCCS torsion angle (°)	
Ni(1)–Ni(2)	2.764(2)	Ni(1)	361.51(19)	L1	1.338(13)	L1	9.4(7)
Ni(2)–Ni(3)	2.712(15)	Ni(2)	368.14(18)	L2	1.343(13)	L2	8.4(7)
Ni(1)–Ni(3)	2.579(2)	Ni(3)	359.12(16)	L3	1.358(13)	L3	7.8(8)
				L4	1.523(12)	L4	76.5(9)

Table S3. Selected bond lengths (Å) and angles (°) for **L$_4$Ni$_3$**. *a*. Uncertainties for the sum of angles are given as the root sum of the squares of the individual estimated standard deviations.

UV-Vis Spectroscopy

General information

The UV-vis spectra were recorded at room temperature with a V-770 Double Beam UV-Visible-NIR Spectrophotometer(Jasco, Inc.) with quartz UV cell.

UV-Vis spectra

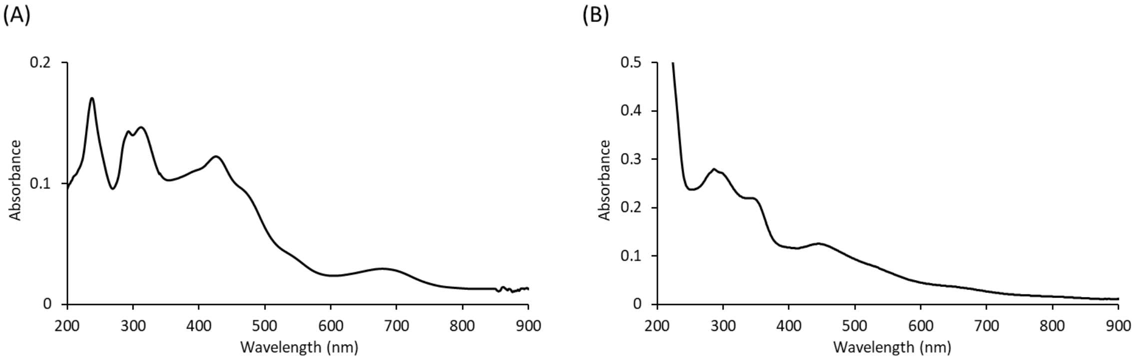


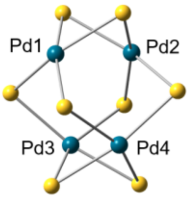
Figure S6. (A) UV-vis absorption of **L$_4$Pd$_4$** (0.025 mM in THF) and (B) **L$_4$Ni$_4$** (0.054 mM in MeCN). Path length = 10 mm.

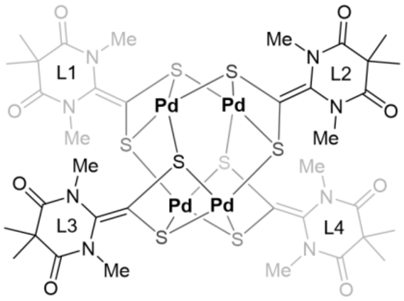
DFT Calculation

General information

Geometry optimizations were performed using Gaussian 16-A03 package[6] with TPSSh functional[7] and Def2-TZVP[8] basis set. In the geometry optimization, the default tight convergence in the SCF cycle was used without any orbital symmetry constraints. Input coordinates were taken from the solid-state structures obtained from X-ray crystallography. To improve the efficiency of the calculations, the DAC mesityl groups were replaced with methyl groups. Wiberg bond indices (WBIs) were calculated from the optimized geometry with the natural atomic orbital (NAO) basis set.[9]

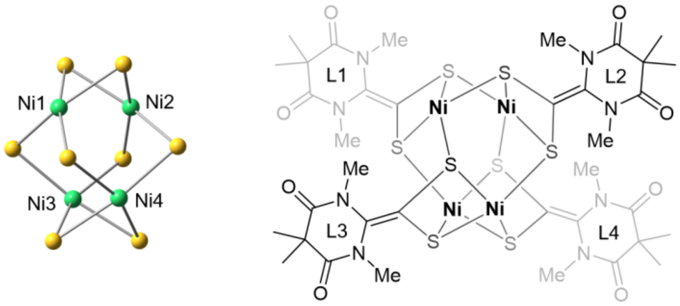
DFT-optimized structural parameters





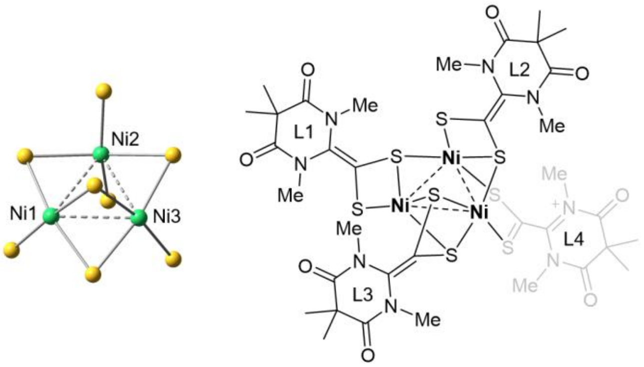
Pd–Pd (Å)				Σ(∠S– Pd –S) (°)[a]		C_{DAC}–C_{CS_2} (Å)		NCCS torsion angle (°)	
Short Pd–Pd		Long Pd–Pd							
Pd(1)–Pd(2)	2.665 (0.18)	Pd(1)–Pd(3)	3.311 (0.08)	Pd(1)	354.0	L1	1.361 (1.58)	L1	2.4
Pd(3)–Pd(4)	2.665 (0.18)	Pd(1)–Pd(4)	3.310 (0.08)	Pd(2)	354.0	L2	1.361 (1.58)	L2	2.4
		Pd(2)–Pd(3)	3.311 (0.08)	Pd(3)	354.0	L3	1.361 (1.58)	L3	2.4
		Pd(2)–Pd(4)	3.310 (0.08)	Pd(4)	354.1	L4	1.361 (1.58)	L4	2.4

Table S4. Selected bond lengths (Å) and angles (°) for $\mathbf{L_4Pd_4}$ from DFT calculation. Wiberg bond indices are shown in parentheses.



Ni–Ni (Å)				Σ(∠S– Ni –S) (°)[a]		C_{DAC}–C_{CS_2} (Å)		NCCS torsion angle (°)	
Short Ni–Ni		Long Ni–Ni							
Ni(1)–Ni(2)	2.402 (0.16)	Ni(1)–Ni(3)	3.077 (0.06)	Ni(1)	355.8	L1	1.359 (1.60)	L1	3.5
Ni(3)–Ni(4)	2.402 (0.16)	Ni(1)–Ni(4)	3.077 (0.06)	Ni(2)	355.8	L2	1.359 (1.60)	L2	3.5
		Ni(2)–Ni(3)	3.077 (0.06)	Ni(3)	355.8	L3	1.359 (1.60)	L3	3.4
		Ni(2)–Ni(4)	3.077 (0.06)	Ni(4)	355.8	L4	1.359 (1.60)	L4	3.6

Table S5. Selected bond lengths (Å) and angles (°) for **L_4Ni_4** from DFT calculation. Wiberg bond indices are shown in parentheses.



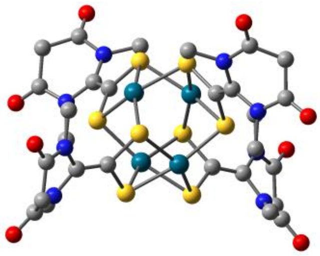
Ni–Ni (Å)		Σ(∠S– Ni –S) (°)		C_{DAC}–C_{CS_2} (Å)		NCCS torsion angle (°)	
Ni(1)–Ni(2)	2.712 (0.11)	Ni(1)	359.9	L1	1.354 (1.60)	L1	2.0
Ni(2)–Ni(3)	2.658 (0.11)	Ni(2)	367.2	L2	1.356 (1.59)	L2	0.6
Ni(1)–Ni(3)	2.557 (0.13)	Ni(3)	359.2	L3	1.346 (1.64)	L3	0.1
				L4	1.480 (1.00)	L4	82.4

Table S6. Selected bond lengths (Å) and angles (°) for **L_4Ni_3** from DFT calculation. Wiberg bond indices are shown in parentheses.

Coordinates of optimized structures

The following optimized geometries were displayed in Cartesian coordinates (atomic unit). E° represents the electronic energy of the optimized structure in Hartree unit.

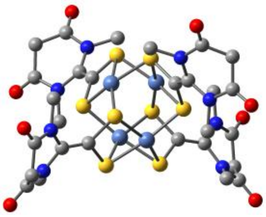
L_4Pd_4 [E° = –5824.6602745]



Charge = 0; Multiplicity = 1;

Atomic coordinates (Cartesian; in atomic unit)			
Pd	-0.918841	7.803218	17.857996
Pd	1.454426	8.409771	16.80807
Pd	1.622362	7.264647	19.90995
Pd	0.896892	9.824036	19.748974
S	-0.569573	6.346087	19.684553
S	2.681073	6.666741	17.883887
S	-1.305313	9.916982	18.897872
S	-0.639616	9.410946	16.163846
S	0.304945	6.418031	16.313324
S	3.079383	9.14242	20.3018
S	2.247485	10.37195	17.858437
S	0.309721	8.330253	21.545414
O	4.264304	1.757294	17.557498
O	-3.262737	14.663567	18.278192
O	-2.03296	13.836232	14.046266
N	2.786059	3.480781	17.710362
O	0.440568	1.432377	15.238544
N	0.764376	3.314266	16.477791
N	-3.234034	6.288981	21.442595
N	-1.872894	12.900058	17.907069
N	-1.226809	12.455673	15.666682
N	6.0178	9.531518	19.26151
N	5.373422	10.635138	17.261307
O	6.886457	12.027578	16.285931
O	-3.458933	8.097808	24.976266
O	-4.835547	4.859119	22.197581
C	1.692025	4.14991	17.129185
C	3.346296	2.388608	17.072577
C	-2.226543	7.213426	21.778574
C	-1.083501	10.678513	17.312113
C	-1.377801	11.965083	16.978087
O	8.11254	9.933878	20.056543
C	-2.150497	13.348952	15.152864
C	4.966294	9.974777	18.436267
C	1.547283	5.502824	17.174279
C	-1.06755	7.32895	21.07366
C	1.207143	2.208224	15.773542
C	-2.837211	13.813755	17.521101
C	3.657484	9.792275	18.763627
C	6.476148	11.470104	17.284586
C	-3.931396	5.6334	22.441363
C	7.160986	10.299799	19.395904
C	-3.159378	7.444811	23.996641
C	6.014714	8.208948	19.900795
H	5.713214	8.267441	20.946947
H	5.337675	7.555394	19.354248
H	7.033855	7.826986	19.85245
C	4.73956	10.389671	15.960405
H	4.239749	9.42304	15.986037
H	4.021925	11.171514	15.709657
H	5.53118	10.388975	15.21198
C	-0.046357	12.158313	14.844441
H	0.774374	11.869886	15.498202
H	-0.246229	11.364311	14.124456
H	0.202892	13.068328	14.299785
C	-1.3254	13.027964	19.262891
H	-1.95169	12.521467	19.998013
H	-0.320998	12.608758	19.280834
H	-1.298387	14.090915	19.499979
C	-3.667036	6.065381	20.058056
H	-3.394024	6.930762	19.456863
H	-3.217706	5.165208	19.637424
H	-4.749102	5.940315	20.075582
C	-0.68756	3.490325	16.614601
H	-0.889984	4.049853	17.525745
H	-1.113442	4.009635	15.7557
H	-1.127204	2.495283	16.673638
C	-2.221756	9.44174	22.960516
H	-1.294367	9.657109	23.491862
H	-2.164349	9.821865	21.942465
H	-3.047091	9.910209	23.495515
N	-2.499065	7.99996	22.914467
C	-3.461413	5.971258	23.838671
H	-4.21681	5.673594	24.560309
H	-2.542982	5.406085	24.041395
C	3.300671	3.822613	19.041825
H	4.194046	4.444763	18.979137
H	2.524639	4.34459	19.598748
H	3.560299	2.887349	19.536514
C	2.712792	2.068943	15.736873
H	2.979228	1.059076	15.438263
H	3.107114	2.769419	14.989958
C	-3.298965	13.648337	16.090393
H	-3.810966	14.549446	15.765052
H	-4.006567	12.810676	16.049575
C	7.104339	11.615956	18.652676
H	8.10658	12.022887	18.553174
H	6.498766	12.318688	19.238758

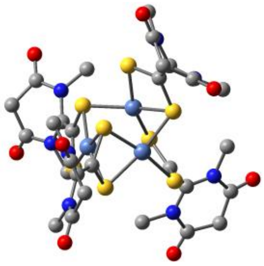
L_4Ni_4 [E° = –11346.6447823]



Charge = 0; Multiplicity = 1;

Atomic coordinates (Cartesian; in atomic unit)			
Ni	-0.77715	7.85626	17.876276
Ni	1.367929	8.38083	16.93121
Ni	1.547391	7.375348	19.834086
Ni	0.913889	9.687152	19.680201
S	-0.480723	6.456541	19.56715
S	2.580499	6.800659	17.960888
S	-1.164695	9.800675	18.923205
S	-0.554766	9.325128	16.229744
S	0.275911	6.528178	16.390151
S	2.961004	9.07494	20.273864
S	2.115798	10.242334	17.87068
S	0.37037	8.371398	21.427682
O	4.26234	1.885769	17.717772
O	-3.139608	14.588597	18.422654
O	-2.038378	13.793876	14.140321
N	2.758041	3.591632	17.81172
O	0.504766	1.498979	15.28581
N	0.772741	3.390056	16.525069
N	-3.185888	6.335968	21.306325
N	-1.771401	12.821486	17.989842
N	-1.191139	12.397939	15.726779
N	5.932905	9.512235	19.233983
N	5.250998	10.557411	17.214018
O	6.733668	11.942629	16.182043
O	-3.430313	8.043923	24.892416
O	-4.805623	4.894284	21.999103
C	1.66985	4.241839	17.198038
C	3.348058	2.498875	17.202971
C	-2.17826	7.247162	21.677646
C	-0.992756	10.611344	17.355406
C	-1.3042	11.895173	17.037399
O	8.028894	9.962135	20.000694
C	-2.12248	13.302519	15.24835
C	4.866488	9.918218	18.408655
C	1.501394	5.589358	17.244762
C	-1.022119	7.385665	20.977248
C	1.246714	2.28303	15.843493
C	-2.738343	13.747512	17.642668
C	3.565699	9.714431	18.744483
C	6.345258	11.403264	17.199413
C	-3.901897	5.658024	22.276218
C	7.068946	10.295642	19.334726
C	-3.132636	7.419442	23.893588
C	5.939762	8.218219	19.928108
H	5.616804	8.314647	20.965127
H	5.283989	7.531159	19.39648
H	6.966171	7.85392	19.914689
C	4.593513	10.277473	15.932619
H	4.139338	9.289148	15.976678
H	3.834103	11.024223	15.697983
H	5.364298	10.309223	15.163718
C	-0.049616	12.080019	14.859455
H	0.798523	11.80284	15.482791
H	-0.282519	11.271413	14.165958
H	0.175564	12.97797	14.28551
C	-1.190049	12.919619	19.333342
H	-1.779132	12.369644	20.068129
H	-0.173589	12.530758	19.30802
H	-1.188419	13.974332	19.605201
C	-3.592743	6.150009	19.908985
H	-3.343173	7.047552	19.345783
H	-3.106279	5.283438	19.459795
H	-4.669513	5.986011	19.908155
C	-0.683088	3.567653	16.597597
H	-0.925898	4.109469	17.509855
H	-1.067774	4.105863	15.730789
H	-1.125734	2.572593	16.615223
C	-2.1453	9.431327	22.934478
H	-1.20399	9.604777	23.456841
H	-2.096801	9.850508	21.931191
H	-2.950545	9.894426	23.50328
N	-2.456123	7.999622	22.835152
C	-3.452683	5.955612	23.689006
H	-4.224632	5.649635	24.389447
H	-2.546206	5.372176	23.893995
C	3.23528	3.96241	19.148692
H	4.094607	4.632019	19.098221
H	2.423901	4.442243	19.693142
H	3.537723	3.042492	19.647314
C	2.753402	2.152926	15.856465
H	3.034438	1.13987	15.582825
H	3.165761	2.842101	15.108718
C	-3.238249	13.607616	16.222514
H	-3.74511	14.520414	15.922458
H	-3.960415	12.782065	16.189771
C	6.994735	11.587739	18.552326
H	7.993772	11.994999	18.425048
H	6.397227	12.305964	19.127883

L$_4$Ni$_3$ [E° = –9838.1542605]



Charge = 0; Multiplicity = 1;

Atomic coordinates (Cartesian; in atomic unit)			
Ni	9.04814	5.817437	20.351239
Ni	9.253664	6.858112	17.913848
Ni	7.219824	5.22779	18.663393
S	7.38941	6.371802	16.789822
S	7.080226	6.808628	20.296785
S	10.832588	4.501278	20.289121
S	7.376199	3.617885	17.210046
S	10.363194	7.517019	19.71366
S	10.536545	5.185605	17.312774
S	8.544429	8.904477	18.137403
S	7.560166	4.168417	20.630118
O	15.652243	3.567369	17.377982
O	7.313713	12.719577	21.468806
O	6.861866	6.555223	11.669806
O	6.705958	2.139243	12.241006
N	10.149139	9.946959	21.784087
N	7.563126	5.749875	13.683908
O	3.65684	7.568044	24.251282
N	11.95573	2.154873	18.169375
O	10.20284	10.434648	24.009669
N	13.520138	3.925021	18.103552
N	5.136813	4.157575	22.822376
O	4.453712	3.194726	24.772257
O	12.587362	0.017397	17.661251
N	8.606428	11.155347	20.433196
C	7.496229	4.821957	15.937091
N	4.716468	6.489953	22.544043
N	7.48795	3.388557	13.982014
C	9.430938	9.021866	19.644787
C	6.822092	5.688009	12.524053
C	14.600374	3.089153	17.712561
C	11.192653	4.415855	18.642332
C	9.591185	10.41253	22.956722
C	9.401486	9.997971	20.585138
C	7.520624	4.664524	14.592079
C	5.485473	5.362964	22.167521
C	12.268444	3.459287	18.298269
C	4.802833	4.186813	24.158467
C	6.469642	5.432357	21.251917
C	7.967812	11.694841	21.529169
C	6.738331	3.198623	12.841197
C	12.920001	1.157218	17.851125
C	4.355158	6.649126	23.864352
C	11.550335	9.523413	21.814563
H	11.649234	8.459575	22.038642
H	12.006623	9.736811	20.849071
H	12.039318	10.092056	22.604736
C	8.164711	10.894332	22.800367
H	7.886968	11.498058	23.659511
H	7.506189	10.017612	22.760209
C	8.51638	11.878841	19.159559
H	9.401946	11.660648	18.566009
H	7.622776	11.598163	18.600736
H	8.463923	12.941541	19.393957
C	5.975538	4.435861	12.414201
H	5.629109	4.318029	11.391654
H	5.105262	4.547185	13.073092
C	8.296277	2.273828	14.475883
H	9.205965	2.670305	14.925592
H	7.755864	1.677019	15.212717
H	8.532439	1.646042	13.617375
C	8.481243	6.881049	13.850621
H	7.99716	7.726427	14.341306
H	9.335904	6.557627	14.442438
H	8.799164	7.190237	12.855276
C	4.903496	5.56784	24.775163
H	4.368884	5.583966	25.720541
H	5.962124	5.783537	24.967395
C	4.191857	7.435291	21.554786
H	4.875407	8.268982	21.384835
H	4.018957	6.909705	20.616367
H	3.255941	7.827775	21.949915
C	5.012883	2.89048	22.09848
H	4.736403	3.09636	21.06521
H	5.94163	2.317378	22.121554
H	4.234111	2.311216	22.592895
C	13.815533	5.373395	18.193176
H	13.634258	5.845795	17.228903
H	13.180161	5.818028	18.953557
H	14.864903	5.46715	18.456892
C	14.351421	1.61218	17.813108
H	14.872533	1.097623	17.005755
H	14.820775	1.272166	18.746114
C	10.555146	1.696641	18.340345
H	10.352135	1.553597	19.400795
H	9.870915	2.434243	17.9222
H	10.471911	0.750562	17.814502

Cyclic Voltammetry

General information

Cyclic voltammograms were recorded at room temperature with a EmStat3-4WE potentiostat (PalmSens). The cell consisted of a glassy carbon working electrode, a Pt wire counter electrode, and an Ag wire pseudo-reference electrode. All potentials are referenced vs. the ferrocene/ferrocenium couple measured as an internal standard.

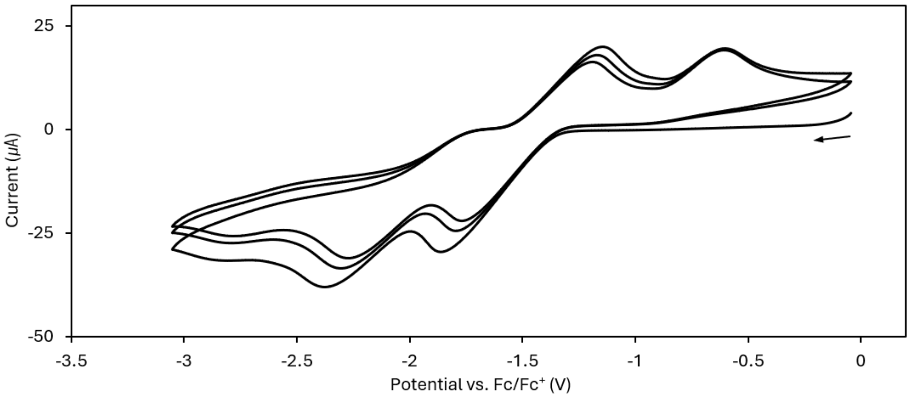


Figure S7. Cyclic voltammogram **L** (1.0 mM) in dry THF. Electrolyte: Bu_4NPF_6 (0.1 M), scan rate = 0.2 V/s. The irreversible reduction of **L** under cyclic voltammetry conditions indicates that the **L**$^{2-}$ form is not stable in its free state without coordination to metal centers such as Pd or Ni.

References

(1) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29* (9), 2176-2179.
(2) Hudnall, T. W.; Moerdyk, J. P.; Bielawski, C. W. *Chem. Commun.* **2010**, *46* (24), 4288-4290.
(3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42* (2), 339-341.
(4) Sheldrick, G. M. *Acta. Cryst.* **2015**, *A71*, 3-8.
(5) Sheldrick, G. M. *Acta. Cryst.* **2015**, *C71*, 3-8.
(6) *Gaussian 16, Revision A.03*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Jr., J. A. M.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J., Gaussian, Inc., Wallingford CT, 2016.
(7) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2007**, *120* (1-3), 215-241.
(8) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297-3305.
(9) (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **2002**, *102* (24), 7211-7218. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78* (6), 4066-4073.