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Alkylation of acylmetalates with alkyl halides to prepare Fischer carbene complexes: an improved protocol

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ABSTRACT

Alkoxy Fischer carbene complexes have been synthesized by alkylation of lithium acylmetalates with alkyl halides in the presence of catalytic amount (5–10 mol %) of *n*-tetrabutylammonium bromide (*n*-Bu_4NBr) restricting the temperature below 55 °C to minimize decomposition of the product. The reaction occurs in a biphasic condition involving water and alkyl halide. The effect of cesium on this alkylation reaction has been studied. The presence of a radical quencher, di-*tert*-butyl phenol, neither affects the yield nor leads to the formation of dimer of di-*tert*-butyl phenol, which rules out the possibility of radical pathway mechanism. The kinetic study and the ^{1}H NMR spectra of products suggest an S_N2 pathway particularly involving alkyl halides.

1. Introduction

Fischer carbene complexes have proven to be useful in the synthesis of a range of interesting and useful organic compounds[1] and suitably substituted alkoxy Fischer carbene complexes of chromium, tungsten or molybdenum are normally used as synthons. These complexes are usually prepared by the treatment of $M(CO)_6$ with organolithium reagents followed by alkylation. Simple alkyl groups such as methyl and ethyl are introduced using Meerwein oxonium salts[2] or methyl fluorosulfate or methyl triflate[3] but these methods are not useful for the incorporation of more complex alkyl groups. Fischer carbene complexes with complex alkoxy groups are synthesized by treating the tetraalkylammonium acylmetalate with different acyl halides like acetyl chloride, acetyl bromide or pivaloyl chloride at low temperature, followed by addition of alcohol.[4] Chromium Fischer carbene complexes are obtained in good yield, but tungsten carbene complexes give moderate yield in this procedure. Direct incorporation of alkyl groups using alkyl halides have been reported earlier[5] but this method is limited to the preparation of only chromium carbene complexes. Moreover the reaction was done in large scale (20 mmol) and variable yields were reported.[5c] In this direction, Matsuyama's method[6] is more general and has covered a wide range of substrates.

2. Results and discussion

2.1. Preparation of Fischer carbene complexes

During the course of our work on the application of metallocarbenes in the synthesis of organic compounds, we wanted to make the Fischer carbene complex **1** using Hoye's[5a] method as it appeared to be simple and straightforward. Unfortunately, we isolated the desired complex **1** in very poor yield (20%) using methyl iodide as an alkylating agent. However, the reaction was performed in 2 mmol scale, which was much lower than the reported scale (30 mmol). The reaction was even tried at elevated temperature (65–70 °C) in aqueous medium according to their procedure, yet the yield was same. Moreover, methyl iodide escaped during heating. Carrying out the reaction in various solvents like DCM, DMF or THF, did not improve the yield. When the reaction was performed in these organic solvents, we observed that the reaction mixture turned green and significant amount of unidentified byproducts were formed. Based on our extensive investigation and guided by earlier reports,[5a,c] we found the optimum condition which involved (a) filtering the aqueous solution of the lithio salt of the transition metal–carbene complex for removing decomposed acylmetalate impurity and unreacted metal hexacarbonyl prior to the addition of the alkyl halides, (b) restricting the temperature below 55 °C to minimize decomposition of the product, (c) performing the reaction in biphasic condition of neat alkyl halides (no organic solvent for dilution) and water to make the reaction faster and move to forward direction.

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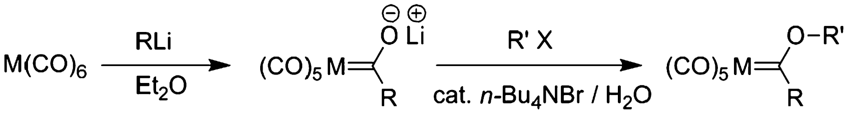
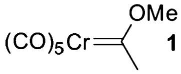
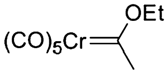
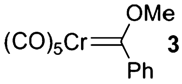
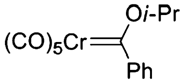
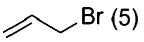
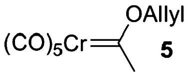
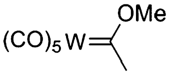
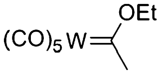
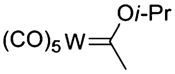
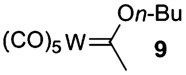
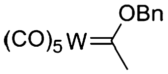
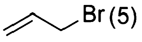
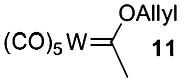
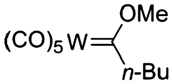
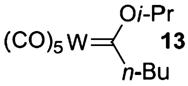
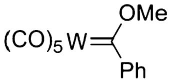
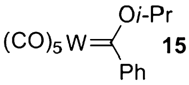
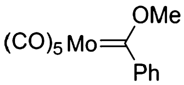
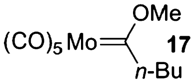
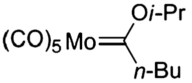
Table 1
Synthesis of alkoxy Fischer carbene complexes



Entry	Metal (M)	R	R′X (equiv)	Rxn. condition temp/time	Product	Yield[a] (%)
1	Cr	CH_3	CH_3I (25)	25 °C/4 h	 **1**	62
2	Cr	CH_3	EtI (5)	50 °C/2 h	 **2**	65
3	Cr	Ph	CH_3I (25)	25 °C/7 h	 **3**	61
4	Cr	Ph	*i*-PrI (5)	55 °C/10 h	 **4**	58
5	Cr	CH_3	 Br (5)	25 °C/1.5 h	 **5**	55
6	W	CH_3	CH_3I (25)	25 °C/8 h	 **6**	60
7	W	CH_3	EtI (5)	55 °C/6 h	 **7**	57
8	W	CH_3	*i*-PrI (5)	55 °C/6.5 h	 **8**	68
9	W	CH_3	*n*-BuI (5)	55 °C/10 h	 **9**	60
10	W	CH_3	$PhCH_2Br$ (5)	25 °C/2.5 h	 **10**	72
11	W	CH_3	 Br (5)	25 °C/6 h	 **11**	70
12	W	*n*-Bu	CH_3I (25)	25 °C/9 h	 **12**	48
13	W	*n*-Bu	*i*-PrI (5)	55 °C/8 h	 **13**	65
14	W	Ph	CH_3I (25)	25 °C/7 h	 **14**	61
15	W	Ph	*i*-PrI (5)	55 °C/12 h	 **15**	50
16	Mo	Ph	CH_3I (25)	25 °C/1.5 h	 **16**	45

(*continued on next page*)

Table 1 (*continued*)

Entry	Metal (M)	R	R′X (equiv)	Rxn. condition temp/time	Product	Yield[a] (%)
17	Mo	*n*-Bu	CH_3I (25)	25 °C/1.5 h	 **17**	35
18	Mo	*n*-Bu	*i*-PrI (5)	40 °C/2 h	 **18**	40

[a] Yields refer to the isolated pure compounds.

Under this optimized condition, we have not only prepared alkoxy Fischer carbene complexes of Cr but several W- and Mo-complexes were also prepared (Table 1). Notably, it was not possible to prepare the W- and Mo-complexes earlier by the direct alkylation method.[5a] All these reactions were repeated 3–4 times in order to ensure reproducibility. In addition, we have done preliminary mechanistic studies of this alkylation reaction.

The complex **1** was prepared in the presence of excess methyl iodide (25 equiv) and 5–10 mol % of *n*-tetrabutylammonium bromide in aqueous medium at room temperature to obtain 62% yield after column purification (entry 1, Table 1). Interestingly, the reaction worked well even in 2 mmol scale. The excess methyl iodide promoted a rapid reaction and minimized decomposition of thermally sensitive product. The completion of the reaction was evident from the disappearance of the yellow color of water layer and appearance of yellow or red color in organic layer. The allylation was done at room temperature with allyl bromide and complex **5** was isolated in 55% yield (entry 5, Table 1). It is worth to mention here that the same complex **5** was prepared previously[5a] using allyl iodide whereas allyl bromide did not work. The alkylation of acylmetalates with unactivated alkyl halides like ethyl, *iso*-propyl, and butyl iodides gave poor yield at room temperature. We found that the reaction proceeded smoothly at 55 °C and gave good yields (entries 2 and 4, Table 1). This is the optimum temperature, above which decomposition started. Moreover, the preparation of tungsten carbene complexes was not reported earlier[5a,c] except only one example where the yield was very poor. Under the modified conditions, we isolated several tungsten complexes in very good to excellent yields (entries 6–15, Table 1). Again the allyl bromide worked well and the allylated complex **11** was isolated in 70% yield after column purification (entry 11, Table 1).

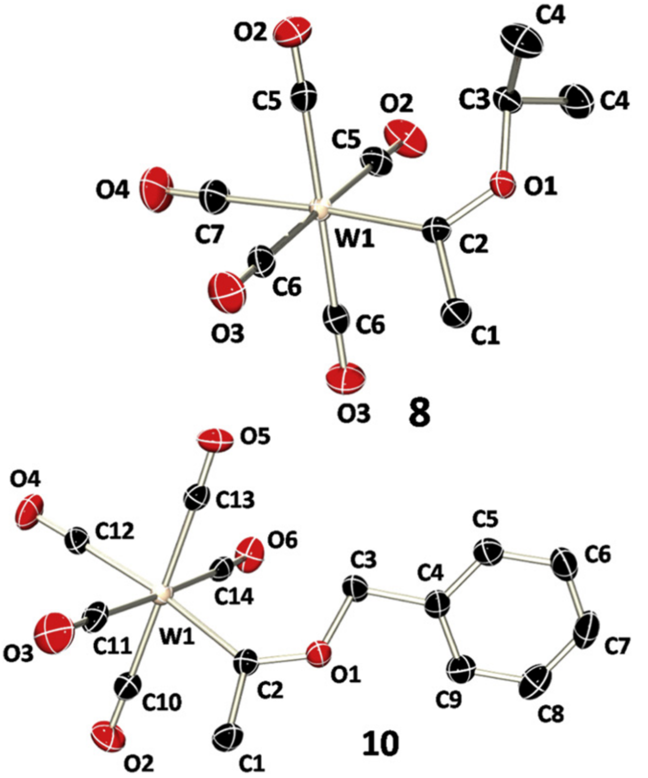


Fig. 1. ORTEP plot of the solid-state molecular structure of **8** and **10**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Next our aim was to prepare alkoxy carbene complexes of molybdenum as methodology for the preparation of alkoxy carbene complexes of molybdenum is still very limited and Hoye's condition was also not effective. Using the modified conditions, we isolated the products with various alkyl halides in reasonably good yields (entries 16–18, Table 1).

Some of the Fischer carbene complexes studied were crystalline solids. Fig. 1 shows the single crystal X-ray structure of compounds **8** and **10**.

2.2. Cesium effect

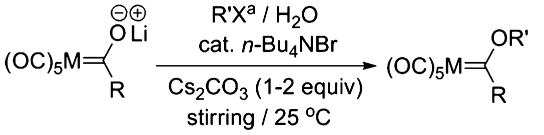
It is known in the literature[7] that cesium increases the nucleophilic character of cesium carboxylate in esterification reaction of *N*-protected amino acids. Therefore, we were interested to see the 'effect of cesium' in our alkylation reaction. The reaction was repeated in the presence of 1–2 equiv of Cs_2CO_3 in aqueous medium. As we have already discussed, at room temperature the reaction gave incomplete conversion with unactivated alkyl halides (Table 2) but interestingly, we observed that cesium has a positive effect in the alkylation reaction at room temperature to increase the yields by 4–13% in every case except for allyl complex **5**. Attempts to improve it by heating the reaction mixture failed to give better results because decomposition became dominant reaction. It was tried in different solvents such as DMF or DCM or THF but in all these cases the yield was very poor and α-*C*-alkylated Fischer carbene was formed as a side product.

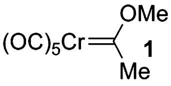
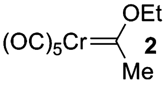
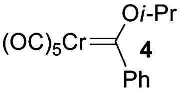
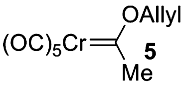
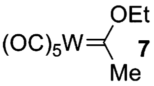
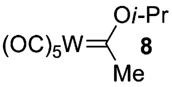
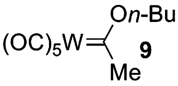
2.3. Mechanistic study

The plausible mechanism of the alkylation reaction has been previously suggested by Hoye et al.[5a] According to them, the reaction perhaps takes place via S_N2 pathway or a radical transfer process but no in depth study of the reaction was carried out.

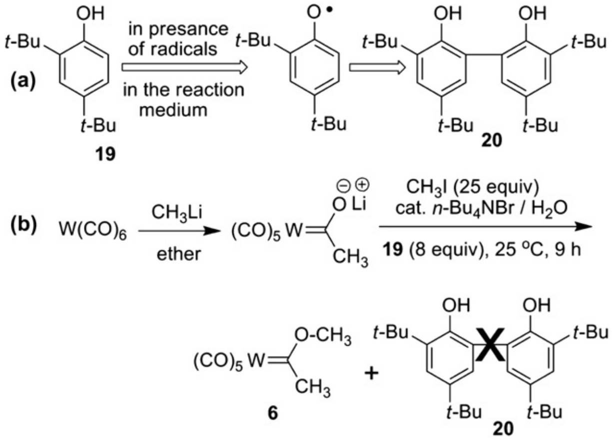
We established that the reaction was not taking place via radical pathway because the yield of the Fischer carbene complex **6** was not affected when the reaction was done in the presence of excess (8 equiv) radical quencher 2,4-di-*tert*-butyl phenol. Moreover, there was no indication of the formation of coupling product 4,4′,6,6′-tetra-*tert*-butyl-2,2′-biphenol (Scheme 1, b), which is known to form if phenoxyl radical is generated in the reaction medium (Scheme 1,a).

Table 2
Effect of cesium in alkylation reaction



Carbene complexes	Time (h)	No Cs_2CO_3 [yield[b] (%)]	Cs_2CO_3 [yield[b] (%)]
 **1**	4	62	66
 **2**	2	10	20
 **4**	3	7	15
 **5**	1.5	55	53
 **7**	8	14	27
 **8**	12	22	32
 **9**	12	14	23

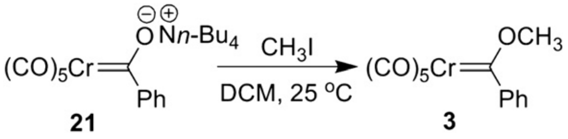
[a] MeI of 25 equiv or 5 equiv of other halides were used.
[b] Yields refer to the isolated pure compounds.



Scheme 1. (a) Dimerization of di-*tert*-butyl phenol in presence of radicals. (b) Alkylation reaction in the presence of radical quencher.

2.4. Kinetics

We have studied the kinetics of alkylation of **21** (an intermediate of the alkylation reaction) with alkyl halide by monitoring the reaction with optical spectroscopy (Scheme 2). It was difficult to monitor the kinetics of the alkylation reaction of lithium acylmetalate under biphasic conditions due to opacity, so we have studied the kinetics in the homogenous phase with alkyl halide. The advantage is that the starting material, **21** and the product, **3** show λ_{max} at 350 nm and 405 nm, respectively, in the UV–visible absorption spectra (Fig. 2).



Scheme 2. Methylation of *n*-tetrabutylammonium salt **21**.

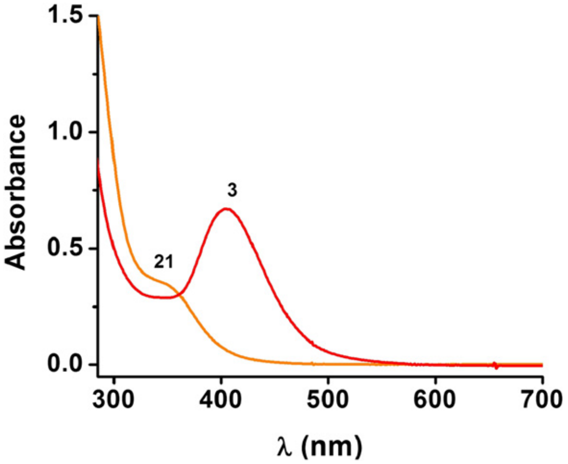


Fig. 2. UV–vis absorption spectra of **21** (concn=1.75×10^{-4} M) and **3** (concn=1.1×10^{-4} M).

Compound **21** (0.71 mM) was taken in deoxygenated dichloromethane in a cuvette (3 mL and 1 cm). To that an excess of methyl iodide in DCM was added to obtain an overall concentration of 0.72 M and optical spectral changes were recorded at 25 °C. The formation of the product was monitored by following the absorbance at 405 nm. Initially, a lag phase was observed for ~4 min and thereafter the reaction shows a pseudo first order conversion of **21** to **3** with an isobestic point at 375 nm (Fig. 3). This is consistent

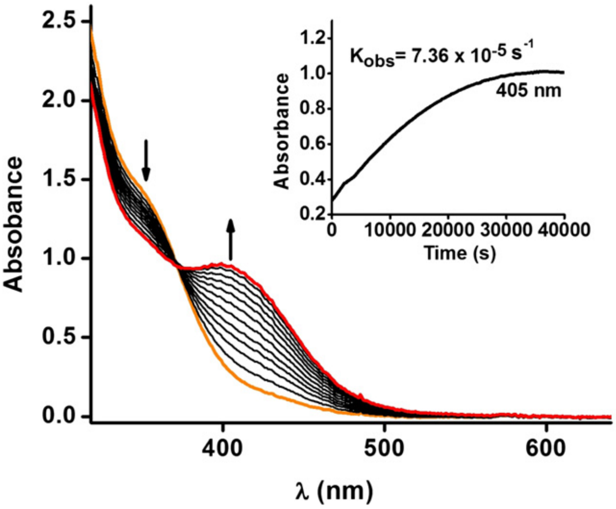


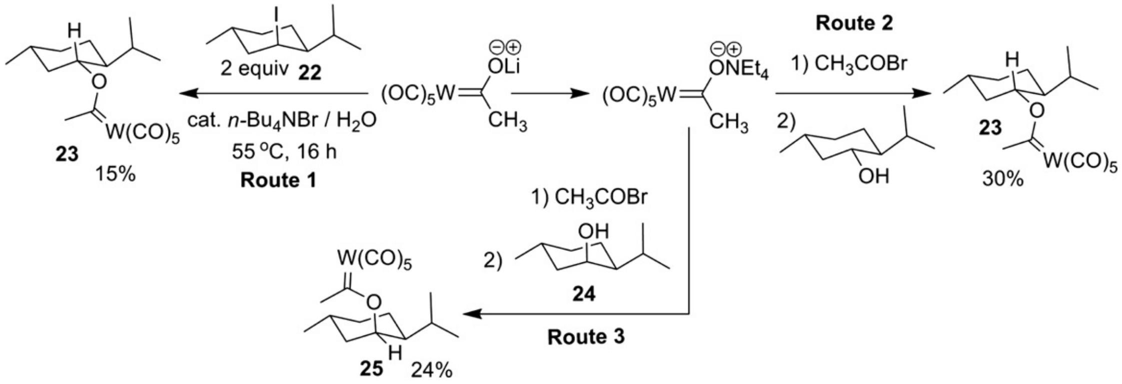
Fig. 3. Spectral changes observed upon mixing of DCM solution of **21** with large excess methyl iodide at 25 °C over 11 h. Concentration of solutions **21** 0.71 mM; CH_3I, 0.72 M. λ_{max} corresponding to **21** starts to decay, λ_{max} corresponding to product, **3** starts to accumulate. Inset: single-wavelength registration (at 405 nm) of the formation of **3** overlayed with a first-order fit; k_{obs} 7.36×10^{-5} s^{-1}.

with the observed reaction rate dependence on the concentration of methyl iodide. Therefore the following rate equation may be suggested for this reaction, rate$=k_{obs}\times$[**21**]; where $k_{obs}=k\times[CH_3I]$ (k is actual rate constant).

2.5. NMR study

The menthyloxy Fischer carbene complex **23** was synthesized from (+)-neomenthyl iodide **22** (route 1, Scheme 3). The complex **23** was isolated in 15% yield as a single product. The specific rotation and ^1H NMR spectrum of the compound **23** indicated that the reaction proceeded with complete inversion of configuration at the reaction center. The neomenthyl iodide **22** (see Supplementary data for spectral data) was synthesized from commercially available optically active (−)-menthol, $[\alpha]_D^{26}$ −45 (c 4.1, $CHCl_3$) using reported procedure;[8] however, no spectral data were included in that paper. The ^1H NMR spectrum of complex **23** was compared with the sample synthesized directly from (−)-menthol by the known method (route 2, Scheme 3).

The optical rotation and the ^1H NMR spectra of both the samples were same and particularly, the proton attached at C–O showed a clear td at 4.90 ppm with J values 10.4 and 3.7 Hz, respectively. The corresponding complex **25**, synthesized by acetylation of tetraethylammonium salt of acylmetalate followed by addition of (+)-neomenthol, **24**, $[\alpha]_D^{27}$ +15.9 (c 6.3, $CHCl_3$) (route 3, Scheme 3), had spectral features clearly different from that of complex **23** (Fig. 4).



Scheme 3. Synthesis of optically active Fischer carbene complexes.

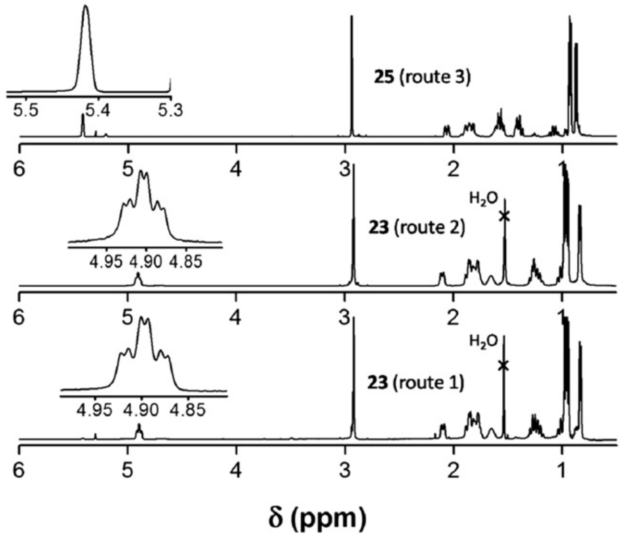


Fig. 4. ^1H NMR spectra ($CDCl_3$, 500 MHz) of (−)-menthyloxy Fischer carbene complex **23** and (+)-neomenthyloxy Fischer carbene complex **25**.

The (+)-neomenthol **24** was synthesized from (−)-menthol in optically active form via the formation of p-nitro-benzoyl ester using DEAD/PPh_3, followed by hydrolysis with K_2CO_3 in MeOH/THF (1:1) (see Supplementary data).

The opposite stereochemical configuration at C1 of the two optically active isomers **23** and **25** was further confirmed by CD spectra (Fig. 5).

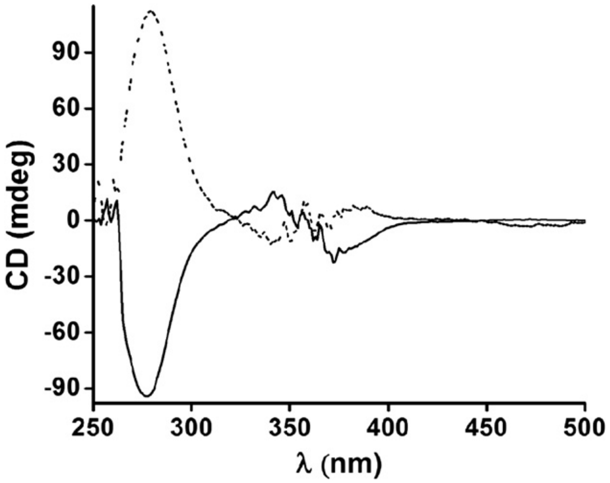


Fig. 5. CD spectra of complex **23** (10^{-2} M in $CHCl_3$, solid line) and complex **25** (4.6×10^{-3} M in $CHCl_3$, dashed line, data plotted after multiplication by three).

3. Conclusions

In conclusion, we have found an optimum condition for the preparation of Fischer carbene complexes of Cr, W, and Mo by direct alkylation of acylmetalates with activated and unactivated alkyl halides. Though this method did not work well (5–10% yield) in case of functionalized alkyl halides ($BrCH_2CO_2Et$, methoxyethoxymethyl chloride) but it could be useful for the large scale preparation of Fischer carbene complexes as alkyl halides are easily available. The effect of cesium ion on the alkylation reaction has been studied. The kinetics and ^1H NMR studies suggest that the alkylation reaction takes place predominantly via S_N2 pathway particularly in case of alkyl halides as was proposed earlier by Hoye.[5a]

4. Experimental section

4.1. General considerations

All reagents were purchased from commercial sources and used without further purification, unless otherwise stated. Petroleum ether (PE) refers to the fraction of petroleum boiling between 40 and 60 °C. DMF, DCM, and THF are the abbreviation of dimethylformamide, dichloromethane, and tetrahydrofuran, respectively. All reactions were carried out in oven-dried glassware under an argon atmosphere using anhydrous solvents, standard syringe, and septum techniques unless otherwise indicated. The aqueous solution of acylmetalates was filtered through a syringe filter, purchased from Sigma–Aldrich. Organic extracts were dried over anhydrous Na_2SO_4 and then filtered prior to removal of all volatiles under reduced pressure on rotary evaporation. Chromatographic purification of products was accomplished using column chromatography on silica gels (mesh 100–200). Thin-layer chromatography (TLC) was carried out on aluminum sheets, Silica Gel 60 F254 (Merck; layer thickness 0.25 mm). Visualization of the developed chromatogram was performed by UV light and/or vanillin stains.

4.2. Physical measurements

Infrared spectra were recorded using an FTIR instrument (Shimadzu FTIR-8300), the frequencies are reported in wave number (cm^{-1}) and intensities of the peaks are denoted as s (strong). ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 and DPX-500 spectrometers, respectively. Chemical shifts are reported in parts per million (ppm). Coupling constants are reported wherever it is necessary in hertz (Hz). Elemental analyses were performed on a Perkin–Elmer 2400 series II CHN analyzer. Solution electronic spectra were measured on an Agilent 8453 diode array spectrophotometer. CD spectra were recorded on a JASCO J-815 CD spectrometer and optical rotations were measured on JASCO P-1020. Optical rotation values reported are uncorrected.

4.3. X-ray crystal structure determination

Crystallographic data for **8** and **10** are provided in Table S1 (Supplementary data). X-ray single crystal data were collected at 150 K using MoKα (λ=0.7107 Å) radiation on a SMART APEX diffractometer equipped with CCD area detector. Data collection and reduction and structure solution/refinement were carried out using the software package of APEX II.[9] Fischer carbene complex **10** was solved by direct method, complex **8** was solved by Patterson method and refined in a routine manner. The non-hydrogen atoms were treated anisotropically. All hydrogen atoms were geometrically fixed. Three hydrogen atoms in methyl group of complex **8** came in six positions due to symmetry of the molecule.

4.4. General procedure

To a stirred suspension of metal hexacarbonyl (2 mmol) in freshly dried ether (8 mL) was added slowly alkyl or phenyl lithium (1–1.6 M, 1.98 mmol, *n*-BuLi in hexane, MeLi and PhLi in ether) at 20 °C under argon atmosphere. The reaction mixture was protected from light and was stirred for 20 min at room temperature. The slurry became a homogeneous yellowish brown or red solution. The solvent was removed under reduced pressure without heating, argon purged ice-cold water (5 mL) was added quickly under argon atmosphere. The aqueous solution was then filtered through a syringe filter to a 10-mL round-bottomed flask. Tetrabutylammonium bromide (5–10 mol %) and organic halide (amount according to Table 1) were added and the biphasic solution was stirred vigorously under argon atmosphere (condition according to Table 1). As the reaction proceeded, the yellow aqueous layer became faint and an orange or red layer formed to the bottom of the round-bottomed flask. The reaction mixture was extracted with petroleum ether (40–60 °C) (3×20 mL). The combined organic extracts were washed with ice-cold water (25 mL), dried over sodium sulfate. The solvent was removed under reduced pressure without heating. Column purification was done under argon or N_2 pressure using petroleum ether (40–60 °C) as eluent.

4.4.1. Pentacarbonyl(1-methoxyethylidene)chromium(0) (***1***)[5a]. Yellow crystalline solid (62%); IR (neat): ν 2064, 1917 (s), 1456, 1261 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 4.71 (br s, 3H, OCH_3), 2.96 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 360.6 (C=Cr), 223.5 (CO_{trans}), 216.5 (CO_{cis}), 67.4 (br, OCH_3), 49.2 (br, CH_3). Anal. Calcd for $C_8H_6O_6Cr$: C, 38.41; H, 2.42. Found: C, 38.71; H, 2.60.

4.4.2. Pentacarbonyl(1-ethoxyethylidene)chromium(0) (***2***). Orange oil (65%); IR (neat): ν 2064, 1917 (s), 1260 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 5.01 (br s, 2H, OCH_2), 2.95 (s, 3H, CH_3), 1.65 (t, *J*=7.0 Hz, 3H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 357.6 (C=Cr), 223.5 (CO_{trans}), 216.6 (CO_{cis}), 77.2 (OCH_2CH_3, merged with $CDCl_3$) [78.7, 75.3, 73.4, br s, OCH_2; observed in acetone-d_6], 50.1, 49.6 (br, CH_3), 15.1 (OCH_2CH_3). Anal. Calcd for $C_9H_8O_6Cr$ C, 40.92; H, 3.05. Found: C, 40.56; H, 3.11.

4.4.3. Pentacarbonyl(methoxy(phenyl)methylene)chromium(0) (***3***)[6b]. Red crystalline solid (61%); IR (neat): ν 2062, 1925 (s), 1449, 1231 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.41 (s, 3H, ArH), 7.30 (s, 2H, ArH), 4.70 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 351.3 (C=Cr), 224.3 (CO_{trans}), 216.3 (CO_{cis}), 153.9 (ArC), 130.5 (ArC), 128.3 (ArC), 123.1 (ArC), 67.3 (OCH_3). Anal. Calcd for $C_{13}H_8O_6Cr$: C, 50.01; H, 2.58. Found: C, 50.27; H, 2.60.

4.4.4. Pentacarbonyl(isopropoxy(phenyl)methylene)chromium(0) (***4***)[6b]. Red crystalline solid (58%); IR (neat): ν 2062, 1925 (s), 1244 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.41–7.44 (m, 3H, ArH), 7.22–7.24 (m, 2H, ArH), 5.66 (br s, 1H, OCH), 1.60 [d, *J*=5.8 Hz, 6H, $OC(CH_3)_2$]; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 326.4 (C=Cr), 224.5 (CO_{trans}), 216.4 (CO_{cis}), 154.0 (ArC), 129.9 (ArC), 128.3 (ArC), 122.5 (ArC), 85.9 (OCH), 22.8 [$OCH(CH_3)_2$]. Anal. Calcd for $C_{15}H_{12}O_6Cr$: C, 52.95; H, 3.55. Found: C, 52.75; H, 3.63.

4.4.5. Pentacarbonyl(1-(allyloxy)ethylidene)chromium(0) (***5***)[5a]. Red oily liquid (poor stability) (55%); IR (neat): ν 2064, 1917 (s), 1258 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.17 (br s, 1H, OCH_2CH=), 5.46–5.54 (m, 4H, OCH_2C=CH_2), 2.99 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 358.8 (C=Cr), 223.4 (CO_{trans}), 216.5 (CO_{cis}), 130.8 (CH=), 120.5 (=CH_2), 81.3 (br, OCH_2), 49.6 (br, CH_3).

4.4.6. Pentacarbonyl(1-methoxyethylidene)tungsten(0) (***6***)[6b]. Yellow crystalline solid (60%); IR (neat): ν 2070, 1929 (s), 1451, 1263 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 4.61 (s, 3H, OCH_3), 2.91 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 333.4 (C=W), 203.6 (CO_{trans}), 197.4 (CO_{cis}), 70.4 (OCH_3), 52.3 (CH_3). Anal. Calcd for $C_8H_6O_6W$: C, 25.16; H, 1.58. Found: C, 25.56; H, 1.74.

4.4.7. Pentacarbonyl(1-ethoxyethylidene)tungsten(0) (***7***). Yellow crystalline solid (57%); IR (neat): ν 2071, 1912 (s), 1258 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 4.87 (q, 2H, *J*=6.8 Hz, OCH_2), 2.89 (s, 3H, CH_3), 1.62 (t, 3H, *J*=7.1 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 330.4 (C=W), 203.6 (CO_{trans}), 197.4 (CO_{cis}), 80.7 (OCH_2), 52.5 (CH_3), 14.9 (OCH_2CH_3). Anal. Calcd for $C_9H_8O_6W$: C, 27.30; H, 2.04. Found: C, 27.02; H, 1.92.

4.4.8. Pentacarbonyl(1-isopropoxyethylidene)tungsten(0) (***8***)[6b]. Yellow crystalline solid (68%); IR (neat): ν 2072, 1910 (s), 1283 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 5.63–5.66 (m, 1H, OCH), 2.86 (s, 3H, CH$_3$), 1.53 [d, 6H, *J*=6.1 Hz, OCH(CH$_3$)$_2$]; ^{13}C NMR (CDCl$_3$, 75 MHz): δ 325.6 (C=W), 203.6 (CO$_{\mathrm{trans}}$), 197.3 (CO$_{\mathrm{cis}}$), 90.0 (OCH), 52.6 (CH$_3$), 22.3 [OCH(CH$_3$)$_2$]. Anal. Calcd for $C_{10}H_{10}O_6W$: C, 29.29; H, 2.46. Found: C, 29.52; H, 2.44.

4.4.9. Pentacarbonyl(1-butoxyethylidene)tungsten(0) (***9***). Yellow oil (60%); IR (neat): ν 2070, 1917 (s), 1265 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.81 (t, *J*=5.9 Hz, 2H, OCH$_2$–), 2.88 (s, 3H, CH$_3$), 1.91–2.00 (m, 2H, OCH$_2$CH$_2$–), 1.51–1.58 (m, 2H, OCH$_2$CH$_2$CH$_2$–), 1.03 (t, *J*=7.4 Hz, 3H, OCH$_2$CH$_2$CH$_2$CH$_3$); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 330.5 (C=W), 203.7 (CO$_{\mathrm{trans}}$), 197.5 (CO$_{\mathrm{cis}}$), 84.7 (OCH$_2$–), 52.3 (CH$_3$), 31.2 (OCH$_2$CH$_2$–), 19.3 (OCH$_2$CH$_2$CH$_2$–), 13.7 (OCH$_2$CH$_2$CH$_2$CH$_3$). Anal. Calcd for $C_{11}H_{12}O_6W$: C, 31.16; H, 2.85. Found: C, 31.06; H, 3.05.

4.4.10. Pentacarbonyl(1-(benzyloxy)ethylidene)tungsten(0) (***10***). Yellow crystalline solid (72%); IR (neat): ν 2066, 1937, 1904, 1260 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.45 (m, 5H, ArH), 5.81 (s, 2H, OCH$_2$), 2.93 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 331.1 (C=W), 203.5 (CO$_{\mathrm{trans}}$), 197.4 (CO$_{\mathrm{cis}}$), 134.0 (ArC), 129.5 (ArC), 129.1 (ArC), 128.7 (ArC), 86.4 (OCH$_2$), 52.5 (CH$_3$). Anal. Calcd for $C_{14}H_{10}O_6W$: C, 36.71; H, 2.20. Found: C, 36.61; H, 2.12.

4.4.11. Pentacarbonyl(1-(allyloxy)ethylidene)tungsten(0) (***11***). Yellowish orange oil (70%); IR (neat): ν 2072, 1915 (s), 1260 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 6.17 (ddt, *J*=16.3, 10.5, 5.8 Hz, 1H, OCH$_2$CH=), 5.51 (ddd, *J*=17.0, 2.6, 1.2 Hz, 1H, OCH$_2$CH=CH$_{\mathrm{cis}}$), 5.46 (ddd, *J*=10.5, 2.1, 1.0 Hz, OCH$_2$CH=CH$_{\mathrm{trans}}$), 5.31 (d, *J*=5.5 Hz, 2H, OCH$_2$–), 2.92 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 331.3 (C=W), 203.5 (CO$_{\mathrm{trans}}$), 197.3 (CO$_{\mathrm{cis}}$), 130.8 (CH=), 120.7 (=CH$_2$), 84.8 (OCH$_2$), 52.4 (CH$_3$).

4.4.12. Pentacarbonyl(1-methoxypentylidene)tungsten(0) (***12***). Orange oil (48%); IR (neat): ν 2070, 1915 (s), 1451, 1258 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 4.60 (s, 3H, OCH$_3$), 3.21 (t, *J*=7.5 Hz, 2H, CH$_2$–), 1.47–1.52 (m, 2H, CH$_2$CH$_2$–), 1.33–1.37 (m, 2H, CH$_2$CH$_2$CH$_2$–), 0.92 (t, *J*=7.2 Hz, 3H, CH$_2$CH$_2$CH$_2$CH$_3$); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 337.9 (C=W), 203.4 (CO$_{\mathrm{trans}}$), 197.5 (CO$_{\mathrm{cis}}$), 70.5 (OCH$_3$), 64.9 (CH$_2$–), 28.7 (CH$_2$CH$_2$–), 22.5 (CH$_2$CH$_2$CH$_2$–), 14.0 (CH$_2$CH$_2$CH$_2$CH$_3$). Anal. Calcd for $C_{11}H_{12}O_6W$: C, 31.16; H, 2.85. Found: C, 31.49; H, 2.91.

4.4.13. Pentacarbonyl(1-isopropoxypentylidene)tungsten(0) (***13***). Yellow crystalline solid (65%); IR (neat): ν 2068, 1913 (s), 1263 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 5.64 (heptet, *J*=6.1 Hz, 1H, OCH), 3.16 (t, *J*=7.5 Hz, 2H, CH$_2$–), 1.52 [d, *J*=6.2 Hz, 6H, OCH(CH$_3$)$_2$], 1.41–1.56 (m, 2H, CH$_2$CH$_2$–), 1.35 (sextet, *J*=7.2 Hz, 2H, CH$_2$CH$_2$CH$_2$–), 0.92 (t, *J*=7.2 Hz, 3H, CH$_2$CH$_2$CH$_2$CH$_3$); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 329.9 (C=W), 203.6 (CO$_{\mathrm{trans}}$), 197.4 (CO$_{\mathrm{cis}}$), 89.8 (OCH), 64.9 (CH$_2$), 28.5 (CH$_2$CH$_2$–), 22.5, 22.3 [CH$_2$CH$_2$CH$_2$– and OCH(CH$_3$)$_2$], 14.1 (CH$_2$CH$_2$CH$_2$CH$_3$). Anal. Calcd for $C_{13}H_{16}O_6W$: C, 34.54; H, 3.57. Found: C, 34.92; H, 3.65.

4.4.14. Pentacarbonyl(methoxy(phenyl)methylene)tungsten(0) (***14***). Orange crystalline solid (61%); IR (KBr): ν 2070, 1929 (s), 1219 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.56–7.58 (m, 2H, ArH), 7.46–7.50 (m, 1H, ArH), 7.40–7.43 (m, 2H, ArH), 4.77 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 322.2 (C=W), 203.6 (CO$_{\mathrm{trans}}$), 197.3 (CO$_{\mathrm{cis}}$), 155.3 (ArC), 131.8 (ArC), 128.2 (ArC), 126.3 (ArC), 70.1 (OCH$_3$). Anal. Calcd for $C_{13}H_8O_6W$: C, 35.16; H, 1.82. Found: C, 35.51; H, 1.60.

4.4.15. Pentacarbonyl(isopropoxy(phenyl)methylene)tungsten(0) (***15***). Orange crystalline solid (50%); IR (neat): ν 2068, 1991, 1977, 1904 (s), 1244 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.50–7.53 (m, 2H, ArH), 7.41–7.48 (m, 3H, ArH), 5.92 (heptet, *J*=6.0 Hz, 1H, OCH), 1.66 (d, *J*=6.2 Hz, 6H, OC(CH$_3$)$_2$); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 316.1 (C=W), 203.7 (CO$_{\mathrm{trans}}$), 197.2 (CO$_{\mathrm{cis}}$), 155.5 (ArC), 131.4 (ArC), 128.0 (ArC), 126.0 (ArC), 88.8 (OCH), 22.4 [OCH(CH$_3$)$_2$]. Anal. Calcd for $C_{15}H_{12}O_6W$: C, 38.16; H, 2.56. Found: C, 38.52; H, 2.45.

4.4.16. Pentacarbonyl(methoxy(phenyl)methylene)molybdenum(0) (***16***). Orange solid (poor stability) (45%); IR (neat): ν 2068, 1925 (s), 1449, 1234 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.57 (m, 2H, ArH), 7.40–7.47 (m, 3H, ArH), 4.86 (s, 3H, OCH$_3$); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 339.8 (C=Mo), 213.7 (CO$_{\mathrm{trans}}$), 205.9 (CO$_{\mathrm{cis}}$), 153.8 (ArC), 132.0 (ArC), 128.2 (ArC), 126.2 (ArC), 69.4 (OCH$_3$).

4.4.17. Pentacarbonyl(1-methoxypentylidene)molybdenum(0) (***17***). Yellow oil (35%); IR (neat): ν 2070, 1921 (s), 1452, 1258 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 4.68 (s, 3H, OCH$_3$), 3.24 (t, *J*=7.5 Hz, 2H, CH$_2$–), 1.45–1.50 (m, 2H, CH$_2$CH$_2$–), 1.31–1.35 (m, 2H, CH$_2$CH$_2$CH$_2$–), 0.91 (t, *J*=7.2 Hz, 3H, CH$_2$CH$_2$CH$_2$CH$_3$); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 355.9 (C=Mo), 213.2 (CO$_{\mathrm{trans}}$), 205.8 (CO$_{\mathrm{cis}}$), 69.4 (OCH$_3$), 62.9 (CH$_2$–), 28.1 (CH$_2$CH$_2$–), 22.4 (CH$_2$CH$_2$CH$_2$–), 13.8 (CH$_2$CH$_2$CH$_2$CH$_3$).

4.4.18. Pentacarbonyl(1-isopropoxypentylidene) molybdenum(0) (***18***). Yellow oil (40%); IR (neat): ν 2068, 1921 (s), 1283 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 5.67 (heptet, *J*=6.2 Hz, 1H, OCH), 3.18 (t, *J*=7.8 Hz, 2H, CH$_2$–), 1.52 (d, *J*=6 Hz, 6H, OCH(CH$_3$)$_2$), 1.42–1.48 (m, 2H, CH$_2$CH$_2$–), 1.30–1.37 (m, 2H, CH$_2$CH$_2$CH$_2$–), 0.91(t, *J*=7.2 Hz, 3H, CH$_2$CH$_2$CH$_2$CH$_3$); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 347.2 (C=Mo), 213.5 (CO$_{\mathrm{trans}}$), 205.8 (CO$_{\mathrm{cis}}$), 89.1 (OCH), 63.0 (CH$_2$–), 28.0 (CH$_2$CH$_2$–), 22.5, 22.2 [CH$_2$CH$_2$CH$_2$– and OCH(CH$_3$)$_2$], 14.0 (CH$_2$CH$_2$CH$_2$CH$_3$).

4.4.19. Pentacarbonyl(1-((1R,2S*,5R*)-2-isopropyl-5-methylcyclohexyl)propan-2-ylidene)tungsten(0)* (***23***). Yellow oil; R_f (hexane) 0.71; $[\alpha]_D^{25}$ −75.4 (*c* 1.4, CHCl$_3$); IR (neat): ν 2070, 1915 (s), 1275 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 4.90 (td, *J*=10.4, 3.7 Hz, 1H, OCH), 2.92 (s, 3H, W=CCH$_3$), 2.10 (br d, *J*=12 Hz, 1H), 1.76–1.89 (m, 4H), 1.65 (br s, 1H), 1.18–1.30 (m, 2H), 0.92–1.04 (m, 7H), 0.84 (d, *J*=7 Hz, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 327.2 (C=W), 203.0 (CO$_{\mathrm{trans}}$), 197.6 (CO$_{\mathrm{cis}}$), 95.8 (OCH), 53.6 (W=CCH$_3$), 47.9, 41.9, 34.2, 31.3, 26.9, 24.3, 22.0, 21.4, 17.3. Anal. Calcd for $C_{17}H_{22}O_6W$: C, 40.34; H, 4.38. Found: C, 40.52; H, 4.07.

4.4.20. Pentacarbonyl(1-((1S,2S*,5R*)-2-isopropyl-5-methylcyclohexyloxy)ethylidene)tungsten(0)* (***25***). Yellow oil; R_f (hexane) 0.66; $[\alpha]^{26}{}_D$ +40.6° (c 1.3, CHCl$_3$); IR (neat): ν 2070, 1915 (s), 1263 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 5.42 (br s, 1H, OCH), 2.94 (s, 3H, W=CCH$_3$), 2.07 (br d, *J*=14.5 Hz, 1H), 1.82–1.89 (m, 2H), 1.54–1.62 (m, 3H), 1.36–1.44 (m, 2H), 1.04–1.09 (m, 1H), 0.92–0.98 (m, 6H), 0.87 (d, *J*=6.5 Hz, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 327.6 (C=W), 203.1 (CO$_{\mathrm{trans}}$), 197.6 (CO$_{\mathrm{cis}}$), 93.7 (OCH), 53.6 (W=CCH$_3$), 47.0, 41.0, 34.7, 29.8, 27.2, 24.4, 22.4, 21.8, 20.0. Anal. Calcd for $C_{17}H_{22}O_6W$: C, 40.34; H, 4.38. Found: C, 40.53; H, 4.01.

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Supplementary data

^{1}H and ^{13}C spectra for all Fischer carbene complexes. CCDC 787311 and 787312 contain crystallographic data for **8** and **10**. This material can be obtained free of charge from the Cambridge

Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.11.016. These data include MOL files and InChiKeys of the most important compounds described in this article.

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