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Synthesis, structure and benzannulation of chalcogen-tethered Fischer carbene complexes

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Abstract

Addition of $PhSH–NEt_3$ or PhSeNa to $Ph{-}C{\equiv}C{-}C(OC_2H_5){=}M(CO)_5$ [M = Cr or W] afforded stable, β-chalcogenide tethered conjugated carbene complexes **3–6** as a mixture of *E,Z*-isomers. The *Z*-configuration was ascribed to those isomers that readily yield cyclometallated complexes. Aminolysis with methylamine yielded corresponding amino carbene complexes as mixtures of *E,Z*-isomers. Alkylation by methyl iodide afforded separable *E,Z*-isomers of dimethylamino complexes. One-step aminolysis of ethoxy carbene complexes with dimethylamine furnished only the *Z*-isomer of the dimethylamino complex. The *Z*-isomer of dimethylamino carbene complexes yielded cyclometallated products on warming. Representative crystal structures of these complexes confirm isomer assignments. Only *E*-isomers of the S or Se-tethered ethoxy complexes undergo benzannulation reaction with alkynes, with loss of chalcogenide atom.

Keywords: Fisher carbene; Chalcogen; Benzannulation

1. Introduction

Fischer carbene complexes with conjugated double or triple bonds are excellent substrates for many useful synthetic transformations [1] including Dötz reaction and various cycloadditions. The unsaturated bonds in conjugation with the carbene moiety can also act as Michael acceptors [2]. We recently reported addition of chalcogen-stabilized diiron clusters to a triple bond activated by a Fischer carbene function [3], and discovered interesting reactivity traits in the resulting complexes [4]. In order to accurately correlate the substitution parameters with modified reactivity of Fischer carbene function in these complexes, we sought to decouple the contribution of the chalcogen atoms from that of the diiron cluster. The present objective was, therefore, to prepare chalcogenide-tethered Fischer carbene complexes, vary the position and number of chalcogenides gradually and systematically, and study the reactivity of each derivative. In this paper, we describe the synthesis and structural characterization of sulfur and selenium tethered Fischer carbene complexes and their aminolysis products, and benzannulation reaction of the alkoxy complexes. We recognize that β-substitution with a chalcogenide element could also give rise to interesting ''push–pull'' molecules relevant for NLO materials [5].

2. Results and discussion

The most straightforward route to desired Fischer carbene complexes with single chalcogenide substituent is nucleophilic addition of reagent RXH (R = alkyl or

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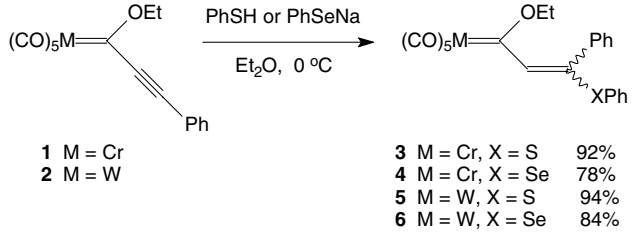
aryl, X = S, Se or Te) to the electrophilic triple bond of an alkynyl carbene complex. For reasons of simplicity and ready availability, initial experiments used Ph—C≡C—C(OEt)=M(CO)$_5$, where M = Cr (**1**), or W (**2**) [6]. Thiophenol was added [7] at 0 °C to a solution of complex **1** or **2** in diethyl ether. Presence of 0.5 equivalents of triethylamine accelerates the addition (1 h); reactions without triethylamine require 3–4 h for completion. Phenylselenide anion was generated in situ from diphenyl diselenide and sodium hydride in refluxing THF according to a reported [8] procedure. A suspension of this anion was subsequently added to the ether solution of complex **1** or **2** at 0 °C (Scheme 1).

For sulfur-containing products, **3** and **5**, the geometrical isomers were non-separable by chromatography. Their relative population in the mixture was estimated from ^{1}H NMR spectra. On the other hand, the selenium analogs yielded *E* and *Z* isomers of **4** and **6** after column chromatography (Chart 1). The *Z*-isomers are identified as **3a**–**6a** and the *E*-isomers are identified as **3b**–**6b** in this paper.

The *E*/*Z* assignment for the complexes **3** and **5** was based on diagnostic ^{1}H NMR signals of ethoxy group and the =CH group. In *E*-isomers, **3b** and **5b**, the olefinic proton (at 6.90 and 6.85 ppm, respectively) is shielded compared to the similar proton in *Z*-isomers, **3a** and **5a** (7.66 and 7.67 ppm, respectively). Both CH_3 and CH_2 signals of the ethoxy group are also similarly shielded in the *E*-isomers, **3b** and **5b**, the significant magnitude of $\Delta\delta$ presumably implies an anisotropic effect of the β-phenyl ring [9]. Similar trend is also observed for the selenium analogs, **4** and **6**. The olefinic proton for *E*-isomer appears at around 7.1 ppm while the olefinic proton for *Z*-isomer is observed at 8 ppm.

By warming complex **3** (*E*:*Z* = 1:1) in benzene at 60 °C for 12 h, the cyclometallated [10] complex **3c** (47%) and pure *E*-isomer **3b** (42%) were isolated after chromatography. From the selenium analog, **4a**, cyclometalated product **4c** was obtained analogously. The cyclometallated products **3c** and **4c** were characterized by their distinctly different CO absorption pattern in IR spectra (see Section 4) and CO signals in the ^{13}C NMR spectra. While the proton NMR signal of the olefinic proton of **3c** overlaps with peaks in the aromatic region, corresponding signal for **4c** is readily identified as a singlet at 7.51



Scheme 1.

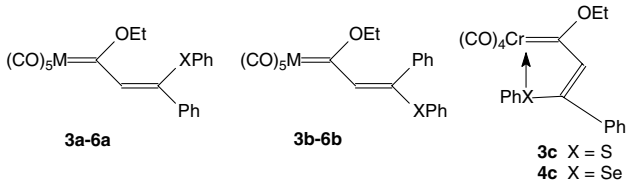
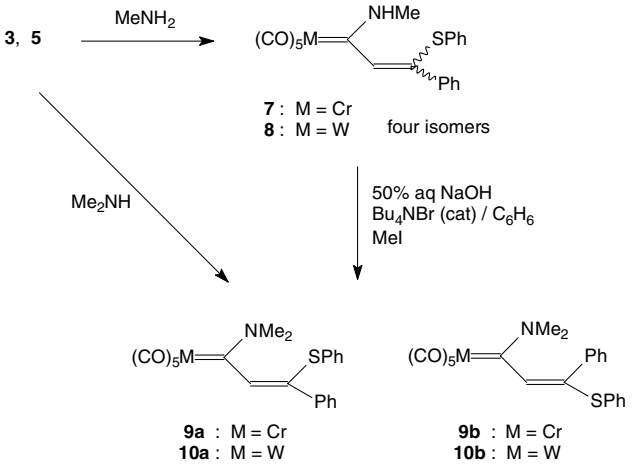


Chart 1.

ppm (shielded with respect to 7.99 ppm in the precursor **4a**). Formation of cyclometalated products provided corroborative evidence to support the *E*–*Z* assignment: only the *Z*-isomer could cyclize in this manner. No such intramolecular complexation was observed for tungsten complexes **5** or **6** under similar condition. At higher temperature (toluene reflux) they tend to decompose rather than internally cyclize. This observation is intriguing because chelation was indeed observed with amino carbene complexes (vide infra). It is conceivable that the nonbonding electron pair on sulfur is delocalized over the π-system to effect the "push–pull" system, they are not available for intramolecular coordination.

Aminolysis of complexes **3** and **5** with methylamine at 0 °C in ether furnished amino carbene complexes **7** and **8**, respectively. In both instances, presence of four geometric isomers was observed in the NMR spectra but the isomers were not separable on column. Both **7** and **8** were thereafter treated with methyl iodide in presence of alkali under PTC condition [11] to afford dimethylamino carbene complexes **9a–b** and **10a–b**, respectively (Scheme 2). These isomers were separated by column chromatography and characterized individually. In ^{1}H NMR spectrum of the minor isomers, **9b** and **10b**, methyl signals of the dimethylamino group are considerably shielded ($\Delta\delta \approx 0.4$–0.6 ppm) due to anisotropic effect of neighboring phenyl ring. Interestingly, when aminolysis was carried out with dimethylamine in one



Scheme 2.

step, the major isomers **9a** and **10a**, were the only products.

Crystal structure of a representative complex, **10a**, was determined in order to confirm the structural assignments. The ORTEP diagram is displayed in Fig. 1.

Crystallographic and data collection parameters and selected bond lengths and angles for complex **10a** are given in Tables 1 and 2, respectively. The amino nitrogen is flat and the angles around it (around 120° each) are consistent with an sp^2-hybridized center. The bond of nitrogen with the carbene carbon is short (1.287 Å) indicating an effective delocalization of the nitrogen lone pair towards the metal–carbene fragment. This, in turn, prevents delocalization of non-bonded electron from sulfur across the π-framework, the bond angles around sulfur reflects an sp^3 hybridization and the S–C(3) bond remains practically a single bond (1.750 Å).

Consistent with this, the distance *C2–C3* corresponds to a normal double bond (1.370 Å). Four carbonyl groups and tungsten form a nearly square planar arrangement, and the carbene ligand is practically perpendicular to this plane and placed *anti* to the fifth carbonyl group (bond angles: *C1–W–C18* 91.2, *C1–W–C22* 90.2, *C1–W–C20* 178.0). The π-plane of this alkene is twisted away from the metal–carbene plane (dihedral angle *W–C1–C2–C3* 103.16). The plane of the amino group is coplanar with the carbene plane (dihedral angle *C16–N–C1–W* 179.71, *C17–N–C1–W* 4.26) but twisted away from the alkene plane (dihedral angle *N–C1–C2–C3* 76.5).

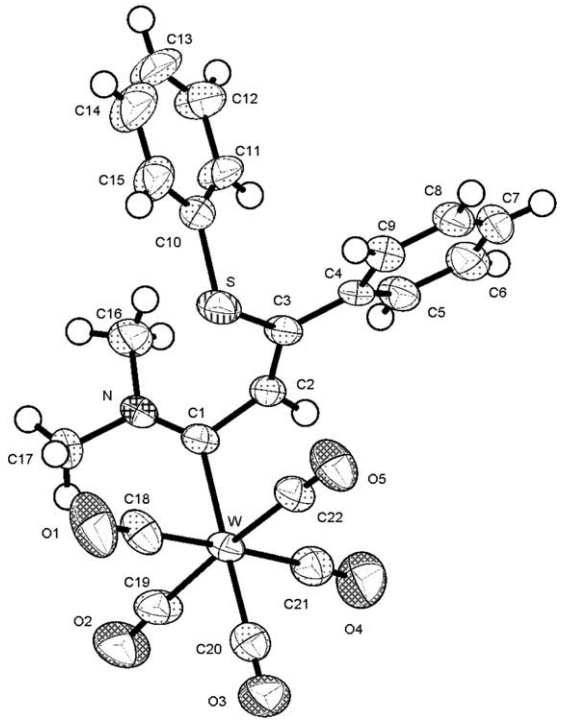


Fig. 1. ORTEP diagram of the complex **10a**. Ellipsoids are drawn at 50% probability.

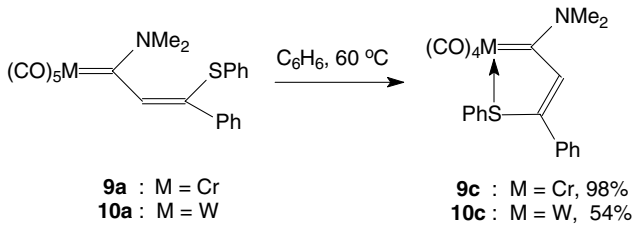
Table 1
Crystallographic and data collection parameters for complex **10a**

Empirical formula	$C_{22}H_{17}NO_5SW$
Formula weight	591.28
Temperature (K)	293(2)
Wavelength (Å)	0.70930
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	20.149(3)
b (Å)	6.1070(18)
c (Å)	18.116(3)
β (°)	91.600(13)
Volume (Å^3)	2228.3(8)
Z	4
Calculated density (Mg/m^3)	1.762
Crystal size (mm)	$0.35 \times 0.25 \times 0.2$
Absorption coefficient (mm^{-1})	5.309
F (0 0 0)	1144
Theta range for data collection	1.01–24.92°
Limiting indices	$-23 \leqslant h \leqslant 23$, $0 \leqslant k \leq 7$, $-21 \leqslant l \leqslant 21$
Reflections collected/unique	5218/3437 [R_{int} = 0.0438]
Completeness to theta = 24.92	87.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3437/0/289
Goodness-of-fit on F^2	1.086
Final R indices [$I > 2$sigma(I)]	R_1 = 0.0420, wR_2 = 0.1110
R indices (all data)	R_1 = 0.0566, wR_2 = 0.1272
Extinction coefficient	0.0033(3)
Largest differential peak and hole (e Å^{-3})	1.604 and −2.427

Table 2
Selected bond lengths (Å) and angles (°) for complex **10a**

W—C(18)	2.012(8)	C(1)—C(2)	1.500(9)
W—C(20)	2.021(9)	C(2)—C(3)	1.370(9)
W—C(22)	2.029(8)	C(18)—W—C(19)	90.7(3)
W—C(21)	2.030(9)	C(20)—W—C(19)	88.0(3)
W—C(19)	2.055(8)	C(22)—W—C(19)	176.0(3)
W—C(1)	2.247(7)	C(3)—S—C(10)	104.4(4)
S—C(3)	1.750(7)	C(1)—N—C(17)	123.0(6)
S—C(10)	1.780(9)	C(1)—N—C(16)	125.9(6)
N—C(1)	1.287(8)	N—C(1)—C(2)	116.2(6)
N—C(17)	1.487(8)	C(3)—C(2)—H(2)	121.1
N—C(16)	1.492(9)	C(4)—C(3)—S	120.7(5)

On warming **9a** in benzene at 60 °C for 6 h, the cyclometallated product **9c** was obtained in 98% yield (Scheme 3). The crystal structure of complex **9c** (Fig. 2) clearly revealed the cyclometalated structure. Crystallographic and data collection parameters of complex **9c** are displayed in Table 3. The sulfur is sp^3 hybridized (bond angles C3–S–C10 103.76, C3–S–Cr 100.42, C10–S–Cr 109.93) while the nitrogen adopts a planar configuration (dihedral angle C16–N–C1–Cr 159.21; C17–N–C1–C2 168.65; C16–N–C1–C2 13.26; bond angle N–C1–C2 114.96) indicative of delocalized lone pair across the carbene framework. The chromium has an octahedral environment (bond angles C18–Cr–C21



Scheme 3.

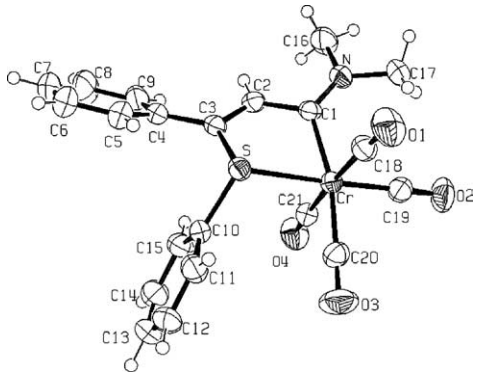


Fig. 2. ORTEP diagram of complex **9c.** Ellipsoids are drawn at 50% probability.

Table 3
Crystal data and structure refinement for complex **9c**

Empirical formula	$C_{21}H_{17}CrNO_4S$
Formula weight	431.42
Temperature (K)	293(2)
Wavelength Å	0.71073
Crystal system, space group	Orthorhombic, *P*212121
Unit cell dimensions	
a (Å)	6.5172(17)
b (Å)	12.672(3)
c (Å)	24.206(6)
Volume (Å^3)	1999.1(9)
Z, calculated density (Mg/m^3)	4, 1.433
Absorption coefficient (mm^{-1})	0.703
F (0 0 0)	888
Crystal size (mm)	$0.39 \times 0.21 \times 0.09$
Theta range for data collection	1.81–23.28°
Limiting indices	$-7 \leqslant h \leqslant 7$, $-14 \leqslant k \leqslant 14$, $-26 \leqslant l \leqslant 26$
Reflections collected/unique	16366/2875 [R_{int} = 0.0292]
Completeness to theta=23.28	99.9%
Maximum and minimum transmission	0.9369 and 0.7701
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2875/0/255
Goodness-of-fit on F^2	1.254
Final *R* indices [$I > 2$sigma(I)]	$R_1 = 0.0264$, $wR_2 = 0.0718$
R indices (all data)	$R_1 = 0.0266$, $wR_2 = 0.0720$
Absolute structure parameter	0.02(2)
Largest differential peak and hole (e Å^{-3})	0.187 and −0.329

175.77; S–Cr–C19 177.32; C1–Cr–C20 167.01), while the chelated ring is envelope-shaped. For the tungsten complex **10a**, under similar condition, this reaction was not complete even after 18 h. While 54% of cyclometallated product **10c** was isolated as a stable solid, about 32% (*Z*, **10a**) of the starting material was recovered after chromatography.

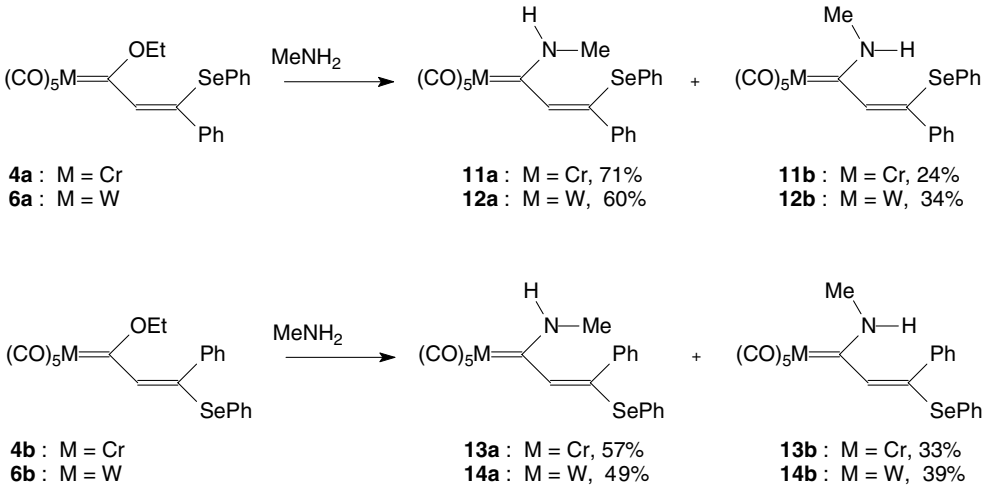
Aminolysis of selenium tethered complexes (**4a** and **6a**) with methylamine yielded corresponding amino carbene complexes (**11a**–**b** and **12a**–**b**, respectively) as depicted in Scheme 4.

The chromium complexes **11a** and **11b** are not separable by column chromatography, but their ratio could be determined based on the ^{1}H NMR spectrum as 3:1. The tungsten analogs (**12a** and **12b**) were separated on column and individually characterized. Similarity of spectral features permitted assignment of NMR peaks of complexes **11a**–**b** in a mixture. Similarly, from the other set of geometrical isomers (**4b** and **6b**) corresponding amino carbene complexes (**13a**–**b** and **14a**–**b**) were obtained. Only the tungsten complexes, **14a** and **14b**, were separated on column while the ratio of **13a** and **13b** in the mixture was determined from ^{1}H NMR spectrum as 1.7:1.

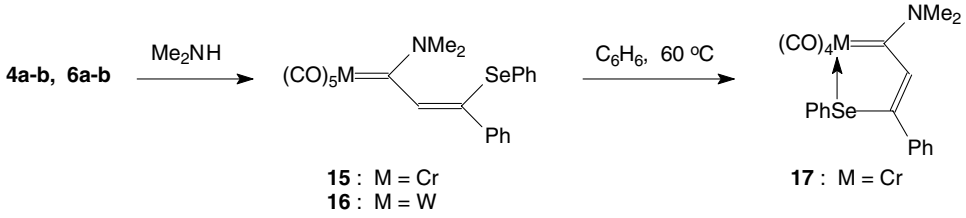
Attempted alkylation of the methylamino group by methyl iodide under alkaline condition yielded acetylene carbene complexes by a rapid elimination of PhSeH. Therefore, the dimethylamino complexes were prepared by direct aminolysis of ethoxy complexes (**4a**–**b** and **6a**–**b**) with dimethylamine (Scheme 5). Surprisingly, the same geometric isomer (*Z*-isomer) of the amino carbene complex was produced (**15** and **16**) irrespective of the configuration of its precursor. The ^{1}H NMR pattern of complexes **15** and **16** are very similar. The configuration of the double bond was readily ascertained when cyclometallated complex **17** was obtained from **15** in 3.5 h. The tungsten complex **16** led to extensive decomposition on prolonged heating.

Once the aminolysis protocol was established, three cyclic secondary amines (pyrrolidine, piperidine and morpholine) were used to access a new set of complexes as shown in Scheme 6. All tungsten carbene derivatives were isolated in very good yields. Several amino derivatives of chromium carbene complexes proved elusive towards isolation. Base-induced elimination of chalcogen substituent contributed to such a situation in certain cases. In some instances the desired complex decomposed during purification by column chromatography. The NMR spectra of all the isolated yellow complexes **18**–**26** are consistent with the assigned structure and are free of other isomeric product signals. Satisfactory elemental analyses (C, H and N) were obtained for all solid complexes.

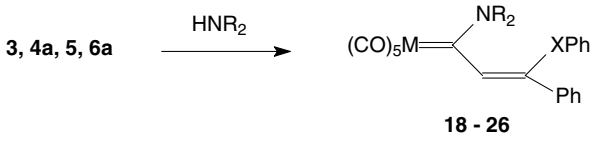
In order to test the reactivity of such chalcogen tethered carbene complexes in benzannulation reaction, the



Scheme 4.



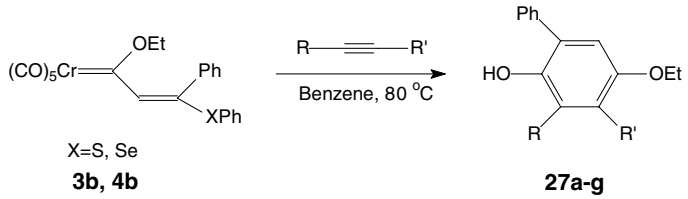
Scheme 5.



	M	X	NR_2	Yield (%)
18	Cr	S		87
19	Cr	Se	–N	97
20	W	S		83
21	W	Se		96
22	W	S	–N	96
23	W	Se		97
24	Cr	S		76
25	W	S	–N O	85
26	W	Se		94

Scheme 6.

E-isomer of both sulfur and selenium adducts, **3b** and **4b**, were treated with mono- and di-substituted acetylenes (Scheme 7). In all cases, a substituted phenol was obtained as the major isolable product, and PhS- or PhSe-group was eliminated [12]. The corresponding *Z*-isomers yield cyclometalated products on warming as discussed above, and these complexes do not undergo further reaction with acetylenes. These results conform to usual reactivity pattern of Fischer carbene complexes. No unusual reaction product was obtained as in reactions of bis-chalcogen tethered carbene complexes reported earlier [4].



	R	R'	Yield(%)
27a	Ph	H	72
27b	Ph	Ph	61
27c	CH_2OCH_3	H	42
27d	Bu	H	62
27e	p-Tolyl	H	75
27f	Naphthyl	H	71
27g	Ferrocenyl	H	45

Scheme 7.

3. Conclusion

In summary, we have reported successful synthesis and structural assignments of a set of α,β-unsaturated Fischer carbene complexes featuring a β-chalcogen substituent. Most of the *E*/*Z* isomers of alkoxy and amino complexes were isolated and spectroscopically characterized. Preliminary attempts of benzannulation revealed that one β-chalcogen substituted alkenyl complexes yield anticipated products without the chalcogen atom.

4. Experimental

4.1. General considerations

All reactions were carried out under an atmosphere of argon. Tetrahydrofuran, ether and benzene were distilled under argon from sodium and benzophenone. Compound **1** and **2**,[6] **3** and **5**[7] were synthesized following reported procedures. All chemicals were purchased from commercial suppliers (Aldrich, Strem, Merck) and used as received. Infrared spectra were recorded on a Shimadzu FTIR-8400 spectrometer and absorptions are expressed in cm^{-1}. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AC200 spectrometer. Elemental analyses were performed by the microanalysis group at NCL using a Carlo-Ebra 1100 automatic analyzer. Satisfactory elemental analysis was not obtained for liquid compounds. Melting points were recorded on a Thermonik Campbell melting point apparatus and are uncorrected.

4.2. General procedure for preparation of compound *3* and *5*

The reactions were carried out in 1–3 mmol scale. To a solution of **1** or **2** (*n* mmol) in ether (5*n* ml) at 0 °C thiophenol (1.1*n* mmol) was added followed by triethylamine (0.5*n* mmol) and allowed to react at 0 °C for 1 h. Solvent was removed and pure product was isolated by flash column chromatography using 5% dichloromethane in petroleum ether as eluent.

Complex ***3***: Brown liquid, 92%. IR ($CHCl_3$): 1926, 2054 (ν_{CO}). ^1H NMR ($CDCl_3$): δ **3a**: 1.84 (t, 3H, $J = 7.2$ Hz, CH_3), 5.21 (q, 2H, $J = 7.2$ Hz, OCH_2), 7.66 (s, 1H, =C*H*); **3b**: 0.81 (t, 3H, $J = 7.2$ Hz, CH_3), 4.53 (q, 2H, $J = 7.2$ Hz, OCH_2), 6.90 (s, 1H, =C*H*); Combined peaks: 6.98–7.64 (m, 10H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 13.9, 15.8 (CH_3), 75.9, 77.3 (OCH_2), 128.1, 128.5, 128.7, 129.6, 130.2, 133.4, 135.6, 136.0, 138.4, 140.9, 142.9 (Ar*C* and =*C*H), 148.3, 174.1 [=*C*(Ph)(SPh)], 216.8, 217.1, 224.2 (*C*O), 324.1, 325.8 (Cr=*C*). Anal. Calc. For $C_{22}H_{16}O_6SCr$: C, 57.39; H, 3.47; S, 6.95. Found C, 57.45; H, 3.51; S, 6.93%.

Complex ***5***: Brown liquid, 94%. IR ($CHCl_3$): 1936, 2064 (ν_{CO}). ^1H NMR ($CDCl_3$): δ **5a**: 1.81 (t, 3H, $J = 7.2$ Hz, CH_3), 5.03 (q, 2H, $J = 7.2$ Hz, OCH_2), 7.67 (s, 1H, =C*H*); **5b**: 0.80 (t, 3H, $J = 7.2$ Hz, CH_3), 4.34 (q, 2H, $J = 7.2$ Hz, OCH_2), 6.85 (s, 1H, =C*H*); Combined peaks: 7.01–7.65 (m, 10H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 13.8, 15.8 (CH_3), 78.5, 79.9 (OCH_2), 128.1, 128.3, 128.8, 129.4, 130.3, 130.6, 133.6, 135.6, 138.6, 139.3 (Ar*C* and =*C*H), 148.1, 152.4 [=*C*(Ph)(SPh)], 197.6, 198.0, 204.0 (CO), 297.0, 298.7 (W=C). Anal. Calc. For $C_{22}H_{16}O_6SW$: C, 44.59; H, 2.70; S, 5.40. Found C, 44.57; H, 2.73; S, 5.42%.

4.3. General procedure for preparation of compounds *4a–b* and *6a–b*

The reactions were carried out in 2–3 mmol scale. Sodium hydride (1.5*n* mmol, 60% suspension in mineral oil) was taken in a two-necked round bottom flask, washed twice with dry hexane and once with dry ether

and dried under vacuum. It was then treated with diphenyl diselenide (0.7*n* mmol) in THF (5*n* ml) and heated under reflux for 1 h to produce a yellow suspension of sodium phenylselenide. It was cooled to 0 °C and added to a solution of alkynyl carbene **1** or **2** (*n* mmol) in ether (2*n* ml) at 0 °C. The reaction mixture was quenched after 5–10 min with water at 0 °C and extracted with ether. The ether layer was dried over sodium sulfate and concentrated under vacuum. The crude product was purified by flash column chromatography using 5–10% dichloromethane in petroleum ether as eluent to afford **4a**–**b**, **6a**–**b** as reddish-brown solid.

*Complex **4a***: Reddish brown solid, 67% (m.p. 74–75 °C). IR ($CHCl_3$): 1934, 2054 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 1.90 (t, 3H, $J = 7.2$ Hz, CH_3), 5.28 (q, 2H, $J = 7.2$ Hz, OCH_2), 6.95–7.25 (m, 10H, Ar*H*), 7.99 (s, 1H, =C*H*). ^{13}C NMR ($CDCl_3$): δ 16.5 (*C*H_3), 77.5 (O*C*H_2), 127.9, 128.4, 128.6, 128.8, 129.6, 135.7, 139.9, 142.6 (Ar*C* and =*C*H), 146.8 [=*C*(Ph)(SePh)], 217.1, 224.3 (*C*O), 323.4 (Cr=*C*). Anal. Calc. For $C_{22}H_{16}O_6SeCr$: C, 52.07; H, 3.15. Found C, 51.97; H, 3.27%.

*Complex **4b***: Reddish brown solid, 11% (m.p. 68–69 °C). IR ($CHCl_3$): 1940, 2054 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 0.81 (t, 3H, $J = 7.2$ Hz, CH_3), 4.54 (q, 2H, $J = 7.2$ Hz, OCH_2), 7.09 (s, 1H, =C*H*), 7.15–7.26 (m, 3H, Ar*H*), 7.28–7.38 (m, 3H, Ar*H*), 7.45–7.55 (m, 2H, Ar*H*), 7.68–7.76 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 14.0 (*C*H_3), 76.1 (O*C*H_2), 127.7, 128.1, 128.4, 130.4, 137.1, 139.4 (Ar*C* and =*C*H), 146.9 [=*C*(Ph)(SePh)], 216.7, 224.1 (*C*O), 327.7 (Cr=*C*). Anal. Calc. For $C_{22}H_{16}O_6SeCr$: C, 52.07; H, 3.15. Found C, 52.05; H, 3.06%.

*Complex **6a***: Reddish brown solid, 71% (m.p. 78–79 °C). IR ($CHCl_3$): 1938, 2062 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 1.86 (t, 3H, $J = 7.2$ Hz, CH_3), 5.07 (q, 2H, $J = 7.2$ Hz, OCH_2), 6.95–7.25 (m, 10H, Ar*H*), 7.98 (s, 1H, =C*H*). ^{13}C NMR ($CDCl_3$): δ 16.3 (*C*H_3), 80.0 (O*C*H_2), 127.9, 128.5, 128.9, 129.3, 129.7, 135.7, 140, 146.2 (Ar*C* and =*C*H), 151.3 [=*C*(Ph)(SePh)], 198.0, 204.1 (*C*O), 296.3 (W=*C*). Anal. Calc. For $C_{22}H_{16}O_6SeW$: C, 41.31; H, 2.50. Found C, 41.39; H, 2.52%.

*Complex **6b***: Reddish brown solid, 13% (m.p. 72–73 °C). IR ($CHCl_3$): 1940, 2064 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 0.80 (t, 3H, $J = 7.2$ Hz, CH_3), 4.35 (q, 2H, $J = 7.2$ Hz, OCH_2), 7.07 (s, 1H, =C*H*), 7.15–7.36 (m, 5H, Ar*H*), 7.40–7.55 (m, 3H, Ar*H*), 7.64–7.75 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 13.9 (*C*H_3), 78.7 (O*C*H_2), 127.6, 127.8, 128.4, 130.5, 137.1, 139.8, 142.7 (Ar*C* and =*C*H), 151.6 [=*C*(Ph)(SePh)], 197.6, 204.0 (*C*O), 299.9 (W=*C*). Anal. Calc. For $C_{22}H_{16}O_6SeW$: C, 41.31; H, 2.50. Found C, 41.07; H, 2.52%.

4.4. Preparation of amino carbene complexes

Amino carbene complexes were prepared by aminolysis of ethoxy carbene complexes. Amino carbene complexes **9b** and **10b** were prepared by aminolysis followed by phase-transfer catalyzed *N*-alkylation.

4.5. General procedure for aminolysis of ethoxy carbene complexes

All the reactions were carried out in 0.2–0.9 mmol scale. To a solution of ethoxy carbene complex (*n* mmol) in ether (10*n* ml) was added 40% aqueous solution of methylamine or dimethylamine (1.5*n* mmol) at 0 °C, stirred at 0 °C for 5–15 min, solvent was removed under reduced pressure. The crude product was purified by flash column chromatography using 25–30% dichloromethane in petroleum ether as eluent.

*Complex **7***: Orange-yellow liquid, 88% (mixture of four isomers) IR ($CHCl_3$): 1925, 2068 (ν_{CO}), 3304, 3376 (ν_{NH}). ^1H NMR ($CDCl_3$): δ 2.69 (d, 3H, $J = 5.3$ Hz, CH_3), 3.20 (d, 3H, $J = 5.3$ Hz, CH_3), 3.25 (d, 3H, $J = 5.3$ Hz, CH_3), 3.68 (d, 3H, $J = 5.3$ Hz, CH_3), 6.50 (s, 1H, =C*H*), 6.69 (s, 1H, =C*H*), 6.97 (s, 1H, =C*H*), 7.08–7.71 (m, 40H, ArC*H* and 1H, =C*H*), 8.13 (bs, 1H, N*H*), 8.46 (bs, 1H, N*H*), 8.77 (bs, 1H, N*H*), 9.00 (bs, 1H, N*H*). ^{13}C NMR ($CDCl_3$): δ 38.5, 39.1 (*C*H_3), 128.2, 128.4, 128.9, 129.4, 129.7, 130.4, 132.9, 133.7, 134.7, 137.6 (Ar*C* and =*C*H), 143.6 [=*C*(Ph)(SPh)], 217.4, 223.0 (*C*O), 240.6, 268.2, 272.4, 275.3 (Cr=*C*). Anal. Calc. For $C_{21}H_{15}NO_5SCr$: C, 56.62; H, 3.37; N, 3.14; S, 7.19. Found C, 56.65; H, 3.42; N, 3.12; S, 7.23%.

*Complex **8***: Yellow liquid, 87% (mixture of four isomers) IR ($CHCl_3$): 1926, 2062 (ν_{CO}), 3311, 3371 (ν_{NH}). ^1H NMR ($CDCl_3$): δ 2.65 (d, 3H, $J = 5.3$ Hz, CH_3), 3.10 (d, 3H, $J = 5.3$ Hz, CH_3), 3.15 (d, 3H, $J = 5.3$ Hz, CH_3), 3.54 (d, 3H, $J = 5.3$ Hz, CH_3) 6.46 (s, 1H, =C*H*), 6.70 (s, 1H, =C*H*), 6.91 (s, 1H, =C*H*), 7.05–7.63 (m, 40H, Ar*H* and 1H, =C*H*), 8.08 (bs, 1H, N*H*), 8.42 (bs, 1H, N*H*), 8.73 (bs, 1H, N*H*), 8.97 (bs, 1H, N*H*). ^{13}C NMR ($CDCl_3$): δ 38.3, 41.4, 41.7 (*C*H_3), 126.7, 128.2, 128.6, 128.9, 129.5, 129.7, 130.3, 133.8, 134.4, 134.8, 138.9 (Ar*C* and =*C*H), 144.9 [=*C*(Ph)(SPh)], 197.9, 198.2, 198.4, 203.1, 203.8 (*C*O), 248.4, 251.7, 254.2 (W=*C*). Anal. Calc. For $C_{21}H_{15}NO_5SW$: C, 43.67; H, 2.59; N, 2.42; S, 5.54. Found C, 43.70; H, 2.63; N, 2.46; S, 5.51%.

*Complex **9a***: Yellow solid, 89% (m.p. 114–115 °C) IR ($CHCl_3$): 1921, 2052 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 3.45 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 6.98–7.17 (m, 6H, Ar*H* and =C*H*), 7.18–7.30 (m, 3H, Ar*H*), 7.52 (d, 2H, $J = 8$ Hz, Ar*H*). ^1H NMR (C_6D_6): δ 2.43 (s, 3H, CH_3), 3.05 (s, 3H, CH_3), 6.64–6.81 (m, 3H, Ar*H*), 6.85 (s, 1H, =C*H*), 6.87–7.04 (m, 3H, Ar*H*), 7.10–7.16 (m, 2H, Ar*H*) 7.57 (d, 2H, $J = 7.6$ Hz, Ar*H*). ^{13}C NMR ($CDCl_3$): 46.4, 50.7 (*C*H_3), 122.9, 126.8, 128.2, 128.6, 128.9, 130.7, 133.5, 138.0 (Ar*C* and =*C*H), 139.9 [=*C*(Ph)(SPh)], 217.6, 223.6 (*C*O), 268.1 (Cr=*C*). Anal. Calc. For $C_{22}H_{17}NO_5SCr$: C, 57.52; H, 3.70; N, 3.05; S, 6.97. Found C, 57.55; H, 3.78; N 2.97; S, 7.12%.

*Complex **10a***: Orange-yellow solid, 91% (m.p. 127–128 °C) IR ($CHCl_3$): 1924, 2061 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 3.45 (s, 3H, CH_3), 3.86 (s, 3H, CH_3), 6.97 (s, 1H, =C*H*), 7.02–7.19 (m, 5H, Ar*H*), 7.20–7.34 (m, 3H, Ar*H*), 7.53 (d, 2H, J = 7.4 Hz, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 44.9, 52.9 (*C*H_3), 124.7, 126.8, 128.4, 128.6, 128.9, 130.6, 133.6, 137.8, 141.1 (Ar*C* and =*C*H), 169.7 [=*C*(Ph)(SPh)], 198.4, 203.5 (*C*O), 249.8 (W=*C*). Anal. Calc. For $C_{22}H_{17}NO_5SW$: C, 44.68; H, 2.88; N, 2.37; S, 5.41. Found C, 44.80; H, 2.88; N, 2.32; S, 5.42%.

*Complex **11a–b***: Orange-yellow liquid, 94% (mixture, **11a**:**11b** = 3:1) IR ($CHCl_3$): 1923, 2054 (ν_{CO}), 3300, 3371 (ν_{NH}). ^1H NMR ($CDCl_3$): δ **11a**: 3.27 (d, 3H, J = 5.2 Hz, CH_3), 8.95 (bs, 1H, N*H*); **11b**: 3.66 (d, 3H, J = 5.3 Hz, CH_3), 8.67 (bs, 1H, N*H*); Combined peaks: 6.56–7.84 (m, 11H, Ar*H* and =C*H*). ^{13}C NMR ($CDCl_3$): δ 38.3, 39.3 (*C*H_3), 124.8, 127.4, 128.5, 129.0, 133.1, 138.1, 138.9, 139.6 (Ar*C* and =*C*H), 144.3 [=*C*(Ph)(SePh)], 217.5, 223.1 (*C*O), 274.3, 276.7 (Cr=*C*). Anal. Calc. For $C_{21}H_{15}NO_5SeCr$: C, 51.21; H, 3.04; N, 2.84. Found C, 51.25; H, 3.08; N, 2.87%.

*Complex **12a***: Yellow solid, 60% (Dec. 117–119 °C) IR ($CHCl_3$): 1927, 2062 (ν_{CO}), 3369 (ν_{NH}). ^1H NMR ($CDCl_3$): δ 3.19 (d, 3H, J = 5.2 Hz, CH_3), 6.97 (s, 1H, =C*H*), 7.05–7.18 (m 3H, Ar*H*), 7.19–7.42 (m, 5H, Ar*H*), 7.46–7.54 (m, 2H, Ar*H*), 8.82 (bs, 1H, N*H*). ^{13}C NMR ($CDCl_3$): δ 38.2 (*C*H3), 126.4, 127.4, 128.5, 128.6, 129.2, 133.1, 138.7 (Ar*C* and =*C*H), 139.3 [=*C*(Ph)(SePh)], 198.5, 203.0 (*C*O), 256.2 (W=*C*). Anal. Calc. For $C_{21}H_{15}NO_5SeW$: C, 40.38; H, 2.40; N, 2.24. Found C, 40.46; H, 2.47; N, 2.22%.

*Complex **12b***: Yellow solid, 34% (Dec. 113–116 °C) IR ($CHCl_3$): 1927, 2062 (ν_{CO}), 3309 (ν_{NH}). ^1H NMR ($CDCl_3$): δ 3.51 (d, 3H, J = 5.3 Hz, CH_3), 7.02–7.41 (m, 9H, Ar*H* and =C*H*), 7.48 (d, 2H, J = 7.8 Hz, Ar*H*), 8.58 (bs, 1H, N*H*). ^{13}C NMR ($CDCl_3$): δ 41.6 (*C*H_3), 127.7, 128.6, 128.9, 129.4, 133.0, 139.5 (Ar*C* and =*C*H), 145.5 [=*C*(Ph)(SePh)], 198.0, 202.9 (*C*O), 254.7 (W=*C*). Anal. Calc. For $C_{21}H_{15}NO_5SeW$: C, 40.38; H, 2.40; N, 2.24. Found C, 40.22; H, 2.53; N, 2.31%.

*Complex **13a–b***: Orange liquid, 90% (mixture, **13a**:**13b** = 1.7:1) IR ($CHCl_3$): 1927, 2054 (ν_{CO}), 3308, 3371 (ν_{NH}). ^1H NMR ($CDCl_3$): δ **13a**: 2.71 (d, 3H, J = 5.3 Hz, CH_3), 6.47 (s, 1H, =C*H*), 8.42 (bs, 1H, N*H*). **13b**: 3.19 (d, 3H, J = 5.5 Hz, CH_3), 6.72 (s, 1H, =C*H*), 8.14 (bs, 1H, N*H*). Combined peaks: 7.05–7.56 (m, 8H, Ar*H*), 7.57–7.84 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 38.7, 39.2 (*C*H_3), 128.2, 128.8, 129.1, 129.6, 130.1, 132.4, 136.2, 136.8 (Ar*C* and =*C*H), 139.8 [=*C*(Ph)(SePh)], 217.6, 223.5 (*C*O), 269.6 (Cr=*C*). Anal. Calc. For $C_{21}H_{15}O_5NSeCr$: C, 51.21; H, 3.04; N, 2.84. Found C, 51.26; H, 3.11; N, 2.89%.

*Complex **14a***: Orange liquid, 49%. IR ($CHCl_3$): 1927, 2060 (ν_{CO}), 3371 (ν_{NH}). ^1H NMR ($CDCl_3$): δ 2.67 (d, 3H, J = 5.2 Hz, CH_3), 6.35 (s, 1H, =C*H*), 7.14–7.52 (m, 8H, Ar*H*), 7.56–7.75 (m, 2H, Ar*H*), 8.33 (bs, 1H, N*H*). ^{13}C NMR ($CDCl_3$): δ 38.4 (*C*H3), 128.3, 128.7, 129.0, 129.2, 130.0, 131.7, 136.0, 136.2 (Ar*C* and =*C*H), 138.5 [=*C*(Ph)(SePh)], 198.5, 203.1 (*C*O), 253.3 (W=*C*). Anal. Calc. For $C_{21}H_{15}O_5NSeW$: C, 40.38; H, 2.40; N, 2.24. Found C, 40.43; H, 2.45; N, 2.27%.

*Complex **14b***: Orange liquid, 39%. IR ($CHCl_3$): 1925, 2060 (ν_{CO}), 3312 (ν_{NH}). ^1H NMR ($CDCl_3$): δ 3.09 (d, 3H, J = 5.3 Hz, CH_3), 6.65 (s, 1H, =C*H*), 7.12–7.53 (m, 8H, Ar*H*), 7.56–7.78 (m, 2H, Ar*H*), 8.01 (bs, 1H, N*H*). ^{13}C NMR ($CDCl_3$): δ 41.4 (*C*H_3), 127.734, 129.1, 129.7, 130.1, 134.6, 136.8 (Ar*C* and =*C*H), 141.1 [=*C*(Ph)(SePh)], 198.1, 203.6 (*C*O), 249.6 (W=*C*). Anal. Calc. For $C_{21}H_{15}O_5NSeW$: C, 40.38; H, 2.40; N, 2.24. Found C, 40.42; H, 2.44; N, 2.29%.

*Complex **15***: Yellow solid, 84% from **4a** and 72% from **4b** (Dec. 93–96 °C). IR ($CHCl_3$): 1927, 2052 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 3.42 (s, 3H, CH_3), 3.90 (s, 3H, CH_3), 6.96–7.35 (m, 9H, Ar*H* and =C*H*), 7.48 (d, 2H, J = 7.6 Hz, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 46.2, 50.6 (*C*H_3), 122.5, 127.4, 128.1, 128.7, 129.1, 133.4, 139.3 (Ar*C* and =*C*H), 140.6 [=*C*(Ph)(SePh)], 217.6, 223.6 (*C*O), 269.6 (Cr=*C*). Anal. Calc. For $C_{22}H_{17}NO_5SeCr$: C, 52.17; H, 3.36; N, 2.77. Found C, 52.07; H, 3.47; N, 2.67%.

*Complex **16***: Yellow solid, 93% from **6a** and 88% from **6b** (m.p. 118–119 °C). IR ($CHCl_3$): 1936, 2058 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 3.41 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 6.98–7.16 (m, 4H, Ar*H* and =C*H*), 7.17–7.31 (m, 5H, Ar*H*), 7.48 (d, 2H, J = 7.2 Hz, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 44.7, 52.8 (*C*H_3), 124.1, 127.4, 128.2, 128.4, 128.6, 129.0, 129.3, 133.3, 138.9 (Ar*C* and =*C*H), 141.7 [=*C*(Ph)(SePh)], 198.4, 203.5 (*C*O), 251.0 (W=*C*). Anal. Calc. for $C_{22}H_{17}NO_5SeW$: C, 41.38; H, 2.66; N, 2.19. Found C, 41.45; H, 2.80; N, 2.09%.

4.6. General procedure for PTC alkylation of amino carbene complexes

Reactions were performed in 0.5–0.7 mmol scale. The carbene complex (n mmol), tetrabutylammonium bromide (0.1n mmol) in benzene (10n ml) was treated with 50% aq NaOH (0.2–0.3 ml) and methyl iodide (1.5n mmol). The reaction was complete at room temperature in 1.5 h (TLC). It was diluted with water and extracted with ether, dried with sodium sulfate, concentrated under reduced pressure and product was purified by flash column chromatography.

*Complex **9b***: Yellow liquid, 22% (along with 52% **9a**) IR ($CHCl_3$): 1929, 2052 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 2.86 (s, 3H, CH_3), 3.57 (s, 3H, CH_3), 6.69 (s, 1H, =C*H*), 7.18–7.49 (m, 8H, Ar*H*), 7.50–7.66 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 46.4, 50.5 (*C*H_3), 127.8, 128.4, 128.7, 129.6, 132.4, 133.8, 135.8 (Ar*C* and =*C*H), 137.5 [=*C*(Ph)(SPh)], 217.5, 223.5 (*C*O), 265.5 (Cr=*C*). Anal.

Calc. For $C_{22}H_{17}NO_5SCr$: C, 57.51; H, 3.70; N, 3.05; S, 6.97. Found C, 57.55; H, 3.73; N, 3.08; S, 6.94%.

*Complex **10b***: Orange-yellow liquid, 26% (along with 65% **10a**) IR ($CHCl_3$): 1926, 2062 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 2.82 (s, 3H, C*H*$_3$), 3.50 (s, 3H, C*H*$_3$), 6.56 (s, 1H, =C*H*), 7.22–7.42 (m, 6H, Ar*H*), 7.43–7.55 (m, 4H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 45.0, 52.9 (*C*H$_3$), 128.5, 128.8, 129.8, 132.3, 134.0, 136.8 (Ar*C* and =*C*H), 137.5 [=*C*(Ph)(SPh)], 198.5, 203.6 (*C*O), 247.7 (W=*C*). Anal. Calc. For $C_{22}H_{17}NO_5SW$: C, 44.67; H, 2.87; N, 2.36; S, 5.41. Found C, 44.70; H, 2.91; N, 2.41; S, 5.39%.

4.7. Chelation of carbene complexes

All reactions were carried out in 0.2–0.5 mmol scale. The carbene complex (*n* mmol) in benzene (10*n* ml) was heated at 60 °C under continuous flow of argon until the reaction was complete (TLC). The reaction mixture was filtered through alumina, concentrated and product was purified by flash column chromatography using 25–40% dichloromethane in pet-ether as eluent.

*Complex **3c***: Deep violet solid (Dec. 81–84 °C) (47% after 12 h, 42% **3b** recovered) IR ($CHCl_3$): 1869, 1921, 2013 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 1.70 (t, 3H, J = 7 Hz, C*H*$_3$)), 5.13 (q, 2H, J = 7 Hz, OC*H*$_2$), 7.01–7.51 (m, 9H, Ar*H* and =C*H*), 7.56–7.89 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 15.5 (*C*H$_3$), 77.3 (O*C*H$_2$), 128.2, 129.2, 129.6, 129.8, 130.9, 133.5, 135.6, 145.1 (Ar*C* and =*C*H), 166.1 [=*C*(Ph)(SPh)], 216.0, 231.3, 232.4 (*C*O), 333.9 (Cr=*C*). Anal. Calc. For $C_{21}H_{16}O_5SCr$: C, 58.33; H, 3.70; S, 7.41. Found C, 58.10; H, 3.59; S, 7.37%.

*Complex **3b***: Brown liquid (42%) IR ($CHCl_3$): 1927, 2054 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 0.81 (t, 3H, J = 7.2 Hz, C*H*$_3$), 4.53 (q, 2H, J = 7.2 Hz, OC*H*$_2$), 6.90 (s, 1H, =C*H*), 7.21–7.41 (m, 5H, Ar*H*), 7.45–7.55 (m, 3H, Ar*H*), 7.57–7.70 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 14.0 (*C*H$_3$), 75.9 (O*C*H$_2$), 127.9, 128.4, 128.6, 128.8, 129.3, 129.9, 130.3, 135.7, 136.1 (Ar*C* and =*C*H), 148.1 [=*C*(Ph)(SPh)], 216.9, 224.2 (*C*O), 326.2 (Cr=*C*). Anal. Calc. For $C_{22}H_{16}O_6SCr$: C, 57.39; H, 3.47; S, 6.95. Found C, 57.42; H, 3.51; S, 6.98%.

*Complex **4c***: Deep violet solid, 98%, (after 10 h) (m.p. 89–91 °C) IR ($CHCl_3$): 1869, 1921, 2012 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 1.69 (t, 3H, J = 7 Hz, C*H*$_3$), 5.14 (q, 2H, J = 7 Hz, OC*H*$_2$), 7.20–7.44 (m, 8H, Ar*H*), 7.51 (s, 1H, =C*H*), 7.60–7.74 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 15.5 (*C*H$_3$), 77.2 (O*C*H$_2$), 128.4, 129.2, 129.9, 130.3, 131.0, 131.6, 134.7, 145.9 (Ar*C* and =*C*H), 163.6 [=*C*(Ph)(SePh)], 216.9, 218.0, 231.7, 233.5 (*C*O), 336.6 (Cr=*C*). Anal. Calc. For $C_{21}H_{16}O_5SeCr$: C, 52.61; H, 3.34. Found C, 52.50; H, 3.46%.

*Complex **9c***: Deep brown solid, 98% (after 6 h) (m.p. 117–118 °C) IR ($CHCl_3$): 1846, 1892, 2002 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 3.51 (s, 3H, C*H*$_3$), 4.03 (s, 3H, C*H*$_3$), 7.16–7.36 (m, 8H, Ar*H* and =C*H*), 7.50–7.63 (m, 3H, Ar*H*). ^1H NMR (C_6D_6): δ 2.13 (s, 3H, C*H*$_3$), 3.48 (s, 3H, C*H*$_3$), 6.62–6.73 (m, 1H, Ar*H*), 6.79 (d, 2H, J = 7.6 Hz, Ar*H*), 6.82–6.92 (m, 3H, Ar*H*), 6.96 (s, 1H, =C*H*), 7.27 (d, 2H, J = 7.6 Hz, Ar*H*), 7.27–7.37 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 44.4 (*C*H$_3$), 54.4 (*C*H$_3$), 128.0, 128.9, 129.4, 130.0, 130.3, 134.9, 136.1, 139.0 (Ar*C* and =*C*H), 164.0 [=*C*(Ph)(SPh)], 218.5, 230.5, 232.0 (*C*O), 267.9 (Cr=*C*). Anal. Calc. For $C_{21}H_{17}NO_4SCr$: C, 58.47; H, 3.94; N, 3.25, S, 7.42. Found C, 58.58; H, 3.98; N, 3.16; S, 7.29%.

*Complex **10c***: Dark brown solid, 54% (after 18 h, 32% **10a** recovered) (m.p. 142–143 °C) IR ($CHCl_3$): 1842, 1902, 2008 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 3.49 (s, 3H, C*H*$_3$), 3.96 (s, 3H, C*H*$_3$), 7.16–7.36 (m, 8H, Ar*H*), 7.49–7.60 (m, 2H, Ar*H*), 7.62 (s, 1H, =C*H*). ^{13}C NMR ($CDCl_3$): δ 43.3, 57.1 (*C*H$_3$), 128.1, 129.1, 129.3, 129.5, 130.0, 130.5, 135.0, 135.4, 141.8, 159.9 (ArC and =*C*H), 163.7 [=*C*(Ph)(SPh)], 202.7, 213.9 (*C*O), 250.9 (W=*C*). Anal. Calc. For $C_{21}H_{17}NO_4SW$: C, 44.76; H, 3.02; N, 2.49; S, 5.68. Found C, 45.02; H, 3.01; N, 2.52; S, 5.91%.

*Complex **17***: Dark brown solid, 98% (after 3.5 h) (Dec. 114–117 °C) IR ($CHCl_3$): 1846, 1900, 2000 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 3.47 (s, 3H, C*H*$_3$), 4.05 (s, 3H, C*H*$_3$), 7.16–7.41 (m, 8H, Ar*H*), 7.46–7.58 (m, 2H, Ar*H*), 7.73 (s, 1H, =C*H*). ^{13}C NMR ($CDCl_3$): δ 44.9, 54.2 (*C*H$_3$), 127.9, 129.0, 129.5, 130.1, 131.3, 136.3, 140.8 (Ar*C* and =*C*H), 162.6 [=*C*(Ph)(SePh)], 230.6, 232.4 (*C*O), 271.4 (Cr=*C*). Anal. Calc. For $C_{21}H_{17}NO_4SeCr$: C, 52.72; H, 3.56; N, 2.93. Found C, 52.73; H, 3.68; N, 2.97%.

4.8. General procedure for aminolysis with cyclic amines

All reactions were carried out in 0.3–0.7 mmol scales. To a solution of ethoxy carbene complex (*n* mmol) in ether (10*n* ml) was added the corresponding cyclic amine (1.2*n* mmol) at 0 °C. After stirring at 0 °C for 5–15 min solvent was removed under reduced pressure. The crude product was purified by flash column chromatography using 25–30% dichloromethane in petroleum ether as eluent.

*Complex **18***: Yellow solid, 87% (m.p. 101–102 °C) IR ($CHCl_3$): 1927, 2052 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 1.98–2.13 (m, 4H, –C*H*$_2$C*H*$_2$–), 3.79 (bs, 2H, NC*H*$_2$), 4.05–4.35 (m, 2H, NC*H*$_2$), 6.97–7.17 (m, 6H, Ar*H* and =C*H*), 7.17–7.28 (m, 3H, Ar*H*), 7.45–7.56 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 25.3, 25.6 (–*C*H$_2$*C*H$_2$–), 56.2, 59.1 (N*C*H$_2$), 122.3, 126.6, 128.1, 128.6, 128.8, 130.4, 133.5, 138.0 (Ar*C* and =*C*H), 141.2 [=*C*(Ph)(SPh)], 217.9, 223.6 (*C*O), 262.9 (Cr=*C*). Anal. Calc. For $C_{24}H_{19}NO_5SCr$: C, 59.38; H, 3.92; N, 2.89; S, 6.60. Found C, 59.46; H, 3.86; N, 2.81; S, 6.66%.

*Complex **19***: Yellow solid, 97% (m.p. 103–104 °C) IR ($CHCl_3$): 1925, 2052 (ν_{CO}). ^1H NMR ($CDCl_3$): δ

1.91–2.59 (m, 4H, –CH_2CH_2–), 3.62–3.96 (m, 2H, NCH_2), 4.04–4.36 (m, 2H, NCH_2), 6.95–7.32 (m, 9H, Ar*H* and =C*H*), 7.35–7.54 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 25.3, 25.6 (–*C*H_2*C*H_2–), 56.0, 58.9 (N*C*H_2), 121.9, 127.3, 127.9, 128.4, 128.6, 128.9, 129.1, 133.1, 139.2 (Ar*C* and =*C*H), 141.6 [=*C*(Ph)(SePh)], 217.9, 223.6 (*C*O), 264.0 (Cr=*C*). Anal. Calc. For $C_{24}H_{19}NO_5$SeCr: C, 54.13; H, 3.57; N, 2.63. Found C, 53.86; H, 3.49; N, 2.54%.

Complex ***20***: Yellow solid, 83% (m.p. 131–132 °C) IR ($CHCl_3$): 1911, 2060 (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 2.03–2.52 (m, 4H, –CH_2CH_2–), 3.75 (t, 2H, J = 6.7 Hz, NCH_2), 3.99–4.18 (m, 2H, NCH_2), 6.95 (s, 1H, =C*H*), 7.00–7.18 (m, 5H, Ar*H*), 7.19–7.31 (m, 3H, Ar*H*), 7.44–7.56 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 24.7, 25.3 (–*C*H_2*C*H_2–), 54.8, 61.3 (N*C*H_2), 124.3, 126.6, 128.2, 128.5, 128.8, 129.6, 130.4, 133.3, 133.7, 137.8 (Ar*C* and =*C*H), 142.3 [=*C*(Ph)(SPh)], 198.7, 203.4 (*C*O), 244.4 (W=*C*). Anal. Calc. For $C_{24}H_{19}NO_5$SW: C, 46.68; H, 3.08; N, 2.27; S, 5.19. Found C, 46.80; H, 3.15; N, 2.22; S, 5.09%.

Complex ***21***: Yellow solid, 96% (m.p. 117–118 °C) IR ($CHCl_3$): 1923, 2060 (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 2.14 (bs, 4H, –CH_2CH_2–), 3.74 (bs, 2H, NCH_2), 4.08 (bs, 2H, NCH_2), 7.06 (d, 3H, J = 6.6 Hz, Ar*H*), 7.13–7.37 (m, 6H, Ar*H* and =C*H*), 7.44 (d, 2H, J = 7.2 Hz, Ar*H*). ^{13}C NMR ($CDCl_3$): 25.1, 25.8 (–*C*H_2*C*H_2–), 54.7, 61.2 (N*C*H_2), 123.7, 127.3, 128.1, 128.4, 128.7, 129.0, 129.4, 133.2, 138.9 (Ar*C* and =*C*H), 142.7 [=*C*(Ph)(SePh)], 198.7, 203.5 (*C*O), 245.7 (W=*C*). Anal. Calc. For $C_{24}H_{19}NO_5$SeW: C, 43.37; H, 2.86; N, 2.11. Found C, 43.28; H, 3.03; N, 2.03%.

Complex ***22***: Yellow solid, 96% (m.p. 96–98 °C) IR ($CHCl_3$): 1919, 2060 (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 1.45–2.15 (m, 6H, –CH_2CH_2CH_2–), 3.66–3.85 (m, 1H, NCH_2), 3.89–4.06 (m, 1H, NCH_2), 4.11–4.31 (m, 1H, NCH_2), 4.34–4.54 (m, 1H, NCH_2), 6.93 (s, 1H, =C*H*), 6.99–7.17 (m, 5H, Ar*H*), 7.17–7.33 (m, 3H, Ar*H*), 7.52 (d, 2H, J = 6.4 Hz, Ar*H*). ^{13}C NMR ($CDCl_3$): 24.2, 27.5 (–*C*H_2*C*H_2*C*H_2–), 54.9, 63.4 (N*C*H_2), 124.3, 126.7, 128.3, 128.6, 128.8, 130.6, 133.9, 137.9 (Ar*C* and =*C*H), 140.9 [=*C* (Ph)(SPh)], 198.4, 203.5 (*C*O), 245.2 (W=*C*). Anal. Calc. For $C_{25}H2_1NO_5$SW: C, 47.54; H, 3.33; N, 2.22; S, 5.07. Found C, 47.44; H, 3.37; N, 2.18; S, 5.09%.

Complex ***23***: Yellow solid, 97% (m.p. 93–96 °C) IR ($CHCl_3$): 1921, 2060 (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 1.58–2.16 (m, 6H, –CH_2CH_2CH_2–), 3.52–3.76 (m, 1H, NCH_2), 3.88–4.25 (m, 2H, NCH_2), 4.28–4.54 (m, 1H, NCH_2), 6.92–7.31 (m, 9H, Ar*H* and =C*H*), 7.34–7.52 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): 24.2, 27.5 (–*C*H_2*C*H_2*C*H_2–), 54.8, 63.3 (N*C*H_2), 123.7, 127.3, 128.1, 128.4, 128.7, 129.0, 129.6, 133.2, 138.9 (Ar*C* and =*C*H), 140.9 [=*C*(Ph)(SePh)], 198.4, 203.6 (*C*O), 246.1 (W=*C*). Anal. Calc. For $C_{25}H_{21}NO_5$SeW: C, 44.25; H, 3.10; N, 2.06. Found C, 44.19; H, 3.31; N, 1.98%.

Complex ***24***: Orange sticky compound, 76%. IR ($CHCl_3$): 1929, 2054 (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 3.62–3.81 (m, 2H, NCH_2), 3.91–4.18 (m, 4H, OCH_2), 4.42–4.57 (m, 2H, NCH_2), 7.01 (s, 1H, =C*H*), 7.05–7.15 (m, 4H, Ar*H*), 7.18–7.31 (m, 3H, Ar*H*), 7.40–7.57 (m, 3H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 55.8, 60.0 (N*C*H_2), 67.3, 67.8 (O*C*H_2), 123.5, 126.9, 128.3, 128.9, 130.8, 133.3, 137.9 (Ar*C* and =*C*H), 138.5 [=*C* (Ph)(SPh)], 217.6, 223.4 (*C*O), 268.1 (Cr=*C*). Anal. Calc. For $C_{24}H_{19}NO_6$SCr: C, 57.48; H, 3.79; N, 2.79; S, 6.38. Found C, 57.51; H, 3.84; N, 2.76; S, 6.41%.

Complex ***25***: Yellow sticky compound, 85%. IR ($CHCl_3$): 1927, 2062 (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 3.61–3.80 (m, 1H, NCH_2), 3.84–4.16 (m, 5H, NCH_2 and OCH_2), 4.36–4.57 (m, 2H, NCH_2), 6.92 (s, 1H, =C*H*), 7.01–7.36 (m, 8H, Ar*H*), 7.43–7.56 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 54.6, 62.2 (N*C*H_2), 67.1, 67.6 (O*C*H_2), 125.2, 126.9, 128.3, 128.6, 128.9, 130.6, 133.4, 137.6 (Ar*C* and =*C*H), 139.7 [=*C*(Ph)(SPh)], 198.2, 203.1, (*C*O), 248.8 (W=*C*). Anal. Calc. For $C_{24}H_{19}NO_6$SW: C, 45.49; H, 3.00; N, 2.21; S, 5.05. Found C, 45.53; H, 3.05; N, 2.23; S, 5.09%.

Complex ***26***: Yellow solid, 94% (m.p. 110–111 °C) IR ($CHCl_3$): 1925, 2062 (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 3.63–3.78 (m, 1H, NCH_2), 3.84–4.09 (m, 5H, NCH_2 and OCH_2), 4.41 (t, 2H, J = 5.4 Hz, NCH_2), 6.96–7.12 (m, 4H, Ar*H* and =C*H*) 7.13–7.27 (m, 5H, Ar*H*), 7.35–7.49 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 54.4, 62.0 (N*C*H_2), 67.2, 67.6 (O*C*H_2), 124.5, 127.5, 128.5, 128.6, 129.1, 133.1, 138.6 (Ar*C* and =*C*H), 140.1 [=*C*(Ph)(SePh)], 198.1, 203.2, (*C*O), 249.9 (W=*C*). Anal. Calc. For $C_{24}H_{19}NO_6$SeW: C, 42.35; H, 2.79; N, 2.06. Found C, 42.51; H, 2.88; N, 1.94%.

4.9. General procedure for the benzannulation reaction

All reactions were carried out in 0.3–0.5 mmol scales. To a solution of ethoxy carbene complex **3b** and **4b** (n mmol) in benzene (3n ml) was added the corresponding acetylene and was heated at 80 °C for 2 h. Then the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography using dichloromethane in petroleum ether as eluant.

Complex ***27a***: Sticky compound, 72%, IR ($CHCl_3$): 3554(ν_{OH}). ^{1}H NMR ($CDCl_3$): δ 1.46 (t, 3H, J = 8 Hz, CH_3), 4.09 (q, 2H, J = 8 Hz, OCH_2), 5.11 (s, 1H, O*H*), 6.91 (s, 2H, Ar*H*), 7.39 –7.63 (m, 10H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 15.2, 64.4, 116.4, 127.9, 129.0, 129.6, 138.0, 143.6,152.9. Anal. Calc. For $C_{20}H_{18}O_2$: C, 82.75; H, 6.21. Found C, 82.63; H, 6.25%.

Complex ***27b***: Sticky compound, 61%, IR ($CHCl_3$): 3543(ν_{OH}). ^{1}H NMR ($CDCl_3$): δ 1.29 (t, 3H, J = 8 Hz, CH_3), 3.99 (q, 2H, J = 8 Hz, OCH_2), 4.97 (s, 1H, O*H*), 7.07 –7.72 (m, 16H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 15.1, 65.8, 116.0, 126.4, 127.4, 127.6, 128.7, 129.6, 131.2, 131.7, 135.7, 136.8, 138.3, 144.2, 150.3. Anal. Calc.

For $C_{26}H_{22}O_2$: C, 85.24; H, 6.01. Found C, 85.13; H, 6.04%.

Complex ***27c***: Sticky compound, 42%, IR ($CHCl_3$): 3373(ν_{OH}). ^{1}H NMR ($CDCl_3$): δ 1.41 (t, 3H, J = 8 Hz, CH_3), 3.46 (s,3H, CH_3), 4.02 (q, 2H, J = 8 Hz, OCH_2), 4.66 (s, 2H, CH_2), 6.68 (d, 1H, J = 4 Hz, ArH), 6.86 (d, 1H, J = 2 Hz, ArH), 7.07 (s, 1H, OH), 7.35 –7.59 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$): δ 15.2, 29.9, 58.5, 64.4, 73.8, 114.6, 116.4, 123.9, 127.5, 128.6, 129.6, 138.2, 146.8, 152.4. Anal. Calc. For $C_{16}H_{18}O_3$: C, 74.41; H, 6.97. Found C, 74.32; H, 7.01%.

Complex ***27d***: Sticky compound, 62%, IR ($CHCl_3$): 3562(ν_{OH}). ^{1}H NMR ($CDCl_3$): δ 0.98 (t, 3H, J = 7 Hz, CH_3), 1.39–1.50 (m, 5H, CH_3 & CH_2), 1.58–1.70 (m, 2H, CH_2), 2.67 (t, 2H, J = 8 Hz, CH_2), 4.02 (q, 2H, J = 8 Hz, OCH_2), 4.94 (s, 1H, OH), 6.66 (d, 1H, J = 4 Hz, ArH), 6.76 (d, 1H, J = 4 Hz, ArH), 7.41–7.50 (m, 5H, ArH) ^{13}C NMR ($CDCl_3$): δ 14.3, 15.2, 22.9, 30.5, 32.2, 64.2, 113.3, 116.5, 128.1, 128.4, 129.4, 130.8, 137.9, 144.5, 152.5. Anal. Calc. For $C_{18}H_{22}O_2$: C, 80.0; H, 8.14. Found C, 79.93; H, 8.21%.

Complex ***27e***: Sticky compound, 75%, IR ($CHCl_3$): 3557(ν_{OH}). ^{1}H NMR ($CDCl_3$): δ 1.47 (t, 3H, J = 8 Hz, CH_3), 2.47 (s, 3H, CH_3), 4.09 (q, 2H, J = 8 Hz, OCH_2), 5.15 (s, 1H, OH), 6.91 (s, 2H, ArH), 7.32 – 7.65 (m, 9H, ArH). ^{13}C NMR ($CDCl_3$): δ 15.2, 21.4, 64.3, 116.1, 127.8, 128.9, 129.4, 129.5, 129.8, 134.9, 137.7, 138.1, 143.6, 152.8. Anal. Calc. For $C_{21}H_{20}O_2$: C, 82.89; H, 6.57. Found C, 82.81; H, 6.61%.

Complex ***27f***: Sticky compound, 71%, IR ($CHCl_3$): 3547(ν_{OH}). ^{1}H NMR ($CDCl_3$): δ 1.46 (t, 3H, J = 8 Hz, CH_3), 4.09 (q, 2H, J = 8 Hz, OCH_2), 4.75 (brs, 1H, OH), 6.91 (d, 1H, J = 2 Hz, ArH), 7.06 (d, 1H, J = 4 Hz, ArH), 7.41–8.00 (m, 12H, ArH). ^{13}C NMR ($CDCl_3$): δ 15.1, 64.3, 116.9, 125.8, 126.1, 126.4, 126.8, 127.6, 128.1, 128.7, 129.6, 134.1, 135.1, 138.2, 144.2, 152.6, 159.7. Anal. Calc. For $C_{24}H_{20}O_2$: C, 84.70; H, 5.88. Found C, 84.64; H, 5.91%.

Complex ***27g***: Sticky compound, 45%, IR ($CHCl_3$): 3562(ν_{OH}). ^{1}H NMR ($CDCl_3$): δ 1.47 (t, 3H, J = 8 Hz, CH_3), 4.07 (q, 2H, J = 8 Hz, OCH_2), 4.30 (s, 5H, FcH), 4.47 (m, 2H, FcH), 4.65 (m, 2H, FcH), 6.90 (s, 2H, ArH), 6.93 (s, 1H, OH), 7.43–7.54 (m, 3H, ArH), 7.69–7.73 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 15.3, 64.3, 67.9, 69.5, 69.7, 71.3, 82.9, 115.4, 124.7, 127.5, 128.5, 129.7, 138.7, 144.4, 152.4. Anal. Calc. For $C_{24}H_{22}O_2Fe$: C, 72.39; H, 5.52. Found C, 72.10; H, 5.75%.

4.10. X-ray crystal structure analysis for complex ***9c***

Single crystals of the complex were grown by slow evaporation of the solution in dichloromethane and hexane. Reddish-brown coloured thin plate of approximate size $0.39 \times 0.21 \times 0.09$ mm, was used for data collection on *Bruker SMART APEX* CCD diffractometer using Mo K_α radiation with fine focus tube with 50 kV and 30 mA. Crystal to detector distance 6.05 cm, 512×512 pixels/frame, Hemisphere data acquisition. Total scans = 4, total frames = 2424, Oscillation/frame $-0.3°$, exposure/frame = 10.0 s/frame, maximum detector swing angle = $-30.0°$, beam center = (260.2, 252.5), in plane spot width = 1.24, SAINT integration, θ range = 1.81–23.28°, completeness to θ of 23.2° is 99.9%. SADABS correction applied, $C_{21}H_{17}CrNO_4S$, M = 431.42. Crystals belong to orthorhombic, space group $P2_12_12_1$, a = 6.517(2), b = 12.672(3), c = 24.206(6) Å, V = 1999.1(9) Å^3, Z = 4, D_c = 1.433 mg m^{-3}, μ(Mo Kα) = 0.703 mm^{-1}, T = 293(2) K, 16366 reflections measured, 2875 unique [$I > 2\sigma(I)$], R value 0.0264, wR_2 = 0.0718. All the data were corrected for Lorentzian, polarization and absorption effects. SHELX-97 (SHELXTL) [13] was used for structure solution and full matrix least squares refinement on F^2. Hydrogen atoms were included in the refinement as per the riding model. Data collection and refinement parameters are listed in Table 3. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 238048.

4.11. X-ray crystal structure analysis for complex ***10a***

Needle like orange single crystals were grown from a solution of **10a** in dichloromethane and hexane. Data were collected on *MACH-3* diffractometer using Mo Kα radiation with fine focus tube. Crystal of size $0.35 \times 0.25 \times 0.20$ mm was used for data collection in 2θ range = 1.01 to 24.92°. All the data were corrected for Lorentzian, polarization and absorption effects. SHELX-97 (SHELXTL)[13] was used for structure solution and full matrix least squares refinement on F^2. Hydrogen atoms were included in the refinement as per the riding model. Data collection and refinement parameters are listed in Table 1. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 238049.

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