

Ligand properties of *N*-heterocyclic and Bertrand carbenes: A density functional study

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Received 30 May 2005; received in revised form 16 July 2005; accepted 16 July 2005

Available online 22 August 2005

Abstract

In order to probe the ligand properties we have examined a series of $\text{Cr}(\text{CO})_5\text{L}$ and $\text{Ni}(\text{CO})_3\text{L}$ complexes using density functional theory (DFT). The ligands included in our study are *N*-heterocyclic carbenes (NHCs) and Bertrand-type carbenes. Our study shows that the carbene–metal bonds of imidazol-2-ylidenes (**1**), imidazolin-2-ylidenes (**2**), thiazo-2-ylidenes (**3**), and triazo-5-ylidenes (**4**) are significantly stronger than those of Bertrand-type carbenes (**5–7**). The force constants of C–O in complexes are related to the property of isolated carbenes such as proton affinity (PA), electronegativity (χ), and charge transfer (ΔN). NHCs and Bertrand-type carbenes are identified as nucleophilic, soft ligands. Carbene stabilization energy (CSE) computations indicate that carbenes **1** and **4** are the most stable species, while **2** and **3** are less stable. In contrast to NHCs, CSE of carbenes **5–7** are much smaller, and their relative stabilities are in the order (amino)(aryl) carbenes **7e–7g** > (amino)(alkyl) carbenes **7a–7d** > (phosphino)(aryl) **6d–6e**, and (phosphino)(silyl) carbenes **5a–5c** > (phosphino)(alkyl) carbenes **6a–6c**.

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Keywords: *N*-heterocyclic carbene; Nucleophilicity; Electrophilicity; Hardness; Electronegativity

1. Introduction

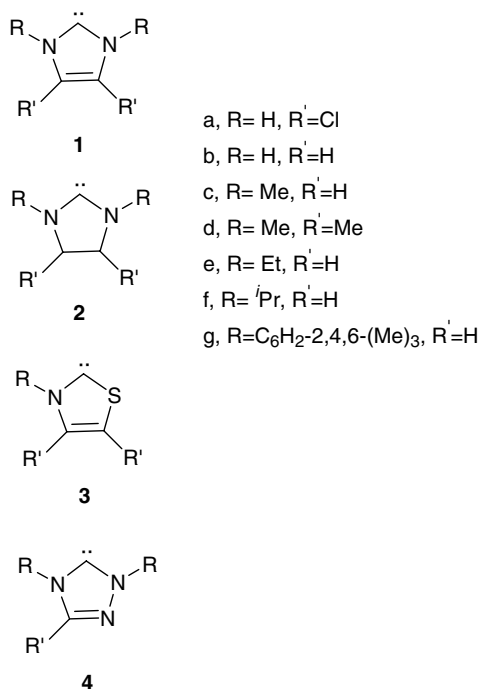
Since the isolation of *N*-heterocyclic carbene (NHC) by Arduengo et al. [1], preparations of NHC have become accessible to chemists [2,3]. Due to their extraordinary properties, NHC ligands were found to be involved in a great variety of catalytic processes [4–7]. The new generation of NHC catalysts have supplemented the role of traditional phosphine catalysts. Moreover, the phosphine ligands are in part replaced by NHCs due to the demonstrated excellence in homogeneous catalysis of the latter. As stated by Herrmann: “a revolutionary turning point in organometallic catalysis is emerging” [6]. One of the most successful applications of NHC is the second-generation Grubbs’ ruthenium–NHC complex, which catalyzes olefin–metathesis reactions [6,7].

NHCs are also shown to be excellent ligands in complexes which catalyze Heck and Suzuki coupling reactions [8,9].

It is generally accepted that NHC binds to metals via σ -bonding, while π -backbonding of NHC is negligible [4]. Theoretical approaches have been applied to enhance our understanding about the bonding nature and the stability of NHCs and carbenes [10–20]. It is known from these studies that, the stability of free NHC is mainly attributed to the p_π – p_π delocalization of nitrogen atoms. Steric effect also contributes to the stability of NHC, however to a smaller extent [14,15]. Dimerization is the most likely reaction path of NHC, and the E_a of dimerization of NHCs having 6π -delocalization (imidazol-2-ylidenes, **1**) are ~ 10 kcal/mol larger than those of imidazolin-2-ylidenes (**2**) [11,16,17]. E_a of dimerization of NHCs are proportional to the singlet–triplet energy separation [11,17]. Theoretical study also shows that the prototype NHC (**1b** and **3b**, Scheme 1)

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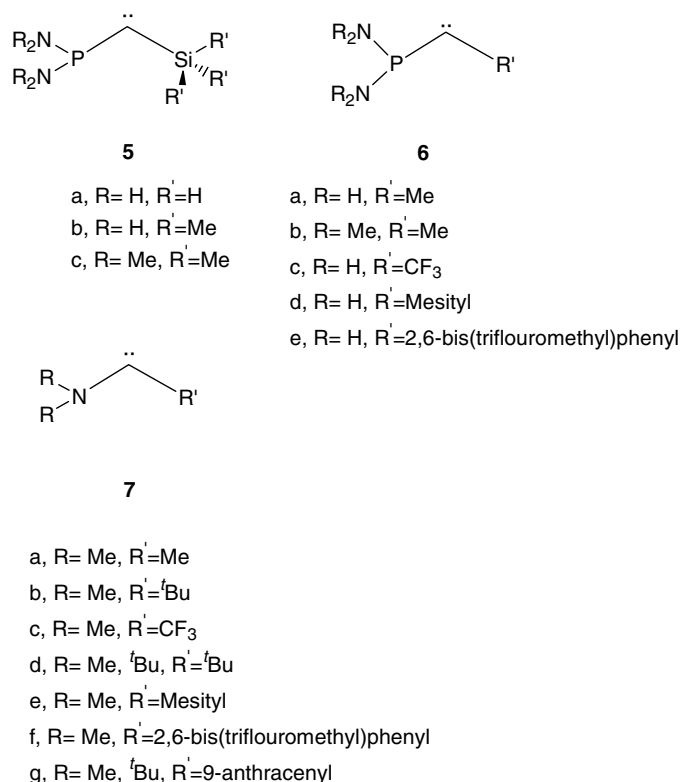
Scheme 1.

are not isolable under normal conditions, because they undergo intermolecular hydrogen transfers readily [18]. With theoretical and experimental efforts, it has been re-

vealed that proton catalyzes NHC dimerizations [19–21]. Thiazo-2-ylidenes (**3**) and triazo-5-ylidenes (**4**) are not used in organometallic catalysis as often as **1** and **2**, however they have demonstrated to be effective organocatalysts in enantioselective reactions [22].

Theoretical study of Boehme and Frenking [23] on MCl (M = Cu, Au, Au) complexes showed that NHC–metal bonds are very strong, and that there is negligible π -backbonding from metal to NHC ligands. Weskamp et al. [24] concluded that the ligand binding energies are in the order $\text{PH}_3 < \text{PMe}_3 < \mathbf{1b}$ for ruthenium(II)-alkylidene compounds. Similar conclusions were obtained from another theoretical study, in which Schwarz et al. [25] concluded that the ligand binding energies in palladium(II) complexes are in the order $\text{PH}_3 < \text{PMe}_3 < \mathbf{1b} < \mathbf{1c}$. Spectroscopic study of Öfele et al. [26] revealed the close relationship between NHC and phosphine complexes.

Another equally important category of carbenes is the series of carbenes synthesized by Bertrand's research group (see Scheme 2). Bertrand's group has successfully isolated the (phosphino)(silyl) [27], (phosphino)(aryl) [28], and (amino)(aryl) [29] carbenes. (Phosphino)(trifluoromethyl) and (phosphino)(alkyl) carbenes were shown to be stable at low temperatures [28,30]. Theoretical aspects and reactivity of these species have been analyzed [29]. The reactions of (phosphino)(silyl) carbenes were studied in great detail; a widespread varieties of



Scheme 2.

reactions typical of transient carbenes, such as insertion to C–H bonds, addition to olefins, and coupling with isocyanides were examined by Bertrand et al. [31].

This report is a summary of our theoretical study on the characters and bonding natures of carbene species mentioned above. The ligand properties are probed using $\text{Cr}(\text{CO})_5\text{L}$ and $\text{Ni}(\text{CO})_3\text{L}$ complexes. The complexes of NHCs **1** and **2** have been reported previously [32].

2. Computational approaches

The theoretical treatment of the systems included in this work was performed by the B3LYP approach using the GAUSSIAN 03 series of programs [33]. The B3LYP approach is a hybrid method, which includes Becke's three-parameter gradient corrected exchange potential [34] and the correlation functional of Lee, Yang, and Parr [35]. In most of the computations, the 6-31G* basis sets were used. The 6-31G* set of Cr, and Ni are Pople's split-valence basis set which consist of the contractions (22s16p4d1f/5s4p2d1f) [36].

Geometries of complexes $\text{Cr}(\text{CO})_5\text{L}$ and $\text{Ni}(\text{CO})_3\text{L}$ were fully optimized. The harmonic vibrational frequencies were computed via analytic energy second derivatives at the B3LYP/6-31G* level. These frequencies were then used to verify genuine minima, and were used to compute zero-point vibrational energy (ZPVE) corrections. ZPVE corrections are included in all energetic calculations. Proton affinities (PA) are computed at the same level of theory. In addition, force constant (in N cm^{-1}) of the C–O bond *trans* to the ligand [$k(\text{C}-\text{O}_{\text{trans}})$] was obtained using the energy second derivatives. In our previous study both $k(\text{C}-\text{O}_{\text{trans}})$ and totally symmetric vibrational frequency [$\nu(\text{CO})$] were used to characterize ligand–metal bonding, and the result shows both quantities are equally good [32]. In this study we will use only $k(\text{C}-\text{O}_{\text{trans}})$ in our discussions.

Another line of pursuing the understanding the role played by the carbenes in complexes, is to study the property of free carbene species. The concept of electrophilicity/nucleophilicity of a carbene was proposed by Mendez and Garcia-Garibay [37], which uses charge transfer (ΔN) to assess the nucleophilicity

$$\Delta N = (\chi_C - \chi_D)/2(\eta_C + \eta_D). \quad (1)$$

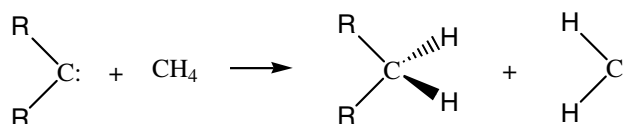
In the above equation χ is the electronegativity [38], and η is the absolute hardness [39]. Within the finite-difference approximation, χ is evaluated by $(\text{IP} + \text{EA})/2$ and η by $(\text{IP} - \text{EA})/2$, where IP and EA are vertical ionization potential and electron affinity, respectively. ΔN is the predicted electron transfer from species D to species C when C and D encounter. In our case, D represents the carbene and C represents $\text{Cr}(\text{CO})_5$ or $\text{Ni}(\text{CO})_3$. The larger extent the electron transfer from the carbene to the complex (positive ΔN), the more nucleophilic the

carbene [37]. In addition to ΔN , χ alone can be used as a measure of the nucleophilicity of carbenes. Sander et al. [40] have shown that nucleophilic carbenes are characterized by low IP and low EA; in contrast, electrophilic carbenes have high IP and high EA. It was thus suggested by Sander et al. that electrophilicity of a carbene is proportional to χ . We will use both quantities, ΔN and χ in our analysis of the electrophilicity/nucleophilicity of carbenes. IP and EA are computed at the B3LYP/6-311++G**//B3LYP/6-31G* level.

A conceptually similar analysis on the scaling of electrophilicity and nucleophilicity of carbenes has been performed by Moss et al. [41,42]. In this approach the “carbene selectivity index” (m_{CXY}) can be derived from experimental data, or from theoretical computations based on frontier orbital theory. Most interestingly, our computed χ values are inversely proportional to m_{CXY} for the carbenes studied by Moss [42]. In the Moss analysis, large m_{CXY} corresponds to nucleophilic addition (small χ), and small m_{CXY} corresponds to electrophilic addition (large χ).

In addition to the aforementioned analysis, Frenking's group has studied NHC complexes using charge decomposition analysis [15], and the energy decomposition analysis of Morokuma [43] and Ziegler [44]. These analyses have resulted in insightful conclusions on the nature of carbenes and their bonding in complexes [15,45].

In order to assess the relative stability of a carbene, we calculated the carbene stabilization energy (CSE) using the following reaction:



The predicted energy of reaction reveals the relative stability of the carbene; i.e., the more endothermic the reaction, the more stable the carbene. In previous theoretical studies, it has been demonstrated that CSEs are proportional to the dimerization barriers of NHCs [17,20]. Nyulászi et al. [13] have studied a series of carbene species, including NHCs, and observed that CSE of carbenes correlates almost linearly with their dimerization reaction energies.

3. Results and discussion

3.1. $\text{Cr}(\text{CO})_5\text{L}$ complexes

The important geometrical parameters of the complexes, $k(\text{C}-\text{O}_{\text{trans}})$, ligand binding energy (D_0), proton affinity (PA), χ , η , and ΔN are summarized in Table 1.

Table 1

Force constants of *trans* C–O [$k(\text{C–O}_{\text{trans}})$, in N cm^{-1}], ligand dissociation energies (D_0 , in kcal/mol), and important geometrical parameters of $\text{Cr}(\text{CO})_5\text{L}$ (bond distances in Å)

	$d(\text{Cr–L})$	$d(\text{Cr–CO}_{\text{trans}})$	$d(\text{C–O}_{\text{trans}})$	$k(\text{C–O}_{\text{trans}})$	D_0	PA	χ	η	ΔN	CSE
1a	2.097	1.882	1.156	17.329	50.0	247.5	4.21	4.78	0.071	102.7
1b	2.107	1.878	1.157	17.210	53.7	258.2	4.08	4.55	0.081	108.4
1c^a	2.161	1.869	1.158	17.068	48.0	266.1	3.85	4.37	0.098	108.8
1d	2.170	1.868	1.159	17.023	47.4	272.4	3.82	4.21	0.102	110.1
1e	2.177	1.867	1.159	17.025	44.3	269.0	3.80	4.28	0.103	114.1
1f	2.185	1.867	1.159	17.015	46.9	271.3	3.73	4.17	0.109	112.3
1g	2.182	1.862	1.160	16.920	46.0	275.7	3.84	4.26	0.100	110.2
2a	2.067	1.890	1.154	17.464	50.7	242.8	4.50	4.64	0.054	85.0
2b	2.101	1.880	1.157	17.230	54.4	260.2	3.96	4.43	0.090	94.9
2c	2.157	1.871	1.158	17.090	46.3	266.1	3.75	4.21	0.107	97.1
2d	2.161	1.870	1.158	17.067	47.0	270.2	3.65	4.10	0.116	95.7
2e	2.173	1.869	1.158	17.065	45.9	268.8	3.64	4.09	0.116	102.0
2f	2.186	1.868	1.158	17.037	45.3	270.7	3.61	4.01	0.120	99.3
2g	2.190	1.863	1.159	16.950	44.4	274.7	3.49	3.82	0.132	100.3
3a	2.073	1.887	1.155	17.427	46.4	239.2	4.26	4.84	0.067	91.6
3b	2.087	1.883	1.156	17.304	49.0	248.6	4.24	4.61	0.071	94.1
3c	2.120	1.877	1.157	17.204	45.8	253.6	4.07	4.50	0.082	94.7
3d	2.129	1.875	1.158	17.145	45.8	260.7	3.92	4.22	0.096	94.7
3e	2.130	1.875	1.158	17.176	45.5	255.4	4.04	4.45	0.085	95.8
3f	2.133	1.875	1.158	17.165	45.6	257.2	4.00	4.38	0.088	96.5
3g	2.131	1.873	1.158	17.107	44.9	260.1	3.84	4.22	0.101	94.9
4a	2.085	1.884	1.156	17.391	48.6	238.0	4.45	4.98	0.055	104.9
4b	2.091	1.882	1.156	17.333	50.0	242.6	4.42	4.87	0.057	107.4
4c	2.141	1.873	1.158	17.181	46.8	253.6	4.13	4.62	0.077	108.0
4d	2.144	1.872	1.158	17.146	47.0	257.7	4.03	4.46	0.085	108.0
4e	2.157	1.871	1.158	17.135	45.4	256.9	4.06	4.53	0.083	109.8
4f	2.161	1.870	1.158	17.114	45.8	260.2	4.00	4.43	0.087	111.4
4g	2.172	1.864	1.159	16.989	43.2	264.8	3.76	4.09	0.108	108.7
5a	2.113	1.881	1.157	17.243	35.6	253.8	3.92	3.91	0.100	48.7
5b	2.258	1.859	1.160	16.934	33.2	260.7	3.76	3.72	0.116	49.4
5c	2.209	1.861	1.160	16.883	32.0	268.9	3.31	3.59	0.150	51.5
6a	2.019	1.909	1.154	17.564	53.7	266.8	3.74	3.69	0.119	36.2
6b	2.031	1.904	1.155	17.430	48.8	274.4	3.24	3.62	0.154	40.1
6c	1.980	1.926	1.151	17.788	45.9	247.8	4.32	4.52	0.054	40.9
6d	2.040	1.905	1.154	17.491	41.2	270.2	3.07	3.66	0.134	45.6
6e	2.040	1.906	1.154	17.551	36.3	254.4	3.58	3.78	0.115	52.1
7a	2.136	1.879	1.158	17.170	49.1	269.5	3.98	3.50	0.128	68.5
7b	2.246	1.866	1.159	17.042	34.0	274.3	3.73	3.33	0.145	63.9
7c	2.114	1.885	1.156	17.346	44.0	247.1	4.50	4.33	0.065	66.6
7d	2.311	1.862	1.159	17.009	18.3	278.5	3.54	3.16	0.162	66.8
7e	2.164	1.875	1.158	17.109	42.8	271.9	3.50	3.17	0.162	74.9
7f	2.168	1.875	1.158	17.171	38.6	259.1	3.81	3.69	0.117	78.8
7g	2.273	1.864	1.159	17.020	27.4	274.5	2.88	3.25	0.171	80.5
CO^b	1.915	1.915	1.150	18.072	39.9	103.8	7.76	6.48	–0.052	

The electronegativity (χ) and absolute hardness (η) (in eV). Charge transfer (ΔN) from ligands to $\text{Cr}(\text{CO})_5$ were computed using Eq. (1).

^a Geometrical parameters from X-ray data are $d(\text{Cr–C}_1) = 2.138$, $d(\text{Cr–CO}_{\text{trans}}) = 1.867$, $d(\text{C–O}_{\text{trans}}) = 1.147$, and $R_x = 2.207$ [26,46].

^b X-ray data (averaged): $d(\text{Cr–L}) = 1.915$, $d(\text{C–O}_{\text{trans}}) = 1.140$ [48].

Our predicted geometrical parameters of the $\text{Cr}(\text{CO})_5\text{L}$ complexes of **1c** and of $\text{Cr}(\text{CO})_6$ are in fine agreement with the X-ray data [26,46–48]. The experimentally determined bond distances are slightly underestimated by DFT. The optimized $d(\text{C–O}_{\text{trans}})$ and $d(\text{Cr–CO}_{\text{trans}})$ are very close among NHC complexes, thus the electronic influence of the *trans* ligands is not noticeably revealed via these geometric parameters. The general trend in $d(\text{Cr–L})$ is that, the metal–ligand distance increases as the size of substituent increases. The overall correlation between χ and ΔN is fairly linear ($R^2 = 0.976$) for carb-

enes **1–7**, thus both quantities are equally good as a measure of the electrophilicity or nucleophilicity of carbene ligands.

Among NHCs, the average electronegativities of thiazol-2-ylidenes (**3**) and triazol-5-ylidenes (**4**) are larger than those of imidazol-2-ylidenes (**1**) and imidazol-2-ylidenes (**2**), and the difference is also seen in their ΔN . **1** and **2** are more nucleophilic (less electrophilic) than **3** and **4**, as we see in the χ and ΔN values. It is also seen that **3** and **4** are harder ligands than **1** and **2**, as shown in their computed η values. Larger substituent groups on

nitrogen decreases the electronegativity of a carbene. With the mesityl substitution on N, **2g**, **3g** and **4g** are the softest and most nucleophilic (smallest η and largest ΔN) in their categories. The electrophilicity/nucleophilicity scale of ligands demonstrates the induced electron density change at the metal center, and the effect is also seen in $k(\text{C}-\text{O}_{\text{trans}})$.

We attempt to probe the influence of carbene ligands using $k(\text{C}-\text{O}_{\text{trans}})$. The force constant of C–O stretching is considered to be proportional to the π -backbonding and σ -withdrawing ability of the ligand. In a previous study, we found that the correlation between $k(\text{C}-\text{O}_{\text{trans}})$ and the C–O totally symmetric frequency [$\nu(\text{CO})$] is fairly linear. The discussion of the electronic influence of ligands thus can be equally well described using either $\nu(\text{CO})$ or $k(\text{C}-\text{O}_{\text{trans}})$ [32]. π -backbonding would result in a short Cr–L distance, long $d(\text{Cr}-\text{CO}_{\text{trans}})$, short $d(\text{C}-\text{O}_{\text{trans}})$ and large $k(\text{C}-\text{O}_{\text{trans}})$. The more nucleophilic (basic) ligands will induce smaller C–O force constants. It has to be noted that $k(\text{C}-\text{O}_{\text{trans}})$ is affected by the change of electron density at the metal and the extent of π -backbonding, the difference in $k(\text{C}-\text{O}_{\text{trans}})$ should not be attributed to π -backbonding alone.

We have noticed that $d(\text{Cr}-\text{L})$ of NHC increases as the size of substituent on N increases from **a** to **g**. In addition, along this line the nucleophilicity of NHC is increased, and $k(\text{C}-\text{O}_{\text{trans}})$ is decreased. These observations suggest that going through **a** to **g** substituents, the σ -donating ability of NHC is increasing, while their π -accepting ability is decreasing. Fig. 1 illustrates $k(\text{C}-\text{O}_{\text{trans}})$ versus ΔN relations for carbenes. We used a reduced number of data for NHC in Fig. 1, so that it can be compared with the results of $\text{Ni}(\text{CO})_3\text{L}$. In the figure, we see that for each type of NHC, $k(\text{C}-\text{O}_{\text{trans}})$ are inversely proportional to ΔN . The correlation suggests that the binding of NHC to the metal is mainly via nucleophilic electron donation. This agrees with previous consensus about NHC, that NHCs are strong σ -donors and poor π -acceptors. The σ -donating ability of carbene ligands is in the **a** to **g** order. Steric repulsion may play a certain role in affecting the electronic property of the complex. However this effect may not be significant, since $d(\text{Cr}-\text{L})$ correlates with ΔN ($R^2 = 0.766$), while ΔN is computed without the inclusion of steric repulsions. At the upper-left corner (**3b**, **4b**) of Fig. 1 are the better π -acceptors and poorer σ -donors; at the lower-right corner (**1f**, **2f**) are the better σ -donors and poorer π -acceptors. The π -accepting ability of **3** and **4** are thus stronger than those of **1** and **2**.

Comparing between NHCs, we see that with the same substituent, **2** (imidazol-2-ylidene) is the most nucleophilic, and that **4** (triazol-5-ylidene) is the least nucleophilic. At the same nucleophilicity (ΔN), **3** corresponds to larger $k(\text{C}-\text{O}_{\text{trans}})$ than **4**, a result that could be attributed to the better π -accepting ability of imi-

dazol-2-ylidenes. As we shall discuss later, a similar trend is also seen in $\text{Ni}(\text{CO})_3\text{L}$ complexes.

CSE of **4** suggests that its stability is comparable to **1**, and both are more stable than the 4,5-saturated compound **2**. **3** has the smallest CSE, and is expected to be the least stable carbene among NHCs. NHCs with Et and ⁱPr (**e** and **f**) substituents are the most stable.

The ligand binding energy D_0 in $\text{Cr}(\text{CO})_5\text{L}$ for NHCs ranges from 43–54 kcal/mol, and are all larger than the binding strength of CO (39.9 kcal/mol). The average D_0 of carbenes **1–4** are similar. **1b–4b** have the largest D_0 values in their categories. D_0 of **2b** is the largest in all studies ligands, as we shall see D_0 of **2b** is also the largest in $\text{Ni}(\text{CO})_3\text{L}$ complexes. It is noted that, our computed D_0 in this study are based on complexes that have more Fisher character, the results for complexes having more Schrock character may be different [49].

The electronic properties of Bertrand carbenes and NHCs are not quite comparable. There are, however, several points which are worthy of mentioning. Firstly, CSE values of Bertrand carbenes are significantly smaller than those of NHCs, indicating that Bertrand carbenes are less stable with respect to dimerization. The CSE values also reveal that **7** is the more stable species among Bertrand carbenes. CSEs of **5** and **6** are comparable, indicating that (phosphino)(silyl) carbene is electronically more stable than (phosphino)(alkyl) and (phosphino)(aryl) carbenes. Secondly, Bertrand carbenes are softer, more nucleophilic than NHCs. And thirdly, in general the ligand binding energies of Bertrand carbenes are smaller than the NHCs.

Among carbenes **5–7**, the relative stability (with respect to dimerizations) suggested by CSE are in the order **7e–7g** (amino)(aryl) > **7a–7d** (amino)(alkyl) > **6d–6e** (phosphino)(aryl), and **5a–5c** (phosphino)(silyl) > **6a–6c** (phosphino)(alkyl) carbenes. Trifluoromethyl substituent increases the electrophilicity significantly as we would expect, the σ -withdrawing effect is seen both in their $k(\text{C}-\text{O}_{\text{trans}})$, χ and ΔN values of **6c** and **7c**. However, the electron withdrawing group does not seem to stabilize the stability of a carbene as shown by CSE.

The bond distances between Cr and the carbene center $d(\text{Cr}-\text{L})$ of NHCs are less variant than those of Bertrand carbenes, Thiazol-2-ylidenes have slightly shorter ligand–metal bonds. For the Bertrand carbenes the $d(\text{Cr}-\text{L})$ distances span a wider range, and are good probe for the steric effects. With the ^tBu group (**7b** and **7d**), $d(\text{Cr}-\text{L})$ are significantly longer (2.246 and 2.311 Å, respectively), and their D_0 are significantly smaller.

Very recently, Bertrand's research group successfully isolated **7g** [50]. Interestingly, we find that **7g** is by far the softest carbene in our study. It is also the most nucleophilic, and the least electronegative species. The CSE of **7g** is 80.5 kcal/mol, the largest among all Bertrand

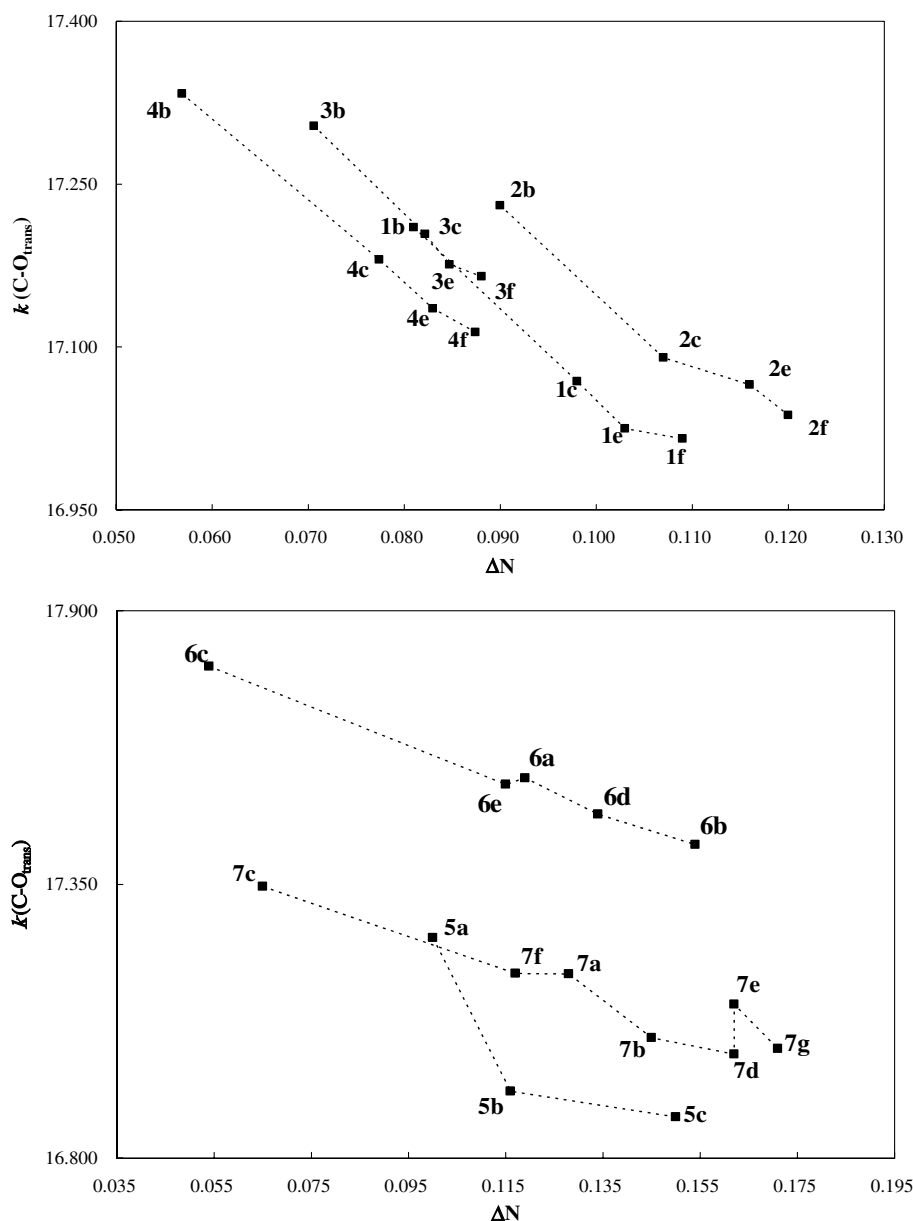


Fig. 1. $k(\text{C-O}_{\text{trans}})$ of $\text{Cr}(\text{CO})_5\text{L}$ complexes vs ΔN of carbenes.

carbenes. Its D_0 and $d(\text{Cr-L})$ are 27.4 kcal/mol and 2.273 Å, respectively; while those of **7d** are 18.3 kcal/mol and 2.311 Å. The comparison shows that the ^tBu group on carbenic center is much more sterically repulsive than anthracene. The trend is also seen in their $\text{Ni}(\text{CO})_3\text{L}$ complexes.

The ligand binding energy in $\text{Cr}(\text{CO})_5\text{L}$ for Bertrand carbenes are much more widely distributed than those of NHCs. Among them, **6** are more strongly bonded to the metal than **5** and **7**. We also see that steric repulsions have a much more significant effect on the ligand–metal binding than the NHCs, ligands having less bulky substituents of **5** and **6** bind more strongly, although in most cases the binding energies are weaker than the NHCs.

3.2. $\text{Ni}(\text{CO})_3\text{L}$ complexes

Table 2 shows results of our computations for $\text{Ni}(\text{CO})_3\text{L}$ complexes. The optimized structures of $\text{Ni}(\text{CO})_3\text{L}$ are close to tetrahedral, thus the force constants are taken from the average of three CO ligands. As expected, the ligand–metal distances are shorter than those of $\text{Cr}(\text{CO})_5\text{L}$. It can also be observed that the force constants of the Ni complexes are larger than those of their Cr counterparts. The D_0 values of the $\text{Ni}(\text{CO})_3\text{L}$ complexes, however, are smaller than those of $\text{Cr}(\text{CO})_5\text{L}$. The predicted geometries of $\text{Ni}(\text{CO})_4$ are in close agreement with X-ray data [39,41]. Similar to the $\text{Cr}(\text{CO})_5\text{L}$ system, the overall correlation between χ and ΔN is fairly linear ($R^2 = 0.978$).

Table 2

Average force constants of C–O, ligand dissociation energies (D_0), ΔN , and important geometrical parameters of Ni(CO)₃L

	$d(\text{Ni-L})$	$d(\text{Ni-CO})$	$d(\text{C-O})$	$k(\text{C-O}_{\text{trans}})$	D_0	ΔN
1b	1.950	1.789	1.154	17.531	45.1	0.065
1c	1.968	1.787	1.155	17.414	43.2	0.080
1e	1.983	1.787	1.155	17.415	43.3	0.084
1f	2.007	1.787	1.155	17.406	39.1	0.090
2b	1.944	1.789	1.155	17.524	45.8	0.073
2c	1.980	1.788	1.155	17.483	42.3	0.088
2e	1.981	1.787	1.155	17.434	42.7	0.096
2f	2.008	1.787	1.155	17.406	37.7	0.099
3b	1.933	1.793	1.153	17.689	42.0	0.055
3c	1.939	1.792	1.153	17.623	41.5	0.066
3e	1.948	1.792	1.153	17.607	41.9	0.068
3f	1.972	1.791	1.154	17.582	37.6	0.071
4b	1.941	1.792	1.153	17.658	43.7	0.043
4c	1.957	1.789	1.154	17.546	43.5	0.062
4e	1.970	1.789	1.154	17.519	43.4	0.067
4f	1.992	1.788	1.154	17.491	39.6	0.071
5a	1.979	1.792	1.153	17.632	29.5	0.081
5b	2.025	1.787	1.155	17.459	29.2	0.095
5c	2.013	1.784	1.156	17.264	27.7	0.125
6a	1.879	1.802	1.151	17.816	44.8	0.098
6b	1.878	1.082	1.152	17.707	40.9	0.129
6c	1.852	1.815	1.148	18.186	35.8	0.040
6d	1.894	1.803	1.151	17.812	36.2	0.109
6e	1.886	1.808	1.150	17.991	32.7	0.094
7a	1.957	1.791	1.154	17.536	44.6	0.107
7b	1.992	1.790	1.155	17.427	36.5	0.121
7c	1.937	1.798	1.152	17.795	40.9	0.051
7d	2.025	1.791	1.155	17.384	24.6	0.136
7e	1.958	1.792	1.154	17.562	41.7	0.136
7f	1.948	1.796	1.152	17.696	39.1	0.097
7g	1.980	1.795	1.154	17.527	30.2	0.143
CO^a	1.811	1.811	1.146	18.484	30.9	-0.056

^a X-ray data (averaged): $d(\text{Ni-CO}) = 1.817$, $d(\text{C-O}) = 1.127$ [52].

As in the Cr(CO)₅L system, $d(\text{C-O})$ and $d(\text{Ni-CO})$ are not sensitive to ligands. The ligand–metal distance $d(\text{Ni-L})$ of NHC increases with larger substituents on N, $k(\text{C-O}_{\text{trans}})$ on the contrary, decreases with larger substituents. The $k(\text{C-O}_{\text{trans}})$ versus ΔN relations are illustrated in Fig. 2, in which one sees that larger NHC substituents not only have longer ligand–metal distances, but also induce a smaller C–O force constant. The π -accepting ability of **3** and **4** are better than **1** and **2**. It also appears that, to a lesser extent **3** are better π -acceptors than **4**, and **2** are better π -acceptors than **1**.

The C–O force constants of complexes of **5–7** span a much wider range than NHCs (Fig. 2). The influence of these ligands on Ni(CO)₃L as seen in the $k(\text{C-O}_{\text{trans}})$ versus ΔN relations is very similar to that in the Cr(CO)₅L system. The relation in Fig. 2 suggests that the π -accepting ability of Bertrand carbene is **6** > **5**, **7**.

ΔN in Table 2 reveals that the nucleophilicity of NHCs are in the order **2** > **1** > **3**, **4**. Bertrand-type carbenes are noticeably more nucleophilic than NHCs. (Amino)(alkyl) and (amino)(aryl) carbenes (**7**) are more nucleophilic than carbenes **5** and **6**. **7g**, followed by **7d** and **7e**, are the most nucleophilic ligands among all

studied carbenes. Trifluoromethyl substitution on the carbonic carbon has a strong influence on the electronic nature of the carbene. As we see in **6c** and **7c**, both are the most electrophilic Bertrand-type carbenes, and have the shortest $d(\text{Ni-L})$ and the largest $k(\text{C-O}_{\text{trans}})$ in their categories.

Among the Cr(CO)₅L and Ni(CO)₃L complexes, we see that NHC ligands bind more strongly to metals than Bertrand carbenes. However, it has been shown by Schoeller et al. [51] that for W(CO)₅L complexes the binding energies of Bertrand carbenes are strong. It has also been demonstrated that for complexes of Schrock type character the binding energies of Bertrand carbenes are stronger than those of diaminocarbenes [49]. Among Bertrand-type carbenes, the binding energies of (phosphino)(silyl) carbenes (**5**) are the smallest, and correspondingly their $d(\text{Ni-L})$ distances are the longest. The ligand binding energies of NHCs are in the order **1**, **2** > **4** > **3**, however the difference is not significant. The **b** substitution (hydrogen on N) increases the ligand binding energy, D_0 of **1b–4b** are the largest in their categories and **2b** has the largest D_0 in all Ni(CO)₃L complexes.

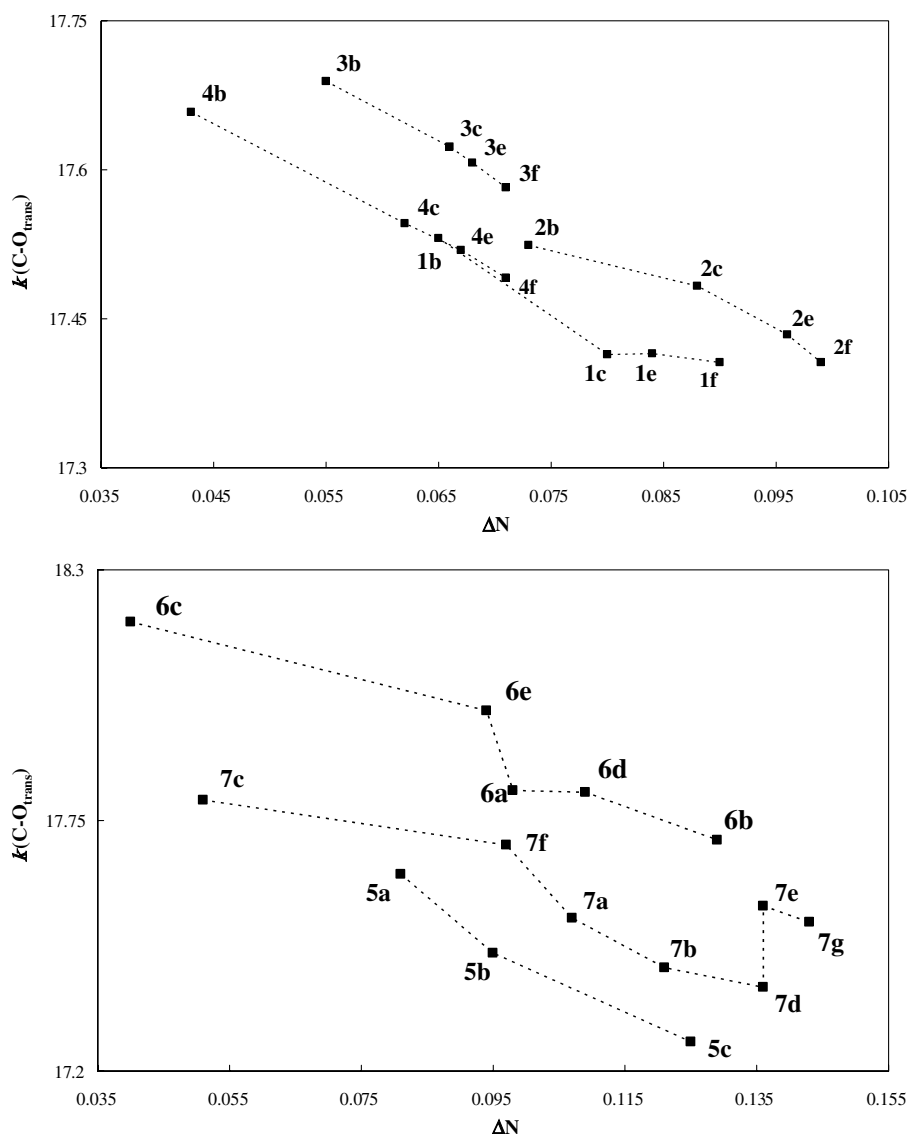


Fig. 2. $k(\text{C-O}_{\text{trans}})$ of $\text{Ni}(\text{CO})_3\text{L}$ complexes vs ΔN of carbenes.

4. Conclusion

A systematic study on the complexes $\text{Cr}(\text{CO})_5\text{L}$ and $\text{Ni}(\text{CO})_3\text{L}$ have been performed using theoretical approaches, with L being NHCs and Bertrand-type carbenes. It has been observed that ligand–metal bonds of NHCs are much stronger than those of Bertrand-type carbenes in these carbenes. Carbene stabilization energy (CSE) calculations indicate that NHCs are more stable than Bertrand-type carbenes. The most stable NHC species are imidazol-2-ylidenes (**1**) and triazo-5-ylidenes (**4**), followed by imidazolin-2-ylidenes (**2**), and the thiazo-2-ylidenes (**3**) are less stable. Among Bertrand-type carbenes (amino)(aryl) carbenes (**7e–7g**) are the most stable, followed by (amino)(alkyl) carbenes (**7a–7d**) and (Phosphino)(silyl) carbenes (**5**). (Phosphino)(aryl) carbenes (**6d–6e**) are less stable, and (phosphino)(alkyl) (**6a–6c**)

carbenes are the least stable species. ΔN computed for both $\text{Cr}(\text{CO})_5\text{L}$ and $\text{Ni}(\text{CO})_3\text{L}$ systems indicate that Bertrand-type carbenes are much more nucleophilic than NHCs. The nucleophilicity is in the order $7 > 5$, $6 > 1$, $2 > 3$, **4**. The $k(\text{C-O}_{\text{trans}})$ versus ΔN relations suggests that **4** is the relatively better π -acceptor among NHCs, and **6** is the better π -acceptor among Bertrand-type carbenes.

Acknowledgements

The authors acknowledge the National Science Council of Taiwan, Republic of China, for supporting this work. We also thank the National Center for High-performance Computing for computer time and facilities.

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