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Supporting Information

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Diels-Alder Reactivity of Binuclear Complexes with Calixarene-like Structures **

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Contents

1. Compounds and their Labels

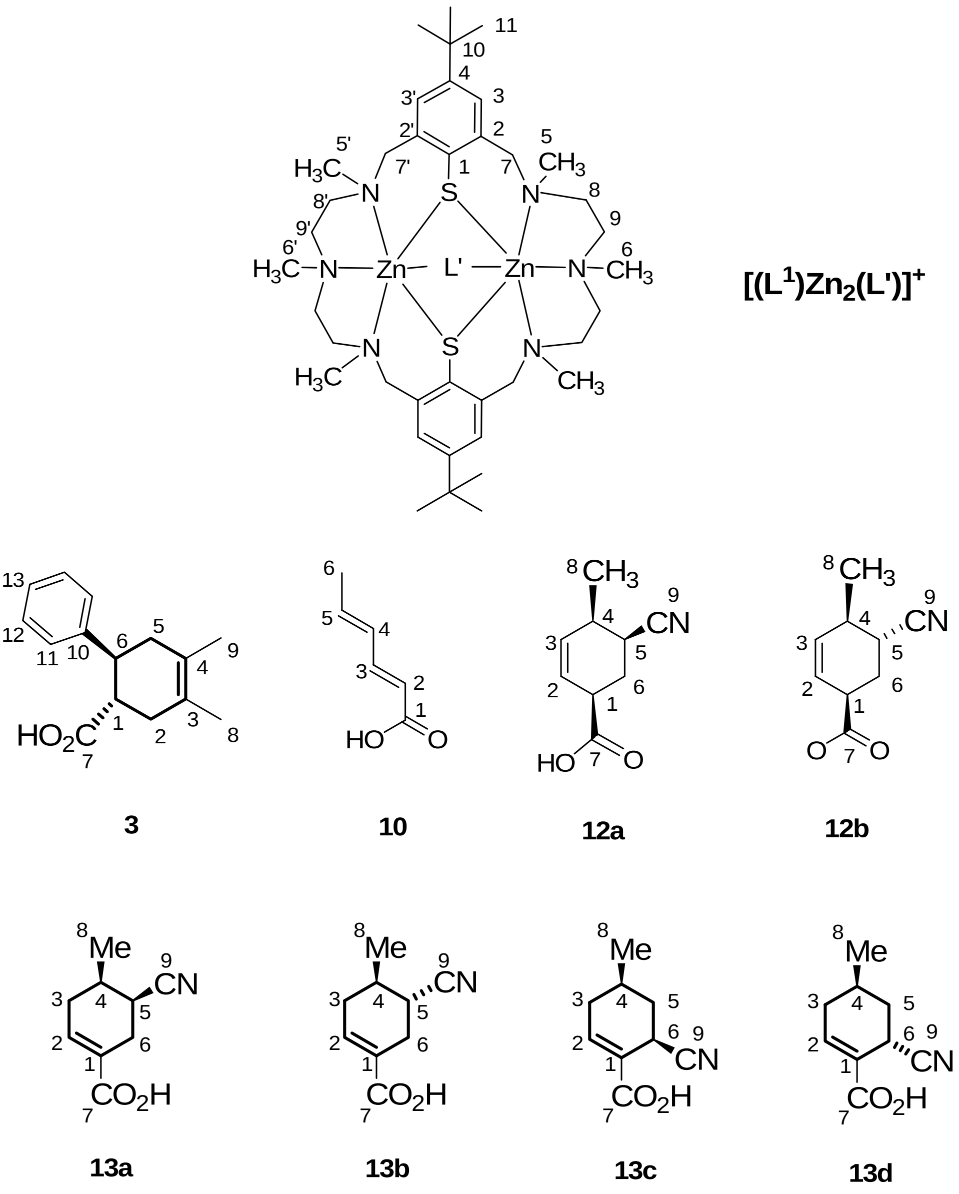
Label	Compound[a]
1	Cinnamic acid
2	2,3-Dimethylbutadiene
3	3,4-Dimethyl-6-phenylcyclohex-3-enecarboxylic acid
4	$[(L^1)Ni_2(Cl)]^+$
5	$[(L^1)Zn_2(OAc)]^+$
6	$[(L^1)Ni_2(O_2CCH{=}CHPh)]^+$
7	$[(L^1)Zn_2(O_2CCH{=}CHPh)]^+$
8	$[(L^1)Ni_2$(3,4-dimethyl-6-phenylcyclohex-3-enecarboxylate)]$^+$
9	$[(L^1)Zn_2$(3,4-dimethyl-6-phenylcyclohex-3-enecarboxylate)]$^+$
10	Sorbinic acid ((2*E*,4*E*)-hexa-2,4-dienoic acid)
11	Acrylonitrile
12a	(1*R*,4*R*,5*S*)-5-cyano-4-methylcyclohex-2-enecarboxylic acid
12b	(1*R*,4*R*,5*R*)-5-cyano-4-methylcyclohex-2-enecarboxylic acid
13a	(4*R*,5*S*)-5-cyano-4-methylcyclohex-1-enecarboxylic acid
13b	(4*R*,5*R*)-5-cyano-4-methylcyclohex-1-enecarboxylic acid
13c	(4*R*,6*R*)-6-cyano-4-methylcyclohex-1-enecarboxylic acid
13d	(4*R*,6*S*)-6-cyano-4-methylcyclohex-1-enecarboxylic acid
14	(2*E*,4*E*)-2-cyanoethyl-hexa-2,4-dienoate
15	$[(L^1)Zn_2$((4*R*,5*S*)-5-cyano-4-methylcyclohex-1-enecarboxylate)]$^+$
16	$[(L^1)Zn_2$((2*E*,4*E*)-hexa-2,4-dienoate)]$^+$
17	$[(L^1)Ni_2$((2*E*,4*E*)-hexa-2,4-dienoate)]$^+$
18a	$[(L^1)Zn_2$((1*R*,4*R*,5*S*)-5-cyano-4-methylcyclohex-2-enecarboxylate)]$^+$
18b	$[(L^1)Zn_2$((1*R*,4*R*,5*R*)-5-cyano-4-methylcyclohex-2-enecarboxylate)]$^+$
19a	$[(L^1)Ni_2$((1*R*,4*R*,5*S*)-5-cyano-4-methylcyclohex-2-enecarboxylate)]$^+$
19b	$[(L^1)Ni_2$((1*R*,4*R*,5*R*)-5-cyano-4-methylcyclohex-2-enecarboxylate)]$^+$
20	1,3-Bis(diacetoxymethyl)-2-bromo-benzene
21	2-Bromobenzene-1,3-dialdehyde
22	1,2-Bis(2,6-diformylphenylthio)ethane
23	Macrobicyclic thioether
24	Permethylated Macrobicyclic thioether
H_2L^2	Hexaazadithiophenolate Macrocycle (H_2L^2).
25	$[(L^2)Zn_2(OAc)]^+$
26	$[(L^2)Zn_2$((2*E*,4*E*)-hexa-2,4-dienoate)]$^+$
27a	$[(L^2)Zn_2$((1R,4R,5S)-5-cyano-4-methylcyclohex-2-enecarboxylate)]$^+$
27b	$[(L^2)Zn_2$((1R,4R,5R)-5-cyano-4-methylcyclohex-2-enecarboxylate)]$^+$

[a] The complexes were isolated as ClO_4^- or BPh_4^- salts.

2. Preparation of Compounds

Materials and methods: Compounds $[(L^1)Ni_2(Cl)]ClO_4$ (**4**$\cdot ClO_4$) and $[(L^1)Zn_2(OAc)]ClO_4$ (**5**$\cdot ClO_4$) were prepared according to literature procedures.[1] All other chemicals were purchased. All syntheses were carried out under a protective atmosphere of argon. Melting points were determined in open glass capillaries and are uncorrected. NMR spectra were recorded on a Bruker AVANCE DPX-200, a Varian Unity 300, or Bruker 400 and 500 spectrometers at 300 K. Chemical shifts refer to solvent signals. Mass spectra were recorded on a MAT 95xP. Infrared spectra were recorded on a Bruker VECTOR 22 FT-IR-Spectrometer and electronic absorption spectra on a Jasco V-570 UV / VIS / NIR spectrometer. Elemental analyses were carried out with a VARIO EL – elemental analyzer. *CAUTION! Perchlorate salts are potentially explosive and should therefore be prepared only in small quantities and handled with appropriate care.*

3,4-dimethyl-6-phenylcyclohex-3-enecarboxylic acid (3). This compound was prepared from cinnamic acid **1** and 2,3-dimethylbutadiene **2** according to literature procedures.[2] The NMR data of **3** are not included in this article. Therefore, they are given here. M.p. 165°C, (Lit: 165-166°C). ^1H NMR (400 MHz, $CDCl_3$, 25°C, TMS, for atom labels see Scheme S1): δ = 1.56 (s, 3 H, C^8H_3), 1.59 (s, 3 H, C^9H_3), 2.30-2.11 (m, 4 H, C^2H_2 + C^5H_2), 2.78 (m, 1 H, C^6H), 3.02 (m, 1 H, C^1H), 7.20-7.10 (m, 5 H, $C^{11-13}H$) ppm. $^{13}C\{^1H\}$NMR (50 MHz, $CDCl_3$, 25°C, TMS): δ = 18.9 (C^8), 19.0 (C^9), 35.7 (C^1), 40.3 (C^6), 43.3 (C^2), 46.7 (C^5), 123.9, 125.7, 126.9, 127.7, 128.8, 144.3 ($C^{3,4,10-13}$), 180.8 (C^7) ppm.



$[(L^1)Zn_2(L')]^+$

3 **10** **12a** **12b**

13a **13b** **13c** **13d**

Scheme S1. Atom labels for compounds $[(L^1)Zn_2(L')]^+$, **3**, **10**, **12a,b**, and **13a-d** used for the assignment of ^{1}H and ^{13}C NMR resonances.

$[(L^1)Ni_2(O_2CCH{=}CHPh)]ClO_4$ (6·ClO_4). To a solution of **4**·ClO_4 (921 mg, 1.00 mmol) in methanol (100 mL) was added a solution of triethylammonium cinnamate (prepared in situ from cinnamic acid **1** (222 mg, 1.50 mmol) and triethylamine (151.8 mg, 1.50 mmol)) in methanol (5 mL). After stirring for 2 h at ambient temperature, the product was precipitated by the addition of solid $LiClO_4{\cdot}3H_2O$ (1.60 g, 10.0 mmol). The green microcrystalline solid was isolated by filtration, washed with 5 mL of cold methanol, and recrystallized once from a mixed ethanol/acetonitrile solvent system. Yield: 744 mg (72 %). M.p. 304°C (decomp.). IR (KBr, cm^{-1}): nu(tilde) = 2961(s), 2866(s), 1642(m) ν(C=C), 1578(s) $\nu_{as}(RCO_2^-)$, 1462(s), 1404(s) $\nu_s(RCO_2^-)$, 1362(m), 1309(w), 1260(w), 1233(w), 1201(w), 1170(w), 1094(vs) $\nu(ClO_4^-)$, 1076(s), 1037(m), 982(w), 931(w), 913(w), 881(w), 826(m), 816(m), 771(m), 702(w), 632(m). UV/Vis (MeCN): $\lambda_{max}(\varepsilon)$ = 358 (2491), 658 (33), 1123 nm (69 $M^{-1}cm^{-1}$). Elemental analysis calcd. for $C_{47}H_{71}ClN_6Ni_2O_6S_2{\cdot}H_2O$ (1033.07 + 18.02): C 53.71, H 7.00, N 8.00, S 6.10, found C 53.80, H 7.01, N 8.29, S 6.51. The tetraphenylborate salt, $[(L^1)Ni_2(O_2CCH{=}CHPh)]BPh_4$ (**6**·BPh_4), was prepared by adding $NaBPh_4$ (342 mg, 1.00 mmol) to a solution of **6**·ClO_4 (103 mg, 0.100 mmol) in methanol (40 mL). The pale-green microcrystalline solid was isolated by filtration, washed with ethanol and dried in air. Yield: 113 mg (90 %). M.p. > 300°C (decomp). IR (KBr, cm^{-1}): nu(tilde) = 3158(vw), 3120(vw), 3053(m), 3031(m), 2961(s), 2863(s), 2806(w), 1641(m) ν(C=C), 1575(s) $\nu_{as}(RCO_2^-)$, 1459(s), 1422(m), 1402(s) $\nu_s(RCO_2^-)$, 1362(m), 1307(w), 1263(w), 1233(w), 1201(w), 1170(vw), 1151(m), 1076(m), 1058(s), 1040(s), 1000(w), 982(w), 929(w), 912(w), 882(w), 822(s), 768(w), 732(s), 703(s), 628(w), 611(m).

$[(L^1)Zn_2(O_2CCH{=}CHPh)]ClO_4$ (7·ClO_4). To a solution of **5**·ClO_4 (958 mg, 1.00 mmol) in methanol (100 mL) was added a solution of triethylammonium cinnamate (prepared in situ from cinnamic acid (1.48 g, 10.0 mmol) and triethylamine (1.02 g, 10.0 mmol)) in methanol (15 mL). After stirring for 12 h at ambient temperature, the solvent was removed under reduced pressure to a final volume of ca. 10 mL. The colorless solid was isolated by filtration and washed with 5 mL of cold methanol. To remove traces of **5**·ClO_4 this material was treated again with a ten-fold molar excess of triethylammonium cinnamate as described above. Recrystallization from a mixed ethanol/acetonitrile solvent system then gave the title compound in analytically pure form. Yield: 837 mg (80 %). Elemental analysis calcd. for

$C_{47}H_{71}ClN_6Zn_2O_6S_2$ (1046.47): C 53.94, H 6.84, N 8.03, S 6.13; found: C 53.60, H 7.00, N 8.14, S 6.33. IR (KBr, cm^{-1}): nu(tilde) = 2961(s), 2867(s), 1641(m) ν(C=C), 1568(s) $\nu_{as}(RCO_2^-)$, 1460(s), 1402(s) $\nu_s(RCO_2^-)$, 1365(w), 1307(w), 1266(w), 1234(w), 1203(w), 1154(vw), 1093(vs) $\nu(ClO_4^-)$, 1044(s), 1004(w), 982(w), 928(w), 913(w), 884(w), 821(m), 771(w), 750(w), 709(w), 688(w), 623(s). ^1H NMR (400 MHz, CD_3CN, 25°C, TMS, for atom labeling see Scheme S1): δ ($[(L^1)Zn_2]^{2+}$-fragment) = 1.06 (s, 18 H, $C^{11}H_3$), 2.43 (m, 4 H, C^8H or C^9H), 2.53 (s, 12 H, C^5H_3), 2.65 (d, ^2J = 11.25 Hz, 4 H, C^7HH), 2.81 (m, 4 H, C^8H or C^9H), 2.91 (s, 6 H, C^6H_3), 3.28 (m, 4 H, C^8H or C^9H), 3.54 (m, 4 H, C^8H or C^9H), 4.44 (d, ^2J = 11.25Hz, 4 H, C^7HH), 7.03 (s, 4 H, C^3H) ppm; δ(coligand) = 5.55 (d, ^3J = 15.89 Hz, 1 H, C$H$$CO_2$), 6.74 (d, ^3J = 15.89, 1 H, ArCH), 7.23 (m, 5 H, ArH) ppm. $^{13}C\{^1H\}$NMR (100 MHz, CD_3CN, 25°C, TMS): δ ($[(L^1)Zn_2]^{2+}$-fragment) = 31.4 (C^{11}), 34.3 (C^{10}), 46.9 (C^5), 49.8 (C^6), 58.4 (C^7), 59.6 (C^8) 64.4 (C^9), 128.7(C^3), 134.9 (C^2), 143.2 (C^1) 145.8 (C^4) ppm; δ (coligand) = 118.3, 125.2, 128.1, 129.5, 129.8, 139.9, 169.6 ppm. The tetraphenylborate salt, $[(L^1)Zn_2(O_2CCH{=}CHPh)]BPh_4$ (**7**·BPh_4), was prepared by adding $NaBPh_4$ (342 mg, 1.00 mmol) to a solution of **7**·ClO_4 (105 mg, 0.100 mmol) in methanol (40 mL). The colorless microcrystalline solid was isolated by filtration, washed with ethanol and dried in air. Yield: 108 mg (85 %). M.p. > 300 °C (decomp). IR (KBr, cm^{-1}): nu(tilde) = 1641(m) ν(C=C), 1568(s) $\nu_{as}(RCO_2^-)$, 1402(s) $\nu_s(RCO_2^-)$, 735(s), 703(s) $\nu(BPh_4^-)$.

Reaction of 6·BPh_4 (or 7·BPh_4) with 2,3-dimethylbutadiene. A glass tube was charged with **6**·BPh_4 (125 mg, 0.100 mmol) [or **7**·BPh_4 (127 mg, 0.100 mmol)] and 2,3-dimethylbutadiene (2.00 g, 24.3 mmol) in toluene (10 mL) and sealed. The suspension was heated to 210°C to give a pale-green (or colorless) solution, which was stirred for further 24 h at 210°C. After cooling to room temperature, the solvent was removed under reduced pressure to give a pale green (or colorless) solid. In both cases the IR spectra (or NMR spectra in the case of **7**·BPh_4)

were identical with those of the starting materials. Recovered yields: **6**·BPh_4 (115 mg, 92 %), **7**·BPh_4 (110 mg, 87 %).

[(L^1)Ni$_2$(3,4-dimethyl-6-phenylcyclohex-3-enecarboxylate)]ClO$_4$ (8·ClO$_4$). This compound was prepared from **4**·ClO_4 (92.1 mg, 0.100 mmol), 3,4-dimethyl-6-phenylcyclohex-3-enecarboxylic acid **3** (34.5 mg, 0.150 mmol) and triethylamine (15.2 mg, 0.150 mmol) by the procedure detailed above for **6**·ClO_4. Yield: 89 mg (80 %). M.p. 340°C (decomp.). IR (KBr, cm^{-1}): nu(tilde) = 2965(s), 2866(s), 1573(s) $\nu_{as}(RCO_2^-)$, 1462(s), 1423(m), 1400(s) $\nu_s(RCO_2^-)$, 1362(m), 1309(w), 1262(w), 1232(w), 1202(w), 1171(m), 1098(s) $\nu(ClO_4^-)$, 1038(s), 1000(m), 930(m), 910(m), 880(m), 828(m), 752(m), 701(w), 623(s). UV/Vis (MeCN): $\lambda_{max}(\varepsilon)$ = 350 (2029), 650 (29), 1112 nm (66 M^{-1}cm^{-1}). Elemental analysis calcd. for $C_{53}H_{81}ClN_6Ni_2O_6S_2\cdot EtOH$ (1115.22 + 46.07): C 56.88, H 7.55, N 7.24, S 5.75, found C 56.61, H 7.77, N 7.00, S 3.96. The tetraphenylborate salt, [(L^1)Ni$_2$(3,4-dimethyl-6-phenylcyclohex-3-enecarboxylate)]BPh_4 (**8**·BPh_4), was prepared by adding $NaBPh_4$ (342 mg, 1.00 mmol) to a solution of **8**·ClO_4 (112 mg, 0.100 mmol) in methanol (40 mL). The pale-green microcrystalline solid was isolated by filtration, washed with ethanol and dried in air. Yield: 120 mg (90 %). M.p. 340°C (decomp). IR (KBr, cm^{-1}): nu(tilde) = 3054(m), 3030(m), 2963(s), 2867(s), 1569(s) $\nu_{as}(RCO_2^-)$, 1459(vs), 1424(m), 1403(s) $\nu_s(RCO_2^-)$, 1364(m), 1308(w), 1267(w), 1232(w), 1203(w), 1170(w), 1153(m), 1131(w), 1080(s), 1045(s), 1000(m), 927(m), 912(m), 884(m), 843(w), 822(m), 734(s), 704(s), 625(m), 612(m). This salt was additionally characterized by X-ray crystallography.

[(L^1)Zn$_2$(3,4-dimethyl-6-phenylcyclohex-3-enecarboxylate)]ClO$_4$ (9·ClO$_4$). This compound was prepared from **5**·ClO_4 (95.8 mg, 0.100 mmol), 3,4-dimethyl-6-phenylcyclohex-3-enecarboxylic acid **3** (230 mg, 1.00 mmol) and triethylamine (1.01 g, 1.00 mmol) by the procedure detailed above for **7**·ClO_4. Yield: 77 mg (68 %). M.p. 300

> °C (decomp.). Elemental analysis calcd. for $C_{53}H_{81}ClN_6Zn_2O_6S_2$ (1128.61 g mol^{-1}): C 56.40, H 7.23, N 7.45, S 5.68 found: C 56.32, H 7.13, N 7.55, S 5.34. IR (KBr, cm^{-1}): nu(tilde) = 2962(s), 2902(s), 2867(s), 1571(s) $\nu_{as}(RCO_2^-)$, 1459(s), 1424(m), 1403(s) $\nu_s(RCO_2^-)$, 1364(m), 1308(w), 1267(w), 1232(w), 1204(w), 1170(m), 1154(m), 1094(vs) $\nu(ClO_4^-)$, 1045(w), 1005(m), 928(m), 912(m), 884(m), 822(m), 750(m), 700(w), 624(s). $^{13}C\{^1H\}$NMR (100 MHz, CD_3CN, 25°C, TMS, for atom labels see Scheme S1): δ ($[(L^1)Zn_2]^{2+}$-fragment) = 31.6 (C^{11}), 34.5 (C^{10}), 46.6 (C^5), 47.1 ($C^{5'}$), 49.9 (C^6), 58.0 (C^7), 58.6 ($C^{7'}$), 59.5 (C^8), 60.1 ($C^{8'}$), 64.6 (C^9), 64.9 ($C^{9'}$), 128.8 (C^3), 128.9 ($C^{3'}$), 135.3 (C^2), 135.7 ($C^{2'}$), 143.7 (C^1), 146.1 (C^4) ppm; δ (coligand) = 19.12 (C^8), 19.52 (C^9), 29.5 (C^2), 31.8 (C^5), 40.0 (C^1), 48.1 (C^6), 123.8, 126.0, 126.5, 127.8, 129.3, 146.5, 178.0 ($C^{3,4,10\text{-}13}$) ppm. The ^{13}C NMR spectrum reveals only half as many signals as expected for a C_1 symmetric species. This indicates fast rotation of the carboxylate residue about the $O_2C{-}R$ bond which leads to a time-averaged C_2-symmetric structure on the NMR time scale.The zinc complex **15** described below reveals a similar behaviour. The fact that **9** has a time-averaged C_2-symmetric structure on the NMR time scale is also supported by ^1H NMR spectroscopy. This is most readily seen by the fact that the four CH_3 groups on the benzylic nitrogens give rise to only two signals: ^1H NMR (400 MHz, CD_3CN, 25°C, TMS): δ ($[(L^1)Zn_2]^{2+}$-fragment) = 1.17 (s, 18 H, $C^{11}H_3$), 2.43 (m, 4 H, C^8H or C^9H), 2.45 (s, 6 H, C^5H_3), 2.53 (s, 6 H, $C^{5'}H_3$), 2.68 (d, ^2J = 11.6 Hz, 4 H, C^7HH), 2.79 (m, 4 H, C^8H or C^9H), 2.88 (s, 6 H, C^6H_3), 3.23 (m, 4 H, C^8H or C^9H), 3.52 (m, 4 H, C^8H or C^9H), 4.41 (m, 4 H, C^7HH), 6.86 (d, 2 H, C^3H), 7.12 (d, 2 H, $C^{3'}H$) ppm; δ (coligand) = 0.93 (m, 2 H, CH_2), 1.103 (m, 1H, CH_2), 1.30 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 1.45 (m, 1 H, CH_2), 3.05 (m, 1 H, $CHCO_2$), 3.44 (m, 1 H, CHPh), 7.10 (m, 5 H, ArH) ppm.

(2*E*,4*E*)-hexa-dienoic-acid (10): ^1H NMR (CD_3OD, 400 MHz, 25°C, CH_3OH, for atom labeling see Scheme S1): δ = 1.85 (d, ^3J = 6.0 Hz, 3 H, C^6H_3), 5.76 (d, ^3J = 15.20 Hz, 1 H, C^2H), 6.21 (m, 2 H, C^4H and C^5H), 7.24 (dd, ^3J = 15.20 Hz, ^3J = 9.53 Hz, C^3H) ppm. Sodium

(2*E*,4*E*)-hexa-dienoate: ^{1}H NMR (D_2O, 400 MHz, 25°C, CH_3OH): δ = 1.74 (d, ^{3}J = 6.8 Hz, 3 H, C^6H_3), 5.74 (d, ^{3}J = 15.20 Hz, 1 H, C^2H), 6.08 (m, 1 H, C^5H), 6.17 (m, 1 H, C^4H), 6.91 (dd, ^{3}J = 15.20 Hz, ^{3}J = 9.53 Hz, C^3H) ppm.

(1*R*,4*R*,5*S*)-5-cyano-4-methylcyclohex-2-enecarboxylic acid (12a) and (1*R*,4*R*,5*R*)-5-cyano-4-methylcyclohex-2-enecarboxylic acid (12b). To a suspension of **18a,b**·ClO_4 (2.13 g, 2.00 mmol) [or **19a,b** (2.10 g, 2.00 mmol)] in water (100 mL) was added conc. hydrochloric acid (10 mL), and the mixture was stirred for four days at ambient temperature. The resulting green solution was concentrated to half of its original volume and extracted with dichloromethane (4 × 50 mL). The combined organic phases were dried with anhydrous magnesium sulfate and evaporated to dryness. Yield: 160 mg (97 %) in the case of **18a,b** [157 mg (95 %) in the case of **19a,b**]. M.p. 58-60°C. Elemental analysis calcd. for $C_9H_{11}NO_2$ (165.19): C 65.44, H 6.71, N 8.48, found C 65.32, H 6.61, N 8.41. ESI-MS(*m*/*z*): 165.08 (M^+). IR (KBr, cm^{-1}): nu(tilde) = 3037(w), 2968(s), 2879(w), 2240(m) ν(CN), 1695(s) ν(RCO_2^-), 1458(m), 1413(s), 1309(w), 1264(m), 1208(s), 1163(m), 1137(w), 1099(m), 1062(m), 1030(w), 915(m), 813(w), 783(w), 763(w), 726(m), 633(m), 592(w), 486(w), 444(w). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25°C): δ (**12a**, major isomer (57%), for atom labeling see Scheme 1 below) = 17.28 (C^8), 23.93 (C^6), 29.74 (C^5), 33.60 (C^4), 40.19 (C^1), 120.21 (C^9), 122.76 (C^3), 132.42 (C^2), 177.74 (C^7) ppm. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ (**12a**, major isomer (57%)) = 1.18 (d, 3 H, C^8H_3), 2.20 (m, 2 H, C^6H_2), 2.38 (m, 1 H, C^4H), 2.55 (m, 1 H, C^5H), 3.15 (m, 1 H, C^1H), 5.72 (m, 1 H, C^2H), 5.76 (m, 1 H, C^3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25°C): δ (**12b**, minor isomer (43%)) = 19.79 (C^8), 26.41 (C^6), 30.25 (C^4), 30.57 (C^5), 38.70 (C^1), 121.65 (C^9), 122.59 (C^3), 133.49 (C^2), 178.12 (C^7) ppm. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ (**12b**, minor isomer (43%)) = 1.21 (d, 3 H,

C^8*H*), 1.90 (m, 1 H, C^6*H*), 2.36 (m, 1 H, C^6*H*), 2.45 (m, 1 H, C^4*H*), 2.86 (m, 1 H, C^5*H*), 3.20 (m, 1 H, C^1*H*), 5.63 (m, 1 H, C^2*H*), 5.76 (m, 1 H, C^3*H*) ppm.

Diels-Alder reaction between triethylammonium (2*E*,4*E*)-hexa-dienoate (10) and acrylonitrile (11). A solution of triethylammonium (2*E*,4*E*)-hexa-dienoate (prepared in situ from (2*E*,4*E*)-hexa-dienoic-acid **10** (1.12 g, 10.0 mmol) and triethylamine (1.02 g, 10.0 mmol)) in acrylonitrile **11** (100 mL) was refluxed for eight days. The solvent was distilled off at reduced pressure to afford an oily residue, which (by NMR spectroscopy) showed the presence of five products derived from sorbinic acid: (4*R*,5*S*)-5-cyano-4-methylcyclohex-1-enecarboxylic acid (**13a**, *ca.* 40 %), (4*R*,5*R*)-5-cyano-4-methylcyclohex-1-enecarboxylic acid (**13b**, *ca.* 28 %), (4*R*,6*R*)-6-cyano-4-methylcyclohex-1-enecarboxylic acid (**13c**, *ca.* 19 %), (4*R*,6*S*)-6-cyano-4-methylcyclohex-1-enecarboxylic acid (**13d**, ca. 7 %), and (2*E*,4*E*)-2-cyanoethyl-hexa-2,4-dienoate (**14**, *ca.* 5 %), besides some polymeric byproducts derived from acrylonitrile. The ester **14** and the polymeric byproducts were separated from the acids **13a-d** by extraction of a 3M aqueous potassium hydroxide solution (3M, 100 mL) with dichloromethane (3 × 100 mL). Chromatographic workup of the combined organic fractions gave 66 mg (4 %) of pure **14** (SiO_2, R_f 0.20). The polymer was discarded. The pH of the aqueous phase was then adjusted to ~ 1 with conc. hydrochloric acid, and the acids **13a-d** were extracted with dichloromethane (3 × 50 mL). The organic phases were combined, dried with anhydrous magnesium sulfate and evaporated to dryness to afford 1.52 g (92 %) of a mixture of the acids **13a-d** as a colorless residue. Pure samples of the three acids **13a,b,d** could be obtained in small amounts by fractional crystallization from water. **13c** could not be obtained in analytically pure form in this way. The analytical data are as follows:

(4*R*,5*S*)-5-cyano-4-methylcyclohex-1-enecarboxylic acid (13a): M.p. 150-152°C. IR (KBr, cm^{-1}): nu(tilde) = 2966(m), 2878(s), 2577(br), 2239(w) ν(CN), 1697(vs) $\nu(RCO_2^-)$, 1638(m) ν(C=C), 1612(w), 1415(s), 1377(w), 1327(w), 1296(w), 1264(s), 1201(m), 1153(m), 997(m), 970(m), 947(m), 919(m), 871(m), 804(w), 742(w), 698(m), 593(w), 470(m). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25°C, for atom labeling see Scheme S1): δ = 18.57 (C^8), 26.91 (C^6), 29.03 (C^4), 30.95 (C^3), 31.19 (C^5), 119.86 (C^9), 125.89 (C^1), 141.43 (C^2), 170.62 (C^7) ppm. ^1H NMR ($CDCl_3$, 500 MHz, 25°C): δ = 1.18 (d, 3H, C^8H_3), 1.98 (m, 1 H, C^4H), 2.22 (m, 1 H, C^3H^a or C^3H^b), 2.41 (m, 1 H, C^3H^a or C^3H^b), 2.54 (m, 1 H, C^6H^a or C^6H^b), 2.77 (m, 1 H, C^6H^a or C^6H^b), 2.96 (m, 1 H, C^5H), 7.12 (m, 1 H, C^2H) ppm. Elemental analysis calcd. for $C_9H_{11}NO_2$ (165.19): C 65.44, H 6.71, N 8.48; found C 65.10, H 6.97, N 8.18. This compound was additionally characterized by X-ray crystallography.

(4*R*,5*R*)-5-cyano-4-methylcyclohex-1-enecarboxylic acid (13b): M.p. 150-152°C. IR (KBr, cm^{-1}): ν = 2962(m), 2931(m), 2870(m), 2813(m), 2622(m), 2240(m) ν(CN), 1677(vs) $\nu(RCO_2^-)$, 1645(s) ν(C=C), 1419(s), 1382(m), 1351(w), 1308(w), 1275(s), 1170(w), 1142(w), 1109(w), 1069(w), 1044(s), 1021(w), 964(s), 841(w), 752(m), 724(m), 603(m), 573(w), 517(w). $^{13}C\{^1H\}$NMR ($CDCl_3$, 125 MHz, 25°C, TMS, for atom labeling see Scheme S1): δ = 19.39 (C^8), 27.06 (C^6), 30.0 (C^4), 32.01 (C^5), 32.78 (C^3), 121.01 (C^9), 126.55 (C^1), 140.97 (C^2), 170.63 (C^7) ppm. ^1H NMR ($CDCl_3$, 500 MHz, 25°C): δ = 1.21 (d, 3H, C^8H_3), 1.98 [m, 2 H, C^4H + (C^3H^a or C^3H^b)], 2.44 (m, 1 H, C^5H), 2.51 [m, 2 H, (C^6H^a or C^6H^b) + (C^3H^a or C^3H^b)], 2.83 (m, 1 H, C^6H^a or C^6H^b), 7.12 (m, 1 H, C^2H) ppm. Elemental analysis calcd. for $C_9H_{11}NO_2$ (165.19): C 65.44, H 6.71, N 8.48; found C 65.50, H 7.01, N 8.46. This compound was additionally characterized by X-ray crystallography.

(4*R*,6*R*)-6-cyano-4-methylcyclohex-1-enecarboxylic acid (13c): This compound could not be obtained in analytically pure form. The presence of this compound in the above mixture is indicated by a dublet for the CH_3 protons at 1.08 ppm in the ^1H NMR spectrum. ^1H NMR ($CDCl_3$, 300 MHz, 25°C): δ= 1.08 (d, ^3J = 9.3 Hz, 3H, C^8H_3) ppm.

(4*R*,6*S*)-6-cyano-4-methylcyclohex-1-enecarboxylic acid (13d): M.p. 154°C. IR (KBr, cm^{-1}): 2967(s), 2926(s), 2890(s), 2606(m), 2528(m), 2234(m) ν(CN), 1679(s) ν(RCO_2^-), 1638(m) ν(C=C), 1459(w), 1428(m), 1381(s), 1288(s), 1272(s), 1235(s), 1171(m), 1111(w), 1098(w), 1074(w), 1026(m), 942(m), 822(m), 783(m), 741(m), 633(w), 609(w), 488(m). $^{13}C\{^1H\}$NMR ($CDCl_3$, 125 MHz, 25°C): δ= 20.96 (C^8), 24.69 (C^4), 26.14 (C^3), 33.57 (C^5), 34.06 (C^6), 120.36 (C^9), 124.53 (C^1), 146.86 (C^2), 169.87 (C^7) ppm. ^1H NMR ($CDCl_3$, 300 MHz, 25°C, for atom labeling see Scheme S1): δ= 1.06 (d, ^3J = 9.3 Hz, 3H, C^8H_3), 1.44 (m, 1 H, C^5H^a or C^5H^b), 1.84 (m, 1 H, C^3H^a or C^3H^b), 1.93-2.13 (m, 2 H, C^4H and (C^5H^a or C^5H^b)), 2.49 (m, 1 H, C^3H^a or C^3H^b), 3.69 (m, 1 H, C^6H), 7.33 (m, 1 H, C^2H) ppm. Elemental analysis calcd. for $C_9H_{11}NO_2$ (165.19): C 65.44, H 6.71, N 8.48; found C 65.00, H 6.81, N 8.68. This compound was additionally characterized by X-ray crystallography.

Isomerization of 12a,b. A solution of **12a**,**b** (16.5 mg, 0.100 mmol) and triethylamine (10 mg, 0.10 mmol) in CD_3CN (1 mL) was placed in a sealed NMR tube and heated for 6h at 75°C. Analysis of the reaction mixture by ^1H NMR spectroscopy revealed the total conversion to a mixture of **13a** and **13b**.

(2*E*,4*E*)-2-cyanoethyl-hexa-2,4-dienoate (**14**). This compound was obtained as a byproduct in the Diels-Alder reaction between triethylammonium (2*E*,4*E*)-hexa-dienoate and acrylonitrile (*vide supra*). An analytical sample was obtained by column chromatography (SiO_2). Colorless, oily liquid. R_f (0.20, dichloromethane). ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C, for atom labeling see Scheme S1): δ = 1.88 (d, 3 H, C^6H_3), 2.73 (m, 2 H, C^8H_2), 4.34 (m, 2 H, C^7H_2), 5.78 (m, 1 H, C^2H), 6.20 (m, 2 H, C^4H + C^5H), 7.30 (m, 1 H, C^3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25°C): δ = 18.75 (C^6), 19.32 (C^8), 59.10 (C^7), 117.55 (C^9), 118.11 (C^2), 130.24 (C^4), 130.45 (C^5), 141.3 (C^3), 167.14 (C^1) ppm.

[(L^1)Zn_2((4*R*,5*S*)-5-cyano-4-methylcyclohex-1-enecarboxylate)]BPh_4 (15·BPh_4). This compound was prepared from **5**·ClO_4 (9.58 mg, 0.0100 mmol), (4*R*,5*S*)-5-cyano-4-methylcyclohex-1-enecarboxylic acid **13a** (16.5 mg, 0.100 mmol) and triethylamine (10 mg, 0.10 mmol) by the procedure detailed above for **7**·ClO_4. The resulting solid of **15**·ClO_4 was redissolved in methanol (20 mL) and a solution of $NaBPh_4$ (171 mg, 0.500 mmol) in methanol (3 mL) was added. The precipitate was filtered, washed with a few milliliters of methanol and recrystallized from a mixed acetonitrile/ethanol solvent system. Yield: 8 mg (62 %). M.p. 268-270°C. Elemental analysis calcd. for $C_{71}H_{94}BN_7O_2S_2Zn_2$ (1283.27): C 66.45, H 7.38, N 7.64, S 5.00; found C 66.26, H 7.38, N 7.53, 5.07. IR (KBr, cm^{-1}): nu(tilde) = 3054(m), 3032(m), 2962(s), 2868(m), 2242(vw) ν(CN), 1653(m) ν(C=C), 1568(s) $\nu_{as}(RCO_2^-)$, 1479(w), 1459(s), 1410(s) $\nu_s(RCO_2^-)$, 1362(m), 1308(w), 1266(w), 1232(w), 1202(w), 1153(w), 1079(m), 1044(m), 912(w), 883(w), 822(m), 746(m), 732(s) $\nu(BPh_4^-)$, 704(s) $\nu(BPh_4^-)$, 626(m), 612(m). $^{13}C\{^1H\}$NMR (125 MHz, CD_3CN, 25°C, TMS, for atom labeling see Scheme S1): δ ($[(L^1)Zn_2]^{2+}$-fragment) = 31.57 (C^{11}), 34.49 (C^{10}), 46.98 + 47.09 (C^5 + $C^{5'}$), 49.88 (C^6), 58.23 + 58.24 (C^7 + $C^{7'}$), 59.76 + 59.51 (C^8 + $C^{8'}$), 64.53 + 64.31 (C^9 + $C^{9'}$), 128.88 + 128.79 (C^3 + $C^{3'}$), 134.86 + 134.95 (C^2 + $C^{2'}$), 143.3 (C^4), 145.9 (C^1) ppm; δ (coligand) = 169.5 (C^7), 132.69 (C^2), 131.85 (C^1), 121.34 (C^9), 31.76 (C^5), 31.10 (C^3), 29.61 (C^4), 28.80 (C^6), 18.58 (C^8); δ (BPh_4^-) = 164.79 (q), 136.74 (q), 126.68 (q), 122.75 ppm. ^{1}H NMR (500 MHz, CD_3CN, 25°C, TMS, for atom labeling see Scheme S1): δ

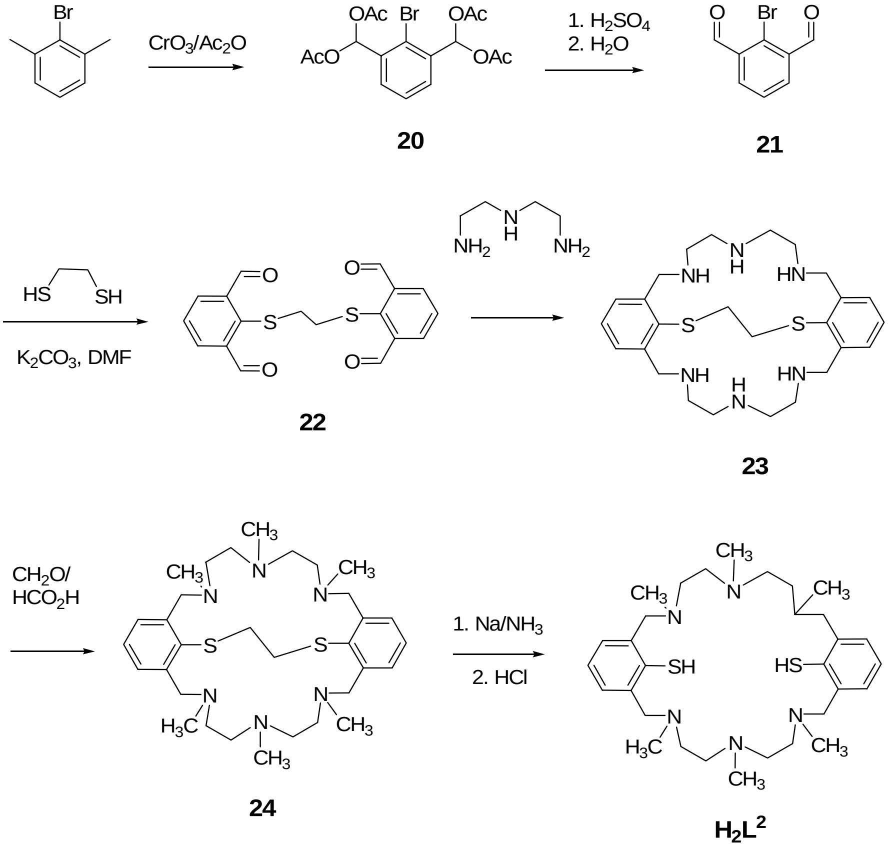
($[(L^1)Zn_2]^{2+}$-fragment) = 1.18 (s, 18 H, $C^{11}H_3$), 2.41 (m, 4 H, C^8H or C^9H), 2.43 (s, 6 H, C^5H_3), 2.47 (s, 6 H, $C^{5'}H_3$), 2.62 (d, ^2J = 11.6 Hz, 2 H, C^7H), 2.63 (d, ^2J = 11.6 Hz, 2 H, $C^{7'}H$), 2.80 (m, 4 H, C^8H or C^9H), 2.89 (s, 6 H, C^6H_3), 3.23 (m, 4 H, C^8H or C^9H), 3.54 (m, 4 H, C^8H or C^9H), 4.42 (d, ^2J = 11.6 Hz, 4 H, C^7H_2), 7.03 (s, 2 H, C^3H), 7.05 (s, 2 H, $C^{3'}H$); δ(coligand) = 0.86 (d, ^3J = 6.32 Hz, 3 H, C^8H_3), 1.40-2.05 (m, 6 H), 5.93 (d, 1 H, C^2H); δ(BPh_4^-): 6.84 (m, 4 H), 6.98 (m, 8 H), 7.26 (m, 8 H). This compound was additionally characterized by X-ray crystallography.

$[(L^1)Zn_2$((2*E*,4*E*)-hexa-2,4-dienoate)]ClO_4 (16·ClO_4). This compound was prepared from **5**·ClO_4 (958 mg, 1.00 mmol), (2*E*,4*E*)-hexa-dienoic-acid (1.12 g, 10.0 mmol) and triethylamine (1.02 g, 10.0 mmol) by the procedure detailed above for **7**·ClO_4. Yield: 735 mg (73 %.). M.p. 348-350°C (decomp.). IR (KBr, cm^{-1}): nu(tilde) = 2962(s), 2867(s), 1651(w) ν(C=C), 1618(w) ν(C=C), 1560(s) $\nu_{as}(RCO_2^-)$, 1461(s), 1423(w), 1406(s) $\nu_s(RCO_2^-)$, 1363(m), 1307(w), 1265(w), 1232(w), 1204(w), 1154(m), 1096(vs) $\nu(ClO_4^-)$, 1043(m), 995(m), 913(m), 882(m), 823(m), 805(m), 624(s). Elemental analysis calcd. for $C_{44}H_{71}ClN_6Zn_2O_6S_2\cdot H_2O$ (1010.43 + 18.02): C 51.39, H 7.15, N 8.17, S 6.24, found C 51.34, H 7.14, N 8.07, S 6.44. $^{13}C\{^1H\}$NMR (50 MHz, CD_3CN, 25°C, TMS, for atom labeling see Scheme S1): δ ($[(L^1)Zn_2]^{2+}$-fragment) = 31.6 (C^{11}), 34.6 (C^{10}), 46.9 (C^5), 50.0 (C^6), 58.6 (C^7), 59.8 (C^8) 64.6 (C^9), 128.9 (C^3), 135.1 (C^2), 143.3 (C^1) 145.9 (C^4); δ (coligand) = 18.4 (C^6), 126.3, 131.2, 135.8, 140.5 (C^{2-5}), 170.3 (C^1) ppm. ^1H NMR (400 MHz, CD_3CN, 25°C, TMS, for atom labeling see Scheme S1): δ ($[(L^1)Zn_2]^{2+}$-fragment) = 1.16 (s, 18 H, ($C^{11}H_3$), 2.43 (m, 4 H, C^8H or C^9H), 2.46 (s, 12 H, C^5H_3), 2.63 (d, ^2J = 11.54 Hz, 4 H, C^7H), 2.80 (m, 4 H, C^8H or C^9H), 2.88 (s, 6 H, C^6H_3), 3.25 (m, 4 H, C^8H or C^9H), 3.53 (m, 4 H, C^8H or C^9H), 4.41 (d, ^2J = 11.54 Hz, 4 H, C^7H), 7.02 (s, 4 H, C^3H); δ (coligand) = 1.65 (d, ^3J = 5.27 Hz, 3 H, C^6H_3), 4.83 (d, ^3J = 15.20 Hz, 1 H, C^2H), 5.76 (m, 2 H, C^4H and C^5H), 6.32 (dd, ^3J = 15.31 Hz, ^3J = 9.53 Hz, C^3H) ppm.

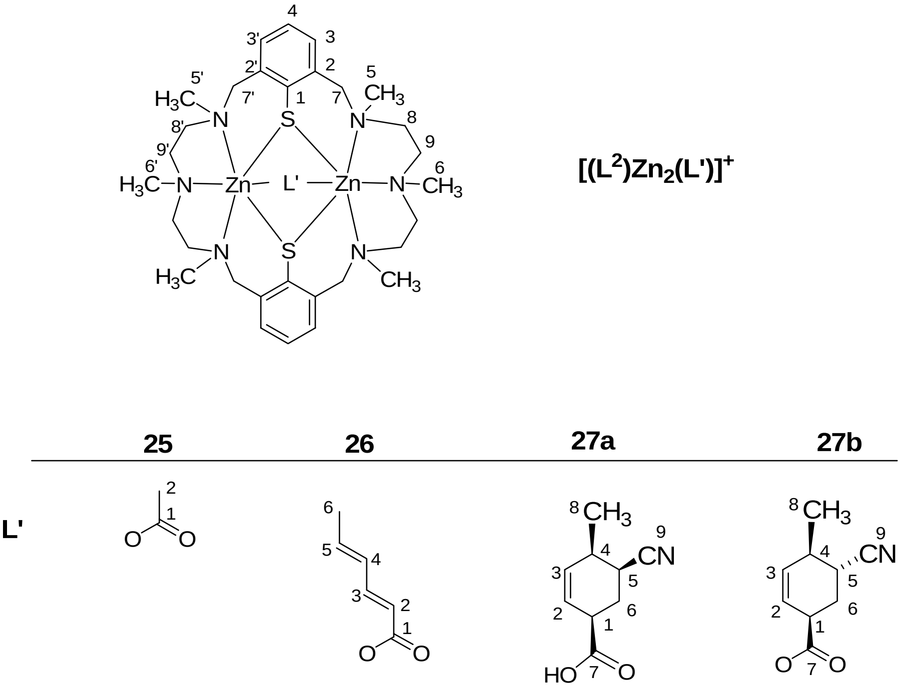
[(L^1)Ni_2((2*E*,4*E*)-hexa-2,4-dienoate)]ClO_4 (17·ClO_4). This compound was prepared from **4**·ClO_4 (92.1 mg, 0.100 mmol), (2*E*,4*E*)-hexa-2,4-dienoic acid **10** (16.8 mg, 0.150 mmol) and triethylamine (15.2 mg, 0.150 mmol) by the procedure detailed above for **6**·ClO_4. Yield: 83 mg (83 %). M.p. 348-350°C (decomp.). IR (KBr, cm^{-1}): nu(tilde) = 2961(s), 2866(s), 1651(m) ν(C=C), 1619(m) ν(C=C), 1567(s) $\nu_{as}(RCO_2^-)$, 1462(s), 1423(w), 1395(s) $\nu_s(RCO_2^-)$, 1362(m), 1308(w), 1264(w), 1233(w), 1201(w), 1153(m), 1096(vs) $\nu(ClO_4^-)$, 1039(s), 993(s), 930(m), 913(m), 881(m), 828(m), 825(m), 807(w), 752(m), 728(m), 623(s). UV/Vis (MeCN): $\lambda_{max}(\varepsilon)$ = 350 (2316), 650 (43), 1120 nm (70 $M^{-1}cm^{-1}$). Elemental analysis calcd. for $C_{44}H_{71}ClN_6Ni_2O_6S_2 \cdot H_2O$ (997.04 + 18.02): C 52.06, H 7.25, N 8.28, S 6.32, found C 52.43, H 7.38, N 8.00, S 5.75. The tetraphenylborate salt, [(L^1)Ni_2((2*E*,4*E*)-hexa-2,4-dienoate)]BPh_4 (**17**·BPh_4), was prepared by adding $NaBPh_4$ (342 mg, 1.00 mmol) to a solution of **17**·ClO_4 (99 mg, 0.100 mmol) in methanol (40 mL). The pale-green microcrystalline solid was isolated by filtration, washed with ethanol and dried in air. Yield: 110 mg (90 %). This salt was additionally characterized by X-ray crystallography.

[(L^1)Zn_2((1*R*,4*R*,5*S*)-5-cyano-4-methylcyclohex-2-enecarboxylate)]ClO_4 (18a·ClO_4) and [(L^1)Zn_2((1*R*,4*R*,5*R*)-5-cyano-4-methylcyclohex-2-enecarboxylate)]ClO_4 (18b·ClO_4). A solution of [(L^1)Zn_2((2*E*,4*E*)-hexa-2,4-dienoate)]ClO_4 (**16**·ClO_4) (2.02 g, 2.00 mmol) in acrylonitrile (100 mL) was refluxed for 56h. The reaction mixture was evaporated to dryness, redissolved in acetonitrile (60 mL), and filtered off from undissolved material. Ethanol (100 mL) was then added and the solution was concentrated in vacuum to ~ 30 mL by using a rotary evaporator. The resulting colorless solid was filtered, washed with ethanol and dried in air. Yield: 2.00 g (94 %). M.p. 288-290°C (decomp.). Elemental analysis calcd. for $C_{47}H_{74}ClN_7O_6S_2Zn_2 \cdot H_2O$ (1063.50 + 18.02): C 52.20, H 7.08, N 9.07, S 5.93, found C 51.88, H 7.21, N 8.95, S 6.30. IR (KBr, cm^{-1}): nu(tilde) = 2963(s), 2869(s), 2239(w) ν(CN), 1590(s) $\nu_{as}(RCO_2^-)$, 1462(s), 1408(s) $\nu_s(RCO_2^-)$, 1364(m), 1305(m), 1267(m), 1232(m), 1203(m), 1170(w), 1154(w), 1096(s) ν(ClO_4^-), 1055(w), 1043(m), 1004(m), 983(m), 928(m), 913(m), 884(m), 823(s), 806(m), 750(m), 624(s). The NMR data described below reveal this product is a ~57:43 mixture of the two isomers: $[(L^1)Zn_2((1R,4R,5S)$-5-cyano-4-methylcyclohex-2-enecarboxylate)]ClO_4 (**18a**·ClO_4) and $[(L^1)Zn_2((1R,4R,5R)$-5-cyano-4-methylcyclohex-2-enecarboxylate)]ClO_4 (**18b**·ClO_4). All attempts to separate these two isomers by fractional crystallization have been unsuccessful. $^{13}C\{^1H\}$NMR (100 MHz, CD_3CN, 25°C, major isomer **18a**, 57%, , for atom labeling see Scheme S1): δ ($[(L^1)Zn_2]^{2+}$-fragment) = 31.64* (C^{11}), 34.52 (C^{10}), 46.96* (C^5), 47.01 ($C^{5'}$), 49.78* (C^6), 58.18 + 58.49 (C^7 + $C^{7'}$), 59.46 + 59.78 (C^8 + $C^{8'}$), 64.36 + 64.58* (C^9 + $C^{9'}$), 128.95* (C^3), 129.02 ($C^{3'}$), 135.13* (C^2), 135.16 ($C^{2'}$), 143.44* (C^1), 146.03 (C^4); δ(coligand) = 16.97 (C^8), 24.74 (C^6), 29.75 (C^5), 33.79 (C^4), 45.16 (C^1), 122.30 (C^9), 126.83 (C^3), 130.44 (C^2), 175.67 (C^7) ppm. $^{13}C\{^1H\}$NMR (100 MHz, CD_3CN, 25°C, minor isomer **18b**, 43%, for atom labeling see Scheme S1): δ ($[(L^1)Zn_2]^{2+}$-fragment) = 31.64* (C^{11}), 34.54 (C^{10}), 46.96* (C^5), 47.07 ($C^{5'}$), 49.78* (C^6), 58.22 + 58.43 (C^7 + $C^{7'}$), 59.50 + 59.72 (C^8 + $C^{8'}$), 64.41 + 64.58* (C^9 + $C^{9'}$), 128.95*(C^3), 129.10 ($C^{3'}$), 135.07 (C^2), 135.13* ($C^{2'}$), 143.44* (C^1), 146.10 (C^4); δ(coligand) = 20.16 (C^8), 27.39 (C^6), 30.08 (C^4), 31.01 (C^5), 42.4 (C^1), 122.68 (C^9), 126.80 (C^3), 130.46 (C^2), 175.88 (C^7). For the $[(L^1)Zn_2]^{2+}$-fragments of **18a**,**b** only the signals for the $N^{Bz}CH_3$ protons are resolved in the 400 MHz ^1H NMR spectrum (400 MHz, CD_3CN, 25°C, TMS): δ ($[(L^1)Zn_2]^{2+}$-fragment, **18a** + **18b**) = 1.25 (s, 18 H, ($C^{11}H_3$), 2.40 (m, 4 H, C^8H or C^9H), 2.43 (s, 3 H, C^5H_3), 2.44 (s, 3 H, $C^{5'}H_3$), 2.46 (s, 3 H, C^5H_3), 2.48 (s, 3, $C^{5'}H_3$), 2.65 (m, 4 H, C^7H_2), 2.80 (m, 4 H, C^8H or C^9H), 2.87 (s, 6 H, C^6H_3), 3.24 (m, 4 H, C^8H or C^9H), 3.52 (m, 4 H, C^8H or C^9H), 4.40 (m, 4 H, C^7H_2), 6.86 (d, 2 H, C^3H), 7.10 (m, 4 H, C^3H) ppm. For the two coligands (**12a**,**b**) only the signals for the olefinic CH protons and the CH_3 protons are resolved in the 400 MHz ^1H NMR spectrum. The other resonances are obscured by the signals of the $[(L^1)Zn_2]^{2+}$-fragments: ^1H NMR (400 MHz, CD_3CN, 25°C, TMS): δ(coligand) = 0.85 (*d*, ^3J = 7.2 Hz, 3 H, C^8H_3), 0.83 (*d*, ^3J = 7.6 Hz, C^8*H*$_3$), 1.70-2.60 (m, 5 H, CH$_2$, 3 × CH), 4.49 (m, 1 H, C*H*), 4.81 (m, 1 H, C*H*), 5.19 (m, 1 H, C*H*), 5.29 (m, 1 H, C*H*) ppm. *Signal not resolved.

[(L^1)Ni$_2$((1*R*,4*R*,5*S*)-5-cyano-4-methylcyclohex-2-enecarboxylate)]ClO$_4$ (19a·ClO$_4$) and [(L^1)Ni$_2$((1*R*,4*R*,5*R*)-5-cyano-4-methylcyclohex-2-enecarboxylate)]ClO$_4$ (19b·ClO$_4$): A solution of [(L^1)Ni$_2$((2*E*,4*E*)-hexa-2,4-dienoate)]ClO$_4$ (**17**·ClO$_4$) (1.99 g, 2.00 mmol) in acrylonitrile (100 mL) was refluxed for 56 h. The reaction mixture was evaporated to dryness, redissolved in acetonitrile (60 mL), and filtered off from undissolved material. Ethanol (100 mL) was then added and the solution was concentrated in vacuum to ~ 10 mL by using a rotary evaporator. The resulting green solid was filtered, washed with ethanol and dried in air. Yield: 1.99 g (95 %). M.p. 341-342°C. Elemental analysis calcd. for $C_{47}H_{74}ClN_7Ni_2O_6S_2 \cdot H_2O$ (1050.10 + 18.02): C 52.85, H 7.17, N 9.18, S 6.00, found C 53.06, H 7.24, N 9.23, S 6.11. IR (KBr, cm^{-1}): nu(tilde) = 2962(s), 2869(s), 2238(w) ν(CN), 1594(s) $\nu_{as}(RCO_2^-)$, 1462(s), 1407(s) $\nu_s(RCO_2^-)$, 1364(m), 1308(m), 1264(m), 1233(m), 1201(m), 1170(w), 1154(w), 1096(s) $\nu(ClO_4^-)$, 1039(s), 1001(w), 981(w), 930(m), 912(m), 881(m), 826(s), 807(m), 752(m), 623(s). UV/Vis(MeCN): $\lambda_{max}(\varepsilon)$ = 346 (2478), 674 (24), 1110 nm (55 M^{-1}cm^{-1}). The NMR data described above for **12a** and **12b** reveal this product is a ~57:43 mixture of the two isomers: [(L^1)Ni$_2$((1*R*,4*R*,5*S*)-5-cyano-4-methylcyclohex-2-enecarboxylate)]ClO$_4$ (**19a**·ClO$_4$) and [(L^1)Ni$_2$((1*R*,4*R*,5*R*)-5-cyano-4-methylcyclohex-2-enecarboxylate)]ClO$_4$ (**19b**·ClO$_4$). All attempts to separate these two isomers by fractional crystallization have been unsuccessful.



Scheme S2. Synthesis of $H_2L^2(HCl)_6$.



Scheme S3. Synthesized zinc complexes of $(L^2)^{2-}$.

1,3-Bis(diacetoxymethyl)-2-bromo-benzene (20). To a suspension of 2-bromo-1,3-dimethylbromobenzene (25.3 g, 137 mmol) in acetic anhydride (270 mL) was added concentrated sulfuric acid (40 mL) dropwise at such rate as to maintain the temperature below –20°C. To the resulting mixture was added a solution of chromium (VI) oxide (46.7 g, 46.4 mmol) in acetic anhydride dropwise while the temperature was kept below –20 °C. Since solutions of chromium (VI) oxide in acetic anhydride appear to be unstable at 30°C, the oxidation agent was prepared and added in 6 portions. After complete addition the green suspension was poured onto ice (5000 ml) with efficient stirring. After standing at room temperature for 12 h the precipitate was filtered off and washed thoroughly with water. Drying in air gave a yellowish solid. Recrystallization from ethanol gave analytically pure material as colourless crystals. Yield: 28.0 g (67.1 mmol, 49%). M.p.: 142–143°C. Elemental analysis calcd. for $C_{16}H_{17}BrO_8$ (417.21): C 46.06, H 4.11, found C 46.00, H 4.14 .^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.13$ (s, 12 H, CH_3CO_2), 7.42 (m, $^3J = 7.83$ Hz, 1 H, Ar*H*), 7.59 ppm (m, $^3J = 7.83$ Hz, 2 H, Ar*H*). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 21.3$, 89.6, 123.5, 128.4, 129.8, 136.7, 168.8 ppm.

2-Bromobenzene-1,3-dialdehyde (21). To a suspension of 1,3-bis-(diacetoxymethyl)-2-bromo-benzene (9.00 g, 21.6 mmol) in methanol (50 mL) was added concentrated sulfuric acid (95 mL) dropwise at 0°C. After complete addition, the resulting orange solution was stirred for futher 1h. Upon dropwise addition of water (220 mL) at 0°C the product precipitated from the solution. It was filtered, washed with water, and dried in air. Recrystallisation from dichloromethane/cyclohexane gave analytically pure material as a colourless crystalline solid. Yield: 3.00 g (65 %). M.p.116–117 °C. Elemental analysis calcd. for $C_8H_5BrO_2$ (213.03): C 45.10, H 2.37, found C 45.20, H 2.44. IR (KBr, cm^{-1}) ν(tilde) = 3350(m), 3065(m), 2999(w), 2869(w), 2465(w), 2134(w), 2134(w), 1998(w), 1957(w), 1830(w), 1703(s) ν(CO), 1679(s), 1573(s), 1444(s), 1374(s), 1300(m), 1234(s), 1162(m), 1029(m), 1009(m), 902(s), 802(s), 690(s), 496(m), 416(w). ^{1}H NMR (400 MHz, 25°C, $CDCl_3$, TMS): δ = 7.56 (t, $^3J_{H,H}$ = 7.83 Hz, 1 H, Ar*H*), 8.14 (d,^{3}J = 7.83 Hz, 2 H, Ar*H*), 10.52 ppm (s, 2 H, ArC*H*O). ^{13}C{^{1}H} NMR (100 MHz, 25°C, $CDCl_3$, TMS): *δ* = 129.5, 133.9, 135.1, 135.9, 191.6 ppm (*C*HO).

1,2-Bis(2,6-diformylphenylthio)ethane (22). To a suspension of anhydrous potassium carbonate (3.31 g, 23.9 mmol) in DMF (50 mL) was added 1,2-ethandithiol (796 mg, 8.45 mmol) and 2-bromobenzene-1,3-dialdehyde (3.60 g, 16.9 mmol) and the reaction mixture was stirred at room temperature for 1 week. After dropwise addition of water (300 mL), the resulting precipitate was filtered off and washed with water. Drying in vacuo gave 1,2-bis(2,6-diformylphenylthio)ethane as a pale yellow powder. Crystallisation from chloroform gave analytical pure material as a pale yellow powder. Yield: 3.00 g, 8.37 mmol (50%). M.p. 210–212°C. Elemental analysis calcd. for $C_{18}H_{14}O_4S_2$ (358.43): C 60.32, H 3.94, S 17.89 found C 60.30, H 4.51, S 17.70. IR (KBr, cm^{-1}): nu(tilde) = 3432(m), 3063(w), 3001(w), 2934(w), 2877(m), 2752(w), 2725(w), 1701(s) ν(CHO), 1679(s) ν(CHO), 1568(s), 1446(m), 1409(m), 1367(s), 1285(w), 1233(s), 1213(m), 1163(w), 1136(w), 1047(w), 1009(w), 903(s), 810(m), 792(m), 740(w), 722(w), 692(m), 503(w), 422(w). ^{1}H NMR (400 MHz, 25°C, $CDCl_3$, TMS): δ = 2.94 (s, 4 H, SC*H*$_2$), 7.63 (t, ^{3}*J* = 8.00 Hz, 2 H, Ar*H*), 8.12 (d, ^{2}*J* = 8.00 Hz, 7.59 Hz, 4H, Ar*H*), 10.71 ppm (s, 4H, ArC*H*O). ^{13}C{^{1}H}NMR (100 MHz, 50°C, DMSO-d_6): δ = 38.8, 129.8, 133.3, 138.3, 139.5, 191.2 ppm.

Macrobicyclic thioether (23). Solutions of 1,2-bis(2,6-diformylphenylthio)ethane (824 mg, 2.30 mmol) in chloroform (100 mL) and of bis-(2-aminoethyl)amine (475 mg, 4.60 mmol) in ethanol (100 mL) were added simultaneously over a period of 5 h to a mixture of dichloromethane (200 mL) and ethanol (50 mL). After complete addition, the reaction mixture was stirred at room temperature for 12 h. The dichloromethane was then removed at reduced pressure and solid sodium borhydride (681 mg, 18.0 mmol) was added. After stirring at room temperature for 2 h, the reaction mixture was acidified to pH 1 with conc. hydrochloric acid and the resulting colourless suspension was evaporated to dryness. Water (200 mL) and dichloromethane (200 mL) were added to the residue and the pH was adjusted to pH 13 with 3M aqueous potassium hydroxide. The layers were separated and the aqueous phase was extracted with dichloromethane (5 × 30 mL). The combined organic fractions were evaporated to dryness. Drying in air gave a white foamy solid. Yield: 1.12g, 2.23 mmol (97 %). M.p.: 161–163°C. Elemental analysis calcd. for $C_{26}H_{40}N_6S_2 \cdot H_2O$ (500.76 + 18.02): C 60.19, H 8.16, N 16.20, S 12.36, found C 60.30, H 8.18, N 16.00, S 12.70. IR(KBr, cm^{-1}): ν(tilde) = 3297(s) ν(NH), 3259(m), 3051(w), 2897(s), 2830(s), 2650(m), 2420(w), 1665(w), 1581(w), 1455(s), 1430(s), 1353(m), 1330(m), 1253(m), 1204(m), 1189(m), 1154(m), 1130(s), 1033(m), 989(m), 970(m), 917(m), 772(s), 738(s), 684(m), 664(w), 627(w), 547(w), 519(w), 501(w), 439(w). ^1H NMR (400 MHz, 25°C, CD_3OD, TMS): δ = 2.88 (m, 16 H, $N(CH_2CH_2)$, 3.21 (s, 4 H, $ArSCH_2$), 3.97 (s, 8 H, $ArCH_2N$), 7.36 ppm (m, 6H, ArH). $^{13}C\{^1H\}$NMR (100 MHz, 25°C, $CDCl_3/CD_3OD$): δ = 36.86 (SCH_2), 48.18 (NCH_2), 48.58 (NCH_2), 53.12 ($ArCH_2$), 129.26 ($C^{Ar}H$), 130.51 ($C^{Ar}H$), 132.99 ($C^{Ar}S$), 144.05 ppm ($C^{Ar}CH_2$).

Permethylated Macrobicyclic thioether (24). To a solution of **23** (1.00 g, 2.00 mmol) in formic acid (10 mL) was added 35% aqueous formaldehyde solution (3 mL) and the resulting mixture was heated under reflux for 12 h. The yellow solution was evaporated to dryness. Water (200 mL) and dichloromethane (200 ml) were added to the slicky residue, the pH was adjusted to pH 13 with 3M aqueous potassium hydroxide solution, and the heterogeneous mixture was stirred vigorously for 30 min. The layers were separated and the aqueous phase was extracted with dichloromethane (5 × 30 mL). The combined organic fractions were dried over K2CO3 and filtered. Methanol was added to the clear solution. On evaporation of the dichloromethane, the permethylated macrocycle **24** was obtained as colorless crystals. Yield: 1.00 g, 1.71 mmol (85 %). M.p.: 165–167°C. Elemental analysis calcd. for $C_{32}H_{52}N_6S_2$ (584.93): C 65.71, H 8.96, N 14.37 S 10.96, found C 65.30, H 8.97, N 14.20, S 11.20. IR (KBr, cm^{-1}): ν(tilde) = 3050(m), 2963(s), 2944(s), 2831(s), 2780(s), 1455(s), 1422(w), 1394(w), 1364(w), 1355(m), 1319(m), 1267(m), 1210(m), 1196(m), 1168(m), 1128(m), 1107(s), 1077(m), 1037(m), 1001(w), 985(m), 953(w), 933(w), 917(m), 821(m), 773(s), 726(w), 694(w), 614(w), 572(w), 555(w), 534(w), 490(w), 444(w), 413(w). ^{1}H NMR (400 MHz, 25°C, $CDCl_3$, TMS): δ = 2.01 (s, 12 H, CH_3NCH_2Ar), 2.23 (s, 6 H, $CH_3N(CH_2CH_2)_2$), 2.58 (s, 16 H, CH_2), 3.11 (s, 4 H, $ArSCH_2$), 3.78 (s, 8 H, $ArCH_2N$), 7.16 (t, ^3J = 7.34 Hz, 2 H, Ar*H*), 7.25 ppm (d, ^3J = 7.34 Hz, 4 H, Ar*H*). $^{13}C\{^1H\}$NMR (100 MHz, 25°C, $CDCl_3$, TMS): δ = 37.5 ($N^{Bz}Me$), 42.5 (NMe), 42.8 (SCH_2), 56.1 (NCH_2), 56.5 (NCH_2), 62.1 ($ArCH_2$), 127.8 ($C^{Ar}CH_2$), 129.6 ($C^{Ar}H$), 134.7 ($C^{Ar}S$), 144.9 ppm ($C^{Ar}H$).

Hexaazadithiophenolate Macrocycle (H_2L^2). A solution of **24** (2.70 g, 4.62 mmol) in tetrahydrofuran (50 mL) was added dropwise to a solution of sodium (1.00 g, 43.4 mmol) in liquid ammonia (50 mL) at –78°C. The resulting blue reaction mixture was kept at –78 °C for a further 60min before solid ammonium chloride (200 mg, 3.70 mmol) was added in small portions to destroy excess reducing agent. The resulting colourless suspension was allowed to warm to room temperature with evaporation of ammonia. After 12 h, the remaining solvent was distilled off at reduced pressure. The residue was taken up in water (20 mL). Conc. hydrochloric acid was added and the mixture was evaporated to dryness. To remove the inorganic salts from the product, the residue was triturated with methanol (7 × 50 mL) and filtered. The solvent was evaporated to about 10 mL. Ethanol was added and the resulting precipitate was filtered and dried in vacuo. This compound could not be obtained in analytically pure form but was pure enough for the preparation of the metal complexes. Yield: 3.08 g (86 %). Elemental analysis calcd. for $C_{30}H_{56}Cl_6N_6S_2$ (777.65): C 46.33, H 7.26, N

10.81, S 8.25, found C 44.10, H 5.81, N 9.69, S 7.95. IR (KBr, cm^{-1}) nu(tilde) = 2961(s), 2827(m), 1630(s), 1464(m), 1248(w), 1172(w), 1114(w), 1049(w), 941(s), 779(s), 729(m), 555(m), 416(w). ^{1}H NMR (400 MHz, 25°C, CD_3OD, TMS): δ = 3.02 (s, 18 H, CH_3N), 3.81-3.96 (m, 16 H, (CH_2CH_2)), 4.71 (s, 8 H, $ArCH_2N$), 7.35 (t, ^3J = 7.34 Hz, 2 H, Ar*H*), 7.67 ppm (d, ^3J = 7.34 Hz, 4 H, Ar*H*). $^{13}C\{^1H\}$NMR (100 MHz, 25°C, D_2O, TMS): 40.3 , 40.4, 50.0, 51.6, 61.9, 122.5, 130.8, 133.4, 149.6 ppm.

$[(L^2)Zn_2(\mu\text{-}OAc)]ClO_4$ (25·ClO_4). To a solution of H_2L^2·6HCl (500 mg, 0.643 mmol) in methanol (20 mL) was added a solution of $Zn(OAc)_2$·$2H_2O$ (283 mg, 1.28 mmol) in methanol (5 mL). A solution of triethylamine (520 mg, 5.14 mmol) in methanol (5 mL) was added and the resulting clear solution was stirred for 2 days at room temperature. Solid $LiClO_4$·$3H_2O$ (1.00 g, 6.23 mmol) was then added. The resulting colourless precipitate was isolated by filtration, washed with methanol and dried in air. The product was recrystallized from an acetonitrile/ethanol mixture. Yield: 468 mg, 0.550 mmol (86%). M.p. 320–321°C. Elemental analysis calcd. for $C_{32}H_{51}ClN_6O_6S_2Zn_2 \cdot H_2O$ (846.15 + 18.02): C 44.48, H 6.18, N 9.73, S 7.42, found C 44.10, H 5.81, N 9.69, S 7.95. IR (KBr, cm^{-1}): nu(tilde) = 2979(s), 2993(s), 2851(s), 2805(s), 1583(s) ν_{as}(OAc), 1460(s), 1433(s) ν_s(OAc), 1395(m), 1365(m), 1350(w), 1312(w), 1295(m), 1269(m), 1203(w), 1171(m), 1095(vs) ν(ClO_4), 1042(s), 1060(s), 1003(m), 959(w), 915(m), 894(w), 824(m), 749(w), 728(w), 663(m), 622(s), 561(m), 533(w), 523(w), 482(w), 411(w). ^{1}H NMR (400 MHz, 25°C, CD_3CN, TMS, for atom labeling see Scheme S3): δ ($[(L^2)Zn_2]^{2+}$-fragment) = 2.38 (m, 4 H, C^8H or C^9H), 2.42 (s, 12 H, C^5H_3), 2.68 (d, ^2J = 11.25 Hz, 4 H, C^7HH), 2.78 (m, 4 H, C^8H or C^9H), 2.89 (s, 6 H, C^6H_3), 3.21 (m, 4 H, C^8H or C^9H), 3.48 (m, 4 H, C^8H or C^9H), 4.40 (d, ^3J = 11.25 Hz, 4 H, C^7HH), 6.91 (t, ^3J = 7.36 Hz, 2 H, C^4H), 7.07 ppm (d, ^3J = 7.36 Hz, 4 H, C^3H); δ (coligand) = 0.82 ppm (s, 3 H, C^2H_3). $^{13}C\{^1H\}$NMR (100 MHz, 25°C, CD_3CN, TMS): δ ($[(L^2)Zn_2]^{2+}$-fragment] = 47.2 (C^5), 50.2 (C^6), 58.4 (C^7), 60.0 (C^8), 64.7(C^9), 123.2 (C^4), 132.3 (C^3), 136.2 (C^2), 147.8 ppm (C^1); δ (coligand) = 19.1 (C^2), 175.5 ppm (C^1). The tetraphenylborate salt, $[(L^2)Zn_2(OAc)]BPh_4$ (**25**·BPh_4), was prepared by adding $NaBPh_4$ (342 mg, 1.00 mmol) to a solution of **25**·ClO_4 (85 mg, 0.100 mmol) in methanol (40 mL). The colorless microcrystalline solid was isolated by filtration, washed with ethanol and dried in air. This salt was additionally characterized by X-ray crystallography.

$[(L^2)Zn_2((2E,4E)$-hexa-2,4-dienoate$)]ClO_4$ (26·ClO_4). To a solution of $[(L^2)Zn_2(OAc)]ClO_4$ (300 mg, 0.354 mmol) in methanol (100 mL) was added a solution triethylammonium (2*E*,4*E*)-hexa-2,4-dienoate (prepared in situ from (2*E*,4*E*)-hexa-2,4-dienoic acid (397 mg, 3.54 mmol) and triethylamine (357 mg, 3.54 mmol)) in methanol (2 mL). After stirring for 12 h at ambient temperature, the solvent was removed under reduced pressure to a final volume of ca. 10 mL. The colourless solid was isolated by filtration and washed with 5 mL cold methanol. To remove traces of unreacted $[(L^2)Zn_2(OAc)]ClO_4$ this material was treated again with a ten fold molar excess of triethylammonium (2*E*,4*E*)-hexa-2,4-dienoate as described above. Recrystallization from a 1:1 mixed ethanol/acetonitrile solvent system then gave the title compound in analytically pure form. Yield: 240 mg, 0.267 mmol (75 %). M.p. 325–328°C. Elemental analysis calcd. for $C_{36}H_{55}ClN_6O_6S_2Zn_2 \cdot H_2O$ (898.22 + 18.02): C 47.19, H 6.27, N 9.17, S 7.00 found C 47.50, H 5.67, N 9.17, S 7.84. IR (KBr, cm^{-1}): nu(tilde) = 2991(s), 1713(m), 1650(m) ν(C=C), 1618(m) ν(C=C), 1585(m), 1559(s) $\nu_{as}(CO_2)$, 1484(m), 1460(s), 1434(s), 1406(s) $\nu_s(CO_2)$, 1375(m), 1352(m), 1333(w), 1311(w), 1296(m), 1269(m), 1204(w), 1172(w), 1096(s) $\nu(ClO_4)$, 1043(s), 998(m), 959(w), 916(m), 894(w), 874(w), 825(m), 804(s), 765(s), 726(w), 691(w), 666(m), 623(s), 561(w), 536(w), 523(w), 482(w), 456(w), 410(w). ^1H NMR (400 MHz, 25°C, CD_3CN, TMS, for atom labeling see Scheme S3): δ ($[(L^2)Zn_2]^{2+}$-fragment) = 2.41 (m, 4 H, C^8H or C^9H), 2.45 (s, 12 H, C^5H_3), 2.65 (d, ^2J = 11.74 Hz, 4 H, C^7HH), 2.80 (m, 4 H, C^8H or C^9H), 2.88 (s, 6 H, C^6H_3), 3.26 (m, 4 H, C^8H or C^9H), 3.51 (m, 4 H, C^8H or C^9H), 4.41 (d, ^2J = 11.74 Hz, 4 H,

C^7H*H*), 6.75 (t, ^{3}J = 7.33 Hz, 2 H, C^4*H*) 6.93 (d, ^{3}J = 7.33 Hz, 4 H, C^3*H*); δ (coligand) = 1.68 (d, ^{3}J = 4.89 Hz, 3 H, C^6H_3), 4.89 (d, ^{3}J = 15.16 Hz, 1 H, C^2*H*), 5.81 (m, 2 H, C^4*H*, C^5*H*), 6.34 ppm (dd, ^{3}J = 15.16 Hz, ^{3}J = 9.78 Hz, 1 H, C^3*H*). ^{13}C{^{1}H}NMR (100 MHz, 25°C, CD_3CN, TMS): δ ([$(L^2)Zn_2]^{2+}$-fragment) = 47.0 (C^5), 49.9 (C^6), 58.4 (C^7), 59.8 (C^8), 64.4 (C^9), 122.8 (C^4), 131.9 (C^3), 135.8 (C^2), 147.3 ppm (C^1); δ (coligand) = 18.5 (C^6), 126.3, 130.9, 136.6, 140.9 ($C^{2\text{-}5}$), 170.2 (C^1).

[$(L^2)Zn_2$((1*R*,4*R*,5*S*)-5-cyano-4-methylcyclohex-2-enecarboxylate)]ClO_4 (27a·ClO_4) and [$(L^2)Zn_2$((1*R*,4*R*,5*R*)-5-cyano-4-methylcyclohex-2-enecarboxylate)]ClO_4 (27b·ClO_4). A solution of [$(L^2)Zn_2$((2*E*,4*E*)-hexa-2,4-dienotate)]ClO_4 (50 mg, 56 μmol) in acrylonitrile (50 mL) was refluxed for 72 h. The reaction mixture was evaporated to dryness, redissolved in acetonitrile (20 mL) and filtered off from undissolved material. Ethanol (20 mL) was then added and the solution was concentrated in vacuum to about 10 mL by using a rotary evaporator. The resulting colourless solid was filtered, washed with ethanol and dried in air. Yield: 46 mg (87 %). M.p. 330–334°C: Elemental analysis calcd. for $C_{39}H_{58}ClN_7O_6S_2Zn_2$ (951.29): C 49.24, H 6.15, N 10.31, S 6.74, found C 48.90, H 6.07, N 10.20, S 7.32. IR (KBr, cm^{-1}): nu(tilde) = 2969(m), 2872(m), 2238(vw) ν(CN), 1588(s) $\nu_{as}(RCO_2)$, 1484 (m), 1461(s), 1433(m), 1407(m) $\nu_s(RCO_2)$, 1387(m), 1367(w), 1352 (w), 1312(w), 1296(m), 1269(m), 1203(w), 1171(w), 1096(s) ν(ClO_4), 1042(s), 1003(w), 959(w), 926 (m), 915(m), 894(w), 825(m), 766(m), 750(w), 728(w), 666(m), 623(s), 561(w), 535(w), 482 (w), 474(w). ^{13}C{^{1}H}NMR (100 MHz, 25°C, CD_3CN, TMS, major isomer **27a**, 55%, for atom labeling see Scheme S3): δ ([$(L^2)Zn_2]^{2+}$-fragment) = 47.53 (C^5), 47.56 ($C^{5'}$), 50.13* ($C^{6,6'}$), 58.70* ($C^{7,7'}$), 59.97 + 60.00 (C^8 + $C^{8'}$), 64.64* ($C^{9,9'}$), 123.16 (C^4), 132.28 (C^3), 132.32 ($C^{3'}$), 136.07 (C^2), 136.10 ($C^{2'}$), 147.79 (C^1); δ (coligand) = 17.32 (C^8), 25.42 (C^6), 30.36 (C^5), 34.93 (C^4), 44.91 (C^1), 122.90 (C^9), 127.17 (C^3), 130.63 (C^2), 176.22 (C^7). *Signal not resolved. ^{13}C{^{1}H}NMR (100 MHz, 25°C, CD_3CN, TMS, minor isomer **27b**, 45%): δ ([$(L^2)Zn_2]^{2+}$-

fragment) = 47.58 (C^5), 47.64 ($C^{5'}$), 50.13* ($C^{6,6'}$), 58.50 + 58.87 (C^7 + $C^{7'}$), 59.77 + 60.16 (C^8 + $C^{8'}$), 64.50 + 64.71 (C^9 + $C^{9'}$), 123.44 (C^4), 132.18 (C^3), 132.20 ($C^{3'}$), 136.16 (C^2), 136.02 ($C^{2'}$), 147.74 (C^1); δ (coligand) = 20.22 (C^8), 28.70 (C^6), 30.38 (C^5), 31.94 (C^4), 42.51 (C^1), 123.16 (C^9), 127.56 (C^3), 130.49 (C^2), 175.81 (C^7). *Signal not resolved. For the $[(L^2)Zn_2]^{2+}$-fragments of **27a,b** only the signals for the $N^{Bz}CH_3$ protons are resolved in the 400 MHz ^{1}H NMR spectrum. The same behaviour was found for compounds **18a,b** (vide supra). ^{1}H NMR (400 MHz, 25°C, CD_3CN, TMS): *δ* ($[(L^2)Zn_2]^{2+}$-fragment] = 2.40 (m, 4 H, C^8H or C^9H), 2.44 (s, 3 H, C^5H_3), 2.47 (s, 6 H, C^5H_3), 2.51 (s, 3 H, C^5H_3), 2.67 (m, 4 H, C^7HH), 2.81 (m, 4 H, C^8H or C^9H), 2.87 (s, 6 H, C^6H_3), 3.25 (m, 4 H, C^8H or C^9H), 3.48 (m, 4 H, C^8H or C^9H), 4.40 (m, 4 H, C^7HH), 6.86 (m, 2 H, C^4H), 7.01 (m, 4 H, C^3H). For the two coligands (**12a,b**) only the signals for the olefinic CH protons and the CH_3 protons are resolved in the 400 MHz ^{1}H NMR spectrum. The other resonances are obscured by the signals of the $[(L^2)Zn_2]^{2+}$ fragments: δ (coligand) = 0.88 (d, ^3J = 6.85 Hz, 3 H, C^8H_3 (**27a**)), 0.89 (d, ^3J = 6.85 Hz, 3 H, C^8H_3 (**27b**)), 1.37-1.79 (m, 5 H, CH_2, 3 × CH), 4.63 (m, 1 H, C*H*), 5.16 (m, 1 H, C*H*), 5.31 (m, 1 H, C*H*).

Hydrolysis of 27a,b. To a suspension of **27a,b**·ClO_4 (340 mg, 0.357 mmol) in water (50 mL) was added conc. hydrochloric acid (5mL), and the mixture was stirred for 3 days at ambient temperature. The resulting colourless solution was extracted with dichlormethane (4×20 mL). The combined organic phases were dried with anhydrous magnesium sulfate and evaporated to dryness to give 47 mg (80 %) of the acids **12a,b** in a 55:45 ratio. The analytical data are identical with those obtained for **12a**,**b** prepared by hydrolysis of **18a**,**b** (vide supra).

3. Kinetic Studies

Solubility considerations and the slow rate of the reactions at millimolar concentrations of acrylonitrile and room temperature dictated that all experiments were carried out in neat acrylonitrile [15.8 mol/l] at 77°C. In a typical experiment, a solution of triethylammonium sorbinate (prepared in situ from sorbinic acid (224 mg, 2.10 mmol) and triethylamine (202 mg, 2.10 mmol)) in acrylonitrile (50 mL) was stirred at 77°C for 192 h. Samples (2 mL) of the reaction mixture were removed at regular intervals, taken to dryness, redissolved in ca 0.5 mL CD_3OD, and then analyzed by ^1H NMR spectroscopy. The relative amounts of educt and products could be quantified by integration of characteristic signals. This procedure was carried out for at least three different concentrations to give reproducible values for the reaction rates. However, the rate data presented in Table S1 below should be taken as indicative rather than definitive.

a) Diels-Alder reaction between triethyl ammonium sorbinate and acrylonitrile.

A solution of triethylammonium sorbinate (prepared in situ from sorbinic acid (224 mg, 2.10 mmol) and triethylamine (202 mg, 2.10 mmol)) in acrylonitrile (50 mL) was stirred at 77°C for 192 h. Samples (2 mL) of the reaction mixture were removed at regular intervals, taken to dryness, redissolved in ca 0.5 mL CD_3OD, and then analyzed by ^1H NMR spectroscopy. The relative amounts of triethyl ammonium sorbinate and the Diels-Alder adducts **13a-d** could be quantified by integration of the respective methyl proton signals at 1.85 ppm (for **10**) and at 1.18 (**13a**), 1.21 (**13b**), 1.08 (**13c**), and 1.06 ppm (**13d**). The pseudo first-order rate constant k' was derived from a plot of $\ln([\mathbf{10}]_t/[\mathbf{10}]_0)$ versus time (see Figure S1). The reaction rates are summarized in Table S1.

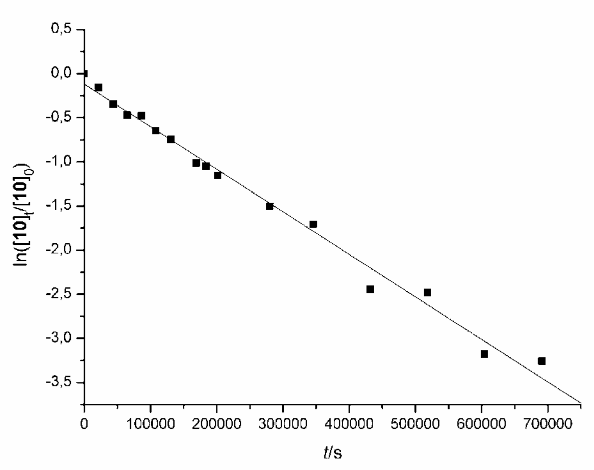


Figure S1. Plot of ln([**10**]$_t$/[**10**]$_0$) vs *t*.

b) Diels-Alder reaction of triethyl ammonium sorbinate with acrylonitrile in the presence of zinc acetate. In this experiment, the influence of zinc(II) salts on the above Diels-Alder reaction was examined. A solution of triethyl-ammonium sorbinate (prepared in situ from sorbinic acid (224 mg, 2.10 mmol), zinc acetate dihydrate (461 mg, 2.10 mmol) and triethylamine (202 mg, 2.10 mmol)) in acrylonitrile (50 mL) was stirred at 77°C for 192 h. Analysis was as described above. The results are listed in Table S1.

c) Diels-Alder Reaction of 16 with acrylonitrile. A solution of $[(L^1)Zn_2((2E,4E)$-hexa-2,4-dienoate$)]ClO_4$ (**16**·ClO_4) (101 mg, 0.100 mmol) in acrylonitrile (50 mL) was stirred at 77°C for 56 h. Samples (2 mL) of the reaction mixture were removed at regular intervals, taken to dryness, redissolved in ca 0.5 mL CD_3OD, and then analyzed by ^1H NMR spectroscopy. The relative amounts of **16** and the Diels-Alder adducts **18a**,**b** could be quantified by integration of the respective *tert*-butyl methyl proton signals at 1.16 ppm (for **16**) and at 1.25 ppm (for **18a**,**b**) (see Figure S2). The pseudo first-order rate constants *k'* were derived from plots of ln([**16**]$_t$/[**16**]$_0$) versus time. This procedure was carried out for four different concentrations of **16** to give reproducible values for the reaction rates. Again, the data presented in Table S1 should be taken as indicative rather than definitive.

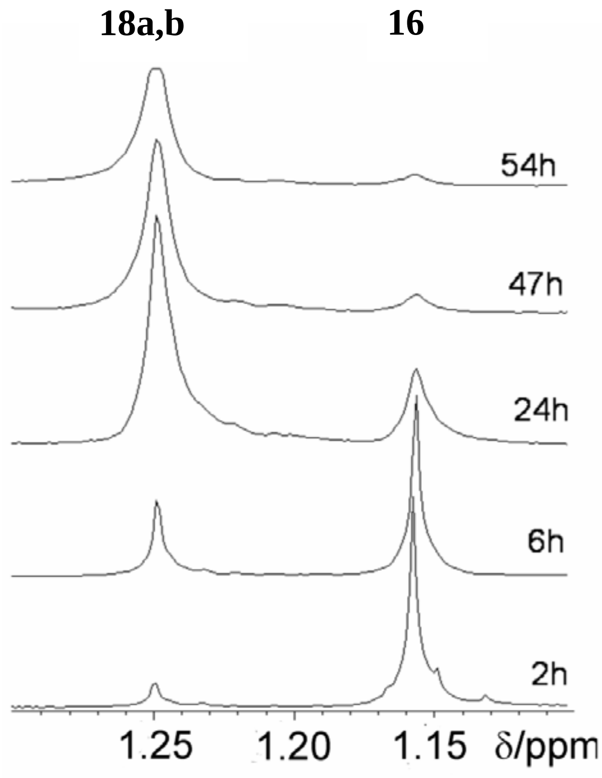


Figure S2. NMR spectral changes during the reaction of **17** with acrylonitrile in the δ = 1.30-1.10 ppm region.

d) Diels-Alder Reaction of 26 with acrylonitrile. A solution of $[(L^2)Zn_2((2E,4E)$-hexa-2,4-dienoate$)]ClO_4$ (**26**$\cdot ClO_4$) (100 mg, 0.111 mmol) in acrylonitrile (50 mL) was stirred at 77°C for 76 h. Samples (2 mL) of the reaction mixture were removed at regular intervals, taken to dryness, redissolved in ca 0.5 mL CD_3OD, and then analyzed by ^1H NMR spectroscopy. The relative amounts of educt **26** and the Diels-Alder adducts **27a**,**b** were quantified by integration of the respective aromatic proton resonances at 6.93 ppm (for **26**) and at 7.01 ppm (for **27a**,**b**) (Figure S4). The pseudo first-order rate constants k' were derived from plots of $\ln([\mathbf{26}]_t/[\mathbf{26}]_0)$ versus time (see Figure S4). Again, the data presented in Table S1 should be taken as indicative rather than definitive.

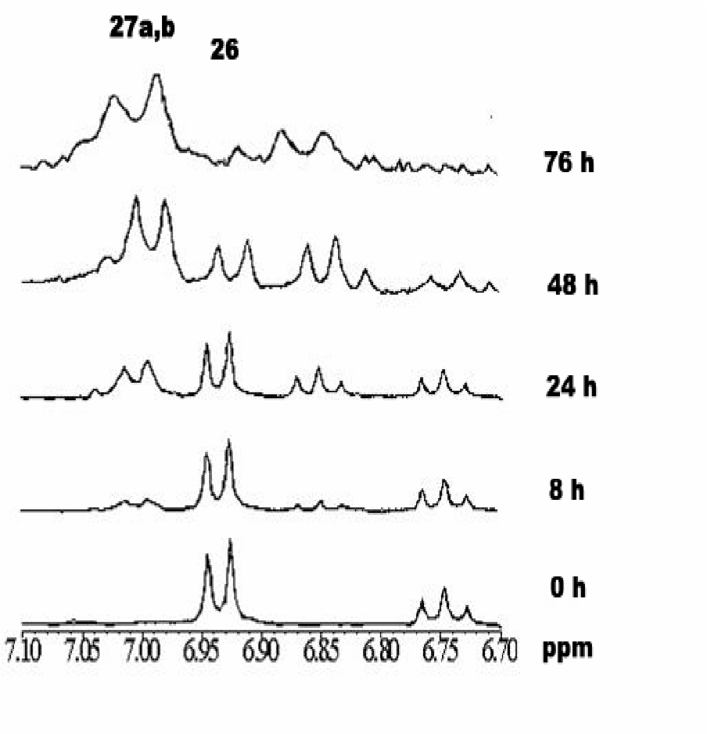


Figure S3. NMR spectral changes during the reaction of **26** with acrylonitrile in the δ = 6.70-7.10 ppm region.

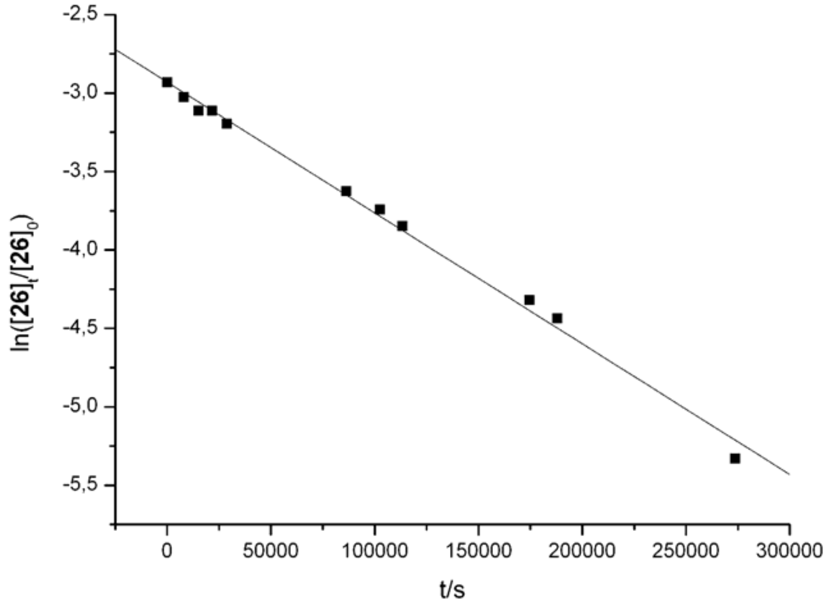


Figure S4. Plot of ln([**26**]$_t$/[**26**]$_0$) vs *t*.

Table S1. Rate constants for the investigated Diels-Alder reactions at 77°C.

No.	conditions	k'[a]/ s^{-1}	k[a]/ $M^{-1}s^{-1}$
1	**10** (42 mM), NEt_3 (42 mM), neat acrylonitrile	4.8×10^{-6}	3.0×10^{-7}
2	**10** (17 mM), NEt_3 (17 mM), neat acrylonitrile	4.9×10^{-6}	3.1×10^{-7}
3	**10** (10 mM), NEt_3 (10 mM), neat acrylonitrile	4.7×10^{-6}	3.0×10^{-7}
4	**10** (42 mM), NEt_3 (42 mM), neat acrylonitrile 2 equiv. $Zn(OAc)_2(H_2O)_2$	4.3×10^{-6}	2.7×10^{-7}
5	**16** (1.0 mM), neat acrylonitrile	1.3×10^{-5}	8.2×10^{-7}
6	**16** (2.0 mM), neat acrylonitrile	1.4×10^{-5}	8.9×10^{-7}
7	**16** (3.0 mM), neat acrylonitrile	1.2×10^{-5}	7.6×10^{-7}
8	**16** (6.0 mM), neat acrylonitrile	1.5×10^{-5}	$1.1\times10^{-6}1$
	10 (42 mM), NEt_3 (42 mM), neat acrylonitrile	4.8×10^{-6}	3.0×10^{-7}
9	**26** (2.24 mM), neat acrylonitrile	8.3×10^{-6}	5.3×10^{-7}
10	**26** (3.0 mM), neat acrylonitrile	8.2×10^{-6}	5.2×10^{-7}
11	**26** (1.0 mM), neat acrylonitrile	8.0×10^{-6}	5.1×10^{-7}

[a] pseudo-first-order rate constant, [b] $k = k'$/[acrylonitrile] = k'/15.8 $mol\cdot l^{-1}$

4. Crystal structure determinations

Single crystals of $[(L^1)Ni_2$(3,4-dimethyl-6-phenylcyclohex-3-enecarboxylate)]-$\cdot BPh_4\cdot 2MeCN$ (**8**$\cdot BPh_4\cdot 2MeCN$), $[(L^1)Zn_2$((4*R*,5*S*)-5-cyano-4-methylcyclohex-1-enecarboxylate)]$BPh_4\cdot EtOH$ (**15**$\cdot BPh_4\cdot EtOH$), and $[(L^1)Ni_2$((2*E*,4E)-hexa-2,4-dienoate)]BPh_4 (**16**$\cdot BPh_4$) and $[(L^2)Zn_2(OAc)]BPh_4$ (**25**$\cdot BPh_4$) were grown by recrystallization from a mixed acetonitrile/ethanol solvent system. Crystals of **13a,b,d** suitable for crystal structure determination were grown by recrystallization from water. The crystals were mounted on glass fibers using perfluoropolyether oil. Intensity data were collected at 210(2) K, using a Bruker SMART CCD diffractometer. Graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) was used throughout. Crystallographic data of the compounds are listed in Table S2. The data were processed with SAINT[3] and corrected for absorption using SADABS[4] (transmission factors: 1.00–0.90 (**8**·BPh_4·$(MeCN)_2$), 1.00-0.84 (**15**·BPh_4·EtOH), 1.00-0.81 (**16**·BPh_4), and 1.00-0.83 (**25**·BPh_4). The structures were solved by using the program SHELXS-86.[5] Refinements were carried out with the program SHELXL-97.[6] PLATON was used to search for higher symmetry.[7] ORTEP-3 was used for the artwork of the structures.[8] Where appropiate all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and given isotropic thermal parameters 1.2 times (1.5 times for CH_3 groups) the thermal parameter of the atoms to which they were attached.

In the crystal structure of **15**·BPh_4·EtOH·a *tert*-butyl group and the coligand were found to be disordered over two positions at site occupancies of 0.54(2)/0.46(2) (C(36a)-C(38a)/C(36b)-C(38b)) and of 0.76(1)/0.24(1) (C(41a)-N7(a)/C(41b)-N7(b)), respectively. The C and N atoms of the disordered groups and the ethanol solvate molecule were refined isotropically. In the crystal structure of **16**·BPh_4 a *tert*-butyl group was found to be disordered over two positions. The site occupancies of the respective positions were refined as follows: C(32a)-C(34a)/C(32b)-C(34b) 0.58(2)/0.42(2).

CCDC-264275 (**8**·BPh_4), CCDC-264276 (**13a**), CCDC-264277 (**13b**), CCDC-264278 (**13d**), CCDC-264279 (**15**·BPh_4·EtOH), CCDC-264280 (**16**·BPh_4) and CCDC-278590 (**25**·BPh_4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

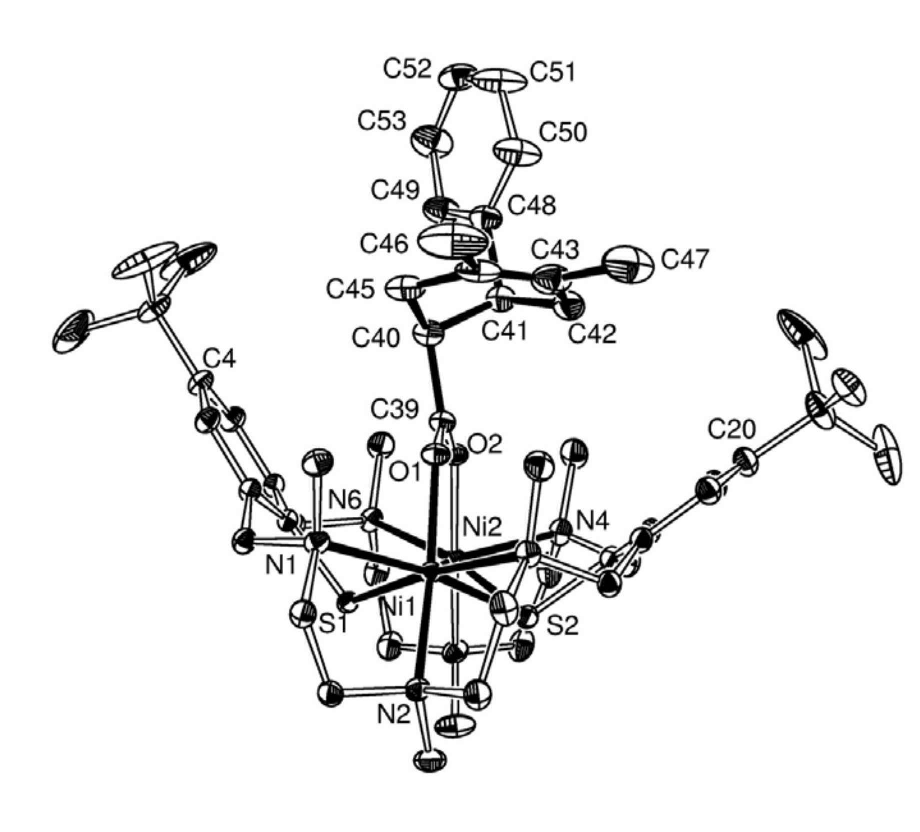


Figure S5. Structure of the dinickel complex **8** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths [Å] for **8**: Ni(1)···Ni(2) 3.487(1), Ni(1)−O(1) 2.043(2), Ni(1)−N(1) 2.285(2), Ni(1)−N(2) 2.173(2), Ni(1)−N(3) 2.223(2), Ni(1)−S(1) 2.480(1), Ni(1)−S(2) 2.4487(8), Ni(2)−O(2) 1.994(2), Ni(2)−N(4) 2.265(2), Ni(2)−N(5) 2.159(2), Ni(2)−N(6) 2.293(2), Ni(2)−S(1) 2.4982(7), Ni(2)−S(2) 2.4256(9).

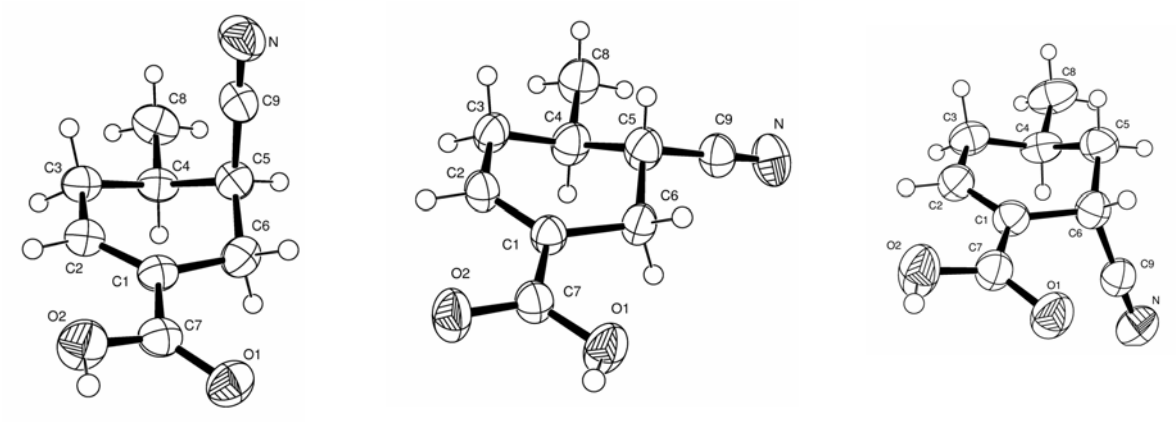


Figure S6. Molecular structures of **13a** (left), **13b** (middle), and **13d** (right) with thermal ellipsoids drawn at the 50% probability level. Note that the labeling is different from the one used in Schem

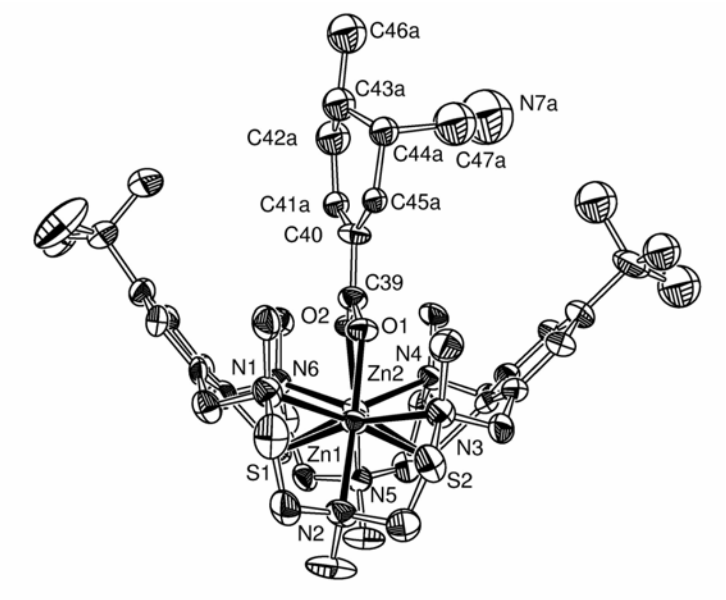


Figure S7. Structure of the dizinc complex **15** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths [Å] for **15**: Zn(1)···Zn(2) 3.439(1), Zn(1)−O(1) 2.031(6), Zn(1)−N(1) 2.331(9), Zn(1)−N(2) 2.244(7), Zn(1)−N(3) 2.348(8), Zn(1)−S(1) 2.571(3), Zn(1)−S(2) 2.508(3), Zn(2)−O(2)

2.031(6), Zn(2)−N(4) 2.245(8), Zn(2)−N(5) 2.233(8), Zn(2)−N(6) 2.419(8), Zn(2)−S(1) 2.506(3), Zn(2)−S(2) 2.565(3).

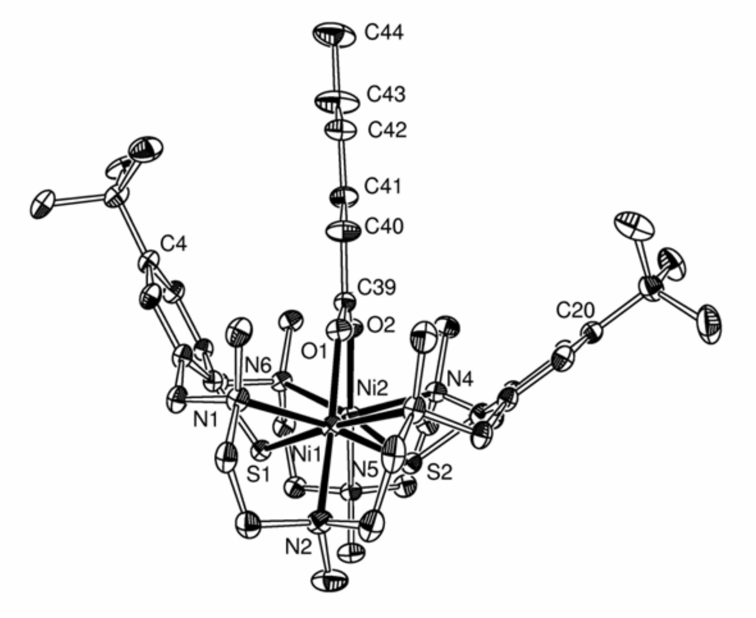


Figure S8. Structure of the dinickel complex **16** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths [Å] for **16**: Ni(1)···Ni(2) 3.472(1), Ni(1)−O(1) 2.011(2), Ni(1)−N(1) 2.293(2), Ni(1)−N(2) 2.164(3), Ni(1)−N(3) 2.239(3), Ni(1)−S(1) 2.494(1), Ni(1)−S(2) 2.438(1), Ni(2)−O(2) 1.998(2), Ni(2)−N(4) 2.235(3), Ni(2)−N(5) 2.150(2), Ni(2)−N(6) 2.309(3), Ni(2)−S(1) 2.505(1), Ni(2)−S(2) 2.434(1).

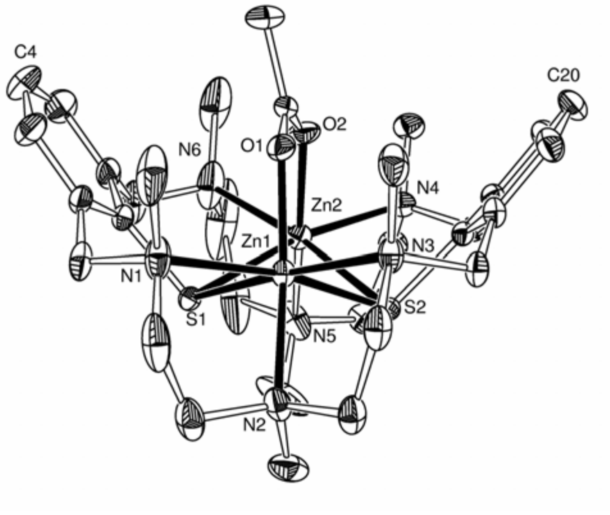


Figure S9. Structure of the dizinc complex **25** with thermal ellipsoids drawn at the 30%

probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths [Å] for **25**: Zn(1)···Zn(2) 3.434(1), Zn(1)−O(1) 2.022(2), Zn(1)−N(1) 2.396(2), Zn(1)−N(2) 2.217(2), Zn(1)−N(3) 2.283(2), Zn(1)−S(1) 2.5136(5), Zn(1)−S(2) 2.5374(5), Zn(2)−O(2) 2.021(2), Zn(2)−N(4) 2.327(2), Zn(2)−N(5) 2.184(2), Zn(2)−N(6) 2.282(2), Zn(2)−S(1) 2.5846(6), Zn(2)−S(2) 2.5348(2).

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Table S2. Crystallographic data for compounds **8**·BPh_4·2MeCN, **13a**, **13b**, **13d**, **15**·BPh_4·EtOH, **16**·BPh_4 and **25**·BPh_4.

Compound	**8**·BPh_4·2MeCN	**13a**	**13b**	**13d**	**15**·BPh_4·EtOH	**16**·BPh_4	**25**·BPh_4
Formula	$C_{81}H_{107}BN_8Ni_2O_2S_2$	$C_9H_{11}NO_2$	$C_9H_{11}NO_2$	$C_9H_{11}NO_2$	$C_{73}H_{100}BN_7O_3S_2Zn_2$	$C_{68}H_{91}BN_6Ni_2O_2S_2$	$C_{56}H_{71}BN_6O_2S_2Zn_2$
M_r [g/mol]	1417.10	165.19	165.19	165.19	1329.27	1216.82	1065.86
Space group	$P1$-bar	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P1$-bar	$P2_1/n$
a, Å	13.396(3)	6.8281(12)	6.9660(16)	9.710(2)	18.166(4)	13.184(3)	18.2959(7)
b, Å	15.493(3)	13.846(2)	6.2217(15)	8.213(2)	20.966(4)	15.618(3)	14.4608(4)
c, Å	20.135(4)	9.1194(16)	19.767(5)	10.932(2)	18.601(4)	17.379(3)	20.4461(8)
α, deg	67.77(3)	90	90	90	90.00	109.00(3)	90.00
β, deg	76.48(3)	91.946(3)	98.061(5)	92.17(3)	91.01(3)	91.31(3)	105.549(3)
γ, deg	86.57(3)	90	90	90	90.00	106.90(3)	90.00
V, $Å^3$	3759(1)	861.7(3)	848.2(3)	871.2(3)	7083(2)	3210.0(11)	5211.5(3)
Z	2	4	4	4	4	2	4
$d_{calcd.}$, g/cm^3	1.252	1.273	1.294	1.259	1.246	1.259	1.358
Cryst. size, mm^3	0.25×0.25×0.25	0.40×0.25×0.25	0.30×0.20×0.20	0.25×0.20×0.20	0.35×0.30×0.20	0.28×0.25×0.25	0.32×0.20×0.10
μ(Mo Kα), mm^{-1}	0.608	0.091	0.092	0.090	0.786	0.700	1.049
2θ limits, deg	2.24–58.48	5.36–57.68	4.16–57.36	5.50–57.8	2.92–57.86	2.50–58.10	6.64–56.00
Measured refl.	39885	5130	7179	5257	21040	24617	24567
Independent refl.	17984	2033	2052	2069	12713	14627	12538
Observed refl.[a]	14147	1294	1046	1276	3944	8955	8552
No. parameters	865	110	110	110	707	758	619
$R1^b$ ($R1$ all data)	0.0388 (0.1161)	0.0401 (0.0922)	0.0647 (0.1755)	0.0434 (0.1165)	0.0799 (0.1929)	0.0399 (0.0914)	0.0355 (0.0777)
w$R2^c$ (w$R2$ all data)	0.0535 (0.1289)	0.0713 (0.1065)	0.1296 (0.2069)	0.0751 (0.1370)	0.2443 (0.2696)	0.0829 (0.1233)	0.0610 (0.0835)
Max, min peaks, e/$Å^3$	1.101, –0.507	0.168, –0.142	0.633, –0.295	0.202, –0.179	0.692, –0.724	0.558, –0.727	0.596, –0.408

[a] Observation criterion: $I > 2\sigma(I)$. [b] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.