Journal of Organometallic Chemistry, 321 (1987) 327–334
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

USE OF AN OPTICALLY ACTIVE GERMANIUM SPECIES FOR THE RESOLUTION OF DIASTEREOISOMERIC TRANSITION METAL COMPLEXES WITH FIVE DIFFERENT AND INDEPENDENT LIGANDS *

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(Received September 22nd, 1986)

Summary

Reaction of optically active MePh(1-$C_{10}H_7$)GeLi with (η^5-C_5H_5)M$(CO)_2$NO (M = Mo, W) results in replacement of CO and formation of anionic species which can be alkylated with CH_3I to afford mixtures of diastereoisomeric complexes, (η^5-C_5H_5)M(CO)(NO)(GeR_3)CH_3 (R_3 = MePh(1-$C_{10}H_7$); M = Mo, W). These complexes are the first in which a transition metal, surrounded by five different ligands shows optical activity. These compounds are not fluxional and show a high optical stability; under forcing conditions decomposition occurs before epimerisation.

Introduction

Optically active transition metal complexes are of much interest [2,3], and a few have been obtained with a square pyramidal geometry. However, up to now, all such complexes contain two identical ligands in order to restrict the number of the possible isomers (30 isomers could exist) [4]. The introduction of a η^5-cyclopentadienyl ligand should lead to a four legged piano stool geometry with 6 possible isomers (i.e. 3 pairs of enantiomers) [5]. Brunner and coworkers [3] restrict the number of isomers to 2 enantiomers by introducing a chelate ligand.

In earlier work [6,7] we described the alkylation of anionic species, as shown in Scheme 1 and observed the formation of 3 geometrical isomers which are configurationally stable up to 100°C. The chirality at the transition metal has been recorded by the magnetic non-equivalence of the CH_2 protons in the benzyl derivative, which shows that each isomer exists as an enantiomeric pair. Under the conditions used [7], only the isomer in which CO and NO are *trans* to each other can be obtained.

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* For a preliminary communication see ref. 1.

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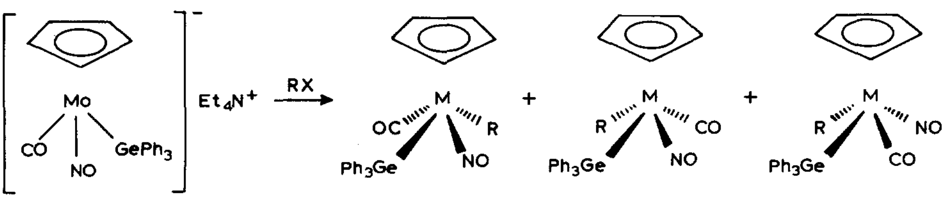


(M = Mo , W ; RX = CH_3I , $PhCH_2Br$)

SCHEME 1

In separate work we have studied the introduction of optically active germanium ligands into transition metal complexes [8] by replacement of a CO ligand. We now report the resolution of diastereoisomeric molybdenum and tungsten species by means of optically active germanium ligands and describe their properties.

Experimental

All experiments were carried out under nitrogen, by standard vacuum line techniques. Solvents were dried, distilled and deoxygenated. Starting materials were commercial products or were prepared by literature methods.

Melting points were taken under vacuum in a Tottoli apparatus and are uncorrected. IR spectra were recorded with a Perkin–Elmer 298 spectrophotometer and NMR spectra with a Varian EM 360 spectrometer. Optical rotations were measured with a Perkin–Elmer 141 polarimeter, ORD spectra were recorded with a Spectropol 1 spectropolarimeter.

Synthesis and resolution of diastereoisomers

The synthesis and resolution of SP5-25-CS(+) and SP5-25-AS(−) (methylphenyl-1-naphthylgermyl)(η^5-cyclopentadienyl)nitrosylcarbonylmethyltungsten are described to illustrate the method.

Optically active MePh-1-$C_{10}H_7$GeLi was prepared by mixing (*R*)-MePh-1-$C_{10}H_7$GeH [9] ($|\alpha|_D^{25}$ + 26°, 2.93 g, 10 mmol) in 20 ml of ether with 10 mmol n-BuLi (10 ml of a 1 *M* solution in ether) then keeping the mixture for 1 h at room temperature. The solution was subsequently added dropwise to a solution of (η^5-C_5H_5)$(CO)_2$NOW [10] (3.34 g, 10 mmol) in 20 ml of ether at room temperature; gas evolution was observed. After 3 h the solvent was pumped off and the residue taken up in 50 ml of CH_2Cl_2 and a solution of 2 g of Et_4NCl in 10 ml of CH_2Cl_2 was added at room temperature. The solution was filtered through a fritted funnel (G4), the solvent pumped off, and the residue taken up in THF. After filtration, the THF was pumped off and the residue dissolved in 30 ml of CH_2Cl_2. Slow addition of 40 ml of hexane produced two layers and the mixture was left at −20°C. After 3–6 days a brown gum had separated, and was freed from solvent and dissolved in 30 ml of THF. Methyl iodide (2 ml) was added from a syringe to this solution at room temperature; after a few minutes an off-white precipitate of Et_4NI appeared and the brown solution turned orange-yellow. The solvent was pumped off and the residue taken up in toluene and filtered. The solution was concentrated and chromatographed on silicagel with toluene/hexane (1/1) as eluant. A yellow band was collected and the solvent removed to leave an orange-yellow solid residue (3.1 g, yield 51%) $|\alpha|_{\mathrm{D}}^{25} - 4.3°$ (1.88 g/l in benzene). ^{1}H NMR, δ (ppm relative to Me_4Si in C_6D_6) 6.8–8.5 (m, aromatic), 4.66 (s, C_5H_5), 1.38 (s) and 1.42 (s) (CH_3Ge), 0.85 (s) and 0.82 (s) (CH_3W). IR (CH_2Cl_2) for both diastereoisomers ν(CO) 2010, ν(NO) 1635 cm^{-1}.

This solid was dissolved in the minimum of boiling hexane and the solution left at −20°C overnight. Orange crystals were obtained, and after 3 crystallizations from toluene/hexane at −20°C these showed a constant rotation $|\alpha|_{\mathrm{D}}^{25} + 163.6°$. (1.284 g/l in benzene) m.p. 140–141°C dec. ^{1}H NMR: signals at δ 1.38 and 0.82 ppm. Analysis. Found: C, 47.11; H, 4.02; N, 2.29. $C_{24}H_{23}GeNO_2W$ calc.: C, 46.94; H, 3.75; N, 2.28%.

The mother liquors from the first crystallization were concentrated and left at −20°C, and the orange crystals obtained were recrystallized from hexane at −20°C 3 times (to constant rotation) $|\alpha|_{\mathrm{D}}^{25} - 144.0°$ (1.194 g/l in benzene) m.p. 118–120°C dec.

A similar procedure starting from (*S*)-MePh-1-$C_{10}H_7GeH$ [9] led to the diastereoisomers with $|\alpha|_{\mathrm{D}}^{25} - 154.8°$ and $|\alpha|_{\mathrm{D}}^{25} + 149.9°$.

Using the *S*-germane (10 mmol) and (η^5-C_5H_5)(CO)$_2$NOMo [10] (2.5 g, 10 mmol) the corresponding diastereoisomers were obtained (1.30 g, yield 25%). ^{1}H NMR (C_6D_6) signals at δ 7–8.3 (m, aromatic), 4.70 (s, C_5H_5), 1.37 (s) and 1.33 (s) (CH_3Ge) 0.80 (s) and 0.78 (s) (CH_3Mo). IR (CH_2Cl_2) ν(CO) 2010, ν(NO) 1650 cm^{-1}.

Less soluble isomer: cream crystals $|\alpha|_{\mathrm{D}}^{25} - 130°$. m.p. 115–116°C. ^{1}H NMR: methyl signals at δ 1.33 and 0.78 ppm. Analysis. Found: C, 54.97; H, 4.59; N, 2.48. $C_{24}H_{23}GeMoNO_2$ calc.: C, 54.80; H, 4.38; N, 2.66%.

More soluble isomer, yellow crystals, $|\alpha|_{\mathrm{D}}^{25} + 123°$, m.p. 78–80°C.

Use of *R*-germane and (η^5-C_5H_5)(CO)$_2$NOMo gave the diastereoisomers with $|\alpha|_{\mathrm{D}}^{25} + 109.3°$ and $|\alpha|_{\mathrm{D}}^{25} - 83°$, which were not crystallized to constant rotation.

Optical rotations are assembled in Table 1 and ORD spectra in Fig. 1.

TABLE 1

OPTICAL ROTATIONS [a] OF (η^5-C_5H_5)(MePh-1-$C_{10}H_7$Ge)(NO)(CO)(CH_3)M

Complex [c]	M	Isomer	$\lvert\alpha\rvert_{\mathrm{D}}^{25}$ (°)	$\lvert\alpha\rvert_{578}^{25}$ (°)	$\lvert\alpha\rvert_{546}^{25}$ (°)	$\lvert\alpha\rvert_{436}^{25}$ (°)	Concentration (g l^{-1})
1	Mo	SP5-25-CS [b]	+107.3	+117.8	+150.2	+384.9	1.052
2	Mo	SP5-25-AS [b]	−83.3	−91.4	−122.2	−246.7	1.236
3	Mo	SP5-25-AR	−130.5	−140.4	−184.4	−483.5	1.816
4	Mo	SP5-25-CR	+123.3	+134.5	+179.6	+380.5	1.792
5	W	SP5-25-CS	+163.6	+176.0	+228.2	+422.1	1.284
6	W	SP5-25-AS	−144.0	−154.9	−211.0	−238.7	1.194
7	W	SP5-25-AR	−154.8	−167.0	−220.9	−402.7	1.634
8	W	SP5-25-CR	+149.9	+160.7	+218.7	+247.2	1.294

[a] In benzene. [b] Not crystallized to constant rotation. [c] 1 and 3, 2 and 4, 5 and 7, 6 and 8 are enantiomers. Their optical rotations do not have the same absolute value owing to the small yields obtained after several crystallizations.

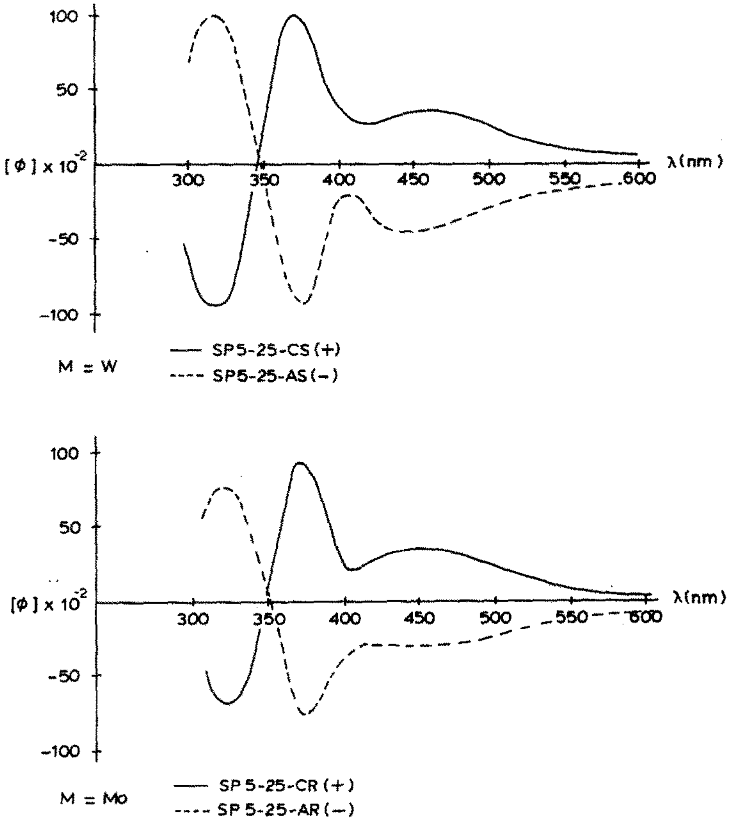


Fig. 1. ORD curves of (η^5-C_5H_5)(MePh-1-$C_{10}H_7$Ge)(NO)(CO)(CH_3)M.

Optical stability of SP5-25-CS(+) (η^5-C_5H_5*)(MePh-1-*$C_{10}H_7$*Ge)(NO)(CO)(*CH_3*)Mo*

The title compound ($\simeq$ 20 mg) was dissolved in 20 ml of benzene to give a solution with a rotation of $|\alpha|_D^{25}$ + 0.119° (cell 1 dm); after 12 h at room temperature the rotation was $|\alpha|_D^{25}$ + 0.118°. The solution was subsequently kept at 60°C; after 30 min the rotation was $|\alpha|_D^{25}$ + 0.101°, and after 1 h only $|\alpha|_D^{25}$ + 0.071°. However much decomposition was observed (the solution had to be filtered before the measurements). The solvent was pumped off, and the ^{1}H NMR spectrum of the residue was identical to that of the starting material and did not show the presence of two diastereoisomers.

Nucleophilic cleavage of SP5-25-AR(−) (η^5-C_5H_5*)(MePh-1-*$C_{10}H_7$*Ge)(NO)(CO)-(*CH_3*)Mo*

To the title compound $|\alpha|_D^{25}$ − 119.0° (139 mg, 0.26 mmol) in 30 ml, of ether at room temperature was added 80 ml of a 0.05 *M* solution of $LiAlH_4$ in ether. The mixture was stirred for 4 h and then treated with 4 *N* HCl. The organic layer was evaporated and the organogermane purified by preparative layer chromatography on silicagel with hexane/benzene 9/1 as eluant, 17.96 mg (yield 25%) $|\alpha|_D^{25}$ − 14.5°. A dihydridogermane was also detected but not identified.

Results and discussion

(a) Synthesis and resolution of diastereoisomers

The reaction of optically active germyllithium [11] with $(\eta^5\text{-}C_5H_5)(CO)_2NOM$ (M = Mo, W) results in a smooth carbon monoxide evolution and formation of the lithium salt. The lithium cation is then replaced by the tetraethylammonium cation (Scheme 2). These salts cannot, however, be crystallized and are obtained as gums which solidify on pumping off the last traces of solvent.

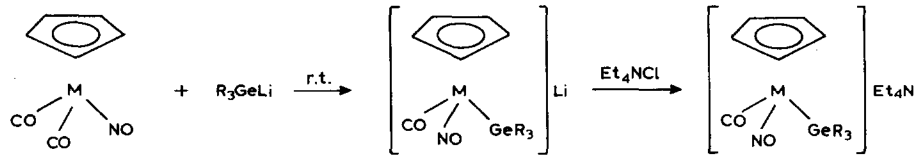
As we pointed out in an earlier paper [8], the course of the reaction may involve nucleophilic attack of the lithium compound at one carbonyl ligand followed by elimination of CO. Such nucleophilic attack on these complexes yielding carbenic species has been described previously [12].

Alkylation of the tetraethyl ammonium salts with MeI is readily carried out and two diastereoisomers are formed in equal amounts (Scheme 3).

As we pointed out above, formation of the six possible isomers [4] is avoided by introducing the germyl ligand at room temperature. This introduction takes place with retention of configuration at germanium, as was expected since optically active germyllithium always reacts with this stereochemistry either with organic substrates [11,13] or with metal carbonyls [8]. The stereochemical result was confirmed by a crystallographic study [14].

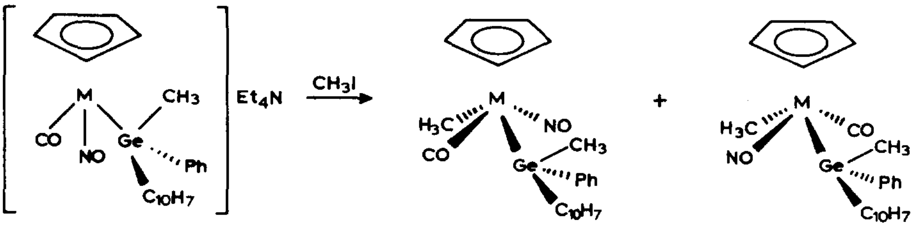
Since the transition metal complex is prochiral, two diastereoisomers are obtained and these can be separated by careful fractional crystallizations.

Attempts at resolution with optically active ammonium salts or optically active alkyl iodides or by functionalization of the cyclopentadienyl ring (with COOH and then formation of a salt of an optically active cation) were unsuccessful.



(M = Mo , W ; R = $CH_3Ph\text{-}1\text{-}C_{10}H_7$ (optically active))

SCHEME 2

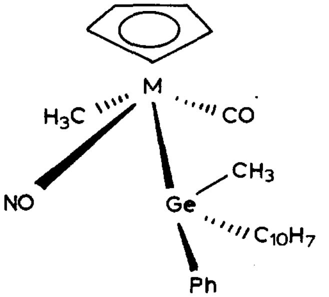


(M = Mo , W)

SCHEME 3

(b) Specification of configuration

The stereochemistry of the complexes is expressed in terms of the convention introduced by Sloan and his coworkers [15]. The configuration of the germanium atom follows that of the transition metal, according to a suggestion of Wojcicki for similar complexes with transition metal–carbon bonds [16] rather than transition metal–germanium bonds. As an example, the following complex possesses the configuration SP5-25-CS:



SP5 defines a pentacoordinated square pyramid, and the priority sequence of the ligands is Ge > C_5H_5 > NO > CO > CH_3 [17], the first digit of the configuration number is the priority number of the lone ligand. The second digit is the priority number of the atom situated diagonally opposite to the most senior ligand in the plane. The chirality symbol is derived by viewing the plane from the position of the lone axial ligand and tracing a path around the square plane from the most senior to the next most senior ligand. If this path is clockwise, C is the assigned chirality symbol; if anticlockwise, the symbol is A. S refers to the configuration at germanium.

Thus, the isomers having the configurations SP5-25-CS and SP5-25-AS are diastereoisomers, while the isomers SP5-25-CS and SP5-25-AR are enantiomers. The attributions of configurations are made by comparison with (methylphenyl-1-naphthylgermyl)(η^5-cyclopentadienyl)nitrosylcarbonylmethyltungsten ($|\alpha|_D^{25}$ + 163.6°) which is known to possess the configuration SP5-25-CS [14]. Table 1 summarizes the configurations of the obtained complexes.

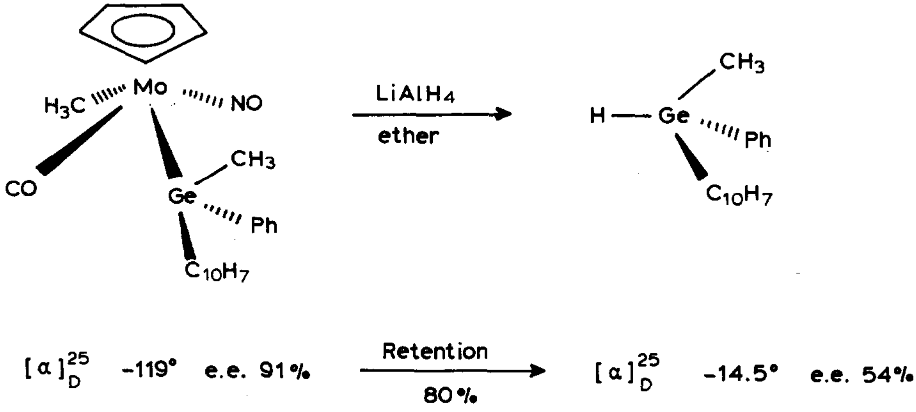
(c) Chiroptical properties

Optically active transition metal complexes have very large specific rotations compared with organic compounds [18]. These large values arise from the fact that the compounds are coloured and have a strong Cotton effect in the visible part of the spectrum.

The ORD curves for the (+) and (−) diastereoisomers, which differ in the transition metal configuration and have the same stereochemistry around germanium, are almost mirror images of each other (Fig. 1), because the ORD is mainly determined by the metal chromophore and the chirality in the germanium ligand makes only minor contributions. This behaviour has been reported previously [3,18].

(d) Configurational stability

These complexes are extremely optically stable: no epimerisation is observed in solution during 12 h at 25°C. This contrasts markedly with the observations of Brunner and coworkers on other optically active square pyramidal complexes of molydenum having five independent ligands [19].



SCHEME 4

Heating of the solution at 60°C caused a slow decomposition. After 1 h the optical rotation was only 60% of the initial value. However, this is not the result of an epimerization but is due to thermal decomposition, the NMR spectrum of the soluble residue being identical to that of the starting complex, with no trace of its diastereoisomer. This is to be compared to the thermal stability of racemic complexes in which germanium is inactive, which do not isomerize up to 100°C and decompose at ≃ 120°C in solution [6,7].

(e) Reactivity and stereochemistry of nucleophilic cleavage

The chemical reactivity of the complexes is very low: they are inert towards $AlCl_3$, HCl, I_2, Ph_3GeLi and CH_3OH. On the other hand, reaction with n-C_4H_9Li, ICl, or $SnCl_4$ leads to decomposition as does UV irradiation in the presence or absence of a phosphine. Furthermore, $LiAlH_4$ cleaves the SP5-25-AR(−) molybdenum complex to give *S*(−) germane (Scheme 4).

The stereochemistry of the cleavage is predominant retention of configuration at germanium, since the relative configurations are the same for the complex in which germanium is *R* and for the hydridogermane in which it is *S*. Since the complex $|\alpha|_D^{25} - 119°$ is diastereochemically pure (confirmed by ^{1}H NMR), its enantiomeric excess is 91% on the assumption that the maximum rotation for the complex is $|\alpha|_D^{25} - 130.5°$. When account is taken of the maximum rotation for the germane, $|\alpha|_D^{25} - 26.7°$, an enantiomeric excess of 54% corresponds to 80% of retention. The transition metal moiety could not be isolated from this reaction, an unsuccessful attempt was made to trap a possible anion with Ph_3GeBr.

Concluding remarks

The first resolutions are described of diastereoisomeric complexes of a transition metal in which the metal is chiral and bears five different and independent ligands. There has been a previous report of optically active complexes of molybdenum with five independent ligands, but two of these ligands are identical [19]. In this work an optically active organogermyl ligand has been used to resolve optically active complexes of a transition metal. The difference between this method and resolution by means of phosphines consists in the fact that the formation of the Ge–metal bond is not reversible so epimerization through a reversible process is avoided.

These complexes show a low reactivity, and no detectable epimerization is observed even at high temperature, decomposition taking place instead.

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