Supporting Information

Cyclic (Alkyl)(amino)carbenes in Organic and Organometallic Methane C-H Activation: a DFT and MCSCF Study

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1. MCSCF Natural Orbital Analysis of CAAC ligands

MCSCF calculation shows that the natural orbital (NO) 39 of 1 and NO 50 of 2 are the π orbitals of the N–C_c bond (NOON = 1.96 e⁻ for both 1 and 2). The NO 38 of 1 and NO 49 of 2 (NOON = 1.97 e⁻ for 1 and 1.98 e⁻ for 2) are the lone pair located on the sp^2 atom (73% on N and 26% on C_c for 1 and 76% on N and 23% on C_c for 2; percentages determined via a Mulliken population analysis). The NO 40 of 1 and NO 51 of 2 are the π^* orbitals of the N–C_c bond, Figure S1. The cyclohexyl substituent on the C_a attached to C_c delocalizes a small amount of electron density onto the amino substituent. In 3, the NO 79 and 78 are both π orbitals of the Dipp substituent on the amino group. NO 77 is calculated to be the lone pair on C_c with 91% of the *e⁻* located on this atom. The electron rich aryl group can delocalize the electron density from the amino group to C_c. The difference in NOON between NO 79 and 80 of 3 is 1.86 e⁻, which is smaller than that of 1 and 2 (1.91 e⁻). The delocalized π -system of the Dipp substituent (3) seems to increase the HOMO-LUMO gap compared to the CAAC ligand with the alkyl substituent (1), particularly the σ -donating ability of the overall CAAC ligand because the one of the frontier orbitals, which is the sp^2 orbital that defines the C_c lone pair (NO 77 in 3) is stabilized.

The NO 35 of **4** is the same as NO 39 of **1** and NO 50 of **2**, which is the π orbital of the N–C_c bond with 76% of the electron density located on N_a and the NO 36 being the π^* orbital of the N–C_c bond as well. But the NO 34 of **4** is the σ orbital between the N_a–N bond and the NO 33 is the σ orbital formed between the sp^2 orbitals from N_a and C_c with 67% of the electron density located on N_a and 33% on the C_c. The NO 30 of **5** is the π orbital of the unsaturated C–C bond and the π orbital of the N-N bond with 85% of the electron density located in the C–C bond π orbital and 12% in the N–N bond π orbital. The NO 29 is the π orbital of the N–C c–C a with only constructive interaction and zero nodes (62% of the *e*-located N_a and 27% on C_c). NO 28 is also the σ orbital formed between the sp^2 orbitals from N_a and C_c with 67% of the electron density located on N_a and 32% on the C_c, similar to that of **4**. The unsaturation of the CAAC ring in **5** changes the properties of the frontier orbitals, with the orbital on the N_a–C_c bond being more delocalized. The calculated electron density plot of the six-membered rings CAAC **6** shows more substantial delocalization than those of the five-membered ring CAACs **1** - **5**. The NO 43 of **6** only has 0.90 *e* (45%) located on the C_c with the remaining electron density spread over other atoms. The NO 44 of **6** is also highly delocalized, which may impact the backbonding properties when functioning as a ligand as compared to five-membered ring CAACs.



Figure S1. MCSCF-calculated frontier orbitals of ligands 1 - 6 with natural orbital occupation numbers. For these simulations, a CAS(8/8) wavefunction was employed in conjunction with the 6-31G(d) basis and 6-31G basis for H atoms.

2. MCSCF-calculated Natural Orbitals of $L_n(Cp)M$ ($L_n = 1$ and 6, M = Co, Rh, Ir) and Mulliken Population Results



Figure S2. MCSCF-calculated natural orbitals of 1(Cp)Co singlet state. A CAS(12/12) wavefunction was employed in conjunction with the 6-31G(d) basis set. 6-31G basis is used for H atoms.

1(Cp)Co singlet natural orbitals	NOON (e ⁻)	Co pop (e ⁻)	C _c pop (e ⁻)
55	0.01	0.01	0.00
54	0.02	0.02	0.00
53	0.02	0.02	0.00
52	0.03	0.03	0.00
51	0.04	0.03	0.01
50	1.96	1.76	0.13
49	1.97	1.92	0.01
48	1.98	1.94	0.00
47	1.99	1.95	0.00
46	1.99	1.52	0.00

Table S1. Mulliken population analysis of active space natural orbitals for 1(Cp)Co singlet state.



Figure S3. MCSCF-calculated natural orbitals of 1(Cp)Co triplet state. A CAS(12/12) wavefunction was employed in conjunction with the 6-31G(d) basis set. 6-31G basis is used for H atoms.

1 (Cp)Co triplet natural orbitals	NOON (e ⁻)	Co pop (e ⁻)	C _c pop (e ⁻)
55	0.019	0.017	0.002
54	0.029	0.025	0.000
53	0.033	0.029	0.002
52	0.057	0.037	0.014
51	1.000	0.949	0.011
50	1.001	0.928	0.019
49	1.936	1.743	0.121
48	1.962	1.912	0.002
47	1.968	1.902	0.019
46	1.987	0.659	0.720

Table S2. Mulliken population analysis of active space natural orbitals for 1(Cp)Co triplet state.



Figure S4. MCSCF-calculated natural orbitals of 1(Cp)Rh singlet state. A CAS(12/12) wavefunction was employed in conjunction with the 6-31G(d) basis set. 6-31G basis is used for H atoms.

l(Cp)Rh singlet natural orbitals	NOON (e ⁻)	Rh pop (e ⁻)	C _c pop (e ⁻)
55	0.018	0.016	0.000
54	0.020	0.016	0.001
53	0.024	0.018	0.001
52	0.054	0.033	0.011
51	0.062	0.028	0.028
50	1.939	1.541	0.352
49	1.958	0.974	0.692
48	1.974	1.840	0.036
47	1.978	1.915	0.002
46	1.981	1.906	0.008

Table S3. Mulliken population analysis of active space natural orbitals for 1(Cp)Rh singlet state.



5152535455Figure S5. MCSCF-calculated natural orbitals of 1(Cp)Rh triplet state. A CAS(12/12) wavefunction was employed in conjunction
with the 6-31G(d) basis set. 6-31G basis is used for H atoms.

(Cp)Rh triplet natural orbitals	NOON (e ⁻)	Rh pop (e ⁻)	C _c pop (e ⁻)
55	0.015	0.115	0.003
54	0.020	0.155	0.001
53	0.027	0.021	0.005
52	0.044	0.022	0.018
51	1.003	0.806	0.035
50	1.005	0.793	0.000
49	1.959	1.741	0.001
48	1.973	0.889	0.000
47	1.981	1.889	0.001
46	1.987	1.876	0.041

Table S4. Mulliken population analysis of active space natural orbitals for 1(Cp)Rh triplet state.



Figure S6. MCSCF-calculated natural orbitals of 1(Cp)Ir singlet state. A CAS(12/12) wavefunction was employed in conjunction with the 6-31G(d) basis set. 6-31G basis is used for H atoms.

1(Cp)Ir singlet natural orbitals	NOON (e ⁻)	Ir pop (e ⁻)	C _c pop (e ⁻)
55	0.018	0.015	0.000
54	0.021	0.017	-0.001
53	0.031	0.018	0.002
52	0.052	0.027	0.011
51	0.066	0.026	0.034
50	1.935	1.361	0.547
49	1.958	1.100	0.197
48	1.970	1.441	0.391
47	1.977	1.729	0.087
46	1.980	1.395	0.266

Table S5. Mulliken population analysis of active space natural orbitals for 1(Cp)Ir singlet state.



5152535455Figure S7. MCSCF-calculated natural orbitals of 1(Cp)Ir triplet state. A CAS(12/12) wavefunction was employed in conjunction
with the 6-31G(d) basis set. 6-31G basis is used for H atoms.

1(Cp)Ir triplet natural orbitals	NOON (e ⁻)	Ir pop (e ⁻)	C _c pop (e ⁻)
55	0.016	0.012	0.001
54	0.020	0.014	0.000
53	0.029	0.023	0.005
52	0.044	0.019	0.020
51	1.003	0.899	0.011
50	1.004	0.794	0.056
49	1.957	1.650	0.228
48	1.971	0.938	0.954
47	1.976	1.837	0.027
46	1.982	1.891	0.012

Table S6. Mulliken population analysis of active space natural orbitals for 1(Cp)Ir triplet state.

3. DFT-calculated Free Energy Profiles of $L_n(Cp)M$ ($L_n = 1, 6$ and 7) for Co, Rh and Ir



Figure S8. Free energy diagram of methane oxidative addition to $L_n(Cp)Co (L_n = 1)$ calculated with DFT ω B97XD/6-31G(d)//6-311++G(d,p) and ECP basis def2-SVP//def2-TZVP for cobalt. Free energies are reported in kcal/mol at 298.15 K and 1 atm.



Figure S9. Free energy diagram of methane oxidative addition to $L_n(Cp)Co$ ($L_n = 6$) calculated with DFT ω B97XD/6-31G(d)//6-311++G(d,p) and ECP basis def2-SVP//def2-TZVP for cobalt. Free energies are reported in kcal/mol at 298.15 K and 1 atm.



Figure S10. Free energy diagram of methane oxidative addition to $L_n(Cp)Co$ ($L_n = 7$) calculated with DFT ω B97XD/6-31G(d)//6-311++G(d,p) and ECP basis def2-SVP//def2-TZVP for cobalt. Free energies are reported in kcal/mol at 298.15 K and 1 atm.



Figure S11. Free energy diagram of methane oxidative addition to $L_n(Cp)Rh$ ($L_n = 1$) calculated with DFT ω B97XD/6-31G(d)//6-311++G(d,p) and ECP basis def2-SVP//def2-TZVP for rhodium. Free energies are reported in kcal/mol at 298.15 K and 1 atm.



Figure S12. Free energy diagram of methane oxidative addition to $L_n(Cp)Rh$ ($L_n = 6$) calculated with DFT ω B97XD/6-31G(d)//6-311++G(d,p) and ECP basis def2-SVP//def2-TZVP for rhodium. Free energies are reported in kcal/mol at 298.15 K and 1 atm.



Figure S13. Free energy diagram of methane oxidative addition to $L_n(Cp)Rh$ ($L_n = 7$) calculated with DFT ω B97XD/6-31G(d)//6-311++G(d,p) and ECP basis def2-SVP//def2-TZVP for rhodium. Free energies are reported in kcal/mol at 298.15 K and 1 atm.



Figure S14. Free energy diagram of methane oxidative addition to $L_n(Cp)Ir$ ($L_n = 1$) calculated with DFT ω B97XD/6-31G(d)//6-311++G(d,p) and ECP basis def2-SVP//def2-TZVP for iridium. Free energies are reported in kcal/mol at 298.15 K and 1 atm.



Figure S15. Free energy diagram of methane oxidative addition to $L_n(Cp)Ir$ ($L_n = 6$) calculated with DFT ω B97XD/6-31G(d)//6-311++G(d,p) and ECP basis def2-SVP//def2-TZVP for iridium. Free energies are reported in kcal/mol at 298.15 K and 1 atm.



Figure S16. Free energy diagram of methane oxidative addition to $L_n(Cp)Ir$ ($L_n = 7$) calculated with DFT ω B97XD/6-31G(d)//6-311++G(d,p) and ECP basis def2-SVP//def2-TZVP for iridium. Free energies are reported in kcal/mol at 298.15 K and 1 atm.