Supporting Information

Quantum chemical and solution phase evaluation of metallocenes as reducing agents for the prospective atomic layer deposition of copper

Gangotri Dey[a], Jacqueline S. Wrench[b], Dirk J. Hagen[a], Lynette Keeney[a], Simon D. Elliott[a*]

*simon.elliott@tyndall.ie

Contents:

Table S1: Spin states of the metallocenes and metallocene based by-products that are studied in the main paper.

Table S2: Positive and negative points of the metallocenes that are studied.

Table S3: Energetic of different metallocenes other than the ones studied in the main paper. These metallocenes do not exist in II oxidation state. Hence, they have been excluded from the main manuscript.

Figure S1: Ball and stick figure of the metallocene based by-products.

Table S1: Spin state of metallocene and metallocene-based by-products for equations 1 and 2. The metal cations can have multiple spin states but only the lowest energy state is presented here. The metallocene compounds are in the formal oxidation state of II and the substituted metallocene compounds in III and IV. The obtained spin states for the metallocene are in accordance with the most stable spin state as described by Swart[54]. In cases where there is spin contamination, the computed UKS spin expectation value $<S^2>$ is listed and in these cases the spin projection technique outlined in section C.i. has been used to compute the spin-pure ground state energy.

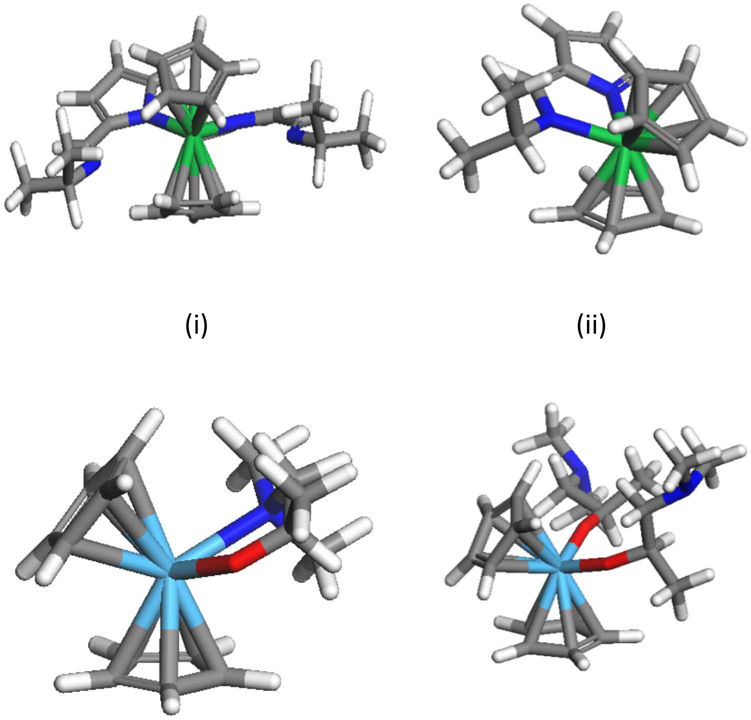
Metallocene	No. of d electrons in the metal of the complex			MCp_2	acac		dmap		PyrAld		PyrIm		$PyrIm^{iPr}$	
	MCp_2	MCp_2L_2	MCp_2L		Eq. 1	Eq. 2	Eq. 1	Eq. 2	Eq. 1	Eq. 2	Eq. 1	Eq. 2	Eq. 1	Eq. 2
VCp_2	3	1	2	Quartet ($<S^2>$=1.74)	Doublet ($<S^2>$= 0.91)	Singlet	Doublet	Singlet	Doublet	Singlet	Doublet	Singlet	Doublet	Singlet
$CrCp_2$	4	2	3	Triplet	Singlet	Quartet ($<S^2>$= 1.69)	Singlet	Quartet	Singlet	Doublet	Singlet	Doublet	Singlet	Quartet ($<S^2>$=3.80)
$FeCp_2$	6	4	5	Singlet	Quintet	Quartet ($<S^2>$= 1.33)	Quintet ($<S^2>$=6.09)	Doublet	Quintet ($<S^2>$=6.12)	Doublet	Singlet	Doublet	Singlet	Doublet
$CoCp_2$	7	5	6	Doublet	Doublet	Singlet	Doublet	Singlet	Doublet	Singlet	Doublet	Singlet	Doublet	Singlet
$NiCp_2$	8	6	7	Triplet	Singlet	Doublet	Quintet	Doublet	Quintet	Doublet	Singlet	Doublet	Singlet	Doublet

Table S2: The positive and negative points of the metallocene that are studied.

	Positive points	**Negative points**
VCp_2	It is commonly available in monomer form. The reactions with different precursors are computed to be exothermic in nature (Table 3).	
$CrCp_2$	Commonly available and exists as monomer form. The reactions are exothermic in nature (Table 3)[44].	In few cases the reaction energies are endothermic.
$FeCp_2$	It is commonly available in monomer form.	Difficult for redox reactions to take place, as the metallocene compound has 18 e^-stability[70].
$CoCp_2$	It is commonly available in monomer form[44] that helps in the reaction as in equation 1 and 2.	Since it is a 19 electron compound, it is not stable. Even if it gives electrons to the system, it will tend to form an ionic compound like $[CoCp_2]^+X^-$[ref:70]. Reaction steps are endothermic as indicated by positive reaction energy.
$NiCp_2$	It is commonly available in monomer form.	It is a 20 e^- species andmight also form an ionic intermediate like $CoCp_2$. It shows an endothermic reaction energy.

Table S3: This table shows the energetics (kJ/mol) of five different copper precursors interacting with metallocene compounds following equations 4 and 5. These metallocene compounds do not exist in oxidation state II. The energetics show them to be excellent candidates as the reducing agents, if produced in oxidation state II, but this may simply reflect the instability of that state. The energies are computed using a PBE/def-SV(P) gas phase model. Exothermicity (negative reaction energy) indicates feasibility of the reaction.

	$Cu(acac)_2$		$Cu(dmap)_2$		$Cu(PyrAld)_2$		$Cu(PyrIm)_2$		$Cu(PyrIm^{iPr})_2$	
	1	2	1	2	1	2	1	2	1	2
$TiCp_2$	-205.8	-532.2	-290.0	-437.1	-221.2	-534.1	-110.4	-511.9	-102.8	-495.9
$ZrCp_2$	-386.9	-658.0	-441.7	-539.8	-406.0	-653.4	-329.3	-634.2	-292.8	-616.9
$HfCp_2$	-452.0	-705.2	-471.1	-603.3	-428.3	-688.0	-362.0	-673.1	-324.6	-654.7
$TaCp_2$	-283.1	-545.6	-319.4	-441.0	-278.5	-586.1	-195.7	-599.1	-184.5	-575.8
$MoCp_2$	-107.1	-247.8	-170.7	-272.7	-156.6	-348.9	-81.1	-369.7	-72.3	-283.2



(i)

(ii)

(iii)

(iv)

Figure S1: Stick model of DFT-optimized structure of (i) $TaCp_2(PyrIm^{iPr})_2$, (ii) $TaCp_2(PyrIm^{iPr})$. These are the by-products from equation 1 and 2 with tantalocene as the reducing agent and $Cu(PyrIm^{iPr})_2$ as the precursor. (iii) $HfCp_2(dmap)$, (iv) $HfCp_2(dmap)_2$. (i) and (iv) shows that the ligand opens in the by-product with just the O atoms attached to the metal, i.e. monodenticity in the by-products as opposed to bidenticity in the original precursor. This happens in many by-products. Colour code: Grey – Carbon, White – Hydrogen, Dark Blue – Nitrogen, Green – Tantalum, Light blue – Hafnium, Red – Oxygen.