structures were then completed by successive difference Fourier syntheses. Reflections with $F_o^2 > 3\sigma(F_o^2)$ were considered observed and were included in the refinement (on F) by full-matrix least squares. Weights were calculated as $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = \sigma^2(I) + (pF_o^2)^2$, $\sigma(I)$ based on counting statistics, and p an instability factor obtained from plots of F_o versus weighted error. After completion of the isotropic refinement of the non-H atoms an empirical absorption correction, using the DIFABS[39] routine, was performed for all structures. Due to the presence of a heavy atom not all H atoms were located on difference Fourier maps of the structures. In some cases macrocyclic and/or urea H atoms were put in calculated positions and treated as riding on their parent atoms. Details concerning the treatment of the H-atoms are in the Supplementary Material. Parameters refined were the overall scale factor, an isotropic extinction parameter g ($F_o = F_c/(1 + gI_c)$), positional and anisotropic thermal parameters for non-H atoms, and positional and isotropic thermal parameters for H-atoms. Refinement converged with shift/error ratios less than unity. Final difference Fourier maps showed features less than 1.0 eÅ^{-3}, mostly near the heavy atom. All calculations were done with SDP.[40]

Acknowledgment. These investigations were supported in part by the Netherlands Technology Foundation (STW), Future Technical Science Branch of the Netherlands Organization for the Advancement of Pure Research (ZWO). We are indebted to Dr. J. C. Hubert for stimulating discussions and to AKZO Research BV for financial support.

Supplementary Material Available: Tables of positional and thermal parameters of all atoms, bond distances and angles, and torsion angles in the macrocycle for the crystal structures of the compounds **12a**, **19a**·H_2O, **16e**·urea, and **20e**·urea (26 pages). Ordering information is given on any current masthead page.

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Synthesis and Catalysis of Novel Mono- and Bis(diene) Complexes of Niobium and X-ray Structures of Binuclear $[Nb(\mu\text{-}Cl)(C_5H_5)(s\text{-}cis\text{-butadiene})]_2$ and Mononuclear $Nb(C_5H_5)(s\text{-}cis\text{-}2,3\text{-dimethylbutadiene})_2$

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Abstract: A series of novel mono(diene)-niobium complexes of the type $NbCl_2(C_5R_5)$(*s-cis*-diene) (R = CH_3, H; diene = 2,3-dimethylbutadiene, isoprene, butadiene) of supine (exo) conformation was synthesized by the 1:1 reaction of $NbCl_4(C_5R_5)$ with (2-butene-1,4-diyl)magnesium or its higher homologue. Using a similar procedure, binuclear niobium-diene complexes, $[Nb(\mu\text{-}Cl)(C_5H_5)(\text{butadiene})]_2$ and $[Nb(\mu\text{-}Cl)(C_5H_5)(\text{isoprene})]_2$, could also be isolated as crystals and the X-ray analysis was applied for the former. The 1:2 reaction of $NbCl_4(C_5R_5)$ with (2-butene-1,4-diyl)magnesium or its derivatives leads to $Nb(C_5R_5)(s\text{-}cis\text{-diene})_2$ of supine-prone (exo-endo) conformation in good yields. A very unusual s-cis,s-trans mixed bis(diene)-metal complex was obtained in the case of $Nb(C_5H_5)(\text{butadiene})_2$ as a mixture with its geometrical isomer bearing two *s-cis*-C_4H_6 ligands. The addition reaction of a deuterium labeled complex $Nb(C_5H_5)(C_6H_6D_4)(C_6H_{10})$ with 2,4-dimethyl-3-pentanone proved the exceedingly high reactivity of the prone-oriented diene relative to the supine diene toward electrophiles. The isolated binuclear Nb-diene complexes and bis(diene)niobium complexes exhibit a fairly good catalytic activity for the polymerization of butadiene, linear dimerization of isoprene, and cyclic trimerization of 1-alkynes. $[Nb(\mu\text{-}Cl)(C_5H_5)(s\text{-}cis\text{-}C_4H_6)]_2$ crystallizes as monoclinic crystals, space group $P2_1/c$ with a = 12.257 (2) Å, b = 8.088 (1) Å, c = 19.049 (4) Å, β = 108.39 (1)°, and z = 4. The complex is diamagnetic in spite of the presence of a long Nb-Nb bond (3.364 (1) Å). A bis(*s-cis*-diene)niobium complex of supine-prone conformation, $Nb(C_5H_5)(2,3\text{-dimethylbutadiene})_2$, crystallizes as orthorhombic crystals, space group *Pnma* with a = 8.961 (1) Å, b = 12.305 (2) Å, c = 13.530 (2) Å, and z = 4.

The chemistry of diene complexes of d-block along with f-block early transition metals (Zr,[1] Ti,[2] Hf,[3] Ta,[4] Th,[5,6] U,[6] etc.) is attracting increasing interests, since these complexes display a distinctive chemistry reflecting their unique M-C bonding property and their ability to perform the highly selective reactions. Previously we have reported unusual orientation of coordinated dienes and remarkable structures for group 5A tantalum-diene complexes (a third transition series metal complex) of the type $TaCl_2(C_5R_5)$(diene) and $Ta(C_5R_5)(\text{diene})_2$,[4] which became accessible by employing (2-butene-1,4-diyl)magnesium or its derivatives as an effective diene-incorporating reagent.[7] The extension of the above chemistry to niobium-diene complexes is of fundamental importance to prove the notable chemical and structural features of the second transition series group 5A metal species, since the

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Table I. Chemical Characterization and EIMS Spectral Data for Niobium–Mono(diene) Complexes

complexes	mp (°C)	metal content, %		mass spectral data (rel intensity)	
		found[a]	calcd	found	calcd[b]
$Cp^*NbCl_2(C_6H_{10})$ (**1**)	130	24.2	24.4	384 [$M^+(^{37}Cl)$, 0.8], 382 [$M^+(^{37}Cl, ^{35}Cl)$, 4.1], 380 [$M^+(^{35}Cl)$, 6.8], 300 [$M^+(^{37}Cl, ^{35}Cl) - C_6H_{10}$, 64.4], 298 [$M^+(^{35}Cl) - C_6H_{10}$, 100.0]	381.2
$Cp^*NbCl_2(C_5H_8)$ (**2**)	125	25.6	25.3	370 [$M^+(^{37}Cl)$, 0.4], 368 [$M^+(^{37}Cl, ^{35}Cl)$, 3.3], 366 [$M^+(^{35}Cl)$, 4.7], 300 [$M^+(^{37}Cl, ^{35}Cl) - C_5H_8$, 65.4], 298 [$M^+(^{35}Cl) - C_5H_8$, 100.0]	367.2
$Cp^*NbCl_2(C_4H_6)$ (**3**)	111	25.4	26.3	356 [$M^+(^{37}Cl)$, 0.7], 354 [$M^+(^{37}Cl, ^{35}Cl)$, 3.6], 352 [$M^+(^{35}Cl)$, 5.1], 300 [$M^+(^{37}Cl, ^{35}Cl) - C_4H_6$, 62.4], 298 [$M^+(^{35}Cl) - C_4H_6$, 100.0]	353.1
$CpNbCl_2(C_6H_{10})$ (**4**)	163	30.2	29.9	314 [$M^+(^{37}Cl)$, 0.3], 312 [$M^+(^{37}Cl, ^{35}Cl)$, 5.8], 310 [$M^+(^{35}Cl)$, 9.0], 230 [$M^+(^{37}Cl, ^{35}Cl) - C_6H_{10}$, 64.7], 228 [$M^+(^{35}Cl) - C_6H_{10}$, 100.0]	311.1
$CpNbCl_2(C_5H_8)$ (**8**)	105	30.0	31.3	300 [$M^+(^{37}Cl)$, 0.7], 298 [$M^+(^{37}Cl, ^{35}Cl)$, 4.8], 296 [$M^+(^{35}Cl)$, 7.1], 230 [$M^+(^{37}Cl, ^{35}Cl) - C_5H_8$, 65.2], 228 [$M^+(^{35}Cl) - C_5H_8$, 100.0]	297.0
$CpNbCl_2(C_4H_6)$ (**9**)	90	34.0	32.8	286 [$M^+(^{37}Cl)$, 0.3], 284 [$M^+(^{37}Cl, ^{35}Cl)$, 5.1], 282 [$M^+(^{35}Cl)$, 7.0], 230 [$M^+(^{37}Cl, ^{35}Cl) - C_4H_6$, 64.2], 228 [$M^+(^{35}Cl) - C_4H_6$, 100.0]	283.0
$[NbCp(\mu\text{-}Cl)(C_5H_8)]_2$ (**5a**)	230	35.8	35.5	526 [$M^+(^{37}Cl)$, 0.1], 524 [$M^+(^{37}Cl, ^{35}Cl)$, 1.0], 522 [$M^+(^{35}Cl)$, 1.4], 263 [$M^+(^{37}Cl)/2$, 1.0], 262 [$M^+(^{37}Cl, ^{35}Cl)/2$, 17.6], 261 [$M^+(^{35}Cl)/2$, 57.1], 195 [$M^+(^{37}Cl, ^{35}Cl)/2 - C_5H_8$, 21.0], 193 [$M^+(^{35}Cl)/2 - C_5H_8$, 100.0]	523.2
$[NbCp(\mu\text{-}Cl)(C_4H_6)]_2$ (**6a**)	216	37.7	37.5	498 [$M^+(^{37}Cl)$, 0.2], 496 [$M^+(^{37}Cl, ^{35}Cl)$, 0.9], 494 [$M^+(^{35}Cl)$, 1.0], 249 [$M^+(^{37}Cl)/2$, 0.9], 248 [$M^+(^{37}Cl, ^{35}Cl)/2$, 10.3], 247 [$M^+(^{35}Cl)/2$, 37.2], 195 [$M^+(^{37}Cl, ^{35}Cl)/2 - C_4H_6$, 32.11, 193 [$M^+(^{35}Cl)/2 - C_4H_6$, 100.0]	495.1

[a] Determined by employing the metal oxide method. [b] Calculated by using atomic weight defined by IUPAC.

Table II. ^1H NMR Data (δ (ppm), J (Hz)) for Niobium–Mono(diene) Complexes and Related Complexes[a]

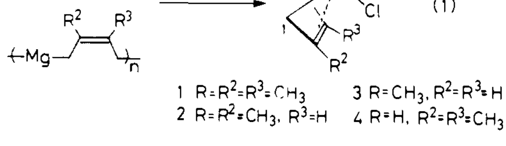
complexes	$\nu_{R^{1a},R^{4a}}$	$\nu_{R^{1s},R^{4s}}$	ν_{R^2,R^3}	$\nu_{C_5R_5}$
$NbCl_2(C_5Me_5)(CH_2CMe{=}CMeCH_2)$ (**1**)	0.44 (d, $J_{1a,1s} = 6.2$)	1.00 (d, $J_{4a,4s} = 6.2$)		1.81
$NbCl_2(C_5Me_5)(CH_2CMe{=}CHCH_2)$ (**2**)	0.79 (d, $J_{1a,1s} = 7.2$)	0.98 (d)	6.69	1.80
	0.96 (dd, $J_{3,4a} = 7.0$)	1.68 (dd, $J_{3,4s} = 6.5$, $J_{4a,4s} = 7.2$)		
$NbCl_2(C_5Me_5)(CH_2CH{=}CHCH_2)$ (**3**)	0.46 (dd, $J_{1a,1s} = 6.0$) ($J_{1a,2} = J_{3,4a} = 7.5$)	1.35 (dd, $J_{4a,4s} = 6.0$) ($J_{1s,2} = J_{3,4s} = 6.5$)	7.07 ($J_{2,3} = 6.2$)	1.77
$NbCl_2(C_5H_5)(CH_2CMe{=}CMeCH_2)$ (**4**)	0.84 (d, $J_{1a,1s} = 6.2$)	1.14 (d, $J_{4a,4s} = 6.2$)		6.05
$NbCl_2(C_5H_5)(CH_2CMe{=}CHCH_2)$ (**8**)	0.76 (d, $J_{1a,1s} = 7.1$)	0.86 (d, $J_{4a,4s} = 6.3$)	6.59	6.01
	0.90 (dd, $J_{3,4a} = 7.5$)	1.65 (dd, $J_{3,4s} = 6.0$)		
$NbCl_2(C_5H_5)(CH_2CH{=}CHCH_2)$ (**9**)	0.32 (dd, $J_{1a,1s} = 6.0$) ($J_{1a,2} = J_{3,4a} = 7.2$)	1.27 (dd, $J_{4a,4s} = 6.0$) ($J_{1s,2} = J_{3,4s} = 6.5$)	7.29 ($J_{2,3} = 6.5$)	6.07
$TaCl_2(C_5H_5)(CH_2CH{=}CHCH_2)$[b]	0.19 (dd, $J_{1a,1s} = 6.5$) ($J_{1a,2} = J_{3,4a} = 7.5$)	0.96 (dd, $J_{4a,4s} = 6.5$) ($J_{1s,2} = J_{3,4s} = 6.5$)	7.03 ($J_{2,3} = 6.5$)	6.06
$TaCl_2(C_5H_5)(CH_2CMe{=}CMeCH_2)$[b]	0.40 (d, $J_{1a,1s} = 6.0$)	0.69 (d, $J_{4a,4s} = 6.0$)		5.98
$[Nb(\mu\text{-}Cl)(C_5H_5)(CH_2CMe{=}CHCH_2)]_2$ (**5a**)	0.86 (d, $J_{1a,1s} = 7.0$)	1.29 (d, $J_{4a,4s} = 7.2$)		
	0.91 (dd, $J_{3,4a} = 7.2$)	1.60 (dd, $J_{3,4s} = 6.5$)	5.28	5.34
$[Nb(\mu\text{-}Cl)(C_5H_5)(CH_2CH{=}CHCH_2)]_2$ (**6a**)	2.62 (dd, $J_{1a,1s} = 6.5$) ($J_{1a,2} = J_{3,4a} = 7.4$)	3.82 (dd, $J_{4a,4s} = 6.5$) ($J_{1s,2} = J_{3,4s} = 7.0$)	5.10 ($J_{2,3} = 6.0$)	5.12

[a] Spectra were measured at 500 MHz in C_6D_6 at 30 °C and analyzed by computer simulation. Numbering system is given in eq 1, 2, and 5. [b] See ref 4.

chemistry of niobium–diene complexes has not yet been well-warranted except for two short communications.[8] Especially noteworthy is the higher tendency of Nb(V) species to be reduced to Nb(IV) species, which has scarcely been seen for tantalum series. We report here the preparation and characterization of a series of mono(*s-cis*-diene) and bis(*s-cis*-diene) complexes of niobium and the first examples of the s-cis,s-trans mixed bis(diene)metal complex along with the X-ray structural studies on a novel binuclear mono(*s-cis*-diene)niobium and on a monomeric bis(*s-cis*-diene)niobium. Quite unique catalysis of these complexes in diene and alkyne oligomerization or polymerization is also described.

Results and Discussion

Synthesis and Characterization of Mono(*s-cis*-diene)–Niobium Complexes. When a tetrahydrofuran solution of 0.8–0.9 equiv of (2,3-dimethyl-2-butene-1,4-diyl)magnesium was added dropwise to a stirred solution of $NbCl_4Cp^*$ ($Cp^* = C_5Me_5$) dissolved in tetrahydrofuran at 0 °C, the solution takes on a lime-green coloration from red brown with the precipitation of a magnesium salt. Removal of the solvent in vacuo and extraction of the product into deoxygenated hexane followed by cooling to −20 °C allowed $NbCl_2Cp^*$(2,3-dimethylbutadiene) (**1**) to be isolated as air and moisture sensitive green crystals in >60% yield (eq 1). The precursor $NbCl_4(C_5R_5)$ (R = CH_3, H) can be synthesized conveniently in high yield upon treatment of $NbCl_5$ with 1 equiv of $SiMe_3(C_5R_5)$.[9] Analogously, the isoprene, butadiene, and 2,3-dimethylbutadiene complexes (**2**, **3**, and **4**) are synthesized starting from the corresponding (2-butene-1,4-diyl)magnesium compounds.



(1)

The mass spectra of **1**–**4** clearly confirm their monomeric nature

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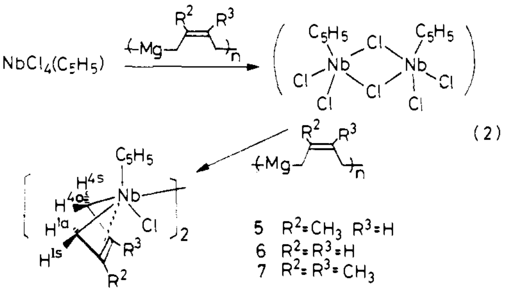
and the chemical characterization supports the proposed constitution (Table I). Improved procedure is required for the isolation of pure mono(butadiene) complex **9** ligated by a less bulky auxiliary ligand (Cp). The ^{1}H NMR spectral data for **1–4** indicate the supine (exo) conformation and the s-cis diene geometry since their spectral patterns (Table II) compare very closely with those of isoelectronic $TaCl_2(C_5R_5)$(*s-cis*-butadiene) and $TaCl_2(C_5R_5)$(*s-cis*-2,3-dimethylbutadiene) reported earlier.[4] The large intensity of $[Nb(C_5R_5)Cl_2]^+$ fragment observed in the EIMS spectra indicates that the Nb–diene bond in $NbCl_2(C_5R_5)$(diene) is weak as compared with its Nb–C_5R_5 and Nb–Cl bonds (see Table I).

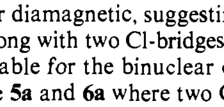
A novel binuclear niobium–diene complex, $[NbClCp(isoprene)]_2$ (**5**), was obtained as a mixture with $NbCl_2Cp$(isoprene) (**8**) in a 75:25 ratio when $NbCl_4Cp$ was treated with 0.7 equiv of (2-methyl-2-butene-1,4-diyl)magnesium (eq 2). The complex **5** can be separated from **8** by repeating the recrystallization from a hydrocarbon solvent as these have a substantial difference in their solubility. An analogous reaction between $NbCl_4Cp$ with (2-butene-1,4-diyl)magnesium (1:0.8 ratio) affords a pure sample of the binuclear complex, $[Nb(\mu\text{-}Cl)Cp(\textit{s-cis}\text{-butadiene})]_2$ (**6**), as the sole product in ca. 55% yield as revealed by the NMR and EIMS spectroscopies (Tables I and II). However, the corresponding reaction of $NbCl_4Cp$ with (2,3-dimethyl-2-butene-1,4-diyl)magnesium did not yield any binuclear complex like **7**. It yields only the mononuclear complex **4**.



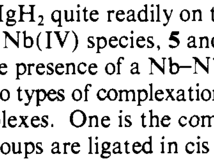
(2)

The magnitude of the coupling constant $J_{2,3}$ (6.0 Hz) for **6** clearly confirms the s-cis geometry. The appreciable downfield shift of H^1 and H^4 signals of **6** in comparison with those for monomeric complexes **1–4** may arise from the increased Nb–C π-bonding interaction (η^4-diene coordination property) as a result of loss of one Cl ligand (electron-withdrawing group).

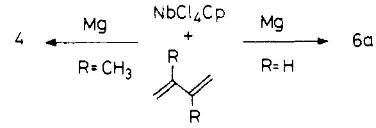
The formation of binuclear complexes is responsible to the reduction of the starting Nb(V) compound to a formally Nb(IV) species by the action of the magnesium compound. Such a function of enediylmagnesium as an equivalence of atomic magnesium has also been reported for magnesium–anthracene adducts, which affords RMgX or MgH_2 quite readily on treating it with RX or H_2.[10] The resulting Nb(IV) species, **5** and **6**, are however diamagnetic, suggesting the presence of a Nb–Nb single bond along with two Cl-bridges. Two types of complexations seem conceivable for the binuclear complexes. One is the complex of the type **5a** and **6a** where two Cp groups are ligated in cis fashion and the other is its trans isomer, **5b** and **6b**. Although the trans geometry has been reported for a closely related niobium–diphenylacetylene complex, $[Nb(\mu\text{-}Cl)(C_5R_5)(ArC{\equiv}CAr)]_2$,[11] the X-ray crystallographic analysis of **6** proved the unique cis geometry opposed to our expectation (vide infra). One of the possible explanations for this is as follows. If the reduction of $NbCl_4Cp$ occurs prior to the diene complexation on the solid surface of the aggregated magnesium–diene adduct, it should give rise to $[NbCl_3Cp]_2$ possessing the Cp ligands in the cis position as a result of steric repulsion between the Cp and the solid surface and then the diene–metal complexation should follow to afford **5a** or **6a**. Recall that (2-butene-1,4-diyl)magnesium is highly aggregated and hence sparingly soluble in THF, while (2-methyl-2-butene-1,4-diyl)magnesium and (2,3-dimethyl-2-butene-1,4-diyl)magnesium have better solubility in THF. Indeed the heterogeneous reaction of $NbCl_4Cp$ on the metallic magnesium surface in the presence of 1,3-butadiene gives rise to only the expected *cis*-$[Nb(\mu\text{-}Cl)Cp(C_4H_6)]_2$ in 23–35% yield. Exceptional is the heterogeneous reaction of $NbCl_4Cp$ with magnesium turnings in the presence of 2,3-dimethylbutadiene, which gives only the monomeric Nb(V) species **4** in 38% yield in place of the binuclear Nb(IV) species. Thus the steric bulk of ligated dienes also plays an important role in determining the reaction courses.



5a R=CH3
6a R=H

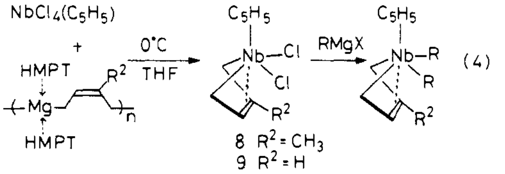


5b R=CH3
6b R=H



(3)

In support of the above prediction, the reaction of $NbCl_4Cp$ with a soluble reducing agent, *i*-PrMgBr or EtMgBr (0.4–0.8 equiv), in the presence of butadiene, gave mononuclear butadiene complex **9** predominantly in 30–45% yield. To further substantiate this assumption, the reaction of $NbCl_4Cp$ with a hexamethylphosphoric triamide adduct, (2-butene-1,4-diyl)magnesium·$(HMPT)_2$ or (2-methyl-2-butene-1,4-diyl)magnesium·$(HMPT)_2$, was examined as these HMPT adducts are freely soluble in THF. Actually these homogeneous reactions gave the desired mono(butadiene) complex **9** and the mono(isoprene) complex **8** in a state of high purity, without accompanying binuclear complexes, **5a** and **6a** (eq 4). In summarizing the above results, we can conclude that the steric bulk of dienes as well as that of auxiliary ligands along with the solubility of the reducing agents serve as crucial factors in controlling the reaction courses. In the hope of developing an alternative route to $[Nb(\mu\text{-}Cl)Cp(butadiene)]_2$, reduction of **9** was also examined. However, complex **9** gives $Nb(C_5H_5)(C_4H_6)R_2$ (R = Me, Bu) in good yields on treatment with CH_3MgBr or C_4H_9MgBr, while the reduction of **9** with magnesium turnings gives bis(butadiene) complex (**17a** and **17b** in a 1.0:0.92 ratio) in 30% yield accompanied by the precipitation of a cluster-like solid as a result of disproportionation of the initially formed product at 0 °C.



(4)

Numerous efforts have been paid to dissociate the binuclear species, **5a** and **6a**, into monomeric species by the coordination of electron donors (PMe_3, PEt_3, pyridine, HMPT, dipyridyl, TMEDA, etc.), but all of these attempts have failed at present because the Nb–Nb bond is so strong that these donors could not induce the bond dissociation, i.e., the addition of these donors to **5a** and **6a** did not alter their ^{1}H NMR spectral patterns even when the mixture is heated to 80 °C in toluene-d_8. The use of trimethylamine oxide or pyridine oxide as a hard base is also ineffective due to the rapid decomposition of the complexes (**5a** and **6a**) presumably due to the oxidation of the metal.

Crystal Structure of $[Nb(\mu\text{-}Cl)(C_5H_5)(butadiene)]_2$ (6a). The solid-state molecular structure of **6a** shown in Figure 1 clearly confirms its dimeric nature. The X-ray experimental data are summarized in Table III and the fractional atomic coordinates in Table IV. The perspective interatomic bond distances and

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(10) Bogdanović, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 262 and references cited therein.

(11) Curtis, M. D.; Real, J. *Organometallics* **1985**, *4*, 940.

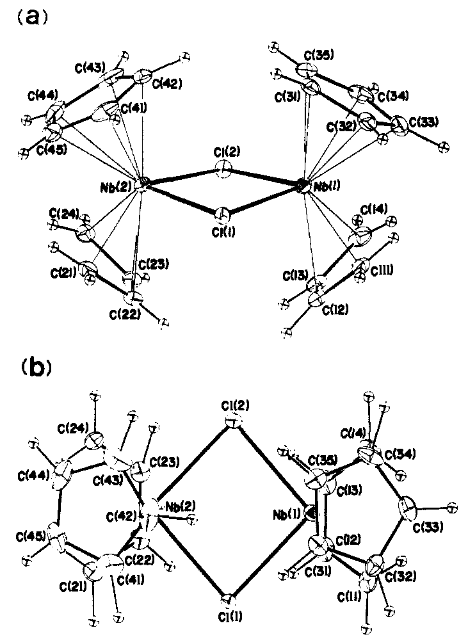

Figure 1. Two molecular projections of [Nb(μ-Cl)(C_5H_5)(C_4H_6)]$_2$ (**6a**) by ORTEP drawings: (a) side view and (b) top view.

Table III. Crystallographic and Experimental Data for **6a** and **15**

	6a	15
formula	$C_{18}H_{22}Cl_2Nb_2$	$C_{17}H_{25}Nb$
formula wt	495.1	322.3
system	monoclinic	orthorhombic
space group	$P2_1/c$	*Pnma*
a, Å	12.257 (2)	8.961 (1)
b, Å	8.088 (1)	12.305 (2)
c, Å	19.049 (4)	13.530 (2)
β, deg	108.39 (1)	
V, Å^3	1791.9 (5.1)	1491.9 (4)
Z	4	4
D_{calcd}, g cm^{-3}	1.835	1.434
F(000), e	984	672
μ (Mo Kα), cm^{-1}	15.3	7.7
crystal size, mm	0.20 × 0.25 × 0.35	0.10 × 0.25 × 0.25
T, °C	20	20
2θ limits,[a] deg	$4 < 2\theta < 65$	$0 < 2\theta < 65$
scan type	θ–2θ	θ–2θ
scan speed, deg min^{-1} in 2θ	4.0	4.0
scan width, deg in 2θ	$2.0 + 0.70 \tan\theta$	$2.0 + 0.70 \tan\theta$
bkgd counting, s	5	5
data collected	$+h,+k,\pm l$	$+h,+k,+l$
unique data	6480	3404
reflctns obsd[b]	4674	1626
no. of params refined	288	136
R(*F*)[c]	0.039	0.056
$R_w(F)$[d]	0.064	0.077

[a] Diffraction data were collected with a Rigaku automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. [b] Reflections were regarded as observed if $|F_o| > 5\sigma(F_o)$. [c] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$, $w^{-1} = \sigma^2(F_o) + g(F_o)^2$.

Table IV. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors[a] for Non-Hydrogen Atoms in **6a**, with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq}
Nb(1)	0.23396 (3)	−0.01166 (5)	0.172732 (19)	2.62
Nb(2)	0.26321 (3)	0.09631 (5)	0.348270 (18)	2.66
Cl(1)	0.09076 (8)	0.09541 (13)	0.23251 (6)	2.33
Cl(2)	0.41054 (9)	0.02473 (14)	0.28465 (6)	2.61
C(11)	0.1194 (5)	0.1396 (7)	0.0741 (3)	4.2
C(12)	0.1926 (6)	0.2585 (7)	0.1199 (3)	4.5
C(13)	0.3115 (6)	0.2378 (7)	0.1392 (3)	5.1
C(21)	0.1749 (5)	0.3344 (6)	0.3705 (3)	3.3
C(22)	0.2363 (5)	0.3860 (6)	0.3213 (3)	3.3
C(23)	0.3549 (5)	0.3566 (6)	0.3425 (3)	3.3
C(24)	0.4073 (4)	0.2784 (6)	0.4124 (3)	3.2
C(31)	0.1495 (5)	−0.2790 (6)	0.1838 (3)	3.3
C(32)	0.1128 (5)	−0.2320 (7)	0.1084 (3)	3.3
C(33)	0.2131 (6)	−0.2278 (7)	0.0848 (4)	4.1
C(34)	0.3073 (5)	−0.2688 (7)	0.1464 (4)	4.4
C(35)	0.2680 (5)	−0.3015 (6)	0.2071 (3)	3.7
C(41)	0.1465 (6)	−0.0825 (9)	0.3950 (4)	7.3
C(42)	0.2252 (7)	−0.1829 (7)	0.3745 (4)	5.8
C(43)	0.3323 (7)	−0.1415 (10)	0.4224 (5)	9.0
C(44)	0.3196 (7)	−0.0210 (9)	0.4700 (4)	6.7
C(45)	0.2098 (8)	0.0161 (8)	0.4539 (4)	6.3

[a] See: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table V. Interatomic Bond Distances (Å) and Angles (deg) for Non-Hydrogen Atoms in **6a** with Estimated Standard Deviations in Parentheses

(a) Bond Distances			
Nb(1)–Nb(2)	3.364 (1)		
Nb(1)–Cl(1)	2.528 (1)	Nb(2)–Cl(1)	2.528 (1)
Nb(1)–Cl(2)	2.531 (1)	Nb(2)–Cl(2)	2.539 (1)
Nb(1)–C(11)	2.309 (6)	Nb(2)–C(21)	2.313 (6)
Nb(1)–C(12)	2.392 (7)	Nb(2)–C(22)	2.399 (6)
Nb(1)–C(13)	2.401 (7)	Nb(2)–C(23)	2.405 (6)
Nb(1)–C(14)	2.311 (7)	Nb(2)–C(24)	2.328 (5)
Nb(1)–C(31)	2.435 (6)	Nb(2)–C(41)	2.394 (8)
Nb(1)–C(32)	2.395 (6)	Nb(2)–C(42)	2.390 (9)
Nb(1)–C(33)	2.378 (7)	Nb(2)–C(43)	2.378 (8)
Nb(1)–C(34)	2.380 (8)	Nb(2)–C(44)	2.396 (9)
Nb(1)–C(35)	2.434 (6)	Nb(2)–C(45)	2.394 (10)
C(11)–C(12)	1.412 (9)	C(21)–C(22)	1.437 (8)
C(12)–C(13)	1.396 (9)	C(22)–C(23)	1.400 (8)
C(13)–C(14)	1.395 (9)	C(23)–C(24)	1.430 (8)
C(31)–C(32)	1 415 (8)	C(41)–C(42)	1.407 (12)
C(32)–C(33)	1.436 (9)	C(42)–C(43)	1.383 (12)
C(33)–C(34)	1.401 (10)	C(43)–C(44)	1.373 (12)
C(34)–C(35)	1.410 (10)	C(44)–C(45)	1.317 (14)
C(31)–C(35)	1.390 (8)	C(41)–C(45)	1.396 (12)
(b) Bond Angles			
Cl(1)–Nb(1)–Cl(2)	96.4 (1)	Cl(1)–Nb(2)–Cl(2)	96.2 (1)
Nb(1)–Cl(1)–Nb(2)	83.4 (1)	Nb(1)–Cl(2)–Nb(2)	83.1 (1)
C(11)–Nb(1)–C(14)	72.7 (2)	C(21)–Nb(2)–C(24)	72.5 (2)
C(11)–C(12)–C(13)	119.2 (6)	C(21)–C(22)–C(23)	118.1 (5)
C(12)–C(13)–C(14)	117.9 (6)	C(22)–C(23)–C(24)	117.7 (5)
C(32)–C(31)–C(35)	108.9 (5)	C(42)–C(41)–C(45)	107.3 (7)
C(31)–C(32)–C(33)	107.1 (5)	C(41)–C(42)–C(43)	105.6 (7)
C(32)–C(33)–C(34)	107.0 (6)	C(42)–C(43)–C(44)	109.0 (8)
C(33)–C(34)–C(35)	109.1 (6)	C(43)–C(44)–C(45)	109.2 (8)
C(31)–C(35)–C(34)	107.9 (6)	C(41)–C(45)–C(44)	108.9 (8)

angles for non-hydrogen atoms are collected in Table V with anisotropic thermal parameters. The molecule contains a non-cyrstallographic symmetry passing through the centroids of C_5H_5 rings, niobium atoms, and midpoints of butadiene inner C–C bonds. The expected additional mirror symmetry passing through two chlorine atoms and normal to the Nb(1)--Nb(2) vector is broken by the unique relative position of two Cp ligands, i.e., one is eclipsed and another is staggered to the butadiene ligand in the molecular projection shown in Figure 1b.

Of particular interest is the the location of the two Cp ligands (or two C_4H_6 ligands) in the cis position (on the same side of the Nb_2Cl_2 core). The molecular structure however does not provide any persuasive reason for the preference of the cis geometry (even the trans geometry seems probable from the view of interspatial interaction among the ligands). The observed geometry may therefore be considered as a result of the heterogeneous reaction on the surface of the magnesium compound as suggested above. The dihedral angle between two Cp rings (58.5°) is smaller than the dihedral angle between the two butadiene planes (83.5°). The distances of four Nb–Cl are comparable (av 2.459 Å) and are slightly longer than those reported for [Nb(C_5H_4Me)(CO)$_2$Cl(μ-Cl)]$_2$ (2.459 Å) and [Nb(C_5H_4Me)(ArC≡CAr)(μ-Cl)]$_2$ (2.235 Å).[11] The Nb_2Cl_2 core adopts a little folded rhombus. Its puckered angle is 10.3°. Strictly planar Nb_2Cl_2 core is reported for [Nb(C_5H_4Me)(CO)$_2$Cl(μ-Cl)]$_2$ while the extensively folded Nb_2Cl_2 core is known for [Nb(C_5H_4Me)(CO)$_2$(μ-Cl)]$_2$ containing semibridged two chlorine atoms.[11] The Nb–Nb distance of 3.364 Å for **6a** is marginally larger when compared with those of [Nb(C_5H_4Me)(CO)$_2$(μ-Cl)]$_2$ (3.056 Å) and [Nb(C_5H_4Me)(ArC≡CAr)(μ-Cl)]$_2$ (3.072 Å), which contain planar Nb_2Cl_2

Table VI. Chemical Characterization and EIMS Spectral Data for Niobium–Bis(diene) Complexes

		metal content, %		mass spectral data (rel intensity)	
complex	mp (°C)	found[a]	calcd	found	calcd[b]
$Cp^*Nb(C_6H_{10})_2$ (**12**)	128	24.5	23.7	392 (M^+, 30.5), 310 ($M^+ - C_6H_{10}$, 70.2), 306 ($M^+ - C_6H_{14}$, 100.0)	392.4
$Cp^*Nb(C_5H_8)_2$ (**13**)	82	25.7	25.5	364 (M^+, 30.7), 296 ($M^+ - C_5H_8$, 71.3), 294 ($M^+ - C_5H_{10}$, 100.0)	364.4
$Cp^*Nb(C_4H_6)_2$ (**14**)	111	28.2	27.6	336 (M^+, 32.5), 282 ($M^+ - C_4H_6$, 68.8), 278 ($M^+ - C_4H_{10}$, 100.0)	336.3
$CpNb(C_6H_{10})_2$ (**15**)	185	29.9	28.8	322 (M^+, 33.1), 240 ($M^+ - C_6H_{10}$, 73.3), 236 ($M^+ - C_6H_{14}$, 100.0)	322.3
$CpNb(C_5H_8)_2$ (**16**)	98	31.0	31.6	294 (M^+, 36.0), 226 ($M^+ - C_5H_8$, 64.9), 224 ($M^+ - C_5H_{10}$, 100.0)	294.2
$CpNb(C_4H_6)_2$ (**17**)	133	35.4	34.9	266 (M^+, 57.1), 212 ($M^+ - C_4H_6$, 86.8), 210 ($M^+ - C_4H_8$, 100.0)	266.2

[a] Determined by the metal oxide method. [b] Calculated using the atomic weight defined by IUPAC.

Table VII. ^{1}H NMR Data (δ (ppm), J (Hz)) for Niobium–Bis(diene) Complexes and Related Complexes[a]

complexes	[supine] [prone]	$\nu_{R^{1a},R^{4a}}$ $\nu_{R^{5a},R^{8a}}$	$\nu_{R^{1s},R^{4s}}$ $\nu_{R^{5s},R^{8s}}$	ν_{R^2,R^3} ν_{R^6,R^7}	$\nu_{C_5R_5}$
$Nb(C_5Me_5)(CH_2CMe{=}CMeCH_2)_2$ (**12**)		−0.01 (d, $J_{1a,1s} = 6.0$)	1.95 (d, $J_{4a,4s} = 6.0$)		1.66
		−0.13 (d, $J_{5a,5s} = 5.8$)	1.06 (d, $J_{8a,8s} = 5.8$)		
$Nb(C_5Me_5)(CH_2CMe{=}CHCH_2)_2$ (**13**)		0.98 (d, $J_{1a,1s} = 6.0$)	2.28 nd)	3.84 (dd)	1.50
		0.54 (dd, $J_{3,4a} = 8.2$)	2.86 (dd, $J_{3,4s} = 7.1$)		
		0.96 (d, $J_{5a,5s} = 6.0$)	2.17 (d)	3.34 (dd)	
		0.01 (dd, $J_{7,8a} = 10.0$)	2.39 (dd, $J_{7,8s} = 8.0$)		
$Nb(C_5Me_5)(CH_2CH{=}CHCH_2)_2$ (**14**)		0.50 (dd, $J_{1a,1s} = 6.5$)	1.77 (dd, $J_{4a,4s} = 6.5$)	4.77 ($J_{2,3} = 7.1$)	1.55
		($J_{1a,2} = J_{3,4a} = 8.2$)	($J_{1s,2} = J_{3,4s} = 6.5$)		
		0.34 (dd, $J_{5a,5s} = 6.0$)	2.19 (dd, $J_{8a,8s} = 6.0$)	3.74 ($J_{6,7} = 8.4$)	
		($J_{5a,6} = J_{7,8a} = 10.0$)	($J_{5s,6} = J_{7,8a} = 9.3$)		
$Nb(C_5H_5)(CH_2CMe{=}CMeCH_2)_2$ (**15**)		0.46 (d, $J_{1a,1s} = 5.8$)	2.37 (d, $J_{4a,4s} = 5.8$)		4.90
		−0.47 (d, $J_{5a,5s} = 5.8$)	1.95 (d, $J_{8a,8s} = 5.8$)		
$Nb(C_5H_5)(CH_2CMe{=}CHCH_2)_2$ (**16**)		0.32 (d, $J_{1a,1s} = 6.0$)	2.22 (d)	4.27 (dd)	4.82
		0.28 (dd, $J_{3,4a} = 7.5$)	2.66 (dd $J_{3,4s} = 6.5$)		
		0.30 (d, $J_{5a,5s} = 6.0$)	1.76 (d)	3.96 (dd)	
		−0.52 (dd, $J_{7,8a} = 10.0$)	1.99 (dd, $J_{7,8s} = 8.0$)		
$Nb(C_5H_5)(CH_2CH{=}CHCH_2)_2$ (**17a**)		0.59 (dd, $J_{1a,1s} = 6.1$)	2.83 (dd, $J_{4a,4s} = 6.1$)	4.57 ($J_{2,3} = 7.3$)	4.84
		($J_{1a,2} = J_{3,4a} = 9.3$)	($J_{1s,2} = J_{3,4s} = 6.2$)		
		0.22 (dd, $J_{5a,5s} = 3.8$)	2.06 (dd, $J_{8a,8s} = 3.8$)	4.29 ($J_{6,7} = 7.4$)	
		($J_{5a,6} = J_{7,8a} = 11.2$)	($J_{5s,6} = J_{7,8s} = 9.8$)		
$Nb(C_5H_5)(CH_2CH{=}CHCH_2)_2$ (**17b**)	s-trans	1.67 (dd, $J_{1a,1s} = 4.2$)	1.48 (dd, $J_{1s,2} = 7.3$)	2.39 ($J_{2,3} = 13.7$, H_2)	4.78
		(dd, $J_{1a,2} = 12.1$)			
		2.57 (dd, $J_{4a,4s} = 1.4$)	2.75 (dd, $J_{3,4s} = 6.0$)	3.16 (H_3)	
		(dd, $J_{3,4a} = 12.7$)			
	s-cis	0.76 (dd, $J_{5a,5s} = 0.1$)	2.20 (dd, $J_{5s,6} = 5.9$)	4.67 ($J_{6,7} = 6.8$, H_6)	
		(dd, $J_{5a,6} = 7.8$)			
		0.82 (dd, $J_{8a,8s} = 0.01$)	2.17 (dd, $J_{7,8s} = 7.2$)	3.65 (H_7)	
		(dd, $J_{7,8a} = 8.3$)			
$Nb(C_5H_5)(CH_2CMe{=}CMeCH_2)$-$(CH_2CH{=}CHCH_2)$		0.48 (d, $J_{1a,1s} = 5.8$)	2.42 (d, $J_{4a,4s} = 5.8$)		4.78
		−0.34 (dd, $J_{5a,5s} = 6.0$)	2.25 (dd, $J_{8a,8s} = 6.0$)	4.33 ($J_{6,7} = 7.7$)	
$Ta(C_5Me_5)(CH_2CMe{=}CMeCH_2)_2$[b]		−0.36 (d, $J_{1a,1s} = 7.5$)	1.14 (d, $J_{4a,4s} = 7.5$)		1.95
		−0.76 (d, $J_{5a,5s} = 11.1$)	1.18 (d, $J_{8a,8s} = 11.1$)		
$Ta(C_5H_5)(CH_2CMe{=}CMeCH_2)_2$[b]		0.05 (d, $J_{1a,1s} = 8.0$)	1.78 (d, $J_{4a,4s} = 8.0$)		5.04
		−0.28 (d, $J_{5a,5s} = 8.0$)	1.45 (d, $J_{8a,8s} = 8.0$)		
$Ta(C_5H_5)(CH_2CH{=}CHCH_2)_2$[b]		0.30 (dd, $J_{1a,1s} = 8.2$)	2.49 (dd, $J_{4a,4s} = 6.2$)	4.93 ($J_{2,3} = 7.0$)	4.88
		($J_{1a,2} = J_{3,4a} = 8.2$)	($J_{1s,2} = J_{3,4s} = 6.5$)		
		0.45 (dd, $J_{5a,5s} = 5.8$)	1.84 (dd, $J_{8a,8s} = 5.8$)	4.40 ($J_{6,7} = 8.5$)	
		($J_{5a,6} = J_{7,8a} = 11.0$)	($J_{5s,6} = J_{7,8s} = 11.0$)		

[a] Spectra were measured at 500 MHz in C_6D_6 at 30 °C and analyzed by computer simulation. Chemical shift values are calibrated by using C_6H_6 as an internal standard, assumed to be 7.2 ppm. [b] See ref 4.

cores and two C_5H_4Me ligands on the opposite side (trans position) of the Nb_2Cl_2 square array. The N-bridged $Nb_2N_2L_2$-type binuclear niobium (2.83–2.92 Å, e.g., $[NbCp_2NCAr)]_2$),[12] S-bridged niobium compounds (3.13–3.16 Å, e.g., $[NbCp_2S]_2$),[13] and O-bridged niobium compound (2.781 Å for $[NbCl_2(OMe)_2\cdot MeOH]_2$)[14] generally exhibit much shorter Nb–Nb bonds. In spite of the anomalously long Nb–Nb bond distance, the complex **6a** maintains the diamagnetic nature as confirmed by the NMR spectroscopy. This is indicative of the presence of direct Nb–Nb spin coupling. Each of the butadiene–Nb units is composed of the bent σ^2, π-metallacyclo-3-pentene structure familiar to tantalum–diene and zirconium–diene complexes, although the bonding property of the limiting π^2-η^4-diene–metal species contributes significantly to the present metallacycle as estimated from the respective C–C bond lengths (vide infra).

Synthesis and Characterization of Bis(diene)–Niobium Complexes. The addition of 2 equiv of (2,3-dimethyl-2-butene-1,4-diyl)magnesium to $NbCl_4Cp^*$ or $NbCl_4Cp$ in tetrahydrofuran resulted in the formation of bis(diene) complexes, $Nb(C_5R_5)$-(2,3-dimethylbutadiene)$_2$, in high yields where R is CH_3 (**12**) or H (**15**). Analogous bis(isoprene) complexes (**13** and **16**) and $NbCp^*$(butadiene)$_2$ (**14**) could be synthesized by the corresponding 1:2 reactions. The chemical characterization and the mass spectral data listed in Table VI clearly confirm the formula given in eq 5. Complexes **12**–**16** exhibit magnetically inequivalent two diene units as deduced from the ^{1}H NMR and they show the spectral pattern characteristic to the bis(diene) complexes of supine-prone (exo-endo) geometry (Table VII). The supine-prone structure has already been established in the case of Ta-

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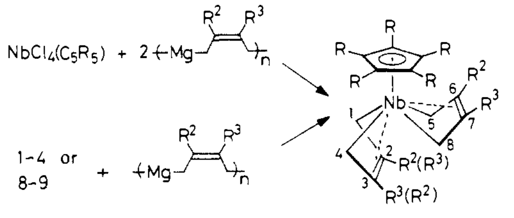
(12) (a) Cotton, F. A.; Roth, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 3734. (b) Lemenovskii, D. A.; Fedin, V. P.; Slovohotov, Yu. L.; Struchkov Yu. T. *J. Organomet. Chem.* **1982**, *228*, 153.

(13) (a) Herrmann, W. A.; Biersack, H.; Ziegler, M. L.; Balbach, B. *J. Organomet. Chem.* **1981**, *206*, C33. (b) Skripkin, Yu. V.; Eremenko, I. L.; Pasynskii, A. A.; Struchkov, Yu. T.; Shklover, V. E. *J. Organomet. Chem.* **1984**, *267*, 285.

(14) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 22.

(C_5R_5)(2,3-dimethylbutadiene)$_2$ (R = H, CH_3) based on the X-ray analyses.[4] The treatment of mono(diene) complexes, **1** and **4**, with (2,3-dimethyl-2-butene-1,4-diyl)magnesium also provides the same complexes, **12** and **15**, respectively, as revealed by the chemical and spectroscopic characterizations (Tables VI and VII).

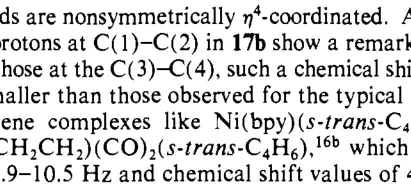


(5)

12 R=R^2=R^3=CH_3 15 R=H, R^2=R^3=CH_3
13 R=R^2=CH_3, R^3=H 16 R=R^3=H, R^2=CH_3
14 R=CH_3, R^2=R^3=H 17a R=R^2=R^3=H

Thus all of the above noted niobium–bis(diene) complexes (**12–16**) assume the supine-prone (exo-endo) geometry although conventional bis(diene) complexes of group 6–8 transition metals are reported to prefer the supine-supine geometry.[15] The preference of the supine-prone geometry for niobium complexes can be explained on the basis of the same molecular orbital argument as described for tantalum–bis(diene) complexes.[4] Comparison of the NMR data of bis(diene) complexes with those of mono(diene) complexes reveals a general trend that syn-protons (at C^1, C^4, C^5, C^8) of the former complexes resonate at lower field as compared with those of mono(diene) complexes, while anti-protons (at C^1, C^4, C^5, C^8) and the olefinic protons (H^2, H^3, H^6, H^7) are shifted to higher field. This change may be ascribed to the combined shielding effect of C_5R_5 and diene ligands as a result of an increased proximity of these ligands.

Very unusual complexation is observed in the reaction of $NbCl_4Cp$ with 2 equiv of (2-butene-1,4-diyl)magnesium and also in the reaction of **9** with 1 equiv of (2-butene-1,4-diyl)magnesium, both of which give rise to a mixture of two isomeric products. All attempts at separation have been failures. However, the 500-MHz ^1H NMR indicates the presence of two isomers (100-MHz NMR spectrum is useless for the assignment). One is the supine-prone bis(s-*cis*-butadiene)niobium complex (**17a**) as can be assigned readily by reference to the NMR data of related complexes (**12–16**), while the other is a new type of bis(diene) complex (**17b**) involving one *s-cis*-butadiene and one *s-trans*-butadiene in a molecule as shown in eq 6 (relative ratio, 1.0:0.93). Computer simulation of the spectrum for **17b** reveals that the *s-trans*-C_4H_6 exhibits the coupling constant $J_{2,3}$ of 13.7 Hz while the $J_{6,7}$ for the *s-cis*-C_4H_6 is 6.8 Hz (Table VII). Furthermore, we can presume on the basis of the chemical shift values that both of these C_4H_6 ligands are nonsymmetrically η^4-coordinated. Although the signals of protons at C(1)–C(2) in **17b** show a remarkable upfield shift from those at the C(3)–C(4), such a chemical shift difference is much smaller than those observed for the typical 1-2-η^2-coordinated diene complexes like Ni(bpy)(*s-trans*-C_4H_6)$_2$[16a] and $Mo(C_5H_4CH_2CH_2)(CO)_2$(*s-trans*-C_4H_6),[16b] which involve $J_{2,3}$ values of 9.9–10.5 Hz and chemical shift values of 4.4–5.4 ppm for the noncoordinated vinyl group. Despite our repeated attempts, single crystals suited for the X-ray analysis have not been obtained as yet.



(6)

17b

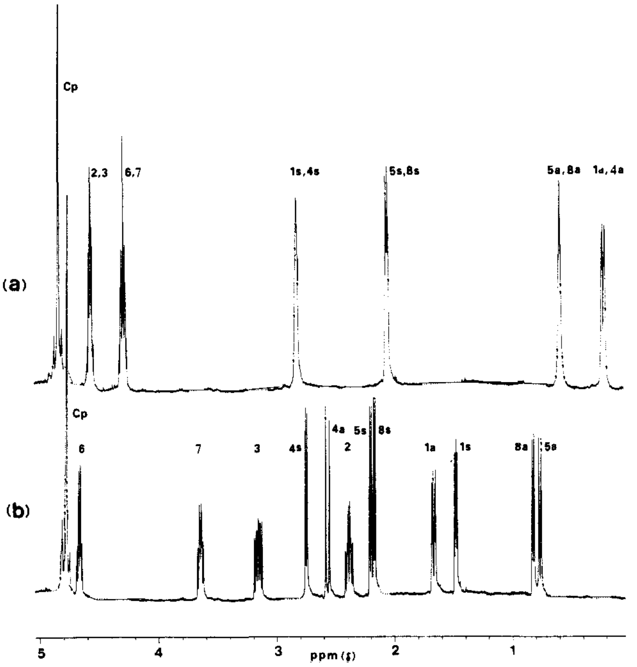


Figure 2. ^1H NMR (500 MHz) spectra of a mixture of two isomers of $Nb(C_5H_5)(C_4H_6)_2$ intentionally separated into (a) NbCp(*supine-s-cis*-C_4H_6)(*prone-s-cis*-C_4H_6) (**17a**) and (b) NbCp(*s-cis*-C_4H_6)(*s-trans*-C_4H_6) (**17b**). The assignment of each signal was made with the help of the decoupling procedure and finally by computer simulation. See eq 5 and 6 for numbering systems.

A set of NMR spectra for the s-cis-,s-cis isomer (**17a**) and the s-trans,s-cis isomer (**17b**) is given separately for clarity in Figure 2, spectra a and b, respectively. This is the first example of the η^4-s-*cis*, η^4-s-*trans* mixed bis(diene) complex throughout the organometallics. Heating or cooling of the mixture in the range of −80 to 80 °C does not induce any interconversion between **17a** and **17b**. The addition of 3 equiv of PR_3 (R = Me, Et), pyridine, or triethylamine to the mixture also did not alter the ratio. Thus the relative ratio must be determined kinetically during the formation of **17**. Further details on the reaction pathway still remain equivocal.

The gated-decoupled ^{13}C NMR spectra were measured to find a difference in the M–C bonding character if any between niobium–diene and tantalum–diene complexes. The spectral data for the binuclear complex **6a** compare very closely to those for the mononuclear complex **9** and to those for a tantalum analogue, $TaCl_2Cp(C_4H_6)$ (Table VIII). Thus the Nb–C_4H_6 units in **6a** and **9** may be best described in terms of the metallacyclo-3-pentene structure. The C–H coupling constants for the terminal carbons of the dienes in **5a–6a**, **8–9**, and **15–16** fall into a narrow range, 145–150 Hz, irrespective of the mode of diene coordination (supine or prone) and the type of complexation (mononuclear or binuclear). These values are intermediate between those (158–161 Hz) observed for conventional η^4-diene–metal complexes of group 6–8 late transition metals[17] and those (123–126 Hz) for group 4A fluxional metallacyclo-3-pentenes, $ZrCp^*_2$(isoprene)[1] and $HfCp^*_2$(butadiene).[3] A remarkable chemical shift difference was observed between the mono(diene) complexes (**5a–6a**, **8–9**) and bis(diene) complexes (**15–16**). The terminal carbons (C-1, C-4) of the former resonate at higher field as compared with those for bis(diene) complexes, reflecting more electron rich metal center of the latter.

To get further insight into the reaction pathway for formation of bis(diene) complexes, a labeling experiment was performed with

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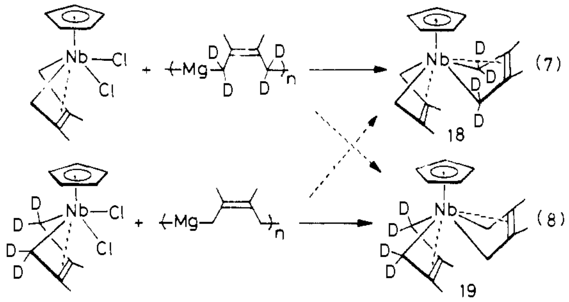
Table VIII. ^{13}C NMR Chemical Shift Values (δ, ppm) and ^{13}C–^{1}H Coupling Constants (Parentheses, Hz) for Niobium–Mono(diene) and Niobium–Bis(diene) Complexes[a]

complexes	$\nu_{C\text{-}1,C\text{-}4}$	$\nu_{C\text{-}2,C\text{-}3}$	$\nu_{C\text{-}5,C\text{-}8}$	$\nu_{C\text{-}6,C\text{-}7}$	$\nu_{C_5R_5}$
NbCl$_2$Cp(IP) (**8**)	63.9 (t, 147)	137.2 (s)			114.8 (d, 170)
	63.4 (t, 146)	123.8 (d, 161)			
NbCl$_2$Cp(BD) (**9**)	60.1 (t, 145)	123.0 (d, 165)			113.2 (d, 167)
[Nb(μ-Cl)Cp(IP)]$_2$ (**5a**)	63.0 (t, 147)	135.1 (s)			100.7 (d, 172)
	63.3 (t, 146)	116.9 (d, 160)			
[Nb(μ-Cl)Cp(BD)]$_2$ (**6a**)	59.6 (t, 147)	122.3 (d, 160)			101.5 (d, 171)
NbCp(DM)$_2$ (**15**)	33.0 (t, 145)	119.7 (s)	33.1 (t, 150)	116.8 (s)	105.6 (d, 168)
NbCp(IP)$_2$ (**16**)	40.5 (t, 148)	120.5 (s)	42.6 (t, 148)	111.3 (s)	97.4 (d, 168)
	40.1 (t, 147)	112.1 (d, 159)	42.3 (t, 147)	98.6 (d, 156)	
NbCp*(BD)$_2^b$ (**14**)	48.41 (t, 149)	107.38 (d, 159)	42.51 (t, 150)	116.23 (d, 157)	105.14 (s)
NbCp(BD$_2^b$ (**17a**)	46.49 (t, 149)	111.12 (d, 159)	41.06 (t, 150)	100.21 (d, 157)	96.40 (d, 174)
NbCp(BD$_2^b$ (**17b**)	35.41 (t, 148)	104.18 (d, 155)	43.06 (d, 151)	69.99 (d, 158)	95.71 (d, 174)
(s-cis,s-trans)	36.54 (t, 150)	106.17 (d, 159)	74.84 (dd, 153, 161)	114.99 (d, 158)	
TaCl$_2$Cp(BD)^c	62.4 (t, 146)	126.1 (d, 169)			112.9 (d, 173)
TaCp(BD)$_2^c$	35.9 (t, 150)	113.8 (d, 156)	37.2 (t, 148)	103.7 (d, 155)	96.9 (d, 172)

[a] In ppm downfield from external Me$_4$Si in CDCl$_3$. Data were collected in C$_6$D$_6$ at 30 °C (22.5 MHz). Assignment of **14** and **15** was made referring to the chemical shift values for **18** and **19** (not shown). BD, butadiene; IP, isoprene; DM, 2,3-dimethylbutadiene. [b] Data were collected at 125.65 MHz. [c] Data from ref 4. Numbering system is given in eq 1, 2, and 5.

tetradeuteriated (2,3-dimethyl-2-butene-1,4-diyl-*1,1,4,4-d*$_4$)-magnesium. If NbCp(2,3-dimethylbutadiene)$_2$ (**15**) is formed through mono(diene) complex **4** keeping its initial supine conformation, the reaction of **4** with deuteriated magnesium–2,3-dimethylbutadiene compound must give rise to the conformer **18** as the sole product, while if the process involves a geometrical change, it should produce another isomer **19**. The ^{1}H NMR chemical shifts for the ensuing product clearly confirm structure **18**. Thus the reaction proceeds cleanly (>95% in puruty) without accompanying isomer **19**. On the other hand, a pure sample of isomer **19** could be obtained on treating NbCpCl$_2$(2,3-dimethylbutadiene-d$_4$) with nondeuteriated (2,3-dimethyl-2-butene-1,4-diyl)magnesium. The above noted sequential (stepwise) reaction will enable us to obtain a variety of mixed bis(diene) complexes by choosing an appropriate combination of niobium and magnesium compounds. Actually, a mixed bis(diene) complex, for example, NbCp(*prone*-s-*cis*-butadiene)(*supine*-s-*cis*-2,3-dimethylbutadiene), could be obtained from the stoichiometric reaction of complex **4** with (2-butene-1,4-diyl)magnesium in good yield (see Table VII).



Crystal Structure of Nb(C$_5$H$_5$)(2,3-dimethylbutadiene)$_2$ (15). As a typical example of niobium–bis(diene) complexes, NbCp-(2,3-dimethylbutadiene)$_2$ (**15**) was subjected to the X-ray crystallographic analysis. Comparison of the molecular structure of **15** with that of isomorphous TaCp(2,3-dimethylbutadiene)$_2$, a well-defined bis(diene)tantalum complex,[4] will surely provide a nice opportunity to find the absolute effect of metal on the coordination geometry along with the M–C bonding property emerged by replacement of Ta with Nb. The structural result of **15** is given in Figure 3 with the numbering scheme. Atomic positional parameters for non-hydrogen atoms are collected in Table IX. Selected bond distances and angles are listed in Table X. The gross structure of **15** resembles very well that of TaCp(2,3-dimethylbutadiene)$_2$ and again assumes the supine-prone geometry in fair agreement with the solution structure. The M–C(terminal) and M–C(central) bond distances of **15** are almost in parallel with the corresponding M–C bond distances found in the tantalum analogue within 0.03 Å. Also comparable are the

Table IX. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors[a] for Non-Hydrogen Atoms in **12**, with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}
Nb	0.12949 (8)	0.2500	0.48721 (5)	2.3
C(1)	0.2093 (8)	0.1376 (7)	0.3635 (5)	3.1
C(2)	0.3500 (7)	0.1943 (6)	0.3834 (5)	2.9
C(5)	0.4881 (10)	0.1287 (10)	0.4061 (7)	4.4
C(11)	0.2686 (9)	0.1344 (7)	0.5870 (5)	3.1
C(12)	0.1827 (8)	0.1929 (6)	0.6584 (5)	3.0
C(15)	0.0822 (13)	0.1260 (10)	0.7282 (8)	4.8
C(21)	−0.1022 (8)	0.1921 (8)	0.4009 (7)	4.3
C(22)	−0.1055 (9)	0.1560 (9)	0.4990 (6)	4.4
C(23)	−0.1174 (12)	0.2500	0.5603 (9)	4.2

[a] See: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table X. Interatomic Bond Distances (Å) and Angles (deg) for Non-Hydrogen Atoms in **15** and Isoelectronic Tantalum Complex, TaCp(C$_6$H$_{10}$)$_2$ (Estimated Standard Deviations)

	15	TaCp(C$_6$H$_{10}$)$_2^d$
	(a) Bond Distances	
Nb/Ta–C(1)	2.286 (8)	2.261 (8)
Nb/Ta–C(2)	2.519 (7)	2.522 (7)
Nb/Ta–C(11)	2.324 (8)	2.292 (6)
Nb/Ta–C(12)	2.467 (7)	2.473 (6)
Nb/Ta–C(21)	2.486 (9)	2.482 (11)
Nb/Ta–C(22)	2.408 (10)	2.411 (13)
Nb/Ta–C(23)	2.424 (11)	2.419 (16)
C(1)–C(2)	1.466 (10)	1.469 (11)
C(2)–C(2′)	1.371 (13)	1.352 (11)
C(11)–C(12)	1.429 (10)	1.475 (10)
C(12)–C(12′)	1.405 (14)	1.343 (11)
C(2)–C(5)	1.509 (14)	1.525 (12)
C(12)–C(15)	1.543 (13)	1.544 (13)
C(21)–C(22)	1.400 (14)	
C(22)–C(23)	1.427 (15)	
C(21)–C(21′)	1.424 (19)	
Nb/Ta–CCP^a	2.253	2.119
Nb/Ta–M1^b	1.820	1.796
Nb/Ta–M2^c	1.838	1.797
	(b) Bond Angles	
C(1)–Nb/Ta–C(1′)	74.4 (3)	74.8 (3)
C(11)–Nb/Ta–C(11′)	75.5 (3)	76.7 (3)
C(1)–C(2)–C(2′)	118.4 (6)	118.4 (7)
C(11)–C(12)–C(12′)	120.2 (7)	120.6 (7)
C(1)–C(2)–C(5)	119.3 (7)	118.5 (7)
C(11)–C(12)–C(15)	117.3 (7)	115.9 (7)
C(2′)–C(2)–C(5)	122.3 (7)	123.1 (7)
C(12′)–C(12)–C(15)	122.2 (7)	123.3 (7)
C(22)–C(21)–C(21′)	108.5 (8)	108.1 (10)
C(22)–C(23)–C(22′)	108.2 (9)	108.8 (13)

[a] CCP: centroid of cyclopentadienyl ligand. [b] M1: midpoint of C(1) and C(1′). [c] M2: midpoint of C(11) and C(11′). [d] See ref 4.

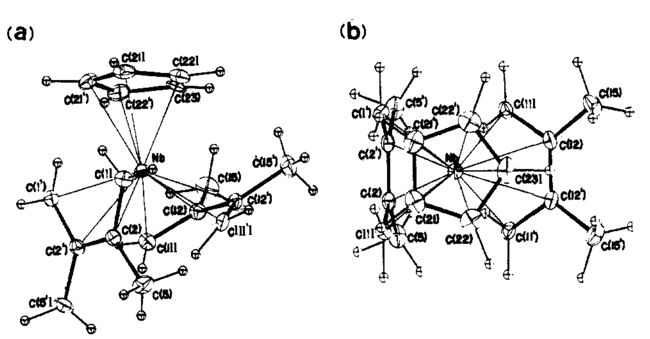
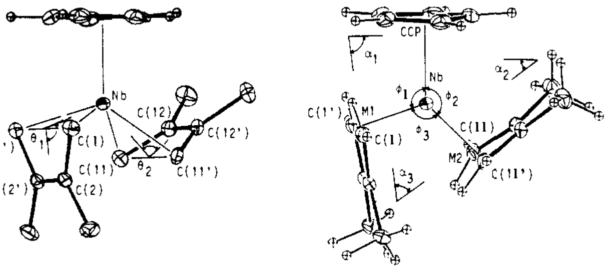


Figure 3. Molecular projections of $Nb(C_5H_5)(s\text{-}cis\text{-}C_6H_{10})_2$ (**15**) by ORTEP drawings: (a) side view and (b) top view.

Table XI. Structural Parameters (deg) in Coordination Geometry for **15** and Related $TaCp(2,3\text{-dimethylbutadiene})_2$



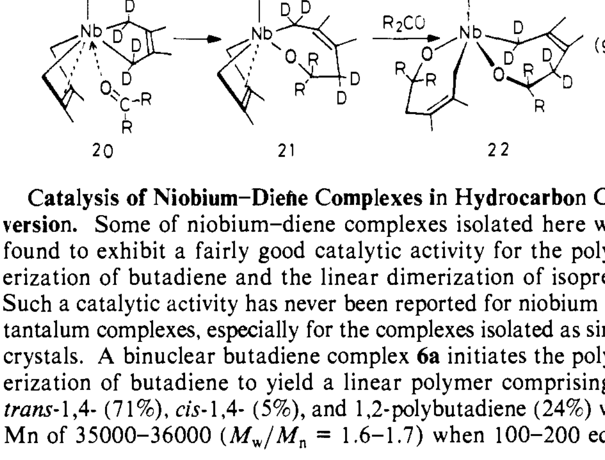
	15	$TaCp(C_6H_{10})_2$
θ_1	101.1	102.5
θ_2	98.8	100.4
α_1	80.5	81.5
α_2	36.0	35.0
α_3	63.5	63.6
ϕ_1	107.6	108.5
ϕ_2	138.2	137.2
ϕ_3	114.2	114.3

coordination geometry around the metal (see ϕ_1, ϕ_2, and ϕ_3 defined in Table XI and dihedral angles between the planes of Cp and *supine*-diene (α_1) and that between the planes of Cp and *prone*-diene (α_2) together with that between planes of two diene units (α_3)).

Inspite of the above noted close resemblance, complex **15** shows an appreciable structural perturbation from the tantalum derivative. Perhaps the most important potentially is the relatively small difference in the C–C bond distances defined by $\Delta l = l$[C–C(external)] − l[C–C(internal)]. Although $TaCp(2,3\text{-dimethylbutadiene})_2$ exhibits a relatively large Δl of 0.132 Å for the *prone*-diene unit, the corresponding value for complex **15** diminishes significantly to 0.024 Å. The binuclear niobium complex **6a** also shows very small Δl of av 0.021 Å. This indicates that the displacement of Ta with Nb commonly causes a slight shift from the σ^2, π-metallacyclic limit to the (π^2-diene)metal limit for the *prone*-diene. Another feature is seen in the relatively small difference between the M–C bond lengths, Δd, defined by d[M–C(terminal)] − d[M–C(central)]. The value $|\Delta d|$ for **15** (av 0.188 Å) is slightly smaller than that (av 0.221 Å) observed for the corresponding tantalum analogue. When the metal–diene complex approaches the σ^2, π-metallacyclo-3-pentene limit as found for $ZrCp_2(2,3\text{-dimethylbutadiene})$ and $HfCp^*(2,3\text{-dimethylbutadiene})$, the value Δd reaches -0.297 and -0.243 Å, respectively. The metal in diene complexes of middle and late transition metals is usually situated in positions directly above the η^4-coordinated diene and hence Δd falls in the region of −0.1 to 0.1 Å. Thus the magnitude of Δd for bis(diene) complex **15** is intermediate between the values reported for the two limits but that for mono(diene) complex **6a** is consistent with the value for η^4-diene–metal complexes. As a consequence the bent angle (θ_1 and θ_2) between the C(terminal)–M–C(terminal) and the diene planes for **15** (98.8°, 101.1°) governs also the intermediates value between the angles reported for group 4A metal–diene complexes (110–120°) and the group 8 metal–diene complexes (75–92°),[18] whereas the bent angle for **6a** (86.6° for Nb(1) and 87.9° for Nb(2)) is almost comparable with those for group 8 metal–diene complexes. The Nb–C(terminal) bond distances for **15** and **6a** are in accord with the Nb–alkyl single bond distance found for $NbCp_2Et(C_2H_4)$ (2.290 Å)[19] and $NbCp_2(CH_2SiMe_2CH_2)$ (2.275 Å),[20] but larger than the Nb–acetylene bonds (2.038–2.125 Å)[21] which possess partially the Nb═C double bond character. On the basis of these structural parameters, it will be safe to say that σ^2, π-metallacyclic property is more pronounced in the mono(diene)niobium complexes while a substantial participation of π^2-η^4-diene–metal type bonding is recognized in the bis(diene)niobium complexes.

Nucleophilic Properties of Bis(diene)–Niobium Complexes. The niobium complexes reported in this article are expected to show pronounced reactivity toward electrophiles because of the high oxophilicity of the niobium metal. Indeed, all of the niobium complexes (**1-4**, **5a-6a**, **12-19**) readily react with aldehydes (CH_3CHO, $i\text{-}C_3H_7CHO$) and ketones (acetone, 2,4-dimethyl-3-pentanone, etc.) as found for $ZrCp_2(diene)$ and $HfCp_2(diene)$, but these are inert to esters (ethyl acetate, methyl acetate) in sharp contrast to the high reactivity of zirconium- and hafnium–diene complexes.[22] Thus, it is obvious that the oxophilicity of niobium–diene complexes is remarkably lower than that of group 4A metal–diene complexes.

By taking advantage of the high oxophilicity of niobium complexes, we have examined here the stoichiometric reaction of deuterium labeled mixed bis(diene)–niobium complexes (**18** and **19**) with 2,4-dimethyl-3-pentanone to evaluate the relative strength of nucleophilicity for each diene lying supine and prone. The 1:1 addition resulted in the selective insertion of the ketone to the *prone*-2,3-dimethylbutadiene-d_4 in **18** and the *prone*-2,3-dimethylbutadiene in **19** (>95%) as confirmed by the NMR analysis of the hydrolysate. Thus it is obvious that the *prone*-diene is much more reactive than the *supine*-diene toward electrophiles. The ketone molecule should access to the metal from the bottom (trans position) through the low-lying vacant dz^2 orbital as has been seen in the X-ray structure of $TaCl_4Cp^*\cdot CH_2{=}PMePh_2$.[23] Then the complex **18** may be transformed into a 16e complex **21**. Further addition of 2,4-dimethyl-3-pentanone leads to a doubly inserted compounds. Nb–olefin interaction is absent in these oxametallacycloheptene units as deduced from the NMR chemical shifts.



(9)

Catalysis of Niobium–Diene Complexes in Hydrocarbon Conversion. Some of niobium–diene complexes isolated here were found to exhibit a fairly good catalytic activity for the polymerization of butadiene and the linear dimerization of isoprene. Such a catalytic activity has never been reported for niobium and tantalum complexes, especially for the complexes isolated as single crystals. A binuclear butadiene complex **6a** initiates the polymerization of butadiene to yield a linear polymer comprising of *trans*-1,4- (71%), *cis*-1,4- (5%), and 1,2-polybutadiene (24%) with Mn of 35000–36000 (M_w/M_n = 1.6–1.7) when 100–200 equiv

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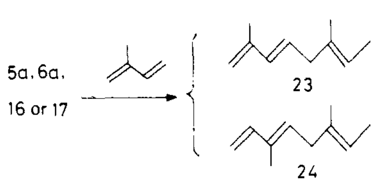
of butadiene was charged to a toluene solution of **6a** and reaction was carried out at 60 °C for 15 h. However, the complex **6a** catalyzes only the linear dimerization in place of the polymerization when isoprene was used under the same conditions. The ensuing isoprene dimer was composed of (*E*)-2,6-dimethyl-1,3,6-octatriene (**23**) (tail-to-head bonded dimer) and (*E*)-3,6-dimethyl-1,3,6-octatriene (**24**) (head-to-head bonded dimer) in a 85:15 ratio (eq 10). The turnover observed in this reaction is 17–22. Similar catalytic linear dimerization has recently been found by us utilyzing a two-component system, TiClCp*-(C_4H_6)/RMgX.[2b] The corresponding binuclear isoprene complex **5a** shows a diminished activity at 60 °C but at 90 °C the same type of dimerization occurred successfully to afford a mixture of **23** and **24** in ca. 85:15 (turnover 12).

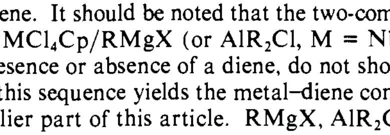


(10)

The bis(diene) complexes (**16** and **17**) show increased catalytic effect (turnover, 35–42) and they give rise again to a mixture of **23** and **24** (ca. 7:3 ratio). When butadiene (100 equiv) was used, complexes **16** and **17** provided trans-1,4-rich polybutadiene in 65–75% selectivity with $M_n = 183\,000$ ($M_w/M_n = 2.0$), $M_n = 129\,000$ ($M_w/M_n = 1.8$), respectively (reaction was carried out at 60 °C for 1 h). Thus bis(diene) complexes show a higher catalytic activity as compared with the binuclear complexes **5a** and **6a**. In contrast, all mono(diene)niobium complexes (**1–4**, **8–9**) and the tantalum analogues with formula $TaCl_2Cp$(diene) and $TaCp(diene)_2$ show no catalytic activity toward both butadiene and isoprene. It should be noted that the two-component catalytic systems, MCl_4Cp/RMgX (or AlR_2Cl, M = Nb, Ta) prepared in the presence or absence of a diene, do not show any catalysis, whereas this sequence yields the metal–diene complexes as noted in an earlier part of this article. RMgX, AlR_2Cl, or other contaminants existing in the two-component catalyst systems should destroy the active center or terminate the propagation reaction.

The linear dimerization of isoprene may proceed through a transient metallacycle formed by the oxidative coupling of two dienes in Nb(η^2-diene)$_2$ species which is in equilibrium with Nb(η^4-diene)$_2$. A similar mechanism has been proposed for the isoprene dimerization catalyzed by $ZrCp_2$(isoprene).[1a] More detailed mechanistic study is under progress on the basis of the stoichiometric reaction of dienes with complexes **5a**, **6a**, and **17**.

All the pure niobium–diene complexes tested here (**5a–6a**, **8–9**, **15–16**) also display a good catalysis for cyclotrimerization of 1-alkynes. For example, 1-butyne (100 equiv) was transformed into a mixture of 1,3,5- and 1,2,4-triethylbenzene (15:85 ratio) in 8 h at 60 °C in toluene in high conversion (75–85%) by the catalytic effect of binuclear complexes, **5a** and **6a**. Bis(diene) complexes (**15**, **16**) also conduct the cyclic trimerization but the catalytic effect is much lower (25–29%) and the ratio of 1,3,5- and 1,2,4-triethylbenzene changes to 62:28. In contrast to the above, mononuclear mono(diene) complexes (**8**, **9**) show extremely low activity under the same reaction conditions (ca. 3–8% conversion). Although the reaction mechanism for the present cyclic trimerization is uncertain at present, we can estimate at least that the cyclic trimerization occurs on the low valent "CpNb" or "CpNbCl" species because above complexes release the coordinated diene quantitatively during the reaction as detected in the NMR spectrum. Indeed, related high-valent metal compounds such as $NbCl_4Cp$ as well as $NbCl_4Cp^*$ show no catalysis.



(11)

Although precise mechanistic studies are required to gain further insight into the catalytic cycle, we can draw an important conclusion from this work that monometallic niobium complexes can serve as a new catalyst for polymerizations and oligomerizations of conjugated dienes and 1-alkynes; nevertheless such a catalytic action has scarcely been reported for the isolated group 5A transition-metal complexes.

Concluding Remarks. Monomeric niobium–mono(diene) complexes of the type $NbCl_2(C_5R_5)$(*s-cis*-diene) were found to assume always the supine conformation and bis(diene) complexes, Nb(C_5R_5)(*s-cis*-diene)$_2$, the unique supine-prone conformation. The large propensity of Nb(V) to be reduced to Nb(IV) species allows the formation of novel binuclear niobium–diene complexes in some favorable cases, while such type of complexation has not yet been received for the tantalum series. A remarkable mixed bis(diene)metal complex containing one *s-cis*-butadiene and one *s-trans*-butadiene ligand in a molecule was first obtained in the case of $NbCp(C_4H_6)_2$. The versatile catalysis of niobium–diene complexes observed in the polymerization or oligomerization of dienes and alkynes will promise further utility of this class of complexes as a potential new type of catalyst for the conversion of various hydrocarbons. The present structural studies provide a good experimental basis for penetrating into the reaction mechanisms for these catalytic reactions.

Experimental Section

All operations involving organometallics were carried out under an argon atmosphere in prepurified Schlenk apparatus. Nonaqueous solvents were thoroughly dried and deoxygenated in a manner appropriate to each and were distilled before use. $NbCl_5$ purchased from Mitsuwa Chemical Co. was used as received. Mass spectra (EI) were recorded on a JEOL DX-300 or a JEOL O ISG spectrometer. ^{1}H NMR spectra (500 MHz) were recorded on a JEOL GSX-500 or a Varian XL-100 spectrometer and analyzed with a Varian Spin Simulation program. ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer.

Preparation of $NbCl_4(C_5H_5)$ and $NbCl_4(C_5Me_5)$. A pure sample of $NbCl_4(C_5H_5)$ was obtained from the reaction of $NbCl_5$ (16.2 g, 60 mmol) in dichloromethane (500 mL) with $SiMe_3(C_5H_5)$ (8.3 g, 60 mmol) at 20 °C according to the procedure reported by Cardoso[9] (mp 180 °C dec). Dark-red crystals of $NbCl_4(C_5Me_5)$ were prepared in the following procedure. To a stirred solution of $NbCl_5$ (1.1 g, 4.1 mmol) in hot toluene (50 mL) warmed to 80 °C was added dropwise $SiMe_3(C_5Me_5)$ (0.9 g, 4.3 mmol) with use of a pressure-equalized dropping funnel. The mixture was stirred at 100 °C for 2 h and was then evaporated to dryness. The residue was washed with two portions of hexane (40 mL) and dried in vacuo to give $NbCl_4(C_5Me_5)$ as microcrystals. Yield, 70%, mp 145 °C. EIMS, *m/z* 368 (M^+). Anal. Calcd for $C_{10}H_{15}Cl_4Nb$: C, 32.47; H, 4.09; Cl, 38.33. Found: C, 32.23; H, 4.15; Cl, 38.56. The present method is superior to the reported preparation method with $Bu_3Sn(C_5Me_5)$[24] with respect to the easy handling and high yield of the product.

$NbCl_2(C_5Me_5)$(diene) (1–3). A solution of (2,3-dimethyl-2-butene-1,4-diyl)magnesium (1.4 mmol) in tetrahydrofuran (5 mL) was added dropwise using a syringe to a stirred solution of $NbCl_4(C_5Me_5)$ (0.6 g, 1.6 mmol) in tetrahydrofuran (15 mL). The mixture was allowed to warm to room temperature and stirred there for 2 h. The color of the solution changed from red to green. The product is extracted into thoroughly deoxygenated hexane (30 mL) and the solution was concentrated into 2 mL in vacuo. Cooling the green solution to −20 °C gave $NbCl_2(C_5Me_5)$(2,3-dimethylbutadiene) (**1**) as green crystals in 65% yield. The results of chemical characterization, mp, EIMS, and NMR data are summarized in Table I and II. By using an analogous procedure, $NbCl_2(C_5Me_5)$(isoprene) (**2**) and $NbCl_2(C_5Me_5)$(butadiene) (**3**) were obtained as green crystals in 60–65% yield. In the case of **3**, recrystallization was carried out in toluene. Anal. of **3** calcd for $C_{14}H_{21}Cl_2Nb$: C, 47.62; H, 5.99; Cl, 20.08. Found: C, 48.01; H, 6.19; Cl, 20.38.

$NbCl_2(C_5H_5)$(2,3-dimethylbutadiene) (4). A suspension of $NbCl_4(C_5H_5)$ (1.1 g, 3.7 mmol) in tetrahydrofuran (50 mL) was placed in a two-necked 100-mL Schlenk flask equipped with an inlet and then cooled to −70 °C. A tetrahydrofuran solution (5 mL) of (2,3-dimethyl-2-butene-1,4-diyl)magnesium (3.5 mmol) was added dropwise to the magnetically stirred suspension with a syringe. The mixture was stirred at 20 °C for 2 h and subsequently evaporated to dryness. After extraction of the product into hexane (40 mL), the salt was separated by filtration or centrifugation with use of a two-necked glass tube. The hexane extract was concentrated followed by cooling to −20 °C to give **4** as green crystals in 53% yield based on $NbCl_4(C_5H_5)$.

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[24] Herrmann, W. A.; Kalcher, W.; Briersack, H.; Bernal, I.; Creswick, M. *Chem. Ber.* **1981**, *114*, 3558.

$NbCl_2(C_5H_5)$(isoprene) (8). The addition of hexamethylphosphoric triamide (HMPT) (0.3 mL, 2 mmol) to a suspension of (2-methyl-2-butene-1,4-diyl)magnesium (2 mmol) in tetrahydrofuran (5 mL) followed by stirring at 30 °C for 1 h results in a homogeneous solution. The resulting orange solution was added to a stirred suspension of $NbCl_4(C_5H_5)$ (0.6 g, 2 mmol) at 0 °C. After the mixture was stirred for 2 h, the solution was evaporated to dryness. The product was recrystallized from oxygen-free hexane to give **8** as green crystals in 61% yield.

$NbCl_2(C_5H_5)$(butadiene) (9). Synthesis was carried out by using a similar procedure as described for **8** on reacting (2-butene-1,4-diyl)magnesium·$(HMPT)_2$ (2 mmol) with $NbCl_4(C_5H_5)$ (0.6 g, 2 mmol). Yield, 75% (green crystals).

[Nb(μ-Cl)(C_5H_5)(isoprene)]$_2$ (5a). A solution of (2-methyl-2-butene-1,4-diyl)magnesium (1.4 mmol) in tetrahydrofuran (5 mL) was dropwise added to a suspension of $NbCl_4(C_5H_5)$ (0.6 g, 2.0 mmol) in THF (10 mL) at −78 °C with magnetic stirring. The mixture was allowed to warm to room temperature, stirred there for 2 h, and evaporated. Then the product was extracted from the residue into hexane (20 mL). The contaminated insoluble materials were removed by centrifugation by using a two-necked glass tube fitted with septum caps. The solution was concentrated to 10 mL followed by cooling to −20 °C to induce the precipitation of the products. The products were recrystallized twice from hexane to give the desired binuclear complex **5a** as red-brown crystals in 55% yield based on $NbCl_4(C_5H_5)$.

[NbCl(C_5H_5)(butadiene)]$_2$ (6a). A suspension of (2-butene-1,4-diyl)magnesium (1.6 mmol) in tetrahydrofuran (5 mL) was added to a chilled suspension of $NbCl_4(C_5H_5)$ (0.6 g, 2.0 mmol) in tetrahydrofuran (10 mL) at −78 °C. Then the mixture was allowed to warm to room temperature with magnetic stirring. After the mixture was stirred for 1 h at 30 °C, the solvent was removed by flash distillation and the product was extracted from the residue with hexane (20 mL). Concentration of the extract followed by cooling to 0 °C gives **6a** as red-brown crystals in 55% yield. For further purification, recrystallization was carried out from hexane. Anal. Calcd for $C_{18}H_{22}Nb_2$: C, 43.67; H, 4.48; Cl, 14.32. Found: C, 42.46; H, 4.00; Cl, 15.82.

NbCp*(diene)$_2$ (12–14). A typical experiment is as follows. A suspension of (2-butene-1,4-diyl)magnesium (7.4 mmol) in tetrahydrofuran (10 mL) was added to a stirred solution of $NbCl_4(C_5Me_5)$ (1.4 g, 3.7 mmol) in tetrahydrofuran (20 mL) at −78 °C. The mixture was allowed to warm to room temperature, and the stirring was continued at 30 °C for 2 h. Filtration of the salt and evaporation of the filtrate gave a brown solid. The hexane extract (40 mL) was concentrated and cooled to −20 °C to give NbCp*(butadiene)$_2$ (**14**) as yellow-brown crystals in 58% yield. The corresponding bis(2,3-dimethylbutadiene) complex (**12**) and bis(isoprene) complex (**13**) were also isolated as yellow-brown crystals in 55–65% yield, using an analogous procedure. The results of chemical characterization, mp, and EIMS data are given in Table VI and NMR data in Table VII.

NbCp(diene)$_2$ (15–17). The bis(2,3-dimethylbutadiene) complex (**15**) and bis(isoprene) complex (**16**) were obtained as yellow-brown crystals (60–65% yields) with essentially the same procedure as described for **12–14**, starting from $NbCl_4Cp$ (0.9 g, 3 mmol) and the corresponding (butenediyl)magnesium (6 mmol). The preparation of NbCp(butadiene)$_2$ (**17**) was done in the following manner. A mixture of (2-butene-1,4-diyl)magnesium (2 mmol) and hexamethylphosphoric triamide (0.7 mL, 4 mmol) in tetrahydrofuran (30 mL) was stirred at 25 °C until it turned to a homogeneous solution (ca. 1 h). The solution was syringed onto a stirred suspension of $NbCl_4Cp$ (0.3 g, 1 mmol) in tetrahydrofuran (10 mL). After being stirred for 2 h, the mixture was evaporated to dryness and the product was extracted into hexane (40 mL). Recrystallization at −20 °C gave **17** as yellow-brown crystals in 45% yield. The product is composed of two isomers, **17a** and **17b**, in an ca. 1:1 ratio. The ^1H and ^{13}C NMR data are given in Tables VII and VIII.

NbCp(C_6H_{10})($C_6H_6D_4$) (18 and 19). The deuteriated precursor $CD_2C(CH_3)C(CH_3)CD_2$ was prepared by the cracking of $CH_3COOCD_2CH(CH_3)CH(CH_3)CD_2OCOCH_3$ at 370 °C in an argon stream, which was obtained on reacting dimethyl 2,3-dimethylsuccinate (6.5 g, 37.4 mmol) with $LiAlD_4$ (1.9 g, 45 mmol) in ether (30 mL) at 30 °C followed by hydrolysis and acylation of the resulting $HOCD_2CH(CH_3)CH(CH_3)CD_2OH$ (4.0 g, 19 mmol) with acetic anhydride (10 mL) at 130 °C. The magnesium adduct of 2,3-dimethylbutadiene-d_4 and its derivative $NbCl_2Cp(C_6H_6D_4)$ were prepared in the same manner as described above. The compound NbCp(*supine*-2,3-dimethylbutadiene)(*prone*-2,3-dimethylbutadiene-d_4) (**18**) was synthesized by the reaction of **4** (0.5 g, 1.6 mmol) with (2,3-dimethyl-2-butene-1,4-diyl-*1,1,4,4*-d_4)magnesium (1.6 mmol) in THF and NbCp(*supine*-2,3-dimethylbutadiene-d_4)(*prone*-2,3-dimethylbutadiene) (**19**) by the 1:1 reaction of $NbCpCl_2(C_6H_6D_4)$ (1.3 mmol) with nondeuteriated (2,3-dimethyl-2-butene-1,4-diyl)magnesium (1.3 mmol). Parity of **18** and **19** is ca. 92% (each contains 8% of the isomer). Yield, 70–75% based on $NbCl_2Cp$(diene). EIMS, 326 (M^+).

Reaction of 18 or 19. To a tetrahydrofuran solution (5 mL) of **18** or **19** (0.2 g, 0.5 mmol) was added 2,4-dimethyl-3-pentanone (0.07 mL) at −78 °C. The mixture was allowed to warm to ambient temperature with magnetic stirring to give the 1:1 adduct.

Adduct 21 from 18. ^1H NMR(C_6D_6) δ 0.61 (d, 2 H, *supine*-C_6H_{10}, anti), 2.18 (d, 2 H, syn-protons), 1.70 (s, 6 H, CH_3), 1.88, 1.90 (s, 6 H, CH_3), 1.01 (d, 12 H, CH_3), 1.97 (m, 2 H, CH), 6.07 (s, 5 H, Cp).

Adduct from 19. ^1H NMR (C_6D_6) δ 1.71 (s, 6 H, *supine*-$C_6H_6D_4$), 2.21 (s, 2 H, $TaCH_2$), 1.88, 1.90, (s, 6 H, CH_3), 1.85 (s, 2 H, CH_2), 1.01 (d, 12 H, CH_3), 1.97 (m, 2 H, CH), 6.07 (s, 5 H, Cp).

X-ray Analyses of 6a and 15. Air-sensitive **6a** and **15** crystals were sealed in thin-walled glass capillary tubes under argon. All X-ray experiments were carried out on a Rigaku automated four-circle diffractometer with graphite monochromatized Mo Kα radiation. The unit cell parameters at 20 °C were determined by a least-squares fit to 2θ values of 25 strong higher angle reflections. The crystal data and experimental conditions for data collection are summarized in Table III. No significant intensity decay was observed during the data collection. The intensity data were corrected for the usual Lorentz and polarization effects but not for absorption. The crystal structures of both complexes were solved by the heavy-atom method and refined by the full-matrix least-squares method as implemented in the X-RAY SYSTEM[25] by the use of observed reflections [$|F_o| > 3s(F_o)$]. After anisotropic refinement of the non-hydrogen atoms, all hydrogen atoms were located in the difference Fourier maps with the help of geometrical calculations and were refined isotropically. The ORTEP drawings were obtained with use of Johnson's program.[26]

All calculations were carried out on an ACOS-850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Acknowledgment. The authors are indebted to Grant-in-Aid for Special Project Research (No. 61225015 and No. 62115007) from the Ministry of Education, Science and Culture, Japan.

Registry No. 1, 114763-65-4; **2**, 114763-66-5; **3**, 114763-67-6; **4**, 114763-68-7; **5a**, 114763-69-8; **6a**, 114763-70-1; **8**, 114763-72-3; **9**, 114763-73-4; **12**, 114763-74-5; **13**, 114763-75-6; **14**, 114763-76-7; **15**, 114763-77-8; **16**, 114763-78-9; **17a**, 114818-68-7; **17b**, 114763-71-2; **18**, 114763-79-0; **19**, 114763-80-3; **21** (R = *i*-Pr) (isomer 1), 114763-82-5; **21** (R = *i*-Pr) (isomer 2), 114763-83-6; $CD_2C(CH_3)C(CH_3)CD_2$, 42185-77-3; $CH_3COOCD_2CH(CH_3)CH(CH_3)CD_2OCOCH_3$, 114763-84-7; $NbCl_5$, 10026-12-7; $SiMe_3(C_5H_5)$, 25134-15-0; $NbCl_4(C_5Me_5)$, 80432-35-5; $NbCl_4(C_5H_5)$, 33114-15-7; $NbCpCl_2(C_6H_6D_4)$, 114789-57-0; $SiMe_3(C_5Me_5)$, 87778-95-8; $HOCD_2CH(CH_3)CH(CH_3)CD_2OH$, 114763-85-8; (2,3-dimethyl-2-butene-1,4-diyl)magnesium, 95251-09-5; (2-methyl-2-butene-1,4-diyl)magnesium, 90823-62-4; (2-butene-1,4-diyl)magnesium, 70809-00-6; (2,3-dimethyl-2-butene-1,4-diyl-*1,1,4,4*-d_4)magnesium, 114763-81-4; 2,4-dimethyl-3-pentanone, 565-80-0; dimethyl 2,3-dimethylsuccinate, 28306-68-5; (2-butene-1,4-diyl)magnesium·$(HMPt)_2$, 114789-58-1.

Supplementary Material Available: Lists of anisotropic temperature factors for non-hydrogen atoms, atomic coordinates for hydrogen atoms with isotropic temperature factors, and bond distances and angles including hydrogen atoms (7 pages); tables of observed and calculated structure factors (69 pages). Ordering information is given on any current masthead page.

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