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## ARTICLE

## Fischer carbene complexes remain favourite targets, and vehicles for new discoveries

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H.G. Raubenheimer<sup>a</sup>Received 00th January 2012,  
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Exciting new variations in Fischer-type carbene complex composition and reactivity have been realised by following or modifying well-established synthetic approaches such as metal carbonyl functionalization and modification of existing carbene ligands. The formation of targeted complexes for organic synthesis, carbene-containing chelates, and polynuclear carbene complexes, by employing 'click chemistry', warrants discussion. Transmetalation and  $\alpha,\alpha$ -dehydrogenation of ethers and amines have come into their own as viable synthetic methods to access carbene complexes with unique properties and activities. Successful mediation of carbene complex formation with pincer ligands has proved its worth. Quantum chemistry has become essential for supporting or initiating mechanistic proposals, but heuristic approaches such as invoking the vinology principle to describe substituted phenylcarbene complexes are still valuable in the interpretation of bonding properties and the classification of complex types. Electrochemical studies now also constitute a powerful part of the experimental characterization tool kit.

### Introduction

Ever since the ground-breaking publication by Fischer and Maasböl fifty years ago,<sup>1</sup> introducing stable, isolable and fully characterized carbene complexes of group 6 metals, the versatility of the carbene ligand class has not failed to fascinate the chemical community. The complete antipodes of Fischer's electrophilic complexes, the nucleophilic, so-called alkylidenes, present in high oxidation state transition metal complexes, were announced 10 years later, in 1974, by Schrock,<sup>2</sup> which opened up the research field even further. Many other types of carbene ligands have now been exposed in detail – see Table 1 for examples.<sup>3</sup> Most of them defy simple categorization as exclusively Fischer or Schrock types.<sup>29</sup> Others have such distinctive and useful coordination influences, making electrophilicity or nucleophilicity not their most significant features. Obviously, the metal and its oxidation state as well as the other ligands present play a role in the large variations in reactivity found, for example, in the simple coordinated secondary, nonheteroatom-stabilized, ligands: CHR (R = aryl).<sup>12,30</sup>

Fischer-type carbene complexes (FCCs) have shown exceptional merit as synthons in organic and organometallic synthesis, and numerous review articles have been devoted to describing and organising the results. The latest of such articles usually contain references to earlier literature.<sup>5,31–33</sup> The important role played by the Spanish research groups, under the leadership of Barluenga, Sierra and others, is worth mentioning

here. Often the applicable mechanisms in the syntheses have been explored by quantum chemical calculations.<sup>34</sup> In addition to yielding organic products, interaction with carbene ligands, using other coordination modes, has afforded numerous coordination complexes.<sup>35</sup>

FCCs have found application in diverse – and sometimes unexpected – research areas. The formation of mixed valence and mixed metal Lindqvist complexes,<sup>36</sup> as well as stable gold and palladium,<sup>37,38</sup> and monodisperse chromium nanoparticles<sup>39</sup> are cases in point.

In this Perspective, classical Fischer carbene complexes of the general form  $L_nM=C(XR^1)R^2$  are considered. With the growing interest in other types of carbene complexes (Table 1), it is remarkable that research into such complexes is still flourishing. Sustained activity and application is stimulated, and guaranteed, by the preparation of new complex variations within the family as well as by a thorough understanding of their bonding (on both quantum chemical and empirical levels) and mechanism of formation. These aspects receive attention here and the literature is reviewed for the past decade. The only other reactions dealt with in depth here are the conversions of one carbene complex to another. Several relevant review articles have appeared during the review period and they are referred to in the appropriate sections.

**Table 1** Selected examples of typical carbene ligands<sup>a</sup>**Preparative results****The Fischer route.**

The synthetic approach followed in the laboratory of E.O. Fischer during the 1970s and 1980s is often still used – sometimes with small modifications – to obtain new and useful compounds or to find new applications for known complex types when the carbene ligands are designed differently to the original ones.

**Polymer-supported carbene complexes.** In contrast to previous approaches to affix carbene complexes to polymer supports by using phosphine ligands or by making the polymer the organic substituent of the carbene complex, more recently, the pentacarbonyl metal fragment was attached via a carefully selected isocyanide as the sixth ligand, starting from a Merrifield resin.<sup>40</sup> The carbene complex preparation then occurs as a solid-phase process by consecutive treatment with RLi and an alkylating agent, methyltriflate (MeOTf), (eqn (1)). In other examples, the linker chain length was increased. Reactions such as aminolysis, cyclopropanation and C–H insertion occur in the solid state, although not always in satisfactory yields. On completion of such a reaction, the starting pentacarbonyl complex, still attached to the resin, can be regenerated by treatment with CO, and the process of carbene formation repeated.

Eqn 1

**Azobenzene-containing carbene ligands.** In a contribution that particularly focussed on experimental variations when using the Fischer synthetic protocol, Garlich-Zschoche and Dötz<sup>41</sup> described the preparation of two unique amphiphilic azobenzene aminosugar carbene complexes of chromium (**1**). Reaction conditions, choice of solvent, the metal attached to the organic group for CO nucleophilic attack, the alkylating agent, and time allowed for the reactions are the most important synthetic variables that were optimised for ensuring acceptable yields (Scheme 1).

**Scheme 1** "Me<sup>+</sup>" = Me<sub>3</sub>OBF<sub>4</sub>.

**Fluorinated carbene complexes.** Replacing the nucleophilic reagent RLi in the Fischer approach with Me<sub>3</sub>SiCF<sub>3</sub> in the presence of fluoride ions and using MeOTf as alkylating agent, the first example of a perfluoroalkyl carbene complex has been prepared (eqn (2)).<sup>42</sup> It should be possible to transfer such a ligand to later transition elements (see below).

Eqn 2

**Unusual CO functionalizations.** The first example of a simple methoxycarbene complex of platinum was prepared by straightforward base attack on coordinated CO, followed by alkylation. The platinum(II) in the produced complex was coordinated by a mediating PCP-type pincer ligand (Scheme 2).<sup>43</sup>

**Scheme 2**

Using another approach, chelated biscarbene complexes of chromium and tungsten could be formed upon consecutive CO functionalizations.<sup>44</sup> 3-Bromo-5-methyl-thiophene was deprotonated by LDA and reacted with M(CO)<sub>6</sub> to form a 2-carbeniate. Subsequent Li/Br exchange with *n*-BuLi effected a second nucleophilic attack on a cis-positioned CO ligand, and alkylation yielded the product (Scheme 3). The preparation and reactivity of di- and polymetallic carbene complexes has been thoroughly dealt with in an earlier review article by Bezuidenhout and Lotz.<sup>45</sup>

**Scheme 3** i LDA; ii M(CO)<sub>6</sub>; iii <sup>*n*</sup>BuLi (all in THF); iv [Et<sub>3</sub>O][BF<sub>4</sub>] (in CH<sub>2</sub>Cl<sub>2</sub>).

Deprotonation of N-coordinated N-methylimidazole in a cationic rhenium complex leads to internal Fischer-like nucleophilic attack on a coordinated CO ligand and affords carbene complex formation upon alkylation.<sup>46</sup> The dinuclear product represents a rare (see below) four-membered carbene–imine chelate eqn (3), Ar' = 3,5-bis(trifluoromethyl)phenyl.

Eqn 3

An as yet unprecedented (methoxy)phospholylcarbene complex prepared according to an established method under carefully controlled conditions (eqn (4)), coordinates to a second (CO)<sub>5</sub>W fragment.<sup>47</sup> The NMR resonance of the carbene carbon in the product at δ 316.9, which is much higher than in known alkoxy(heteroaryl) carbene complexes (see references later in the text), indicates the possibility of unique reactivity, which has indeed been found.

Eqn 4

**Changing the carbene ligand.**

Certainly, the most versatile method to provide access to Fischer carbene complexes involves modification of an existing coordinated carbene. Numerous such reactions have been described previously, many of them in the course of utilizing carbene complexes in organic synthesis.<sup>4</sup>

**Cycloadditions and condensations.** Alkynyl esters in the presence of N-methylmorpholine-N-oxide (NMO) and Fischer carbene complexes such as (CO)<sub>5</sub>M=C(OEt)Ph or (CO)<sub>5</sub>M=C(OEt)C≡CPh (M = Cr, W) undergo self-

condensation and coordination to the  $(\text{CO})_5\text{M}$  unit to afford pyran-2-ylidene Fischer complexes in relatively low yields (eqn (5)).<sup>48</sup> The exact mechanism of the transformation is still uncertain, although it seems likely that the NMO activates the original carbene complexes by other means than simply by ligand oxidation. Various other methods of preparing pyran-2-ylidene complexes are known.<sup>4</sup>

Eqn 5

Aumann and co-workers found remarkable differences between  $(\beta\text{-imino})\text{ethoxy-}$  and  $(\beta\text{-imino})\text{thioethoxycarbene}$  complexes of chromium and tungsten in reactions with imido-yl chlorides (Scheme 4).<sup>49</sup> The preference for either a metallic ( $\text{di-}\pi\text{-methane}$ ) rearrangement (MDPMR) to yield (alkoxy)amino-carbene complexes (**2**), or an  $\alpha\text{-cyclization}$  to afford thermolabile, coordinated pyrroles, is determined by an intricate interplay of kinetic and thermodynamic factors. A key role is played by a common intermediate carbene complex.

**Scheme 4**  $\text{M} = \text{Cr or W}$ ;  $\text{R}^1 = \text{organic group}$ ,  $\text{R}^2 = \text{alkyl or aryl}$ ,  $\text{R}^3 = \text{H or Me}$ ,  $\text{R}^4 = \text{alkyl or aryl}$ .

In a reaction that once again illustrates the versatility of alkynyl FCCs,<sup>4</sup> Sierra and co-workers<sup>50</sup> have shown that such compounds react with tropothione by formal regioselective  $[8 + 2]$  cycloaddition (Scheme 5) to give cycloheptathiophenecarbene complexes (**4**). DFT quantum chemical calculations indicate the intermediate formation of a nonaromatic, zwitterionic allene adduct (**I**).

Subsequent to the appearance of the Bezuidenhout review mentioned above, Baeza, Casarrubios and Sierra<sup>51</sup> published an important paper. They succeeded in showing that Fischer aminocarbene complexes of chromium and tungsten that contain both internal and terminal alkyne units in their organic side chains can be effectively converted into dinuclear, trinuclear, and tetranuclear carbene complexes by using 'click chemistry' with organic azides. The 1,3-dipolar addition reactions catalyzed by Cu(I) occurred readily and in good yields, although a few exceptions were noted. A highly diverse range of structures were constructed, but only a few representative examples (**3–5**) are shown in Scheme 6. Pauson–Khand cyclization of the (allyl)amino ( $\text{R}^1 = \text{allyl}$ ) and alkyne substituents at the carbene carbon of selected compounds leads to a large number of C–C bond formations and CO insertions during bicyclic ring formation. (Amino)vinyl Fischer carbenes still exist at the periphery of the newly constructed molecules of increased complexity. In a simplified graphic version (Scheme 7), the cyclization in only one carbene unit is shown.

**Scheme 5**

**Scheme 6**

**Scheme 7**

**$\alpha\text{-Deprotonation of Fischer carbene complexes.}$**  The acidity of  $\alpha\text{-hydrogens}$  attached to the carbene carbon atom in Fischer carbene complexes is well known and has often been utilized in the past for their modification of the complexes by deprotonation and electrophilic addition. Recent contributions from Raubenheimer's laboratory have been reviewed in this journal.<sup>52</sup> These include the formation of elusive four-membered carbene–heteroatom chelates as well as the preparation of remote NHC carbene complexes *via* the stereoselective generation of  $\alpha,\beta\text{-unsaturated}$  Fischer carbenes.

The groups of Ortega-Alfaro and Alvarez-Toledano<sup>52</sup> combined efforts in preparing more examples of carbene-S and carbene-N five-membered chelates by reaction of  $\alpha\text{-deprotonated}$  aminocarbene complexes with PhNCS and employing two different alkylating agents, and ultrasound activation in one instance, to afford **6** and **7** (Scheme 8).

**Scheme 8**

In a very interesting application, Sarkar and co-workers<sup>53</sup> deprotonated standard  $(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Me}$  to allow the introduction of two polyethylene glycol (PEG) tethers by allyl attachment to the carbanionic centre (**8**, Scheme 9). The resulting product, when  $n = 7$ , is sufficiently soluble in water (55 mg/l) to be biochemically useful. Bovine serum albumin reacts, by aminolysis, with this 'PEGylated' carbene complex to produce a bioconjugate with marker (heavy metal;  $\nu_{\text{CO}}$ ) characteristics (Scheme 10). In a recent contribution, first protein and then rabbit IgG were immobilized on gold and glass surfaces by reaction with a Fischer carbene function.<sup>54</sup>

**Scheme 9**

Anionic metaloxycarbene complexes of the Fischer-type were found to react with a variety of metal complexes, by different pathways, to form unusual products, depending on the R-group in  $[(\text{CO})_5\text{MC}(\text{O})\text{R}]^-$  and the second metal employed. Particularly interesting are examples of isomorphous, *mer*-configured, tris 'complexes of complexes' of Cr(III), Fe(III) and Co(III), that form when  $\text{R} = 4\text{-methyl-2-thiazolyl}$ .<sup>52</sup>

**Scheme 10**

Alkene–carbene and alkyne–carbene chelates are well known. López-Cortéz and co-workers<sup>56</sup> reported the first examples of allene–aminocarbene complexes prepared by a rare functionalization of primary (amino)(ferrocenyl)carbene complexes of Cr, Mo and W (eqn (6)).

Eqn 6

**Transmetallation.**

Important contributions towards the preparation of new carbene complexes by transmetallation (or metal exchange) using, particularly, Rh, Pd and (later) Au as metals to replace Cr or W, have been made by the Spanish schools. Developments that have taken place after the appearance of the last review article by Gómez-Gallego *et al.*<sup>57</sup> are discussed below.

Sierra and co-workers<sup>58</sup> recently showed, both experimentally and theoretically, that carbene transmetallation from Cr to Rh or Pd is a key step in the catalyzed formation of quinolone alkaloids by cyclization of group 6 (2-aminoethyl)-carbene complexes.

Barluenga and co-workers<sup>59</sup> succeeded in preparing the first examples of mixed complexes that contain both Fischer carbene and NHC ligands coordinated to Rh(I) (eqn (7)), whereas Fañanás-Mastral and Aznar<sup>60</sup> made gold complexes bearing NHC and alkenylcarbene ligands by reacting  $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{CH}=\text{CHPh}$  with  $(\text{NHC})\text{AuCl}$  in the presence of  $\text{AgSbF}_6$ . Various *remote* NHCs, prepared from Fischer carbenes, were transferred to Rh and Au to prepare the first such compounds of the latter element.<sup>61</sup>

Eqn 7

Strasser *et al.*<sup>62</sup> utilized  $(\text{tht})\text{AuCl}$  to transfer a FCC that carries a 2-phenylthiazol-5-yl group from  $(\text{CO})_5\text{W}$  to isolobal  $\text{AuCl}$  (eqn (8)). The single proton on the thiazole ring exhibits an unusual shape and positional variation with temperature in its NMR spectra, probably because of  $\text{Au}\cdots\text{H}$  hydrogen bonding interaction.<sup>63</sup> It is interesting that tungsten carbeniates are also readily transferable from W to Au when suitable complex fragments of the two metals are used.

Eqn 8

Although diheterocarbene complexes are not discussed in detail in this paper (see, for example, references 10 and 11 for recent articles on them), one very interesting example is mentioned below. Ruiz and co-workers<sup>64</sup> prepared such a complex positioned within an N-heterometallic carbene ligand that is coordinated to gold (**10**), by double deprotonation, metallation with  $(\text{Ph}_3\text{P})\text{AuCl}$ , and final alkylation of a diaminecarbene complex of manganese(I) carbonyl. A reasonable schematic rationalization of the process, which includes metal exchange and internal nucleophilic attack on coordinated CO, is given in Scheme 11. Upon heating, the kinetic zwitterionic product (**9**) also reacts by a formal exchange of Me and Ph groups. Again, all metal–carbene interactions are represented by double bonds to allow the arrow formalism to be applied.

Various other intermolecular metal exchange reactions in bi- and polymetallic systems have been dealt with in the review article by Bezuidenhout and Lotz,<sup>45</sup> and are not repeated here. A very recent example, however, deserves attention.

**Scheme 11**

As mentioned above, facile transmetallation of typical heteroatom-stabilized FCCs of Cr and W occurs with different gold(I) complexes. In the absence of a heteroelement in the diphenylcarbene complex of pentacarbonyltungsten, the reaction stops halfway and a cationic gold adduct (**11**) is formed (Scheme 12).<sup>65</sup> Such a compound with chromium as central metal is unstable, even at  $-50\text{ }^\circ\text{C}$ , and converts rapidly with loss of CO to form a bimetallic complex (**12**) in which the chromium atom is in contact with an *ipso* carbon of one of the phenyl groups, shielding it electronically. The contrasting smooth and complete transmetallation known for alkoxy-carbene complexes can, however, be accomplished by placing two methoxy groups in the *para* positions of the phenyl rings of the starting chromium carbene complex. Cationic penta- and tetracarbonyl dinuclear products still form initially, but spontaneously convert to form a linear, diarylcarbene-gold complex (eqn (9)).<sup>66</sup>

**Scheme 12**

Eqn 9

These results, as well as NMR measurements and crystal structure data, indicate that Fischer-like carbene complexes stabilized by remotely positioned heteroatoms can be generated not only by 1,2-insertion of a six-membered aromatic ring ('vinology principle'<sup>67</sup> – see below), but by a 1,4-insertion of the  $\text{C}_6\text{H}_4$  ring ('extended vinology') between the heteroatom fragment, e.g., OMe, and the carbene carbon. At any particular moment, only one of the two anisyl rings participates in  $\pi$ -electron delocalization towards the carbene carbon atom.

 **$\alpha,\alpha$ -Dehydrogenation.**

Inspired and guided by the results obtained in the groups of Bergman, Bercaw, Caulton and, particularly, Carmona, who all showed that carbene complexes can be formed by double C–H activation, Grubbs, Whited and others investigated  $\alpha,\alpha$ -dehydrogenation in ethers and amines by using an anionic pincer-supported iridium complex as the active metal center. The results were reported in a series of important papers that appeared between 2008 and 2010. Examples of their carbene complex syntheses are shown in Scheme 13.<sup>68–71</sup> A few general conclusions regarding synthetic aspects can be drawn from the papers.

- Ozerov's PNP imidophosphine ligand ( $\text{PNP} = [\text{N}(\text{2-}i\text{Pr}_2\text{-4-Me-C}_6\text{H}_3)_2]^-$ )<sup>71</sup> serves as an excellent support for Ir(I), facilitating  $\alpha,\alpha$ -H-activation in the substrates, and allowing the isolation of

- relatively stable carbene complexes and the characterization of intermediates (reaction type 1, Scheme 13).
- b) Two mole equivalents of norbornylene are required per (PNP)Ir to ensure complete double dehydrogenation of the starting complex, (PNP)IrH<sub>2</sub>: the first to initiate the reaction and then again to form the kinetic carbene complex product when the starting complex is regenerated by the eliminated H<sub>2</sub> reacting with an intermediate.
- c) In contrast with the dehydrogenation of methyl ethers to give square planar Ir(I) carbene complexes, (PNP)Ir effects octahedral aminocarbene(dihydro)Ir(III) complexes by double C–H activation of methylamines (reaction 2).<sup>70</sup> The latter result is in agreement with an earlier report by Manzano and co-workers<sup>73</sup> who found that a PAPP bidentate PN ligand (PAPP = 1,2-[1-(dimethylamino)ethyl]-1-(diphenylphosphino)ferrocene) installed at Ru(II) effectively activates the attached aminomethyl unit to give a chelated aminocarbene ligand, (eqn (10)), whereas two related but less rigid and weaker bonded PN bidentate ligands, PPFA (2-[1-(dimethylamino)ethyl]-1-(diphenylphosphino)ferrocene) and PTFA ([η5-cyclopentadienyl][η5-4-(endo-dimethylamino)-3-(diphenylphosphino)-4,5,6,7-tetrahydro-1H-indenyl]) of iron(II) are not prone to such conversion.
- d) The dihydride formed according to the procedure followed by Grubbs and co-workers when using THF as substrate (reaction 3, Scheme 13) is structurally related to the products mentioned in c. Heating leads to the expulsion of H<sub>2</sub>.<sup>71</sup>
- e) Carbenes are not always formed during C–H activation with dehydrogenated (PNP)IrH<sub>2</sub>. Other outcomes include the formation of vinyl ethers (reaction 4) and activated (e.g., by oxidative addition, reaction 5) or decarbonylated (reaction 6) products.<sup>71</sup>
- f) Detailed quantum chemical calculations carried out by Yates and co-workers<sup>74</sup> support the mechanisms postulated by experimentation and give an excellent interpretation of the role played by norbornylene by invoking a unique autocatalytic interplay between thermodynamics and kinetics during carbene complex formation.

In 2009, a short review article was published that deals mainly with *reactions* of the Fischer type iridium carbene complexes.<sup>68</sup> Certainly, one of the most unusual reactions is carbon dioxide reduction coupled with oxygen atom transfer to the Fischer carbene.<sup>75–77</sup>

### Scheme 13

Eqn 10

Schneider and co-workers<sup>78</sup> also used PNP pincer ligands for activating THF towards carbene formation along another synthetic route. Their chelating ligands of the types (HPNP)<sup>R</sup> (R = <sup>t</sup>Pr, <sup>t</sup>Bu) react with [IrCl(COE)<sub>2</sub>]<sub>2</sub> (COE = cyclooctene) in the presence of NaX (X = BPh<sub>4</sub>) or TIX (X = PF<sub>6</sub>) to give the carbene complexes indicated in (eqn (11)). Obvious differences to the Grubbs' system are the neutral pincer ligand employed by

the Schneider group compared to Grubbs' PNP amide, and the manner in which the active Ir(I) complex is generated. Important steps in the proposed, and experimentally supported, mechanism include cyclooctenyl complex formation by oxidative substitution, Cl<sup>−</sup> abstraction, reductive elimination, and COE recoordination. Then, presumably, follows a slow α,α-dehydrogenation, leading to the formation of a carbene(dihydride) complex by COE substitution, as proposed by Yates and co-workers<sup>74</sup> for the Grubbs' reactions.

Using advanced mass spectrometry and collision-induced dissociation (CID) supported by DFT calculations, Chen and co-workers<sup>79</sup> proposed the generation of gaseous, cationic, secondary FCCs (**13**, **14**) from an adduct formed between [(IMes)Au]<sup>+</sup> and 1-ethoxy-2-methoxy ethane (Scheme 14). The description of the postulated model intermediate, **II**, as an 'agostic complex' could be contentious, since the possibility of agostic interactions in gold(I) chemistry – albeit in solution or the solid state – has essentially been ruled out in a recent article.<sup>63</sup>

Eqn 11

### Scheme 14

#### Insertions into Si–C and Si–H bonds.

CO insertion into Si–C bonds of actinide and early transition metal complexes is a well-established pathway to enolate complexes. Using an Fe(II) complex bearing the tridentate tetravalent silene ligand tris(3-trimethylsilyl-2-mercaptophenyl)methylsilane, Kawaguchi and co-workers<sup>80</sup> showed that treatment with CO results in an insertion of the molecule into one (substituted) phenyl–Si bond with concomitant C-coordination to form an iron–carbene bond. Two other CO molecules bind to iron to increase its coordination number from four to six (**15** in eqn (12)). The close positioning of one of the thiolato sulphur atoms to the carbene carbon atom (1.872(4) Å) bears analogy to a thiametallacyclopropane complex, an intermediate during thiolysis of alkoxy carbene complexes that contain thiol ligands.<sup>81</sup>

Eqn 12

Recently, in a highlight contribution, an unprecedented insertion of XylNC into a Si–H bond in a reaction between η<sup>3</sup>-H<sub>2</sub>SiRR' σ-complexes of Ru(I) and the isocyanide was discovered (Scheme 15).<sup>82</sup> NMR studies at low temperatures indicate that an adduct is initially formed in which the isocyanide is associated with a six-coordinated Si centre. DFT computational modelling of the subsequent product formation shows 1,1-hydrosilation (isocyanide insertion into the Si–H bond), iminoformyl migration to Ru, and N-bonding to Si to afford the aminocarbene product **16**. The carbene ligand features one γ-agostic (3c2e) Si–H→Ru bond and a weaker

Ru–H Si association, in which the ruthenium provides the bridging hydride.

### Oxidative substitution.

The formation of (generally cyclic) carbene complexes by oxidative substitution was pioneered independently by the research groups of Lappert<sup>83</sup> and Stone<sup>84</sup> in the early 1970s. Later, it was applied to the preparation of *normal* and *abnormal* (some of them *remote*) pyridylidenes.<sup>23</sup> Fürstner and co-workers<sup>85</sup> used the approach to prepare prototypical Fischer-type aminocarbene complexes of Pd(II) (eqn (13)). The method also lends itself to the formation of acyclic diaminocarbene complexes of Pd and Ni or diheterocarbene complexes of Pd; but these types, like NHCs and CAACs (see Table 1), have developed independently and are not discussed here.

### Scheme 15

Eqn 13

### Experimental kinetic and thermodynamic studies

The results discussed here are important in the context of converting one carbene complex to another. Since the 1980s, Bernasconi and co-workers have made important contributions towards understanding the thermodynamic and kinetic acidities of CH-active FCC complexes of group 6 metals. In one of the latest papers on this topic, Bernasconi and Ragains<sup>86</sup> report on deprotonation studies of  $[\text{Cp}^*(\text{CO})_2\text{Fe}=\text{C}(\text{OMe})\text{Me}]^+$ , and use the opportunity to consider and briefly compare the different factors that determine proton transfer from both kinetic (using intrinsic rate constants,  $k_o$ ) and thermodynamic (using  $\text{pK}_a$  as parameter) viewpoints. Owing to the complexity of the many mutually supporting and opposing structural influences, rationalization of data is possible, but correct comparative predictions for given compounds in terms of rate of deprotonation or acid strength is unattainable.

The research group of Bernasconi has also published numerous articles on nucleophilic substitution at the carbene carbon atom. Their latest contribution<sup>87</sup> elaborates on two important results: (i) in the reaction of thiolate anions with Fischer type alkoxycarbene complexes, the leaving group expulsion is rate limiting with thiolates that are weak bases, whereas the nucleophilic attachment step is rate determining when such bases are strong; and (ii) weak base thiolates are inferior leaving groups compared to aryloxides of comparable basicities.

Rate constants for postulated tetrahedral adduct formation during hydrolysis of arylcarbene complexes,  $(\text{CO})_5\text{Cr}=\text{C}(\text{OR}^1)\text{Ar}$ , with  $\text{OH}^-$ , are adversely affected by an increase in the steric bulk of group  $\text{R}^1$ . Such effects are similar to those found in the hydrolysis of esters, but they are more

accentuated in carbene complexes.<sup>88</sup> Both the carbanionic and anionic amide nucleophiles malonitrile,  $\text{CH}(\text{CN})_2^-$ , and cyanamide,  $\text{N}\equiv\text{CNH}^-$ , are more reactive nucleophiles for substituted alkoxy- or thioalkoxy carbene complexes than  $\text{OH}^-$ .<sup>89,90</sup>

### Theoretical approaches

A review article appeared in 2005 summarizing the status of quantum chemical calculations for Fischer- (and Schrock-) type carbene complexes.<sup>91</sup> Of importance is that it clearly shows that the interpretations of bonding in carbene complexes in terms of simple heuristic models based on experiment, measurement, and intuition have been substantiated by elaborate calculations. Interpretations are based on various procedures by making use of charge or energy partitioning. In doing this, new concepts have been defined that have not necessarily all been embraced yet by all experimental chemists. Dichotomies may arise between heuristic models and quantum mechanical interpretations, for example: stronger 'orbital interactions' do not necessarily translate into stronger chemical bonds; and calculated electron densities, in many examples, do not always concur with formal mesomeric structures.

On the other hand, the relative contributions by  $\sigma$ - and  $\pi$ -interactions in the metal–C(carbene) bond in terms of a Dewar–Chatt–Duncanson-type interpretation have now been placed on a firm footing, while an earlier proposal by Wang and co-workers,<sup>92</sup> and others,<sup>91</sup> to describe the  $\pi$ -interaction in the M–C(carbene)–X fragment of a FCC by a (3c4e) bond has not been refuted.

### Structure and reactivity studies combined with quantum chemical calculations.

Dedicated quantum mechanical calculations have also been used to interpret or supplement various experimental investigations. The calculations by Yates in the context of Grubbs'  $\alpha, \alpha$ -hydrogen activations, and the rationalization of carbene complex formation by mass spectroscopic activation, as discussed above, are such examples. These, and a few others, are highlighted below.

**Conformation of Fischer type carbene complexes.** Fischer carbene complexes,  $(\text{CO})_5\text{M}=\text{C}(\text{OR}^1)\text{R}^2$ , usually occur as *anti* isomers around the C(carbene)–O bond in the crystalline state. For the first time, by using DFT calculations and accepting correspondence between the vacuum and crystalline states, the observation has been explained in terms of  $\sigma_{\text{CH}}$  and  $\sigma_{\text{CH}}^*$  (situated on the alkyl group,  $\text{R}^2$ ) donor–acceptor interactions with symmetry-related  $\pi$  orbitals of neighbouring CO ligands.<sup>93</sup> The more obvious destabilizing steric repulsion between groups attached to the carbene carbon atom plays a decisive role in alkynylcarbene complexes, making the *syn*-conformation the preferred one. Complexes with *syn*-conformations are more polar than their *anti* analogues and are the preferred orientations in more polar solvents.

**Carbene complex ionization.** ESI-MS studies coupled with deuterium labelling, and DFT calculations to identify lowest energy intermediates, enabled Sierra and co-workers<sup>94,95</sup> to explain the ionization mechanisms of alkenyl and alkynyl FCCs and to demystify the role played by the additive (Ad), tetrathiafulvalene (TTF).

Three generalized mechanisms for the processes involving single electron transfer (SET) by hydrogen atom transfer (HAT), are shown in Scheme 16. All of them require an abstractable hydrogen atom positioned  $\alpha$ ,  $\beta$  or  $\gamma$  to the carbene carbon atom, respectively. The ionization of alkynylcarbene complexes in (c) is accompanied by internal hydrogen migration. Complexes in (a) and (b) are detected in the mass spectrometer as  $[M-H]^-$  anions whereas the fragment ions  $[M-H-CO]^-$  are observed in ionizations such as in (c). The mediating additive, TTF, acts neither as an electron carrier nor as a base, but as a hydrogen atom abstractor.

**Photochemistry.** Quantum chemistry is essential for understanding the versatile and extremely useful photochemistry of Cr(0) and Mo(0) FCCs. After studying the electronic transitions, reactivities, ligand modifications, important solvent effects, operative mechanisms, and selectivity in such complexes, Sierra and co-workers summarized their most important results in a review article.<sup>96</sup>

**Electrochemistry.** Various groups have reported on the redox profiles of FCCs in the review period. In almost all cases, the interpretation of the results supported and extended by quantum chemical calculations, is in accordance with earlier work.<sup>97,98</sup> The current viewpoint is that, for example, oxidation occurs at the central metal and reduction at the carbene ligand, with most of the additional electronic charge centred at the carbene carbon atom and partly delocalized over attached heteroatoms and conjugated heteroaromatic rings. The delocalization is indicated by the shape of the LUMO orbitals of the neutral complexes or the HOMOs of the formed anionic radicals.<sup>99-102</sup>

A number of further developments regarding FCCs have been reported, some of which are summarized below.

- Conjugation of the carbene complexes with an analogue of natural nucleic acids by aminolysis affects the electrochemical activity of the organometallic fragment modestly, and exploitation as electrochemical probes in bio-organometallic chemistry can be foreseen.<sup>103</sup>
- A direct major influence on the oxidation potential of the carbene complexes is the  $\pi$ -acidity of the ligands attached to the metal.<sup>99</sup>

#### Scheme 16

- Increasing the effective electronegativity of X in complexes of the type  $(CO)_5M=C(XR^1)R^2$  (X = O, NR<sup>3</sup>, S; R<sup>1</sup> = alkyl; R<sup>2</sup> = alkyl, aryl; R<sup>3</sup> = H, alkyl) and the electron-withdrawing influence of groups R<sup>4</sup> in

$(CO)_5M=C(XR^1)C_6H_5R^4-p$ , the more readily the reduction occurs.<sup>99,101</sup>

- The heteroatom in furyl and thienyl substituents plays a similar role as X and (amino)furylcarbenes are reduced more readily than their thienyl analogues.<sup>99</sup> It is unclear why the order is reversed in alkoxycarbenes.<sup>101</sup>
- Carbene complexes of iron and chromium become stronger oxidants with the increased electron delocalization in the formed radical anion when R<sup>2</sup> = C(O)Me in aminocarbene complexes. The low-lying LUMO orbital of the neutral complex (or the HOMO of the radical anion) is delocalized over N, C(carbene), the aromatic ring, and attached carbonyl group in the *para* position. Such complexes are even much easier reduced than those with R<sup>2</sup> = CF<sub>3</sub>, where the LUMO is exclusively localized on the C(carbene)–N portion of the molecule.<sup>104</sup> This result is particularly interesting since conjugative stabilization of the carbocationic carbene carbon atom by phenyl or substituted phenyl groups is generally of little importance.<sup>100,105,106</sup> The electron charge of the added electron is much better delocalized in 2-heteroaryl substituents than in substituents linked in the 3-position.<sup>103</sup> Extending delocalization by the addition of a second conjugated thienyl group to an existing one facilitates reduction even further.<sup>107</sup>
- Support for the atomic location of the single electron after one-electron oxidations and reductions in a variety of carbene complexes, including examples of Fe(0) and Mn(I), emanated from DFT calculations, ESR measurements, and mass spectrometry.<sup>99,102</sup>
- Most authors report one-electron oxidation and reduction steps, but two-electron reductions have also been found for aminocarbene complexes, depending on the electrodes used.<sup>99,101</sup> Further oxidation of the central metal has also been observed.
- Newly characterized and DFT-studied *fac* and *mer* isomers of the complexes  $(CO)_6(dppe)Cr=C(XR^1)R^2$  (X = O, NH; R<sup>1</sup> = Et, Cy; R<sup>2</sup> = 2-thienyl, 2-furyl) participate in various reactions during cyclic voltammetric study (Scheme 17).<sup>108</sup> The equilibrium between the neutral complexes in solution favours the lower energy *mer* isomer by way of a fast conversion. The *fac*<sup>+</sup> cation rapidly and quantitatively converts to the *mer*<sup>+</sup> isomer, which is the only one that exhibits a reduction peak in the cyclic voltammogram. Related redox relationships have been postulated earlier for disubstituted phosphine and phosphite derivatives of chromium hexacarbonyl.<sup>109</sup>

#### Scheme 17

**Mechanistic considerations.** Extending the comprehensive kinetic studies undertaken by Bernasconi and co-workers on the aminolysis of methoxy and thiomethoxy carbene complexes of Cr(0) and W(0), Solà and co-workers<sup>110</sup> undertook the first *computational* study of the mechanisms of such reactions; they concentrated on a chromium family. The detailed calculations



take into account various reaction routes as well as solvent effects. The results indicate a stepwise process, including two transition states, that takes place by the initial formation of a tetrahedral zwitterionic intermediate, **III**. The rate-determining step is the initial nucleophilic attack by  $\text{NH}_3$ , which is inhibited by  $\pi$ -donation from the heteroatom X. The subsequent two steps in which  $\text{MeXH}$  is eliminated and the product formed, are in accordance with earlier proposals made by Bernasconi's group.<sup>111</sup>

### III

#### Other bonding considerations.

Despite the fact that Hoveyda–Grubbs precatalysts and their derivatives (Scheme 18) contain no heteroatom attached to the carbene carbon atom, they can be classified as belonging to the Fischer carbene family on the basis of the vinology principle<sup>112</sup> (referred to earlier) with the anchored, remote *o*-O<sup>i</sup>Pr group fulfilling a stabilizing role by  $\pi$ -conjugation with the electron-deficient carbene carbon atom.<sup>67</sup> The most important modifications that have been made to such catalysts to change their performance emerge from in steric or electronic effects. Substituents *ortho* to the O<sup>i</sup>Pr group cause a structural distortion and increased rate of metathesis reaction,<sup>112</sup> whereas nearly the same effect is achieved by substituting the aromatic ring in the position *para* to the O<sup>i</sup>Pr group by electron withdrawing  $\text{NO}_2$ .<sup>114</sup> Stability of the Ru–O bond in the chelate is however increased (and activity decreased) by better  $\pi$ -delocalization (aromaticity) in the chelate ring, caused by the correct positioning of annelated aromatic rings (Scheme 18).<sup>67</sup> This active field of research with its own unique and complicated mechanistic uncertainties<sup>115</sup> has been reviewed.<sup>116,117</sup>

#### Scheme 18

#### Conclusions

The wealth of new Fischer type carbene complexes prepared during the past 10 years holds challenges and can serve as a basis for investigation by organic chemists, theoreticians, kineticists and bio-inorganic chemists. The often unique processes utilized, including certain transmetallations, cycloadditions,  $\alpha,\alpha$ -dehydrogenations and even oxidative additions, should inspire synthetic organometallic chemists to find new novel methods of preparation and to further enlarge the existing library of FCCs.

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#### Notes and references

<sup>a</sup> Department of Chemistry and Polymer Science, University of Stellenbosch, Matieland 7602, South Africa. E-mail: hgr@sun.ac.za

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Fifty years after their introduction, Fischer-type carbene complexes still enthrall synthetic and theoretical chemists interested in their preparation and characterization.