Table III. Summary of Retention Volumes in Toluene for the Ferrocene Oligomers[a]

oligomer	retentn vol (mL)
1:8 diferrocenylnaphthalene (1a)	18.36
2:2 oligomer (4a)	17.84
2:3 oligomer (3a)	16.72
3:3 oligomer (4b)	16.40
3:4 oligomer (3b)	14.15
4:5 oligomer (3c)	13.80

[a] 500- and 100-Å Ultrastyragel columns in series, using toluene at 1 mL/min.

As the solution began to reflux, 0.532 g of 1,8-diiodonaphthalene as a solution in 10 mL of THF was slowly dripped into the reaction over the course of 5 h.

When the addition was complete, the reaction was allowed to continue refluxing with periodic monitoring by gel permeation HPLC (500- and 100-Å Ultrastyragel columns linked in series, THF at 1.0 mL/min). After only 3 h the reaction had produced a molecular weight distribution typical of the 3:4 and 4:5 range of oligomers. Typically, the 1,8 diferrocenylnaphthalene dominated these reactions, but here it was seen in only small amounts. At this point, black particles in the solution suggested decomposition of the Pd(0) catalyst and another 5 mol was added.

After 12 h a large amount of orange precipitate had formed. Its lower solubility in THF made characterization of the product distribution by HPLC unreliable in this solvent. The reaction was run for a total of 36 h at reflux and then worked up as described for the other syntheses.

Attempts to separate the oligomers by column chromatography gave poor resolution due to the wide range of molecular weights and the low solubility of the higher oligomers in solvent combinations which resolve the lower molecular weight species. The product distribution was therefore fractionated in the following series of extractions. In order to compare the fractions to the characterized oligomers, the gel permeation chromatography was performed in toluene which readily solubilized all of the fractions

(500- and 100-Å Ultrastyragel columns in series, toluene at 1.0 mL/min). A table of retention volumes in toluene for the known oligomers appears in Table III for comparison.

Extracting the crude product with diethyl ether gave the first fraction which contained all of the lower molecular weight oligomers (1,8-diferrocenylnaphthalene through the 3:4 oligomer), as confirmed by the distribution of the retention volumes in the HPLC. This material weighed 77 mg, or approximately 17% of theoretical product yield.

The remaining solid was then washed with benzene to give the second fraction (56 mg). This fraction contained a small amount of oligomer in the 3:4 and 4:5 range. Molecular weight determination of this fraction gave $M_w = 1600$ and $M_n = 940$.

The third and final fraction was collected by Soxhlet extraction of the remaining solids in benzene to give 55 mg of product as a dark red powder. A molecular weight determination carried out on this material gave $M_w = 6000$ and $M_n = 3600$.

Registry No. 1a, 94161-70-3; 1b, 112461-16-2; 3a (M = F), 113792-95-3; 3a (M = Ru), 113792-98-6; 3b (M = Fe), 113792-96-4; 3b (M = Ru), 113793-00-3; 3c (M = Fe), 113792-97-5; 3c (M = Ru), 113793-01-4; 3d (M = Ru), 113830-86-7; 56 (M = Ru), 113792-99-7; (PPh3)2PdCl2, 13965-03-2; ferrocene, 102-54-5; dilithioferrocene, 33272-09-2; ferrocenylzinc chloride, 94161-76-9; diiodonaphthalene, 1730-04-7; ruthenocene, 1287-13-4; dilithioruthenocene, 60898-13-7; ruthenocenylzinc chloride, 113793-02-5; α-naphthylferrocene, 94161-77-0.

Synthesis, X-ray Structure, and Nucleophilic Properties of Mixed Bis(diene)tantalum Complexes Ta(η^5-C5R5)(η^4-C4H6)(η^4-C6H10)

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Mixed bis(diene) complexes of tantalum have been synthesized in a stepwise manner either by reaction of TaCl2L(butadiene) of supine (exo) geometry (L = C5Me5, C5H5) with (2,3-dimethyl-2-butene-1,4-diyl)magnesium or by reaction of TaCl2L(2,3-dimethylbutadiene) of supine geometry with (2-butene-1,4-diyl)magnesium. In the former reaction, the initial geometry of the coordinated diene changes from supine to prone (endo) while, in the latter reaction, the supine geometry of the 2,3-dimethylbutadiene ligand was maintained. Ta(C5Me5)(prone-butadiene)(supine-2,3-dimethylbutadiene) (6a) thus obtained crystallizes in space group *Pbca* with a = 14.173 (3) Å, b = 16.524 (3) Å, c = 15.344 (3) Å, and Z = 8. The reaction of 6a with 2,4-dimethyl-3-pentanone revealed the higher reactivity of the butadiene unit lying prone compared with dimethylbutadiene lying supine.

Introduction

Bis(diene) complexes of group 5A early transition metals (Ta,[1] Nb[2]) of the type LM(diene)2 (L = C5H5, C5Me5) were

recently found to exhibit a novel supine–prone (exo–endo) structure (1),[3] where the metal–diene moieties consist of
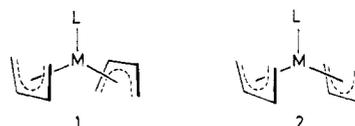
(1) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410.

the bent metallacyclo-3-pentene framework. By contrast, all the bis(diene) complexes of middle and late transition metals with the formula LM(diene)$_2$ (M = Fe,[4] Rh,[5] Ir,[6] Mn;[7] L = Cp, Cl, CO) are known to always prefer the supine–supine (exo–exo) structure **2**, where dienes are bound to the metal as η^4-diene ligands. The unique diene orientation observed for bis(diene)tantalum complexes prompted us to further synthesize mixed bis(diene) complexes where the dienes are coordinated to the metal in two different ways. The chemistry of this type of complexes should provide fundamental information about the essential factor in determining the final mode of diene orientation (supine, prone) and is useful to elucidate the subtle differences in M–C bonding and chemical reactivity existing between the supine and prone dienes. Similar mixed bis(diene) complexes have recently been synthesized in the case of Fe(diene)$_2$·PR$_3$.[8]

Results and Discussion

Preparation of (Butadiene)(2,3-dimethyl-butadiene)tantalum Complexes. As a typical example of the stepwise synthesis pursuing mixed bis(diene) complexes, the reaction of 16e Ta(C$_5$Me$_5$)Cl$_2$(*s-cis*-butadiene) (**3a**) of supine geometry with 1 equiv of (2,3-dimethyl-2-butene-1,4-diyl)magnesium (**4a**) was examined (eq 1).
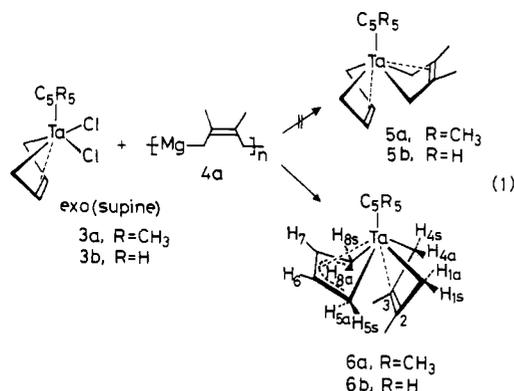

This reaction sequence gave the desired monomeric 18-electron mixed bis(diene) complex Ta(C$_5$Me$_5$)(*s-cis*-butadiene)(*s-cis*-2,3-dimethylbutadiene) in good yield (70%). If the π-interaction between the metal and the olefinic C(2)–C(3) bond in **3a** is strong enough, the formation of the bis(diene) complexes should proceed keeping the supine geometry of the butadiene ligand to give **5a**. However, a geometrical change in **6a** is expected if the severe steric repulsion between C$_5$Me$_5$ and 2,3-dimethylbutadiene ligands in **5a** causes skeletal rearrangement. The X-ray analysis of the resultant complex clearly showed its geometry to be **6a** (discussed later). Thus it is obvious that the orientation of the *s-cis*-butadiene changes from supine

to prone during the reaction. A similar geometrical change (from supine–supine to supine–prone or prone–prone) is reported for the photoinduced rearrangement of ZrCp(η^4-butadiene)(η^3-allyl).[9]
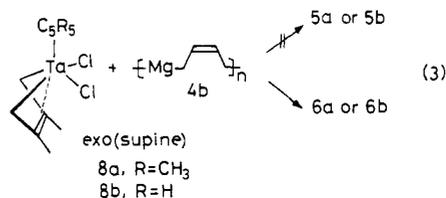
For the above geometrical change, two reaction pathways are conceivable. One is the geometrical change after the formation of the mixed bis(diene) complex, and the other is the skeletal rearrangement before the formation of the bis(diene) complex. The thermodynamic rearrangement after the formation of bis(diene) complexes may be ruled out since not only the present complex **6a** but also the related homo bis(diene)tantalum complexes Ta(C$_5$H$_5$)-(butadiene)$_2$ and Ta(C$_5$H$_5$)(2,3-dimethylbutadiene)$_2$ that we reported earlier[1] do not show any appreciable change in their NMR spectra on heating in *o*-xylene up to the point where decomposition occurs (ca. 110 °C). Absence of the exothermic rearrangement is further evidenced by the variable-temperature NMR studies of a deuterium-labeled complex, TaCp(supine-2,3-dimethylbutadiene)-(prone-2,3-dimethylbutadiene-d_4), prepared by reacting TaCl$_2$Cp(2,3-dimethylbutadiene) with [MgCD$_2$C(CH$_3$)C-(CH$_3$)CD$_2$]. No rearrangement was observed in the NMR spectra at temperatures of 20–100 °C. If the rearrangement occurs, it should provide a mixture of geometrical isomers that can be readily assigned on the basis of the chemical shifts and the relative intensity ratio of diene resonances.

Therefore, we can estimate that the formation of bis-(diene) complexes most likely proceeds through a 16e transition state, **7** (eq 2). In this step, the 1,4-η^2-bonded
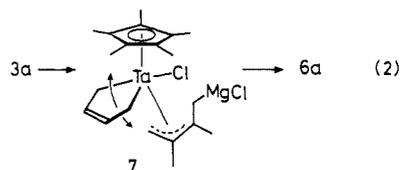
butadiene unit can be flipped upward (the rapid transformation of **7** into **6a** precludes our efforts in isolating species **7**). As a consequence, we can presume that the steric repulsion between Cp* (C$_5$Me$_5$) and the 2,3-dimethylbutenyl ligand in **7** is a significant factor in determining the final mode of diene orientations.

To verify this idea, we have examined the successive incorporation of the two dienes in the reversed order. The reaction of TaCl$_2$(C$_5$Me$_5$)(2,3-dimethylbutadiene) (**8a**) (supine geometry) with (2-butene-1,4-diyl)magnesium (**4b**) proceeds to give Ta(C$_5$Me$_5$)(*s-cis*-butadiene)(*s-cis*-2,3-dimethylbutadiene) (eq 3) whose NMR and X-ray parame-

ters are the same as those for **6a** obtained from **3a** and (2,3-dimethyl-2-butene-1,4-diyl)magnesium (see eq 1). This means that the initial supine geometry of 2,3-dimethylbutadiene is conserved in this case and the less bulky butadiene ligand is incorporated into the prone position.

To gain further insight into the steric effect of alkyl substituents on the mode of diene orientation, the stoi-

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(3) The terms prone and supine were used to describe the orientation of the coordinated dienes. The conventional naming, exo and endo, does not seem suitable for the present unique stereochemistry.

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Table I. ¹H NMR Parameters for the Mixed Bis(diene)tantalum and Related Homo Bis(diene)tantalum Complexes[a]

complexes	L	diene (supine)[c] diene (prone)	chem shifts, ppm			coupling consts, Hz			
			ν_{1s}, ν_{4s} ν_{5s}, ν_{8s}	ν_{1a}, ν_{4a} ν_{5a}, ν_{8a}	ν_2, ν_3 ν_6, ν_7	$J_{1s,1a(4s,4a)}$ $J_{5a,5s(8a,8s)}$	$J_{1s,2(3,4s)}$ $J_{5s,6(7,8s)}$	$J_{1a,2(3,4a)}$ $J_{5a,2(7,8a)}$	$J_{2,3}$ $J_{6,7}$
6a	C₅Me₅	C₆H₁₀	1.70	−0.08		−7.5			
		C₄H₆	1.58	0.04	4.34	−5.8	8.5	11.0	8.5
10a	C₅Me₅	C₅H₈	1.29, 2.06	0.88, 0.16	1.93 (Me), 4.62	−7.4	8.0	6.2	
		C₄H₆	1.88	−0.13	4.28	−5.8	8.5	10.8	8.3
11a	C₅Me₅	C₆H₁₀	1.53	−0.10		−8.2			
		C₅H₈	1.29, 1.34	0.08, 0.13	2.06 (Me), 4.28	−7.5	8.2	6.5	
6b	C₅H₅	C₆H₁₀	2.10	0.35		−7.2			
		C₄H₆	1.89	−0.23	4.53	−6.0	8.0	11.0	8.2
10b	C₅H₅	C₅H₈	1.28, 2.45	0.50, 0.22	1.77 (Me), 4.47	−7.5	8.1	6.2	
		C₄H₆	1.70	0.04	4.58	−6.0	9.0	11.0	8.1
11b	C₅H₅	C₆H₁₀	2.02	0.30		−8.0			
		C₅H₈	1.75, 1.69	−0.14, −0.26	1.79 (Me), 4.26	−7.5	7.1	6.0	
12[b]	C₅H₅	C₄H₆	2.49	0.30	4.93	−6.2	8.2	6.5	7.0
		C₄H₆	1.84	0.45	4.40	−5.8	9.5	11.0	8.4
13[b]	C₅H₅	C₆H₁₀	1.78	0.05		−8.0			
		C₆H₁₀	1.45	−0.28		−8.0			

[a] Spectra (500 MHz) measured in C₆D₆ at 30 °C were analyzed by computer simulation. Chemical shifts for Cp and Cp* are 4.83–5.04 and 1.52–1.62 ppm, respectively. Numbering system is given in eq 1 and 4. [b] See ref 1. [c] C₄H₆ = butadiene; C₅H₈ = isoprene; C₆H₁₀ = 2,3-dimethylbutadiene.

chiometric reactions of TaCp*Cl₂(isoprene) (9a) with (2-butene-1,4-diyl)magnesium and (2,3-dimethyl-2-butene-1,4-diyl)magnesium were also examined. The former reaction gives rise to only 10a without geometrical change while the latter gave 11a selectively with geometrical change. Thus, the subtle difference in the steric bulk of the diene ligands effectively reflects the final mode of diene orientations.

The substitution of C₅Me₅ group with the less bulky C₅H₅ ligand also leads to the same result. For example, the 1:1 reaction of supine TaCl₂(C₅H₅)(butadiene) (3b) (its structure has been-well established by X-ray analysis)[1] with (2,3-dimethyl-2-butene-1,4-diyl)magnesium yielded Ta(C₅H₅)(butadiene)(2,3-dimethylbutadiene) (6b) with geometrical change, while the reaction of TaCl₂(C₅H₅)-(2,3-dimethylbutadiene) (8b) of supine geometry with nonsubstituted (2-butene-1,4-diyl)magnesium (4b) again produced 6b without any change in the 2,3-dimethylbutadiene orientation as revealed by the NMR studies (eq 1 and 3). In a similar fashion, TaCl₂(C₅H₅)(isoprene) (9b) reacts with 4a to give 100% pure 11b ligated by prone-isoprene while it gives 10b ligated by supine-isoprene by a major reaction (80%) with magnesium–butadiene adduct (4b). Heating these complexes to 100 °C in toluene did not induce the interconversion between them, indicating that the relative ratio (10b/11b) is determined kinetically,

(4)
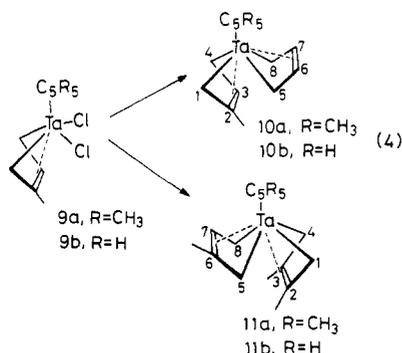
not thermodynamically. In summarizing the above results, we can conclude that the bulk of auxiliary ligands (C₅H₅, C₅Me₅) has no discernible effect in determining the mode of diene orientation while the steric bulk of the alkyl substituents on the diene ligand plays a vital role in determining the whole geometry; i.e., the bulky diene ligand
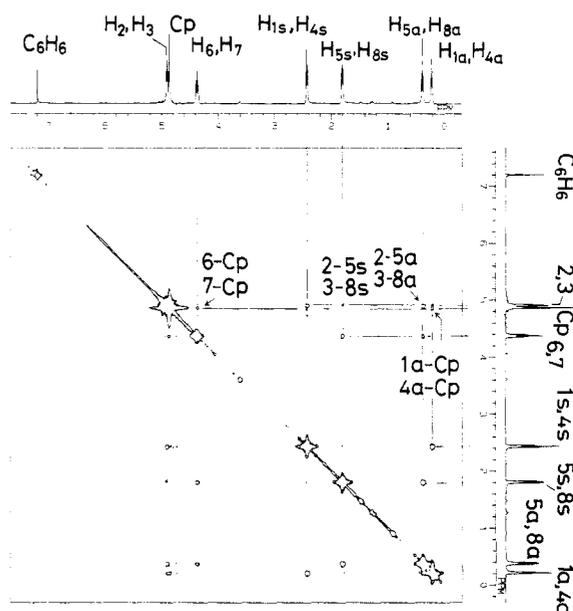

Figure 1. The absorption phase 2D NOE spectrum (500 MHz) of TaCp(butadiene)₂ (12) in C₆D₆ at 35 °C obtained by using $(\pi/2)-t_1-(\pi/2)-\tau_m-(\pi/2)-t_2$ pulse sequence. A total of 2048K spectra were aquired with a t_1 increment of 0.25 ms to give a sweep width in both dimensions of 5 KHz. The data matrix was zero filled to 256 × 2K, and a 2-Hz line broadening was applied prior to Fourier transformation. The $\pi/2$ pulse width was 5.8 μs, τ_m was 1500 ms, and the delay between acquisitions was 2 s. The numbering system for each signals follows that given in eq 1.

always occupies the supine position.

¹H and ¹³C Nuclear Magnetic Resonance Studies. The ¹H NMR parameters of the prone butadiene unit in 6b (obtained by computer simulation) are consistent with those of Ta(C₅H₅)(butadiene)₂ (12) reported previously and are summarized in Table I. The assignment of supine and prone dienes in 12 was established on the basis of the 2D-NOE NMR spectrum (Figure 1), which displays cross peaks among the protons: H₆–Cp, H₇–Cp, H₁ₐ–Cp, H₄ₐ–Cp, H₂–H₅ₛ, H₃–H₈ₛ, H₂–H₅ₐ, and H₃–H₈ₐ. The NMR parameters for crystallographically well-established tantalum complexes 6a (this work) and TaCp(C₆H₁₀)₂[1] also support the above assignment. It is obvious from these data that the chemical shift values (av) for syn protons (H₁ₛ,H₄ₛ) in the supine dienes are always larger (ca. 0.2–0.6 ppm) than

Table II. ^{13}C NMR Chemical Shift Values (δ)^a and ^{13}C–^{1}H Coupling Constants (Hz) for Mixed Bis(diene)tantalum Complexes^a

	supine		prone		
complexes^c	C-1 (C-4)	C-2 (C-3)	C-5 (C-8)	C-6 (C-7)	L
TaCp*(DM)(BD) (6a)	47.6 (t, 141)	116.4 (s)	40.4 (t, 146)	105.4 (d, 156)	10.0 (q, 126)
TaCp(DM)(BD) (6b)	33.6 (t, 139)	111.3 (s)	36.3 (t, 147)	103.2 (d, 155)	97.0 (d, 166)
TaCp*(IP)(BD) (10a)	43.8 (t, 143)	131.5 (s)	42.4 (t, 144)	107.6 (d, 162)	11.3 (q, 127)
	44.1 (t, 141)	112.0 (d, 160)			
TaCp*(DM)(IP) (11a)	51.5 (t, 140)	114.9 (s)	42.3 (t, 146)	131.8 (s)	11.6 (q, 126)
			42.0 (t, 147)	108.2 (d, 155)	
TaCp(DM)(IP) (11b)	48.2 (t, 141)	112.8 (s)	40.0 (t, 147)	132.4 (s)	98.2 (q, 125)
			39.5 (t, 147)	106.3 (d, 154)	
TaCp(BD)$_2$ (12)^b	35.9 (t, 150)	113.8 (d, 156)	37.2 (t, 148)	103.7 (d, 155)	97.0 (d, 169)
TaCp(DM)$_2$ (13)^b	43.9 (t, 138)	117.2 (s)	43.8 (t, 140)	114.7 (s)	98.4 (d, 171)

^{a} In ppm downfield from the external SiMe$_4$. Data were collected at 22.5 MHz in C$_6$D$_6$ at 30 °C. See eq 1 and 4 for numbering system. ^{b} See ref 1. ^{c} BD = butadiene; IP = isoprene; DM = 2,3-dimethylbutadiene.

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors^a for Non-Hydrogen Atoms in 6a with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}, Å^2
Ta	0.24270 (3)	0.45912 (3)	0.10369 (3)	2.58
C(1)	0.1429 (9)	0.4852 (8)	−0.0068 (8)	4.1
C(2)	0.1189 (7)	0.5554 (6)	0.0446 (8)	2.8
C(3)	0.0951 (8)	0.5447 (8)	0.1305 (8)	3.5
C(4)	0.0975 (8)	0.4607 (8)	0.1631 (9)	4.3
C(5)	0.1245 (10)	0.6395 (8)	0.0035 (9)	4.9
C(6)	0.0704 (9)	0.6155 (8)	0.1904 (9)	4.6
C(11)	0.2787 (11)	0.5424 (11)	0.2229 (11)	6.3
C(12)	0.3669 (10)	0.5194 (9)	0.1890 (12)	5.6
C(13)	0.3896 (9)	0.5287 (9)	0.0979 (13)	6.1
C(14)	0.3260 (10)	0.5636 (9)	0.0384 (11)	5.4
C(21)	0.2242 (8)	0.3233 (7)	0.0343 (9)	3.1
C(22)	0.3203 (7)	0.3496 (6)	0.0260 (7)	2.7
C(23)	0.3588 (8)	0.3493 (7)	0.1111 (8)	3.2
C(24)	0.2851 (11)	0.3329 (8)	0.1715 (8)	4.1
C(25)	0.2038 (9)	0.3110 (7)	0.1205 (8)	3.5
C(26)	0.1607 (10)	0.2997 (8)	−0.0414 (11)	4.8
C(27)	0.3714 (11)	0.3601 (10)	−0.0573 (10)	5.5
C(28)	0.4642 (9)	0.3509 (8)	0.1306 (11)	4.8
C(29)	0.2985 (14)	0.3215 (11)	0.2681 (10)	6.6
C(30)	0.1149 (11)	0.2754 (9)	0.1581 (13)	6.0

^{a} See Hamilton, W. C. *Acta Crystallogr.* 1959, *12*, 609.

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

Bond Distances			
Ta–C(1)	2.250 (12)	C(2)–C(5)	1.527 (18)
Ta–C(2)	2.537 (11)	C(3)–C(6)	1.527 (18)
Ta–C(3)	2.558 (12)	C(11)–C(12)	1.407 (25)
Ta–C(4)	2.251 (14)	C(12)–C(13)	1.442 (27)
Ta–C(11)	2.346 (17)	C(13)–C(14)	1.407 (26)
Ta–C(12)	2.409 (18)	C(21)–C(22)	1.436 (16)
Ta–C(13)	2.379 (20)	C(22)–C(23)	1.415 (15)
Ta–C(14)	2.320 (16)	C(23)–C(24)	1.423 (18)
Ta–C(21)	2.497 (12)	C(24)–C(25)	1.440 (19)
Ta–C(22)	2.430 (10)	C(21)–C(25)	1.369 (17)
Ta–C(23)	2.453 (11)	C(21)–C(26)	1.520 (20)
Ta–C(24)	2.408 (15)	C(22)–C(27)	1.479 (18)
Ta–C(25)	2.522 (12)	C(23)–C(28)	1.524 (20)
C(1)–C(2)	1.445 (17)	C(24)–C(29)	1.506 (24)
C(2)–C(3)	1.373 (16)	C(25)–C(30)	1.506 (23)
C(3)–C(4)	1.474 (18)		

Bond Angles			
C(1)–Ta–C(4)	74.2 (5)	C(21)–C(22)–C(23)	106.5 (9)
C(11)–Ta–C(14)	77.9 (6)	C(22)–C(23)–C(24)	108.6 (10)
Ta–C(1)–C(2)	83.7 (7)	C(23)–C(24)–C(25)	106.3 (11)
C(1)–C(2)–C(3)	118.6 (10)	C(21)–C(25)–C(24)	108.6 (11)
C(2)–C(3)–C(4)	116.2 (11)	C(22)–C(21)–C(26)	124.8 (11)
Ta–C(4)–C(3)	84.0 (8)	C(25)–C(21)–C(26)	125.1 (12)
C(1)–C(2)–C(5)	119.5 (10)	C(21)–C(22)–C(27)	125.2 (10)
C(4)–C(3)–C(6)	121.5 (11)	C(23)–C(22)–C(27)	127.5 (10)
C(3)–C(2)–C(5)	121.8 (10)	C(22)–C(23)–C(28)	124.0 (11)
C(2)–C(3)–C(6)	122.3 (11)	C(24)–C(23)–C(28)	126.5 (11)
Ta–C(11)–C(12)	75.3 (10)	C(23)–C(24)–C(29)	124.9 (13)
C(11)–C(12)–C(13)	121.8 (16)	C(25)–C(24)–C(29)	127.2 (13)
C(12)–C(13)–C(14)	122.1 (17)	C(21)–C(25)–C(30)	127.2 (13)
Ta–C(14)–C(13)	74.9 (11)	C(24)–C(25)–C(30)	124.1 (13)
C(22)–C(21)–C(25)	109.3 (11)	Ta–C(21)–C(22)	70.5 (6)

those for syn protons (H$_{5s}$,H$_{8s}$) in the prone dienes. In addition, the replacement of the bulky Cp* ligand with the less bulky Cp ligand commonly results in the downfield shift of the syn protons in both supine and prone dienes. This is ascribed to the diminished electron donating property of the Cp ligand. The magnitude of $J_{2,3}$ and $J_{6,7}$ clearly confirms the s-cis coordination for the butadiene ligands (see eq 1 for numbering scheme).

The measurement of the ^{13}C–^{1}H coupling constant was carried out for the present complexes since it offers important information on the extent of sp^2 or sp^3 hybridization for coordinated diene carbons. It is possible to calculate the percent of s carbon atoms on the basis of Newton's semiempirical rule[10a] and hence the hybridization approximated by $n = (1 − s)/s$ for sp^n. The validity of this calculation for the present system is confirmed by observing $n = 1.95$–2.05 for CH carbons in Cp and $n = 2.95$–3.1 Cp* methyls.[10b] The n values for the terminal carbons of the prone butadiene (2.45–2.47) in 6a and 6b are a little smaller than the corresponding values (2.57–2.62) of the supine-2,3-dimethylbutadiene. This

suggests the presence of more pronouced metal–carbon π-bonding character in the prone-butadiene ligand as compared with the supine-2,3-dimethylbutadiene ligand. The large chemical shift dispersion for the inner protons of butadiene in bis(diene) complexes 6a,b, 10a,b, and 11a,b (4.3–4.9 ppm) is ascribed to the combined magnetic shielding effect by C$_5$R$_5$ and diene ligands (the corresponding protons in mono(diene) complexes 3a and 3b resonate at ca. 7.2 ppm).

X-ray Structure of Ta(C$_5$Me$_5$)(butadiene)(2,3-dimethylbutadiene) (6a). The X-ray diffraction study of Ta(C$_5$Me$_5$)(butadiene)(2,3-dimethylbutadiene) clearly confirms the structure 6a where the s-*cis*-butadiene lies prone. The ORTEP drawings of 6a are given as two different projections in Figure 2 with atomic numbering scheme. Final atomic coordinates for non-hydrogen atoms is listed in Table III, and relevant interatomic bond distances and angles are listed in Table IV.

Table V summarizes the geometrical parameters to define the coordination sphere of the Ta atom in 6a in com-

(10) (a) Newton, M. D.; Schulmann, T. M.; Manus, M. M. *J. Am. Chem. Soc.* 1974, *96*, 17. (b) This calculation is applicable to vast majority of neutral hydrocarbons and organometallics except for highly rehybridized molecules such as CHF$_3$ and some metal–CH$_3$ species. See, for example: George, C. L.; Ed. *Topics in Carbon-13 NMR Spectroscopy*; Wiley-Interscience: Toronto, 1976; Vol. 2. Mann, B. E., Taylor, B. E.; Eds. *^{13}C NMR Data for Organometallic Compounds*; Academic: London, 1981.
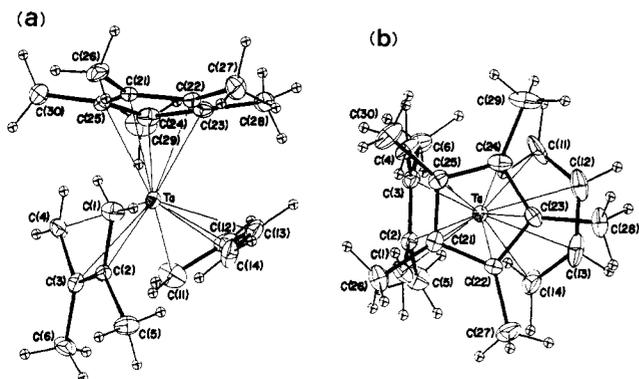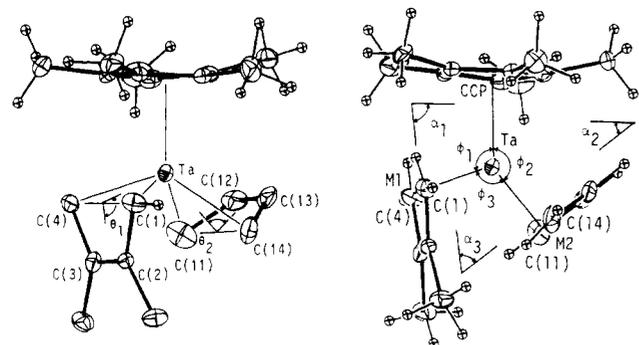
(a)

(b)

Figure 2. Two molecular projections of **6a** by ORTEP drawings: (a) side view and (b) top view.

Table V. Structural Parameters (deg) in Coordination Geometry for 6a and Related Complexes

	6a	13	14
θ_1	103.9	102.5	98.9
θ_2	96.6	100.4	112.0
α_1	81.8	81.5	83.5
α_2	38.6	35.0	18.5
α_3	59.6	63.6	78.6
ϕ_1	109.5	108.5	103.1
ϕ_2	137.4	137.2	142.1
ϕ_3	113.1	114.3	114.6

parison with those in $Ta(C_5H_5)(2,3\text{-dimethylbutadiene})_2$ (**13**) and $Ta(C_5Me_5)(2,3\text{-dimethylbutadiene})_2$ (**14**) which we reported earlier.[1] We observed a marked difference in the dihedral angle θ_2 among **6a**, **13**, and **14**. The magnitude of θ_2 for **14** is remarkably larger than the magnitude in **6a** and **13**, of θ_2 and consequently α_2, the dihedral angle between C_5R_5 and prone diene ligands, for **14** (18.5°) becomes smaller than α_2, in **6a** (38.6°) and **13** (35.0°). The severe steric congestion between the methyl groups in C_5Me_5 and 2,3-dimethylbutadiene in **14** may imply the above difference. The α_1 angles are, however, comparable throughout all these complexes.

The C(2)–C(3) bond (1.373 Å) in the 2,3-dimethylbutadiene moiety in **6a** is shorter by 0.07 and 0.10 Å than its C(1)–C(2) and C(3)–C(4) bonds, respectively. The metal–terminal carbon bonds Ta–C(1) (2.250 Å) and Ta–C(4) (2.251 Å) are significantly shorter (average 0.30 Å) than the Ta–C(2) and Ta–C(3) bonds. The bent angle defined by the C(1)–C(2)–C(3)–C(4) and C(1)–Ta–C(4) planes is 103.9°. Thus, the Ta–(2,3-dimethylbutadiene) unit in **6a** is best described as bent metallacyclo-3-pentene structure as commonly found for group 4A transition-metal–diene complexes.[11] In contrast to the above, the

Table VI. Selected Bond Distances (Å) in 6a and Related Complexes

	6a	13	3b
Ta–C(1) Ta–C(4)	2.251 (av)	2.261	2.258 (av)
Ta–C(2) Ta–C(3)	2.548 (av)	2.522	2.417 (av)
C(1)–C(2) C(3)–C(4)	1.460 (av)	1.469	1.456 (av)
C(2)–C(3)	1.373	1.352	1.375
Ta–C(11) Ta–C(14)	2.333 (av)	2.292	
Ta–C(12) Ta–C(13)	2.394 (av)	2.473	
C(11)–C(12) C(13)–C(14)	1.407 (av)	1.475	
C(12)–C(13)	1.442	1.343	
Ta–CCP[a]	2.148	2.119	2.088
Ta–M1[b]	1.795	1.796	1.811
Ta–M2[c]	1.815	1.797	

[a] Centroid of cyclopentadienyl ligand. [b] Midpoint of C(1) and C(4). [c] Midpoint of C(11) and C(14).

prone butadiene unit shows a short–long–short bond alternation; i.e., the external C–C bonds C(11)–C(12) and C(13)–C(14) are slightly (average 0.04 Å) shorter than the internal C(12)–C(13) bonds. The bond lengths between Ta and butadiene terminal carbons [Ta–C(11) and Ta–C(14)] are only slightly longer than those for the Ta–butadiene internal carbons [Ta–C(12) and Ta–C(13)]. Judging from these C–C and Ta–C bond lengths, a substantial participation of the π-bonded η^4-diene character is expected for the prone Ta–butadiene unit in **6a**.

Although the gross structural features of **6a** are similar to those of $TaCp(2,3\text{-dimethylbutadiene})_2$ (**13**) and $TaCl_2Cp(\text{butadiene})$ (**3b**), close comparison of these structures reveals several perturbations as shown in Table VI. The Ta–C and C–C bond lengths for the supine 2,3-dimethylbutadiene in **6a** is very close to those for the supine dienes in **13** and **3b**. However, the Ta–C(11) and Ta–C(14) bonds for the prone butadiene unit in **6a** is significantly longer than the corresponding bonds for the prone diene in **13** along with the supine dienes in **6a**, **13**, and **3b**. On the other hand, the averaged bond distance of tantalum–butadiene inner carbons, Ta–C(12) and Ta–C(13), in **6a** is remarkably shorter than the corresponding bonds in **13** along with the Ta–C(2) and Ta–C(3) bonds in **6a**, **13**, and **3b**. The relatively large π-bonding property of the prone butadiene in **6a** may invoke such a marked difference.

The Ta–C(terminal) bond distances in the present complexes are nearly equal to the Ta–C bond distances in Ta-ethylene (2.257 Å)[12] and those in tantalacyclopentanes (2.217 Å),[13] while the Ta–acetylene complexes have shortened M–C bond distances (ca. 2.07 Å) because of their metal–carbene character.[14]

Selective Reaction of Mixed Bis(diene)tantalum Complexes with Electrophiles. By taking advantage of the different modes of diene orientation that emerged in the present mixed bis(diene) complexes, one can estimate the relative reactivities of supine and prone dienes toward electrophiles. On the addition of 1 equiv of 2,4-dimethyl-3-pentanone (a ketone useful for facile NMR assignment) to **6b** at 0 °C in toluene, the 1:1 insertion proceeds selectively (95%) at the prone butadiene ligand to

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(12) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169.

(13) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1980**, *19*, 3106.

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

produce a 16e compound, 16, which involves a set of supine σ^2, π-metallacyclopentene and (Z)-oxametallacyclic units as confirmed by the NMR and EIMS spectroscopy (eq 5).

(5)
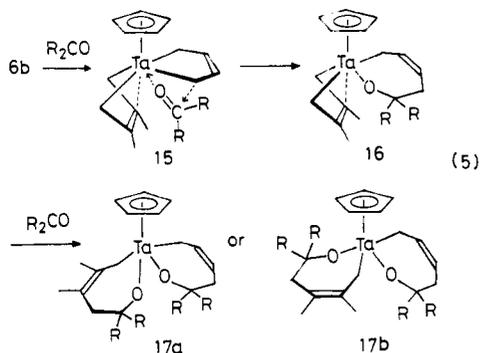
Similarly the 1:1 reaction of a deuterium-labeled homo bis(diene) complex, $Ta(C_5H_5)$(supine-2,3-dimethyl-butadiene)(prone-2,3-dimethylbutadiene-d_4) (13-d_4), with 2,4-dimethyl-3-pentanone or acetone gave the corresponding 1:1 addition compound whose structure is essentially the same as 16. In summarizing above reactions, we can conclude that the prone diene ligand possesses a higher reactivity toward electrophiles than the supine diene, irrespective of the bulkiness of the coordinated diene. Further addition of the ketone at elevated temperature (60 °C) finally produced complex 17a (or 17b) containing two oxametallacycloheptene units in the molecule. The resulting compound exhibits monomeric nature as revealed by the EIMS spectroscopy. The mode of the present ketone insertion reaction compares closely with that reported for $ZrCp_2$(diene) and $HfCp_2$(diene) which give rise to (Z)-oxametallacyclo-4-heptene derivatives by reactions with a variety of carbonyl compounds.[15] As a consequence, a reaction pathway through the four-center 16e transition-state 15 is proposed also for the present ketone insertion reaction. However, all of the tantalum-diene complexes (6a, 12–14) turn out to be completely inert toward esters, alkenes(1-pentene, 2-pentene), and dienes (butadiene, isoprene) at 30–80 °C in sharp contrast to the proper reactivity of group 4A metal–diene complexes.[16] The use of low-valent tantalum diene complexes in place of the present 18e complexes will be necessary to conduct the ester or alkene insertion reaction.

Concluding Remarks

A series of mixed bis(diene)tantalum complexes could be prepared in a pure form by incorporating two dienes stepwisely using the appropriate (2-butene-1,4-diyl)magnesium derivatives. The bulky diene ligands always prefer the supine orientation and are less reactive toward electrophiles as compared with the prone dienes. All the bis(diene)tantalum complexes comprise of s-cis-coordinated dienes while the novel s-trans, s-cis mixed bis(diene) complex was found in the case of $NbCp(C_4H_6)_2$.[2]

The present reaction sequences may have a broad application in the preparation of a wide range of mixed bis(diene) complexes of the type LM(diene-1)(diene-2) from $M(L)X_4$ or $M(L)X_2$(diene) (M = group 5–8 elements;

Table VII. Crystallographic and Experimental Data for 6a

formula	$C_{20}H_{31}Ta$
system	orthorhombic
space group	*Pbca*
a, Å	14.173 (3)
b, Å	16.524 (3)
c, Å	15.344 (3)
V, Å^3	3593.4 (1.1)
Z	8
D_{calcd}, g cm^{-3}	1.672
F(000), e	1792
μ(Mo Kα), cm^{-1}	91.7
cryst size, mm	0.25 × 0.25 × 0.40
T, °C	20
2θ limits,^{a} deg	$4 < 2\theta < 65$
scan type	$\theta/2\theta$
scan speed, deg min^{-1} in 2θ	4.0
scan width, deg in 2θ	$2.0 + 0.70 \tan\theta$
bkgd counting, s	5
data collected	+*h*,+*k*,+*l*
unique data	6495
reflctns obsd^b	3763
no. of params refined	315
$R(F)^c$	0.061
$R_w(F)^d$	0.083

^{a} Diffraction data were collected with a Rigaku automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. ^{b} Reflections were regarded as observed if $|F_o| > 3\sigma(F_o)$. $^c R(F) = \sum||F_3| - |F_c||/\sum|F_o|$. $^d R_w(F) = [\sum w(|F_3| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

diene-1 and diene-2 = butadiene, isoprene, 2,3-dimethyl-butadiene, 1,4-diphenylbutadiene, etc).

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 deoxygenated by vacuum distillation before use. The crystalline $TaCl_5$ (Mitsuwa Chem.) was used as received. ^{1}H NMR spectra were obtained on a JEOL GX-500 spectrometer and are analyzed with a Varian spin simulation program. ^{13}C NMR spectra were run on a JEOL FX-90Q spectrometer (22.5 MHz). The mass spectra (EI) were recorded on a JEOL DX-300 spectrometer at 70 eV.

X-ray Analysis of 6a. An air-sensitive single crystal of 6a was sealed in a thin-walled glass capillary tube under argon. All X-ray experiments were carried out on a Rigaku automated four-circle diffractometer with graphite-monochromatized Mo Kα radiation. The unit cell parameters at 20 °C were determined by a least-squares fit to 2θ values of 25 strong higher angle reflections. The crystal data and experimental conditions for data collection are summarized in Table VII. No significant intensity decay of the standard reflections was observed during the data collection. The intensity data were corrected for the usual Lorentz and polarization effects but not for absorption. The crystal structure was solved by the conventional heavy-atom method and was refined by the full-matrix least-squares method as implemented in the X-ray system by the use of observed reflections $[|F_o| - >3\sigma(R_o)]$.[17] After anisotropic refinement of the non-hydrogen atoms, all hydrogen atoms were located in the difference Fourier maps with the help of geometrical calculations and were refined isotropically.

All calculations were carried out on an ACOS S850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka, Japan.

Preparation of $TaCl_4(C_5Me_5)$. The preparation method reported by Herrmann et al.[18] was modified by using air-stable nontoxic $SiMe_3(C_5Me_5)$ in place of $SnBu_3(C_5Me_5)$. To a stirred solution of $TaCl_5$ (1.8 g, 5.0 mmol) in 40 mL of hot toluene (80 °C) was added dropwise $SiMe_3(C_5Me_5)$ (1.0 g, 5.0 mmol) with a syringe. An orange powder precipitates immediately after mixing.

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(18) (a) Herrmann, W. A.; Kalcher, W.; Briersack, H.; Bernal, I.; Creswick, M. *Chem. Ber.* 1981, 114, 3558. (b) Yasuda, H.; Okamoto, T.; Nakamura, A. *Organomet. Synth.*, in press.

The mixture was stirred for 1 h at 100 °C and then concentrated to 20 mL. The resulting orange powder was filtered, washed with hexane (20 mL), and dried in vacuo to give $TaCl_4(C_5Me_5)$ in ca. 70% yield: mp 220 °C; EIMS, m/z 456 (M⁺); ¹H NMR (CDCl₃) δ 2.73. Anal. Calcd for $C_{10}H_{15}Cl_4Ta$: C, 26.23; H, 3.30; Cl, 30.96. Found: C, 26.15; H, 3.62; Cl, 30.79.

Preparation of Ta(C₅R₅)(C₄H₆)(C₆H₁₀) (6a,b). Ta-(C₅Me₅)(butadiene)(2,3-dimethylbutadiene) (6a) was prepared according to the method previously noted starting from $TaCl_4$-(C₅Me₅).[1] Ta(C₅H₅)(butadiene)(2,3-dimethylbutadiene) (6b) was prepared in the following manner. A suspension of (2-butene-1,4-diyl)magnesium (2 mmol) in tetrahydrofuran (40 mL) was added to a stirred solution of $TaCl_2(C_5H_5)$(2,3-dimethylbutadiene) (0.8 g, 2 mmol) at -78 °C. After the mixture was allowed to warm to room temperature, stirring was continued at 30 °C for 2 h. Then the mixture was evaporated to dryness, and the product was extracted into hexane (50 mL). The extract was concentrated and chilled to -20 °C to induce the precipitation of 6b as pale yellow crystals in 70% yield: mp 108 °C; EIMS, m/z (relative intensity) 382 (M⁺, 41), 328 (M⁺ - C₄H₆, 11), 324 (M⁺ - C₄H₆ - H₄, 100), 300 (M⁺ - C₆H₁₀, 20), 296 (M⁺ - C₆H₁₀ - H₄, 26). Anal. Calcd for $C_{15}H_{21}Ta$: C, 47.19; H, 5.54; Ta, 47.33. Found: C, 47.05; H, 5.35; Ta, 47.51 (metal oxide method).

The reaction of $TaCl_2(C_5H_5)$(butadiene) (0.7 g, 2 mmol) with (2,3-dimethyl-2-butene-1,4-diyl)magnesium (2 mmol) under the same reaction conditions also gave the same mixed bis(diene) complex 6b in 75% yield.

Preparation of Ta(C₅R₅)(C₄H₆)(C₅H₈) (10a,b). To a stirred solution of $TaCl_2(C_5Me_5)(C_5H_8)$ (9a)(2.3 g, 5.0 mmol) in THF (40 mL) was dropwise added a suspension of (2-butene-1,4-diyl)-magnesium (5.0 mmol) in THF (10 mL) at -78 °C. The mixture was allowed to warm to 20 °C, and stirring was continued for 5 h. The color of the solution changes from purple to brown during the reaction. Then the mixture was evaporated to dryness, and the product was extracted into hexane (50 mL). Concentration of the solution to 15 mL followed by cooling to -20 °C resulted in the precipitation of $Ta(C_5Me_5)(C_4H_6)(C_5H_8)$ (10a) as pale yellow crystals in 70% yield: mp 110 °C; EIMS m/z (relative intensity) 438 (M⁺, 51), 384 (M⁺ - C₄H₆, 44), 380 (M⁺ -C₄H₁₀, 100), 370 (M⁺ - C₅H₈, 20). Anal. Calcd for $C_{19}H_{29}Ta$: C, 52.06; H, 6.67; Ta, 41.28. Found: C, 51.97; H, 6.58; Ta, 41.45.

In a similar procedure, Ta(C₅H₅)(C₄H₆)(C₅H₈) (10b) was obtained from 9b and (2-butene-1,4-diyl)magnesium as pale yellow crystals in 72% yield: mp 96-98 °C. EIMS, m/z (relative intensity) 368 (M⁺, 41), 314 (M⁺ - C₄H₆, 15), 300 (M⁺ - C₅H₈, 14), 310 (M⁺ - C₄H₁₀, 100). Anal. Calcd for $C_{14}H_{19}Ta$: C, 45.66; H, 5.20; Ta, 49.14. Found: C, 45.64; H, 5.15; Ta, 49.20. This sample contains another geometrical isomer, Ta(C₅H₅)(supine-C₄H₆)-(prone-C₅H₈) (20%).

Preparation of Ta(C₅R₅)(C₅H₈)(C₆H₁₀) (11a,b). In essentially the same procedure as described for 6b and 10a,b, Ta-(C₅Me₅)(C₅H₈)(C₆H₁₀) (11a) was prepared from 9a and (2,3-dimethyl-2-butene-1,4-diyl)magnesium in 68% yield: mp 98 °C; EIMS, m/z (relative intensity) 466 (M⁺, 53), 398 (M⁺ - C₅H₈, 52), 384 (M⁺ - C₆H₁₀, 63), 394 (M⁺ - C₅H₁₂, 100), 380 (M⁺ - C₆H₁₀, 41). Anal. Calcd for $C_{21}H_{33}Ta$: C, 54.07; H, 7.13; Ta, 38.80. Found: C, 54.01; H, 6.98; Ta, 39.00.

In a similar procedure, Ta(C₅H₅)(C₅H₈)(C₆H₁₀) (11b) was prepared in a state of high purity from 9b and (2,3-dimethyl-2-butene-1,4-diyl)magnesium in 65-73% yield: mp 101 °C; EIMS, m/z (relative intensity) 396 (M⁺, 38), 342 (M⁺ - C₄H₆, 13), 314 (M⁺ - C₆H₁₀, 15), 310 (M⁺ - C₄H₁₀). Anal. Calcd for $C_{16}H_{23}Ta$: C, 48.49; H, 5.85; Ta, 45.66. Found: C, 48.39; H, 5.78; Ta, 45.80.

Preparation of Ta(C₅H₅)(C₆H₁₀)(C₆H₆D₄). A deuterium-labeled diene, $CD_2C(CH_3)C(CH_3)CD_2$, was prepared by thermal cracking of $CH_3CO_2CD_2CH(CH_3)CH(CH_3)CD_2OCOCH_3$ (370 °C in argon). The diester was obtained by reacting dimethyl 2,3-dimethylsuccinate (6.5 g, 37.4 mmol) with LiAlD₄(1.9 g, 45 mmol) in ether (50 mL) at 30 °C followed by hydrolysis and acylation of the resulting $HOCD_2CH(CH_3)CH(CH_3)CD_2OH$ (4.0 g, 19 mmol) with acetic anhydride (10 mL) at 130 °C. The magnesium adduct of $CD=C(CH_3)C(CH_3)=CD_2$ was prepared as described earlier.[1] The reaction of TaCl₂Cp(supine-2,3-dimethylbutadiene) (2.0 g, 5 mmol) with $MgCD_2C(CH_3)C(CH_3)CD_2$ (5.0 mmol) in tetrahydrofuran (25 mL) at 25 °C for 5 h yielded TaCp(supine-C₆H₁₀)(prone-C₆H₆D₄) (96%) and TaCp(supine-C₆H₆D₄)(prone-

C_6H_{10})(4%) in 82% isolated yield. Their NMR and analytical data are identical with those for $TaCp(C_6H_{10})_2$ (see ref 1): EIMS, m/z (relative intensity) 410 (M⁺, 30.5), 328 (M⁺ - C₆H₁₀, 8.3), 324 (M⁺ - C₆H₆D₄, 8.9), 324 (M⁺ - C₆H₁₄, 51), 320 (M⁺ - C₆H₁₀D₄, 49).

Reaction of 6b with 2,4-Dimethyl-3-pentanone. A tetrahydrofuran solution (40 mL) of 2,4-dimethyl-3-pentanone (0.3 mL, 2 mmol) was added to a stirred solution of Ta(C₅H₅)(butadiene)(2,3-dimethylbutadiene) (6b) (0.8 g, 2 mmol) in 10 mL of tetrahydrofuran at -78 °C. The mixture was allowed to warm to room temperature, stirred at room temperature for 1 h, and then evaporated to dryness. The resulting product was extracted into hexane, and the solution was cooled to -20 °C to induce the precipitation of the 1:1 adduct (16, R = i-C₃H₇) as a pale yellow semisolid in ca. 93% yield: EIMS, m/z (relative intensity) 496 (M⁺, 17.5), 431 (M⁺ - Cp, 50.4), 414 (M⁺ - C₆H₁₀, 12.6), 349 (M⁺ - Cp- C₆H₁₀, 100); ¹H NMR (C₆D₆) δ 0.32 (d, J = 7.5 Hz, 2 H, anti protons in C₆H₁₀), 2.05 (d, 2 H, syn protons in C₆H₁₀), 1.80 (s, 6 H, CH₃ in C₆H₁₀), 2.63 (d, J = 8.1 Hz, TaCH₂), 2.36 (d, J = 8.2 Hz, OCH₂), 5.02 (dd, J = 11.0 Hz, TaCH₂CH=), 6.20 (dd, 1 H, CH=CH₂O), 0.98 (d, 12 H, CH₃), 2.01 (m, 2 H, CH(CH₃)₂, 5.82 (s, 5 H, Cp). Anal. Calcd for $C_{22}H_{35}OTa$: C, 53.22; H, 7.11; Ta, 36.44. Found: C, 53.08; H, 7.01; Ta, 36.85. Hydrolysis products of 16 (R=i-C₃H₇) consist of 2-methyl-3-isopropyl-6-hepten-3-ol (48%), 2,3-dimethyl-3-butene (17%), and 2,3-dimethyl-2-butene (35%) as determined by gas chromatography.

To the 1:1 adduct 16 (0.5 g, 1 mmol) was added 2,4-dimethyl-3-pentanone (0.1 mL, 1 mmol) at 0 °C. Heating of the mixture at 60 °C for 30 min affords the 1:2 adduct 17 in 92% GC yield (analysis of the hydrolyzate). Cooling of the hexane extract to -45 °C resulted in the precipitation of 17 as a pale yellow semisolid: EIMS, m/z (relative intensity) 610 (M⁺, 5.7), 545 (M⁺ - Cp, 100), 530 (M⁺ - Cp - CH₃, 61.6), 278 (TaCpO₂, 23.5); ¹H NMR (C₆D₆) [C₄H₆ side] δ 2.65 (d, J = 8.0 Hz, 2 H, TaCH₂), 2.50 (d, J = 8.2 Hz, 2 H, CH₂), 6.65 (dt, J = 11.2 Hz, 1 H, TaCH₂CH=), 5.49 (dt, 1 H, CH=), 0.98 (d, 12 H, CH₃), 2.02 (m, 2 H, CH(CH₃)₂, [C₆H₁₀ side] δ 2.32 (s, 2 H, TaCH₂), 2.24 (s, 2 H, CH₂), 1.80, 1.82 (s, 6 H, CH₃), 1.01 (d, 12 H, CH₃), 2.03 (m, 2 H, CH(CH₃)₂), 5.78 (s, 5 H, Cp). Anal. Calcd for $C_{29}H_{49}OTa$: C, 57.03; H, 8.09; Ta, 29.63. Found: C, 56.98; H, 8.03; Ta, 30.04 (metal oxide method).

Reaction of 13-d_4 with 2,4-Dimethyl-3-pentanone. A tetrahydrofuran solution (10 mL) of 2,4-dimethyl-3-pentanone (0.2 mL, 1.3 mmol) was added to a chilled solution of TaCp(supine-C₆H₁₀)(prone-C₆H₆D₄) (13-d_4) (0.5 g, 1.3 mmol) in 10 mL of tetrahydrofuran. The mixture was stirred at 20 °C for 3 h, and then the product was hydrolyzed. The product comprises a tetradeuteriated alcohol and a nondeuteriated one in 95:5 ratio as confirmed by the EIMS and NMR spectroscopies. 2,5,6-Trimethyl-3-isopropyl-6-hepten-3-ol-4,4,7,7-d_4: EIMS, m/e 198 (M⁺); ¹H NMR (CDCl₃) δ 0.95 (d, 12 H, CH₃ in C₃H₇), 1.05 (d, 3 H, CH₃), 1.76 (m, 2 H, CH in C₃H₇), 1.94 (s, 3 H, CH₃), 2.18 (m, 1 H, CH), 2.01 (s, 1 H, OH); GC yield, 95%.

Reaction of 13-d_4 with Acetone. The 1:1 addition reaction was carried out in essentially the same manner as described above. The hydrolysis product of the adduct contains 2,4,5-trimethyl-5-hexen-2-ol-3,3,6,6-d_4 (94%) and its nondeuteriated isomer (6%) as revealed by the EIMS and NMR spectra: ¹H NMR (CDCl₃) for the latter compound δ 1.05 (d, 3 H, C4-CH₃), 1.18 (s, 6 H, C1 and C2CH₃), 1.78 (m, 2 H, C3CH₂), 1.25 (s, 1 H, OH), 2.17 (m, 1 H, C4CH), 4.82, 4.89 (m, 2 H, CH₂=); GC yield, 92%.

Registry No. 3b, 95250-97-8; 4a, 95251-09-5; 4a-d_4, 114763-81-4; 4b, 70809-00-6; 6a, 95251-08-4; 6b, 116004-78-5; 8b, 95250-99-0; 9a, 95251-01-7; 9b, 95250-98-9; 10a, 115982-89-3; 10b (isomer 1), 115982-90-6; 10b (isomer 2), 116051-20-8; 11a, 116004-79-6; 11b, 116004-80-9; 13-d_4 (isomer 1), 115982-91-7; 13-d_4 (isomer 2), 116004-81-0; 16, 115982-92-8; 17, 115982-93-9; SiMe₃(C₅Me₅), 87778-95-8; TaCl₄(C₅Me₅), 71414-47-6; $CH_3CO_2CD_2CH(CH_3)CH$-(CH₃)CD₂OCOCH₃, 114763-84-7; $CD_2C(CH_3)C(CH_3)CD_2$, 42185-77-3; $HOCD_2CH(CH_3)CH(CH_3)CD_2OH$, 114763-85-8; TaCl₅, 7721-01-9; dimethyl 2,3-dimethylsuccinate, 28306-68-5; 2,4-di-

methyl-3-pentanone, 565-80-0; 2-methyl-3-isopropyl-6-hepten-3-ol, 38443-89-9; 2,3-dimethyl-3-butene, 563-78-0; 2,3-dimethyl-2-butene, 563-79-1; 2,5,6-trimethyl-3-isopropyl-6-hepten-3-ol-4,4,7,7-d_4, 115982-94-0; 2,5,6-trimethyl-3-isopropyl-6-hepten-3-ol, 115982-95-1; 2,4,5-trimethyl-5-hexen-2-ol-3,3,6,6-d_4, 115982-96-2; 2,4,5-trimethyl-5-hexen-2-ol, 115982-97-3; acetone, 67-64-1.

Preparation and Structure of Ru3(CO)7(μ3-η²-C6H4)(μ-PPhFc)2

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Heating Ru3(CO)10(PFcPh2)2, FcH = Fe(η^5-C5H5)2, in refluxing cyclohexane affords a good yield, 83%, of the μ3-benzyne complex Ru3(CO)7(μ3-η²-C6H4)(μ2-PPhFc)2 (2e), which was characterized by X-ray diffraction. It crystallizes in the monoclinic system, space group $P2_1/n$, with cell constants a = 17.872 (2) Å, b = 13.017 (1) Å, c = 18.547 (2) Å, and β = 101.50 (1)°; the final R value of 0.028 was obtained by using 3526 observed reflections. The Fc groups are trans with respect to the plane of the Ru3 triangle. The benzyne fragment, which seems to have partially localized bonds, is planar and makes an angle of 64.0 (2)° with the plane of the Ru3 triangle. NMR studies of the fluxional behavior of the benzyne fragment, a 180° rotation, indicate that the motion is less facile than is found in related Os3 systems.

Introduction

Dehydrobenzene, benzyne, is a highly reactive molecule[1] which can be trapped as simple η^2-bound metal complexes such as 1 (M = Ta)[2] and μ3-η^2-bound complexes such as 2a.[3,4a] Some examples of μ4-η^2-binding are known, e.g. 3.[4]

1
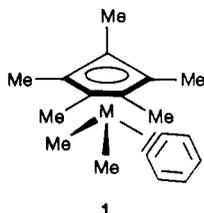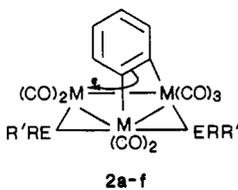
a, M = Os, ERR' = PPh2; **b**, M = Ru, ERR' = PPh2; **c**, M = Os, ERR' = PMe2; **d**, M = Os, ERR' = AsMe2; **e**, M = Ru, ERR' = PFcPh; **f**, M = Ru, ERR' = PFcPh, PPh2

There are few reports concerning the possibility that dehydroferrocene, ferrocyne, has an independent existence.[5] One of the objectives of our current research efforts is to establish if ferrocyne can be trapped as a metal complex by using similar techniques to those used for the preparation of 1-3. Hope in this endeavor is fueled by work showing that complexes such as 4 are stable.[6]
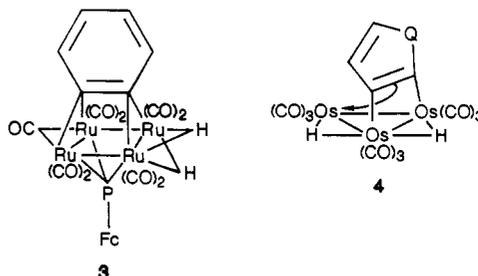
3   4

Furthermore, the dehydrocyclopentadienyl ion seems to be capable of transient existence.[7] This paper describes an attempt to trap ferrocyne by pyrolysis of the complex Ru3(CO)10(PFcPh2)2,[8] FcH = Fe(η^5-C5H5)2. It seems that P-Ph bond cleavage is more facile than P-Fc so that the principal product is 2e. The crystal structure of this new compound is described as are NMR studies of the fluxional

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