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Novel route to niobocene-allyl compounds by hydrometalation of conjugated dienes with $NbH(C_5H_5)_2$(olefin)

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Abstract

Niobium hydrido-olefin complexes, $NbH(C_5H_5)_2$(olefin), are found to react readily with conjugated dienes such as butadiene, isoprene, and pentadiene, to give $Nb(C_5H_5)_2(\eta^3$-allyl) derivatives of *syn* or *syn,syn* geometry, in > 80% yields with high regioselectivity. All the complexes were isolated as crystals and their structures were determined by NMR and EIMS spectroscopy. The reaction pathway leading to *syn*- or *syn,syn*-η^3-allylniobium compounds is discussed on the basis of the regiochemistry of the products and the results of a deuterium labeling experiment. These complexes react readily with aldehydes to give homoallyl alcohols upon hydrolysis of the products. The corresponding tantalum derivatives were found to be inert to all dienes tested.

Introduction

Hydrido-olefin complexes of Group 5A metallocenes of the formula MHL_2(olefin) ($M = Nb$, Ta; $L = C_5H_5$, C_5Me_5) are among the thermally most stable olefin complexes of metal hydrides and have been conveniently synthesized by reaction of $NbCl_2(C_5H_5)_2$ [1], $TaCl_2(C_5H_5)_2$ [2] or $NbCl_2(C_5Me_5)_2$ [3] using a variety of alkylmagnesium halides. This reaction proceeds by dehydrometalation of the initially formed alkylmetal species. An ethylene complex, $NbH(C_5H_5)_2(C_2H_4)$, is known to react with ethylene only under elevated pressure to afford $NbC_2H_5(C_5H_5)_2(C_2H_4)$, while the hydrido complex is generally inert to other olefins [4]. We have found that $NbH(C_5H_5)_2$(olefin) complexes are reactive toward conjugated dienes and yield various allyl compounds of the type $Nb(C_5H_5)_2(\eta^3$-$CHR^1CR^2CHR^3)$. Here we describe the reactions and the factors that determine the regio- and stereo-chemistry of the ensuing alkyl-substututed allylniobium compounds.

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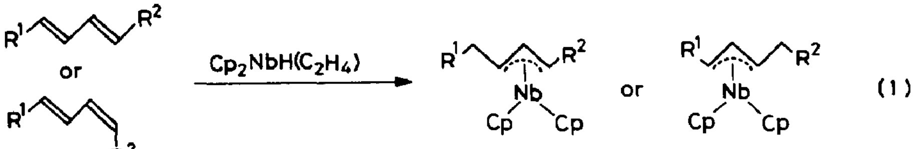
Results and discussion

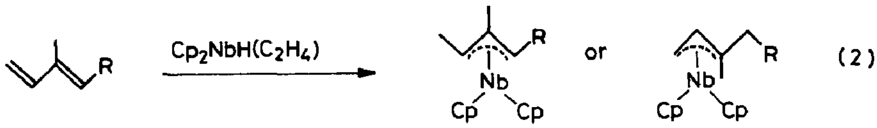
Novel route to dicyclopentadienyl(allyl)niobium compounds

The reactions of a series of conjugated dienes with $NbH(C_5H_5)_2(C_2H_4)$ were found to provide allylniobium compounds of the type $Nb(C_5H_5)_2(\eta^3\text{-allyl})$ in high yields (80–90%) (see eqs. 1, 2). The coordinated ethylene is readily expelled at 25 °C by the attack of a conjugated diene and the hydride is transferred to the sterically less-crowded diene terminus. Thus the niobium hydrido-olefin complexes serve as a convenient reagent for the preparation of 1,2- or 1,3-dialkyl-substituted allylniobium compounds starting from butadiene, (*E*,*E*)- and (*E*,*Z*)-2,4-hexadiene, (*E*)- and (*Z*)-1,3-pentadiene (see eq. 1), 3-methyl-1,3-pentadiene and isoprene (see eq. 2). All the allyl niobium compounds synthesized here were isolated as air-sensitive pale-yellow crystals by recrystallization from hexane (Table 1). Analogous $NbH(C_5H_5)_2$(olefin)-type complexes containing propene, 1-butene or styrene also



(1)

1, $R^1 = R^2 = H$
2, $R^1 = R^2 = CH_3$
3a, $R^1 = H$, $R^2 = CH_3$ 3b



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4a, R=H 4b
5a, $R = CH_3$ 5b

Table 1

Characterization of allylniobium compounds prepared from $NbHCp_2$(ethylene) and dienes

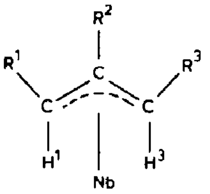
Complexes	M.p. (°C)	EIMAS spectra, *m*/*z* (relative intensity)	Elemental analysis (Found (calcd.)(%)) C	H
1	110	278(M^+, 3.8), 224(Cp_2NbH^+, 100) 223(Cp_2Nb^+, 14.5)	60.41 (60.44)	6.08 (6.16)
2	91	306(M^+, 4.1), 223(Cp_2Nb^+, 100)	62.55 (62.75)	6.67 (6.91)
3a	128	292(M^+, 7.9), 224(Cp_2NbH^+, 100) 223(Cp_2Nb^+, 10.6)	61.39 (61.65)	6.32 (6.55)
4a	139	306(M^+, 7.5), 224(Cp_2NbH^+, 100), 223(Cp_2Nb^+, 18.5)	62.67 (62.75)	6.78 (6.91)
5a	115	292(M^+, 8.5), 224(Cp_2NbH^+, 100), 223(Cp_2Nb^+, 16.5)	61.62 (61.65)	6.45 (6.55)

Table 2

^1H NMR parameters for niobocene-allyl compounds [a]

$Cp_2Nb(R^1CH^1CR^2CH^3R^3)$			Chemical shifts (δ, ppm)						Coupling constants (Hz) [c]				
R^1	R^2	R^3	$\nu(H^1)$	$\nu(R^1)$	$\nu(R^2)$	$\nu(H^3)$	$\nu(R^3)$	$\nu(Cp)$	$J(H^1,R^1)$	$J(H^1,R^2)$	$J(R^1,R^2)$	$J(R^2,H^3)$	$J(H^3,R^3)$
H	H	CH_3 (**1**)	0.51	2.65	2.29	1.46	2.01	4.54 4.14	−4.4	13.6	9.5	11.5	5.6
CH_3	H	C_2H_5 (**2**)	1.17	1.95	2.33	1.61	2.28 1.33	4.48 4.11	5.5	13.8		13.7	5.7
CH_3	H	CH_3 (**3a**)	1.17	1.97	2.34	1.17	1.97	4.50 4.15	5.5	13.9		13.9	5.5
CH_3	CH_3	CH_3 (**4a**)	0.97	1.88	1.52	0.97	1.88	4.53 4.04	5.8				5.8
H	CH_3	CH_3 (**5a**)	0.62	2.73	1.59		1.89	4.54 4.09	−5.0				5.5
H	H	H [b]	0.75	2.95	2.18	0.75	2.95	4.53 4.08	−4.5	14.9	9.5	14.9	−4.5
H	CH_3	H [b]	0.86	2.90	1.60	0.86	1.60	4.49 4.10	−4.8				−4.8

Numbering scheme

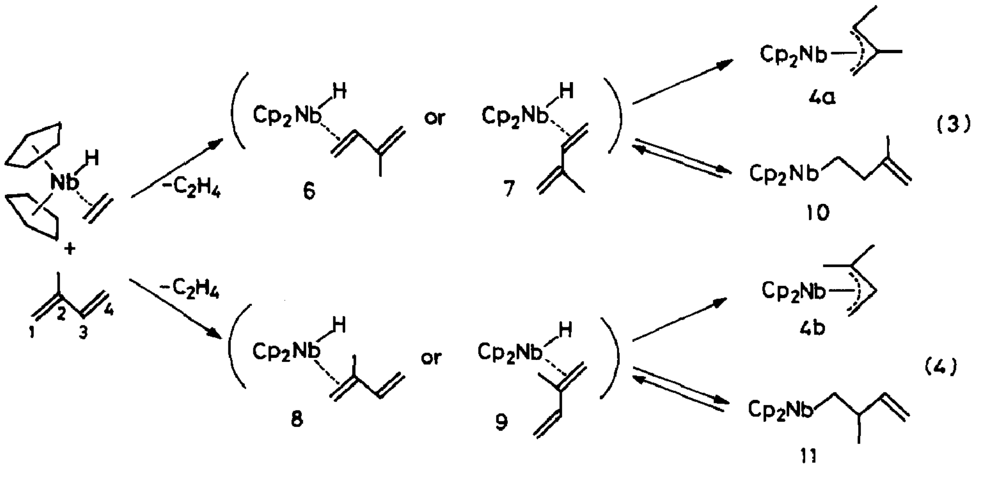


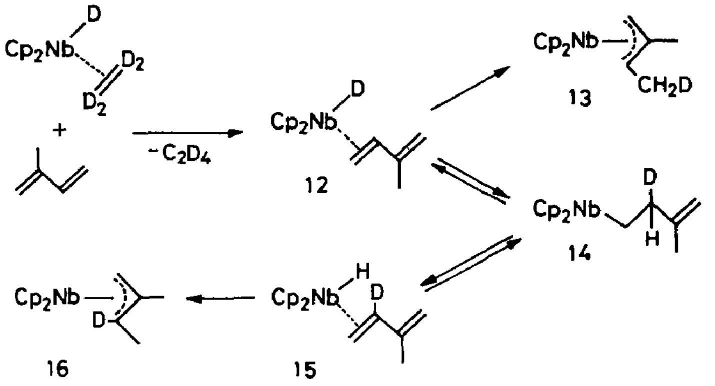
[a] Parameters were determined by the computer simulation of the 100 MHz NMR spectra (C_6D_6 at 30 ° C). Chemical shifts are expressed in ppm downfield from TMS calibration with C_6H_6 as internal standard, assumed to be at 7.2 ppm. [b] Prepared by reaction of Cp_2NbCl_2 with allylmagnesium bromide. [c] $J(H^1,H^3)$ and $J(H^1,H^3)$ (R = H) are in the ranges $-0.5 \sim -0.9$ and $-0.1 \sim -0.2$ Hz, respectively.

induce the same type of reactions. Similar hydrometalations of conjugated dienes leading to allylmetal compounds have been known in the case of $NbH_3(C_5H_5)_2$ [4a], $ZrCl(H)(C_5H_5)_2$ [5], $RhH(PR_3)_4$ [6], etc. in addition to transient metal hydride complexes containing Ti [7], Ni [8], Pd [9], and Pt [10]. Although the corresponding (1,2- or 1,3-dialkylallyl)niobium compounds are available by an alternative route (i.e. the reaction of $NbCl_2(C_5H_5)_2$ with allylmagnesium halides), the yield is always low (10–20%) [11]. Thus the present method is superior to the conventional methods with respect to yield and purity, especially in the preparation of (1,3-disubstituted-allyl)niobium compounds. All of the allylniobium compounds are monomeric, as revealed by the mass spectroscopic analysis, and always assume the thermodynamically more favored *syn*- or *syn,syn*-allyl structure as deduced from one or more ^1H NMR parameters, such as $J(H^1,R^2)$ and/or $J(R^2,H^3)$ of 13.5–14.2 Hz (Table 2).

Although two regioisomers are conceivable for each compound derived from pentadiene (eq. 1), isoprene or 3-methyl-1,3-pentadiene (eq. 2), only the sterically more favorable isomers **3a**, **4a** and **5a** instead of **3b**–**5b** were formed selectively.

The factors controlling the reaction pathway are thought to be (1) the mode of diene orientation for the intermediates (*endo* and *exo* orientation and the bonding preference of the metal toward C(1)–C(2) or C(3)–C(4) bond), (2) conformational stability of the product (*syn*- or *anti*-allyl structure) and (3) electronic stability of the product (16e or 18e species). For example, four kinds of isomers, **6**–**9**, are probable intermediates for the isoprene complex. The results reveal that the reaction proceeds through either **6** (*endo*-form) or **7** (*exo*-form) in which the isoprene is ligated to the metal at its C(3)–C(4) moiety, rather than at the sterically more hindered C(1)–C(2) part as in **8** and **9** (eq. 4). The *endo*-orientation **6** may be sterically more favorable than the *exo*-orientation **7** since the analogous 1-alkene hydrido complexes, $NbH(C_5H_5)_2$(1-alkene), usually take on the more stable *endo*-form as a result of steric repulsion between C_5H_5 and the alkyl group in the 1-alkenes [1]. In the subsequent step hydride transfer should take place onto the C(4) carbon of the isoprene unit to lead to the electronically more stable η^3-allylmetal species (**4a** or **4b**) (d^2, 18e species) (see eqs. 3 and 4) rather than electron deficient 16e species, **10** or **11**, which would result if hydride transfer is to the C(3)





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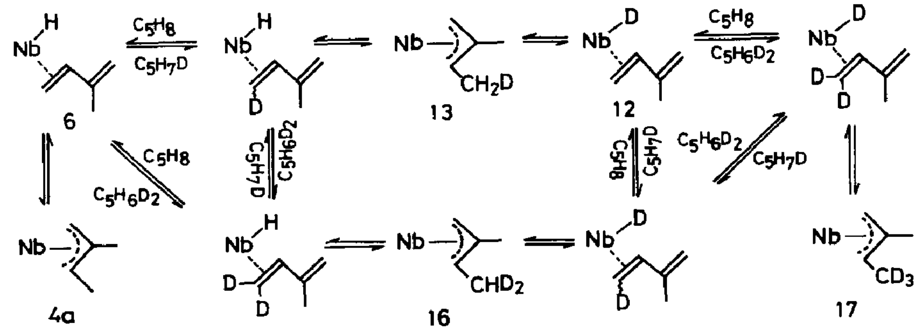
carbon. As a result of the above reactions, complex **4a** was obtained as the sole product. Thus the formation of sterically more congested complex **4b** was completely suppressed probably because of the strong steric repulsion between C_5H_5 and the *anti*-methyl group of **4b** and also because of the steric hindrance between C_5H_5 and the isoprene methyls of **8** and **9**. This interpretation is supported by the fact that 4-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, 2,3-dimethylbutadiene, and 2,5-dimethyl-2,4-hexadiene are completely inert to $NbH(C_5H_5)_2(C_2H_4)$ even under vigorous conditions (80 °C, 15 h). If hydride transfer onto these dienes is possible, it must give rise to sterically very congested η^3-allyl compounds where one or two anti-position(s) are occupied by methyl group(s). In light of this we propose the mechanism as shown in eq. 3, which involves sterically favored *endo* species **6** as the key intermediate and electronically preferred d^2, 18e complex **4a** as the final product.

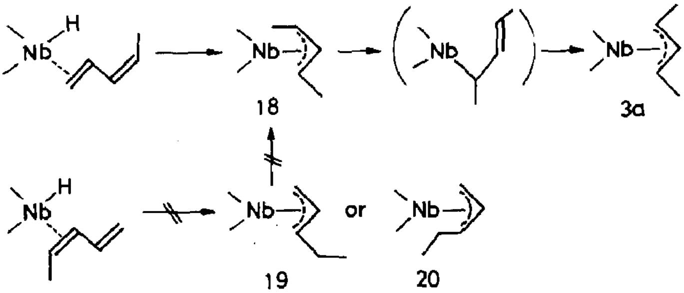
To gain further insight into the reaction pathways, a deuterium labeling experiment was performed using $NbD(C_5H_5)_2(C_2D_4)$ of 95% purity. If there is an equilibrium between **14** and **12** or between **14** and **15** (hydride addition and elimination at the β-carbon), deuterium scrambling should occur to give, for example, **16**, while direct attack of deuteride on the C(4)-carbon (α-carbon) of isoprene should give rise only to the formation of the methyl deuterated compound **13**. The ^1H NMR spectra of the hydrolysis products clearly confirm the absence of complex **16**, while multiple deuteration occurred on the methyl group of **13**. This means that the above reaction sequence involves a diene–diene ligand exchange process as shown in eq. 6. The extent of deuteration for the hydrolysis product and



(6)

the recovered isoprene is summarized in Table 3 (C_5H_9D, $C_5H_8D_2$ and $C_5H_7D_3$ are 4-d_1-, 4-d_2- and 4-d_3-2-methylbutenes, respectively, and C_5H_7D, $C_5H_6D_2$ and $C_5H_5D_3$ are 4-d_1-, 4-d_2- and 4-d_3-isoprene, respectively, as identified by the NMR and mass spectra). If the deuterium scrambling occurs freely and rapidly as in eq. 6, the addition of excess isoprene (40 equiv.) to $NbD(C_5H_5)_2(C_2D_4)$ should give rise to the non-deuterated species $NbH(C_5H_5)_2(C_5H_9)$ as the major product which in turn gives C_5H_{10} upon hydrolysis. However, the resulting product gave C_5H_{10}, C_5H_9D and $C_5H_8D_2$ in a ratio of 85/15/10 after reaction at 60 °C for 6 h. Thus the interconversion takes place rather slowly, indicating that the equilibrium is largely shifted to η^3-allylniobium species (e.g. **13**) from deuterido-diene species (e.g. **12**) in solution.

In order to elucidate the reaction pathway for the formation of *syn,syn*-allyl type complexes from (*Z*)-1,3-pentadiene and (*Z,E*)-2,4-hexadiene, a 1/1 reaction between $NbH(C_5H_5)_2(C_2H_4)$ and (*Z*)- or (*E*)-1,3-pentadiene was examined in toluene-d_8. The temperature was raised from −78 to 70 °C with periodical monitoring of the NMR spectra. The reaction began at ca. −10 °C in both cases, at the same time the ligated ethylene was released. In the case of (*Z*)-1,3-pentadiene, resonances assignable to the (*E,Z*)-isomer (**18**) were observed at −10 °C ~ 30 °C (half-life time, 22 min at 25 °C), i.e., 1.10 (*anti*-H, *J*(H,H) 13.6 Hz, *J*(H,CH_3) 5.0 Hz), 2.40 (*syn*-H, *J*(H,H) 9.5 Hz), 1.94 (central-H), 1.43 (*anti*-CH_3), 1.92 (*syn*-CH_3). This complex changed to the (*syn,syn*)-isomer (**3a**) within 30 min when temperature was raised to 50 °C (eq. 7). The rearrangement of (*syn,anti*)- to (*syn,syn*)-species should occur through a σ-bonded intermediate on the NMR time scale. Any other species ascribable to **19** or **20** was not detected. When (*E*)-1,3-pentadiene was used, the complex changed to *syn,syn*-allyl compound **3a** directly. Therefore, the reaction process involving a 1,3-shift of **19** or **20** to **3a** or **18** can be ruled out for the present transformation (eq. 7). The reaction of the resulting $Nb(C_5H_5)_2(\eta^3$-allyl) (e.g. **4a**)



18 3a 19 20 (7)

with PMe_3 or pyridine (4 equiv.) was tested by monitoring the transformation of **4a** into $Nb(C_5H_5)_2(\eta^1$-allyl) · Donor adduct, since a similar transformation has been reported for the reactions of $NbH(C_5H_5)_2$(olefin) with these donors, which afford $Nb(C_5H_5)_2$(alkyl) · Donor quantitatively [12]. As a result, no complexation was observed in these cases.

Preparation of bis(cyclopentadienyl)(allyl)tantalum compounds

Several allylic tantalum compounds of the type $Ta(C_5H_5)_2(\eta^3$-allyl) can be synthesized in low yield (10–15%) by treating $TaCl_2(C_5H_5)_2$ with allylmagnesium halides or 2-butenylmagnesium halides [10]. The reaction of $TaH(C_5H_5)_2$(olefin) (olefin = ethylene, propene and styrene, see Experimental) with conjugated dienes,

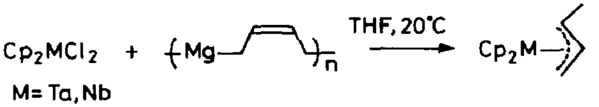
Table 3

Extent of deuteration in the complex and in the recovered isoprene

Charged NbD/C_5H_8 ratio	Hydrolysis of the complex (%)			Recovered isoprene (%)		
	C_5H_{10}	C_5H_9D	$C_5H_8D_2$	C_5H_8	C_5H_7D	$C_5H_6D_2$
1/2	32	60	8	89	9	2
	(53.2)	(37.4)	(8.8)	(66)	(31)	(3)
1/4	44	52	4	91	8	1
	(71.6)	(25.3)	(3.0)	(80)	(19)	(1)
1/8	63	36	1	95	5	0
	(84.2)	(15.0)	(0.1)	(89)	(10)	(1)
1/40	85	15	0	99	1	0
	(96.5)	(3.4)	(0.0)	(98)	(2)	(0)

[a] Relative ratio was determined based on the EIMS spectroscopic data using authentic samples, C_5H_{10} and C_5H_9D obtained by hydrolysis or deuterolysis of $Nb(C_5H_5)_2(C_5H_9)$ (**4a**). Values in parentheses are the calculated values obtained by assuming that diene–diene exchange occurs freely, leading to triple deuteration.

however, was found to be ineffective for preparation of $Ta(C_5H_5)_2(\eta^3$-allyl)-type complexes because the tantalum hydrido-olefin complexes are completely inert to all the dienes noted above even under vigorous conditions (60–100 °C for 12 h). During the course of this study, we have found that the reaction of $M(C_5H_5)_2Cl_2$ with (2-butene-1,4-diyl)magnesium [13] gave $M(C_5H_5)_2(\eta^3$-2-butenyl) (M = Ta, Nb) in high yield (> 65%). However the corresponding reaction with (2-methyl-2-butene-1,4-diyl)magnesium gave an inseparable complex mixture. The proton source for the above reaction may have been the solvent, THF.



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Nucleophilic properties of allyl-niobium and -tantalum compounds

Zirconium-diene [14] and titanium-olefin complexes [15] are known to show versatile reactivity toward saturated and unsaturated carbonyl compounds (aldehydes, ketones, esters), and toward nitriles and heterocumulenes (isocyanates, ketenes, CO_2 [16]. Hydrido-olefin complexes of the type $MH(C_5R_5)_2$(olefin) (M = Nb, Ta; R = H, CH_3), however, exhibit extremely low reactivity toward these electrophiles even under vigorous conditions. Only hydrometalation occurred in low yields (40%) when $NbH(C_5H_5)_2(C_2H_4)$ was treated with 2-methylpropanal at 80 °C. Aliphatic ketones such as 3-pentanone and 2,4-dimethyl-3-pentanone are completely inert to both niobium and tantalum hydrido-olefin complexes under similar conditions.

In sharp contrast to the hydrido-olefin complexes, the present allylic niobium and tantalum compounds show good reactivity toward the aliphatic aldehydes and ketones. Currently *threo-* and *erythro*-selective additions of allylmetal compounds to aldehydes are being extensively studied as an important subject in organic synthesis [17]. Therefore we have explored the reaction of allylniobium and allyltantalum

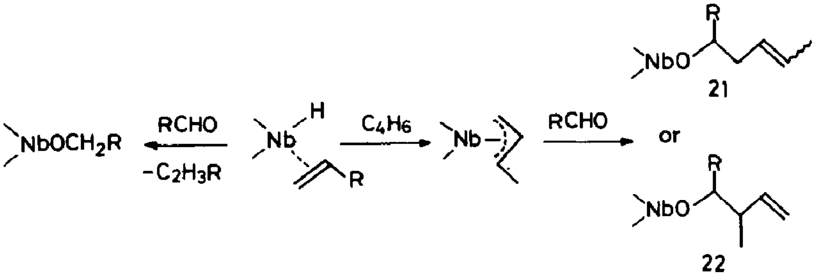
Table 4

Threo/erythro isomer ratio for the adduct of 2-methylpropanal with allylniobium compounds

Complexes	Regioselectivity (%)	*Threo/erythro* ratio (%)	Yield (%)
1	100	54/46	79
3a	99	71/29	72
5a	98	67/33	68
$Cp_2Ta(CH_2CHCHCH_3)$	100	79/21	66

[a] Reaction was carried out in toluene at 60 °C for 6 h.

compounds with an aldehyde to evaluate their potential utility. The addition of $M(C_5H_5)_2(\eta^3\text{-allyl})$ (M = Nb, Ta) to one equiv. of 2-methylpropanal was found to proceed regioselectively ($>$ 98%) at the substituted carbon of the allyl moiety to give **22** in 70–90% yield, but the diastereoselectivity was very poor (65–75%) (Table 4). The poor selectivity may be ascribed to the low oxophilicity of the present allylmetal compounds. The reaction is initiated at ca. 60 °C in the present case whereas allyl-titanium and -zirconium compounds show high reactivity toward aldehydes and ketones even at -90 °C [17].



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Experimental

All operations were carried out under argon using standard vacuum-line techniques. Solvents were dried over benzophenonesodium and thoroughly degassed by vacuum distillation before use. Crystals of $NbCl_5$ and $TaCl_5$ (Mitsuwa Chem.) were used as received. ^1H NMR spectra were recorded on a JEOL GX-500 or a Varian XL-100 instrument and analyzed by computer simulation with the NEC LAOCN-98 program. The mass spectra (EI) were recorded on a JEOL DX-300 instrument at 70 eV.

Preparation of $NbH(C_5H_5)_2$(ethylene). This complex was prepared in close analogy to Klazinga and Teuben's method [1]. An ether solution of ethylmagnesium bromide (6.4 mmol, 8 ml) was added to a suspension of $NbCl_2(C_5H_5)_2$ (1.0 g, 3.4 mmol) in ether (30 ml) at -78 °C. The mixture was allowed to warm to 25 °C with magnetic stirring. The mixture was stirred at that temperature for 3 h, and evaporated to dryness. The residue was then extracted with degassed hexane (30 ml). The extract was concentrated and cooled to -20 °C to give $NbH(C_5H_5)_2$(ethylene) as pale-yellow crystals in 55–65% yield. m.p. 85 °C. EIMAS (rel. intensity) m/z 253 ($M^+ + 1$, 2.5), 252 (M^+, 20.1), 251 ($M^+ - H$, 1.9), 224 ($M^+ - C_2H_4$, 100), 223

($M^+ - C_2H_5$, 69). Full ^{1}H NMR data (500 MHz) were obtained by computer simulation of the spectrum in C_6D_6 at 30 °C (numbering scheme, $Nb(C_5H_5)_2H^e(H^aH^bC{=}CH^cH^d)$) δ 1.18 (dd, H^a, $J_{a,c}$ 10.9 Hz, $J_{a,d}$ 11.0 Hz), 1.18 (dd, H^b, $J_{b,c}$ 10.9 Hz, $J_{b,d}$ 11.0 Hz), 0.66 (dd, H^c, $J_{c,d}$ 0 Hz), 0.66 (dd, H^d), −0.82 (t, H^e, $J_{a,e} = J_{b,e} = 1.8$ Hz), 4.50 (s, Cp).

Preparation of $NbH(C_5H_5)_2$(propene). An ether solution of propylmagnesium bromide (6.4 mmol, 8 ml) was added to an ether suspension (30 ml) of $NbCl_2(C_5H_5)_2$ (1.0 g, 3.4 mmol) at −78 °C. After the usual work-up, as described above, $NbH(C_5H_5)_2$(propene) was isolated as pale-yellow crystals in ca. 55% yield (ratio of *endo/exo*, 64/36) [18*]. m.p. 82 °C. EIMS (rel. intensity) m/z 266 ($M^+ = 1$, 4.2), 266 (M^+, 18.5), 224 (Cp_2NbH^+, 100), 223 (Cp_2Nb^+, 73). ^{1}H NMR parameters for the *endo*-isomer (numbering scheme $Nb(C_5H_5)_2H^e[H^a(CH_3^b)C{=}CH^cH^d]$) δ 2.02 (ddq, H^a, $J_{a,b}$ 6.4 Hz, $J_{a,c}$ 9.9 Hz, $J_{a,d}$ 12.1 Hz), 1.96 (d, H^b), 0.53 (dd, H^c, $J_{c,d}$ −3.9 Hz), 1.05 (dd, H^d), −2.91 (s, $J_{a,e} = J_{b,e} = J_{c,e} = J_{d,e} = 0$ Hz), 4.49 and 4.63 (s, Cp). ^{1}H NMR parameters for the *exo*-isomer, $Nb(C_5H_5)_2H^e[H^aH^bC{=}CH^c(CH_3^d)]$: δ 0.87 (dd, H^a, $J_{a,b} = -5.5$ Hz, $J_{a,c}$ 10.1 Hz), 1.49 (dd, H^b, $J_{a,d}$ 12.3 Hz), 1.27 (ddq, H^c, $J_{c,d}$ 6.5 Hz), 1.67 (d, H^d), −3.15 (dd, H^e, $J_{a,e}$ 1.4 Hz, $J_{b,e}$ 1.8 Hz), 4.49 and 4.52 (s, Cp).

Preparation of $Nb(C_5H_5)_2H$(styrene). A tetrahydrofuran solution (8 ml) of $C_6H_5CH_2CH_2MgBr$ (5.2 mmol) was added dropwise to a tetrahydrofuran solution (30 ml) of $NbCl_2(C_5H_5)_2$ (0.75 g, 2.6 mmol) at −70 °C. The mixture was stirred at 25 °C for 3 h, evaporated to dryness, and extracted with degassed hexane (25 ml). Concentration of the extract followed by cooling to −20 °C afforded $NbH(C_5H_5)_2$(styrene) as pale-yellow crystals, in 42% yield, of which 98% is *endo*-isomer. m.p. 136 °C, EIMS (rel. intensity) m/z 329 ($M^+ + H$, 4.3), 328 (M^+, 21.6), 224 (Cp_2NbH^+, 100), 223 (Cp_2Nb^+, 59.8). ^{1}H NMR parameters (C_6D_6 at 30 °C) for the *endo*-isomer: δ 3.36 (dd, H^a, $J_{a,c}$ 10.1 Hz, $J_{a,d}$ 13.3 Hz) 6.94, 7.26 and 7.53 (m, H^b, C_6H_5), 0.95 (dd, H^c, $J_{c,d}$ −5.5 Hz), 1.32 (dd, H^d), −2.36 (s, H^e, $J_{a,e} = J_{b,e} = J_{d,e} = 0$ Hz), 4.40 and 4.52 (s, Cp).

Preparation of $NbD(C_5H_5)_2(CD_2CD_2)$. An ether solution of CD_3CD_2MgBr (12.5 mmol, 16 ml, deuterium content 98%) prepared from CD_3CD_2Br and Mg was added dropwise to a suspension of $NbCl_2(C_5H_5)_2$ (2.0 g, 6.8 mmol) in ether (30 ml) at −40 °C. The mixture was stirred at 25 °C for 45 min and then evaporated to dryness. The product was extracted with hexane to give $NbD(C_5H_5)_2(CD_2CD_2)$ in 95% purity as analyzed by EIMS. Prolonged reaction in ether (5 h) resulted in the formation of $NbD(C_5H_5)_2(CD_2CD_2)$ (72%) and $NbH(C_5H_5)_2(CD_2CD_2)$ (27%). The corresponding reaction in THF at 25 °C for 4 h gave $NbH(C_5H_5)_2(CH_2CH_2)$ as the major product probably due to an H–D exchange reaction between the α-protons of THF and the metal deuteride in $Nb(C_5H_5)_2D(CD_2CD_2)$. The use of dimethoxyethane was also unsuited because of the substantial H–D exchange.

Preparation of $TaH(C_5H_5)_2$(olefin). Synthesis of tantalumhydrido-olefin complexes was by the procedure reported by Teuben et al. [2]. To a tetrahydrofuran suspension (25 ml) of $TaCl_2(C_5H_5)_2$ (0.8 g, 2.1 mmol) was added a solution of C_2H_5MgBr, $CH_3CH_2CH_2MgBr$ or $C_6H_5CH_2CH_2MgBr$ (4.2 mmol) in tetrahydrofuran (6.5 ml) at −78 °C. The mixture was warmed to 30 °C with stirring for 4 h

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* Reference number with asterisk indicates a note in the list of references.

and then evaporated to dryness. The residue was extracted with degassed hexane (30 ml). Concentration of the extract, followed by gradual cooling to −20 °C gave pale-yellow crystals of the corresponding $TaH(C_5H_5)_2$(olefin) in 35–42% yield. Each of these complexes exists as the single isomer. The ^1H NMR parameter (C_6D_6 at 30 °C, 500 MHz) determined by computer simulation are shown below.

$Ta(C_5H_5)_2H^e(H^aH^bC{=}CH^cH^d)$ δ 0.87 (t, H^a, $J_{a,c} = J_{a,d} = 11.0$ Hz), 0.87 (t, H^b, $J_{b,c} = J_{b,d} = 11.0$ Hz), 0.37 (t, H^c, $J_{c,d}$ 0 Hz), 0.37 (t, H^d). −3.31 (t, H^e, $J_{a,e} = J_{b,e} = 2.7$ Hz, $J_{c,e} = J_{d,e} = 0$ Hz), 4.50 (s, Cp).

$Ta(C_5H_5)_2H^e[H^a(CH^b_3)C{=}CH^cH^d]$ (*endo*-isomer) δ 0.86 (ddq, H^a, $J_{a,b}$ 7.0 Hz, $J_{a,c}$ 10.8 Hz, $J_{a,d}$ 11.9 Hz), 2.38 (d, H^b), 0.13 (dd, H^c, $J_{c,d}$ −6.0 Hz), 1.70 (dd, H^d), −3.13 (s, H^e, $J_{a,e} = J_{b,e} = J_{c,e} = J_{d,e} = 0$ Hz), 4.45 and 4.58 (s, Cp).

$Ta(C_5H_5)_2H^e[H^a(C_5H^b_5)C{=}CH^cH^d]$ (*endo*-isomer) δ 2.92 (dd, H^a, $J_{a,c}$ 10.5 Hz, $J_{a,d}$ 12.8 Hz), 6.93, 7.30 and 7.56 (m, H^b, C_6H_5), 0.77 (dd, H^c, $J_{c,d}$ 0 Hz), 1.01 (dd, H^d), −2.15 (s, $J_{a,e} = J_{b,e} = J_{c,e} = J_{d,e} = 0$ Hz, $J_{c,d}$ −6.8 Hz), 4.38 and 4.50 (s, Cp).

Preparation of $Nb(C_5H_5)_2(\eta^3$-2-butenyl) (1). A benzene solution (15 ml) of butadiene (3.5 mmol) was added by syringe to a suspension of $NbH(C_5H_5)_2(C_2H_4)$ (0.63 g, 2.5 mmol) in benzene (8 ml) at 5 °C placed in a 30-ml Schlenk tube. The mixture was heated to and kept at 60 °C for 4 h, and was then evaporated to dryness. The residue was extracted with dry, thoroughly deoxygenated hexane (20 ml). The extract was concentrated and cooled to −20 °C, which resulted in the separation of $Nb(C_5H_5)_2(\eta^3\text{-}C_4H_7)$ (**1**) as dark-green crystals. Typical yield, 87%.

*Preparation of $Nb(C_5H_5)_2(\eta^3$-alkenyl) (**2**, **3a**, **4a** and **5a**).* These complexes were prepared in essentially the same way as described for **1**. The reaction of $NbH(C_5H_5)_2(C_2H_4)$ (0.6 g, 2.5 mmol) with (*E*,*E*)- or (*E*,*Z*)-2,4-hexadiene, (*E*)- or (*Z*)-1,3-pentadiene, isoprene or 3-methyl-1,3-pentadiene (5 mmol) in benzene at 60 °C for 4 h gave the corresponding allylniobium compounds (**2–5a**) as dark-green crystals in 87–93% yield.

Deuterium labeling experiment

A benzene solution (8 ml) of $NbD(C_5H_5)_2(CD_2CD_2)$ (0.5 g, 2 mmol) was added to a benzene solution (3 ml) of isoprene (4, 8, 16 or 80 mmol). After the mixture had been heated at 60 °C for 4 h, volatiles were distilled in vacuo and collected in a liquid-nitrogen condenser-trap. The isoprene present in the distillate was isolated by preparative gas chromatography and subjected to mass and NMR spectroscopy. The residue was hydrolyzed in toluene and the product was separated into individual components (2-methyl-1-butene, 2-methyl-2-butene and 3-methyl-1-butene in a ratio of 18/70/12) in a gas chromatograph fitted with a Si-DC-550-packed column. Deuterium content was determined by mass spectroscopy with the authentic samples of C_5H_{10} and $C_5H_8D_2$ being obtained, respectively, from the hydrolysis and the deuterolysis of the isoprenemagnesium adduct, and C_5H_9D was obtained by deuterolysis of C_5H_9MgBr.

Addition of allylmetal compounds to 2-methylpropanal.

To a benzene solution (8 ml) of the allylniobium compound (**1**, **3a** or **5a**) or $Ta(C_5H_5)_2(CH_2CH{=}CHCH_3)$ (2 mmol) was added 2-methylpropanal (2 mmol) dissolved in benzene (2 ml) at 5 °C. The mixture was stirred at 60 °C for 6 h and then hydrolyzed. (The reaction did not proceed at 25 °C.) The resulting alcohol was distilled and separated into *threo*- and *erythro*-isomers by gas chromatography. The individual isomers were identified as described elsewhere on the basis of the NMR spectra [17].

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