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Dimethylgermanethione Trapping by Benzynezirconocene. X-ray Crystal Structure of $Cp_2ZrSGe(Me)_2(o\text{-}C_6H_4)$

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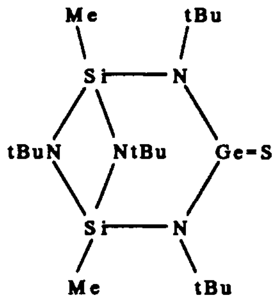
Summary: In boiling heptane the reaction of the trimer $[Me_2GeS]_3$ with bis(η^5-*tert*-butylcyclopentadienyl)diphenylzirconium, $(tBuCp)_2ZrPh_2$, led in good yield to the dimetallacycle $[(tBuCp)_2Zr—S—Ge(Me)_2(o\text{-}C_6H_4)]$ (**1**). This complex probably results from the insertion of the monomer germanethione $[Me_2Ge{=}S]$ into the Zr—C bond of the transient benzynezirconocene formed from the diphenyl complex. A similar reaction starting from $[Me_2GeS]_3$ and $Cp_2Zr(CH_3)C_6H_5$ in boiling benzene afforded the complex $Cp_2Zr—S—Ge(Me)_2(o\text{-}C_6H_4)$ (**2**). **1** and **2** have been fully characterized by ^1H NMR and mass spectrometry. An X-ray diffraction study carried out on **2** confirmed the presence of the five-membered heterocycle. Crystal data for $C_{18}H_{20}GeSZr$: orthorhombic, *Pbca*, a = 14.779 (3) Å, b = 14.810 (2) Å, c = 16.333 (3) Å, V = 3575 Å^3, Z = 8, R = 0.029.

Most of the germanethiones [$R_2Ge = S$] are known as transient species and dialkylgermanethiones have been detected by trapping in an argon matrix.[1,2] Only one cyclic germanethione has been isolated and characterized by Veith.[1]



Probably the most convenient method to obtain germanethiones involves a β-elimination reaction from suitable reagents.[4] Among these reagents, hexaalkyltrigermatrithianes affording dialkylgermanethiones by a moderate thermolysis are good candidates.[5] Dialkylgermanethiones are very easily polymerized but represent active electrophiles which readily react with many σ-bonds such as Ge–O, Si–O, Si–Cl,[5] C–O (epoxides), C–S (episulfides),[6] and some dipoles 1–3.[7]

Moreover, the transient benzynezirconocene species [the benzynebis(cyclopentadienyl)zirconium species] can result from the thermolysis of diphenylzirconocene[8–10] or methylphenylzirconocene.[11] Buchwald[12] also reported on the isolation and characterization of the benzynezirconocene in its complex with trimethylphosphine. This useful transient reagent appears very efficient regarding insertion reactions and combines with many unsaturated substrates (alkenes, alkynes, aldehydes, ketones, nitriles, etc.).[13] Because germanethione and benzynezirconocene are generated in similar conditions of thermolysis, it seemed reasonable to us to put these two unstable species together with a good chance for their combination and stabilization.

Experimental Section

Materials and Methods. All reactions were routinely carried out in Schlenk type glassware under argon. Solvents were distilled from a sodium or potassium benzophenone ketyl complex prior to use. Microanalyses were performed by the "Service d'Analyse du CNRS". Melting points were measured with a Kofler beam without any correction. ^1H NMR spectra were recorded on a Bruker WM400 spectrometer operating at 400.13 MHz and referenced to TMS (external).

^{13}C NMR spectra were recorded using a Bruker AC200 spectrometer operating at 50.32 MHz and referenced to TMS (external). Mass spectra were obtained from the "Service Central de Spectrométrie de Masse du CNRS" (electronic ionization = 70 eV).

Trimeric dimethylgermanium sulfide was prepared according to the published procedure.[14,15] Bis(*tert*-butylcyclopentadienyl)diphenylzirconium and methylphenylzirconocene were synthesized according to the literature.[16–18]

Preparation of $(tBuCp)_2ZrSGe(Me)_2(o\text{-}C_6H_4)$ (1). A solution of bis(*tert*-butylcyclopentadienyl)diphenylzirconium (0.29 g, 0.59 mmol) and trimeric dimethylgermanium sulfide (0.08 g, 0.20 mmol) in 20 mL of heptane was refluxed for 18 h. The solution had changed from colorless to pale yellow. At this time,

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Table I. Crystallographic Data for $Cp_2\overline{ZrSGe(Me)_2(o\text{-}C}_6H_4)$ (2)

molecular formula	$C_{18}H_{20}GeSZr$
fw	432.23
cryst syst	orthorhombic
space group	*Pbca* (No. 61)
cell dimens	
a, Å	14.779 (3)
b, Å	14.810 (2)
c, Å	16.333 (3)
V, Å^3	3574.8
Z	8
ρ_{calc}, g·cm^{-3}	1.606
linear abs, μ, cm^{-1}	23.375
F(000)	1728
λ(Mo Kα radiation), Å	0.71073
scan type	ω–2θ
scan speed, deg·min^{-1}	1.5–8.3
scan width, deg	$\Delta\omega = 0.9 + 0.347 \tan\theta$
octants collcd	*h* 0–17, *k* 0–17, *l* 0–19
θ range, deg	2–25
no. of reflns measd	3263
temp, K	296 (1)
decay, %	–3.2, corrected
cutoff for obsd data	$I \geq 2\sigma(I)$
no. of unique obsd data (NO)	1856
no. of variables (NV)	250
transm coeff (ψ scan)	83.554–99.997
R(*F*)	0.029
GOF	2.603
peaks in final ΔF map, e/Å^3	–0.27 to +0.31
largest Δ/σ in final cycle	0.04

the solvent was removed in vacuo to yield 0.37 g of a yellow oily residue which was 90% pure by ^{1}H NMR analysis; yield 92% (the impurity was identified as small amounts of $(Me_2GeS)_3$). ^{1}H NMR (C_6D_6): δ 0.73 (s, 6, Ge–CH$_3$), 1.26 (s, 9, tBu), 5.38 (m, 2, Cp), 5.81 (m, 2, Cp), 5.94 (m, 2, Cp), 6.44 (m, 2, Cp), 6.73–7.01 (m, 4, Ph). Mass spectrometry: *m/z* 544 (M$^{•+}$, 20), 487 (M–tBu, 15), 332 ((tBuCp)$_2$Zr, 60).

Preparation of $Cp_2\overline{ZrSGe(Me)_2(o\text{-}C}_6H_4)$ (2). A solution of methylphenylzirconocene (0.63 g, 2.01 mmol) and trimeric $(Me_2GeS)_3$ (0.28 g, 0.69 mmol) in 20 mL of benzene was refluxed for 18 h. During this time, the solution became gradually pale yellow. The solvent was removed, and the residue was washed two times with pentane. The crude product was recrystallized from a toluene/pentane 1/1 mixture leading to yellow crystals (0.56 g, yield 65%). Mp: 188–189 °C. ^{1}H NMR (C_6D_6): δ 0.74 (s, 6, Ge–CH$_3$), 5.93 (s, 10, Cp), 6.70 (d, 1, Ph, *J* = 7.3 Hz), 7.00–7.12 (m, 3, Ph). ^{13}C NMR (CDCl$_3$): δ 4.9 (Ge–CH$_3$), 113.8 (Cp), 124.3 (Ph), 126.5 (Ph), 131.8 (Ph), 137.5 (Ph). Mass spectrometry: *m/z* 432 (M$^{•+}$, 28), 417 (M – CH$_3$, 32), 402 (M – 2CH$_3$, 8), 220 (Cp$_2$Zr, 27). Anal. Calcd for $C_{18}H_{20}ZrGeS$: C, 50.00; H, 4.63. Found: C, 50.17; H, 4.74.

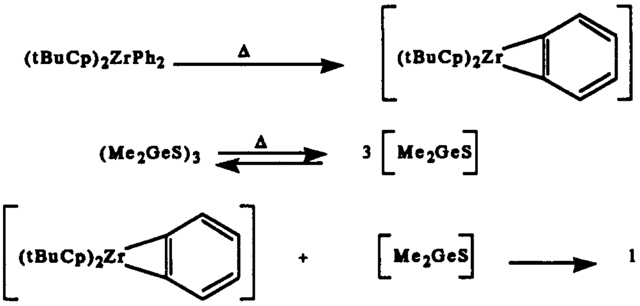
Crystallographic Studies. Crystals suitable for X-ray analysis were grown by slow cooling of a solution of 2 in a toluene/pentane 1/1 mixture. A yellow triangular prismatic crystal (approximate dimensions 0.3 × 0.3 × 0.1 mm) was mounted on an Enraf-Nonius CAD4 diffractometer. The crystal data and data collection parameters are summarized in Table I. The unit cell was determined and refined from 25 randomly selected reflections obtained by use of the CAD4 automatic routines. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction (ψ scan) was made. All calculations were carried out by use of the Enraf-Nonius SDP package.[18] Neutral-atom scattering factors and anomalous dispersion corrections were those given by Cromer and Waber.[19] The structure was solved and refined by conventional three-dimensional Patterson, difference Fourier, and full-matrix least-squares methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of all the hydrogen atoms were calculated by the HYDRO program of SDP. These atoms were refined on the carbon atoms bearing them and included in the final calculations with B_{iso} fixed at the values equal to 1.3B_{eq} for the corresponding carbon atoms (Table II).

Table II. Positional Parameters and Their Estimated Standard Deviations for $Cp_2\overline{ZrSGe(Me)_2(o\text{-}C}_6H_4)$ (2)

atom	*x*	*y*	*z*	*B*,[b] Å^2
Zr	0.24631 (4)	0.29248 (4)	0.51252 (3)	2.712 (9)
Ge	0.38648 (4)	0.41955 (4)	0.63897 (4)	3.10 (1)
S	0.3092 (1)	0.4495 (1)	0.5258 (1)	4.14 (4)
C1	0.3515 (4)	0.2294 (4)	0.5980 (3)	2.8 (1)
C2	0.4008 (4)	0.2886 (4)	0.6480 (3)	2.8 (1)
C3	0.4638 (4)	0.2566 (4)	0.7040 (4)	3.3 (1)
C4	0.4802 (4)	0.1650 (4)	0.7122 (4)	3.9 (1)
C5	0.4324 (5)	0.1052 (4)	0.6651 (4)	4.4 (2)
C6	0.3686 (4)	0.1362 (4)	0.6101 (4)	3.7 (1)
C7	0.3279 (5)	0.4706 (5)	0.7350 (4)	5.7 (2)
C8	0.5054 (4)	0.4741 (4)	0.6269 (4)	4.8 (2)
C11	0.1583 (5)	0.2473 (8)	0.6368 (5)	9.6 (3)
C12	0.1185 (5)	0.2040 (5)	0.5697 (6)	8.0 (2)
C13	0.0798 (4)	0.2706 (7)	0.5237 (5)	7.0 (2)
C14	0.0950 (5)	0.3474 (6)	0.5605 (6)	7.7 (2)
C15	0.1404 (5)	0.3365 (7)	0.6265 (5)	8.6 (2)
C16	0.3349 (5)	0.1945 (6)	0.4151 (4)	6.0 (2)
C17	0.3520 (5)	0.2776 (6)	0.3918 (4)	6.1 (2)
C18	0.2759 (7)	0.3163 (6)	0.3631 (4)	7.4 (2)
C19	0.2062 (5)	0.2529 (8)	0.3702 (4)	8.5 (3)
C20	0.2465 (7)	0.1752 (5)	0.4036 (4)	6.6 (2)
CP1[a]	0.1184	0.2811	0.5834	
CP2	0.2831	0.2433	0.3887	

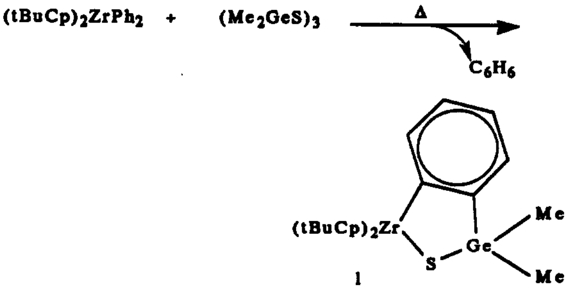
[a] CP are the gravity centers of the cyclopentadienyl rings. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Scheme I



Results and Discussion

After the reflux with heptane for 18 h, the mixture of bis(*tert*-butylcyclopentadienyl)diphenylzirconium and the trimer $(Me_2GeS)_3$ afforded a viscous yellow liquid, after the solvent was removed. The ^{1}H NMR spectrum of the liquid clearly indicated the presence of the highly preponderant compound 1 in which the sulfur atom is directly bonded to the zirconium atom (eq 1).



(1)

The formation of complex 1 is interpreted as the result of the insertion of the monomer dimethylgermanethione into the Zr–C bond of benzynezirconocene according to Scheme I.

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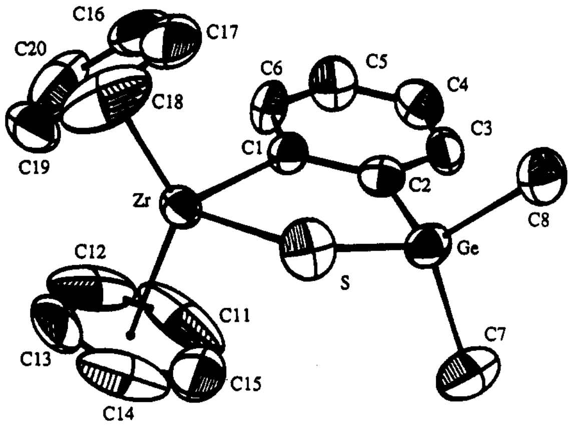
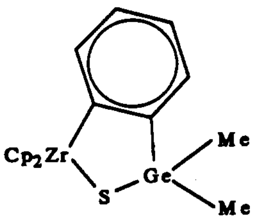


Figure 1. ORTEP drawing of $Cp_2\overline{ZrSGe(Me)_2(o\text{-}C_6H_4)}$. Thermal ellipsoids are at the 50% probability level.

To our knowledge, this is the first example of insertion of an inorganic fragment containing a heteroatom into the Zr–C bond of an arynezirconocene, to give, in this case, a dimetallacycle with both an early-transition-metal atom and a main-group metalloid atom linked together by a chalcogen and a phenyl group.

The regioisomer in which the metal is attached to the germanium atom can be immediately discarded by reference to previous results reported in the literature. As a rule, the insertion of ketones and nitriles into a Zr–C bond respectively leads to the regioselective formation of Zr–O and Zr–N bonds due to the electrophilic nature of the metal.[11,20,21]

The unsubstituted cyclopentadienyl complex 2 could not be obtained under the same experimental conditions, but it was formed as a yellow solid from refluxing $Cp_2Zr(Ph)CH_3$ and $(Me_2GeS)_3$ in benzene for 18 h. Higher temperatures only afforded an unidentified mixture.



2

The spectroscopic features for the complexes synthesized agree very well with the proposed structures. In the ^1H NMR spectra, the signal observed near 0.7 ppm clearly corresponds to the methyl protons bonded to the germanium atom. The *tert*-butyl groups appear at 1.26 ppm for complex 1, and the diastereotopic protons of the substituted cyclopentadienyl rings give, as expected, four multiplets in the range 5.4–6.4 ppm. In addition, one of the benzene protons in 1 and 2 is shielded (6.7 ppm) compared to the normal chemical shift observed for the benzene ring. This signal probably corresponds to the proton close to the zirconium atom, as suggested in the literature.[22] The shift effects are much less sensitive for the ^{13}C NMR spectra.

Structure of 2. The molecular structure of 2 (Figure 1) is typical of bent metallocenes. The coordination polyhedron around the zirconium atom defined by the cyclopentadienyl ring centroids, the sulfur, and one carbon atom of the phenyl group is a tetrahedron.

Table III. Selected Bond Distances (Å) and Angles (deg) for $Cp_2\overline{ZrSGe(Me)_2(o\text{-}C_6H_4)}$ (2)

Zr ··· Ge	3.4783 (8)	CP1–Zr–CP2[a]	131.2
Zr–S	2.514 (2)	S–Zr–C1	94.2 (1)
ZR–C1	2.298 (5)	S–Zr–CP1	109.8
Zr–CP1	2.223	S–Zr–CP2	107.0
Zr–CP2	2.216	C1–Zr–CP1	103.3
Ge–S	2.217 (2)	C1–Zr–CP2	104.8
Ge–C2	1.958 (5)	Zr–S–Ge	94.44 (6)
Ge–C7	1.944 (7)	S–Ge–C2	108.5 (2)
Ge–C8	1.944 (7)	Ge–C2–C1	121.3 (4)
C1–C2	1.402 (8)	Zr–C1–C2	117.0 (4)

[a] CP are the gravity centers of the cyclopentadienyl rings.

The Zr–S bond length of 2.514 (2) Å (Table III) lies in the range observed for some zirconocenethiolates, $[Cp_2Zr(SPh)]_2O$ 2.542 (2) and 2.554 (2) Å,[23] $(Cp_2Zr)_2(\mu\text{-}S(CH_2)_3S)_2$ 2.482 (2)–2.516 (2) Å,[24] and $(tBuCp)_2ZrTeC_6H_4S$ 2.529 (2) Å,[25] and for an η^2-thioaldehyde complex $Cp_2Zr(SCHMe)(PMe_3)$ 2.529 (3) and 2.520 (3) Å.[26] This range of distances is typical for the compounds in which the sulfur atom conserves its electron lone pairs and indicates a single Zr–S σ bond. Note that, in the compound $Cp_2ZrCl(S_2CNEt_2)$ with a chelating dithiocarbamate ligand, where the third frontier orbital of zirconium is involved in the bonding and where the sulfur atoms have a nature different from that of 2, the Zr–S distances are as long as 2.635 (2) and 2.723 (2) Å.[27]

The Zr–C1(phenyl) bond length of 2.298 (5) Å is close to the values found in the compounds with a zirconium to aromatic carbon bond: $Cp_2Zr(CH(SiMe_3)_2)Ph$ 2.324 (7) Å,[28] $(tBuCp)_2Zr(C_5H_4)_2Fc$ 2.284 (2) Å,[29] and $(Me_5C_5)ZrPh(Me_4C_5CH_2)$ 2.285 (5) Å.[30]

The Ge—S bond length equal to 2.217 (2) Å is close to the range of corresponding distances measured in a series of compounds containing tetrahedral germanium bound to the monodentate dithiophosphate ligands (2.22–2.28 Å).[31] It is slightly longer than the values of 2.181 (4) and 2.196 (6) Å observed in the germylene complex $(CO)_5CrGe(SR)_2$[32] but clearly longer than the Ge=S double bond length of 2.063 (2) Å found by Veith in its cyclic germanethione.[1] It indicates that the Ge—S bond is a single σ bond. Together with the earlier statement on a single nature of the Zr—S bond, the geometrical parameters observed for 2 confirm its formation as a result of an insertion of the Ge=S double bond into the zirconium–carbon bond of intermediate benzynezirconocene.

The five-membered heterocycle ZrSGeC2C1 is not planar. The sulfur atom lies 0.56 Å outside the plane of the $-ZrC_6H_4Ge-$ unit. The dihedral angle between the ZrSGe plane and that of the phenyl ring C1 to C6 is equal to 20.5 (3)° (supplementary material). The phenyl ring plane is put off the ZrSC1 one, bisecting that of the Cp ligands by 14.6°. These distortions in the five-membered heterocycle

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are due to the geometrical constraints and probably to the packing effects and may explain the observation that the angle between the normals to the Cp ligand planes (128.0°) differs by about 3° from the Cp1–Zr–Cp2 (centroids) angle (131.2°).

We are currently trying to extend this reaction to other main-group derivatives. Reaction of the dimetallacycles with various electrophilic reagents leading to new heterocyclic systems will be reported in due time.

Supplementary Material Available: Tables of the anisotropic thermal parameters, hydrogen atom coordinates, complete bond distances and angles, and least-squares planes (6 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

Experimental Observation of the Barrier to Rotation around the Metal–Arene Bond in [1,4-Bis(4,4-dimethyl-3-oxopentyl)-2,3,5,6-tetraethylbenzene]molybdenum Tricarbonyl

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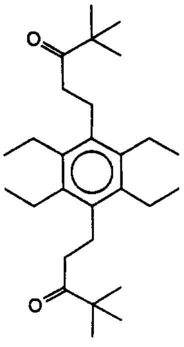
Summary: The barrier to rotation about the metal–arene bond in **1**-Mo is deduced from variable-temperature ^{13}C NMR studies. The dynamic stereochemistry of **1**-Mo is compared to that of **1**-Cr and the free arene **1**. The results indicate that the tripod rotation barrier is primarily steric in nature.

The debate over the magnitude of the barrier to rotation about the metal–arene bond in (hexaethylbenzene)chromium tricarbonyl has been settled by studies on desymmetrized analogues.[1,2] It has also been demonstrated that the alkyl groups on the arene and the metal tripod mesh complementarily;[3] the motion of the alkyl groups gate the motion of the tripod.[1] In order to better understand the physical nature of this barrier we have investigated the periodic effect of substituting chromium by molybdenum. Herein we report the experimental observation of the barrier to rotation about the molybdenum–arene bond in [1,4-bis(4,4-dimethyl-3-oxopentyl)-2,3,5,6-tetraethylbenzene]molybdenum tricarbonyl, 1-Mo.



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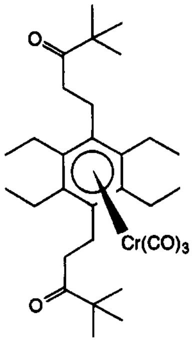
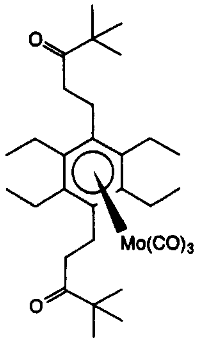


1-Cr



1-Mo

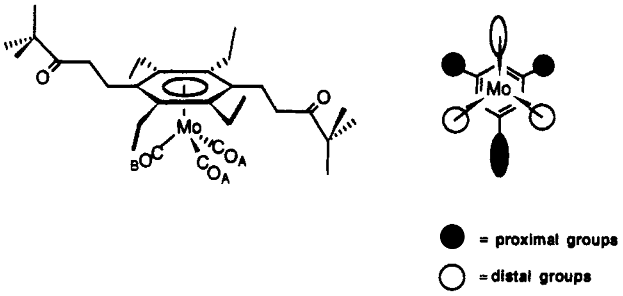


Figure 1. Structure of 1-Mo (Chem 3-D) and projection down the Mo–arene bond.

Synthesis of 1-Mo was accomplished by reaction of 1[4] with tris(acetonitrile)tricarbonylmolybdenum[5] in dioxane for 5 h at reflux under an atmosphere of argon. The product was purified by chromatography on silica gel (31% yield).

The symmetry analysis is the same as for the chromium compound. The static symmetry of 1-Mo is C_s and should give rise to two types of carbon monoxide sites in a ratio of 2:1 as well as two nonequivalent oxopentyl arms in a ratio of 1:1 (Figure 1). Tripod rotation produces a dynamic symmetry of $C_s \times C_3$, rendering the carbon monoxide sites equivalent but leaving the oxopentyl arms nonequivalent. Alkyl group rotation introduces yet greater dynamic symmetry and renders the oxopentyl arms equivalent. Thus independent probes for the tripod and for the ethyl group motion are established.

The ^{13}C NMR spectrum of 1-Mo shows one signal each for the methyl carbons of the *tert*-butyl groups, the tertiary carbon of the *tert*-butyl group, and the carbon monoxide carbon at room temperature. At −80 °C both the methyl carbon signal of the *tert*-butyl groups and the tertiary carbon signal of the *tert*-butyl group carbon have split into two peaks ($\delta\nu = 9.2$, 14.3 Hz), respectively, of equal intensity whereas the carbon monoxide carbon signal remains a sharp singlet. At −140 °C in $CDCl_2F$[6] the carbon monoxide signal also splits into two peaks ($\delta\nu = 130$ Hz)

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[4] Details on the synthesis of 1 can be found in the supplementary material to ref 2.

[5] Tris(acetonitrile)tricarbonylmolybdenum was synthesized as described in: Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433.

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