Supplementary Data

Structural Study of Model Rhodium(I) Carbonylation Catalysts Activated by Indole-2-/ Indoline-2-Carboxylate Bidentate Ligands and Kinetics of Iodomethane Oxidative Addition

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INDEX

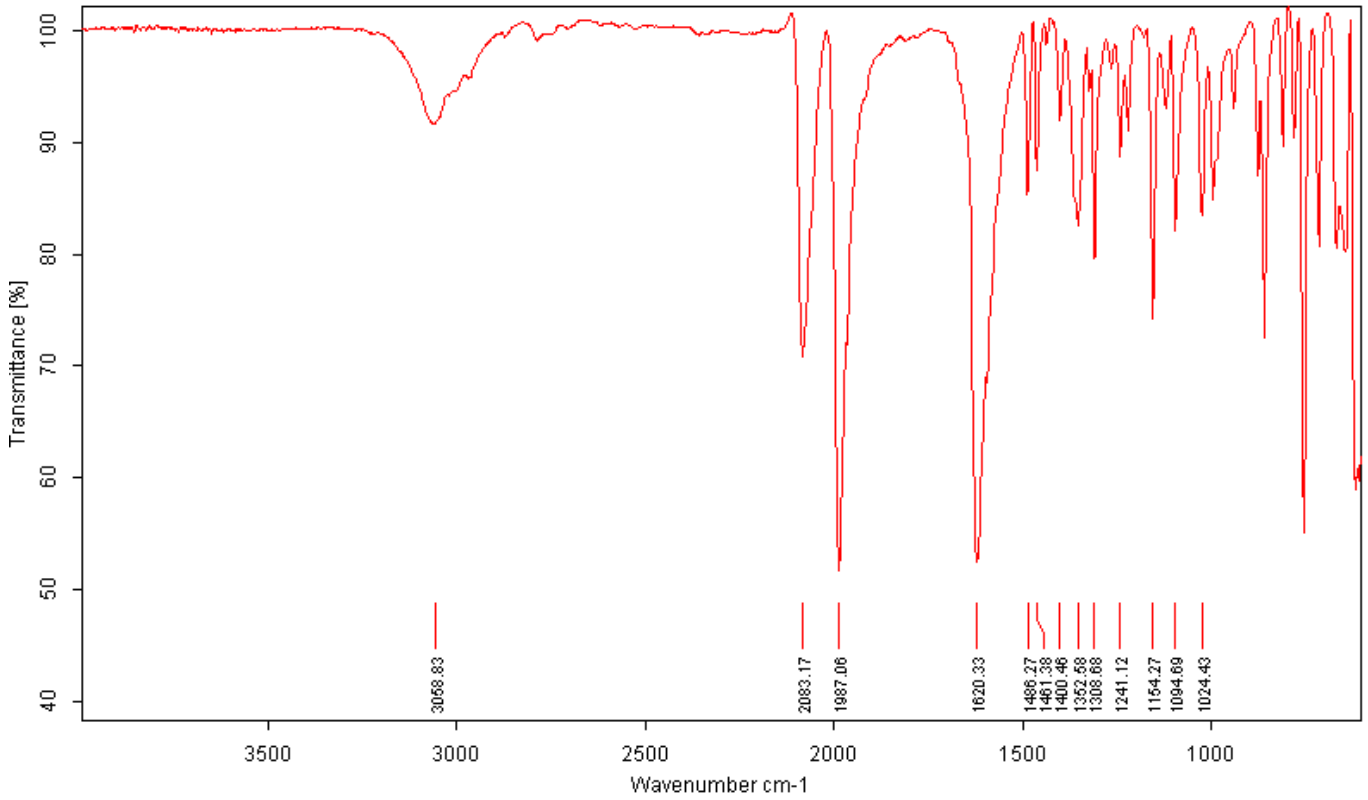


Figure S1: ATR IR spectrum of [Rh(indoli)(CO)$_2$] (A1)

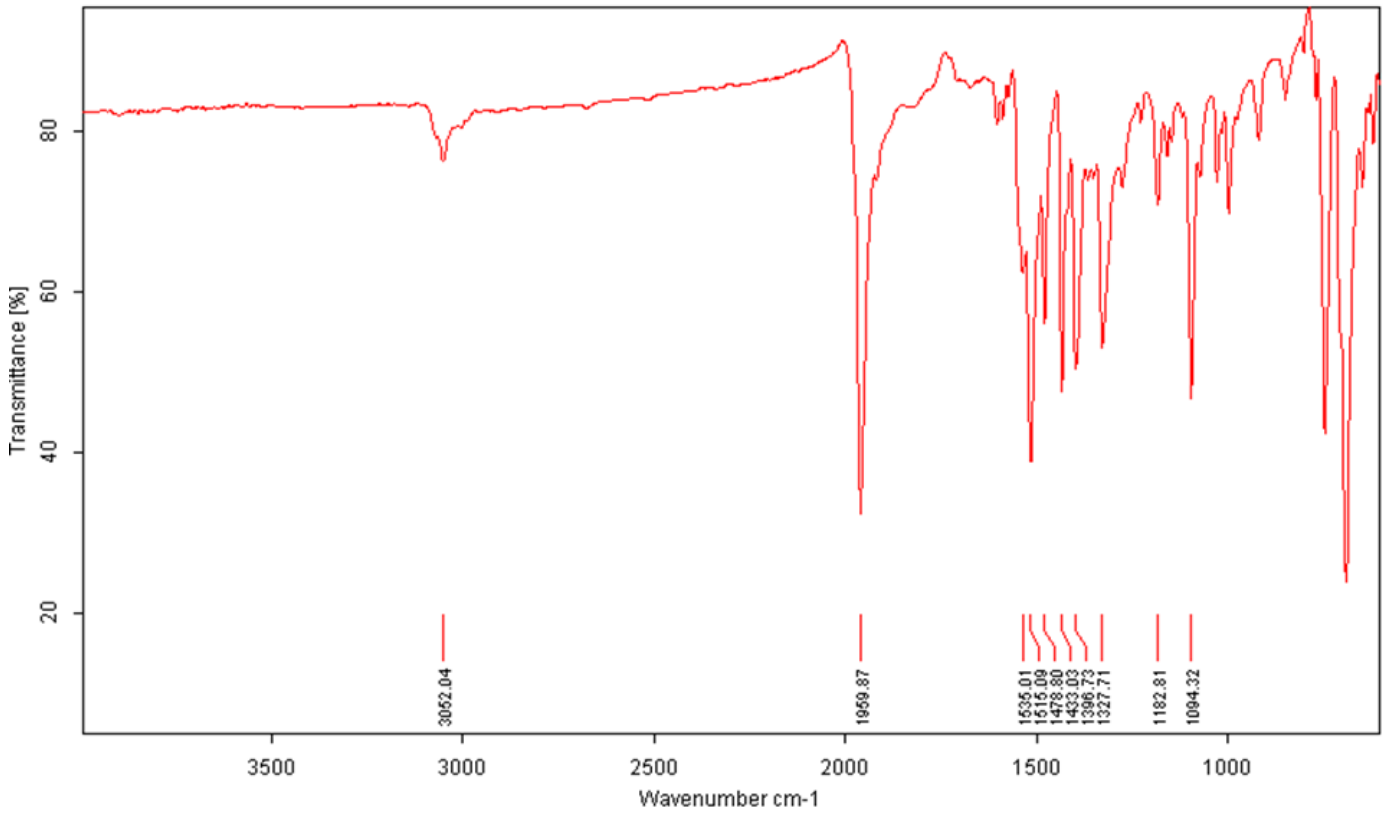


Figure S2: ATR IR spectrum of [Rh(indoli)(CO)(PPh_3)] (A2)

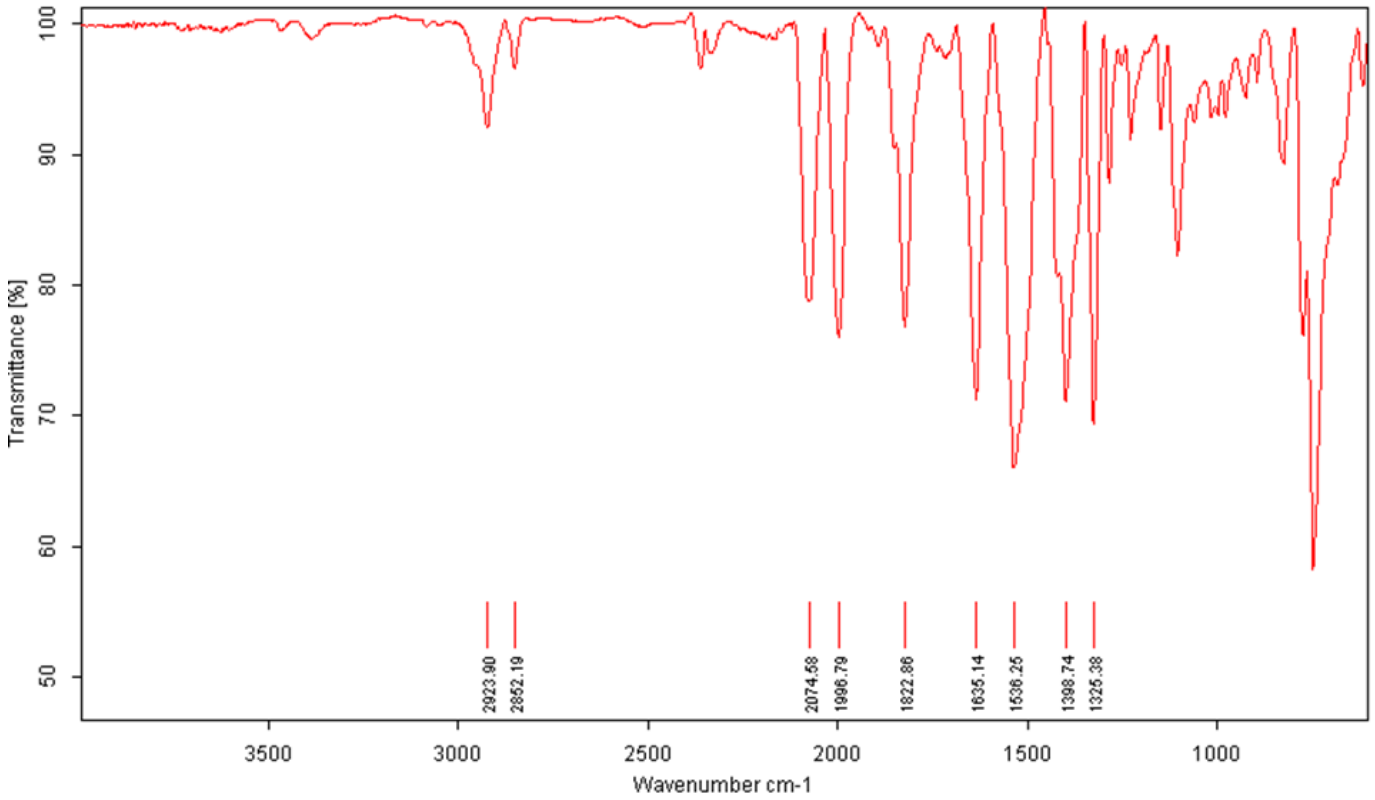


Figure S3: ATR IR spectrum of [Rh(indol)($CO)_2$] (B1)

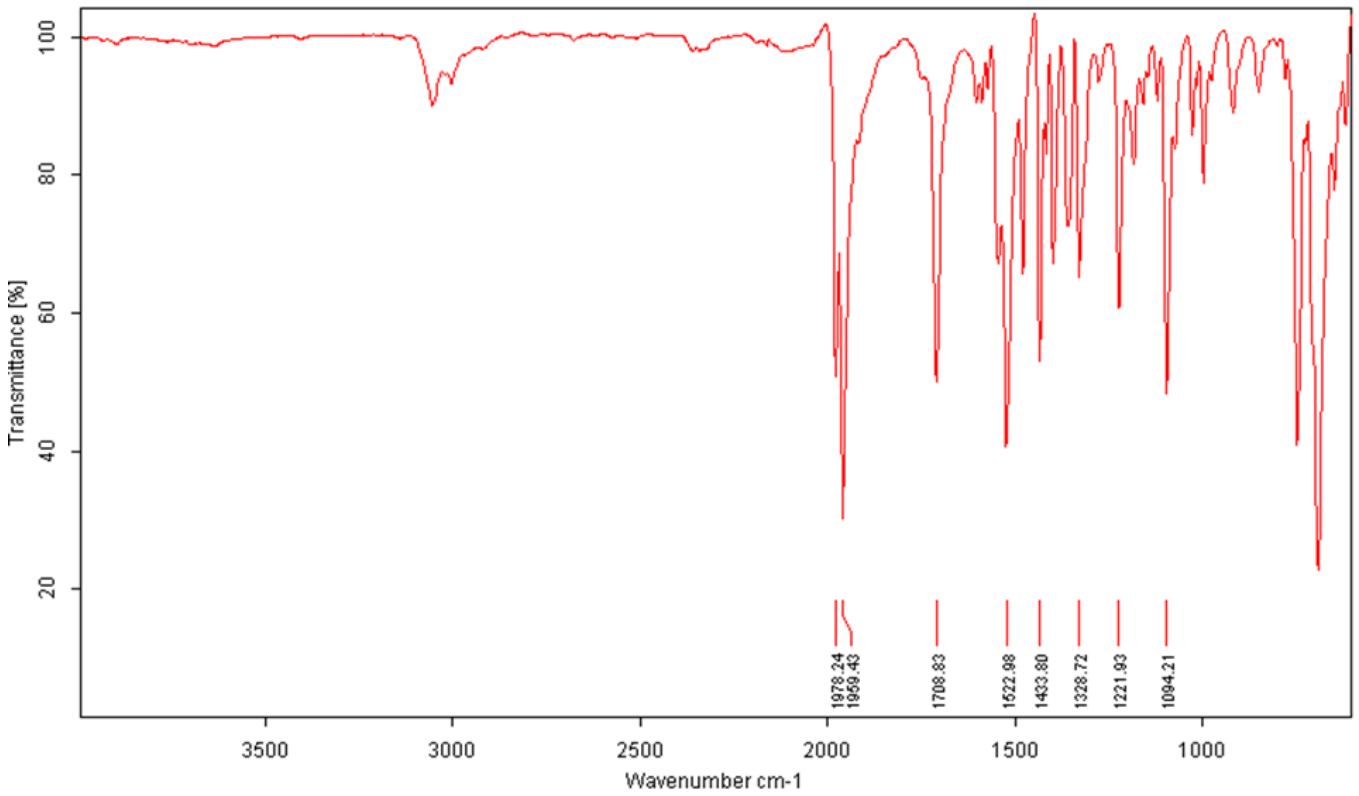


Figure S4: ATR IR spectrum of [Rh(indol)(CO)(PPh_3)Rh(CO)($PPh_3)_2$] (B2)

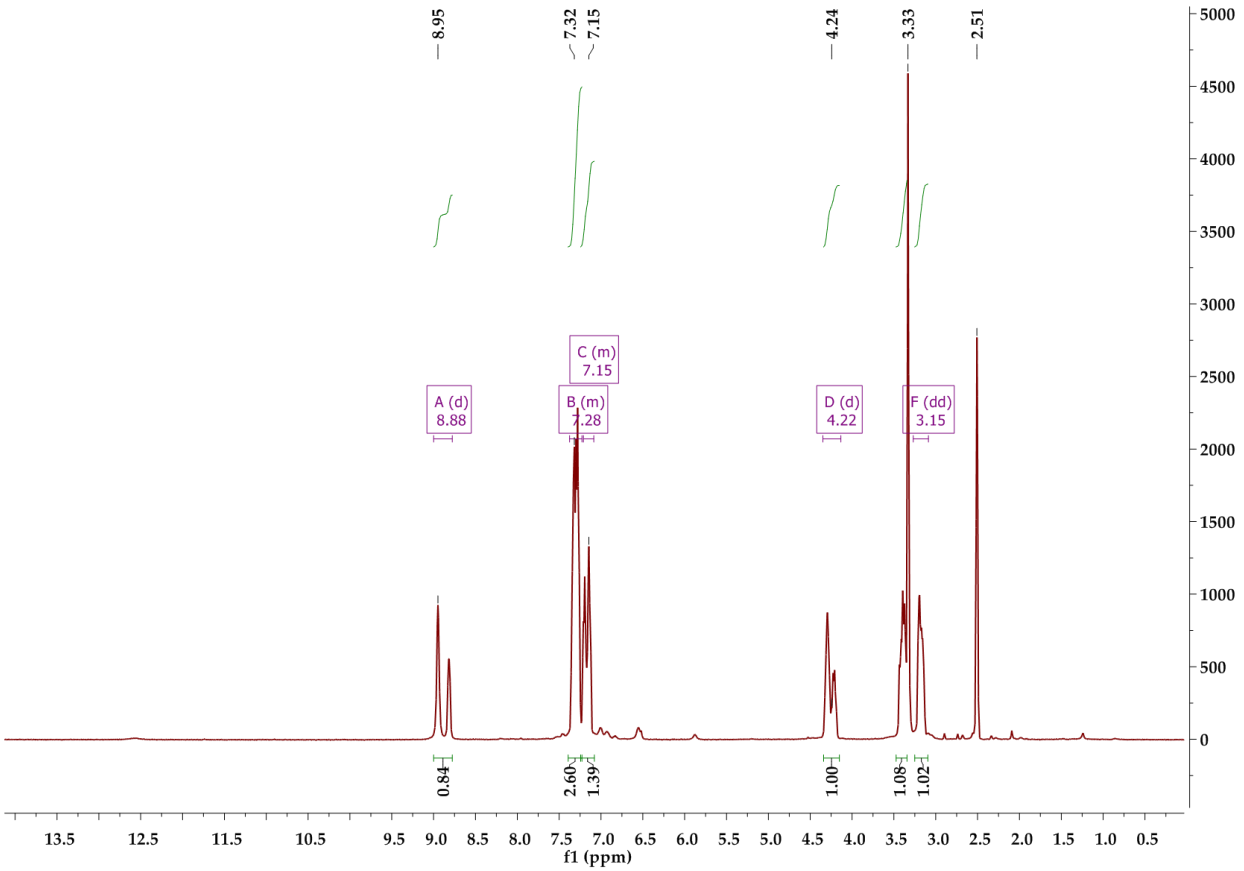


Figure S5: ^{1}H NMR spectrum (DCM) of [Rh(indoli)(CO)$_2$] (A1)

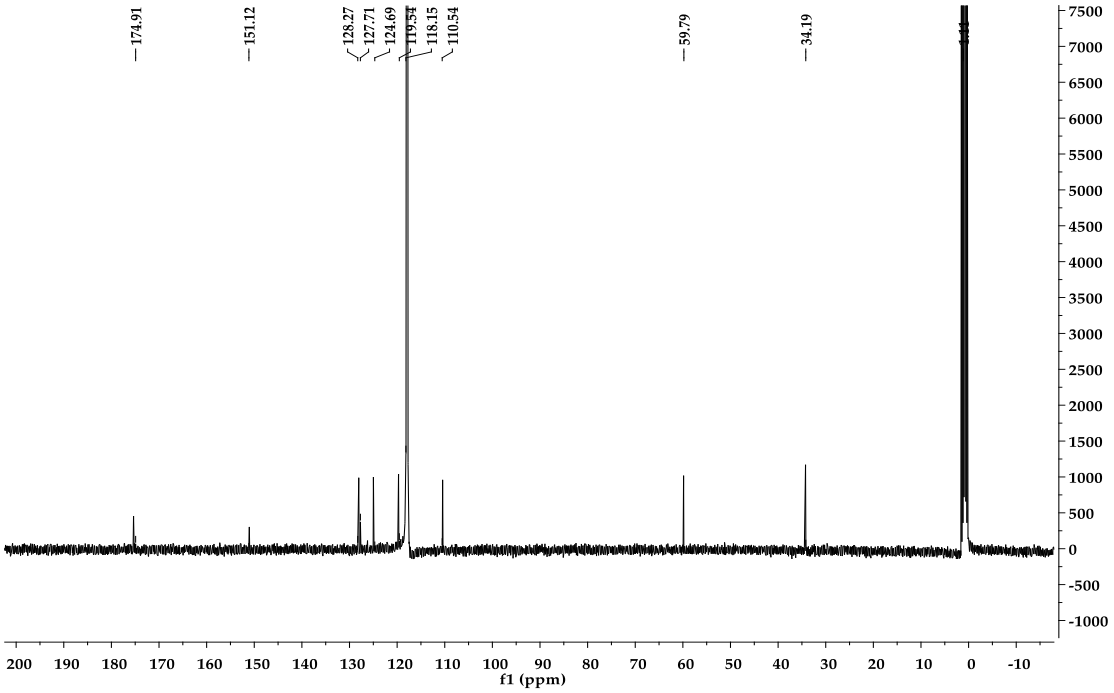


Figure S6: ^{13}C NMR spectrum of the IndoliH ligand in Acetonitrile d$_3$. The signals 1.1 and 118.2 refer to the deuterated acetonitrile solvent.

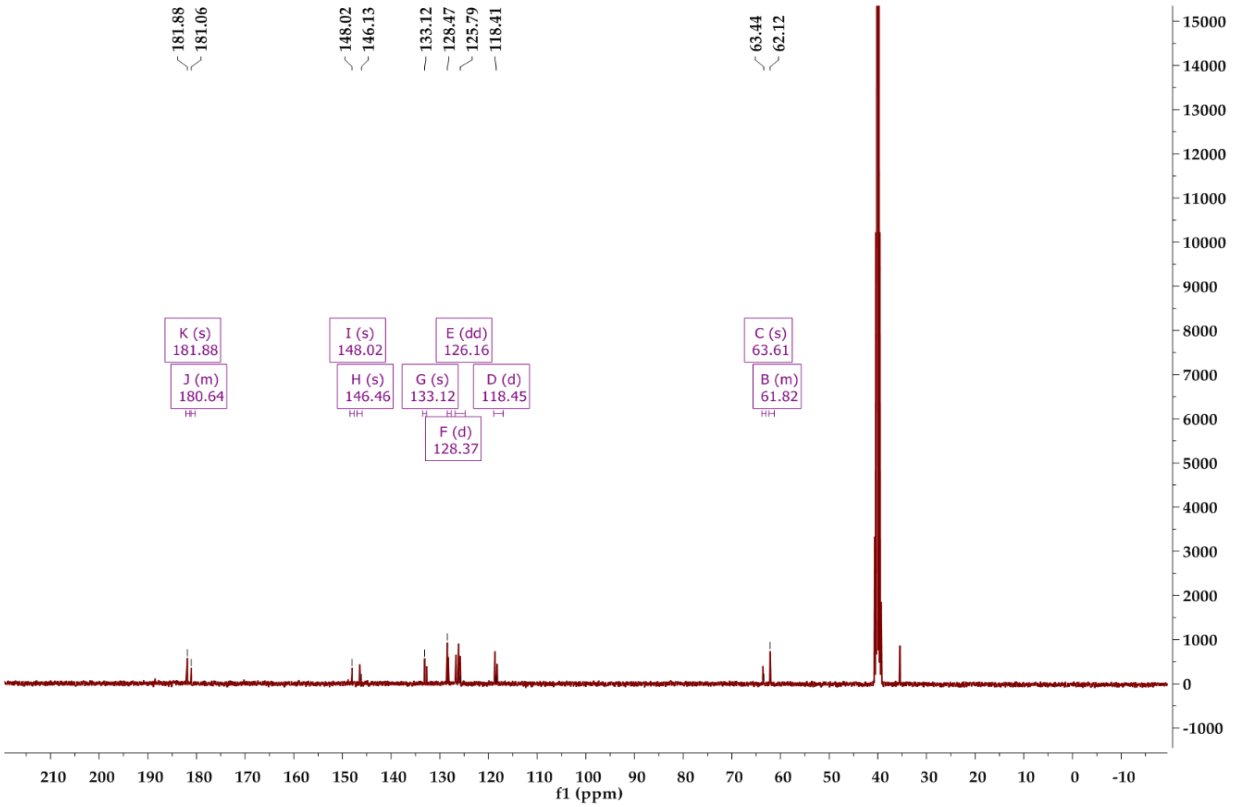


Figure S7: ^{13}C NMR spectrum (DCM) of [Rh(indoli)(CO)$_2$] (A1)

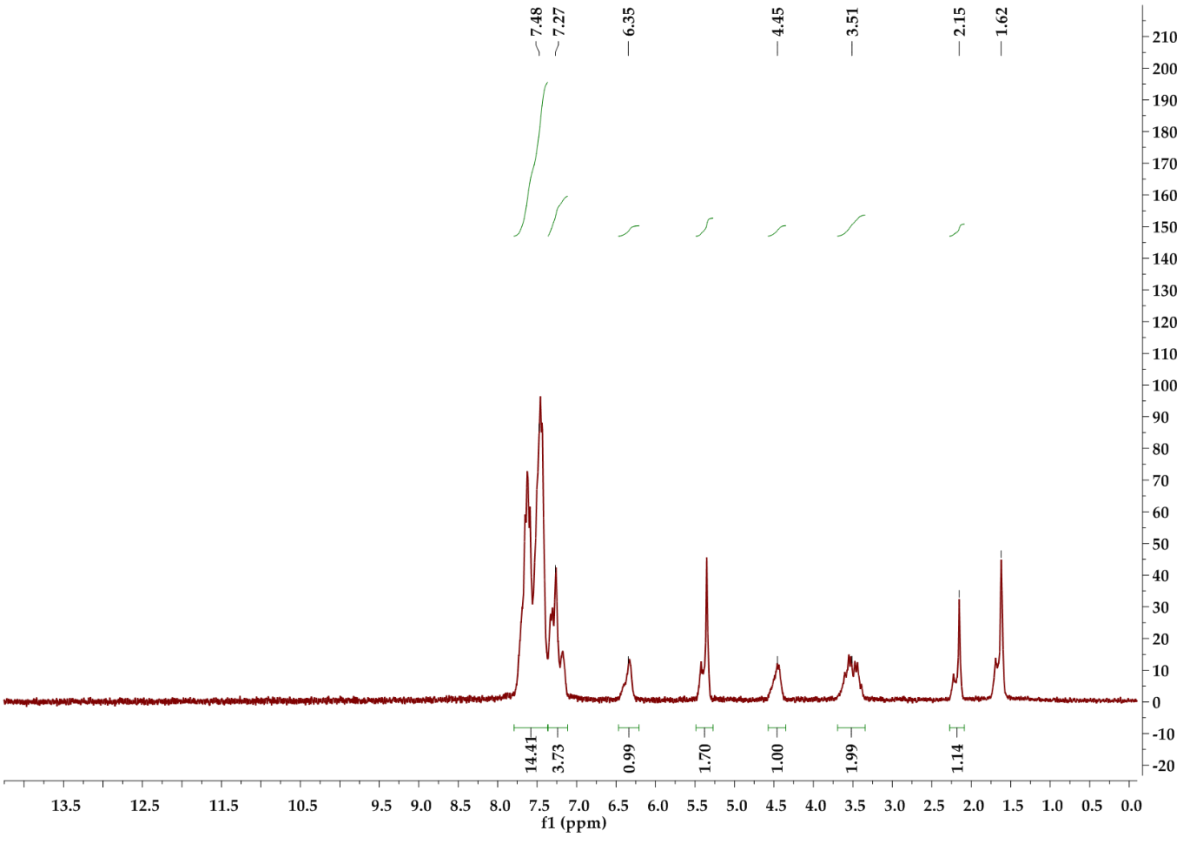


Figure S8: ^{1}H NMR spectrum (DCM) of [Rh(indoli)(CO)(PPh$_3$)] (A2)

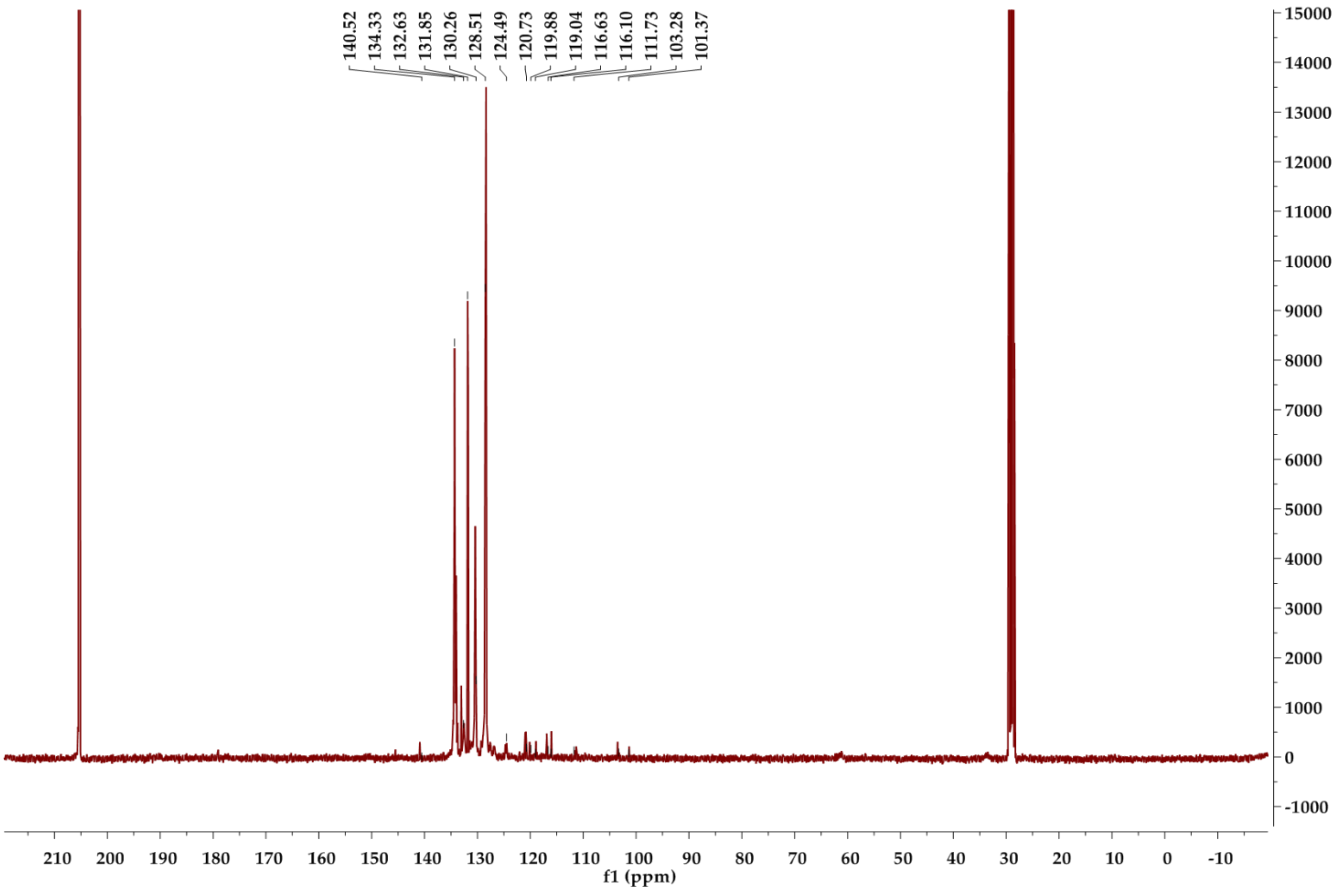


Figure S9: ^{13}C NMR spectrum (Acetone-d_6) of [Rh(indoli)(CO)(PPh_3)] (A2)

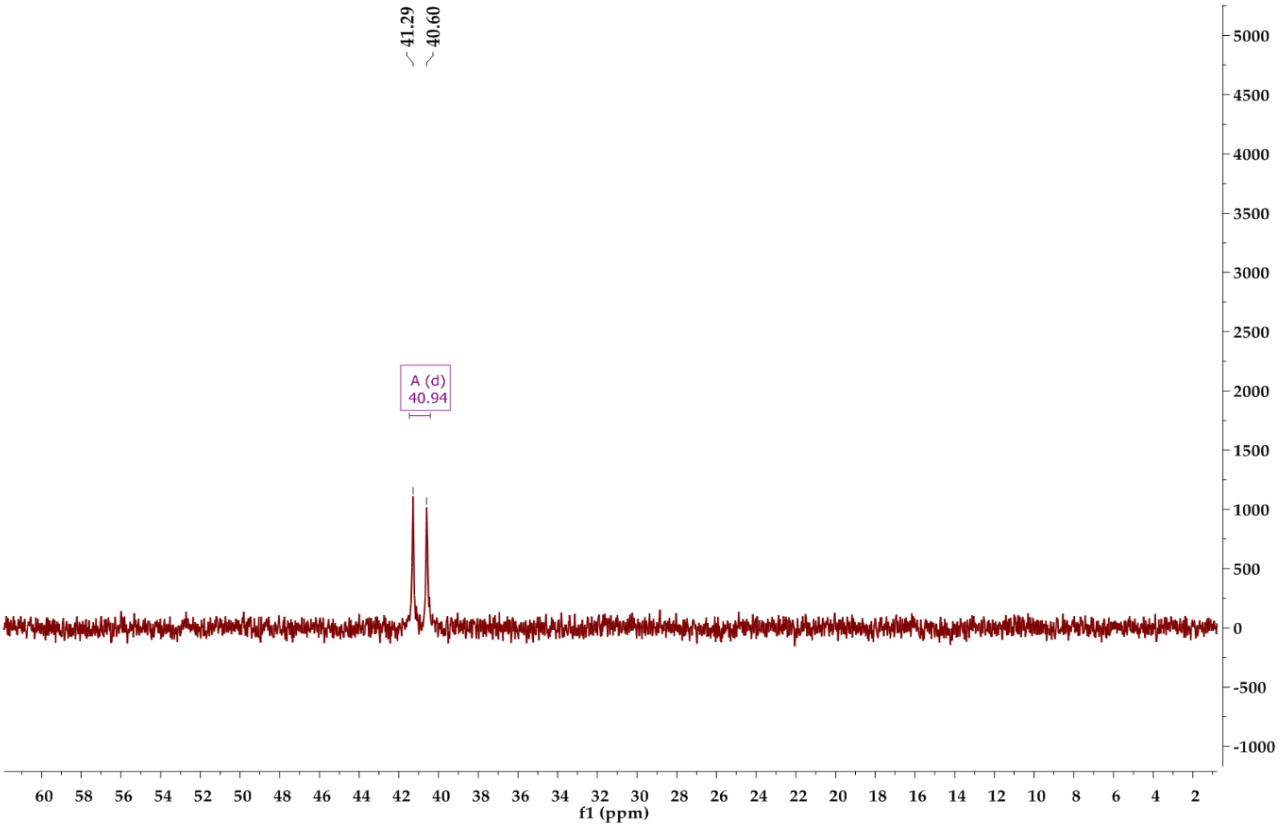


Figure S10: ^{31}P NMR spectrum (DCM) of [Rh(indoli)(CO)(PPh_3)] (A2)

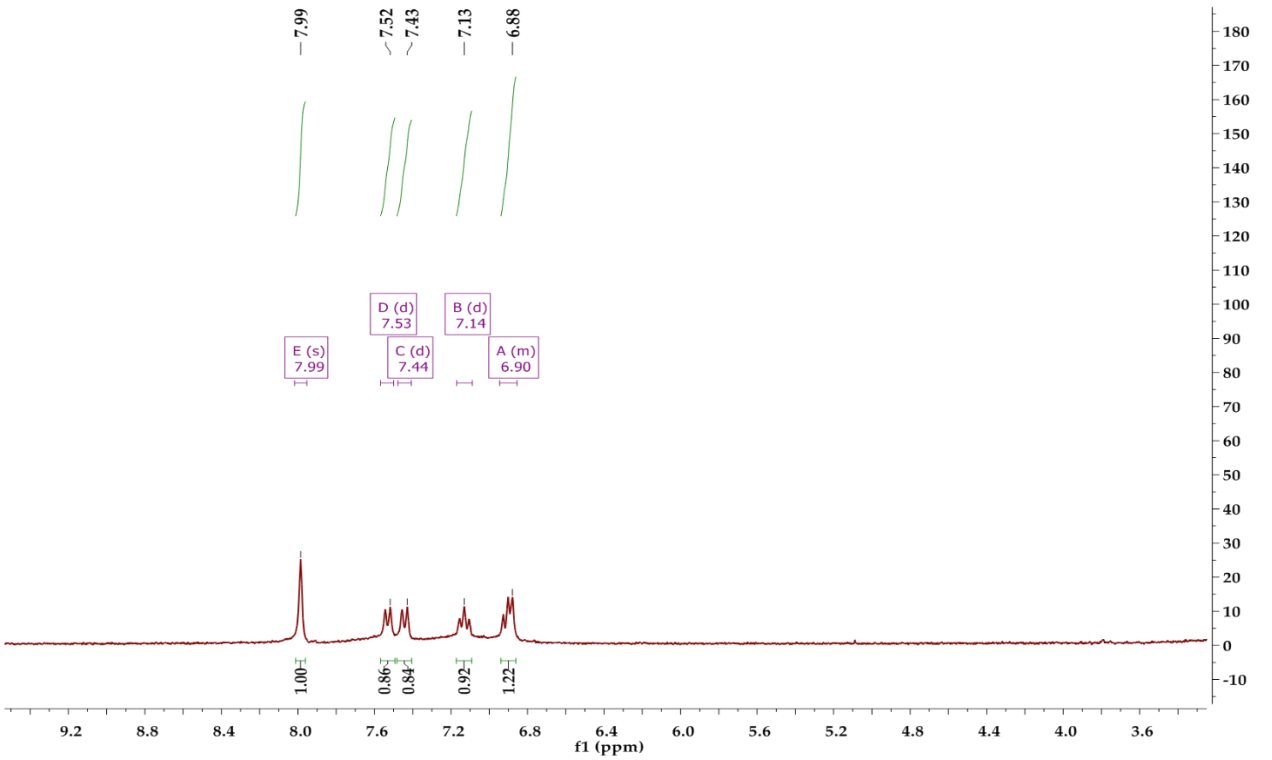


Figure S11: ^{1}H NMR spectrum (DCM) of [Rh(indol)(CO)$_2$] (B1)

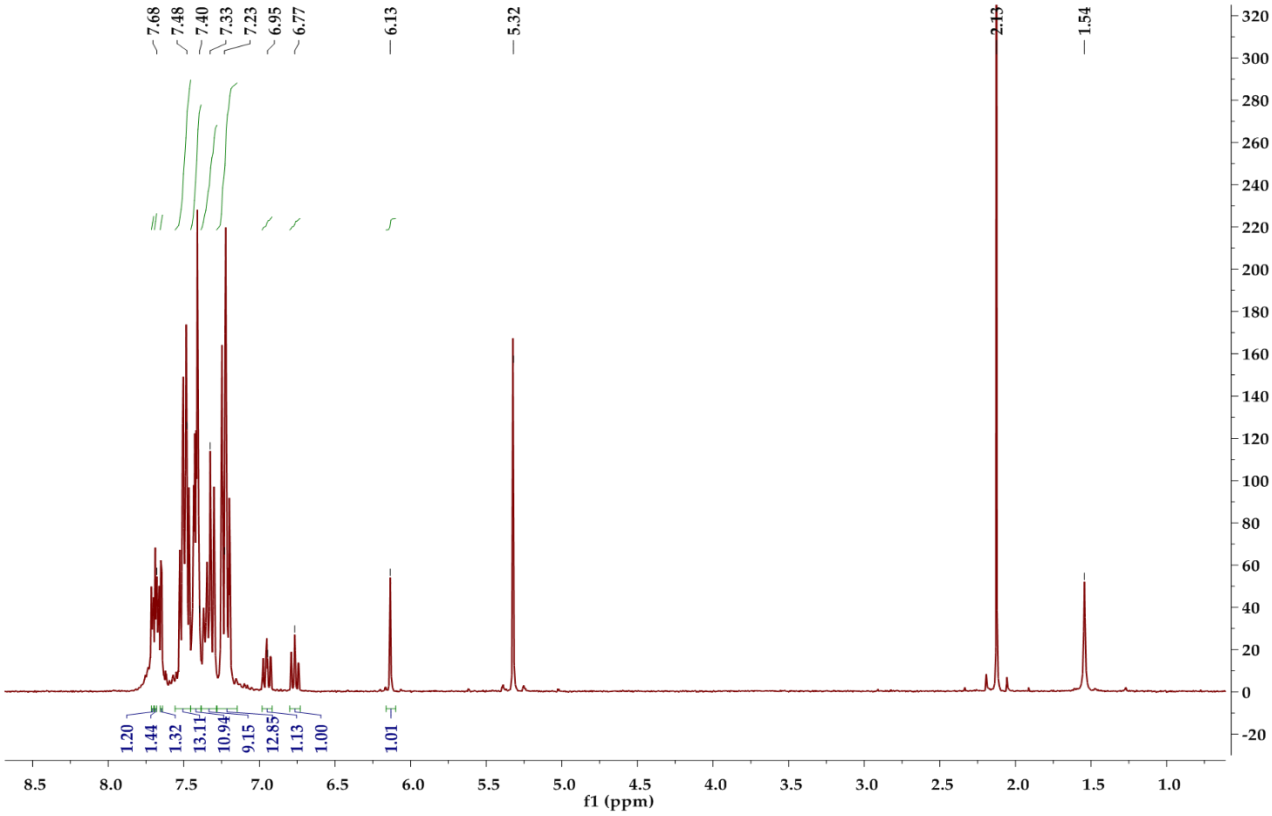
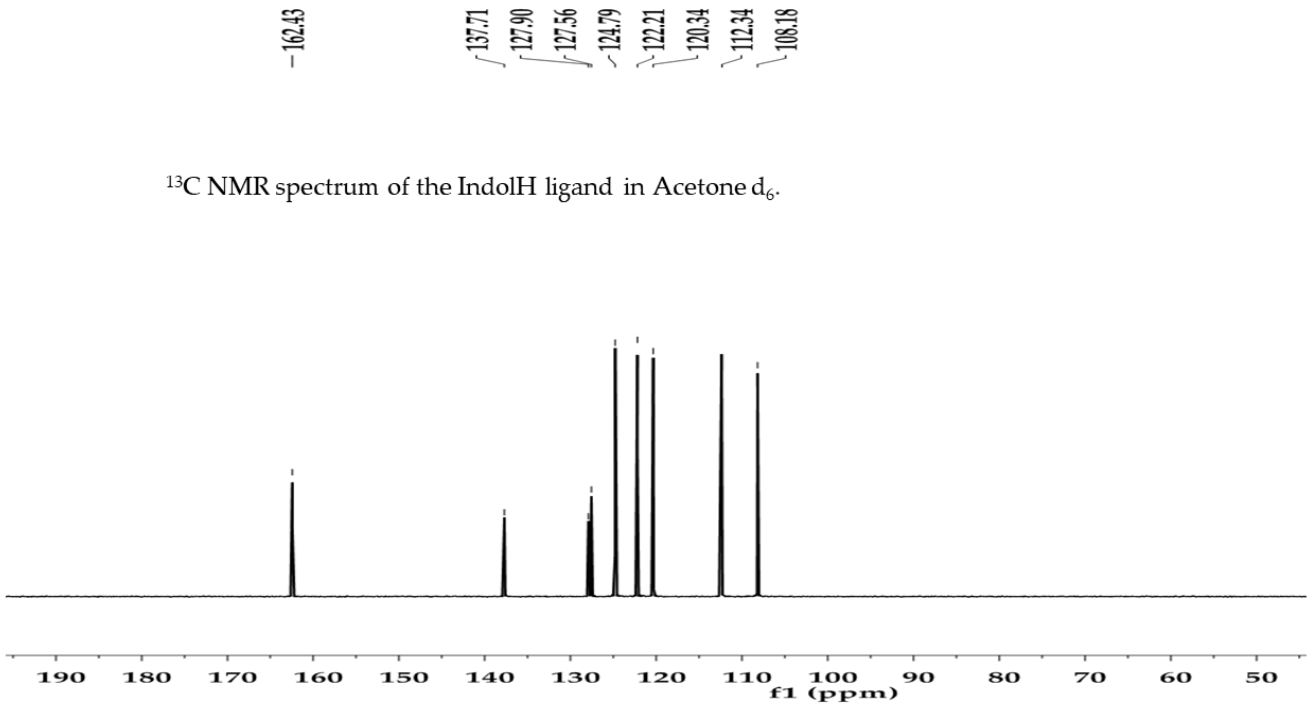


Figure S12: ^{1}H NMR spectrum (DCM) of [Rh(indol')(CO)(PPh$_3$)Rh(CO)(PPh$_3$)$_2$] (B2)



^{13}C NMR spectrum of the IndolH ligand in Acetone d_6.

Figure S13: ^{13}C NMR spectrum (Acetone-d_6) of IndolH

^{13}C NMR spectrum of the [Rh(indol)$(CO)_2$] (**B1**) in Acetone d_6

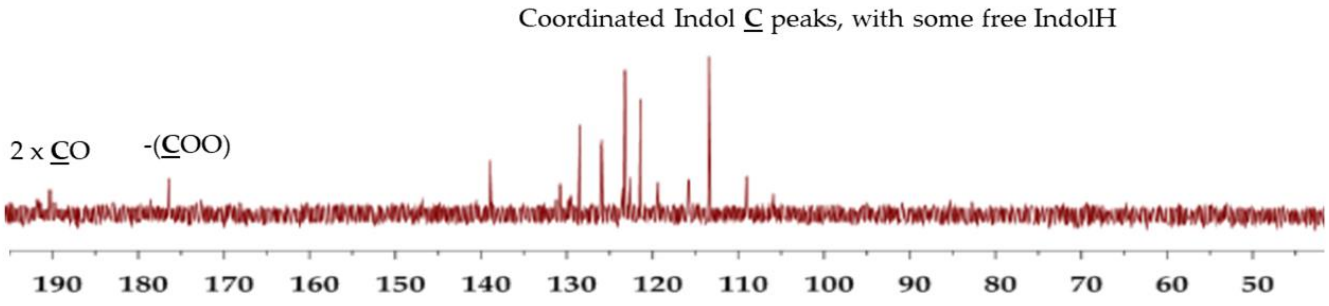


Figure S14: ^{13}C NMR spectrum (Acetone-d_6) of [Rh(indol)$(CO)_2$] (B1)

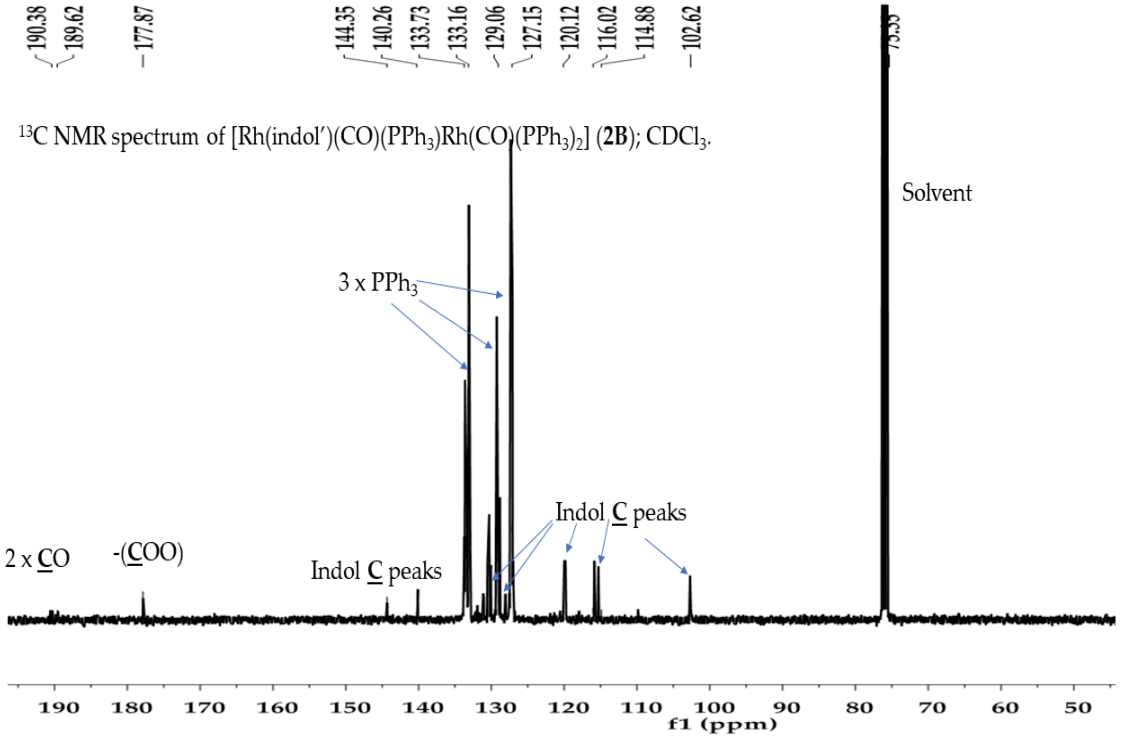


Figure S15: ^{13}C NMR spectrum ($CDCl_3$) of [Rh(indol')(CO)(PPh_3)Rh(CO)(PPh_3)$_2$] (B2)

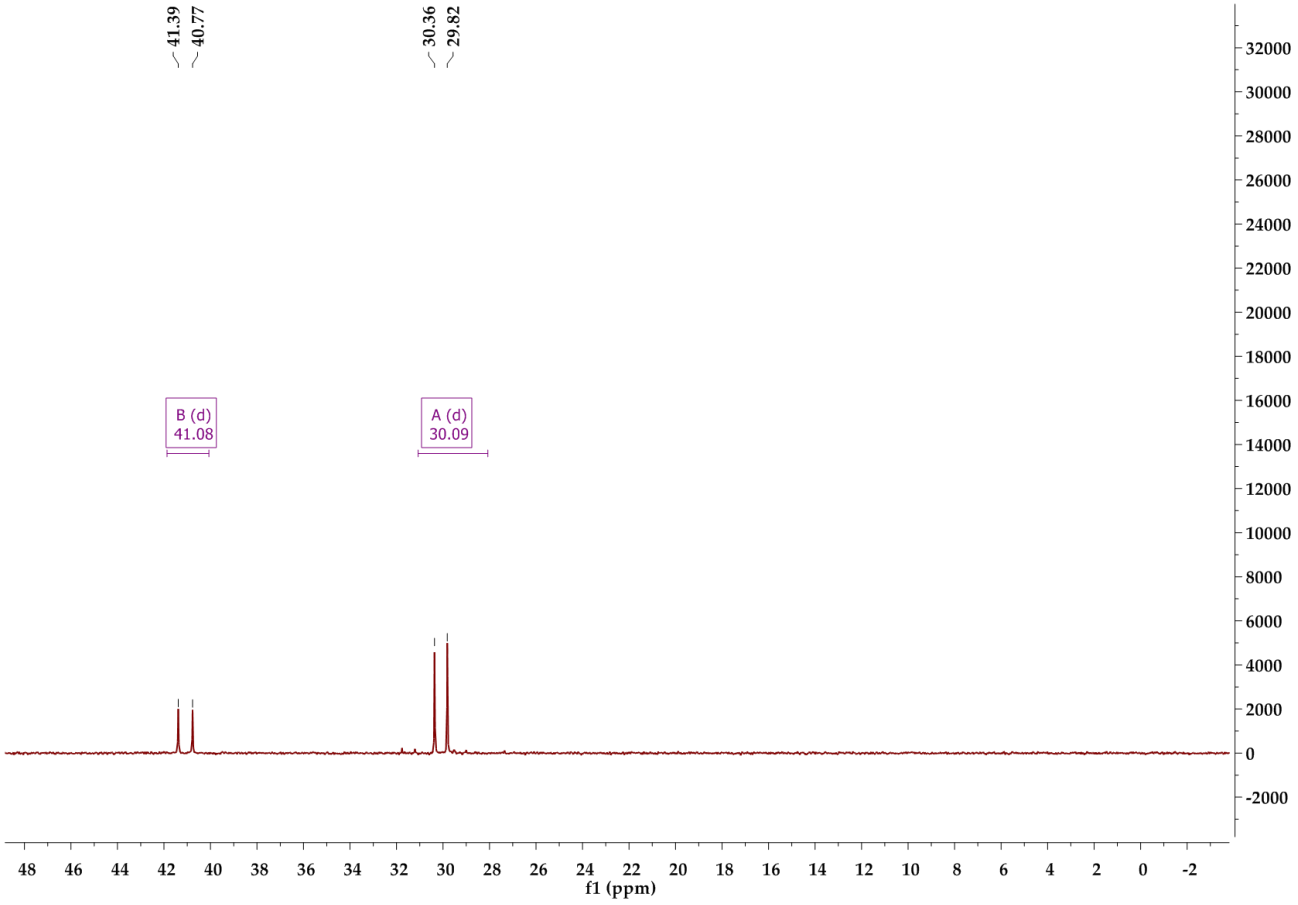


Figure S16: ^{31}P NMR spectrum (DCM) of [Rh(indol')(CO)(PPh_3)Rh(CO)(PPh_3)$_2$] (B2)

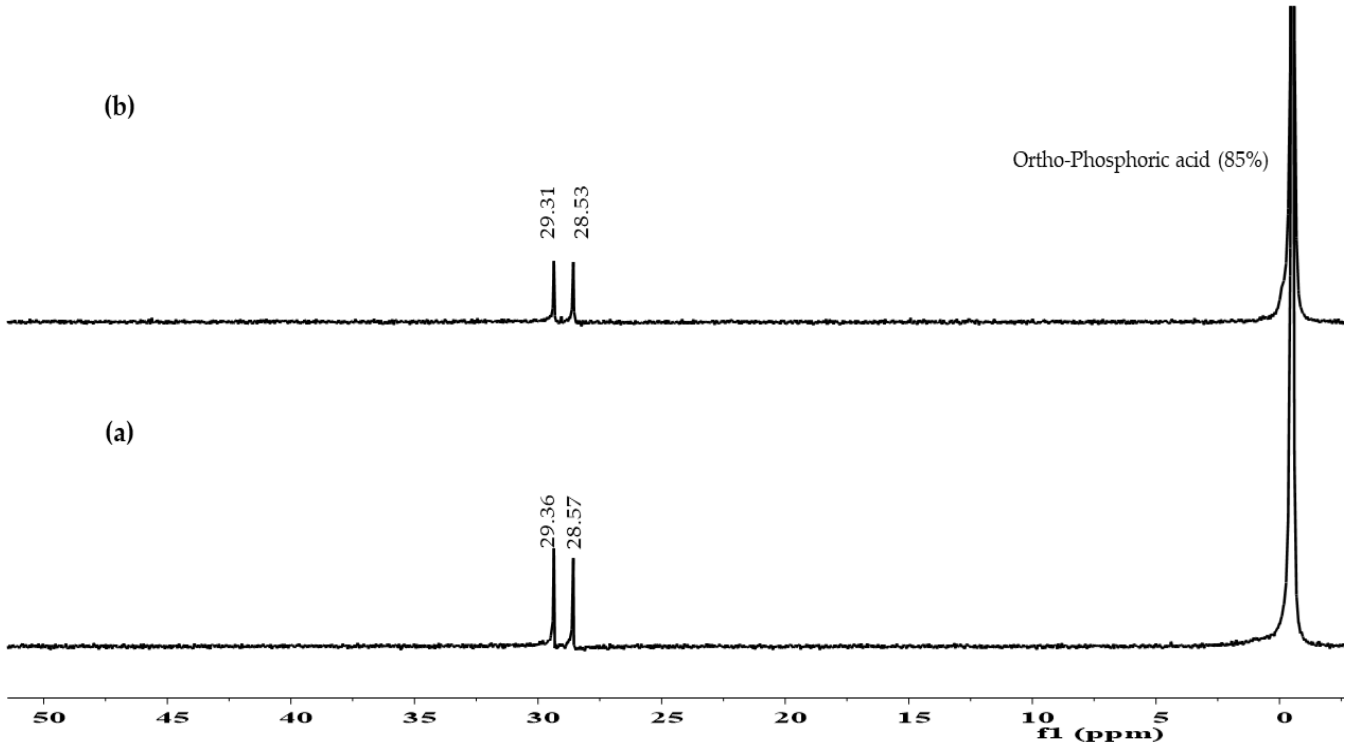


Figure S17: ^{31}P NMR spectrum (DCM) of (a) *trans*-[RhI(CO)(PPh$_3$)$_2$] (B4) and (b) *trans*-[RhClCO)(PPh$_3$)$_2$]

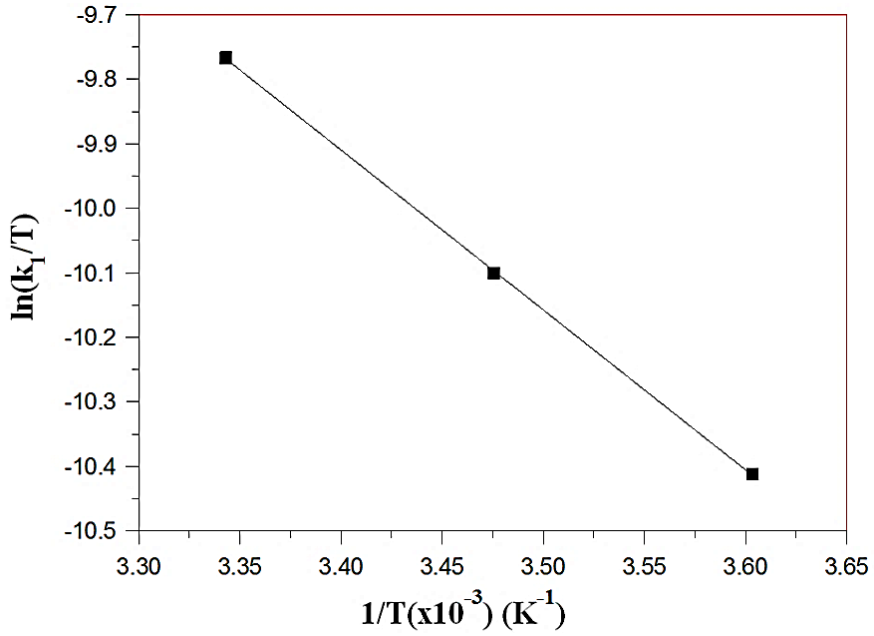


Figure S18: Eyring plot: k_1 rate constant (DCM): iodomethane oxidative addition to [Rh(indoli)(CO)(PPh$_3$)] (A2).

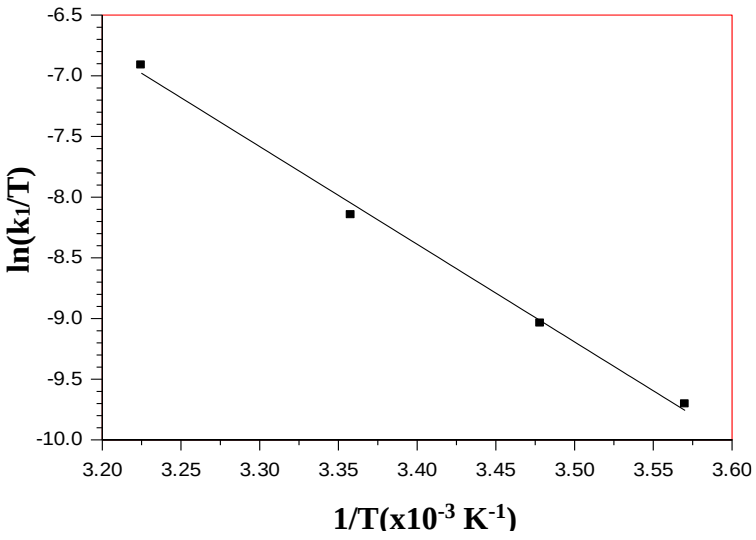


Figure S19: Eyring plot: OA k_1 rate constant to [Rh¹(Indol')(CO)(PPh₃)Rh²(CO)(PPh₃)₂] (B2) in dichloromethane.

Table S1: Comparison of selected crystallographic data in [Rh¹(Indol')(CO)(PPh₃)-Rh²(CO)(PPh₃)₂].(CH_3COCH_3) (**B2a**) with an isostructural thiourea molecule reported by Kemp et al. [Ref see ms]

Complex	[Rh¹(Indol')(CO)(PPh₃)Rh²(CO)(PPh₃)₂].(CH_3COCH_3) (**B2a**)	[Rh(nbnpt)(CO)(PPh₃)Rh(CO)-(PPh₃)₂].(CH_3COCH_3) [a)]
Bond length (Å)		
Rh1-P1	2.2626(14)	2.275(3)
Rh2-P2	2.3355(14)	2.328(3)
Rh2-P3	2.3415(14)	2.330(3)
Rh1-C	1.784(5)	1.773(1)
Rh2-C	1.800(6)	1.744(1)
O1···N1 (Bite distance)	2.654(1)	-
Periphiral H-H distance [b)]	16.90(3)	-
Bond angle (°)		
P1-Rh1-C	90.07(17)	89.7(4)
P2-Rh2-C	91.37(16)	88.6(4)
P3-Rh2-C	86.54(16)	88.5(4)
P2-Rh2-P3	171.80(5)	174.78(1)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
Temperature (° K)	100	298
a (Å)	14.097(2)	12.282(3)
b (Å)	14.280(2)	26.539(5)
c (Å)	17.942(3)	20.079(4)
α (°)	93.451(6)	90
β (°)	112.987(5)	100.20(2)
γ (°)	115.164(6)	90
Z	2	4
Volume (Å³)	2896.4(8)	6441(2)

a) nbnpt⁻ = *N*-benzoyl-*N'*-phenylthiourea anion [Ref see ms]; b) H14--H94 distance; outermost H-atoms on periphery of **B2**, and when including the H-atom radii, total distance is > 1.7 nm

Table S2: Comparison of geometric parameters and crystal data of *trans*-[Rh(CO)(I)(PPh_3)$_2$].(CH_3COCH_3) (**B5a**) and similar structure found in the literature.

Complex	**B5a**	Basson *et al.* structure [Ref see ms]
Bond length (Å)		
Rh-P1	2.3178(9)	2.336 (2)
Rh-P1i	2.3178(9)	2.316 (2)
Rh-I	2.7103(7)	2.683 (1)
Rh-C	1.725(5)	1.81 (1)
C-O	0.995(5)	1.14 (1)
Bond angle (°)		
I-Rh-P1	87.59(3)	88.54 (6)
I-Rh-P1i	92.40(3)	91.19 (6)
C-Rh-P1	85.99(18)	89.9 (3)
C-Rh-Pi	85.99(18)	91.0(3)
I-Rh-C	176.2(2)	176.3(3)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	11.974(5)	9.823(2)
b (Å)	20.289(5)	15.340(2)
c (Å)	8.335(5)	21.980(3)
β (°)	98.311(5)	95.51(1)
Z	2	4