FULL PAPER

Binuclear biscarbene complexes of furan

Chantelle Crause,^a Helmar Görls^b and Simon Lotz^{*a}

^a Department of Chemistry, University of Pretoria, Pretoria, 0002, South Africa

^b Friedrich-Schiller-Universität, Institut für Anorganische und Analytische Chemie, Lessingstrasse 8, D-07743, Jena, Germany

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Carbene complexes of chromium and tungsten with a bridging furan substituent were synthesized from lithiated furan precursors and metal hexacarbonyls. The binuclear biscarbene complexes $[(CO)_5M{C(OEt)-C_4H_2O-C(OEt)}-M'(CO)_5]$ (M = M' = Cr (3), W (4)) were obtained as well as the corresponding monocarbene complexes $[M{C(OEt)-C_4H_3O}(CO)_5]$ (M = Cr (1), W (2)). A method of protecting the carbene moiety during the metal acylate stage was used to increase not only the yields of the binuclear Fischer biscarbene complexes 3 and 4 but to establish a method to synthesize analogous mixed heterobinuclear carbene complexes (M = W, M' = Cr (5)) in high yields. The binuclear biscarbene complexes 3 and 5 were reacted with 3-hexyne and yielded the corresponding benzannulated monocarbene complexes $[M{C(OEt)-C_{14}H_{17}O_3}(CO)_5]$ (M = Cr (6), W(7)). Complex 5 reacted regioselectively with the benzannulation reaction occurring at the chromium–carbene centre. The major products from refluxing 3 in the presence of $[Pd(PPh_3)_4]$ were a monocarbene-ester complex $[Cr{C(OEt)-C_4H_2O-C(O)OEt}(CO)_5]$ (8), the 2,5-diester of furan (9) and a carbene–carbene coupled olefin EtOC(O)–C_4H_2O-C(OEt)=C(OEt)–C_4H_2O-C(O)OEt (10). X-Ray structure analysis of 4 and 6 confirmed the molecular structures of the compounds in the solid state and aspects of electron conjugation between the transition metals and the furan substituents in the carbene ligands were investigated.

Introduction

The carbene carbon atom in Fischer carbene complexes is a highly reactive electrophilic centre, being affected by the metal fragments and the carbene substituents. Binuclear transition metal complexes containing conjugated bridges have recently attracted considerable interest, since electronic communication between the metal centres could lead to interesting physical and chemical properties.1 Application of transition metal monocarbene complexes in organic synthesis is also an exciting and already established area of research focussing not only on the carbocationic carbene carbon atom but also on unsaturated side chains.² Homonuclear bimetallic carbene complexes with conjugated even-numbered carbon atoms ranging from C₄ to C_{14} and heteronuclear bimetallic carbene complexes with C_3 bridges have been reported by using reactive carbene precursors in coupling reactions.3 Bimetallic homonuclear biscarbene complexes with one-dimensional conjugated phenylene⁴ and benzene derivatives⁵ acting as bridging units are also known. By contrast, similar chain compounds with conjugated heteroarene moieties instead of carbon units have received far less attention. It has been reported that thiophene derivatives can be useful components of electronic materials,6 have stabilities surpassing that of polyenes⁷ and conduct electrons with better efficiency than their phenyl analogues.8 Consequently, heteroaromatic units are attractive alternative π -spacers in bimetallic compounds and we have reported results of homonuclear bimetallic biscarbene complexes with linking thiophene9 and thiophene derivatives.10

Synthetic methods to prepare mixed transition metal binuclear biscarbene complexes with arene units linking carbene carbon atoms remain a challenging synthetic problem. Maiorana and co-workers¹¹ reported the synthesis of a bimetallic (Cr,W) complex containing a bithiophene unit as bridging substituent in a mixed metal Fischer biscarbene complex. The objective of this study was to investigate potential non-linear optical properties of Fischer carbene complexes. In a second approach, the groups of Hegedus and Semmelhack¹² used acyl halides or *in situ* generated chloroimine intermediates that were treated with nucleophilic transition metal complexes to afford mononuclear aminocarbene complexes. Based on this method, Dvorak and co-workers¹³ studied the reaction of tertiary diamides and

metal carbonyl dianions in the presence of chlorotrimethylsilane to prepare a series of Cr or Fe homonuclear bimetallic biscarbene complexes as well as one mixed Cr,Fe bis(aminocarbene) complex linked by a benzene moiety in the 1,3-positions.

The synthesis of carbene complexes with modified substituents, the stepwise exploitation of two different transition metal carbene centres for different carbon-carbon coupling reactions, the resulting regioselectivity determined by a specific metal fragment, and the electronic and structural features of such binuclear biscarbene complexes are but some of many important topics of research that have been neglected and are of interest in our laboratories. In this paper we report the synthesis of bimetallic biscarbene complexes with a bridging furan spacer which was used to highlight the challenge of synthesizing mixed transition metal biscarbene complexes with bridging heteroarene substituents in high yields, the role of the heteroatom in the bridging heteroarene to determine the conformation of the biscarbene complex in the solid state and the testing of known monocarbene reaction pathways for carbene modification and carbon-carbon coupling reactions.

Results and discussions

Synthesis of the biscarbene complexes

Chromium and tungsten carbene complexes of furan were synthesized from reacting lithiated furan (path A)¹⁴ and dilithiated furan (path C) with metal carbonyls as shown in Scheme 1. Furan can be monolithiated quantitatively and quickly with butyllithium¹⁵ and Chadwick and Willbe established optimum conditions for the preparation of 2,5-dilithiofuran.¹⁶

Route C shows the synthesis of homonuclear biscarbene complexes and entails the generation of 2,5-dilithiofuran in hexane followed by the addition of two equivalents of the metal carbonyl to form a dilithium diacyl metallate. Subsequent quenching of the dilithium salt with triethyloxonium tetrafluoroborate yielded amongst others the desired heteronuclear biscarbene complex. This route afforded both the monocarbene, $[M(CO)_5{C(OEt)furyl}] (M = Cr 1, M = W 2)$ and biscarbene complexes $[(CO)_5{M{C(OEt)-C_4H_2O-C(OEt)}M(CO)_5] (M = Cr 3, W 4)$. A by-product of the reaction was a monocarbene



Scheme 1 Synthesis of dinuclear biscarbene complexes of furan.

furan complex with an ester group in the 5-position of the furan substituent.⁹ The corresponding chromium complex $[Cr(CO)_5{C(OEt)-C_4H_2O-C(O)OEt}]$ 8 was isolated and fully characterized. This method characteristically yields significant amounts of the butyl carbene complexes, $[M(CO)_5{C(OEt)Bu}]$, and furyl monocarbene complexes (1, 2) and low amounts of the targeted biscarbene complexes (3, 7%; 4, 2%). A possible explanation for this is the fact that the reaction is carried out under mild conditions (low temperatures) and that the second deprotonation of the intermediate furyl anionic complex was incomplete.

A method (path B) based on the one used by Maiorana and co-workers11 for bithiophene was modified to improve the yield of the furan biscarbene complexes 3 and 4 and to access the heteronuclear bimetallic biscarbene complex 5. The method involves the stepwise generation of acyl metallates from the reaction with lithiated furan and metal carbonyls. The second metallation at the 5' position was achieved with LDA at low temperatures (Maiorana used "BuLi instead). Method B is based on a single pot reaction studied by Aoki et al.¹⁷ in which they reacted $[M(CO)_5{C(OLi)R}]$ (R = heteroarenes) with LDA at -78 °C followed by an appropriate organic electrophile, water and finally Et₃OBF₄. This "anionic protection" strategy of an electrophilic carbene carbon atom without substantially reducing the acidity of the proton in the 5-position of the furyl substituent, accounts for the formation of the dianionic carbene precursor in high yields. It is during this sequential addition that a heteronuclear dimetallic biscarbene complex, $[(CO)_5Cr{C(OEt)-C_4H_2O-C(OEt)}W(CO)_5]$ (5), becomes readily accessible by adding a different metal hexacarbonyl in the second step. Not only was the heteronuclear dimetallic complex 5 isolated in a yield of 47%, but the yields of the homonuclear dimetallic complexes could also be increased significantly (3, 39%; 4, 40%). The alkylation step needs to be carried out in dichloromethane as the biscarbene complexes are unstable in aqueous medium. Alkylation in water of $Li_2[Cr_2(CO)_{10} \{C(O) C_4H_2C(O)$] afforded only 8 and none of the corresponding dichromium biscarbene complex. The reactions also yielded the butyl- and furyl monocarbene complexes as well as the diisopropylamino carbene complex, [M(CO)₅{C(OEt)NⁱPr₂}], in low yields. The tungsten biscarbene complex 4 could be stored for months under argon atmosphere in the solid state, but the chromium analogue 3 was less stable.

Benzannulation of biscarbene metal complexes (Dötz reaction)

Whilst the reaction of monocarbene complexes containing heteroaromatic substituents and alkynes has been investigated extensively¹⁸ the same does not hold for the analogous bimetallic biscarbene complexes. In a study by Wulff *et al.*¹⁹ the reactivity of aryl monocarbene complexes of chromium and tungsten

with 3-hexyne was investigated. The chromium complexes had the highest selectivity to the carbonyl inserted benzannulated product (phenol) with the optimal conditions being found with higher metal complex concentrations and with less polar and/or coordinating solvents.

Very few accounts of the reactions of biscarbene complexes with alkynes exist and as far as we are aware none with heteroarene substituents that could provide the required unsaturated bond for the benzannulation reactions. Whereas the chromium biscarbene complex, $[(CO)_5Cr\{C(OEt)-C_6H_4-C(OEt)-p\}Cr(CO)_5]$ reacted with one molecule of diphenylacetylene in the usual way affording **A** (Fig. 1), the binuclear diphenyl biscarbene complexes react with two molecules of diphenylacetylene under similar conditions to afford the anticipated binaphthol derivative **B** for chromium and the indene derivative **C** for tungsten (Fig. 1).²⁰



Fig. 1 Benzannulation products from biscarbene complexes with phenylene and biphenylene bridging substituents.²⁰

Other examples include the double benzannulation of an annulene derivative²¹ and the biscarbene from binaphtol that yielded phenanthrene $Cr(CO)_3$ complexes with axial and planar chirality.²² Replacement of arene by heteroarene substituents, could, in the light of these observations, lead to interesting new coordination complexes and novel heteroarene compounds.

The reaction conditions used by Wulff¹⁹ were adapted for the reactions of the biscarbene complexes **3**, **4** and **5** with 3hexyne. These complexes presented the opportunity to evaluate a number of factors that could influence the product distribution. Not only could the influence of a second carbene functionality be evaluated but also the effect of a different metal moiety. The present study deals only with the major products formed and no attempt was made to isolate intermediates or minor organic products. Since the reactivity of both chromium and tungsten complexes was evaluated, reaction conditions were

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chosen which would suit both metals. The reactions of the biscarbene metal complexes with 3-hexyne was carried out in toluene at 80 °C with a metal concentration of 0.1 mol dm⁻³ and 4 molar equivalents of alkyne. Higher metal complex concentrations were not accessible due to the limited solubility of these compounds in toluene. Reactions were allowed to proceed for 24 h after which the major product was isolated with column chromatography and the results are presented in Scheme 2 and Table 1. The monocarbene chromium complex 6 was the major product isolated from the reaction of 3 with 3-hexyne and the corresponding binuclear product with a π -coordinated $Cr(CO)_3$ moiety was not observed. Complex 4 did not react at all under these conditions. This seems to indicate that either the bimetallic nature of the metal complex or the furan substituent contributes to the lower reactivity of the bimetallic complex. For the mixed Cr,W-binuclear biscarbene complex 5, the formation of 7 was found and could be expected since it is generally known that chromium carbene complexes are more reactive than their tungsten analogues. This result demonstrates the potential of using heteronuclear dimetal biscarbene complexes in benzannulation reactions to regioselectively discriminate between the different metal carbene ligands.



Scheme 2 Monobenzannulation of binuclear biscarbene complexes with furylene substituents.

Carbene transfer reactions

Early work on the reactivity of Fischer carbene complexes focussed on the ability of these complexes to act as stable carbene sources.²³ Examples have been cited in which the

 Table 1
 Benzannulation reactions

carbene ligand is transferred to another metal centre.²⁴ Fischer and Beck²⁵ reported the transfer of a carbene ligand from Cp(CO)(NO)M(CXPh) (M = Cr, Mo, W; X = OMe, NMe₂) to photochemically generated Fe(CO)₅. Carbene exchange at elevated temperatures between alkoxychromium carbene complexes and W(CO)₆ to form alkoxytungsten carbene complexes and Cr(CO)₆ has been reported.²⁶ Fischer and co-workers²⁷ studied thermal carbene-carbene coupling reactions of several monocarbene complexes by refluxing carbene complexes in hexane. Stone and co-workers28 reported on the stoichiometric transmetallation of Group VI Fischer carbene complexes to coordinatively unsaturated metal centres to yield mixed metal binuclear complexes with μ -carbene ligands. Fischer carbene complexes have also been used to prepare gold carbene complexes by reaction with chloroauric acid.29 Sierra and coworkers³⁰ have reported results showing that carbene complexes participate effectively in carbene-carbene coupling reactions when Pd(0) or Pd(II) catalysts were used. According to the proposed mechanism one requires the transfer of carbenes to the palladium centre to facilitate a carbene-carbene coupling reaction intramolecularly via a pallada-propane intermediate. For the carbene transfer reaction to a palladium centre a threemembered heterometallic dimetallapropane is required.

Initial work in this laboratory was aimed at the thermal coupling of carbene complexes to afford new binuclear biscarbene complexes with a growing spacer between the two identical metal fragments. Important is the retention of π conjugation through the spacer ligand in the final product as this extended conjugated system could facilitate metal-to-metal communication and impart charge-transfer properties to the molecule. In the synthesis of bimolybdenum biscarbene complex with a bridging dithieno[3,2-*b*:2',3'-*d*]thiophene substituent, a molybdenum biscarbene with a carbene–carbene coupled bridging unit was isolated in low yield (Fig. 2).³¹



Fig. 2 Example of a biscarbene dimolybdenum complex with an extended conjugated spacer unit. $^{\rm 31}$

Thermal studies in hexane with this complex showed that the extended spacer was unfortunately more reactive towards



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oxygen and subsequent ester formation than the initial precursor biscarbene dimolybdenum complex. As a result, an oxygen atom replaced the metal fragment to afford a monocarbene complex with a terminal ester function. This discouraged us to further pursue carbene-carbene coupling reactions by refluxing binuclear biscarbene complexes in hexane. It was anticipated that the Pd catalyst could catalyse repetitive carbene-carbene coupling reactions and provide access to extended polyenes containing chainlike disubstituted furan units in polymeric materials. The binuclear biscarbene chromium complex 3 was refluxed in a thf solution in the presence of $Pd(PPh_3)_4$ until the precursor was totally converted. Complex (8) and a mixture of esters could be isolated (Scheme 3, Table 2). We have observed previously that the thiophene analogue, [(CO)₅Cr{C(OEt)- $C_4H_2S-C(OEt)$ Cr(CO) was not stable in ether solutions, resulting in the formation of 2,5-monocarbene ester complexes similar to 8.9 The major product of this reaction after 12 h of refluxing was the 2,5-diester of furan (9) and a cis-trans mixture of the carbene-carbene coupled diester, 10. The presence of 8 was detectable by thin layer chromatography shortly after initiation of the reaction in thf but was totally converted into 9 within the first 0.5 h. The experiment was repeated in hexane and it was possible to isolate and characterize 8 as well as higher yields of 10. These results indicated that ester formation was in strong competition with carbene-carbene coupling and that this reaction was most likely also catalysed by palladium.

Characterization

The carbene complexes were characterised using NMR and infrared spectroscopy and mass spectrometry. Although analogous methoxy monocarbene complexes of furan (1, 2) are known,¹⁴ the spectral data of the ethoxy derivatives are given for comparative purposes. Connor and Jones synthesized a series of monocarbene complexes of chromium with heteroaromatic substituents, [Cr(CO)₅{C(XR)C₄H₃Y}] (RX = OMe, NH₂; Y = O, S, NMe) in order to study the extent to which the heteroatom Y affects the donation of electrons to the empty carbene carbon p-orbital.¹⁴ Final confirmation of the molecular structures of **4** and **6** were obtained from single crystal X-ray diffraction studies.

The coordination of a metal fragment *via* a carbene carbon to furan has a profound effect on the electronic environment of the ring protons and is clearly reflected in the ¹H and ¹³C NMR spectra. The ¹H NMR data for the mono- and biscarbene complexes with furan substituents are given in Table 3. The chemical shift of free furan (7.38 (H2,5) and 6.3 (H3,4) ppm) and the predicted values for a 2-furylester derivative (7.15 (H3), 6.52 (H4) and 7.63 (H5)) are used as reference values.³² The



Scheme 3 Compounds with extended conjugated spacer units.

 Table 2
 Palladium catalysed carbene–carbene coupling reactions of 3



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Complex	IR^{a} (ν /cm ⁻¹ in hexane)	¹ H NMR (<i>ð</i> /ppm, <i>J</i> /Hz in CDCl ₃)	¹³ C NMR (<i>ð</i> /ppm in CDCl ₃)
1^b	2061 (s), 1990 (w), 1946 (s), 1960 (vs)	6.96 (dd, 3.6 , 0.8 , H3), 6.56 (dd, 3.6 , 1.6 , H4), 7.82 (dd 1.6 , 0.8 H5), 513 (-7 0) 1.63 (r -70) (-70)	311 (Cl, carbene), 224 (Cr(CO) ₅ , <i>trans</i>), 217 (Cr(CO) ₅ , <i>cis</i>), 164 (C2), 112 (C3), 113 (C4), 150 (C5), 76 15 (Cr(CF))
7	2069 (s), 1986 (w), 1943 (s), 1956 (vs)	7.13 (dd 3.60 , 8.9), 8.90 , 6.00 (dd 3.60 , 1.67 , 1.70 , 1.20 , 1.13 (dd 1.60 , 8.13 , 6.00 (dd 3.50 , 1.6 , 1.44), 7.86	285 (CC), 75, 15 (CC), 17 (CO), 17 (W(CO), 197 (W(CO), cis), 166 (C2), 115 (C3), 113 (C4), 150 (C5), 78, 15 (WCOE), 150 (C5), 78, 150 (C5), 150 (C5), 78, 150 (C5), 15
e	2054 (s), 1995 (w), 1955 (s), 1962 (vs)	7.22 (s, H3, H4); 5.22 (q, 7.0) 1.72 (t, 7.0) (CrCOEt)	313 (CC), 54 (CC), 54 (Cr(CO), <i>trans</i>), 216 (Cr(CO), <i>cis</i>), 162 (C2, C5), 119 (C3, C4); 77, 15 (Cr(COF))
4	2062 (s), 1990 (w), 1950 (s), 1957 (vs)	7.29 (s, H3, H4); 4.97 (q, 7.0) 1.70 (t, 7.0) (WCO <i>Et</i>)	286 (C1, C6 carbene), 203 (W(CO) ₅ , <i>trans</i>), 197 (W(CO) ₅ , <i>cis</i>), 166 (C2, C5), 121 (C3, C4); 79, 15 (WCOF)
Ś	2057 (s), 1992 (w), 1955 (s), 1955 (vs)	7.31 (d, 4.0, H3(W)), 7.20 (d, 4.0, H4); 4.93 (q, 7.1) 1.70 (t - 7.1) (WCO.F.)	313 (G, carbene), 224 (Cr(CO) ₅ , <i>trans</i>), 216 (Cr(CO) ₅ , <i>cis</i>), 286 (C1 carbene), 203 (W(CO) ₅ , <i>trans</i>) 197 (W(CO) ₇ , <i>cis</i>) 166 (C2) 121 (C3) 119 (C4) 162 (C5) 79 15 (WCOF) 76 15 (Cr(OF))
9	2059 (s), 1989 (w), 1947 (s), 1959 (vs)	7.20 (s, H3), 4.86 (s, OH); 2.69, 2.78 (br), 1.17 (t) (2 × ArEt); 4.44, 1.50 (t) (ArOEt); 5.18 (q) 1.68 (t) (ArOEt); $ArEtOEt$	313 (C1, carbene), 224 (Cr(CO),, <i>trans</i>), 217 (Cr(CO)), <i>cis</i>), 162 (C2), 103, 117, 122, 137, 137, 144, 149 (aromatic carbons), 21, 19, 15 (2 × Ar <i>Et</i>), 69, 16 (Ar <i>OEb</i>); 76, 16 (CrCO <i>Et</i>)
٢	2064 (s), 1986 (w), 1946 (s), 1956 (vs)	7.40 (s, H3), 5.12 (s, OH); 2.69, 2.78 (br), 1.18 (t) (2 × 7.78) (s, H3), 2.15 (t) (ArOEt); 4.97 (q) 1.65 (t) (MrOEt)	287 (Cl, carbene), 204 (W(CO) ₅ , <i>trans</i>), 197 (W(CO) ₅ , <i>cis</i>), 165 162 (C2), 106, 118, 123, 136, 138, 144, 149 (aromatic carbons); 21, 19, 15, 15 ($2 \times \operatorname{Ar}Eh$); 69, 15 (ArOEt); 78, 16 (WCOEt)
×	2062 (s), 1988 (w), 1944 (s), 1958 (vs)	7.19 (d. 3.6, H3), 6.82 (d, 3.6, H4); 5.19 (q, 7.0) 1.66 (t, 7.0) (CrCOEt); 4.41 (q, 7.1) 1.40 (t, 7.1) (C(O)OEt)	315 (Cl, carbene), 224 (Cr(CO) ₅ , <i>trans</i>), 216 (Cr(CO) ₅ , <i>cis</i>), 163 (C2), 118 (C3), 110 (C4), 158 (C5); 76, 15 (CrCOE <i>i</i>); 62, 14 (C(O)OE <i>t</i>)
" Carbonyl re	gion. ^b Also see ref. 14.		

assignment of the furan protons is clear from the coupling constants and is also in line with the prediction for a furyl ester. In all spectra the methylene quartet and the methyl triplet of the ethoxy substituents of the carbene carbon and ester displayed the largest downfield shift which is consistent with the strong electron-withdrawing character of the $M(CO)_5{C(C_4H_3O)}$ and the ester groups. Since ¹H and ¹³C NMR spectroscopy unambiguously discriminates between the various methylene protons of the ethoxy groups in these compounds, it was the method of choice to use as a probe to study product formation in the reactions of biscarbene complexes and $[Pd(Ph_3)_4]$. Typical spectral ranges for ¹H NMR (¹³C NMR) chemical shifts (δ , ppm) are: 5.0–5.2 (75–77) for Cr=C(OCH₂Me)R, 5.0–4.9 (78–79) for $W = C(OCH_2Me)R$, 4.3–4.4 (61–62) ppm for $O = C(OCH_2Me)R$, 3.9-4.1 (67-69) ppm for trans-RC(OCH₂Me)=C(OCH₂Me)R and 3.7–3.8 ppm for cis-RC(OCH₂Me)=C(OCH₂Me)R. The chemical shifts of the methylene protons of the ethoxy carbene moiety are fairly characteristic for a specific metal and less sensitive to the number and type of carbene substituents. On the other hand the number of carbene ligands as well as the nature of the transition metal involved, determines the chemical shifts of the ring protons of the furan substituent. Single resonances are observed for the ring protons in the symmetrical homonuclear bimetallic biscarbene complexes with δ values in between the highest and lowest values for the corresponding monocarbene complexes. In the biscarbene complexes two metal moieties compete to drain electron density from the double bonds in the furan ring, thus deshielding both H3 and H4 as opposed to H3 and H5 in the monocarbene complexes, a phenomenon that can be explained by π -resonance effects. The assignment of chemical shifts for 5 was made by comparison to the homonuclear bimetallic complexes. An unequal deshielding of H3 and H4 reflects the competitive withdrawal of electron density from 2,5disubstituted furan by different carbone carbons in 5 and by an ester and a carbene in 8. The ester group has a smaller deshielding effect on the adjacent proton (H4) compared to that of a carbene substituent on H3. The ¹³C NMR data supports the proton data and chemical shifts are determined by the type of metal, the carbone carbon or furyl substituent. Carbone carbon and carbonyl carbon resonances are in good agreement with data reported for other group 6 pentacarbonyl carbene complexes.³³

The pentacarbonyl metal fragment has C_{4v} symmetry and of the three infrared active absorption bands the $A_1^{(2)}$ band is by far the more sensitive for electronic properties of the unique ligand.³⁴ For carbene complexes 1-8, which represent good π -acceptor ligands, the $A_1^{(2)}$ band is found at higher wavenumbers compared to the E band. The $A_1^{(2)}$ band is also found at lower wavenumbers for W compared to the corresponding Cr complexes. This effect can be seen when comparing Cr complexes 1 and 3 with W complexes 2 and 4. The mixed metal complex 5 did not show the expected doubling of peaks due to the presence of two different metals. The four peaks observed were however very broad and the poor resolution indicated that the peaks for the carbonyl ligands on the different metals overlap to a great extent. A molecular ion peak, M⁺, was observed in the mass spectra for each of the furan complexes and a general fragmentation pattern was recognized which consisted of the stepwise fragmentation of the carbonyl ligands and carbene-ethoxy moiety.

X-Ray crystallography

Several attempts were made to obtain crystals of especially the heteronuclear dimetallic biscarbene complex but suitable crystals were only obtained for the tungsten biscarbene complex **4**. Crystals of this biscarbene complex were afforded from a hexane–dichloromethane (5 : 1) solution as deep purple needlelike crystals. Crystals of **6** were formed from a concentrated hexane solution cooled to 0 °C. Single crystal X-ray diffraction studies confirmed the molecular structure of the complexes as depicted by the ball-and-stick plots in Figs. 3 and 4.



Fig. 3 Ball-and-stick representation of complex 4.



Fig. 4 Ball-and-stick representation of complex 6.

Although the structure of furan in the gas phase has been determined by microwave spectroscopy,³⁵ the experimental results for the gas phase differ substantially from those reported for the crystalline phase.³⁶ Liescheski and Rankin³⁷ determined the molecular structure of furan by several structural analyses using various combinations of data from gas-phase electron diffraction, rotational spectroscopy and liquid crystal NMR spectroscopy. The best structure obtained confirms the results of the earlier microwave structures, except for the position of

Table 4 Selected bond lengths (Å) and angles (°) for 4, 6 and furan³⁶

the hydrogen atoms. The geometrical parameters for furan, assuming planarity and C_{2v} symmetry as well as selected bond lengths and angles determined for complexes **4** and **6** are tabulated in Table 4.

The six ligands, five carbonyl groups and one carbene, are arranged octahedrally around each metal centre. The W-C(carbene) bond lengths in 4 differ significantly from each other, but is comparable to values of approximately 2.1 Å found in literature³⁸ and agrees excellently with the observed value in the corresponding thiophene biscarbene complex.9 The thiophene biscarbene tungsten complex does not exhibit such a discrepancy between the two metal-carbene carbon bonds (2.154 vs. 2.156 Å). This could be due to the orientation of the tungsten carbene fragments with respect to the furan ring. Fig. 3 shows clearly that the tungsten atoms are on different sides of the furan ring. In the analogous thiophene compound the metal moieties are on the same side of the thiophene ring, opposite to the sulfur atom.9,39 The planarity of the furan ring, carbene carbons and metal atoms in the solid state would facilitate electron delocalisation. The torsion angle O(1)-C(5)-C(4)-C(3)is $0.0(3)^{\circ}$ indicating that the furan ring is planar. On both sides of the heterocycle, the furyl ring, carbene carbon and metal atom are also in the same plane with torsion angles of 180.0(2)and -180.0(2)° for W-C(1)-C(2)-O(1) and W'-C(6)-C(5)-C(4), respectively. On comparing the bond lengths of the furan ring in complex 4 with the bond lengths of uncoordinated furan, evidence is found of electron delocalisation through the ring. All the bonds were equalized to within 0.08 Å with the C(3)-C(4)bond shorter in the complex while the C(2)-C(3) and C(4)-C(5)bonds are fractionally longer. The bond angles within the ring are also within 3° of each other. This delocalisation is carried through to the C(carbene)-C(furyl) bond which is also shorter than normal C–C single bonds (1.448 and 1.464 vs. 1.51(3) Å).

The bond lengths within the fused ring system are not similar, with large deviations in the C(3)–C(3a) and C(5)–C(6) bonds. This deformation indicates incomplete electron delocalisation through the π -system. This may be attributed to electronic rather than steric factors since the rings are coplanar as shown by the torsion angle of 179.4(3)° through the fused ring system. Interestingly, the carbene carbon is bent out of the plane formed by the ring systems as can be seen from the torsion angle of 167.7(3)° for Cr–C(1)–C(2)–C(3) thus electron delocalisation from the aromatic system to the carbene moiety would be inhibited. This leads to the conclusion that the observed stabilisation of the carbene moiety by the aromatic substituent is by inductive effects and not electron delocalisation.

	$4\left(M=W\right)$	$6\left(M=Cr\right)$		$4\left(M=W\right)$	$6 \left(\mathbf{M} = \mathbf{C} \mathbf{r} \right)$
$\begin{array}{l} M-C(1) \\ M'-C(6) \\ M-C(trans-CO) \\ M-C(cis-CO)_{av} \\ M'-C(trans-CO) \\ M'-C(cis-CO)_{av} \\ C(1)-C(2) \\ C(2)-C(3) \\ C(3)-C(4) \\ C(4)-C(5) \\ C(4)-C(9) \\ C(5)-C(6) \\ O(1)-C(2) \\ O(1)-C(9) \\ O(1)-C(5) \end{array}$	2.166(6) 2.139(6) 2.044(7) 2.051(5) 2.046(6) 2.038(5) 1.448(8) 1.382(8) 1.414(7) 1.366(8) 	2.051(7) 	$\begin{array}{l} M-C(1)-C(2)\\ M-C(1)-O(3/4)\\ C(2)-C(1)-O(3/4)\\ C(2)-O(1)-C(5/9)\\ O(1)-C(5/9)-C(4)\\ C(5/9)-C(4)-C(3)\\ C(3)-C(2)-O(1)\\ C(4)-C(3)-C(2)\\ C(5)-C(6)-O(2)\\ O(2)-C(6)-W\\ C(5)-C(6)-W\\ \end{array}$	123.0(4) 131.4(4) 105.6(5) 107.4(4) 109.5(5) 107.7(5) 108.7(5) 106.7(5) 102.2(5) 132.4(4) 125.4(4)	125.4(4) 130.2(4) 104.3(5) 105.0(4) 111.3(5) 105.6(5) 110.5(5) 107.5(5) —
 Furan ³⁶ O–C(2) C(2)–C(3) C(3)–C(4)	1.364(1) 1.364(1) 1.430(2)		C(2)–O–C(5) O–C(2)–C(3) C(2)–C(3)–C(4)	106.74(7) 110.49(7)	

Conclusions

We have shown optimised reaction conditions to synthesize mixed metal binuclear Fischer biscarbene complexes by using an anionic metal acylate protection strategy and a stepwise addition of metal carbonyl precursors. We have demonstrated how one could use $[(CO)_5Cr{C(OEt)-C_4H_2O-C(OEt)}W(CO)_5]$ and $[(CO)_5Cr{C(OEt)-C_4H_2O-C(OEt)}Cr(CO)_5]$ as precursors in benzannulation reaction to synthesize analogous monocarbene complexes of Cr and W with similar modified carbene ligands. The tungsten monocarbene complex is not obtainable starting from $[(CO)_5W{C(OEt)-C_4H_2O-C(OEt)}W(CO)_5]$. This represents but one example of exploiting the regioselectivity induced by different transition metal fragments in binuclear biscarbene complexes and far wider applications in organic syntheses are obvious. In order to gain deeper insight into the conformational preferences of binuclear biscarbene complexes and the role of the heteroatom in the bridging heteroarene moiety, DFT calculations are presently being carried out. In the solid state a differerent conformer is found for the bridging furan compare to bridging thiophene and N-methylpyrrole in binuclear biscarbene complexes.

Experimental

General remarks

All reactions were performed in an inert atmosphere of either nitrogen or argon with dry solvents by using standard Schlenk and vacuum-line techniques. Column chromatography was carried out under a nitrogen atmosphere using silica gel (particle size 0.063-0.200 nm) as stationary phase. Solvents were dried and distilled under an atmosphere of nitrogen before use. Ether, tetrahydrofuran, hexane and toluene were distilled from sodium metal, with benzophenone as indicator in the case of the ethereal solvents. Chloroform and dichloromethane were distilled from phosphorus pentoxide. TMEDA was distilled before use. All other reagents were purchased from commercial suppliers and used without further purification. All NMR spectra were recorded in degassed deuterated chloroform on a Bruker ARX-300 spectrometer. Chemical shifts were referenced to chloroform. ¹H and ¹³C NMR spectra were measured at 300.133 and 75.469 MHz, respectively. Infrared spectra were recorded on a BOMEM Michelson-100 FT-IR spectrophotometer with a NaCl cell using hexane as solvent. Mass spectra were recorded at 70 eV on a Perkin-Elmer RMU-6H instrument using the electron impact method. Melting points were recorded on a hot stage Gallenkamp melting point apparatus and are uncorrected.

Synthesis

Route A.

Synthesis of monocarbene metal complexes via monolithiated furan. 2.0 mmol of furan was dissolved in 10 ml of hexane and a slight excess of n-butyllithium 1.27 ml (2.03 mmol) was added at 0 °C and the reaction was stirred for 30 minutes at room temperature. The reaction mixture was cooled to -10 °C and 10 ml THF was added. 2.0 mmol of M(CO)₆ was added at $-70 \degree$ C and the temperature was allowed to rise to room temperature. Stirring was maintained for a further 15 minutes during which the colour of the reaction mixture usually changed to red-brown. The solvent was removed in vacuo, the reaction residue was redissolved in 10 ml of dichloromethane and cooled to -20 °C. A solution of 0.40 g (2.08 mmol) triethyloxonium tetrafluoroborate in 10 ml of dichloromethane was added. The cooling bath was removed and stirring was continued for a further hour. The mixture was washed with dichloromethane through a filter containing silica gel. The solvent was removed in vacuo and the remainder purified on a silica gel column. Products were isolated starting with hexane as eluting agent and increasing the polarity gradually by adding dichloromethane to the eluting agent.

Route B.

Synthesis of biscarbene metal complexes via monolithiated furan followed by deprotonation of a metal acylate. 2.0 mmol of furan was dissolved in 10 ml of thf and 1.25 ml (2 mmol) of *n*-butyllithium was added at 0 °C and the reaction was stirred for 30 minutes. 2.0 mmol of $M(CO)_6$ was added at -40 °C and the temperature was allowed to rise to room temperature. Stirring was maintained for a further 15 min during which the colour of the reaction mixture usually changed to orange-brown. The reaction mixture was cooled to -78 °C and a thf solution of LDA (2.4 mmol, prepared according to Brandsma)¹⁵ was added. Stirring was maintained at this temperature for 1 h after which the reaction was warmed to -40 °C. 2.0 mmol of M(CO)₆ was added and the temperature was allowed to rise to room temperature. The colour of the reaction mixture usually changed to dark brown. The solvent was removed in vacuo, the reaction residue was redissolved in 10 ml of dichloromethane and cooled to -20 °C. A solution of 0.78 g (4.05 mmol) triethyloxonium tetrafluoroborate in 10 ml of dichloromethane was added. An immediate colour change to dark purple was observed. The cooling bath was removed and stirring was continued for a further hour. The mixture was washed with dichloromethane through a filter containing silica gel. The solvent was removed in vacuo and the remainder purified on a silica gel column. Products were isolated starting with hexane as eluting agent and increasing the polarity gradually by adding dichloromethane to the eluting agent.

Route C.

Dilithiation of furan¹⁶. 0.14 g (2.0 mmol) of furan was dissolved in 10 ml of hexane. 0.75 ml (5.0 mmol) of TMEDA and 3.1 ml (5 mmol) of a 1.6 mol dm⁻³ solution of *n*-butyllithium in hexane were added at room temperature. The mixture was refluxed for 30 minutes and then cooled to 0 °C.

Synthesis of biscarbene metal complexes via dilithiated furan. 2.0 mmol of furan was dilithiated as specified above. The reaction mixture was cooled to -40 °C and 4.0 mmol of M(CO)₆ as well as 5 ml thf was added. The temperature was allowed to rise to room temperature. Stirring was maintained for a further 15 min during which the colour of the reaction mixture usually changed to dark brown. The solvent was removed in vacuo, the reaction residue was redissolved in 10 ml of dichloromethane and cooled to -20 °C. A solution of 0.78 g (4.05 mmol) triethyloxonium tetrafluoroborate in 10 ml of dichloromethane was added. An immediate colour change to dark purple was observed. The cooling bath was removed and stirring was continued for a further hour. The mixture was washed with dichloromethane through a filter containing silica gel. The solvent was removed in vacuo and the remainder purified on a silica gel column. Products were isolated starting with hexane as eluting agent and increasing the polarity gradually by adding dichloromethane to the eluting agent.

Characterisation of products. 1: Red solid; mp 103–106 °C; $C_{12}H_8O_7Cr$ (316.25) calc. C 45.57, H 2.57%, found: C 45.81 H 2.76%. Yield: Method A 0.15 g (24%), method B 0.18 g (29%) and method C 0.48 g (76%); MS (EI): m/z 316 [M⁺], stepwise fragmentation of five carbonyl ions to give the principal ion (I = 100%) [M⁺ – 5CO].

2: Red solid; mp 117–119 °C; $C_{12}H_8O_7W$ (448.09) calc. C 32.16, H 1.81%, found: C 32.55, H 1.97%. Yield: Method A 0.29 g (34%), Method B 0.11 g (13%) and method C 0.67 g (79%); MS (EI): m/z 448 [M⁺], stepwise fragmentation of five carbonyl ligands to give the principal ion (I = 100%) [M⁺ – 5CO].

3: Purple solid; $C_{20}H_{12}O_{13}Cr_2$ (564.3) calc. C 42.57, H 2.14%, found: C 42.86, H 2.33%. Yield: Method A 0.08 g (7%) and Method B 0.44 g (39%); MS (EI): m/z 564 [M⁺]

4: Purple solid; $C_{20}H_{12}O_{13}W_2$ (828.0) calc. C 28.99, H 1.46%, found: C 23.17 H 1.66%. Yield: Method A 0.03 g (2%) and Method B 0.66 g (40%); MS (EI): m/z 828 [M⁺].

Table 5Crystal data and structure refinement of 4 and 6

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
M 828.00482.40 T/K 183(2)183(2) $\lambda/Å$ 0.710730.71073 $Crystal system$ MonoclinicTriclinicSpace group $C2/m$ $P\bar{1}$ Unit cell dimensions $a/Å$ 23.8784(9) $a/Å$ 23.8784(9)7.569(2) $b/Å$ 7.6038(3)10.524(3) $c/Å$ 13.3500(6)14.093(4) $a/°$ 9088.52(1) $\beta/°$ 97.435(3)78.24(2) $\gamma/°$ 9086.29(2) $V/Å^3$ 2403.5(2)1096.6(5) Z 42 $D_c/Mg m^{-3}$ 2.2881.461 μ/mm^{-1} 9.6290.573 $F(000)$ 1536500	
T/K 183(2)183(2) $\lambda/Å$ 0.710730.71073Crystal systemMonoclinicTriclinicSpace group $C2/m$ $P\bar{1}$ Unit cell dimensions $a/Å$ 23.8784(9) $a/Å$ 23.8784(9)7.569(2) $b/Å$ 7.6038(3)10.524(3) $c/Å$ 13.3500(6)14.093(4) $a/°$ 9088.52(1) $\beta/°$ 97.435(3)78.24(2) $\gamma/°$ 9086.29(2) $V/Å^3$ 2403.5(2)1096.6(5) Z 42 $D_c/Mg m^{-3}$ 2.2881.461 μ/mm^{-1} 9.6290.573 $F(000)$ 1536500	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
$\begin{array}{cccc} Crystal system & Monoclinic & Triclinic \\ Space group & C2/m & P\bar{1} \\ Unit cell dimensions & & & \\ a/\mathring{A} & 23.8784(9) & 7.569(2) \\ b/\mathring{A} & 7.6038(3) & 10.524(3) \\ c/\mathring{A} & 13.3500(6) & 14.093(4) \\ a/^{\circ} & 90 & 88.52(1) \\ \beta/^{\circ} & 97.435(3) & 78.24(2) \\ \gamma/\hat{A}^{3} & 2403.5(2) & 1096.6(5) \\ Z & 4 & 2 \\ D_{c}/Mg m^{-3} & 2.288 & 1.461 \\ \mu/mm^{-1} & 9.629 & 0.573 \\ F(000) & 1536 & 500 \\ \end{array}$	
Space group Unit cell dimensions $C2/m$ $P\bar{1}$ $a/Å$ 23.8784(9)7.569(2) $b/Å$ 7.6038(3)10.524(3) $c/Å$ 13.3500(6)14.093(4) $a/^{\circ}$ 9088.52(1) $\beta/^{\circ}$ 97.435(3)78.24(2) $\gamma/^{\circ}$ 9086.29(2) $V/Å^3$ 2403.5(2)1096.6(5) Z 42 $D_c/Mg m^{-3}$ 2.2881.461 μ/mm^{-1} 9.6290.573 $F(000)$ 1536500	
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Z 4 2 $D_c/\mathrm{Mg}\mathrm{m}^{-3}$ 2.288 1.461 μ/mm^{-1} 9.629 0.573 $F(000)$ 1536 500	
$\begin{array}{ccc} D_{\rm c}/{\rm Mgm^{-3}} & 2.288 & 1.461 \\ \mu/{\rm mm^{-1}} & 9.629 & 0.573 \\ F(000) & 1536 & 500 \end{array}$	
μ/mm^{-1} 9.629 0.573 F(000) 1536 500	
F(000) 1536 500	
Crystal size/mm $0.10 \times 0.10 \times 0.08$ $0.09 \times 0.08 \times 0.07$	
θ Range for data collection/° 2.15–27.50 2.42–21.05	
Index ranges, hkl -29 to 30, -9 to 9, -16 to 17 -7 to 7, -10 to 10, -14 to 14	
Reflections collected 9142 3571	
Independent reflections (R_{int}) 2775 (0.0735) 2175 (0.047)	
Completeness to $\theta = 27.50^{\circ}$ 93.4 91.6	
Absorption correction Semi-empirical —	
Max., min. transmission 0.286, 0.197 —	
Refinement method Full-matrix least-squares on F^2 Full-matrix least-squares on F^2	
Data/restraints/parameters 2775/0/187 2175/0/289	
Goodness-of-fit on F^2 0.977 1.106	
Final <i>R</i> indices $[I > 2\sigma(I)]$ R1 = 0.0269, wR2 = 0.0586 R1 = 0.0500, wR2 = 0.1181 R1 = 0.0202, wR2 = 0.0586 R1 = 0.0500, wR2 = 0.1181	
<i>R</i> Indices (all data) $R1 = 0.0336$, $wR2 = 0.0599$ $R1 = 0.0821$, $wR2 = 0.1373$	
Largest diff. peak, hole/e A^{-3} 0.772, -1.397 0.251, -0.295	

5: Purple solid; $C_{20}H_{12}O_{13}CrW$ (696.1) calc. C 34.52, H 1.74%, found: C 34.71 H 1.95%. Yield: Method B 0.68 g (47%); MS (EI): m/z 696 [M⁺].

8: Red solid; $C_{15}H_{12}O_9Cr$ (388.3) calc. C 46.39, H 3.13%, found: C 46.61 H 3.26%. Yield: Method A 0.02 g (2%) and method B 0.17 g (15%); MS (EI): m/z 388 [M⁺], stepwise fragmentation of five carbonyl ions to give the principal ion (I = 100%) [M⁺ – 5CO].

Reactions of metal carbene complexes.

Benzannulation of a biscarbene metal complex and 3-hexyne¹⁹. 0.45 ml (4 mmol) 3-hexyne was added to a stirred solution of 1 mmol of the biscarbene metal complex in 10 ml toluene. The reaction mixture was stirred at 80 °C for 24 h. The solvent was removed under reduced pressure and the remainder purified by column chromatography on silica gel. Starting with hexane as eluting agent and increasing the polarity gradually by adding dichloromethane to the eluting agent isolated products. Several organic products were formed but no attempt was made to isolate and characterise non-metal containing compounds.

*Palladium catalysed carbene–carbene coupling reactions*³⁰. The carbene complex (1 mmol) and 0.1 molar equivalents of Pd(PPh₃)₄ was refluxed in 10 ml of thf for 3 h. The solvent was removed under reduced pressure and the remainder purified by column chromatography on silica gel. Products were isolated starting with hexane as eluting agent and increasing the polarity gradually by adding dichloromethane. This experiment was repeated in hexane and refluxed overnight.

X-Ray crystallography

Data were collected at -90 °C on a Nonius-Kappa CCD diffractometer using graphite-monochromated Mo-K α radiation. Data were corrected for Lorenz polarization effects but not for absorption.^{40,41} The structures were solved by direct methods (SHELXS)⁴² and refined by full-matrix least squares techniques against F^2 (SHELXL-97).⁴³ The hydrogen

atoms of the structures were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. XP software (SIEMENS Analytical Xray Instruments. Inc.) was used for structure representations. Crystal data and other experimental procedures and refinement parameters are given in Table 5.

CCDC reference numbers 240666 (4) and 240667 (6).

See http://www.rsc.org/suppdata/dt/b4/b419148j/ for crystallographic data in CIF or other electronic format.

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