Electronic Supplementary Information (ESI)

$d^8\cdots d^{10}$ $Rh^I\cdots Au^I$ Interactions in Rh 2,6-Xylylisocyanide Complexes with $Au(CN)_2^-$: Bond Analysis and Crystal Effects

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EXPERIMENTAL GENERAL SECTION

All reactions were carried out under N_2 atmosphere. The solvents were purified according to standard procedures.[1] $[Rh(COD)Cl]_2$,[2] $[Rh(COD)_2]BF_4$,[3] (COD = 1,5-Cyclooctadiene), $[Rh(CNXylyl)_4]Cl$,[4] were prepared according to literature procedures. The Xylylisocyanide and $K[Au(CN)_2]$ were purchased from commercial suppliers and used as received. Infrared spectra were recorded with Perkin–Elmer Frontier (4000–200 cm^{-1}) equipped with an ATR accessory (Attenuated total reflection) for the direct registration of solid samples. Visible absorption spectra of solutions were recorded in a Shimadzu UV-2550 spectrophotometer. The NMR spectra were recorded with Bruker Avance 400 Ultrashield, and Varian 500/54 Premium Shielded instruments. The ^{1}H and ^{13}C NMR spectra are referenced to tetramethylsilane (TMS), while ^{19}F NMR spectra are referenced to $CFCl_3$. MALDI-TOF mass spectrometry was carried out using a Bruker Autoflex instrument. The elemental analyses were performed with a Carlo Erba 1108 microanalyzer (Vigo University).

Experimental procedure for X-ray Crystallography

A crystal was attached to a glass fiber and transferred to an Agilent Supernova diffractometer with an Atlas CCD area detector. Data collection was performed with Mo-Kα radiation (λ = 0.71073 Å) and in some cases at low temperature due to the problems associated with loss of solvent crystallization molecules. Data integration, scaling and empirical absorption correction was carried out using the CrysAlisPro program package.[5] The crystals were kept at 298 K or 180 K during data collection. Using Olex2,[6] the structure was solved with the olex2.solve[7] and refined with Shelx program.[8] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealized positions and refined using the riding model. Refinement proceeded smoothly to give the residuals shown in Tables ESI1 and ESI2. CCDC 1894639-1894644 contains the supporting 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].

The technical measurements were carried out with equipment of the LTI services or the IU CINQUIMA (both of the University of Valladolid) unless otherwise stated.

SYNTHESIS AND CHARACTERIZATION OF THE COMPOUNDS

$[Rh(CNXylyl)_4](BF_4)$ (1)

Xylylisocyanide (132 mg, 1.01 mmol) in dry dichloromethane (20 mL) was added slowly to a solution of $[Rh(COD)_2](BF_4)$ (100 mg, 0.246 mmol) in dry dichloromethane (10 mL) and the mixture was stirred at room temperature for 1h. The solution was concentrated by evaporation under reduced pressure and precipitated with diethyl ether (10 mL). The yellow solid was washed with diethyl ether. Yield: 155 mg (88 %).

Suitable single crystals of **1** (Figure 1, below) for X-ray Crystallography were obtained layering diethyl ether in a solution of the compound in chloroform at 250 K.

^{1}H NMR (499.72 MHz, $CDCl_3$ 298 K, Figure ESI1): δ 7.31 (m, 4H, H_p), 7.19 (m, 8H, H_m); 2.46 (s, 24H, CH_3).

^{19}F NMR (470.15 MHz, $CDCl_3$ 298 K, Figure ESI2): δ –154.51 ($^{10}BF_4$), –154.56 ($^{11}BF_4$).

^{13}C {^{1}H} NMR (125.67 MHz, $CDCl_3$ 298 K, Figure ESI3 and ESI4): δ 148.20 (4C, Rh–*C*N), 135.30 (8C, C_{Ph}–Me), 130.44 (4C, C_{Ph}–H_p), 128.55 (8C, C_{Ph}–H_m), 125.94 (4C, C_{Ph}–N), 18.78 (8C, *C*H_3).

IR (ATR, neat, cm^{-1}): 2129 ($\nu_{CNXylyl}$), 1046-1031(ν_{BF4^-}). MS (MALDI-TOF): *m/z*: calcd for [M^+-BF_4^-] (M^+ = $C_{36}H_{36}N_4Rh^+$): 627.1990; found: 627.1998; *Anal*. calcd for $C_{36}H_{36}BF_4N_4Rh$: C 60.52, H 5.08, N 7.84; found C 60.31, H 5.00, N 7.61.

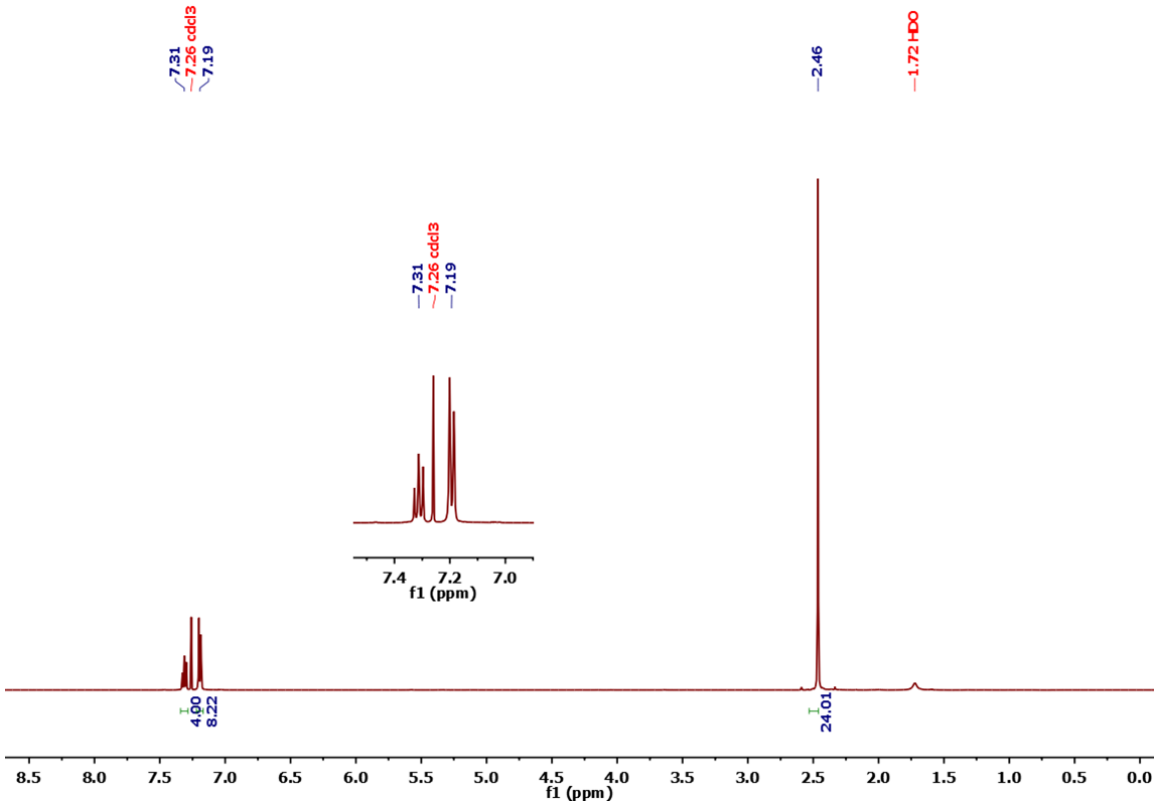

Figure ESI1. ^{1}H NMR spectrum of **1** at 298 K in $CDCl_3$

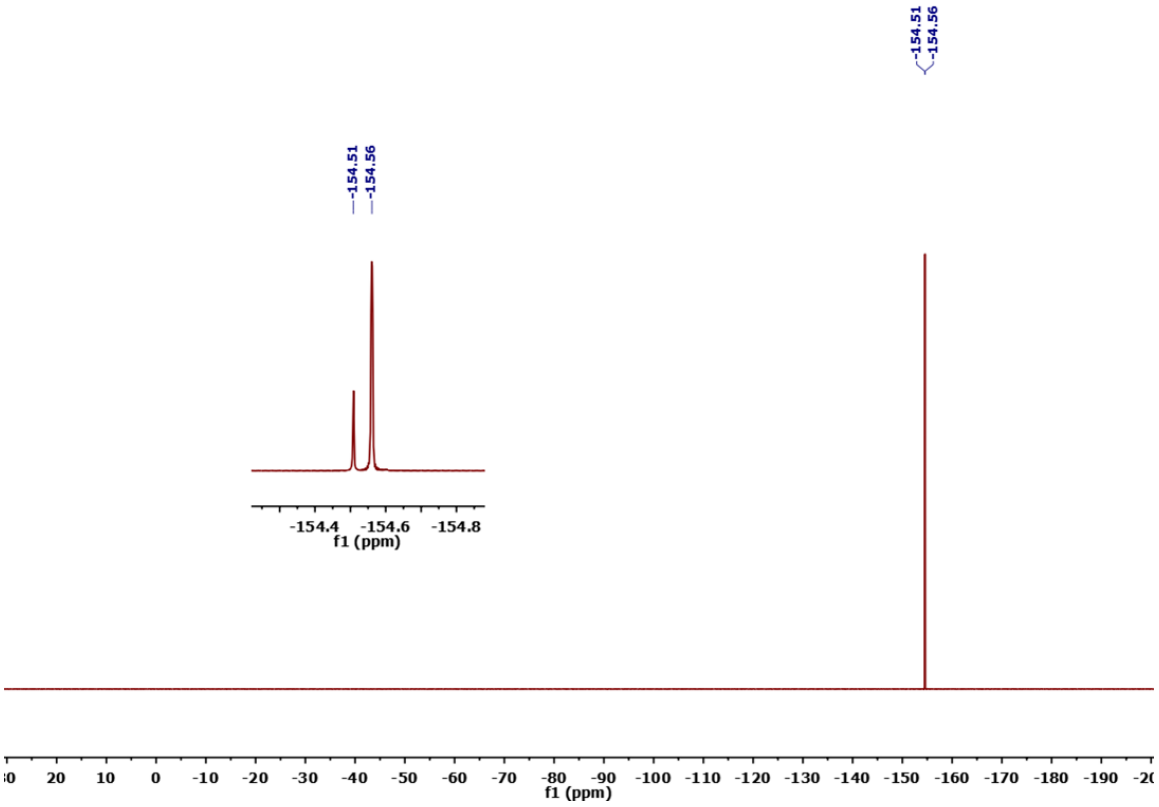

Figure ESI2. ^{19}F NMR spectrum of **1** at 298 K in $CDCl_3$

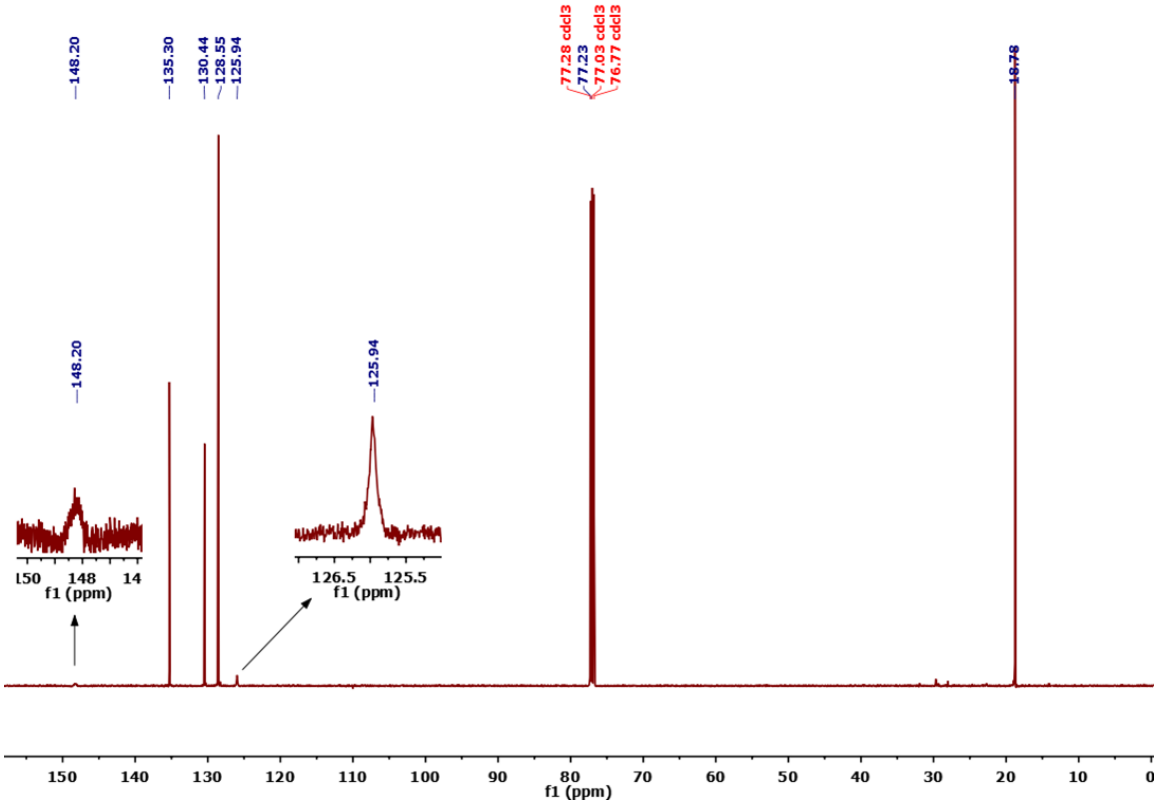

Figure ESI3. $^{13}C\{^{1}H\}$ NMR spectrum of **1** at 298 K in $CDCl_3$

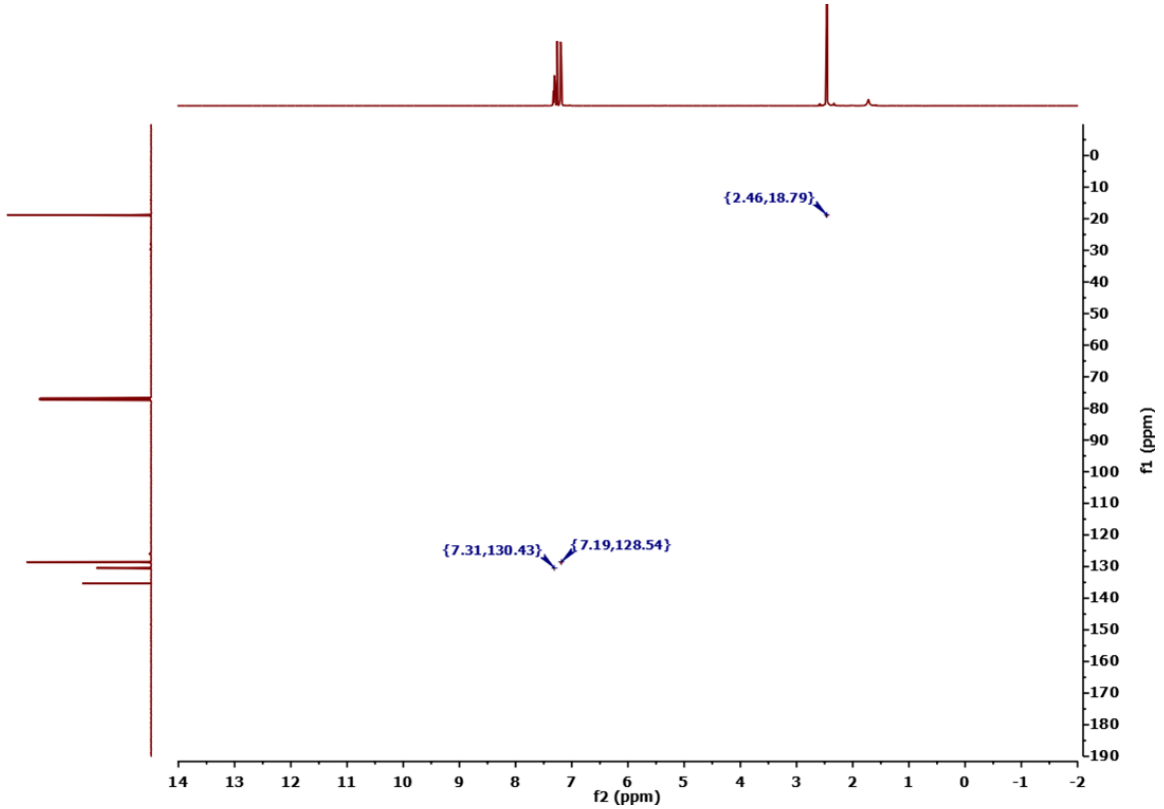

Figure ESI4. 2D-HSQC spectrum of **1** at 298 K in $CDCl_3$

[Rh(CNXylyl)$_4$][Au(CN)$_2$] (2)

Potassium dicyanoaurate(I) (24.2 mg, 0.084 mmol) was dissolved in acetone (10 mL) and was added dropwise to a yellow solution of **1** (50.0 mg, 0.070 mmol) in 20 mL of acetone. The mixture was stirred at room temperature for 1 h and the solution darkened. The solvent was evaporated under reduced pressure and the purple solid obtained was washed with distilled water (3 × 10 mL) and then with diethyl ether (2 × 5 mL). Yield: 50 mg, 82%.

^{1}H NMR (499.72 MHz, CD_2Cl_2 298 K, Figure ESI5): δ 7.32 (m, 4H, *H*$_p$), 7.21 (m, 8H, *H*$_m$); 2.49 (s, 24H, C*H*$_3$).

^{13}C {^{1}H} NMR (125.67 MHz, CD_2Cl_2 298 K, Figure ESI6 and ESI7): δ 150.21 (2C, Au–*C*N), 149.04 (4C, Rh–*C*N), 135.47 (8C, *C*$_{Ph}$–Me), 129.97 (4C, *C*$_{Ph}$–H$_p$), 128.27 (8C, *C*$_{Ph}$–H$_m$), 126.33 (4C, *C*$_{Ph}$–N), 18.66 (8C, *C*H$_3$).

IR (ATR, neat, cm^{-1}): 2133 ($\nu_{CNXylyl-Rh}$), 2193 (ν_{CN-Au}). MS (MALDI-TOF): *m/z*: calcd [M^+-(Au(CN)$_2^-$)] (M^+ = $C_{36}H_{36}N_4Rh^+$): 627.1990; found: 627.201 *Anal*. calcd for $C_{38}H_{36}AuN_6Rh$: C 52.07, H 4.14, N 9.59; found C 51.81, H 3.99, N 9.45.

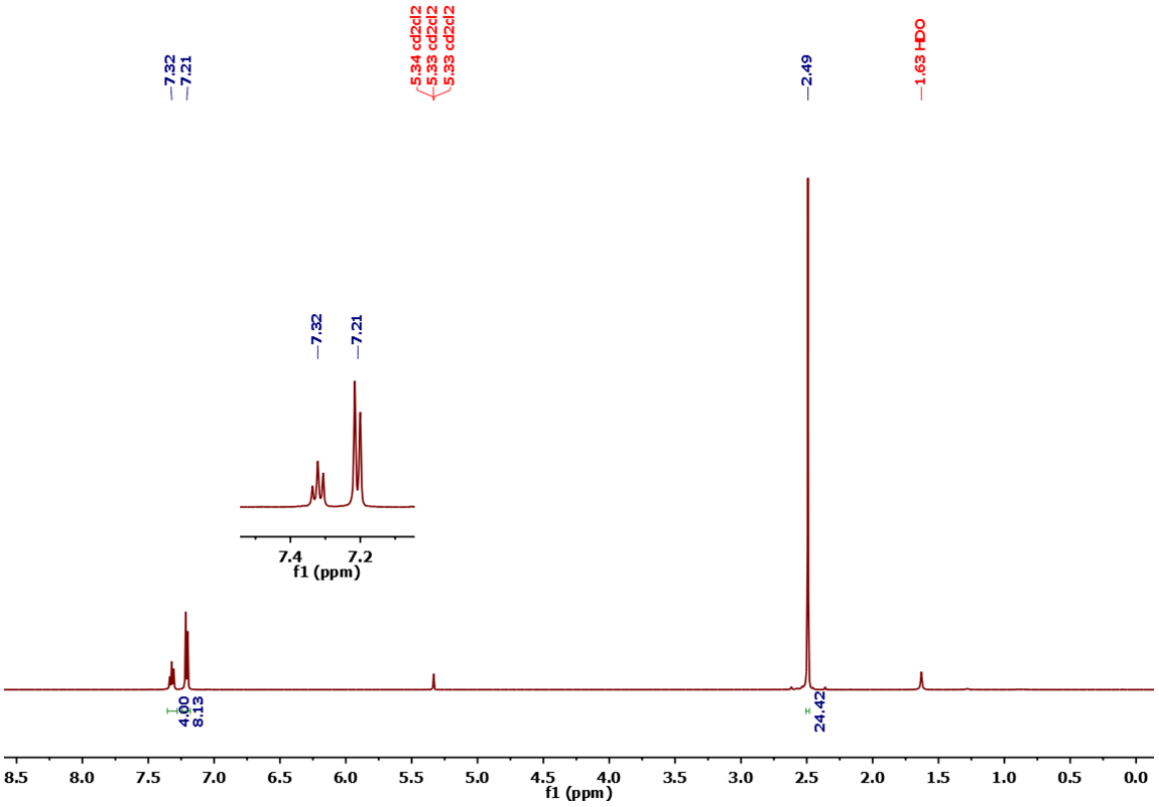

Figure ESI5. ^{1}H NMR spectrum of **2** at 298 K in CD_2Cl_2

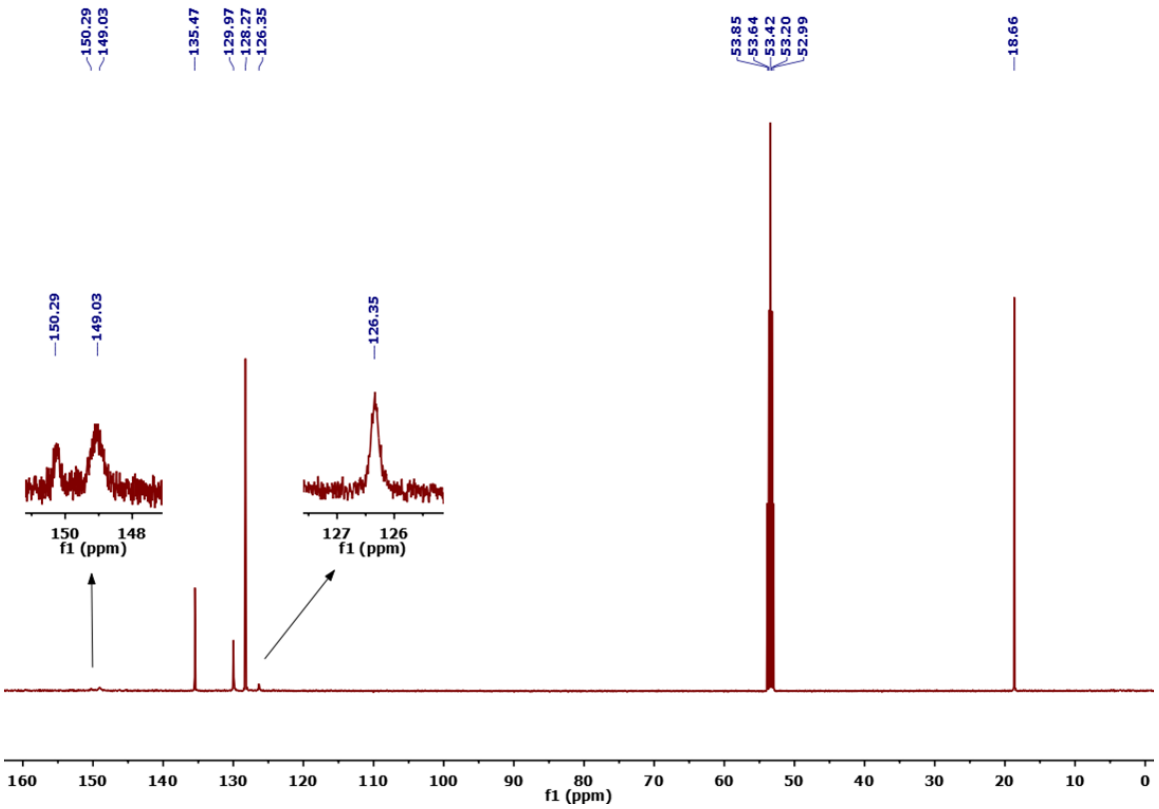

Figure ESI6. ^{13}C{^{1}H} NMR spectrum of **2** at 298 K in CD_2Cl_2

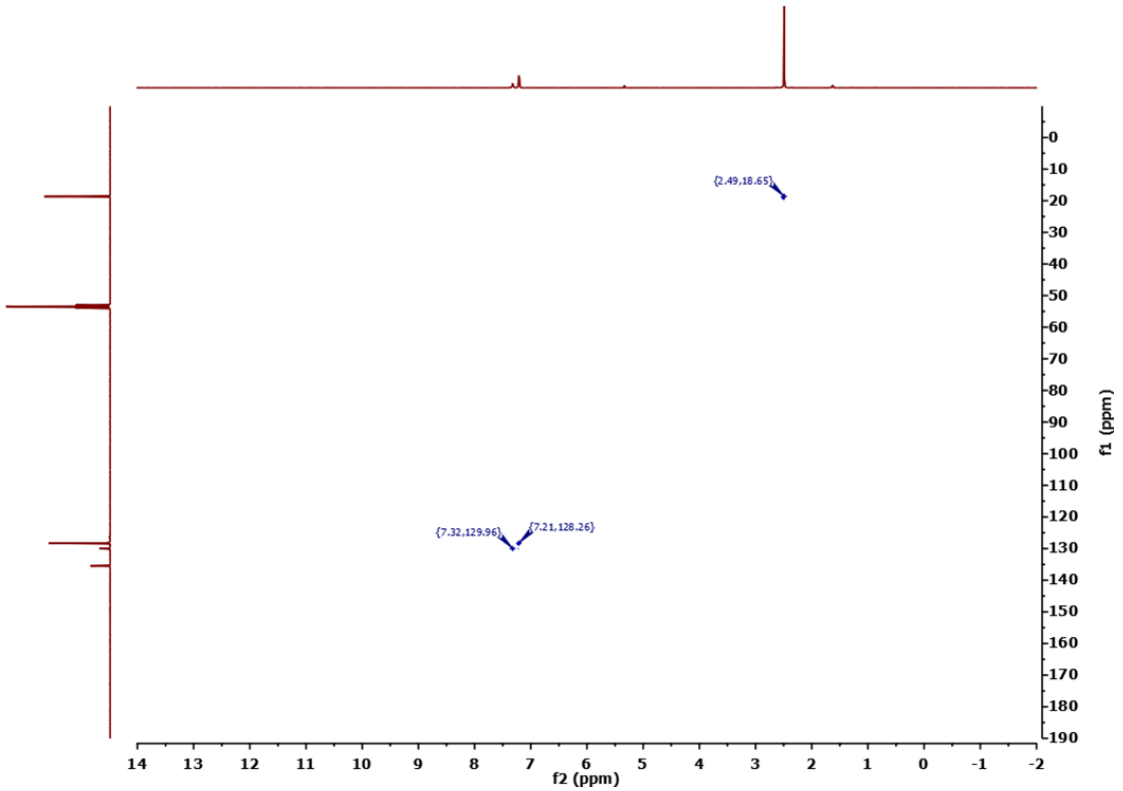

Figure ESI7. 2D-HSQC spectrum of **2** at 298 K in CD_2Cl_2

The different crystals of **2** were studied by X-Ray diffraction (Figure 2). A photograph with single crystals of each polymorph were shown in Figure ESI8. Examples of *Inter-unit* π-π stacking interactions are collected in Figure ESI9.

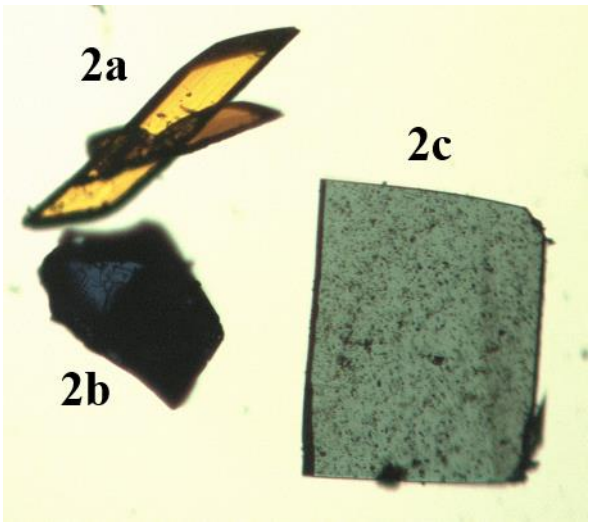

Figure ESI8. Microphotograph of single crystals of **2a**, **2b** and **2c**.

- **2a**: orange crystals were obtained slow diffusion of diethyl ether into a concentrated solution of the compound in chloroform at 250 K.
- **2b**: deep blue crystals were obtained slow evaporation at room temperature of a solution of the compound in a solvent mixture with acetone and *n*-heptane at room temperature.
- **2c**: deep green crystals were obtained by slow diffusion of *n*-hexane into diluted solution of the compound in dichloromethane at room temperature.

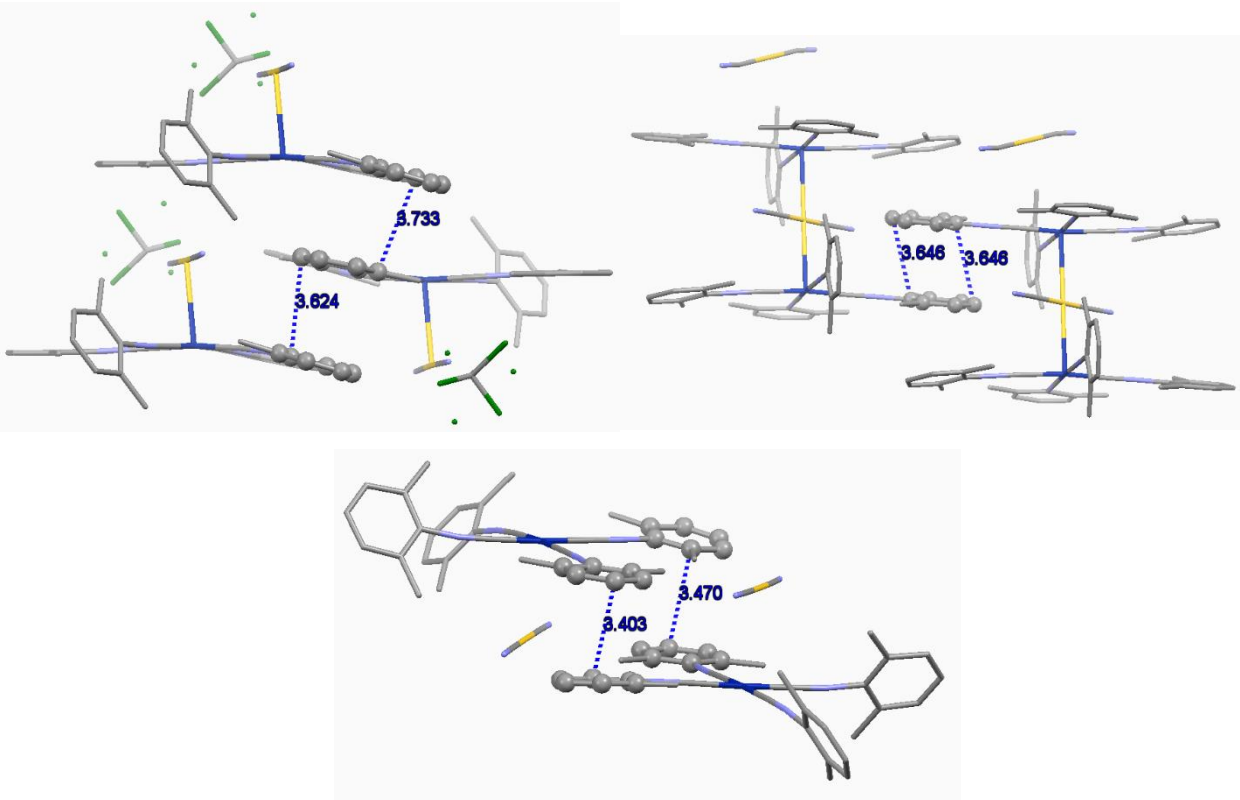

Figure ESI9. Extended structures of **2a** (above, left), **2b** (above, right) and **2c** (below). *Inter-unit* π-π stacking distances in Å.

[Rh(CNXylyl)$_4$]$_2$[Au(CN)$_2$][Au$_2$(CN)$_3$] (3)

During the crystallization of **2a** by slow diffusion of diethyl ether into a concentrated solution of [RhL$_4$][Au(CN)$_2$] (**2**) in chloroform at 250 K purple crystals of **3** suitable for X-ray diffraction appeared as a byproduct after several days. The structure is depicted in Figure 3.

[Rh(CN)(CNXylyl)$_3$] (4)

NaCN (5.0 mg, 0.110 mmol) was added to a solution of [Rh(CNXylyl)$_4$]Cl (35.0 mg, 0.053 mmol) in acetone (20 mL) with a few drops of added water. The mixture was stirred at room temperature for 30 minutes. Then, the solution was filtered to remove NaCl and evaporated to dryness. The green solid was washed with *n*-hexane to remove free CNXylyl (2 × 5 mL) and extracted with 10 mL of

CH_2Cl_2. Then, *n*-hexane (10 mL) was added and the solution was concentrated in vacuum and cooled to –20 ºC. The yellow solid obtained was filtered, washed with *n*-hexane (3 × 5 mL) and vacuum dried. Yield: 22 mg (80 %).

Suitable yellow single crystals of **4** (Figure ESI10) for X-ray Crystallography were obtained by slow evaporation of a diethyl ether solution of the compound.

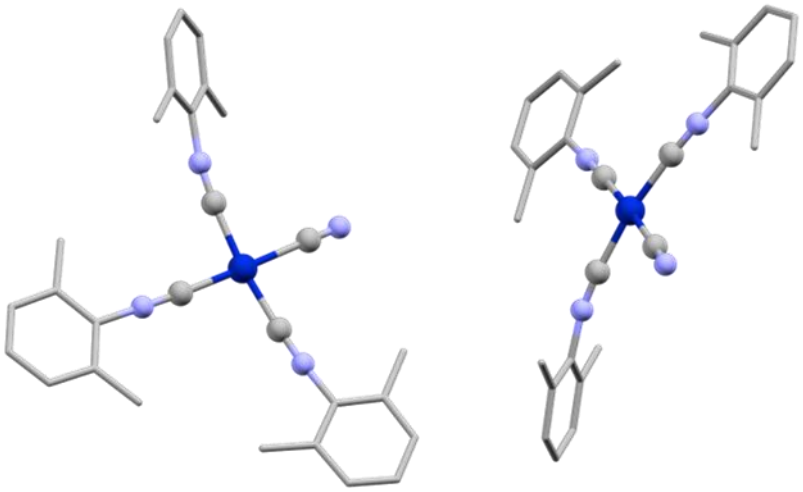

Figure ESI10. X-ray structure of **4** in balls and sticks view. The asymmetric unit contains two slightly different molecules.

^{1}H NMR (499.72 MHz, CD_2Cl_2 298 K, Figure ESI11): δ 7.24 (m, 3H, H_p), 7.15 (m, 6H, H_m), 2.49 (br, 18H, CH_3).

IR (ATR, neat, cm^{-1}): 2178 ($\nu_{CN\text{-}Rh}$), 2117 ($\nu_{CNXylyl\text{-}Rh}$), 2105 ($\nu_{CNXylyl\text{-}Rh}$). MS (MALDI-TOF): *m/z*: calcd [M^+-(CN^-)] (M^+ = $C_{28}H_{27}N_4Rh$): 496.1260; found: 496.1276; *Anal*. calcd for $C_{28}H_{27}N_4Rh$: C 64.37, H 5.21, N 10.72; found C 64.21, H 5.31, N 10.90.

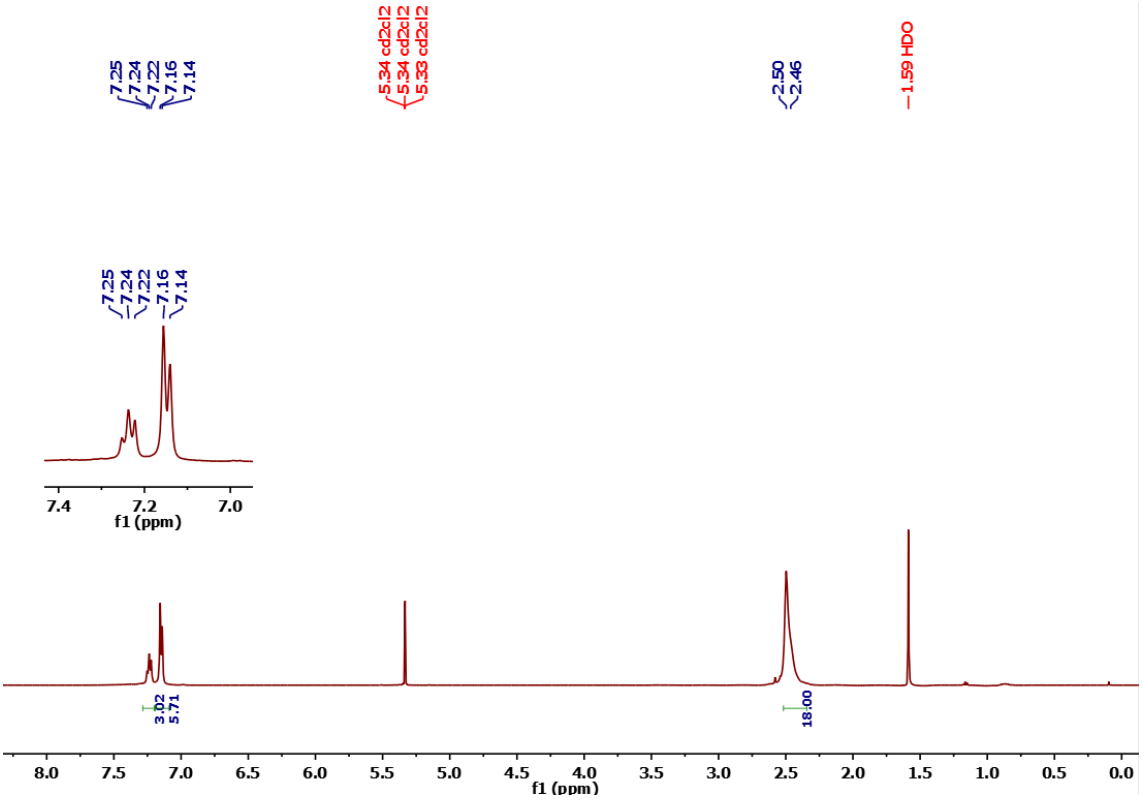

Figure ESI11. ^{1}H NMR spectrum of **4** at 298 K in CD_2Cl_2

REFINEMENT DATA OF THE X-RAY STRUCTURES

Table ESI1. Crystal data and structure refinements for complexes **1**, **2a** and **2b** (L = CN-2,6-Xylyl).

	$[RhL_4](BF_4)$ (**1**)	$[\{L_4Rh\}\{Au(CN)_2\}]\cdot CHCl_3$ (**2a**)	$[\{L_4Rh\}_2\{Au(CN)_2\}][Au(CN)_2]$ (**2b**)
Empirical formula	$C_{36}H_{36}BF_4N_4Rh$	$C_{39}H_{37}AuCl_3N_6Rh$	$C_{38}H_{36}AuN_6Rh$
Formula weight	714.41	995.97	876.60
Temperature/K	294	180.00(14)	294
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	11.7907(7)	7.6734(5)	11.7657(4)
b/Å	11.9943(7)	15.7599(12)	13.0544(5)
c/Å	13.0642(7)	17.8463(10)	13.1851(5)
α/°	103.531(5)	110.029(6)	96.657(3)
β/°	103.457(5)	90.594(5)	102.564(3)
γ/°	93.287(4)	99.495(6)	109.808(3)
Volume/$Å^3$	1734.70(18)	1994.7(2)	1819.62(12)
Z	2	2	2
$\rho_{calc}g/cm^3$	1.368	1.658	1.600
μ/mm^{-1}	0.544	4.323	4.514
F(000)	732.0	976.0	860.0
Crystal size/mm^3	0.232 × 0.137 × 0.062	0.449 × 0.13 × 0.087	0.239 × 0.082 × 0.025
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.944 to 58.914	6.838 to 59.216	6.884 to 59.112
Index ranges	$-12 \le h \le 15$, $-16 \le k \le 13$, $-16 \le l \le 17$	$-9 \le h \le 10$, $-21 \le k \le 21$, $-23 \le l \le 16$	$-15 \le h \le 15$, $-17 \le k \le 14$, $-14 \le l \le 18$
Reflections collected	12167	13755	12812
Independent reflections	7867 [Rint = 0.0364, Rsigma = 0.0853]	9062 [Rint = 0.0393, Rsigma = 0.0792]	8305 [Rint = 0.0369, Rsigma = 0.0959]
Data/restraints/parameters	7867/0/423	9062/0/487	8305/0/426
Goodness-of-fit on F^2	1.042	1.064	1.012
Final R indexes [I>=2σ (I)]	R1 = 0.0631, wR2 = 0.1041	R1 = 0.0493, wR2 = 0.0976	R1 = 0.0543, wR2 = 0.0663
Final R indexes [all data]	R1 = 0.1268, wR2 = 0.1331	R1 = 0.0788, wR2 = 0.1174	R1 = 0.1309, wR2 = 0.0858
Largest diff. peak/hole/$eÅ^{-3}$	0.45/-0.43	1.44/-1.37	0.88/-0.67

Table ESI2. Crystal data and structure refinements for complexes **2c**, **3** and **4** (L = CN-2,6-Xylyl).

	$[\{L_4Rh\}\{Au(CN)_2\}]_\infty$ (**2c**)	$[\{L_4Rh\}_2\{Au(CN)_2\}\{Au_2(CN)_3\}]_\infty \cdot 4CHCl_3$ (**3**)	$[Rh(CN)L_3]$ (**4**)
Empirical formula	$C_{38}H_{36}N_6RhAu$	$C_{40.5}H_{38}Au_{1.5}Cl_6N_{6.5}Rh$	$C_{28}H_{27}N_4Rh$
Formula weight	876.60	1223.48	522.44
Temperature/K	294	180.00(14)	294
Crystal system	monoclinic	triclinic	triclinic
Space group	P21/c	P-1	P-1
a/Å	16.9315(8)	7.6734(5)	8.6127(3)
b/Å	6.7987(4)	15.7599(12)	14.8452(5)
c/Å	31.6402(12)	17.8463(10)	20.5926(7)
α/°	90	110.029(6)	88.376(3)
β/°	98.038(4)	90.594(5)	78.045(3)
γ/°	90	99.495(6)	82.826(3)
Volume/Å^3	3606.4(3)	1994.7(2)	2555.63(15)
Z	4	2	4
ρ_{calc}g/cm^3	1.615	1.658	1.358
μ/mm^{-1}	4.555	4.323	0.69
F(000)	1720.0	976.0	1072
Crystal size/mm^3	0.189 × 0.116 × 0.022	0.449 × 0.13 × 0.087	0.387 × 0.126 × 0.033
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.664 to 59.524	6.838 to 59.216	6.556 to 59.414
Index ranges	-22 ≤ h ≤ 23, -6 ≤ k ≤ 8, -34 ≤ l ≤ 39	-9 ≤ h ≤ 10, -21 ≤ k ≤ 21, -23 ≤ l ≤ 16	-8 ≤ h ≤ 11, -19 ≤ k ≤ 18, -26 ≤ l ≤ 28
Reflections collected	23992	13755	17904
Independent reflections	8694 [Rint = 0.0651, Rsigma = 0.1005]	9062 [Rint = 0.0393, Rsigma = 0.0792]	11736 [R_{int} = 0.0290, R_{sigma} = 0.0810]
Data/restraints/parameters	8694/0/423	9062/0/487	11736/0/607
Goodness-of-fit on F^2	0.934	1.064	1.07
Final R indexes [I>=2σ (I)]	R1 = 0.0471, wR2 = 0.0492	R1 = 0.0493, wR2 = 0.0976	R_1 = 0.0583, wR_2 = 0.0814
Final R indexes [all data]	R1 = 0.1380, wR2 = 0.0703	R1 = 0.0788, wR2 = 0.1174	R_1 = 0.1270, wR_2 = 0.1073
Largest diff. peak/hole/eÅ^{-3}	0.48/-0.64	1.44/-1.37	0.60/-0.51

COMPUTACIONAL SECTION

Density functional theory (DFT) calculations reported in this work were carried out using the dispersion corrected hybrid functional ωB97X-D developed by Head-Gordon and Chai,[9] and the Gaussian09 software.[10] The choice of this level of theory is based on the satisfactory results obtained in previous theoretical studies on related Rh/Au transmetalation.[11] C and H atoms were described using the double-ζ basis set 6-31G(d,p), whereas the same basis set plus diffuse functions was employed to describe the more electronegative N. Rh and Au metals were described using the effective core potential LANL2DZ[12] including f-polarization functions (exponents: 1.350 for Rh and 1.050 for Au).[13]

Single point calculations were used to study the Rh···Au interaction in Figures 4 and 6 with the X-Ray data of **2a** without the solvent molecule and an anionic symmetric fragment of **2b**. Geometry relaxations in gas phase deforms drastically the structures driving apart both metal centres. This happens because all other intermolecular stabilizing interactions such as *inter-unit* π-π stacking determine the solid state structure and cannot be dealt with in this work.

Selected relevant Molecular Orbitals (MO)

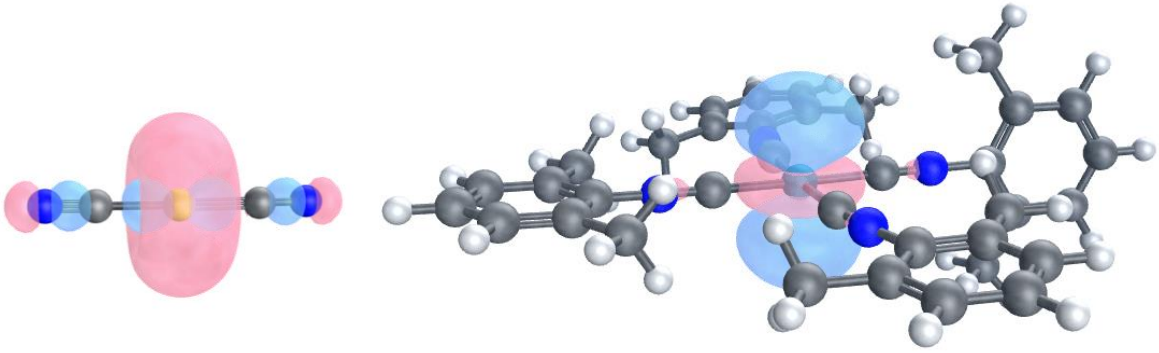

Figure ESI12. Left: HOMO (isovalue = 0.10) of $[Au(CN)_2]^-$ formed by $5d_z^2$ + 6s of gold. Right: HOMO of $[RhL_4]^+$ which mainly consist in a $4d_z^2$ atomic orbital of rhodium.

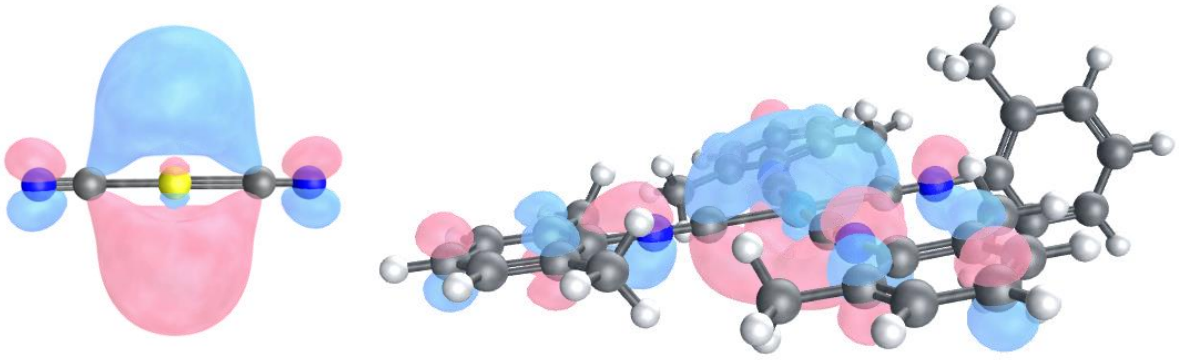

Figure ESI13. Left: LUMO (isovalue = 0.07) of $[Au(CN)_2]^-$ mostly formed by a $6p_x$ of gold. Right: LUMO (isovalue = 0.07) of $[RhL_4]^+$ with highly delocalized π density.

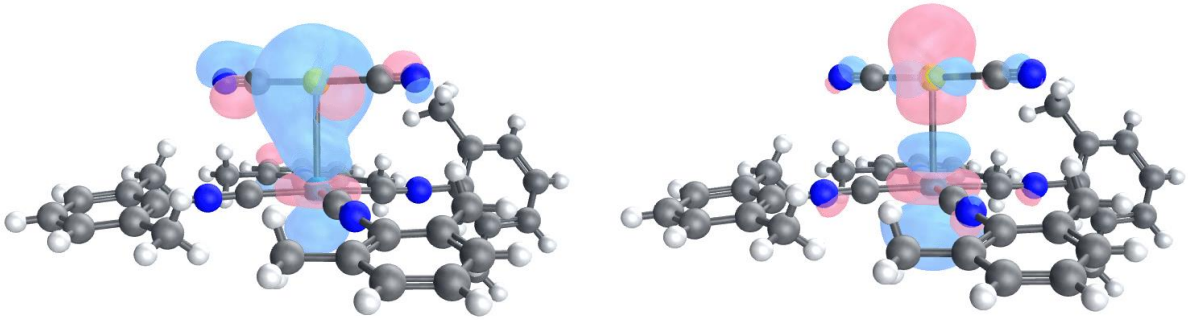

Figure ESI14. Selected occupied Molecular Orbitals (isovalue = 0.10) of polymorph **2a** depicted in Figure 4. Left: σ HOMO-3. Right: σ* HOMO.

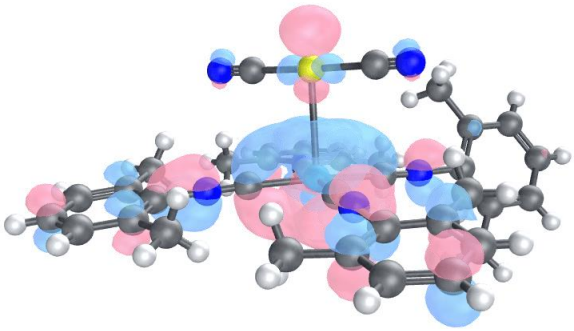

Figure ESI15. LUMO (isovalue = 0.07) of [{L_4Rh}{Au(CN)$_2$}] (**2a**).

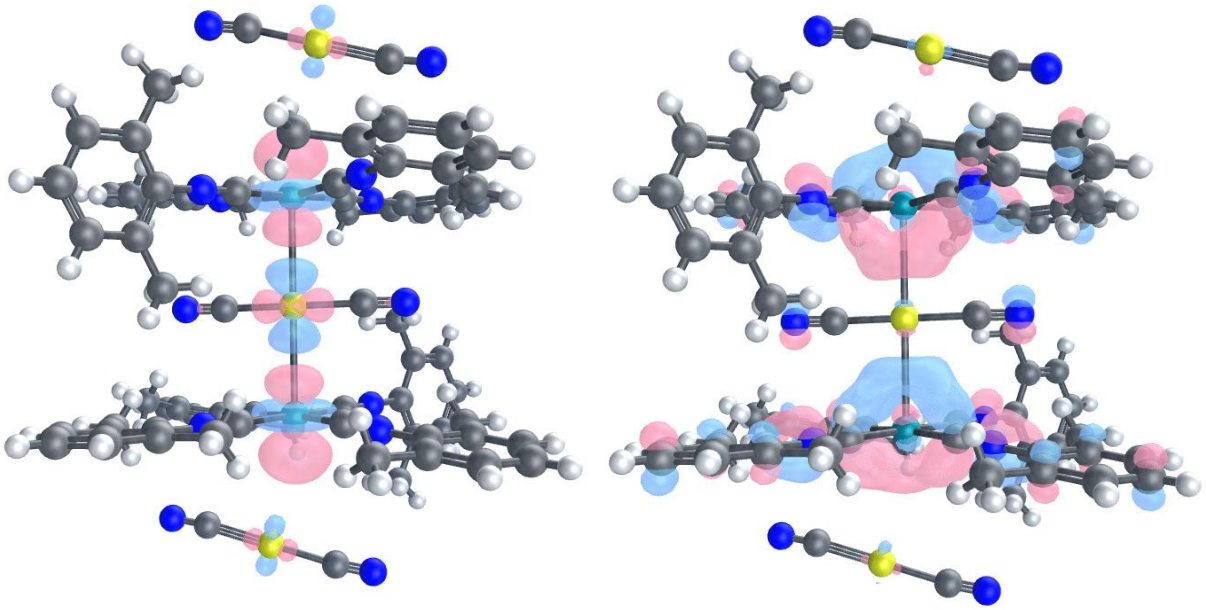

Figure ESI16. Frontier Molecular Orbitals of the selected symmetric fragment ($Au^a\cdots Rh\text{-}Au^b\text{-}Rh\cdots Au^a)^-$ of polymorph **2b** depicted in Figure 6. Left: HOMO σ* (isovalue = 0.10). Right: LUMO (isovalue = 0.07).

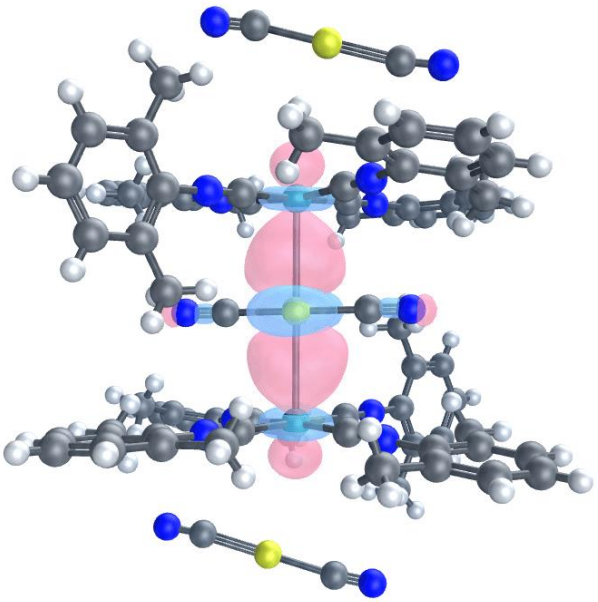

Figure ESI17. Highly stable completely bonding orbital (σ) of the core Rh-Au-Rh. Occupied Molecular Orbital (isovalue = 0.07) of the selected symmetric fragment $(Au^{a}\cdots Rh\text{-}Au^{b}\text{-}Rh\cdots Au^{a})^{-}$ of polymorph **2b**.

Rest of relevant data

Table ESI3. Mulliken Charges of the metal atoms (gold and rhodium) in the $[Au(CN)_2]^-$ anion, $[RhL_4]$ cation, polymorphs **2a** and **2b** $(Au^{a}\cdots Rh\text{-}Au^{b}\text{-}Rh\cdots Au^{a})^{-}$.

	Au	**Rh**
$[Au(CN)_2]^-$	0.516	-
$[RhL_4]^+$	-	0.369
$[\{L_4Rh\}\{Au(CN)_2\}]$ (2a)	0.477	0.403
$[\{L_4Rh\}_2\{Au^{b}(CN)_2\}][Au^{a}(CN)_2]$ (2b)	0.436^{a}, 0.426^{b}	0.416

Table ESI4. Contribution of the different atomic orbitals from gold and rhodium in the HOMO and HOMO-3 orbitals depicted in Figure 4. In bold the numbers up to 0.1 in absolute value and in a grey cell the most important contribution for each molecular orbital.

	Au		**Rh**	
Atomic Orbital	**HOMO**	**HOMO-3**	**HOMO**	**HOMO-3**
1S	**-0.11024**	**0.12859**	**0.10358**	0.05067
2S	**0.15340**	**-0.18391**	**-0.10801**	-0.05393
3S	**-0.23229**	**0.27218**	**0.22086**	0.09591
4PX	-0.00254	-0.01091	-0.00215	-0.00225
4PY	-0.00520	0.01257	-0.00173	-0.00446
4PZ	0.02686	0.01297	0.04181	-0.00716
5PX	0.00674	0.00215	0.00016	-0.00191
5PY	0.01110	-0.0015	0.02723	-0.00494
5PZ	-0.05875	-0.02581	-0.09957	-0.00954
6PX	0.00122	0.0019	-0.00310	-0.00072
6PY	0.00125	-0.00276	0.00589	-0.00661
6PZ	0.00705	-0.01269	-0.01421	-0.01101
7D0	**-0.32715**	0.00182	**0.62484**	**0.31123**
7D+1	-0.01543	-0.03003	-0.04858	0.00568
7D-1	**0.11844**	**0.24256**	**-0.14618**	-0.02978
7D+2	-0.04748	**0.23131**	-0.00478	0.00758
7D-2	**-0.23145**	**0.46917**	0.00183	0.01713
8D0	-0.06347	0.01822	**0.16029**	0.08222
8D+1	-0.00736	-0.00569	-0.01278	0.00347
8D-1	0.02324	0.04437	-0.03771	-0.00761
8D+2	-0.01566	0.05111	0.00565	0.00607
8D-2	-0.06607	0.10852	-0.00210	0.00622
9F0	-0.00153	-0.00095	-0.00025	0.00083
9F+1	0.00003	-0.00045	-0.00011	-0.00001
9F-1	0.00112	0.00142	0.00052	-0.00103
9F+2	0.00017	0.00001	0.00017	0.00025
9F-2	-0.00019	-0.00054	0.00000	0.00001
9F+3	-0.00028	-0.00123	0.00004	-0.00035
9F-3	-0.00005	-0.00025	0.00040	-0.00030

Table ESI4 collects the contributions of the two metal centres in the occupied molecular orbitals of **2a** shown in Figure 4 (for **2b** it is similar but more complex). No significant *p* density is present in these orbitals. Rh has a higher contribution than Au in the HOMO and *viceversa* for HOMO-3.

Cartesian coordinates of all the calculated species

$[Au(CN)_2]^-$

79	0.000006	0.030036	-0.000027
6	-2.001463	-0.033885	0.000750
6	2.001478	-0.033136	-0.000188
7	3.163988	-0.140971	0.000164
7	-3.164064	-0.140561	-0.000345

$[Au_2(CN)_3]^-$

79	-2.591558	-0.000217	-0.000039
6	-4.585949	0.001467	0.000068
6	-0.598181	-0.001341	0.000000
7	0.564421	-0.001528	0.000130
7	-5.751694	0.002570	0.000148
79	2.592339	-0.000241	0.000020
6	4.553337	0.001537	-0.000023
7	5.719133	0.002702	-0.000102

$[RhL_4]^+$

45	-0.339454	-0.058704	-0.077566
7	1.301997	-2.736132	-0.061741
7	2.536596	1.195245	-0.051184
7	-1.492467	2.861381	-0.071235
7	-3.159506	-1.456130	0.004090
6	-1.134277	1.751547	-0.078367
6	-2.117258	-0.936039	-0.039106
6	1.449723	0.774282	-0.072437
6	0.617851	-1.791529	-0.069130
6	4.550553	1.773025	-1.210380
6	3.860986	1.610970	-0.000342
6	2.240111	-3.760723	-0.044159
6	-4.401692	-2.073365	0.068167
6	-1.756135	4.224731	-0.036889
6	1.789898	-5.086335	-0.107602
6	-5.545241	-1.261901	0.053624
6	5.885981	2.160557	-1.128063
1	6.452621	2.297232	-2.043493
6	-4.442514	-3.472640	0.149468
6	3.865425	1.536999	-2.527776
1	3.456906	0.522780	-2.591837
1	4.562460	1.674285	-3.355833
1	3.029603	2.230396	-2.668379
6	4.439008	1.815937	1.260842
6	-0.672932	5.089769	0.184251
6	-6.778313	-1.904449	0.123490
1	-7.686397	-1.310132	0.114632
6	-3.074417	4.661665	-0.223109
6	0.718995	4.550185	0.369987
1	0.760613	3.838101	1.201406
1	1.424095	5.357028	0.576167
1	1.060201	4.021686	-0.527249
6	6.492786	2.372046	0.105714
1	7.534428	2.672342	0.147960
6	2.759495	-6.085765	-0.087430
1	2.448996	-7.124497	-0.136914
6	-5.422708	0.234209	-0.024209
1	-4.902166	0.628391	0.855478
1	-6.406433	0.703883	-0.074989
1	-4.851988	0.540606	-0.907167
6	-5.700115	-4.065923	0.219651
1	-5.773001	-5.146631	0.286869
6	-6.855644	-3.291065	0.206406
1	-7.825909	-3.772754	0.263092
6	4.111078	-5.767455	-0.005805
1	4.850732	-6.560699	0.009400
6	3.637271	1.621644	2.517777
1	2.774983	2.296257	2.545275
1	4.246936	1.816425	3.401378
1	3.248863	0.600138	2.591424
6	0.321439	-5.397858	-0.190290
1	-0.206980	-5.037277	0.698423
1	0.157220	-6.473635	-0.269951
1	-0.135900	-4.918589	-1.062045
6	5.777007	2.201870	1.286549
1	6.260265	2.369117	2.243740
6	4.523485	-4.440052	0.055492
1	5.580700	-4.203524	0.119844
6	3.595456	-3.402554	0.036376
6	-4.184670	3.675536	-0.456872
1	-4.004365	3.087050	-1.362702
1	-5.141908	4.186982	-0.570073
1	-4.269635	2.973779	0.379034
6	-3.297099	6.035538	-0.181090
1	-4.304978	6.412840	-0.321239
6	-0.950079	6.453707	0.218123
1	-0.139529	7.155171	0.387944
6	-3.173132	-4.278072	0.156347
1	-2.617202	-4.139646	-0.777169
1	-3.386822	-5.342095	0.270552
1	-2.516024	-3.971274	0.977040
6	-2.247676	6.922201	0.037397
1	-2.442512	7.988918	0.068237
6	4.013092	-1.958425	0.093423
1	3.704931	-1.422263	-0.811053
1	5.096370	-1.867275	0.186452
1	3.555482	-1.445591	0.946524

$[\{L_4Rh\}\{Au(CN)_2\}]$ (**2a**, no $CHCl_3$)

79	0.121598	-0.458383	2.465686
45	0.259108	0.175248	-0.554757
7	-0.503183	-2.825756	-1.027737
7	0.492140	3.285171	-0.467628
7	-2.830163	0.493676	-0.676426
6	-0.143264	-1.738755	-0.849607
6	-1.131292	1.118340	2.702208
6	1.361977	-2.027915	2.295879
6	0.464720	2.125494	-0.461383
7	3.328646	-0.288639	-0.673383
6	-1.695085	0.416176	-0.632053
7	2.088942	-2.878601	2.219451
7	-1.791021	1.869834	2.814157
6	2.196525	-0.126658	-0.606077
6	-4.249193	0.527371	-0.670720
6	0.346531	4.675434	-0.563009
6	1.501379	5.425461	-0.778264
6	-0.061247	-5.154065	-1.269321
6	-4.864553	1.182674	-1.721628
6	-0.558365	-6.433031	-1.437925
1	0.026229	-7.153225	-1.493193
6	-2.363293	-4.278819	-1.332806
6	4.739885	-0.475611	-0.774808
6	-0.951477	-4.118740	-1.233855
6	-4.906692	-0.120119	0.361531
6	-1.931799	-6.645531	-1.525298
1	-2.255274	-7.511468	-1.619965
6	-6.271497	1.184107	-1.692672
1	-6.747016	1.626139	-2.358711
6	-2.823843	-5.584447	-1.472724
1	-3.737093	-5.748517	-1.531246
6	2.841607	4.798915	-0.827854
1	3.026232	4.368786	0.010659
1	3.504094	5.473624	-0.993381
1	2.865588	4.147952	-1.532897
6	4.966329	2.026093	-0.879126
1	4.214716	2.077398	-1.473075
1	5.641158	2.649665	-1.160364
1	4.684891	2.239997	0.013138
6	5.526360	0.645218	-0.905723
6	-4.154818	-0.733905	1.510916
1	-3.431177	-1.266013	1.171942
1	-4.748249	-1.290370	2.020720
1	-3.805646	-0.038549	2.072436
6	-0.927791	5.207908	-0.446486
6	5.217099	-1.782345	-0.779086
6	6.897782	0.437802	-1.031958
1	7.467304	1.167751	-1.114033
6	-4.107718	1.846901	-2.816303

1	-3.603810	2.581871	-2.458164
1	-4.721972	2.175357	-3.478174
1	-3.508652	1.215343	-3.221323
6	-6.950812	0.534953	-0.682212
1	-7.880757	0.516136	-0.700523
6	7.416343	-0.822922	-1.035821
1	8.333499	-0.943732	-1.129437
6	1.301164	6.817299	-0.917447
1	2.037170	7.369598	-1.051765
6	-6.293872	-0.085225	0.349175
1	-6.776297	-0.483102	1.038985
6	-3.307764	-3.125934	-1.307863
1	-3.192298	-2.633679	-0.492222
1	-4.209830	-3.449741	-1.361022
1	-3.130642	-2.550253	-2.056594
6	1.427023	-4.890221	-1.160910
1	1.907732	-5.713240	-1.280148
1	1.625386	-4.529191	-0.293973
1	1.691928	-4.265580	-1.837792
6	6.592045	-1.921863	-0.901257
1	6.965959	-2.773144	-0.893702
6	-1.051377	6.583093	-0.609676
1	-1.891128	6.978459	-0.549101
6	-2.120764	4.335219	-0.152587
1	-2.224720	3.688505	-0.854361
1	-2.910001	4.879471	-0.100211
1	-1.988656	3.883475	0.682740
6	0.054400	7.370954	-0.859843
1	-0.051422	8.285613	-0.990053
6	4.303756	-2.960273	-0.615160
1	4.813930	-3.771707	-0.681985
1	3.635075	-2.945518	-1.302494
1	3.879724	-2.919954	0.245650

(Au···Rh-Au-Rh···Au)$^{-}$ of **(2b)**

79	0.000000	0.000000	0.000000
6	-0.633087	3.528593	0.785738
6	1.652581	2.607643	1.971900
6	2.906962	2.415439	-0.387833
6	0.540855	3.174728	-1.756578
7	-1.599384	3.954665	1.269269
7	2.006497	2.414537	3.049772
7	4.027301	2.118934	-0.525085
7	0.231112	3.328001	-2.831931
45	1.073338	2.875214	0.118742
6	-2.671276	4.455446	2.027305
6	2.443168	2.172731	4.346743
6	5.395149	1.802102	-0.589304
6	-0.120788	3.483510	-4.185567
6	-3.746687	4.995971	1.328451
6	3.066879	3.203019	4.987674
6	6.106533	1.865079	0.572934
6	0.853011	3.248848	-5.133741
6	-4.784062	5.503151	2.131818
1	-5.527200	5.894019	1.728875
6	3.493049	2.958584	6.326199
1	3.941516	3.614064	6.810989
6	7.459251	1.536927	0.509974
1	7.979489	1.556052	1.280602
6	0.491894	3.406742	-6.452119
1	1.118182	3.252133	-7.122011
6	-4.716986	5.431691	3.482935
1	-5.425860	5.764119	3.985354
6	3.227790	1.758574	6.867653
1	3.465435	1.614196	7.755386
6	8.025369	1.183040	-0.693817
1	8.930276	0.973887	-0.732852
6	-0.757492	3.781498	-6.784547
1	-0.976474	3.882559	-7.682353
6	-3.646857	4.889515	4.131421
1	-3.630731	4.867785	5.060707
6	2.635929	0.750200	6.192724
1	2.509037	-0.072233	6.609518
6	7.276905	1.133171	-1.830871
1	7.683126	0.887763	-2.629201
6	-1.717450	4.020275	-5.832595
1	-2.572152	4.280829	-6.089471
6	-2.577998	4.369542	3.406124
6	2.215465	0.931659	4.890716
6	5.920927	1.439690	-1.828352
6	-1.412500	3.871970	-4.483996
6	-3.814858	5.047235	-0.142289
1	-2.952721	5.280088	-0.494864
1	-4.459977	5.707853	-0.409239
1	-4.078466	4.188712	-0.479754
6	3.344023	4.538046	4.359335
1	4.059121	4.451182	3.723441
1	3.596985	5.165577	5.040560
1	2.554824	4.852241	3.912321
6	5.488022	2.293835	1.887534
1	4.788848	1.682317	2.125522
1	5.123405	3.177890	1.795613
1	6.160603	2.295414	2.572537
6	2.244058	2.830860	-4.724503
1	2.655947	3.538154	-4.223343
1	2.767220	2.647623	-5.508982
1	2.193873	2.039841	-4.183048
6	-1.343993	3.792711	4.055869
1	-1.205492	2.896242	3.741070
1	-1.458343	3.783125	5.009080
1	-0.581734	4.332792	3.830473
6	1.504844	-0.128586	4.141494
1	0.568039	0.079318	4.104978
1	1.629310	-0.971073	4.583472
1	1.856530	-0.179923	3.249984
6	5.074381	1.383925	-3.042217
1	4.859877	2.276177	-3.324277
1	4.265426	0.906454	-2.845783
1	5.549582	0.933823	-3.743589
6	-2.416009	4.131007	-3.401088
1	-2.573528	3.321142	-2.910002
1	-3.238277	4.432546	-3.793957
1	-2.077844	4.805390	-2.808007
6	-1.073275	0.262263	1.649546
7	-1.681679	0.437439	2.600239
6	0.633087	-3.528593	-0.785738
6	-1.652581	-2.607643	-1.971900
6	-2.906962	-2.415439	0.387833
6	-0.540855	-3.174728	1.756578
7	1.599384	-3.954665	-1.269269
7	-2.006497	-2.414537	-3.049772
7	-4.027301	-2.118934	0.525085
7	-0.231112	-3.328001	2.831931
45	-1.073338	-2.875214	-0.118742
6	2.671276	-4.455446	-2.027305
6	-2.443168	-2.172731	-4.346743
6	-5.395149	-1.802102	0.589304
6	0.120788	-3.483510	4.185567
6	3.746687	-4.995971	-1.328451
6	-3.066879	-3.203019	-4.987674
6	-0.853011	-3.248848	5.133741
6	4.784062	-5.503151	-2.131818
1	5.527200	-5.894019	-1.728875
6	-3.493049	-2.958584	-6.326199
1	-3.941516	-3.614064	-6.810989
6	-7.459251	-1.536927	-0.509974
1	-7.979489	-1.556052	-1.280602
6	-0.491894	-3.406742	6.452119
1	-1.118182	-3.252133	7.122011
6	4.716986	-5.431691	-3.482935
1	5.425860	-5.764119	-3.985354
6	-3.227790	-1.758574	-6.867653
1	-3.465435	-1.614196	-7.755386
6	-8.025369	-1.183040	0.693817
1	-8.930276	-0.973887	0.732852
6	0.757492	-3.781498	6.784547
1	0.976474	-3.882559	7.682353
6	3.646857	-4.889515	-4.131421
1	3.630731	-4.867785	-5.060707
6	-2.635929	-0.750200	-6.192724
1	-2.509037	0.072233	-6.609518
6	-7.276905	-1.133171	1.830871
1	-7.683126	-0.887763	2.629201
6	1.717450	-4.020275	5.832595
1	2.572152	-4.280829	6.089471
6	2.577998	-4.369542	-3.406124
6	-2.215465	-0.931659	-4.890716

6	-5.920927	-1.439690	1.828352	1	-2.767220	-2.647623	5.508982	1	3.238277	-4.432546	3.793957
6	1.412500	-3.871970	4.483996	1	-2.193873	-2.039841	4.183048	1	2.077844	-4.805390	2.808007
6	3.814858	-5.047235	0.142289	6	1.343993	-3.792711	-4.055869	6	1.073275	-0.262263	-1.649546
1	2.952721	-5.280088	0.494864	1	1.205492	-2.896242	-3.741070	7	1.681679	-0.437439	-2.600239
1	4.459977	-5.707853	0.409239	1	1.458343	-3.783125	-5.009080	79	-3.670982	-6.141008	0.000000
1	4.078466	-4.188712	0.479754	1	0.581734	-4.332792	-3.830473	6	-4.472325	-5.357952	1.631917
6	-3.344023	-4.538046	-4.359335	6	-1.504844	0.128586	-4.141494	7	-5.044489	-5.021306	2.515873
1	-4.059121	-4.451182	-3.723441	1	-0.568039	-0.079318	-4.104978	6	-2.869639	-6.924064	-1.631918
1	-3.596985	-5.165577	-5.040560	1	-1.629310	0.971073	-4.583472	7	-2.297475	-7.260710	-2.515873
1	-2.554824	-4.852241	-3.912321	1	-1.856530	0.179923	-3.249984	79	3.670982	6.141008	0.000000
6	-5.488022	-2.293835	-1.887534	6	-5.074381	-1.383925	3.042217	6	2.869639	6.924064	1.631918
1	-4.788848	-1.682317	-2.125522	1	-4.859877	-2.276177	3.324277	7	2.297475	7.260710	2.515873
1	-5.123405	-3.177890	-1.795613	1	-4.265426	-0.906454	2.845783	6	4.472325	5.357952	-1.631917
1	-6.160603	-2.295414	-2.572537	1	-5.549582	-0.933823	3.743589	7	5.044489	5.021306	-2.515873
6	-2.244058	-2.830860	4.724503	6	2.416009	-4.131007	3.401088				
1	-2.655947	-3.538154	4.223343	1	2.573528	-3.321142	2.910002				

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