Multimetal Fischer carbene complexes of Group VI transition metals: synthesis, structure and substituent effect investigation†

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Fischer carbene complexes of tungsten with substituents containing up to two additional different transition metals, with all the metals in electronic contact with the carbene carbon atom, were synthesised and studied both in solution and in the solid state. For the complexes of the type \([\text{W(CO)}_5\{\text{C(OR)}_2\text{R}\}])\), the substituents chosen were heteroaromatic 2-benzothienyl (2-BT), or 2-BT \(\pi\)-bonded to a chromium tricarbonyl fragment \([\text{Cr(CO)}_3(2-\eta^5\text{-BT})])\) or ferrocenyl (Fc) as the R-substituent, while the OR- substituted was systematically varied between an ethoxy or a titanoxo group, to yield the complexes 1b (\(\text{R}' = \text{Et}, \text{R} = 2\text{-BT}\)), 2b (\(\text{R}' = \text{Et}, \text{R} = \text{Cr(CO)}_3(2-\eta^5\text{-BT})\)), 3b (\(\text{R}' = \text{TiCp}_2\text{Cl}, \text{R} = 2\text{-BT}\)), 4b (\(\text{R}' = \text{TiCp}_2\text{Cl}, \text{R} = \text{Cr(CO)}_3(2-\eta^5\text{-BT})\)), 5b (\(\text{R}' = \text{Et}, \text{R} = \text{Fc}\)) and 6b (\(\text{R}' = \text{TiCp}_2\text{Cl}, \text{R} = \text{Fc}\)). The structural features and their relevance to bonding in the multimetal carbene compounds of both these tungsten and the analogous chromium complexes were investigated as they represent indicators of possible reactivity sites in multimetal carbene assemblies. The possibility of using DFT calculations to quantify the effect of metal-containing substituents on the carbene ligands was tested and correlated with experimental parameters by employing methods such as vibrational spectroscopy, molecular orbital analysis, and cyclic voltammetry.

Introduction

The activation of simple organic molecules by more than one transition metal constitutes an area of research that has grown in importance. The applications of carbones as active or auxiliary ligands in organic synthesis and catalysis, however, are mostly focused on monocarbene systems. Examples of large assemblies of carbene units (carbene supramolecular chemistry) are scarce and only a few carbene complexes are known to be part of small metal organic frameworks (MOFs).1 In fact very few studies on multimetal carbene complexes or multicarbene metal complexes have been recorded.2

The first examples of chromium Fischer carbene complexes with substituents containing an additional two transition metals, with all three metals in electronic contact with the carbene carbon atom, were synthesised in our laboratories (Fig. 1).3 Monometal and dimetal substituted carbene complexes were derived from a lithiated benzothienyl substituent (2-BT) or \([\text{Cr(CO)}_3(\eta^5\text{-2-BT})])\), followed by alkylation of the acyl metalate by triethylxomium tetrafluoroborate or other electronic format see DOI: 10.1039/c1dt10183h

† CCDC reference numbers 810995–810999. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10183h

Fig. 1 Multimetal carbene complexes of chromium.
It was concluded that stabilisation occurs by conjugative release of electrons from the heteroarene substituent R rather than specific $\pi \rightarrow \rho$ donation. Hence the electronic character of the carbene carbon atom is more strongly influenced by the X group than either the metal or the R group.

Experimental

General considerations

All operations were carried out under an inert atmosphere of nitrogen or argon gas using standard Schlenk techniques. Solvents were dried and distilled under an atmosphere of nitrogen. Diethyl ether, hexane and THF were distilled from sodium metal, with benzophenone as indicator for the ethereal solvents. Dichloromethane was distilled from phosphorous pentoxide. Most chemicals were used without prior purification, unless stated otherwise. W(CO)$_6$, Cr(CO)$_6$, benzo[\(\eta\)-thiophene, ferrocene, $\eta$-BuLi (1.6 mol dm$^{-3}$) solution in hexane) and titanocene dichloride were used as purchased. Triethylsilium tetrafluoroborate was prepared according to Fish and Rosenblum’s method. Column chromatography using silica gel 60 (0.0063–0.200 mm) or neutral aluminum oxide 90 as the stationary phase was used for all separations, and columns were cooled by circulating ice-water through the column jackets. Melting points were not recorded due to decomposition during heating. NMR spectra were recorded on a Bruker AVANCE 500 spectrometer. $^1$H NMR spectra were recorded at 500.139 MHz and $^{13}$C NMR spectra at 125.75 MHz. The signal of the deuterated solvent was used as reference, e.g. $^1$H CDCI$_3$, 7.24 ppm, benzene-$d_6$ 7.15 ppm and $^{13}$C CDCI$_3$, 77.00 ppm, benzene-$d_6$ 128.00 ppm. FAB-MS spectra were recorded on a VG 70SEQ Mass Spectrometer, with the resolution for FAB = 1000 in a field of 8 kV. Nitrobenzyl alcohol was used as the solvent and as the internal standard.

Synthesis of 1–6

The general method for the synthesis of the chromium carbene complexes as described before was employed to prepare the tungsten analogues (Scheme 1). The ferrocenyl ethoxycarbene complexes of both chromium and tungsten (5a and 5b) are known, and their structures have been reported. The relevant (hetero)arene (benzo[\(\eta\)-thiophene, [Cr(CO)$_3$(\(\eta\)-2-BT)] or FcI) (5 mmol) was stirred while adding $\eta$-BuLi (5.5 mmol, 1.5 M, 3.66 mL) in 40 mL of THF at $-20^\circ$C under an inert N$_2$ atmosphere. Stirring was continued for 2 h. [W(CO)$_3$] (5 mmol) was added at $-78^\circ$C, resulting in the reaction mixture changing to a darker color, while stirring for 1 h. Stirring was then continued for an additional 30 min at RT. THF solvent was evaporated under reduced pressure. Et$_3$OBF$_4$ (6 mmol, 1.15 g) or TiCp$_2$Cl$_2$ (6 mmol, 1.49 g) in dichloromethane was added to the reaction mixture at $-30^\circ$C and stirred until reaction completion. LiBF$_4$/LiCl salts were removed by filtration and the reaction products were separated by column chromatography using hexane/dichloromethane (4:1) as the eluent. The products were recrystallised by solvent layering using hexane/dichloromethane (1:1). The atom numbering system employed in the NMR spectra is given in Fig. 2. No $^{13}$C NMR spectra could be obtained for 3b and 4b due to the decomposition of these complexes in solution over the long accumulation times required for recording of these complexes’ NMR spectra.

![Fig. 2 Atom numbering system used for NMR spectral data.](image)

[W(CO)₅{(C≡OEt)[{(t⁵²}→-2-Br)Cr(CO)₅}] (3b) (abbreviated as WBTcEtR): yield 1.63 g (37%), dark brown crystals. Anal. found (calc. for C₃₈H₅ₐO₅SCrW): C 35.83 (35.10), H 1.65 (1.55)%. NMR, 500 MHz (CDCl₃); 1H: 8.05 (s, 1H, H₃), 6.07 (d, 1H, H₄, J = 6.7 Hz) 5.64 (m, 1H, H₅), 5.25 (m, 1H, H₆, J = 6.5 Hz), 6.29 (dd, 1H, H₇, J = 6.5 Hz), 4.98 (q, 2H, CH₂, J = 7.1 Hz), 1.67 (t, 3H, CH₃, J = 7.1 Hz).); 13C (C₃₈H₅ₐO₅SCrW): 79.1 (s, 1H, H₃), 5.00 (d, 1H, H₄, J = 6.5 Hz) 4.56 (m, 1H, H₅, J = 6.5 Hz), 5.13 (d, 1H, H₁, J = 6.5 Hz), 4.24 (q, 2H, CH₂, J = 7.0 Hz), 0.94 (t, 3H, CH₃, J = 7.0 Hz); IR ν(CO) (hexane): W(CO)₅: 2067 m (A₁⁻), 1980 vw (B), 1945 vs (E). Cr(CO)₅: 1945 vs (A₁⁻), 1907 s (E). UV (CH₂Cl₂) 325 (L: π → π⁺), 449, 55 (M → L). FAB-MS; m/z = 650 (M⁺).

[W(CO)₅{(C≡OTiCp₂Cl)F} (4b) (abbreviated as WFCETi): yield 2.35 g (83%), dark brown crystals. Anal. found (calc. for C₃₈H₅ₐO₅STiW): C 37.98 (38.20), H 1.76 (1.81)%). NMR, 500 MHz (CDCl₃); 1H: 7.95 (d, 1H, H₃, J = 0.8 Hz), 5.11 (d, 1H, H₄, J = 6.7 Hz), 4.57 (m, 1H, H₅), 4.15 (m, 1H, H₆), 2.22 (dd, 1H, H₇, J = 6.7, 0.8 Hz), 5.88, 5.85 (Cp’s); IR, ν(CO) (hexane): 2060 m, 1969 s, 1930 vs, 1900 s. UV (Å × nm⁻¹, CH₂Cl₂) 325 (L: π → π⁺), 494, 57 (M → L). FAB-MS; m/z = 844 (M⁺).

[W(CO)₅{(C≡OEt)F} (5b) (abbreviated as WFCETi): yield 2.35 g (83%), dark brown crystals. Anal. found (calc. for C₃₈H₅ₐO₅STiW): C 38.32 (38.5), H 1.76 (1.81)%. NMR, 500 MHz (CDCl₃); 1H: 4.78 (dd, 2H, H₁, H₃, J’ = 2.2, 1.8 Hz), 4.27 (dd, 2H, H₄, H₄, J = 2.3, 1.7 Hz) 3.92 (s, 5H, Fe–Cp), 4.49 (q, 2H, CH₂, J = 7.0 Hz), 0.95 (t, 3H, CH₃, J = 7.0 Hz); 13C: 303 (C₁), 191 (CO₂), 198 (CO₃₉), n.o. (C₂), 74 (C₃,C₃˪), 71 (C₄,C₄˪), 68 (Fe–Cp), 78 (CH₂), 15 (CH₃); IR ν(CO) (hexane): 2065 w (A₁⁻), 1975 w (B and A₁⁻), 1927 s (E). FAB-MS; m/z = 566 (M⁺).

Crystal structure determination

Single crystals suitable for data collection were obtained for 1b–4b and 6b. Crystallographic and structure refinement data are given in Table 1. The X-ray crystal structure analyses were performed using data collected at 20 °C on a Siemens P4 diffractometer fitted with a Bruker 1 K CCD detector using graphite-monochromated, Mo-Kα radiation by means of a combination of phi and omega scans. Data reductions were performed using SAINT⁺¹⁴ and the intensities were corrected for absorption using SADABS.¹⁴ The structures were solved by direct methods using SHELXTL¹⁴ and refined by full-matrix least squares using SHELX-97.¹⁴ In the structure refinements all hydrogen atoms were included in calculated positions and treated as riding on the atom to which they are attached. All non-hydrogen atoms (except for the minor occupied sites of disordered atoms) were refined with anisotropic displacement parameters. All isotropic displacement parameters for hydrogen atoms were calculated as $X × U_{eq}$ of the

<table>
<thead>
<tr>
<th>Complex</th>
<th>1b</th>
<th>2b</th>
<th>3b</th>
<th>4b</th>
<th>6b</th>
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<tr>
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<td>C₃₈H₅₉Cl₂STiCH₂Cl</td>
<td>C₃₈H₅₉CrO₅SW</td>
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<td>783.55</td>
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<td>Triclinic</td>
<td>Monoclinic</td>
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<td>P1</td>
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<td>11.3533(6)</td>
<td>8.4597(6)</td>
<td>11.2280(5)</td>
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<td>11.6693(6)</td>
<td>10.8010(8)</td>
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<td>90</td>
<td>90</td>
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<td>104.638(16)</td>
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<td>2539.2(6)</td>
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<td>9495</td>
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<td>0.0305</td>
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<td>290</td>
<td>419</td>
<td>325</td>
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<td>0.0264</td>
<td>0.0444</td>
<td>0.0307</td>
<td>0.0413</td>
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<td>wR₁ (all data)</td>
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<td>0.0709</td>
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<td>0.0871</td>
<td>0.0996</td>
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<td>Absolute structure (Flack) parameter</td>
<td>0.027(14)</td>
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</table>
atom to which they are attached, X = 1.5 for methyl hydrogens and 1.2 for all other hydrogens. Crystallographic and structure refinement data are given in Table 1. In the structure of 3b some disorder of the thienyl ring was observed with a minor orientation (sof = 0.156(7)) arising from an alternate conformer of the η⁶-tricarbonylchromium-benzol[b]thien-2-yl group with the thienyl ring rotated c.a. 180° with respect to the η⁶-tricarbonylchromium-benzene moiety. The parameters for the major orientations were refined freely. The minor orientation atoms S(1a) and C(8a)–H(8a) were refined with isotropic displacement parameters and with the bond lengths to neighbouring atoms constrained to approximately equal the corresponding bond lengths in the major orientation. Two site occupation factors, one for the major orientation positions S(1), C(8) and H(8) and one for the minor orientation positions S(1a), C(8a) and H(8a), were refined but constrained to sum to 1.0.

Vibrational spectroscopy

Solution IR spectra were recorded on a Perkin–Elmer Spectrum RXI FT-IR spectrophotometer with dichloromethane as the solvent. Only the vibration bands in the carbonyl-stretching region (ca. 1600–2200 cm⁻¹) were recorded for the solution IR. Solid state Fourier Transform infrared (FTIR) spectra were obtained under vacuum as a 1% w/w CsI disk using a Bruker IFS 113 spectrometer over the region 125–4000 cm⁻¹ with a spectral resolution of 4 cm⁻¹. OPUS 5.5 software was used for data processing. Experimental solid-state Raman spectra were obtained using a dispersive Raman spectrometer. All dispersive spectra were obtained by exciting the samples with the 647.1 nm (red) line of a Spectra-Physics 5012 Krypton-ion laser. For the solid-state spectra, an Olympus confocal microscope with a 50x objective was used to focus the laser light on the sample. The scattered light was dispersed and recorded by means of a Dilor XY multichannel Raman spectrometer equipped with a liquid nitrogen-cooled Wright Generation 1 CCD detector. A Linkam RMS 90 cell was employed to obtain the solid-state Raman spectrum for all the complexes measured at non-ambient conditions of ~196 °C, as degradation of the samples was seen at room temperature. All Raman spectra were obtained from the same samples as used for solid state FTIR: as CsI pellets, to allow heat dissipation by the solvent. Only the vibration bands in the carbonyl-stretching region were separated from the test solution by a salt bridge containing 0.10 M Bu4NPF6, which was synthesised by metathesis of Bu4Br and HPF6, recrystallised from dichloromethane/hexane, and dried under vacuum. HPLC grade dichloromethane was used as the solvent in all experiments. Once opened, the solvent was kept under argon and contact with the atmosphere was minimised. Additional purification was not deemed necessary or desirable. Cyclic voltammetry was carried out with EG&G 173/175/179 potentiostatic instrumentation. The working electrode was a 1 mm diameter platinum disk, and the counter electrode was a platinum wire. The reference was a Metrohm Ag/AgCl electrode filled with dichloromethane/Bu4NPF6 and saturated with LiCl: this was separated from the test solution by a salt bridge containing 0.10 M Bu4NPF6 in CH2Cl2.

Results and discussion

Molecular structures

The crystallographic molecular structures of 1b–4b and 6b, are shown in Fig. 3–7 together with the atom numbering schemes used for the structural data.

Computational details

The calculations reported were obtained with the GAUSSIAN 03 suite of programmes. Each complex was modelled using spin restricted DFT wavefunctions (RB3LYP) with effective core potentials basis set LANL2DZ. No symmetry constraints were applied and only the default convergence criteria were used during the geometric optimizations. The complexes were all modelled in the singlet spin state and the optimized structures were confirmed to be minima energy conformations as the vibrational frequency analysis yielded no imaginary frequencies. RMS deviations between the optimized molecular structures and the crystal structures using the non-hydrogen atoms were calculated with the ‘RMS Compare Structures’ utility in CHEMCRAFT Version 1.5.19 Good agreements between experimental and theoretical structures were obtained, reflected by RMSD values in the range of 0.10–0.16 Å for the chromium complexes, and 0.06–0.19 Å for the tungsten complexes.

Electrochemical studies

Voltammetric experiments were performed under a blanket of nitrogen that was saturated with solvent. The electrolyte was 0.10 M Bu4NPF6, which was synthesised by metathesis of Bu4Br and HPF6, recrystallised from dichloromethane/hexane, and dried under vacuum. HPLC grade dichloromethane was used as the solvent in all experiments. Once opened, the solvent was kept under argon and contact with the atmosphere was minimised. Additional purification was not deemed necessary or desirable. Cyclic voltammetry was carried out with EG&G 173/175/179 potentiostatic instrumentation. The working electrode was a 1 mm diameter platinum disk, and the counter electrode was a platinum wire. The reference was a Metrohm Ag/AgCl electrode filled with dichloromethane/Bu4NPF6 and saturated with LiCl: this was separated from the test solution by a salt bridge containing 0.10 M Bu4NPF6 in CH2Cl2.

As observed for the chromium complexes,1 the thienyl and the ferrocenyl cyclopentadienyl ring are approximately coplanar with the carbene moiety (W(1), C(6), O(6), C(7)), with torsion angles W(1)–C(6)–C(7)–S(1)/C(11) ranging from 165.5(2)° to 180.0°, thus allowing resonance stabilisation between the carbene ligand and the adjacent ring. The most significant features of the structures are the long Ti(1)–O(6) bond lengths of 2b (1.931(2) Å), 4b (1.921(3) Å) and 6b (1.901(6) Å), compared to that of typical terminal titanium(iv) alkoxides (1.855 Å in [TiCp2(OEt)Cl]) 28 The very short C(6)–O(6) bond distances of these complexes (1.279(4), 1.280(5) and 1.273(11) Å, respectively), as well as the near-linear bond angles for C(6)–O(6)–Ti(1) (171.7(3), 174.6(3) and 175.4(7)°, respectively), is indicative of O(6)→C(6) π-donation occurring at
Fig. 4 ORTEP\textsuperscript{13} + POV-Ray\textsuperscript{44} drawing of the molecular structure of 2b. Atomic displacement ellipsoids are shown at the 50\% probability level.

Fig. 5 ORTEP\textsuperscript{13} + POV-Ray\textsuperscript{44} drawing of the molecular structure of 3b. Atomic displacement ellipsoids are shown at the 50\% probability level. The minor positions of the disordered atoms –S(1a) and C(8a)-H(8a) are shown as small arbitrary sized spheres and with their bonds in a lighter colour.

Fig. 6 ORTEP\textsuperscript{13} + POV-Ray\textsuperscript{44} drawing of the molecular structure of 4b. Atomic displacement ellipsoids are shown at the 50\% probability level.

Fig. 7 ORTEP\textsuperscript{13} + POV-Ray\textsuperscript{44} drawing of the molecular structure of 6b. Atomic displacement ellipsoids are shown at the 50\% probability level.

The W–C(carbene) bond distances fall in the range 2.179(7)–2.253(9) Å, which is typical for alkoxy carbene complexes of W(CO)\textsubscript{5}.\textsuperscript{22} The longest tungsten-carbene bond length is associated with complex 6b, where the π-delocalisation of the ferrocene ring (Fig. 9)\textsuperscript{21} as well as inductive effects towards stabilizing the carbene carbon atom requires less back bonding from the W(CO)\textsubscript{5}-moiety.

The structures containing a Cr(CO)\textsubscript{3}-fragment π-bonded to the benzothienyl substituent (3b and 4b) result in shorter W–C(carbene) bond distances than the corresponding counterparts 1b and 2b without the π-Cr(CO)\textsubscript{3} group (Table 2). The π-bond of a metal to a heteroarene acts as an ‘electron sink’,\textsuperscript{24} disrupting the prevalent aromaticity of the ring and exerts an electron withdrawing inductive effect causing increased ring participation in carbene stabilisation.\textsuperscript{25} The W–C(carbene) bond distances can be listed in order of increasing bond length, as a measure of the amount of back donation required from the tungsten carbonyl centre towards carbene stabilisation:

\[
\begin{align*}
\text{WBCrEt}_3 \ (2.179(7) \text{ Å}) &< \ W\text{BTEt}_1 \ (2.201(5) \text{ Å}) < \ \text{WBCrTi}_4 \ (2.207(4) \text{ Å}) < \ \text{WBTi}_2 \ (2.211(4) \text{ Å}) < \ \text{WFcEt}_5 \ (2.215(4) \text{ Å}) < \ \text{WFcTi}_6 \ (2.253(9) \text{ Å})
\end{align*}
\]

This order reflects the extreme cases of greater donor ability of the ferrocenyl substituent and the ionic character of the titanoxycarbene vs. the electron withdrawing effect of the π-Cr(CO)\textsubscript{3} moiety and the ‘less’ donating ethoxy substituent. However, no clear trend about the effect of different combinations of these metal-containing substituents can be ascertained.

\section*{Crystal packing}

Packing of both the chromium\textsuperscript{1} and tungsten crystal structures obtained seemed to be mostly governed by closest-packing, except in the case of 6a and 6b. The previously characterised chromium ferrocenyl carbene complex 6a (Fig. 10)\textsuperscript{16} crystallised in the \(P2_1/n\) space group with one dichloromethane solvent molecule per complex molecule. The complex molecules display π-stacking
of the ferrocenyl Cp-rings, stacked one above the other, separated by 3.584 Å. The corresponding tungsten complex 6b crystallised in the Pna2₁ space group, and no solvent inclusion is observed. In both cases, however, the crystal packing is such that pockets are formed, which in the case of 6a is filled with two dichloromethane molecules (Fig. 11). The cell volumes of the different structures indicate that although tungsten has a considerably larger atomic volume of 2539.2(6) Å³, as demonstrated in Fig. 11 (left, bottom), in which two of the solvent molecules in the crystal packing of 6a have been deleted from the pocket, compared to the much smaller empty space/pocket of 6b in Fig. 11(right, bottom).

Substituent effect investigation

An attempt was made to correlate the donor properties of the various carbene ligands in the complexes listed in Scheme 1 with respect to both the C=O stretching frequencies and bond lengths. With the aid of DFT calculations, the A¹ band, the mode associated with the stretching of the C–O bond trans to the carbene ligand, was chosen as probe, as it was expected to be most affected by the electronic environment. To exclude solvent effects, solid, crystalline samples of complexes 3a and 3b (MBTCrEt); 4a and 4b (MBTCTi); and 6a and 6b (MFcTi) (M = Cr, W) were obtained and solid state infrared and Raman spectra measured. The IR data displayed clearly resolved spectra, with the expected localised Cᵥ pattern of the IR-active A¹; A¹ and E-modes for a M(CO)₅L-system. Although all four modes (A¹, A¹, B₁, and E) are Raman-active, only two bands were confidently observed in the Raman spectra: the A¹ and (E + A¹) bands. Due to accidental degeneracy, the E and the A¹ bands cannot be resolved in the solid state. In addition, the A¹ band (trans v(CO)) was not observed in the presence of titanoxycarbene substituents due to distortional effects, as illustrated in Fig. 12. From the crystal structures of these complexes, it can be seen that the Cl-atom of the titanoxo substituent protrudes in between two C–O stretching frequencies and bond

Table 2: Selected bond lengths (Å) and bond angles (°) for the tungsten carbene complexes

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>1b</th>
<th>2b</th>
<th>3b</th>
<th>4b</th>
<th>6b</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(1)–C(6)</td>
<td>2.201(5)</td>
<td>2.211(4)</td>
<td>2.179(6)</td>
<td>2.207(4)</td>
<td>2.253(9)</td>
</tr>
<tr>
<td>C(6)–O(6)</td>
<td>1.315(6)</td>
<td>1.279(4)</td>
<td>1.317(8)</td>
<td>1.280(5)</td>
<td>1.273(11)</td>
</tr>
<tr>
<td>C(6)–C(7)</td>
<td>1.469(7)</td>
<td>1.474(5)</td>
<td>1.459(7)</td>
<td>1.492(3)</td>
<td>1.461(6)</td>
</tr>
<tr>
<td>O(6)–C(18)</td>
<td>1.447(6)</td>
<td>1.391(2)</td>
<td>1.459(7)</td>
<td>2.006(6)</td>
<td>2.008(13)</td>
</tr>
<tr>
<td>W(1)–C(6)</td>
<td>2.018(6)</td>
<td>2.007(4)</td>
<td>2.011(7)</td>
<td>2.006(13)</td>
<td>2.022(27)</td>
</tr>
<tr>
<td>W(1)–C(2,3,4,5)</td>
<td>1.756(5)</td>
<td>1.755(4)</td>
<td>1.778(5)</td>
<td>1.432(14)</td>
<td>1.272(9)</td>
</tr>
</tbody>
</table>

* Averaged value (the errors shown are the standard deviations, σ, for the n components averaged).
Fig. 11 Mercury® views along the a-axis to indicate presence of pocket/channel of 6a and 6b, as well as space-filled representations (from which solvent molecules of 6a have been deleted).

Fig. 12 ν(CO) region of the Raman spectra of complexes 2b, 4b and 6b, showing the disappearance of the A1 band due to distortion effect of -TiCp2Cl substituent.

Fig. 13 Mercury® space-filled representation of the Cl-atom protruding between two cis-CO ligands of complex 6b.

employed to assist in the assignment of a M=C carbene stretching frequency. However, the modelled data indicated that no pure ν(M=C carbene) mode exists. Instead, a bending vibration or scissor mode could be identified from the calculations. A representative overlay of the measured experimental IR and Raman spectra and the calculated spectra used for assignment is demonstrated in Fig. 14. The IR spectra illustrated in Fig. 14 also display the ring-C–H deformation δ(C aromatic–H) modes. The δ(CC carbene) scissor mode consists of a ‘stretching’ displacement of the carbene carbon atom towards the central metal atom, with contribution
Fig. 14 Comparitive experimental (bold) and unscaled calculated (thin line) IR (left) and Raman (right) spectra of the \( \delta(\text{CC}_{\text{carbon}} \text{O}) \) scissor mode for the chromium complexes.

Table 3 Experimental IR and Raman data of substituent influenced vibrational bands (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Assignment</th>
<th>3a CrBTCrEt</th>
<th>4a CrBTCrTi</th>
<th>6a CrFcTi</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu(\text{CO}) ) ( A_1 )</td>
<td>IR 1963</td>
<td>IR 1934</td>
<td>IR 1921</td>
</tr>
<tr>
<td>( \delta(\text{CC}_{\text{carbon}} \text{O}) )</td>
<td>893</td>
<td>741</td>
<td>742</td>
</tr>
<tr>
<td>Assignment</td>
<td>3b WBTCrET</td>
<td>4b WBTCrTi</td>
<td>6b WFeTi</td>
</tr>
<tr>
<td>( \nu(\text{CO}) ) ( A_1 )</td>
<td>IR 1960</td>
<td>IR 1913</td>
<td>IR 1928</td>
</tr>
<tr>
<td>( \delta(\text{CC}_{\text{carbon}} \text{O}) )</td>
<td>895</td>
<td>746</td>
<td>748</td>
</tr>
</tbody>
</table>

IR: infrared, R: Raman
A striking result of the literature MO calculations on the carbene complexes was the marked separation of the LUMO from all of the other molecular orbitals. The energy differences between the LUMO's and the next-closest lying molecular orbitals were calculated, (Table 4) to determine if the energy differences between the LUMO's and the next-closest lying orbitals was reversed. This once again demonstrates the donating properties of the ferrocenyl group, and the largest electrophilicities of the tricarbonyl. This was not greatly influenced by R for a specific X-group, provided that X was an organic fragment. But if R = Fc, redox potentials decreased by more than 200 mV. Similarly for decreasing donor strength of X into C_carbene p orbital, increased redox potentials were observed.

When electrophilic indices were calculated by Frenking et al. for Fischer carbene complexes, it was found that π-donor substituents reduce the electrophilicity of the complexes, as a result of the acceptor orbital in the carbene becoming occupied by π-donation. The values listed in Table 4 appear to adhere to the above statement. Thus for every fixed [M(CO)5{C(OX)(aryl)}] (X = Et or TiCp2Cl), the electrophilicity increases following the order Fe < 2-benzothienyl < 2-η^2-benzo[θ]thienyl chromium tricarbonyl. This once again demonstrates the donating properties of the ferrocenyl group, and the largest electrophilicities of the π-bonded Cr(CO)3-substituted carbene complexes in line with the acceptor character of these substituents. Due to the greatly differing nature of these substituents, a greater impact on the carbene electrophilicity is effected by these ring-substituents, compared to the results of Connor et al. where the nature of the heteroatom substituent, rather than the arene-substituent or the metal, more strongly influenced the electronic nature of the carbene carbon atom. In the case of the ferrocenyl and benzothienyl complexes, higher electrophilicity indices were calculated for the titanoxycarbenes. For the [Cr(CO)3(2-η^2-BT)]-substituted complexes, higher ω-values were obtained for the ethoxycarbene complexes, as expected from previous results where the donating character of the acyl-like oxygen of the titanoxycarbenes were demonstrated.

### Table 4  Calculated molecular orbital energy differences (eV) and electrophilicity indices (eV)

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>2a</th>
<th>3a</th>
<th>4a</th>
<th>5a</th>
<th>6a</th>
</tr>
</thead>
<tbody>
<tr>
<td>(LUMO) – (HOMO)</td>
<td>3.3632</td>
<td>2.9414</td>
<td>2.6176</td>
<td>2.7085</td>
<td>3.6932</td>
<td>3.1315</td>
</tr>
<tr>
<td>(LUMO + 1) – (LUMO)</td>
<td>1.5374</td>
<td>0.3320</td>
<td>1.7387</td>
<td>0.4827</td>
<td>1.0198</td>
<td>0.0460</td>
</tr>
<tr>
<td>η</td>
<td>3.4915</td>
<td>3.7864</td>
<td>4.6486</td>
<td>4.5005</td>
<td>2.5919</td>
<td>2.5919</td>
</tr>
</tbody>
</table>

Cyclic voltammetry

For carbene complexes of the type [M(CO)3C(X)R] (M = Cr, Mo and W), cyclic voltammetry showed that the primary oxidation of these complexes corresponded to a one electron transfer. The value of $E_{1/2}$ was not greatly influenced by R for a specific X-group, provided that X was an organic fragment. But if R = Fc, redox potentials decreased by more than 200 mV. Similarly for decreasing donor strength of X into C_carbene p orbital, increased redox potentials were observed.

### Table 5  Voltammetric data (V)^a

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>2a</th>
<th>3a</th>
<th>4a</th>
<th>6a</th>
<th>1b</th>
<th>2b</th>
<th>4b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation $E_{1/2}$</td>
<td>+0.97</td>
<td>+0.74</td>
<td>+1.00</td>
<td>+0.93</td>
<td>+0.84</td>
<td>+1.19</td>
<td>+1.03</td>
<td>+1.11</td>
</tr>
<tr>
<td>Reduction $E_{1/2}$</td>
<td>–0.21</td>
<td>–0.95</td>
<td>–1.09</td>
<td>–0.88</td>
<td>–1.05</td>
<td>–1.03</td>
<td>–1.05</td>
<td>–1.10</td>
</tr>
</tbody>
</table>

a 1.0 mm [carbene complex] in CH2Cl2/0.10 M Bu4NPF6 under N2 (g) at –75 °C. The working electrode was a 1.0 mm diameter platinum disk, and the scan rate was 0.50 V s^-1. A ferrocene internal standard had $E_{1/2} = +0.52$ V. $E_p$ = peak potential of irreversible cathodic waves, or first reduction wave of reversible waves. These values correspond to the irreversible anodic wave peak potential $E_p$ of the tungsten complexes.
chromium and tungsten complexes, the ethoxy substituted complexes only showed one cathodic wave, while the cyclic voltammograms of the titanoxycarbene complexes displayed several waves. The peak potentials of reductions listed in Table 5 are ascribed to carbene ligand-centred reductions. For monomeric chromium complexes only one reversible anodic wave, corresponding to oxidation of the pentacarbonyl metal centre, is observed. The same is true for the tungsten complexes, although the oxidation waves are only partially reversible.

The complexes containing a second metal moiety, either Fe or 2-BTCr(CO)3, displayed another oxidation wave at lower potential, showing that the two metal moieties in each complex function as separate, localised redox centres, in contrast to results obtained showing that the two metal moieties in each complex function as metal can be made, as it is not an electronically delocalised system.

A more positive potential for 3a is obtained than for 1a, due to the electron withdrawing effect of the Cr(CO)3-, in 3a, decreasing the ease of oxidation. This was also found to be valid for titanoxycarbene complex 4a vs. 2a.

In turn, when the -OEt -OTiCp2Cl fragments are compared, the increased donating character of the titanocarbene fragment reflects in the lower oxidation potentials obtained for these complexes 2a and 4a in relation to their ethoxy counterparts 1a and 3a.

Conclusions

Obtaining information directly regarding substituent effects from the preliminary vibrational investigation proved non-trivial. The use of Raman spectroscopy vs. IR to monitor structural changes due to symmetry breaking was clearly shown from the disappearance of the Raman-active A1 band. In combination with modelling data, the novel assignment of the Raman/IR-active δ(CCCarbeneO) band as a promising probe for substituent effect, was achieved.

The effect of both the heteroatom substituent as well as the (hetero)arene substituent, and in addition, different combinations of the above could be qualitatively gauged.

With the introduction of metal-containing fragments on both carbene substituents, modification of the electronic and steric nature of the carbene ligand can be effected by both the heteroatom and the (hetero)aryl substituent, in contrast with previous studies where organic fragments only were utilized.44 6

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