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 [[SiMe₂]₃₂(C₅H₆)₂], which were presented in a recent lecture. TiOi, and MOCl₂ [M = Ti, Zr; Cp = C₅H₅, C₅Me₅] react with the monolithium salt of the ligand to give mono-[TiOi]([n⁵-C₅H₅][SiMe₂]₂(C₅H₆)] and mixed dicyclopentadienyl-type ([TiCp₂Cl₂][n⁵-C₅H₅][SiMe₂]₂(C₅H₆)) complexes. TiOi reacts with the dillithium salt of the ligand to give mixtures of cis- and trans-[TiOi]₂([SiMe₂]₂([n⁵-C₅H₅]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 ([M(CO)₃H]([SiMe₂]₂([n⁵-C₅H₅]₂)) are prepared by reacting [Mo(CO)₃mesitylene] and [W(CO)₆(MeCN)₃] with ([SiMe₂]₂(C₅H₆)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 ([TiCp₂Cl₂][n⁵-C₅H₅][SiMe₂]₂(C₅H₆)) with [Mo(CO)₃mesitylene] and [W(CO)₆(MeCN)₃] provide cis and trans heterodinuclear ([TiCp₂Cl₂][M(CO)₃H]([SiMe₂]₂([n⁵-C₅H₅]₂)) complexes that can be transformed into their chloro and imido derivatives. Reactions of MC₄ (M = Ti, Zr) with the dillithium salt of the doubly silyl-bridged dicyclopentadienyl ligand in a 1:1 molar ratio leads to metalocene-type [TiCl₂][SiMe₂]₂([n⁵-C₅H₅]₂) complexes, which react with different alkylation agents to give mono- and dialkyll 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 anza ligands in relation to their catalytic applications in Ziegler-Natta polymerization of olefins to produce highly stereoregular ioe 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-carbonhydrogen activation reactions, and the presence of silyl groups with empty 3d 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 complexes. New complexes, 1-7 of this type were isolated by the reactions represented in Scheme 1.

![Scheme 1](image-url)
All these compounds were identified by elemental analyses and their structures were studied by NMR spectroscopy. The $^1$H 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 $\delta$ 5.50 and $\delta$ 7.50. On the other hand, the metalloocene 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 [(SiMe$_2$)$_2$(η$^5$-C$_5$H$_5$)$_2$]$^2^-$ 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 reported $^5$ the isolation of the trans monocy clopentadienyl-type titanium complex [(TiCl$_3$)$_2$(SiMe$_2$)$_2$(η$^5$-C$_5$H$_5$)$_2$] and several other cis and trans group 4 bent metalloccenes have been reported $^6$ more recently. Whereas the reaction of TiCl$_4$ with the dithiylamidate of the ligand in toluene led to the selective formation of trans-[(TiCl$_3$)$_2$(SiMe$_2$)$_2$(η$^5$-C$_5$H$_5$)$_2$] $^5$ in 30% yield, the similar reaction with the dithiylamide in toluene (see Scheme 3) always afforded a mixture of the cis isomer 8 and trans isomers, which can be separated by recrystallization from toluene. A similar behavior has been observed $^6$ for the reaction of [Ti(η$^5$-C$_5$H$_5$)Cl$_3$] with the dithiylamide salt of the ligand, which leads to a mixture of the cis and trans mixed bent metalloccenes [(TiCl$_2$(η$^5$-C$_5$H$_5$)$_2$)Cl][(SiMe$_2$)$_2$(η$^5$-C$_5$H$_5$)$_2$] and the related [Ti(η$^5$-C$_5$H$_5$)Cl] 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 [(TiCl$_2$(μ-O))Cl][(SiMe$_2$)$_2$(η$^5$-C$_5$H$_5$)$_2$] $^9$ by elemental analysis and the $\nu$(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 [(TiCl)$_2$(μ-O)][(SiMe$_2$)$_2$(η$^5$-C$_5$H$_5$)$_2$]$_2$(μ-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](https://example.com/figure1.png)

Figure 1. – ORTEP representation of complex 10. Selected distances (Å): Ti(1)–Cl(1) 2.28(2), Ti(1)–O(1) 1.803(4), Ti(1)–O(2) 1.98(4). Selected angles (°): Ti(1)–O(2)–Ti(2) 160.7(2), Ti(1)–O(2)–Ti(2) 153.0(3).
diititanium [TiMe$_3$] (SiMe$_2$)$_2$ (η$^5$-C$_5$H$_3$)$_2$] 11 complex and the tetramethyl dititanium derivative cis-[(TiMe$_2$Cl)$_2$- (SiMe$_2$)$_2$ (η$^5$-C$_5$H$_3$)$_2$] 12, even in the presence of 2 equiv excess of the alkylation agent. Both compounds were characterized by elemental analysis and NMR spectroscopy.

The $^1$H 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 pseudodoublet and pseudo-triplet due to the cyclopentadienyl ring protons are observed in the $^1$H 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 tianocene [(Ti(η$^5$-C$_5$Me$_3$)$_2$Cl)$_2$ (SiMe$_2$)$_2$ (η$^5$-C$_5$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 reported$^7$ stereoselective synthesis of cis 13 and trans 13 isomers of [(Mo(CO)$_3$H)$_2$ (SiMe$_2$)$_2$ (η$^5$-C$_5$H$_3$)$_2$] cannot be extended to the related tungsten compounds cis 14 and trans 14, which were always obtained$^8$ as a mixture of both stereoisomers (Scheme 4); they cannot be interconverted because an irreversible
process takes place to give complex 15 with Si–Si coupling by heating to 90°C, as was verified 9 for the cis 13 and trans 13 molybdenum isomers by means of labelled 1NMR studies.

The isolation and characterization of neutral chloro-tricarbonyl [[M(CO)3Cl]2[(SiMe2)2(η5-C5H5)2]] (M = Mo, W) and metal-metal-bonded tricarbonyl [[M(CO)3]2-[(SiMe2)2(η5-C5H5)2]] (M = Mo, W) complexes, anionic tricarbonyl metallaclate [[M(CO)3Cl][[(SiMe2)2(η5-C5-H5)2]]3- (M = Mo, W) derivatives, and cationic molybdenum tricarbonyl [[(Mo(CO)5L)2[(SiMe2)2(η5-C5-H5)2]]2+ compounds with coordinated acetylene and phosphine ligands have been recently reported 10. We have also reported 11 the oxidation of the chloro-tricarbonyl complexes with PCl5 to give paramagnetic cis and trans tetrachloro metal(V) [[MCl3L][(SiMe2)2(η5-C5-H5)2]] (M = Mo, W) complexes that react with primary amines to give paramagnetic dichloro-imido [[MCl2(NR)]2[(SiMe2)2(η5-C5-H5)2]] (M = Mo, W) compounds. The imido-tungsten derivatives can be further oxidized with PCl5 to the related tungsten(VI) trichloro-imido [[WCl3(NR)]2[(SiMe2)2(η5-C5-H5)2]] compounds.

More recently we isolated 12 the cis 16 and trans 16 dinuclear nitrosyl dicarbonyl molybdenum [[Mo(CO)4(NO)][[(SiMe2)2(η5-C5-H5)2]] complexes (see Scheme 5 for cis compounds) by reactions with the p-MeC6H4SO2N((NO)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 isonoyde adducts with PCl5 took place with partial loss of the ligand, leading to the formation of the 18-electron dichloro-nitrosyl-isonoyde 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 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

![Diagram]

Scheme 5.
the \textit{cis} 16 complex, with the two almost exactly coplanar cyclopentadienyl rings.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{complex_16}
\caption{ORTEP representation of complex \textit{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).}
\end{figure}

**Heterodinuclear compounds containing the bridging ligand**

Recently we also isolated \textit{13} new \textit{cis} and \textit{trans} heterodinuclear compounds containing group 4 and group 6 metal fragments (Scheme 6). Reacting [Mo(CO)\textsubscript{5}mesitylene] and M(CO)\textsubscript{5}(MeCN)\textsubscript{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 \textit{cis} 25, \textit{cis} 26, \textit{trans} 25, and \textit{trans} 26 compounds \{[TiCp\textsubscript{5}Cl\textsubscript{2}][M(CO)\textsubscript{5}H]\}, although the reasons for the selective formation of the \textit{cis} or the \textit{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-\(\eta^2\)-dicyclopentadienyl ligand.

The \textit{1}H NMR spectra of both \textit{cis} and \textit{trans} compounds show two AA'BB' 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 \textit{trans} isomers. The molecular structure of complex \textit{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 \textit{cis} 26 reacts with dichloromethane to give the carbonyl derivative \textit{cis}–\{[TiCpCl\textsubscript{2}][WCl\textsubscript{2}(t-BuN)] \([\text{SiMe}_2]_2(\eta^2-C_2H_2)_2]\} \textit{cis} 27 which can be oxidized with PCl\textsubscript{3} to give the paramagnetic tetrachloro-tungsten complex \textit{cis}–\{[TiCpCl\textsubscript{2}](WCl\textsubscript{2})(\text{SiMe}_2)_2(\eta^2-C_2H_2)_2]\}. Complex \textit{cis} 28 reacts with t-BuNH\textsubscript{2} to give the imido derivative \textit{cis}–\{[TiCpCl\textsubscript{2}][WCl\textsubscript{2}(t-BuN)] \([\text{SiMe}_2]_2(\eta^2-C_2H_2)_2]\} \textit{cis} 29, which can be further oxidized with PCl\textsubscript{3} to yield the tungsten(VI) compound \textit{cis}–\{[TiCpCl\textsubscript{2}][XCl\textsubscript{2}(t-BuN)] \([\text{SiMe}_2]_2(\eta^2-C_2H_2)_2]\} \textit{cis} 30. All these compounds were identified by their analytical composition and the diamagnetic derivatives were structurally characterized by NMR spectroscopy.
Group 4 metalloocene-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 metalloocene represented by the recently reported titanium \(^{14}\), zirconium \(^{15}\), and hafnium \(^{16}\) derivatives (Scheme 7).

![Scheme 7](image)

More recently \(^{17}\) we isolated new zirconium complexes with \(\beta\)-containing alkyl substituents. Reacting toluene solutions of \([\text{ZrCl}_2(\text{SiMe}_2)_2(\eta^2-\text{C}_5\text{H}_5)_2])^{15b}\) with one equivalent of MgCICl (R = Et, n-Pr, i-Pr) at temperatures lower than 15°C led to the chloro-alkyl complexes \([\text{ZrCl}(\text{SiMe}_2)_2(\eta^2-\text{C}_5\text{H}_5)_2])\) (R = Et 31, n-Pr 32, i-Pr 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 33 contain a mixture of the n-Pr and the i-Pr derivatives in an equilibrium determined by \(\beta\)-hydrogen elimination. Thermal decomposition of the diethyl complex 34 led to the formation of the dinuclear \([\text{ZrCl}_2(\mu-\text{C}_5\text{H}_5)_2(\text{SiMe}_2)_2(\eta^2-\text{C}_5\text{H}_5)_2])\) 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 31 and 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. Martin, 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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