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Process for preparing transition metal complexes containing 1,3-disubstituted cyclopentadienyl ligands

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(71) Applicant(s)
Witco GmbH

(72) Inventor(s)
Richard Lisowsky

(74) Agent/Attorney
DAVIES COLLISON CAVE,GPO Box 3876,SYDNEY NSW 2001

(56) Related Art
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(12) PATENT ABSTRACT (11) Document No. AU-A-40612/95
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(54) Title
PROCESS FOR PREPARING TRANSITION METAL COMPLEXES CONTAINING 1,3-DISUBSTITUTED CYCLOPENTADIENYL LIGANDS

(51)[6] International Patent Classification(s)
C07F 017/00 **C07F 017/02**

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(71) Applicant(s)
WITCO GMBH

(72) Inventor(s)
NAME NOT GIVEN

(74) Attorney or Agent
DAVIES COLLISON CAVE , GPO Box 3876, SYDNEY NSW 2001

(57)

The invention relates to an improved process which, starting from 2-cyclopenten-1-ones substituted in the 3 position, gives high yields of 1,3-dialkylcyclopentadienes which are directly metallated and reacted to give the corresponding 1,3-dialkylcyclopentadienyl-transition metal complexes.

Abstract:

Process for preparing transition metal complexes containing 1,3-disubstituted cyclopentadienyl ligands

The invention relates to an improved process which, starting from 2-cyclopenten-1-ones substituted in the 3 position, gives high yields of 1,3-dialkylcyclopentadienes which are directly metallated and reacted to give the corresponding 1,3-dialkylcyclopentadienyl-transition metal complexes.

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ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Applicant(s): Witco GmbH
Ernst-Schering-Strasse 14
D-59192 BERGKAMEN
GERMANY

Address for Service: DAVIES COLLISON CAVE
Patent & Trade Mark Attorneys
Level 10, 10 Barrack Street
SYDNEY NSW 2000

Invention Title: Process for preparing transition metal complexes containing 1,3-disubstituted cyclopentadienyl ligands

The following statement is a full description of this invention, including the best method of performing it known to me:-

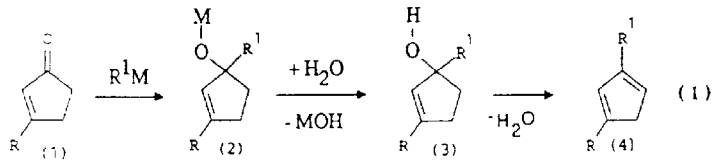
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Process for preparing transition metal complexes containing 1,3-disubstituted cyclopentadienyl ligands

The invention relates to an improved process which, starting from 2-cyclopenten-1-ones substituted in the 3 position, gives high yields of 1,3-dialkylcyclopentadienes which can be directly metallated and converted into the corresponding 1,3-dialkylcyclopentadienyl-transition metal complexes.

Owing to the wide variety of possible uses of the abovementioned transition metal complexes as catalysts in organic synthesis and, in particular, in the polymerization of olefins, the efficient industrial preparability of sandwich complexes which are disubstituted on the cyclopentadienyl radicals has become increasingly important (EP-A-0 128 045, EP-A-0 366 290, EP-A-0 283 739, EP-0 582 480, US-A 4 874 880).

The preparation of such compounds is known in principle. The procedure according to equation 1 can generally be used for this purpose,



(I)

where

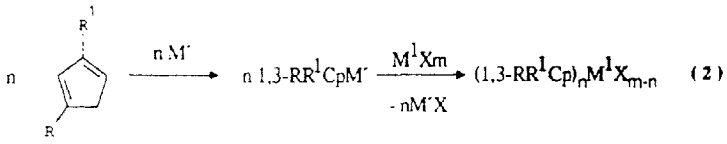
M can be Li, MgCl, MgBr,

R, R^1 (identical or different) can be alkyl or aryl

radicals.

A disadvantage of this procedure was hitherto that after the reaction of 3-alkylcyclopenten-1-ones with Grignard compounds or lithium alkyls, the resulting alkoxide (2) first had to be hydrolyzed by means of water and isolated as alcohol (3) before, after separate catalytic dehydration and work-up, the desired 1,3-dialkylcyclopentadiene component (4) was then obtained and could only be used for the further reaction after separate drying (Tetrahedron 1965, 21, 2313; Chem. Ber. 1976, 109, 329; J. Organomet. Chem., 1991, 417, 9).

It was therefore an object of the invention to simplify the reactions I., II. and III. (equation 1) to such a degree as to provide a process which allows, in one reaction without isolation of the intermediates, the synthesis of high yields of 1,3-disubstituted cyclopentadienes which can then be reacted to give the corresponding transition metal complexes, e.g. according to equation 2:



M' = metallating agent

M^1 = transition metal

X = Cl, Br, I

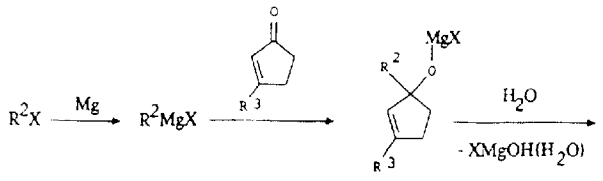
m = oxidation state of M^1

n ≤ m

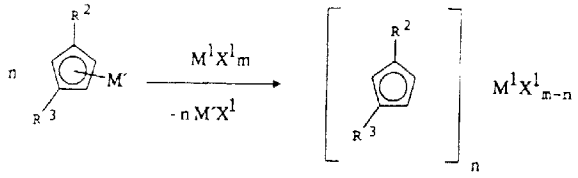
It has now surprisingly been found that the above reaction (equation 1) for preparing 1,3-dialkylcyclopentadienes allows, particularly when using Grignard compounds, the formation of the alcohol and the dehydration in an advantageous manner in situ without isolation of intermediates.

Furthermore, the magnesium salt thus formed simultaneously acts as desiccant and thus allows the immediate use of the solution obtained for preparing 1,3-dialkylcyclopentadienyl-transition metal complexes, since, owing to the solution of 1,3-dialkylcyclopentadiene being formed in anhydrous form, the latter can be treated immediately with moisture-sensitive metallating agents (Na, NaH, Li alkyls), converted into 1,3-RR^1CpM' and then reacted by conventional methods with transition metal salts (equation 3):

1.)



2.)



where R^2, R^3 = independently of one another, C_1-C_{20}, substituted or unsubstituted, alkyl, alkenyl cycloalkyl, aryl arylalkyl radicals,

X = Cl, Br, I

M' = metallating agent such as Li, Na, K, NaH, KH, Li alkyls

M^1 = Sc, Ti, Zr, Hf, Fe, V, Cr

X^1 = Cl, Br, I

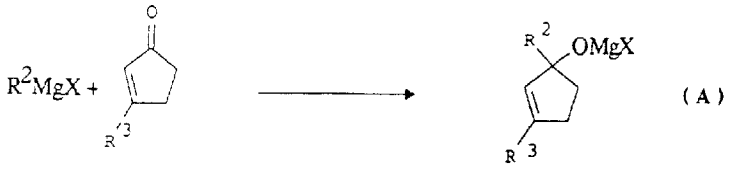
m = oxidation state of M^1

n ≤ m.

The reaction procedure of the invention according to equation 3 is not possible for the processes of the prior art, since the alcohol prepared according to

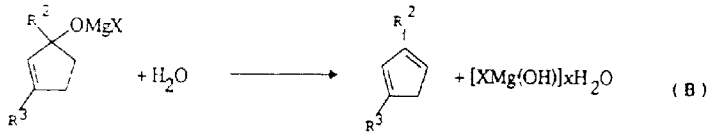
equation 1, stage II, first has to be isolated and subsequently separately dehydrated according to equation 2, stage III, and the water liberated in this reaction has to be completely removed before the further reaction according to equation 2 can be carried out to give the transition metal complexes.

The invention provides a process for preparing 1,3-disubstituted cyclopentadienyl-transition metal complexes, which is characterized in that, in a first stage, cyclopent-2-en-1-ones substituted in the 3 position are reacted with Grignard compounds according to equation (A)



(A)

and the alkoxides formed are hydrolyzed with stoichiometric amounts of water and dehydrated in a step according to equation (B)



(B)

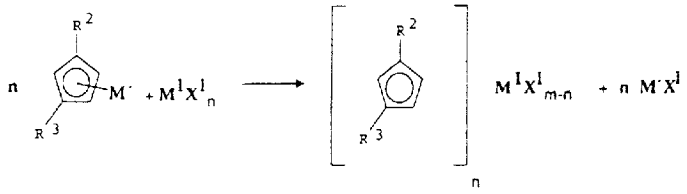
where R^2, R^3, independently of one another, C_1-C_{20}, substituted or unsubstituted alkyl, alkenyl cycloalkyl, aryl arylalkyl radicals,

X = Cl, Br, I

and, in a second stage, directly metallated by methods known per se according to equation (C)



(C)



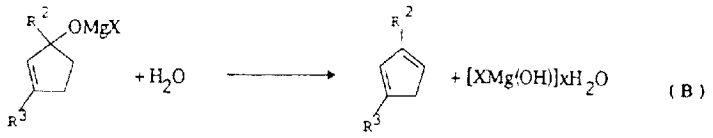
where M′ is metallating agent, M^1 is Sc, Ti, Zr, Hf, Fe, V Cr, X^1 is Cl, Br, I, m is oxidation state of M^1, $n \leq m$, and reacted with transition metal halides to give the corresponding complexes.

The invention also provides a process for preparing 1,3-disubstituted cyclopentadienyl compounds, characterized in that , in a first stage, cyclopent-2-en-1-ones substituted in the 3 positions are reacted with Grignard compounds according to the equation (A)



(A)

and the alkoxides formed are hydrolyzed with stoichiometric amounts of water and dehydrated in a step according to equation (B)



(B)

where R^2, R^3, independently of one another, are C_1-C_{20} substituted or unsubstituted alkyl, alkenyl-, cycloalkyl-,-aryl-, or arylalkyl radicals, and X is Cl, Br or I

Other aspects of the invention are described hereinafter.

The Grignard compounds R^2MgX used according to equation (A) are commercial products or can be prepared by the generally well known methods by reaction of the corresponding organochlorine, organobromine or organoiodine compounds with metallic magnesium as described for example, in Houben-Weyl, Volume XIII/2a -

Metallorganische Verbindungen Be, Mg, Ca, Sr, Ba, Zn, Cd; p. 47 - Organomagnesiumverbindungen - Georg Thieme Verlag Stuttgart - 1973.

Preference is given to using compounds R^2MgX in which R^2 is a substituted or unsubstituted alkyl radical or cycloalkyl radical having 1 to 20 carbon atoms.

The cyclopent-2-en-1-ones substituted in the 3 position which are used according to the invention can be prepared by literature methods (J. Chem. Soc., 1952, 1127; German Laid-Open Application (DE-OS) 23 12 504; Tetrahedron Lett., 1965, 21, 2313; Synthesis, 1972, 397; Bull. Soc. Chiem., 1970, 2981). The radicals R^3 are substituted or unsubstituted alkyl, alkenyl, cycloalkyl, aryl or arylalkyl radicals having 1 to 20 carbon atoms, with compounds in which R^3 is methyl or phenyl radical being particularly preferred according to the invention.

The reaction of the Grignard compounds with the cyclopent-2-en-1-ones substituted in the 3 position is preferably carried out in a molar ratio of 1:1 in ethers, preferably in diethyl ether, tert-butyl methyl ether and, in particular, tetrahydrofuran, at temperatures of from -20°C to 120°C, preferably from 0°C to 70°C.

The cyclopentenone compounds, if desired dissolved in ether, is [sic] metered continuously or in portions into the ethereal solution of the Grignard compound and the reaction mixture is continued [sic] for about one to three hours after addition is complete.

After the reaction is complete, the magnesium alkoxide formed is hydrolyzed at room temperature by

addition of a preferably stoichiometric amount of water. The hydrolysis and dehydration taking place in one step are finally completed at elevated temperatures of about 20 - 100°C, preferably at about 70°C, for 1 - 3 h.

The hydrolysis and dehydration steps of reaction (B) is performed in a ratio of hexane and/or heptane:ether = 1:1 to 4:1.

The magnesium salt formed completely binds the water present in the reaction mixture, so that cooling to room temperature and removal of the precipitated magnesium salt gives a clear, solid-free and water-free solution which can be used directly for the reaction with a metallating agent and can then be reacted with a transition metal halide according to equation (C) to give the corresponding transition metal complexes.

This reaction is carried out by generally known methods as are described, for example, in "Chemistry of organozirconium and -hafnium compounds", D.J. Cardin, M.F. Lappert, C.L. Raston; 1986, Ellis Horwood Limited; "Organometallic Chemistry of Titanium, Zirconium, and Hafnium" 1974 - Academic Press New York and London, P.C. Wailes, R.S.P. Coutts, H. Weigold; Gmelin - Handbuch der anorganischen Chemie - Supplement to 8th edition - Volumes 10 and 11, "Zirconium- and Hafnium organische Verbindungen", p. 26 ff - Verlag Chemie, Weinheim - 1973.

Examples

1. Preparation of bis(1-methyl-3-octylcyclopentadienyl)zirconium dichloride

17.26 g (0.71 mol) of magnesium turnings were introduced into 30 ml of tetrahydrofuran (THF), and 2 g of octyl bromide were added to initiate the Grignard

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reaction. After the Grignard had started, the remaining octyl bromide (total of 115.9 g; 0.6 mol) dissolved in 70 ml of THF was metered in in such a way that gentle refluxing occurred.

After addition was complete, the mixture was allowed to react further for another 2 h under reflux.

The mixture was then cooled to 0°C and the 3-methyl-2-cyclopenten-1-one (0.5 mol, 48.1 g), dissolved in 20 ml of THF and 80 ml of hexane, was added at this temperature.

After the metered addition, the mixture was allowed to react further for 3 h at room temperature (RT).

At RT, 170 ml of hexane and the stoichiometric amount of water necessary for the hydrolysis (0.6 mol, 10.8 g) were then added.

After addition was complete, the mixture was refluxed for another 2 h, subsequently cooled to RT and the magnesium salt was removed. The clear, solids-free filtrate was introduced first, and butyllithium (2.5 molar in hexane, 0.4 mol, 160 ml) was added at RT over a period of 30 minutes. The mixture was stirred further for 1 h at 50°C.

46.6 g of zirconium tetrachloride (0.2 mol) were then added at 0°C, the mixture was stirred for 1 h at RT and for 2 h under reflux.

The precipitated LiCl was subsequently removed and the solvent was distilled off.

The remaining residue was recrystallized from

hexane. This gave 77.4 g of product (yield: 71%)

Zr (calc.: 16.74) found: 16.9

Cl (calc.: 13.02) found: 13.3

^{1}H-NMR: ($CDCl_3$)

6.1 - 5.8 (m, 6 H, Cp); 2.6 - 2.35 (m, 4H, $-CH_2-$); 2.2 (s, 6 H, $-CH_2$);

1.6 - 1.1 (m, 24 H, $-(CH_2)_6-$); 0.85 (t, 6 H, $-CH_3$)

2. **Preparation of bis(1-i-butyl-3-methylcyclopentadienyl)zirconium dichloride**

Procedure and starting materials as in 1.); except that 0.6 mol of i-butyl chloride was used in place of the octyl bromide. This gave 61.4 g of product (yield: 71%)

Zr (calc.: 21.1) found: 20.8

Cl (calc.: 16.4) found: 16.1

^{1}H-NMR: ($CDCl_3$)

(see Fig. 1)

3.a) **Preparation of bis(1-n-butyl-3-methylcyclopentadenyl)zirconium dichloride**

Procedure and starting materials as in 1.); 0.6 mol of n-butyl chloride was used in place of octyl bromide. This gave 67.5 g of product (yield: 78%)

Zr (calc.: 21.1) found: 20.7

Cl (calc.: 16.4) found: 16.1

^{1}H-NMR: ($CDCl_3$)

6.1 - 5.9 (m, 6 H, Cp); 2.65 - 2.38 (m, 4 H, $-CH_2-$); 2.2 (s, 6 H, $-CH_3$);

1.6 - 1.25 (m, 8 H, $-CH_2CH_2-$); 0.9 (t, 6 H, $-CH_3$)

3.b) Preparation of bis(1-n-butyl-3-methylcyclopentadienylzirconium dichloride with isolation of the intermediate 1-n-butyl-3-methylcyclopentadiene

19.44 g of magnesium turnings (0.8 mol) were introduced into 40 ml of THF, and 1 g of n-butyl chloride was added to initiate the Grignard reaction.

After the Grignard reaction had started, a further 63.8 g of n-butyl chloride (total of 0.7 mol), dissolved in 150 ml of tetrahydrofuran, were added dropwise in such a way that gentle refluxing occurred.

After addition was complete, the mixture was reacted further for another 2 h under reflux. It was then cooled to 0°C and 67.3 g of 3-metyl-2-cyclopenten-1-one [sic] (0.7 mol), dissolved in 40 ml of tetrahydrofuran and 140 ml of hexane, were metered in.

The mixture was subsequently stirred at RT for another 2 h.

200 ml of hexane were then added at RT and 12.6 g (0.7 mol) of H_2O were slowly metered in.

After the addition of the water, the mixture was refluxed for another 1 h. After cooling to RT, the precipitated magnesium salts were removed and the filtrate was freed of solvent. The residue remaining after stripping off the solvent was examined by means of ^{1}H-NMR and showed absolutely no remaining undehydrated alcohol, 1-n-butyl-3-methylcyclopent-2-en-1-ol [see Figure 2.) and compare also reaction using n-butyllithium in place of n-butyl-Grignard - 4.) comparative example to 3.b)]

The residue was then distilled at 45°C/mbar

[sic]. This gave 85 g of distillate.

70 g of the distillate were introduced into 200 ml of pentane and 26 ml of tetrahydrofuran and, at RT, 146 ml of butyllithium (2.5 molar in hexane; 0.365 mol) were added dropwise. After addition of the butyllithium, the mixture was refluxed for another 30 min. 42.5 g (0.183 mol) of zirconium tetrachloride were introduced into the reaction mixture which had been cooled to 0°C. It was then refluxed for another 1 hour.

After cooling to RT, the precipitated LiCl was removed and the filtrate was cooled to -20°C. The precipitated product was filtered off and dried.

This gave 65.5 g of product (83% of theory)

^{1}H-NMR identical to that in Example 3.a)

4. Comparative Example to 3.b): butyllithium was used in place of Grignard

41.6 ml of butyllithium (2.5 molar in hexane; 104 mmol) were introduced first at -10°C.

Over a period of 45 min, a mixture of 27 ml of hexane, 9 ml of THF and 10 g of 3-methyl-2-cyclopenten-1-one (0.104 mol) was added dropwise. After the addition was complete, the mixture was stirred for 4 h at RT. 1.87 g of water (0.104 mol) were then added dropwise, the mixture was stirred for 1 h at RT and for 1 h under reflux, cooled and filtered. The filtrate was freed of solvent and examined by means of ^{1}H-NMR. Only the pure alcohol 1-n-butyl-3-methylcyclopent-2-en-1-ol was detectable.

^{1}H-NMR ($CDCl_3$): (see Figure 3.)

Dehydration had not occurred and thus 1-butyl-3-methylcyclopentadiene had not been formed.

5. Preparation of bis(1-ethyl-3-methylcyclopentadienyl)zirconium dichloride

Procedure and starting materials as in 1.); 0.6 mol of ethyl bromide was used in place of octyl bromide. This gave 51.2 g of product (yield: 68%)

Zr (calc.: 24.23) found: 23.5

Cl (calc.: 18.83): found: 18.6

^{1}H-NMR: ($CDCl_3$):

6.1 - 5.9 (m, 6 H, Cp); 2.72 - 2.49 (m, 4 H, CH_2-); 2.2 (s, 6 H, -CH_3):

1.15 (d, 6 H, -CH_3)

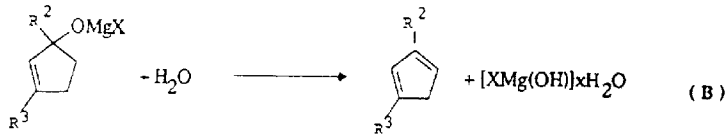
The claims defining the invention are as follows:

1. Process for preparing 1,3-disubstituted cyclopentadienyl-transition metal complexes, characterized in that, in a first stage, cyclopent-2-en-1-ones substituted in the 3 position are reacted with Grignard compounds according to equation (A)



(A)

and the alkoxides formed are hydrolyzed with stoichiometric amounts of water and dehydrated in a step according to equation (B)



(B)

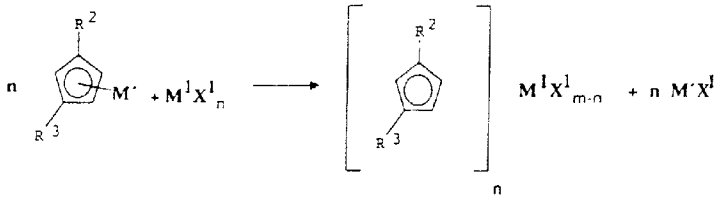
where R^2, R^3, independently of one another, C_1-C_{20}, substituted or unsubstituted alkyl, alkenyl cycloalkyl, aryl, arylalkyl radicals,

X = Cl, Br, I

and, in a second stage, directly metallated by methods known per se according to equation (C)



(C)



where M' = metallating agent

M^1 = Sc, Ti, Zr, Hf, Fe, V, Cr

X^1 = Cl, Br, I

m = oxidation state of M^1

n ≤ m

and reacted with transition metal halides to give the corresponding complexes.

2. Process for preparing 1,3-disubstituted cyclopentadienyl-transition metal complexes according to claim 1, characterized in that the Grignard compounds R^2MgX used are compounds in which R^2 is an n-butyl, i-butyl, n-octyl radical.

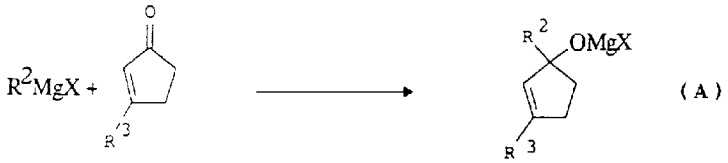
3. Process for preparing 1,3-disubstituted cyclopentadienyl-transition metal complexes according to claim 1, characterized in that the substituted cyclopent-2-en-1-one compounds used are ones in which R^3 is a methyl or phenyl radical.

4. A process for preparing 1,3-disubstituted cyclopentadienyl-transition metal complexes according to claim 1, characterized in that the Grignard compound R^2MgX in equation (A) is used in tetrahydrofuran as solvent.

5. A process for preparing 1,3-disubstituted cyclopentadienyl-transition metal complexes according to claim 1, characterized in that the reaction (B) is carried out in a ratio of hexane and/or heptane:ether = 1:1 to 4:1.

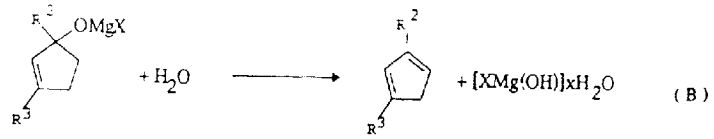
6. A process for preparing1,3-disubstituted cyclopentadienyl-transition metal complexes according to claim 1, characterized in that the cyclopentadiene derivative CpR^2R^3 obtained according to reaction (B) is isolated before the further reaction.

7. A process for preparing 1,3-disubstituted cyclopentadienyl compounds, characterized in that , in a first stage, cyclopent-2-en-1-ones substituted in the 3 positions are reacted with Grignard compounds according to the equation (A)



(A)

and the alkoxides formed are hydrolyzed with stoichiometric amounts of water and dehydrated in a step according to equation (B)



(B)

where R^2, R^3, independently of one another, are C_1-C_{20} substituted or unsubstituted alkyl, alkenyl-, cycloalkyl-, aryl-, or arylalkyl radicals, and X is C1, Br or I.

8. A process for preparing 1,3-disubstituted cyclopentadienyl-compounds according to claim 7, characterized in that the Grignard compounds R^2MgX used are compounds in which R^2 is a n-butyl, i-butyl or n-octyl-radical.

9. A process for preparing 1,3-disubstituted cyclopentadienyl-compounds according to claim 7, characterized in that R^3 is a methyl or phenyl radical.

10. A process for preparing 1,3-disubstituted cyclopentadienyl-compounds according to claim 7, characterized in that the Grignard compound R^2MgX in equation (A) is dissolved in tetrahydrofuran.

11. 1,3-disubstituted cyclopentadienyl-transition metal complexes when prepared according to any one of claims 1 to 6.

12. A process for producing 1,3-disubstituted cyclopentadienyl-transition metal complexes according to any one of claims 1 to 6 substantially as hereinbefore described with reference to the Examples.

DATED this 24th day of February 1999

WITCO GMBH

By their Patent Attorneys
DAVIES COLLISON CAVE

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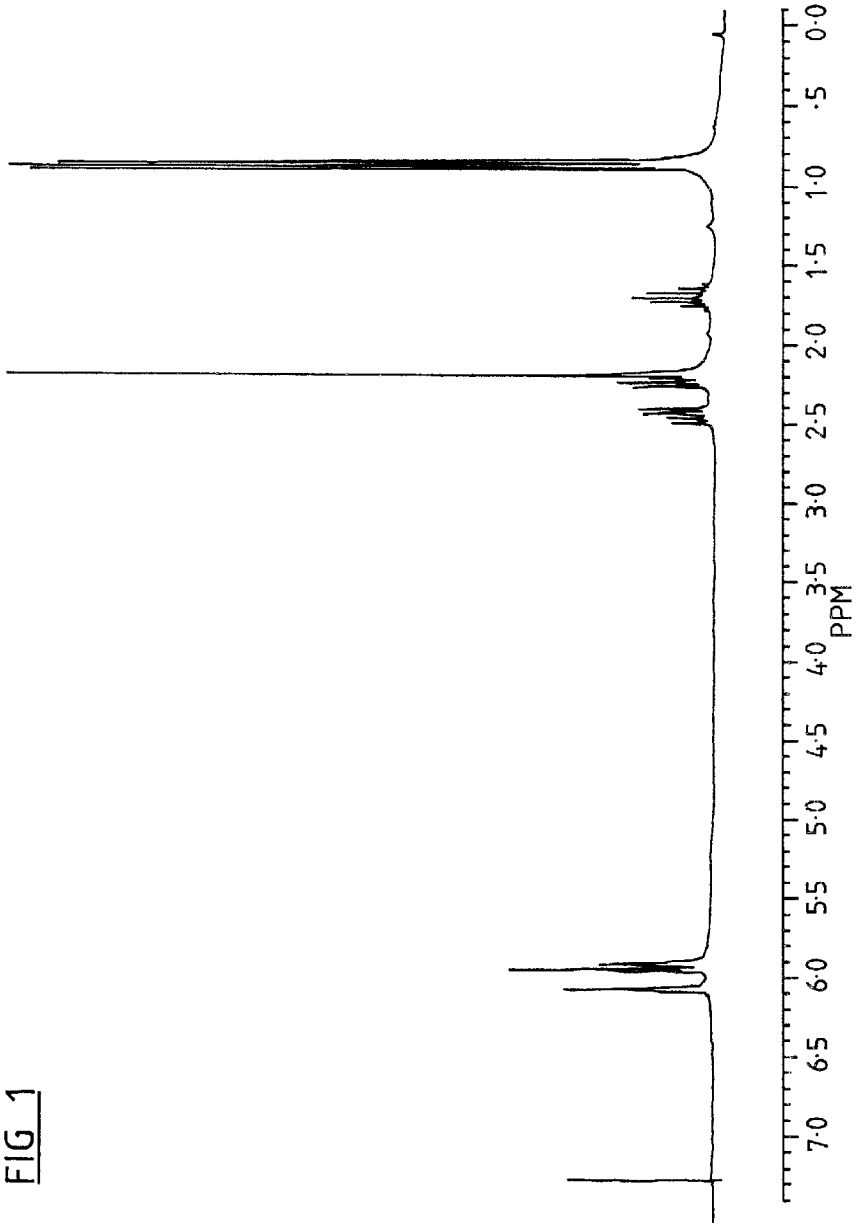


FIG 1

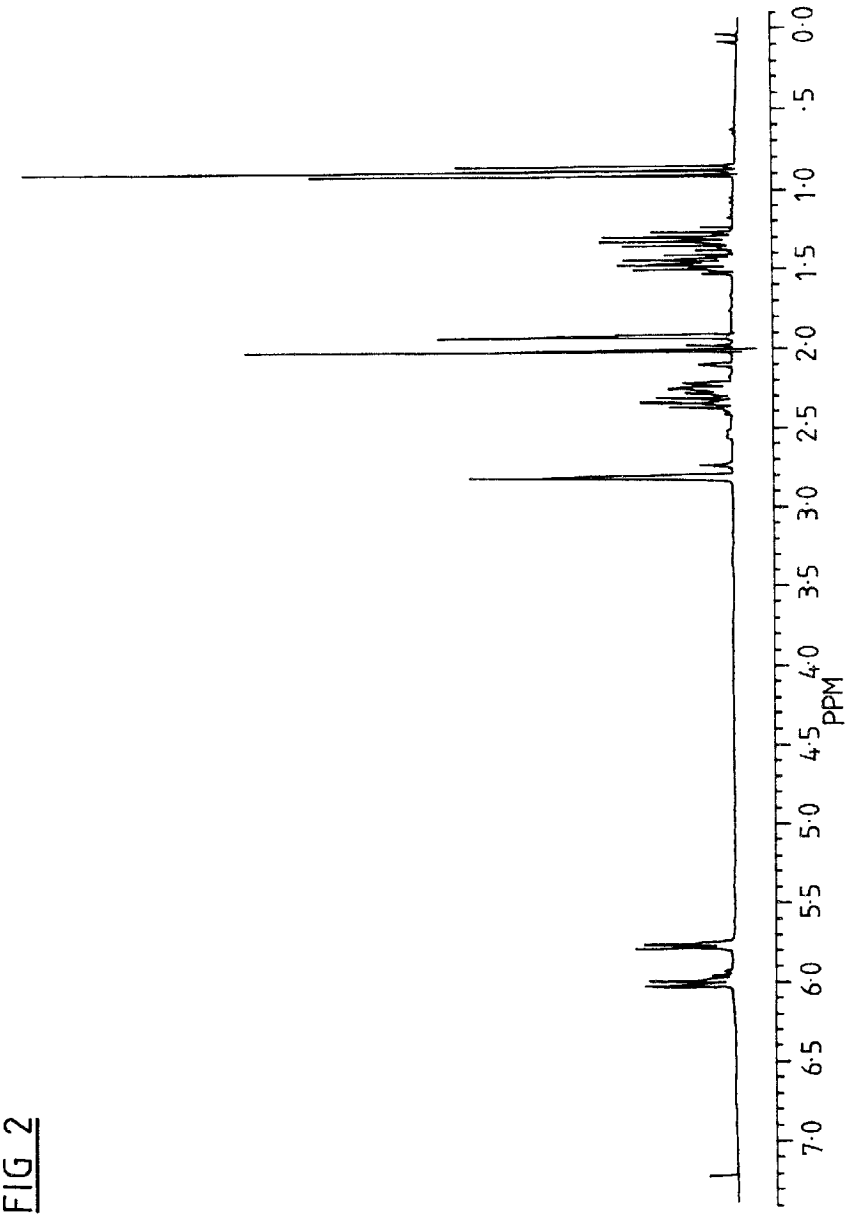


FIG 2

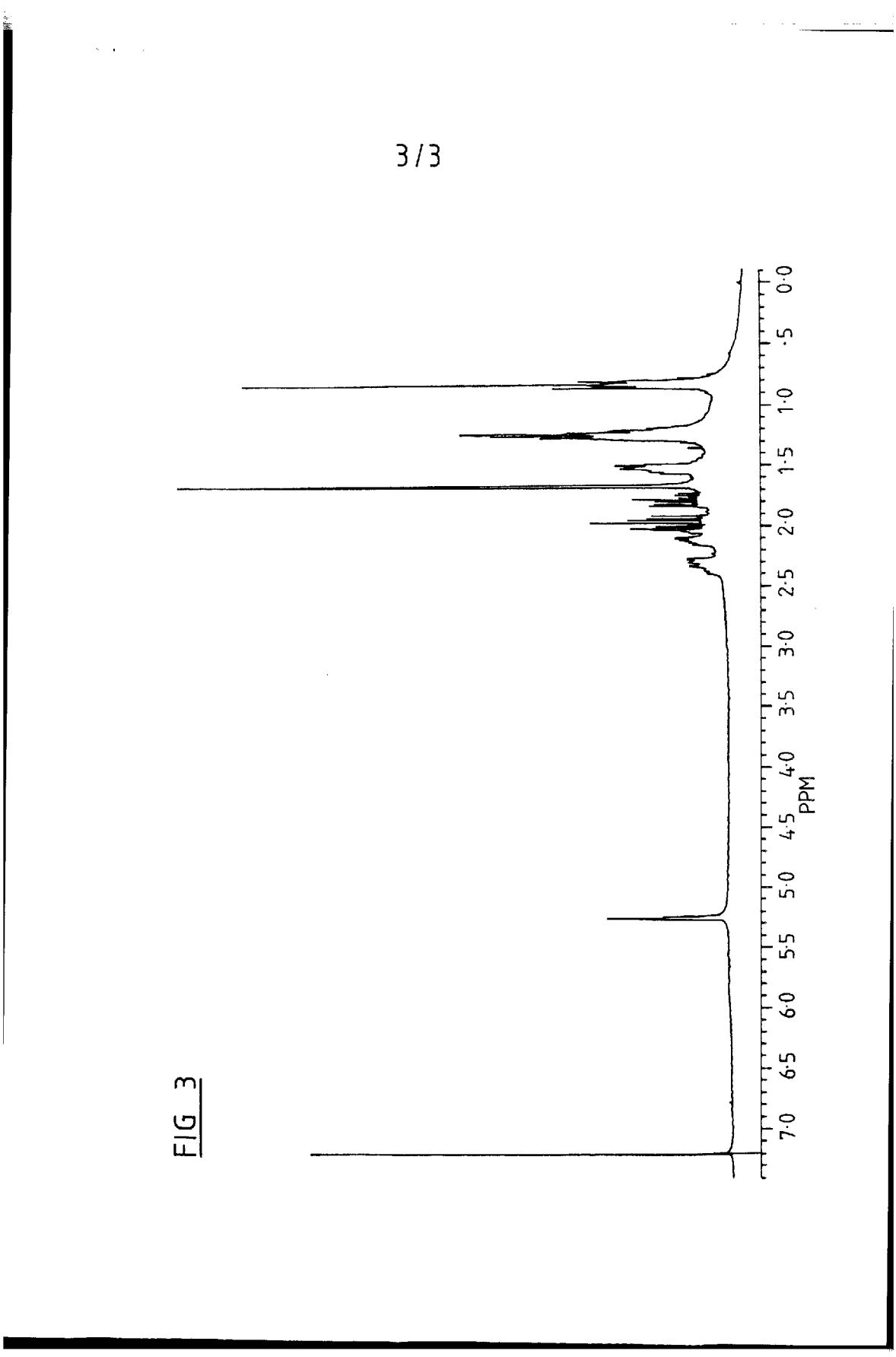


FIG 3