4058 *Organometallics* **1991**, *10*, 4058–4066

Facile Synthesis and Stereochemistry of Alkyne Complexes of Cp_2MH and $Cp_2MCH_2CH_2R$ (M = Nb, Ta)

Hajime Yasuda* and Hitoshi Yamamoto

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724, Japan

Takashi Arai and Akira Nakamura*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Jie Chen, Yasushi Kai,* and Nobutami Kasai

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Received February 14, 1991

Hydridoniobium–olefin complexes of type $Cp_2NbH(RCH{=}CH_2)$ (R = H, CH_3, C_6H_5) were found to readily react with propyne, 1-butyne, 2-butyne, and phenylacetylene under mild conditions to afford air-sensitive blue crystals of alkyl–alkyne complexes, $Cp_2NbCH_2CH_2R$(alkyne), in high yield. Resulting complexes prefer the exo geometry in sharp contrast to the endo preference of the starting materials. An unusual α-agostic interaction was observed in the ethyl group of $(C_5H_5)_2NbCH_2CH_3(CH_3C{\equiv}CCH_3)$, which crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 12.930$ (6) Å, $b = 14.498$ (7) Å, $c = 7.590$ (5) Å, and $Z = 4$. Bulky 1-alkynes such as 3,3-dimethyl-1-butyne, (trimethylsilyl)acetylene, and diphenylacetylene behave in a different manner and gave rise to the formation of hydridoniobocene complexes of the type Cp_2NbH(alkyne) with exo geometry. $(C_5H_5)_2NbH[(CH_3)_3CC{\equiv}CH]$ belongs to the monoclinic space group $P2_1$, with $a = 6.037$ (1) Å, $b = 14.428$ (3) Å, $c = 8.218$ (2) Å, $\beta = 105.96$ (1)°, and $Z = 2$. An analogous structure was found in $(C_5H_5)_2NbH[(CH_3)_3SiC{\equiv}CH)]$, which crystallizes in the monoclinic space group $P2_1$, with $a = 6.149$ (4) Å, $b = 14.727$ (4) Å, $c = 8.579$ (5) Å, $\beta = 104.78$ (5)°, and $Z = 2$. The reaction of the alkene complexes with excess $(CH_3)_3SiC{\equiv}CH$ and 1-phenyl-1-propyne afforded insertion products formulated by $Cp_2NbCH{=}CHR(CH{\equiv}CR)$. All the alkyne complexes were inert to CO, CO_2, PR_3, pyridine, and even carbonyl compounds. Cp_2TaH(alkene) complexes also react with alkynes in a similar manner.

Introduction

Intramolecular migration of hydridometal or alkylmetal to the coordinated C–C unsaturation has been considered to be the key reaction in initiation and propagation of the Ziegler–Natta type polymerizations and oligomerizations.[1] However only limited evidences have been accumulated for this type of addition reaction using, for example, $[Cp_2WH(CH_2{=}CH_2)]^+PF_6^-$ and $[Cp_2W(CO)Me]^+PF_6^-$.[2] Cp_2MH(alkene) (M = Nb, Ta; Cp = C_5H_5) may serve as an useful starting material to gain new information on this insertion process, since these are typical examples of the stable hydridometal–alkene complexes with moderate reactivity. Conjugated dienes have been found to readily react with these hydrido-alkene complexes, liberating the ligated olefin to yield a series of η^3-allyl–metal complexes, as previously noted.[3] Since alkynes commonly exhibit higher π-donating and accepting properties as compared with alkenes and dienes, we have confined our attention to the reaction of Cp_2MH(alkene) with alkynes in order to clarify the reaction courses (ligand exchange and hydrometalation) and exact stereochemistry of the resulted alkyne complexes (exo, endo) and to collect fundamental information on the intramolecular migratory insertion of ligated ethylene or alkynes into a M–H or M–R bond in Nb(III) and Ta(III) species. Although a considerable amount of X-ray works on niobium–alkyne complexes have been reported (vide infra), the majority of these are unsuited as the model for the present study.

Results and Discussion

Reaction and Molecular Structure of Monosubstituted Alkynes with Cp_2MH(alkene) (M = Nb, Ta). (a) Formation of Alkyl–Alkyne Complexes. An ethylene complex of hydridoniobium, $Cp_2NbH(CH_2{=}CH_2)$,[4] was found to react cleanly and smoothly with a variety of monosubstituted alkynes such as propyne, 1-butyne, and phenylacetylene under argon at 40–60 °C in toluene. Strict exclusion of air and moisture is required for these reactions. The color of the solution turns green from brown during the reaction, and the products were isolated as air-sensitive green crystals in >70% yield by recrystallization from degassed hexane. Their EIMS and ^1H NMR studies coupled with elemental analysis indicated the formation of novel alkyne complexes formulated by $Cp_2NbCH_2CH_3(RC{\equiv}CH)$ (see Experimental Section). Thus the attack of an alkyne causes migratory insertion of the ligated ethylene into the Nb–H bond, forming a Nb–ethyl bond, accompanied by the coordination of incoming alkyne to the metal (eq 1). The mode of this reaction corresponds well to that observed in reactions of $Cp_2MH(CH_2{=}CH_2)$ (M = Ta,[5] Nb[6]) with CO and isonitrile, which afford $Cp_2NbCH_2CH_3$(donor) in high yield.

---

(1) (a) Cossee, P. *Tetrahedron Lett.* **1960**, *17*, 12. (b) Boor, J. *Ziegler-Natta Catalysts and Polymerization*; Academic Press: New York, 1979; p 670. (c) Reichert, K. H. In *Transition Metal Catalyzed Polymerization. Alkenes and Dienes*; Quirk, R. P., Ed.; Hawood Academic Publishers: New York, 1983; Part B, p 465. (d) Yasuda, H.; Nakamura, A. *Rev. Chem. Intermed.* **1986**, *6*, 365.

(2) (a) Francis, B. R.; Green, M. L. H.; Roberts, G. G. *J. Chem. Soc., Chem. Commun.* **1971**, 1290. (b) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 761.

(3) Yasuda, H.; Arai, T.; Okamoto, T.; Nakamura, A. *J. Organomet. Chem.* **1989**, *361*, 161.

(4) (a) Klazinga, A. H.; Teuben, J. H. *J. Organomet. Chem.* **1980**, *194*, 309. (b) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 5420.

(5) (a) Klazinga, A. H.; Teuben, J. H. *J. Organomet. Chem.* **1980**, *192*, 75. (b) Eichner, M. E.; Alt, H. G.; Raush, M. D. *J. Organomet. Chem.* **1984**, *264*, 309.

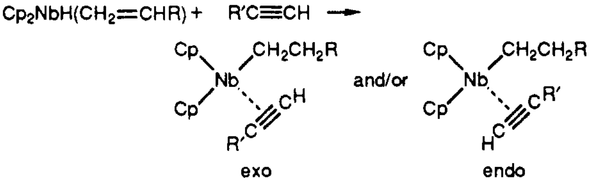
0276-7333/91/2310-4058$02.50/0

Table I. ^1H NMR Parameters for Cp_2MR(alkyne) and Cp_2MH(alkyne) (M = Nb, Ta) in C_6D_6

complex	chemical shift (δ), ppm (coupling constant, Hz)			
	H^1	H^2	H^3	H^4
$Cp_2NbCH^3{}_2CH^4{}_3(CH^1{}_3C{\equiv}CH^2)$ (1)				
exo 79%	2.58 (d, 1.74)	6.79 (d)	2.07 (q, 7.15)	1.87 (t)
endo 21%	2.37 (d, 1.73)	8.19 (d)	1.84 (q, 5.78)	1.76 (t)
$Cp_2NbCH^3{}_2CH^4{}_3(CH^{1'}{}_3CH^1{}_2C{\equiv}CH^2)$ (2)				
exo 81%	2.75 (dq, 1.54, 7.23) 1.35 (t, 7.23) (1′)	6.78 (d)	2.02 (q, 7.05)	1.84 (t)
endo 19%	2.63 (dq, 1.54, 7.30) 1.22 (t, 7.30) (1)	8.14 (d)	2.01 (q, 6.22)	1.80 (t)
$Cp_2NbCH^3{}_2CH^4{}_3(C_6H^1{}_5C{\equiv}CH^2)$ (3)				
exo 93%	7.2–7.7 (m)	7.15 (s)	2.11 (q, 7.15)	1.88 (t)
endo 7%	7.2–7.7 (m)	8.19 (s)	1.83 (q, 7.05)	1.57 (t)
$Cp_2TaCH^3{}_2CH^4{}_3(CH^1{}_3C{\equiv}CH^2)$ (4)				
exo 87%	2.91 (s)	7.42 (s)	2.50 (q, 7.14)	2.01 (t)
endo 13%	2.74 (s)	9.02 (s)	2.46 (q, 7.03)	1.98 (t)
$Cp_2NbH^3(t\text{-}Bu^1C{\equiv}CH^2)$ (5)				
exo 100%	1.80 (s)	7.52 (d, 8.21)	−0.08 (d, 8.21)	
$Cp_2NbH^3(Me^1{}_3SiC{\equiv}CH^2)$ (6)				
exo 100%	0.36 (s)	9.18 (d, 7.90)	−0.77 (d, 7.90)	
$Cp_2NbCH^3{}_2CH^4{}_3(CH^1{}_3C{\equiv}CCH^2{}_3)$ (7)	2.43 (s)	2.21 (s)	1.98, 1.97 (m)	1.91 (m)
$Cp_2NbCH^3{}_2CH^3{}_2CH^4{}_3(CH^1{}_3C{\equiv}CCH^2{}_3)$ (8)	2.20 (s)	1.99 (s)	1.62 (m)	1.57 (t)
$Cp_2NbCH^3{}_2CH^4{}_2C_6H_5(CH^1{}_3C{\equiv}CCH^2{}_3)$ (9)	2.68 (s)	2.40 (s)	2.12 (t)	2.07 (t)
$Cp_2TaCH^3{}_2CH^4{}_3(CH^1{}_3C{\equiv}CCH^2{}_3)$ (10)	2.52 (s)	2.26 (s)	1.82 (q, 7.15)	1.77 (t)
$Cp_2NbH^3(C_6H^1{}_5C{\equiv}CC_6H^25)$ (11)	7.2–8.3 (m)	7.2–8.3 (m)	−0.23 (s)	
$Cp_2NbH^3(C_6H^1{}_5C{\equiv}CCH^2{}_3)$ (12)	7.2–8.3 (m)	2.30 (s)	−0.18 (s)	

Table II. ^{13}C NMR Parameters for $Cp_2MCH_2CH_3$(alkyne) and Cp_2MH(alkyne) (M = Nb, Ta)

complex		chemical shift (δ), ppm				
		C^1	C^2	C^3	C^4	C^5
$Cp_2NbC^4H_2C^5H_3(C^1H_3C^2{\equiv}C^3H)$ (1)	exo	21.8	158.8	127.0	13.8	21.0
	endo	11.9	137.2	138.4	14.3	21.4
$Cp_2NbC^4H_2C^5H_3(C^{1'}H_3C^1H_2C^2{\equiv}C^3H)$ (2)	exo	30.5, 23.0	165.7	126.5	14.3	20.9
	endo	20.3, 20.9	144.0	137.5	14.1	21.3
$Cp_2NbC^4H_2C^5H_3(C^1{}_6H_5C^2{\equiv}C^3H)$ (3)	exo	120–140	160.1	124.6	14.2	20.8
	endo	120–140	138.0	137.0	14.3	23.0
$Cp_2NbH(t\text{-}Bu^1C^2{\equiv}C^3H)$ (5)	exo	37.2, 32.3	165.6	116.0		
$Cp_2NbH(Me^1{}_3SiC^2{\equiv}C^3H)$ (6)	exo	1.1	144.7	147.8		
$Cp_2NbC^4H_2C^5H_3(C^1H_3C^2{\equiv}C^3C^{1'}H_3)$ (7)		20.0 (exo) 9.6 (endo)	147.9	130.2	12.7	21.6
$Cp_2NbH(C^1{}_6H_5C^2{\equiv}C^3C^{1'}{}_6H_5)$ (11)		120–140 (exo) 120–140 (endo)	149.2	139.0		



(1)

1: R = H, R′ = CH_3
2: R = H, R′ = C_2H_5
3: R = H, R′ = C_6H_5
4: R = H, R′ = CH_3 (metal, Ta)

All of the resulting products, $Cp_2NbCH_2CH_3(CH_3C{\equiv}CH)$ (1), $Cp_2NbCH_2CH_3(C_2H_5C{\equiv}CH)$ (2), and $Cp_2NbCH_2CH_3(C_6H_5C{\equiv}CH)$ (3), comprise two geometrical isomers, endo and exo, as confirmed by the NMR studies. ^1H and ^{13}C NMR parameters for the resulting alkyne complexes are summarized in Tables I and II, respectively. The most striking is the preferential formation of the exo isomer. This trend contrasts sharply to the behavior of starting alkene complexes, which favor the endo geometry as a result of severe steric congestion between Cp and alkyl substituent on the ligated alkene. The exo content increases with increasing bulkiness of alkyl substituents. The assignment of exo and endo isomers of the alkyne complexes was made on the basis of the 2D-NOESY NMR spectrum with reference to the X-ray structure of a related complex $(C_5H_5)_2NbCH_2CH_3$(2-butyne) (vide infra). Alkyne CH signals of the exo isomers (6.7–7.2 ppm) generally show upfield shift as compared with those of the endo isomers (8.1–9.1 ppm). As a typical example, the ^1H NMR spectrum of $Cp_2NbCH_2CH_3(CH_3C{\equiv}CH)$ (1) is illustrated in Figure 1, which displays cross peaks among several groups; propyne CH···CH_2 and CH_3 of $NbCH_2CH_3$(exo isomer), propyne CH_3···CH_2 and CH_3 of $NbCH_2CH_3$(endo isomer). Thus, the steric repulsion between Nb–alkyl and alkyne–alkyl plays a key role for preferential formation of the exo isomer. No geometrical interconversion was observed in solution even at high temperature (90 °C) to indicate that the isomer ratio is determined kinetically. An attempt to conduct the intramolecular migration of the ethyl group into the ligated propyne in the presence of PMe_3 or PEt_3 (5 equiv) has failed because 1 is inert to PR_3 at 40–100 °C in toluene.

The present method is effective also for synthesis of the corresponding tantalum–alkyne complexes, as evidenced by the reaction of $Cp_2TaH(CH_2{=}CH_2)$ with propyne, although this reaction required more vigorous reaction conditions (100 °C). The EIMS and NMR spectral patterns of the resulting tantalum–propyne complex 4 is virtually identical with those of the corresponding niobocene derivative 1.

---

(6) (a) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670. (b) Gibson, V. C.; Bercaw, J. E.; Bruton, W. J., Jr.; Sanner, R. D. *Organometallics* **1986**, *5*, 976. (c) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134.

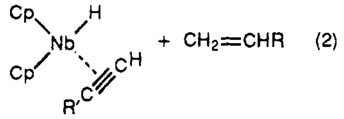
Table III. Summary of Crystallographic and Experimental Data for Complexes $Cp_2NbH(Me_3CC{\equiv}CH)$ (5), $Cp_2NbH(Me_3SiC{\equiv}CH)$ (6), and $Cp_2Nb(CH_2CH_3)(MeC{\equiv}CMe)$ (7)

	5	6	7
formula	$C_{16}H_{21}Nb$	$C_{15}H_{21}SiNb$	$C_{16}H_{21}Nb$
fw	306.2	322.3	306.2
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1$	$P2_1$	$P2_12_12_1$
temp, °C	20	20	20
a, Å[a]	6.307 (1)	6.149 (4)	12.930 (6)
b, Å	14.428 (3)	14.727 (4)	14.498 (7)
c, Å	8.218 (2)	8.579 (5)	7.590 (5)
β, deg	105.96 (1)	104.78 (5)	
V, Å^3	688.2 (2)	751.1 (6)	1422.8 (1.2)
Z	2	2	4
D_{calcd}, g cm^{-3}	1.478	1.657	1.574
$F(000)$, e	316	332	632
μ(Mo Kα), cm^{-1}	9.1	10.6	6.1
2θ range, deg[b]	$4 < 2\theta < 60$	$4 < 2\theta < 60$	$4 < 2\theta < 60$
scan width, deg in 2θ	$2.0 + 0.70 \tan \theta$	$2.0 + 0.70 \tan \theta$	$2.0 + 0.70 \tan \theta$
background, s	5	5	5
no. of reflns measd	2047	2282	2566
no. of reflns obsd[c]	2007	2184	2235
no. of variables	237	237	238
GOF[d]	1.001	0.996	1.021
R[e]	0.027	0.034	0.048
R_w[f]	0.040	0.055	0.053

[a] Least-squares refinement of the θ values for 25 reflections with $2\theta > 25°$. [b] Intensity data were collected on a Rigaku four-circle diffractometer using graphite-monochromatized Mo Kα radiation by the θ–2θ scan method. [c] $|F_o| > 3\sigma(F_o)$. [d] $[\sum w(|F_o| - |F_c|)^2/(n - m)$, where n and m are the number of reflections used and variables refined, respectively. [e] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [f] $R_w = [\sum(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$, $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$, and $g = 0.003$ for all the complexes.

(b) Formation of Hydrido–Alkyne Complexes. The behavior of bulky 1-alkynes differs greatly from that of propyne and 1-butyne; i.e. the reaction of 3,3-dimethyl-1-butyne (t-$BuC{\equiv}CH$) with $Cp_2NbH(RCH{=}CH_2)$ (R = H, CH_3) led to the formation of an alkyne complex of hydridoniobocene, $Cp_2NbH(t\text{-}BuC{\equiv}CH)$ (5), selectively and in high yield (eq 2). This type of complexation was

$Cp_2NbH(CH_2{=}CHR) + R'C{\equiv}CH \longrightarrow$



$+ CH_2{=}CHR$ (2)

exo

5: R = H, R' = t-C_4H_9

6: R = H, R' = Me_3Si

confirmed in terms of the ^1H NMR and EIMS spectroscopies. We can readily assign the signal at −0.08 ppm to Nb–H on the basis of signal ratio and chemical shift. The Nb–H resonance shows an upfield shift by 0.2–0.3 ppm as compared with the Nb–H resonances of the precursor Cp_2NbH(alkene) (see the full assignment of $Cp_2NbH(CHR{=}CH_2)$ (R = H, CH_3) reported in a previous paper).[3,6] Since appreciable magnetic interaction was observed ($^3J_{H-H}$ = 8.2 Hz) between the CH of ligated t-$BuC{\equiv}CH$ and Nb–H, exo geometry is most probable. The exact structure was finally determined by the X-ray crystallographic analysis (vide infra). Similarly $(CH_3)_3SiC{\equiv}CH$ also provides a hydrido–alkyne complex, $(C_5H_5)_2NbH[(CH_3)_3SiC{\equiv}CH)]$ (6), of exo geometry, as the sole product. The formation of hydrido–alkyne complexes in place of alkyl–alkyne complexes may result from strong π-donation of t-$BuC{\equiv}CH$ or $(CH_3)_3SiC{\equiv}CH$, which prompted a ligand-exchange reaction between the ligated alkene and an incoming alkyne prior to the migratory insertion of ethylene or propene into the Nb–H bond. The reaction pathway via β-elimination of $Cp_2NbCH_2CH_3(t\text{-}BuC{\equiv}CH)$ can be ruled out from the variable-temperature NMR studies; i.e. formation of such species was undetected at −70–60 °C. Thus the reaction courses to yield either alkylmetal or hydridometal are determined owning to the delicate balance of steric and electronic effects of substituents on the ligated alkyne molecule. The steric congestion between Nb–H and the t-Bu group of the alkyne may inhibit the formation of the endo isomer. Resulting complexes 5 and 6 are again inert to PMe_3 and pyridine (5 mol equiv) even at 120 °C in toluene, and no intramolecular hydrometalation occurred.

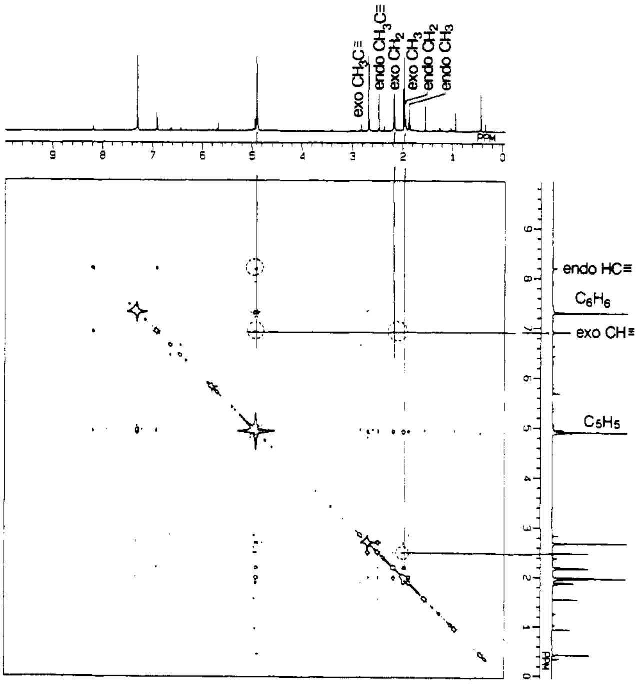


Figure 1. 2D-NOEZY NMR spectrum of $Cp_2NbCH_2CH_3(CH_3C{\equiv}CH)$ (1) in C_6D_6 at 30 °C.

(c) Molecular Structure of $Cp_2NbH(RC{\equiv}CH)$ [R = t-Bu (5), $(CH_3)_3Si$ (6)]. Crystallographic and experimental data of the 3,3-dimethyl-1-butyne complex 5 are compiled in Table III, and selected bond distances and angles, in Table IV. Final atomic coordinates are shown

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for $Cp_2NbH[(CH_3)_3CC{\equiv}CH)]$ (5) and $Cp_2NbH[(CH_3)_3SiC{\equiv}CH)]$ (6) with Estimated Standard Deviations in Parentheses

	5	6
	(a) Bond Distances	
Nb–C(1)	2.160 (4)	2.164 (7)
Nb–C(2)	2.191 (4)	2.214 (6)
Nb–C(11)	2.426 (7)	2.418 (9)
Nb–C(12)	2.408 (7)	2.404 (9)
Nb–C(13)	2.430 (6)	2.428 (8)
Nb–C(14)	2.446 (7)	2.437 (8)
Nb–C(15)	2.431 (5)	2.406 (7)
Nb–C(16)	2.461 (9)	2.420 (12)
Nb–C(17)	2.451 (9)	2.432 (12)
Nb–C(18)	2.411 (8)	2.390 (11)
Nb–C(19)	2.430 (7)	2.406 (13)
Nb–C(20)	2.437 (6)	2.405 (11)
Nb–H(2)	1.63 (8)	1.64 (8)
Si–C(2)		1.844 (12)
Si–C(3)		1.864 (13)
Si–C(4)		1.864 (12)
Si–C(5)		1.862 (8)
C(1)–C(2)	1.288 (6)	1.282 (9)
C(2)–C(3)	1.525 (6)	
C(3)–C(4)	1.532 (8)	
C(3)–C(5)	1.540 (7)	
C(3)–C(6)	1.529 (7)	
C(11)–C(12)	1.426 (9)	1.419 (13)
C(11)–C(15)	1.396 (8)	1.382 (12)
C(12)–C(13)	1.404 (9)	1.408 (12)
C(13)–C(14)	1.406 (9)	1.411 (11)
C(14)–C(15)	1.388 (9)	1.390 (11)
C(16)–C(17)	1.325 (12)	1.333 (17)
C(16)–C(20)	1.408 (11)	1.422 (16)
C(17)–C(18)	1.427 (12)	1.395 (16)
C(18)–C(19)	1.378 (10)	1.376 (17)
C(19)–C(20)	1.364 (10)	1.362 (17)
Nb–CCP(1)	2.114 (8)	2.105 (10)
Nb–CCP(2)	2.136 (9)	2.108 (11)
Nb–C(Cp)(av)	2.433 (7)	2.416 (10)
C(1)–H(1)	0.92 (7)	0.85 (8)
	Bond Angles	
C(1)–Nb–C(2)	34.2 (2)	34.0 (2)
Nb–C(1)–C(2)	74.1 (3)	75.1 (4)
Nb–C(2)–C(1)	71.5 (3)	70.8 (4)
Nb–C(2)–C(3)	150.8 (3)	
Nb–C(2)–Si		147.5 (3)
C(1)–C(2)–Si		141.7 (5)
C(1)–C(2)–C(3)	137.7 (4)	
C(2)–Si–C(3)		109.8 (4)
C(2)–Si–C(4)		109.4 (4)
C(2)–Si–C(5)		111.5 (3)
C(2)–C(3)–C(4)	109.0 (4)	
C(2)–C(3)–C(5)	110.6 (4)	
C(2)–C(3)–C(6)	110.6 (4)	
C(3)–Si–C(4)		109.3 (4)
C(3)–Si–C(5)		107.5 (5)
C(4)–Si–C(5)		109.3 (4)
C(4)–C(3)–C(5)	110.0 (4)	
C(4)–C(3)–C(6)	109.3 (4)	
C(5)–C(3)–C(6)	107.3 (4)	
C(11)–C(12)–C(13)	107.2 (6)	108.2 (8)
C(11)–C(15)–C(14)	109.0 (5)	110.7 (7)
C(12)–C(11)–C(15)	107.5 (6)	106.5 (8)
C(12)–C(13)–C(14)	108.3 (6)	107.7 (7)
C(13)–C(14)–C(15)	108.0 (6)	106.9 (7)
C(16)–C(17)–C(18)	108.6 (8)	107.7 (11)
C(16)–C(20)–C(19)	107.5 (6)	105.5 (10)
C(17)–C(16)–C(20)	108.8 (8)	109.7 (11)
C(17)–C(18)–C(19)	106.6 (7)	107.6 (10)
C(18)–C(19)–C(20)	108.4 (6)	109.4 (11)
CCP(1)–Nb–CCP(2)	133.7 (5)	134.9 (5)
Nb–C(1)–H(1)	143 (4)	153 (6)
C(1)–Nb–H(2)	71 (3)	70 (3)
C(2)–C(1)–H(1)	142 (4)	131 (5)

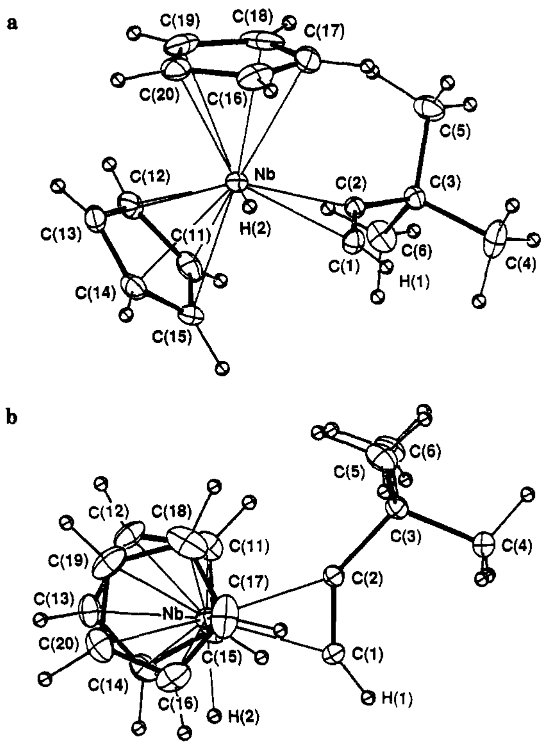


Figure 2. ORTEP drawings of $Cp_2NbH(t\text{-}BuC{\equiv}CH)$ (5): (a) side view; (b) top view.

Table V. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors for Non-Hydrogen Atoms in $Cp_2NbH[(CH_3)_3CC{\equiv}CH]$ (5) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq}, Å^2
Nb	0.16619 (3)	0.2500 (0)	0.07209 (3)	2.34
C(1)	–0.0477 (6)	0.1644 (3)	0.1828 (6)	2.9
C(2)	0.158 (1)	0.1311 (3)	0.2362 (5)	2.3
C(3)	0.279 (1)	0.0536 (3)	0.3530 (5)	2.7
C(4)	0.105 (1)	0.0052 (5)	0.429 (1)	4.9
C(5)	0.480 (1)	0.0925 (5)	0.495 (1)	4.4
C(6)	0.380 (2)	–0.0172 (4)	0.255 (1)	4.2
C(11)	0.254 (2)	0.1287 (4)	–0.1048 (6)	3.9
C(12)	0.385 (1)	0.2087 (5)	–0.1221 (6)	4.1
C(13)	0.227 (1)	0.2767 (4)	–0.2044 (6)	3.8
C(14)	0.003 (1)	0.2402 (5)	–0.2348 (5)	3.7
C(15)	0.022 (1)	0.1503 (4)	–0.1727 (6)	3.5
C(16)	0.148 (2)	0.3936 (5)	0.230 (2)	4.7
C(17)	0.266 (2)	0.3334 (5)	0.342 (1)	5.4
C(18)	0.473 (2)	0.3108 (4)	0.300 (1)	5.9
C(19)	0.475 (1)	0.3629 (5)	0.160 (1)	5.1
C(20)	0.274 (2)	0.4129 (4)	0.112 (1)	4.4

in Table V. The molecular structure of 5 is shown in Figure 2 by ORTEP drawing. The overall geometry around the Nb atom is described as a very hindered trigonal bipyramid with CCP(1), CCP(2), and C(1) at basal positions and C(2) and H(2) at axial positions (CCP: centroid of cyclopentadienyl ligand). The molecule represents a wedgelike sandwich structure with an angle of 47.6° between the closely planar cyclopentadienyl rings. Figure 2b clearly indicates the exo geometry for alkyne coordination; i.e. the *tert*-butyl group of the alkyne locates in the exo position to release steric interaction with Nb–H(2). C(1), C(2), H(1), and H(2) are coplanar with Nb in line with general structural features of pentacoordinated niobocene derivatives. The Nb–C(2) distance (2.191 Å) is slightly longer than the Nb–C(1) length (2.160 Å) of 6 and also the corresponding Nb–C length (2.18 Å) reported for $NbCp_2(OOCCMe_3)(C_2Ph_2)$[7] as a result of steric re-

---

[7] Pasynskii, A. A.; Skripkin, Yu. V.; Eremenko, I. L.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1979**, *165*, 39.

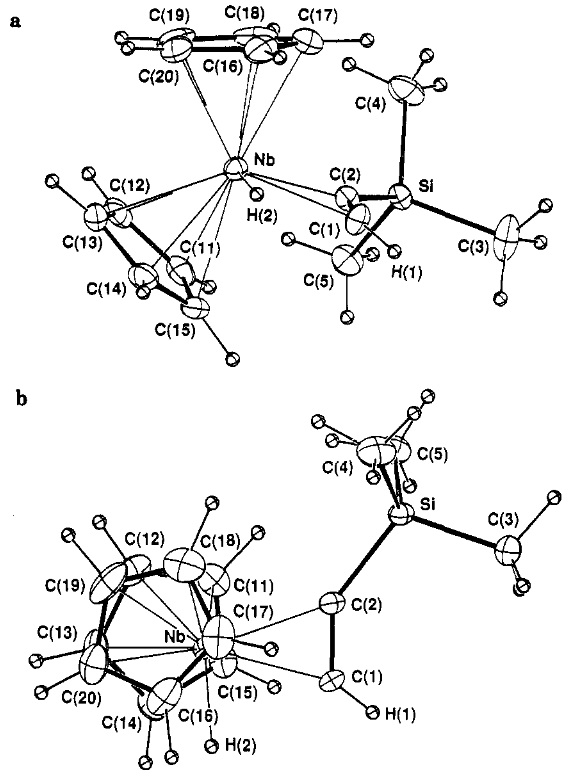


Figure 3. ORTEP drawings of $Cp_2NbH[(CH_3)_3SiC{\equiv}CH]$ (6): (a) side view; (b) top view.

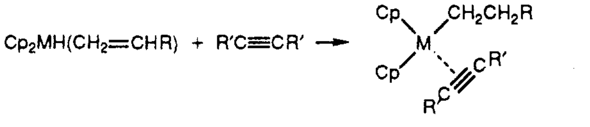
pulsion between *t*-Bu and Cp groups. The Nb–H(2) distance (1.63 Å) resembles that in $(C_5H_5)_2NbH_3$ (average 1.65 Å).[8] The C(1)–C(2) bond distance (1.288 Å) of the ligated alkyne is lengthened from that of the noncoordinated alkyne molecules. Both *t*-Bu and H groups bend away from the metal with a C(2)–C(1)–H(1) angle of 142° and a C(1)–C(2)–C(3) angle of 137.7°. The elongated C≡C and large deviation of the C(1)–C(2)–R angle from 180° may originate from strong d–π* back-bonding of alkynes. As a consequence, the present complexes may be viewed as a metallacyclo-2-propene in a formal +5 oxidation state, as was found for $(C_5H_4CH_3)NbCl_2(C_2Ph_2)$ (C≡C length of 1.307 Å),[9] $NbCl_3(PhCCSi\text{-}t\text{-}BuMe_2)(THF)_2$ (1.306 Å),[10] $NbCp_2(OOCCMe_3)(C_2Ph_2)$ (1.259 Å),[7] $NbCl_2(C_4H_8S)(C_2Ph_2)$ (1.301 Å),[11] $(C_5Me_5)TaCl_2(C_2Ph_2)$ (1.337 Å),[12] and $Nb[C_2(OSiMe_3)_2](dmpe)$ (1.310 Å).[13] Metallacyclic preference was also found in a series of niobium–diene and tantalum–diene complexes of type $MCl_2(C_5Me_5)(diene)$[14] and $M(C_5Me_5)(diene)_2$.[14]

Whole geometry of $Cp_2Nb[(CH_3)_3SiC{\equiv}CH]$ (6) (Figure 3) resembles with that of 5, although a slight difference is seen in their mode of alkyne coordination. The selected molecular dimensions are shown in Table IV, and final atomic coordinates, in Table VI. The bulky $(CH_3)_3Si$ group again points away from the H(2) atom so that the silyl group locates at the exo position to minimize the steric interaction. The Nb–C(2) bond in 6 (2.214 Å) shows a slightly longer distance as compared with that in 5 (2.191 Å), while the Nb–C(1) length of 6 (2.164 Å) is comparable with that of 5. Enlargement of the C(1)–C(2)–Si angle (141.7°) suggests weak interaction of this alkyne to the metal relative to the *t*-BuC≡CH in 5. In a special case, a nearly linear angle (178°) was observed, as reported for $(C_5Me_5)_2Yb$(2-butyne), where the alkyne is bound very loosely.[15] The Si atom in 6 and C(3) in 5 are slightly out of the C(1), C(2), Nb plane. The dihedral angles between the planes composed of Nb, C(1), C(2) and C(1), C(2), C(3)/Si are 1.86 and 0.66° for 5 and 6, respectively. The H(2)–Nb–C(1) angle (70°) is approximately equal to that in complex 5 (71°), while these angles are larger than the H–Nb–H angle in Cp_2NbH_3 (average 63°).

Table VI. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors for Non-Hydrogen Atoms in $Cp_2NbH[(CH_3)_3SiC{\equiv}CH)]$ (6) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq}, Å^2
Nb	0.150123 (7)	0.250000 (0)	0.068564 (4)	2.94
Si	0.29053 (3)	0.047500 (8)	0.37000 (2)	3.09
C(1)	−0.0619 (2)	0.16939 (4)	0.1810 (1)	3.9
C(2)	0.1359 (2)	0.13601 (3)	0.23398 (7)	3.1
C(3)	0.0945 (3)	−0.01434 (6)	0.4663 (2)	6.8
C(4)	0.5175 (3)	0.10146 (6)	0.5294 (1)	6.0
C(5)	0.4172 (2)	−0.03761 (4)	0.2587 (1)	4.8
C(11)	0.2507 (3)	0.12600 (4)	−0.08409 (8)	4.7
C(12)	0.3720 (2)	0.20383 (5)	−0.1113 (1)	5.0
C(13)	0.2167 (3)	0.26788 (3)	−0.19679 (8)	4.7
C(14)	−0.0004 (3)	0.23027 (3)	−0.22103 (8)	4.6
C(15)	0.0260 (2)	0.14467 (3)	−0.15058 (8)	4.2
C(16)	0.1305 (3)	0.39241 (5)	0.2052 (2)	6.1
C(17)	0.2325 (4)	0.33465 (5)	0.3203 (2)	6.4
C(18)	0.4355 (3)	0.30908 (5)	0.2887 (2)	6.6
C(19)	0.4553 (3)	0.35586 (5)	0.1541 (2)	6.9
C(20)	0.2665 (3)	0.40638 (4)	0.0957 (2)	6.0

Reaction of Disubstituted Alkyne with Cp_2MH(alkene) (M = Nb, Ta) and Molecular Structure of the Product. (a) Formation of Alkyl–Alkyne Complexes. The reactions of disubstituted alkynes with $Cp_2NbH(CH_2{=}CH_2)$ were explored in order to understand the steric as well as electronic effect of the substituents. Although the linear structure of disubstituted alkyne is expected to prevent or interfere with the access of alkyne molecule to the metal center due to its large steric interaction with both Cp and Nb–R groups, 2-butyne was found to react readily with $Cp_2NbH(CH_2{=}CH_2)$ to afford an ethylniobocene complex, $Cp_2NbCH_2CH_3(CH_3C{\equiv}CCH_3)$ (7), as the sole product in 70–80% yield under mild conditions (60 °C) in toluene (eq 3). Similarly, propene and styrene complexes, $Cp_2NbH(RCH{=}CH_2)$ where R = CH_3, C_6H_5, react with 2-butyne to yield $Cp_2NbCH_2CH_2CH_3(CH_3C{\equiv}CCH_3)$ (8) and $Cp_2NbCH_2CH_2C_6H_5(CH_3C{\equiv}CCH_3)$ (9), respectively. Their ^1H NMR and EIMS spectral data support this formulation. An attempt to synthesize the corresponding alkyl(alkyne) complexes by an alternative route starting from Cp_2NbCl(alkyne) and Grignard reagent was unsuccessful because it forms a complex mixture.



(3)

7: M = Nb, R = H, R′ = CH_3
8: M = Nb, R = CH_3, R′ = CH_3
9: M = Nb, R = C_6H_5, R′ = CH_3
10: M = Ta, R = H, R′ = CH_3

---

(8) Wilson, R. D.; Koetzle, T. F.; Hart, D. W.; Kvick, A.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1775.

(9) Cartic, M. D.; Real, J. *Organometallics* **1985**, *4*, 940.

(10) Hartung, J. B., Jr.; Pedersen, S. F. *Organometallics* **1990**, *9*, 1414.

(11) Cotton, F. A.; Roth, W. J. *Inorg. Chim. Acta* **1984**, *85*, 17.

(12) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387.

(13) Bianconi, P. A.; Vrtis, R. N.; Rao, C. P.; Williams, I. D.; Engeler, M. P.; Lippard, S. L. *Organometallics* **1987**, *6*, 1968.

(14) (a) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410. (b) Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 5008.

(15) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 941.

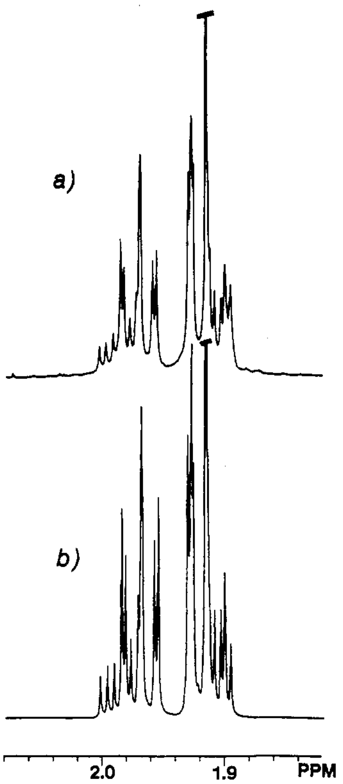


Figure 4. (a) ^1H NMR spectrum (500 MHz) of the ethyl group with an α-agostic bond in $Cp_2NbCH_2CH_3(CH_3C{\equiv}CCH_3)$ (7). (b) Simulation spectrum.

Especially noteworthy is the unique ^1H NMR spectral pattern of the ethyl group in 7, as illustrated in Figure 4a, while the Nb–ethyl group in $Cp_2NbCH_2CH_3(CH_3C{\equiv}CH)$ shows a normal A_2B_3 pattern (J_{AB} = 7.65 Hz). Computer simulation of the 500-MHz ^1H NMR spectrum of 6 (Figure 4b) reveals an abnormal ABX_3 pattern for the ethyl group, indicating the presence of an unusual agostic interaction between an α-hydrogen of the ethyl and the Nb center: J_{AB} = 27.15, J_{AX} = 7.47, J_{BX} = 7.84 Hz. The ^{13}C NMR spectrum of the CH_2 group shows a slight difference between the two $^1J(^{13}C-^1H)$ values (135 and 140 Hz).

The mode of reaction between $Cp_2TaH(CH_2{=}CH_2)$[4] and 2-butyne is essentially the same as that described for the niobocene derivatives, as revealed by NMR analysis. The isolated yellow sample of $Cp_2TaCH_2CH_3(CH_3C{\equiv}CCH_3)$ (10) however shows no agostic interaction in solution presumably due to a larger ionic radius of the metal.

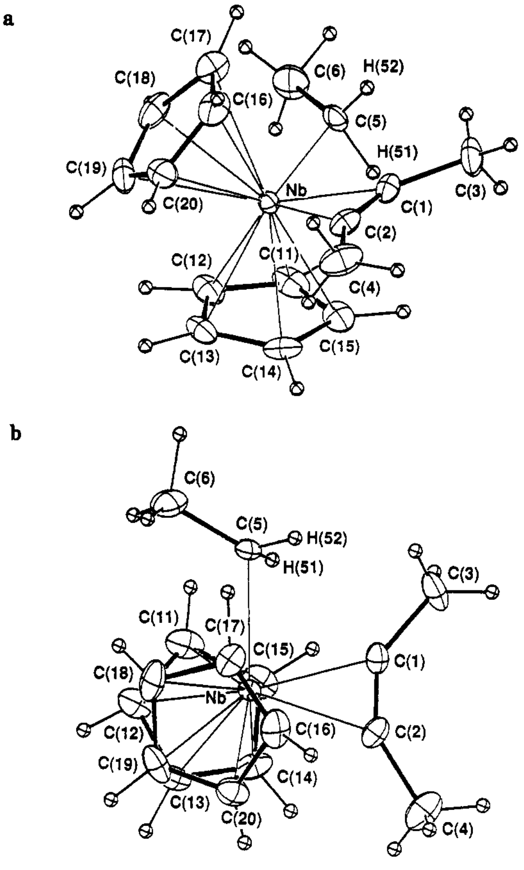


Figure 5. ORTEP drawings of $Cp_2NbCH_2CH_3(CH_3C{\equiv}CCH_3)$ (7): (a) side view; (b) top view.

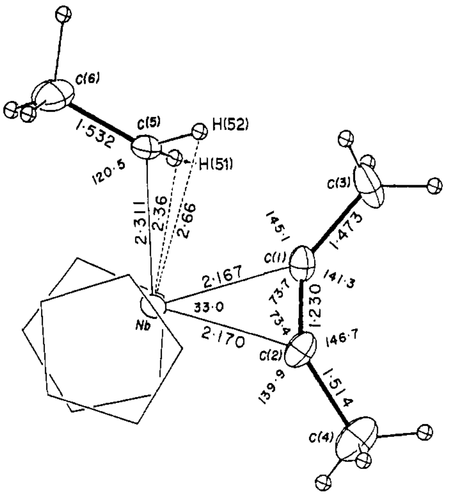


Figure 6. Important structural parameters for the α-agostic interaction within the $NbCH_2CH_3$ part in 7.

(b) Molecular Structure of $(C_5H_5)_2NbCH_2CH_3(CH_3C{\equiv}CCH_3)$ (7). The X-ray structural analysis of 7 clearly confirmed close approach of an α-hydrogen of the Et group to the metal. Figure 5 shows an ORTEP drawing of the molecule with the atom-labeling scheme, and Figure 6 shows important structural parameters for 7. Crystallographic and experimental data are collected in Table III, and important bond distances and angles, in Table VII. Atomic coordinates are shown in Table VIII. The most striking feature of this molecule lies in unique Nb–CH_2 interaction, which resulted in the distorted geometry of the sp^3 C(5) center; i.e. Nb–C(5)–C(6), Nb–C(5)–H(51), Nb–C(5)–H(52), C(6)–C(5)–H(51), and H(51)–C(5)–H(52) angles are 120.5, 79, 103, 123, and 100°, respectively. This abnormal geometry suggests the presence of an α-agostic interaction between H(51) and Nb. The Nb–H(51) bond (2.36 Å) is indeed significantly shorter than the nonbonded Nb–H(52) (2.66 Å). The Nb, C(1), C(2), and C(5) atoms form a good plane within 0.08 Å, from which H(51) deviates 0.93 Å toward the opposite side of C(6). The observed M–C–H(α) angle (79°) compares closely with that (70°) of the well-known α-agostic methyl complex, $TiCl_3Me(dmpe)$.[21,16b] This is the first example of an α-agostic ethyl complex, although several β-agostic ethyl complexes have already been reported, e.g. $TiCl_3Et(dmpe)$,[16] $[Co(C_5Me_5)Et(\eta^2\text{-}C_2H_4)]^+$,[17] $Sc(C_5Me_5)_2Et$,[18] and

---

[16] (a) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 802. (b) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K.; Shultz, A. J.; Williams, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629.

[17] Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117.

[18] Thompson, M. E.; Baxter, S. M.; Ray Bulls, A.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

Table VII. Selected Bond Distances (Å) and Bond Angles (deg) for $Cp_2Nb(CH_2CH_3)(CH_3C{\equiv}CCH_3)$ (7) with Estimated Standard Deviations in Parentheses

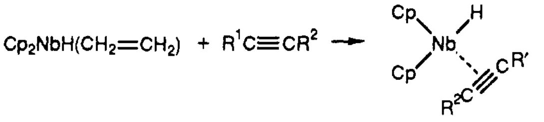
(a) Bond Distances			
Nb–C(1)	2.167 (11)	Nb–C(2)	2.170 (13)
Nb–C(5)	2.311 (11)	Nb–C(11)	2.472 (15)
Nb–C(12)	2.446 (14)	Nb–C(13)	2.432 (16)
Nb–C(14)	2.425 (14)	Nb–C(15)	2.436 (14)
Nb–C(16)	2.463 (16)	Nb–C(17)	2.469 (14)
Nb–C(18)	2.440 (18)	Nb–C(19)	2.460 (14)
Nb–C(20)	2.461 (14)	C(1)–C(2)	1.230 (17)
C(1)–C(3)	1.47 (2)	C(2)–C(4)	1.51 (3)
C(5)–C(6)	1.53 (2)	C(11)–C(12)	1.41 (2)
C(11)–C(15)	1.42 (2)	C(12)–C(13)	1.39 (2)
C(13)–C(14)	1.44 (2)	C(14)–C(15)	1.44 (2)
C(16)–C(17)	1.34 (2)	C(16)–C(20)	1.38 (2)
C(17)–C(18)	1.45 (2)	C(18)–C(19)	1.42 (2)
C(19)–C(20)	1.37 (2)	Nb–CCP(1)	2.122
Nb–CCP(2)	2.152	Nb–C(Cp)(av)	2.450 (15)
Nb–H(51)	2.36 (13)	Nb–H(52)	2.66 (10)
C(5)–H(51)	1.09 (13)	C(5)–H(52)	0.90 (10)
(b) Bond Angles			
C(1)–Nb–C(2)	33.0 (4)	C(17)–C(16)–C(20)	111.8 (14)
Nb–C(1)–C(2)	73.7 (8)	C(16)–C(17)–C(18)	106.1 (13)
Nb–C(2)–C(1)	73.4 (8)	C(17)–C(18)–C(19)	106.4 (14)
Nb–C(1)–C(3)	145.1 (9)	C(18)–C(19)–C(20)	107.7 (13)
Nb–C(2)–C(4)	139.9 (11)	C(16)–C(20)–C(19)	108.0 (13)
C(2)–C(1)–C(3)	141.3 (12)	CCP(1)–Nb–CCP(2)	131.4
C(1)–C(2)–C(4)	146.7 (14)	Nb–C(5)–H(51)	79 (7)
Nb–C(5)–C(6)	120.5 (10)	Nb–C(5)–H(52)	103 (6)
C(12)–C(11)–C(15)	108.2 (13)	H(51)–C(5)–H(52)	100 (9)
C(11)–C(12)–C(13)	109.8 (13)	C(6)–C(5)–H(51)	123 (7)
C(12)–C(13)–C(14)	107.7 (14)	C(6)–C(5)–H(52)	122 (6)
C(13)–C(14)–C(15)	107.4 (13)	CCP(1)–Nb–CCP(2)	131.4
C(11)–C(15)–C(14)	106.9 (12)		

$Co(C_5H_5)Et(PR_3)$ (R = Me, OME).[19] In general, both α- and β-alkyl agostic complexes exhibit an electronically deficient structure and α-agostic complexes are limited to methyl or bulky alkyl complexes such as $TiCl_3Me(dmpe)$,[20,16b] $Ti(C_5Me_5)(CH_2Ph)_3$,[21] $Zr(CH_2SiMe_3)_4(dmpe)$,[22] and $Th(C_5Me_5)(CH_2CMe_3)_2$[23] whose M–C–H(α) angles are in the range 70–94°. The present molecule however exhibits formally 18e structure in conflict with the reported complexes. Hence a weak α-agostic interaction is expected for this molecule. In fact its Nb–C(5)–C(6) angle (120.5°) and the Nb–C(5) bond distance (2.311 Å) are deviated only a little from those (118.7° and 2.316 Å) reported for a nonagostic complex, $Nb(C_5H_5)_2Et(CH_2{=}CH_2)$.[4b] Therefore the observed α-agostic interaction is estimated to arise from severe steric congestion around the metal, which causes weakening of the metal–alkyne bond and/or electronic shift of Cp ligand from η^5- into η^3-coordination. Indeed, slightly longer Nb–C(1) and Nb–C(2) distances (2.167 and 2.170 Å) as compared with conventional Nb–alkyne bonds and expansion of C(3)–C(1)–C(2) and C(4)–C(2)–C(1) angles (141.3 and 146.7°) are observed for 7 in support of the above prediction, although exact η^3-coordination could not be detected crystallographically.

(c) Formation of Hydride–Alkyne Complexes. Diphenylacetylene and 1-phenyl-1-propene differ markedly from 2-butyne in their mode of reactions with $Cp_2NbH(CH_2{=}CH_2)$. Ethylene–alkyne ligand exchange predominated in these cases as a result of stronger π-acidity of these alkynes. The ^1H NMR spectrum of the resulting $Cp_2NbH(C_6H_5C{\equiv}CC_6H_5)$ (11) is consistent with that of the hydride–alkyne complex synthesized from Cp_2NbH_3 and diphenylacetylene.[24] Similarly, 1-phenyl-1-propyne reacts with the ethylene complex to give a hydridoniobocene complex, $Cp_2NbH(CH_3C{\equiv}CC_6H_5)$ (12), under mild conditions (60 °C for 6 h), as identified by ^1H NMR analysis (eq 4). The corresponding tantalum complexes, $(C_5H_4Me)_2TaH(RC{\equiv}CR')$ R = R' = C_3H_7; R = CH_3, R' = *t*-Bu), have already been synthesized from $(C_5H_4Me)_2TaH_3$ and alkynes.

Table VIII. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors for Non-Hydrogen Atoms in $Cp_2Nb(CH_2CH_3)(CH_3C{\equiv}CCH_3)$ (7) with Estimated Standard Deviations in Parentheses

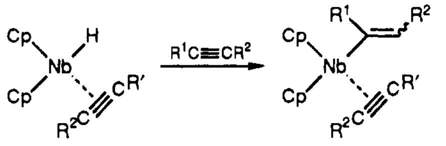
atom	*x*	*y*	*z*	B_{eq}
Nb	0.09064 (5)	0.29836 (5)	–0.29127 (8)	2.59
C(1)	0.1292 (7)	0.1801 (7)	–0.453 (2)	3.7
C(2)	0.1614 (7)	0.1628 (7)	–0.304 (2)	4.0
C(3)	0.124 (2)	0.140 (2)	–0.631 (3)	6.1
C(4)	0.215 (2)	0.094 (2)	–0.186 (3)	6.9
C(5)	0.054 (1)	0.3480 (7)	–0.574 (2)	3.9
C(6)	0.020 (2)	0.448 (2)	–0.607 (2)	6.8
C(11)	–0.0996 (7)	0.313 (2)	–0.307 (2)	5.6
C(12)	–0.0662 (8)	0.360 (1)	–0.155 (2)	5.0
C(13)	–0.0237 (8)	0.298 (2)	–0.037 (2)	4.5
C(14)	–0.0286 (7)	0.208 (1)	–0.115 (2)	4.9
C(15)	–0.0750 (7)	0.218 (1)	–0.287 (2)	5.1
C(16)	0.2768 (8)	0.331 (1)	–0.262 (3)	5.5
C(17)	0.239 (1)	0.398 (1)	–0.365 (2)	5.1
C(18)	0.168 (2)	0.4507 (8)	–0.256 (3)	5.9
C(19)	0.170 (1)	0.409 (1)	–0.087 (2)	5.4
C(20)	0.236 (1)	0.335 (1)	–0.095 (2)	4.8



(4)

11: $R^1 = R^2 = C_6H_5$
12: $R^1 = CH_3$, $R^2 = C_6H_5$

Of significant importance is the conversion of this complex into an alkenyl–alkyne complex, $Cp_2NbC(CH_3){=}CHC_6H_5(CH_3C{\equiv}CC_6H_5)$, under special conditions in the presence of 2–5 equiv of alkynes at an elevated temperature (120 °C), as a result of hydrometalation (eq 5).



(5)

$R^1, R^2 = Me_3Si$, H or CH_3, C_6H_5

$Cp_2NbH[(CH_3)_3SiC{\equiv}CH]$ can conduct similar addition reaction toward $(CH_3)_3SiC{\equiv}CH$. This type of hydride migration (intermolecular addition) has recently been found for $Cp_2NbH(RC{\equiv}CR)/(R'C{\equiv}CR')$ (R = Me, Ph, $SiMe_3$; R' = MeO_2C) or Cp_2NbH_3/alkyne reaction systems.[25] Although $NbCl_5$ and $TaCl_5$ are known to catalyze the alkyne polymerization to yield high molecular weight linear polyalkynes,[26] no polymerization initiated by re-

---

(19) (a) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443. (b) Crackness, R. G.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1005.

(20) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1410.

(21) Mena, M.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1118.

(22) Cayias, J. Z.; Babaian, E. A.; Hrncir, D. C.; Bott, S. G.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1986**, 2743.

(23) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Kay Fair, C.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40.

(24) (a) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (b) McGrady, N. D.; McDade, C.; Bercaw, J. E. In *Organometallic Compounds: Synthesis, Structure and Theory*; Shapiro, B. L., Ed.; Texas A & M University Press: College Station, TX, 1983; p 46.

(25) (a) Herberich, G. E.; Hessner, B.; Mayer, H. *J. Organomet. Chem.* **1986**, *314*, 123. (b) Herberich, G. E.; Mayer, H. *Organometallics* **1990**, *9*, 2655. (c) Herberich, G. E.; Hoeveler, U. E. M.; Savvopoulos, I. *J. Organomet. Chem.* **1990**, *399*, 35.

(26) (a) Cotton, F. A.; Hall, W. T.; Cann, K. J.; Karol, F. J. *Macromolecules* **1981**, *14*, 233. (b) Masuda, T.; Niki, A.; Osobe, E.; Higashimura, T. *Macromolecules* **1985**, *18*, 311.

acting **6** or **1–5** with excess $(CH_3)_3SiC{\equiv}CH$ even at 120–140 °C for 20 h in toluene. The observed catalytic inactivity of $Cp_2Nb[CH_2{=}CHSi(CH_3)_3][CH{\equiv}CSi(CH_3)_3]$ as well as Cp_2MH(alkyne) and Cp_2MR(alkyne) (M = Nb, Ta) may be responsible for their electronically sufficient 18e structure together with their relatively weak Lewis acidity.

Nucleophilic Properties of Alkyne Complexes. In order to understand the chemical properties of the resulting alkyl–alkyne and hydrido–alkyne complexes, the reactions of CO, CO_2, $P(CH_3)_3$, pyridine, acetone, and propanal with $Cp_2NbCH_2CH_3(CH_3C{\equiv}CH)$ (**1**), $Cp_2NbCH_2CH_3(CH_3C{\equiv}CCH_3)$ (**7**), and Cp_2NbH(*t*-BuC≡CH) (**5**) were explored at 60–100 °C for 5 h. If their alkyl, hydride, or alkyne group exhibits sufficient nucleophilic property, a reaction should take place to give insertion products including a $Cp_2NbCR{=}CRCH_2CH_3$(donor) or $Cp_2NbCR{=}CHR$(donor) type complex, which is available from the reaction of $Cp_2NbH(CO)$ with alkynes bearing an electron-withdrawing CF_3 or CN group.[27] In the case of $Cp_2Ti(PhC{\equiv}CPh)$, a ketone is known to react readily to give the insertion product.[28] However, no coordination or no addition occurred in all of the present reactions (only starting materials were recovered unchanged). These results indicate the presence of very poor nucleophilic properties for the present complexes presumably due to their 18e structure. In contrast, low-valent $NbCl_n$(alkyne)[10,29] and $TaCl_n$(alkyne)[30] complexes have recently been reported to react readily with several carbonyl compounds.

Experimental Section

All reactions and other manipulations were performed under argon by using a high-vacuum technique. Solvents were dried over Na/K alloy and thoroughly degassed and distilled before use. Pure Cp_2NbH(alkene) and Cp_2TaH(alkene) were obtained according to the known method.[3] ^1H NMR spectra were recorded on a JEOL GX-500 or a JEOL GX-270 spectrometer and analyzed with a Varian spin simulation program. ^{13}C NMR were run on a JEOL GX-270 spectrometer at 67.5 MHz. The mass spectra were recorded on a JEOL DX-300 spectrometer at 40–70 eV.

Preparation of $Cp_2NbC_2H_5(CH_3C{\equiv}CH)$ (1). A benzene solution (10 mL) of propyne (0.3 mL, 6 mmol) was added to $Cp_2NbH(C_2H_4)$ (0.63 g, 2.5 mmol) dissolved in benzene (10 mL). The mixture was heated to 60 °C in a sealed Schlenk tube, kept there for 4 h, and then evaporated to dryness. The residue was extracted with hexane (20 mL). Then, the extract was filtered, concentrated, and cooled to −20 °C to induce the precipitation of $Cp_2NbC_2H_5(CH_3C{\equiv}CH)$ as yellow-green crystals. The typical yield is 72–76% (NMR yield, >95%), mp 133 °C. EIMS: *m/z* (species, relative intensity) 292 (M^+, 12), 252 ($M^+ - C_2H_4$, 11), 224 (Cp_2Nb^+ + 1, 100), 223 (Cp_2Nb^+, 61). Anal. Calcd for $C_{15}H_{19}Nb$: C, 61.65; H, 6.51; Nb, 31.83. Found: C, 61.35; H, 6.88; Nb, 31.6 (oxidation method).

Preparation of $Cp_2NbC_2H_5(RC{\equiv}CH)$ [R = CH_3CH_2 (2), C_6H_5 (3)]. To a benzene solution (10 mL) of $Cp_2NbH(C_2H_4)$ (0.63 g, 2.5 mmol) was added 1-butyne (0.5 mL, 6 mmol) or phenylacetylene (0.6 g, 6 mmol) in benzene. The mixture was heated to 60 °C, and the product was isolated as yellow-green crystals in essentially the same way as described for **1**. $Cp_2NbC_2H_5(C_2H_5C{\equiv}CH)$ (**2**): yield, 74%, mp 104 °C. EIMS: *m/z* (species, relative intensity) 306 (M^+, 7), 252 ($Cp_2NbC_2H_5^+$, 16), 224 (Cp_2NbH^+, 100), 223 (Cp_2Nb^+, 91). Anal. Calcd for $C_{16}H_{21}Nb$: C, 62.76; H, 6.86; Nb, 30.37. Found: C, 62.79; H, 7.05; Nb, 30.2. $Cp_2NbC_2H_5(C_6H_5C{\equiv}CH)$ (**3**): yield, 71%, mp 135 °C. EIMS: *m/z* (species, relative intensity) 354 (M^+, 17), 252 ($Cp_2NbC_2H_5^+$, 49), 224 (Cp_2NbH^+, 100). Anal. Calcd for $C_{20}H_{21}Nb$: C, 67.81; H, 5.93; Nb, 26.25. Found: C, 67.35; H, 6.13; Nb, 26.5 (oxidation method).

Preparation of $Cp_2TaC_2H_5(CH_3C{\equiv}CH)$ (4). A toluene solution (5 mL) of propyne (0.3 mL, 6 mmol) or 1-butyne (0.5 mL, 6 mmol) was added to $Cp_2TaH(C_2H_4)$ (0.85 g, 2.5 mmol) dissolved in toluene (10 mL). The mixture was shielded in a Schlenk tube, heated to 100 °C, and maintained there for 3 h. Then the solution was evaporated to dryness, and the residue was extracted into hexane (30 mL). Filtration and concentration of the extract followed by cooling to −20 °C caused the precipitation of yellow crystals. Recrystallization of the crude product from hexane gave $Cp_2TaC_2H_5(CH_3C{\equiv}CH)$ in 56% yield. $Cp_2TaC_2H_5(CH_3C{\equiv}CH)$ (**4**): mp 126 °C. EIMS: *m/z* (species, relative intensity) 380 (M^+, 10), 340 ($Cp_2TaCH_2CH_3^+$, 18), 312 (Cp_2TaH^+, 100), 311 (Cp_2Ta^+, 34). Anal. Calcd for $C_{15}H_{19}Ta$: C, 47.37; H, 5.00; Ta, 47.62. Found: C, 47.21; H, 5.08; Ta, 47.4 (oxidation method).

Preparation of $Cp_2NbH(RC{\equiv}CH)$ [R = *t*-Bu (5), $(CH_3)_3Si$ (6)]. To a benzene solution (20 mL) of Cp_2NbH(propene) (0.51 g, 2.0 mmol) was added 3,3-dimethyl-1-butyne (0.5 mL, 4.0 mmol) or (trimethylsilyl)acetylene (0.6 mL, 4 mmol). The mixture was allowed to warm to 60 °C with magnetic stirring, kept there for 3 h, and then evaporated to dryness. The resulting marine blue solid was extracted with hexane (30 mL). The extract was concentrated to 7–8 mL and then cooled to −20 °C to obtain yellow-green crystals of **5** or **6**. Cp_2NbH(*t*-BuC≡CH) (**5**): mp 150 °C. EIMS: *m/z* (species, relative intensity) 306 (M^+, 14.6), 224 (Cp_2NbH^+, 100). $Cp_2NbH[(CH_3)_3SiC{\equiv}CH]$ (**6**): mp 162 °C. EIMS: *m/z* (species, relative intensity) 322 (M^+), 224 (Cp_2NbH^+, 100).

Preparation of $Cp_2NbCH_2CH_2R(CH_3C{\equiv}CCH_3)$ [R = H (7), CH_3 (8), C_6H_5 (9)]. The ethylene, propene, and styrene complexes of Cp_2NbH (2 mmol, see ref 3 for preparation method) were allowed to react with 2-butyne (4 mmol) and isolated as crystals as described for **1–3**. $Cp_2NbC_2H_5(CH_3C{\equiv}CCH_3)$ (**7**): mp 157 °C. EIMS: *m/z* (species, relative intensity) 306 (M^+, 7), 252 ($Cp_2NbC_2H_5^+$, 31), 224 (Cp_2NbH^+, 100), 223 (Cp_2Nb^+, 95). Anal. Calcd for $C_{16}H_{21}Nb$: C, 62.76; H, 6.86; Nb, 30.45. Found: C, 62.55; H, 7.15; Nb, 30.3, $Cp_2NbC_3H_7(CH_3C{\equiv}CCH_3)$ (**8**): mp 78 °C. EIMS: *m/z* (species, relative intensity) 321 (M^+H, 0.8), 320 (M^+, 4.2), 266 ($Cp_2NbC_3H_7^+$, 17.7), 226 (Cp_2NbH^+, 100), 223 (Cp_2Nb, 73.6). $Cp_2NbCH_2CH_2C_6H_5(CH_3C{\equiv}CCH_3)$ (**9**) EIMS: *m/z* (species, relative intensity), 383 (M^+H, 0.7), 382 (M^+, 4.5), 328 ($Cp_2NbC_2H_4Ph^+$, 18.2), 224 (Cp_2NbH^+, 100), 223 (Cp_2Nb^+, 74.0).

Preparation of $Cp_2TaC_2H_5(CH_3C{\equiv}CCH_3)$ (10). A toluene solution (20 mL) of $Cp_2TaH(C_2H_4)$ (1.0 g, 3.0 mmol) and 2-butyne (6.0 mmol) was stirred at 100 °C for 4 h. After the usual workup, complex **10** was obtained as yellow crystals in 67% yield, mp 145 °C. EIMS: *m/z* (species, relative intensity) 394 (M^+, 32), 340 ($Cp_2TaC_2H_5^+$, 100), 312 (Cp_2TaH^+, 68), 311 (Cp_2Ta^+, 26). Anal. Calcd for $C_{16}H_{21}Ta$: C, 48.74; H, 5.33; Ta, 45.93. Found: C, 48.23, H, 5.17; Ta, 46.

Preparation of $Cp_2NbH(C_6H_5C{\equiv}CC_6H_5)$ (11). A benzene solution (20 mL) of Cp_2NbH(propene) (0.51 g, 2.0 mmol) was added to a solution of diphenylacetylene (0.45 g, 2.5 mmol) in benzene (5 mL) with magnetic stirring. The mixture was stirred for 4 h at 60 °C, and then the solvent was removed by flash distillation. The residue was extracted into hexane (30 mL). The extract was concentrated into 10 mL and cooled to −20 °C to obtain complex **11** as dark green crystals in 85% yield, mp 105 °C. EIMS: *m/z* (species, relative intensity) 403 (M^+, 100), 402 (M^+, 22), 223 (Cp_2Nb^+, 75). Anal. Calcd for $C_{24}H_{21}Nb$: C, 71.66; H, 5.23; Nb, 23.12. Found: C, 71.25; H, 5.33; Nb, 23.4.

Preparation of $Cp_2NbH(CH_3C{\equiv}CC_6H_5)$ (12). Cp_2NbH(ethylene) (0.63 g, 2.5 mmol) was allowed to react with methylphenylacetylene (0.4 g, 4 mmol) and the product was isolated in essentially the same manner as described for **11**. EIMS: *m/z* (species, relative intensity) 342 (M^+, 5), 226 ($M^+ - CH_3C_2C_6H_5$, 21), 224 (Cp_2NbH^+, 100), 223 (Cp_2Nb^+, 62). ^1H NMR (C_6D_6): δ 7.3–8.8 (C_6H_5, d), 4.82 (Cp, s), 2.65 (CH_3, s), −0.25 (Nb–H, s).

Reaction of $CpNbH(C_2H_4)$ with Excess $(CH_3)_3SiC{\equiv}CH$ and 1-Phenylpropyne. To a benzene solution (15 mL) of $Cp_2NbH(C_2H_4)$ (0.63 g, 2.5 mmol) was added methylphenyl-

---

[27] Amaudrut, J.; Leblanc, J.-C.; Moise, C.; Sala-Pala, J. *J. Organomet. Chem.* **1985**, *295*, 167.

[28] Shur, V. B.; Burlakov, V. V.; Yanovsky, A. I.; Petrovsky, P. V.; Struchkov, Yu. T.; Volpin, M. E. *J. Organomet. Chem.* **1985**, *297*, 51.

[29] (a) Williams, A. C.; Sheffels, P.; Sheehan, D.; Livinghouse, T. *Organometallics* **1989**, *8*, 1566. (b) Hartung, J. B., Jr.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 5468.

[30] (a) Takai, K.; Kataoka, Y.; Utimoto, K. *J. Org. Chem.* **1990**, *55*, 1707. (b) Strickler, J. R.; Bruck, M. A.; Vexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 266.

acetylene (0.6 g, 5 mmol) or (trimethylsilyl)acetylene (10 mL, 7 mmol). The mixture was heated to 70 °C and stirred there for 6 h. The solution was concentrated by evaporation, and hexane (10 mL) was added to induce the precipitation of the red-brown insertion product (35-41%), $Cp_2NbC(CH_3){=}CHPh(CH_3C{\equiv}CPh)$. EIMS: *m/z* (species, relative intensity) 456 (M^+, 0.5), 340 ($M^+ - C_2MePh$, 21), 224 (Cp_2NbH^+, 100), 223 (Cp_2Nb^+, 59). ^1H NMR (C_6D_6): δ 6.96 (CH=, d), 4.61 (Cp, s), 1.86, 1.94 (Me, s), 7.2-8.9 (C_6H_5, m). $Cp_2NbCH{=}CHSiMe_3(HC{\equiv}CSiMe_3)$. EIMS: *m/z* (species, relative intensity) 420 (M^+, 4), 322 ($M^+ - CHCSiMe_3$, 72), 224 (Cp_2NbH^+, 100), 223 (Cp_2Nb^+, 61). ^1H NMR (C_6D_6): δ 7.57 (CH≡, s), 4.73, 4.80 (CH=CH, d), 4.50 (Cp, s), 1.47, 1.49 ($SiMe_3$, s).

Reaction of Alkyne Complexes with CO, CO_2, $P(CH_3)_3$, and Carbonyl Compounds. Alkyne complexes 1 and 7 were used to examine their reactivity toward donor molecules. Gaseous CO and CO_2 (>20 mmol) were bubbled in a benzene solution (10 mL) of 1 and 7 (2.0 mmol) at 60 °C for 2 h, but no change was observed in their ^1H NMR spectra. A 1:2 mixture of 1 or 7 and $P(CH_3)_3$ or pyridine in toluene-d_8 sealed in a NMR tube was heated to 100 °C for 3 h. No spectral or color change was observed during this procedure. The complexes 1 and 7 were also inert to acetone and propanal (charged in a 1:3 ratio) even at 80 °C in toluene. Further heating to 120 °C resulted in the production of a complex mixture containing mesityl oxide derived from aldol type condensation of the carbonyl compound.

Structure Determination of 5-7. Single crystals of 5-7 sealed in a thin-walled glass capillary under argon were mounted on a Rigaku automated four-circle diffractometer. Relevant crystal and data statistics are summarized in Table III. The unit cell parameters at 20 °C were determined by a least-squares fit to 2θ values of 25 strong high-angle reflections. Each sample showed no significant intensity decay over the duration of data collection. The crystal structures of the above complexes were all solved by the heavy-atom method and refined by full-matrix least squares as implemented in the XRAY-76 system utilizing the observed reflections [$|F_o| > 3\sigma(F_o)$]. In the subsequent refinements, the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the amplitudes of observed and calculated structure factors, respectively. After the anisotropic refinement of non-hydrogen atoms for 5-7, all hydrogen atoms were located in the difference Fourier maps with the help of geometrical calculations and were refined isotropically.

Acknowledgment. We are indebted to a Grant-in-Aid for scientific research (No. 1490012) from the Ministry of Education, Science, and Culture, Japan.

Registry No. 1 (exo isomer), 136736-44-2; 1 (endo isomer), 136780-80-8; 2 (exo isomer), 136736-45-3; 2 (endo isomer), 136780-81-9; 3 (exo isomer), 136736-46-4; 3 (endo isomer), 136780-82-0; 4 (exo isomer), 136736-47-5; 4 (endo isomer), 136780-83-1; **5**, 136736-48-6; **6**, 136736-49-7; **7**, 136736-50-0; **8**, 136736-51-1; **9**, 136736-52-2; **10**, 136736-53-3; **11**, 77299-70-8; **12**, 136736-54-4; $Cp_2NbC(CH_3){=}CHPh(CH_3C{\equiv}CPh)$, 136736-55-5; $Cp_2NbCH{=}CHSiMe_3(HC{\equiv}CSiMe_3)$, 136736-56-6; $Cp_2NbH(C_2H_4)$, 11105-70-7; $Cp_2TaH(C_2H_4)$, 66786-38-7; Cp_2NbH(propene), 123620-30-4; Cp_2NbH(styrene), 123620-31-5.

Supplementary Material Available: Listings of additional bond lengths and angles, hydrogen atom parameters, and anisotropic thermal parameters for 5-7 (9 pages); tables of the observed and calculated structure factors (82 pages). Ordering information is given on any current masthead page.

Notes

Role of $[Cp^*Mo(\mu\text{-}S)]_2S_2CH_2$ in Dichloromethane Hydrogenolysis

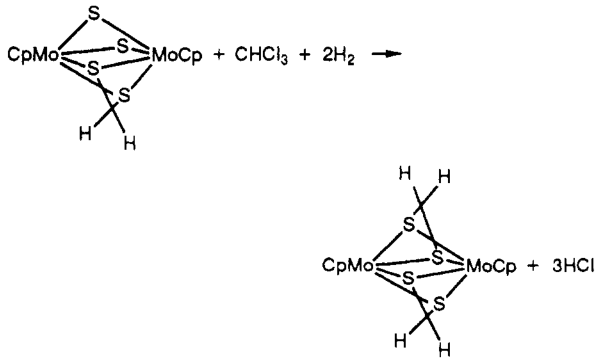
M. Maciejewski Farmer, R. C. Haltiwanger, F. Kvietok, and M. Rakowski DuBois*

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

Received March 13, 1991

Summary: The reaction of $(Cp^*MoS)_2S_2CH_2$ ($Cp^* = C_5Me_5$) with dichloromethane under 1-2 atm of H_2 at 50 °C led to the hydrogenolysis of dichloromethane and the formation of $(Cp^*MoS_2CH_2)_2$ (**1**). Complex **1** crystallized in space group $P\bar{1}$ with unit cell dimensions a = 7.992 (2) Å, b = 8.354 (3) Å, c = 10.624 (5) Å, α = 88.11 (3)°, β = 74.15 (3)°, γ = 62.83 (2)°, and V = 603.6 (4) Å^3. The X-ray diffraction study of **1** verified that the two Cp^*Mo units were symmetrically bridged by two η^2 methanedithiolate ligands. When $(Cp^*MoS)_2S_2CH_2$ was reacted with dichloromethane under nitrogen rather than hydrogen pressure, the cationic product $[(Cp^*Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2Cl)]Cl$ (**2**) was formed. Complex **2** reacted with hydrogen to form **1** and is, therefore, a likely intermediate in the dichloromethane hydrogenolysis.

Several years ago we reported that the dinuclear molybdenum(IV) complex $[CpMo(\mu\text{-}S)]_2S_2CH_2$ reacted slowly with chloroform under 1-3 atm of hydrogen to form $[CpMoS_2CH_2]_2$ and HCl as shown in eq 1.[1,2] In recent studies of the analogous (pentamethylcyclopentadienyl)molybdenum(IV) complex, $[Cp^*Mo(\mu\text{-}S)]_2S_2CH_2$, we observed that the bis(methanedithiolate) product was formed in good yield in reactions with dichloromethane under hydrogen. We report here the characterization of a probable intermediate in this unusual hydrogenolysis reaction and some novel reaction chemistry of these deriv-



(1)

---

[1] McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329.

[2] Weberg, R. T. Ph.D. Thesis, University of Colorado, Boulder, CO, 1986.

0276-7333/91/2310-4066$02.50/0