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Some group 4 metallocene derived carbene complex chemistry

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Abstract

Many metal carbonyls add to reactive (η^2-olefin) group 4 metallocene type complexes (e.g. (η^2-aryne)titanocene or -zirconocene, (butadiene)$ZrCp_2$) forming metallacyclic titanoxy- or zirconoxycarbene complexes. The metallacyclic (π-allyl)zirconoxycarbene complex derived from (*s-trans*-η^4-butadiene)zirconocene and hexacarbonyltungsten adds to organic carbonyl substrates to give nine-membered metallacyclic carbene complexes $Cp_2\overline{ZrOC[{=}W(CO)_5]CH_2CH{=}CHCH_2CR^1R^2O}$, exhibiting *trans*-C=C double bonds. The zirconoxycarbene complexes undergo stereoselective base-induced alkylation and Wittig-olefination reactions. Oxygen-bridged dimeric (η^2-formaldehyde)zirconocene is obtained in high yield upon treatment of the carbon monoxide hydrozirconation product with methyllithium. The $[(\eta^2\text{-}CH_2O)ZrCp_2]$-dimer undergoes various insertion reactions with aluminum hydride or boron hydride reagents. Metal carbonyl complexes insert selectively into one metallaoxirane Zr–C bond of $[(\eta^2\text{-}CH_2O)ZrCp_2]_2$ to give cyclic $Cp_2\overline{ZrOC[{=}ML_n]CH_2O}$ containing zirconoxycarbene complexes.

Introduction

Carbene complex chemistry has undergone a remarkable development in recent years. Mononuclear electrophilic heteroatom stabilized Fischer type carbene complexes $L_nM{=}C(R)OR'$ have been prepared from most transition elements. Such complexes have found widespread applications in organic synthesis and catalysis [1]. "Schrock-type" alkylidene complexes, $L_nM{=}CR^1R^2$, have been used as new stoichiometric nucleophilic reagents as well as catalysts for organic syntheses [2]. Binuclear μ-CH_2 or μ-CR_2 complexes represent other interesting classes of carbene complexes.The (μ-alkylidene)$[ML_n]_m$ species show a wide range of interesting chemical and structural features. Metal–metal bonded late transition element (μ-methylene)M_2L_n compounds and μ-alkylidene complexes of early transition and main group metal complex fragments (e.g. Tebbe's reagent) are representative examples at opposite ends of the bridging alkylidene complex spectrum [3].

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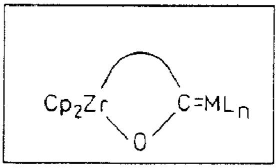
Zirconium complexes have recently contributed to the development of the chemistry of several types of carbene complexes. In this article, we will focus on the formation and some selected chemical features of zirconoxycarbene complexes (**1**) and of compounds containing the metallaoxirane unit (**2**). The former can be regarded as specifically modified Fischer-type carbene complexes. The later are related to the binuclear methylene bridged $L_nM(\mu\text{-}CH_2)ML_n$ complexes. Characteristic chemical features of the $Cp_2\overline{Zr(CH_2O})$ complexes, beyond their well known ability of methylene transfer, shall be discussed in the second part of this account.



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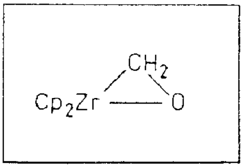

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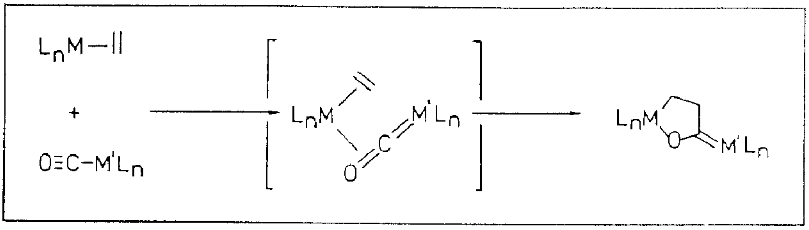
Zirconoxycarbene complexes

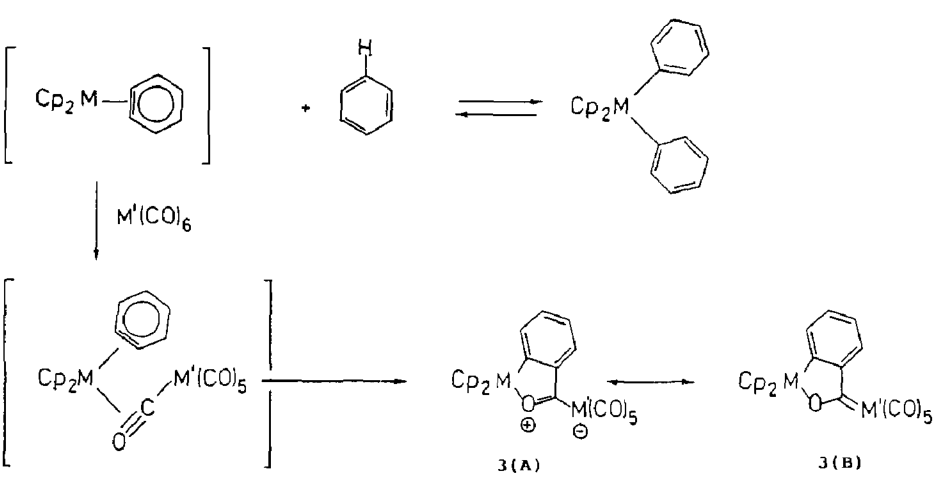
Many heteroatom stabilized metal carbene complexes can be prepared from metal carbonyls by modifying Fischer's method; i.e. by adding a nucleophilic reagent to the carbonyl carbon center followed by attaching an appropriate electrophile to the oxygen atom [4]. Since this two step reaction sequence has to rely on well defined stability/reactivity requirements with regard to the acyl metallate anion intermediate involved, a variety of alternative "non-nucleophilic" routes to Fischer-type carbene complexes have been developed [5].

We have discovered a method that makes use of the high reactivity of group 4 bent metallocene mono-olefin complexes and related species. These complexes add to many metal carbonyls forming binuclear carbonyl-bridged reactive intermediates. The $(\eta^2\text{-alkene})(\mu\text{-}\eta^1:\eta^2\text{-O}{\equiv}\text{CM})$ metallocenes undergo a subsequent rapid (probably concerted electrocylic) ring-closure reaction to yield five-membered metallacyclic metaloxycarbene complexes directly.



Typical examples are the reactions of thermally generated $(\eta^2$-aryne)titanocene or -zirconocene which cleanly react with the group 6 $M(CO)_6$ metal carbonyls to give metallacyclic benzannelated titanoxy- and zirconoxycarbene complexes **3** (M = Ti, Zr), respectively [6].

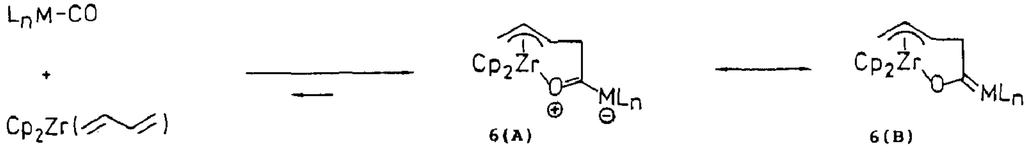
Figure 1 shows the molecular structure of a typical example of this class of compounds. Complex **4** has been prepared starting from bis(t-butylcyclopentadienyl)zirconium diphenyl (**5**). Thermolysis of **5** at 80 °C in the presence of hexacarbonyltungsten resulted in the formation of the five-membered metallacyclic



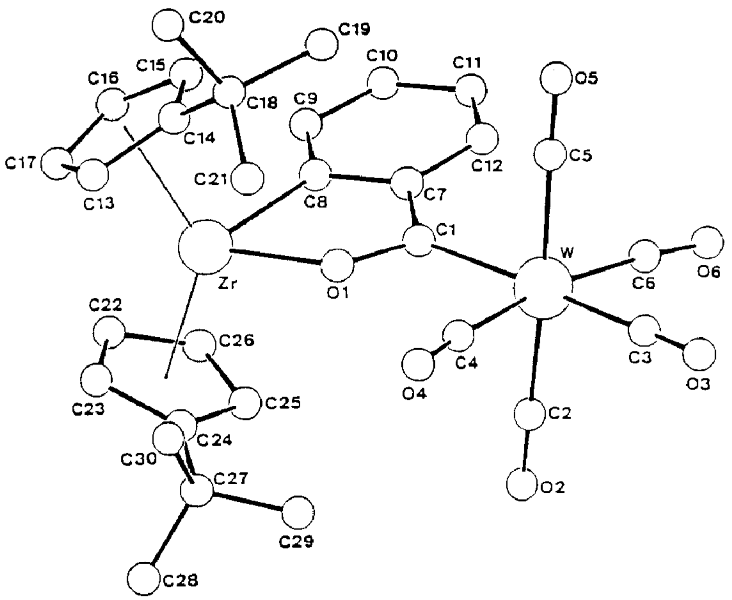
U. Dorf (1985) M= Ti, Zr ; M' = Cr, Mo, W (52% yield)

zirconoxycarbene complex (4). Noteworthy is the rather short O(1)–C(1) bond length of **4** indicating a pronounced acyl metallate character.

(Conjugated diene)zirconocene and -hafnocene complexes have been used extensively to convert metal carbonyls into metal carbene complexes. For most examples there is experimental evidence that the (*s-trans*-η^4-diene)metallocene reacts much more easily with added $L_nM{-}C{\equiv}O$ substrates as compared to its more nucleophilic (*s-cis*-conjugated-diene)MCp_2 isomer. Usually the five-membered σ-allyl metaloxycarbene complexes obtained as primary products in the electrocyclic ring closure reaction are not stable under the reaction conditions but rearrange to the more stable π-allyl metallocene isomers **6**. The zirconoxycarbene complexes **6** derived from the metal carbonyl complexes of various transition elements by addition of (*s-trans*-η^4-butadiene)zirconocene have been isolated in good yields (typical examples: $Cr(CO)_6$ (51% yield), $Mo(CO)_6$ (61%), $W(CO)_6$ (73%), $CpV(CO)_4$ (72%), $Fe(CO)_5$ (76%), $Fe(PPh_3)(CO)_4$ (53%), $CpCo(CO)_2$ (51%), $(ClCp)Co(CO)_2$ (54%), $CpRh(CO)_2$ (47%), $Ru_3(CO)_{12}$ (71%), $(dppe)Ru_3(CO)_{10}$ (56%)). According to the X-ray crystal structure analyses of many examples the acyl metallate resonance form **6**(A) contributes significantly to the description of the structural properties of these metallacyclic (π-allyl)zirconoxycarbene complexes [7].



The (π-allyl)zirconocene moiety of **6** is a carbon nucleophile that adds cleanly to organic carbonyl compounds. Carbon–carbon coupling takes place at the allyl-CH_2 terminus exclusively. Complex **6a** adds one equivalent of acetone to give the nine-membered metallacyclic zirconoxycarbene complex **7** (56% isolated yield). Remarkably, product **7** contains a *trans*-C=C double bond.Therefore, the nine-



Selected bond distances (Å)

Zr-O(1)	2.082(7)
O(1)-C(1)	1.31(2)
C(1)-W	2.229(8)
W-C(3)	2.00(1)

Fig. 1. A view of the molecular structure of the metallacyclic zirconoxycarbene complex **4** as determined by X-ray diffraction.

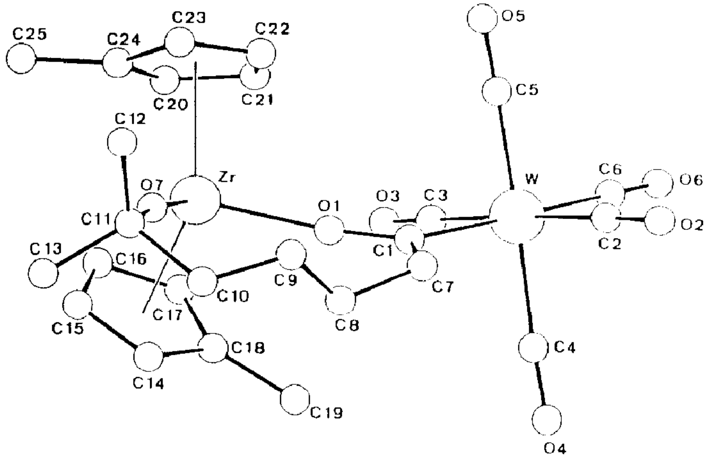
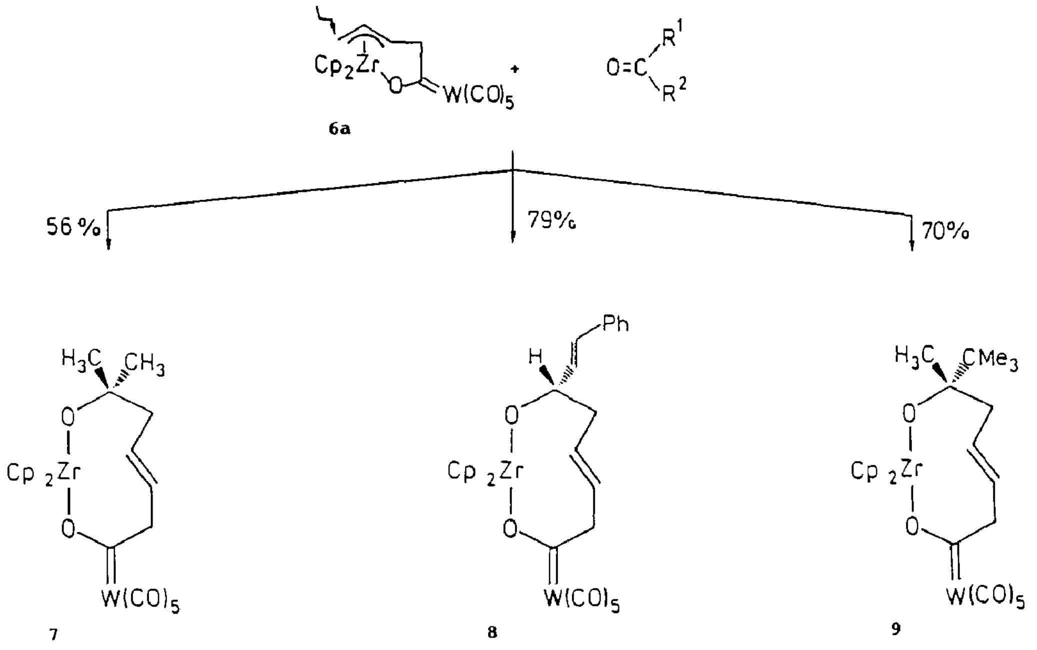


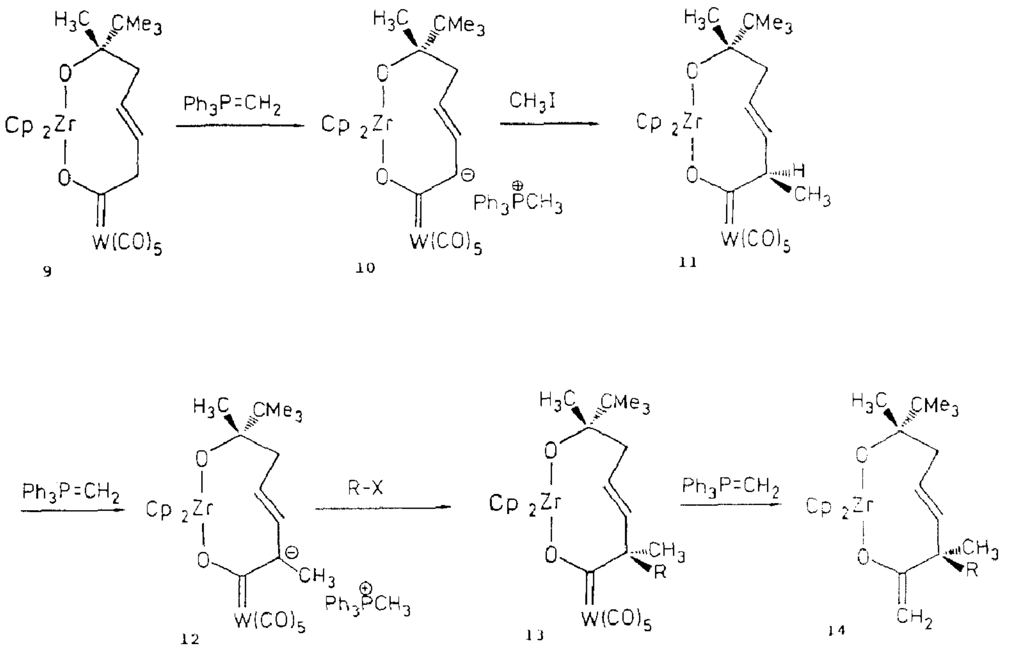
Fig. 2. Molecular structure of the metallacyclic zirconoxycarbene complex $\overline{(MeCp)_2ZrOC[=W(CO)_5]\text{-}}$ $\overline{CH_2CH=CHCH_2C(CH_3)_2O}$ in the crystal.



membered metallacycle features a chiral ground-state conformation. This gives rise to the observation of signals due to diastereotopic methyl groups, Cp-ligands, and methylene groups by NMR spectroscopy. The activation barrier of enantiomerization of **7** is rather high [$\Delta G^{\ddagger}$ (50 °C) 16.6 kcal/mol; to be compared with *trans*-cyclononene: $\Delta G^{\ddagger}$ (-10 °C) ≈ 19 kcal/mol and *trans*-cyclodecene: $\Delta G^{\ddagger}$ (3 °C) ≈ 12 kcal/mol]. Figure 2 shows the chiral metallacyclic structure of the corresponding bis(methylcyclopentadienyl)zirconocene analogue [8].

Complex **6a** adds exclusively to the O=C-functionality of α,β-unsaturated carbonyl compounds (e.g. cinnamaldehyde, two diastereoisomers **8a** and **8b**, 60/40 ratio). Only one diastereomer (**9**) is obtained when pinacolone is added to the (π-allyl)zirconoxycarbene complex **6a**. The X-ray crystal structure analysis shows that the bulky t-butyl substituent occupies an equatorial position at the chiral nine-membered metallacycle of **9** [9].

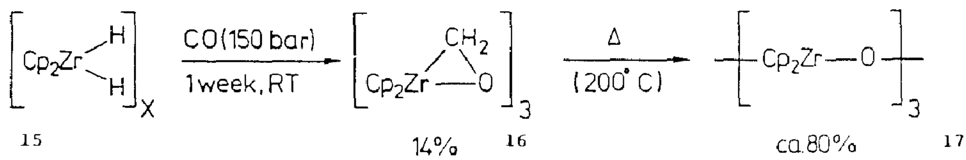
Complex **9** has been treated with various bases. The ylide $Ph_3P{=}CH_2$ abstracts a proton at the ring carbon atom adjacent to the metal carbene complex functionality. The resulting carbanionic complex **10** was isolated (using the bulky $Ph_3PCH_3^+$ cation) and characterized spectroscopically. Alkylation (e.g. with methyl iodide) takes place stereoselectively.The diastereoisomer **11** featuring *cis*-1,5-dimethyl substitution is obtained with ca. 80% d.e. Subsequent treatment of **11** with additional $Ph_3P{=}CH_2$ produces the methyl-substituted anion **12**. Similarly addition of various alkylation reagents (e.g. CD_3I, CH_3CH_2I) occurred diastereoselectively, giving **13**. Treating **13** with a further equivalent of a phosphorus ylide cannot result in deprotonation. Consequently, a slow Wittig-olefination reaction of the zirconoxycarbene complex occurs instead. This organometallic analogue of the (unknown)



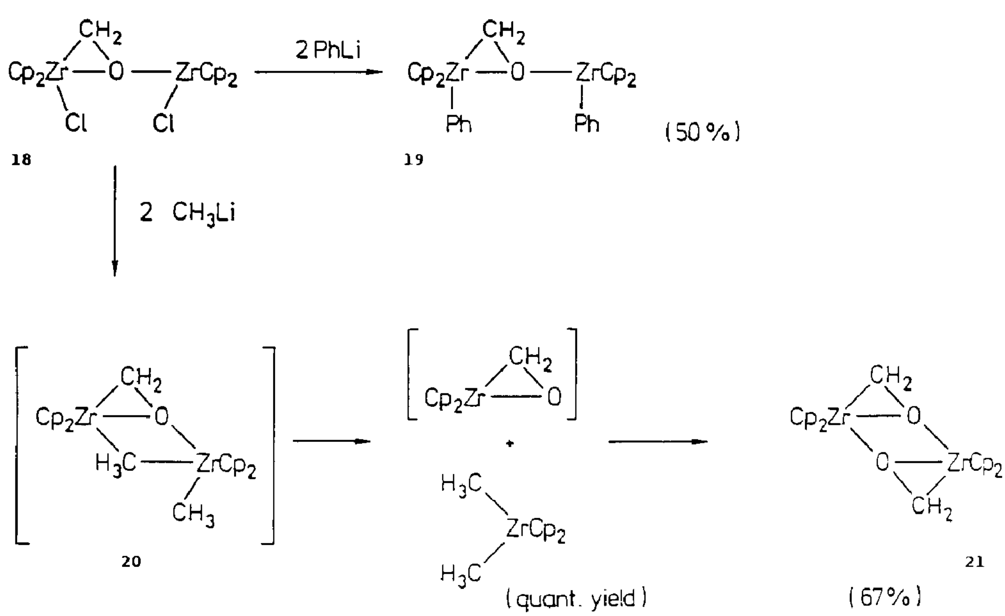
Wittig-olefination of a carboxylate anion produces an enolate, in this case the metallacyclic zirconium enolate **14** [10].

(η^2-Formaldehyde)zirconocene

Previously we have shown that a (η^2-formaldehyde)zirconocene complex is formed upon prolonged treatment of oligomeric dihydridozirconocene **15** with carbon monoxide. The cyclotrimeric metallaoxirane **16**, (the X-ray structure of which is shown in Fig. 3), is obtained in a rather low yield. Complex **16** shows chemical properties similar to μ-methylene complexes. Upon thermolysis (200 °C) all three CO derived CH_2 groups of **16** are cleaved giving the known cyclotrimeric $[Cp_2ZrO]_3$ metal oxide framework (**17**) [11]. This observation is of interest in view of the continuing search for molecular Fischer–Tropsch models [12].



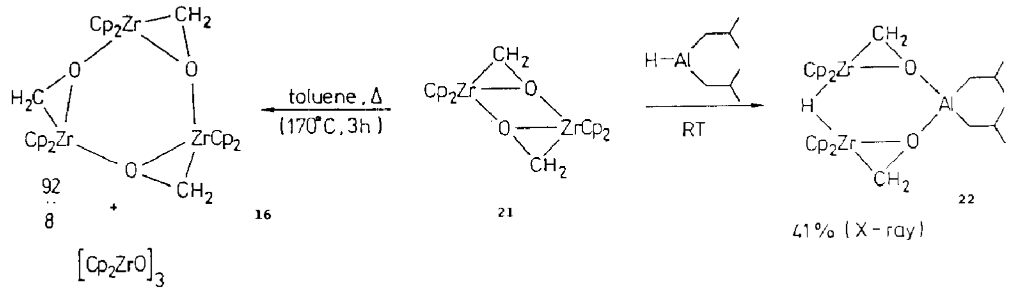
Floriani et al. have shown that $[\mu(O\text{-}\eta^1 : C,O\text{-}\eta^2\text{-}CH_2O)(Cp_2ZrCl)_2]$ (**18**) is formed upon hydrozirconation of carbon monoxide [13]. We have treated **18** with two molar equivalents of phenyllithium to obtain the substitution product **19** [14]. Reaction of **18** with methyllithium takes a different course. We assume that the methyl-bridged binuclear intermediate **20** is formed which is not stable under the reaction conditions. Cleavage leads to dimethylzirconocene (isolated in almost quantitative yield)



and (η^2-formaldehyde)zirconocene. The latter is not stable as a monomer and consequently we isolated the (η^2-CH_2O)$ZrCp_2$ dimer **21** (67% yield).

Complex **21** was characterized by X-ray diffraction. A view of the molecular structure of the cyclodimeric (η^2-formaldehyde)zirconocene complex and a comparison of characteristic bond lengths of $[(\eta^2\text{-}CH_2O)ZrCp_2]_2$ (**21**) and $[(\eta^2\text{-}CH_2O)ZrCp_2]_3$ (**16**) (see Fig. 3) is given in Fig. 4. Both formaldehyde-zirconocene complexes exhibit rather long Zr–C and C–O bond lengths, indicating pronounced σ-complex (metallaoxirane) character. In both complexes **21** and **16** the Zr–O bonds connecting monomeric $\overline{\mathrm{ZrCO}}$ units are slightly longer than the metal oxygen distances within the metallaoxirane structural subunits.

Upon thermolysis of the (η^2-formaldehyde)zirconocene dimer **21** in toluene at 170 °C the thermodynamically favoured cyclotrimeric $[(\eta^2\text{-}CH_2O)ZrCp_2]_3$ complex **16** is formed. Addition of diisobutylaluminumhydride to $[(\eta^2\text{-}CH_2O)ZrCp_2]_2$ (**21**) results in insertion of hydride. The remaining AlR_2 unit ends up between the mononuclear metallaoxirane moieties giving **22** [15*].



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* Reference number with asterisk indicates a note in the list of references.

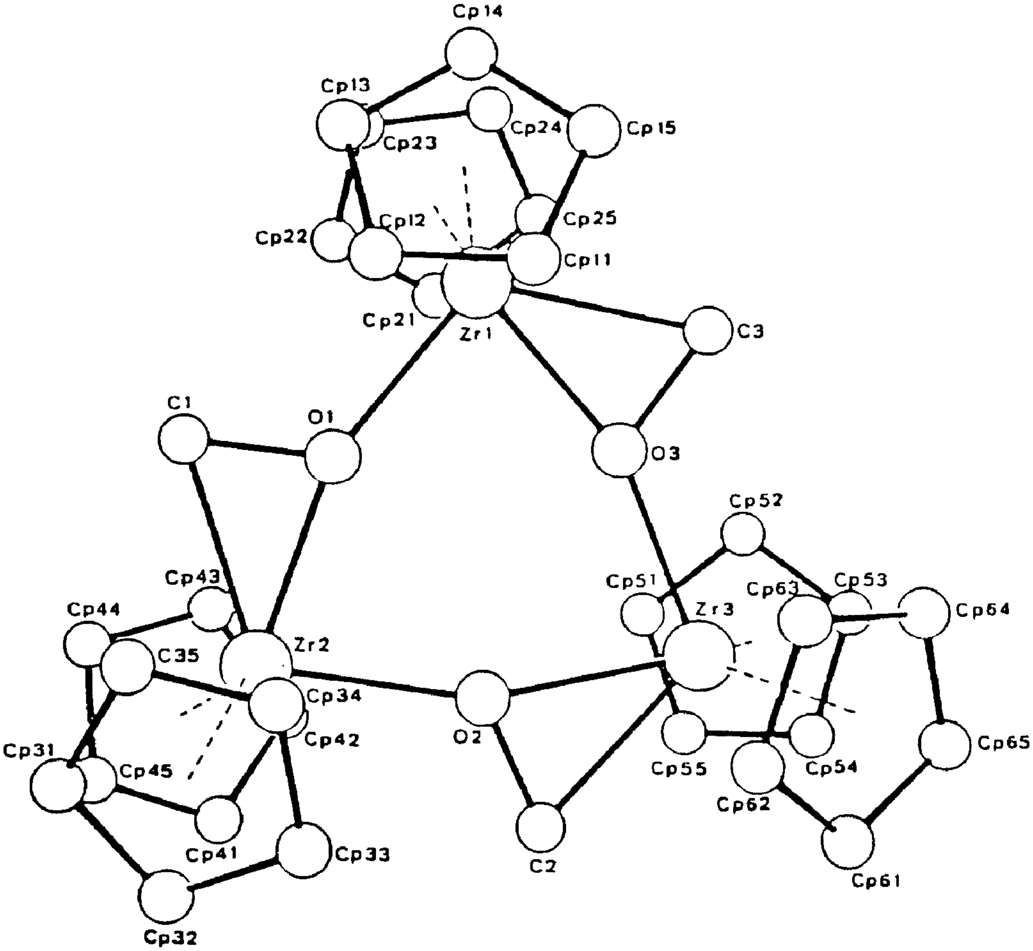
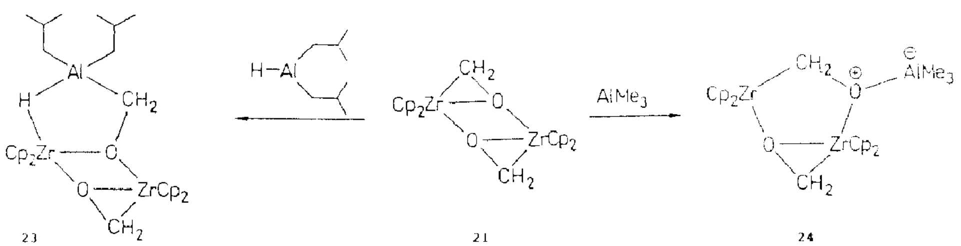


Fig. 3. A projection of the molecular structure of cyclotrimeric (η^2-formaldehyde)zirconocene (**16**), obtained by carbonylation of $[Cp_2ZrH_2]_x$.

Under kinetic control the reaction of $HAl(isoC_4H_9)_2$ with $[(\eta^2\text{-}CH_2O)ZrCp_2]_2$ **21** results in a different product. The Zr–O bonds connecting the mononuclear subunits are retained. Instead, insertion of the HAl group into one metallaoxirane Zr–C bond is observed.The resulting reaction product **23** contains a five-membered metallacycle featuring five different ring atoms (Zr, O, C, Al, H). At room temperature complex **23** rearranges to **22**. The reaction of **21** with trialkylaluminum reagents results in a different product type. Addition of $AlMe_3$ to a metallaoxirane oxygen atom leads to the ring-opened product **24**.



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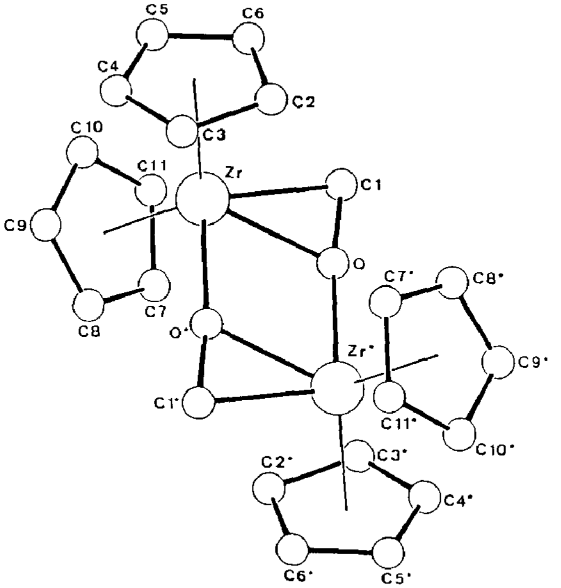


selected bond distances (Å)

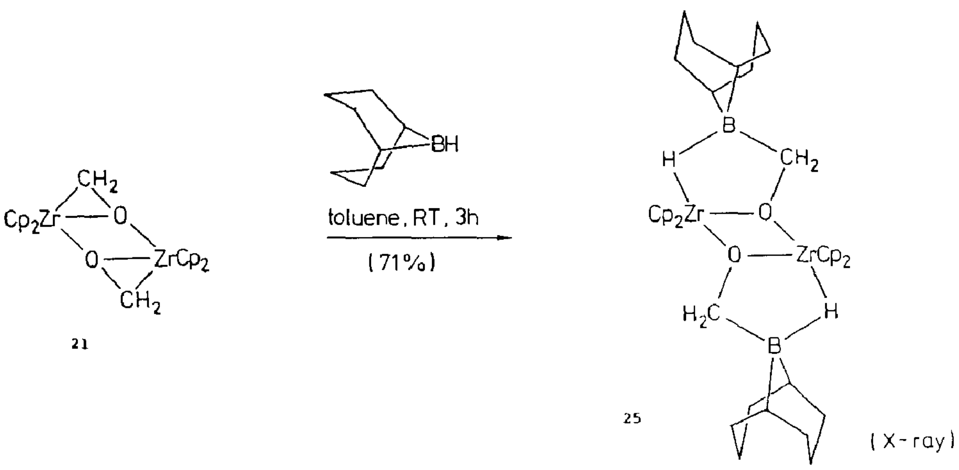
	$[Cp_2Zr(CH_2O)]_2$	$[Cp_2Zr(CH_2O)]_3$ †
C(1)–O	1.395(4)	1.427
Zr–C(1)	2.243(3)	2.275
Zr–O	2.103(2)	2.135
O–Zr*	2.200(2)	2.179

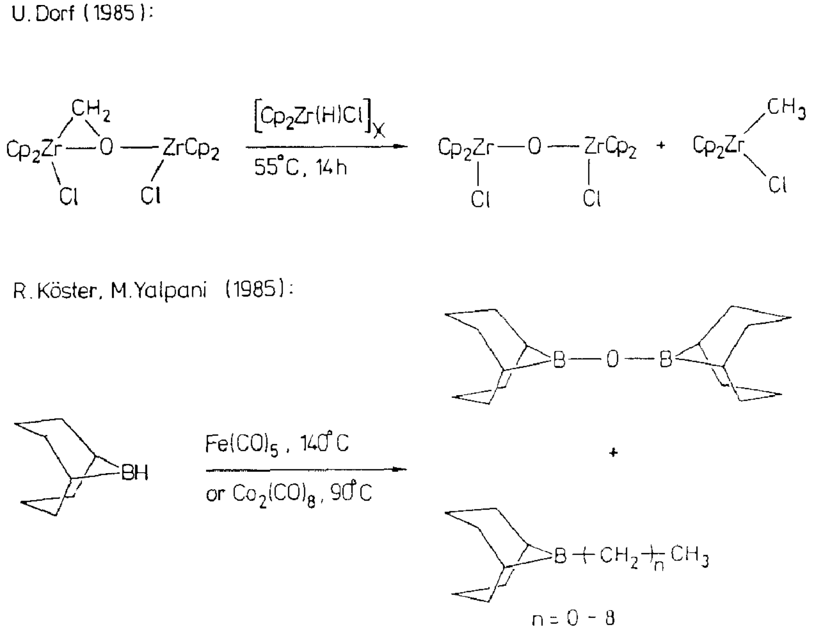
† averaged

Fig. 4. Molecular geometry of $[(\eta^2\text{-}CH_2O)ZrCp_2]_2$ (**21**).

Cyclodimeric (η^2-formaldehyde)zirconocene (**21**) reacts with two molar equivalents of 9-borabicyclo[3.3.1]nonane by B–H insertion into the metallaoxirane Zr–C bonds.The $\overline{\text{ZrOCH}_2\text{[B]H}}$ containing dimer **25** was identified by an X-ray crystal structure analysis.

Complex **25** can be regarded as a model of an intermediate stage of the process leading to insertion of the metallaoxirane CH_2 group into the B–H bond of the 9-BBN reagent. It is well known that CO-derived metallaoxirane CH_2 groups can be inserted into transition metal–hydrogen bonds to yield metallocene bonded σ-methyl ligands [16]. Analogous three-membered $\text{[B]}\overline{\text{OCH}_2\text{[B]}}$ type compounds may poten-

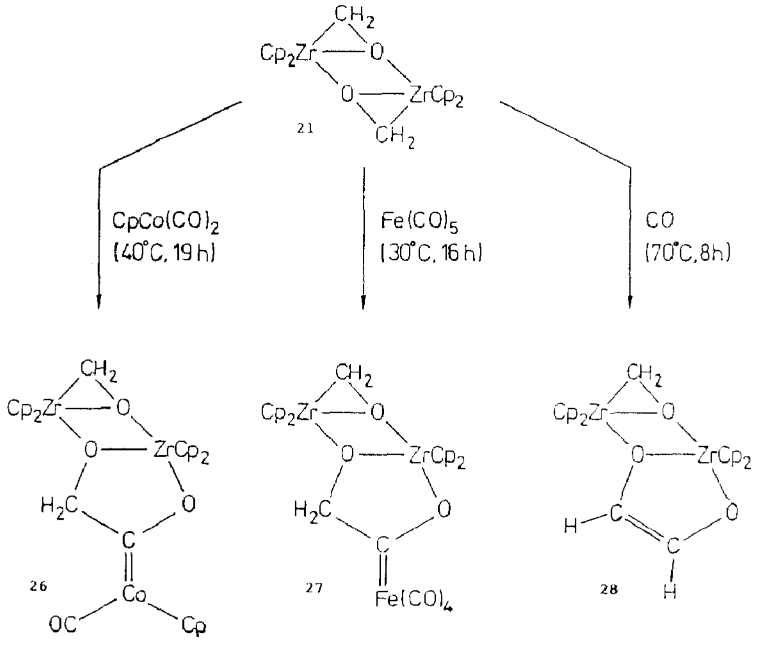




Scheme 1. Two selected examples of importance to the development of homogeneous Fischer–Tropsch type processes.

tially serve as reactive intermediates in reductive CO coupling reactions employing the 9-BBN reagent (see Scheme 1) [17].

The complex $[(\eta^2\text{-}CH_2O)ZrCp_2]_2$ can be carbonylated further. At ambient pressure only one equivalent of carbon monoxide per cyclodimer is adsorbed to



selectively convert one metallaoxirane unit into a metal bound endiolate ligand. The resulting product **28** is also formed if **21** is treated with $Fe(CO)_5$. In this case the metal carbene complex **27** is formed in addition to **28**. The zirconoxycarbene moiety of **27** is formed by formally inserting an Fe-bound carbonyl ligand into the Zr–C bond of a $Cp_2\overline{Zr{-}O{-}C}H_2$ moiety. The reaction of $[(\eta^2\text{-}CH_2O)ZrCp_2]_2$ (**21**) with $CpCo(CO)_2$ proceeds much cleaner. Treatment of this metal carbonyl complex with **21** at 40 °C for 19 h cleanly yields the metallaoxirane containing zirconoxycarbene complex **26**.

Conclusions

The reaction of (η^2-formaldehyde)zirconocene with metal carbonyls shown above indicate that the two topics described and discussed in this account are in fact rather closely related. The examples presented involve rather different modes of activating the carbon monoxide molecule. Metal activated carbonyl groups can be added to other unsaturated ligands forming the metaloxycarbene complexes. Reaction of CO with the early transition metal hydride ultimately leads to the reduction of CO to CH_2 groups. We are hopeful that combining such different types of CO-converting reactions may eventually open up novel ways of utilizing the carbon monoxide molecule [18].

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