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Reaction of lithiated thiophene-derived aminocarbene complexes with inorganic halides: Preparation of a heteroatom containing mono- and multicarbene complexes

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ABSTRACT

The reaction of lithiated pentacarbonyl [(*N*,*N*-dimethylamino) (2-thienyl)carbene]chromium (0) or pentacarbonyl [(*N*,*N*-dimethylamino) (2-thienyl)carbene]tungsten (0) with $SOCl_2$, $COCl_2$, Me_3SiCl, Me_2SiCl_2, Me_3SnCl and $SnCl_4$ afforded the corresponding carbene complexes, in which the chlorine was substituted with a 2-thienyl amino carbene moiety. Reaction with S_2Cl_2 afforded the corresponding biscarbene sulphide. In contrast, reactions with the phosphorous chlorides PCl_3, $POCl_3$, $PhPCl_2$ and Ph_2PCl were unsuccessful. The trimethylstannyl derivative was successfully used in Stille coupling with 4-nitroiodobenzene. The molecular structure of the tungsten tetracarbene derived from $SnCl_4$ was obtained.

1. Introduction

Although more than 50 years have passed since the preparation of the first carbene complexes by Fischer and Maasböl [1], these compounds are still inspiring for chemists. They have many applications, not only in organic synthesis [2] but also in material sciences [3], and their electrochemistry [4] has attracted considerable attention. Recently, attention has turned to the less-developed chemistry of Fischer multicarbene complexes [5], which, aside from their synthetic applications, have been studied for their potential use in material science. In particular, studies have focused on the electrochemistry and structure of the complexes containing a conjugated bridge [4].

We have recently described the lithiation of aminocarbene complexes derived from five membered heterocycles. These lithiated complexes can further react with a number of electrophiles [6] or can be used, after transmetalation to zinc, as reagents in Negishi reaction, giving new modified aminocarbene [7] or biscarbene complexes [8]. In the course of our study of electrochemical behaviour of the bridged Fischer multicarbenes complexes [9] we have turned our attention to the reaction of lithiated carbene complexes with inorganic halides. We envisioned that this simple methodology allows an access to multicarbene complexes bridged by a heteroatom spacer that will extend our knowledge of electrochemical properties of the Fischer multicarbenes. Moreover, such complexes could potentially be used in specific interactions with other substrates or surfaces in material science and for further derivatization. Similar approach was described by Helmut Fischer, who developed the synthetic route to multicarbene complexes based on the reaction of metalated alkynyl and polyalkynyl Fischer carbenes containing terminal $-C{\equiv}CH$ group with inorganic and organometallic halides. Series of bis-, tris- and tetrakis (ethynylcarbene) heteropolymetallic complexes, including those containing heteroatom in the bridging ligand, were prepared by this methodology [10].

2. Results and discussion

First, we turned our attention to reactions with phosgene. The reaction of thiophene-derived aminocarbene **1a** afforded, after metalation and reaction with phosgene, the expected ketone **2a** in low yield (Scheme 1). The ketone **2a** was also prepared from **1a** in two steps. The carbene **1a** was lithiated and reacted with carbene

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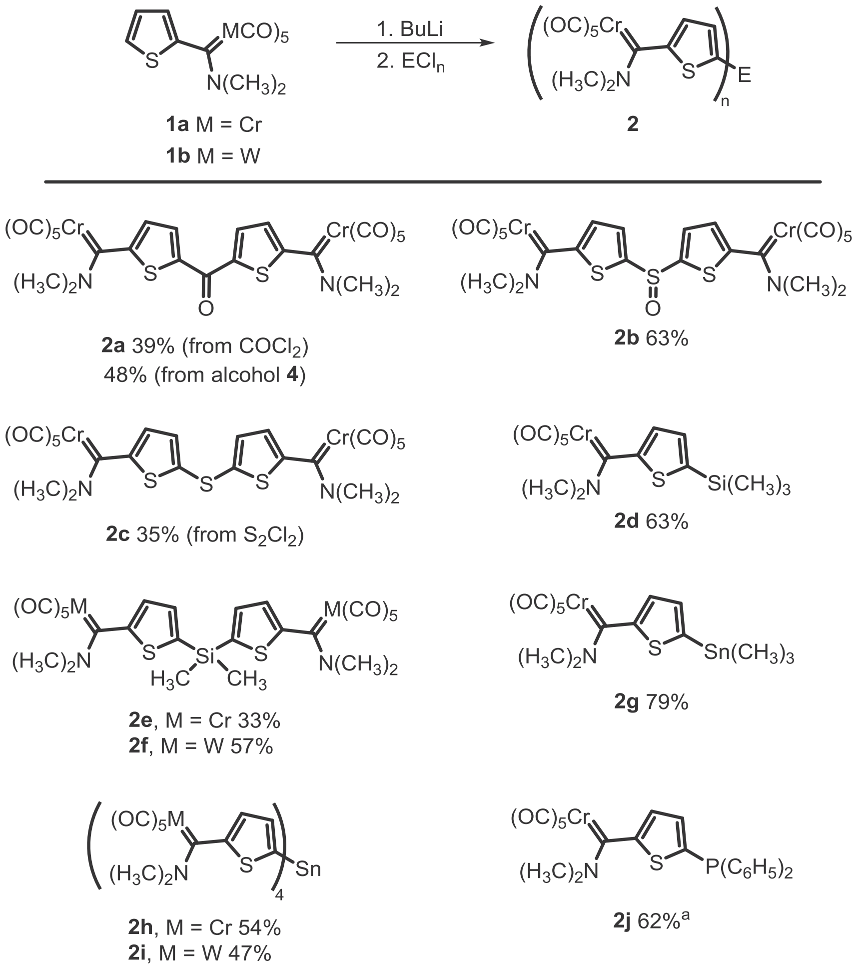


[a]Complex was not obtained in pure form.

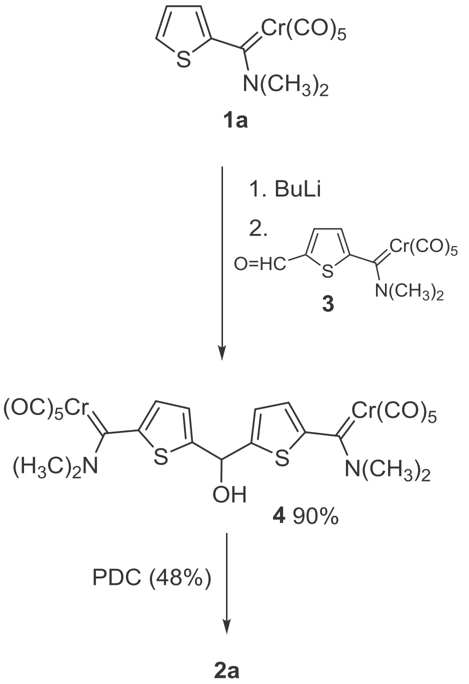
Scheme 1. Reaction of lithiated **1** with inorganic halides.

aldehyde **3** [6], forming the corresponding secondary alcohol **4** in a 90% yield. The alcohol was then oxidized to **2a** using pyridinium dichromate (PDC), while the Dess-Martin reagent gave no reproducible results in this case (Scheme 2).

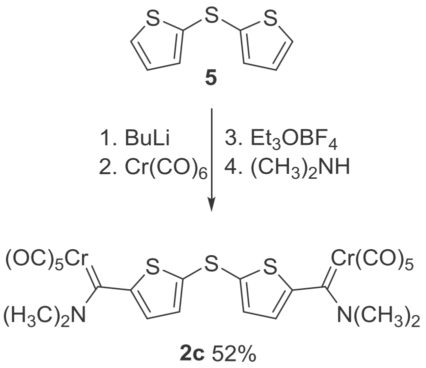
Similarly, the reaction of lithiated **1a** with thionyl chloride produced the sulfoxide **2b** in medium yield (63%) (Scheme 1). The other sulphur electrophile tested was sulphur monochloride (S_2Cl_2). Because organic disulphides are known to form sulphides upon treatment with organolithiums [11], the formation of the sulphide **2c** rather than a disulphide was expected in this case. Indeed, the sulphide **2c** was the only isolated carbene product in this reaction. The structure of **2c** was confirmed by independent synthesis starting from di(thiophen-2-yl)sulphide (**5**). After double lithiation, sulphide **5** was converted to the corresponding bis-alkoxy-carbene, which, without isolation, gave the sulphide **2c** by reaction with dimethylamine (Scheme 3).

Lithiated **1a** also easily reacted with trimethylsilyl chloride, giving **2d** in a 63% yield, while its reaction with dichlorodimethylsilane gave the corresponding biscarbene **2e** in low (33%) yield. The reaction of lithiated tungsten carbene **1b** was more successful in this case, giving the corresponding tungsten biscarbene complex **2f** in a 57% yield. Attempts to prepare a tetracarbene by the reaction of the lithiated **1a** with $SiCl_4$ were unsuccessful, probably for sterical reasons, and only an inseparable mixture of carbene products was obtained. The reaction of lithiated **1a** with chlorotrimethylstannane proceeded smoothly, giving, according to the TLC and NMR of the crude reaction mixture, the expected trimethylstannyl derivative **2g** as virtually the only product in quantitative yield. However, all attempts to isolate analytically pure **2g** by column chromatography on silica or alumina using various solvent mixtures were unsuccessful, affording only starting **1a**, because of quantitative destannylation. Fortunately, the crystallisation of the crude product from dichloromethane/*n*-hexane gave pure **2g** in a 79% yield. The reaction of a lithium salt of **1a** with $SnCl_4$ was also attempted. This reaction, in contrast to the reaction with $SiCl_4$, afforded the desired tetracarbene complex **2h** in a 54% yield after flash chromatography and crystallisation. However, the obtained product was unstable, decomposing within several days, even in a fridge under an argon atmosphere. The same reaction with the lithiated tungsten analogue **1b** gave the corresponding tungsten tetracarbene **2i** in a 47% overall isolated yield (Scheme 1). This compound, in contrast to the chromium complex **2h**, was stable, and we were able to obtain crystal suitable for X-ray analysis (Fig. 1). The instability of **2h** compared to **2i** might be rationalized by generally higher thermodynamic and kinetic stability of the complexes of *5d* elements over *3d* elements.

The obtained crystal structure of **2i** revealed the expected tetrahedral arrangement of four thiophene groups around the tin



Scheme 2. Alternative preparation of the ketone **2a**.



Scheme 3. Preparation of biscarbene **2c** from di(thiophen-2-yl)sulphide (**5**).

atom. Three of the aminocarbene groups [$Me_2N{-}C{=}W(CO)_5$] were roughly perpendicular to the thiophene ring, which is normal [12]. The fourth aminocarbene group was slightly shifted from the perpendicular angle, and its torsion angle ($W\text{-}C_{carb}\text{-}C_{2th}\text{-}C_{3th}$) was −107.9 (5)°. The above tetracarbenes, **2h** and **2i,** are rare examples of multicarbenes in which the carbene groups are not attached to the skeleton through their oxygen or nitrogen atoms.

The reactions with phosphorous halides were not successful. Attempts with PCl_3, $POCl_3$ and $C_6H_5PCl_2$ gave only deeply coloured solutions, presumably the result of electron transfer processes. Inseparable mixtures of unidentified products were obtained in all of these experiments. In the case of the reaction of $(C_6H_5)_2PCl$ with lithiated **1a** at −78 °C, the desired carbene complex **2j** was identified by the ^1H (see Experimental). However, it proved to be very unstable, and we have not been able to obtain a pure compound by chromatography. Attempts at crystallisation were also unsuccessful in this case. This is somewhat surprising because structurally similar mono-, bis- and tris-ethoxy-carbene complexes of chromium derived from tri (2-furyl)phosphine have been prepared and characterised [13].

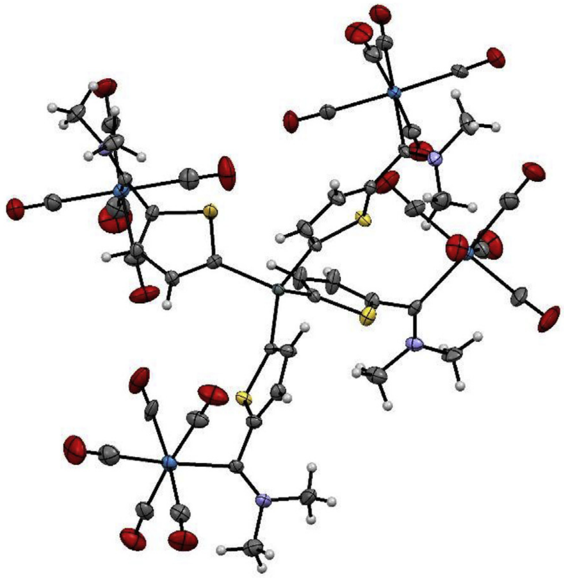
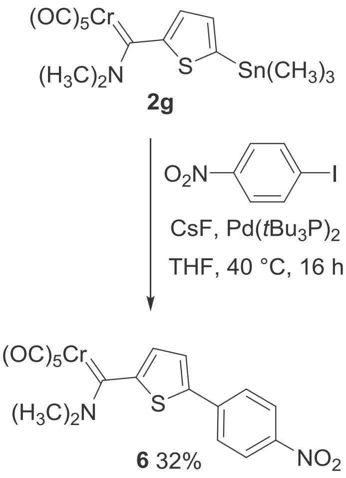


Fig. 1. Molecular structure of tetracarbene complex **2i**. ADP elipsoids are shown at the 50% probability level.

Trialkylstannyl derivatives are common reagents in the Stille cross-coupling reaction. Therefore, the ability of the trimethylstannyl carbene **2g** to participate in this reaction was tested in its reaction with 4-nitroiodobenzene. The best conditions were eventually found using Pd (tBu_3P)$_2$ in combination with CsF as an additive (Scheme 4). The product of the cross-coupling reaction **6** was thus obtained in a 32% yield. A similar result was achieved using the crude non-crystallised carbene **2g**.

In conclusion, the reactions of lithiated, thiophene-derived aminocarbene complexes of chromium and tungsten with $SOCl_2$, $COCl_2$, Me_3SiCl, Me_2SiCl_2, Me_3SnCl and $SnCl_4$ provide a new approach to the mono- and multicarbene complexes. The low yield of several carbenes is partly the result of losses during the separation from polar by-products and losses by crystallisation. The detailed study of the influence of the bridge on the electronic communication between the metal atoms is currently under the study in our laboratories.



Scheme 4. Stille reaction of trimethylstannyl carbene **2g**.

3. Experimental

3.1. General information

All reactions were performed under an argon atmosphere. The solvents were dried and degassed by standard procedures; silica gel (Merck, Geduran Si 60, 63–200 μm) was used for the column chromatography. Pentacarbonyl [(*N*,*N*-dimethylamino) (2-thienyl) carbene]chromium (0) (**1a**) [9a], pentacarbonyl [(*N*,*N*-dimethylamino) (2-thienyl)carbene]tungsten (0) (**1b**) [6] and pentacarbonyl [(*N*,*N*-dimethylamino) (5-formyl-2-thienyl)carbene]chromium (0) [6] (**3**) were prepared by the reported procedures; other compounds were purchased.

3.2. X-ray structure determination

The crystal of **2i** suitable for X-ray analysis was obtained by the diffusion of *n*-hexane into a solution of **2i** in dichloromethane.

The structure of **2i** was measured using a D8 VENTURE equipped with a photon CMOS detector with Mo-Ka ($\lambda = 0.71073$ Å) radiation at 180 K. The structure was in a monoclinic system, $P\ 2_1/c$ space group with the lattice parameters $a = 22.9535\ (9)$Å, $b = 16.3125\ (7)$ Å, $c = 16.1365\ (6)$Å, $\alpha = 90°$, $\beta = 96.7174\ (13)°$, $\gamma = 90°$, $Z = 4$, $V = 6000.5\ (4)$Å^3, $D_c = 2.178$ g/cm^3 and μ(Cu–K α) = 8.262 mm^{-1}. The data reduction and absorption correction were done using the Apex3 software. The structure was solved by charge flipping using the Superflip software and refined, using full-matrix least-squares on the *F* squared value in the Crystals software, to the final values $R = 0.0278$ and $wR = 0.0513$, using 14371 independent reflections ($\Theta_{max} = 27.950°$), 731 parameters and no restraint. The MCE software was used to visualize residual electron density maps. In accordance with common practice, the hydrogen atoms attached to carbon atoms were place geometrically, with U_{iso}(H) in range 1.2–1.5 U_{eq} of the parent atom (C). The structure was deposited into the Cambridge Structural Database under number CCDC 1846761.

3.3. General procedure for the reaction of lithiated Fischer aminocarbene complexes **1a** and **1b** with inorganic chlorides

Butyllithium (1.0 equiv.) was added to a solution of carbene complex **1a** or **1b** (1.0 equiv.) in dry THF (7 mL/mmol) cooled to −78 °C. The resultant mixture was stirred for 30 min at −78 °C, followed by the addition of the inorganic chloride. The mixture was then stirred without cooling, and after 2 h, alumina (3 g/mmol) was added and the solvents were evaporated *in vacuo*. Column chromatography then afforded the target compounds.

*Biscarbene complex **2a***. The general procedure starting from aminocarbene complex **1a** (0.198 g, 0.60 mmol) and phosgene (0.21 mL of a 15% solution in toluene, 0.3 mmol) afforded after column chromatography (silica gel, hexane/EtOAc 1:1) 0.08 g of the title compound (39%) as an orange crystalline solid. The analytical sample was obtained by crystallisation from a hexane/DCM mixture. Mp 115 °C (dec). ^{1}H NMR (CDCl$_3$): δ 3.33 (s, 6H, CH$_3$), 4.08 (s, 6H, CH$_3$), 6.64 (d, *J* = 3.8 Hz, 2H, CH$_{\mathrm{th}}$), 7.82 (d, *J* = 3.8 Hz, 2H, CH$_{\mathrm{th}}$). ^{13}C NMR (CDCl$_3$): δ 47.0 (NCH$_3$), 51.5 (NCH$_3$), 118.9 (CH$_{\mathrm{th}}$), 133.2 (CH$_{\mathrm{th}}$), 140.7 (C$_{\mathrm{th}}$), 159.3(C$_{\mathrm{th}}$), 178.3 (C=O), 216.4 (CO$_{\mathrm{cis}}$), 223.2 (CO$_{\mathrm{trans}}$), 268.8 (C$_{\mathrm{carbene}}$). IR (ATR): ν 2053 (m), 1901 (s), 1598 (m), 1537 (m), 1514 (m), 1429 (m), 1398 (m), 1320 (m), 1294 (m), 1219 (m) cm^{-1}. Calcd for $C_{25}H_{16}Cr_2N_2O_{11}S_2$: C, 43.61; H, 2.34; N, 4.07; S, 9.31. Found: C, 43.30; H, 2.20; N, 3.82; S, 8.95.

*Two steps procedure: Biscarbene alcohol **4***. Butyllithium 0.4 mL (0.88 mmol, 2.2 M in hexanes) was added to a solution of 0.265 g (0.8 mmol) of **1a** in dry THF (16 mL) cooled to −78 °C. The resultant mixture was stirred for 30 min at −78 °C followed by addition of the solution of 0.360 g (1 mmol) **3** in THF (5 mL). Then the mixture was stirred 2 h at −78 °C. The reaction was then quenched with aqueous solution of NH$_4$Cl, water layer was extracted with ether, dried over Na$_2$SO$_4$ and concentrated *in vacuo*. Column chromatography on silica (DCM/hexane 2:1) afforded 0.50 g (90%) of **4** in the form of yellow foam.

^{1}H NMR (acetone-d$_6$): δ 3.35 (s, 6H, CH$_3$), 4.05 (s, 6H, CH$_3$), 5.83 (s, 1H, CH), 6.33 (s, 1H, OH), 6.47 (d, *J* = 3.6 Hz, 2H, CH$_{\mathrm{th}}$), 6.95 (d, *J* = 3.3 Hz, 2H, CH$_{\mathrm{th}}$). ^{13}C NMR (acetone-d$_6$): δ 47.2, 52.2, 68.3, 118.3, 124.9, 148.9, 153.8, 217.9, 224.8, 264.5. Calcd for $C_{25}H_{18}Cr_2N_2O_{11}S_2$: C, 43.48; H, 2.63; N, 4.06; S 9.29. Found: C, 43.15; H, 2.75; N, 4.11; S, 9.55.

*Oxidation of the biscarbene alcohol **4***. PDC (0.752 g, 2 mmol) was added to the solution of **4** (0.500 g, 0.72 mmol) in dry DCM (20 mL) cooled to 0 °C. The mixture was stirred at that temperature for 4 h and the reaction was quenched with aqueous solution of NH$_4$Cl. Water layer was extracted with DCM, dried over NaSO$_4$ and concentrated *in vacuo*. Column chromatography on silica (EtOAc/hexane 1:1) afforded 0.238 g (48%) of **2a**.

*Biscarbene complex **2b***. The general procedure starting from aminocarbene complex **1a** (0.330 g, 1.0 mmol), BuLi (0.45 mL of 2.22 M solution in hexanes, 1 mmol) and SOCl$_2$ (0.030 mL, 0.4 mmol) afforded after chromatography (silica, hexane/EtOAc 1:1, then 1:2) **2b** (0.180 g, 63%) in the form of yellow foam. ^{1}H NMR (CDCl$_3$): δ 3.22 (s, 6H, CH$_3$), 3.99 (s, 6H, CH$_3$), 6.51 (d, *J* = 4 Hz, 2H, H$_{\mathrm{th}}$), 7.42 (d, *J* = 4 Hz, 2H, H$_{\mathrm{th}}$). ^{13}C NMR (CDCl$_3$): δ 47.2, 51.6, 118.0, 130.7, 145.8, 158.0, 216.4, 223.3, 267.6. IR (ATR): ν 2053 (m), 1979 (w), 1886 (s), 1615 (m), 1532 (m), 1423 (m), 1396 (m), 1259 (s), 1218 (s) cm^{-1}. Calcd for $C_{24}H_{16}Cr_2N_2O_{11}S_3$: C, 40.68; H, 2.28; N, 3.95; S, 13.57. Found: C, 40.38; H, 2.54; N, 3.88; S, 13.93.

*Biscarbene complex **2c***. The general procedure starting from aminocarbene complex **1a** (0.330 g, 1.0 mmol), BuLi (0.45 mL of 2.22 M solution in hexanes, 1 mmol) and S$_2$Cl$_2$ (0.036 mL, 0.45 mmol) afforded after column chromatography (silica gel, hexane/DCM 3:1) 0.120 g of the title compound (35%) as a yellow-orange glass. ^{1}H NMR (CDCl$_3$): δ 3.21 (s, 6H, CH$_3$), 3.96 (s, 6H, CH$_3$), 6.35 (d, *J* = 4 Hz, 2H, CH$_{\mathrm{th}}$), 7.08 (d, *J* = 4 Hz, 2H, CH$_{\mathrm{th}}$). ^{13}C NMR (CDCl$_3$): δ 46.8 (CH$_3$), 51.4 (CH$_3$), 118.0 (CH$_{\mathrm{th}}$), 133.76 (CH$_{\mathrm{th}}$), 134.8 th, 156.8 th, 216.6 (CO$_{\mathrm{cis}}$), 223.4(CO$_{\mathrm{trans}}$), 268.6 (C$_{\mathrm{carbene}}$). IR (ATR): ν 2053 (m), 1978 (w), 1884 (s), 1616 (m), 1533 (m), 1420 (m), 1395 (m), 1210 (w) cm^{-1}. Calcd for $C_{24}H_{16}Cr_2N_2O_{10}S_3$: C, 41.62; H, 2.33; N, 4.04; S, 13.89. Found: C, 41.34; H, 2.43; N, 4.06; S, 14.25.

*Preparation from di(thiophen-2-yl)sulphide (**5**)*. Butyllihium (8.33 mL of 2.40 M solution in hexanes, 20.0 mmol) was added to a solution of thiophene (1.682 g, 20 mmol) in dry THF (20 mL) cooled to −78 °C. The resultant mixture was stirred for 30 min at −78 °C followed by addition of sulphur (0.321 g, 10 mmol) and the reaction mixture was stirred for another 15 h at ambient temperature. Then the reaction mixture was diluted with ether (100 mL), washed with HCl (30 mL, 1 M solution), water (3 × 50 mL), and brine (50 mL). The organic layer was dried over MgSO$_4$, concentrated under reduced pressure to give the crude sulphide **5** as a yellow oil. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 6.94–6.97 (m, 2H), 7.20–7.22 (m, 2H), 7.32–7.35 (m, 2H), in accordance with literature [14]. Such prepared sulphide **5** was used in the next step without purification. Butyllithium (1.09 mL, of 2.44 M solution in hexanes, 2.65 mmol) was added to the solution of sulfide **5** (0.250 g, 1.26 mmol) in dry THF (10 mL) cooled to −78 °C. The resultant mixture was stirred for 30 min at room temperature followed by addition of chromium hexacarbonyl (0.554 g, 2.52 mmol), and the mixture was stirred for 2 h at room temperature, the solvents were then removed under reduce pressure. The isolated residue was dissolved in 15 mL of water, the solution was cooled to 0 °C, and triethyloxonium tetrafluoroborate (0.570 g, 3.0 mmol) was added in one portion. The mixture was stirred for 10 min at 0 °C, alkoxycarbene complex was isolated by extraction (3 × 30 mL EtOAc:THF, 1:1), the organic layer was dried over $MgSO_4$, and concentrated under reduce pressure. The isolated crude carbene complex was dissolved in dry THF (10 mL), and dimethylamine (2.0 mL, 2 M ethereal solution) was added. After 2 h, the solvents were removed under reduce pressure, and column chromatography (silica gel, DCM:hexane, 1:2) gave the title compound 0.450 g (52%) as yellow foam. The ^{1}H NMR was identical with that of the compound obtained from S_2Cl_2.

*Pentacarbonyl[(N,N-dimethylamino) (5-trimethylsilyl-2-thienyl) carbene]chromium(0) (**2d**).* The general procedure starting from aminocarbene complex **1a** (0.330 g, 1.0 mmol), BuLi (0.44 mL of 2.22 M solution in hexanes, 1 mmol) and trimethylsilylchloride (0.11 mL, 0.9 mmol) afforded after chromatography (silica, hexane/DCM 2:1) 0.230 g (63%) of **2d** as yellow crystalline solid. Mp 98 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 0.35 (s, 9H, $3CH_3$), 3.25 (s, 3H, CH_3), 4.02 (s, 3H, CH_3), 6.62 (d, $J = 3.4$ Hz, 1H, H_{th}), 7.06 (d, $J = 3.4$ Hz, 1H, H_{th}). ^{13}C NMR ($CDCl_3$): δ −0.1 ($SiCH_3$), 46.6 (CH_3), 51.4 (CH_3), 119.7 (CH_{th}), 133.9 (CH_{th}), 138.3 (C_{th}), 158.0 (C_{th}), 216.9 (*cis*-CO), 223.8 (*trans*-CO), 270.6 C-carb.). IR (ATR): ν 2051 (m), 1974 (m), 1903 (s), 1889 (s), 1537 (m), 1509 (w), 1434 (w), 1399 (w), 1290 (w) cm^{-1}. Calcd for $C_{15}H_{17}CrNO_5SSi$: C, 44.66; H, 4.25; N, 3.47; S, 7.95. Found: C, 44.77; H, 4.24; N, 3.46; S, 8.01.

*Biscarbene complex **2e**.* The general procedure starting from aminocarbene complex **1a** (0.218 g, 0.66 mmol), BuLi (0.29 mL of 2.22 M solution in hexanes, 0.72 mmol) and dichlorodimethylsilane (0.036 mL, 0.3 mmol) afforded after chromatography (silica, hexane/DCM 2:1) 0.07 g (33%) of **2e** as yellow crystalline solid. The analytical sample was obtained by crystallisation from a hexane/DCM mixture. Mp 142 °C (dec). ^{1}H NMR ($CDCl_3$): δ 0.62 (s, 6H, $2CH_3$), 3.19 (s, 6H, $2CH_3$), 3.98 (s, 6H, $2CH_3$), 6.60 (d, $J = 3$ Hz, 2H, H_{th}), 7.13 (d, $J = 3$ Hz, 2H, H_{th}). ^{13}C NMR ($CDCl_3$): δ 0.4 ($SiCH_3$), 46.6 (CH_3), 51.3 (CH_3), 119.7 (CH_{th}), 135.2 (C_{th}), 135.4 (CH_{th}), 158.9 (C_{th}), 216.7 (*cis*-CO), 223.7 (*trans*-CO), 269.8 C-carb.). IR (ATR): ν 2050 (m), 1908 (m), 1872 (s), 1536 (m), 1504 (m), 1429 (m), 1399 (m), 1293 (w), 1217 (m), 1156 (w) cm^{-1}. Calcd for $C_{26}H_{22}Cr_2N_2O_{10}S_2Si$: C, 43.45; H, 3.09; N, 3.90; S, 8.92. Found: C, 43.46; H, 33.06; N, 3.97; S, 9.05.

*Biscarbene complex **2f**.* The general procedure starting from aminocarbene complex **1b** (0.470 g, 1.01 mmol), BuLi (0.45 mL of 2.42 M solution in hexanes, 1.09 mmol) and dichlorodimethylsilane (0.036 mL, 0.5 mmol) afforded after chromatography (silica, hexane/DCM 2:1) 0.281 g (57%) of **2f** as yellow crystalline solid. The analytical sample was obtained by crystallisation from a hexane/DCM mixture. Mp 121 °C (dec). ^{1}H NMR ($CDCl_3$): δ 0.67 (s, 6H, $2CH_3$), 3.23 (s, 6H, $2CH_3$), 3.6 (s, 6H, $2CH_3$), 6.70 (d, $J = 3.2$ Hz, 2H, H_{th}), 7.20 (d, $J = 3.4$ Hz, 2H, H_{th}). ^{13}C NMR ($CDCl_3$): δ −0.3 ($SiCH_3$), 45.1 (CH_3), 53.7 (CH_3), 120.6 (CH_{th}), 135.3 (CH_{th}), 135.7 (C_{th}), 160.0 (C_{th}), 198.2 ($^1J_{W\text{-}C} = 126$ Hz, *cis*-CO), 204.0 ($^1J_{W\text{-}C} = 126$ Hz, *trans*-CO), 250.7 ($^1J_{W\text{-}C} = 92$ Hz, C-carb.). IR (ATR): ν 2058 (m), 1867 (s), 1536 (m), 1504 (w), 1429 (w), 1401 (w), 1294 (w), 1252 (w), 1215 (w) cm^{-1}. Calcd for $C_{26}H_{22}N_2O_{10}S_2SiW_2$: C, 31.79; H, 2.26; N, 2.85; S, 6.53. Found: C, 31.72; H, 2.25; N, 2.84; S, 6.45.

*Pentacarbonyl[(N,N-dimethylamino) (5-trimethylstannyl-2-thienyl)carbene]chromium(0) (**2g**).* Butyllithium (0.92 mL of 2.44 M solution in hexanes, 2.24 mmol) was added to a solution of carbene complex **1a** (0.664 g, 2.0 mmol) in dry THF (14 mL) cooled to −78 °C. The resultant mixture was stirred for 30 min at −78 °C followed by addition of the solution of chlorotrimethylstannane (0.627 g, 3.15 mmol) in THF (4 mL). The mixture was then stirred 30 min at −78 °C, and then 2 h without cooling. Water (100 mL) was then added, the product was extracted to diethylether (3 × 25 mL), dried over $MgSO_4$ and the solvents were evaporated *in vacuo*. Crystallisation of obtained oil from a hexane/dichloromethane mixture afforded 0.779 g (79%) of **2g** in the form of grey-yellow crystals. Mp 59–62 °C (dec). ^{1}H NMR (acetone-d_6): δ 0.39 (s, 9H, $^2J_{Sn\text{-}H} = 58$ Hz, $3CH_3$), 3.32 (s, 3H, CH_3), 4.08 (s, 3H, CH_3), 6.74 (d, $J = 3.2$ Hz, 1H, H_{th}), 7.14 (d, $J = 3.3$ Hz, $^3J_{Sn\text{-}H} = 25$ Hz, 1H, H_{th}). ^{13}C NMR ($CDCl_3$): δ −9.1 ($SnCH_3$), 46.1 (CH_3), 51.2 (CH_3), 119.6 (CH_{th}, $^2J_{Sn\text{-}C} = 40$ Hz), 134.9 (CH_{th}, $^3J_{Sn\text{-}C} = 29$ Hz), 135.6 (C_{th}), 159.1 (C_{th}), 217.1 (*cis*-CO), 224.0 (*trans*-CO), 264.2 C-carb.). IR (ATR): ν 2050 (m), 1972 (w), 1898 (s), 1886 (s), 1617 (w), 1532 (m), 1396 (w), 1211 (w), 1153 (w) cm^{-1}. Calcd for $C_{15}H_{17}CrNO_5SSn$: C, 36.47; H, 3.47; N, 2.84; S, 6.49. Found: C, 36.46; H, 3.54; N, 2.85; S, 6.57.

*Chromium tetracarbene **2h**.* The general procedure starting from aminocarbene complex **1a** (0.668 g, 2.02 mmol), BuLi (0.87 mL of 2.42 M solution in hexanes, 2.1 mmol) and $SnCl_4$ (0.85 mL of 0.53 M solution in hexane, 0.45 mmol) afforded after flash chromatography (silica 40–63 μm, hexane/DCM 2:1, then 1:1) 0.350 g (54%) of **2h** as yellow crystalline solid. The analytical sample was obtained by crystallisation from a hexane/DCM mixture. Mp 147 °C (dec). ^{1}H NMR ($CDCl_3$): δ 3.26 (s, 12H, CH_3), 4.04 (s, 12H, CH_3), 6.80 (d, $J = 3.3$ Hz, $^4J_{Sn\text{-}H} = 5$ Hz, 1H, H_{th}), 7.29 (d, $J = 3.4$ Hz, $^3J_{Sn\text{-}H} = 35$ Hz, 1H, H_{th}). ^{13}C NMR ($CDCl_3$): δ 46.8 (CH_3), 51.5 (CH_3), 119.8 ($^2J_{Sn\text{-}C} = 64$ Hz, CH_{th}), 128.2 (C_{th}), 138.0 ($^3J_{Sn\text{-}C} = 43$ Hz, CH_{th}), 160.4 (C_{th}), 216.7 (*cis*-CO), 223.6 (*trans*-CO), 269.4 C-carb.). IR (ATR): ν 2052 (m), 1970 (w), 1914 (s), 1598 (m), 1519 (m), 1483 w), 1447 (w), 1391 (m), 1257 (w), 1210 (w), 1061 (w) cm^{-1}. Calcd for $C_{48}H_{32}Cr_4N_4O_{20}S_4Sn$: C, 40.04; H, 2.24; N, 3.89; S, 8.91. Found: C, 39.67; H, 2.55; N, 3.97; S, 9.16.

*Tungsten tetracarbene **2i**.* The general procedure starting from aminocarbene complex **1b** (0.926 g, 2.0 mmol), BuLi (0.82 mL of 2.44 M solution in hexanes, 2.0 mmol) and $SnCl_4$ (0.91 mL of 0.50 M solution in hexane, 0.45 mmol) was used. By flash chromatography (silica 40–63 μm) some starting **1b** was washed out by hexane/DCM 2:1 and further elution with hexane/DCM 1:1 afforded 0.177 g (18%) of **2i** as yellow crystalline solid. The analytical sample was obtained by crystallisation from a hexane/DCM mixture. The third fraction which was contaminated by intensively violet impurity gave, after two crystallizations from a hexane/DCM mixture, another 0.290 g (29%) of **2i**. Mp 125 °C (dec). ^{1}H NMR ($CDCl_3$): δ 3.26 (s, 12H, CH_3), 3.98 (s, 12H, CH_3), 6.85 (d, $J = 3.4$ Hz, $^4J_{Sn\text{-}H} = 5$ Hz, 1H, H_{th}), 7.32 (d, $J = 3.4$ Hz, $^3J_{Sn\text{-}H} = 35$ Hz, 1H, H_{th}). ^{13}C NMR ($CDCl_3$): δ 45.2 (CH_3), 53.8 (CH_3), 120.6 ($^2J_{Sn\text{-}C} = 64$ Hz, CH_{th}), 128.5(C_{th}), 137.8 ($^3J_{Sn\text{-}C} = 43$ Hz, CH_{th}), 161.6 ($^2J_{W\text{-}C} = 24$ Hz, C_{th}), 198.1 ($^1J_{W\text{-}C} = 126$ Hz, *cis*-CO), 203.8 ($^1J_{W\text{-}C} = 126$ Hz, *trans*-CO), 250.0 ($^1J_{W\text{-}C} = 93$ Hz, C-carb.). IR (ATR): ν 2060 (m), 1881 (s), 1536 (m), 1420 (w), 1399 (w), 1216 (w), 1155 (w) cm^{-1}. Calcd for $C_{48}H_{32}W_4N_4O_{20}S_4Sn$: C, 29.31; H, 1.64; N, 2.85; S, 6.52. Found: C, 29.39; H, 1.53; N, 2.95; S, 6.52.

*Pentacarbonyl[(N,N-dimethylamino) (5-diphenylphosphino-2-thienyl)carbene]chromium(0) (**2**j).* The general procedure starting from aminocarbene complex **1a** (0.165 g, 0.5 mmol), BuLi (0.22 mL of 2.5 M solution in hexanes, 0.55 mmol) and Ph_2PCl (0.11 mL, 0.6 mmol) afforded after chromatography (silica, hexane/DCM 2:1) 0.160 g (62%) of orange foam. According to the ^{1}H NMR it was virtually pure **2j**, however ^{13}C NMR revealed impurities in aromatic region. All further attempts to obtain pure compound have failed. ^{1}H NMR ($CDCl_3$): δ 3.19 (s, 9H, CH_3), 3.94 (s, 9H, CH_3), 6.57 (dd, $^3J_{HH} = 3.5$ Hz, $^4J_{P\text{-}H} = 1.5$ Hz, 3H, H_{th}), 7.16 (dd, $^3J_{HH} = 3.5$ Hz, $^3J_{P\text{-}H} = 6.1$ Hz, 3H, H_{th}), 7.3–7.42 (m, 10H, H_{Ph}).

*Cross-coupling reaction of trimethylstannyl complex **2g**.* A solution of carbene complex **2g** (0.240 g, 0.486 mmol) in dry THF (2 mL) was added to a mixture of CsF (0.096 g, 0.631 mmol), 4-nitroiodobenzene (0.249 g, 1.0 mmol), and Pd ($tBu_3P)_2$. The resultant mixture was stirred for 16 h at 40 °C, then concentrated under reduce pressure, and column chromatography (silica gel, DCM:hexane, 1:2) gave the complex **6** 0.060 g (32%) as an orange oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.32 (s, 3H), 4.03 (s, 3H), 6.56 (d, $J = 3.3$ Hz, 1H), 7.37 (d, $J = 3.3$ Hz, 1H), 7.67–7.71 (m, 2H), 8.21–8.26 (m, 2H), in accordance with ref. [7].

Declarations of interest

None.

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