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'Supine' or 'prone' ligands: geometric preference of conjugated diene, 1-azadiene, and 1,4-diazadiene ligands on half-metallocene complexes of early transition metals

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Dedicated to Professor H. Brunner on the occasion of his 65th birthday and for his contribution to organometallic chemistry

Abstract

The two terms defined originally, *supine* and *prone*, describing the orientation of an *s-cis*-1,3-diene ligand bound to half-metallocene fragments of niobium and tantalum are considered to include various new examples of diene complexes. Typically, bis(diene) complexes of these fragments predominantly prefer one *supine* and one *prone* diene ligands. The *supine/prone* preference of various mono- and bis(diene), bis(allyl) and (allyl)(diene) complexes together with 1-azadiene and 1,4-diazadiene complexes is also described. Structural features and unique reactivity of these two different diene coordination modes are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Supine and *prone*; Half-metallocene fragments; Diene complexes

1. Introduction

Rich stereochemistry has been observed in coordination of conjugated 1,3-diene to transition metals. *s-cis*-1,3-Diene complexes of transition metals have a general tendency that early transition metals favor a M–C σ-bonding and a metallacyclopent-3-ene as a canonical form, while late transition metals favor a π-bonding and an η^4-diene coordination mode [1][1]. In the case of ML(diene)$_2$-type complexes where two diene ligands
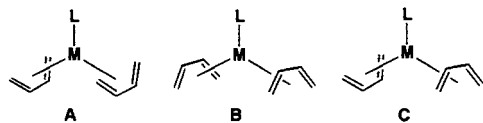
coordinate to a metal center, three coordination modes, A, B, and C in Scheme 1, are generally possible. Bis(diene) complexes of late transition metal such as Fe(L)(butadiene)$_2$ (L = Co, PR$_3$) [2,3], Ru(CO)(diene)$_2$ [4], RhCl(butadiene)$_2$ [5,6], IrCl(butadiene)$_2$ [7], and Mn(L)(butadiene)$_2$ (L = CO, PR$_3$) [8,9] have been reported to have mode A, but there is no example of mode B. On the other hand, we reported in 1985 a series of bis(diene) complexes of niobium and tantalum, $(\eta^5$-C$_5$R$_5$)M(diene)$_2$ (**1**) (M = Nb, Ta; R = H, Me; diene = butadiene, isoprene, 2,3-dimethylbutadiene), and demonstrated that these complexes adopt a categorically new geometry, mode C [10]. In organometallic complexes, terms '*endo*' and '*exo*' have been used for describing the orientation of hydrogen atoms on the conjugated organic ligands toward the metal center. Hence, in order to describe the orientation of diene units, we defined *supine* and *prone* orientations as illustrated in Fig. 1.

supine: having front or ventral part upwards.
prone: having front or ventral part downwards.
(Oxford Dictionary)

Scheme 1.

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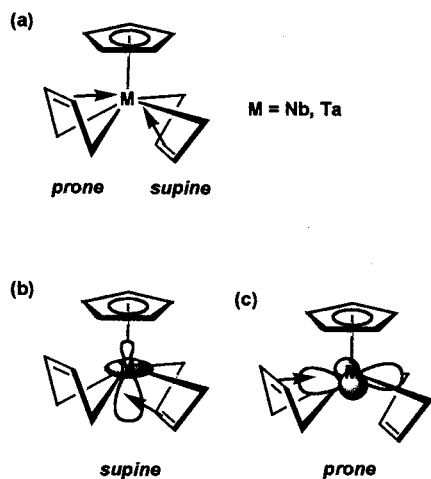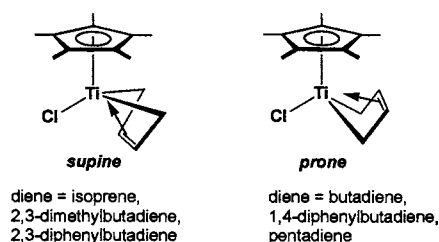[1] The *s-trans* coordination mode of 1,3-diene is not included.

Fig. 1. (a) Molecular structure of bis(diene) complexes **1**. (b) Orbital interaction (donation from filled pπ to the vacant d-orbital (d$_{z^2}$) of the metal). (c) Orbital interaction (donation from filled pπ to the vacant d-orbital (d$_{x^2-y^2}$) of the metal).

diene = isoprene, 2,3-dimethylbutadiene, 2,3-diphenylbutadiene

diene = butadiene, 1,4-diphenylbutadiene, pentadiene

Scheme 2.

We have already proposed in 1985 a simple rationalization of the observed preference of CpM fragments (M = Group 5 metals) for the *supine–prone* geometry based on an EHMO analysis [10]. Fig. 1(b) and (c) indicate the most important orbital interactions for the *supine–prone* geometry (mode C).

Recent years have seen many other important examples of mono- and bis(diene) complexes of transition metals; the difference in oxidation state of the metal center as well as the choice of auxiliary ligands are important for determining the geometry throughout the transition metals. The orientation of allyl group(s) of bis(allyl) and (allyl)(diene) complexes is also conceptually described by using the same *supine/prone* notation. Moreover, analogous to the diene complexes, some new complexes with 1-aza-1,3-diene (abbr. AD) or 1,4-diaza-1,3-diene (abbr. DAD) ligand have been prepared recently and the similar descriptions are available. With many of these new experimental findings, the rationalization of their preferential geometry should be considered again, and we propose some new conceptions for the geometrical aspects of the diene ligand and its heteroatom derivatives upon coordination.

Table 1
Crystallographically characterized *supine/prone* geometric preference of some mono-η^4-*s-cis*-1,3-diene half-metallocene complexes of early transition metals [a]

Complex	Diene ligand	Ref.
Cp*TiCl(BD)	*Prone*	[11]
Cp*TiCl(1,4-DPBD)	*Prone*	[11]
Cp*TiCl(2,3-DPBD)	*Supine*	[11]
(η^5:η^1-C$_5$Me$_4$SiMe$_2$N^{t}Bu)Ti(HD)	*Prone*	[23]
Cp*HfCl(pyridine)(DMBD)	*Supine*	[50]
Cp*HfCl(DMBD)	*Supine*	[50]
[CpNb(μ-Cl)(BD)]$_2$	*Supine*	[13]
CpTaCl$_2$(BD)	*Supine*	[10]
Cp*TaMe(OTf)(IP)	*Supine*	[16]
Cp*Ta(benzyne)(BD)	*Supine*	[51]
Cp*Ta(CH$_2$Ph)$_2$(BD)	*Supine*	[52]
Cp*Ta(=CH$_2$Ph)(PMe$_3$)(BD)	*Supine*	[53]
[CpMo(μ-Br)(BD)]$_2$	*Supine*	[29]
CpMo(NO)(DMBD)	*Supine*	[54]
CpMoCl$_2$(BD)	*Supine*	[55]
Cp*ReCl$_2$(TMBD)	*Supine*	[56]

[a] Abbreviations: BD, 1,3-butadiene; IP, isoprene; DMBD, 2,3-dimethyl-1,3-butadiene; 2,3-DPBD, 2,3-diphenyl-1,3-butadiene; 1,4-DPBD, 1,4-diphenyl-1,3-butadiene; TMBD, 1,2,3,4-tetramethylbutadiene; HD, 2,4-hexadiene.

2. Substitution effect on the coordination modes of the diene ligand

Substitution effect on the diene ligand of early transition metal complexes is important, and a remarkable difference in the *supine/prone* geometrical isomerism was found for complexes having different substituent(s) on the diene. Substitution at the central carbons of the diene gives rise to the *supine* geometry in the case of Cp*Ti(diene)Cl (**2**), whereas the *prone* geometry was found for unsubstituted diene such as 1,3-butadiene and 1,4-diphenyl-1,3-butadiene [11] (Scheme 2). This may be explained simply by the steric effect of the substituent(s) since internal substitution(s) gave rise to the *supine* isomer. The bonding nature of the diene coordinated to the titanium atom is quite different depending on the coordination geometry. The ^{1}H-NMR spectral data indicated pronounced σ-bonding at the terminal carbons for the *supine* diene, whereas the *prone* diene exists in the doubly π-coordinated state. Thus, the diene–titanium bonding in the *prone* isomer is rather similar to the diene–metal bond generally found for late transition metals. This preference for the *prone* coordination is now rationalized by the electronic effect of formally divalent titanium center, which does not form two strong metal–carbon σ-bonds. Absence of any related dialkyl complexes, CpTiCl(R)$_2$, corroborate this. Most of mono-diene half-metallocene complexes of other early transition metals were found to be *supine*-isomer presumably due to the M–C σ-bonding character of the early transition metal diene complexes; typical examples are shown in Table 1.

In the case of mixed bis(diene) tantalum complexes **1**, the geometric preference of substituted diene was different from unsubstituted one; our experimental finding indicates that the 2,3-disubstituted diene, i.e. dimethylbutadiene, of Cp*Ta(butadiene)(2,3-dimethylbutadiene) prefers the *supine* coordination, while the unsubstituted one, i.e., butadiene, the *prone* orientation [13]. Since the *supine* diene is found to be stronger σ-binder (σ^{2}π-type) to the metal, this is consistent with the established tendency of 2,3-di-substituted diene for the *supine* geometry.

3. Structural similarity between η-cyclopentadienyl ligand and η-*s-cis*-1,3-butadiene ligand

When one looks at the series of isoelectronic complexes as shown in Fig. 2, similarity of series (a) complexes, diene complexes of Group 4–6 metals, in their structure is apparent. The other series (b) diene complexes shown in Fig. 2(b) also indicate similarity of the structure among Mn, Ru, and Co diene complexes. The *s-cis* diene ligand behaves like Cp but one carbon less.
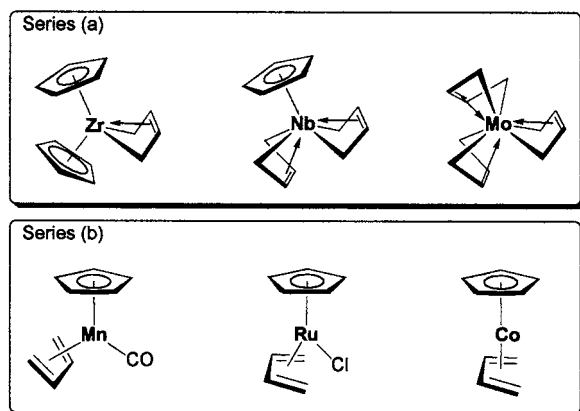

Fig. 2. Isoelectronic series of mixed CpM(diene) complexes of early transition metals [series (a)] and late transition metals [series (b)].
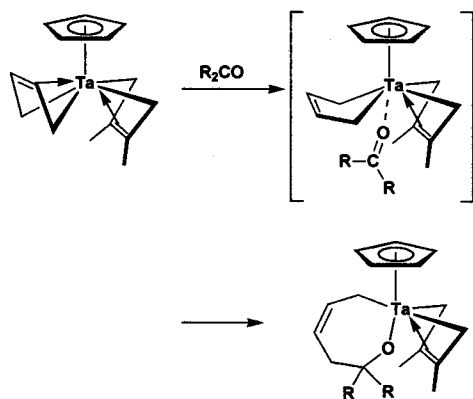

Fig. 3. Reaction between bis(diene) complex, CpTa(η^4-*prone*-butadiene)(η^4-*supine*-2,3-diemthylbutadiene), with organic carbonyls.

It is noteworthy that the CpCo(diene) complex has a paralleled Cp/diene structure, which is structurally similar to ferrocene. It is proposed that the CpCo(diene) may be called 'norferrocene' to indicate its similarity in molecular structure. The *s-cis* diene complexes of ruthenium, Cp*Ru(diene)Cl, predominantly have *prone* structure where the diene is nearly parallel to the cyclopentadienyl ring [12], and hence the Cp*Ru(diene) part, though Cl compensates the electron deficiency, is assumed to have ferrocene-like stereochemistry.

4. Reactivity difference between *supine* and *prone* diene ligands

It is of interest that *supine* and *prone* diene ligands exhibit different reactivity. The addition reaction of organic carbonyl compounds to the diene ligands of CpTa(diene)$_2$ proved the exceedingly high reactivity of the *prone* diene to give metallacyclic compounds as shown in Fig. 3 [13,14]. This difference may be ascribed to the first coordination of carbonyl group to the vacant d($x^2 - y^2$) orbital (Fig. 1), which dominantly interacts with the occupied pπ-orbitals of the *prone* diene ligand, and then a carbonyl group inserts into a M–C bond of the *prone* diene ligand.

Another example is that one of two dienes was replaced by ligand exchange reaction; the reaction of (η^5-C$_5$H$_4$Me)Nb(butadiene)$_2$ with cyclooctatetraene afforded (η^5-C$_5$H$_4$Me)Nb(η^4-*supine*-butadiene)(η^3-C$_8$H$_8$) [15]. Moreover, mono-diene complexes (η^5-C$_5$R$_5$)MCl$_2$(diene) (M = Nb, Ta; R = H, CH$_3$) in the presence of excess amounts of MAO were found to catalyze living polymerization of ethylene [16,17]. Almost the same catalytic activities were accomplished by using the corresponding bis(diene) systems (η^5-C$_5$R$_5$)M(diene)$_2$/MAO (M = Nb, Ta; R = H, CH$_3$) [16,18]. These findings clearly indicated that one of two diene ligands selectively reacted with excess amounts of MAO to give the same catalytically active species, [(η^5-C$_5$R$_5$)(η^4-diene)M–Me]$^+$, which are isoelectronic to the corresponding cationic alkyl metallocene species of Group 4 metals, [Cp$_2$MR]$^+$. The intact *supine* diene ligand was found to control the catalyst activity presumably by the steric and electronic effects. With 2,3-diemthylbutadiene as the diene ligand in the catalysis, which showed the highest activity among complexes with other dienes, the polymerization proceeded most rapidly at temperatures above 30 °C. Thus, it is important to point out the unique spectator role of the diene ligand since any coordinated dienes have generally been expected to be activated by only intramolecular reactions. Various diene complexes upon treated with boron or aluminum compounds, Cp$_2$Zr(butadiene)/B(C$_6$F$_5$)$_3$ [19,20], Cp$_2$Zr(butadiene)/AlR$_2$X [21], (η^5-C$_5$H$_3$-(SiMe$_3$)$_2$-1,3)M(CH$_2$Ph)(diene) (M = Zr, Hf)/B(C$_6$F$_5$)$_3$

Table 2
Crystallographically characterized *supine/prone* geometric preference of some bis(*s-cis*-1,3-diene), bis(allyl), (*s-cis*-1,3-diene)(allyl) half-metallocene complexes of early transition metals [a]

Complex	*Supine* ligand(s)	*Prone* ligand(s)	Ref.
CpZr(allyl)(BD)	Allyl, BD	–	[25]
Cp*Hf(1,2,3-Me$_3$–allyl)(1,2-Me$_2$–butadiene)	–	1,2,3-Me$_3$–allyl, 1,2-Me$_2$–butadiene	[26]
CpNb(DMBD)$_2$	DMBD	DMBD	[13]
Cp*Nb(BD)(η^3-COT)	BD	COT	[57]
CpTa(BD)$_2$	BD	BD	[10]
Cp*Ta(DMBD)$_2$	DMBD	DMBD	[10]
Cp*Ta(BD)(DMBD)	DMBD	BD	[14]
Cp*Ta(BD)(η^3-COT)	BD	COT	[58]
Cp*Ta(1-phenylallyl)$_2$	1-Phenylallyl, 1-phenylallyl	–	[27]
CpCr(allyl)$_2$	Allyl, allyl	–	[28]
CpMo(BD)(allyl)	BD, allyl	–	[29]
CpMo(BD)(allyl)	BD	Allyl	[29]
[CpMo(BD)(C$_3$H$_4$CH$_2$PMe$_3$)]$^+$	BD	C$_3$H$_4$CH$_2$PMe$_3$	[30]
CpMo(allyl)$_2$	Allyl, allyl	–	[31]

[a] Abbreviations: BD,1,3-butadiene; DMBD, 2,3-dimethyl-1,3-butadiene; COT, 1,3,5,7-cyclooctatetraene.

[22] and (η^5:η^1-C$_5$Me$_4$SiMe$_2$N^{t}Bu)Ti(diene)–B(C$_6$F$_5$)$_3$ [23,24], were found to be unique catalysts for olefin polymerization.

5. Bis(allyl) and (Allyl)(diene) complexes

Some typical examples of bis(allyl) and (allyl)(diene) complexes of Zr [25], Hf [26], Ta [27], Cr [28], and Mo [29–32] are shown in Table 2. In the middle of d-elements, 18-e rules nicely describe thermally stable species. For example, allyl–diene complexes CpMo-(diene)(allyl) are isoelectronic (18e) to bis(diene) complexes of niobium and tantalum [29,30,32]. The *supine/prone* preference has also been investigated for these mixed ligand complexes. It is of interest that the thermodynamically stable *supine–supine* isomer of CpZr(allyl)(diene) was reversibly converted to the *prone–prone* one by photo irradiation [33].

6. Coordination modes of 1-hetero-1,3-butadiene complexes

Heteroatom substitution on diene units provides unique coordination geometry because of various types of M-heteroatom bondings. The coordination of 1-aza-1,3-butadiene (abbr. AD) to a metal is much flexible than that of conventional diene ligand [34]; being not only *supine/prone* modes for η^4-*s-cis*-AD but also η^2-C=N or η^2-C=C coordination modes. Some AD and related complexes of early transition metals are summarized in Table 3.

We prepared AD complexes having Cp*TaCl$_2$ fragments, in which the AD ligand coordinates in a *supine* fashion. On the basis of NMR spectral data, the AD

ligation proves to have a significant contribution of an η^1-*N*-η^3-allyl canonical form (Scheme 3) [27,35]. Similar an η^3-allyl contribution was already reported for a mesityl oxide complex, CpTa(*supine*-η^4-MEO) (MEO, mesityl oxide) [36]. Methyl methacrylate (MMA) and methyl acrylate (MA) coordinate also in a *supine*-fash-

Table 3
Crystallographically characterized *supine/prone* geometric preference of some 1-azabutadiene, 1-oxabutadiene, and 1,4-diazabutadiene half-metallocene complexes of early transition metals [a]

Complex	Hetero-diene ligand	Ref.
CpTiCl(1-*o*-Tol-3-Me-AD)	*Supine*	[59]
Cp*TaCl$_2$(Ph-AD)	*Supine*	[34]
Cp*Ta(CH$_2$Ph)$_2$(η^2-*C,N*-Ph-AD)	η^2-C=N	[38]
Cp*TaCl$_2$(*p*-MeO-C$_6$H$_4$-DAD)	*Supine*	[42]
Cp*NbCl$_2$(*p*-MeO-C$_6$H$_4$-DAD)	*Supine*	[42]
Cp*TaCl$_2$(^{i}Pr-DAD)	*Supine*	[43]
Cp*TaCl(CH$_2$Ph)	*Supine*	[42]
(*p*-MeO-C$_6$H$_4$-DAD)		
Cp*TaMe$_2$(*p*-MeO-C$_6$H$_4$-DAD)	*Prone*	[42]
Cp*Ta(CH$_2$Ph)$_2$(Cy-DAD)	*Prone*	[42]
Cp*Ta(-CC^{t}Bu)$_2$(^{i}Pr-DAD)	*Supine*	[43]
Cp*Ta(-CC^{t}Bu)$_2$(^{t}Bu-DAD)	*Prone*	[43]
Cp*TaMe$_2$(^{i}Pr-DAD)	*Prone*	[43]
Cp*Ta(S^{t}Bu)$_2$(η^2-*C,N*-^{i}Pr-DAD)	η^2-C=N	[43]
Cp*TaCl$_2$(MMA)	*Supine*	[38]
Cp*TaCl$_2$(MA)	*Supine*	[37]
CpTaCl$_2$(MEO)	*Supine*	[36]
Cp*Ta(η^4-*supine*-butadiene)(Cy-DAD)	Mode D	[38]

[a] Abbreviations: 1-*o*-Tol-3-Me-AD, 1-*o*-tolyl-3-methyl-4-phenyl-1-aza-1,3-butadiene; Ph-AD, 1,4-diphenyl-1-aza-1,3-butadiene; *p*-MeO-C$_6$H$_4$-DAD, 1,4-di(*p*-methoxyphenyl)-1,4-diaza-1,3-butadiene; ^{i}Pr-DAD, 1,4-di(isopropyl)-1,4-diaza-1,3-butadiene; Cy-DAD, 1,4-di(cyclohexyl)-1,4-diaza-1,3-butadiene; MMA, methyl methacrylate; MA, methyl acrylate; MEO, mesityl oxide.
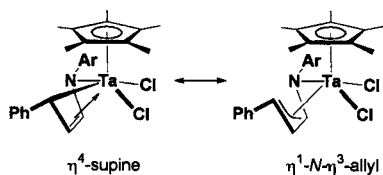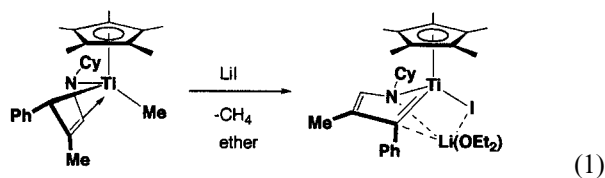
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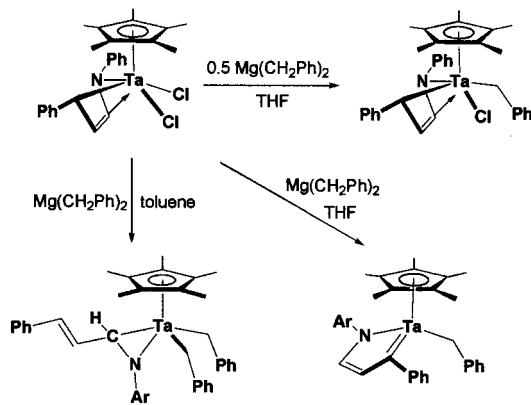
Scheme 4.

ion to the half-metallocene fragment of tantalum [37,38].

As a result of hetero-atom incorporation, a unique reactivity at the coordinated ligand was realized. A methyl complex, CpTiMe(*supine*-η^4-CyN=CHCMe=CHPh), gradually decomposed via η-hydrogen elimination at the AD ligand to give a metallacyclic titanium–carbene complex and methane (Eq. (1)) [39].

(1)

Alkylation of dichloro-AD complexes of tantalum effectively affects the coordination mode. For example, benzylation of the dichloro complexes gave several interesting tantalum complexes having the AD ligand; monobenzylation, giving Cp*TaCl(CH$_2$Ph)(*supine*-η^4-Ph-AD) (Ph-AD = 1,4-diphenyl-1-aza-1,3-butadiene), did not change the coordination mode, while dibenzylation afforded an η^2-*C,N*-imine complex Cp*Ta(CH$_2$Ph)$_2$(η^2-*C,N*-Ph-AD) together with a cyclic tantalum–carbene complex (Scheme 4) depending on the kind of solvent, toluene or THF. These observations are attributed to the congestion between two benzyl groups that enforce the formation of nascent benzylidene species and then abstract the H4 proton from their AD ligand.

7. Coordination modes of 1,4-diaza-1,3-butadiene complexes

The 1,4-diaza-1,3-butadiene (abbr. DAD) ligand coordinates to the metal center in several modes, *N,N'*-chelation (D, E, and F) and η^2-*C,N*-imine (G) (Chart 1) [40,41]. The mode-F has been reported for many late transition metal complexes. By tuning the substituent(s) on the DAD ligand, niobium and tantalum complexes having three coordination modes, D, E, and G, have been prepared [42–45]. Furthermore, the $\sigma^2\pi$-endi-amido ligand (mode E) can adopt two isomers, i.e. *supine* and *prone*.
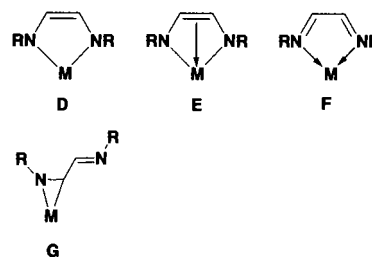

Chart 1.

Dichloro complexes (η^5-C$_5$R$_5$)MCl$_2$(η^4-*supine*-R-DAD) (M = Nb, Ta; R = H, Me) [R-DAD = 1,4-di(R)-1,4-diaza-1,3-butadiene; R = alky, aryl] generally adopt the *supine* isomer [42,44] except for a bulky substituted DAD complex; Cp*TaCl$_2$(η^4-*prone*-^{t}Bu-DAD) (^{t}Bu-DAD = 1,4-di(*tert*-butyl)-1,4-diaza-1,3-butadiene) [43]. Much bulkier ligand, 1,4-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene [abbr. (^{i}Pr)$_2$C$_6$H$_3$-DAD], afforded Cp*TaCl$_2$(η^2-*C,N*-(^{i}Pr)$_2$C$_6$H$_3$-DAD), in which the DAD ligand coordinates to the tantalum center in η^2-*C,N*-imine coordination (mode-G). Such the η^2-*C,N*-coordination of the DAD ligand has also been reported for a niobium complex, [Nb(η^4-^{t}Bu-DAD)(η^2-*C,N*-^{t}Bu-DAD)]$_2$(η-^{t}Bu-DAD) [46], and a tantalum complex, Cp*Ta(S^{t}Bu)(η^2-*C,N*-^{t}Bu-DAD) [43].

The orientation of the DAD ligand changes on alkylation of these dichloro complexes. As illustrated in Scheme 5, the *supine*-DAD ligand flips to the *prone*-one in dimethyl complexes Cp*TaMe$_2$(η^4-*prone*-DAD) and bis(benzyl) complexes Cp*M(CH$_2$Ph)$_2$(η^4-*prone*-DAD) (M = Ta, Nb) [42].

These bis(benzyl) complexes are thermally stable in the solid state, but in solution these gradually decomposed to give the corresponding benzylidene complexes Cp*M(=CHPh)(η^4-*prone*-DAD) (M = Ta, Nb) with the release of toluene [42]. The similar halfmetallocene-di-azadiene complexes of zirconium and hafnium have been prepared and were found to have *supine* geometry [45]. Alkylation of these complexes did not change the orientation of DAD ligand.
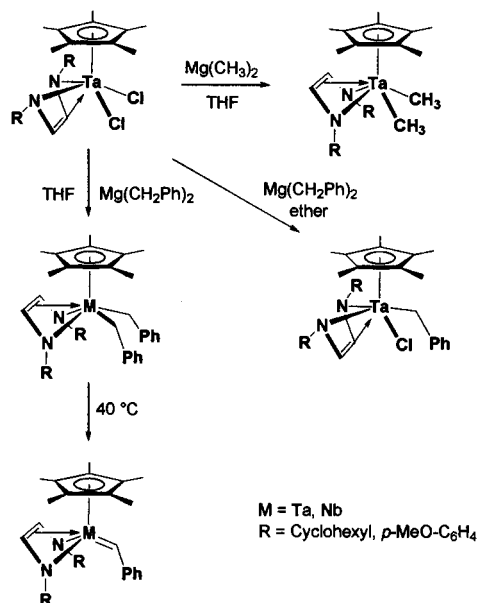
Scheme 5.
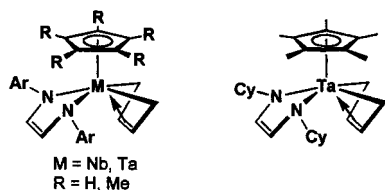
Scheme 6.

8. Synthesis and characterization of 16-electron mixed-ligand 1,4-diazadiene-diene complexes

A series of 16-electron mixed-ligand complexes having both diene and 1,4-diazadiene ligands were prepared (Scheme 6). In mixed ligand complexes $(\eta^5\text{-}C_5R_5)M(\eta^2\text{-}N,N'\text{-DAD})(\eta^4\text{-}supine\text{-diene})$ (M = Nb, Ta; R = H, Me), a DAD ligand coordinates to the tantalum as metalla-2,5-diazacyclopent-3-ene (mode D) and the diene coordinates in an $\eta^4\text{-}supine$ fashion [42,44]. It is notable that these complexes show characteristic intense red or purple color due to LMCT bands, where electrons of the filled $N(p\pi)$ orbital are donated to the empty $Ta(d\pi^*)$ orbital, in accordance with the metalla-2,5-diazacyclopent-3-ene structure (mode D). This interaction somewhat stabilizes the coordinative unsaturation at the 16-electron tantalum center, as theoretically pointed out for 16-electron half-sandwich transition metal complexes [47–49].

9. Conclusion

We have corroborated our previously proposed stereochemical definition, *supine/prone*, for describing the relative orientation of *s-cis*-1,3-diene units. The nature of diene–metal bonding, e.g. physical properties and versatile reactivities, depends on the coordination mode of the diene ligand. Additionally, 1-azadiene (AD) and 1,4-diazadiene (DAD) complexes are also discussed for their stereochemical preference, *supine* and *prone* isomers.

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