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Density functional investigation of incorporation of functional additives to neutral salicylaldiminato Ni(II) polymerization catalyst

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Abstract

A recent density functional study by Chan et al. (*Organometallics* 19 (2000) 2741) on the mechanism of ethylene polymerization using neutral Ni(II) salicylaldiminato catalysts revealed that there is no direct correlation between activation energy required for ethylene insertion to Ni–C (alkyl) bond and reported turnover frequency (TOF). With this background using density functional method (B3LYP/LANL2DZ), an attempt has been made to investigate the variation in TOF due to incorporation of functional additives in the neutral Ni(II) salicylaldiminato catalyzed polymerization of ethylene. Reasonably good correlation is observed between ln(TOF) of the catalysts on the one hand, and Ni–O (additive) bond dissociation energy or the topological parameters of electron density of the Ni–O (additive) bond on the other. Taking this correlation and comparison of orbital interactions of various species involved into account, a probable mechanism for ethylene polymerization in the presence of the additives is suggested.

Keywords: Density functional; Functional additives; Turnover frequency; Ethylene polymerization catalyst; Bond dissociation energy; Electron density

1. Introduction

In recent years, homogeneous metallocene and non-metallocene catalysts have profoundly impacted the polyolefin industry [1–5]. Among the many promising research approaches the neutral salicylaldiminato Ni(II) complexes reported by Grubbs and co-workers are especially noteworthy for several reasons [6]. First, these complexes are easily synthesized and can polymerize ethylene with activities comparable to that of the early metallocene catalysts [1–3]. Second, unlike the metallocenes they do not require a co-catalyst such as MAO [1,6]. Third and most importantly, unlike the traditional Ziegler–Natta and metallocene catalysts, they retain their activities even in the presence of functional additives such as ethers, esters, ketones, alcohols, and even water. This expands the horizon of their potential application significantly [6a].

Computational methods as a tool for mechanistic investigations of homogeneous catalytic reactions in general and olefin polymerization reactions in particular are well established [7–9]. Recently, by using density functional theory Chan et al. [10] investigated the polymerization mechanism of the earlier version of the Grubbs' catalysts [6b] where triphenylphosphine is one of the ligands. The results of this study are in broad agreement with the generally accepted mechanism of polymerization.

Thus phosphine dissociation followed by complexation by ethylene initiates the polymerization process, while insertion of ethylene into an existing Ni–C bond provides the mechanism for chain propagation. However, the addition of electron-withdrawing or -releasing substituents on the 5-position of the salicylaldiminato ring, i.e. *para* to the carbon with the phenolic oxygen, was found to result only in small changes in the energies of these basic mechanistic steps. Thus, no direct correlation between the energies of these steps and the

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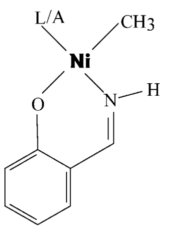
experimentally reported turnover frequencies (TOF) of the catalysts could be established.

As mentioned earlier, in a more recent publication [6a], Younkin et al. showed that the Ni(II) salicylaldiminato complexes with acetonitrile rather than triphenyl phosphine as the neutral ligand are more active precatalysts. They also reported the effects of oxygen donor atom containing functional additives such as dimethoxy ethane, diethyl ether, water, acetone, ethanol and ethyl acetate on the TOF of a specific precatalyst. While the addition of dimethoxy ethane and diethyl ether resulted in TOF in the range ca. 0.3–0.5, with ethanol and water it was between ca. 0.02 and 0.05. With ethyl acetate and acetone as the additives, the TOF was in the range of ca. 0.07–0.08.

In the present work by using density functional theory, the variation in TOF due to the incorporation of polar functional additives has been investigated. The TOF correlates reasonably well with the bond dissociation energy (DE) and the topological parameters of the electron density (ED) of the Ni-additive bond. Based on this model we also predict the activity of the nickel catalyst in the presence of other functional additives that have not been experimentally tried so far.

2. Methodology

The model catalyst structures shown in Fig. 1 have been obtained using hybrid density functional method B3LYP [11] (three parameter Becke's exchange energy functional along with correlation functional due to Lee et al.). The LANL2DZ basis set which include a double zeta valence basis set (8s5p5d)/[3s3p2d] for Ni with the Hay and Wadt ECP replacing core electrons up to 2p and Huzinaga–Dunning double zeta basis set for all other atoms has been used throughout the calculations.



L and A are ligands and additives respectively.

Complex	L
1a	**P(CH$_3$)$_3$**
1b	**CH$_3$CN**
	A
2a	**H$_2$O**
2b	**(C$_2$H$_5$)$_2$O**
2c	**C$_2$H$_5$OH**
2d	**CH$_3$COOC$_2$H$_5$**
2e	**CH$_3$COCH$_3$**
2f	**(CH$_3$OCH$_2$)$_2$**
2g	**THF**
2h	**2,5-Dimethyl THF**
2i	**(CH$_3$)$_2$CHOH (isopropanol)**
2j	**Di-isopropyl ether**
2k	**DMSO**

Fig. 1. Model system used throughout this work.

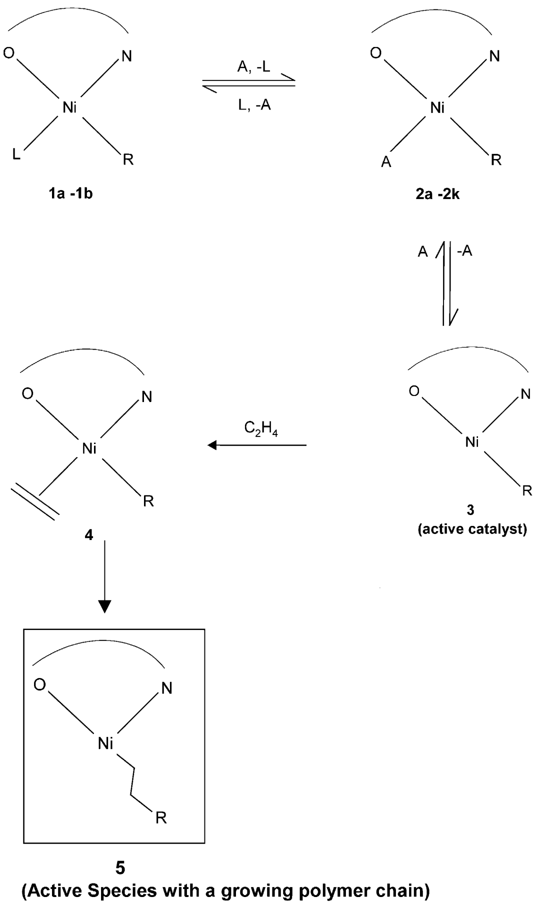
The model catalyst structures studied herein are those proposed by Grubbs and co-workers with L = P(CH$_3$)$_3$ and CH$_3$CN and structures resulting from the replacement of L by polar functional additives A, where A = H$_2$O, C$_2$H$_5$OH, (C$_2$H$_5$)$_2$O, (CH$_3$OCH$_2$)$_2$, CH$_3$COOC$_2$H$_5$, CH$_3$COCH$_3$. As already mentioned, Younkin et al. reported the experimentally determined TOF for these additives [6a]. In addition to these, we have also investigated the structures and energetics of complexes where A = tetrahydrofuran (THF), isopropyl alcohol, 2,5-dimethyl THF, di-isopropyl ether and dimethyl sulfoxide (DMSO), i.e. additives for which experimentally determined TOF is not available.

Some of the mechanistic aspects of the catalytic process have been investigated on the basis of molecular orbital interactions. The bonding features of all the structures have been obtained from topological analysis of ED. This allows us to compare the effect of addition of different functional additives on the metal center. All the calculations have been performed using ab initio program GAUSSIAN-94 [12].

3. Results and discussion

The catalytic cycle proposed by Younkin et al., is based on the generally accepted mechanisms for polymer chain initiation, propagation and termination steps [6a]. Chan et al. had shown earlier that there was no direct correlation of the energetics of any of these elementary steps (viz. chain initiation, propagation and termination) with the activities of the first generation Grubbs catalysts [10,6b]. On the basis of these observations we assume that in the presence of a large excess of a functional additive 'A', the mechanism of polymerization is as shown in Scheme 1. The only extension introduced in this mechanism over the one proposed by Younkin et al., is a matter of fine detail, i.e. the explicit involvement of complexes **2** and **3** as intermediates.

When L is PPh$_3$, the conversion of **1**–**2** involves the generation of free PPh$_3$. However, while three phosphinated complexes, **1** and two others (not shown in Scheme 1) have been identified by ^{31}P-NMR spectroscopy, free PPh$_3$ has not been observed [6a]. This is because PPh$_3$ generated in the conversion of **1**–**2** is consumed in at least two other reaction steps of the proposed catalytic cycle [6a]. Both **5** and a hydridic intermediate formed by β-hydride transfer in the chain termination step, react with PPh$_3$ to give the stable phosphinated complexes observed by ^{31}P-NMR spectro-



Scheme 1. The boxed species is one of the catalytic intermediates proposed by Younkin et al. and the entry point onto their catalytic cycle [6a]. **1a**–**1b**, **2a**–**2k**, L and A are defined in Fig. 1. R = Ph in the precatalyst but assumed to be Me for computation.

scopy. These equilibria must reduce the concentration of free PPh_3 to a great extent, and if the steady-state concentration of free PPh_3 is negligible, it would not be observed by NMR.

Instead of a S_N1 type stepwise conversion of **1**–**4** involving the co-ordinatively unsaturated intermediate **3**, it is possible that the reaction proceeds by an associative mechanism. In other words, the reaction between **1** or **2** with ethylene might take place in a concerted manner without going through an intermediate like **3** and leading directly to the formation of **4**. Although the addition of varying amounts of PPh_3 has been found to result in a drastic reduction of the overall rate of the reaction [6a], this observation does not help to differentiate between the dissociative or associative pathways. Because of the following reasons, the dissociative mechanism has been assumed and the associative pathway not investigated in any detail.

First, considerations based on molecular orbital interactions seem to favor the dissociative pathway (see later). Second, a dissociative mechanism was assumed explicitly by Chan et al. [10] and implicitly by Younkin et al. [6a]. The mechanism proposed in the latter work has complex **5** as one of the crucial catalytic intermediates [6a]. Third, for the ethylene oligomerization reaction in the SHOP process, there is spectroscopic evidence for the formation of a three co-ordinate Ni(II) complex similar to **3** or **5** as a catalytic intermediate [7g].

3.1. Dissociation energy and structures

The co-ordination geometry assumed for calculating the model structures of **1**, **2** and **3** are based on the structures proposed in the earlier works [6a,6b,10]. Two structures arising from the *cis*- or *trans*-orientations of the Ni–CH_3 bond with respect to the ‘Ni–N’ bond are possible for **3**. Considering the stability of the *cis*-structures over the *trans* ones for all the complexes studied by Chan et al. [10], and as has been observed experimentally [6b], we have considered only the *cis*-structures.

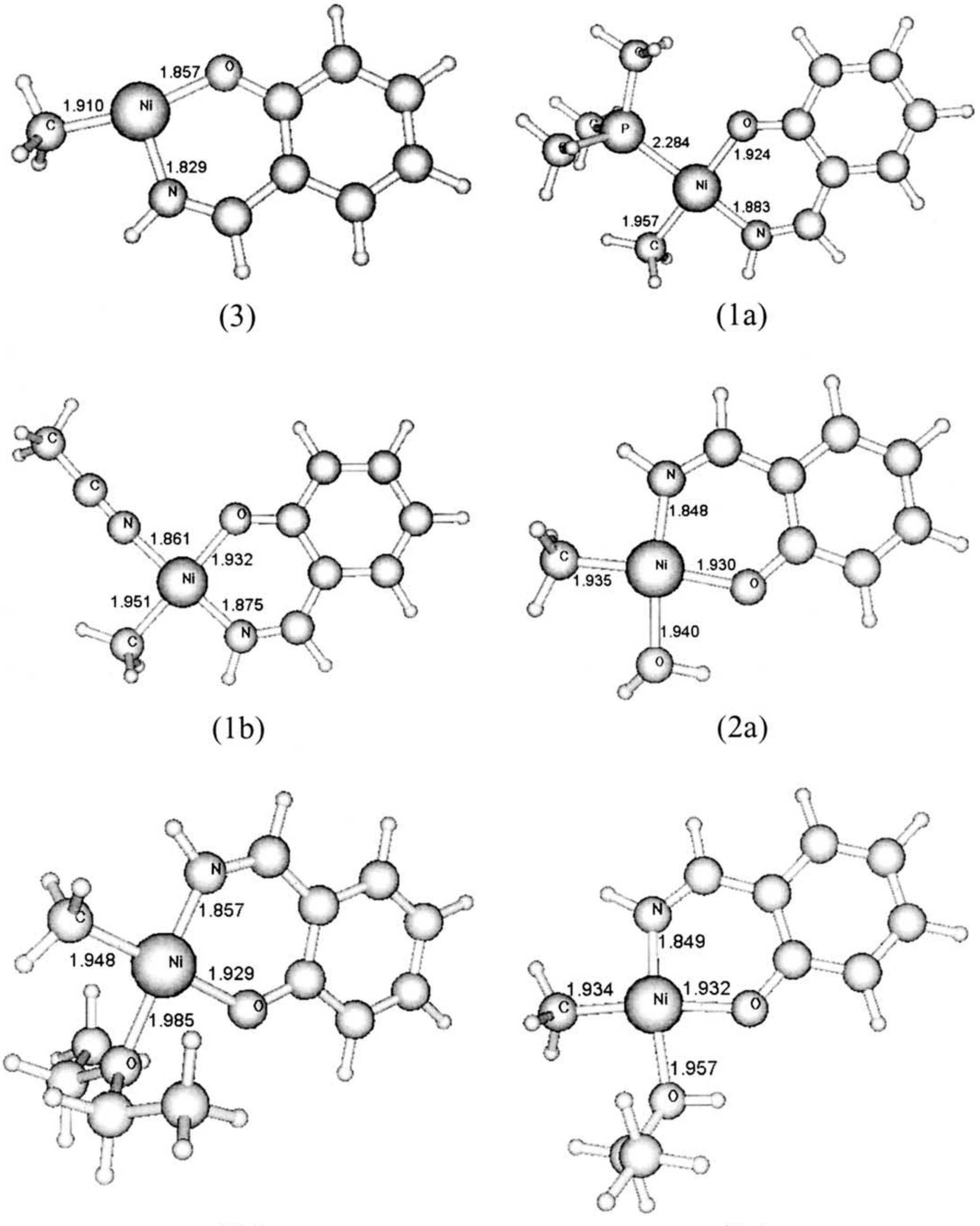
The optimized structures of **1a**–**1b**, **2a**–**2k** and **3** for different ‘L’ and ‘A’ are portrayed in Fig. 2. Complexes **1** and **2** have square planar geometries, and for the latter complexes one of the oxygen atoms of ‘A’ is bound to the nickel atom. This bond is designated as ‘Ni–O(A)’. The theoretically computed total energies of all the structures, the DEs of the ‘Ni–O(A)’ bond and the experimentally determined TOF are given in Table 1.

When A is dimethoxy ethane two structures for **2**, one with *trans*- and the other with *cis*-geometry of dimethoxy ethane, have been found. The DE of the latter is less than the former by 3.52 kcal mol^{-1}. Thus, we expect isomerization of the *trans*-structure to the *cis*-form before dissociation of the additive takes place. In Fig. 2, only the *cis*-structure **2f** is shown.

With ethyl acetate as the additive, two structures, one with nickel binding to carbonyl oxygen and the other where nickel binds to oxygen of the ‘OC_2H_5’ group, are found. The former is stable by 3.23 kcal mol^{-1} than the latter and hence only the former structure is considered in the discussion (see **2d** in Fig. 2).

The DE of the ‘Ni–L’ bond of **1b** is found to be less than that of **1a** by about 1.46 kcal mol^{-1} (see Table 1). This is in accordance with Younkin et al.’s observation that the family of precatalyst with L = acetonitrile is about two to three times as active as the ones where L = PPh_3 [6a]. The fact that the calculated DE of the ‘Ni–P’ bond is for L = PMe_3 and not for PPh_3, has also been addressed. Considerations based on molecular orbital interactions indicate that just like the Ni–PMe_3 bond, the Ni–PPh_3 bond is stronger than the Ni–acetonitrile bond (see later).

Amongst the functional additives, high DE is required for **2a** and **2c** i.e. where the additive is water and ethanol, respectively. Low TOF is obtained with both these additives (cf. Table 1). Diethyl ether and dimethoxy ethane give high TOF and the corresponding



(3) (1a)

(1b) (2a)

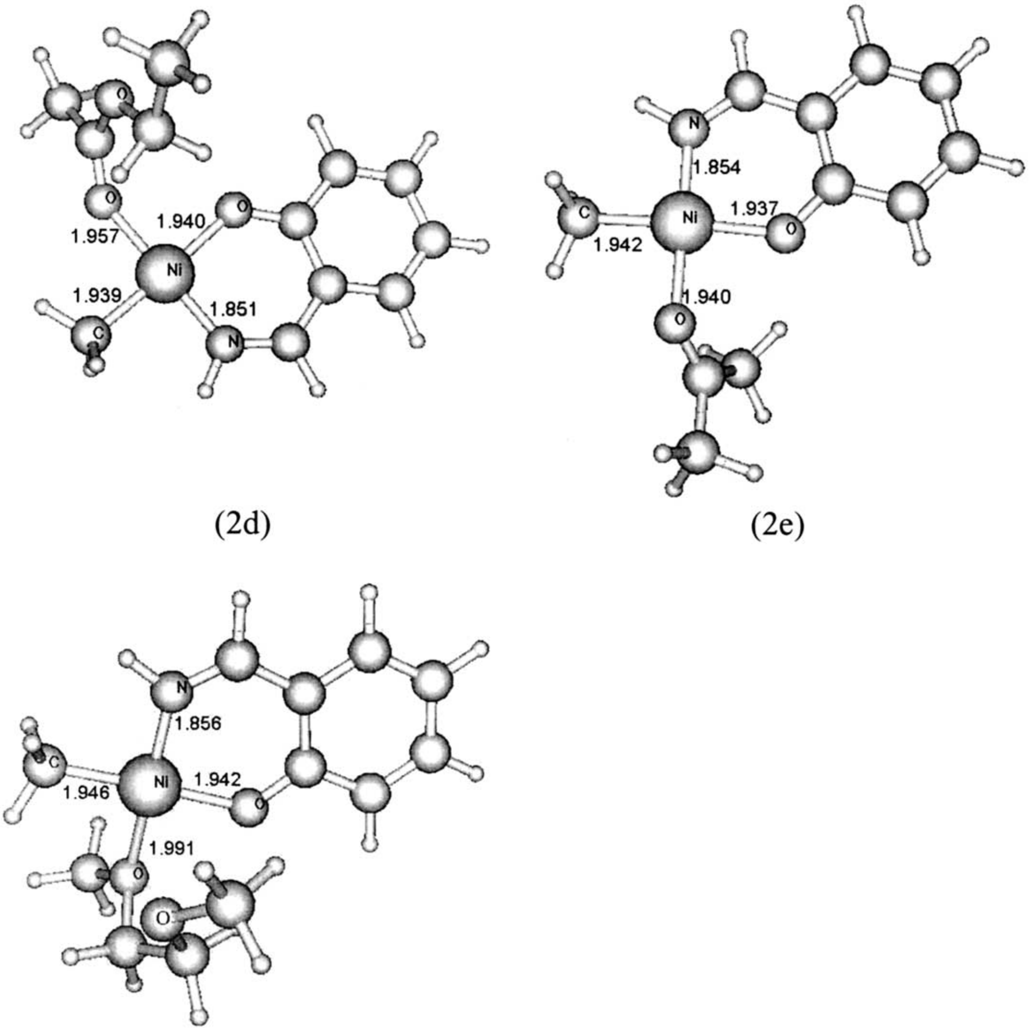
(2b) (2c)

Fig. 2. Ni(II) catalyst with different ligands and additives at B3LYP/LANL2DZ level. All structures have been calculated, however, structures of experimentally reported systems are shown herein with relevant bond lengths reported in Angstrom units. All the structures have been visualized by using MSE_PROP molecular modeling software [17].

DEs in **2b** and **2f** are low (cf. Table 1). The DE of complex **2e** with additive acetone is in between that of **2a** and **2b** and the TOF is slightly higher than that of **2a** and considerably less than that of **2b**. However, for a more quantitative relationship, we consider variation of ln(TOF) with negative of dissociation energy (−DE). The correlation coefficient $r = 0.83$ has been obtained.

It may be noted that while the TOF has been measured in solution, the calculated dissociation energies refer to values expected in the gas phase. Considerations based on a simple Born–Haber type thermodynamic cycle show that for calculating the DE in solution, the difference in the solvation energies of **2a**–**2k** and dissociated free ‘A’ must be taken into account.

The dissociation energies for **2g** and **2h** indicate that with THF and 2,5-dimethyl THF as additives, the TOF should be between that of acetone and ethanol. Simi-



(2d) (2e)

(2f)

Fig. 2 (*Continued*)

larly since **2i**, the isopropanol adduct, has a DE close to that of **2a** and **2c** its TOF is predicted to be similar to that of **2a** and **2c**. The DE of **2j** is low whereas that of **2k** is very high. Thus di-isopropyl ether as an additive would probably give TOF close to that of diethyl ether and dimethoxy ethane, whereas DMSO would give very low TOF.

Since the emphasis of this study is on the 'Ni–O(A)' bond, comparison of this bond length for different 'A' is of interest. The shortest 'Ni–O(A)' distance of 1.940 Å is found for **2a** and **2e** i.e. with additives H_2O and acetone. These two additives give low TOF. The complex **2f** with additive dimethoxy ethane has highest TOF and the longest 'Ni–O(A)' bond (1.991 Å). Among the hypothetical additives for which experimental data are not available, complexes **2k** and **2j** have the shortest (1.920 Å) and the longest (1.996 Å) 'Ni–O(A)' bonds, respectively. The corresponding additives, DMSO and di-isopropyl ether, are thus predicted to give low and high TOF, respectively.

The energy differences between the frontier orbitals of ethylene and **2a**–**2k** or **3** are shown in Table 2. Clearly the energy difference between the HOMO of ethylene and the LUMO of **3** is less than that between HOMO of ethylene and LUMO of **2a**–**2k**. To a first approximation this energy difference is a measure of the likely π-forward donation from ethylene to **3**, or **2a**–**2k**.

Table 2 also shows results on the π-back donation estimated from the energy difference between the LUMO of ethylene and HOMO of complexes **2a**–**2k** or **3**. From the data it is apparent that π-forward donation would be favored for **3**, but π-back donation for **2a**–**2k**. In metal–ethylene complexes such as Zeise's salt, the contribution of π-forward donation to the total binding energy has been estimated [13] to be ca. 75%. In other words, in these complexes π-forward donation

Table 1
Total energies [a] (in au) of **1a**, **1b**, **2a**–**2k**, **3** and dissociation energies (ΔE) (in kcal mol^{-1}) of Ni–L/A [b] bonds in **1a**, **1b**, **2a**–**2k** for the model system [c] at the B3LYP/LANL2DZ level

Complex	E(B3LYP)	ΔE [d] (B3LYP)	TOF [e]
3	−609.51375		
1a, L = PMe_3	−735.77905	27.43	
1b, L = CH_3CN	−742.28341	25.97	
2a, A = H_2O	−685.97615	30.17	0.05
2b, A = $O(C_2H_5)_2$	−843.17850	21.08	0.31
2c, A = C_2H_5OH	−764.58279	29.22	0.02
2d, A = CH_3COOEt	−917.21126	21.94	0.07
2e, A = CH_3COCH_3	−802.68184	24.18	0.08
Cis-**2f**, A = $(CH_3OCH_2)_2$ [f]	−918.36283	20.63	0.49
2g, A = THF	−841.97291	25.40	
2h, A = (2,5-dimethyl THF)	−920.59562	23.40	
2i, A = (*I*-Pr–OH)	−803.89577	29.56	
2j, A = $(i\text{-}Pr)_2O$	−921.79975	21.00	
2k, A = DMSO	−774.61353	37.30	

[a] The B3LYP/LANL2DZ energies (in au) of free ligands/additives, respectively are: $PMe_3 = -126.22158$; $H_2O = -76.41432$; $O(C_2H_5)_2 = -233.63116$; $C_2H_5OH = -155.02248$; $CH_3CN = -132.72828$; $CH_3COCH_3 = -193.12955$; *trans*-$(CH_3OCH_2)_2 = -308.81620$; $(CH_3)_2CH{-}OH = -194.33492$; THF = −232.41878; 2,5-dimethyl THF = −311.04458; $CH_3COOEt = -307.66254$; $((CH_3)_2CH)_2O = -312.25253$; DMSO = −165.04034.

[b] L corresponds to ligand and A corresponds to additive in this table.

[c] The model system has been defined in Fig. 1.

[d] Dissociation energy defined as $\Delta E = E$ (**3**) + E (L/A) − E((**1a**)/(**1b**)/(**2a**–**2k**)).

[e] Turnover frequency of catalyst's polyethylene (PE) production in 10^6 g of PE mol^{-1} of Ni h^{-1}.

[f] Calculations show that structure with *trans*-conformation has substantially higher DE (see text for details).

Table 2
HOMO–LUMO energy difference ΔE (in eV) of the frontier orbitals of ethylene and **2** or **3**

Complex	$\Delta E = E_{HOMO}(\mathbf{2}) - E_{LUMO}$(ethylene)	$\Delta E = E_{HOMO}$(ethylene) − $E_{LUMO}(\mathbf{2})$
2a	5.338	5.813
2b	5.067	6.054
2c	5.293	5.839
2d	5.141	5.980
2e	5.169	5.850
2f	5.023	6.073

$E_{HOMO}(\mathbf{3}) - E_{LUMO}$(ethylene) = 5.714 eV; E_{HOMO}(ethylene) − $E_{LUMO}(\mathbf{3})$ = 5.224 eV.

may be reasonably expected to be more important than π-back donation. Thus the formation of **4** is more likely to proceed through the stepwise dissociative mechanism involving **3**, rather than a direct concerted reaction between ethylene and **2a**–**2k**.

As mentioned earlier by using frontier orbital interactions, we have also explored the effect of having PPh_3 rather than PMe_3 or acetonitrile as 'L'. This has been done to see whether or not compared to both these phosphines, acetonitrile produces a more labile Ni–L bond. The energy gap between the HOMO of 'L' and LUMO of **3** for L = PMe_3, PPh_3 and CH_3CN are 3.809, 3.792 and 6.802 eV, respectively. The energy gaps involving the other pair of frontier orbitals, i.e. HOMO of **3** and LUMO of 'L' are 7.347, 5.046 and 6.258 eV for PMe_3, PPh_3 and CH_3CN, respectively. Both σ-donation and π-back donation estimates thus indicate that acetonitrile would be more weakly bound than both the phosphines.

3.2. Topological analysis of electron density

To study the effect of 'A' on the bonding features of **2a**–**2k**, topological analysis of ED has been performed. The topological analysis involves location and characterization of critical points (CP) in ED distribution and their interpretation [14]. The ED, Laplacian of ED and bond ellipticity are the parameters used for the analysis. The negative Laplacian is an indicator of a covalent bond, whereas positive Laplacian indicates non-bonding or closed shell interaction between the two atoms [15]. The bond ellipticity defined from eigenvalues λ_i of the Hessian matrix of ED as $\varepsilon = (\lambda_1/\lambda_2 - 1)$ where λ_1 and λ_2 are magnitudes of negative eigenvalues with $\lambda_1 > \lambda_2$, is an indicator of the extent of double bond character. In addition, the bond ellipticity provides a measure of structural stability, the bonds with large ε values are prone to rupture [16].

A detailed topological analysis of ED involving location and characterization of all bond critical points (BCP) in ED distribution has been carried out for all the structures, however only some of the representative parameters are shown in Table 3.

The 'Ni–Me' bond (1.910 Å) of **3** is longer than that of **1a**, **1b** and **2a**–**2k**. Accordingly, the ED values at the corresponding bond CPs are also lower. When the ED values of the 'Ni–Me' bonds of **3** and **2a**–**2k** are compared, maximum changes are observed for the additives ethanol, acetone and dimethoxy ethane.

In the case of dimethoxy ethane, i.e. complex **2f**, the two 'Ni–O(A)' distances are 1.991 and 3.097 Å. The latter distance is indicative, if at all, of a very weak bonding interaction and the co-ordination geometry around the nickel atom is in that of a pseudo square pyramid. In case of some complexes, hydrogen bonding has been observed between ligating oxygen atom of the salicylaldiminato backbone and a hydrogen atom of A (viz. as in ethanol, dimethoxy ethane, isopropanol, THF, 2,5-dimethyl THF and ethyl acetate) leading to stabilization of the catalyst.

As all the additives bind to nickel via oxygen atoms, the ED properties of the 'Ni–O(A)' bond are critical for comparing the propensity of the additive towards dissociation. From Table 3 it is clear that complex **2a**

Table 3
Electron density and Laplacian of ED and bond ellipticities at some BCP of Ni(II) catalysts (model system [a]) **1a**, **1b**, **2a**–**2k** and **3** having different ligands at the B3LYP/LANL2DZ level geometry

Ligand/ additive	Location of CP [b] in the specified bond	$\rho(r)$	$\nabla^2\rho(r)$	ε
3	Ni–CH$_3$	0.1196	0.2424	0.000
1a	Ni–CH$_3$	0.1082	0.2287	0.006
	Ni–P	0.0727	0.2110	0.016
	P–C	0.1288	−0.0913	0.105
	P–C′	0.1307	−0.1020	0.098
1b	Ni–CH$_3$	0.1099	0.2174	0.021
	Ni–N (L)	0.0969	0.6501	0.127
	N≡C bond (L)	0.4215	0.0466	0.014
	C–C bond (L)	0.2403	−0.5232	0.001
2a	Ni–CH$_3$	0.1137	0.2282	0.009
	Ni–O (A)	0.0764	0.5782	0.030
	O–H (A)	0.3118	−1.4300	0.021
	O–H′ (A)	0.3284	−1.5000	0.021
2b	Ni–CH$_3$	0.1110	0.2303	0.013
	Ni–O (A)	0.0687	0.5167	0.251
	O–C (A)	0.2081	−0.2509	0.052
2c	Ni–CH$_3$	0.1139	0.2298	0.007
	Ni–O (A)	0.0740	0.5438	0.031
	O–H bond (A)	0.3130	−1.4080	0.022
	O–C bond (A)	0.2069	−0.2330	0.025
	(O)H···O [c]	0.0264	0.1470	2.035
	C–C bond (A)	0.2285	−0.4642	0.038
	P–C′	0.1307	−0.1020	0.098
2d	Ni–CH$_3$	0.1130	0.2192	0.022
	Ni–O (A)	0.0687	0.5534	0.152
	O=C bond (A)	0.3484	−0.4535	0.029
	(O)C–CH$_3$ bond (A)	0.2382	−0.4997	0.037
	C–O bond (A)	0.2807	−0.4831	0.005
	(Ni)O···H(CH$_2$ A) [c]	0.0141	0.0589	0.122
2e	Ni–CH$_3$	0.1122	0.2212	0.020
	Ni–O (A)	0.0752	0.5824	0.175
	O=C bond (A)	0.3388	−0.3300	0.043
	C–C bond (A)	0.2393	−0.5086	0.020
	C–C bond (A)	0.2374	−0.4953	0.027
cis-**2f**	Ni–CH$_3$	0.1116	0.2274	0.014
	Ni–O (A)	0.0096	0.0222	0.124
	Ni–O (A)	0.0661	0.5164	0.263
	O–C bond (A)	0.2243	−0.3307	0.075
	O–C bond (A)	0.2208	−0.3117	0.032
	C–C bond (A)	0.2386	−0.5203	0.028
	C–O bond (A)	0.2099	−0.2552	0.062
	C–O bond (A)	0.2133	−0.2613	0.026
	(C)H···O [c]	0.0037	0.0143	0.328
	(C)H···O [c]	0.0121	0.0524	0.161
2g	Ni–CH$_3$	0.1135	0.2266	0.018
	Ni–O (A)	0.0721	0.5402	0.196
	O–C bond (A)	0.2011	−0.2316	0.064
	O–C bond (A)	0.2051	−0.2405	0.053
	(O)H···O [c]	0.0098	0.0499	7.722
2h	Ni–CH$_3$	0.1114	0.02302	0.015
	Ni–O (A)	0.0723	0.05492	0.252
	O–C bond (A)	0.2030	−0.2347	0.047
	O–C bond (A)	0.2001	−0.2273	0.045
	(CH$_3$)H···O(A) [c]	0.0072	0.0300	0.056
2i	Ni–CH$_3$	0.1137	0.2290	0.008
	Ni–O (A)	0.0745	0.5446	0.028
	O–C bond (A)	0.2034	−0.2281	0.023
	O–H bond (A)	0.3132	−1.4030	0.022
	(O)H···O [c]	0.0260	0.1467	2.643
2j	Ni–CH$_3$	0.1116	0.2276	0.017
	Ni–O (A)	0.0645	0.4946	0.267
	C–O bond (A)	0.2009	−0.2330	0.034
	C–O bond (A)	0.2019	−0.2376	0.024
2k	Ni–CH$_3$	0.1128	0.2233	0.016
	Ni–O (A)	0.0827	0.5837	0.118
	O–S	0.1639	−0.1200	0.054

[a] The model system has been defined in Fig. 1.

[b] The convention used for location of CP is as follows: L, ligand and A, additive the details of which appear already in caption of Fig. 1; occurrence of (A/L) after atom implies atom is part of additive; occurrence of (A/L) after description of bond location implies that both the atoms of bond are part of additive.

[c] Hydrogen bond between salicylaldiminato oxygen attached to Ni and hydrogen of OH/CH group of additive.

with additive water has highest ED at the bond CP (0.0764 au), whereas it is lowest for *cis*-complex **2f** with additive dimethoxy ethane viz. 0.0661 au. The corresponding TOF values are expectedly second lowest and highest. Similar broad reverse relationships between the ED values at the ‘Ni–O(A)’ bond CP and TOF are observed for all the other cases too. The overall correlation of ED value with ln(TOF) is 0.76. Using this correlation we predict that di-isopropyl ether may be a superior additive and DMSO an inferior one compared to those for which experimental data are available.

As mentioned earlier, the bond ellipticity is also a measure of the lability of the bond (higher ellipticity indicates higher lability) and hence we have treated it similar to that of DE for obtaining correlation with TOF. The ellipticity values of ‘Ni–O(A)’ bond CP for all the additives show trends in accordance with the corresponding TOF. The overall correlation between bond ellipticity and ln(TOF) is 0.93.

4. Concluding remarks

The variation in the TOF of Grubbs’ catalyst due to incorporation of polar functional additives has been investigated by density functional method. The dissociation energies of the ‘Ni–L’ (L = PMe$_3$, PPh$_3$ or acetonitrile) or ‘Ni–A’ (A = polar additives with oxygen atom donor) bonds provide a better correlation with the ln(TOF), than the insensitive Ni–C (alkyl) insertion energy barriers reported earlier [10]. The ED topological parameters of these complexes have also been studied.

Both ED and ellipticity values at the 'Ni–O(A)' bond show a good correlation with the corresponding ln(TOF) and for the latter parameter the correlation is remarkably good. However, the finer adjustments in the reported TOF values of the catalysts may be attributed to solvation effects of **2** and free 'A'. Based on these observations and comparison of orbital interactions of various species involved, a probable mechanism (cf. Scheme 1) for ethylene polymerization in presence of functional additives is suggested.

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