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REACTIVITY OF (η^3-ALLYL)DICARBONYLNITROSYL IRON COMPLEXES WITH DIMETHYL MALONATE AND DIISOBUTYL MALONATE

Misbah Tabassam[1], Amna Farooq[1], Muhammad Imran[1*], Syeda Robina Gillani[2], Saima Saqib[3], Zaid Mehmood[1] and Liviu Mitu[4*]

[1]Institute of Chemistry, University of the Punjab, Lahore, Pakistan
[2]Department of Chemistry, University of Engineering and Technology, Lahore, Pakistan
[3]Department of Chemistry, Govt. Postgraduate College for Women, Samanabad, Lahore, Pakistan
[4]Department of Chemistry, University of Pitesti, Pitesti-110040, Romania

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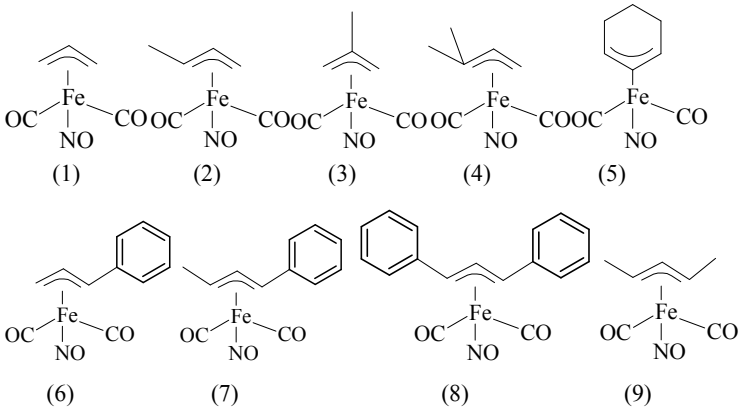
ABSTRACT. In this paper, we describe the reactivity of our previously reported (η^3-allyl)dicarbonylnitrosyl iron complexes (**1**–**9**). In this context, stoichiometric reactions of **1**–**9** with dimethyl malonate and di-iso-butyl malonate were carried out. The regioselectivity of the resulting products (**10**–**25**) was determined by gas chromatoraphic analysis of reaction mixtures. These products were purified by column chromatography and then structurally characterized by IR, ^{1}H NMR, ^{13}C NMR spectroscopies and mass spectrometry. Effect of different ligands L (L = CO, PPh_3, SIMES (1,3-di-tert-butylimidazolium hexafluoro phosphate), BUSI(1,3-bis(2,4,6-trimethyl-phenyl)-4,5-dihydro-3H-imidazol-1-ium hexafluorophosphate)) and their influence on the substitution pattern has also been studied. The introduction of variable substituents exhibited diverse reactivities. Generally, it was observed that the reactivity decreased by increasing the size of substituentin (η^3-allyl)dicarbonylnitrosyl iron complexes (**1**–**9**). Strong impact on the reactivity was observed due to substitution pattern of the allyl moiety. A considerable reduction in the conversion ratio from 81% to 68% was observed in repositioning the substituent from C-3 to C-2 position.

KEY WORDS: Iron, Stoichiometric reactions, Column chromatography, Dimethyl malonate

INTRODUCTION

Metal-allyl complexes are very well known compounds, both stoichiometrically and catalytically, in organic synthesis [1]. The addition of an allyl metal complex to a carbonyl compound has been extensively used for carbon-carbon bond forming process [2, 3]. η^3-allyl metal complexes can be synthesized from various organic precursors. Iron allyl complexes were reported previously as versatile intermediate in organic synthesis [4–6]. The influence of steric and electronic effects of the incoming ligand was reported using substituted cyclopentadienyl iron complexes to develop a green chemistry approach [7]. Catalysis based on such metal complexes have been recognized as powerful synthetic tool in organic synthesis. Roustan *et al.* reported the first Fe–catalyzed allylic substitution and observed good regioselectivity, where substitution preferentially occurred at the carbon atom bearing the leaving group in the starting material [8]. It is further established in the literature that iron allyl complexes posssessed amphiphilic reactivitirs towards both nucleophiles and electrophiles [9–11]. In the above same context of literature, in this paper we report the reactivity of following (η^3-allyl) iron complexes with dimethyl malonate and di-iso-butyl malonate, which we were synthesized and reported by our group previously [12]:

*Corresponding author. E-mail: imran_inorganic@yahoo.com, ktm7ro@yahoo.com



The purpose of this study is to investigate the stoichiometric reaction's effect of different ligands on stoichiometric reactions which will be a good source of knowledge for further cayalytic applications of these complexes. The regioselectivity of the nucleophilic substitution products as determined by gas chromatographic analysis, purification by column chromatography and subsequent characterization by IR, ^{1}H-NMR, ^{13}C-NMR spectroscopies and mass spectrometry is part of this manuscript.

EXPERIMENTAL

Materials and methods

All the reactions and necessary work out were performed in an inert atmosphere using high vacuum Schlenk techniques. All chemicals were purchased from E-Merck (Darmstadt, Germany). Nuclear magnetic resonance (NMR) spectra were recorded by using $CDCl_3$ as solvent with Brucker Avance 300 spectrometer at 300 MHz and Brucker Avance 500 spectrometer at 500 MHz. The IR instrument used was Brucker Vector 22 FT-IR spectrometer. Column chromatography separations were carried out with silica gel 60(230–400 mesh) from Merck using pressure by means of compressed air. Low resolution mass spectrometry (LRMS) and high resolution mass spectrometry (HRMS) of the allyl iron complexes was carried out using Brucker Type micro-TOF-Q (ESI). The capillary gas chromatography was measured on focus GC Thermo Finnigan (carrier gas: H_2, column: DBI, 25 m long, 0.2 μm phase thickness).

*I. Reactions of (η^3-allyl)dicarbonylnitrosyl iron (**1–9**) complexes with dimethyl malonate*

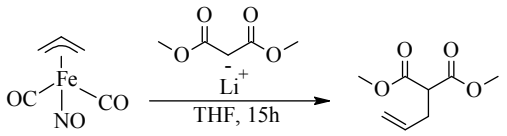
General method of the reactions of these complexes (**1–9**) with nucleophiles is described as follow.

General method (I)

In an oven dried 10 mL Schlenk tube, was added lithium hydride (8.0 mg, 1 mmol) under nitrogen followed by 1 mL dry THF at room temperature. The resulting suspension was cooled to 0 °C and then dimethyl malonate (114 μL, 131 mg, 1 mmol) was added. Finally, the Schlenk tube was closed and suspension was stirred at this temperature for 30 min at 0 °C and then further 30 min at room temperature. This freshly deprotonated nucleophile (lithium salt of dimethyl malonate) was added to a 1 mmol solution of the respective (η^3-allyl)dicarbonyl-

nitrosyl iron (**1**, **2**, **4–9**) complexes in 10 mL dry THF under nitrogen and again the Schlenk tube was closed. The reaction mixture was stirred for 15 h at room temperature, after that, the reaction mixture was extracted with diethyl ether and the combined ethereal extracts were washed successively with 4 M hydrochloric acid and distilled water. Then dried over a mixture of sodium sulfate and charcoal (1:1), solvent was evaporated under vaccum to produce the crude products (**10–17**), which were then column chromatographed on silica gel using isohexane/diethyl ether as eluent (ratio was different as described below). The resulting final products were subsequently characterized by IR, ^{1}H NMR, ^{13}C NMR and microanalysis.

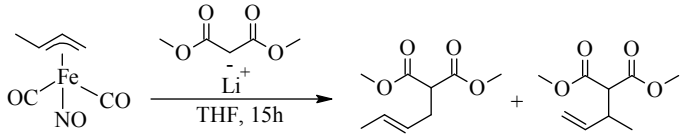
I.1. Reaction of (π-allyl)dicarbonylnitrosyl iron with dimethyl malonate



(1) (10)

*2-Allyl-malonic acid dimethyl ester (**10**)*. Colourless liquid, R_f 0.32, yield: 80%. IR, υ/cm $^{-1}$: 2956 (w), 1732 (s), 1643 (w), 1435 (m), 1340 (w), 1236 (m), 1195 (m), 1152 (s), 1025 (w), 997 (w), 921 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 5.70–5.83 (*m*, 1H, CH_2=C*H*), 5.15 (*dd*,1H, *J* = 1.48,2.99 Hz, CH_2=CH), 5.04–5.09 (*m*, 1H, C*H*$_2$=CH), 3.74 (*s*, 6H, OC*H*$_3$), 3.47 (*t*, 1H, J = 7.57 Hz, C*H*COOCH$_3$), 2.65 (*t*, 2H, *J* = 7.23 Hz, =CHC*H*$_2$); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ (ppm): 169.0 (*C*=O), 133.8 (=CH), 117.8 (=*C*H$_2$), 52.8 (*C*HCO), 51.5 (O*C*H$_3$), 32.8 (*C*H$_2$); microanalytical data: C calculated 55.81, found 55.77, H calculated 7.02, found 7.06.

I.2. Reaction of (1-methyl-π-allyl)dicarbonylnitrosyl iron with dimethyl malonate



(2) (11) (11A)

75 : 25

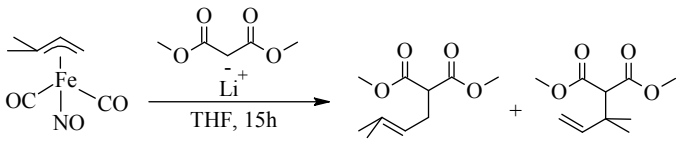
The crude product was column chromatographed using isohexane/diethyl ether (5:1) (yield: 72%) and it was the mixture of two isomers, i.e. linear and branched having regioisomeric ratio (75:25) as determined by capillary gas chromatography.

*(a) Linear isomer 2-but-2enyl-malonic acid dimethylester (**11**)*. R_f 0.32; IR, υ/cm^{-1}: 2955 (w), 1738 (s), 1438 (m), 1265 (m), 1195 (m), 1151 (s), 1023 (w), 971 (w); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 5.56 (*m*, 1H, CH_3CH=C*H*), 5.37 (*m*, 1H, CH_3C*H*=CH), 3.71 (*s*, 6H, OC*H*$_3$), 3.39 (*t*, 1H, *J* = 7.3 Hz, C*H*COOCH$_3$), 2.57 (*m*, 2H, =CHC*H*$_2$),1.64 (*d*,3H, *J* = 6.1 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$)δ (ppm): 169.0 (*C*=O), 128.2, 126.5 (=*C*H), 52.8 (*C*HCO), 52.2 (O*C*H$_3$), 32.5 (*C*H$_2$), 18.0 (*C*H$_3$); microanalytical data: C calculated 58.05, found 58.04, H calculated 7.58, found 7.55.

*(b) Branched isomer 2-(1-methyl-allyl)-malonic acid dimethyl ester (**11A**)*. R_f 0.40; IR, υ/cm^{-1}: 3084 (m), 3024 (s), 3019 (m), 3004 (m), 2955 (s), 1723(s), 1643 (m), 1438 (m), 1269 (m), 1198 (s), 1151 (m), 921 (w); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 5.73 (*ddd*, 1H, J = 17.6, 10.4, 8.0

Hz, C*H*=CH$_2$), 5.05 (*d,* 1H, *J* = 17.6 Hz, CH=C*H*$_2$), 4.97 (*d,* 1H, *J* = 10.2 Hz, CH=C*H*$_2$), 3.70 (*s*, 3H, OC*H*$_3$), 3.66 (*s*, 3H, OC*H*$_3$), 3.28 (*d*, 1H, *J* = 8.4 Hz, C*H*COOCH$_3$), 2.91 (*m,* 1H, CH$_3$C*H*CH=CH$_2$), 1.06 (*d,* 3H, *J* = 7.68 Hz, C*H*$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ (ppm): 169.0, 168.8 (*C*=O), 139.6 (=*C*H), 114.9 (=*C*H$_2$), 57.50 (*C*HCO), 52.33 (O*C*H$_3$), 38.06 (*C*H$_2$), 17.9 (*C*H$_3$); microanalytical data: C calculated 58.05, found 58.01, H calculated 7.58, found 7.63.

I.3. Reaction of (1,1-dimethyl-π-allyl)dicarbonylnitrosyl iron with dimethyl malonate



(4) (12) (12A)

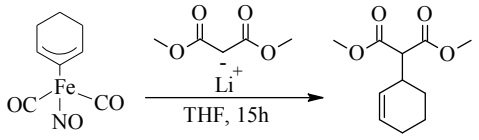
94 : 6

The crude product was column chromatographed as described above using isohexane/diethyl ether (8:1) (yield: 78 %). There were two isomers linear and branced (94:6) as determined by capillary gas chromatography.

*(a) Linear isomer 2-(3-methyl-but-2enyl)-malonic acid dimethyl ester (**12**)*. R$_f$ 0.45; IR, υ/cm^{-1}: 2955 (w), 2918 (w), 1733 (s), 1435 (m), 1335 (w), 1239 (m), 1213 (m), 1197.9 (m), 1147 (s), 1039 (m), 961 (w), 827 (w), 782 (w), 698 (w); ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 5.05 (*t*, 1H,*J*= 7.47 Hz, =C*H*), 3.73 (*s*, 6H, OC*H*$_3$), 3.37 (*t*, 1H, *J* = 7.69 Hz, C*H*COOCH$_3$), 2.59 (*t*, 2H, *J* = 7.47, =CHC*H*$_2$),1.68 (*s*,3H,C*H*$_3$), 1.63 (*s*, 3H, C*H*$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ (ppm): 170.8 (*C*=O), 134.2 (=*C*), 120.8 (=*C*H), 53.8 (*C*HCO), 53.1 (O*C*H$_3$), 29.3 (*C*H$_2$), 27.2, 19.4 (*C*H$_3$); microanalytical data: C calculated 59.98, found 59.96, H calculated 8.05, found 8.07.

*(b) Branched isomer 2-(1,1-dimethyl-allyl)-mlonic acid dimethyl ester (**12A**)*. R$_f$ 0.42; IR, υ/cm^{-1} : 2955 (w), 1736 (s), 1435 (m), 1245 (m), 1142 (s), 1220 (m); ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 6.01 (*dd,* 1H, *J* = 17.2, 10.8 Hz, C*H*=CH$_2$), 5.00 (*d,* 1H,*J* = 17.2 Hz, CH=C*H*$_2$), 4.98 (*d,* 1H, *J* = 10.8 Hz, CH=C*H*$_2$), 3.66 (*s*, 6H, OC*H*$_3$), 3.34 (*s*, 1H, C*H*COOCH$_3$), 1.19 (*s,* 6H, *C*(C*H*$_3$)$_2$); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ (ppm): 169.0 (*C*=O), 144.9 (=*C*H), 112.6 (=*C*H$_2$), 60.5 (*C*HCO), 52.2 (O*C*H$_3$), 39.2 (*C*), 25.3(*C*H$_3$); microanalytical data: C calculated 59.98, found 59.93, H Calculated 8.05, found 8.07.

I.4. Reaction of (π-cyclohexenyl)dicarbonylnitrosyl iron with dimethyl malonate

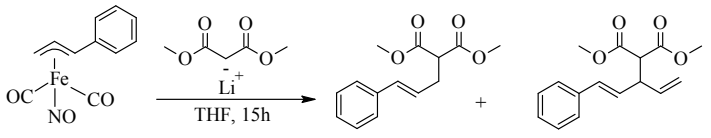


(5) (13)

*2-Cyclohex-2-enyl-malonic acid dimethyl ester (**13**)*. Colourless liquid, R$_f$ 0.34; yield: 77%; IR, υ/cm^{-1}: 2952 (w), 1731 (s), 1650 (w), 1434 (m), 1326 (w), 1249 (m), 1195 (m), 1141 (s), 1018 (m); ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 5.74 –5.81 (*m*, 1H, CH$_2$C*H*=CH), 5.51 (*d*, 1H,

J = 10.5 Hz, $CH_2CH{=}CH$), 3.74 (*s*, 6H, OCH_3), 3.29 (*d*, 1H, *J* = 9.48 Hz, $CHCOOCH_3$), 2.85–2.96 (*m*, 1H, $CH{=}CHCHCH_2$),1.95–2.04 (*m*, 2H, CH_2), 1.72–1.82 (*m*, 2H, CH_2), 1.53–1.59 (*m*, 2H, CH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$)δ (ppm): 169.2 (C=O), 131.1, 127.5 (=CH), 57.2 (CHCO), 52.6 (OCH_3), 35.4 (CH), 26.8, 25.0, 21.2 (CH_2); microanalytical data: C calculated 62.25, found 62.21, H calculated 7.60, found 7.63.

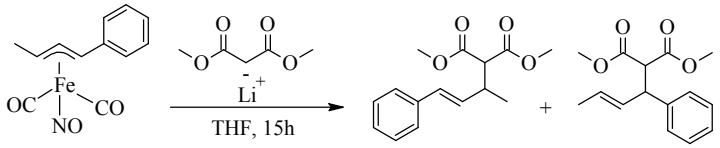
I.5. Reaction of (1-phenyl-π-allyl)dicarbonylnitrosyl iron with dimethyl malonate



The capillary gas chromatography of the product indicated that regioisomeric ratio of linear and branched was 100:0. The resulting crude product was column chromatographed on silica gel using isohexane/diethyl ether (6:1).

*2-(3-Phenyl-propenyl)-malonic acid dimethyl ester (**14**)*. Colourless liquid, R_f 0.52; yield: 80%; IR, υ/cm^{-1}: 2954 (w), 2848 (w), 1732 (s), 1650 (w), 1494 (w), 1435 (m), 1337 (w), 1231 (m), 1154 (m), 1025 (w), 968 (w), 747 (w), 696 (w); ^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm): 7.21–7.35 (*m*, 5H, Ar–*H*), 6.48 (*d*, 1H, *J* = 15.7 Hz, Ar–C*H*=CH), 6.14 (*dt*, 1H, *J* = 7.14, 15.5 Hz, Ar–CH=C*H*), 3.74 (*s*, 6H, OCH_3), 3.53 (*t*, 1H, *J* = 7.90 Hz, C*H*$COOCH_3$) 2.81 (*m*, 2H, $=CHCH_2$); ^{13}C NMR (75.4 MHz, $CDCl_3$)*δ* (ppm): 169.1 (*C*=O), 136.6, 132.9, 128.2, 127.1, 126.0, 125.2 (Ar*C*H& =*C*H), 51.7 (*C*HCO), 52.6 (OCH_3), 32.4 (CH_2); microanalytical data: C calculated 67.73, found 67.70, H calculated 6.50, found 6.52.

I.6. Reaction of (phenyl-methyl-π-allyl)dicarbonylnitrosyl iron with dimethyl malonate

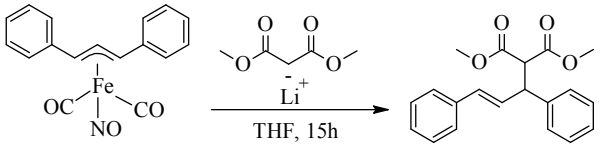


Single isomer was obtained in good yield that was purified by column chromatographed on silica gel using isohexane/diethyl ether (8:1).

*2-(1-Methyl-3-phenyl-allyl)-malonic acid dimethyl ester (**15**)*. Colourless oil, R_f 0.30; yield: 62%; IR, υ/cm^{-1}: 3027 (w), 2953 (w), 1733 (s), 1668 (w), 1609 (w), 1493 (w), 1449 (w), 1434 (m), 1246 (m), 1192 (m), 1155 (m), 1070 (w), 1020 (m), 967 (m), 747 (s), 692 (s); ^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm): 7.21–7.40 (*m*, 5H, Ar–*H*), 6.45 (*d*, 1H, *J* = 15.76 Hz, Ar–C*H*=CH),6.12 (*dd*, 1H, *J* = 8.54, 15.83 Hz, ArCH=C*H*), 3.74 (*s*, 3H, OCH_3), 3.67(*s*, 3H, OCH_3), 3.40 (*d*, 1H, *J* = 8.98 Hz, C*H*$COOCH_3$), 3.06–3.18(*m*, 1H, CH=CHC*H*), 1.19 (*d*, 3H, J = 6.79 Hz, $-CH_3$) ; ^{13}C NMR (75.4 MHz, $CDCl_3$) *δ* (ppm): 168.50 (*C*=O), 131.09, 128.39, 127.65,

127.28, 126.16, (Ar<u>C</u>H and =<u>C</u>H), 57.70 (<u>C</u>HCO), 52.30, 52.22 (O<u>C</u>H$_3$), 37.62 (<u>C</u>HCH$_3$), 18.37 (<u>C</u>H$_3$); microanalytical data: C calculated 68.68, found 68.72, H calculated 6.92, found 6.87.

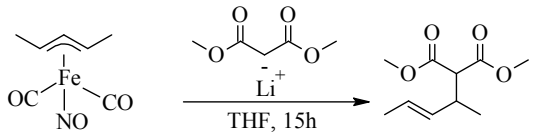
I.7. Reaction of (1,3-diphenyl-π-allyl)dicarbonylnitrosyl iron with dimethyl malonate



(8) (16)

*2-(1,3-Diphenyl-allyl)-malonic acid dimethyl ester (**16**)*. Colourless oil, R_f 0.62, yield: 58%; IR, υ/cm^{-1}: 1765 (s), 1741 (s), 1604 (w), 1495 (m), 1460 (m), 1439 (s), 1325 (m), 1267 (s), 1171 (s), 1022 (w), 965 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.20–7.35 (*m*, 10H, Ar–*H*), 6.49 (*d*, 1H, *J* = 15.9 Hz, Ar–C*H*=CH),6.33 (*dd*, 1H, *J* = 8.4, 15.9 Hz, ArCH=C*H*), 4.27 (*dd*, 1H, *J* = 11.1, 8.4 Hz, ArC*H*CH(COOCH$_3$)$_2$), 3.96 (*d*, 1H, *J* = 11.1 Hz, C*H*(COOCH$_3$)$_2$), 3.70 (*s*, 3H, OC*H*$_3$), 3.53 (*s*, 3H, OC*H*$_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$)δ (ppm): 168.1, 167.8 (*C*=O),140.1, 136.6 131.5, 129.63, 129.0, 128.4, 127.65, 127.6, 127.2, 126.8,126.3 (Ar*C*H and =*C*H), 57.4 (*C*HCO), 52.4 (O*C*H$_3$), 52.22 (O*C*H$_3$), 49.1 (*C*H); microanalytical data: C calculated 74.06, found 74.09, H calculated 6.21, found 6.19.

I.8. Reaction of (1,3-dimethyl-π-allyl)dicarbonylnitrosyl iron with dimethyl malonate



(9) (17)

*Methyl(R)-2-carbomethoxy-3-methylhex-4-enoate (**17**)*. Colourless oil, R_f 0.41, yield: 78%; IR, υ/cm^{-1}: 3031 (w), 2953 (w), 2881 (w), 1731(s), 1435 (s); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 5.28–5.58 (*m*, 2H, CH$_3$C*H*=C*H*), 3.73 (*s*, 3H, OC*H*$_3$), 3.70 (*s*, 3H, OC*H*$_3$), 3.27 (*d*, 1H, *J* = 9.1 Hz, C*H*(COOCH$_3$)$_2$), 2.80–2.98 (*m*, 1H, CH$_3$C*H*(COOCH$_3$)$_2$),1.64 (*d*, 3H, *J* = 6.2 Hz C*H*$_3$CH=CH), 1.06 (*d*, 3H, *J* = 6.8 Hz, C*H*$_3$CHCH(COOCH$_3$)$_2$); ^{13}C NMR (75.4 MHz, $CDCl_3$)δ (ppm): 168.3, 168.77 (*C*=O), 132.22, 126.31 (=*C*H), 57.96 (*C*HCO), 52.29 (O*C*H$_3$), 52.18 (O*C*H$_3$), 37.39 (*C*HCH$_3$),18.51 (*C*H$_3$), 17.84 (*C*H$_3$); microanalytical data: C calculated 59.98, found 59.93, H calculated 8.05, found 8.01.

*II. Reactions of (η^3-allyl)dicarbonylnitrosyl iron (**1–9**) complexes with diisobutyl malonate*

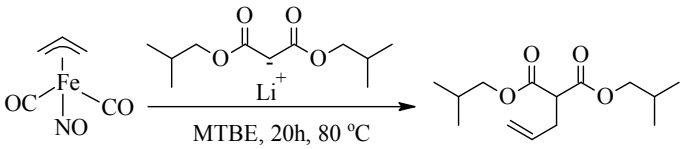
General method of the reactions of (π-allyl)dicarbonylnitrosyl iron (**1–7**, **9**) with di-iso-butyl malonate is described as under.

General method (II)

Oven dried 10 mL Schlenk tube having a stirring bead was charged with lithium hydride (8.0 mg, 1 mmol) at room temperature. Then 1 mL of dry THF was added and stirred for 2 min at room temperature followed by cooling it to 0 °C. At this temperature di-iso-butyl malonate (216

μL, 1 mmol) was then added and the suspension was re-stirred at this temperature for 30 min at 0 °C. Finally, it was stirred again for further 30 min at room temperature. This freshly lithium salt of di-iso-butyl malonate was added to a 1mmol solution of the respective (η^3-allyl)-dicarbonylnitrosyl iron (**1–7**, **9**) complexes in 10 mL dry methyl-tert-butyl ether (MTBE) under nitrogen in a 50 mL Schlenk flask. The Schlenk flask was closed and the reaction mixture was heated to 80 °C for 20 h. During this course, % conversion with respect to lithium salt of di-iso-butyl malonate was checked by GC analysis after three, five and twenty hours. After 20 h reaction mixture was cooled to room temperature, acidified with 4 M hydrochloric acid and extracted with diethyl ether. The combined ethereal extracts was washed with distilled water, dried over mixture of sodium sulphate and charcoal (1:1), filtered. The resulting crude products (**18–25**) was column chromatographed on silica gel using petroleum ether/diethyl ether as eluent and the products was characterized by IR, ^{1}H NMR, ^{13}C NMR , GC/MASS and HRMS.

II.1. Reaction of (π-allyl)dicarbonylnitrosyl iron with diisobutyl malonate

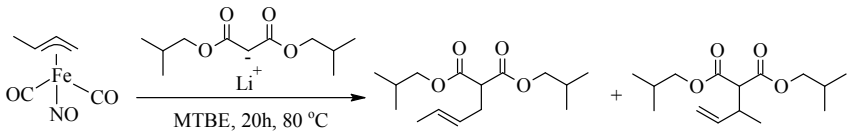


(1) (18)

The resulting crude yellowish oil was purified by column chromatography on silica gel. Elution with petroleum ether/ethyl acetate (5:1) gave the product.

*2-Allyl-di-iso-butyl malonate (**18**)*. Colourless oil, R_f 0.70, yield: 80%; IR, υ/cm^{-1}: 2963 (m), 2876 (w), 1735 (vs), 1644 (w), 1470 (w), 1378 (w), 1333 (w), 1271 (m), 1234 (m), 1152 (m), 1056 (w), 1022 (w), 918 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.79 (*tdd*,1H, J = 17.4,10.2, 6.7 Hz, 1H CH_2=C*H*), 5.16–5.14 (*m*, 2H, =CH_2), 3.97–3.87 (*m*, 4H, CH_2CH(CH_3)$_2$), 3.47 (*t*, J = 7.5 Hz, 1H, O(O)CC*H*C(O)O), 2.69–2.63 (*m*, 2H, CH_2), 2.01–1.85 (*m*, 2H, CH_2C*H*(CH_3)$_2$), 0.93 (*d*, J = 6.7 Hz, 12H, CH_2CH(CH_3)$_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm): 169.0 (*C*=O), 134.1 (=*C*H), 117.5 (=*C*H_2), 71.4 (O*C*H_2), 51.8 (*C*HCO), 32.8 (*C*H_2), 27.7 (*C*H(CH_3)$_2$), 19.0 (CH(*C*H_3)$_2$); GC/MS (EI, 70 eV) *m/z* (%): 256 (11) [M^+], 200 (30) [MH^+ –$CH_2CH(CH_3)_2$], 183 (5) [M^+–$OCH_2CH(CH_3)_2$], 155 (6) [M^+–C(O)$OCH_2CH(CH_3)_2$], 144 (100) [MH_2^+ –$CH_2CH(CH_3)_2$–$CH_2CH(CH_3)_2$], 127 (66) [MH^+–$CH_2CH(CH_3)_2$–$OCH_2CH(CH_3)_2$], 98 (57) [M^+–C(O)$OCH_2CH(CH_3)_2$–$CH_2CH(CH_3)_2$], 57 (95) [$CH_2CH(CH_3)_2^+$], 41 (28) [$CH_2CH{=}CH_2^+$]; HRMS data: $C_{14}H_{24}O_4$, calculated 256.1675, found 256.1666.

II.2. Reaction of (1-methyl-π-allyl)dicarbonylnitrosyl iron with diisobutyl malonate



(2) (19) (19A)

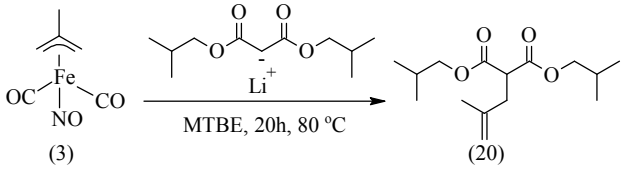
75 : 25

The resulting crude yellowish oil was purified by column chromatographed using petroleum ether/diethyl ether (5:1) as eluent (yield: 81%). The resulting product was a mixture of two isomers linear and branced (75:25) as determined by capillary gas chromatography.

*(a) Linear isomer 2-((E)-but-2enyl)-di-iso-butyl malonate (**19**)*. R_f 0.75; IR, υ/cm^{-1}: 2962 (m), 2876 (w), 2358 (w), 1735 (vs), 1470 (w), 1378 (w), 1332 (w), 1266 (w), 1226 (m), 1150 (m), 1020 (w), 967 (w); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 5.61–5.49 (*m*, 1H, CH_3CH=C$\underline{H}$), 5.34–5.33 (*m*, 1H, $CH_3C\underline{H}$=CH), 3.91 (*dd*, *J* = 6.7, 1.5 Hz, 4H, C$\underline{H}_2$CH$(CH_3)_2$), 3.41 (*t*,*J* = 7.7 Hz, 1H, OOCC$\underline{H}$COO), 2.61 –*2*.56 (*m*, 2H, C$\underline{H}_2$), 2.00–1.87 (*m*, 2H, $(CH_3)_2C\underline{H}CH_2$),1.63 (*dd*, *J* = 6.2, 1.3 Hz, 3H, =CHC$\underline{H}_3$), 0.92 (*d*, *J* = 6.7 Hz, 12 H, $CH_2CH(C\underline{H}_3)_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm): 169.2 (C=O), 128.3, 126.6 (=CH), 71.4 (O$\underline{C}H_2$),52.3 ($\underline{C}$HCO), 31.9 ($\underline{C}H_2$), 27.7 ($\underline{C}H(CH_3)_2$),19.0 (CH($\underline{C}H_3)_2$), 17.9 ($\underline{C}H_3$); GC/MS (EI, 70eV) *m/z* (%): 270 (33) [M^+], 214 (16) [M^+ –$CH_2CH(CH_3)_2$], 158 (59) [M^+–CH_2CH=$CHCH_3$–$CH_2CH(CH_3)_2$], 141 (30) [M^+–$CH_2CH(CH_3)_2$–$CH_2CH(CH_3)_2$–CH_3], 112 (100) [M^+ –$CH_2CH(CH_3)_2$–C(O)O$CH_2CH(CH_3)_2$], 57 (50) [$CH_2CH(CH_3)_2^+$]; HRMS: $C_{15}H_{26}O_4$, calculated 270.1831, found 270.1836.

*(b) Branched isomer 2-(but-3en-2yl)-di-iso-butyl malonate (**19A**)*. R_f 0.72; IR, υ/cm^{-1}: 2962 (s), 2876 (w), 1734(s), 1470 (m), 1377 (m), 1147 (s), 1015 (m), 916 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.86–5.74 (*m,* 1H, C$\underline{H}$=CH_2), 5.13 – 5.00 (*m,* 2H, CH=C$\underline{H}_2$), 3.93–3.87 (*m*, 4H, $CH_2CH(CH_3)_2$), 3.32 (*d*, *J* = 8.7 Hz, 1H, OOCC$\underline{H}$COO), 3.03–2.90 (*m*, 1H, CH_3CH), 2.01–1.86 (*m,* 2H, $CH_2C\underline{H}(CH_3)_2$), 1.12 (*d, J* = 6.5 Hz, 3H, =CHCHC$\underline{H}_3$), 0.92 (*d*, *J* = 6.9 Hz, 12H, $CH_2CH(C\underline{H}_3)_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm): 168.4, 168.3 ($\underline{C}$=O), 139.9 (=$\underline{C}$H), 115.4 (=$\underline{C}H_2$), 71.4, 71.3 (O$\underline{C}H_2$), 57.9 ($\underline{C}$HCO), 37.9 ($\underline{C}HCH_3$), 27.6 ($\underline{C}H(CH_3)_2$), 19.0 (CH($\underline{C}H_3)_2$), 18.0 ($\underline{C}H_3$); GC/MS (EI, 70eV) *m/z* (%) : 284 (22) [M^+], 211 (7) [M^+ –$OCH_2CH(CH_3)_2$], 183 (20) [M^+–O$COCH_2CH(CH_3)_2$], 155 (20), 69 (100) [$(CH_3)_2$–CCH=CH_2^+], 57 (46) [$CH_2CH(CH_3)_2^+$]; HRMS: $C_{14}H_{24}O_4$, calculated 270.1831, found 270.1825.

II.3. Reaction of (2-methyl-π-allyl)dicarbonylnitrosyl iron with diisobutyl malonate

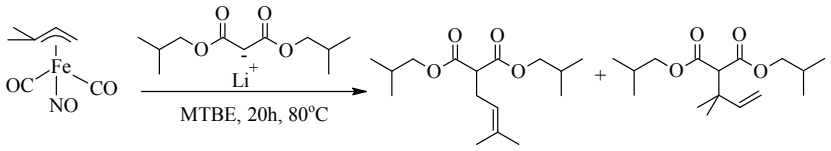


(3) (20)

The resulting crude yellowish oil was purified by column chromatography on silica gel. Elution with done with petroleum ether / ethyl acetate (10:1).

*2-(Prop-1-en-2-yl)-iso-butyl malonate (**20**)*. colourless oil, R_f 0.50, yield: 70%; IR, υ/cm^{-1}: 3081 (w), 2963 (m), 2876 (w), 2358 (w), 1735 (vs), 1652 (w), 1470 (w), 1286 (m), 1225 (m), 1149 (s), 1015 (w), 942 (vw), 895 (w); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 4.76 (*d*, *J* = 16.3 Hz, 2H, =C$\underline{H}_2$), 3.93–3.90 (*m*, 4H, C$\underline{H}_2$CH$(CH_3)_2$), 3.62 (*t*, *J* = 7.8 Hz, 1H, OOCC$\underline{H}$COO), 2.62 (*dd*, *J* = 7.7 Hz, 2H, CH_2=CCH_2) 2.03 – 1.87 (*m*, 2H, $(CH_3)_2C\underline{H}CH_2$),1.76 (*s*, 3H, CH_2=CC$\underline{H}_3$), 0.93 (*d*, *J* = 6.7 Hz, 12 H, $CH_2CH(C\underline{H}_3)_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm): 169.2 ($\underline{C}$=O), 141.7 (=$\underline{C}$), 112.2 (=$\underline{C}H_2$), 71.5 (O$\underline{C}H_2$), 50.6 ($\underline{C}$HCO), 36.5 ($\underline{C}H_2$), 27.7 ($\underline{C}H(CH_3)_2$), 22.3 ($\underline{C}H_3$), 19.0 (CH($\underline{C}H_3)_2$); GC/MS (EI, 70 eV) *m/z* (%): 270 (24) [M^+], 197 (4) [M^+ –$OCH_2CH(CH_3)_2$], 169 (20) [M^+–C(O)O$CH_2CH(CH_3)_2$], 141 (27) [M^+ –$CH_2CH(CH_3)_2$–$CH_2CH(CH_3)_2$–CH_3], 114 (100) [M^+ –C(O)O$CH_2CH(CH_3)_2$–C_4H_7], 57 (65) [$CH_2CH(CH_3)_2^+$]; HRMS: $C_{15}H_{26}O_4$, calculated 270.1831, found 270.1826.

II.4. Reaction of (1,1-dimethyl-π-allyl)dicarbonylnitrosyl iron with diisobutyl malonate



(4) (21) (21A)

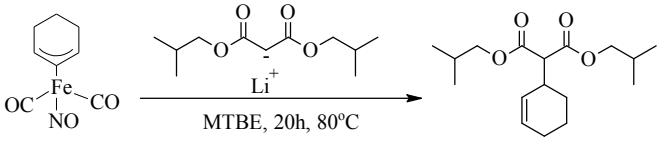
93 : 7

GC analysis indicated that reaction mixture contained two isomers linear and branched (93:7). The resulting crude yellowish oil was purified by column chromatography using petroleum ether /diethyl ether (5:1) (yield: 80 %) and it was the mixture of two isomers linear and branced.

*(a) Linear isomer 2-(3-methyl-but-3-enyl)-di-iso-butyl malonate (**21**)*. R_f 0.78; IR, υ/cm^{-1}: 2962 (m), 2875 (w), 1732 (s), 1470 (m), 1377 (m), 1330 (m), 1269 (m), 1236 (m) 1211 (m), 1145 (s), 1033 (m), 980 (m), 943 (w), 825 (w), 781 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm): 5.07 (*t*, *J* = 7.5 Hz, 1H, C=C*H*), 3.90 (*d*, *J* = 6.6 Hz, 4H, CH_2CH(CH$_3$)$_2$), 3.36 (*t*, *J* = 7.6 Hz, 1H, OOCC*H*COO), 2.60 (*t*, *J* = 7.5 Hz, 2H, =CHCH_2) 1.99–1.88 (*m*, 2H, (CH$_3$)$_2$C*H*CH$_2$), 1.67 (*s*, 3H, =CCH_3), 1.63 (*s*, 3H, =CCH_3), 0.92 (*d*, *J* = 6.8 Hz, 12 H, CH$_2$CH(CH_3)$_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$)δ (ppm): 169.4 (*C*=O), 134.9 (=*C*), 119.8 (=*C*H), 71.3 (O*C*H$_2$), 52.3 (*C*HCO), 27.7, 27.6 (*C*H(CH$_3$)$_2$), 25.8 (*C*H$_2$), 19.0 (CH(*C*H$_3$)$_2$), 17.8 (*C*H$_3$); GC/MS (EI, 70 eV) *m/z* (%): 284 (43) [M$^+$], 229 (2) [M$^+$ –CH=C(CH$_3$)$_2$], 211 (10) [M$^+$–OCH$_2$CH(CH$_3$)$_2$], 172 (14) [M$^+$ –CH=C(CH$_3$)$_2$–CH$_2$CH(CH$_3$)$_2$], 126 (100) [M$^+$–CH$_2$CH(CH$_3$)$_2$–C(O)OCH$_2$CH(CH$_3$)$_2$], 69 (33) [CH$_2$CH=C(CH$_3$)$_2^+$],57 (42) [CH$_2$CH(CH$_3$)$_2^+$]; HRMS: $C_{16}H_{28}O_4$, calculated 284.1988, found 284.1990.

*(b) Branched isomer 2-(2-dimethyl-allyl)-di-iso-butyl malonate (**21A**)*. R_f 0.42; IR, υ/cm^{-1}: 2962 (m), 2876 (m), 1754 (m), 1731 (s), 1470 (m), 1369 (w), 1321 (m), 1238 (m), 1215 (m), 1129 (s), 1021 (m), 968 (w), 915 (m), 679 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm): 6.05 (*dd, J* = 17.2, 10.8 Hz, 1H, C*H*=CH$_2$), 5.05–5.00 (*m*, 2H, =CH_2), 3.91–3.85 (*m*, 4H, CH_2CH(CH$_3$)$_2$), 3.38 (*s*, 1H, OOCC*H*COO), 1.96–1.88 (*m*, 2H, (CH$_3$)$_2$C*H*CH$_2$), 1.25 (*s*, 6H, =CCH_3), 0.92 (*d*, *J* = 6.9 Hz, 12 H, CH$_2$CH(CH_3)$_2$); ^{13}C NMR (75.4 MHz, $CDCl_3$)δ (ppm): 168.1 (*C*=O), 145.0 (=*C*H), 112.2 (=*C*H$_2$), 71.2 (O*C*H$_2$) 61.1 (*C*HCO), 38.8 (*C*(CH$_3$)$_2$), 27.6 (*C*H(CH$_3$)$_2$), 25.2 (C(*C*H$_3$)$_2$), 19.1 (CH(*C*H$_3$)$_2$); GC/MS (EI, 70eV) *m/z* (%) : 284 (22) [M$^+$], 211 (7) [M$^+$–OCH$_2$CH(CH$_3$)$_2$], 183 (20) [M$^+$ –OCOCH$_2$CH(CH$_3$)$_2$], 155 (20), 69 (100) [(CH$_3$)$_2$CCH=CH$_2^+$], 57 (46) [CH$_2$CH(CH$_3$)$_2^+$]; HRMS: $C_{16}H_{28}O_4$, calculated 284.1988, found 284.1982.

II.5. Reaction of (π-cyclohexenyl)dicarbonylnitrosyl iron with diisobutyl malonate

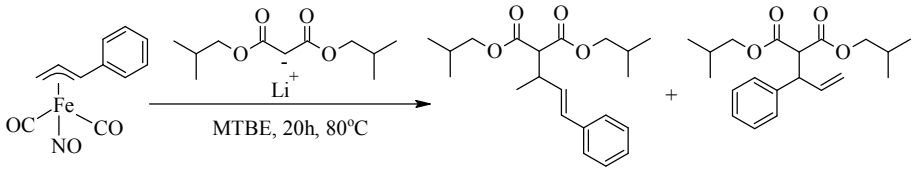


(5) (22)

The resulting crude yellowish oil was purified by column chromatography using petroleum ether/ethyl acetate (10:1) system.

*2-(Cyclohex-2-enyl)-di-iso-butyl malonate (**22**)*. Colourless oil, R_f 0.62, yield: 54%; IR, υ/cm^{-1}: 2975 (m), 2942 (m), 1758 (vs), 1752 (vs), 1472 (w), 1482 (w), 1321 (m), 1195 (s),1011 (m), 762 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 5.79–5.74 (*m*, 1H, CHC*H*$_2$=CH$_2$),5.59–5.54 (*m*, 1H, CHCH$_2$=C*H*$_2$), 3.94–3.91 (*m*, 4H, C*H*$_2$CH(CH$_3$)$_2$), 3.29 (*d*, *J* = 9.4 Hz, 1H, OOCC*H*COO), 2.96–2.86 (*m*, 1H, C*H*CH$_2$=CH$_2$) 2.03–1.88 (*m*, 4H, C*H*$_3$and (CH$_3$)$_2$C*H*CH$_2$), 1.85–1.67 (*m*, 2H, CH$_2$), 1.63–1.51 (*m*, 1H, C*H*$_2$), 1.45–1.35 (*m*, 1H, C*H*$_2$), 0.93 (*d*, *J* = 6.8 Hz, 12 H, CH$_2$CH(C*H*$_3$)$_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$)δ (ppm): 168.8, 168.7 (*C*=O), 129.6, 127.8 (=*C*H), 71.5 (O*C*H$_2$), 57.5 (*C*HCO), 35.4 (*C*H), 27.8 (*C*H(CH$_3$)$_2$), 26.9, 25.1, 21.1 (*C*H$_2$), 19.2 (CH(*C*H$_3$)$_2$); GC/MS (EI, 70 eV) *m/z* (%): 296 (23) [M$^+$], 240 (10) [MH$^+$–CH$_2$CH(CH$_3$)$_2$], 223 (8) [M$^+$–OCH$_2$CH(CH$_3$)$_2$], 194 (46) [M$^+$–C(O)OCH$_2$CH(CH$_3$)$_2$], 184 (16) [MH$_2^+$ –CH$_2$CH(CH$_3$)$_2$–CH$_2$CH(CH$_3$)$_2$], 138 (100) [M$^+$–CH$_2$CH(CH$_3$)$_2$–C(O)OCH$_2$CH(CH$_3$)$_2$], 81 (22) [M$^+$–H(COO*i*-Bu)$_2$], 57 (15) [CH$_2$CH(CH$_3$)$_2^+$]; HRMS: $C_{17}H_{28}O_4$, calculated 296.1988, found 284.1995.

II.6. Reaction of (1-phenyl-π-allyl)dicarbonylnitrosyl iron with diisobutyl malonate



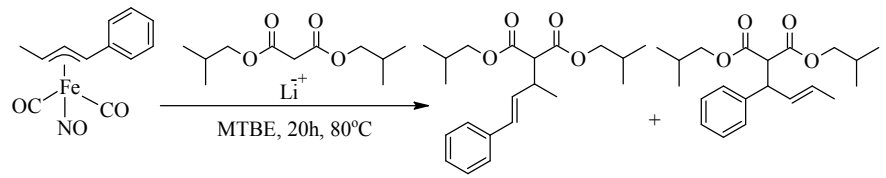
(6) (23) (23A)

98 : 2

GC analysis revealed that reaction mixture contained two isomers linear and branched in the ratio of 98:2. The resulting crude oil was purified by column chromatography using petroleum ether/ethyl acetate (9:1) as eluent.

2-cinnamyl-di-iso-butyl malonate (23). Colourless oil, R_f 0.41, yield: 62%; IR, υ/cm^{-1}: 2961 (m), 2875 (w), 1731 (vs), 1469 (m), 1331 (m), 1263 (m), 1223 (s), 1149 (s), 1021 (m), 966 (m), 745 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.34–7.16 (*m*, 5H, Aryl-*H*), 6.48 (*d*, *J* = 15.8 Hz, 1H, Ar-CH), 6.16 (*td*, *J* = 15.8 Hz, 1H, Ar-CH=C*H*), 3.98–3.87 (*m*, 4H, C*H*$_2$CH(CH$_3$)$_2$), 3.54 (*t*, *J* = 7.5 Hz, 1H, O(O)CC*H*C(O)O), 2.85–2.79 (*m*, 2H, Ar-CH=CHC*H*$_2$) 2.01–1.87 (*m*, 1H, (CH$_3$)$_2$C*H*CH$_2$),0.92 (*d*, *J* = 6.7 Hz, 12 H, CH$_2$CH(C*H*$_3$)$_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$)δ (ppm): 169.0 (*C*=O),137.0, 132.8, 128.5, 127.4, 126.2, 125.6 (Ar and =*C*H), 71.5 (O*C*H$_2$), 52.1 (*C*HCO), 32.2 (*C*H$_2$), 27.7 (*C*H(CH$_3$)$_2$), 19.0 (CH(*C*H$_3$)$_2$); GC/MS (EI, 70eV) *m/z* (%) : 333 (100) [MH$^+$], 317 (2) [M$^+$–CH$_3$], 277 (22) [MH$_2^+$–CH$_2$CH(CH$_3$)$_2$], 230 (16) [MH$^+$–PhCH=CH], 174 (15) [M$^+$–C(O)OCH$_2$CH(CH$_3$)$_2$–CH$_2$CH(CH$_3$)$_2$], 129 (13) [MH$^+$ –C(O)OCH$_2$CH(CH$_3$)$_2$–PhCH=CH], 117 (30) [PhCH=CHCH$_2^+$], 57 (8) [CH$_2$CH(CH$_3$)$_2^+$]; HRMS: $C_{17}H_{28}O_4$, calculated 332.1988, found 332.1991.

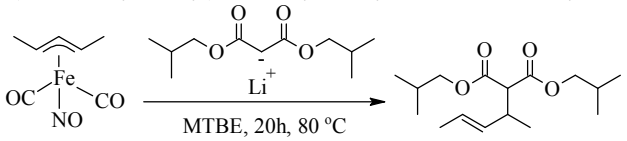
II.7. Reaction of (phenyl-methyl-π-allyl)dicarbonylnitrosyl iron with diisobutyl malonate



(7) (24) (24A)

It was indicated by GC analysis that conversion rate and % conversion was very low and also observed that the product might be a mixture of two regioisomers that could not be separated and purified by column chromatography and hence could not be characterized further.

II.8. Reaction of (1,3-dimethyl-π-allyl)dicarbonylnitrosyl iron with diisobutyl malonate



(9) (25)

The resulting crude yellowish oil was purified by column chromatography on silica gel. Elution was carried out with petroleum ether/ethyl acetate (9:1).

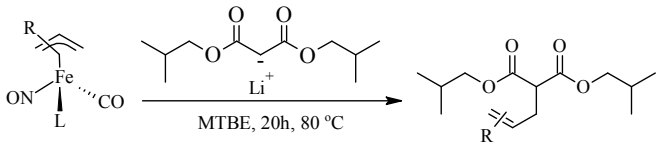
*2-(2-Pent-3-en-2-yl)-di-iso-butyl malonate (**25**)*. Colourless oil, R_f 0.42, yield: 32%; IR, υ/cm^{-1}: 2962 (m), 2876 (w), 1753 (m), 1733 (s),1470 (m), 1394 (w), 1377 (m), 1284 (m), 1242 (m),1171 (m), 1145 (s), 1053 (w), 1014 (m), 966 (m), 944 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.55–5.48 (*m*, 1H, CH_3CH=C*H*), 5.40–5.35 (*m*, 1H, CH_3CH=CH), 3.94–3.84 (*m*, 4H, $CH_2CH(CH_3)_2$), 3.27 (*d*,*J* = 9.2 Hz, 1H, OOCC*H*COO), 2.94–*2*.87 (*m*, 1H, CH_3CH), 1.98–1.88 (*m*, 2H, $(CH_3)_2CHCH_2$),1.62 (*dd*, *J* = 6.2, 1.3 Hz, 3H,CH=CHCH_3), 1.08 (*d*, *J* = 6.8, 3H, CHCH_3),0.93 (*d*, *J* = 7.0 Hz, 6 H, $CH_2CH(CH_3)_2$),0.92 (*d*, *J* = 7.0 Hz, 6 H, $CH_2CH(CH_3)_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$)δ (ppm): 168.6, 168.5 (*C*=O), 132.6, 126.1 (=*C*H), 71.3, 71.2 (O*C*H_2), 58.4 (*C*HCO), 37.2 (*C*HCH_3), 27.7, 27.6 (*C*$H(CH_3)_2$),19.0 ($CH(CH_3)_2$), 18.7, 17.9 (*C*H_3); GC/MS (EI, 70eV) *m/z* (%): 284 (14) [M^+], 173 (57) [MH^+ –$CH(CH_3)_2$–$(CH_3)CHCH$=$CHCH_3$], 155 (46) [MH^+–$OCH_2CH(CH_3)_2$–$CH_2CH(CH_3)_2$], 137 (100) [M^+ –$OCH_2CH(CH_3)_2$–$OCH_2CH(CH_3)_2$], 127 (43) [MH^+ –$C(O)OCH_2CH(CH_3)_2$–$CH_2CH(CH_3)_2$], 111 (37) [M^+ –$C(O)OCH_2CH(CH_3)_2$–$OCH_2CH(CH_3)_2$], 82 (4) [M^+ –$C(O)OCH_2CH(CH_3)_2$–$C(O)OCH_2CH(CH_3)_2$]; HRMS: $C_{16}H_{28}O_4$, calculated 284.1988, found 284.1995.

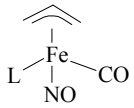
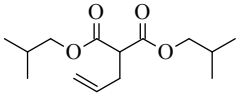
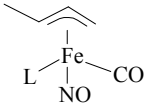
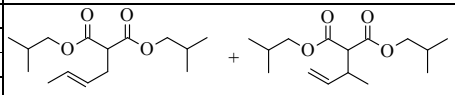
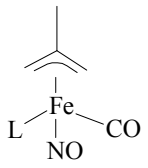
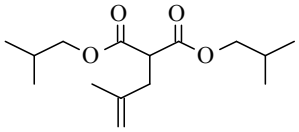
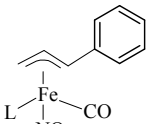
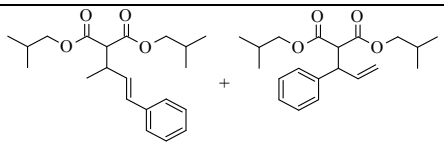
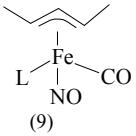
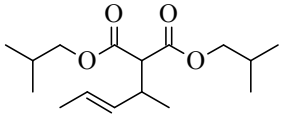
III. Effect of different ligand on stoichiometric reaction of allyl iron complexes with nucleophiles

General procedure (III)

10 mL Schlenk tubes was separately charged at room temperature with different ligands such as triphenylphosphine (26.2 mg, 0.1 mmol), 1,3-di-tert-butylimidazolium hexafluoro phosphate SIMES*PF_6 (45.2 mg, 0.1 mmol), 1,3-Bis(2,4,6-trimethyl-phenyl)-4,5-dihydro-3H-imidazol-1-ium hexafluorophosphate BUSI*PF_6 (33.6 mg, 0.1 mmol) under nitrogen atmosphere. Then dry methyl tert-butyl ether (MTBE) (1 mL) was added. Then Schlenk tube was closed and heated upto 60°C for 1h. After cooling to the room temperature, (π-allyl)dicarbonylnitrosyl iron (**1**) (0.1 mmol) was added, the Schlenk tube was closed and the reaction mixture was again heated to 60 °C for 20 h. After cooling to the room temperature, di-iso-butyl malonate (0.1 mmol) which was freshly deprotonated with 1 equivalent lithium hydride (0.1 mmol) in dry THF (0.5 mL) was added. Again the Schlenk tube was closed and resulting slurry was heated to 80 °C. % conversion and regioisomeric ratio was determined by GC analysis after 20 h and the results are given in Table 1.

Table 1. Effect of different ligands on stoichiometric allylations using performedπ-allyl Fe-complexes.



No.	(π-allyl)Fe(CO)$_2$(NO)	L	a : b	Yield (%)
1.	 (1)	CO	 (18)	80
		PPh_3		12
		SIMES		–
		BUSI		17
2.	 (2)	CO	 (19) 75 : (19A) 25	81
		PPh_3		–
		SIMES		–
		BUSI		25
3.	 (3)	CO	 (20)	68
		PPh_3		–
		SIMES		–
		BUSI		11
4.	 (6)	CO	 (23) 98 : (23A) 2	62
		PPh_3		–
		SIMES		–
		BUSI		8
5.	 (9)	CO	 (25)	32

RESULTS AND DISCUSSION

The reactivity of our earlier reported (η^3-allyl)dicarbonylnitrosyl iron complexes (**1−9**) were studied [12]. These complexes have amphiphilic character and react with nucleophile as well as electrophile. Stoichiometric reactions of (**1−9**) with two nucleophiles like dimethyl malonate and di-iso-butyl malonate were carried out. It has been found that carbon nucleophiles

preferentially reacted with less hindered site of (η^3-allyl)dicarbonylnitrosyl iron complexes (**1−9**). This resulted the corresponding alkylated allyl products formation in high yields. Gas chromatographic analysis of the reaction mixtures were used to determine the regioselectivity of the nucleophilic substitution products (**10−25**). Column chromatography was used for the purification and different techniques like, IR, ^{1}H NMR, ^{13}C NMR spectroscopies and mass spectrometry were used for the characterization of the products. Effect of different ligands L (L = PPh_3, SIMES, BUSI) and structure of allyl moiety on stoichiometric reactions of allyl iron complexes with nucleophiles were also studied and the results are tabulated in the Table 1.

Strong impact on the reactivity of stating bis-carbonyl complexes was observed due to substitution pattern of the allyl moiety. Relying on the substitution pattern loss of reactivity noticed by the introduction of one substituent. A methyl group at C-3 of the allyl ligand has only a slight influence, however, a considerable reduction in the conversion ratio from 81% to 68% (entries 2 and 3, Table 1) resulted in reposition the substituent to C-2 position. Moreover, the substituent's electronic nature assumes a significant partin the reaction. Replacing the substituent from methyl to a phenyl group brings about lost reactivity, the product with only 62% conversion (entry 2 and 4, Table 1) is formed. A much more considerable change was noticed upon the second substituent introduction. Presentation of a methyl or phenyl aggregate at C-3 of the allyl ligand prompt a considerable loss in reactivity or even decomposition (entry 5, Table 1). However, the presentation of an extra methyl group at C-1 of the allyl ligand indicated just a minor impact on the reactivity. A side from the impact on the reactivity, the impact on the regioselective course of the allylation is additionally significant. Though one aliphatic substituent has just a minor effect on the reaction rate with clear inclination for the formation of the linear substitution product and a significant change induced in reactivity due to the position and nature of a second substituent. The presentation of a methyl moiety at C-3 of the allyl ligand brings about a noteworthy decrease in the conversion ratio down to 32% or even to decomposition of the beginning material (entries 5, Table 1). Presentation of an extra substituent at C-1 of the allyl ligand, notwithstanding, brought about a reactive π-allyl Fe-complex that was changed over into suitable product in 89% transformation. The impact of the substitution design on both regioselectivity and reactivity of the reaction is comparable to the impacts seen in π-allyl Pd-chemistry [13, 14]. As can be observed from Table 1, the addition of mono-dentate ligands like triphenylphosphine (PPh_3), 1,3-di-tert-butyl imidazolium hexafluoro-phosphate (SIMES*PF_6), 1,3-bis(2,4,6-trimethyl-phenyl)-4,5-dihydro-3H-imidazole-1-ium-hexafluoro- phosphate (BUSI*PF_6) prompt low or no change instead complex decomposition was seen. These results demonstrate that (η^3-allyl)dicarbonylnitrosyl iron complexes evidence various reactivities, relying on the reaction specifications and the structures of the iron complexes.

CONCLUSION

Stoichiometric reactions of these previously synthesized complexes with various nucleophiles were performed, the regioselectivity of these nucleophilic substitution products were resolved. These results demonstrated that (η^3-allyl)dicarbonylnitrosyl iron complexes eshibited appreciable to good reactivities depending upon the structures of the iron complexes and the reaction specifications. The nature of substituent with reference to their electronic cloud and regioselective course of the allylation have played a significant role in these reactions. The considerable lost in reactivity or even decomposition was observed by repositioning methyl substituent or by replacement of methyl to a phenyl substituent.

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