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A Dimethyl Complex of a Niobium−Butadiene Fragment, Cp*(η^4-C_4H_6)$NbMe_2$, Is a Carbene Precursor with Reactivity Similar to That of Dimethyltitanocene

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Summary: The dimethyl complex Cp(*η^4*-*C_4H_6*)*$NbMe_2$ *(***2***) was found to be thermally unstable, and its thermolysis generated a nascent methylidene species that was trapped by carbonyl compounds, giving olefinic products. Addition of norbornene and acenaphthylene to the carbene species gave rise to metallacyclobutane derivatives Cp*(*η^4*-*C_4H_6*)* $\overline{Nb[CH_2CH(C_5H_8)CH}]$ *(***4***) and Cp*(*η^4*-*C_4H_6*)* $\overline{Nb[CH_2CH(C_{10}H_6)CH}]$ *(***8***), respectively. The structure of* ***4*** *was determined by X-ray analysis. Complex* ***4*** *was found to be a catalyst for the ROMP of norbornene.*

Introduction

The monomeric alkylidene complexes of transition metals have been well-established.[1] Among them, complexes having one or two cyclopentadienyl ligands have also attracted much interest, since Tebbe and Parshall have isolated Cp_2TiCH_2 stabilized by organoaluminum.[2,3] Grubbs *et al.* have demonstrated that titanacyclobutanes are excellent precursors of $Cp_2Ti{=}CHR$ species.[1d,4−10] Recently, dialkyltitanocenes were found to be other precursors of alkylidene species that were trapped by carbonyl compounds and cyclic olefins to give olefins and polymers, respectively.[11−15] On the other hand, dimethyl complexes of zirconocene and hafnocene are more thermally stable and did not exhibit similar reactivity toward such substrates, but they are catalysts for the olefin polymerization on combination with relevant cocatalysts. Since Cp(diene)M fragments (M = Nb, Ta) are isoelectronic and isolobal with group 4 metallocene fragments Cp_2M, a 14-electron species, Cp*(diene)Ta (Cp* = pentamethylcyclopentadienyl) was found to stabilize various reactive species such as benzyne,[16] benzylidene,[17] and cationic alkyls.[18] We also found that a dimethyltantalum complex, Cp*(diene)$TaMe_2$, was thermally stable and functions as a unique initiator of the living polymerization of ethylene.[18−20] Herein we report the synthesis and reactions of the analogous dimethylniobium complex Cp*(η^4-C_4H_6)$Nb(CH_3)_2$ (**2**), whose thermolysis afforded a nascent methylidene species that was trapped by norbornene or acenaphthylene to give metallacyclobutane derivatives. The structure of the norbornene-inserted product was revealed by a single-crystal X-ray analysis. It is noteworthy that the observed difference between niobium and tantalum is correlated to the well-known difference between titanocene and zirconocene.

Results and Discussion

Treatment of Cp*(η^4-C_4H_6)$NbCl_2$ (**1**)[21] with 2 equiv of MeMgI in THF afforded **2** as air- and moisture-sensitive dark green crystals in 84% yield. Complex **2** was thermally unstable and gradually decomposed (the half-life in C_6D_6 at 20 °C was approximately 21 h). Thus, **2** was characterized on the basis of its ^1H NMR spectrum, which displayed a broad singlet at δ −0.03 due to two methyl groups bound to the niobium atom together with three signals for the butadiene moiety and a singlet for the Cp* ligand. Reaction of **2** with an excess of methanol afforded exclusively a methyl methoxy complex; the selective formation of a monomethoxy complex corresponds to the reported fact that dialkyl-

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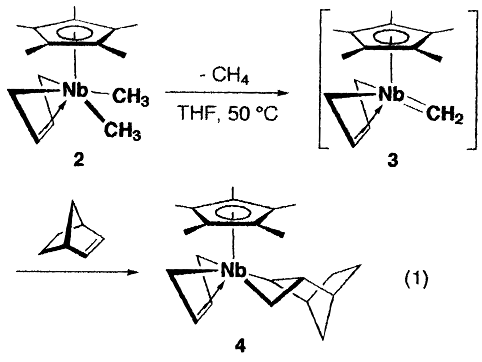
zirconocene similarly reacted with an excess of methanol to give alkylmethoxyzirconocene in quantitative yield.[22,23] Monitoring the thermolysis of **2** by ^{1}H NMR spectroscopy revealed the elimination of methane, suggesting the formation of the nascent carbene complex "Cp*(η^4-C_4H_6)Nb=CH_2" (**3**). Until now we could not isolate any carbene complex using PMe_3; however, the reaction products proved the formation of **3**. Reaction of **2** with carbonyl compounds such as 3-pentanone and cyclopentanone proceeded readily to give the corresponding olefinic products 2-ethyl-1-butene (55%) and methylenecyclopentane (42%), respectively. Complex **2** reacts also with ethyl acetate to give 2-ethoxy-1-propene (28%). These correspond to the reported fact that the titanium carbene species derived from dimethyltitanocene was trapped effectively by ketones and aldehydes,[11] and this type of reactivity of alkylideneniobium complex was preceded in the work of Schrock.[1b]

When a solution of **2** in the presence of norbornene was heated to 50 °C for 18 h, the dark green color of the solution faded to dark brown and then Cp*(η^4-C_4H_6)Nb[$CH_2CH(C_5H_8)CH$] (**4**) was isolated as air-sensitive dark brown crystals in 32% yield. In the ^{1}H NMR spectrum of **4**, the signal due to the metallacyclobutane moiety was quite similar to that of $Cp_2Ti[CH_2CH(C_5H_8)CH]$ (**5**),[9] (DIPP)$_3$Ta[CH(^{t}Bu)CH(C_5H_8)CH] (**6**; DIPP = 2,6-diisopropylphenoxy),[24] and (^{t}BuO)$_2${2,6-(^{i}Pr)$_2C_6H_3$N}-W[CH(^{t}Bu)CH($C_7H_4F_6$)CH] (**7**).[25] The most distinctive characteristic is the H_β resonance that appears far upfield (δ −1.69), which is much higher than that of the corresponding β-hydrogens of **5** (δ 0.14), **6** (δ 0.88), and **7** (δ 2.77). Complex **4** was stable as a solid and in solution at room temperature, but at 75 °C complex **4** in C_6D_6 decomposed gradually to the extent of 70% in 12 h. Complex **4** was found to be a catalyst for the ring-opening metathesis polymerization (ROMP) of norbornene, giving a poly(norbornene) (M_n = 2900, M_w/M_n = 4.78) at 65 °C over 30 h in toluene. Complex **4** was inferior in selectivity of stereochemistry at the double bond (*cis* 91%) of the poly(norbornene) as compared to that (*cis* 97−99%) of a tantalum benzylidene species derived from Cp*(η^4-C_4H_6)Ta(CH_2Ph)$_2$.[17]



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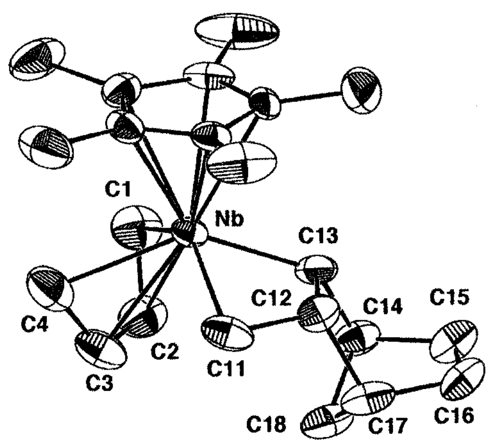


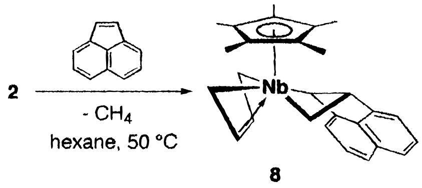
Figure 1. ORTEP drawing of complex **4** with the numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 4

Nb−C(1)	2.26(1)	Nb−C(2)	2.40(1)
Nb−C(3)	2.38(1)	Nb−C(4)	2.28(1)
Nb−C(21)	2.452(10)	Nb−C(22)	2.453(9)
Nb−C(23)	2.488(8)	Nb−C(24)	2.462(8)
Nb−C(25)	2.460(9)		
Nb−C(11)	2.17(1)	Nb−C(13)	2.16(1)
Nb···C(12)	2.44(1)		
Nb−C(11)−C(12)	79.7(5)	Nb−C(13)−C(12)	79.6(6)
C(11)−Nb−C(13)	77.7(4)	C(11)−C(12)−C(13)	116.8(9)

Figure 1 shows an ORTEP drawing of **4**. Selected bond distances and angles are given in Table 1. Complex **4** has a four-legged piano-stool geometry comprised of C(1), C(4), C(11), and C(13) and has a puckered-metallacyclobutane structure with an angle of 29.6° between the Nb−C(11)−C(13) and C(11)−C(12)−C(13) planes, confirming the addition of "Nb=CH_2" to norbornene in an *exo* fashion to minimize the steric interaction with the Cp* ligand. The niobacyclic ring system in **4** is essentially similar to the tantalacyclic ring system in **6**. The bond distances of Nb−C(11) and Nb−C(13) are 2.17(1) and 2.16(1) Å, respectively, which are comparable to the corresponding bond distances (2.14(1) Å) found for **6**.

The reaction between **2** and acenaphthylene proceeded in a fashion similar to that described for **4**. When a hexane solution of **2** and acenaphthylene was heated to 50 °C for 18 h, the new product Cp*(η^4-C_4H_6)Nb[$CH_2CH(C_{10}H_6)CH$] (**8**) was obtained in 27% yield.[26]



(2)

The structure of **8** was characterized on the basis of its NMR spectroscopy as well as X-ray analysis. The ^{1}H

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(26) The crystal structure of **8** was determined by X-ray analysis; however, the quality of data was not good enough to be discussed in detail. **8**: $C_{27}H_{31}Nb$, fw = 448.45, crystal size 0.30 × 0.30 × 0.20 mm, monoclinic, space group $P2_1/n$ (No. 14) with $a = 8.490(5)$ Å, $b = 20.075(5)$ Å, $c = 12.954(4)$ Å, $\beta = 93.25(3)°$, $V = 2204(1)$ Å^3, $Z = 4$, $d_{calcd} = 1.351$ g cm^{-3}, 1439 reflections ($2\theta_{max} = 55.0°$, $2\theta-\omega$ scan, 23 °C), $R = 0.079$, $R_w = 0.084$.

and ^{13}C NMR spectra of **8** displayed signals for a metallacyclic ring system together with one set each for the butadiene and η^5-Cp* ligands. The β-proton in the niobacyclic ring of **8** was observed at δ 1.46, a value which is shifted to lower field due to their benzylic positions.

Thus, the dimethyl complex **2** is found to be a carbene precursor whose reactivity is similar to that found for the dimethyltitanocene. We determined the crystal structure of niobacyclobutane **4** and demonstrated that **4** is the intermediate of the ROMP of norbornene.

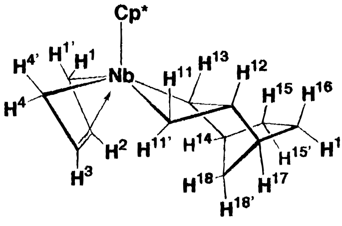
Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by use of the standard Schlenk technique under an argon atmosphere. NbCl$_2$(η^5-C$_5$Me$_5$)(η^4-buta-1,3-diene) (**1**) was prepared according to the literature.[21] Hexane, THF, and toluene were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. Methanol was refluxed over magnesium and distilled under argon. Benzene-d_6 was distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation before use. Norbornene (bicyclo[2.2.1]hept-2-ene) from Aldrich Chemical Co., Inc., was refluxed over sodium and distilled prior to use. Acenaphthylene was sublimed before use.

The ^{1}H (500, 400, and 270 MHz) and ^{13}C (68 MHz) NMR spectra in C$_6$D$_6$ were measured on a JEOL JNM-GX500, a JEOL JNM-GSX400, or a JEOL JNM-EX270 spectrometer. When C$_6$D$_6$ was used as the solvent, the spectra were referenced to the residual solvent protons at δ 7.20 in the ^{1}H NMR spectra (δ 128.0 (triplet for C$_6$D$_6$); ^{13}C NMR). Assignments in ^{1}H and ^{13}C NMR spectra for several complexes were aided by 2D ^{1}H−^{1}H NOESY and 2D ^{1}H−^{13}C COSY spectra, respectively. Elemental analyses were performed at Elemental Analysis Center, Faculty of Science, Osaka University. All melting points of all complexes were measured in sealed tubes under an argon atmosphere and were not corrected. Gel permeation chromatographic (GPC) analyses were carried out at 40 °C using a Shimadzu LC-10A liquid chromatograph system and a RID-10A differential refractometer, equipped with a Shodex KF-806L column. THF was used as the eluent at a flow rate of 0.8 mL/min, and sample concentrations of 0.5 mg/mL were applied. The GPC column was calibrated versus commercially available polystyrene standards (Aldrich).

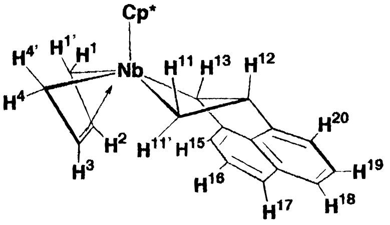
Preparation of Nb(η^5-C$_5$Me$_5$)(η^4-buta-1,3-diene)(CH$_3$)$_2$ (2). To a solution of **1** (0.297 g, 0.842 mmol) in THF (50 mL) cooled to −78 °C was added CH$_3$MgI (2.2 equiv, 1.86 mmol) in ether (0.62 M, 3.0 mL) *via* syringe. The reaction mixture was stirred for 1 h at 25 °C. The color of the solution changed from light green to dark green. All volatiles were removed under reduced pressure to give a residue, from which the product was extracted with hexane (50 mL). Recrystallization from toluene (0.4 mL) and hexane (1.5 mL) at −20 °C afforded **2** as dark green crystals in 84% yield; mp 98−100 °C dec. Complex **2** is thermally unstable, and the content of **2** was decreased to ca. 47% after 21 h at 20 °C; it decomposed about 60% by heating to 45 °C for 6 h. ^{1}H NMR (270 MHz, C$_6$D$_6$, 303 K): δ −0.41 (2H, br, =CH_2 anti), −0.03 (6H, br s, −CH_3), 0.90 (2H, br, =CH_2 syn), 1.68 (15H, s, C$_5$$Me_5$), 6.74 (2H, br, =C$H$−).

Preparation of $\overline{\mathrm{Nb[CH_2CH(C_5H_8)CH}}$]($\eta^5$-C$_5Me_5$)($\eta^4$-buta-1,3-diene) (4). To a solution of **1** (0.208 g, 0.589 mmol) in THF (60 mL) cooled to −78 °C were added norbornene (1.2 equiv, 0.70 mmol) in THF (0.50 M, 1.40 mL) and CH$_3$MgI (2.2 equiv, 1.30 mmol) in ether (0.55 M, 2.35 mL) *via* syringe. The reaction mixture was warmed to 20 °C; the color of the solution changed from light green to dark green, indicating the formation of **2**. When the reaction mixture was stirred for 18 h at 50 °C, the color of the solution changed from dark green to dark brown. Removal of all volatiles under reduced pressure gave a residue, which was extracted with hexane (40 mL). Recrystallization from toluene (0.2 mL) and hexane (0.8 mL) at −20 °C afforded **4** as dark brown crystals in 32% yield; mp 120−121.5 °C dec. Complex **4** decomposed about 70% by heating at 75 °C for 12 h. The 2D ^{1}H−^{1}H NOESY spectrum indicated neighboring protons in the molecule, *e.g.* H^2−H^{14} (m), H^2−H^{18} (m), H^3−H$^{11'}$ (m), H^3−H^{18} (m), H^{13}−H^{15} (s), H^{12}−H^{16} (s), H$^{11'}$−H^{18} (m), H$^{11'}$−H^{17} (m), and so on. ^{1}H NMR (500 MHz, C$_6$D$_6$, 303 K): δ −1.69 (1H, m, H^{12}), −0.33 (1H, m, H$^{1'}$), −0.31 (1H, m, H$^{4'}$), 0.91 (1H, m, H$^{18'}$), 1.14 (1H, m, H^{16}), 1.27 (1H, m, H^{18}), 1.35 (1H, m, H^{15}), 1.39 (1H, m, H^1), 1.52 (1H, m, H^4), 1.64 (1H, m, H$^{16'}$), 1.64 (15H, s, C$_5$$Me_5$), 1.74 (1H, m, H$^{15'}$), 2.12 (1H, m, H$^{11'}$), 2.29 (1H, m, H^{11}), 2.34 (1H, m, H^{14}), 2.53 (1H, m, H^{17}), 3.08 (1H, d, J = 8.0 Hz, H^{13}), 5.43 (1H, m, H^3), 5.80 (1H, m, H^2). ^{13}C NMR (68 MHz, C$_6$D$_6$, 303 K): δ 10.9 (q, $^1J_{\mathrm{CH}}$ = 127 Hz, C$_5$$Me_5$), 15.3 (d, $^1J_{\mathrm{CH}}$ = 143 Hz, C^{12}), 30.0 (t, $^1J_{\mathrm{CH}}$ = 130 Hz, C^{16}), 34.9 (t, $^1J_{\mathrm{CH}}$ = 132 Hz, C^{18}), 35.6 (t, $^1J_{\mathrm{CH}}$ = 130 Hz, C^{15}), 45.0 (d, $^1J_{\mathrm{CH}}$ = 148 Hz, C^{17}), 47.2 (d, $^1J_{\mathrm{CH}}$ = 140 Hz, C^{14}), 51.9 (t, $^1J_{\mathrm{CH}}$ = 146 Hz, C^1), 53.8 (t, $^1J_{\mathrm{CH}}$ = 148 Hz, C^4), 72.4 (br, C^{11}), 110.2 (d, $^1J_{\mathrm{CH}}$ = 163 Hz, C^2), 113.5 (s, C_5Me$_5$), 114.0 (d, $^1J_{\mathrm{CH}}$ = 163 Hz, C^3), 114.2 (br, C^{13}). In the ^{13}C NMR spectra C^{11} and C^{13} were observed as broad signals and their chemical shift values are determined on the basis of 2D ^{1}H−^{13}C COSY spectra. Anal. Calcd for C$_{22}$H$_{33}$Nb: C, 67.68; H, 8.52. Found: C, 67.00; H, 8.43.



Numbering Scheme for **4**

Preparation of $\overline{\mathrm{Nb[CH_2CH(C_{10}H_6)CH}}$]($\eta^5$-C$_5Me_5$)($\eta^4$-buta-1,3-diene) (8). To a solution of **1** (0.308 g, 0.873 mmol) in THF (50 mL) cooled to −78 °C were added acenaphthylene (1.1 equiv, 0.97 mmol) in THF (0.24 M, 4.10 mL) and CH$_3$MgI (2.2 equiv, 1.92 mmol) in ether (0.62 M, 3.10 mL) *via* syringe. The reaction mixture was warmed to 20 °C, and the solution changed from light green to dark green. All volatiles were removed under reduced pressure to give a residue, from which the product was extracted with hexane (50 mL). The hexane solution of the product was concentrated to ca. 25 mL and was heated to 50 °C for 14 h. The color of the solution changed from dark green to dark brown. Recrystallization from toluene (1.0 mL) and hexane (2.5 mL) at −20 °C afforded **8** as dark brown crystals in 27% yield; mp 128−134 °C dec. The 2D ^{1}H−^{1}H NOESY spectrum indicated neighboring protons in the molecule, *e.g.* H^1−H^{15} (w), H^3−H$^{11'}$ (m), H$^{11'}$−H^{20} (m), and so on. ^{1}H NMR (500 MHz, C$_6$D$_6$, 303 K): δ −0.21 (1H, m, H$^{1'}$), −0.09 (1H, m, H$^{4'}$), 0.96 (1H, m, H^1), 1.33 (1H, m, H^4), 1.46 (1H, br, H^{12}), 1.71 (15H, s, C$_5$$Me_5$), 2.38 (1H, dd, J = 8.5 and 11.6 Hz, H^{11}), 3.30 (1H, dd, J = 3.7 and 8.6 Hz, H$^{11'}$), 4.02 (1H, m, H^2), 4.96 (1H, m, H^3), 5.19 (1H, d, J = 6.0 Hz, H^{13}), 6.71 (1H, m, H^{15}), 7.51 (1H, d, J = 7.0 Hz, H^{20}), 7.40−7.45 (3H, two triplet and one doublet) and 7.63 (1H, d, J = 8.1 Hz) for H^{16}, H^{17}, H^{18}, and H^{19}. ^{13}C NMR (100 MHz, C$_6$D$_6$, 303 K): δ 11.3 (q, $^1J_{\mathrm{CH}}$ = 127 Hz, C$_5$$Me_5$), 20.7 (d, $^1J_{\mathrm{CH}}$ = 145 Hz, C^{12}), 53.8 (t, $^1J_{\mathrm{CH}}$ = 154 Hz, C^1), 55.6 (t, $^1J_{\mathrm{CH}}$ = 151 Hz, C^4), 74.1 (br, C^{11}), 110.7 (d, $^1J_{\mathrm{CH}}$ = 159 Hz, C^{15}), 111.6 (br, C^{13}), 113.8 (s, C_5Me$_5$), 115.5 (d, $^1J_{\mathrm{CH}}$ = 161 Hz, C^2), 117.0 (d, $^1J_{\mathrm{CH}}$ = 159 Hz, C^3), 120.7 (d, $^1J_{\mathrm{CH}}$ = 161 Hz, C^{20}), singlets at 132.8, 137.4, 150.4, and 158.9 ppm are for C^{14}, C^{21}, C^{22}, and C^{23}, 120.1 (d, $^1J_{\mathrm{CH}}$ = 157 Hz), 123.8 (d, $^1J_{\mathrm{CH}}$ = 156 Hz), and two peaks overlapped by C$_6$D$_6$ for C^{16}, C^{17}, C^{18}, and C^{19}. Anal. Calcd for C$_{27}$H$_{31}$Nb: C, 72.32; H, 6.97. Found: C, 71.74; H, 6.94.



Numbering Scheme for **8**

Preparation of Nb(OCH$_3$)(CH$_3$)(η^5-C$_5$Me$_5$)(η^4-buta-1,3-diene). Complex **2** (ca. 4 mg, ca. 0.01 mmol) was dissolved in 0.6 mL of C$_6$D$_6$ in a 5 mm NMR tube. To the dark green solution was added excess (ca. 10 equiv) MeOH (ca. 3 μL, ca. 0.10 mmol) at 25 °C. The solution was yellow. The NMR tube was sealed, and the ^{1}H NMR was measured. ^{1}H NMR (270 MHz, C$_6$D$_6$, 303 K): δ −0.06, 0.32, 0.52, 1.44 (4H, m, =CH_2), 0.21 (3H, s, Nb−CH_3), 1.80 (15H, s, C$_5$$Me_5$), 3.86 (3H, s, O$Me$), 5.90, 6.68 (2H, m, =C$H$−).

Polymerization of Norbornene. A solution of **4** (11 mg, 0.027 mmol) in toluene (1.0 mL) was mixed with a solution of norbornene (100 equiv, 2.7 mmol) in toluene (1.36 M, 2.0 mL) at 25 °C. After the solution was stirred at 65 °C for 30 h, methanol (20 mL) was added to the resulting yellow brown solution to precipitate a pale yellow polymer (12% chemical yield, M_n = 2900, M_w/M_n = 4.78), which was washed with methanol and then dried in vacuo. ^{1}H NMR (270 MHz, C$_6$D$_6$, 303 K): δ 1.21 (q (br), 1.49 (br), 1.92 (br), 2.09 (br), 2.95 (br), 5.39 (br); all signals are due to the cis geometry in the C=C bond of the polymer. The cis content was estimated to be 91%.

Methylenation of Carbonyl Compounds by Complex 2. Complex **2** (ca. 5 mg, ca. 0.02 mmol) was dissolved in 0.6 mL of C$_6$D$_6$ in a 5 mm NMR tube. To the dark green solution was added the carbonyl compound, and the mixture was then heated to 50 °C. The reaction was monitored by ^{1}H NMR spectroscopy, and the chemical yield was estimated on the basis of the integral of the product in the ^{1}H NMR spectrum.

Crystallographic Data Collection and Structure Determination of 4. Crystals of **4** suitable for X-ray diffraction studies were sealed in glass capillaries under an argon atmosphere, and then each crystal of the complex was mounted on a Rigaku AFC-5R four-circle diffractometer for data collection using Mo Kα radiation. Relevant crystal and data statistics are summarized in Table 2. The unit cell parameters at 23 °C were determined by a least-squares fit to 2θ values of 20 strong higher reflections for all complexes. Three standard reflections were chosen and monitored every 100 reflections. Empirical absorption correction was carried out on the basis of an azimuthal scan. Every sample showed no significant intensity decay during the data collection. The structures of all complexes were solved by direct methods (SHELXS 86)[27] and refined by the full-matrix least squares method. Measured nonequivalent reflections with $I > 3.0\sigma(I)$ were used for the structure determination. In the subsequent refinement the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$, where $w^{-1} = \sigma^2(F_o) = \sigma^2(F_o^2)/(4F_o^2)$. The positions of all non-hydrogen atoms for all complexes were found from a difference Fourier electron density map and refined anisotropically. All hydrogen atoms were placed in calculated positions (C−H = 0.95 Å) and kept fixed. All calculations were performed using the TEXSAN crystallographic software package, and illustrations were drawn with ORTEP.

Table 2. Crystal Data and Details of the Solution and Refinement of the Structure of 4

formula	C$_{22}$H$_{33}$Nb
fw	390.41
cryst syst	orthorhombic
space group	Pbca
a, Å	15.419(3)
b, Å	28.667(2)
c, Å	8.760(2)
Z	8
V, Å^3	3872(1)
D_{calcd}, g/cm^{-3}	1.339
F(000)	1648
radiation	Mo Kα
cryst size, mm	0.2 × 0.2 × 0.2
abs coeff, cm^{-1}	6.21
scan mode	$\omega-2\theta$
temp, C	23
scan speed, deg/min	8
scan width, deg	0.68 + 0.35 tan θ
2θ_{max}, deg	55.0
no. of unique data	5011
no. of unique data ($I > 3\sigma(I)$)	1672
no. of variables	216
R^a	0.053
$R_w{}^b$	0.059
GOF	1.57
Δ, e Å^{-3}	0.88, −0.69

[a] $R = \Sigma||F_o| - |F_c||/|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. Function minimized: $\Sigma w(|F_o| - |F_c|)^2$.

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Supporting Information Available: Tables of final positional parameters, final thermal parameters, bond distances and angles, and best planes for **4** together with an ORTEP drawing giving its complete atom-numbering scheme (13 pages). Ordering information is given on any current masthead page.

OM9610051

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(27) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R. Eds.; Oxford University Press: Oxford, U.K., 1985; p 179.