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Convenient synthesis of dithiafulvene carbene complexes as potential precursors of extended TTF

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Abstract—The condensation of α-carbanion of Fischer-type carbene complex with 2-thiomethyl-1,3-dithiolium salts **1** gave new heterocyclic organometallic carbenes **2** potentially precursors of extended TTF. Reaction of allylic carbanion **4** derived from (methoxypropenyl)pentacarbonyl carbene complex afforded a mixture of monoheterocyclic condensation products **7** and diheterocyclic carbene complexes **8** produced from successive α and γ attacks of the heterocyclic cations.

Activation of acidic hydrogens and stabilization of carbanions are some of the most common properties of electron-withdrawing organometallic fragments.[1] Polyalkylation, and polyfunctionalization were carried out under slightly basic conditions resulting in interesting developments in organic synthesis, for example, a rapid route to dendrimers using the 18 electron cationic complexes $[CpFe\{\eta^6\text{-}C_6H_5\text{–}(CH_3)_6\}]^+$.[2]

In methoxy Fischer-type carbene complexes, an exceptional class of metal carbonyl compounds, which are widely used for organic and organometallic synthetic applications,[3] the electron-accepting pentacarbonylmetal moiety makes the hydrogen α to the carbenic carbon highly acidic[4] ($pK_a = 12.3$ for the (methoxymethyl)pentacarbonylchromium carbene). α-Carbanions can be obtained under different slightly basic conditions.[5] Their reactions with a wide range of electrophiles, including organic[6] and organometallic[7] cyclic cations have proved to proceed easily, leading in some cases to diaddition products.

In this way, we have previously reported that the carbanion obtained from the (methoxymethyl)pentacarbonyl metal carbene complex reacted with aromatic pyrylium salts to give, depending on the heterocyclic ring substitution, highly substituted benzophenones[8] or γ-methylenecarbenecomplexes.[9]

Moreover, the same carbanion condenses with pyranylidene acetaldehydes to give new heterocyclic unsaturated push–pull carbene complexes,[10] some of which could have interesting NLO properties.[11] We have been able to extend the condensation reaction to allylic carbanion produced from the (propenylmethoxy)pentacarbonyltungsten carbene complex and NEt_3. Using this base with heterocyclic aldehydes leads only to the formation of the γ adducts.[10]

As several active methylene compounds have proved for a long time to react with 1,3 dithiolium salts in basic media,[12] we anticipated that using 2-methylthio-1,3-dithiolium cations as electrophiles should provide a convenient route to 1,3-dithiol-2-ylidene carbene complexes. Extension of the organometallic chemistry of the dithiafulvene group, essentially, as far as we know restricted to ferrocene derivatives,[13] is of interest as the carbene complexes of group 6 metal would be potential precursors of extended TTF, bearing electron rich 1,2 dialkoxy ethylene part, by Pd^0 catalytic self dimerization.[14]

In this communication we wish to report reaction of α and allylic carbanions of Fischer carbene complexes

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Keywords: Allylic anion carbene complex; Dithiolium salt; Addition condensation reaction; Extended TTF.

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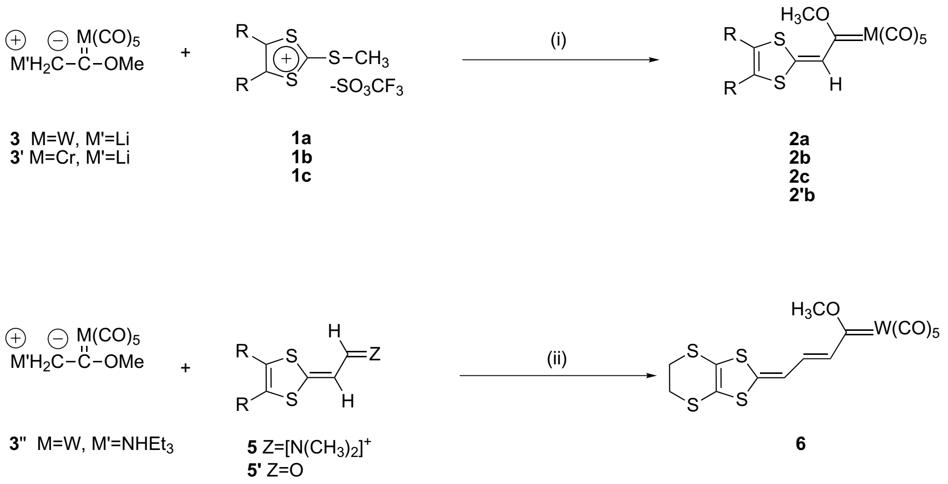


Scheme 1. Reagents and conditions: yield (%): (i) (THF), −78 °C to room temperature (1 h) then hydrolysis; (ii) NEt_3–TMSCl=$Si(CH_3)_3Cl$ (THF), room temperature (1 h). **a**: R = H, **b**: R = CO_2Me, **c**: R = R = S–$(CH_2)_2$–S, **2a** (M = W) (41%), **2b** (M = W) (49%), **2c** (M = W) (68%), **2′b** (M = Cr) (77%), **6** (30% using **5** (Z = $N(CH_3)_2^+$) or 50% using **5′** (Z = O)).

with the strongly electrophilic 1,3 dithiolium salts, which is easily carried out. We have shown that allylic anion carbene complex reaction leads to the unexpected main formation of addition condensation products, produced from successive α and γ carbon reactivity.

Carbanions **3** and **3′** (**3**, M = W; **3′**, M = Cr, M′ = Li), generated from *n*-butyllithium (1 equiv) and the corresponding Fischer carbene complexes reacted with 2-thiomethyl-1,3-dithiolium salts **1a**,**b**,**c**. After hydrolysis and chromatographic purification on silicagel (eluent: light petroleum ether) red (**2a**, **2b**, **2′b**) or pink (**2c**) complexes were obtained in moderate to good yields (Scheme 1).[15]

The formation of organometallic carbenes **2** was the result of carbanion addition to the carbon 2 of the thiolium salt followed by thiomethanol elimination. In addition a reaction between the carbanion **3″** (M = W, M′ = $NHEt_3$) and the heterocyclic iminium salt **5** (Z = $[N(CH_3)_2]^+$) allowed the vinilogous carbene **6** in moderate yield to be obtained. Using aldehyde **5′**[16] (Z=O) in the presence of TMSCl improved the yield. The new complexes were fully characterized by ^1H NMR, ^{13}C NMR and mass spectroscopy. According to the ability of the lone pair electrons on the sulfur atoms to form the partial aromatic stabilized dithiolium structure in the presence of a strong acceptor group, the carbenic carbon resonates at high field (δ ^{13}C for **2a** ($CDCl_3$) = 269.6 ppm)[17] (Fig. 1). It is noteworthy that the two $COOCH_3$ electron-withdrawing groups in **2b** seem to partly offset this effect (δ ^{13}C for **2b** ($CDCl_3$) = 278.0 ppm).

With this result in hand, we next turned our attention to the reactivity of allylic anion **4** towards **1** (Scheme 2). As BuLi adds to the (methoxymethyl)pentacarbonyltungstene carbene in a 1–4 fashion, we decided to use triethylamine as a base in order to form **4**, as previously mentioned.[10] Under these basic conditions, the first attempt with **1a** failed. An inseparable mixture of products was obtained (TLC observation). On the other hand, when the 4 and 5 positions of the heterocycle in **1b** and **1c** were substituted and 2 equiv of NEt_3 were used a cleaner reaction took place with an overall moderate yield (34–47%) leading after chromatographic silicagel separation to the monoheterocyclic carbenes **7**, as

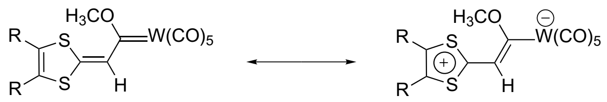
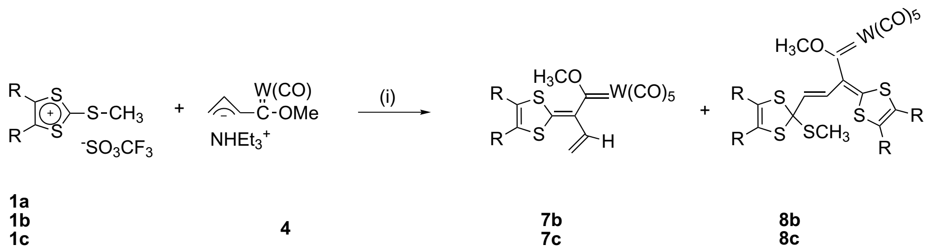
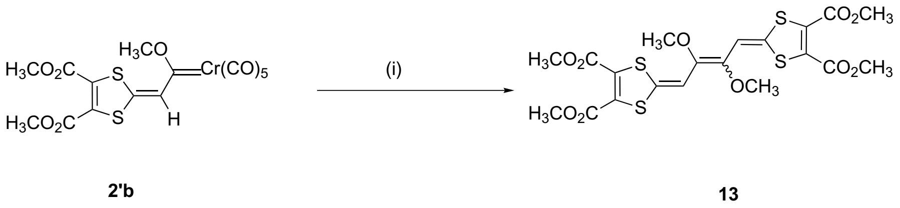


Figure 1.



Scheme 2. Reagents and conditions: yield (%): (i) NEt_3 (THF), room temperature. **a**: R = H, **b**: R = CO_2Me, **c**: R = R = S–$(CH_2)_2$–S, **7b** (16%), **7c** (17%), **8b** (18%), **8c** (30%).



Scheme 3. Reagents and conditions: yield (%): (i) $Pd(PPh_3)_2Cl_2$, NEt_3 (THF); **13** (40%).

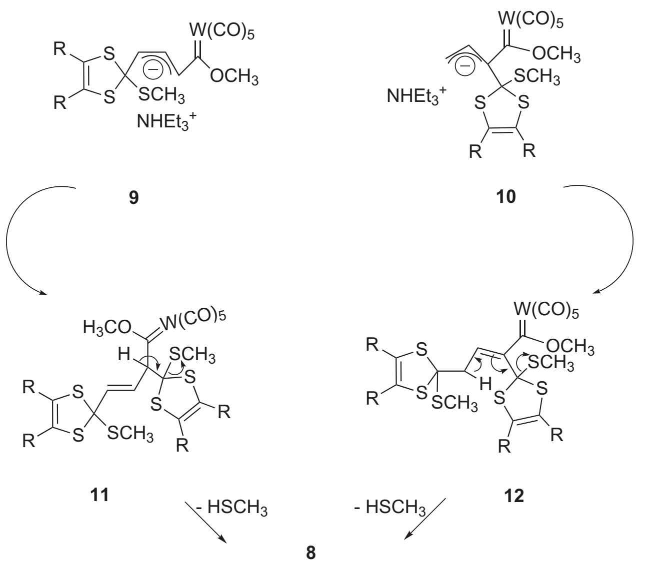


Figure 2. Possible routes for **8** formation.

well as to the diheterocyclic carbenes **8** as the main product (Scheme 2).

The structure of **7** and **8** was confirmed by 2D NMR sequences (HMQC, HMBC, ^{1}H, ^{13}C correlations).[18] In carbene **8b**,**c** the double bound was formed in the *trans* configuration ($J_{HH} > 15\,Hz$). The formation of **7** was the result of the initial attack of the heterocyclic cation to the α carbon of the allylic anion **4**. α-Reactivity is not unprecedented in allylic anion chemistry of Fischer-type complex. Despite steric influence of the metalcarbonyl group, α regioisomer formation predominates in the reaction mixture when RI derivatives are opposed, under kinetic control, to the allylic anion generated by LDA in THF from the (propenylpyronylidino)pentacarbonyl chromium carbene complex.[19] Only the bulky trimethylsilylchloride[19] and nonenolizable aldehydes gave complete γ selectivity.[20]

On the other hand, the formation of **8** is to the best of our knowledge, a more unusual feature in allylic chemistry.[21] Complexes **8** are thought to arise from the attack of the heterocyclic electrophile **1** to the α or γ carbons of the allylic anions **9** and **10** obtained from a first addition step, followed by a deprotonation leading to the diheterocyclic products **11** or (and) **12** and finally to **8** by a subsequent elimination of thiomethanol (Fig. 2). It is noteworthy that the γ condensation monoheterocyclic complex **6** was not present in the final reaction mixture. However, hydrolysis performed at the beginning of the reaction allowed the detection of complex **6** (TLC observation). This behaviour proved that a part of **8** formation arises from the γ monoheterocyclic anion **9**.

The formation of **8** should be the consequence of two determining factors (i) the electronic-withdrawing effect of the metalcarbonyl group, which favours the formation and allows the stabilization of the allylic anions **9** and **10**; (ii) the strong electrophilic capacity of the heterocyclic cation towards **9** and **10**.

Finally, in this experiment where the complex **2′b** was made to react with $Pd(PPh_3)_2Cl_2$ in the presence of NEt_3 could be used to give the expected extended tetrathiafulvene **13** (40% yield mixture of isomers 80/20%)[14,16,22,23] (Scheme 3).

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15. General procedure for the formation of complexes **2**: at −78 °C, 0.8 mL of a 2.5 M solution of *n*-butyllithium (2×10^{-3} M) was added to a solution of (methoxymethyl)pentacarbonylcarbene complex (2×10^{-3} M) in dry THF (10 mL) in a N_2 atmosphere. Thiolium salt (2×10^{-3} M) was then added. The solution was stirred for 1 h. The reaction was quenched by adding ice and cold water. The reaction mixture was extracted with diethylether and the organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by means of silica gel column chromatography (eluent ether–petroleum ether 40–60%). Selected spectroscopic data for **2a**: ^{1}H NMR ($CDCl_3$, 500 MHz, δ): 7.87 (1H, dd, $^5J = 1.4$ Hz, $^5J = 0.4$ Hz); 6.99 (1H, dd, $^3J = 6.5$ Hz, $^5J = 0.4$ Hz); 6.98 (1H, dd, $^3J = 6.5$ Hz, $^5J = 0.4$ Hz); 4.52 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 269.6, 203.4, 198.5, 161.0, 128.8, 125.3, 120.8, 66.4; ν_{max} (KBr)/cm^{-1} 2057, 1912, 1426, 1304, 1207, 1105, 1026, 680, 621, 611; MS (FAB) calcd 481.9115; found 481.9109 for $C_{11}H_6O_6S_2W$.
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17. For comparison, the carbenic carbon of analogous γ-methylenepyran carbene complexes resonates at a lower field (282–286 ppm).[9a] The dithiofulvene fragment seemed to be a more electron-donating group than the methylenepyran group.
18. Selected spectroscopic data for **7b**,**c**:
    7b ^{1}H NMR (THF-d_8, 500 MHz, δ): 7.87 (1H, dd, $^3J = 17.6$ Hz, $^3J = 10.3$ Hz); 5.85 (1H, d, $^3J = 10.7$ Hz); 5.55 (1H, d, $^3J = 17.6$ Hz); 4.70 (3H, s); 3.87 (3H, s); 3.85 (3H, s); ^{13}C NMR (THF-d_8, 75 MHz, δ): 278.1, 203.2, 199.3, 160.2, 159.9, 156.9, 139.8, 137.0, 132.5, 125.7, 66.8, 53.8; ν_{max} (KBr)/cm^{-1} 2060, 1977, 1904, 1735, 1721, 1421, 1396, 1243, 719, 597; MS (FAB) calcd 623.93181; found 623.9361 for $C_{17}H_{12}O_{10}S_2W$.
    Compound **7c**: ^{1}H NMR ($CDCl_3$, 500 MHz, δ): 6.93 (1H, dd, $^3J = 17.8$ Hz, $^3J = 10.6$ Hz); 5.75 (1H, d, $^3J = 10.6$ Hz); 5.49 (1H, d, $^3J = 17.8$ Hz); 4.59 (3H, s); 3.37 (4H, s); ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 270.7, 202.8, 198.7, 156.9, 138.9, 137.1, 124.7, 120.3, 116.5, 65.4, 28.8, 28.5; ν_{max} (KBr)/cm^{-1} 2057, 1886, 1362, 1275, 1179, 1127, 1025, 718; MS (FAB) calcd 597.8867; found 597.8871 for $C_{15}H_{10}O_6S_4W$.
    Compound **8b**: ^{1}H NMR (THF-d_8, 500 MHz, δ): 7.34 (1H, d, $^3J = 15.5$ Hz); 6.39 (1H, d, $^3J = 15.5$ Hz); 4.70 (3H, s); 3.87 (3H, s); 3.74 (6H, s); 2.53 (3H, s); ^{13}C NMR (THF-d_8, 75 MHz, δ): 275.8, 199.0, 161.0, 160.0, 158.4, 137.7, 135.9, 80.3, 53.9, 53.1, 15.4; ν_{max} (KBr)/cm^{-1} 2059, 1919, 1720, 1571, 1433, 1390, 1255, 597, 571; MS (FAB) calcd 887.8966; found 887.8975 for $C_{25}H_{20}O_{14}S_5W$.
    Compound **8c**: ^{1}H NMR ($CDCl_3$, 500 MHz, δ): 7.29 (1H, d, $^3J = 15.3$ Hz); 6.06 (1H, d, $^3J = 15.3$ Hz); 4.58 (3H, s); 3.37 (4H, s); 3.29 (4H, s); 2.50 (3H, s); 2D NMR (HMQC/HMBC, $CDCl_3$, 500 MHz, ^{13}C δ): 270.4, 135.5, 134.7, 65.3, 30.4, 28.9; ν_{max} (KBr)/cm^{-1} 2053, 1924, 1360, 1310, 1144; MS (FAB) $[M-SCH_3]^+$ calcd 788.7975; found 788.7968 for $C_{20}H_{13}O_6S_8W$.
    During the 2D NMR (HMBC) sequence product **8c** is evoluting. This observation is in agreement with the mass spectroscopy analysis, which shows the good leaving capacity of the thiomethyl group.
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23. Spectroscopic data for **13**: ^{1}H NMR (THF-d_8, 500 MHz, δ): major: 6.32 (2H, s); 3.76 (6H, s); 3.75 (6H, s); 3.48 (6H, s); minor: 6.25 (2H, s); 3.76 (6H, s); 3.75 (6H, s); 3.62 (6H, s); ^{13}C NMR (THF-d_8, 75 MHz, δ): major: 160.7, 154.4, 105.8, 61.8; 53.3; MS (FAB) calcd 547.9939; found 547.9937 for $C_{20}H_{20}O_{10}S_4$.