

Supporting Information

Computational details:

The intermediates and stationary points of complexes **2-4** are fully optimized at B3LYP level¹⁻³ of DFT using Gaussian09 program.⁴ The metal and P centers were described with the Stuttgart RECPs and associated basis sets (SDDALL)⁵ with a set of d-orbital polarization functions on P ($\zeta = 0.387$).⁶ The 6-31G** basis sets were used for all other atoms.⁷⁻⁸ The stationary points were fully characterized via analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one imaginary eigenvalue). Energies include a correction for zero point energies (E) and free energies (G) at 298.15 K. The single point calculations of the B3LYP optimized geometries were performed to incorporate the effect of various solvents such as toluene, tetrahydrofuran, acetone and acetonitrile via the polarized continuum model (PCM) approach.⁹⁻¹¹

Table S1. Computed energetics of **1_{exp}**, **2**, and **3** in kcal/mol for CO₂ insertion reactions

CO ₂ insertion steps	1_{exp} ^[a]		2		3 ^[b]	
	ΔE^\ddagger (ΔG^\ddagger)	$\Delta E_{R,E}$ ($\Delta G_{R,E}$)	ΔE^\ddagger (ΔG^\ddagger)	$\Delta E_{R,E}$ ($\Delta G_{R,E}$)	ΔE^\ddagger (ΔG^\ddagger)	$\Delta E_{R,E}$ ($\Delta G_{R,E}$)
First CO ₂	8.2 (22.8)	-12.8 (1.5)	12.0 (23.8)	-7.8 (3.3)	28.1 (38.8)	-7.6 (5.1)
Second CO ₂	-	-	29.2 ^[b] (34.5)	-6.9 ^[b] (0.7)	28.7 (38.1)	-6.8 (4.2)
Third CO ₂	-	-	-	-	30.6 (40.1)	-2.8 (8.2)

[a] Gas phase energetics are taken from *Inorg. Chem.* **2012**, *51*, 9683. [b] Energetics correspond to the concerted CO₂ insertion pathway, wherein the stepwise pathway does not operate.

Method and Basis set Testing:

Table S2. Various method and basis set test on the relative energies (kcal/mol) of **4-Ir** isomers.

Methods	$\Delta E (\Delta G)$ of 4-Ir			
	Isomer 1	Isomer 2	Isomer 3	Isomer 4
B3LYP	0.0 (0.0)	4.4 (4.1)	8.9 (8.7)	11.0 (11.1)
BLYP	0.0 (0.0)	3.9 (4.0)	9.1 (8.9)	10.8 (11.0)
BP86	0.0 (0.0)	4.3 (4.1)	9.6 (9.3)	11.1 (11.1)
B3P86	0.0 (0.0)	4.5 (4.1)	9.5 (9.1)	11.4 (11.0)
PBEPBE	0.0 (0.0)	4.3 (4.4)	9.9 (9.9)	11.1 (11.0)
PBE1PBE	0.0 (0.0)	4.6 (4.4)	9.5 (9.1)	11.2 (11.0)
B3PW91	0.0 (0.0)	4.4 (4.1)	9.3 (9.1)	11.2 (11.1)
M06	0.0 (0.0)	4.6 (4.8)	8.4 (8.2)	10.4 (10.1)
M06L	0.0 (0.0)	4.3 (4.3)	8.4 (8.3)	9.7 (9.2)
B97D	0.0 (0.0)	3.6 (3.1)	9.0 (7.9)	10.2 (9.2)
Basis Sets				
B3LYP(6-311++G**)/B3LYP(6-31G**)	0.0 (0.0)	3.5 (3.3)	8.5 (8.3)	10.8 (10.8)

In order to validate the B3LYP method¹⁻³, nine other methods *viz.* BLYP, BP86,¹²⁻¹³ B3P86, PBEPBE,¹⁴⁻¹⁵ PBE1PBE,¹⁶ B3PW91,¹⁷⁻¹⁸ M06,¹⁹ M06L²⁰ and B97D²¹ have also been used to test the relative stability of the isomers of **4-Ir**. All the methods consistently reproduced the same stability trend with B3LYP method, wherein the **isomer 1** is more stable than other three isomers by 4 – 11 kcal/mol. Hence the more stable **isomer 1** is taken for computing the CO₂ insertion reactions and the B3LYP method is used overall.

Table S3. Various method and basis set test on the activation (ΔG^\ddagger) and reaction free energies ($\Delta G_{R,E}$) (kcal/mol) of **4-Ir** for the successive CO₂ insertion reactions.

Methods	ΔG^\ddagger ($\Delta G_{R,E}$) of 4-Ir		
	4→6	6→8	8→10
B3LYP	18.6 (-7.8)	25.1 (-5.3)	33.3 (-1.1)
B3LYP-D3	9.1 (-13.9)	11.3 (-13.2)	22.6 (-7.6)
PBE1PBE	12.9 (-13.7)	20.4 (-10.3)	28.4 (-5.7)
M06	12.5 (-9.1)	15.7 (-7.5)	26.8 (-3.5)
M06L	13.7 (-5.2)	20.3 (-5.2)	28.3 (-1.1)
Basis Sets			
B3LYP-D3(SDDALL,6-311++G**)//B3LYP(SDDALL,6-31G**)	11.1 (-11.8)	17.7 (-10.6)	28.4 (-4.3)

In order to validate the B3LYP method on the activation (ΔG^\ddagger) and reaction free energies ($\Delta G_{R,E}$) of **4-Ir** for the successive CO₂ insertions, four different methods *viz.* B3LYP-D3, PBE1PBE,¹⁶ M06¹⁹ and M06L²⁰ have been used along with the higher basis set calculations B3LYP-D3(SDDALL,6-311++G**)//B3LYP(SDDALL,6-31G**). All the methods consistently reproduced the same trend with the B3LYP method and also indicates that the rate determining step is associated with the insertion of third CO₂ molecule. Hence, the B3LYP method has been chosen to model the CO₂ insertion reactions of **4-Ir**, **4-Rh** and **4-Co** species.

Solvent effect Testing:

Table S4. Computed activation and reaction energies (kcal/mol) of **4-Ir** for the consecutive CO₂ insertion steps in various solvents.

CO ₂ insertion steps	4-Ir ^[a]		4-Ir ^[b]		4-Ir ^[c]		4-Ir ^[d]	
	ΔE^\ddagger (ΔG^\ddagger)	$\Delta E_{R,E}$ ($\Delta G_{R,E}$)	ΔE^\ddagger (ΔG^\ddagger)	$\Delta E_{R,E}$ ($\Delta G_{R,E}$)	ΔE^\ddagger (ΔG^\ddagger)	$\Delta E_{R,E}$ ($\Delta G_{R,E}$)	ΔE^\ddagger (ΔG^\ddagger)	$\Delta E_{R,E}$ ($\Delta G_{R,E}$)
4→6	16.7 (15.3)	-21.9 (-11.1)	16.6 (12.7)	-24.5 (-13.7)	16.5 (11.8)	-25.6 (-14.8)	16.4 (11.5)	-25.8 (-15.1)
6→8	19.5 (23.0)	-19.3 (-7.8)	19.3 (21.5)	-21.5 (-10.0)	19.2 (21.0)	-22.4 (-10.9)	19.1 (20.8)	-22.6 (-11.1)
8→10	22.2 (31.3)	-15.0 (-3.1)	21.3 (29.7)	-17.8 (-6.0)	20.9 (29.1)	-19.1 (-7.3)	20.7 (28.9)	-19.5 (-7.6)

[a] Energetics including toluene solvent corrections, [b] Energetics including THF solvent corrections, [c] Energetics including acetone solvent corrections, [d] Energetics including acetonitrile solvent corrections.

The effect of various solvents such as toluene ($\epsilon = 2.4$), tetrahydrofuran ($\epsilon = 7.4$), acetone ($\epsilon = 20.5$) and acetonitrile ($\epsilon = 35.7$) have been tested for the CO₂ insertion reactions of **4-Ir** species. The increase in the polarity of solvents effectively reduced the activation free energy in the order **4-Ir** in toluene > **4-Ir** in THF > **4-Ir** in acetone > **4-Ir** in acetonitrile and this is in good agreement with solvent effect of the CO₂ insertion of [(PMe₃)₄Ru(η^2 -NHC₆H₄)] complex.²²

Figure S1. Computed isomers of $[\text{Ir}(\eta^2\text{-NHCH}_2\text{PMe}_2)_3]$ (**4-Ir**) with relative energies (kcal/mol) at B3LYP method. Bond lengths are in Å.

Figure S2. Computed isomers of $[\text{Rh}(\eta^2\text{-NHCH}_2\text{PMe}_2)_3]$ (**4-Rh**) with relative energies (kcal/mol) at B3LYP method. Bond lengths are in Å.

Figure S3. Computed isomers of $[\text{Co}(\eta^2\text{-NHCH}_2\text{PMe}_2)_3]$ (**4-Co**) with relative energies (kcal/mol) at B3LYP method. Bond lengths are in Å.

Figure S4. Optimized intermediates and transition states for CO₂ insertion into the Ir-N bonds of [Ir(η²-NHCH₂PMe₂)₃] (**4-Ir**). Selected distances and torsion angles are given in Å and degrees, respectively. The vibrational modes of transition states are shown by arrows.

Figure S5. Optimized intermediates and transition states for CO₂ insertion into the Rh-N bonds of [Rh(η²-NHCH₂PMe₂)₃] (**4-Rh**). Selected distances and torsion angles are given in Å and degrees, respectively. The vibrational modes of transition states are shown by arrows.

Figure S6. Optimized intermediates and transition states for CO₂ insertion into the Co-N bonds of [Co(η^2 -NHCH₂PMe₂)₃] (**4-Co**). Selected distances and torsion angles are given in Å and degrees, respectively. The vibrational modes of transition states are shown by arrows.

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