

Supplementary Information

Insights into the ligand effects of rhodium catalysts toward reductive carbonylation of methanol to ethanol

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Table S1

Reaction conditions and reductive carbonylation performances of used Co-based catalysts

reference	S1	S2	S3	S4	S4	S4	S5
catalyst system	Co	Co	Co	Co	Co	Co	Co-Ru
promotor	none	none	I ₂	none	HI	HI	I ₂
ligand	none	PBu ₃	n-Bu ₃ P	PPh ₃	none	PPh ₃	PPh ₃
reaction pressure, (MPa)	34	19.6 ^a	13.5 ^a	30	30	30	27
H ₂ /CO molar ratio	0.9	1	2	1	1	1	1.5
temperature, (°C)	190	230	195	200	200	190	170
solvent	none	benzene	1,4-dioxane	none	none	none	toluene
reaction time	2	4.5 ^b	4.33	2	2	2.5	6
methanol conversion	30	37.1	52.2	7.4	69	47	—
molar selectivity, (%)							
dimethyl ether	11.3	—	0.7	} 2.3	} 6.8	} 2.9	7
methyl ethyl ether	0	0.9	0.8				0
diethyl ether	1.0	—	—				13
acetaldehyde	2.0	—	1.3	0		3.2	0
dimethyl acetal	5.2	—	3.7	42	41	13	—
methyl acetate	17.4	—	3.4	} 3.4	20	16	18
ethyl acetate	—	—	0.7				0
ethanol	37.5	77.6	74.4	1.2	5.9	9.2	58

^a initial pressure. ^b activation time 3.0 h, reaction time 1.5h.

Table S2

Crystallographic Data for the X-ray Diffraction Analysis of $[\text{Rh}_2(\mu\text{-I})(\mu\text{-CO})(\text{CO})_2(\text{dppm})_2]^+$, $[\text{Rh}(\text{COCH}_3)_2(\text{dppe})]$, $[\text{Rh}(\text{COCH}_3)_2(\text{dppp})]$ and $[\text{Rh}(\text{COCH}_3)_2(\text{dppb})]$

	$[\text{Rh}_2(\mu\text{-I})(\mu\text{-CO})(\text{CO})_2(\text{dppm})_2]^+$	$[\text{Rh}(\text{COCH}_3)_2(\text{dppe})]$	$[\text{Rh}(\text{COCH}_3)_2(\text{dppp})]$	$[\text{Rh}(\text{COCH}_3)_2(\text{dppb})]$
empirical formula	$\text{C}_{53}\text{H}_{44}\text{IO}_3\text{P}_4\text{Rh}_2$	$\text{C}_{28}\text{H}_{27}\text{I}_2\text{OP}_2\text{Rh}$	$\text{C}_{29}\text{H}_{29}\text{I}_2\text{OP}_2\text{Rh}$	$\text{C}_{30}\text{H}_{31}\text{I}_2\text{OP}_2\text{Rh}$
CCDC Number	1527246	1527365	1527366	1527367
cryst dims, mm^3	$0.176 \times 0.143 \times 0.112$	$0.165 \times 0.144 \times 0.112$	$0.25 \times 0.2 \times 0.15$	$0.187 \times 0.156 \times 0.112$
temp, K	133(2)	133(2)	130	133(2)
cryst syst	Triclinic	Triclinic	Monoclinic	Orthorhombic
space group	P-1	P-1	P 21/n 1	Pna2 ₁
a, Å	14.3031(12)	9.0991(9)	10.2587(6)	22.8849(16)
b, Å	18.7654(16)	10.2694(10)	10.1737(6)	9.1204(6)
c, Å	20.9726(17)	14.8252(14)	27.0921(16)	14.2625(10)
α , deg	81.030(2)	92.239(2)	90	90
β , deg	84.861(2)	94.083(2)	95.0890(10)	90
γ , deg	79.291(2)	99.430(2)	90	90
V, Å ³	5452.8(8)	1361.3(2)	2816.4(3)	2976.9(4)
Z	4	2	4	4
fw, amu	1185.48	798.14	812.17	826.20
calcd density, g/cm^3	1.444	1.947	1.915	1.843
F(000)	2356	768	1568	1600
final R indices [$I > 2\sigma(I)$]	R1 = 0.0530, wR2 = 0.1060	R1 = 0.0298, wR2 = 0.0539	R1 = 0.0270, wR2 = 0.0543	R1 = 0.0251, wR2 = 0.0438
R indices (all data)	R1 = 0.0932, wR2 = 0.1189	R1 = 0.0425, wR2 = 0.0580	R1 = 0.0341, wR2 = 0.0567	R1 = 0.0296, wR2 = 0.0455
GOF	0.894	0.984	1.045	1.026
θ , deg	25.242	25.242	25.242	25.242
scan width, Å	0.71073	0.71073	0.71073	0.71073
index ranges	-17 ≤ h ≤ 16, -22 ≤ k ≤ 21, -25 ≤ l ≤ 25	-8 ≤ h ≤ 11, -12 ≤ k ≤ 12, -18 ≤ l ≤ 18	-11 ≤ h ≤ 14, -14 ≤ k ≤ 14, -38 ≤ l ≤ 33	-25 ≤ h ≤ 28, -11 ≤ k ≤ 10, -17 ≤ l ≤ 14

Table S3

Selected interatomic distances (Å) and bond angles (deg) for [Rh(dppp)(COCH₃)I₂] in different temperature.

	[Rh(dppp)(COCH ₃)I ₂]	
CCDC Number	1014689	1304156
Temp, K	110	295
Solvent	methylene chloride	methanol
P1-Rh-P2, deg	90.96(3)	90.49(5)
Rh-C(O)-C(H3), deg	112.7(2)	113.1(4)
I1-Rh-I2, deg	88.696(11)	89.15(2)
Rh-C(O), Å	1.979(3)	1.981(6)
Rh-I1, Å	2.6975(3)	2.6768(5)
Rh-I2, Å	2.6975(3)	2.7263(5)
Rh-P1, Å	2.2863(5)	2.276(1)
Rh-P2, Å	2.2863(5)	2.299(1)
Ref	s6	s7

Table S4

The catalytic performance of various Rh-based catalyst in the reductive carbonylation of methanol. Results are expressed as mean ± standard error ^a.

Catalyst Composition	Carbonylates product distribution (mol%) ^b						
	EtOH	MeOEt	Et ₂ O	DMAc	EtOAc	MeOAc	AcOH
Rh-based catalyst	15.6±0.3	8.0±0.1	0.0±0	1.1±0.1	2.5±0.1	72.3±1.1	0.5±0.1
Rh(dppm)-based catalyst	22.7±0.6	0.0±0	0.0±0	2.6±0.1	4.7±0.2	63.5±1.1	6.5±0.2
Rh(dppe)-based catalyst	39.6±1.1	12.1±0.3	0.7±0.1	1.6±0.1	4.3±0.1	41.7±1.1	0.0±0
Rh(dppp)-based catalyst	59.0±1.1	15.9±0.3	1.2±0.1	2.3±0.1	3.4±0.1	17.7±0.6	0.5±0.1
Rh(dppb)-based catalyst	4.3±0.1	4.9±0.2	0.0±0	1.3±0.1	1.9±0.1	87.6±1.1	0.0±0

^a Error was calculated from three experiments.

^b The product distribution excluded dimethyl ether because it was formed from the reaction between methanol and methyl iodide ^{s8}. EtOH = ethanol, MeOEt = ethyl methyl ether, Et₂O = diethyl ether, DMAc = dimethyl acetal, EtOAc = ethyl acetate, MeOAc = methyl acetate, AcOH = acetic acid.

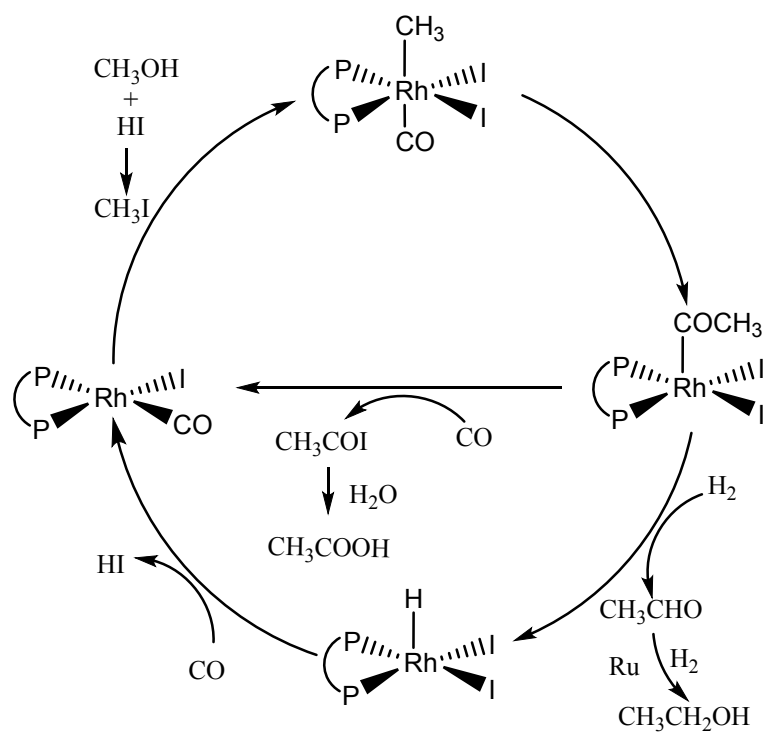


Fig. S1 Catalytic cycle for methanol carbonylation and reduction carbonylation catalyzed by Rh(diphosphine)-based catalysts.

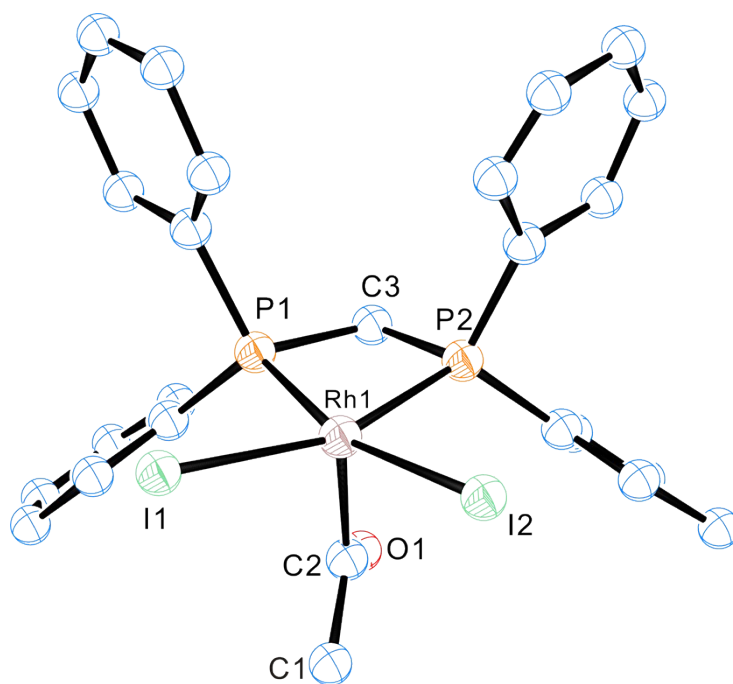


Fig. S2. Molecular structures of complex [Rh(COCH₃)I₂(dppm)].

Characterizing Data

$[\text{Rh}_2(\mu\text{-I})(\mu\text{-CO})(\text{CO})_2(\text{dppm})_2]^+$ (Rh-dppm complex) ^1H NMR (500MHz, CDCl_3): $\delta=4.37\text{-}4.52$ (m, 4H), 7.16 (s, 5H), 7.28-7.32 (m, 7H), 7.40-7.44 (m, 12H), 7.60-7.75 (m, 16H) ppm, ^{31}P NMR (202.46MHz, CDCl_3): $\delta=27.68$ (d, $J_{\text{Rh-P}}=94.55\text{Hz}$, 4P) ppm.

$[\text{Rh}(\text{COCH}_3)_2(\text{dppe})]$ (Rh-dppe complex) ^1H NMR (500MHz, CDCl_3): $\delta=2.15\text{-}2.28$ (m, 2H), 2.77(s, 3H), 3.08-3.21 (m, 2H), 7.30-7.34 (m, 4H), 7.41-7.48 (m, 6H), 7.50-7.53 (m, 6H), 7.84-7.88 (m, 4H) ppm. ^{31}P NMR (202.46MHz, CDCl_3): $\delta=70.39$ (d, $J_{\text{Rh-P}}=139.3\text{Hz}$, 2P) ppm.

$[\text{Rh}(\text{COCH}_3)_2(\text{dppp})]$ (Rh-dppp complex). ^1H NMR (500MHz, CDCl_3): $\delta=1.60\text{-}1.69$ (m, 1H), 2.42-2.50 (m, 3H), 3.06 (s, 3H), 3.08-3.17 (m, 2H), 7.24-7.26(m, 3H), 7.28-7.42 (m, 13H), 7.64-7.68(m, 4H) ppm. ^{31}P NMR (202.46MHz, CDCl_3): $\delta=17.8$ (d, $J_{\text{Rh-P}}=161.97\text{ Hz}$, 2P) ppm.

$[\text{Rh}(\text{COCH}_3)_2(\text{dppb})]$ (Rh-dppb complex). ^1H NMR (500MHz, CDCl_3): $\delta=1.12$ (s, 2H), 1.58 (s, 2H), 2.41-2.47 (m, 2H), 2.73 (s, 3H), 3.24-3.32 (m, 2H), 7.31-7.34(m, 4H), 7.36-7.39(m, 6H), 7.46-7.54 (m, 6H), 7.66-7.70(t, 4H) ppm. ^{31}P NMR (202.46MHz, CDCl_3): $\delta=31.96$ (d, $J_{\text{Rh-P}}=139.3\text{ Hz}$, 2P) ppm.

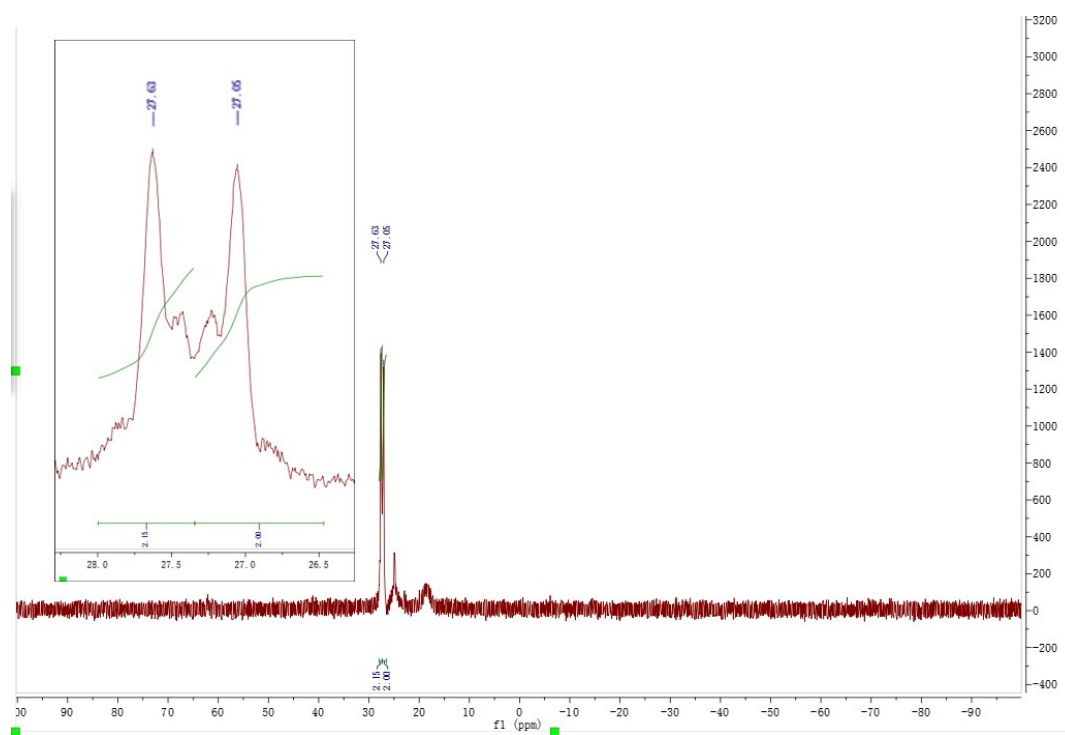
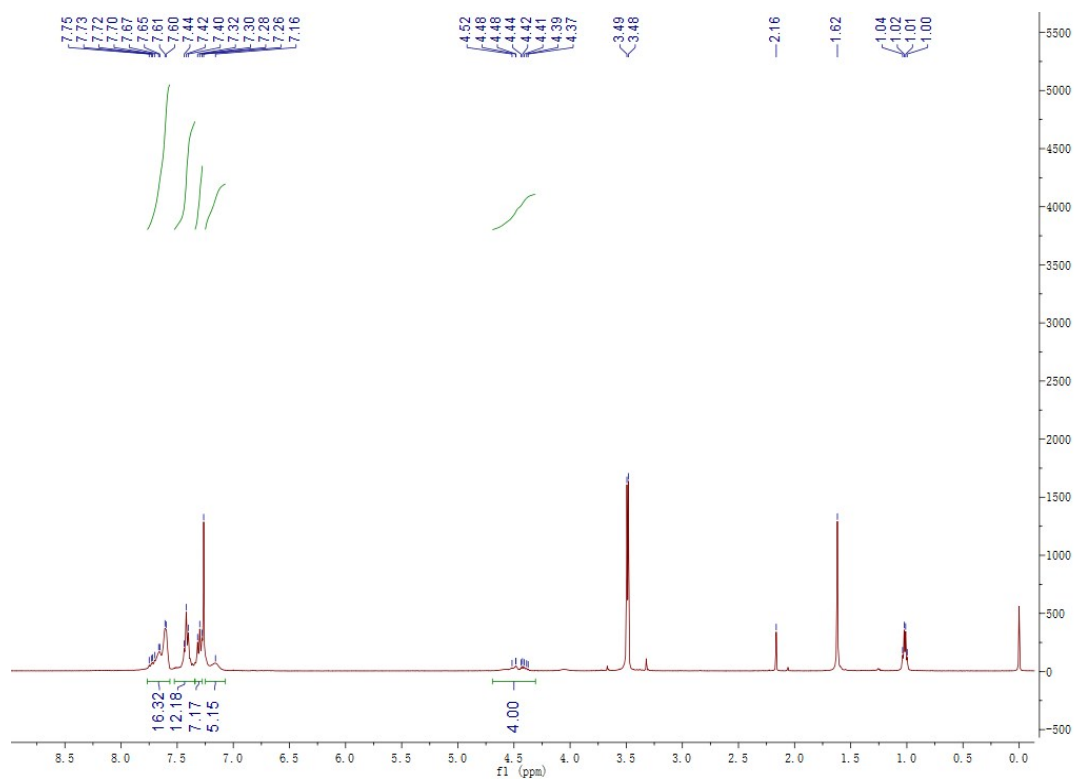


Fig. S3 ^1H and ^{31}P NMR spectra of $[\text{Rh}_2(\mu\text{-I})(\mu\text{-CO})(\text{CO})_2(\text{dppm})_2]^+$.

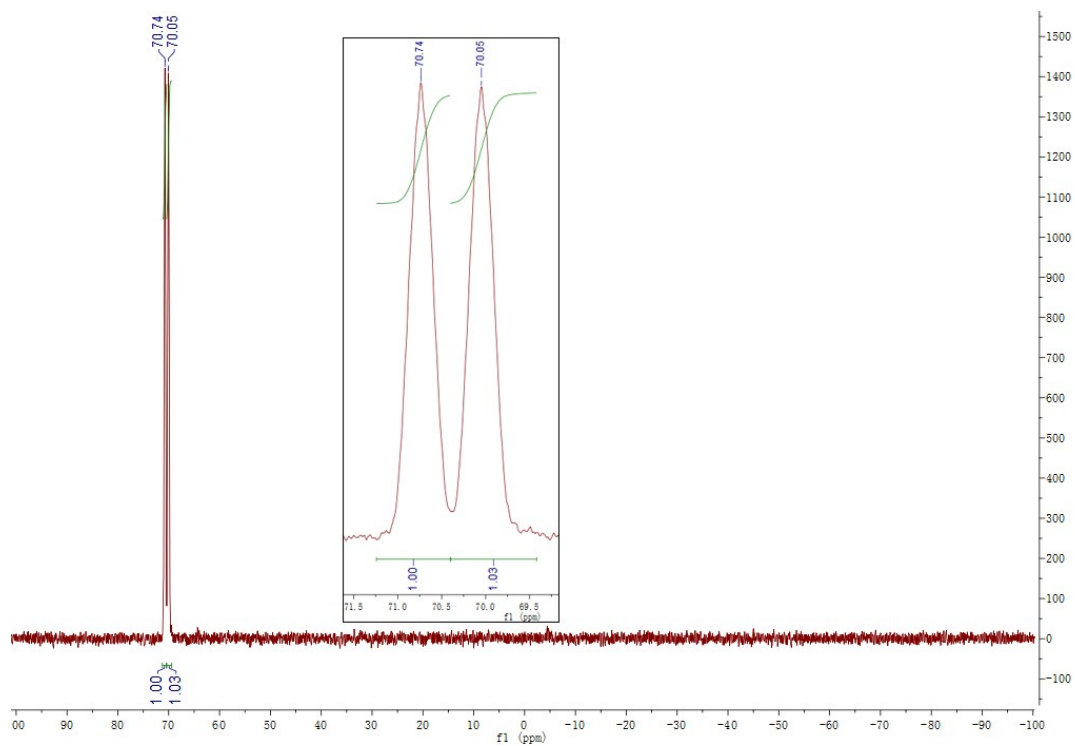
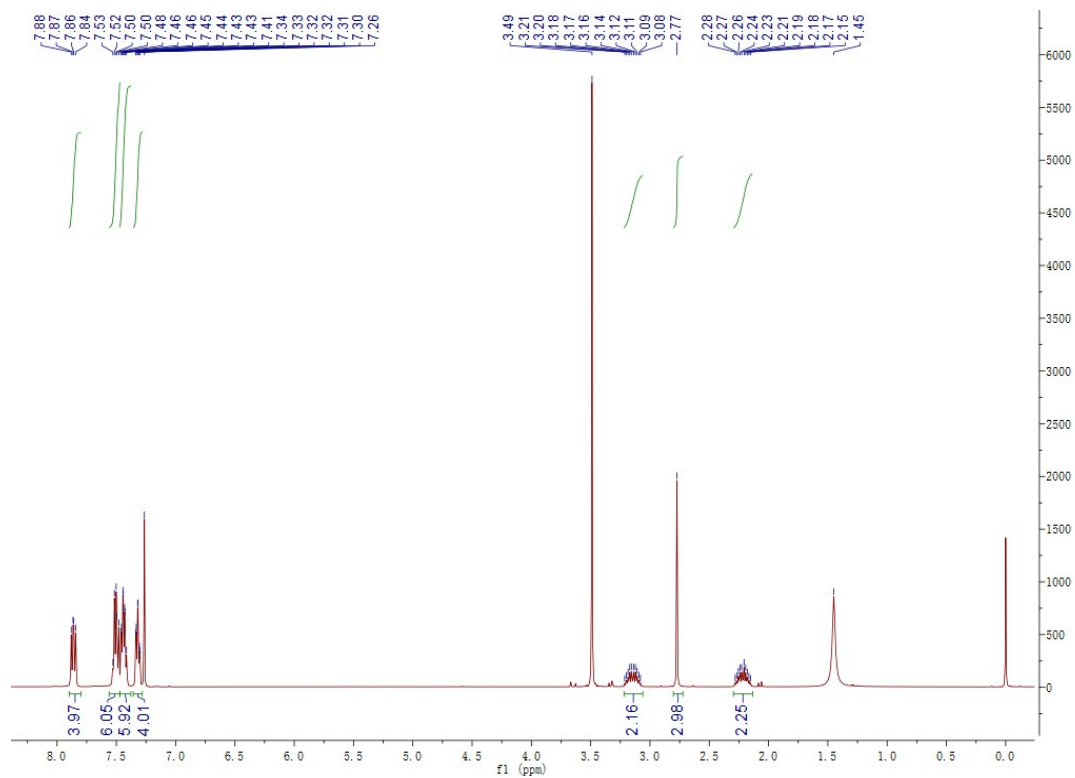


Fig. S4 ¹H and ³¹P NMR spectra of [Rh(COCH₃)₂(dppe)].

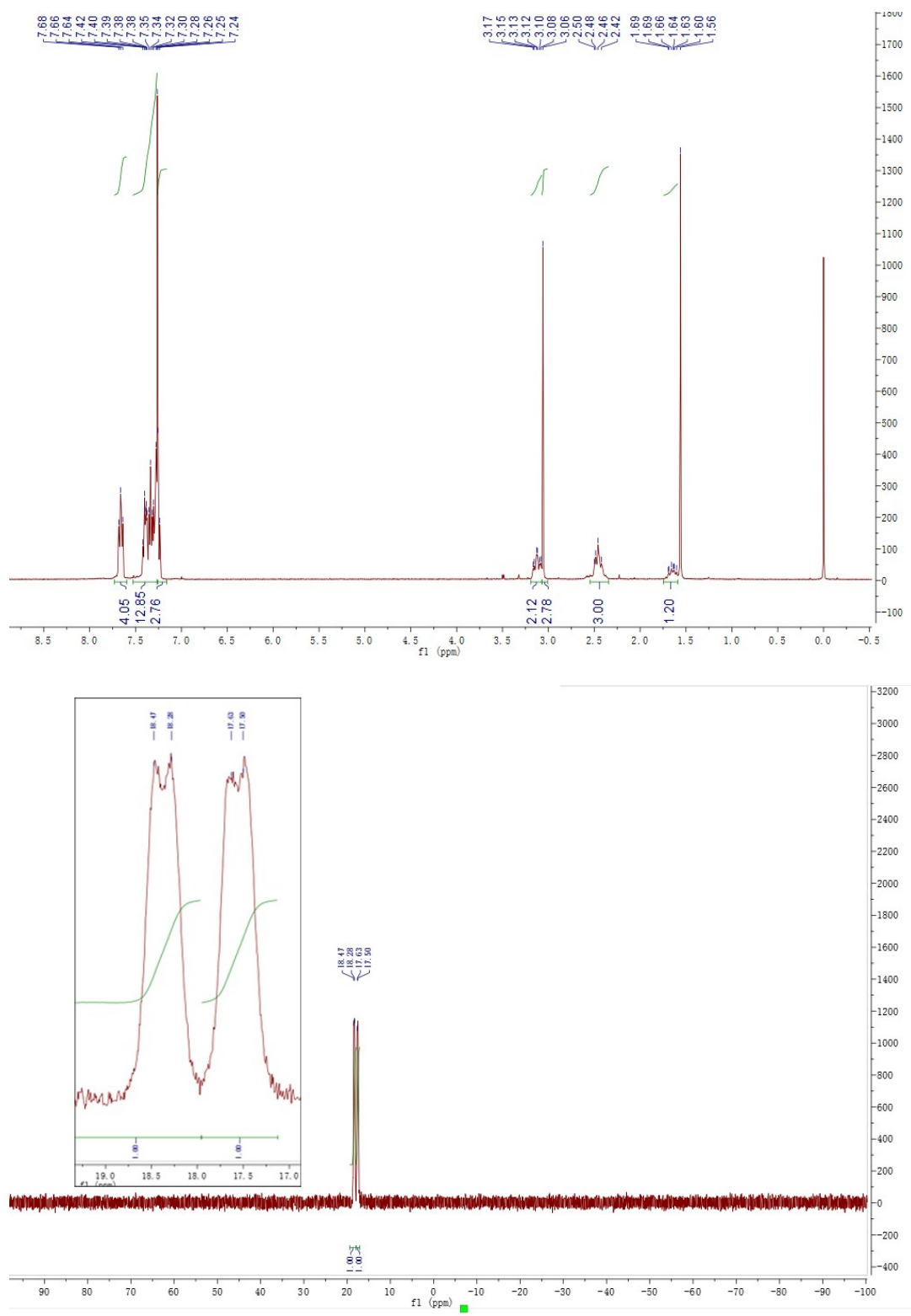


Fig. S5 ^1H and ^{31}P NMR spectra of $[\text{Rh}(\text{COCH}_3)_2(\text{dpp})]$.

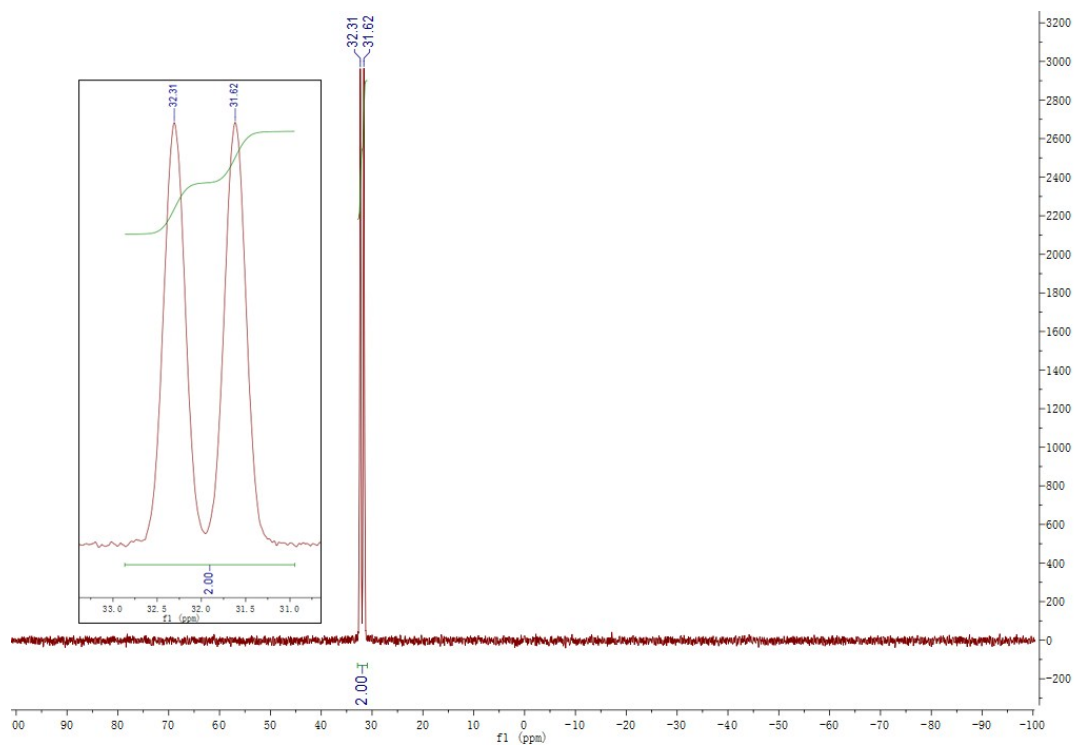
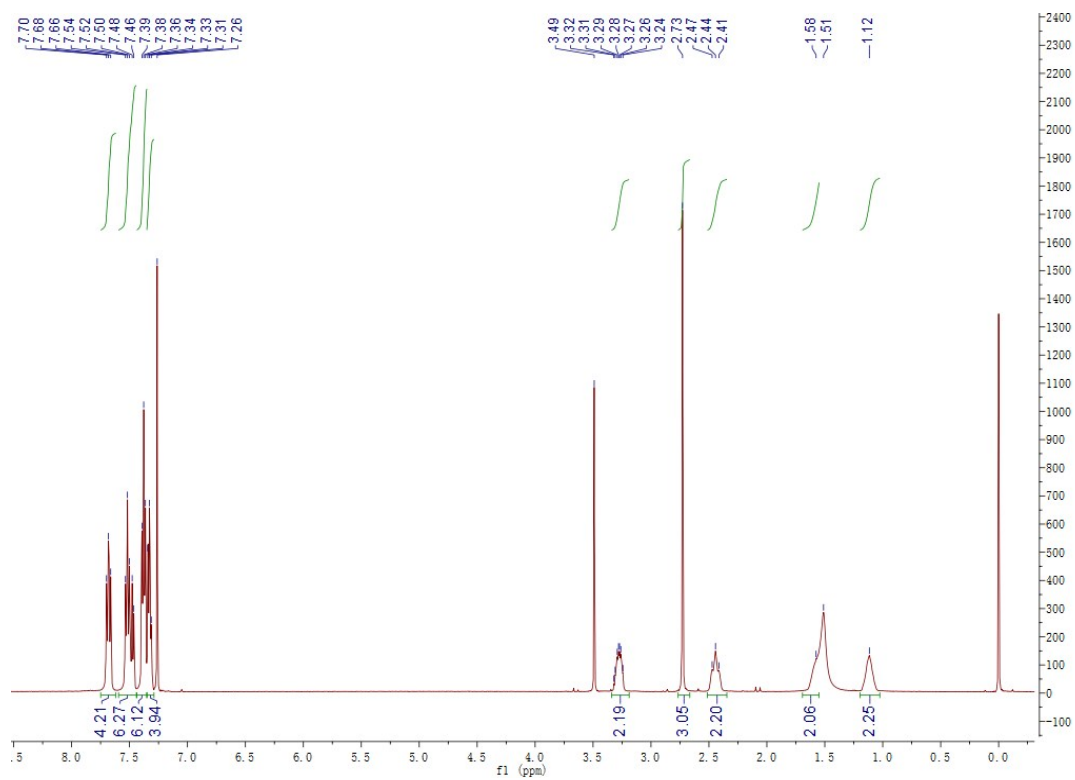


Fig. S6 ¹H and ³¹P NMR spectra of [Rh(COCH₃)₂(dppb)].

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