

Early transition-metal compounds with doubly silyl-bridged dicyclopentadienyl ligands

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Received July 8, 1996; accepted December 11, 1996.

Abstract. – In this paper we present a summary of the different types of complexes formed by the group 4 and 6 metals with ligands resulting from the doubly bridged bis(dimethylsilyl) dicyclopentadiene $[(\text{SiMe}_2)_2(\text{C}_5\text{H}_4)_2]$, which were presented in a recent lecture¹. TiCl_4 and $\text{MCp}'\text{Cl}_3$ [$\text{M} = \text{Ti}, \text{Zr}$; $\text{Cp}' = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5$] react with the monolithium salt of the ligand to give mono $[(\text{TiCl}_3)\{(\eta^5\text{-C}_5\text{H}_3)(\text{SiMe}_2)_2(\text{C}_5\text{H}_4)\}]$ and mixed dicyclopentadienyl-type $[(\text{TiCp}'\text{Cl}_2)\{(\eta^5\text{-C}_5\text{H}_3)(\text{SiMe}_2)_2(\text{C}_5\text{H}_4)\}]$ complexes. TiCl_4 reacts with the dilithium salt of the ligand to give mixtures of *cis*- and *trans*- $[(\text{TiCl}_3)_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ dinuclear compounds, which are transformed into their μ -oxo and methyl derivatives by hydrolysis and alkylation, respectively, with MgClMe . Related *cis* and *trans* homodinuclear group 6 metal hydrido-carbonyls $[\{\text{M}(\text{CO})_3\text{H}\}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ are prepared by reacting $[\text{Mo}(\text{CO})_3\text{mesitylene}]$ and $[\text{W}(\text{CO})_3(\text{MeCN})_3]$ with $[(\text{SiMe}_2)_2(\text{C}_5\text{H}_4)_2]$. The hydrido-carbonyl compounds can be transformed into their anionic tricarbonyl metallate derivatives; neutral nitrosyl, chloro, imido and metal-metal-bonded tricarbonyl species; and cationic carbonyl and related compounds. Reactions of the mixed titanocene complexes $[(\text{TiCp}'\text{Cl}_2)\{(\eta^5\text{-C}_5\text{H}_3)(\text{SiMe}_2)_2(\text{C}_5\text{H}_4)\}]$ with $[\text{Mo}(\text{CO})_3\text{mesitylene}]$ and $[\text{W}(\text{CO})_3(\text{MeCN})_3]$ provide *cis* and *trans* heterodinuclear $[(\text{TiCp}'\text{Cl}_2)\{\text{M}(\text{CO})_3\text{H}\}\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ complexes that can be transformed into their chloro and imido derivatives. Reactions of MCl_4 ($\text{M} = \text{Ti}, \text{Zr}$) with the dilithium salt of the doubly silyl-bridged dicyclopentadienyl ligand in a 1:1 molar ratio leads to metallocene-type $[(\text{TiCl}_2)\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ complexes, which react with different alkylating agents to give mono- and dialkyl compounds. The chemical behavior and thermal stability of these compounds has also been studied.

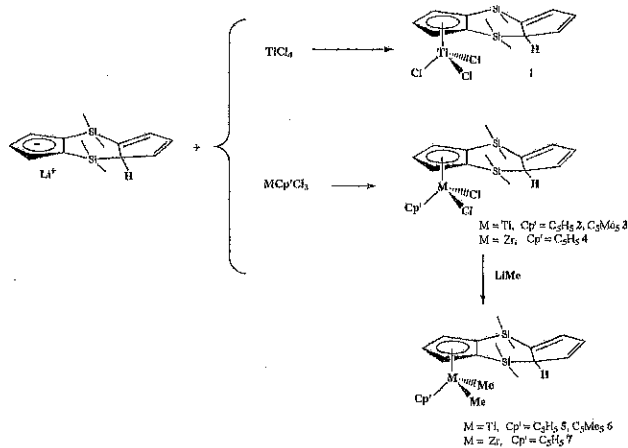
Introduction

Extensive studies have been undertaken of complexes containing the so-called *ansa* ligands in relation to their catalytic applications² in Ziegler-Natta polymerization of olefins to produce highly stereoregular *iso* and *syndio* tactic polymers. The use of bridged silyl-dicyclopentadienyl ligands provides access to new types of mono- and bent dicyclopentadienyl-type metal complexes. In addition, these ligands are more rigid systems that avoid the participation of ring-carbon-hydrogen activation reactions, and the presence of silyl groups with empty 3*d* electron-withdrawing silicon orbitals enhances the accessibility of lower oxidation states.

Complexes with one metal-coordinated cyclopentadienyl ring

Use of the ligand as a monoanion has led to the isolation

of several mixed dicyclopentadienyl titanium complexes³. New complexes, **1-7** of this type were isolated⁴ by the reactions represented in Scheme 1.



Scheme 1.

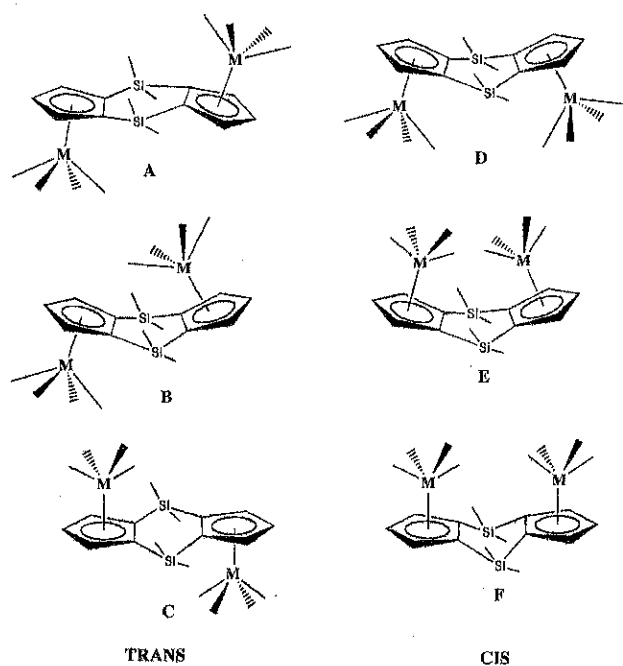
All these compounds were identified by elemental analyses and their structures were studied by NMR spectroscopy. The ^1H NMR spectra show a common behavior; they exhibit four resonances arising from the four inequivalent methyl groups bonded to silicon, one singlet arising from the cyclopentadiene ring sp^3 carbon atom, and six multiplets arising from the six inequivalent hydrogen atoms bonded to the cyclopentadiene and cyclopentadienyl rings between δ 5.50 and δ 7.50. On the other hand, the metallocene complexes show a singlet arising from the additional cyclopentadienyl protons or methyl groups (Cp^*) and two more resonances are observed for the dimethyl derivatives.

Homodinuclear compounds containing the bridging ligand

Titanium complexes

The doubly SiMe_2 -bridged dicyclopentadienyl $[(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2]^{2-}$ dianion is a rigid system that allows the coordination of two metal fragments that occupy *cis* or *trans* positions with respect to the faces of the rings, a quality that gives rise to the different structural conformations A–F represented in Scheme 2.

We reported⁵ the isolation of the *trans* monocyclopentadienyl-type titanium complex $[(\text{TiCl}_3)_2\{(\text{SiMe}_2)_2$



Scheme 2.

$(\eta^5\text{-C}_5\text{H}_3)_2]$, and several other *cis* and *trans* group 4 bent metallocenes have been reported⁶ more recently.

Whereas the reaction of TiCl_4 with the dithallium salt of the ligand in toluene led to the selective formation of *trans*- $[(\text{TiCl}_3)_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]^5$ **8** in 30% yield, the similar reaction with the dilithium salt in toluene (see Scheme 3) always afforded a mixture having a variable proportion of the *cis* **8** and *trans* **8** isomers, which can be separated by recrystallization from toluene. A similar behavior has been observed⁶ for the reaction of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_3]$ with the dilithium salt of the ligand, which leads to a mixture of the *cis* and *trans* mixed bent metallocenes $[\{\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_5)\}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$, whereas the related $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3]$ compound led only to the *trans* isomer. Addition of a stoichiometric amount of water in the presence of 2 equiv. of NEt_3 to a THF solution containing a mixture of *cis* **8** and *trans* **8** resulted in the selective hydrolysis of the *trans* isomer, which was transformed into an oxo compound insoluble in all organic solvents. It was characterized as the μ -oxo complex $[\{\text{TiCl}_2(\mu\text{-O})\}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ **9** by elemental analysis and the $\nu(\text{M-O-M})$ IR absorption observed at 760 cm^{-1} , but no NMR study could be made, owing to its lack of solubility. However, a solution of *cis* **8** in saturated benzene afforded yellow crystals of the dimer $[\{\text{TiCl}\}_2(\mu\text{-O})\}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}_2(\mu\text{-O})_2$ **10**, which was characterized by NMR spectroscopy; its crystal structure was determined by diffraction methods (see Fig. 1).

The alkylation of the *trans* **8** and *cis* **8** complexes with MgClMe gave, respectively, the hexamethyl

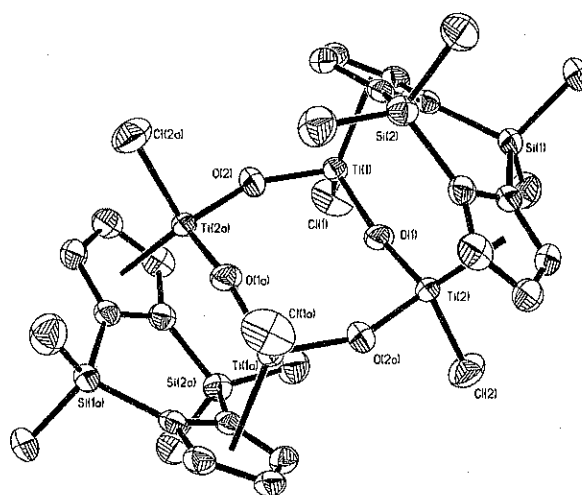
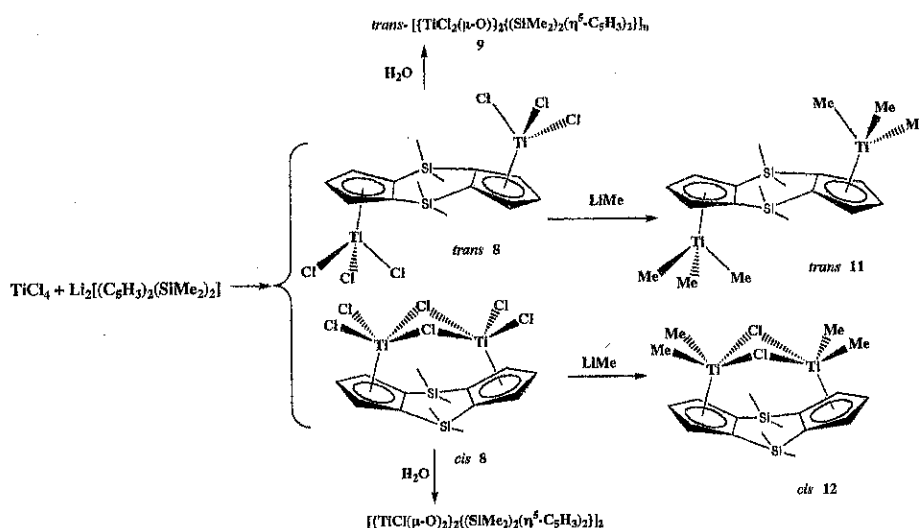


Figure 1. – ORTEP representation of complex **10**. Selected distances (Å): $\text{Ti}(1)\text{-Cl}(1)$ 2.268(2), $\text{Ti}(1)\text{-O}(1)$ 1.803(4), $\text{Ti}(1)\text{-O}(2)$ 1.798(4). Selected angles ($^\circ$): $\text{Ti}(1)\text{-O}(2)\text{-Ti}(2)$ 160.7(2), $\text{Ti}(1)\text{-O}(2)\text{-Ti}(2\text{A})$ 153.0(3).



Scheme 3.

dititanium $[(\text{TiMe}_3)_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ **11** complex and the tetramethyl dititanium derivative $\text{cis-}[(\text{TiMe}_2\text{Cl})_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ **12**, even in the presence of 2 equiv excess of the alkylating agent. Both compounds were characterized by elemental analysis and NMR spectroscopy.

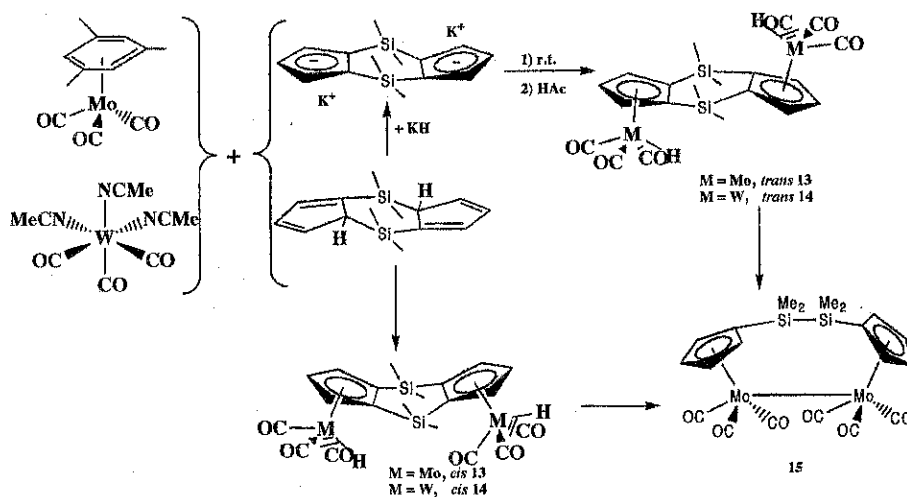
The ^1H and ^{13}C NMR spectra of the *trans* isomers **8** and **11** show one singlet for the four equivalent SiMe_2 groups, whereas two signals are observed for the *cis* compounds **8** and **12** corresponding to the two pairs of equivalent methyl groups. The expected pseudo-doublet and pseudo-triplet due to the cyclopentadienyl ring protons are observed in the ^1H NMR spectra of all the *cis* and *trans* compounds between 6.19 and 6.95. The Ti-Me resonances were observed as one singlet at 1.21

and 0.92 for complexes **11** and **12**, respectively.

All the *trans* group 4 metal complexes reported show an almost planar disposition of the two cyclopentadienyl rings, whereas the *cis* bent titanocene $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ complex **6** exhibits a boat conformation with both metal fragments located on the external faces of the rings.

Molybdenum and tungsten complexes

The reported⁷ stereoselective synthesis of *cis* **13** and *trans* **13** isomers of $[\{\text{Mo}(\text{CO})_3\text{H}\}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ cannot be extended to the related tungsten compounds *cis* **14** and *trans* **14**, which were always obtained⁸ as a mixture of both stereoisomers (Scheme 4); they cannot be interconverted because an irreversible



Scheme 4.

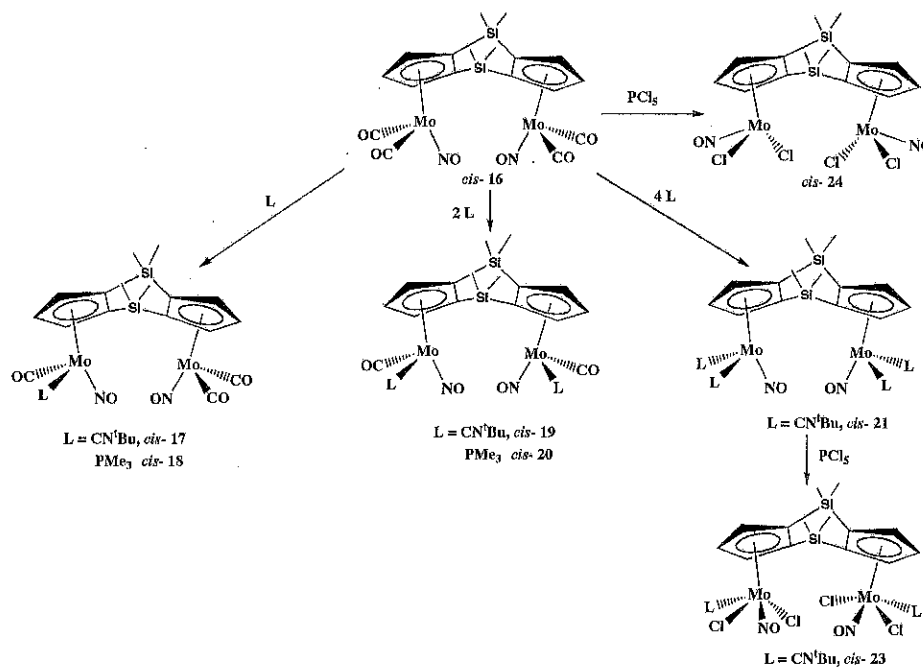
process takes place to give complex **15** with Si-Si coupling by heating to 90 °C, as was verified⁹ for the *cis* **13** and *trans* **13** molybdenum isomers by means of labelled ¹NMR studies.

The isolation and characterization of neutral chloro-tricarbonyl $[\{M(\text{CO})_3\text{Cl}\}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ (M=Mo, W) and metal-metal-bonded tricarbonyl $[\{M(\text{CO})_3\}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ (M=Mo, W) complexes, anionic tricarbonyl metallate $[\{M(\text{CO})_3\text{Cl}\}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{-H}_3)_2\}]^{2-}$ (M=Mo, W) derivatives, and cationic molybdenum tricarbonyl $[\{\text{Mo}(\text{CO})_3\text{L}\}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{-H}_3)_2\}]^{2+}$ compounds with coordinated acetylene and phosphine ligands have been recently reported¹⁰. We have also reported¹¹ the oxidation of the chloro-tricarbonyl complexes with PCl_5 to give paramagnetic *cis* and *trans* tetrachloro metal(V) $[\text{MCl}_4]_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}$ (M=Mo, W) complexes that react with primary amines to give paramagnetic dichloro-imido $[\{\text{MCl}_2(\text{NR})\}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ (M=Mo, W) compounds. The imido-tungsten derivatives can be further oxidized with PCl_5 to the related tungsten(VI) trichloro-imido $[\{\text{WCl}_3(\text{NR})\}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ compounds.

More recently we isolated¹² the *cis* **16** and *trans* **16** dinuclear nitrosyl dicarbonyl molybdenum $[\{\text{Mo}(\text{CO})_2(\text{NO})\}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ complexes (see Scheme 5 for *cis* compounds) by reactions with the *p*- $\text{MeC}_6\text{H}_4\text{SO}_2\text{N}(\text{NO})\text{Me}$ ("diazald") of the corresponding tricarbonyl hydride or the anionic derivative. Complexes *cis* **16** and *trans* **16** react with different ligands in

various molar ratios to give the mono-, di-, and tetrasubstituted compounds **17–21**. Oxidation of the isocyanide adducts with PCl_5 took place with partial loss of the ligand, leading to the formation of the 18-electron dichloro-nitrosyl-isocyanide complexes **22–23**, whereas the oxidation of the carbonyl derivatives produced the 16-electron dichloro-nitrosyl compounds *cis* **24** and *trans* **24** with a total loss of carbon monoxide.

All these compounds were analytically identified and structurally characterized by NMR spectroscopy, the molecular structure of some being studied by X-ray diffraction methods. The ¹H NMR spectra of all the compounds having a *cis* disposition of the two metal fragments show two singlets for the two pairs of inequivalent methyl-silyl groups, whereas those having the two metal fragments in a *trans* configuration show only one singlet for all four equivalent groups. The ¹H NMR spectra of the monosubstituted complexes **17–18**, which have one chiral center, and the disubstituted compounds **19–20**, which have two chiral centers, show the expected behavior for asymmetric molecules. The molecular structure of the *trans* complex **21** belongs to type **A**, whereas that of complex *trans* **19** belongs to the new type **C** shown in Scheme 2. All the reported *cis* complexes belong to the structural dispositions **D–E** shown in Scheme 2, **E** being the typical disposition known for compounds containing some type of additional bridging group between the two metal fragments. However, the *cis* **16** and *cis* **17** complexes show the unprecedented **F** disposition illustrated in Figure 2 for



Scheme 5.

the *cis* **16** complex, with the two almost exactly coplanar cyclopentadienyl rings.

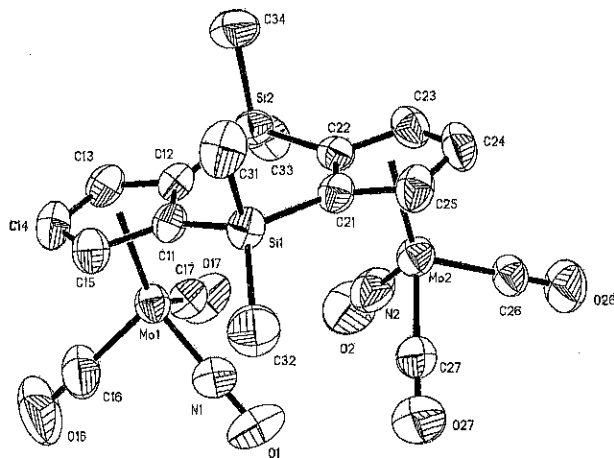


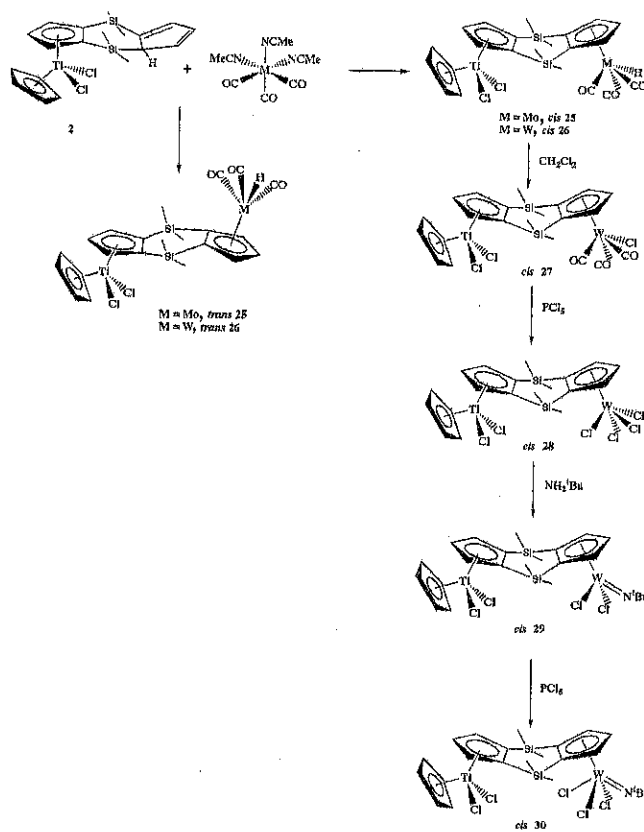
Figure 2. – ORTEP representation of complex *cis* **16**. Selected distances (Å): Mo(1)–C(16) 1.964(6), Mo(1)–N(1) 1.823(5), C(16)–O(16) 1.155(7), N(1)–O(1) 1.187(6).

Heterodinuclear compounds containing the bridging ligand

Recently we also isolated ¹³ new *cis* and *trans* heterodinuclear compounds containing group 4 and group 6 metal fragments (Scheme 6). Reacting [Mo(CO)₃mesitylene] and M(CO)₃(MeCN)₃ (M=Mo, W) with complexes **2** and **3**, which contain only one coordinated cyclopentadienyl ring of the monoanionic ligand, led to the formation of the heterodinuclear *cis* **25**, *cis* **26**, *trans* **25**, and *trans* **26** compounds [(TiCp'Cl₂){M(CO)₃H}], although the reasons for the selective formation of the *cis* or the *trans* isomer or of a mixture of both are not known. These complexes contain one titanocene moiety and one hydrido-tricarbonyl metal (Mo, W) fragment bridged by the dimethylsilyl-η⁵-dicyclopentadienyl ligand.

The ¹H NMR spectra of both *cis* and *trans* compounds show two AA'B spin systems for the protons of the inequivalent cyclopentadienyl rings and two singlets for the two pairs of inequivalent methyl silyl groups, although they can be easily distinguished by the difference between the chemical shifts of the two latter signals, which is smaller for the *trans* isomers. The molecular structure of complex *cis* **26** was studied by X-ray diffraction methods and is shown in Figure 3 along with the most significant bond distances and angles.

Complex *cis* **26** reacts with dichloromethane to give the carbonyl derivative *cis*-[(TiCpCl₂){W(CO)₃Cl}]{(SiMe₂)₂(η⁵-C₅H₃)₂} (*cis* **27**) which can be oxidized with PCl₅ to give the paramagnetic tetrachloro-tungsten complex *cis*-[(TiCpCl₂){WCl₄}]{(SiMe₂)₂(η⁵-C₅H₃)₂}



Scheme 6.

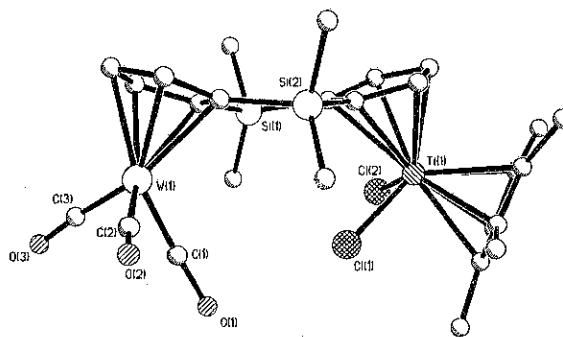
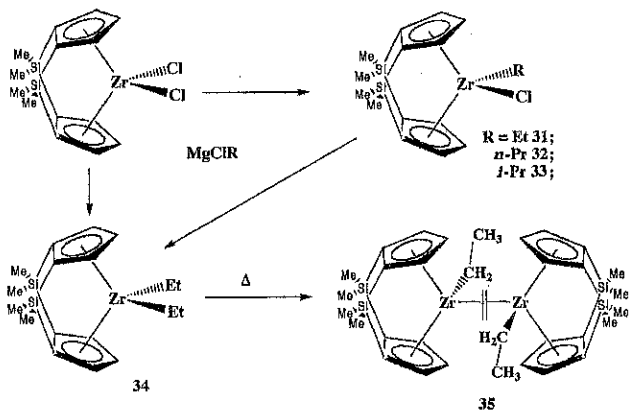


Figure 3. – Perspective view of complex *cis* **26**. Selected distances (Å): W(1)–C(1) 1.972(2), C(1)–O(1) 1.253(2), Ti(1)–Cl(1) 2.324(4).

(*cis* **28**). Complex *cis* **28** reacts with *t*-BuNH₂ to give the imido derivative *cis*-[(TiCpCl₂){WCl₂(*t*-BuN)}]{(SiMe₂)₂(η⁵-C₅H₃)₂} (*cis* **29**), which can be further oxidized with PCl₅ to yield the tungsten(VI) compound *cis*-[(TiCpCl₂){XCl₃(*t*-BuN)}]{(SiMe₂)₂(η⁵-C₅H₃)₂} (*cis* **30**). All these compounds were identified by their analytical composition and the diamagnetic derivatives were structurally characterized by NMR spectroscopy.

Group 4 metallocene-type complexes

In the dianion form the bis(dimethylsilyl) dicyclopentadienyl ligand can also be coordinated as a chelate system to give a new type of *ansa* metallocene represented by the recently reported titanium¹⁴, zirconium¹⁵, and hafnium¹⁶ derivatives (Scheme 7).



Scheme 7.

More recently¹⁷ we isolated new zirconium complexes with β -containing alkyl substituents. Reacting toluene solutions of $[\text{ZrCl}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ ^{15b} with one equivalent of MgClR ($\text{R} = \text{Et}$, $n\text{-Pr}$, $i\text{-Pr}$) at temperatures

lower than 15 °C led to the chloro-alkyl complexes $[\text{ZrClR}\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ ($\text{R} = \text{Et } \mathbf{31}$, $n\text{-Pr } \mathbf{32}$, $i\text{-Pr } \mathbf{33}$). The related dialkyl compounds could not be isolated in the solid, although solutions containing pure components were studied by NMR spectroscopy. Toluene solutions of complex $\mathbf{33}$ contain a mixture of the $n\text{-Pr}$ and the $i\text{-Pr}$ derivatives in an equilibrium determined by β -hydrogen elimination. Thermal decomposition of the diethyl complex $\mathbf{34}$ led to the formation of the dinuclear $[(\text{ZrEt})_2(\mu\text{-C}_2\text{H}_4)\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ $\mathbf{35}$ complex containing one bridging ethylene molecule. All these compounds were identified by their analytical composition and structurally characterized by NMR spectroscopy, the molecular structure of complexes $\mathbf{31}$ and $\mathbf{35}$ being studied by X-ray diffraction methods.

Acknowledgements

This research is included in the EEC COST-D2/03/92 Project and is financially supported by DGICYT Project 92-0178-C. I am also indebted to P. Gómez-Sal, A. Martín, and A. Manzanero for the determination of X-ray crystal structures. An excellent group of students: F. Amor, M. Calvo, J. Cano, A. Cano, F. J. Fernández, A. Gil, R. Gómez-García, A. I. Pérez, E. Royo, and B. Royo (Postdoctoral Fellow), carried out the experimental work.

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