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Supporting information for article:

Chemistry of transition-metal complexes containing functionalized phosphines: synthesis and structural analysis of rhodium(I) complexes containing allyl and cyanoalkylphosphines

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S1. Spectroscopy data

S1.1. Analytical data for [Rh(acac)(CO)(^{t}BuP($CH_2CH=CH_2$)$_2$] (2a):

$^{31}P\{^1H\}$NMR ($CDCl_3$): 55.68 (d, $^1J_{PRh}$ = 170.0 Hz). ^1H NMR ($CDCl_3$): 1.27 (d, $^3J_{HP}$ = 14.49 Hz, 9H, ^{t}Bu), 1.86 (s, 3H, CH_3–acac), 2.04 (s, 3H, CH_3–acac), 2.67(m, 2H, P–CH_2), 5.14 (m, 4H, C=CH_2), 5.43 (s, H–acac), 6.01 (m, 2H, CH=C); $^{13}C\{^1H\}$NMR ($CDCl_3$): 27.13 (s, CH_3–acac), 27.62 (bs, CH_3 – ^{t}Bu), 27.92 (d, $^1J_{CP}$ = 24.55 Hz, PCH_2), 32.99 (d, $^1J_{CP}$ = 26.42 Hz, C –^{t}Bu), 100.53 (s, CH–acac), 118.52 (s, =CH_2), 132.20 (s, CH=), 184.88 (s, C –O–acac), 187.90 (s, C–O–acac), 189.80 (dd, $^1J_{CRh}$ = 75.96 Hz, $^2J_{CP}$ = 24.27 Hz, CO).

S1.2. Analytical data for [Rh(acac)(CO)(^{t}BuP(CH_2CN)$_2$)] (2b):

$^{31}P\{^1H\}$NMR ($CDCl_3$): 61.9 (d, $^1J_{Rh-P}$= 184.5 Hz). ^1H NMR ($CDCl_3$): 1.37 (d, $^3J_{PH}$=16.6, 9H, (CH_3)C), 1.94 (s, 3H, CH_3-acac), 2.08 (s, 3H, CH_3-acac), 3.18 (m, 4H, CH_2CN), 5.51 (s, 1H, H-acac). $^{13}C\{^1H\}$NMR ($CDCl_3$): 11.7(d, $^1J_{PC}$= 15.34, PCH_2), 27.02 (s, CH_3), 27.53 (d, J= 5.64 Hz, CH_3), 34.52 (d, $^1J_{PC}$= 24.47, C(CH3)), 101.13 (s, HC-acac), 114.25 (d, $^2J_{PC}$= 6.7 Hz, CN), 184.92 (s, C-O-acac), 188.42 (s, C-O-acac), 188,7 (bs, CO). $C_{14}H_{20}N_2O_3PRh$

S1.3. Analytical data for [Rh(acac)(CO)[PhP($CH_2CH=CH_2$)$_2$)] (2c):

$^{31}P\{^1H\}$NMR ($CDCl_3$): 35.87 (d, $^1J_{Rh-P}$= 171.9 Hz). ^1H NMR ($CDCl_3$): 1.86 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.9-3.1 (m, 4H, CH_2P), 5.16-5.09 (m, 4H, CH=CH_2), 5.46 (s, 1H, H-acac) 5.85 (m, 2H, CH=CH_2), 7.4 (m, 3H, H-Phenyl), 7.84 (m, 2H, H-Phenyl). $^{13}C\{^1H\}$NMR ($CDCl_3$): 27.17 (s, CH_3), 27.64 (d, J= 5.43 Hz, CH_3), 31.0 (d, J= 28.54 Hz, CH_2P), 100.73 (s, HC-acac), 119.22 (s, CH=CH_2), 128.14 (d, J= 9.96 Hz, C-m-Phenyl), 130.31 (s, p-C-Phenyl), 132.16 (s, CH=CH_2), 132.62 (d, J= 10.26 Hz, 0-C-Phenyl), 185.19 (s, C-O), 187.79 (s, C-O), 189.08 (dd, $^1J_{Rh-C}$= 76.03 Hz, $^2J_{P-C}$= 24.77 Hz, CO).

S1.4. Analytical data for [Rh(acac)(CO)(PhP(CH_2CN)$_2$)] (2d):

$^{31}P\{^1H\}$NMR ($CDCl_3$): 39.57 (d, $^1J_{Rh-P}$= 188.1 Hz). ^1H NMR ($CDCl_3$): 1.94 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 3.42 (m, 4H, CH_2P), 5.55 (s, 1H, H-acac), 7.54 (m, 3H, H-phenyl), 7.8 (m, 2H, H-phenyl). $^{13}C\{^1H\}$NMR ($CDCl_3$): 40.49 (d, $^1J_{P-C}$= 21.36 Hz, CH_2P), 27.05 (s, CH_3), 27.53 (d, J= 6.14 Hz, CH_3), 101.3 (d, $^3J_{Rh-C}$= 1.62 Hz, HC-acac), 113.96 (d, $^2J_{PC}$= 6.8 Hz, CN), 128.07 (d, ^{1}JPC= 50.97 Hz, i-C-Phenyl), 129.32 (d, $^3J_{PC}$= 11.44 Hz, C-m-Phenyl), 132.5 (d, $^2J_{PC}$= 13.6 Hz, o-C-Phenyl), 133.02 (d, $^4J_{PC}$= 2.16 Hz, p-C-Phenyl), 185.28 (s, C-O), 187.13 (dd, $^1J_{Rh-C}$= 73.65 Hz, $^2J_{P-C}$= 26.76 Hz, CO), 188.2 (s, C-O).

S1.5. Analytical data for [Rh(CO)(acac)($Ph_2PCH_2CH=CH_2$)] (2e):

$^{31}P\{^{1}H\}$NMR ($CDCl_3$): 43.7 (d, $^{1}J_{Rh-P}$= 172.9 Hz). ^{1}H NMR ($CDCl_3$): 1.81 (s, 3H, CH_3), 2.1 (s, 3H, CH_3), 3.32 (m, 2H, C$\underline{H}_2$P), 4.9 (m, 2H, CH=C$\underline{H}_2$), 5.5 (s, 1H, H-acac) 5.9 (m, 1H, C$\underline{H}$=CH_2), 7.4-7.7 (m, 10H, H-Phenyl). $^{13}C\{^{1}H\}$NMR ($CDCl_3$): 26.95 (s, CH_3), 27.52 (d, $^{5}J_{P-C}$= 5.22 Hz, CH_3), 33.3 (d, $^{2}J_{P-C}$= 28.7 Hz, CH_2P), 100.7 (s, H$\underline{C}$-acac), 118.7 (s, $\underline{C}$H=CH_2), 128.0 (d, J= 9.4 Hz, C-m-Phenyl), 130.2 (s, p-C-Phenyl), 132.2 (s, CH=$\underline{C}H_2$), 132.9 (d, J= 10.26 Hz, 0-C-Phenyl), 185.2 (s, C-O), 187.6 (s, C-O), 188.8 (dd, $^{1}J_{Rh-C}$= 75.7 Hz, $^{2}J_{P-C}$= 24.9 Hz, CO).

S1.6. Analytical data for [Rh(acac)(CO)[Ph_2PCH_2CN)] 2f:

$^{31}P\{^{1}H\}$NMR ($CDCl_3$): 45.0 (d, $^{1}J_{Rh-P}$ = 178.6 Hz); ^{1}H NMR ($CDCl_3$): 1.94 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 3.56 (d, $^{2}J_{PH}$ = 8.7 Hz, 2H, CH_2P), 5.6 (s, 1H, Hacac), 7.5 (m, 6H, Harom), 7.85 (m, 4H, Harom); $^{13}C\{^{1}H\}$NMR ($CDCl_3$): 16.07 (d, $^{1}J_{PC}$ = 18.8, $\underline{C}H_2$P), 27.05 (s, CH_3), 27.56 (s, CH_3), 101.08 (s, HCacac), 116 (s, CN), 128.81 (d, J_{PC} = 10.7 Hz, m – C), 131.2 (bs, i – C), 131.5 (s, p- C), 133.0 (d, J_{PC} = 12.1, o-C), 185.2 (s, CH_3), 187.9 (bs, CO), 188.1 (s, CH_3)

S1.7. Analytical data for [Rh(acac)(CO)[$^{i}Pr_2NP(CH_2CH=CH_2)_2$)] (2g):

$^{31}P\{^{1}H\}$NMR ($CDCl_3$): 73.9(d, $^{1}J_{Rh-P}$= 180.7 Hz). ^{1}H NMR ($CDCl_3$): 1.36 (d, $^{3}J_{HH}$= 6.8 Hz, 12H, $(C\underline{H}_3)_2$CH), 1.91 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.92 (m, 4H, C$\underline{H}_2$P), 3.75 (m, , 2H, $(CH_3)_2C\underline{H}$) 5.13 (m, 4H, CH=C$\underline{H}_2$), 5.48 (s, 1H, H-acac) 6.09 (m, 2H, C$\underline{H}$=CH_2). $^{13}C\{^{1}H\}$NMR ($CDCl_3$): 24.27 (d, $^{3}J_{PC}$= 1.79 Hz, $(\underline{C}H_3)_2$CH), 27.2 (s, CH_3), 27.7 (d, J= 5.66 Hz, CH_3), 36.3 (d, $^{2}J_{P-C}$= 32.66 Hz, CH_2P), 48.62 (d, $^{2}J_{P-C}$= 2.83 Hz, $(CH_3)_2\underline{C}$H), 100.55 (d, $^{3}J_{Rh-C}$= 1.68 Hz, HC-acac), 118.0 (bs, $\underline{C}$H=CH_2), 132.0 (bs, CH=$\underline{C}H_2$), 185.06 (s, C-O-acac), 187.93 (s, C-O-acac), 190.03 (dd, $^{1}J_{Rh-C}$= 78.12 Hz, $^{2}J_{P-C}$= 25.2 Hz, CO).

S1.8. Analytical data for [Rh(acac)(CO)($Ph_2PCH_2CH_2CN$)] (2h):

$^{31}P\{^{1}H\}$NMR ($CDCl_3$): 46 ppm (d, $^{1}J_{PRh}$= 174Hz). ^{1}H NMR ($CDCl_3$): 1.90ppm (s, 3H, C$\underline{H}_3$); 2.10 (s, 3H, C$\underline{H}_3$); 2.48 (m, 2H, $PCH_2C\underline{H}_2CN$); 2.80 (m, 2H, P$\underline{C}H_2CH_2CN$); 5.52 (s, 1H, H_{acac}); 7.67-7.48 (m, 10H, $H_{arom.}$). $^{13}C\{^{1}H\}$NMR ($CDCl_3$): 13.10 ppm (d, $PCH_2\underline{C}H_2CN$, $^{2}J_{PC}$= 6.85Hz), 22.90 (d, P$\underline{C}H_2CH_2CN$, $1J_{PC}$=28.6Hz), 27.14 (s, CH_3); 27.59 (d, $^{3}J_{RhC}$= 5.56Hz, CH_3), 119.15 (d, $^{3}J_{PC}$= 20.60Hz, $PCH_2CH_2\underline{C}N$,); 128.73 (d, $C_{3,5}$, J_{PC}=10.44Hz); 130.98 (s, C_4); 132.80 (d, C_1, J_{P-C}=11.5Hz); 185.17 (s, C_7); 188.30 (dd, $^{1}J_{RhC}$=71.4Hz; $^{2}J_{PC}$=25.3Hz, $\underline{C}$O).

S1.9. Analytical data for Rh(acac)(CO)($^{t}Bu_2PCH_2CH_2CN$)] (2i):

$^{31}P\{^{1}H\}$NMR ($CDCl_3$): 83.10 (d, J_{PRh}=158Hz); ^{1}H NMR ($CDCl_3$): 1.33 (d, $^{3}J_{PH}$=13.8, 18H, $(CH_3)C$), 1.94 (s, 3H, CH_3-acac); 2.07 (s, 3H, CH_3-acac); 2.50 (m, 2H, $PCH_2C\underline{H}_2CN$); 2.70 (m, 2H, P$\underline{C}H_2CH_2CN$); 5.52 (s, 1H, H-acac); 7.67-7.48 (m,10H); $^{13}C\{^{1}H\}$NMR ($CDCl_3$): 14.33 (d, $^{2}J_{PC}$ = 4.97 Hz, $PCH_2C\underline{H}_2CN$), 14.97 (d, $^{1}J_{PC}$= 18.46Hz, P$\underline{C}H_2CH_2CN$,); 26.07 (s, CH_3acac), 26.76 (d, $^{3}J_{RhC}$= 5.18, CH_3acac), 29.02 (d, $^{2}J_{PC}$= 3.81 Hz, C($\underline{C}H_3$)), 34.3 (dd, $^{1}J_{PC}$= 21.97, $^{2}J_{RhC}$= 1.9 Hz, $\underline{C}(CH_3)$), 100.02 (d,

$^3J_{RhC}$= 3.1 Hz, HCacac), 118.8 (d, $^3J_{PC}$= 17.35, PCH_2CH_2CN); 184.03 (s, CH_3C-O-), 187.56 (s, CH_3C-O-), 189.20 (dd, J_{RhC}= 75.4Hz, $^2J_{PC}$= 23.5 Hz, CO).

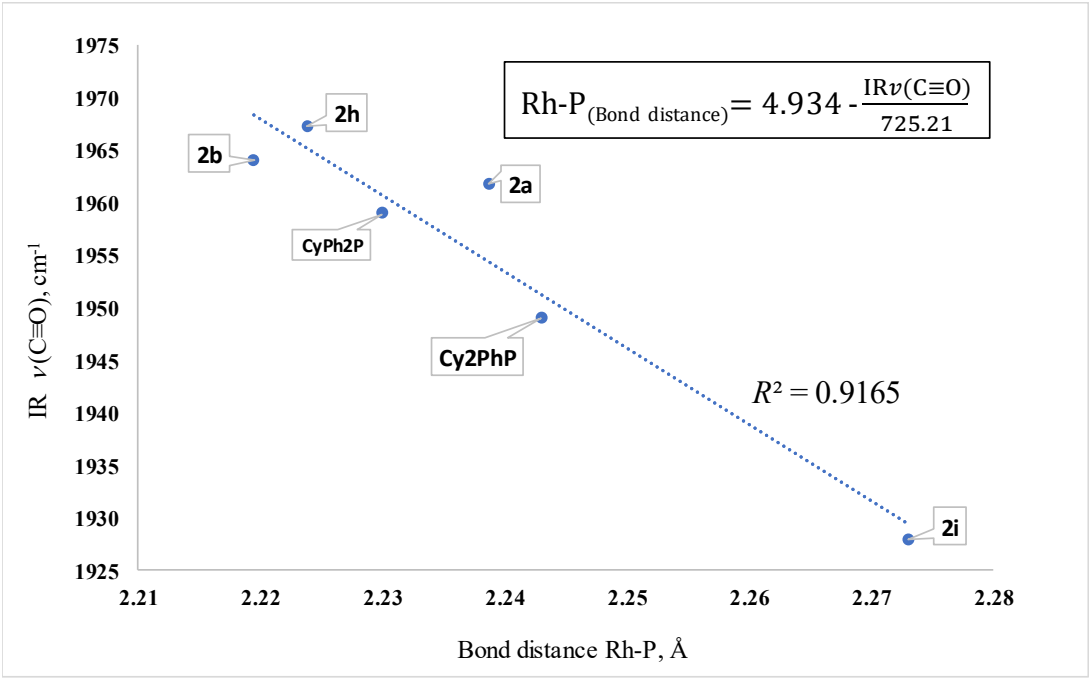


Figure S1 Dependence of IR ν(C≡O) band *vs* Rh-P distance for the selected Rh-complexes [Rh(acac)(CO)(PRR'$_2$)].

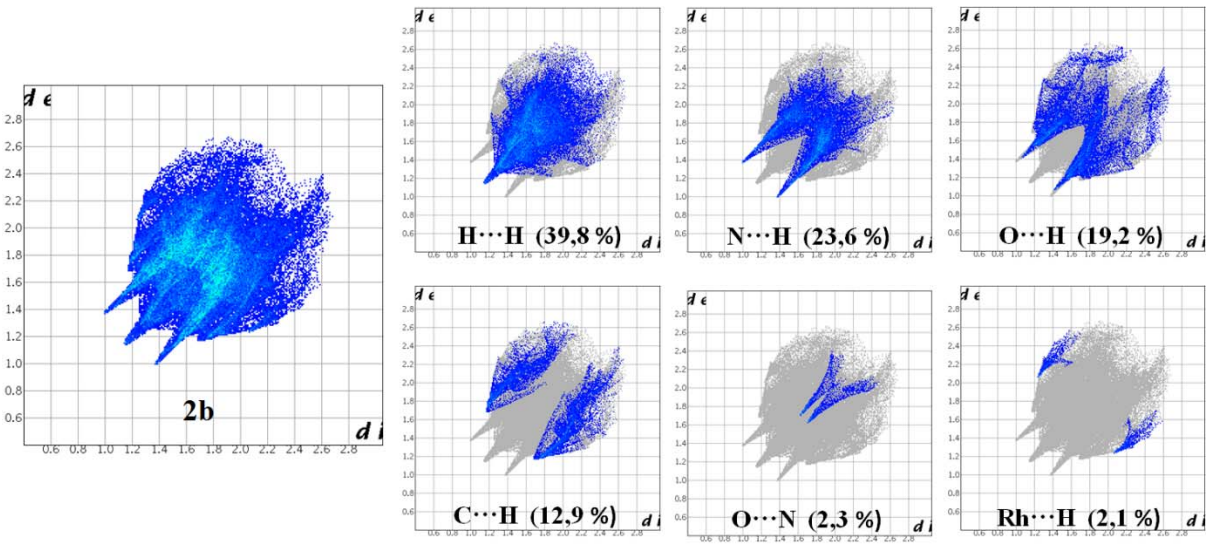
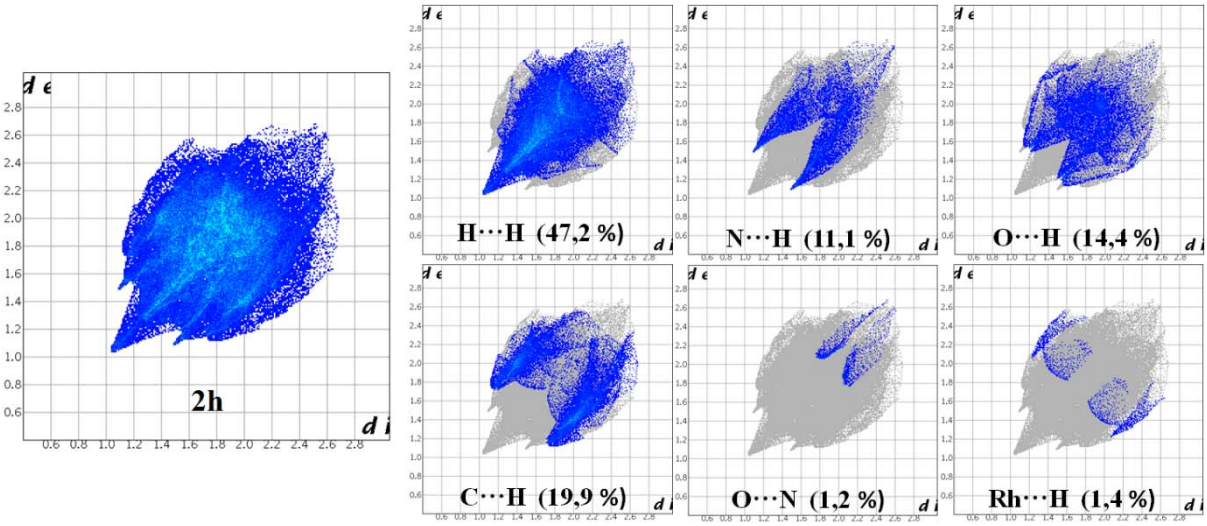
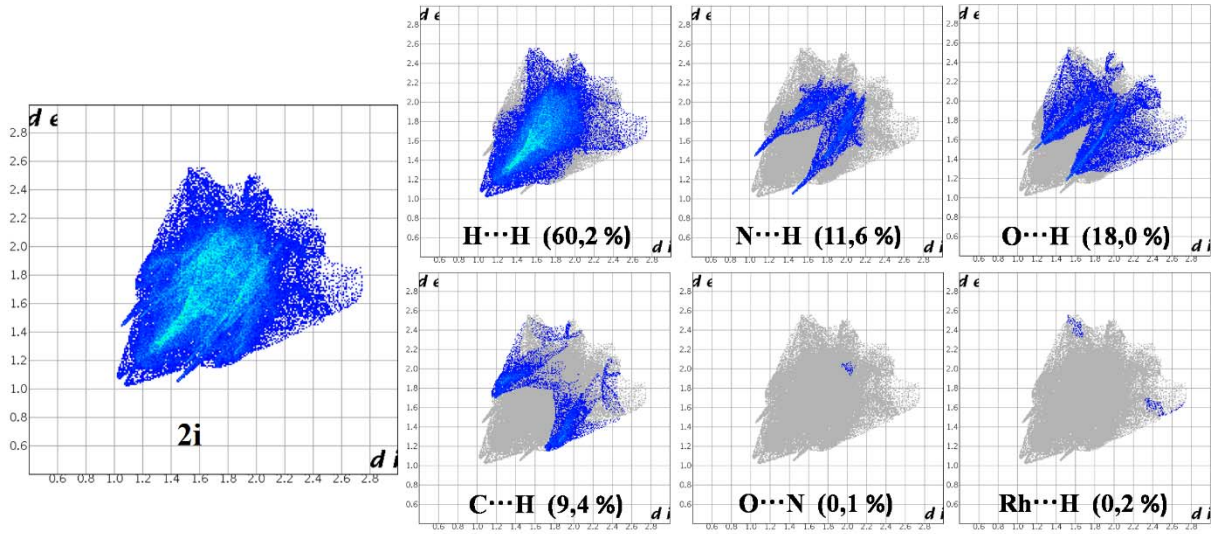


Figure S2 Fingerprint (FP) plot for **2b**, showing the percentages of contacts contributed to the total Hirshfeld surface area.



1 **Figure S3** Fingerprint (FP) plot for **2h**, showing the percentages of contacts contributed to the total
2 Hirshfeld surface area.

3



4 **Figure S4** Fingerprint (FP) plot for **2i**, showing the percentages of contacts contributed to the total
5 Hirshfeld surface area.

6

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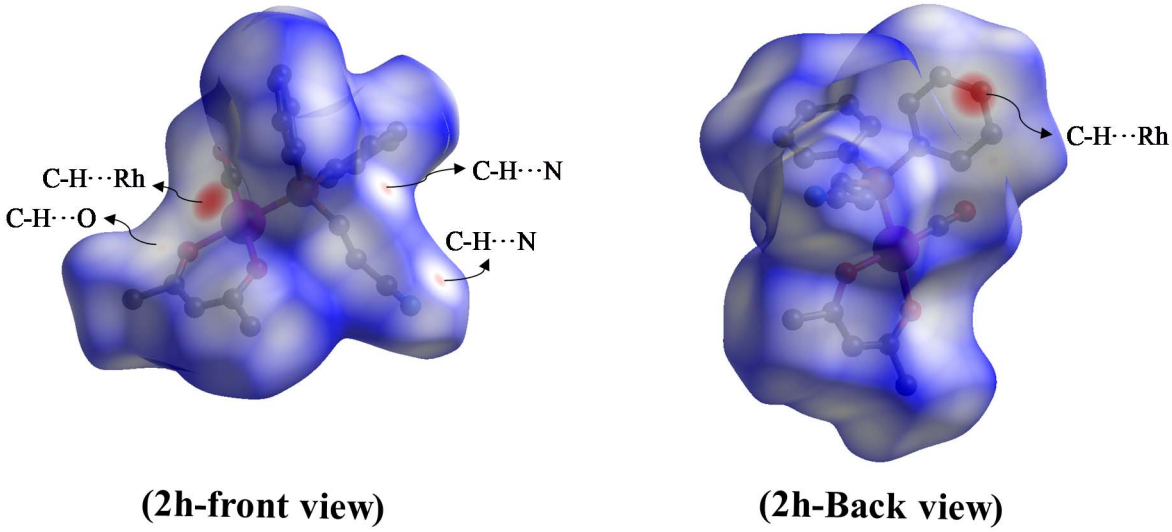

Figure S5 Front and back view of the HS for compound **2h**. Both HS were plotted with the same color code: -0.2238 (blue) to 1.2300 (red).

Table S1 Torsion angles comparison from geometry data obtained from single-crystal XRD and DFT calculation at the B3YLP/DGDZVP level of theory.

Compound	The substituent on phosphine ligand		Torsion angles, (°)		
			From XRD data	From DFT (B3YLP/ DGDZVP)	Differences
2b	Cyanoalkyl	O1–Rh1–P1–C11	-142.0	-139.1	-2.9
		O1–Rh1–P1–C13	-27.0	-25.6	-1.4
		Rh1–P1–C11–C12	162.2	171.5	-9.3
		Rh1–P1–C13–C14	-73.9	-62.5	-11.4
	tert–Butyl	O1–Rh1–P1–C7	93.2	94.3	-1.1
		Rh1–P1–C13–C14	178.4	199.5	-21.1
		Rh1–P1–C13–C14	52.5	77.2	-24.7
		Rh1–P1–C13–C14	62.6	-39.7	-22.9
2h	Cyanoalkyl	O1–Rh1–P1–C13	16.4	9.5	6.9
		Rh1–P1–C13–C14	68.0	68.2	-0.2
	Phenyl	O1–Rh1–P1–C7	135.9	128.6	7.3
		O1–Rh1–P1–C16*	-101.5*	-108.0	6.5
		Rh1–P1–C7–C8	-11.6	-13.3	1.7
		Rh1–P1–C16A–C17A	-87.1	-83.2	-3.9
2i	Cyanoalkyl	O1–Rh1–P1–C13	20.3	18.8	1.5
		Rh1–P1–C13–C14	57.6	59.6	-2.0
	tert-Butyl	O1–Rh1–P1–C7	91.5	-92.2	0.7
		O1–Rh1–P1–C11	138.2	137.5	0.7
		Rh1–P1–C7–C8	179.7	181.7	1.9
		Rh1–P1–C7–C9	-54.9	-54.7	-0.2
		Rh1–P1–C7–C10	60.4	61.3	-0.9
		Rh1–P1–C11–C12	-35.7	-34.8	-0.9
		Rh1–P1–C11–C16	-153.6	-154.5	0.9
		Rh1–P1–C11–C17	82.2	83.0	-0.8

*Mean value involving both P-C_{ipso} (P1-C16A and P1-C16B) orientations for disordered phenyl rings.

Table S2 Comparison of selected bond distances (Å) around the Rh environment obtained from single-crystal XRD and DFT calculation at the B3YLP/DGDZVP level of theory. Distance values from DFT calculations are given in square brackets.

	2b	**2h**	**2i**
Rh1-P1	2.2194(9) [2.30967]	2.2244(12) [2.31731]	2.272(2) [2.35393]
Rh1-O1	2.033(4) [2.09585]	2.044(3) [2.10008]	2.048(6) [2.10428]
Rh1-O2	2.057(4) [2.10550]	2.077(3) [2.11459]	2.081(6) [2.11880]
Rh1-C6(CO)	1.805(6) [1.86869]	1.806(5) [1.86784]	1.790(11) [1.86089]

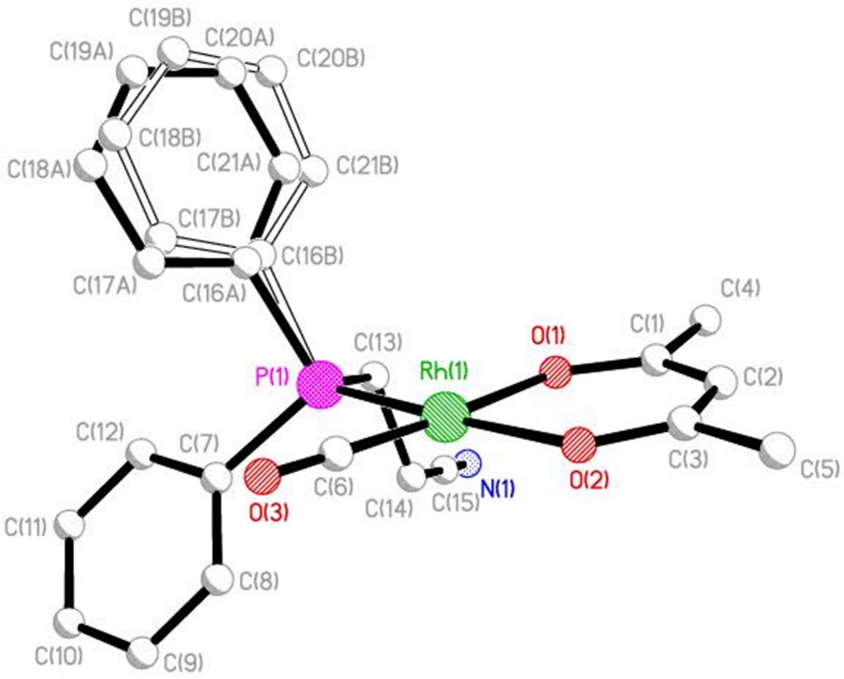

Figure S6 Representation of the molecular structure of **2i** showing the disordered phenyl group (C16-C21) which was modelled with two orientations in a same plane. H-atoms were omitted for clarity. Atoms are displayed with IDP indicated as spheres of arbitrary size.