noted that the analogous square-pyramidal nitride cluster[27] does exist.

Somorjai lists no examples of a small adsorbate on the long bridge site of a (110) face of a fcc crystal, although Weinberg has suggested such a site for O on Ir.[28] Nevertheless there is indirect evidence that carbon may bind to a (110) face in the manner described above. The (100) and (110) surfaces of fcc Pt, Ir, and Au are not stable; they undergo reconstruction.[29] Models for the (1 × 2) reconstruction of the (110) surface have been proposed, all of which destroy the butterfly sites for carbon.[30] What is intriguing is that small amounts of carbon have been found in many cases to stabilize the unreconstructed surface.[29,31] It is also interesting that in one of these cases carbon has been found to considerably enhance the ability of the surface to dissociate CO.[29]

Another way to have carbon on the surface is to start with a carbide. The appropriate carbides are those with the rock-salt structure exemplified by NbC. Here the metal lattice is fcc, and carbon sits in octahedral holes. Since both a square pyramid and a butterfly are fragments of an octahedron, it is clear that if the rock-salt structure is cut appropriately, carbon will have the environment we are looking for. Once again the appropriate cuts are (100) and (110), the main difference from the previous case being that the coverage of carbon is required to be 1 × 1. In the case of carbon on an fcc surface, C–C repulsion keeps the density of carbon atoms from getting as high as 1 × 1. The importance of high coverage is that in this case the butterfly or square-pyramidal "clusters" are not well isolated from one another, and this may affect their properties.

Even less is known about the surface of a carbide than about the carbonaceous surface of a metal. Rock-salt surfaces such as those of TaC and TiC have been shown to have high catalytic activity in hydrogenation as well as in Fisher–Tropsch chemistry, provided that the surfaces were activated by heating them in a vacuum.[32] In the only single crystal study on surfaces of this structure, a (111) surface in which the surface is composed entirely of metal atoms was found to be better than a (100) surface at adsorbing O_2, H_2, and N_2.[33]

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Registry No. **1**, 11087-47-1; **2**, 74792-04-4.

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Transition-Metal Complexes Corresponding to the Insertion into a Group 4B Element–Carbon Bond. 3. Reactivity of Complexes with Unsaturated Carbon–Carbon Bonds. Crystal Structure of (η^5-Cyclopentadienyl)(triphenylgermyl)(η^3-hexenyl)nitrosylmolybdenum

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Anions of the type $[(\eta^5\text{-}C_5H_5)(CO)(L)(M_{4B}Ph_3)M_T]^-$ (L = CO, NO; M_{4B} = Si, Ge, Sn; M_T = Mn, Mo, W) react with allyl halides, affording neutral σ-bonded alkenyl derivatives. These new complexes can rearrange to η^3-allyl complexes and also lose (allyl)M_{4B} to give η^2-allyl complexes. According to the nature of both the transition metal and the group 4B metal η^1, η^3, or η^2 complexes are obtained. A mechanism for these successive reactions is proposed. Butenyl and hexenyl iodides also react with the anions, affording η^1 complexes that can eliminate CO and rearrange to a η^3 ligand as shown by X-ray structure determination.

Introduction

In previous papers,[1,2] we reported the synthesis and reactivity of (η^5-cyclopentadienyl)transition metal anions that contain a transition metal–group 4B metal σ bond. These anions were nucleophilic enough to undergo alkylation with alkyl iodides or benzyl bromides (Scheme I). The neutral complexes thus obtained were quite unreactive (Mo, W)[1] or showed a peculiar reactivity (Mn).[2] We describe here the reactions of these anions with unsaturated halides and the reactivity of the neutral complexes thus obtained. The X-ray structure of a η^3-allylic

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Table I. Elemental Analyses of New Complexes

compd	formula	found (calcd), % C	H	N	Mn
1	$(\eta^5\text{-}C_5H_5)(CO)(NO)(GePh_3)(\eta^1\text{-allyl})Mo$ $C_{27}H_{25}GeMoNO_2$	56.72 (57.49)	4.51 (4.44)	2.55 (2.48)	
2	$(\eta^5\text{-}C_5H_5)(CO)(NO)((\eta^2\text{-allyl})SnPh_3)Mo$ $C_{27}H_{25}MoNO_2Sn$	53.07 (53.15)	4.10 (4.10)	2.27 (2.30)	
3	$(\eta^5\text{-}C_5H_5)(CO)(NO)((\eta^2\text{-allyl})SnPh_3)W$ $C_{27}H_{25}NO_2SnW$	46.43 (46.44)	3.62 (3.58)	2.02 (2.01)	
4	$(\eta^5\text{-}CH_3C_5H_4)(CO)_2(SiPh_3)(\eta^1\text{-allyl})Mn$ $C_{29}H_{27}MnO_2Si$	70.73 (71.00)	5.32 (5.55)		11.13 (11.20)
5	$(\eta^5\text{-}CH_3C_5H_4)(CO)_2(GePh_3)(\eta^1\text{-allyl})Mn$ $C_{29}H_{27}GeMnO_2$	65.02 (65.10)	5.12 (5.09)		
7	$(\eta^5\text{-}C_5H_5)(NO)(CO)(\eta^1\text{-butenyl})(GePh_3)Mo$ $C_{28}H_{27}GeMoNO_2$	58.13 (58.17)	5.06 (4.67)	2.40 (2.42)	
8	$(\eta^5\text{-}C_5H_5)(NO)(GePh_3)(\eta^3\text{-allyl})Mo$ $C_{26}H_{25}GeMoNO$	58.42 (58.26)	4.71 (4.67)	2.64 (2.61)	
9	$(\eta^5\text{-}C_5H_5)(NO)(GePh_3)(\eta^3\text{-benzyl})Mo$ $C_{30}H_{27}GeMoNO$	61.59 (61.48)	4.57 (4.61)	2.36 (2.73)	
10	$(\eta^5\text{-}CH_3C_5H_4)(CO)_2((\eta^2\text{-allyl})SiPh_3)Mn$ $C_{29}H_{27}MnO_2Si$	71.02 (71.00)	5.52 (5.55)		
11	$(\eta^5\text{-}C_5H_5)(NO)(GePh_3)(\eta^3\text{-butenyl})Mo$ $C_{27}H_{27}GeMoNO$	58.59 (58.95)	4.61 (4.91)	2.46 (2.55)	
12	$(\eta^5\text{-}C_5H_5)(NO)(GePh_3)(\eta^3\text{-hexenyl})Mo$ $C_{29}H_{31}GeMoNO$	60.35 (60.26)	5.46 (5.37)	2.33 (2.42)	

Table II. Physical Properties of New Complexes

complex	ν_{CO},[a] cm^{-1}	ν_{NO},[a] cm^{-1}	color	mp, °C	yield, %
1	2026	1650	yellow	220-221	96
2	1960	1620	yellow	119-120	69
3	1960	1605	yellow	146-147	78
4	1968 1908		yellow	195-196	52
5	1965 1910		yellow	89-91	42
7	2020	1650	orange-yellow	104-105 dec	80
8		1620	yellow	190 dec	86
9		1610	orange	147-148 dec	22
10	1950 1885		yellow	118-118.5	40
11		1620	yellow	151-152	49
12		1625	yellow	151-152	31[b]

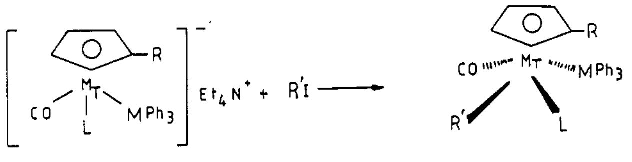
[a] In CH_2Cl_2. [b] Overall yield starting from the corresponding anion.

complex is also reported.

Experimental Section

All experiments were carried out under nitrogen, using standard vacuum line techniques. Solvents were dried, distilled, and deoxygenated. Starting materials were commercial products or were prepared according to the literature. Complex **6** is prepared as described in ref 2.

Scheme I



M_T = Mo, W; L = NO; M = Ge, Sn; R = H

M_T = Mn; L = CO; M = Si, Ge; R = CH_3

R' = CH_3, C_2H_5

Melting points were taken under vacuum with a Tottoli apparatus. IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer and NMR spectra with a Varian EM 360 or EM 390 spectrometer (chemical shifts, ppm, relative to Me_4Si). Elemental analyses are reported in Table I.

Preparation of Complexes 1, 4, and 5. Preparation of complex **1** is given as an example. To a solution of $[(\eta^5\text{-}C_5H_5)(NO)(CO)(GePh_3)Mo]Et_4N$ (**1**) (prepared at room temperature in order to avoid the formation of isomers, 326 mg, 0.5 mmol) in 20 mL of THF at -78 °C was added 250 μL (excess) of allyl iodide. The reaction mixture was allowed to warm slowly to room temperature. A pale yellow solution and a white precipitate formed. The solvent was pumped off and the residue dissolved in toluene. The solution was filtered through a fritted funnel (G4) and chromatographed on silica gel (hexane/toluene, 1/1); the yellow band was collected. The solution was concentrated to ~10 mL, and ~15 mL of hexane was added. Standing at -20 °C yielded 270 mg of **1** as yellow crystals.

Table III. ^{1}H NMR Data for Complexes 1, 4, and 5 in C_6D_6

complex	δ(C_6H_5)	δ(CH=)	δ(CH_2=)	δ(C_5H_5 or C_5H_4)	δ(CH_2M_T)	δ(CH_3)
1	7.77 (m), 7.20 (m)	6.30 (m)	4.84 (m)	4.77 (s)	2.50 (d, *J* = 8 Hz)	
4	7.90 (m), 7.20 (m)	6.40 (m)	5.10 (m)	4.03 (m), 3.83 (m)	2.80 (d, *J* = 7 Hz)	1.40 (s)
5	7.80 (m), 7.26 (m)	6.30 (m)	5.20 (m)	4.06 (m), 3.83 (m)	2.77 (d, *J* = 8 Hz)	1.40 (s)

Table IV. ^{1}H NMR Data for Complexes 2, 3, and 10

complex	δ(C_6H_5)	δ(C_6H_5 or C_5H_4)	δ(CH=)	δ(CH_2=)	δ(CH_2)	δ(CH_3)
2[a]	7.65 (m), 7.17 (m)	4.77 (s)	3.73 (m)	2.66,[b] 1.33 (t)	2.23,[b] 1.96[b]	
2[c]	7.52 (m), 7.35 (m)	5.47 (s)	3.82 (m)	2.72,[b] 1.41 (t)	2.40,[b] 2.09[b]	
3[c]	7.52 (m), 7.34 (m)	5.50 (s)	3.50 (m)	2.87,[b] 1.45 (m)	2.08 (m)	
10[a]	7.63 (m), 7.13 (m)	3.70[d]	3.30 (m)	2.90,[b] 1.13 (m)	2.13,[b] 1.80[b]	1.43 (s)

[a] In C_6D_6. [b] Doublet of doublets. [c] In CD_2Cl_2. [d] Broad singlet.

Table V. ^{1}H NMR Data for Complexes 6 and 7 in C_6D_6

complex	$\delta(C_6H_5)$	$\delta(CH{=})$	$\delta(CH_2{=})$	$\delta(C_5H_5$ or $C_5H_4)$	$\delta(CH_2)$	$\delta(CH_2M_T)$	$\delta(CH_3)$
6	7.90 (m), 7.23 (m)	5.99 (m)	5.01 (m)	4.07 (m), 3.77 (m)	2.48 (m)	2.08 (m)	1.38 (s)
7	7.68 (m), 7.10 (m)	5.90 (m)	5.03 (m)	4.73 (s)	2.53 (m)	1.70 (m)	

Table VI. ^{1}H NMR Data for Complexes 8 and 9 in C_6D_6

complex	$\delta(C_6H_5)$	$\delta(C_5H_5)$	$\delta(CH{=})$	$\delta(CH_2)$
8	7.70 (m), 7.20 (m)	4.82 (s), 4.57 (s)	4.2-3.6 (m)	3.2-2.8 (m), 2.1-1.2 (m)
9	7.9-5.1[a]	4.6 (s), 4.29 (s)		3.00 (d), 2.05 (d, J = 10 Hz)

[a] Several multiplets. These spectra are difficult to interpret due to the presence of exo and endo conformers. For 9 the chemical shifts for the benzyl protons appear to be the same for exo and endo isomers; they are diastereotopic due to the chirality at Mo.

Complexes 4 and 5 were prepared similarly from $[(\eta^5\text{-}CH_3C_5H_4)(CO)_2(Ph_3Si)Mn]Et_4N$[3] and $[(\eta^5\text{-}CH_3C_5H_4)(CO)_2(Ph_3Ge)Mn]Et_4N$.[4]

Physical properties are shown in Table II and ^{1}H NMR spectra in Table III.

Preparation of Complexes 2 and 3. These complexes are prepared by using the same procedure as above, starting with $[(\eta^5\text{-}C_5H_5)(CO)(NO)(SnPh_3)Mo]Et_4N$[1] or $[(\eta^5\text{-}C_5H_5)(CO)(NO)(SnPh_3)W]Et_4N$[1] and allyl bromide or iodide. Their physical properties are reported in Table II and their ^{1}H NMR spectra in Table IV.

Mass spectrum for 2 (m/e assignment for ^{120}Sn and ^{98}Mo): 611 (molecular peak).

Preparation of Complex 7. A procedure similar to those above with the corresponding anion and 1-iodo-3-butene led to complex 7. Its physical properties are reported in Table II, and its ^{1}H NMR spectrum is reported in Table V (compared with that of 6).

Thermal Reaction of 1 and Its Benzyl Analogue. A solution of complex 1 (282 mg, 0.5 mmol) in THF (30 mL) was refluxed for 30 min. After this time the IR absorptions at 2026 and 1650 cm^{-1} had disappeared while one at 1625 cm^{-1} had appeared. No decomposition was observed. Solvent was pumped off and the residue dissolved in toluene. The solution was then filtered and hexane added. Standing at −20 °C afforded 230 mg of 8 as yellow crystals.

The same procedure with the benzyl analogue[1] afforded 9. Their physical properties are reported in Table II and ^{1}H NMR spectra in Table VI.

Thermal Reaction of Complexes 4 and 5. A solution of complex 4 (490 mg, 1 mmol) in THF (30 mL) was refluxed for 30 min. The reaction was monitored by IR spectrscopy; the absorption bands of 4 had disappeared and been replaced by new bands at 1950 and 1890 cm^{-1}. Solvent was pumped off and the residue crystallized from hexane at −20 °C. Yellow crystals of 10 were obtained (196 mg) (Tables II and IV). Complex 5, under the same conditions, underwent the same type of reaction as shown by IR spectroscopy (ν(CO) absorptions at 1960 and 1900 cm^{-1}); however the η^2-allylic complex could not be crystallized.

Reaction of Allyltriphenylsilane with $(\eta^5\text{-}CH_3C_5H_4)(CO)_3Mn$. A solution of $Ph_3(allyl)Si$ (900 mg, 3 mmol) and methylcymanthrene (660 mg, 3 mmol) in 100 mL of THF was irradiated with a 100-W Hanovia lamp overnight. Solvent was pumped off and the residue was crystallized from hexane at −20 °C. Complex 10 was obtained (725 mg, yield 49%) and was shown to be identical with the complex arising from the thermal reaction of 4.

Attempted Reaction of Allyltriphenylsilane and of Allyltriphenylstannane with $(\eta^5\text{-}C_5H_5)(CO)_2(NO)Mo$. Treatment of equimolar amounts of $(\eta^5\text{-}C_5H_5)(CO)_2(NO)Mo$[5] with both allyltriphenylsilane[6] or -stannane[7] in refluxing toluene showed no reaction. When the solution was irradiated with a 100-W Hanovia lamp, no reaction was noticed after 3 h. However with a 450-W Hanovia lamp decomposition took place after 2 h.

Treatment of 2 and 10 with PPh_3. A solution of 2 (583 mg, 0.95 mmol) and PPh_3 (250 mg, 0.95 mmol) in 20 mL of toluene was refluxed for 3 h. After this time IR absorption at 1960 cm^{-1} had disappeared and been replaced by another at 1910 cm^{-1}. Solvent was pumped off and the residue chromatographed on silica gel. Hexane/toluene (8/2) eluted allyltriphenyltin (278 mg, yield 75%) identical with an authentic sample,[7] and hexane/toluene (5/5) eluted a red band. The red solution was concentrated and left at −20 °C; red crystals of $(\eta^5\text{-}C_5H_5)(CO)(NO)(PPh_3)Mo$ (320 mg, yield 69%) were obtained and identified with an authentic sample.[8]

Similar treatment of 10 with the equimolar amount of PPh_3 afforded triphenylallylsilane (yield 70%)[6] and $(\eta^3\text{-}CH_3C_5H_4)(CO)_2(PPh_3)Mn$(yield 85%).[9]

Thermal Reaction of 7. A solution of 7 (577 mg, 1 mmol) in 20 mL of THF was heated at 50 °C for 30 min. After this time IR absorptions due to 7 had disappeared and a new band at 1620 cm^{-1} was observed. Solvent was pumped off and the residue taken up in toluene, and the solution filtered. Addtion of hexane and standing at −20 °C afforded 270 mg of 11 (Table II).

^{1}H NMR (C_6D_6): $\delta(C_6H_5)$ 7.75 (m), 7.12 (m), $\delta(C_5H_5)$ 4.80 (s), 4.61 (s) (corresponding to isomers exo and endo); other signals at δ 3.9–3.3 (m), 2.9 (m), 2.4–1.0 (multiplets), 1.8 (d, J = 9 Hz) and 1.1 (d, J = 9 Hz) (these doublets could correspond to the methyl groups in the exo and endo isomers).

Preparation of 12. To a solution of $[(\eta^5\text{-}C_5H_5)(NO)(CO)(GePh_3)Mo]Et_4N$[1] (652 mg, 1 mmol) in 20 mL of THF was added 600 μL (excess) of hexenyl iodide at room temperature, and the reaction mixture was stirred overnight. The IR spectra showed absorptions at 2010, 1655, and 1625 cm^{-1}. The solution was refluxed for 1 h, and the IR absorptions at 2010 and 1655 cm^{-1} corresponding to the η^1 complex disappeared as the one at 1625 cm^{-1} increased. Solvent was then pumped off, the residue dissolved in toluene, and the solution filtered. Addition of hexane and standing at −20 °C afforded 180 mg of 12 (Table II).

^{1}H NMR (C_6D_6): $\delta(C_6H_5)$ 7.8 (m), 7.2 (m), $\delta(C_5H_5)$ 4.87 (s), 4.7 (s) (corresponding to the exo and endo isomers); other signals at δ 4.1–3.4 (m), 3.2–2.7 (m), 2.2–1.8 (m), 1.7–1.1 (m), and two superimposed triplets centered at δ 0.83 (corresponding to the methyl groups of the endo and exo isomers).

Crystal Preparation. Crystals of complex 12 were grown by slowly cooling a toluene–hexane solution to −18 °C in a nitrogen atmosphere. Large yellow plates were obtained. Preliminary X-ray photography established a monoclinic unit cell of space group $P2_1/_n$ (from the systematic absences). A small block cut from a plate was sealed inside a Lindeman glass capillary with the [001] direction parallel to the Φ axis of the diffractometer.

X-ray Data Collection. Data were collected on a CAD-4 automated diffractometer with graphite-monochromated Mo K$\bar{\alpha}$ radiation (λ = 0.710 69 Å). Lattice constants given in Table VII came from a least-squares refinement of 22 reflections obtained at medium and high angles. The intensities of three standard reflections were monitored after intervals of 60 min. No significant change in these intensities occurred during data collection (4°

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Table VII. Summary of Crystal Data, Intensity Collection, and Refinement

formula	$C_{29}H_{31}GeMoNO$
cryst system	monoclinic
space group	$P2_1/n$
a, Å	9.257 (2)
b, Å	20.950 (4)
c, Å	13.375 (3)
β, deg	98.03 (2)
vol, Å^3	2568
mol wt	578.1
Z	4
d(calcd), g cm^{-3}	1.495
d(measd), g cm^{-3}	1.49 (1)
cryst size, mm^3	0.30 × 0.30 × 0.08
cryst color	yellow
recrystn solvent	toluene/hexane
mp, °C	151-152
method of data collectn	moving cryst, moving counter
radiatn (graphite monochromated)	Mo Kα
μ, cm^{-1}	16.46
2θ limits, deg	4-50
no. of unique reflecns	4643
no. of obsd (indep) reflecns	1848 (1725)
final no. of variables	279
R_F	0.043
R_{wF}	0.062
error of fit	0.96

$< 2\theta < 50°$). The structure amplitudes were obtained after the usual Lorentz and polarization reduction. No absorption corrections were applied because of the relatively small values of μ.

A total of 4945 scans including 302 redundant data were measured for compound **12**. Equivalent reflections $00l$ and $00\bar{l}$ were averaged to give a set of 1848 observed intensities [$\sigma(I)/I < 0.35$] in which were kept the 123 $0kl$–$0k\bar{l}$ pairs.

Structure Determination and Refinement. The Mo and Ge coordinates were given by direct methods (MULTAN80 program) and were checked in a Patterson calculation. A subsequent Fourier map revealed the three phenyl rings, the nitrosyl group, and the cyclopentadienyl ring. After two cycles of least-squares refinement, a difference Fourier synthesis gave six carbon atoms corresponding to the main configuration of the hexenyl ligand. Two cycles of least-squares and a new difference Fourier map revealed the three other disordered atoms. During the remaining calculations the exo and endo isomers were considered to have atomic peaks C(1), C(3), and C(6) in common, and the atoms C(2a) and C(2b), C(4a) and C(4b), and C(5a) and C(5b) were given occupancies of 0.66 and 0.34, respectively. [As suggested by one of the reviewers, it should be noted that the thermal parameters of the resolved a atoms, larger than those of the b atoms, is indicative of some error in the occupancy factors. With the assumption of equal thermal parameters for the two sets of resolved atoms, a ratio of approximately 57:42 can be deduced.] These parameters were estimated from the last difference Fourier map; after refinement by two cycles of least squares, no further change was allowed to occur, and a final difference Fourier map gave no electron density higher than ±0.6.

The atomic scattering factors were taken from Doyle and Turner.[10] The scale factor and the positional and thermal atomic parameters were refined by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = [(0.5\ \sigma(F_o))^2 + (0.07|F_o|)^2]^{-1}$. The residuals R and R_w along with the error of fit appear in Table VII. The final values of the positional atomic parameters are listed in Table VIII. Lists of thermal parameters (Table IX) and observed and calculated structure factors (Table X) are available as supplementary material.

Table VIII. Fractional Atomic Coordinates ($\times 10^4$) for Compound **12**[a]

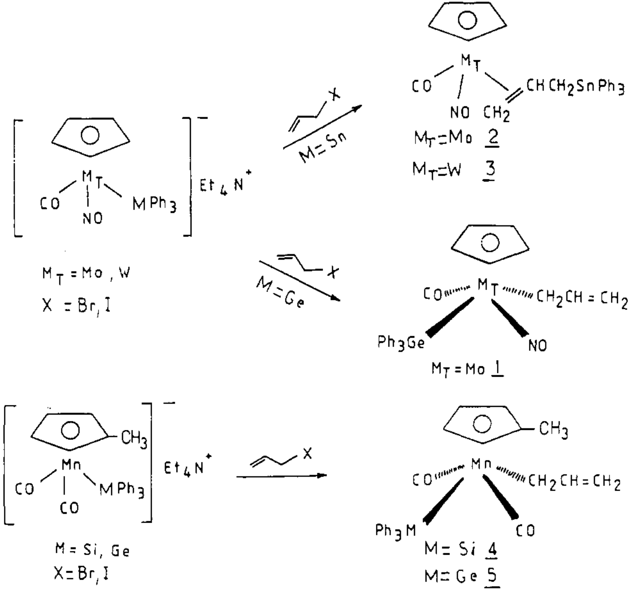
atom	x	y	z
Mo	3860.9 (11)	3990.2 (4)	2528.2 (8)
Ge	6477.8 (12)	4316.7 (5)	2222.7 (9)
N	4602 (12)	3204 (5)	2608 (8)
O	5028 (13)	2671 (5)	2749 (9)
Cp(1)	3082 (15)	3966 (7)	4115 (10)
Cp(2)	4449 (18)	4266 (7)	4225 (9)
Cp(3)	4371 (14)	4837 (6)	3713 (9)
Cp(4)	2886 (16)	4930 (6)	3254 (11)
Cp(5)	2077 (16)	4356 (8)	3495 (11)
C(1)	3710 (16)	4260 (7)	820 (10)
C(2a)[b]	2377 (26)	4213 (11)	1031 (17)
C(2b)	3118 (33)	3754 (15)	848 (22)
C(3)	1792 (16)	3645 (7)	1451 (10)
C(4a)	1789 (30)	2958 (14)	1007 (19)
C(4b)	1109 (43)	3034 (19)	1572 (29)
C(5a)	1206 (34)	2517 (16)	1714 (23)
C(5b)	1877 (60)	2460 (28)	1086 (40)
C(6)	1202 (22)	1816 (9)	1293 (15)
C(11)	7889 (11)	4015 (5)	3403 (7)
C(12)	8399 (14)	3396 (5)	3399 (9)
C(13)	9281 (15)	3162 (6)	4255 (10)
C(14)	9699 (13)	3525 (6)	5102 (9)
C(15)	9191 (13)	4154 (6)	5091 (9)
C(16)	8281 (13)	4400 (5)	4247 (9)
C(21)	7197 (11)	3921 (5)	1033 (8)
C(22)	8016 (15)	4267 (6)	455 (9)
C(23)	8576 (16)	4006 (7)	−373 (10)
C(24)	8321 (16)	3366 (8)	−587 (11)
C(25)	7479 (14)	3006 (7)	−43 (10)
C(26)	6930 (14)	3275 (6)	785 (10)
C(31)	6895 (12)	5233 (5)	2101 (7)
C(32)	8348 (13)	5472 (5)	2329 (9)
C(33)	8632 (19)	6123 (6)	2205 (10)
C(34)	7506 (20)	6534 (7)	1926 (11)
C(35)	6044 (17)	6320 (6)	1692 (10)
C(36)	5773 (15)	5668 (5)	1795 (9)

[a] Estimated standard deviations are in parentheses. [b] The carbon atoms labeled a correspond to the exo configuration. The b labeling refers to the endo configuration (see text).

Results and Discussion

(a) Reaction of Transition-Metal Anions with Allyl Halides. Treatment of tetraethylammonium salts of transition-metal anions (Scheme II) with both allyl iodide or bromide at low temperature (−78 °C) results in displacement of halide and formation of neutral complexes. However, the complexes obtained belong to two different classes, depending on the group 4B metal attached to the transition metal.

Scheme II



In the case of silicon and germanium, the η^1-allyl complexes **1**, **4**, and **5** are obtained. Their formation is easily

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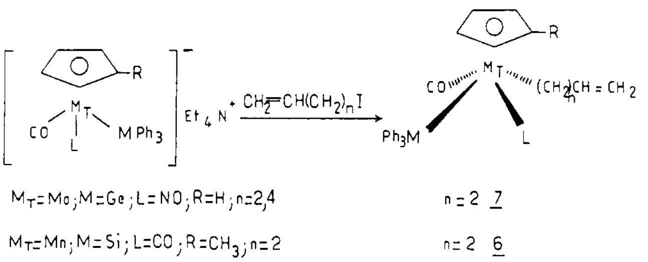
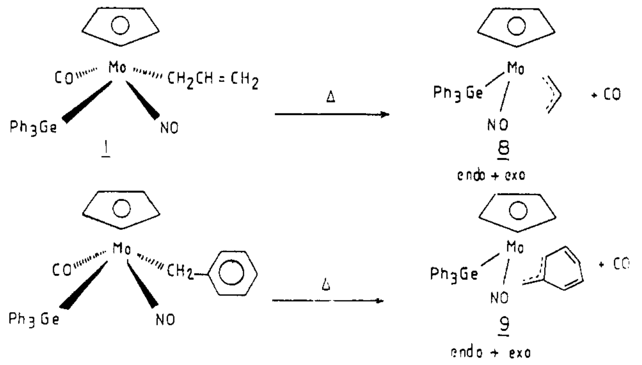
[10] Doyle, P. A.; Turner, P. S. *Acta Crystallogr., Sect. A* **1968** *A24*, 390.

Scheme III



Scheme IV



explained in light of the alkylations with methyl or ethyl iodides.[1,2] The geometry of these type of complexes has already been discussed elsewhere[1,2,11,12] and shown to be trans. In order to avoid the formation of cis isomers, the anions are prepared at room temperature, since we showed previously that anions prepared at −78 °C give a mixture of cis and trans isomers after alkylation.[1]

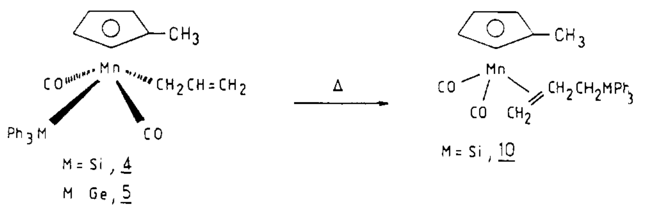
For tin-containing anions the η^2-allylic complexes **2** and **3** are obtained instead. The mechanism of formation of these complexes will be discussed in d.

(b) Reaction of Transition-Metal Anions with Non-Allylic Unsaturated Halides. Tetraethylammonium salts of transition-metal anions react also with unsaturated halides (butenyl iodide, hexenyl iodide) affording the σ-bonded alkenyl derivatives **6**[2] and **7** (the η^1-hexenyl derivative of Mo was identified by IR spectroscopy but not isolated, see d) (Scheme III). In this reactions, tin-containing anions are inert, as we observed previously in the case of ethyl iodide.[1]

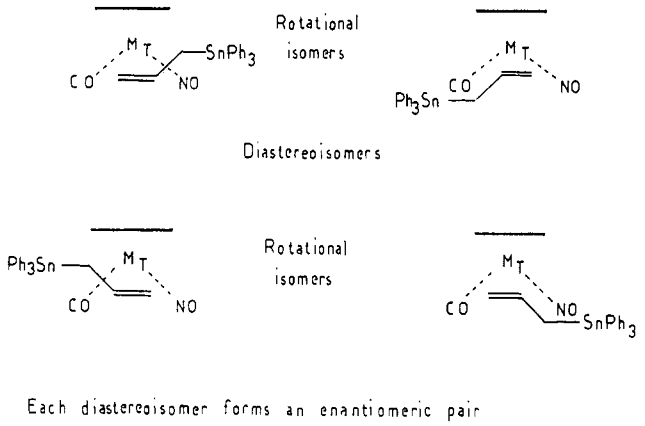
(c) Thermal Reaction of σ-Allyl and σ-Benzyl Complexes. Molybdenum–germanium complexes having allyl or benzyl σ bonds evolve carbon monoxide rapidly when refluxed in THF, and the corresponding η^3-allyl **8** or η^3-benzyl **9** complexes are obtained (Scheme IV). Although the reaction takes place quantitatively (as shown by IR spectroscopy), yields are poor after crystallization (especially for **9**). These complexes exist as an equilibrium mixture of two conformers (exo and endo);[13,14] indeed their ^{1}H NMR spectra are very complex due to the superposition of the spectra of the two conformers; however, two singlets, due to the resonances of the cyclopentadienyl protons are well distinguishable.

In the case of **8** the isomer ratio is shown to be temperature dependent. From the integration of the two cyclopentadienyl resonances, this ratio shows a variation from 1.2 at +55 °C to 1.9 at +110 °C in toluene.

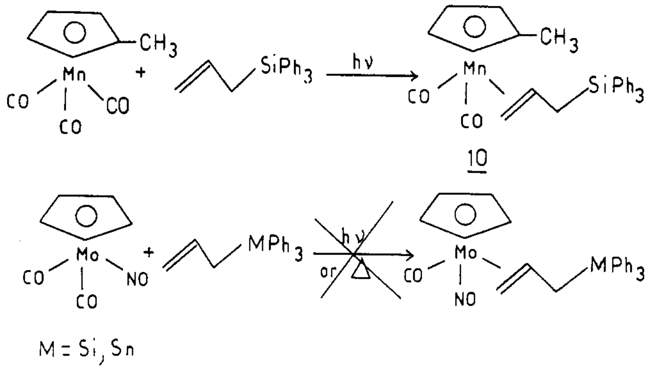
Scheme V



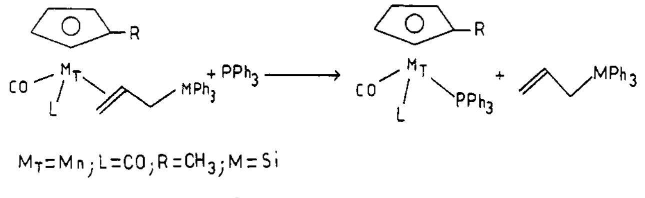
Scheme VI



Scheme VII



Scheme VIII



On the other hand, the manganese η^1-allyl complexes, when heated in THF, undergo reductive elimination of allylsilane or -germane (respectively) and the η^2-allylic complexes are obtained (Scheme V). This result is to be compared to the reaction of the tin-containing anions of molybdenum and tungsten since the only complex obtained is also the η^2-allylic one instead of the expected η^1-allylic complex.

The η^2-allylic complexes may also show rotational isomerism.[15] In the case of manganese two enantiomers are possible (each one showing two rotamers). For the molybdenum and tungsten complexes two diastereoisomers can be obtained (each one showing two rotamers and also two enantiomers)[15] (Scheme VI). The complexity of the

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(11) Colomer, E.; Corriu, R. J. P.; Vioux, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 476.

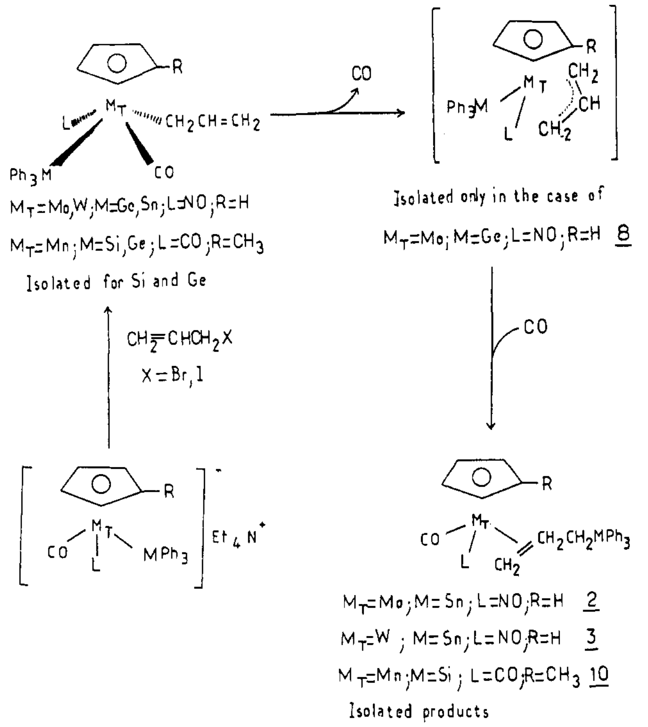
(12) Cerveau, G.; Colomer, E.; Corey, E. R.; Corriu, R. J. P.; Vioux, A., to be submitted for publication in *Organometallics*.

(13) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 3388.

(14) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

(15) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 2570.

Scheme IX



^1H NMR spectra of complexes **2** and **3** may indicate the presence of diastereoisomers even if the melting points of these complexes are sharp (cf. complex **12**).

It is noteworthy that triphenylallylsilane replaces easily one carbonyl in methylcymantrene by UV irradiation, while the same reaction does not take place with the parent molybdenum complexes neither thermally nor photochemically (Scheme VII).

In η^2-allyl complexes, the olefin is easily replaced by a phosphine to afford the free olefin and the phosphine-containing complex (Scheme VIII).

(d) Proposal of Mechanism for the Thermal Reactions. In light of the set of reactions described above one may reasonably assume that in all cases the first step is the formation of the η^1-allyl complexes, followed by thermal reaction to the η^2- or η^3-allylic ones.

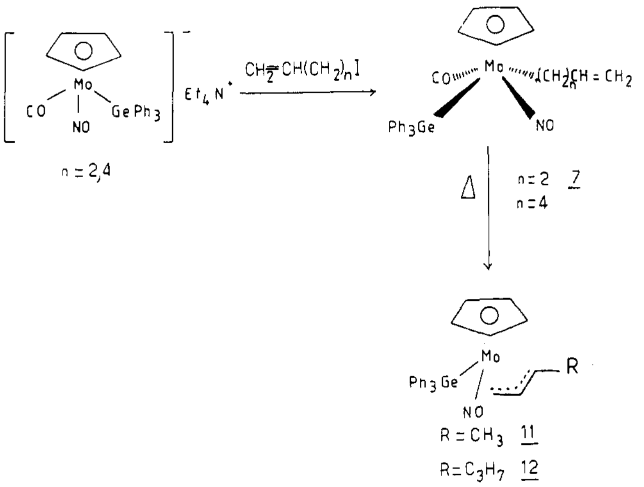
However, for tin-containing anions, even at low temperature (-78 °C), the η^1-allyl complex cannot be detected. This may be due to a extremely short half-life and may be related to the lack of reactivity of these anions that are only alkylated by methyl iodide.[1]

It is difficult to assume that the deinsertion of the transition metal-carbon bond takes place directly since both ligands are trans to each other and since the reaction requires mild conditions (in refluxing THF it takes only a few minutes, and moreover if the allylation of the anion is carried out at room temperature, instead of -78 °C, a mixture of both η^1- and η^2-allylic complexes is obtained in the case of manganese). Moreover, we have already shown that the methyl derivatives are isomerically stable up to 80 °C and decomposition takes place above this temperature without isomerization.[1]

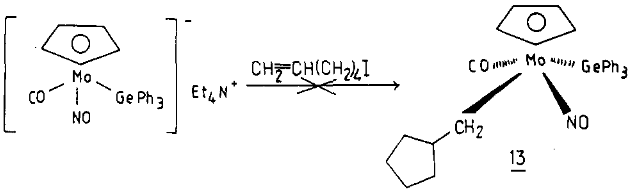
This high isomeric stability seems to exclude isomerization to a square-pyramidal complex in which the allyl and group 4B metal ligands are cis. Transient formation of the η^3-allyl complex via a reversible dissociation of carbon monoxide would show the η^3-allyl and the group 4B metal vicinal, allowing the deinserstion of the transition metal (Scheme IX).

In some cases the η^1-allyl complex is isolated (complexes **1**, **4**, **5**), and then thermal reaction leads to the η^3-allyl one and the reaction stops (this is the case for the formation of **8**) or undergoes deinsertion and formation of the M_{4B}-allyl bond and the η^2-allyl complexes are obtained (compounds **2**, **3**, and **10**).

Scheme X



Scheme XI



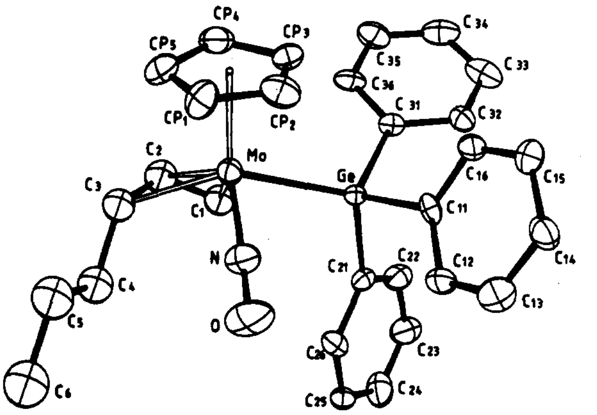


Figure 1. ORTEP diagram of complex **12** showing 30% probability ellipsoids.

(e) Thermal Reaction of η^1-Butenyl and η^1-Hexenyl Complexes. When complex **7** is refluxed in THF, carbon monoxide evolves rapidly and the corresponding η^3-butenyl complex **11** is obtained (Scheme X). This type of reaction has already been observed for iron complexes.[16]

The ^1H NMR spectrum of **11** shows two cyclopentadienyl resonances corresponding to two different isomers (see f) in a 1/1.5 ratio.

The same type of reaction occurs with the η^1-hexenyl derivative. In this case the σ complex is not isolated. Indeed, after treatment of the Mo-Ge anion with 1-iodo-5-hexene, the solution is refluxed to yield the η^3-hexenyl complex **12**. Its ^1H NMR spectrum shows also two isomers in a 1/1 ratio (see f).

It is noteworthy that no η^1-cyclopentylmethyl complex **13** (Scheme XI) is obtained, showing that the attack on

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(16) Green, M. L. H.; Smith, M. J. *J. Chem. Soc. A* **1971**, 3220.

Table XI. Bond Lengths (Å) for Complex 12 (Esd's in Parentheses)

Mo-Ge	2.6038 (15)	C(11)-C(12)	1.38 (1)
Mo-N	1.78 (1)	C(12)-C(13)	1.40 (2)
Mo-Cp(1)	2.34 (1)	C(13)-C(14)	1.37 (2)
Mo-Cp(2)	2.33 (1)	C(14)-C(15)	1.40 (2)
Mo-Cp(3)	2.38 (1)	C(15)-C(16)	1.41 (2)
Mo-Cp(4)	2.42 (1)	C(16)-C(11)	1.39 (1)
Mo-Cp(5)	2.36 (1)		
Mo-C(1)	2.34 (1)	C(21)-C(22)	1.37 (2)
Mo-C(2a)	2.31 (2)	C(22)-C(23)	1.40 (2)
Mo-C(2b)	2.31 (3)	C(23)-C(24)	1.38 (2)
Mo-C(3)	2.34 (1)	C(24)-C(25)	1.37 (2)
		C(25)-C(26)	1.40 (2)
N-O	1.19 (1)	C(26)-C(21)	1.41 (2)
C(1)-C(2a)	1.31 (3)		
C(2a)-C(3)	1.45 (2)	C(31)-C(32)	1.43 (2)
C(3)-C(4a)	1.56 (3)	C(32)-C(33)	1.40 (2)
C(4a)-C(5a)	1.48 (4)	C(33)-C(34)	1.36 (2)
C(5a)-C(6)	1.57 (4)	C(34)-C(35)	1.42 (2)
C(1)-C(2b)	1.20 (3)	C(35)-C(36)	1.40 (2)
C(2b)-C(3)	1.58 (3)	C(36)-C(31)	1.40 (2)
C(3)-C(4b)	1.45 (4)		
C(4b)-C(5b)	1.58 (7)	Cp(1)-Cp(2)	1.40 (2)
C(5b)-C(6)	1.53 (6)	Cp(2)-Cp(3)	1.37 (2)
		Cp(3)-Cp(4)	1.44 (2)
Ge-C(11)	2.01 (1)	Cp(4)-Cp(5)	1.48 (2)
Ge-C(21)	1.99 (1)	Cp(5)-Cp(1)	1.42 (2)
Ge-C(31)	1.97 (1)		

Table XII. Selected Bond Angles (deg) for Complex 12 (Esd's in Parentheses)

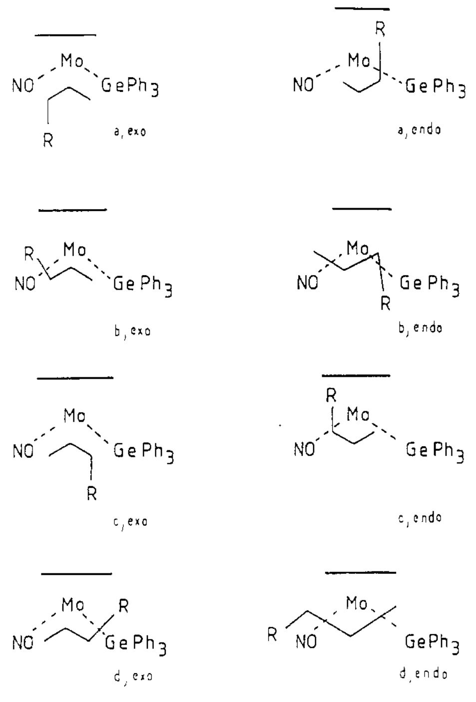
N-Mo-Ge	83.9 (3)	Mo-Ge-C(11)	108.2 (3)
N-Mo-C(1)	104.6 (5)	Mo-Ge-C(21)	116.0 (3)
N-Mo-C(2a)	114.6 (6)	Mo-Ge-C(31)	117.8 (3)
N-Mo-C(2b)	85.4 (8)	C(11)-Ge-C(21)	104.1 (4)
N-Mo-C(3)	91.5 (5)	C(21)-Ge-C(31)	104.4 (4)
N-Mo-Cp[a]	123	C(31)-Ge-C(11)	105.0 (4)
Cp-Mo-Ge	108		
Cp-Mo-C(1)	133	C(1)-C(2a)-C(3)	124.0 (20)
Cp-Mo-C(2a)	116	C(2a)-C(3)-C(4a)	126.3 (17)
Cp-Mo-C(2b)	146	C(3)-C(4a)-C(5a)	108.4 (24)
Cp-Mo-C(3)	113	C(4a)-C(5a)-C(6)	109.8 (26)
Ge-Mo-C(1)	73.3 (4)		
Ge-Mo-C(2a)	105.3 (6)	C(1)-C(2b)-C(3)	122.5 (24)
Ge-Mo-C(2b)	93.5 (8)	C(2b)-C(3)-C(4b)	124.7 (22)
Ge-Mo-C(3)	133.0 (4)	C(3)-C(4b)-C(5b)	113.5 (37)
		C(4b)-C(5b)-C(6)	112.2 (41)
Mo-N-O	173.2 (9)		

[a] Cp is the calculated center of the cyclopentadienyl ring with coordinates 0.3373, 0.4471, and 0.3760.

the organic iodide does not involve radical anions.[17] Indeed, the hexen-5-yl radical is known to cyclize into cyclopentylmethyl radical.[18]

(f) Description of the Structure of Complex 12. The labeling of the atoms is given in Figure 1. Bond lengths and angles are listed in Tables XI and XII. The cyclopentadienyl ring and the triphenylgermyl moiety show no unusual features. The nitrosyl group is approximately linear with a Mo–N–O angle of 173.2 (9)°, thus indicating a three-electron donor ligand.[19] The molybdenum–germanium bond length, 2.604 (2) Å, is significantly shorter than the bond length reported for *trans*-η^5-$C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C_6H_5$[20] (2.658 (2) Å). The average of the molybdenum–carbon distances for the 2-hexenyl ligand, 2.330 Å, is comparable with the average of the molybdenum–cyclopentadienyl atoms distances (2.366 Å).

Scheme XII



Possible isomers for complex 12, R = n-C_3H_7

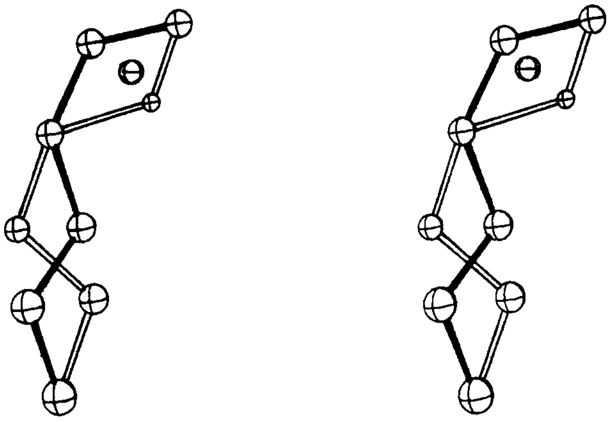


Figure 2. Stereoscopic view of complex 12 showing the two observed conformations. The exo conformation is represented with the plain black bonds. The thermal ellipsoids are at the 10% probability level.

Four diastereomers (a–d) should be expected for complex 12, each of them having two conformers exo and endo, thus leading to eight kinds of molecules (Scheme XII).

The structure determination reveals disorder of the 2-hexenyl ligand (see Experimental Section). This disorder corresponds to a mixture (ratio 57/42) of two isomers: a, exo, and d, endo, in the solid state. One should have expected a preferred crystallization of one of the two observed isomers out of the solution of the crude product. Since the above ratio is not favoring markedly one of them, we suppose the two isomers to have close physical properties; as a matter of fact, an examination of figure 2 shows that these isomers display roughly the same shape and bulkiness due to common atoms C(1), C(2), and C(6).[21]

---

[17] Felkin, H.; Knowles, P. J.; Meunier, B. *J. Organomet. Chem.* **1978**, *146*, 151.

[18] Lamb, R. C.; Ayers, P. W.; Toney, M. K.; Garst, J. F. *J. Am. Chem. Soc.* **1966**, *88*, 4261 and references therein.

[19] Wilson, R. D.; Bau, R. *J. Organomet. Chem.* **1980**, *191*, 123.

[20] Chan, L. Y. Y.; Dean, W. K.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1067.

[21] At this point we have to say that carbon C(6) being in common with both isomers was a hypothesis chosen in order to handle a simpler model for refinement; the large thermal parameter for atom C(6) (B = 8.9), compared with the other carbon atoms C(5) and C(4), shows that disorder also exists to some extent for this atom (see Table X).

The common feature to isomers a, exo, and d, endo, is to have the propyl group *R* only in the vicinity of the nitrosyl ligand. On the other hand, it is likely that the six other isomers (Scheme XII) undergo steric hindrance between the propyl group and either the cyclopentadienyl ring or the triphenylgermyl moiety. The mechanism leading to this isomerization is not perfectly clear at the present time and does not seem to be just a rotation of the allylic ligand like that of cyclopentadienyl rings in ferrocene. Actually Faller et al.[22] have proposed an isomerization mechanism involving the decoordination of the η^3-allylic to an η^1-allylic ligand.

Conclusion

The reaction of anions $[(\eta^5\text{-}C_5H_5)(CO)(L)(M_{4B}Ph_3)M_T]^-$ with unsaturated iodides seems to be general, with some limitations however. Allyl iodides give the neutral σ-bonded square-pyramidal complexes in which the allyl and the group 4B metal ligands are trans to each other.

These complexes may undergo thermal reaction to η^2-allyl complexes via η^3-allyl ones. According to the nature of M_T and M_{4B} the η^1-, η^3-, or η^2-allylic complexes can be isolated. Nethertheless the reaction pathway seems to be the same in all cases, but the reaction can stop and give the η^3 intermediate.

σ complexes bearing ω-alkenyl ligands undergo thermal reaction to η^3-allylic ones, with isomerization of the chain. This structure is established unambiguously by an X-ray structure determination. Interestingly, among the possible isomers, the two having less steric hindrance are obtained.

Acknowledgment. We are grateful to Dr. J. C. Promê, Centre de Recherche de Biochimie et de Gênétique Cellulaires, Toulouse, for the recording and calculations of mass spectra by field desorption and to R. Astier and Dr. E. Philippot of the laboratoire de Chimie Minêrale, Chimie des Matériaux, E.R.A. 314, Universitê des Sciences et Techniques du Languedoc, for the help with X-ray data collection on a Nonius CAD-4 diffractometer

Registry No. **1**, 89958-46-3; **2**, 89958-47-4; **3**, 89958-48-5; **4**, 89975-08-6; **5**, 89958-49-6; **6**, 89958-50-9; **7**, 89975-09-7; **8**, 89958-51-0; **9**, 89958-52-1; **10**, 89958-53-2; a,*exo*-**11**, 89958-54-3; d,*endo*-**11**, 90025-74-4; a,*exo*-**12**, 89958-55-4; d,*endo*-**12**, 90129-08-1.

Supplementary Material Available: A table of vibrational thermal parameters (Table IX) and a listing of observed and calculated structure factors (Table X) (13 pages). Ordering information is given on any current masthead page.

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[22] Faller, J. W.; Shvo, Y.; Chao, K.; Murray, H. H. *J. Organomet. Chem.* **1982**, *226*, 251.

Preparation of Group 4A Complexes Containing Tri-*tert*-butylmethoxide (tritox), a Steric Cyclopentadienyl Equivalent

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Received January 12, 1984

Li(tritox), $((CH_3)_3C)_3COLi$, reacts stoichiometrically with MCl_4 (M = Zr, Ti) to form $(tritox)_2ZrCl_3{\cdot}Li(OEt_2)_2$ (**1**), $(tritox)_2MCl_2$ (M = Zr (**2**), Ti (**4**)), and $(tritox)TiCl_3$ (**5**). From $TiCl_3$ and Li(tritox) (1:2), a complex tentatively formulated as "$(tritox)_2TiCl$" (**3**) was obtained; **3** yielded the corresponding dichloride **4** upon treatment with CCl_4. Derivatization of the M(IV) chlorides with CH_3Li produced $(tritox)_2M(CH_3)_2$ (M = Zr (**6**), Ti (**7**)) and $(tritox)Ti(CH_3)_3$ (**8**). Controlled alcoholysis of $Zr(CH_2Ph)_4$, $Zr(CH_2C(CH_3)_3)_4$, and **6** with (tritox)H gave $(tritox)Zr(CH_2Ph)_3$ (**9**), $(tritox)Zr(CH_2C(CH_3)_3)_3$ (**10**), and $(tritox)_3ZrCH_3$ (**11**), respectively. An X-ray structure determination of **1** showed the tritox units equatorially disposed in this pseudo-tbp complex. Crystal data: monoclinic, $P2_1/c$, $a = 12.946$ (3) Å, $b = 14.026$ (3) Å, $c = 26.257$ (4) Å, $\beta = 121.016$ (12)°, $Z = 4$, and $T = -75$ °C. Standard refinement procedures yielded an R factor of 0.079 from 4346 data where $|F_o| \geq 3\sigma(|F_o|)$. The spatial resemblence of tritox to cyclopentadienyl (Cp) is discussed; the short Zr–O bonds (1.895 Å average) and near linear Zr–O–C ∠'s (169° average) of **1** also suggest that tritox may function as a five-electron donor, like Cp.

Introduction

An important challenge confronting the organometallic chemist concerns the synthesis of complexes that are coordinatively unsaturated, since this characteristic is necessary for observation of metal-centered reactivity.[1] One approach to this problem involves the use of both neutral and anionic ancillary ligands that sterically "saturate" a metal center that may remain coordinatively and electronically unsaturated. For example, by using bis(trimethylsilyl)amide, a number of workers have prepared low coordinate $M[N(Si(CH_3)_3)_2]_n$ complexes that span the periodic table.[2,3] In a similar fashion, sterically comparable phosphide ligands are currently being exploited.[4] Bulky neutral ligands, principally phosphines (PR_3, R = cyclohexyl, *tert*-butyl, etc.), have been used to prepare several

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[1] Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980.

[2] Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273.

[3] (a) Anderson, R. A. *Inorg. Chem.* **1979**, *18*, 1724. (b) Simpson, S. J.; Turner, H. W.; Anderson, R. A. *Ibid.* **1981**, *20*, 2991. (c) Tilley, T. D.; Zalkin, A.; Anderson, R. A.; Templeton, D. H. *Ibid.* **1981**, *20*, 551. (d) Anderson, R. A. *Ibid.* **1979**, *18*, 2929.

[4] (a) Baker, R. T.; Krusic, P. J.; Tulip, T. H.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 6763. (b) Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1437 and references therein.

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