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
2. MCSCF-calculated natural orbitals of Ln(Cp)M (Ln = 1 and 6, M = Co, Rh, Ir) and Mulliken population results
3. DFT-calculated free energy profiles of Ln(Cp)M (Ln = 1, 6 and 7) for Co, Rh and Ir
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 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 sp² atom (73% on N and 26% on C for 1 and 76% on N and 23% on 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 bond, Figure S1. The cyclohexyl substituent on the Cα attached to Cc 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 Cc with 91% of the e⁻ located on this atom. The electron rich aryl group can delocalize the electron density from the amino group to Cc. 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 sp² orbital that defines the Cc 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–Cc bond with 76% of the electron density located on Nα and the NO 36 being the π* orbital of the N–Cc bond as well. But the NO 34 of 4 is the σ orbital between the Nα–N bond and the NO 33 is the σ orbital formed between the sp² orbitals from Nα and Cc with 67% of the electron density located on Nα and 33% on the Cc. 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–Cc–Cc with only constructive interaction and zero nodes (62% of the e⁻ located Nα and 27% on Cc). NO 28 is also the σ orbital formed between the sp² orbitals from Nα and Cc with 67% of the electron density located on Nα and 32% on the Cc, 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 Nα–Cc 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 Cc with the remaining electron density spread over other atoms. The NO 44 of 6 is also highly delocalized, which may impact the back-bonding 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.

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

<table>
<thead>
<tr>
<th>$1$(Cp)Co singlet natural orbitals</th>
<th>NOON (e⁻)</th>
<th>Co pop (e⁻)</th>
<th>Cc pop (e⁻)</th>
</tr>
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<tr>
<td>55</td>
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<td>0.01</td>
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</tr>
<tr>
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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.

<table>
<thead>
<tr>
<th>1(Cp)Co triplet natural orbitals</th>
<th>NOON (e-)</th>
<th>Co pop (e-)</th>
<th>Cc pop (e-)</th>
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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.

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

<table>
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<tr>
<th>1(Cp)Rh singlet natural orbitals</th>
<th>NOON (e⁻)</th>
<th>Rh pop (e⁻)</th>
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Figure S5. MCSCF-calculated natural orbitals of \( (\text{Cp})\text{Rh} \) 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.

<table>
<thead>
<tr>
<th>( (\text{Cp})\text{Rh} ) triplet natural orbitals</th>
<th>NOON (e(^{-}))</th>
<th>Rh pop (e(^{-}))</th>
<th>C(_{5}) pop (e(^{-}))</th>
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Table S4. Mulliken population analysis of active space natural orbitals for \( (\text{Cp})\text{Rh} \) 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.

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

<table>
<thead>
<tr>
<th>1(Cp)Ir singlet natural orbitals</th>
<th>NOON (e⁻)</th>
<th>Ir pop (e⁻)</th>
<th>Cₖ pop (e⁻)</th>
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Figure S7. MCSCF-calculated natural orbitals of $\text{I}(\text{Cp})\text{Ir}$ 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.

<table>
<thead>
<tr>
<th>$\text{I}(\text{Cp})\text{Ir}$ triplet natural orbitals</th>
<th>NOON (e$^{-}$)</th>
<th>Ir pop (e$^{-}$)</th>
<th>C$_{\text{c}}$ pop (e$^{-}$)</th>
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Table S6. Mulliken population analysis of active space natural orbitals for $\text{I}(\text{Cp})\text{Ir}$ triplet state.
3. DFT-calculated Free Energy Profiles of Ln(Cp)M (Ln = 1, 6 and 7) for Co, Rh and Ir

Figure S8. Free energy diagram of methane oxidative addition to Ln(Cp)Co (Ln = 1) calculated with DFT ωB97XD/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 Ln(Cp)Co (Ln = 6) calculated with DFT ωB97XD/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 Ln(Cp)Co (Ln = 7) calculated with DFT ωB97XD/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 ωB97XD/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 ωB97XD/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 ωB97XD/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 Ln(Cp)Ir \((L_n = 1)\) calculated with DFT ωB97XD/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 Ln(Cp)Ir \((L_n = 6)\) calculated with DFT ωB97XD/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 Ln(Cp)Ir \((L_n = 7)\) calculated with DFT ωB97XD/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.