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Chiral acyclic diaminocarbene complexes of palladium(II), platinum(II) and gold(I) from metal-mediated coupling of isocyanides with chiral amino acid amides

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Materials and instrumentation. Solvents, isocyanides and amino acid amides were obtained from commercial sources and used as received without further purification. Complexes *cis*-[$MCl_2(CNR)_2$] (**1**, **2**)[S1-S3] and [AuCl(CNR)] (**3**, **4**)[S4,S5] were synthesized according to the previously reported methods. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX and Vertex 70 instruments in KBr pellets. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ESI mass-spectra were obtained on a VARIAN 500-MS LC ion trap mass-spectrometer in MeOH (or in MeCN) (ion spray voltage: +5 kV, capillary voltage: 30 V, RF loading: 100%). ^{1}H, $^{13}C\{^{1}H\}$ and all 2D NMR spectra were recorded on a Bruker Avance II+ 400MHz (UltraShield™ Magnet) and Bruker Avance II+ 500MHz (UltraShield™ Plus Magnet) spectrometers at ambient temperature.

Computational Details. The single point calculations for model structures of dimers **(*L/D*-7)$_2$** carried out using the PBE0-D3/def2-TZVP (refs. S6,S7) level of theory with the help of Gaussian-09 program package.[S8] The topological analysis of the electron density distribution with the help of the atoms in molecules (QTAIM) method developed by Bader,[S9] and diagrams of electron localization function (ELF) performed by using the Multiwfn program (version 3.7).[S10]The Cartesian atomic coordinates for all model structures are presented in **Tables S4**–**S5**.

Synthetic work. A solution of any of *cis*-[$MCl_2(CNXyl)_2$] (M = Pd **1**; M = Pt **2**) or [AuCl(CNR^1)] (R^1 = Cy **3**; Xyl **4**) (0.1 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of the amino acid amide (L-$HProNH_2$ L-**5**, D-$HProNH_2$ D-**5**, *L*-$HPheNH_2$ L-**6**) (0.105 mmol) in CH_2Cl_2 (0.5 mL) and heated at 40 °C during 10 h (for **1** and **2**) or 8 h (for **3** and **4**). Then solvent was removed with the stream of nitrogen, washed with three 2-mL portions of Et_2O (for **1** and **2**) or hexane (for **3** and **4**) and dried at RT yielding product as colourless solids.

cis-[$PdCl_2$(CNXyl){C(L-$ProNH_2$)NHXyl}] (L-**7**) colourless solid, 84%. ^{1}H NMR (400 MHz, CD_3OD) δ: 7.40−7.06 (m, 6*H*, $C_{ar}H$), 6.84 (d, $^{3}J_{HH}$ 6.9 Hz, 0.9*H*, NH), 5.80 (dd, $^{3}J_{HH}$ 8.4 and 2.2 Hz, 1*H*, NCH), 3.93−3.84 (m, *H*) and 3.70 (dt, $^{3}J_{HH}$ 10.9 and 7.6 Hz, 1*H*, NCH_2), 2.61, 2.31 and 2.10 (3s, 12*H*, Me from Xyl), 2.58−2.12 (m, overlapped with Me signals, 4*H*, C−CH_2). ^{13}C NMR (101 MHz, CD_3OD, 25°C) δ: 175.1 (C=O), 174.8 ($C_{carbene}$=N), 138.1, 137.6, 136.1, 135.9, 130.1, 129.0 and 127.8 (aryls), 67.5 (NCH), 49.9 (NCH_2), 30.4 and 23.4 (C−CH_2 from *L*-Pro), 18.8 and 17.7 (Me from Xyl). IR (KBr, ν/cm^{-1}): 3179, 3064 (N−H), 2968, 2872 (C−H), 2200 (C≡N), 1683 (C=O), 1543 ($C_{carbene}$−N). MS (ESI^+), *m/z*: 519 $[M - Cl]^+$, 701 $[2M - 3HCl - Cl - 2CNXyl]^+$, 868 $[2M - 2HCl - Cl - CNXyl]^+$, 904 $[2M - HCl - Cl - CNXyl]^+$ (calcd. 519, 701, 868, 904). MS (ESI^-), *m/z* ;384 $[M - HCl - H - CNXyl]^-$], 517 $[M - HCl - H]^-$, 771 $[2M - 2HCl - 2CNXyl - H]^-$, 902 $[2M - 2HCl - CNXyl - H]^-$, 997 $[2M - 3HCl - H]^-$ (calcd. 384, 517, 771, 902, 997). Found (%): C, 48.59, H, 5.21; N, 9.37. Calc. for $C_{23}H_{28}N_4Cl_2OPd{\bullet}0.25CH_2Cl_2$ (%): C, 48.56; H, 4.99; N, 9.74.

cis-[$PdCl_2$(CNXyl){C(D-$ProNH_2$)NHXyl}] (D-**7**): colourless solid, 91%. ^{1}H NMR (400 MHz, CD_3OD) δ: 7.39–7.11 (m, 6H, arylsH), 6.84 (d, ^{3}J 6.9 Hz, 0.8H, NH), 5.80 (dd, ^{3}J 8.4 and 2.2 Hz, 1H, NCH), 3.89 and 3.70 (2m, 2H, NCH_2), 2.61, 2.31, and 2.10 (3s, 12H, Me from Xyl), 2.45–2.20 (m, 4H, C–CH_2). ^{13}C NMR (101 MHz, CD_3OD) δ: 175.2 (C=O), 174.8 ($C_{carbene}$=N), 138.1, 137.6, 136.1, 135.9, 130.1, 129.0, and 127.9 (aryls), 67.5 (NCH), 49.9 (NCH_2), 30.4 and 23.4 (C–CH_2 from D-Pro), 18.8 and 17.6 (Me from Xyl). IR (KBr, ν/cm^{-1}): 3181 and 3066 (N–H), 2962 and 2857 (C–H), 2200 (C≡N), 1681 (C=O), 1543 ($C_{carbene}$–N). MS (ESI^+), *m/z*: 519 $[M - Cl]^+$, 701 $[2M - 3HCl - Cl - 2CNXyl]^+$, 868 $[2M - 2HCl - Cl - CNXyl]^+$, 904 $[2M - HCl - Cl - CNXyl]^+$, 1071 $[2M - Cl]^+$ (calcd. 519, 701, 868, 904, 1071). MS (ESI^-), *m/z*: 384 $[M - HCl - H - CNXyl]^-$, 517 $[M - HCl - H]^-$, 771 $[2M - 2HCl - 2CNXyl - H]^-$, 902 $[2M - 2HCl - CNXyl - H]^-$, 997 $[2M - 3HCl - H]^-$ (calcd. 384, 517, 771, 902, 997). Calcd. for $C_{23}H_{28}N_4Cl_2OPd{\cdot}0.75CH_2Cl_2$ (%): C, 46.19; H, 4.82; N, 9.07. Found (%): C, 46.74; H, 4.86; N, 9.49.

cis–[PtCl₂(CNXyl){C(L–ProNH₂)NHXyl}] (L–**8**)*:* colourless solid, 64%. ^{1}H NMR (400 MHz, CD_3OD, major rotamer) δ: 7.43–7.01 (m, 6H, arylsH), 6.83–6.71 (m, 0.9H, NH), 5.76–5.66 (m, 1H, NCH), 3.93–3.82 and 3.72–3.60 (2m, 2H, NCH_2), 2.52, 2.27 and 2.08 (3s, 12H, Me from Xyl, overlapped with CH_2), 2.60–1.98 (m, 4H, C–CH_2, overlapped with Me). ^{13}C NMR (101 MHz, CD_3OD) δ: 175.4 (C=O), 168.9 ($C_{carbene}$=N), 138.8, 138.0, 135.8, 135.7, 129.4, 128.7, 128.0 and 127.8 (aryls and C≡N), 67.1 (NCH), 49.0 (NCH_2), 30.0 and 23.4 (C–CH_2 from L–Pro), 18.6, 17.7 and 17.5 (Me). IR (KBr, ν/cm^{-1}): 3222 (N–H), 2938 and 2865 (C–H), 2188 (C≡N), 1684 (C=O), 1543 ($C_{carbene}$–N). MS (ESI$^+$), *m/z*: 665 [M + Na]$^+$, 738 [M – Cl + CNXyl]$^+$, 607 [M – Cl]$^+$ (calcd. 665, 738, 607). MS (ESI$^-$), *m/z*: 641 [M – H]$^-$ (calcd. 641). Calcd. for $C_{23}H_{28}N_4Cl_2OPt$ (%): C, 43.00; H, 4.39; N, 8.72. Found (%): C, 43.38; H, 4.34; N, 8.48.

cis–[PtCl₂(CNXyl){C(D–ProNH₂)NHXyl}] (D–**8**)*:* colourless solid, 76%. ^{1}H NMR (400 MHz, CD_3OD, major rotamer) δ: 7.42–7.02 (m, 6H, arylsH), 6.83–6.77 (m, 0.9H, NH), 5.75 (dd, ^{3}J 8.2 and 2.2 Hz, 1H, NCH), 3.96–3.85 and 3.80–3.63 (2m, 2H, NCH_2), 2.52, 2.28 and 2.08 (3s, 12H, Me from Xyl, overlapped with CH_2), 2.57–2.00 (m, 4H, C–CH_2, overlapped with Me). ^{13}C NMR (101 MHz, CD_3OD) δ: 175.5 (C=O), 168.9 ($C_{carbene}$=N), 138.6, 138.0, 135.7, 135.6, 129.4, 128.7, 127.9 and 127.7 (aryls and C≡N), 67.0 (NCH), 49.0 (NCH_2), 30.0 and 23.4 (C–CH_2 from D–Pro), 18.6, 17.6 and 17.5 (Me). IR (KBr, ν/cm^{-1}): 3230 (N–H), 2980, 2930 and 2866 (C–H), 2186 (C≡N), 1627 (C=O), 1543 ($C_{carbene}$–N). MS (ESI$^+$), *m/z*: 665 [M + Na]$^+$, 738 [M – Cl + CNXyl]$^+$, 607 [M – Cl]$^+$ (calcd. 665, 738, 607). MS (ESI$^-$), *m/z*: 641 [M – H]$^-$ (calcd. 641). Calcd. for $C_{23}H_{28}N_4Cl_2OPt$ (%): C, 43.00; H, 4.39; N, 8.72. Found (%): C, 43.12; H, 4.23; N, 8.52.

cis–[PdCl₂(CNXyl){C(L–PheNH₂)NHXyl}] (L–**9**)*:* colourless solid, 65%. ^{1}H NMR (400 MHz, CD_3OD, major rotamer) δ: 7.90 (s, 1.3H, NH_2), 7.42–7.06 (m, 11H, arylsH), 7.00 (br s, 0.7H, NH), 5.67 (br s, 2.4H, CH_2Cl_2), 4.09 (dd, ^{3}J 8.4 and 6.0 Hz, 1H, NCH), 3.25 (dd, ^{3}J 14.1 and 6.0 Hz, 1H) and 3.05 (dd, ^{3}J 14.2 and 8.4 Hz, 1H, CH_2), 2.48, 2.41 and 2.23 (3s, 12H, Me from Xyl). ^{13}C NMR (101 MHz, CD_3OD) δ: 175.1 ($C_{carbene}$=N), 172.0 (C=O), 137.6, 135.9, 131.9 (C≡N), 130.9, 130.7, 130.4, 130.3, 129.6 and 129.1 (aryls), 55.8 (NCH), 38.8 (CH_2), 19.3 and 18.6 (Me from Xyl). IR (KBr, ν/cm^{-1}): 3421, 3326, 3221 and 3182 (N–H), 3058, 3020, 2972 and 2915 (C–H), 2199 (C≡N), 1683 (C=O), 1556 ($C_{carbene}$–N). MS (ESI+), *m/z*: 569 [M – Cl]$^+$, 837 [2M – 2CNXyl – 2HCl – Cl]$^+$, 968 [2M – CNXyl – 2HCl – Cl]$^+$, 1171 [2M – Cl]$^+$ (calcd. 569, 837, 968, 1171). MS (ESI$^-$), *m/z*: 434 [M – HCl – H – CNXyl]$^-$, 472 [M – H – CNXyl]$^-$ (calcd. 434, 472). Calcd. for $C_{27}H_{30}N_4Cl_2OPd{\cdot}0.5CH_2Cl_2$ (%): C, 51.10; H, 4.83; N, 8.67. Found (%): C, 51.26; H, 4.97; N, 8.77.

[AuCl{C(L–ProNH₂)NHXyl}] (L–**10**)*:* colourless solid, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23–7.05 (m, 3H, arylsH), 6.96, 6.36 and 5.57 (3br s, 3H, NH/NH_2), 5.05 (br d, ^{3}J 6.0 Hz, 1H, CH), 3.76–3.40 (m, 2H, NCH_2), 2.53–1.85 (m, 10H, CCH_2 from Pro and Me, overlapped with 2.26 s). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.0 ($C_{carbene}$=N), 180.1 (C=O), 138.5, 131.3, 131.0 and 128.9 (aryls), 68.2 (CH from Pro), 45.4 (NCH_2), 29.2 and 24.1 (CCH_2), 22.3 and 19.0 (Me). IR (KBr, ν/cm^{-1}): 3325, 3256, 3052 (N–H), 2956 and 2871 (C–H), 1677 (C=O), 1543 ($C_{carbene}$=N). MS (ESI$^+$), *m/z*: 500 [M + Na]$^+$, 573 [M – Cl + CNXyl]$^+$, 442 [M – Cl]$^+$ (calcd. 500, 573, 442). MS (ESI$^-$), *m/z*: 476 [M – H]$^-$ (calcd. 476). Calcd. for $C_{14}H_{19}N_3ClOAu$ (%): C, 35.20; H, 4.01; N, 8.80. Found (%): C, 35.46; H, 3.95; N, 8.65.

[AuCl{C(D–ProNH₂)NHXyl}] (D–**10**)*:* colourless solid, 86%. ^{1}H NMR (400 MHz, MeOD) δ: 7.31–7.06 (m, 3H, arylsH), 5.50 (s, 0.4H, $C_{carbene}$NH), 5.00 (dd, ^{3}J 8.4 and 2.3 Hz, 1H, CH), 3.76–3.46 (m, 2H, NCH_2), 2.55–1.95 (m, 10H, CCH_2 from Pro and Me, overlapped with 2.31 and 2.26 s). ^{13}C NMR (101 MHz, MeOD) δ: 192.8 ($C_{carbene}$=N), 177.4 (C=O), 140.3, 137.9, 137.4, 129.3, 129.2 and 129.0 (aryls), 69.2 (CH from Pro), 48.4 (NCH_2, overlapped with solvent), 31.0 and 25.0 (CCH_2), 19.1 and 19.0 (Me). IR (KBr, ν/cm^{-1}): 3325, 3246, 3180 (N–H), 2950 and 2874 (C–H), 1676 (C=O), 1541 ($C_{carbene}$=N). MS (ESI$^+$), *m/z*: 573 [M – Cl + CNXyl]$^+$, 442 [M – Cl]$^+$ (calcd. 573, 442). MS (ESI$^-$), *m/z*: 476 [M – H]$^-$ (calcd. 476). Calcd. for $C_{14}H_{19}N_3ClOAu$ (%): C, 35.20; H, 4.01; N, 8.80. Found (%): C, 35.33; H, 4.15; N, 8.72.

[AuCl{C(L–ProNH₂)NHCy}] (L–**11**)*:* colourless solid, 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.95 and 6.31 (2s, 2H, NH_2), 6.03 (d, ^{3}J 8.2 Hz, 1H, $C_{carbene}$NH), 4.95 (d, ^{3}J 7.5 Hz, 1H, CH from Pro), 4.12–4.06 (m, 1H, CH from Cy), 3.61–3.52 and 3.28–3.22 (2m, 2H, NCH_2), 2.30–2.01 (m, 6H, CCH_2 from Pro and α–CH_2 from Cy), 1.80–1.70 and 1.50–1.10 (2m, 6H, β– and γ–CH_2 from Cy). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.1 ($C_{carbene}$=N), 175.1 (C=O), 68.6 (CH from Pro), 59.9 (CH from Cy), 46.8 (NCH_2), 34.6 (β–CH_2 from Cy), 33.8 (α–CH_2 from Cy), 29.9, 25.0, 24.9 and 24.0 (CCH_2 from Pro and γ–CH_2 from Cy). IR (KBr, ν/cm^{-1}): 3295 and 3181 (N–H), 2930 and 2854 (C–H), 1673 (C=O), 1554 ($C_{carbene}$=N). MS (ESI$^+$), *m/z*: 529 [M – Cl + CNCy]$^+$, 875 [2M – Cl]$^+$ (calcd. 529, 875). MS

(ESI⁻), *m/z*: 454 [M – H]⁻, 490 [M + Cl]⁻ (calcd. 454, 490). Calcd. for $C_{12}H_{21}N_3ClOAu$ (%): C, 31.63; H, 4.64; N, 9.22. Found (%): C, 33.08; H, 5.06; N, 8.96.

[AuCl{C(D–ProNH₂)NHCy}] (D–**11**)*:* colourless solid, 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.96 and 6.33 (2s, 2H, NH_2), 6.03 (d, ^{3}J 8.2 Hz, 1H, $C_{carbene}NH$), 4.96 (d, ^{3}J 7.6 Hz, 1H, CH from Pro), 4.16–4.02 (m, 1H, CH from Cy), 3.62–3.52 and 3.29–3.19 (2m, 2H, NCH_2), 2.35–1.92 (m, 6H, CCH_2 from Pro and α–CH_2 from Cy), 1.82–1.67 and 1.53–1.10 (2m, 6H, β– and γ–CH_2 from Cy). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.1 ($C_{carbene}$=N), 175.0 (C=O), 68.6 (CH from Pro), 59.8 (CH from Cy), 46.8 (NCH_2), 34.7 (β–CH_2 from Cy), 33.8 (α–CH_2 from Cy), 29.9, 25.2, 25.0, 24.8, 24.0 and 22.4 (CCH_2 from Pro and γ–CH_2 from Cy). IR (KBr, ν/cm⁻¹): 3293 and 3172 (N–H), 2930 and 2854 (C–H), 1675 (C=O), 1554 ($C_{carbene}$=N). MS (ESI⁺), *m/z*: 529 [M – Cl + CNCy]⁺, 478 [M + Na]⁺, 875 [2M – Cl]⁺ (calcd. 529, 478, 875). MS (ESI⁻), *m/z*: 454 [M – H]⁻, 490 [M + Cl]⁻ (calcd. 454, 490). Calcd. for $C_{12}H_{21}N_3ClOAu$ (%): C, 31.63; H, 4.64; N, 9.22. Found (%): C, 31.48; H, 4.72; N, 9.03.

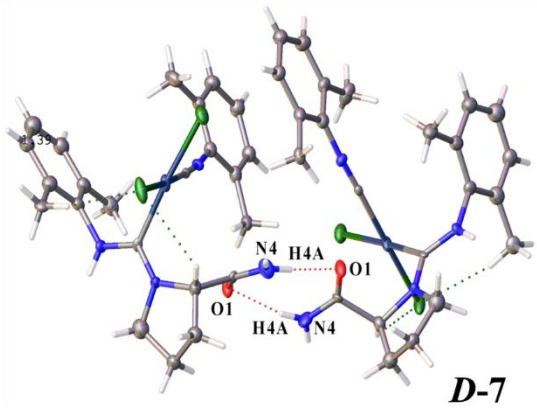

Figure S1. Views of hydrogen bonds in dimer of D-**7**.

Table S1. Selected bond lengths and angles in the structure of D-**7**.

	Length, Å		**Angle, °**
C1–N1	1.097(19)	N1–C1–Pd1	175.1(14)°
C2–N1	1.326(16)	N2–C10–Pd1	122.6(12)°
C10–N2	1.328(19)	N3–C10–N2	120.3(15)°
C10–N3	1.27(2)	N3–C10–Pd1	116.9(10)°
C10–Pd1	2.040(15)	O1–C24–N4	130.1(16)°
C11–N2	1.489(17)	C1–N1–C2	173.2(16)°
C20–N3	1.44(3)	C10–N2–C11	123.7(14)°
C23–N3	1.49(2)	C10–N3–C20	124.5(17)°
C24–N4	1.28(2)	C10–N3–C23	128.9(15)°
C24–O1	1.203(19)	C20–N3–C23	106.6(16)°
Cl2–Pd1	2.306(5)	C1–Pd1–C10	91.6(6)°
Cl1–Pd1	2.348(5)	C1–Pd1–Cl2	176.8(5)°
		C1–Pd1–Cl1	86.9(5)°
		C10–Pd1–Cl2	91.0(5)°
		C10–Pd1–Cl1	175.9(5)°
		Cl2–Pd1–Cl1	90.7(2)°

Table S2. Selected bond lengths and angles in the structure of L-**7**.

	Length, Å		**Angle, °**
C1–N1	1.150(15)	N1–C1–Pd1	176.8(14)°
C2–N1	1.332(12)	N1–C2–C3	117.7(8)°
C10–N2	1.344(16)	N1–C2–C7	122.0(7)°
C10–N3	1.230(17)	N2–C10–Pd1	120.9(11)°

C10–Pd1	2.020(13)	N3–C10–N2	118.7(13)°
C11–N2	1.421(16)	N3–C10–Pd1	120.4(10)°
C20–N3	1.503(16)	N3–C20–C21	106.9(13)°
C23–N3	1.51(2)	N3–C23–C24	107.5(11)°
C24–N4	1.34(2)	N4–C24–C23	115.1(14)°
C24–O1	1.252(17)	O1–C24–C23	122.7(13)°
C25–Cl3	1.715(18)	O1–C24–N4	122.0(13)°
C25–Cl4	1.729(19)	C1–N1–C2	170.0(14)°
C25–Cl5	1.78(2)	C10–N2–C11	126.5(13)°
Cl1–Pd1	2.365(4)	C10–N3–C20	125.8(12)°
Cl2–Pd1	2.308(4)	C10–N3–C23	125.6(12)°
		C20–N3–C23	108.6(12)°
		C1–Pd1–C10	92.5(6)°
		C1–Pd1–Cl1	86.3(4)°
		C1–Pd1–Cl2	176.6(5)°
		C10–Pd1–Cl1	175.2(5)°
		C10–Pd1–Cl2	90.5(4)°
		Cl2–Pd1–Cl1	90.88(13)°

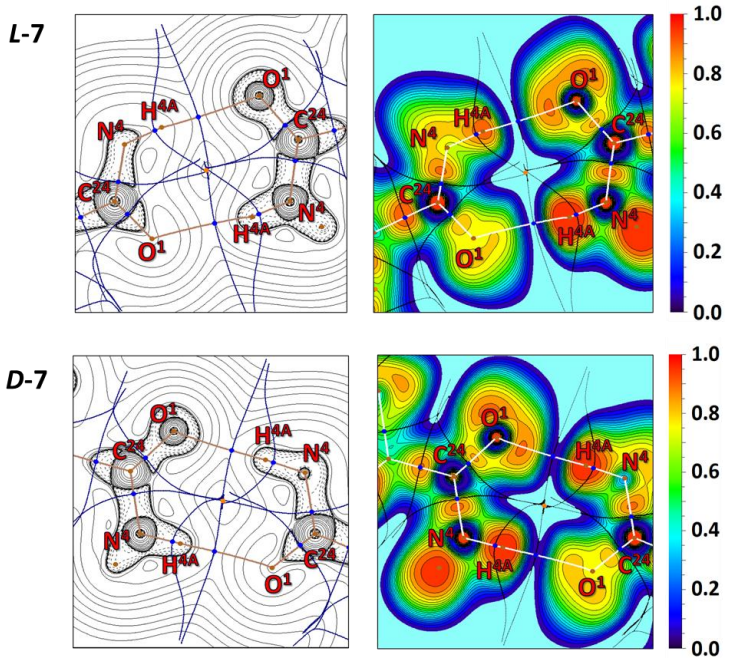

Figure S2. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(r)$ (left panel), visualization of electron localization function (ELF, right panel) for N4–H4···O1=C24 intermolecular contacts in **(**L/D-**7)**$_2$. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, ring critical points (3, +1) – in orange, bond paths are shown as pale brown lines (white for ELF diagram), length units – Å, and the color scale for the ELF map is presented in a.u.

Table S3. Values of the density of all electrons – ρ(**r**), Laplacian of electron density – $\nabla^2\rho$(**r**), energy density – H_b, potential energy density – V(**r**), and Lagrangian kinetic energy – G(**r**) (Hartree) at the bond critical points (3, –1), corresponding to XBs in all adducts, bond lengths – *l* (Å), as well as energies for these contacts E_{int} (kcal/mol), defined by three approaches. N4–H4···O1=C24

Crystal	ρ(**r**)	$\nabla^2\rho$(**r**)	H_b	V(**r**)	G(**r**)	E_{int}[a]	E_{int}[b]	E_{int}[c]	l
L-**7**	0.017	0.077	0.004	–0.011	0.016	3.5	4.3	5.7	2.099(11)
D-**7**	0.023	0.095	0.003	–0.017	0.020	5.3	5.4	7.2	1.98(7)

[a] $E_{int} = -V(\mathbf{r})/2$. [b] $E_{int} = 0.429G(\mathbf{r})$. [c] $E_{int} = 0.57G(\mathbf{r})$.

Table S4. Cartesian atomic coordinates for the structure of L-**7**.

	X	Y	Z
C	18.778334000	16.114820000	4.423004000
C	20.572622000	14.593593000	4.980179000
C	20.183030000	13.264035000	4.860489000
C	21.109393000	12.247458000	5.065475000
H	20.848172000	11.357770000	4.985709000
C	22.423184000	12.560437000	5.388774000
H	23.043544000	11.879282000	5.524821000
C	22.812776000	13.887569000	5.507087000
H	23.693817000	14.097411000	5.722955000
C	21.888577000	14.904147000	5.302102000
C	22.193758000	16.364719000	5.366762000
H	21.394683000	16.867403000	5.190626000
H	22.524435000	16.585115000	6.240164000
H	22.858813000	16.581815000	4.708566000
C	18.802143000	13.009284000	4.471155000
H	18.653752000	12.062072000	4.428851000
H	18.213621000	13.392333000	5.131854000
H	18.630441000	13.405143000	3.620659000
C	17.269748000	18.327515000	5.489203000
C	16.226507000	16.583077000	6.917221000
C	14.867264000	16.371998000	6.721866000
C	14.315342000	15.120078000	6.972250000
H	13.405969000	14.977515000	6.841775000
C	15.124827000	14.079239000	7.415239000
H	14.756187000	13.242515000	7.582666000
C	16.484070000	14.292744000	7.610594000
H	17.025928000	13.596352000	7.907258000
C	17.035992000	15.542237000	7.360209000
C	18.440688000	15.697514000	7.658745000
H	18.714420000	16.594844000	7.450169000
H	18.590962000	15.526467000	8.590726000
H	18.949517000	15.077935000	7.132001000
C	13.971202000	17.536574000	6.302265000
H	13.067435000	17.227185000	6.210599000
H	14.008906000	18.224401000	6.970063000
H	14.277053000	17.886893000	5.462816000
C	17.843314000	20.474702000	6.397191000
H	18.346688000	20.101285000	7.141755000
H	16.967424000	20.737799000	6.722705000
C	18.568388000	21.661114000	5.816629000
H	18.220633000	22.496964000	6.166755000
H	19.522390000	21.615307000	5.990949000
C	18.284851000	21.520394000	4.416125000
H	17.426861000	21.924429000	4.209352000
H	18.967157000	21.965311000	3.891404000
C	18.256714000	20.161722000	4.109335000
H	17.657500000	19.996376000	3.351963000
C	19.704698000	19.569729000	3.805297000
N	19.633272000	15.481582000	4.685770000
N	16.769771000	17.944175000	6.658582000
H	16.757391000	18.515303000	7.301575000
N	17.722107000	19.511500000	5.340623000
N	20.059659000	19.778382000	2.596021000
H	20.886265000	19.699676000	2.370276000
H	19.472804000	19.997881000	2.006916000
O	20.364840000	19.261602000	4.762812000
Cl	15.315294000	18.249876000	3.078906000
Cl	17.265419000	15.869774000	1.858625000
Pd	17.200054000	17.151293000	3.824832000
C	24.509666000	16.114820000	2.455696000
C	22.715378000	14.593593000	1.898521000
C	23.104970000	13.264035000	2.018211000
C	22.178607000	12.247458000	1.813225000
H	22.439828000	11.357770000	1.892991000

C	20.864816000	12.560437000	1.489926000
H	20.244456000	11.879282000	1.353879000
C	20.475224000	13.887569000	1.371613000
H	19.594183000	14.097411000	1.155745000
C	21.399423000	14.904147000	1.576598000
C	21.094242000	16.364719000	1.511938000
H	21.893317000	16.867403000	1.688074000
H	20.763565000	16.585115000	0.638536000
H	20.429187000	16.581815000	2.170134000
C	24.485857000	13.009284000	2.407545000
H	24.634248000	12.062072000	2.449849000
H	25.074379000	13.392333000	1.746846000
H	24.657559000	13.405143000	3.258041000
C	26.018252000	18.327515000	1.389497000
C	27.061493000	16.583077000	-0.038521000
C	28.420736000	16.371998000	0.156834000
C	28.972658000	15.120078000	-0.093550000
H	29.882031000	14.977515000	0.036925000
C	28.163173000	14.079239000	-0.536539000
H	28.531813000	13.242515000	-0.703966000
C	26.803930000	14.292744000	-0.731894000
H	26.262072000	13.596352000	-1.028558000
C	26.252008000	15.542237000	-0.481509000
C	24.847312000	15.697514000	-0.780045000
H	24.573580000	16.594844000	-0.571469000
H	24.697038000	15.526467000	-1.712026000
H	24.338483000	15.077935000	-0.253301000
C	29.316798000	17.536574000	0.576435000
H	30.220565000	17.227185000	0.668101000
H	29.279094000	18.224401000	-0.091363000
H	29.010947000	17.886893000	1.415884000
C	25.444686000	20.474702000	0.481509000
H	24.941312000	20.101285000	-0.263055000
H	26.320576000	20.737799000	0.155995000
C	24.719612000	21.661114000	1.062071000
H	25.067367000	22.496964000	0.711945000
H	23.765610000	21.615307000	0.887751000
C	25.003149000	21.520394000	2.462575000
H	25.861139000	21.924429000	2.669348000
H	24.320843000	21.965311000	2.987296000
C	25.031286000	20.161722000	2.769365000
H	25.630500000	19.996376000	3.526737000
C	23.583302000	19.569729000	3.073403000
N	23.654728000	15.481582000	2.192930000
N	26.518229000	17.944175000	0.220118000
H	26.530609000	18.515303000	-0.422875000
N	25.565893000	19.511500000	1.538077000
N	23.228341000	19.778382000	4.282679000
H	22.401735000	19.699676000	4.508424000
H	23.815196000	19.997881000	4.871784000
O	22.923160000	19.261602000	2.115888000
Cl	27.972706000	18.249876000	3.799794000
Cl	26.022581000	15.869774000	5.020075000
Pd	26.087946000	17.151293000	3.053868000

Table S5. Cartesian atomic coordinates for the structure of D-**7**.

	X	Y	Z
C	7.912278000	17.479418000	9.251050000
C	9.727818000	15.933203000	8.595762000
C	9.371233000	14.591908000	8.668722000
C	10.334448000	13.607227000	8.490375000
H	10.096362000	12.709251000	8.538813000
C	11.654248000	13.963841000	8.237718000
H	12.299319000	13.303040000	8.118361000
C	12.010833000	15.305136000	8.164758000
H	12.894143000	15.542205000	7.996409000
C	11.047618000	16.289817000	8.344455000

C	11.445515000	17.761516000	8.239069000
H	10.673378000	18.312778000	8.386421000
H	12.111699000	17.960502000	8.900937000
H	11.800796000	17.935379000	7.364617000
C	7.925324000	14.155455000	8.963264000
H	7.876793000	13.197121000	8.973262000
H	7.655167000	14.499268000	9.817611000
H	7.342807000	14.498576000	8.281372000
C	6.444625000	19.754830000	8.364722000
C	5.746675000	18.046275000	6.724474000
C	4.511673000	17.423531000	6.852830000
C	4.344251000	16.114172000	6.417772000
H	3.518496000	15.696454000	6.503487000
C	5.414007000	15.427556000	5.853009000
H	5.302748000	14.551190000	5.561561000
C	6.649009000	16.050300000	5.724653000
H	7.365267000	15.591466000	5.346585000
C	6.816431000	17.359660000	6.159710000
C	8.179717000	17.891920000	5.847604000
H	8.251490000	18.795990000	6.164642000
H	8.843096000	17.348775000	6.279676000
H	8.321372000	17.874781000	4.898112000
C	6.909925000	21.969031000	7.462181000
H	6.021180000	22.181829000	7.137968000
H	7.447238000	21.663514000	6.714801000
C	7.538298000	23.179923000	8.095851000
H	7.138227000	24.001546000	7.767842000
H	8.495816000	23.206909000	7.940987000
C	7.218676000	22.953713000	9.556401000
H	7.825697000	23.461914000	10.117517000
H	6.310841000	23.232723000	9.750691000
C	7.379574000	21.479352000	9.810410000
H	6.845283000	21.192890000	10.579651000
C	8.840704000	21.016286000	9.944170000
Cl	6.512029000	17.049885000	11.811404000
Cl	4.544287000	19.531281000	10.780507000
N	8.795044000	16.840706000	8.883548000
N	6.059774000	19.368941000	7.136563000
H	5.994045000	19.985911000	6.540278000
N	6.840348000	20.909834000	8.525504000
N	9.351664000	21.104109000	11.175031000
O	9.534306000	20.678301000	8.959210000
Pd	6.401574000	18.464898000	9.919309000
C	3.431045000	18.323051000	7.437861000
H	2.567827000	18.012078000	7.157330000
H	3.562460000	19.223475000	7.128673000
H	3.482555000	18.304688000	8.396379000
H	10.240953000	20.917818000	11.214213000
H	8.979859000	21.503304000	11.876257000
C	13.830722000	17.479418000	11.015600000
C	12.015182000	15.933203000	11.670888000
C	12.371767000	14.591908000	11.597928000
C	11.408552000	13.607227000	11.776275000
H	11.646638000	12.709251000	11.727837000
C	10.088752000	13.963841000	12.028932000
H	9.443681000	13.303040000	12.148289000
C	9.732167000	15.305136000	12.101892000
H	8.848857000	15.542205000	12.270241000
C	10.695382000	16.289817000	11.922195000
C	10.297485000	17.761516000	12.027581000
H	11.069622000	18.312778000	11.880229000
H	9.631301000	17.960502000	11.365713000
H	9.942204000	17.935379000	12.902033000
C	13.817676000	14.155455000	11.303386000
H	13.866207000	13.197121000	11.293388000
H	14.087833000	14.499268000	10.449039000
H	14.400193000	14.498576000	11.985278000

C	15.298375000	19.754830000	11.901928000
C	15.996325000	18.046275000	13.542176000
C	17.231327000	17.423531000	13.413820000
C	17.398749000	16.114172000	13.848878000
H	18.224504000	15.696454000	13.763163000
C	16.328993000	15.427556000	14.413641000
H	16.440252000	14.551190000	14.705089000
C	15.093991000	16.050300000	14.541997000
H	14.377733000	15.591466000	14.920065000
C	14.926570000	17.359660000	14.106940000
C	13.563283000	17.891920000	14.419046000
H	13.491510000	18.795990000	14.102008000
H	12.899904000	17.348775000	13.986974000
H	13.421628000	17.874781000	15.368538000
C	14.833075000	21.969031000	12.804469000
H	15.721820000	22.181829000	13.128682000
H	14.295762000	21.663514000	13.551849000
C	14.204702000	23.179923000	12.170799000
H	14.604773000	24.001546000	12.498808000
H	13.247184000	23.206909000	12.325663000
C	14.524324000	22.953713000	10.710249000
H	13.917303000	23.461914000	10.149133000
H	15.432159000	23.232723000	10.515959000
C	14.363426000	21.479352000	10.456240000
H	14.897717000	21.192890000	9.686999000
C	12.902296000	21.016286000	10.322480000
Cl	15.230972000	17.049885000	8.455246000
Cl	17.198713000	19.531281000	9.486143000
N	12.947956000	16.840706000	11.383102000
N	15.683226000	19.368941000	13.130087000
H	15.748955000	19.985911000	13.726372000
N	14.902652000	20.909834000	11.741146000
N	12.391336000	21.104109000	9.091619000
O	12.208695000	20.678301000	11.307440000
Pd	15.341426000	18.464898000	10.347341000
C	18.311955000	18.323051000	12.828789000
H	19.175173000	18.012078000	13.109320000
H	18.180540000	19.223475000	13.137977000
H	18.260445000	18.304688000	11.870271000
H	11.502047000	20.917818000	9.052437000
H	12.763141000	21.503304000	8.390393000

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