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PAPER

Rhenium ethoxy- and hydroxycarbene complexes with thiophene substituents†

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Reaction of mono- and dilithiated thiophene (a), bithiophene (b) and 2,5-dibromothiophene (c) with $[\text{Re}_2(\text{CO})_{10}]$ afforded, after subsequent alkylation with triethyloxonium tetrafluoroborate, tetra- and binuclear Fischer carbene complexes, $[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OEt})\{\text{C}_4\text{H}_2\text{S}\}_n\text{X}\}]$, $n = 1$, $\text{X} = \text{H}$ (**1a**); $n = 2$, $\text{X} = \text{H}$ (**1b**); $n = 1$, $\text{X} = \text{Br}$ (**1c**); $n = 1$, $\text{X} = \text{C}(\text{OEt})\text{Re}_2(\text{CO})_9$, (**2a**); $n = 2$, $\text{X} = \text{C}(\text{OEt})\text{Re}_2(\text{CO})_9$ (**2b**), as major products. The dirhenium acylate intermediates from this reaction not only gave the expected novel ethoxycarbene complexes with alkylation but after rhenium–rhenium bond breaking afforded a number of minor products. The ^1H NMR spectrum of the crude reaction mixture revealed the formation of four metal hydride complexes and aldehydes. Protonation with HBF_4 instead of alkylation with Et_3OBF_4 significantly increased the yields of the hydride complexes, which enabled the positive identification of three of these complexes. In addition to the known compounds $[\text{Re}(\text{CO})_5\text{H}]$ and $[\text{Re}_3(\text{CO})_{14}\text{H}]$ (**3**), a unique complex displaying a hydroxycarbene fragment connected to an acyl fragment *via* an $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond and a $\text{Re}\cdots\text{H}\cdots\text{Re}$ bond linking the two Re centers, $[(\mu-\text{H})\{\text{Re}(\text{CO})_4\text{C}(\text{OH})\{\text{C}_4\text{H}_2\text{S}\}_n\text{H}\}\{\text{Re}(\text{CO})_4\text{C}(\text{O})\{\text{C}_4\text{H}_2\text{S}\}_n\text{H}\}]$, $n = 1$ (**4a**) or $n = 2$ (**4b**), were isolated. The formation of thiophene aldehydes, $\text{H}\{\text{C}(\text{O})\}_m\{\text{C}_4\text{H}_2\text{S}\}_n\text{C}(\text{O})\text{H}$ ($m = 0$ or 1 and $n = 1$ or 2), were observed and the novel monocarbene complexes with terminal aldehyde groups, $[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OEt})\{\text{C}_4\text{H}_2\text{S}\}_n\text{C}(\text{O})\text{H}\}]$, $n = 1$ (**5a**) and $n = 2$ (**5b**) could be isolated. A higher yield of **5b** was obtained after stirring crystals of **2b** in wet THF. The crystal structures of **1a**, **2a**, **4a** and **5b** are reported.

Introduction

The stability and versatility of N-heterocyclic carbenes in coordination chemistry has recently sparked interest in the less stable singlet hydroxycarbenes.¹ Hydroxycarbene and acyl/formyl complexes are proposed to be important intermediates in CO reductions such as in the Fischer–Tropsch process (Fig. 1),² and calculations have suggested that Fischer hydroxycarbene species could be key intermediates in hydroformylation and aldehyde decarbonylation reactions.³ Fischer and Riedel synthesized the first transition metal hydroxycarbene complexes of rhenium in 1968 by protonation of a metal acylate.⁴ A large number of hydroxycarbene complexes stabilized by hydrogen bonding have been reported.⁵

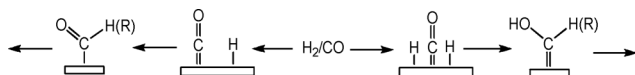


Fig. 1 Acyl/formyl and hydroxycarbene units as potential building blocks in the Fischer–Tropsch process.²

Casey and co-workers⁶ noted the simultaneous presence of rhenium acyl-hydride and rhenium hydroxycarbene complexes in solution. The dual nature and properties of these rhenium species in solution were investigated by using a cyclopentadienyl pendant hydroxycarbene ligand. They showed that an equilibrium existed between this ligand and a cyclopentadienylacyl-hydrido ligand in solution (Fig. 2) and that this mixture of tautomers was seen to decompose under thermal reaction conditions to give aldehydes.

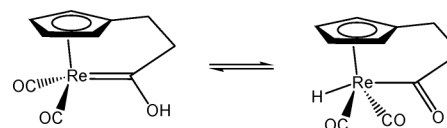
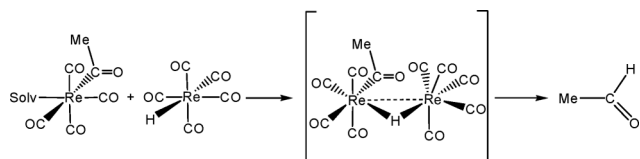


Fig. 2 Casey's hydroxycarbene and hydrido-acyl tautomers.⁶

Reaction pathways for the conversion of Group 7 transition metal-hydrides $[\text{M}(\text{CO})_5\text{H}]$ ($\text{M} = \text{Mn}, \text{Re}$), by Group 7 metal-acyls $[\text{M}(\text{CO})_5\text{C}(\text{O})\text{Me}]$, to give aldehydes have been investigated.⁷ Kinetic studies by Norton and co-workers revealed that, for rhenium complexes, the reaction proceeded through an intermediate with a bridging hydride ligand (Scheme 1).⁷ The hydrogen ligand was transferred to the acyl fragment, converted to the acyl-hydride and subsequently, after reductive elimination, afforded the aldehyde and dirhenium nonacarbonyl. Examples of stable mononuclear acyl-hydride complexes have been reported.⁸

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Scheme 1 Hydrogen transfer mechanism proposed by Norton.⁷

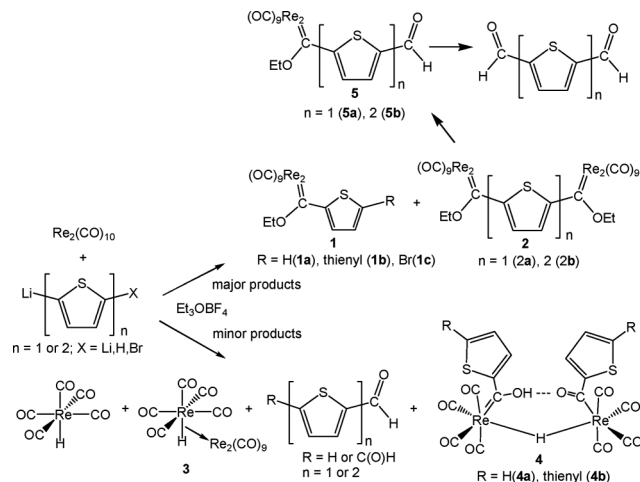
The synthesis and reactivity of rod-like biscarbene complexes with bridging heteroarene spacers, obtained from $[M(CO)_6]$ ($M = Cr, W, Mo$) precursors, have been studied extensively in our laboratories and it was noted that the reactivity of the carbene functionality increased on going from mono- to biscarbene complexes.⁹ In this study, the alkylation and protonation of reaction mixtures containing rhenium acylates of mono- and dilithiated thiophene and thiophene derivatives afforded a variety of major and minor products. Although no mono- or dirhenium hydroxycarbene or acyl complexes could be isolated after protonation of the acylates, a unique dirhenium complex containing a hydroxycarbene and an acyl ligand was obtained. The molecular structure of the thiophene complex was confirmed by single crystal X-ray diffraction and showed an 8-membered dirhenium metallacycle consisting of two acyl ligands held together by an acidic and a hydridic hydrogen. The novel bisethoxycarbene complexes are the first examples of two dirhenium nonacarbonyl fragments being attached to each other with a conjugated biscarbene spacer ligand. The biscarbene complexes when reacted with water gave monocarbene complexes with terminal aldehyde groups and bisaldehydes.

Results and discussion

Synthesis of ethoxycarbene complexes

Thiophene was readily monolithiated with *n*-butyllithium in THF at low temperature ($-20\text{ }^\circ\text{C}$) and subsequently reacted with one equivalent of $[Re_2(CO)_{10}]$ at $-70\text{ }^\circ\text{C}$. The solvent was replaced with dichloromethane and the reaction mixture alkylated with Et_3OBF_4 . Complex **1a** was obtained in almost 80% yield. In an attempt to prepare biscarbene complexes, thiophene was reacted with two equivalents of *n*-butyllithium and two equivalents of dirhenium decacarbonyl. However, very little of the tetra-rhenium biscarbene complex with a thiophene linker between the carbene ligands **2a** (5%) was formed, instead over 60% of the monocarbene complex **1a** and some decomposition products were afforded. This was ascribed to poor dilithiation that was observed for thiophene under the chosen reaction conditions. Higher yields of **2a** could be achieved by reacting 2.5 equivalents of *n*-butyllithium with 2,5-dibromothiophene instead of thiophene in lithium-halogen exchange reactions. In this instance the product distribution was 42% **2a**, 21% **1a** and 13% of a 5-bromo-2-thienylethoxycarbenedirheniumnonacarbonyl complex, $[Re_2(CO)_9\{C(OEt)C_4H_4SBr\}]$ (**1c**). This method was recently successfully employed in our laboratories to make biscarbene chelate complexes of thiophene for group 6 transition metals.¹⁰ By contrast, bithiophene was readily dilithiated with two equivalents of *n*-BuLi under the above reaction conditions. Purification on a silica gel column using hexane-dichloromethane mixtures with increasing polarity gradients afforded the tetra-rhenium biscarbene complex **2b** in *ca.* 60% yield while very little of **1b** formed. A much

higher yield of **1b** is possible from the monolithiated bithienyl precursor. The very stable Fischer carbene complexes **1a**, **1b**, **1c** and less stable complexes **2a**, **2b** are representative of the major products formed after alkylation of the rhenium acylates (Scheme 2).



Scheme 2 Fischer carbene and hydride complexes of thiophene derivatives after Et_3OBF_4 alkylation.

The first examples of dimetal nonacarbonyl monocarbene complexes of Group 7 transition metals were synthesized many years ago.¹¹ The tetra-rhenium complexes (**2**) are the first examples of two dirhenium carbene complexes attached by a single conjugated heteroarene disubstituted spacer, resulting in electronic communication between the metal centers. Recently we reported the first examples of tetra-rhenium biscarbene complexes with ferrocendiy and titanocendioxy bridging spacer ligands.¹² All attempts to synthesize dirhenium biscarbene complexes from $[Re_2(CO)_{10}]$ precursor and lithiated thiophenes failed. We ascribe this to both electronic and steric factors. The Re-Re bond is relatively weak and a bulky carbene ligand in an electronically favoured equatorial position will be in a *cis*-position relative to the second $Re(CO)_4(\text{carbene})$ -fragment. A dirhenium biscarbene complex, $[Re_2(CO)_8\{C(OEt)SiPh_3\}_2]$, displaying one carbene ligand in an axial and the other in an equatorial position was synthesized by Fischer and Rustemeyer.¹³

The ethoxycarbene complexes were studied by NMR, infrared spectroscopy and mass spectrometry (see Experimental) and the data confirmed the assigned structures. The mass spectra of the complexes gave two major fragmentation routes. In the first, carbonyl ligands are cleaved from the molecular ion in a stepwise manner, while in the second instance, the rhenium-rhenium bond was cleaved initially and fragment ions such as $[Re(CO)_5]^+$, $Re(CO)_4(\text{carbene})^+$, $[Re(CO)_6]^+$ and $[Re(CO)_5(\text{carbene})]^+$, were prominent in the spectra of all the new carbene compounds. In the carbonyl region of the infrared spectra recorded in hexane, the typical 9-band pattern of equatorially substituted dirhenium nonacarbonyl complexes was observed for **1** and **2**.¹⁴

The electron withdrawing carbene carbon is directly attached to the 2-position of the thienyl rings (Fig. 3) which, compared to thiophene, manifests in a large downfield shift of especially the adjacent (H3) protons in the 1H NMR spectra of **1** and **2**. The chemical shifts of H3 are very similar for **1b** and **2b** but differ from

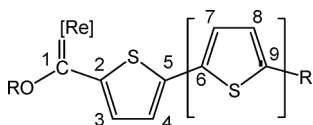


Fig. 3 Atom labeling for NMR assignments.

those for **2a** which is upfield from **1a**. We ascribe this to a reduction in resonance delocalization to the carbene carbon due to a large twist between the thiophene plane and the carbene planes (Fig. 5, *vide infra*). In the ^{13}C NMR spectra the rhenium carbene carbon signals are observed around 290–300 ppm and the resonances of the rhenium carbonyls are scrambled and appear as a broadened signal at 195 ppm. Confirmation of the molecular structures of **1a** (Fig. 4) and **2a** (Fig. 5) were obtained by solid state crystal structure determinations. Compared to the analogous biscarbene complexes of Cr and W, the methylene protons of the ethoxy substituents of **2** resonate at *ca.* 0.5 ppm upfield in the ^1H NMR spectra.

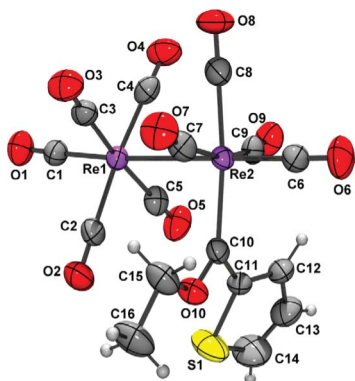


Fig. 4 The molecular structure of $[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OEt})_4\text{H}_3\text{S}\}]$ (**1a**). Atomic displacement ellipsoids are shown at the 50% probability level.¹⁵

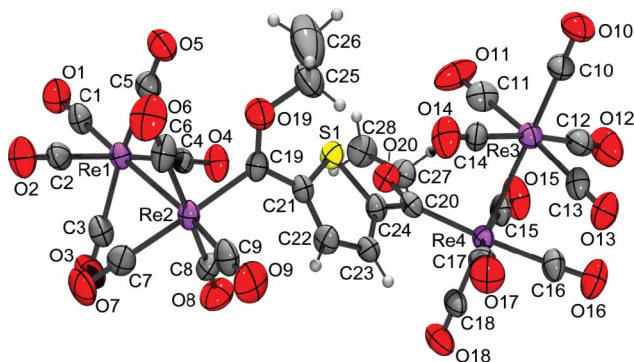


Fig. 5 The molecular structure of $[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OEt})_4\text{H}_2\text{SC}(\text{OEt})\} \text{Re}_2(\text{CO})_9]$ (**2a**). Atomic displacement ellipsoids are shown at the 50% probability level.¹⁵

Hydrolysis of biscarbene complexes

The formation of **5** as well as increased yields of aldehydes were noted during column chromatography on silica gel while the ethoxycarbene complexes were purified. Their formation was tentatively ascribed to the reaction of the biscarbene complexes

with trace amounts of water during chromatography. To test this assumption, crystals of the bisethoxycarbene complex **2b** were dissolved in wet THF and stirred overnight. After removing the solvent the reaction mixture was examined by ^1H NMR spectroscopy and thin layer chromatography. The presence of some unreacted **2b**, **5b**, bisaldehydes and decomposition products was confirmed. Scheme 3 shows the stepwise conversion of bisethoxycarbene complexes to dialdehydes. During the reaction of the ethoxycarbene with water the ethoxy substituent was presumably replaced by a hydroxy substituent. This reaction follows the pattern of the well-known aminolysis reactions of Fischer carbene complexes.¹⁶ The hydrolysis of alkoxycarbene complexes of chromium to give aldehydes under certain reaction conditions was noted earlier in kinetic studies by Bernasconi.¹⁷ The proposed reaction sequence was supported by the isolation and characterization of **5**. The formation of hydroxycarbene intermediates is also supported by results found in our laboratories indicating the hydrolysis of a titanoxo substituent of a dirhenium ferrocenylcarbene complex.¹² In spite of not being able to isolate a hydroxycarbene or acyl complex with the exception of **4** (Fig. 8), the sequence from ethoxycarbene to hydroxycarbene to acyl-hydride to aldehyde was assumed. Support for the formation of hydroxycarbene and acyl-hydride intermediates comes from the work of Fischer⁴ and Casey.⁶

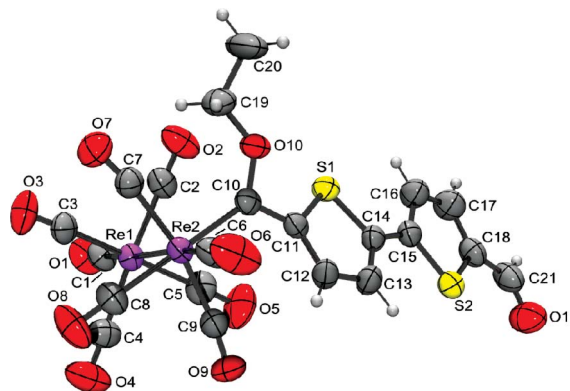
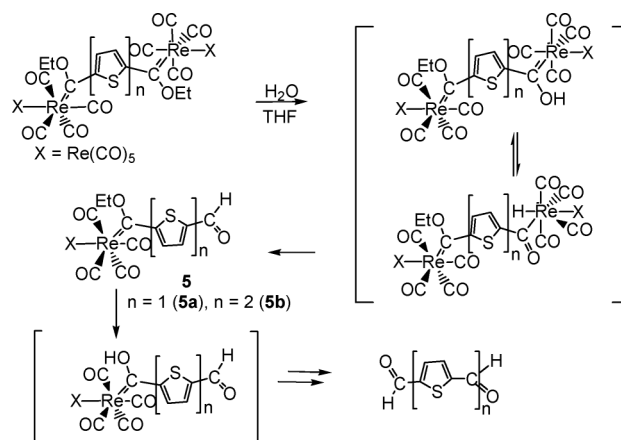


Fig. 6 The molecular structure of $[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OEt})_4\text{H}_2\text{SC}(\text{O})\text{H}\}]$ (**5b**). Atomic displacement ellipsoids are shown at the 50% probability level.¹⁵



Scheme 3 Proposed pathway for the formation of **5** and dialdehydes.

The ^1H NMR chemical shifts of **5** for both H3 and H4 were again shifted downfield compared to the same resonances of thiophene demonstrating the electron withdrawing effects of the ethoxycarbene and the aldehyde substituents. These chemical shifts were smaller for **5** compared to the same shifts in **1** and **2**. In the ^{13}C NMR spectra the rhenium carbene carbon signals are found at around 290–300 ppm, the resonances of the rhenium carbonyls are scrambled and appear as a broadened signal at 195 ppm and the aldehyde carbon peaks present at around 185 ppm. The same fragment ions found for **1** and **2** were again present in the mass spectra of **5** and similar patterns observed in the infrared spectra of **1** and **2** were observed for **5** in the carbonyl region.

Protonation instead of alkylation of rhenium acylates

The presence of minor byproducts in the reaction mixture during the synthesis of the ethoxycarbene complexes was indicated by ^1H NMR spectra for the reaction mixtures of both thiophene (Fig. 7) and bithiophene. The ^1H NMR resonances revealed four hydride species, one of which contained a terminal hydride ligand and the other three displayed signals representative of bridging hydride ligands.¹⁸ The total yield of the minor complexes was less than 10% for bithiophene and almost 15% for thiophene. The ^1H NMR spectra were measured immediately after reactions and before purification of the products and also revealed the formation of thiophene and bithiophene aldehydes. Importantly, this showed that the minor products were already present in the reaction mixture at this early stage of the reaction and revealed another source of hydrogens in the reaction mixture.

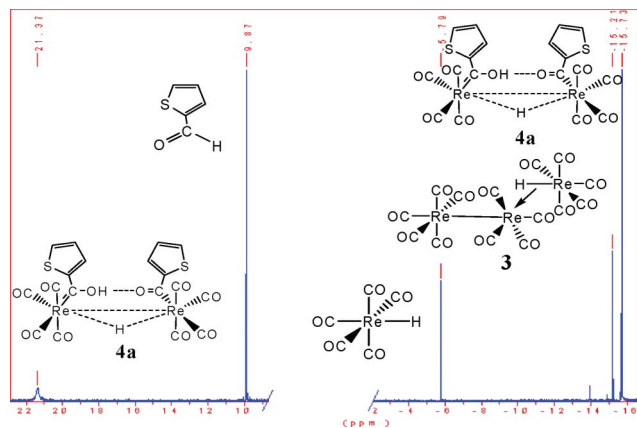


Fig. 7 ^1H NMR spectrum of the metal hydrides and aldehyde formed during the reaction with thiophene (thiophene region omitted).

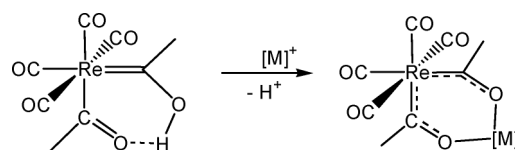
In a control experiment the dirhenium acylate, after the lithiation of the thiophene and subsequent reaction with dirhenium decacarbonyl, was protonated in THF with HBF_4 instead of alkylated with Et_3OBF_4 . Now, more than 40% of products consisting of the aldehydes and the same hydride species found before were present in the reaction mixture. Estimation of the relative yields and confirmations of the presence of all the minor products in the reaction mixtures were obtained from ^1H NMR spectral data and the relative peak intensities. The thiophene aldehydes, $\text{HC(O)}\{\text{C}_4\text{H}_2\text{S}\}_n$ ($n = 1$ or 2 , $\text{R} = \text{H}$ or C(O)H) which formed, were predominately the bisaldehyde for bithiophene and a

monoaldehyde from the monocarbene thiophene precursors. The hydrogens of the aldehydes typically resonate around 10 ppm in their ^1H NMR spectra. Sufficient quantities of the other hydrido-complexes **3** and **4** were present in the reaction mixture to enable purification and full characterization. Protonation instead of alkylation afforded **3** in a much higher yield, and the yield of **4** was almost doubled.

The *in situ* formation of $[\text{Re}(\text{CO})_5\text{H}]$ in the reaction mixture was noted in the ^1H NMR spectra and a signal at -5.79 ppm was assigned to the chemical shift of this hydride. The chemical shift is similar to the value of -5.88 ppm reported in literature for $[\text{Re}(\text{CO})_5\text{H}]$.¹⁹ The formation of $[\text{Re}(\text{CO})_5\text{H}]$ was ascribed to a transfer of hydrogens from either the solvent during Re–Re bond breaking or by the protonation of $[\text{Re}(\text{CO})_5]^-$ with HBF_4 . In addition to the terminal hydride signal at -5.76 ppm, signals of bridging hydrides for **3** and **4** are observed in the range -14 to -16 ppm (Fig. 7).¹⁸ A low intensity peak in the bridging hydride region *ca.* -14 ppm could not be assigned. With no evidence available we cannot exclude the possibility that it originates from an unstable Norton-type⁷ dirhenium hydrido-thienylacyl intermediate (see Scheme 1). A secondary product, trirhenium hydride $[\text{Re}_3(\text{CO})_{14}\text{H}]$ (**3**) with a hydride chemical shift at -15.21 ppm was isolated and represents the coordination of $[\text{Re}(\text{CO})_5\text{H}]$ to a coordinatively unsaturated dirhenium nonacarbonyl species during the reaction. This product has been reported previously and is accessible from ultraviolet photolysis of neat $[\text{Re}(\text{CO})_5\text{H}]$ in high yields.²⁰ Complex **3** was previously prepared by Cheng and Wang in 50% yield from the photochemical reaction of dirhenium decacarbonyl and triphenylsilane or thiophene.²¹ Confirmation of the structure of **3** was obtained by a single crystal structure determination, but since this structure had already been reported,²¹ it is not included.

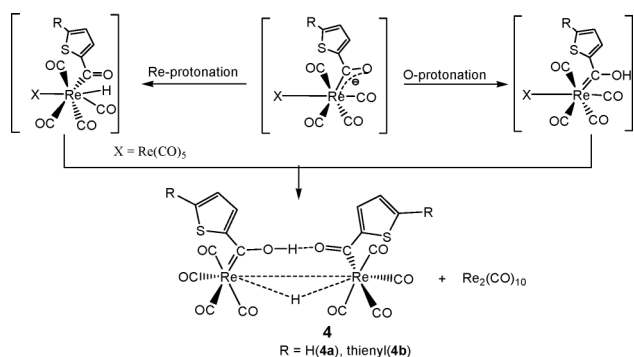
The unique hydroxycarbene-acyl complex containing a bridging hydrido ligand $[(\mu\text{-H})_2\{\text{Re}(\text{CO})_4\text{C(O)}\{\text{C}_4\text{H}_2\text{S}\}_n\text{H}\}_2]$ ($n = 1$ **4a** or $n = 2$ **4b**) was purified by column chromatography with dichloromethane and displayed a hydride signal at -15.73 ppm (**4a**) and a broadened signal for the protonic hydrogen at 21.5 ppm. The formation of **4** is significant and reveals the simultaneous presence of hydroxycarbene and acyl species in the reaction mixture. No stable monorhenium hydroxycarbene or acyl complexes could be isolated from any of the reactions and we suspect they are unstable intermediates unless trapped in a stable conformation such as **4**.

The presence of a hydroxycarbene and an acyl ligand in a single monorhenium complex $[\text{Re}(\text{CO})_4\{\text{C(O)Me}\}\{\text{C(OH)Me}\}]$ was reported many years ago by Lukehart and co-workers.²² Once deprotonated this complex acted as an organometallo-ligand and displayed coordination properties to other metal ions (Scheme 4). Similar systems of platinum- β -diketones were documented more recently by Steinborn and co-workers.²³



Scheme 4 Lukehart's metalla-acac ligand.²²

Based on previous work and this study it is clear that different reaction mechanisms and pathways for the formation of **4** can be proposed. This aspect was not investigated and Scheme 5



Scheme 5 Proposed reaction route for **4** based on the protonation of the dirhenium acylate.

represents a simplification of intermediates in an otherwise complex reaction mixture. The scheme uses dirhenium intermediates that contain both acyl-hydride and hydroxycarbene ligands and is based on the protonation of the dirhenium acylate. However, the fact that the Re–Re bond could already have been cleaved at this stage of the reaction must still be taken into consideration. Protonation at the oxygen (shown on the right) and at the metal center (shown on the left) afford hydroxycarbene and acyl intermediates, respectively. Complex **4** can be constructed after Re–Re bond cleavage and the combination of the rhenium acyl-hydride and hydroxycarbene fragments. The co-existence of mononuclear rhenium acyl-hydride and hydroxycarbene isomers in equilibrium studies was established by Casey and co-workers (Scheme 2).⁶ In the context of this study, complex **4** can be seen as consisting of two unstable intermediates that are trapped in a stable assembly by intermolecular hydrogen bonding and a bridging hydride. The kinetic studies by Norton⁷ were based on a hydrogen transfer process from a rhenium hydride to a rhenium acyl and with both such species present in the reaction mixture, many alternative reaction routes for **4** can be proposed.

The infrared spectra in the carbonyl region of **4a** and **4b** measured in dichloromethane displays one very strong $\nu(\text{CO})$ band just above 2000 cm^{-1} and 7 weak carbonyl stretching bands over the range $2110\text{--}1950\text{ cm}^{-1}$. The pattern of the signals and their relative intensities was not the same as those observed for mononuclear $\text{Re}(\text{CO})_5$ (C_{4v}), *cis*- $\text{Re}(\text{CO})_4$ (C_{2v}) or dinuclear *eq*- $\text{Re}_2(\text{CO})_9$ (C_2) metal fragments.¹⁴

In the ^1H NMR spectra of **4**, H3 are more deshielded compared with the same chemical shifts for **1** and **2**. Proton signals of hydroxycarbene substituents are reported to resonate between 12–14 ppm in their ^1H NMR spectra.²⁴ The ^1H NMR spectra of **4** displayed unbroadened peaks for both the hydride hydrogens as well as those of the thienyl rings and represent symmetrical, dirhenium compounds with fully interchangeable fragments. The two Re–acylthienyl fragments in **4** are separated or connected by two hydrogen atoms in a large 8-membered dimetallacycle. By moving both the hydrogens to one of the Re metals in **4a**, two fragments can be generated, one represents a neutral hydride-hydroxycarbene and the other a coordinatively unsaturated acyl complex. If cleaved in such a way that each rhenium retains one of the hydrogens, two fragments emerge that can be formally described as $\text{Re}(\text{II})$ and $\text{Re}(\text{0})$ fragments.²⁵ A very large difference in chemical shift between the protonic bridging hydrogen (much deshielded by the oxygen atoms) and the hydridic bridging

hydrogen (shielded by the rhenium atoms) of 37.10 ppm was found for **4a** in the ^1H NMR spectrum. Interestingly, the Shvo catalyst,²⁶ $\text{Ru}_2[(\mu\text{-H})\{2,5\text{-Ph}_2\text{-3,4-Tol}_2(\eta^5\text{-C}_4\text{CO})\}_2](\text{CO})_4(\mu\text{-H})$, displayed a protonic hydrogen with a proton signal at *ca.* 8 ppm (21.37 ppm for **4a**) and a hydridic proton signal at -17.75 ppm (-15.73 ppm for **4a**).

The dinuclear Shvo catalyst is a well-known reversible hydrogenation catalyst and was recently used in a dual catalytic system with rhodium to effect in tandem, first hydroformylation and thereafter hydrogenation of terminal olefins into linear alcohols.²⁷ In the Shvo catalyst there is a keto-enol pair, whereas in **4** an acyl-hydroxycarbene pair is incorporated. Both of these represent organometallic versions of keto-enol tautomers. In the ^{13}C NMR spectra of **4** the acyl/hydroxycarbene carbon atoms resonate at around 260 ppm, which is representative of a carbon displaying properties intermediate between those of a Fischer carbene and an acyl ligand.

Crystal and molecular structures of complexes

Single crystal X-ray diffraction studies confirmed the molecular structures of **1a**, **2a**, **4a** and **5b**. These compounds are representative of all the major complex types reported in this study. ORTEP + POV-Ray¹⁵ drawings of the molecular structures of **1a**, **2a**, **4a** and **5b** showing the atom numbering schemes are shown in Fig. 4–6 and 8. Selected bond distances (\AA) and bond angles ($^\circ$) relevant to the carbene ligands are listed in Table 1.

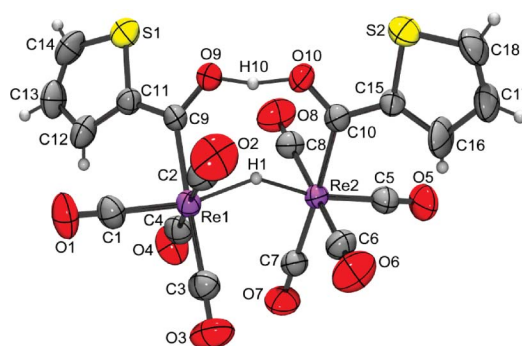


Fig. 8 The molecular structure of $[(\mu\text{-H})\{\text{Re}(\text{CO})_4\text{C}(\text{OH})\text{C}_4\text{H}_5\text{S}\}\{\text{Re}(\text{CO})_4\text{C}(\text{O})\text{C}_4\text{H}_5\text{S}\}]$ (**4a**). Only the major components of the disordered thienyl rings are shown. Atomic displacement ellipsoids are shown at the 50% probability level.¹⁵

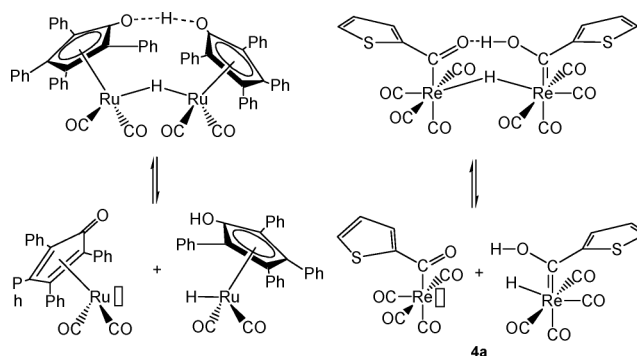
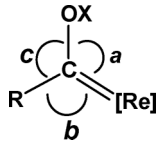


Fig. 9 Similarities and differences between the Shvo catalyst²⁶ and **4a**.

Table 1 Selected bond distances (Å) and bond angles (°) for rhenium carbene complexes


Complex	Bond distances (Å)				Bond angles (°)		
	Re–Re	Re–C _{carbene}	C _{carbene} –(R)	C _{carbene} –O	<i>a</i>	<i>b</i>	<i>c</i>
1a	3.0899(3)	2.125(5)	1.461(7)	1.335(6)	129.9(4)	124.9(4)	105.2(4)
2a	3.0434(6)	2.093(10)	1.476(14)	1.303(13)	119.1(7)	122.7(7)	118.2(9)
	3.0569(7)	2.076(10)	1.480(12)	1.338(12)	131.5(6)	124.1(7)	104.5(8)
4a	3.3622(2)	2.158(4)	1.453(5)	1.273(4)	123.6(3)	124.6(3)	111.7(3)
		2.173(4)	1.446(6)	1.283(4)	122.0(3)	124.7(3)	113.2(3)
5b	3.0770(3)	2.117(4)	1.460(6)	1.323(5)	130.9(3)	125.0(3)	104.1(3)

The electronically favoured position for the carbene ligand in dirhenium complexes is in the equatorial position *cis* to the rhenium–rhenium bond. Neutral rhenium carbonyl complexes require one X-type ligand²⁵ which is a Re(CO)₅-fragment in the above complexes. The unsubstituted Re(CO)₅ fragment represents a rather bulky ligand bonded to the other rhenium fragment containing the carbene ligand. As a result, for **1a**, **2a** and **5b**, the ligands in the equatorial plane containing the carbene ligand are in an approximately staggered conformation with respect to the carbonyl ligands in the adjacent plane. The orientation of the ligands in **4a** is determined by the two bridging hydrogen atoms of the 8-membered dimetallacycle. The thienyl rings are orientated so that the sulfur atom is approximately *cis* to the ethoxy or hydroxycarbene substituent about the C_{carbene}–C_{thienyl} bond in the complexes.²⁸ In **4a** minor orientations of the thienyl rings were also observed with the rings rotated *ca.* 180° about the C_{carbene}–C_{thienyl} bonds with respect to the major orientations so that the sulfur atoms are *trans* to the hydroxy substituents. The site occupation factors of these minor orientations are 0.062(6) and 0.122(6). The sulfurs in the bithiophene moiety in **5b** are *trans* to each other. In the refinements of **1a**, **2a** and **5b**, all hydrogen atoms were included in calculated positions. In the refinement of **4a** all the hydrogen atom positions, except for those associated with the minor orientations of the thiophene rings, were located from difference Fourier maps. However, except for the bridging hydrogen atoms, H1 and H10, all hydrogen atoms were included in calculated positions. H1 and H10 were freely refined with individual isotropic atomic displacement parameters (adp). The relatively large adp refined for the bridging hydroxy hydrogen, H10, (0.15(3) Å²) suggests that the site may be disordered with H10 alternately occupying sites closer to O9 or O10. No attempt was made to resolve the disorder. For **4a**, the Re–Re bond distance is *ca.* 0.3 Å longer (3.3622(2) Å for **4a** vs. an average of 3.067(20) Å for **1a**, **2a** and **5b**) due to the bridging hydride ligand, which forms a formal 3-center 2-electron bond. The rhenium–carbene distances display double bond character with an sp²-hybridized carbene carbon atom which defines a carbene plane: Re, C_{carbene}, O (or C), C. A second plane is defined by the thienyl ring and ideally, because of π-conjugation, should be coplanar with the carbene plane. In **2a**, ignoring steric effects, one could expect the bridging biscarbene spacer to lie in a single plane between the rhenium atoms. This plane will bisect two carbonyl ligands of the adjacent equatorial

plane. Because of some congestion in the area between the two rhenium atoms the ethoxy substituents in **2a** are twisted into positions above and below the plane of the spacer ligand. As a consequence the ethoxy substituents are oppositely orientated relative to their metal fragments. Notably the oxygen lone pairs of one are towards the ring and the other towards the metals. Sierra reported a favoured positioning of oxygen lone pairs away from the metal carbonyl fragment in monocarbene complexes to minimise interactions of the lone pairs with the “carbonyl wall”.²⁹ A large deviation from coplanarity between the carbene and thiophene planes is found, with Re–C_{carbene}–C_{2,thienyl}–C_{3,thienyl} torsion angles of –44.2(14)° and –36.7(14)°. As a result, the bond distances and angles differ around the atoms in the spacer ligand. Also the Re₂(CO)₉ fragments lie approximately perpendicular to each other in **2a** unlike in the analogous, symmetrical, bithiophene structure of **2b** where they are paralleled.³⁰

Complex **4a** has the longest rhenium–carbon(carbene/acyl) bonds and shortest carbon(carbene/acyl)–oxygen bonds, which is expected because of the dual nature of the two ligands in the structure, *i.e.* each representing the average of an acyl and a hydroxycarbene ligand. The Re–C distances of 2.158(4) and 2.173(4) Å are longer than the average of 2.10(2) Å for the Re–C_{carbene} distances in **1a**, **2a** and **5b**. The C_{carbene/acyl}–OH distances of 1.273(4) and 1.283(4) Å in **4a** are shorter than the average of 1.325(16) Å for the corresponding distances of the ethoxycarbene substituents in **1a**, **2a** and **5b** but longer than the C–O_{formyl} distance of 1.186(7) Å in **5b**. The C_{carbene}–C_{thienyl} bond lengths are similar in all the complexes. The angles around the carbene carbon atoms, as listed in Table 1, show variations according to the nature of the substituents. In **1a**, **5b** and for the second carbene in **2a**, the ethyl groups are in their commonly observed position *i.e.* rotated towards the “carbonyl wall” (and hence the oxygen lone pair is directed towards the thienyl sulfur atom). Thus for these carbenes the Re–C_{carbene}–O angles (*a*) are opened out to approximately 130° or greater due to steric crowding between the ethyl and carbonyl groups and there are concomitant closing of the O–C_{carbene}–C_{thienyl} angles (*c*) to approximately 105° or less (possibly enhanced by an attractive interaction between the oxygen lone pair and the thienyl sulfur atom). The Re–C_{carbene}–C_{thienyl} angles (*b*) are governed by steric interactions between the thienyl ring and the “carbonyl wall” and show little variation within all the complexes. For the first carbene in **2a**, the ethyl group is orientated away from the

“carbonyl wall” thus there is no steric crowding (and no possible interaction between the oxygen lone pair and the thienyl sulfur atom) and the bond angles around this carbene are all much closer to the ideal sp^2 -value of 120° . In **4a** there are no ethyl groups, however the possibility of oxygen lone pair...thienyl sulfur interactions do exist and the c -angles are intermediate between those in **1a**, **2a**(2) and **5b** and the ideal sp^2 -value, together with a concomitant slight opening of the a -angles.

Conclusions

The study showed that the site of alkylation/protonation of the rhenium acylate and a subsequent equilibrium between an acyl-hydride and a hydroxycarbene intermediate during the synthesis of Fischer carbene complexes can be of value in the attempt to understand the reaction progress and the product composition. Although not stable, the existence of monorhenium hydroxycarbene or hydrido-acyl intermediates were clearly confirmed by the structure of **4a**, the NMR spectra of reaction mixtures and the composition of isolated secondary products. The fact that Fischer,⁴ Casey,⁶ Norton,⁷ and others^{2,5,8,23} described the formation of aldehydes from either acyl-hydride or hydroxycarbene precursors is significant. It was clear that hydroxycarbene and acyl-hydride intermediates in the above study are but two sides of the same coin and could probably be considered as such in appropriate catalytic cycles involving hydroformylation processes. A possible connection between hydroxycarbene complexes and the formation of alcohols (Shvo catalysis) could not be established in this study, but future investigations with type-4 compounds in catalytic processes have started in our laboratories and are at a preliminary stage. The potential catalytic properties of $[Re_2(CO)_{10}]$ and related complexes in homogeneous catalysis have until recently received little attention in the literature.³¹

Experimental

General procedures

All manipulations involving organometallic compounds made use of Schlenk techniques and operations were carried out under an inert atmosphere. Hexane, THF and dichloromethane were dried and deoxygenated by distillation prior to use. $[Re_2(CO)_{10}]$, *n*-butyllithium (1.6 mol dm^{-3} solution in hexane) and bithiophene were used as purchased and triethyloxonium tetrafluoroborate was prepared according to literature procedures.³² Thiophene was purified before use according to literature procedures,³³ and lithiations were carried out according to Brandsma.³⁴ Column chromatography using silica gel 60 (0.063–0.200mm) or neutral aluminium oxide 90 (activity II–III) as the stationary phase was used for all separations. Circulating ice water through the column jackets cooled the columns. NMR spectra were recorded on Bruker ARX-300 and AVANCE 500 spectrometers. 1H NMR spectra were recorded at 300.135 and 500.139 MHz and ^{13}C NMR spectra at 75.49 and 125.75 MHz, respectively. The signal of the deuterated solvent was used as reference, e.g. 1H $CDCl_3$ 7.24 ppm and ^{13}C $CDCl_3$ 77.00 ppm. IR spectra were recorded on a Perkin–Elmer Spectrum RXI FT-IR spectrophotometer. All spectra were recorded using either dichloromethane or hexane as solvent. Only the vibration bands in the carbonyl-stretch region (*ca.* 1600–

2200 cm^{-1}) were recorded. 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 solvent and internal standard.

Crystal structure determination

The crystal data collection and refinement details for complexes **1a**, **2a**, **4a** and **5b** are summarized in Table 2. The X-ray crystal structure analyses were performed using data collected at 293(2) K on a Siemens P4 diffractometer fitted with a Bruker 1 K CCD detector using graphite-monochromated Mo- $K\alpha$ radiation by means of a combination of ϕ and ω scans. Data reductions were performed using SAINT+³⁵ and intensities were corrected for absorption using SADABS.³⁵ The structures were solved by direct methods using SHELXTS³⁵ and refined by full-matrix least-squares using SHELXTL³⁵ and SHELXL-97.³⁶

Synthesis of complexes

(i) *Reactions of dithiated thiophenes with dirhenium decacarbonyl.* The dropwise addition of 1.4 cm^3 (2.2 mmol) of a 1.6 mol dm^{-3} hexane solution of *n*-BuLi to 20 cm^3 of a cooled ($-10^\circ C$) THF solution containing 0.084 g (1.0 mmol) of thiophene afforded a light yellow solution after 30 min. The solution was cooled to $-78^\circ C$ and 1.30 g (2 mmol) of $[Re_2(CO)_{10}]$ was added in small portions over 10 min, resulting in a gradual change of colour from yellow to orange. After stirring for 0.5 h in the cold, the reaction mixture was warmed to room temperature. Stirring was continued for another hour and the mixture was stripped of solvent under reduced pressure. The residue was dissolved in dichloromethane to give a red solution, cooled to $-30^\circ C$ and carefully treated with 0.40 g (2 mmol) of triethyloxonium tetrafluoroborate which was dissolved in 15 cm^3 of dichloromethane. After stirring for 1 h and allowing the reaction mixture to warm to room temperature, the dark red-brown coloured solution was washed through a plug of silica gel with dichloromethane. The solution was evaporated under reduced pressure to give a dry residue, and purified with column chromatography using hexane/dichloromethane mixtures as eluent. During chromatography, the polarity of the eluent was increased gradually by increasing the ratio dichloromethane to hexane. The first zone consisted of a large amount of unreacted white $[Re_2(CO)_{10}]$ (0.53 g) followed by 0.47 g (0.61 mmol, 61%) of an orange solid, **1a** (yields given in brackets are based on the limiting agent used). A third, dark red band afforded 0.061 g (0.042 mmol, 4.2%) of the target complex **2a**. The last product that was isolated had a yellow colour and gave 0.119 g (0.145 mmol, 14.5%) of **4a**. The presence of other zones representing compounds in low yield *i.e.* $C_4H_3SC(O)H$, **3** and **5a** (see (iii) below) were observed during column chromatography, but were not isolated from this reaction mixture.

(ii) *Reaction with 2,5-dibromothiophene instead of thiophene to improve the yield of 2a.* The same procedure was followed as in (i) above with the exception that 0.242 g (1.0 mmol) of 2,5-dibromothiophene was used instead of thiophene and reacted with 2.2 equivalents of *n*-BuLi and 2.0 equivalents of $[Re_2(CO)_{10}]$. During chromatography, the polarity of the eluent was increased gradually by increasing the ratio dichloromethane to hexane as above. The major product from this reaction was

Table 2 Crystal structure data for **1a**, **2a**, **4a** and **5b**

Complex	1a	2a	4a	5b
Formula	C ₁₆ H ₈ O ₁₀ Re ₂ S	C ₂₈ H ₁₂ O ₂₀ Re ₄ S	C ₁₈ H ₈ O ₁₀ Re ₂ S ₂	C ₂₁ H ₁₀ O ₁₁ Re ₂ S ₂
<i>M_r</i>	764.68	1445.24	820.76	874.81
Crystal size/mm	0.30 × 0.21 × 0.12	0.38 × 0.28 × 0.22	0.32 × 0.27 × 0.25	0.32 × 0.28 × 0.25
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	9.5491(6)	12.3975(16)	14.2721(8)	9.5208(8)
<i>b</i> /Å	13.0140(8)	12.4762(16)	12.2456(7)	13.1481(11)
<i>c</i> /Å	16.4648(10)	13.8030(18)	13.1170(7)	20.6062(17)
α (°)	90	112.639(1)	90	90
β (°)	101.206(1)	105.394(1)	97.280(1)	101.041(1)
γ (°)	90	98.378(1)	90	90
<i>V</i> /Å ³	2007.1(2)	1824.6(4)	2274.0(2)	2531.7(4)
<i>Z</i>	4	2	4	4
<i>D_c</i> /g cm ⁻³	2.531	2.631	2.397	2.295
μ (Mo-K α)/mm ⁻¹	12.206	13.363	10.871	9.775
<i>F</i> (000), e	1400	1312	1512	1624
<i>hkl</i> range	-10 ≤ <i>h</i> ≤ 11, -14 ≤ <i>k</i> ≤ 15, -20 ≤ <i>l</i> ≤ 7	-13 ≤ <i>h</i> ≤ 15, -15 ≤ <i>k</i> ≤ 5, -16 ≤ <i>l</i> ≤ 17	-16 ≤ <i>h</i> ≤ 14, -15 ≤ <i>k</i> ≤ 15, -16 ≤ <i>l</i> ≤ 7	-11 ≤ <i>h</i> ≤ 11, -16 ≤ <i>k</i> ≤ 16, -8 ≤ <i>l</i> ≤ 25
θ Range for data collection (°)	2.68 to 26.53	2.52 to 26.44	2.59 to 26.53	2.54 to 26.47
Completeness to $\theta = 25.0^\circ$ (%)	99.7	96.6	98.6	99.6
Max./min. transmission	0.231/0.067	0.053/0.028	0.066/0.047	0.087/0.062
Refl. Measured	10576	9557	11867	13364
Refl. Unique	3829	6497	4209	4809
<i>R</i> _{int}	0.0365	0.0286	0.0197	0.0248
Parameters Refined	264	480	314	326
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0274	0.0475	0.0179	0.0244
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0690	0.1239	0.0451	0.0623
<i>R</i> ₁ [all data]	0.0297	0.0540	0.0209	0.0266
<i>wR</i> ₂ [all data]	0.0705	0.1321	0.0466	0.0637
GoF (F ²)	1.127	1.041	1.077	1.165
$\Delta\rho_{\text{min}}$ (max/min)/e Å ⁻³	1.444/-1.213	3.879/-2.568	0.687/-0.569	0.774/-0.932
CCDC-Nr.	824376	824377	790280	824378

0.609 g (0.42 mmol, 42%) of **2a**. Other products isolated in order were 0.114 g (0.13 mmol, 13%) of **1c** and 0.16 g (0.21 mmol, 21%) of **1a**, then **2a**, followed by 0.063 g (0.08 mmol, 8%) of an orange-red solid **5a**. According to ¹H NMR spectrum and peak intensities of the reaction mixture, 0.0098 g (0.07 mmol, 8%) of 2,5-thiophenedicarbaldehyde was also present in the mixture.

(iii) *Protonation of the reaction mixture instead of alkylation.* The same procedure was followed as in (i) with the exception that the reaction mixture was protonated instead of being alkylated. After the monolithiation of 0.042 g (0.50 mmol) of thiophene with 0.33 cm³ (0.55 mmol) of *n*-BuLi and subsequent reaction with 0.325 g (0.5 mmol) of [Re₂(CO)₁₀], an ethereal solution of HBF₄ was added dropwise to the reaction mixture (-20 °C), and the progress of the reaction was monitored by thin layer chromatography. Addition of HBF₄ was terminated after product formation was completed. The reaction solution turned yellow-brown in colour. Four products were identified by NMR spectroscopy, of which three could be isolated. The major product, 0.026 g (0.23 mmol, 46%) of 2-thiophenecarbaldehyde was isolated as a light yellow oil, followed by 0.057 g (0.06 mmol, 12%) of **3** and 0.115 g (0.14 mmol, 28%) of **4a**.

(iv) *Protonation of the reaction mixture from the 2,5-dibromothiophene substrate.* In the case of the protonation of the reaction mixture starting from 2,5-dibromothiophene much decomposition occurred and no rhenium complexes could be isolated, but the major product that was isolated was the organic compound 2,5-thiophenedicarbaldehyde.

(v) *Reaction of 2a with water.* Crystals of **2a**, 0.51 g (0.35 mmol), were dissolved in 10 cm³ of THF, 0.5 cm³ of water was added and the mixture stirred overnight at room temperature. The colour of the solution changed from dark red to orange-red. 0.045 g (0.031 mmol, 8.9%) of unreacted **2a** remained in the reaction mixture. In addition, a major organometallic product was isolated and a second organic compound identified by ¹H NMR spectroscopy. The major product was 0.111 g (0.14 mmol, 40%) of a red solid **5a** and according to a ¹H NMR spectrum and peak intensities of the reaction mixture, 0.010 g (0.07 mmol, 20%) of 2,5-thiophenedicarbaldehyde was also present in the mixture. Decomposition products could not be recovered from the column.

1a: Anal. Calcd. (%) for Re₂C₁₆H₈O₁₀S (764.7 g mol⁻¹): C 25.13, H 1.05, Found: C 25.44, H 1.13. MS-FAB (EI POS) *m/z* 763.6 and 765.6 (M⁺). IR (hexane, cm⁻¹): ν(CO) 2103 (w), 2071 (w), 2042 (m), 2015 (vs), 2002 (s), 1994 (s), 1977 (w), 1955 (m), 1945 (w). ¹H NMR (δ (ppm) in CDCl₃): 7.65 (d, H3, 1H, *J* = 4.4 Hz), 7.11 (dd, H4, 1H, *J* = 4.4, 4.7 Hz), 7.65 (d, H5, 1H, *J* = 4.7 Hz), 4.51 (q, CH₂, 2H, *J* = 7.0 Hz), 1.58 (t, CH₃, 3H, *J* = 7.0 Hz). ¹³C NMR (δ (ppm) in CDCl₃): 294.8 (C1), 193 (br, CO), 157.9 (C2), 132.8 (C3), 127.6 (C4), 132.5 (C5), 77.3 (CH₂), 14.6 (CH₃).

1c: Anal. Calcd. (%) for Re₂C₁₆H₇O₁₀SBr (843.6 g mol⁻¹): C 22.78, H 0.83, Found: C 22.93, H 0.92. MS-FAB (EI POS) *m/z* 843 (M⁺). IR (hexane, cm⁻¹): ν(CO) 2106 (w), 2070 (w), 2040 (m), 2015 (vs), 2003 (s), 1991 (s), 1973 (w), 1951 (m), 1946 (w). ¹H NMR (δ (ppm) in CDCl₃): 7.54 (d, H3, 1H, *J* = 4.4 Hz), 7.09 (d, H4, 1H, *J* = 4.4, 4.7 Hz), 4.48 (q, CH₂, 2H, *J* = 6.9 Hz), 1.58 (t,

CH₃, 3H, $J = 6.9$ Hz). ¹³C NMR (δ (ppm) in CDCl₃): 290.7 (C1), 191 (br, CO), 158 (C2), 135.3 (C3), 134.6 (C4), not obs. (C5), 77.5 (CH₂), 14.5 (CH₃).

2a: Anal. Calcd. (%) for Re₄C₂₈H₁₂O₂₀S (1445.4 g mol⁻¹): C 23.27, H 0.84. Found: C 23.43, H 0.93. MS-FAB (EI POS) m/z not obs. (M⁺). IR (hexane, cm⁻¹): ν (CO) 2102 (w), 2045 (s), 2029 (m), 2012 (w), 2001 (vs), 1994 (vs), 1983 (m), 1954 (m). ¹H NMR (δ (ppm) in CDCl₃): 7.47 (s, H3, H3', 2H), 4.47 (q, CH₂, 4H, $J = 7.0$ Hz), 1.57 (t, CH₃, 6H, $J = 7.0$ Hz). ¹³C NMR (δ (ppm) in CDCl₃): 295.6 (C1), 193 (br, CO), 161.0 (C2, C2'), 130.3 (C3, C3'), 77.5 (CH₂), 14.6 (CH₃).

3: Anal. Calcd. (%) for Re₃C₁₄HO₁₄ (951.7 g mol⁻¹): C 17.66, H 0.11. Found: C 17.83, H 0.14. MS-FAB (EI POS) m/z 951.1 and 953.1 (M⁺). IR (hexane, cm⁻¹): ν (CO) 2147 (w), 2101 (m), 2046 (s), 2016 (s), 1989 (vs), 1961 (s), 1922 (s). ¹H NMR (δ (ppm) in CDCl₃): -15.25 (s) ¹³C NMR (δ (ppm) in CDCl₃): 193 and 196 (CO).

4a: Anal. Calcd. (%) for Re₂C₁₈H₈O₁₀S₂ (820.9 g mol⁻¹): C 26.34, H 0.99. Found: C 26.48, H 1.03. MS-FAB (EI POS) m/z 820.6 and 822.6 (M⁺). IR (hexane, cm⁻¹): ν (CO) 2106 (w), 2091 (w), 2043 (w), 2023 (w), 2012 (vs), 2008 (sh, m), 1985 (w), 1968 (w), 1961 (w). ¹H NMR (δ (ppm) in CDCl₃): 21.37 (br, OH, 1H), -15.73 (s, Re-H, 1H), 8.09 (d, H3, 2H, $J = 4.0$ Hz), 7.28 (dd, H4, 2H, $J = 4.4, 3.3$), 7.86 (d, H5, 2H, $J = 3.3$ Hz). ¹³C NMR (δ (ppm) in CDCl₃): 260.3 (C1), 186 (br, CO), 159.4 (C2) 139.4 (C3), 128.8 (C4), 136.6 (C5).

5a: Anal. Calcd. (%) for Re₂C₁₇H₈O₁₁S (792.8 g mol⁻¹): C, 25.78; H, 1.02. Found: C, 25.97, H, 1.13. MS-FAB (EI POS) m/z 792.4 and 794.4 (M⁺). IR (hexane, cm⁻¹): ν (CO) 2103 (w), 2071 (w), 2042 (m), 2015 (vs), 2002 (s), 1994 (s), 1977 (w), 1955 (m), 1945 (w). ¹H NMR (δ (ppm) in CDCl₃): 9.95 (s, C(O)H, 1H), 7.82 (d, H3, 1H, $J = 4.1$ Hz), 7.71 (d, H4, 1H, $J = 4.1$ Hz), 4.39 (q, CH₂, 2H, $J = 7.0$ Hz), 1.72 (t, CH₃, 3H, $J = 7.0$ Hz). ¹³C NMR (δ (ppm) in CDCl₃): 295.0 (C1), 196.1 (CO), 183.5 (C(O)H), 162.1 (C2), 135.1 (C3), 133.3 (C4), 155.3 (C5), 77.2 (CH₂), 14.2 (CH₃).

(vi) *Reaction of dilithiated bithiophene with dirhenium decacarbonyl*. The same procedure given in (i) was followed. The dropwise addition of 1.4 cm³ (2.2 mmol) of a 1.6 mol dm⁻³ hexane solution of *n*-BuLi to 20 cm³ of a THF solution containing 0.166 g (1.0 mmol) bithiophene afforded a white suspension during stirring. Adding [Re₂(CO)₁₀] in small portions gave a gradual change of colour from yellow to orange to red. The solvent was removed under reduced pressure and the residue dissolved in dichloromethane to give a dark red-brown solution which was alkylated with triethyloxonium tetrafluoroborate. The reaction residue was again purified with column chromatography using hexane/dichloromethane mixtures as eluent. The first zone collected from the column consisted of unreacted [Re₂(CO)₁₀] (0.13 g) and 0.057 g (0.06 mmol, 3%) of **3**. The next zone consisted of 0.051 g (0.06 mmol, 6%) of an orange solid **1b**. The red-purple major band afforded 0.885 g (0.58 mmol, 58%) of the target complex **2b** and the following orange zone 0.122 g (0.14 mmol, 14%) of **5b**. The last product isolated gave 0.044 g (0.045 mmol, 4.5%) of a light yellow complex **4b**. The presence of other zones representing compounds in low yield were noted and 0.007 g (0.03 mmol, 3%) of 2,9-H(O)CC₄H₂S-C₄H₂SC(O)H could be isolated.

(vii) *Protonation instead of alkylation*. The same procedure was followed as that in (vi) with the exception that the reaction mixture was protonated instead of being alkylated. After the lithiation (0.5 cm³, 0.80 mmol of a 1.6 M solution of *n*-BuLi)

of 0.124 g (0.75 mmol) bithiophene and reaction with 0.487 g (0.75 mmol) [Re₂(CO)₁₀], an ethereal solution of HBF₄ was added dropwise and the progress of the reaction monitored by thin layer chromatography. The major products were 0.135 g (0.14 mmol, 19%) of **3**, 0.010 g (0.05 mmol, 6.7%) of C₄H₃S-C₄H₂SC(O)H, 0.035 g (0.158 mmol, 21%) of 2,9-H(O)CC₄H₂S-C₄H₂SC(O)H, and 0.17 g (0.173 mmol, 23%) of **4b**.

(viii) *Reaction of 2b with water*. Crystals of **2b**, 0.5 g (0.35 mmol), were dissolved in 10 cm³ of THF, 0.5 cm³ of water was added and the mixture stirred overnight at room temperature. The colour of the solution changed from dark red to orange-red. Products isolated were 0.068 g of unreacted **2b**, 0.141 g (0.160 mmol, 46%) of the red solid **5b** and 0.020 g (0.021 mmol, 6%) of **3**. According to the ¹H NMR spectrum and peak intensities of the reaction mixture, 0.0087 g (0.039 mmol, 11%) of 2,9-bithiophenedicarbaldehyde was also present in the mixture. Decomposition products could not be recovered from the column.

1b: Anal. Calcd. (%) for Re₂C₂₀H₁₀O₁₀S₂ (846.9 g mol⁻¹): C, 28.34; H, 1.19. Found: C, 28.57; H, 1.28. MS-FAB (EI POS) m/z 845.4 and 847.4 (M⁺). IR (hexane, cm⁻¹): ν (CO) 2102 (w), 2041 (m), 2017 (s), 2001 (vs), 1994 (vs), 1977 (w), 1972 (w), 1954 (m), 1944 (w). ¹H NMR (δ (ppm) in CDCl₃): 7.73 (d, H3, 1H, $J = 4.6$ Hz), 7.18 (d, H4, 1H, $J = 4.6$ Hz), 7.35 (d, H7, 1H, $J = 4.6$ Hz), 7.05 (dd, H8, 1H, $J = 4.6, 1.3$ Hz), 7.35 (d, H9, 1H, $J = 4.6$ Hz), 4.54 (q, CH₂, 2H, $J = 7.0$ Hz), 1.60 (t, CH₃, 3H, $J = 7.0$ Hz). ¹³C NMR (δ (ppm) in CDCl₃): 289.8 (C1), 193 (br, CO), 155.9 (C2), 145.6 (C3), 136.2 (C5), 136.0 (C6), 128.4 (C9), 127.0, 125.9, 124.1 (C4, C7, C8), 77.4 (CH₂), 14.6 (CH₃).

2b: Anal. Calcd. (%) for Re₄C₃₂H₁₄O₂₀S₂ (1527.4 g mol⁻¹): C, 25.16; H 0.92. Found: C, 25.33; H, 0.99. MS-FAB (EI POS) m/z not obs. (M⁺). IR (hexane, cm⁻¹): ν (CO) 2102 (w), 2045 (s), 2029 (m), 2012 (w), 2001 (vs), 1994 (vs), 1983 (m), 1954 (m). ¹H NMR (δ (ppm) in CDCl₃): 7.71 (d, H3, H3', 2H, $J = 4.6$ Hz), 7.30 (d, H4, H4', 2H, $J = 4.6$ Hz), 4.52 (q, CH₂, 4H, $J = 7.1$ Hz), 1.62 (t, CH₃, 6H, $J = 7.0$ Hz). ¹³C NMR (δ (ppm) in CDCl₃): 291.0 (C1), 193 (br, CO), 158.4 (C2, C2'), 142.7 (C3, C3'), 125.6 (C4, C4'), 135.4 (C5, C5'), 77.7 (CH₂), 14.6 (CH₃).

4b: Anal. Calcd. (%) for Re₂C₂₆H₁₂O₁₀S₄ (985.2 g mol⁻¹): C, 31.70; H, 1.23. Found: C, 31.98; H, 1.35. MS-FAB (EI POS) m/z 985.4 and 987.4 (M⁺). IR (hexane, cm⁻¹): ν (CO) 2108 (w), 2092 (w), 2040 (w), 2021 (w), 2012 (vs), 2005 (sh, m), 1981 (w), 1967 (w), 1960 (w). ¹H NMR (δ (ppm) in CDCl₃): 21.4 (br, OH, 1H), -15.74 (s, Re-H, 1H), 8.01 (d, H3, 1H, $J = 3.8$ Hz), 7.34 (d, H4, 1H, $J = 3.8$ Hz), 7.48 (d, H7, 2H, $J = 3.8$ Hz), 7.31 (t, H8, 1H, $J = 3.8$ Hz), 7.74 (dd, H9, 2H, $J = 3.8$ Hz). ¹³C NMR (δ (ppm) in CDCl₃): 259.1 (C1), 193 (br, CO), 152.5 (C2) 141.1, 134.9, 126.5, 125.9, 124.0 (C3, C4, C7, C8, C9), C5 and C6 were not observed.

5b: Anal. Calcd. (%) for Re₂C₂₆H₁₂O₁₀S₄ (985.2 g mol⁻¹): C, 31.70; H, 1.23. Found: C, 31.98; H, 1.35. MS-FAB (EI POS) m/z 985.4 and 987.4 (M⁺). IR (hexane, cm⁻¹): ν (CO) 2108 (w), 2092 (w), 2040 (w), 2021 (w), 2012 (vs), 2005 (sh, m), 1981 (w), 1967 (w), 1960 (w). ¹H NMR (δ (ppm) in CDCl₃): 9.95 (s, C(O)H, 1H), 7.70 (d, H3, 1H, $J = 4.1$ Hz), 7.23 (d, H4, 1H, $J = 4.1$ Hz), 7.06 (d, H7, 1H, $J = 4.4$ Hz), 7.34 (d, H8, 1H, $J = 4.4$ Hz), 4.42 (q, CH₂, 2H, $J = 7.0$ Hz), 1.61 (t, CH₃, 3H, $J = 7.0$ Hz).

Aldehydes. The presence of aldehydes were confirmed by comparison of physical properties and spectroscopic measurements (¹H and ¹³C NMR spectra) of authentic samples (Sigma Aldrich).

2-thiophenecarbaldehyde. Oily substance, ^1H NMR (δ (ppm) in CDCl_3): 9.80 (C(O)H, 1H), 7.77 (d, H3, 1H, $J = 3.8$ Hz), 7.04 (d, H4, 1H, $J = 3.8$ Hz), 7.30 (d, H5, 2H, $J = 3.8$ Hz).

2,5-thiophenebiscarbaldehyde. Off white solid, ^1H NMR (δ (ppm) in CDCl_3): 9.95 (C(O)H, 2H), 7.72 (2, H3, H4, 2H).

2-bithiophenecarbaldehyde. Light yellow solid, ^1H NMR (δ (ppm) in CDCl_3): 9.83 (C(O)H, 1H), 7.66 (d, H3, 1H, $J = 3.8$ Hz), 7.23 (d, H4, 1H, $J = 3.8$ Hz), 7.23 (d, H7, 1H, $J = 3.8$ Hz), 7.04 (t, H8, 1H, $J = 3.8$ Hz), 7.30 (d, H9, 2H, $J = 3.9$ Hz).

2,9-bithiophenebiscarbaldehyde. Yellow solid, ^1H -NMR (δ (ppm) in CDCl_3): 9.89 (C(O)H, 2H), 7.70 (d, H3, H3', 2H, $J = 4.1$ Hz), 7.40 (d, H4, H4', 1H, $J = 3.9$ Hz). ^{13}C -NMR (δ (ppm) in CDCl_3): 182.6 (C(O)H), 144.8 (C2, C9) 143.8 (C5, C6), 136.9 (C3, C8), 126.5 (C4, C7).

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References

- 1 P. R. Schreiner, H. P. Reisenauer, P. C. Pickard, A. C. Simmonett, W. D. Allen, E. Matyus and G. Császár, *Nature*, 2008, **453**, 906–911; D. Gerbig, H. P. Reisenauer, C-H. Wu, D. Ley, W. D. Allen and P. R. Schreiner, *J. Am. Chem. Soc.*, 2010, **132**, 7273–7275.
- 2 M. A. Garralda, *Dalton Trans.*, 2009, 3635–3645; J. R. Moss, and W. A. Herrmann, *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, 1996; E. L. Muettterties and J. Stein, *Chem. Rev.*, 1979, **79**, 479–490; W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 117–130.
- 3 M. Sola and T. Ziegler, *Organometallics*, 1996, **15**, 2611–2618.
- 4 E. O. Fischer and A. Riedel, *Chem. Ber.*, 1968, **101**, 156–161.
- 5 Examples of relevant hydroxycarbene complexes: E. O. Fischer and A. Maasbol, *Chem. Ber.*, 1967, **100**, 2445–2456; J. R. Moss, M. Green and F. A. G. Stone, *J. Chem. Soc., Dalton Trans.*, 1973, 975–977; K. P. Darst and C. M. Lukehart, *J. Organomet. Chem.*, 1979, **171**, 65–71; R. J. McKinney and F. G. A. Stone, *Inorg. Chim. Acta*, 1980, **44**, 227–228; J. Chatt, G. J. Leigh, C. J. Pickett and D. R. Stanley, *J. Organomet. Chem.*, 1980, **184**, C64; K. P. Darst, P. G. Lenkert, C. M. Lukehart and L. T. Warfield, *J. Organomet. Chem.*, 1980, **195**, 317–324; R. J. Klingler, J. C. Huffman and J. K. Kochi, *Inorg. Chem.*, 1981, **20**, 34–40; C. P. Casey, H. Sakaba and T. L. Underiner, *J. Am. Chem. Soc.*, 1991, **113**, 6673–6674; P. L. Motz, D. M. Ho and M. Orchin, *J. Organomet. Chem.*, 1991, **407**, 259–269; D. Steinborn, M. Gerisch, C. Bruhn and J. A. Davies, *Inorg. Chem.*, 1999, **38**, 680–683; M. W. Esterhuysen and H. G. Raubenheimer, *Eur. J. Inorg. Chem.*, 2003, 3861–3869.
- 6 C. P. Casey, C. J. Czerwinski and R. K. Hayashi, *J. Am. Chem. Soc.*, 1995, **117**, 4189–4190; C. P. Casey, C. J. Czerwinski, K. A. Fusie and R. K. Hayashi, *J. Am. Chem. Soc.*, 1997, **119**, 3971–3978.
- 7 (a) K. E. Warner and J. R. Norton, *Organometallics*, 1985, **4**, 2150–2160; (b) B. C. Martin, K. E. Warner and J. R. Norton, *J. Am. Chem. Soc.*, 1986, **108**, 33–39; M. J. Nappa, R. Santi and J. Halpern, *Organometallics*, 1985, **4**, 34–41; (c) M. J. Nappa, R. Santi, S. P. Diefenbach and J. Halpern, *J. Am. Chem. Soc.*, 1982, **104**, 619–621.
- 8 Examples of relevant hydrido-acyl complexes see: D. Milstein, *Organometallics*, 1982, **1**, 1549–1551; D. Milstein, *Acc. Chem. Res.*, 1984, **17**, 221–226; E. F. Landvatter and T. B. Rauchfuss, *Organometallics*, 1982, **1**, 506–513; K. Wang, T. J. Emge, A. S. Goldman, C. Li and S. P. Nolan, *Organometallics*, 1995, **14**, 4929–4936; G. Brockaart, R. El Mail, M. A. Garralda, R. Hernández, L. Ibarlicea and J. Santos, *Inorg. Chim. Acta*, 2002, **338**, 249–254.
- 9 Y. M. Terblans, M. H. Roos and S. Lotz, *J. Organomet. Chem.*, 1998, **566**, 133–142; S. Lotz, C. Crause, A. O. Olivier, D. C. Liles, H. Görls, M. Landman and D. I. Bezuidenhout, *Dalton Trans.*, 2009, 697–710; C. Crause, H. Görls and S. Lotz, *Dalton Trans.*, 2005, 1649–1657.
- 10 N. A. Van Jaarsveld, D. C. Liles and S. Lotz, *Dalton Trans.*, 2010, **39**, 5777–5779.
- 11 R. B. King, *J. Am. Chem. Soc.*, 1963, **85**, 1922–1926; C. P. Casey, *J. Chem. Soc. D*, 1970, 1220–1221; C. P. Casey and R. L. Anderson, *J. Am. Chem. Soc.*, 1971, **93**, 3554–3555; C. P. Casey, C. R. Cyr, R. L. Anderson and D. F. Marten, *J. Am. Chem. Soc.*, 1975, **97**, 3053–3059; E. O. Fischer, E. Offhaus, J. Müller and D. Nöthe, *Chem. Ber.*, 1972, **105**, 3027–3035.
- 12 D. I. Bezuidenhout, S. Lotz, M. Landman and D. C. Liles, *Inorg. Chem.*, 2011, **50**, 1521–1533.
- 13 E. O. Fischer and P. Rustemeyer, *J. Organomet. Chem.*, 1982, **225**, 265–277; U. Schubert, K. Ackermann and P. Rustemeyer, *J. Organomet. Chem.*, 1982, **231**, 323–334; E. O. Fischer, P. Rustemeyer, O. Orama, D. Neugebauer and U. Schubert, *J. Organomet. Chem.*, 1983, **247**, 7–19.
- 14 D. I. Bezuidenhout, D. C. Liles, P. H. Van Rooyen and S. Lotz, *J. Organomet. Chem.*, 2007, **692**, 774–783.
- 15 L. J. Faruggia, ORTEP-3 for Windows - a version of ORTEP-III with graphical user interface, *J. Appl. Crystallogr.*, 1997, **30**, 565C. J. Cason, 2004. POV-RAY for Windows. Persistence of Vision, Raytracer Pty. Ltd, Victoria, Australia. URL: <http://www.povray.org>.
- 16 H. Werner, E. O. Fischer, B. Heckl and C. G. Kreiter, *J. Organomet. Chem.*, 1971, **28**, 367–389; S. Lotz, M. Landman, D. I. Bezuidenhout, A. J. Olivier, D. C. Liles and P. H. Van Rooyen, *J. Organomet. Chem.*, 2005, **690**, 5929–5937.
- 17 C. F. Bernasconi, *Chem. Soc. Rev.*, 1997, **26**, 299–307.
- 18 D. Michos, X-L. Luo and R. H. Crabtree, *Inorg. Chem.*, 1993, **32**, 2118–2122.
- 19 M. A. Urbancic and J. R. Shapley, *Inorg. Synth.*, 1990, **28**, 165–168.
- 20 W. Fellmann and H. D. Kaesz, *Inorg. Nucl. Chem. Lett.*, 1966, **2**, 63–65; J. K. Hoyano and W. A. G. Graham, *Inorg. Chem.*, 1972, **11**, 1265–1269.
- 21 C. S. Yang, C. P. Cheng, L. W. Guo and Y. Wang, *J. Chin. Chem. Soc.*, 1985, **32**, 17–22.
- 22 C. M. Lukehart and J. V. Zeile, *J. Am. Chem. Soc.*, 1976, **98**, 2365–2376; C. M. Lukehart, G. P. Torrence and J. V. Zeile, *J. Am. Chem. Soc.*, 1975, **97**, 6903–6904; C. M. Lukehart, G. P. Torrence and J. V. Zeile, *Inorg. Chem.*, 1976, **15**, 2393–2397; C. M. Lukehart and J. V. Zeile, *J. Am. Chem. Soc.*, 1977, **99**, 4368–4372.
- 23 D. Steinborn, *Dalton Trans.*, 2005, 2664–2671; D. Steinborn and S. Schwieger, *Chem.–Eur. J.*, 2007, **13**, 9668–9678.
- 24 E. O. Fischer, G. Kreis and F. R. Kreissl, *J. Organomet. Chem.*, 1973, **56**, C37–C40; D. H. Gibson, S. K. Mandal, K. Owens and J. F. Richardson, *Organometallics*, 1990, **9**, 1936–1942.
- 25 M. L. H. Green, *J. Organomet. Chem.*, 1995, **500**, 127–148.
- 26 Y. Shvo, D. Czarkie and Y. Rahamim, *J. Am. Chem. Soc.*, 1986, **108**, 7400–7402; C. P. Casey, S. W. Singer, D. R. Powell, R. K. Hayashi and M. Kavana, *J. Am. Chem. Soc.*, 2001, **123**, 1090–1100; R. M. Bullock, *Chem.–Eur. J.*, 2004, **10**, 2366–2374; R. Karvembu, R. Prabhakaran and K. Natarajan, *Coord. Chem. Rev.*, 2005, **249**, 911–918 and references therein; B. L. Conly, M. K. Pennington-Boggio, E. Boz and T. J. Williams, *Chem. Rev.*, 2010, **110**, 2294–2312.
- 27 K. Takahashi, M. Yamashita, T. Ichihara, K. Nakano and K. Nozaki, *Angew. Chem. Int. Ed.*, 2010, **49**, 1–4.
- 28 M. Landman, H. Görls and S. Lotz, *J. Organomet. Chem.*, 2001, **617**–**618**, 280–287; M. Landman, J. Ramontja, M. van Staden, D. I. Bezuidenhout, P. H. van Rooyen, D. C. Liles and S. Lotz, *Inorg. Chim. Acta*, 2010, **363**, 705–717; D. C. Liles and S. Lotz, *Acta. Cryst.*, 2006, **E62**, m331–m334.
- 29 D. M. Andrada, M. E. Zoloff Michoff, I. Fernandez, A. M. Granados and M. A. Sierra, *Organometallics*, 2007, **26**, 5854–5858.
- 30 D. C. Liles, A. J. Olivier, S. Lotz and M. Landman, *Unpublished results*.
- 31 H. Dong and H. Berke, *Adv. Synth. Catal.*, 2009, **351**, 1783–1788; Y. Yang, O. Blacque, T. Fox, C. M. Frech and H. Berke, *Organometallics*, 2009, **28**, 5493–5504; Y. Kuminobu, T. Matsuki and K. Takai, *J. Am. Chem. Soc.*, 2009, **131**, 9914–9915.
- 32 H. Meerwein, *Org. Synth.*, 1966, **46**, 113–115.
- 33 G. M. Spies and R. J. Angelici, *Organometallics*, 1987, **6**, 1897–1903.
- 34 L. Brandsma, S. F. Vasilevsky and H. D. Verkruisje, *Application of Transition Metal Catalysis in Organic Synthesis*, Springer-Verlag, Berlin/Heidelberg, 1998, 4–6.
- 35 SAINTE Version 6.45, SADABS Version 2.10, SHELXTS and SHELXTL Version 6.14, Bruker AXS Inc, Madison, WI, USA, 2001.
- 36 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **A64**, 112–122.