

Transition metal carbene chemistry⁷: Nucleophilic substitution reactions of imidazolide and benzimidazolide ions with Fischer carbene complexes in MeOH [☆]

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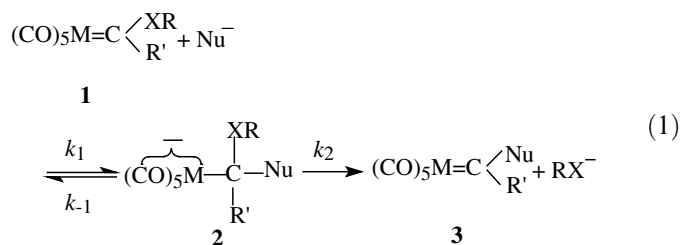
Abstract

Rate constants for the nucleophilic substitution reactions of imidazolide (IZ^-) and benzimidazolide (BIZ^-) ions with **4-Cr-Z** and **5** in MeOH at 25 °C are reported and Hammett ρ values are evaluated to be 1.50 ± 0.10 and 1.51 ± 0.08 for **4-Cr-Z-IZ**⁻ and **4-Cr-Z-BIZ**⁻ reactions, respectively. The comparable reactivity and also almost identical ρ values for these reactions indicate that there is no difference in sensitivity towards electronic effects due to slightly bigger size of BIZ^- over IZ^- and bond formation at the transition states are equally progressed. The higher ρ values for these reactions compared to those with a wide range of nucleophiles may arise mainly due to lower polarity of the solvent MeOH which enhances the requirement for stabilization of the negative charge in the transition state by the Z-substituents.
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Keywords: Fischer carbene complexes; Nucleophilic substitution; Imidazolide and benzimidazolide ions; Hammett plots

1. Introduction

Since the discovery by Fischer and Maasböl [1] in 1964 the group 6 Fischer carbene complexes have been demonstrated as highly valuable building blocks in organic synthesis. In recent years, extensive research activities are focused on the nucleophilic substitution reactions, because of their highly electrophilic nature at the carbene carbon [2–4]. Nucleophilic substitution reactions of alkoxy or alkylthio groups of carbene complexes are best described by Eq. (1), which generally proceeds via a tetrahedral

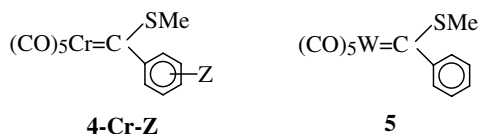


intermediate **2**, in analogy to the reaction of carboxylic esters with nucleophiles. Though, in most synthetic applications the common nucleophiles used include amines [2,4–8], hydrazine [2,9], oximes [2,10], alkoxide ions [2,4,11], thiolate ions [2,4,12–14], carbanions [14–19], (mainly aryl and alkyl lithium) as well as others [2,20–22], the first kinetic investigation on nucleophilic substitution reaction was that of Werner et al. who studied the reaction of **4-Cr-Z** with several primary aliphatic amines (*n*-BuNH₂, C₆H₁₁NH₂, C₆H₅CH₂NH₂) in *n*-decane, dioxane, methanol and dioxane-methanol (1:1) [8]. There have been few other kinetic studies in the early literature; these investigations focused mainly on reactions with amines [4,23–25] and

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phosphines [4,26,27] in weakly polar organic solvents. More recently, a number of kinetic studies with alcohol [28,29], alkoxide ions [28,29], water [30–34], OH^- [30–34], thiol [35–37], thiolate ions [35–37], amines [34,38–42], carbanion [43] and DABCO [44] in polar (mainly in water–acetonitrile mixtures) solvent were reported. Noticeably absent from this list is the reaction of negatively charged nitrogen bases. We here intended to report, for the first time, the nucleophilic substitution reactions of thiomethyl carbene complexes **4-Cr-Z** and **5** with imidazolidide (IZ^-) and benzimidazolidide (BIZ^-) ions in dry methanol.



2. Results and discussion

With neutral nucleophiles such as phosphines [4,26,27] and amines [2,4–8,34,38–46], the nucleophilic attack on the carbene carbon leads to zwitterionic intermediates such as **6–9**; if there is an acidic proton on the intermediate as in the case of **8**, the reaction can proceed further to product by elimination of ROH, otherwise the reaction stops at the adduct stage.

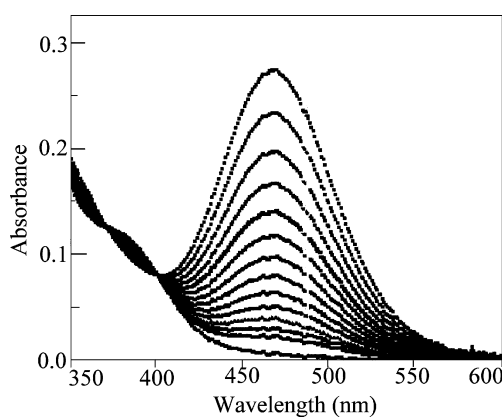
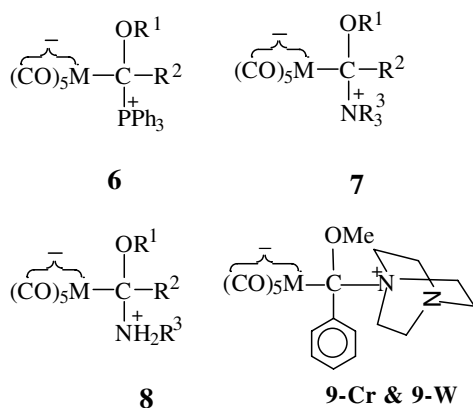


Fig. 1. Time resolved spectra for the reaction of **4-Cr-NMe₂** with IZ^- in dry MeOH at 25 °C. First spectrum was taken immediately after mixing and the last one at 2000 s. Intermediate spectra were recorded at 2 s time interval.

In the present investigation, the kinetics was carried out in dry MeOH throughout the study under pseudo-first-order conditions, with the carbene complexes as the minor component. All measurements were performed in a Hewlett-Packard 8453 Agilent diode array UV–vis spectrophotometer, rates were monitored at λ_{max} of the substrates.

The reactions of IZ^- and BIZ^- with **4-Cr-Z** and **5** lead to the substitution products **4-Cr-Z-IZ** and **4-Cr-Z-BIZ** respectively, as shown in Eq. (2) for the reactions with IZ^- .

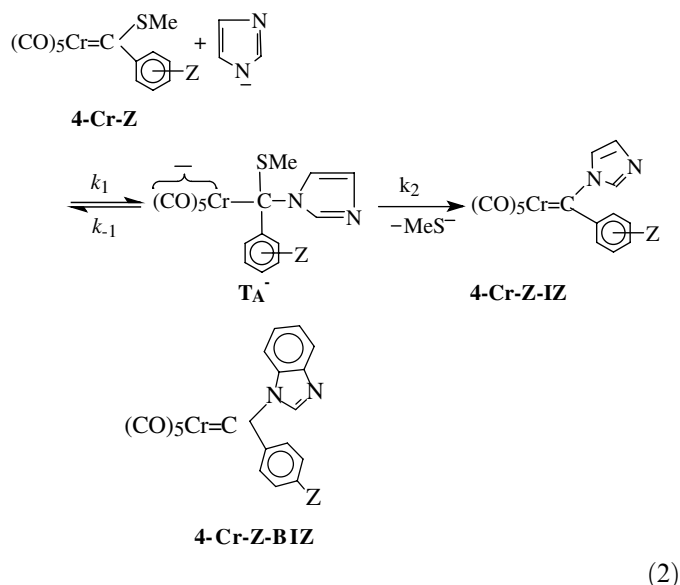
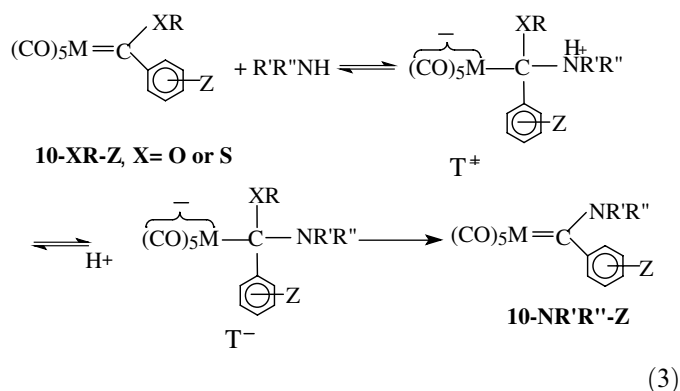


Fig. 1, which is representative one, shows time-resolved spectra for the reaction of IZ^- with **4-Cr-NMe₂**. The spectra were constructed from a kinetic trace. It shows a blue shift in $\text{M}(\text{d}\pi) \rightarrow \text{L}(\text{p}\pi^*)$ (carbene) MLCT band for the amine carbene complexes. These spectral changes are very similar to those observed in the reaction of **10-XMe-Z** ($\text{X} = \text{O}$ or S) with different primary and secondary amines to form the corresponding amine substituted derivatives as in Eq. (3) [34,38–42].

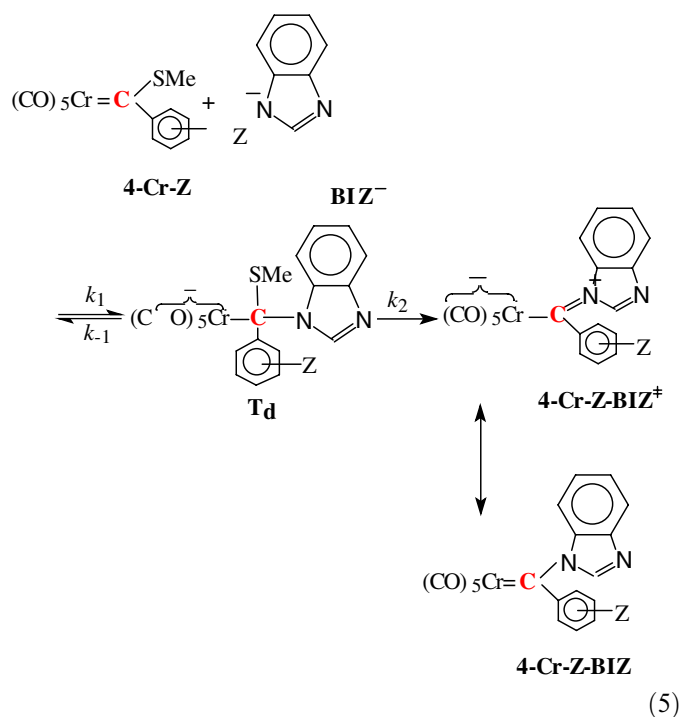


The presence of clear isosbestic points indicates that the reaction is quite clean. The simplest mechanism as outlined in Eq. (2) accounts for our experimental observations with T_A^- as the steady-state intermediate. According to this mechanism, the slopes of the plots of k_{obs} vs. $[\text{Nu}^-]$ ($\text{Nu}^- = \text{IZ}^-$ or BIZ^-) are given by Eq. (4)

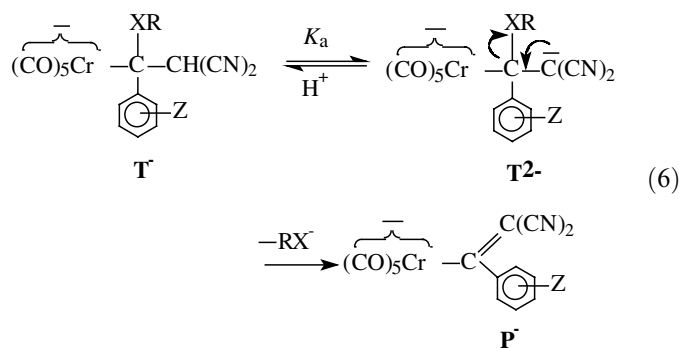
$$\text{slope} = \frac{k_1 k_2}{k_{-1} + k_2} \quad (4)$$

Two special cases may arise: (1) If $k_2 \gg k_{-1}$ slope = k_1 while for (2) $k_2 \ll k_{-1}$, slope = $K_1 k_2$ ($K_1 = k_1/k_{-1}$).

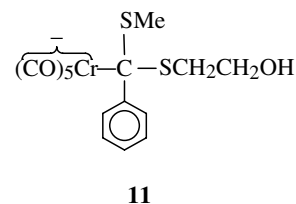
As discussed elsewhere [47], accumulation of the intermediate to detectable levels during the reaction depends on two conditions: (i) thermodynamic or equilibrium condition: $K_1[\text{Nu}^-] > 1$, and (ii) kinetic condition: $k_1[\text{Nu}^-] > k_2$. The former requires a combination of strong nucleophile and strongly electron-withdrawing groups (M(CO)₅, XR) while the latter requires a combination of strong nucleophile and relatively sluggish leaving group; both conditions must be met. It has been shown that reactions of **4-Cr-Z** and **10-XMe-Z** with different primary and secondary amines [34,38–42], no accumulation of intermediate was encountered; because for the reactions with neutral amines the strong electronic push by the amines leads to high k_2 values and hence lower k_1/k_2 ratios. The nucleophilicities of IZ^- and BIZ^- are expected to be at least as that of the most nucleophilic neutral amines and hence thermodynamic conditions, $K_1[\text{Nu}^-] > 1$, should be met. Regarding the kinetic conditions, as MeS^- is a better leaving group than MeO^- and also a strong electronic push in the k_2 step by IZ^-/BIZ^- lowers the k_1/k_2 ratio and hence disfavors the detection of intermediate as in Eq. (5). This is because the leaving group departure is enhanced by the electronic push from the nitrogen lone pair, leading to stabilization of the transition state resulting from the developing product resonance (**4-Cr-Z-BIZ**[±] ↔ **4-Cr-BIZ**)



Analogous explanations were furnished to account for **4-Cr-Z-OH**⁻ [30,33] and **4-Cr-Z-HC(CN)₂**⁻ [43] reactions as outlined in Eq. (6)



This has also been demonstrated by the non-existence of the intermediate in the HR-MS spectrum run immediately after mixing IZ^- with **4-Cr-Cl**. So condition (1) fits well with our experimental observations (Fig. 2) and all the evaluated k_1 values are summarized in Table 1. A large number of kinetic investigations of the reactions of **4-Cr-Z** and related carbene complexes with a variety of nucleophiles have been reported in recent years [4,23–44]. $\text{HOCH}_2\text{CH}_2\text{S}^-$ was found to react with **4-Cr-H** or its tungsten analogue **5** reversibly to form the respective tetrahedral adducts **11** [37] which were found to be quite stable particularly in the time scale (ms) of these experiments and do not proceed to the substitution product by expulsion of the MeS^- group but, upon addition of acid, they revert back to starting materials. These experiments allowed a determination of $k_1 = 6.60 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ as well as of $k_{-1} = 1.78 \times 10^{-3} \text{ s}^{-1}$ and $K_1 = k_1/k_{-1} = 3.07 \times 10^5 \text{ M}^{-1}$ [37].



For the reactions of IZ^- and BIZ^- with **4-Cr-Z** and **5** the respective tetrahedral intermediates do not accumulate to detectable level and **4-Cr-Z-IZ**/**4-Cr-Z-BIZ** were found to be final products in dry MeOH (Fig. 2).

Table 1

Rate constants for the reactions of **4-Cr-Z** and **5** with IZ^- and BIZ^- in dry MeOH with $I = 0.10 \text{ M}$ (NaClO_4) and at 25°C

4-Cr-Z	σ	$k_1/\text{M}^{-1} \text{ s}^{-1}$ (BIZ ⁻)	$k_1/\text{M}^{-1} \text{ s}^{-1}$ (IZ ⁻)
4-CF ₃	0.54	10.3 ± 0.34	11.34 ± 0.46
3-Cl	0.37	5.83 ± 0.15	6.55 ± 0.20
4-Cl	0.23	3.70 ± 0.15	4.84 ± 0.28
4-F	0.06	2.26 ± 0.18	2.86 ± 0.20
4-H	0.00	1.05 ± 0.02	1.07 ± 0.20
4-Me	-0.17	0.77 ± 0.02	0.93 ± 0.01
4-OMe	-0.27	0.50 ± 0.005	0.65 ± 0.04
4-NMe ₂	-0.83	0.099 ± 0.004	0.12 ± 0.01
5		4.02 ± 0.15	4.05 ± 0.06

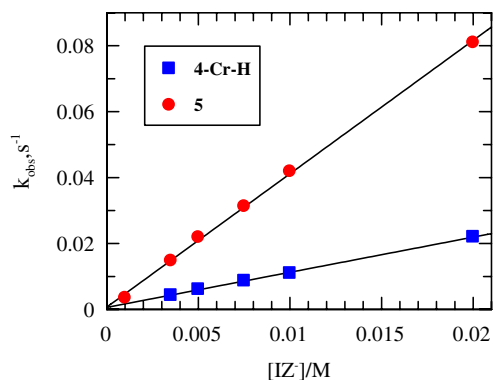


Fig. 2. Representative plots of k_{obs} (s^{-1}) vs. $[\text{IZ}^-]$ for the reaction of IZ^- with **4-Cr-H** and **5**.

ρ values. A closer inspection of Table 1 reveals that surprisingly the two nucleophiles have almost identical reactivity towards a particular Fischer carbene complex. Based on steric consideration, as reactions of Fischer carbene complexes are quite sensitive to steric effects in the transition state, and $\text{p}K_{\text{a}}$ values (14.2 and 12.3 for imidazole and benzimidazole, respectively [48]) it is expected that IZ^- should react faster than BIZ^- . The plausible explanation for the comparable reactivity of the two nucleophiles is based on product stabilizing resonance effect, which is probably the dominating effect over the others two. The number of resonance structures for **4-Cr-Z-BIZ** $^{\pm}$ is higher than that of **4-Cr-Z-IZ** $^{\pm}$, due the involvement of benzene ring in the resonance, and hence the observed reactivity trend.

Hammett plots for the reactions of **4-Cr-Z** with IZ^- and BIZ^- provide excellent linear fit with ρ values 1.50 ± 0.10 and 1.51 ± 0.08 , respectively (Fig. 3). Table 2, incorporates the ρ values for this and related other systems investigated previously. The positive values imply that electron withdrawing substituents stabilize the transition state. The other main factor that can account for the positive ρ values is a destabilization of the carbene complexes, which is best understood in terms of an increased electron deficiency on

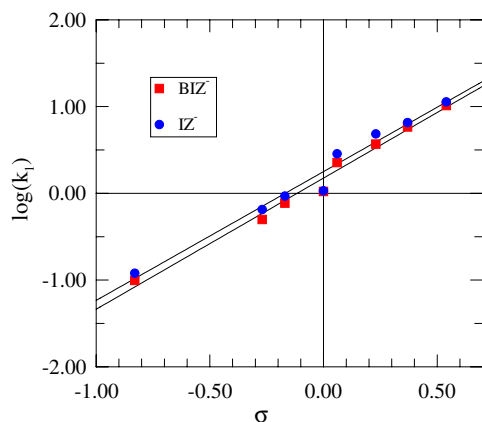


Fig. 3. Hammett plots for the reaction of IZ^- and BIZ^- with **4-Cr-Z** in dry MeOH.

Table 2
Hammett ρ values in 50%MeCN–50%water (v) at 25 °C

Nucleophiles	4-Cr-Z
IZ^-	1.50 ^a
BIZ^-	1.51 ^a
DABCO	$0.89 \pm 0.07^{\text{b}}$
$\text{CH}(\text{CN})_2^-$	$0.69 \pm 0.05^{\text{c}}$
<i>n</i> -BuNH ₂	0.59 ^d
$\text{HOCH}_2\text{CH}_2\text{S}^-$	0.78 ^e
OH^-	1.16 ^f

^a This work in dry MeOH.

^b Ref. [44].

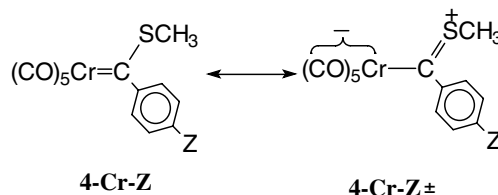
^c Ref. [43].

^d $(\text{CO})_5\text{Cr}=\text{C}(\text{SCH}_2\text{CH}_2\text{OH})\text{C}_6\text{H}_5\text{-Z}^{37}$, Ref. [40].

^e Ref. [37].

^f Ref. [43].

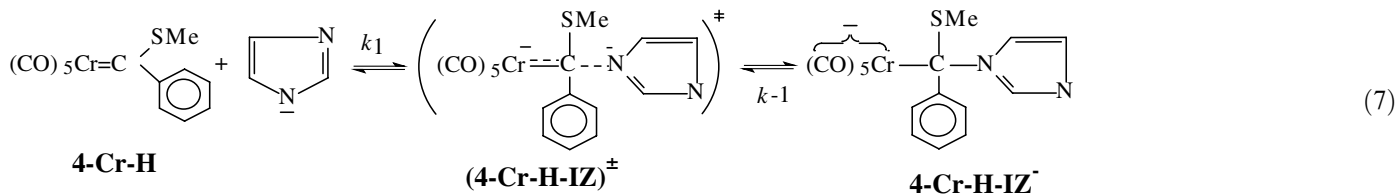
the carbene carbon, as the positive charge developed on the sulfur atom through π -donation is more localized than the negative charge on $(\text{CO})_5\text{Cr}$ moiety of **4-Cr-Z** $^{\pm}$.



A critical inspection of Table 2 reveals that the **4-Cr-Z**+ IZ^- or BIZ^- reactions provide the highest ever known ρ -values. To explain this observation it is justifiable to compare these with **4-Cr-Z**+ OH^- reactions, as in both cases the nucleophiles are negatively charged species. In both cases, partial negative charges reside on $\text{M}(\text{CO})_5$ moiety as well as on the nucleophiles (IZ^- , BIZ^- or OH^-). Now how the stabilization of negative charge in the transition state is influenced by the electron withdrawing substituents is the key to determine the magnitude of ρ -values. A major factor that is likely to contribute to the higher ρ -values for the IZ^- and BIZ^- reactions is the lower polarity of MeOH solvent [29] ($\epsilon = 32.6$) compared to that of 50% MeCN–50% water ($\epsilon = 58.8$). This, just as the case with a less polar solvent, enhances the requirement for stabilization of the charge in the transition state by the Z-substituents. The change in nucleophiles from OH^- to IZ^- or BIZ^- may cause in reduction of ρ -values due to more electron-withdrawing nature of azolide ions than OH^- contributing enhanced stabilization of tetrahedral adduct (T_d) and transition state leading to it. It is apparent that solvent polarity effect predominates over this electron-withdrawing inductive effect and hence the higher ρ -values for the **4-Cr-Z**+ IZ^- or BIZ^- reactions.

Cr vs. W. Nucleophilic addition to the tungsten carbene complexes is slightly favored over the addition to chromium complexes. The higher k_1 values for the reactions of IZ^- and BIZ^- with the tungsten carbene complex **5** compared to the corresponding chromium carbene complexes ($k_1(\mathbf{5})/k_1(\mathbf{4-Cr-H}) = 3.83$ and 3.78 , respectively follow the previously observed reactivity patterns [28,31,36,44].

To explain the reactivity order $\text{Cr} < \text{W}$, it is necessary to consider a number of factors that may potentially affect the transition state (Eq. (7))



In the transition state (**4-Cr-H-IZ**)[‡] the negative charge mostly resides on the metal atom [35–37]. The stabilization of this negative charge may occur either through its dispersion into the 5CO groups or through the electron-withdrawing inductive/field effect of the X atom. As the charge delocalization has made very little progress in the transition state [49], the stabilization of the **TS** by charge dispersion into the 5CO groups will be insignificant. Regarding the influence of sulfur atom, the electron withdrawing inductive/field effects are expected to contribute almost equally in both **4-Cr-H** and **5**. The experimental electronegativity (χ/amu) values are 0.137 and 0.162 for Cr and W, respectively [50]. So the control of the nucleus on the additional negative charge on the metal and hence stabilization of the negative charge in the transition state will be higher in **5** over **4-Cr-H** and consequently an enhanced reactivity **5** over **4-Cr-H** is apparent.

3. Experimental section

3.1. Materials

IZ and BIZ (Aldrich) were of analytical grade and purified by sublimation method. MeCN was distilled over CaH₂ before use. HCl and KOH solutions were prepared using analytical grade reagents (Merck India) and standardized by acid–base titrations using suitable indicator. The carbene complexes used as substrates were obtained from previous studies. The Lithium salts of IZ and BIZ were prepared by treating them with *n*-butyl lithium under Ar atmosphere at liquid N₂ temperature in diethyl ether. The solid product thus obtained was filtered and thoroughly washed with dry MeCN. The purity of the samples was checked by titration against HCl in MeOH using phenolphthalein as indicator.

3.2. Instrumentation and kinetic experiments

HR-MS spectra were recorded on a Qtof Micro YA263 instrument. UV–vis spectra and kinetics of the reactions were recorded in a UV–vis diode array spectrophotometer, model Agilent 8453, interfaced with peltier – a digital tem-

perature control system. The reactions were followed under pseudo-first-order conditions with the carbene complexes as the minor component and by monitoring their disap-

pearance at appropriate wavelength. The reactions were carried out in dry MeOH at 25 °C. Typical substrate concentrations were $(5\text{--}9) \times 10^{-5}$ M. The absorbance, over specified time intervals, was recorded for at least five half-lives which give nice single exponential decay curve, manifesting a first-order dependence on the complexes. The absorbance-time data thus obtained were fitted with the HP-8453 system program to get the pseudo-first-order rate constants. The data thus obtained for triplicate runs were found to fall within the error limit $\pm 5\%$.

3.3. Synthesis of 4-Cr-Cl-IZ

4-Cr-OMe-IZ was generated by reacting **4-Cr-Cl** and **IZ**[−] in dry MeCN for about 3 h and the solvent was then removed under reduced pressure. The resulting residue was then treated with small volume of water and extracted with diethylether. The ether-extract was then subjected to roto-evaporation to get the impure product, which was then purified by column chromatography using silica-gel and extracting with MeCN. The solvent was then removed and resulting material was then analyzed by HR-MS. (*m/z*; electrospray): 383.5 (MH⁺), 204 (MH⁺–H–C₆H₄Cl–C₃H₃N₂), 176 (M–C₆H₄Cl–C₃H₃N₂–CO), 148 (M–C₆H₄Cl–C₃H₃N₂–2CO), 120 (M–C₆H₄Cl–C₃H₃N₂–3CO).

Acknowledgments

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