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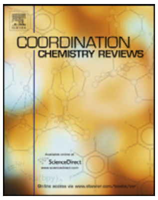

Review

η^5,η^1-Coordinated cyclopentadienyl transition metal complexes featuring σ-metal–carbon *ansa* bridges

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Dedicated to Prof. Fausto Calderazzo on the occasion of his 80th birthday.

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ABSTRACT

An overview of η^5,η^1-coordinated transition metal *ansa* complexes is given. These compounds bear one or more coordinated cyclopentadienyl moieties connected with a η^1-bridging σ-bonded carbon chain featuring a length of at least two carbon atoms. Synthetic approaches, as well as characterisation and applications are described.

1. Introduction

This review gives an overview on the synthetic pathways and spectroscopic data of transition metal *ansa* complexes featuring η^5-bonded cyclopentadienyl ring connected via a σ-bonded carbon bridge to the metal centre. The prospective use of these compounds in industrially relevant chemical processes will require access to tailored catalysts. *Ansa* bridged compounds, in general, have attracted considerable attention in the last decades due to their versatility in catalytic reactions. In these compounds, a cyclopentadienyl fragment containing a chain-like substituent coordinates to a metal or another ligand, forming a handle-like bridging structure in the process (hence the name "*ansa*", from latin: handle). This class of compounds can be divided into two subclasses (Scheme 1).

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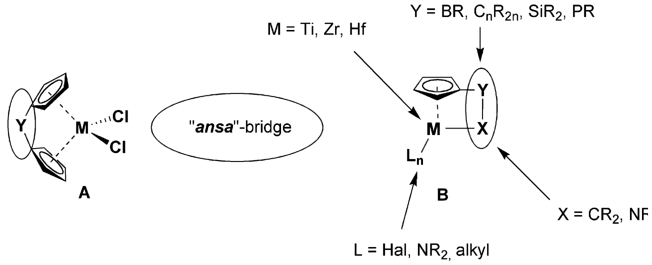


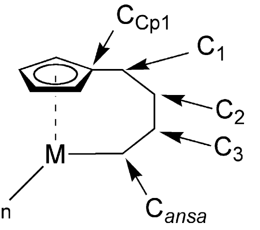
Scheme 1. General structure of *ansa* compounds.

The majority of *ansa* compounds – the *ansa* metallocenes – features two π-coordinated aromatic ligands such as Cp that are linked via an *ansa* bridge (**A**). On the other hand, there is a second class where the *ansa* bridge tethers the metal and one π-coordinated ligand via a metal–ligand σ-bond (**B**).

Fine examples for the well-known *ansa* metallocene class of compounds are the so-called "constrained geometry catalysts" (CGC) of group IV transition metals, which have been widely applied in olefin polymerisation reactions and achieved an unparallelled importance in the field. On an industrial scale, these catalysts play a significant role in the industrial polymerisation of olefins to polyethylene, polypropylene or polystyrene, which amounted to ca. 130 million tons per year in 2006, comprising 60% of the worldwide plastic production [1]. A plethora of CGC catalysts is available by variation of the metal centre, the use of different cyclopentadienyl substituents (H, CH_3, indenyl, fluorenyl, etc.), donor substituents (X) and cyclopentadienyl-*ansa* linkage (Y) (Scheme 1) [2,3]. In general, CGC exhibit electronic and steric properties intermediate between those of *ansa* metallocenes **B** and non-bridged half-sandwich catalysts [3].

In recent years, the π,σ-coordinated *ansa* compounds of class **B** gained attraction not only for polymerisation catalysis, but also found application in the catalytic epoxidation of olefins. The industrial scale of epoxide production ranges from millions of tons per year (ethylene and propylene oxides) to a few grams per year for fine chemicals [4]. Among a huge variety of catalysts, group VI elements in high oxidation states are able to catalyse the oxidation of a variety of compounds. Although ethylene and propylene oxide are the industrially most significant compounds, there is also a need for highly stereo- and enantioselective catalysts for the fabrication of more complex epoxides, which are often used as intermediates for the synthesis of fine chemicals, pharmaceuticals and aroma and flavour molecules [5–8]. Besides the well-known and highly active *Sharpless*- and *Jacobsen*-type catalysts, methyltrioxorhenium (MTO), as well as several other Re(VII), Mo(VI), and V(III) compounds have been found to catalyse olefin epoxidation, sometimes with high to very high enantiomeric excesses (*ee*) [9–17].

Many catalyst systems based on Mo and W have been extensively studied and applied in asymmetric epoxidation catalysis, but were found to give only moderate *ee* values [18–24]. These systems can be improved by performing the catalytic experiments at lower temperatures, yet leading to a significant loss of activity in all cases [25,26]. In recent years, $CpM(CO)_3R$ compounds (M = Mo, W, R = halide, alkyl) have been thoroughly examined in epoxidation catalysis. Amongst these, *ansa*-type complexes, which had first been described by Eilbracht et al. [94] in the late 1970s, have attracted attention due to their potential applications in the field of asymmetric catalysis [27–34]. Recently, our efforts in the search for a broadly applicable epoxidation catalyst have led us to examine several cyclopentadienyl derivatives of Mo and W, which show promising performances in the field of catalytic epoxidation [35–43]. These compounds offer many ways for varying the catalyst structure, such as a fine-tuning of the electronic situation at the metal centre or the introduction of bulky chiral-inducing groups by modifying the Cp moiety or the *ansa* bridge. Additionally, the *ansa* functionality offers extra possibilities of heterogenisation in greater distance from the metal, thus minimising the impact of the anchor on the electronic environment of the catalytic centre.



Scheme 2. Denotation of the *ansa* handle.

2. Scope and limitations

This review focuses on transition metal *ansa* complexes bearing at least one η^5-coordinated cyclopentadienyl moiety, ligated by an alkyl chain of at least two carbon atoms length. This alkyl chain is also η^1-σ-coordinated to the metal centre. Despite that this type of compounds has been partially reviewed for η^1-coordinated heteroatomic *ansa* bridges [2a,b,e,44], even including only the most recent compounds would expand the article out of proportions. Therefore, this article is restricted to transition metal complexes bearing exclusively carbon atoms in the *ansa* bridge. However, heteroatomic substituents at the *ansa* bridge will be dealt with. This article also excludes bimetallic complexes where a second metal is inserted between the η^5-CpM moiety and the η^1-*ansa* bridge. We also only chose compounds with the *ansa* bridge being at least two carbon atoms, since a single carbon atom in the bridge often leads to complexes with a η^6-fulvene-type ligand instead of a η^5,η^1-coordinated *ansa* ligand where the η^1-coordinated *ansa* bridge is purely σ-bound to the metal centre [45]. The *ansa* compounds are categorised in sections according to the corresponding transition metal subgroups and the synthetic routes are used as additional structuring element in each section.

Since the approach to this topic is mostly synthetic, the focus is set on reaction pathways, yields and analytics, however, applications are summarised as well, where available. The comparison of a large quantity of compounds requires a uniform notation and the article will use Scheme 2: starting from the cyclopentadienyl moiety, the ring carbon bearing the *ansa* bridge is denoted C_{Cp1}. The first *ansa* bridge carbon attached to C_{Cp1} is denoted C_1 and those following (for bridge lengths greater than two carbon atoms) are denoted C_2 and C_3. The carbon attached to the metal is denoted C_{ansa}.

All analytical data are summarised in a table at the end of each section (see Tables 1, 3, 4, 6–9). For X-ray analyses, bond lengths for M–C_{ansa} are given, as well as the average M–C_{Cp} and M–$Cp_{centroid}$ ($Cp_{centroid}$ is defined as the geometric centre of the Cp pentagon) distances (if available). Also, to enable a comparison of the ring strain induced in the complexes by the *ansa* bridge, the M–C_{Cp1} distance and/or the $Cp_{centroid}$–M–C_{ansa} angle is given. Also, the analytics part contains ^1H and ^{13}C NMR data for C_{ansa}, as well as ^{31}P NMR and IR data for phosphorus-containing ligands or carbonyls. However, most of the earlier publications do not include ^{13}C NMR spectroscopy.

3. Group IV: Ti, Zr, Hf

In 1991, Erker et al. synthesised the *ansa* metallocenes **1a** and **1c** (Scheme 3) via thermolysis of $(Me_3C\text{–}Cp)CpTiPh_2$ and $(Me_3C\text{–}Cp)_2TiPh_2$ in order to use these new complexes in propene

Table 1
Analytical data for group IV *ansa* compounds.

Compound	Cit.	Selected bond lengths and angles				^{1}H NMR C$_{ansa}$ (ppm)	^{13}C NMR C$_{ansa}$ (ppm)
		M–C$_{ansa}$ (Å)	M–Cp$_{centroid}$ M–Cp$_{average}$[a] (Å)	M–C$_{Cp1}$ (Å)	∢ Cp–M–C$_{ansa}$		
1a	[46]	–	–	–	–	−1.94 −0.08	57.6
1b	[46]	–	–	–	–	−2.25 0.06	57.6
1c	[48]	–	–	–	–	−3.0 0.52	29.96
2	[49]	2.19 2.18	[a]	[a]	[a]	−3.09 −3 −0.04 −0.34	63.48 72.70
3a	[49]	2.208	2.44	[a]	[a]	1.98–2.03	78.4
3b	[49]	2.215	2.437	[a]	[a]	1.55–1.61	86.2
4a	[50]	–	–	–	–	−2.60 −0.02	46.8
4b	[50]	–	–	–	–	−2.57 −0.52	45.3
4c	[50]	–	–	–	–	−2.57 −0.30	[b]
5a	[50]	–	–	–	–	11.92	312.0
5b	[50]	–	–	–	–	2.19	80.2 217.8
5c	[50]	–	–	–	–	–	305.7
5d	[50]	–	–	–	–	–	95.3 245.6
5e	[50]	–	–	–	–	−1.28	75.8 206.2
6	[50]	–	–	–	–	−3.05 −0.38	47.9
7a	[51]	2.209	2.369	–	105	–	103.81 101.45
7b	[51]	2.179	2.341	–	105.7	–	102.71
7c	[52]	[b]	[b]	–	[b]	–	103.6 102.1
7d	[52]	2.189	2.349	–	107	–	103.5 92.4
7e	[52]	[b]	[b]	–	[b]	–	102.2 90.9
8	[51]	2.196	2.391	–	150.4	–	101.32
9a	[51]	2.343	2.510	–	100.3	–	104.11 100.73
9b	[53]	2.359	2.515	–	–	–	106.89 106.84 98.42 94.52
10a	[51]	2.326	2.521	–	101.6	–	102.43 99.23
10b	[51]	2.361	2.538	–	100.6	–	–
11a	[52]	[b]	[b]	–	[b]	–	102.6
11b	[52]	2.259	2.370	–	104	–	101.4
11c	[52]	2.241	2.392	–	105.4	–	–
11d	[52]	2.751	2.360	–	104	–	103.3 100.8
12a	[56]	2.328	2.067	–	–	–	128.2
12b	[56]	2.389	2.193	–	–	–	113.3
12c	[56]	2.364	2.183	–	–	–	113.6
13a	[57]	–	–	–	–	–	103.0 101.7
13b	[57]	–	–	–	–	104.6	102.8
13c	[57]	2.224	2.369	–	105.9	–	103.2
14	[57]	2.233	2.414	–	106	–	93
15	[57]	2.172	2.346	–	105.7	–	102.4 100.2
16	[57]	[b]	[b]	[b]	[b]	[b]	[b]
17	[57]	2.156	2.338	–	104.8	–	106.9 103.8
18a	[58]	2.173	2.024	–	105.9	–	–
18b	[58]	2.199	2.207	–	105.3	–	–
18c	[58]	[b]	[b]	[b]	[b]	–	[b]
18d	[58]	[b]	[b]	[b]	[b]	[b]	[b]
18e	[58]	[b]	[b]	[b]	[b]	[b]	[b]
19a	[58]	2.285	2.285	–	103.2	–	–
19c	[58]	2.394	2.394	[b]	100.6	–	[b]

Table 1 (*Continued*)

Compound	Cit.	Selected bond lengths and angles				^{1}H NMR C$_{ansa}$ (ppm)	^{13}C NMR C$_{ansa}$ (ppm)
		M–C$_{ansa}$ (Å)	M–Cp$_{centroid}$ M–Cp$_{average}$[a] (Å)	M–C$_{Cp1}$ (Å)	∢ Cp–M–C$_{ansa}$		
19d	[58]	[b]	[b]	[b]	[b]	[b]	[b]
19e	[58]	2.425	2.428	–	100.1	–	–
20	[59]	2.183	2.013	–	103.56	1.44	80.30
21	[60]	2.173	2.0577	–	104.99	[b]	[b]
22	[61]	[b]	[b]	[b]	[b]	−0.54 −2.09	37.8
23	[61]	[b]	[b]	[b]	[b]	−0.15 0.75	13.0
24a	[62]	–	–	–	–	–	199.7
24b	[62]	–	–	–	–	–	215.8
25a	[62]	–	–	–	–	–	201.7
25b	[62]	–	–	–	–	–	200.6
26a	[65]	–	–	–	–	–	171.1 180.8
26b	[65]	–	–	–	–	–	–
27a	[65]	–	–	–	–	–	–
27b	[68]	2.342	2.172	–	–	0.30 −1.22	[b]
28a	[66]	–	–	–	–	−0.05	5.4
28b	[66]	–	–	–	–	−0.11	7.6
29	[67]	–	–	–	–	–	163.0
30	[70]	–	–	–	–	0.71	74.9–126.2
31	[70]	–	–	–	–	0.07 −2.17	64.9–27.2
32	[70]	2.3002.294	2.529 2.517	–	[b]	[b]	[b]
33a	[71]	–	–	–	–	–	191.1
33b	[71]	–	–	–	–	–	184.1
33c	[71]	–	–	–	–	–	187.4
34a	[72]	–	–	–	–	–	185.8
34b	[72]	–	–	–	–	–	188.4
34c	[72]	–	–	–	–	–	184.2
34d	[72]	–	–	–	–	–	189.7
34e	[72]	–	–	–	–	–	186.0
34f	[72]	–	–	–	–	–	183.9
35a	[72]	–	–	–	–	–	184.8
35b	[72]	–	–	–	–	–	–
35c	[72]	–	–	–	–	–	184.4
36a	[72]	–	–	–	–	–	186.0
36b	[72]	–	–	–	–	–	188.9
36c	[72]	–	–	–	–	–	186.1
36d	[72]	–	–	–	–	–	186.8
36e	[72]	–	–	–	–	–	180.8
36f	[72]	–	–	–	–	–	–
36g	[72]	–	–	–	–	–	183.2
37	[74]	–	–	–	–	2.43 −1.36	61.2
38a	[74]	–	–	–	–	1.91–3.05	59.5
38b	[74]	–	–	–	–	0.86–2.2	52.5
38c	[74]	–	–	–	–	0.82–2.05	42.5 60.9
39a	[74]	–	–	–	–	0.02 −0.42	54.6 54.0
39b	[74]	–	–	–	–	0.00 0.78–1.57	67.7 26.9–48.0
39c	[74]	–	–	–	–	0.16 0.73–1.82	60.9 26.0–46.6
39d	[74]	–	–	–	–	0.61 −0.13 0.78–1.83	52.7 50.5–67.5
40	[73]	–	–	–	–	–	181.8
41	[80]	–	–	–	–	[b]	[b]
42	[75]	–	–	–	–	−0.27 −0.09	56.8–60.3
43	[75]	–	–	–	–	0.51 0.70	53.4–52.0
44	[75]	–	–	–	–	0.01	52.2–56.9
45	[75]	–	–	–	–	0.25	64.0–125.0
46	[75]	–	–	–	–	−0.11	97.4–184.4
47a	[76]	–	–	–	–	0.06 0.76–1.49	23.5–48.9 68.2–124.8
47b	[76]	–	–	–	–	0.25 0.72–2.02	26.5–43.5 67.3–125.6

Table 1 (*Continued*)

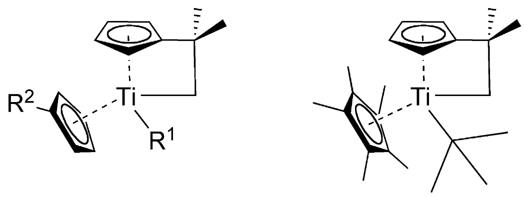
Compound	Cit.	Selected bond lengths and angles				^{1}H NMR C$_{ansa}$ (ppm)	^{13}C NMR C$_{ansa}$ (ppm)
		M–C$_{ansa}$ (Å)	M–Cp$_{centroid}$ M–Cp$_{average}$[a] (Å)	M–C$_{Cp1}$ (Å)	∢ Cp–M–C$_{ansa}$		
47c	[76]	–	–	–	–	−0.06 0.54 0.71–1.88	23.8–51.4 106.1–124.9
48a	[76]	–	–	–	–	0.25 0.98	26.6–115.2 127.1–178.3
48b	[76]	–	–	–	–	0.38 0.82–1.01	125.3–185.4
49a	[76]	–	–	–	–	0.25 0.98	26.6–115.2 127.1–178.3
49b	[76]	–	–	–	–	0.38 0.82–1.01	125.3–185.4
50a	[76]	–	–	–	–	0.11	44.7–125.3 127.4–178.3
50b	[76]	–	–	–	–	0.21 0.77–1.08	123.1–185.9
51a	[76]	–	–	–	–	0.11	44.7–125.3 127.4–178.3
51b	[76]	–	–	–	–	0.21 0.77–1.08	123.1–185.9
51c	[76]	–	–	–	–	0.18 0.88	34.4–57.0 144.5–177.3
51d	[76]	–	–	–	–	0.17 0.31	22.8–57.0 124.7–183.9
52	[76]	–	–	–	–	0.01 0.87–1.56	23.3–48.9 37.1–124.8
53	[76]	–	–	–	–	−1.44 0.83–0.96	66.0 183.4
54	[77]	–	–	–	–	–	186.9
55a	[77]	–	–	–	–	–	186.5
55b	[77]	–	–	–	–	–	[b]
55c	[77]	–	–	–	–	–	186.0
55d	[77]	–	–	–	–	–	185.9
55e	[77]	–	–	–	–	–	183.4
55f	[77]	–	–	–	–	–	185.9
56	[81]	2.254	2.532	–	–	–	150.2/131.1
57a	[78]	–	–	–	–	–	186.1
57b	[78]	–	–	–	–	–	189.3
57c	[82]	–	–	–	–	–	[b]

[a] Inconclusive crystallographic data due to racemic crystallization.

[b] No values available.

polymerisation catalysis [46]. Through elimination of benzene, an intramolecular C–H activation takes place and the C2 *ansa* bridge is formed [47]. After 2 h at 80 °C the thermolysis is quantitative. Other groups also reported the formation of C2 bridges by thermolysis using titanium and zirconium precursors (**1b, 1d**) [48].

Another way to introduce *ansa* bridges is the reductive coupling of double bonds to the metal centre [49]. This reaction can be divided into two parts. First, the titanocene dichloride precursor undergoes a reductive elimination by loss of the chloride atoms, followed by an oxidative addition of the double bonds to the metal centre to form complexes **2** and **3a**,**b** (Scheme 4); therefore the titanocene dichloride precursors were treated with magnesium in THF leading to yields of about 85%.



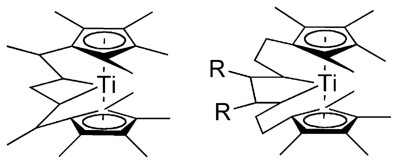
1a R^1 = Ph, R^2 = H
1b R^1 = Ph, R^2 = CMe$_3$
1c R^1 = CH$_2$Ph, R^2 = H

1d

Scheme 3. Ti and Zr *ansa* compounds obtained via thermolysis of (Me$_3$C–Cp)CpMPh$_2$ and (Me$_3$C–Cp)$_2$. MPh$_2$.

Van der Heijden and Hessen slightly changed the reaction conditions as they did not use pure magnesium but bis(neopentyl)magnesium in diethyl ether as reducing agent. They obtained the *ansa* complexes **4a–c** in up to 85% yield. **4a** was reacted with PMe$_3$ to give a “tucked-in” alkylidene complex **5a** in 30% yield, as well as a (bis)*ansa* compounds **6** (Scheme 5) [50]. The reactivity of complex **5** towards unsaturated organic compounds was also examined (Scheme 6).

In order to increase the Lewis acidity of the metal centre, Wang et al. introduced carboranes as a new type of *ansa* bridge [51]. Metal amide M(NR$_2$)$_4$ precursors were reacted with the new carborane ligands under amine elimination to obtain the complexes **7a**, **8**, **9a** and **10** with yields between 68% and 86% (Scheme 7). Further



2

3a R = H
3b R = CH$_3$

Scheme 4. Bis(*ansa*) compounds obtained via reductive coupling.

Table 2
Application of group IV *ansa* compounds in olefin polymerisation.

Compound	Cit.	Substrate	Al/metal (molar ratio)	T (°C)	Activity [a][g(polyme)/g(metal) h bar] [b][g(polyme)/mmol(metal) h bar (atm)] [c][g(polyme)/g(metal) h]
1a[1,3,5,13]	[46]	Propylene	1/122	−20	390[a]
1a[1,3,5,13]	[46]	Propylene	1/97	−40	260[a]
1c[1,3,5,13]	[46]	Propylene	1/190	−20	350[a]
1c[1,3,5,13]	[46]	Propylene	1/260	−40	40[a]
33a[1,3,6,14]	[71]	Ethylene	2500/1	60	1203[b]
33b[1,3,6,14]	[71]	Ethylene	2500/1	60	2006[b]
33c[1,3,6,14]	[71]	Ethylene	2500/1	60	3374[b]
30[2,3,6,14]	[72]	Ethylene	×	60	1900000[c]
36a[2,3,7,14]	[72,85]	Ethylene	3000/1	60	790400[c]
36b[2,3,7,14]	[72,85]	Ethylene	3000/1	60	1810700[c]
36a[2,3,8,14]	[72,85]	Ethylene	1000/1	60	95000[c]
36b[2,3,8,14]	[72,85]	Ethylene	1000/1	60	42000[c]
36a[2,3,9,14]	[72,85]	Ethylene	x	60	272000[c]
36b[2,3,9,14]	[72,85]	Ethylene	x	60	296000[c]
36c[2,3,7,14]	[72]	Ethylene	3000/1	60	1231600[c]
36d[2,3,7,14]	[72]	Ethylene	3000/1	60	1040000[c]
36e[2,3,7,14]	[72]	Ethylene	3000/1	60	1413700[c]
36f[2,3,7,14]	[72]	Ethylene	3000/1	60	ca. 1400000[c]
34a[2,3,7,14]	[72]	Ethylene	3000/1	60	2850000[c]
34b[2,3,7,14]	[72]	Ethylene	3000/1	60	2460000[c]
34b[2,3,7,14]	[72]	Ethylene	3000/1	60	1325000[c]
34f[2,3,7,14]	[72]	Ethylene	3000/1	60	1007000[c]
35c[2,3,7,14]	[72]	Ethylene	3000/1	60	2222900[c]
37[2,3,7,14]	[72]	Ethylene	3000/1	60	41700[b]
38a[2,3,7,14]	[72]	Ethylene	3000/1	60	105300[b]
38b[2,3,7,14]	[72]	Ethylene	3000/1	60	123800[b]
38c[2,3,7,14]	[72]	Ethylene	3000/1	60	59900[b]
39a[2,3,7,14]	[74]	Ethylene	3000/1	60	35800[b]
39b[2,3,7,14]	[74]	Ethylene	3000/1	60	68100[b]
39c[2,3,7,14]	[74]	Ethylene	3000/1	60	327300[b]
39d[2,3,7,14]	[74]	Ethylene	3000/1	60	163900[b]
40[2,3,7,14]	[73]	Ethylene	3000/1	60	310000[c]
40[3,7,13]	[73]	Propylene	3000/1	60	39400[c]
42[2,3,7,14]	[75]	Ethylene	3000/1	60	2640000[c]
43[2,3,7,14]	[75]	Ethylene	3000/1	60	1420000[c]
54[2,3,14]	[77]	Ethylene	3000/1	60	31600[c]
55a[2,3,14]	[77]	Ethylene	3000/1	60	553000[c]
55b[2,3,14]	[77]	Ethylene	3000/1	60	308000[c]
55c[2,3,14]	[77]	Ethylene	3000/1	60	1280000[c]
55d[2,3,14]	[77]	Ethylene	3000/1	60	267000[c]
55e[2,3,14]	[77]	Ethylene	3000/1	60	1330000[c]
55f[2,3,14]	[77]	Ethylene	3000/1	60	1157600[c]
Dimer of **8**[1,4,10,15]	[51]	Ethylene	1500/1	60	2730[b]
Dimer of **8**[1,4,10,15]	[51]	Ethylene	1500/1	60	3340[b]
12a[1,4,11,16]	[56]	Ethylene	1500/1	30	0.0000012[b]
12a[1,4,11,16]	[56]	Ethylene	1500/1	50	0.00000053[b]
12a[1,4,11,16]	[56]	Ethylene	1500/1	70	0.00000093[b]
12b[1,4,11,16]	[56]	Ethylene	1500/1	50	0.0000043[b]
12b[1,4,11,16]	[56]	Ethylene	1500/1	70	0.000005[b]
12b[1,4,11,16]	[56]	Ethylene	1500/1	90	0.0000053[b]
56[1,3,12,15]	[81]	Ethylene	1000/1	r.t.	40[b]

Reaction conditions: data obtained after 1 h reaction time; [1]toluene, [2]pentane; cocat. = [3]MAO, [4]MMAO; [5]m(Ti) = 0.025–0.050 g; [6]m(cat.) = 1–5 mg, [7]m(cat.) = 0.2–1.5 mg for homogeneous catalysis; [8]0.4–0.5 g for heterogeneous catalysis (as polymer); [9]0.15 g for heterogeneous catalysis (PHT); [10]n(cat.) = 3.0 μmol; [11]c(cat.) = 2.158 nM; [12]n(cat.) = 0.05 μmol; [13]propylene condensed into solution, educt pressure; [14]10 bar; [15]1 atm; [16]1 bar.

Table 3
Analytical data for group V *ansa* compounds.

Compound	Cit.	Selected bond lengths and angles					^{1}H NMR	^{13}C NMR
		M-C$_{ansa}$ (Å)	M–Cp$_{centroid}$	M–Cp$_{average}$[a] (Å)	M–C$_{Cp1}$ (Å)	∢ Cp–Fe–C$_{ans}$	C$_{ansa}$ (ppm)	C$_{ansa}$ (ppm)
58	[86]	2.312	2.223	2.522	[b]	98.4	4.50	62.6
59a	[87]	2.291	[b]		[b]	102.5	[a]	[a]
59b	[87]	–	–		–	–	[a]	[a]
60	[89]	–	–		–	–	–	178.3
61	[91]	–	–		–	–	[a]	[a]
62	[90]	–	–		–	–	–	173.9
63	[92]	2.326	[b]		[b]	[b]	−0.29	40.8
64	[93]	–	–		–	–	–	165.8

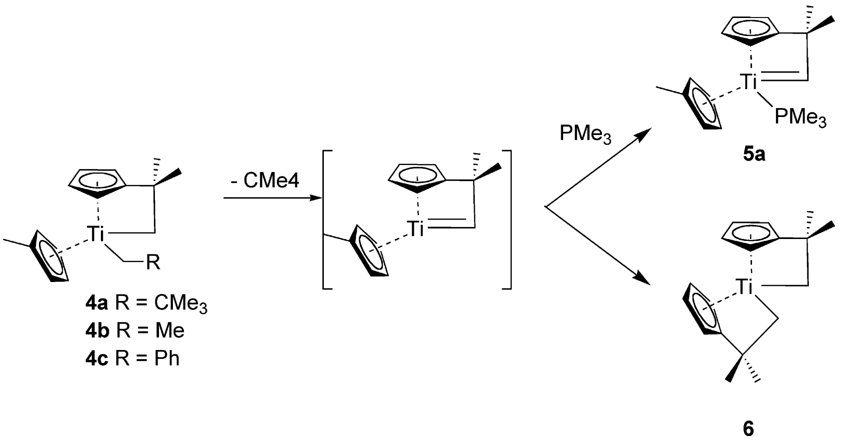
[a] No values given for r.t. NMR due to η^{1}-η5 shift.

[b] Value not given.

Table 4
Analytical data for Mo and W *ansa* compounds.

Compound	Cit.	Selected bond lengths and angles					^{1}H NMR	^{13}C NMR	IR
		M–C_{ansa} (Å)	M–$Cp_{centroid}$	M–$Cp_{average}$ (Å)	M–C_{Cp1} (Å)	∢ Cp–Fe–C_{ansa}	H–C_{ansa} (ppm)	C_{ansa} (ppm)	ν(CO) (cm^{-1})
65a	[94,104]	–	–		–	–	−0.58	−49.7	2012, 1920
65b	[94,104]	2.36	2.311		2.29	[b]	−0.25	−61.7	2008, 1910
66a	[94]	–	–		–	–	1.7	4.8	2000, 1895
66b	[95,102]	2.337	2.011	2.346	2.356	109.2	1.2	−7.4	2005, 1915
67	[100]	–	–		–	–	2.32	[a]	2005, 1910
68	[100]	–	–		–	–	–	[a]	2015, 1915
69a	[101]	–	–		–	–	−0.92	−35.8	2005, 1940, 1912
69b	[101]	–	–		–	–	−0.74	[a]	2008–1894
70a	[101]	–	–		–	–	0.17	−32.2	[a]
70b	[101]	–	–		–	–	0.2–0.4	[a]	2008–1894
73	[103]	–	–		–	–	−0.43	[a]	2006, 1962, 1892
74	[103]	–	–		–	–	–	[a]	2010, 1930, 1900
75a	[106]	2.347	1.974	2.313	2.287	92.68	−0.11 0.50	−36.41	2003 1903
75b	[106]	–	–		–	–	−0.07	−17.48	1999, 1902
76a	[107]	–	–		–	–	0.40	−25.9	[a]
76b	[107]	–	–		–	–	0.46	−38.2	[a]
77a(syn:anti)	[108,109]	–	–		–	–	0.83: 0.25 0:0	[a]	1975, 1918 + sh
78a	[108,109]	–	–		–	–	0.75 −0.75	[a]	1935
77a (W)	[109,110]	–	–		–	–	0.01 0.20	[a]	1989, 1978, 1911, 1906
78a (W)	[109,110]	2.287	1.974	2.299	2.317	90.8	−0.18 −0.94	[a]	1926
80	[111]	2.313	2.297		2.296	[b]	[a]	[a]	[a]
81a	[112,113]	2.273 2.268	2.28	2.281	2.295 2.292	[b]	−0.37 −1.42	[a]	–
81b	[115]	–	–		–	–	9.96 11.42	[a]	–
81b$^+$$PF_6^-$	[116]	–	–		–	–	[c]	[c]	–
82	[114]	–	–		–	–	−0.25 −0.8	[a]	–
83a	[115]	–	–		–	–	−0.8 −0.9	[a]	–
84	[115]	–	–		–	–	−0.7 −0.8	[a]	–
85	[112]	–	–		–	–	0.6 1.1	[a]	–
86a	[117]	–	–		–	–	0.6	[a]	2022, 1957, 1930
86b	[117]	–	–		–	–	0.06–0.42	[a]	2015, 1943, 1927
87b	[117]	–	–		–	–	[a]	[a]	2014, 1919, 1896
88	[118]	2.405	2.355		2.423	[b]	4.22	[a]	2014, 1940, 1934
89a	[119]	2.20	1.99	2.32	2.35	104.6	–	116.5	2028, 1956, 1941
89b	[119]	–	–		–	–	–	115.6	2024, 1940, 1934
90a	[119,123]	–	–		–	–	–	116.1	2027, 2019, 1952, 1945
90b	[119,123]	2.29	1.99	2.328	2.362	115.2	–	116.1	2025, 1942, 1936
92b	[124]	–	–		–	–	2.79	55.5	–
94a	[126]	2.210	1.991	2.339	[b]	[b]	–	156.9	2049, 2032, 1964, 1937
94b	[126]	–	–		–	–	–	151.8	2048, 2043, 1967, 1944
94c	[126]	–	–		–	–	–	[a]	2032, 2008, 1935, 1910
95a	[127]	–	–		–	–	−0.41, −0.89	[a]	–
96a	[127]	–	–		–	–	–	[b]	[b]
97 (R-/S-)	[127]	2.271/2.273	1.944/1.950	2.289/2.289	2.293/2.304	92.13/91.31	−3.21	−39.3	1991
72	[101]	–	–		–	–	–	[a]	2035, 1960, 1938
71	[101]	–	–		–	–	–	[a]	2035, 1960, 1938

[a] Analytical data not available.
[b] Value not given.
[c] Paramagnetic compound.



Scheme 5. *Ansa* compounds obtained by van der Heijden.

Table 5
Mo and W *ansa* compounds in epoxidation catalysis.

Compound	Cit.	Substrate	Yield[b] (%)	TOF (h^{-1})	Yield[c] (%)	TOF (h^{-1})
65a	[128]	Cyclooctene	–		92[e]	250
65a	[128]	Styrene	–		50[f]	–
65a	[128]	1-Octene	–		45[f]	–
66a	[43]	Cyclooctene	–		quant.	660
75a	[106]	Cyclooctene	–		55	–
75a	[106]	*trans*-β-Methylstyrene	20[e]	*ee* N/A	66[e]	15% ee
75b	[106]	Cyclooctene	–		65	–
75b	[106]	*trans*-β-Methylstyrene	–		50[e]	7% ee
76a	[107]	Cyclooctene	quant.	750	–	
76a[d]	[107]	Cyclooctene	30	3650	–	
76a	[107]	cis-Stilbene	35[e]	140	–	
76a	[107]	1-Octene	45[e]	40	–	
65b	[128]	Cyclooctene	–		10[e]	25
66b	[43]	Cyclooctene	–		45	200
76b	[107]	Cyclooctene	15	160	–	

[a] Reaction conditions: DCM, Cat:substrate:oxidant(TBHP) = 1:100:200.

[b] At r.t. after 90 min.

[c] At 55 °C (Mo)/90 °C (W) after 90 min.

[d] Cat:substrate:oxidant(TBHP) = 1:1000:2000.

[e] After 4 h.

[f] After 24 h.

Table 6
Analytical data for Re *ansa* compounds.

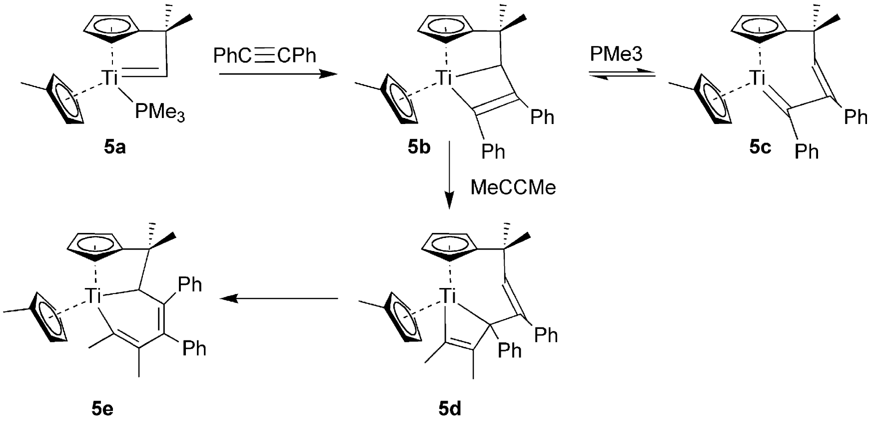
Compound	Cit.	Selected bond lengths and angles				^{1}H NMR	^{13}C NMR	IR
		M–C$_{ansa}$ (Å)	M–Cp$_{centroid}$M–Cp$_{average}$[a] (Å)	M–C$_{Cp1}$ (Å)	∢ Cp–Fe–C$_{ansa}$	C$_{ansa}$ (ppm)	C$_{ansa}$ (ppm)	ν(CO) (cm^{-1})
99	[132]	–	–	–	–	–	–	1898, 1819, 1515
100	[132]	–	–	–	–	–	234.3	2020, 1951, 1925, 1624
102	[132]	–	–	–	–	–	230.9	
103	[131]	–	–	–	–	–	[a]	1902 1822 1505
105	[132]	–	–	–	–	–	13.3	1863 1786
106a	[132]	2.329	2.294	2.320	103.6	3.84	27.0	2027 1928
106b	[132]	–	–	–	–	4.25	30.6	2026 1931

[a] Analytical data not available.

treatment with Me_3SiCl leads to substitution of an amide ligand by a chloride moiety (**7b**). Complex **10a** reacts with ammonium salts to chlorine-bridged dimers.

The chloride complex **7b** was used as the starting compound for several ligand exchange reactions leading to complexes **7c**–**7e** [52]. The reaction of **7b** and **7e** with a variety of nitriles gave the compounds **11a**–**d**. Due to their relative binding strength, **11a**–**d** were exclusively formed by inserting the nitrile solely into the Ti–C bond and not into the Ti–N bond.

In the next step, compound **9a** was used as a precursor to be treated first with Me_3SiCl and then $Li_2C_2B_{10}H_{10}$ to give **9b** in 60% yield after two days [53]. Other reactivity tests were carried out with **7a**. The compound was treated with alkynes under irradiation to form dimers linked by unsaturated carbon chains [54]. Moreover, a large variety of isocyanides and cyanides were reacted with **7a**. The cyanides insert into the M–C$_{ansa}$ bond to give complexes with *N*-heteroatomic *ansa* bridges [55]. To improve the catalytic behaviour of these carborane *ansa* complexes, the steric and electronic environment was changed by introducing an additional Cp* ligand forming new group IV complexes (**12a**–**c**) [56]. Subsequently, Wang et al. created carborane *ansa* complexes starting from the dilithium salt of the carborane Cp moiety. After addition of Ti(=NR)$Cl_2(Py)_3$ (R = alkyl, aryl) to the corresponding ligands in toluene the *ansa* complexes **13a–c** were formed in up to 70% yield. An indenyl analogue **14** was prepared in a similar way with a yield of 42%. **13a** was used as a precursor for several ligand exchange reac-



Scheme 6. Reactivity of **5a** towards unsaturated organic molecules.

Table 7
Analytical data for Fe *ansa* compounds.

Compound	Cit.	Selected bond lengths and angles				^{1}H NMR	^{13}C NMR	IR
		M–C$_{ansa}$ (Å)	M–Cp$_{centroid}$ M–Cp$_{average}$[a] (Å)	M–C$_{Cp1}$ [Å]	∢ Cp–Fe–C$_{ansa}$	C$_{ansa}$ (ppm)	C$_{ansa}$ (ppm)	ν(CO) (cm^{-1})
107a	[136]	2.096	2.114	2.120	[b]	1.00 1.09	[a]	2039, 2007, 1970, 1957
107b	[133,137]	2.15	2.12	2.11	130[d]	–	–	2036, 2024, 1992, 1981, 1970, 1951, 1932
108	[137]	2.111	2.12	2.178	[b]			
109a	[138]	–	–	–	–	–	[a]	
109b	[138]	–	–	–	–	–	[a]	2020, 1985–1965, 1640
110	[138]	1.960	2.098	2.068	[b]	–	[a]	2032, 2005, 1985–1965, 1630
111	[139]	–	–	–	–	–	[a]	2060, 1990, 1635
114	[94]	–	–	–	–	1.1	[a]	1990, 1935
112a	[94,140]	–	–	–	–	–	[a]	2000, 1960, 1940, 1915, 1640,1620
112b	[139]	–	–	–	–	–	–	2020,1955,1643
112c	[139]	–	–	–	–	–	–	2010, 1960, 1950, 1920, 1680, 1635
112d	[103]	–	–	–	–	–	[a]	2020, 1970, 1942, 1630
112e	[103]	–	–	–	–	–	[a]	2020, 1955, 1670, 1630
112f	[103]	–	–	–	–	–	[a]	2015, 1955, 1630
113b	[139]	–	–	–	–	−0.65 0.15	[a]	[a]
113c	[139]	–	–	–	–	0.64	−28.4	2001, 1944
113d	[103]	–	–	–	–	−0,18	[a]	[a]
113f	[103]	–	–	–	–	–	[a]	1988, 1925
117a	[103]	–	–	–	–	0.84	[a]	1990, 1930
117b	[103]	–	–	–	–	0.22	[a]	[a]
116a	[103]	–	–	–	–	–	[a]	2013, 1953, 1635
116b	[103]	–	–	–	–	–	[a]	[a]
115	[139]	–	–	–	–	–	[a]	2030,2010,1990, 1968, 1962, 1943, 1922, 1918, 1640, 1592
118	[141]	–	–	–	–	−0.35	[c]	1985, 1923
119	[141]	1.956	2.110	2.129	118.2	–	50.21	2005, 1955, 1640
120	[141]	–	–	–	–	0.8	5	1990, 1930
121a	[143]	–	–	–	–	–	233.8	2020, 1990, 1630
121b	[143]	1.977	2.098	2.042	[b]	–	233.8	2018, 1990, 1630
121c	[143]	–	–	–	–	–	233.7	2020, 1990, 1622
121d	[143]	–	–	–	–	–	232.7	2020, 1970, 1622
122a	[143]	–	–	–	–	–	238.0	2040, 1980, 1620
122b	[143]	–	–	–	–	–	237.5	2040, 1980, 1620
122c	[143]	–	–	–	–	–	237.8	2020, 1980, 1610
122d	[143]	–	–	–	–	–	237.9	2020, 1985, 1620
122e	[143]	–	–	–	–	–	237.7	2020, 1980, 1620
123	[144]	1.96	1.764 2.136	2.073	[b]	–	[c]	2011, 1952, 1638
124	[145,146]	2.201	1.717	[b]	120.1	4.02	117.4	–
126b	[147]	–	–	–	–	2.47	[a]	2020, 1965, 1670
126c	[147]	–	–	–	–	2.53	[a]	2020, 1965, 1670
126a	[147]	2.070	2.100	2.097	–	2.56	[a]	2030, 1980, 1685

[a] Analytical data not available.
[b] Values not given.
[c] Not observed.
[d] Approximate value, calculated geometrically.

tions, replacing the imido ligand by sulfur, oxygen or *N*-heterocyclic ligands (**15**–**17**) [57].

Recently, similar reactions were performed with the diamido complex **7a**. The amido ligands were replaced by MeNH(CH$_2$)$_n$NHMe (n = 2, 3) to form additional metallacycles **18a–e** [58]. Starting from **18**, macrocycles such as **19** and various dimers were prepared (Scheme 8).

A few years after the first carborane *ansa* complexes, the synthesis of an *ansa* titanocene bearing two *ansa* bridges at the same Cp ring was reported [59]. Compound **20** was prepared by reduction of [TiCl$_2${(η^5-C$_5$Me$_4$(CH$_2$CMe = CH$_2$)}$_2$] with magnesium in THF. The reduction of the precursor results in an unstable π-coordination between the metal centre and one of the double bonds of the isobutene ligand. This transition state brings a vicinal methyl group of the Cp ring close to the metal centre, inducing hydrogen abstraction by the metal. In a follow-up step, the coordinated double bond inserts into the newly created Ti–H bond to form **20** (Scheme 9).

One of the longest carbon *ansa* bridges was generated by serendipity. In 2006, Mach et al. reacted [TiCl$_2$(η^5-C$_5$H$_5$)$_2$] with an excess of magnesium and but-2-yne to give **21**. The reaction was carried out in THF at 60 °C for 3 h to give a yield of 67% [60].

Zwitterionic zirconocene *ansa* complexes (Scheme 10) were developed by van der Heijden et al. As precursor for this zwitterionic complex, **22** was used, which was formed by thermolysis of Cp(t-BuC$_5$H$_4$)ZrNp$_2$ in benzene at 80 °C over 16 h. Treating this complex with B(C$_6$F$_5$)$_3$ led to compound **23** [61].

Later, zwitterionic titanocene complexes **24** were created in 2002 by Deckers and Hessen similar to zirconocene zwitterions by treatment with B(C$_6$F$_5$)$_3$ in pentane with a yield of 66%. Additional experiments with non-zwitterionic precursors gave **25a** and **25b** [62].

As early as 1978, Schrock et al. assumed an intramolecular C–H activation after reduction of dichloro zirconocenes with Na/Hg [63]. In 1987, Marks and co-workers synthesised *ansa* zirconocenes by thermal elimination of one ligand, leading to C–H activation [64]. One of the first group IV *ansa* bis-cyclopentadienyl complexes with a σ-M–C *ansa* bridge was prepared by Erker and co-workers in 1986 (Scheme 11). The compounds were obtained employing two

Table 8
Analytical data for Ru *ansa* compounds.

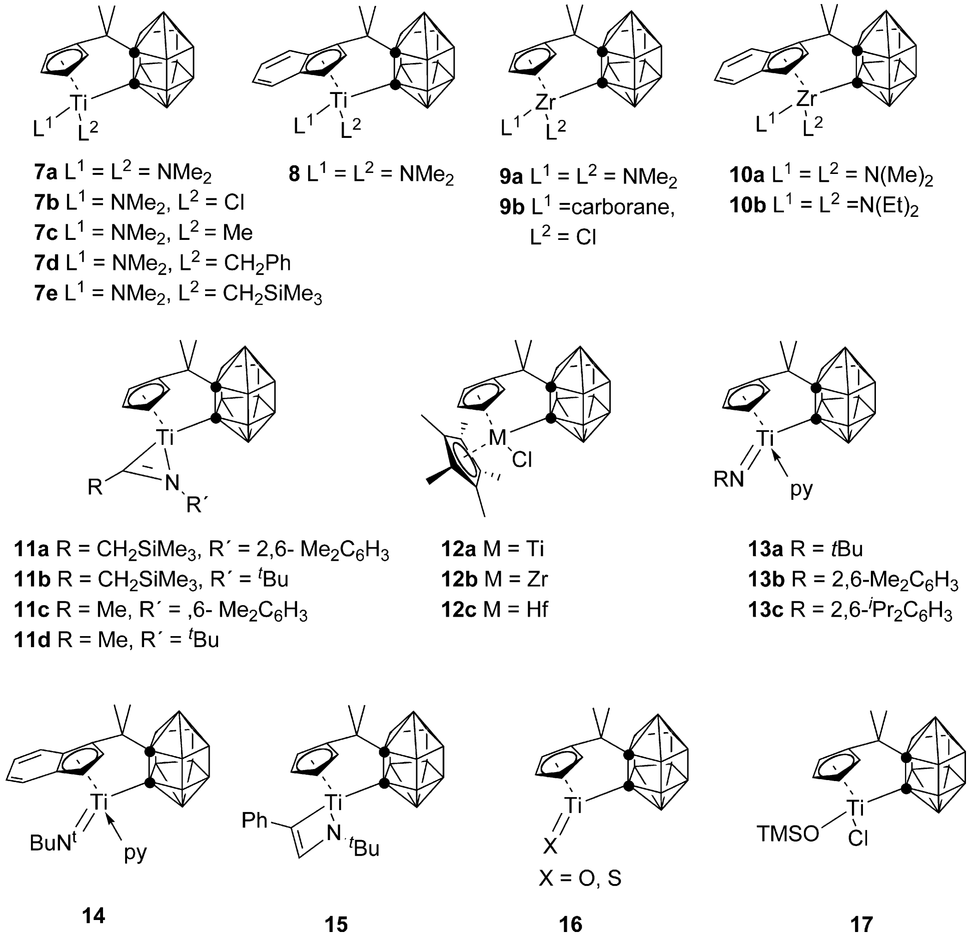
Compound	Cit.	Selected bond lengths and angles				^{1}H NMR	^{13}C NMR	^{31}P NMR	IR
		M–C$_{ansa}$ (Å)	M–Cp$_{centroid}$ M–Cp$_{average}$[a] (Å)	M–C$_{Cp1}$ (Å)	∢ Cp–Fe–C$_{ansa}$	C$_{ansa}$ (ppm)	C$_{ansa}$ (ppm)	P$_{ligand}$	ν(CO) (cm^{-1}) (ppm)
128	[148,149]	2.18	2.245	2.34	[c]	–	[a]	–	[a]
129a	[151]	–	–	–	–	4.51	37.4	–	2018, 1960
129b	[151]	–	–	–	–	4.40	34.6	–	2017, 1959
130a	[151]	–	–	–	–	–	[a]	–	2033, 2014, 1974, 1963
130b	[151]	2.076	1.892	[b]	111.5	–	129.4	–	2046, 2029, 1988, 1975
130c	[151]	2.054	1.888	[b]	[b]	–	132.5	–	2047, 2033, 1998, 1983
131a	[151]	–	–	–	–	–	109.3	–	2042, 2032, 1978
131b	[152]	–	–	–	–	–	108.6	–	2043, 2029, 1986, 1976
132a	[153]	2.061	[b]	[b]	[b]	–	114.0	–	2048, 2029, 1981, 1959, 1943
132b	[153]	–	–	–	–	–	111.7	–	1944, 1927, 1980, 1944
133	[145,146]	2.275	1.863	[b]	117.3	2.44	[a]	4.65	–
134	[145,146]	2.266	1.870	[b]	117.6	5.40	[a]	54.2	–
135	[145,146]	2.276	1.878	[b]	120.0	5.3	[a]	53.4	–
136a	[154]	2.009	[b]	[b]	[b]	–	247.7	49.13	1772
136b	[154]	–	–	–	–	–	257.6	93.69 91.32	[a]
136c	[154]	–	–	–	–	–	245.7	63.36 56.76	[a]
136d	[154]	–	–	–	–	–	254.9	96.5	[a]
137a	[158]	2.213	2.230	[b]	111.8	–	[c]	–	–
137b	[159]	2.141	2.218	[b]	114.3	–	[c]	81.03	–
137c	[159]	–	–	–	–	–	[c]	41.47	–
137e	[159]	2.144	2.211	[b]	115.0	–	[c]	13.23	–
137f	[159]	2.260	2.237	[b]	110.0	–	[c]	–	–
137g	[159]	2.142	1.882 2.230	[b]	115.0	–	[c]	148.2	–
137h	[159]	2.167	1.876 2.232	[b]	113.8	–	[c]	135.4	–
137i	[159]	2.095	2.174	[b]	117.8	–	[c]	–	–
137j	[159]	2.111	1.799 2.166	[b]	118.7	–	[c]	–	–
137k	[159]	–	–	–	–	–	[c]	–	–
137l	[159]	2.095	1.771 2.142	[b]	120.1	–	[c]	–	–
137m	[159]	2.098	1.773 2.149	[b]	120.3	–	[c]	–	–
137n	[159]	2.102	1.785 2.157	[b]	119.2	–	[c]	–	–
137o	[159]	2.217	1.798 2.171	[b]	117.2	–	[c]	–	–
137p	[159]	2.149	1.864 2.220	[b]	115.2	–	[c]	–	–
137q	[159]	2.105	1.833 2.207	[b]	116.3	–	[c]	58.1	–
137r	[159]	–	–	–	–	–	[c]	36.8	–
138	[158]	2.219	2.282	[b]	111.9	–	[c]	–	–
139	[158]	2.228	2.358	[b]	113.0	–	[c]	–	–
140	[161]	2.141 2.150	1.841 1.843 2.204 2.206	[b]	110.9 111.2	–	[c]	–	–
141	[163]	2.105	2.268	2.280	[b]	–	[c]	–	–
142	[163]	2.116 2.234	2.247 2.221	2.221 2.217	[b]	–	[c]	–	–
143a	[164]	2.131	1.863 2.271	[b]	113.6	–	[c]	–	–
143b	[164]	2.156	1.886 2.243	[b]	113.6	–	[c]	–	–
143c	[164]	–	–	–	–	–	[c]	–	–
144a	[164]	2.186	1.848 2.210	[b]	111.7	–	[c]	–	–
144b	[164]	2.179	1.862 2.226	[b]	112.2	–	[c]	–	–
144c	[164]	2.182	1.867 2.228	[b]	111.9	–	[c]	–	–

[a] Analytical data not available.
[b] Value not given.
[c] Not observed in spectrum.

Table 9
Analytical data for Ni *ansa* compounds.

Compound	Cit.	^{1}H NMR C$_{ansa}$ (ppm)	^{13}C NMR C$_{ansa}$ (ppm)	IR ν(CO) (cm^{-1})
145	[165]	–	20.9	2045, 1685
146	[100,167]	–	[a]	2040, 1675
147	[100,167]	2.24	[a]	2010
148	[167]	–	[a]	2060, 1725
148	[167]	–	[a]	2060, 1710
150	[103]	–	[a]	[a]
151	[103]	–	[a]	[a]

[a] Analytical data not available.



7a $L^1 = L^2 = NMe_2$
7b $L^1 = NMe_2$, $L^2 = Cl$
7c $L^1 = NMe_2$, $L^2 = Me$
7d $L^1 = NMe_2$, $L^2 = CH_2Ph$
7e $L^1 = NMe_2$, $L^2 = CH_2SiMe_3$

8 $L^1 = L^2 = NMe_2$

9a $L^1 = L^2 = NMe_2$
9b L^1 =carborane, $L^2 = Cl$

10a $L^1 = L^2 = N(Me)_2$
10b $L^1 = L^2 = N(Et)_2$

11a R = CH_2SiMe_3, R´ = 2,6- $Me_2C_6H_3$
11b R = CH_2SiMe_3, R´ = ^{t}Bu
11c R = Me, R´ = ,6- $Me_2C_6H_3$
11d R = Me, R´ = ^{t}Bu

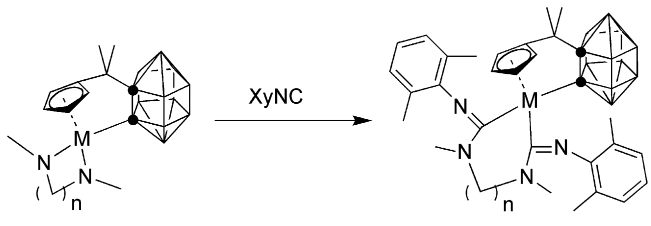
12a M = Ti
12b M = Zr
12c M = Hf

13a R = *t*Bu
13b R = 2,6-$Me_2C_6H_3$
13c R = 2,6-$^i Pr_2C_6H_3$

X = O, S

14 **15** **16** **17**

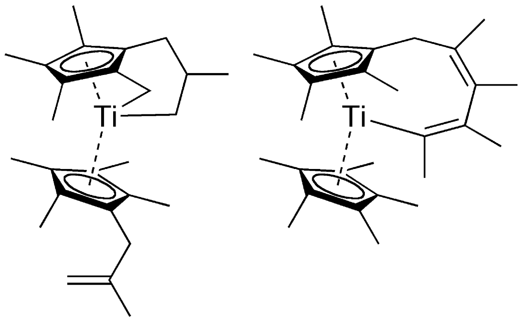
Scheme 7. Compounds with carborane *ansa* bridges.



18a M = Ti, n = 2
18b M = Ti, n = 3
18c M = Zr, n = 2
18d M = Zr, n = 3
18e M = Hf, n = 3

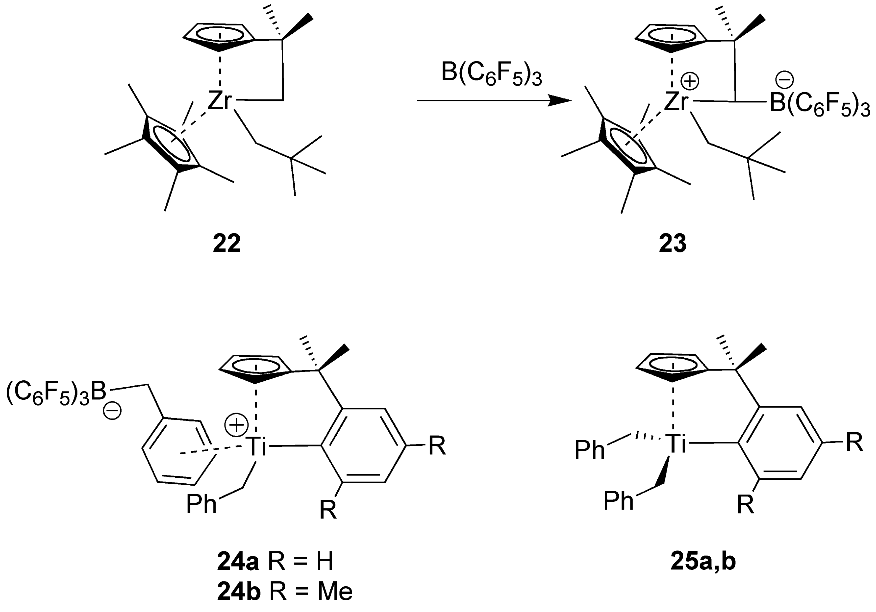
19a,c-e

Scheme 8. Carborane *ansa* compounds with macrocyclic ligands.



20 **21**

Scheme 9. Compound **20** bearing 2 *ansa* bridges and **21** bearing the to date longest *ansa* bridge.



22 **23**

24a R = H
24b R = Me

25a,b

Scheme 10. Zwitterionic *ansa* compounds and similar compounds.

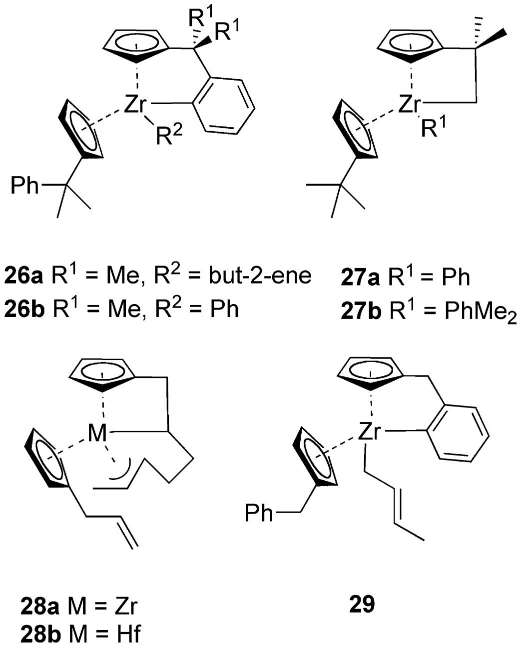
different synthetic approaches. Either the *ansa* complexes were prepared via reduction of dihalide complexes with magnesium butadiene, or alternatively, thermolysis of alkyne ligated precursors was employed as bridge building method. The complex **26a** was obtained by the Mg-reduction route in diethyl ether in 73% yield. The thermolysis products **26b** and **27a** were synthesised in yields of about 80% [65]. Following the Mg-reduction route, the complexes **28a** and **28b** were synthesised in toluene with yields of 75% and 73% [66].

Similar to **26a**, a new complex **29** was synthesised treating bis(benzyl-cyclopentadienyl)zirconium dichloride with two equivalents of vinyllithium. The reaction was carried out in THF and diethyl ether at r.t. to give a yield of 57% [67].

Legrand et al. investigated complex **27a** with respect to the reactivity of selenium insertion and the reaction with unsaturated organic molecules such as nitriles, alkynes and ketones [68]. In the following step, the focus was set on sterically hindered complexes. **27b** was obtained by methane elimination from (t-BuCp)$_2$ZrMe($C_6H_3Me_2$) after 2.5 h in refluxing benzene. This complex reacted with selenium to a bis-selenide moiety.

Pirio et al. used compounds **27a** in 2004 as starting material together with bis(alkynyl)phosphane to build metallacycles (Scheme 11). In these metallacycles Zr is part of an indenyl system, ligated with phenyl and alkynylphosphane [69].

Peifer et al. examined the self-immobilising ability of *ansa* complexes into the growing polymer chain. The heterogenisation takes place through insertion of the alkenyl ligands into the growing polymer chain. For these investigations, compounds **30** and **31** were synthesised by treating zirconocene halide precursors with LiAlH(t-BuO)$_3$ in THF in 40–70% yield (Scheme 12) [70].



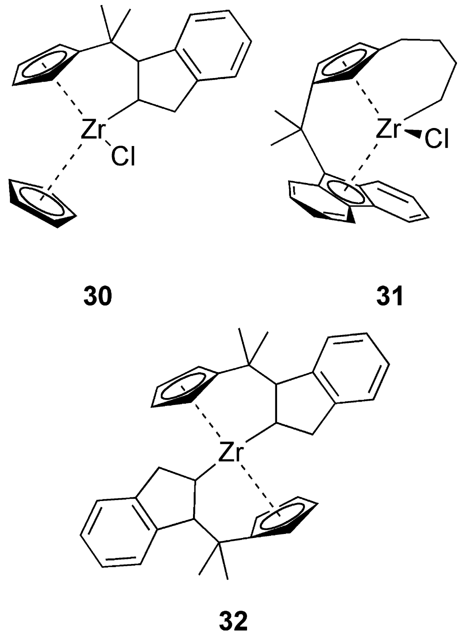
26a R^1 = Me, R^2 = but-2-ene
26b R^1 = Me, R^2 = Ph

27a R^1 = Ph
27b R^1 = PhMe$_2$

28a M = Zr
28b M = Hf

29

Scheme 11. *Ansa* compounds obtained via Mg-reduction or thermolysis.



30 **31**

32

Scheme 12. Zr *ansa* compounds by Peifer and Alt.

In an attempt to improve the catalytic performance of known metallocene catalysts, Alt et al. synthesised a variety of *ansa* compounds with a second heteroatomic *ansa* bridge (Scheme 13). Compounds **33a–c** were obtained in 90% yield by reacting titanocene dichlorides and zirconocene dichlorides with butyllithium in toluene [71]. These metallocenes bear an *ansa* bridge that includes a σ-bound phenyl ring that significantly changes the steric environment at the metal centre, leading to more stabilised, catalytically active cationic complexes (see Section 3.1).

Using zirconocene dichloride precursors bearing two indenyl ligands, Alt et al. obtained **32** through a chloride-butyl exchange induced by BuLi followed by immediate elimination of butane. A yield of up to 31% was achieved after 7 h at r.t. in hexane [70]. A large variety of zirconocene *ansa* complexes (**34–36**) was synthesised by treating dichlorozirconocene precursors with BuLi. The reactions were carried out in toluene for 6 h at r.t. in yields between 60% and 98% [72]. Complexes **37–40** were prepared in an analogous fashion in 2002 [73,74]. In 2003, Licht and Alt continued their work and synthesised **42–46** using the same procedure as before, in yields between 71% and 92% [75]. **45** and **46** appeared as coproducts in the same reaction with a ratio of 40:60 and an overall yield of 94% (Scheme 14).

Other compounds were obtained from the reaction of zirconocene dichlorides with lithium organyls other than BuLi (**47**–**53**) in yields ranging between 85% and 97% [76]. Additionally, several halide substituted complexes **54**–**55** were synthesised (Scheme 15) employing the same reaction procedure. The yields varied from 84% to 94% [77]. The reaction of Cp-substituted zirconocenedichlorides with EtLi led to **57a,b** in 75% and 85% yield, respectively [78].

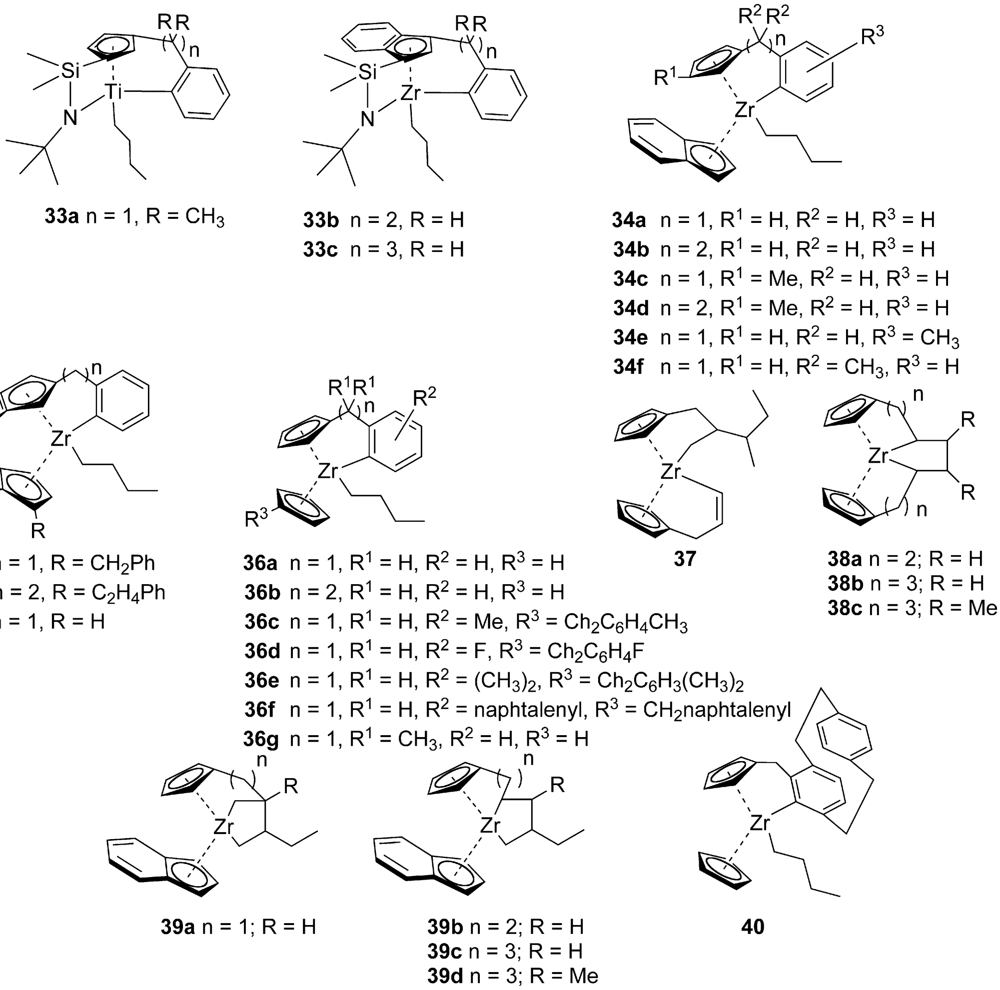
In the same year, Pool et al. synthesised **41** according to a procedure of Chirik et al. [79,80] via thermal elimination of isobutene (t-BuCp)ZrH($C_6H_3Me_2$)i-Bu in quantitative yield. In 2003, Takeuchi et al. synthesised a zirconocene *ansa* complex **56** with a ligated Rh moiety where the *ansa* bridge consisted of a η^1-coordinated indenyl. The zirconocene dichloride precursor, already bearing the Rh(cod) unit, was reacted with $AlMe_3$ under methane elimination in toluene at r.t. for 24 h and **57a,b** were obtained in 38% yield [81].

A new hafnium complex was synthesised in a similar way to other group IV metals by using a Hf chloride precursor and suitable lithium organyls (Scheme 16). **57c** was obtained in boiling toluene for 16 h in 20% yield [82].

3.1. Polymerisation catalysis with group IV complexes

Generally, the *ansa* compound has to be activated with a co-catalyst, usually methylaluminoxane (MAO) or MMAO (MAO with longer aliphatic chains). MAO tethers a halide or organic ligand as an anion, leading to a cationic metal complex (Scheme 17). This cationic complex represents the catalytically active species [83]. Other possible activators are boron compounds [61].

The well-known mechanism of polymer building with *Ziegler-Natta* catalysts is shown in Scheme 18. Ethylene coordinates to the electrophilic metal centre and subsequently inserts into the



33a n = 1, R = CH_3

33b n = 2, R = H
33c n = 3, R = H

34a n = 1, R^1 = H, R^2 = H, R^3 = H
34b n = 2, R^1 = H, R^2 = H, R^3 = H
34c n = 1, R^1 = Me, R^2 = H, R^3 = H
34d n = 2, R^1 = Me, R^2 = H, R^3 = H
34e n = 1, R^1 = H, R^2 = H, R^3 = CH_3
34f n = 1, R^1 = H, R^2 = CH_3, R^3 = H

35a n = 1, R = CH_2Ph
35b n = 2, R = C_2H_4Ph
35c n = 1, R = H

36a n = 1, R^1 = H, R^2 = H, R^3 = H
36b n = 2, R^1 = H, R^2 = H, R^3 = H
36c n = 1, R^1 = H, R^2 = Me, R^3 = $Ch_2C_6H_4CH_3$
36d n = 1, R^1 = H, R^2 = F, R^3 = $Ch_2C_6H_4F$
36e n = 1, R^1 = H, R^2 = $(CH_3)_2$, R^3 = $Ch_2C_6H_3(CH_3)_2$
36f n = 1, R^1 = H, R^2 = naphtalenyl, R^3 = CH_2naphtalenyl
36g n = 1, R^1 = CH_3, R^2 = H, R^3 = H

37

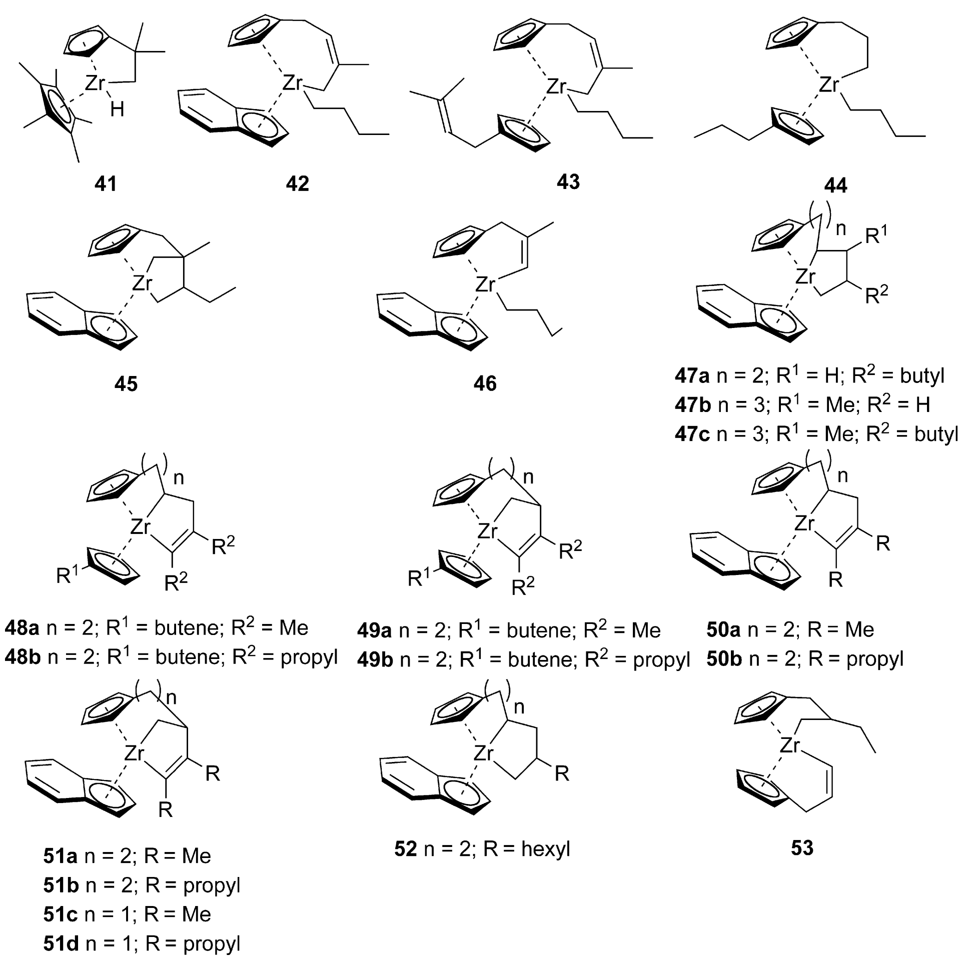
38a n = 2; R = H
38b n = 3; R = H
38c n = 3; R = Me

39a n = 1; R = H

39b n = 2; R = H
39c n = 3; R = H
39d n = 3; R = Me

40

Scheme 13. *Ansa* compounds by Alt et al., part one.



41 **42** **43** **44**

45 **46**

47a n = 2; R^1 = H; R^2 = butyl
47b n = 3; R^1 = Me; R^2 = H
47c n = 3; R^1 = Me; R^2 = butyl

48a n = 2; R^1 = butene; R^2 = Me
48b n = 2; R^1 = butene; R^2 = propyl

49a n = 2; R^1 = butene; R^2 = Me
49b n = 2; R^1 = butene; R^2 = propyl

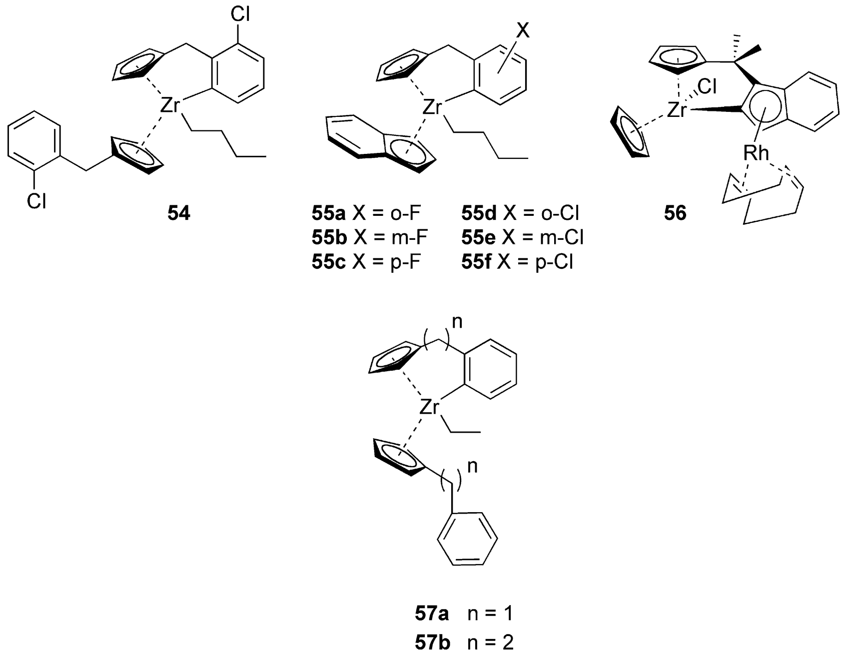
50a n = 2; R = Me
50b n = 2; R = propyl

51a n = 2; R = Me
51b n = 2; R = propyl
51c n = 1; R = Me
51d n = 1; R = propyl

52 n = 2; R = hexyl

53

Scheme 14. *Ansa* compounds by Alt et al., part two.



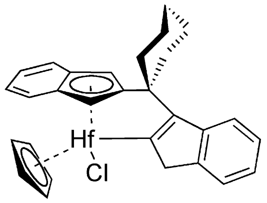
54

55a X = o-F
55b X = m-F
55c X = p-F
55d X = o-Cl
55e X = m-Cl
55f X = p-Cl

56

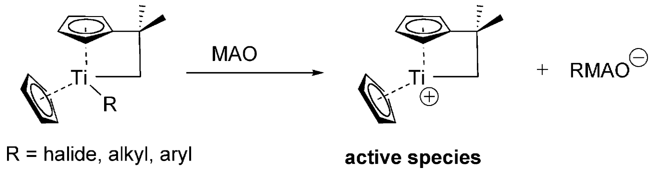
57a n = 1
57b n = 2

Scheme 15. Halide and Cp-substituted *ansa* compounds.



57c

Scheme 16. Hf *ansa* compound **57c**.



Scheme 17. Catalytically active species for olefin polymerisation.

M–C bond. Repeating this step leads to polymers. Termination of the reaction is reached by reduction of the metal centre or just by stopping olefin addition [84].

For industrial purposes, homogenous catalysis is not as useful as heterogeneous catalysis, because of complicated separation procedures of the reaction mixture and worse recyclability. A special way of heterogenisation, a form of self-immobilisation by connecting the complex into the polymer chain, was introduced by Licht and Alt. The catalytically active complex is tethered to the polymer as shown in Scheme 19. The obtained polymer can be isolated and reused in catalysis [85].

The data of the catalyses are summarised in Table 2. Polymerisation experiments with *Ziegler* type catalysts containing **1a**,**c** showed that these *ansa* metallocenes are less active than their unbridged analogues [46]. Alt et al. tested their compounds in ethylene and propylene polymerisation [70–78]. **36a** and **36b** were also tested as heterogeneous catalysts. For this purpose these compounds were immobilised by polymerisation and the complex was activated by a supported co-catalyst, partially hydrolysed trimethylaluminium (PHT) [85]. Wang et al. applied their carborane complexes in ethylene polymerisation [51,56]. Complexes **22** and **23** were tested in the catalytical conversion of 1-pentene. **23** turned out to be a highly selective but quickly deactivating catalyst for the head-to-tail dimerisation of 1-pentene, whereas **22** tended to produce higher oligomers. The catalyses were carried out at 20 °C and for **22** $Ph_3C[B(C_6F_5)_4]$ was used as a cocatalyst [61].

4. Group V: Nb, Ta

The interest in *ansa* metallocenes for polymerisation catalysis led Green and co-workers to synthesise the first representatives of group V *ansa* metallocenes. **58** (Scheme 20) was obtained via reaction of $Li[Me_2C(C_5H_5)_2]$ with $Nb(\eta^5\text{-}C_5H_5)(N^tBu)Cl_2$ in THF at r.t. in 38% yield [86]. Compound **58**, obtained as a racemic mixture, has two chiral centres, one at the pseudotetrahedrally coordinated Nb atom and another at the chiral carbon of the σ-cyclopentadienyl group.

Herrmann et al. reported similar imido niobocene and tantalocene complexes **59a**,**b**, obtained by reaction of a tris(amido)imido complex of the corresponding metal with $Me_2C(C_5H_5)_2$ in refluxing toluene [87]. These complexes were thermally stable up to more than 200 °C, but highly sensitive to moisture. Further studies in solution with **59a** indicated a rapid change of the hapticity, with both cyclopentadienyl units changing between η^5- and η^1-coordination [88].

The extension of the η^1-Cp fragment to an indenyl moiety was achieved by reaction of the precursor with the corresponding ligand in refluxing toluene for 9 h to give **60** in 77% yield [89]. Further reaction of **60** with TMSCl resulted in a η^3-coordinated indenyl species. The same synthetic route led to **62**, which bears an aromatic σ-C_6H_5 *ansa* bridge [90]. This complex was obtained by refluxing the precursor in di-*n*-butylether at 160 °C for 4 d in 15% yield. The complex is reported to be extremely sensitive to air and moisture.

In order to verify the η^5-η^1 shift in **59a**, Green and co-workers synthesised a similar compound, **61**, with an *tert*-butylimido unit and a secondary amine as ligands [91]. Low-temperature NMR solution studies confirmed the shift in hapticity which had been observed by Herrmann et al.

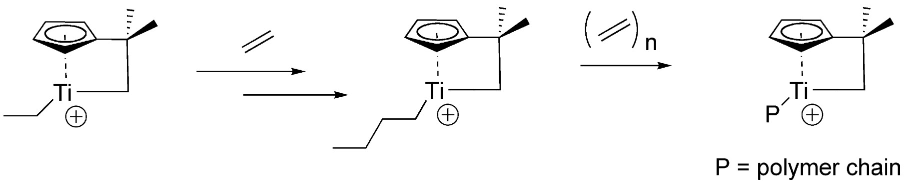
The use of early transition metal alkylidene complexes for ROMP or alkene metathesis led McCamley and co-workers to synthesise the cationic *ansa* compound **63** with a bridge length of two carbon atoms [92]. The *ansa* bridge was generated by a *tert*-butyl substituent from the $[Nb(\eta^5\text{-}C_5H_4Bu^t)_2(CH_2Ph)_2]$ precursor upon treatment with $AgBPh_4$ in THF at 0 °C.

Besides the one representative synthesised by Herrmann et al., only one more Ta *ansa* complex (**64**) is known [93]. Starting from the η^5-coordinated $[Ar\text{-}CMe_2\text{-}\eta^5\text{-}C_5H_4]TaMe_3Cl$, addition of PrMgCl in Et_2O at −50 °C and warming to r.t. produced **64** in 33% yield as a single isomer. In solution, two isomers exist in a 80:20 ratio, owing to the orientation of the methyl substituent on the coordinated propene moiety.

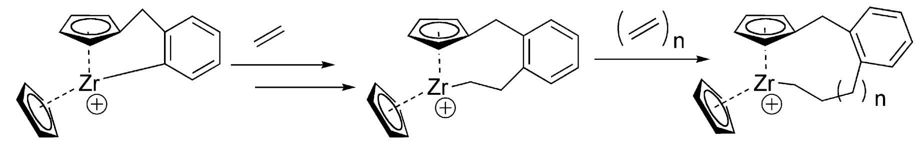
5. Group VI: Mo, W

5.1. Mo and W compounds

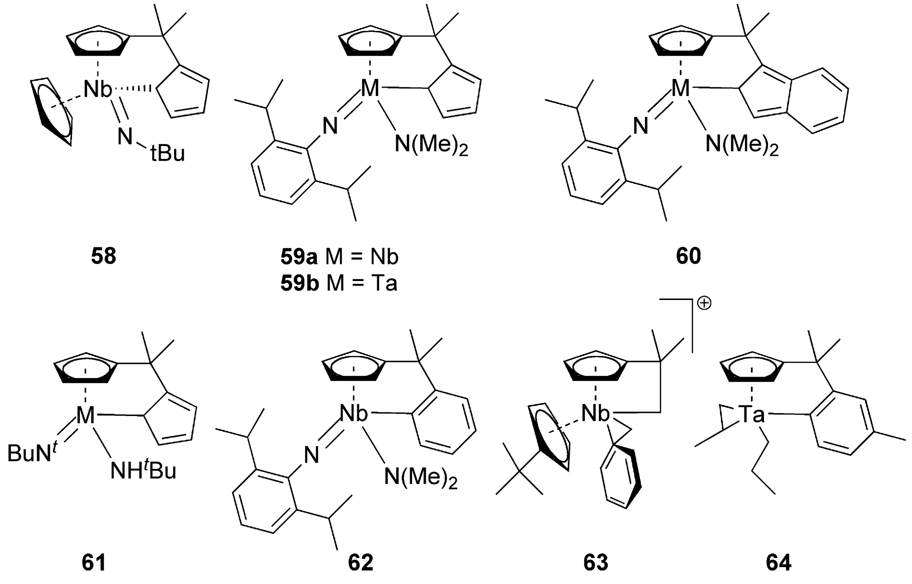
In 1976, Eilbracht published the synthesis of molybdenum *ansa* compounds featuring an *ansa* bridge length of two and four carbon atoms (Scheme 21) [94]. The metal precursor $Mo(CO)_3L_3$ ($L=CH_3CN$, thf) was reacted with spiro-annulated compounds (Scheme 21), namely spiro[4,4]hepta-1,3-diene and spiro[4,4]nona-1,3-diene, in hexane at r.t. to give the compounds **65a** and **66a** in 17% and 20% yield, respectively. The structural assessment was performed via IR, UV–Vis and ^1H NMR spectroscopy to rule out a possible alternative fulvene-like coordination [95]. The crystal structure shows a highly strained system with a short Mo–$Cp_{centroid}$ distance in comparison to other Mo cyclopentadienyl complexes [96–99] and C_{Cp}–C_1–C_{ansa} and C_1–C_{ansa}–Mo angles of 99° and 92°, respectively. Most likely, the driving force of this reaction is the formation of the η^5-cyclopentadienyl moiety by cleavage of one of the C–C bonds in the cyclopropyl moiety of the spirocycle. The metal is then inserted into the bond and a η^1-bound



Scheme 18. Polymerisation of ethylene with *Ziegler-Natta* catalysts.



Scheme 19. Self-immobilisation by ethylene insertion into the M–C_{ansa} bond.

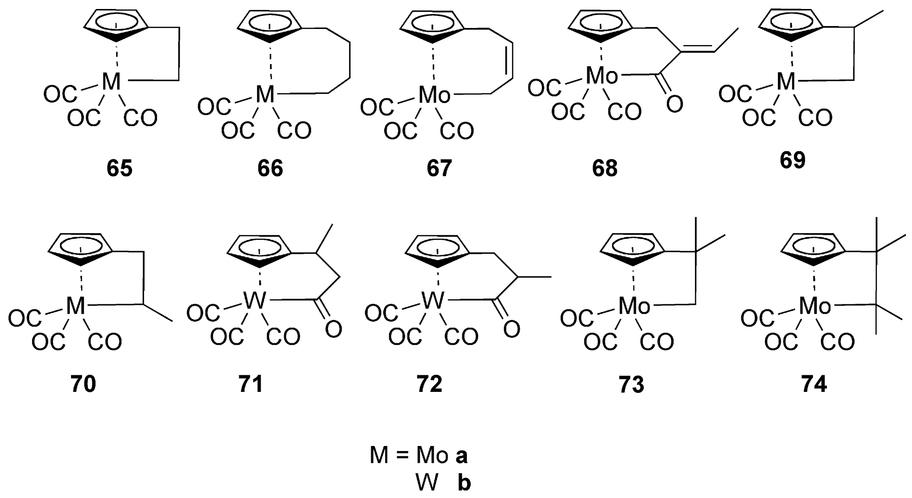


Scheme 20. Group V *ansa* compounds.

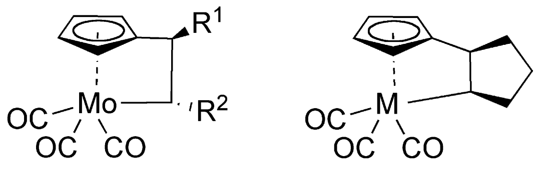
alkyl bridge is formed. Further experiments were carried out with several spirocycles substituted at the cyclopropane ring to determine the mechanism and stereoselectivity of this type of reaction. Reaction of 1-vinylspiro[2,4]hepta-4,6-diene with $Mo(CO)_3(thf)_3$ in hexane at 60 °C gave the acyl *ansa* complex **67** and the alkenyl *ansa* complex **68**. The author suggested a preferred cleavage of the higher substituted C_{Cp}–C bond of the spirocyclic cyclopropyl moiety and a complexed cyclopentadienyl-allyl system as reaction intermediate [100].

Methyl substitution of the spirocyclic 1-position and reaction of the methylated ligand with the Mo precursor in THF at r.t. resulted in two isomers **69a** and **70a** in 40% and 20% yield, respectively. In contrast to the reaction with the vinyl spirocycle, the less substituted isomer **69a** is preferably formed due to steric reasons [101]. Similar to the molybdenum compounds **65a** and **66a**, Eilbracht and co-workers synthesised the analogous tungsten compounds **65b** and **66b** in 38% and 50% yield, respectively [95,102]. Small quantities of a carbonyl-inserted acyl *ansa* complex could also be detected. Similarly, reactions with the substituted spirocycles lead to the tungsten analogues **69b** and **70b**, as well as the corresponding acyl *ansa* isomers **71** and **72** [101].

If both protons of the 1-position of the spirocycle are substituted by methyl groups, only the less substituted C–C bond of the cyclopropyl moiety is cleaved and compound **73**, with both methyl groups attached to the C_1 atom, is obtained in 79% yield. The tetramethylated derivative **74** is obtained in 61% yield under the same reaction conditions [103]. In contrast to tungsten and iron compounds, discussed later in this section and in Section 7, no formation



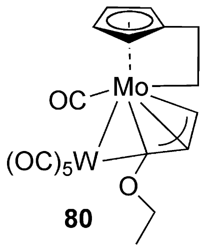
Scheme 21. Mo and W *ansa* compounds by Eilbracht et al.



75a R^1 = Ph, R^2 = H
75b R^1 = Me, R^2 = Me

76a M = Mo
76b M = W

Scheme 22. *Ansa* compounds bearing chiral bridging units.



80

Scheme 24. A heterobimetallic Mo–W-*ansa* compound **80**.

of acyl *ansa* complexes is reported for molybdenum at r.t., with the single exception of **67**, which is formed by a different reaction mechanism.

The topic was revisited in 2000 by Royo and co-workers, who used the metal precursor $\mathrm{M(CO)_3(1,3,5\text{-}C_6H_3Me_3)}$ (M = Mo, W) in the reaction with spiro[2,4]hepta-4,6-diene in THF at r.t. to obtain **65a** in 30% and **65b** in 72% yield. The authors claimed **65a** to be moisture and temperature sensitive. Also, the X-ray crystal structure of **65b** has been reported. **65b** features bond lengths of $\mathrm{W{-}C}_{ansa}$ of 2.36 Å, the $\mathrm{W{-}C_{Cp1}}$ bond length is 2.29 Å and the average $\mathrm{W{-}C_{Cp}}$ distance is 2.32 Å [104].

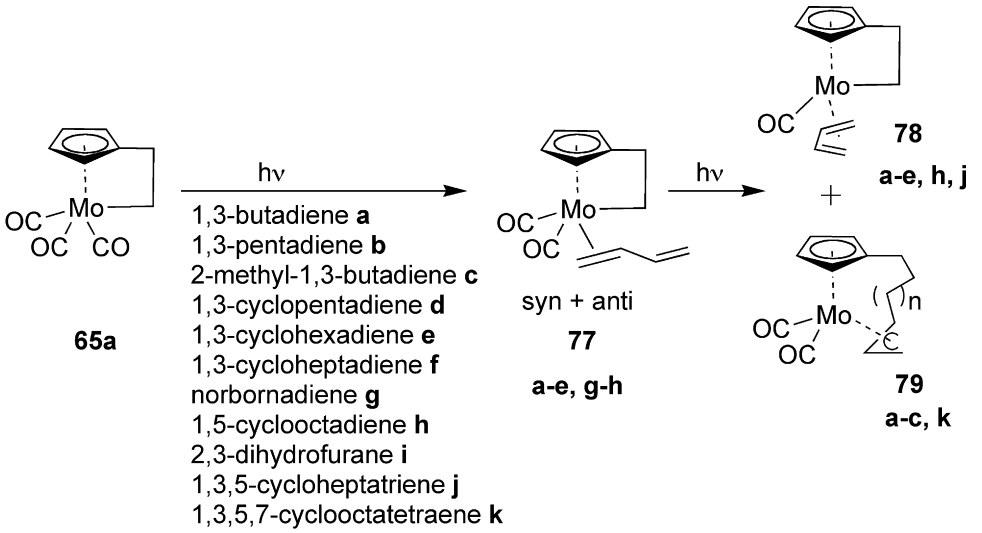
The interest in cyclopentadienyl molybdenum carbonyl compounds as precursors for asymmetric epoxidation catalysts led Kühn and co-workers to investigate several alkyl *ansa* compounds with chiral *ansa* bridges. Some success with enantioselective catalysis has been achieved using non-*ansa* cyclopentadienyl molybdenum compounds bearing a menthyl moiety as chiral-inducing agent; however, the free rotation of the menthyl-substituted cyclopentadienyl moiety along the $\mathrm{Cp_{centroid}{-}Mo}$ axis led to only moderate enantiomeric excess (*ee*). These menthyl compounds were tested in epoxidation catalysis as homogenous and heterogeneous catalysts immobilised on MCM-41 and MCM-48 [105]. To avoid this rotation, fixation of the Cp ring by an *ansa* bridge was considered. An *ansa* menthylcyclopentadienyl molybdenum compound has not been synthesised so far, but compounds **75a,b** (Scheme 22) were prepared via Eilbracht's method from the corresponding chiral spirocycles in 75% and 60% yield, respectively [106]. X-ray crystallographic analysis shows the $\mathrm{Mo{-}C}_{ansa}$ bond at 2.347 Å and the $\mathrm{Mo{-}C_{Cp}}$ distances at 2.287–2.338 Å. The $\mathrm{Mo{-}Cp_{centroid}}$ distance is 1.974 Å.

In addition, similar Mo and W compounds **76a** and **76b** have been obtained in good yields through a similar reaction procedure using *cis*-1,2-cyclopentanediol as the precursor for the corresponding *cis*-spirocycle [107].

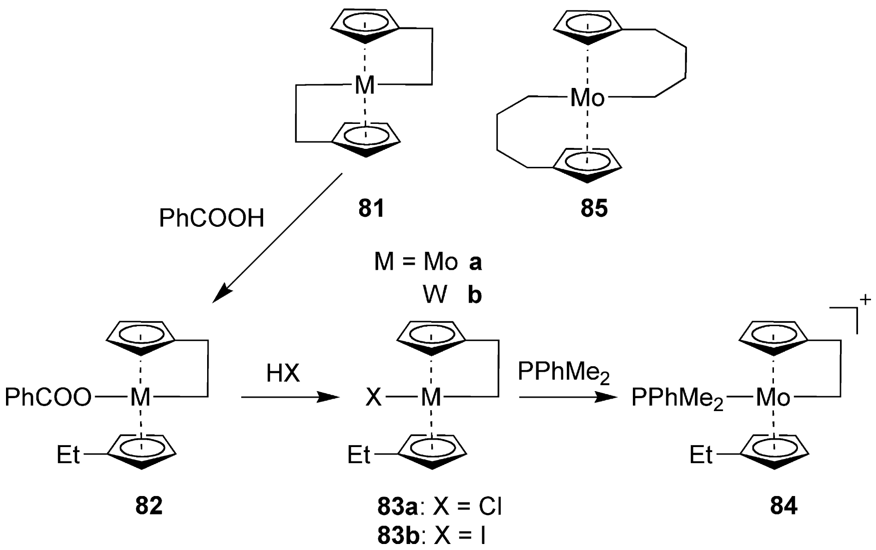
Kreiter et al. analysed the photochemistry of **65a** with a variety of dienes (Scheme 23). The reaction of **65a** with **a**–**c** under irradiation at −20 °C or −47 °C gave, in all cases, a mixture of compounds. IR and NMR monitoring of the reaction showed the formation of a dicarbonyl complex **77**, which decomposed upon further irradiation to another dicarbonyl *ansa* complex **78** and a η^3-coordinated vinylic monocarbonyl complex **79** [108].

Further studies of the photochemistry of **65a** under similar reaction conditions with the dienes **d**–**k** yielded either the *ansa* compound **77** (**d**,**e**,**g**–**h**), where one double bond of the diene is η^2-coordinated to the metal centre, or the *ansa* compound **78** (**c**,**d**,**h**,**j**), where the diene is η^4-coordinated with both double bonds. Compounds **77h** and **78h** were only observed in trace amounts, while the diene **k** reacted to the η^3-allylic insertion compound **79k** [109]. Similar reaction patterns have been observed in the W analogue of **65a** with a variety of cyclic [109] and acyclic [110] dienes. An unexpected outcome of these experiments was also the heterobimetallic compound **80** (Scheme 24) [111].

Green and co-workers obtained the first bis(*ansa*)-complex **81a** of molybdenum through co-condensation of Mo atoms with spiro[4,4]hepta-1,3-diene at −197 °C in 15–25% yield [112]. **81a** is air-sensitive and volatile, but stable up to 110 °C *in vacuo*. The compound possesses a high ring strain, as shown by the distances between $\mathrm{Cp_{centroid}{-}Mo}$ (1.93 Å) and $\mathrm{Mo{-}C}_{ansa}$ (2.271 Å and 2.286 Å) and bond angles of $\mathrm{Cp_{centroid}{-}C_{Cp}{-}C_1}$ and $-\mathrm{C}_{1'}$ (23°), respectively [113]. Treatment of **81a** with benzoic acid in THF led to cleavage of one of the $\mathrm{Mo{-}C}_{ansa}$ bonds and formation of **82a** in 79% yield, and the benzoate ligand can be exchanged with a chloride ligand through reacting **82a** with TMSCl to give **83a** in 50% yield



Scheme 23. Photochemical reactivity of **65a** towards dienes.



Scheme 25. Reactivity of the bis(*ansa*) compound **81**.

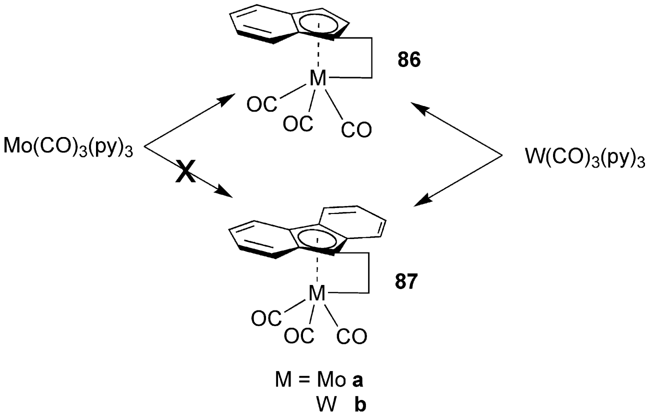
(Scheme 25). Upon addition of PMe_2Ph and NH_4PF_6, the ionic complex **84a** is formed in 70% yield [114]. A similar reactivity has been observed for the W analogue **81b** [115]. Additionally, **81b** can be oxidised by $AgPF_6$ to give $\mathbf{81b}^{+}PF_6^{-}$ [116].

Co-condensation of Mo atoms with spiro[4,4]nona-1,3-diene under similar conditions led to the bis(*ansa*) compound **85** in 12% yield [114]. **85** is only moderately moisture sensitive and highly soluble in non-polar solvents. **85** was subjected to a variety of follow-up variations, all of which led to Mo–C_{ansa} bond breaking.

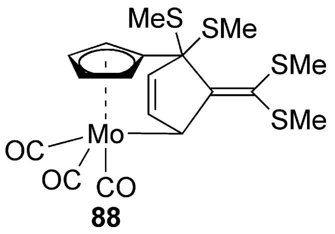
Ustynyuk et al. took the ring-expanding step from cyclopentadienyl to indenyl and fluorenyl [117]. Reaction of $M(CO)_3(py)_3$ with spirocyclopropane-1,1-indene in the presence of $BF_3{\cdot}THF$ led, for M = Mo, to the highly unstable (η^5,η^1-indenyl-C_2H_4)-alkyl *ansa* complex **86a** in 6% yield, as well as to a η^6-coordinated arene complex (Scheme 26). Spirocyclopropane-9,9-fluorene, however, was not converted to the corresponding *ansa* complex. Instead, only the η^6-arene complex was formed. For M = W, both the stable indenyl complex **86b** (15% yield) and the unstable fluorenyl complex **87b** were obtained.

In contrast to group VIII metal complexes discussed in Section 7, the reaction of aryl and alkyl substituted fulvenes with $Mo(CO)_3L_3$ (L = CH_3CN) does not lead to *ansa* compounds with a η^1-coordinated cyclopentadiene as a bridge unit. Only with 6,6-bis(methylthio)fulvene, very small quantities (2% yield) of the thermally unstable compound **88** could be isolated (Scheme 27). The coordinating ligand is a dimeric bis(methylthio)-fulvene. The reaction mechanism is believed to proceed via a η^6-coordinated fulvene complex. This intermediate adds a second fulvene molecule and dimerises under formation of a C–C–σ-bond. The vacancy at the Mo is then saturated by the formation of a Mo–C–σ-bond to the second carbon in the β-position to the double bond of the ligated fulvene [118]. The X-ray crystallographic structure exhibits a Mo–C_{ansa} distance of 2.405 Å. All carbon atoms of the η^5-cyclopentadienyl moiety are within a distance of 2.30–2.37 Å from the Mo centre.

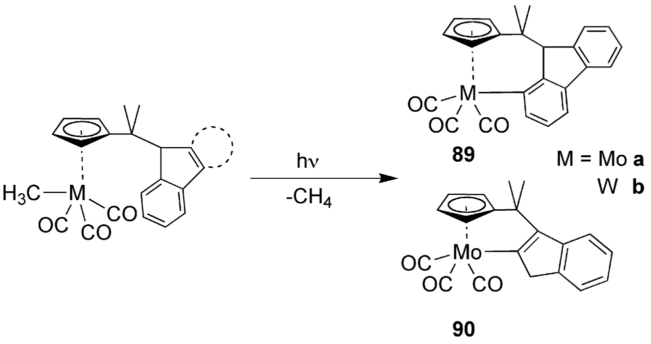
Alt et al. studied similar *ansa* compounds with η^1-coordinated fluorenyl ligands (Scheme 28). Irradiation of a THF solution of a fluorenyl-substituted cyclopentadienyl molybdenum and tungsten tricarbonyl methyl complex led to hydrogen abstraction at the C_1-position of the fluorenyl moiety and subsequent dealkylation of the methyl substituent as CH_4 [119]. The reaction also takes place if two of the carbonyl ligands are replaced by an acetylene ligand. The



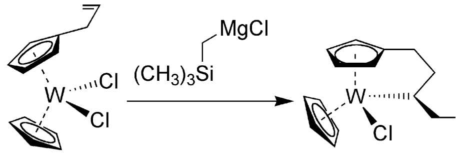
Scheme 26. Indenyl and fluorenyl *ansa* compounds by Ustynyuk et al.



Scheme 27. Compound **88** bearing a dimerised fulvene-type ligand.



Scheme 28. Mo *Ansa* compounds by Alt et al.



91 **92**

Scheme 29. Compound **92** obtained by Cooper et al.

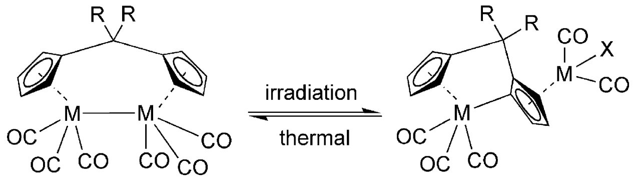
resulting compounds have been extensively studied with respect to their bonding characteristics [120,121].

The η^1-coordinated fluorenyl *ansa* compounds **89a** and **89b** have been characterised by ^{1}H and ^{13}C NMR. Similar reactions with indenyl as a substituent in a pentane solution led to olefin complexes instead of η^1-coordinated indenyl *ansa* compounds [122], but photolysis in toluene afforded both the indenyl and the fluorenyl *ansa* compounds **89** and **90** [123]. The crystal structure for **90a** shows the Mo–C$_{ansa}$ distance at 2.202 Å and the Cp-carbons are within a distance of 2.30–2.35 Å from the metal centre. The Cp$_{\text{centroid}}$–Mo–C$_{ansa}$ angle is 104.6° and the Mo–C$_{ansa}$–C$_2$ angle is 119°. For **89b**, the Mo–C$_{ansa}$ distance is 2.29 Å and the Cp-carbons are in the range of 2.30–2.36 Å from the metal centre. The Cp$_{\text{centroid}}$–Mo–C$_{ansa}$ angle is 115.2° and the Mo–C$_{ansa}$–C$_2$ angle is 122.0°.

Cooper and co-workers studied the reactivity of allyl-substituted tungstenocene dichlorides with lithium alkyls and *Grignard* reagents [124]. These nucleophilic reagents could in principle attack at different locations in the tungstenocene derivative, such as the metal centre with its chlorine ligands, the Cp rings or the allyl group.

Depending on the substituents at the allylic system and the nucleophiles, the reaction occurs mostly at the metal centre through substitution of the chlorine ligand with the nucleophile. In one case, reaction of the tungstenocene **91** with (Me_3SiCH_2)MgCl in ether/THF at r.t. for 12 h produced the alkyl *ansa* complex **92** in 68% yield (Scheme 29). The *S*,*S*-configuration of **92** was determined via ^{1}H NMR chemical shifts in the ABCD pattern of the substituted cyclopentadiene and a mechanism for the sole formation of this enantiomer was proposed.

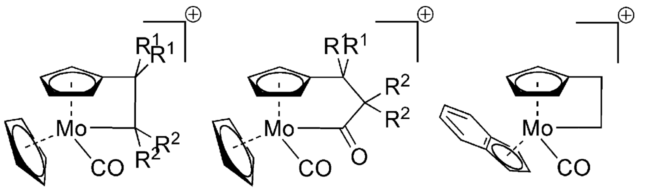
Bitterwolf et al. studied the Nujol matrix photochemistry of a η^5-Cp:η^3-Cp coordinated allylic Mo *ansa* compound at 77 K [125]. Photolysis at 500 and 360 nm, respectively, gave three distinct decomposition species, two of which were η^5-Cp:η^1-Cp coordinated species. These species are isomers, originating from the two mesomeric structures of the η^3-allyl ligand. If "free" CO is present in the matrix, a third carbonyl may be added to these species. Further irradiation experiments with the bimetallic compounds **93** gave, under sunlight irradiation in deuterated benzene/$CHCl_3$ (80:20) the bimetallic compounds **94a–c** in quantitative yields (Scheme 30). The conversion was shown to be reversible, as **94a**–**c** are converted back to **93a–c** at r.t. within 12 h. **94a** has been crystallised and the structure shows a Mo–C$_{ansa}$ distance of 2.210 Å and a Mo–Cp$_{\text{centroid}}$ distance of 1.991 Å [126].



93a M = Mo, R = H
93b M = Mo, R = Me
93c M = W, R = H

94a M = Mo, X = Cl, R = H
94b M = Mo, X = Cl, R = Me
94c M = W, X = H, R = H

Scheme 30. Irradiation behaviour of **93**.



95 **96** **97**

$R^2 = R^2 = H$ **a**
$R^1 = H, R^2 = Me$ **b**
$R^1 = Me, R^2 = H$ **c**

Scheme 31. *Ansa* compounds obtained by Romão et al.

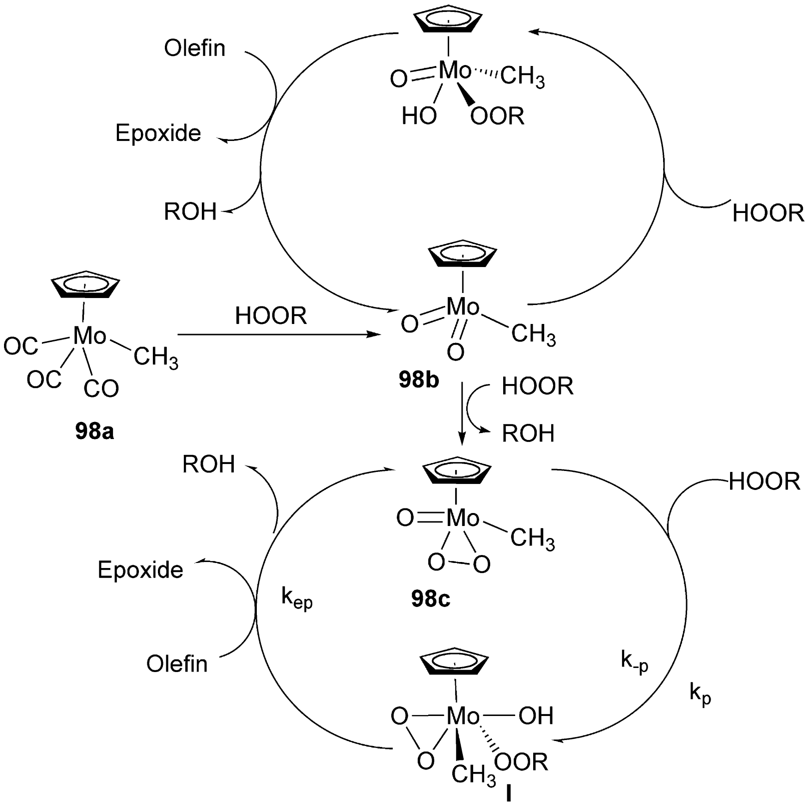
The interest in the anti-tumor activity of groups IV–VI metallocenes led Romão et al. to add a contribution to the molybdenum *ansa* family very recently (Scheme 31). In spite of minor side-products, the ionic compounds **95**, **96** and **97** were synthesised by the spirocycle method. Reaction of $CpMo(CO)_2(CH_3CN)_2$ with spiro[4,4]hepta-1,3-diene in DCM at r.t. for 16 h and subsequent precipitation with Et_2O led mainly to η^4-coordination of the diene moiety of the spirocycle. Additionally, **95a** and **96a** were detected by ^{1}H NMR in the crude reaction mixture, both in a level of 7%. Complexes **95a** and **96a** are not believed to be decomposition products of the η^4-coordinated spirocycle species, but rather to be formed by a mechanism which is yet to be determined.

Reaction with the 1,1-dimethylspiro[4,4]hepta-1,3-diene yielded two isomers of the η^4-coordinated spirocycle species with the methyl groups having either an *endo* or an *exo* conformation. Based on ^{1}H NMR studies, the *exo* isomer is believed to convert into a mixture of **95b,c** and **96b,c**. In contrast to this, the indenyl species **97** was formed quantitatively upon reaction of (indenyl)$Mo(CO)_2(CH_3CN)_2$ with spiro[4,4]hepta-1,3-diene and a crystal structure has been obtained [127].

5.2. Catalytic applications

Compounds **65**, **66**, **75** and **76** have been examined in the catalytic epoxidation of olefins [43,106,107,128] and the results (yields and TOFs, if available) are summarised in Table 5. The complexes show catalytic activity at room temperature, as well as at elevated temperatures. As expected, the Mo compounds show a greater activity than their W counterparts. Cyclic olefins are converted in very good yields, even at r.t. Terminal olefins, which are comparatively hard to oxidise, have been converted to their corresponding epoxides, although only in low yields. Complexes **76a** and **76b** also show good stereoselectivity in epoxidations with *cis*- and *trans*-stilbene, giving mainly (>95%) the corresponding *cis*- and *trans*-stilbene oxide [107]. As expected, the enantiomeric excess (*ee*) achieved with the chiral catalysts **75a** and **75b** was quite low for catalyses at elevated temperatures, beginning at 25% *ee* at reaction start and declining to 15% and 7%, respectively after several hours [106].

The mechanistic features of this type of reaction are currently under intensive investigation. Reactions with the similar, non-bridged compound $CpMo(CO)_3CH_3$ **98a** and the oxidant TBHP gave the dioxo species **98b** (1 eqiv. TBHP) and the oxoperoxo species **98c**. (2 eqiv. TBHP) Both compounds are active in the epoxidation of olefins and a general reaction mechanism has been proposed (Scheme 32) [129].



Scheme 32. Proposed mechanism for the catalytic epoxidation of olefins by $CpMo(CO)_3CH_3$.

6. Group VII: Re

The first CpRe σ-alkyl *ansa* complex was reported by Casey et al. in 1995 [130]. Starting from $CpRe(CO)_3$, the Cp moiety was functionalised with ethylene oxide. Subsequent treatment with *n*-BuLi and an insertion of one carbonyl ligand into the alkyl chain resulted in the negatively charged *ansa* compound **99** (Scheme 33). Protonation of the highly moisture-sensitive **99** with HCl yielded the hydridic complex **100**, as well as the hydroxycarbene **101**. The two structures exist in an equilibrium and the ratio of **100**:**101** is strongly solvent-dependent, with protic solvents stabilising the hydroxycarbene **101**. **100** features a four-legged piano-stool configuration at the Re centre, with a Re–C_{ansa} distance of 1.98 Å and an *ansa* bond angle of 118.6°. Methylation of **99** with MeI gave the methyl acyl *ansa* complex **102** in 45% yield [131].

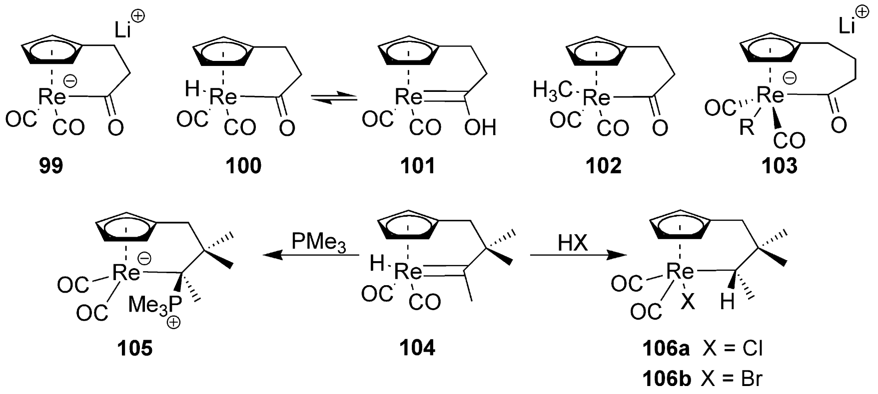
The authors suggested that the *ansa* tether introduces significant strain which destabilises the hydroxycarbene **101**, but leaves the metal acyl hydride **100** unstrained. In general, the four-legged piano-stool geometry has wider L–M–L and narrower $Cp_{centroid}$–M–L angles. To test that hypothesis, the *ansa* bridge was prolonged by one carbon atom in compound **103**. Subsequent methylation at the oxygen atom gave only the corresponding hydroxycarbene and no metal acyl hydride complex was detected. The hydroxycarbene species can also be used to generate oxygen-free three-membered *ansa* bridges. If **99** is alkylated to the corresponding ethoxycarbene species and both acidic protons at the central carbon of the *ansa* bridge are substituted with methyl groups, further alkylation with MeLi leads to the methylcarbene **104**. Treatment of **104** with PMe_3 or HX (X = Cl, Br) leads either to the zwitterionic *ansa* complex **105** or the halogenated **106** in 50%, respectively quantitative yields [132]. **106a** features a Re–C_{ansa} bond length of 2.329 Å and a Re–C_{ansa} angle of 113.2°.

7. Group VIII: Fe, Ru

7.1. Fe

Of the group VIII metals, only Fe and Ru compounds have been described bearing bear σ-alkyl *ansa* bridges. In 1976, Behrens and Weiss confirmed the structure of the bimetallic complex bis(6,6-pentafulvene)pentacarbonyldiiron **107a** [133], which was proposed earlier [134,135]. **107a** was obtained in 0.9% yield from reacting $Fe_2(CO)_9$ with fulvene in THF. Reaction with 6,6-dimethylfulvene led to **107b** under the same reaction conditions [136]. A Fe–C_{ansa} bond length of 2.150 Å and an *ansa* bond angle of 103.9° were observed. The same reaction with 6,6-diethylfulvene led to complex **108** [137].

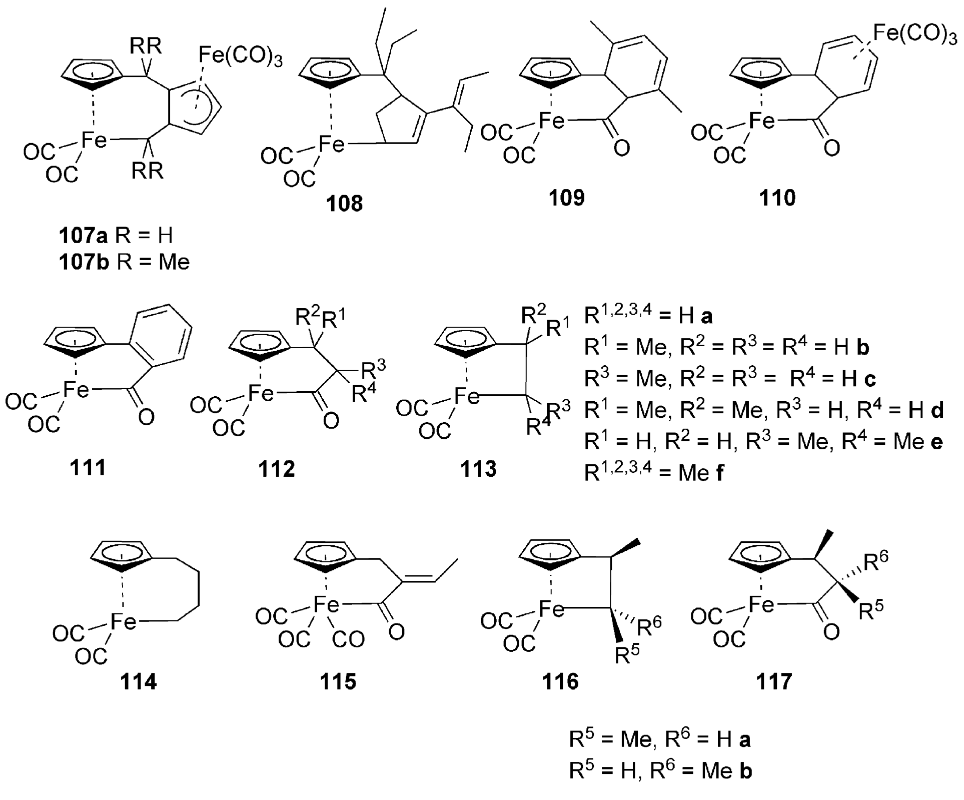
The groups of Eilbracht and Moriarty transferred the method of reacting spiro-annulated compounds with metal carbonyls to iron as the metal centre (Scheme 34). The reaction proceeded as described in Section 5 *via* C–C bond cleavage at the cyclopropane unit of the spirocycle, followed by forming the η^5-cyclopentadienyl system, alkyl migration and sometimes insertion of a carbonyl into the alkyl chain. Spiro[2,4-cyclopentadiene-1,7′-norcara-2′,4′-diene] reacted with $Fe_2(CO)_9$ to the monometallic compound **109** in 7% yield, as well as the bimetallic compound **110** in 28% and 33% yield, respectively, depending on the reaction conditions. X-ray crystallographic studies of **110** show a Fe–C_{ansa} bond length of 1.960 Å. The $Fe(CO)_3$ moiety is η^4-coordinated to the diene of the *ansa* bridge [138]. Later examination of the same reaction also gave **111** as a side product [139]. Spiro[4.4]nona-1,3-diene reacted with $Fe_2(CO)_9$ in refluxing benzene to the alkylene-bridged *ansa* compound **114** in very low yields (2%), while reaction of the carbonyl precursor with spiro[4.4]hepta-1,3-diene yielded the three-carbon-bridged acyl complex **112a** in 22% yield [94]. Further



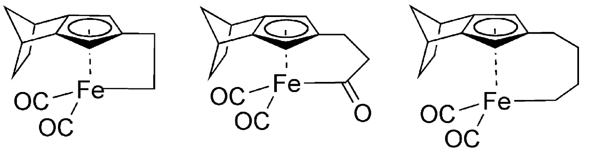
Scheme 33. Re *ansa* compounds.

studies of these compounds revealed that an excess of $Fe_2(CO)_9$ increases the yield to 45% [94]. Functionalisation, especially methylation of the cyclopropane ring of the spirocycle led to a variety of products **112b–e**. The acyl complexes **112b** and **112c** were obtained as the main products with yields of 17% and 10% and a mixture of **113b** and **113c** in 8% yield. The compounds with the methyl group bound to the carbon attached to the Cp unit were thermally more stable than the compounds where the methyl group is attached to the C_{ansa}. Examination of the stereoselectivity of the reaction with (*E*)- and (*Z*)-dimethylspiro[2,4]hepta-4,6-diene showed a product distribution independent of the spiro configuration. For the alkyl compounds, a *Z*:*E* ratio of 2.2:1 is observed and for the acyl compounds, the ratio changes to 5.7:1 [139]. A dimethylated spiroligand precursor leads to a similar product distribution **112d,e** and **113d** in low to very low yields. The steric hindrance of the two methyl units has a larger impact than the single methyl group in compounds **112b–e**. While **112d** was obtained in higher yields than **112e** and was also thermally more stable, **113e** could not be obtained. The tetramethylated compounds **112f** and **113f** could be synthesised in 20% yield by reaction with the corresponding tetramethylated spirocycle, though in the case of **113f** the reaction conditions had to be altered [103]. Reaction of 1-vinylspiro[2.4]hepta-4,6-diene with $Fe_2(CO)_9$ gave the acyl complex **115**, as well as a variety of unstable compounds [139].

Paquette et al. introduced a series of *ansa* compounds **118–120** (Scheme 35), where the Cp moiety was replaced by a η^5-coordinated dicyclopentadiene [141]. Refluxing the metal precursor (benzylideneacetone)iron tricarbonyl with the corresponding spirocycle in DCM led directly to the alkyl complex **118**, although in low yields. Changing the reaction condition to that of refluxing benzene led to the carbonyl-inserted acyl complex **119** in 50% yield. A similar reaction with a four-membered spirocycle in benzene for 20 h gave the alkyl *ansa* complex **120** in 89% yield. Under slightly different reaction conditions, a η^4-cyclopentadiene complex was formed with the intact spirocycle as a ligand.

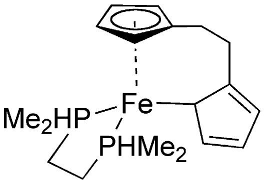


Scheme 34. Fe *ansa* compounds obtained by Eilbracht and Moriarty.



118 **119** **120**

Scheme 35. *Ansa* compounds by Paquette et al.



124

Scheme 37. *Ansa* compound **124** obtained via η^5-η^1 shift.

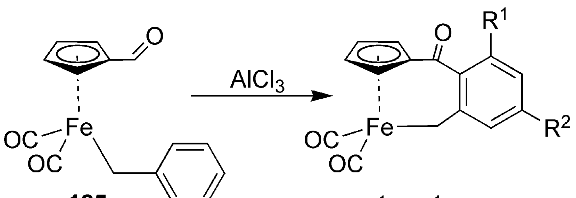
The spirocyclic synthesis route was revisited by Liu and co-workers in 1998. They observed a slow conversion from the spirocyclic η^4-cyclopentadiene complex to the acyl *ansa* complex **112a**, according to IR measurements of the carbonyl stretching vibration [142]. The conversion was solvent-dependent, being faster in polar solvents and slower in unpolar solvents. A series of reactions was carried out, leading to ring-opened products as well as to carbene complexes.

Nakanishi et al. synthesised two acyl *ansa* complexes **121** and **122** from the corresponding cyclopentadienyl and indenyl ligand precursors through triple carbonylation and a double acylation of the Cp moiety (Scheme 36). The crystal structure of **122** has been reported, as well as a ligand exchange reaction of one of the carbonyls with (trimethyl)phosphite [143].

Kerber et al. reacted 2,2′-biindenyl with BuLi, $Fe_2(CO)_9$ and $Fe(CO)_4I_2$ to yield the acyl *ansa* complex **123** in 9% yield. **123** exhibits a tautomerisation between the acyl and the hydroxycarbene form as discussed in Section 6. As with nearly all *ansa* compounds with a cyclopentadienyl fragment as part of the *ansa* bridge, the two Cp units are almost perpendicular to each other. A Fe–C_{ansa} bond length of 1.961 Å and a Fe–$Cp_{centroid}$ distance of 1.764 Å have been observed. A mechanism for the formation of **123** has been given, involving the formation of a $Fe(CO)_4^-$ unit bound in a η^1-fashion to one of the cyclopentadienyls of the biindenyl ligand. The next step involves an increase in hapticity of one indenyl ring from η^1 to η^3, with migration of the other from iron to CO. Finally, η^5-coordination is achieved with CO expulsion [144].

Manners et al. have extensively studied the effects that induce a shift in Cp hapticity for group VIII metallocenes. Although the work was focused mainly on *ansa* complexes with silicon in the three-membered *ansa* bridge, a carbon-bridged *ansa* compound **124** (Scheme 37) was reported. **124** was formed from the reaction of ethane-bridged [2]ferrocenophane with dmpe upon irradiation in 83% yield. X-ray analysis showed a Fe–C_{ansa} bond length of 2.201 Å and a Fe–$Cp_{centroid}$ distance of 1.717 Å. The bond angles of $Cp_{centroid}$–Fe–C_{ansa} are 120.1° and the Cp ring is almost in plane with the C_1 atom. The η^1-coordinated Cp undergoes a 1,2-shift that can be observed on the NMR time scale, while the η^5-coordinated Cp retains its hapticity [145,146].

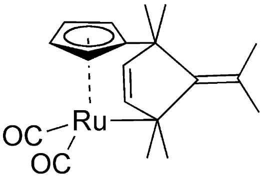
A different approach was employed by Orlova et al., who treated an acyl-substituted Cp iron complex **125** with $AlCl_3$ (Scheme 38).



125

126a $R^1 = R^1 = H$
126b $R^1 = Me, R^2 = H$
126c $R^1 = H, R^2 = Me$

Scheme 38. *Ansa* compounds by Orlova et al.



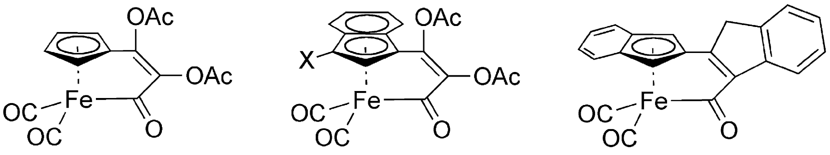
128

Scheme 39. Ru *ansa* compound **128** with a dimeric fulvene derivative.

The *Lewis*-acid induced a *Friedel-Crafts*-acylation at the phenyl ring, resulting in the corresponding C_4-bridged *ansa* complex **126a**. Methyl substitution at the *meta* position of the phenyl ring led to two isomers **126b** and **126c**. The X-ray crystal structure exhibits a Fe–C_{ansa} bond length of 2.070 Å and a Fe–C_{ansa} angle of 113.9° [147].

7.2. Ru

In 1976, Weiss and Behrens synthesised a compound which they believed was the ruthenium analogue to the bis(6,6-pentafulvalene)pentacarbonyldiiron complex **127** by reaction of $Ru_3(CO)_{12}$ with dimethylfulvalene in 39% yield [148]. The mechanism is supposed to involve a Ru–fulvene biradical, which then, depending on the substitution at the fulvene *exo* double bond, facilitates the addition of a second fulvene. X-ray crystallographic studies showed the structure to adopt a slightly different configuration **128** (Scheme 39). The Fe–C_{ansa} bond has a length of 2.18 Å



121a R = CH_3
121b R = CH_2CH_3
121c R = cyclo-C_6H_{11}
121d R = C_6H_5

122a X = Me3Si, R = CH_3
122b X = H, R = CH_3
122c X = H, R = CH_2CH_3
122d X = H, R = cyclo-C_6H_{11}
122e X = H, R = C_6H_5

123

Scheme 36. *Ansa* compounds by Nakanishi et al.

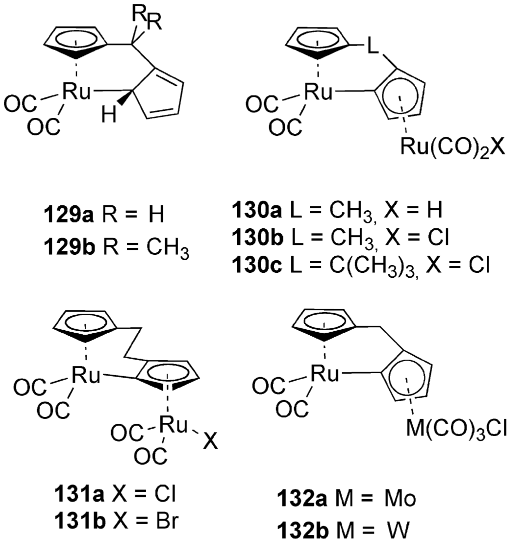
and a Cp$_{centroid}$–Fe distance of 1.929 Å [149]. Attempts to transfer the spirocyclic synthetic method to Ru met with limited success, giving only diruthenium complexes [150].

Bitterwolf et al. succeeded in synthesising *ansa* compounds of the type $(\eta^5\text{-}C_5H_5)Ru(CO)_2(\eta^1\text{-}C_5H_5)$ with a bridge length of four carbon atoms via thallium reagents with $[Cl_2Ru(CO)_3]_2$ (Scheme 40) [151]. While reaction of the metal precursor with 2 equiv. $Tl_2(C_5H_4CH_2C_5H_4)$ in benzene produced the monometallic compound **129a**, the reaction with $Tl_2(C_5H_4C(CH_3)_2C_5H_4)$ yielded the corresponding compound **129b**, as well as the bimetallic complexes **130a–c**, where an additional $Ru(CO)_2X$ unit is coordinated to the η^1-bound cyclopentadienyl unit. Reaction of $[Cl_2Ru(CO)_3]_2$ with a $Tl_2(\eta^5,\eta^5C_5H_4C_2H_4C_5H_4)$-TlBr or -TlCl mixture yielded similar bimetallic products **131a,b**. With the exception of **131**, all complexes adopt a piano-stool conformation at the Ru centres, with the Cp units perpendicular to each other [152].

Along these lines, two heterobimetallic compounds **132a** and **132b** with molybdenum and tungsten have been prepared [153]. Obtained only as side-products, their limited accessibility prevented further studies besides X-ray analysis. Again, both Cp rings are perpendicular to each other.

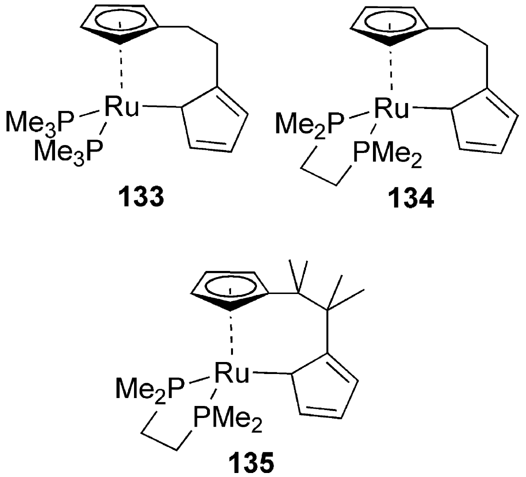
In addition to several other *ansa* complexes with silicon in the three-membered *ansa* bridge, Manners and co-workers synthesised **133** and **134** during the course of their investigations into shifts in Cp hapticity for group VIII metallocenes (Scheme 41). **133** and **134** were readily obtained in quantitative yield by stirring ethane-bridged [2]rutheno-cenophane with PMe_3 or dmpe at r.t. [144]. Complex **133** exhibits a slightly higher ring strain compared to its iron analogue **124** due to a greater covalent radius of the Ru atom. The X-ray crystal structure showed an analogous conformation to **124**, with a Cp$_{centroid}$–Ru distance of 1.863 Å being slightly longer than in **124**, and a Fe–C$_{ansa}$ bond length of 2.275 Å. The complex is stable in boiling toluene and no reconversion to the ruthenophane was observed. Experiments with **134** and **135** concerning photocontrolled ring-opening polymerisation (ROP) showed that the η^1-bound cyclopentadiene cannot be converted to a Cp anion, suggesting a stronger M–σ–η^1–Cp bond. The Ru complexes are inactive in ROP reactions [146].

The reaction of $(\eta^5\text{–}C_5H_4\text{–}COCH_3)(L)_2RuCl$ with ethynylbenzene in boiling MeOH for 4 h results in 3-carbon-bridged acyl *ansa* compounds **136a–d** with a yield greater than 60% (Scheme 42). The η^1-carbon bearing an oxygen originates from the Cp-acetyl group and the formation of the *ansa* compound is believed to proceed via an acetylide complex, subsequent formation of a cationic vinylidene complex followed by oxygen transfer from the acetyl group to the vinylidene carbon [154].



129a R = H
129b R = CH_3
130a L = CH_3, X = H
130b L = CH_3, X = Cl
130c L = $C(CH_3)_3$, X = Cl
131a X = Cl
131b X = Br
132a M = Mo
132b M = W

Scheme 40. *Ansa* compounds by Bitterwolf et al.

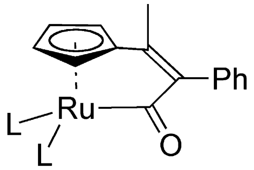


133 **134** **135**

Scheme 41. *Ansa* compounds by Manners et al.

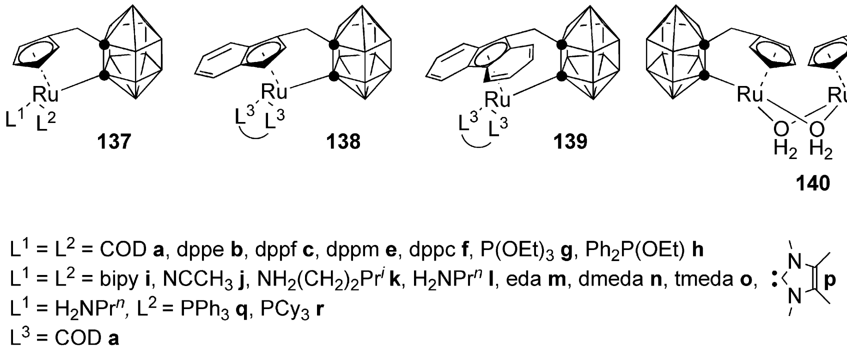
Since it was found that the η^1-coordination of the *ansa* bridge in Ti, Zr and Hf complexes remained intact under polymerisation conditions [51,155–157], the carborane *ansa* moiety was also extended to ruthenium compounds by Xie and co-workers to conduct studies concerning their stability and reactiveness. These investigations resulted in a number of cyclopentadienyl, indenyl and fluorenyl compounds. Starting from the carborane, subsequent dilithiation, treatment of $Li_2C_2B_{10}H_{10}$ with either 6,6-dimethylfulvene, 6,6-dimethylbenzofulvalene or dibenzofulvene and finally reaction with $[RuCl_2(COD)]_x$ gave the corresponding 18 valence electron *ansa* complexes **137a**–**139a** in 50–80% yield (Scheme 43) [158].

The complexes show a distorted tetrahedral geometry. They are soluble in polar solvents, but insoluble in *n*-hexane. It was found that the stability of the compounds decreases with an increasing steric demand of the functionalised Cp ligand. While **137a** is stable in air in the solid state and in solution, **139a** is sensitive to air. According to the X-ray structures, the distance between the metal and the COD ligand decreased from **137a** to **139a**. This was interpreted as being caused by increased back-bonding between Ru and COD because of the increased electron donating strength of fluorenyl in comparison to indenyl or cyclopentadienyl. The COD ligand can be irreversibly displaced by other ligands, such as tertiary phosphines (except PPh_3 or PCy_3) or bidentate aromatic amines to yield complexes **137b–i** [159]. The COD ligand in **137a** proved to be the most labile and thus, **137a** was chosen as model complex for



136a L = 2 PPh_3
136b L = chiraphos
136c L = BINAP
136d L = dppe

Scheme 42. *Ansa* compounds obtained from an acetyl-substituted Cp ligand precursor.



137 **138** **139** **140**

$L^1 = L^2$ = COD **a**, dppe **b**, dppf **c**, dppm **e**, dppc **f**, $P(OEt)_3$ **g**, $Ph_2P(OEt)$ **h**
$L^1 = L^2$ = bipy **i**, $NCCH_3$ **j**, $NH_2(CH_2)_2Pr^i$ **k**, H_2NPr^n **l**, eda **m**, dmeda **n**, tmeda **o**, **p**
$L^1 = H_2NPr^n$, $L^2 = PPh_3$ **q**, PCy_3 **r**
L^3 = COD **a**

Scheme 43. Ru compounds bearing carborane *ansa* bridges.

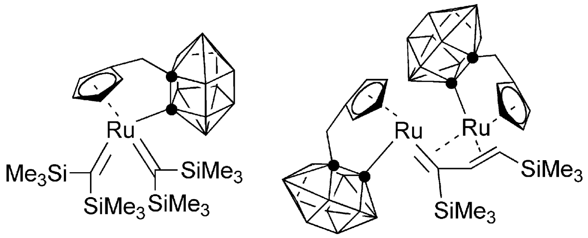
the substitution of COD. Continuing this line of research, a variety of COD displacement reactions were also attempted with several amines, nitriles and carbenes. The reactions leading to **137k** and **137l** were found to be reversible due to the lability of the amine ligand coordination, meaning that a large excess of amine has to be used. Compounds **137k** and **137l** with the weakly coordinated ligands $NH_2(CH_2)_2Pr^i$ and H_2NPr^n were reacted with PPh_3 and PCy_3, but only one ligand was substituted even under harsh reaction conditions (**137q, 137r**). Displacement of the primary amine ligands with bidentate amines **m**–**o** was only achieved at elevated temperatures and the acetonitrile ligated complex **137j** requires prolonged reaction times. With the exception of **137l** and **137j**, all other compounds are stable against moisture and air. Upon exposure to moisture, **137j** decomposes to the dimeric compound **140**. Complexes **137j** and **137l** bear the most labile ligands and are considered to be potential catalyst precursors. All compounds are obtained with yields >70%. The complexes have been electrochemically studied, showing the redox processes to be one-electron and reversible and the electron-richness of the Ru centre decreases in the order **137p** > **137m** ≫ **137q** > **137l** > **137g** [159].

It was attempted to convert **137a** to the corresponding hydride complex; however, the η^1-coordination at the metal centre changed from C to B [160]. According to DFT calculations, the ligand substitution of COD with H_2/PR_3 is thermodynamically favorable. However, the metal–boron coordinated complex is found thermodynamically more stable than the metal–carbon coordinated complex. This implies that all metal–carbon coordinated Ru carboranyl complexes are kinetic products which do not isomerise to the more stable isomer because of a high energetic barrier. Exchanging the ligands to hydrides lowers the barrier and isomerisation becomes possible.

Since transition metal catalysed organic transformation of alkynes often involve vinylidene intermediates [161], the bis(acetonitrile) compound **137j** was reacted with several alkynes bearing aryl and silyl substituents. In the case of aryl alkynes, the aromaticity of the Cp ring was broken upon reaction of **137j** to yield tricyclic Ru complexes [162]. Treatment of **137j** with excess bis(trimethylsilyl)ethyne in toluene yielded the air- and moisture-sensitive mononuclear bis(vinylidene) species **141** (Scheme 44). This is the first representative of a mononuclear bis(vinylidene) complex and could only be synthesised because of the sterically demanding ancillary ligand, as well as bulky alkyne substituents.

Treatment of **137j** with excess trimethylsilyl ethyne in toluene yielded the air- and moisture-sensitive bimetallic species **142**, where one Ru atom is η^4-bound to the vinylvinylidene group and the other Ru is coordinated to a B–H bond of the carborane cage [163]. Both Ru atoms adopt a three-legged piano-stool geometry if each C=C is viewed as a ligand.

Further, the bis(isopropylamine) complex **137l** was reacted with several aryl and alkyl alkynes [164]. It was found that the nature of the products strongly depends on the electron density of the alkyne. For electron-rich alkynes, the formation of aminocarbene complexes **143** is favored, but for electron-deficient alkynes, the products shift to enamine coordination complexes **144** (Scheme 45). The solvent also plays an important role. The reaction of **137l** with ethynylbenzene in DCM gave a aminocarbene:enamine ratio of 76:24, while the same reaction in toluene gave a ratio of 32:68.

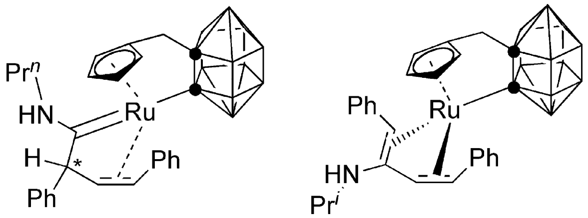


141 **142**

Scheme 44. Ru *ansa* compounds originating from bis(trimethylsilyl)alkenyl ligand precursors.

8. Group X: Ni

Eilbracht synthesised the first nickel *ansa* compounds (Scheme 46). The reaction of spiro[4.4]hepta-1,3-diene with $Ni(CO)_4$ in boiling hexane gave the acyl-bridged *ansa* complex **145** [165]. One C–C cyclopropane bond is broken during the reaction and the nickel moiety is inserted, forming the *ansa* complex. Ni-acyl compounds tend to decompose through decarbonylation [166] and the uncommon stability of this complex is thought to be because this decomposition pathway is blocked. The loss of the CO

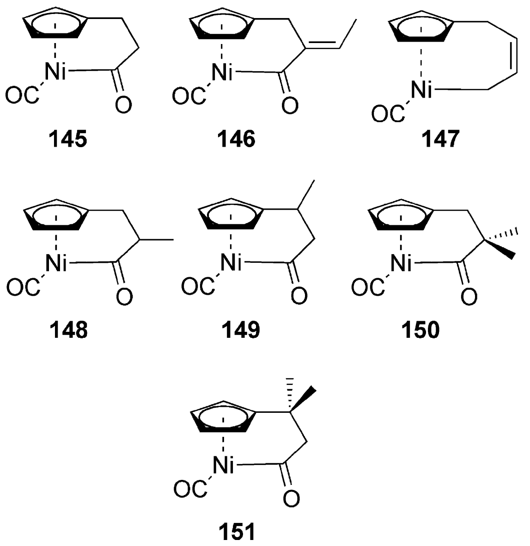


143 **144**

R = Ph **a**
p-tolyl **b**
^{n}Bu **c**

R = Ph **a**
p-ClC_6H_4 **b**
p-BrC_6H_4 **c**

Scheme 45. *Ansa* compounds obtained from the reaction of **137l** with alkynes.



Scheme 46. Ni *ansa* compounds by Eilbracht et al.

moiety would cause a too high ring strain in the system and thus is energetically unfavored.

Variation at the cyclopropane unit of the spirocycle by vinyl or methyl groups resulted in the acyl *ansa* complexes **146**–**151**. Ring-opening of 1-vinylspiro[2,4]hepta-4,6-diene occurred preferably at the C_{Cp}–C_{vinyl} bond, leading to only one acyl-bridged isomer **146** and an olefinic four carbon-bridged compound **147** [100]. If one or two methyl groups are used instead of a vinyl group, a mixture of isomers **148**–**151** results, with the methyl groups preferentially attached to the less sterically demanding C_{Cp} as opposed to the vinylic *ansa* **147** [167]. In contrary to the Fe derivatives, no reaction occurred between $Ni(CO)_4$ and the 1,1,2,2-tetramethylspiro[2.4]hepta-4,6-diene [103]. All compounds were obtained in quite low yields, the main product being dimers or nickelocenes, with **150** and **151** only being detected via NMR and not isolated.

9. Conclusions and outlook

The described π,σ-coordinated *ansa*-type class of compounds, where the *ansa* bridge tethers the metal and one π-coordinated ligand (usually cyclopentadiene) via a metal–ligand σ-bond, features a rich and diverse chemistry. Numerous synthetic approaches and many possibilities to vary different moieties of the compounds are available, such as the metal centre itself or its electronic environment, in particular the ligand system and the *ansa* bridge itself. The easy modification of these compounds enables the synthesis of specially tailored molecules, a property which is invaluable for e.g. catalyst design.

As these *ansa* compounds already show a promising potential in several catalytic applications such as olefin polymerisation or epoxidation, further research in the field of *ansa* compounds will likely focus on improving known polymerisation catalysts or building enantioselective catalyst systems with chirality-inducing functionalities at the *ansa* bridge, as well as methods to heterogenise these systems in order to make them more attractive for industrial applications. Also, in the case of more recently described and examined compounds such as the molybdenum(VI) *ansa* complexes, the mechanistic aspects of their reactivity with various oxidants in the catalytic epoxidation of olefins are currently under investigation and further catalyst design in this area will be determined by these results.

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