Ligand Architecture on Stereocontrol of Half-Metallocene Benzylidene Complexes of Tantalum

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Dedicated to Professor R. R. Schrock for his distinguished and continuous contributions to inorganic and organometallic chemistry.

Abstract: This brief review discloses our studies on half-metallocene benzylidene complexes of tantalum bearing 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, *o*-xylylene, 1,4-diaryl-1,4-diaza-1,3-butadiene, or 1-aryl-4-phenyl-1-aza-1,3-butadiene as an auxiliary ligand. These auxiliary ligands can control the stereochemistry of the benzylidene moiety and induce intriguing reactivity. Furthermore, the butadiene and *o*-xylylene complexes catalyze ring opening metathesis polymerization of norbornene to respectively give polymers with *cis*- and *trans*-C=C bonds. Such selectivity can be attributed to control of the stereochemistry of the propagating alkylidene chain end by the auxiliary ligand: the butadiene complex favors the *anti*-rotamer while the *o*-xylylene complex favors the *syn*-one.

Keywords: benzylidene complexes; half-metallocene complexes; ligand design; polymerization; ROMP; tantalum

1 Introduction

Since alkylidene complexes of niobium and tantalum were discovered by Professor Schrock (Figure 1),[1–9] many alkylidene complexes of early transition metals bearing various types of supporting ligands have been reported.[10–32] Notable feature of these Schrock-type alkylidene complexes compared with that of the Fischer-type carbene complexes is their versatility and applicability as catalysts for olefin metathesis reactions including ring-opening metathesis polymerization of cyclic olefins and as reagents for alkene formation from carbonyl compounds.[5,7,9–11,33–35] We have demonstrated that half-metallocene-diene fragments of group 5 metals are isoelectronic and isolobal to metallocene fragments of group 4 metals.[36–40] Figure 2 shows some typical alkylidene complexes of group 4 metals[41,42] and group 5 metals[43,44] with isoelectronic fragments. This review briefly describes our studies on the synthesis and characterization of benzylidene complexes of tantalum and their stereochemistry of the benzylidene moiety, which was tunable and was highly depending on the kinds of ancillary ligands such 1,3-butadiene (**1**),[45,46] 2,3-dimethyl-1,3-butadiene (**6**),[47] *o*-xylylene (**7**),[46] 1,4-diaryl-1,4-diaza-1,3-butadiene (**8**),[48] and 1,4-diaryl-1-aza-1,3-butadiene (**9**).[49,50] It is of interest that in the case of half-metallocene benzylidene complexes of group 5 metals there are *anti*- and *syn*-isomers with different stereochemistry of alkylidene moiety relative to the cyclopentadienyl ligand.

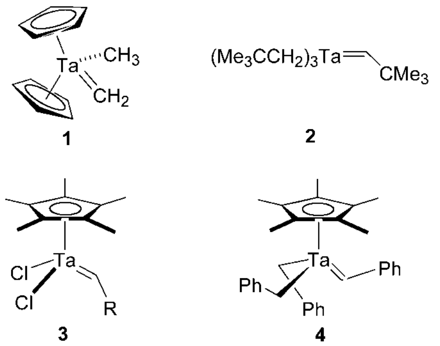

Figure 1. Some alkylidene complexes by Prof. Schrock.

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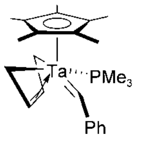

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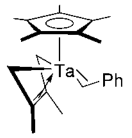

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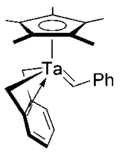

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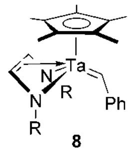

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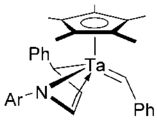

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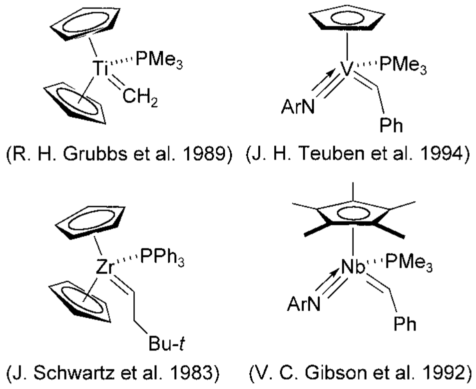


Figure 2. Some alkylidene complexes with isoelectronic fragments.

2 Benzylidene Complexes of Tantalum with Butadiene, 2,3-Dimethylbutadiene, or *o*-Xylylene Ligand

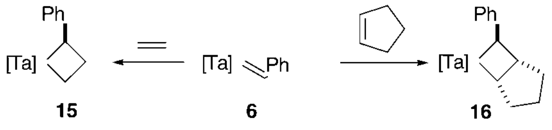
The dibenzyltantalum complex $Ta(CH_2Ph)_2Cp^*(\eta^4$-*supine*-$C_4H_6)$ (**10**) was prepared by reaction of $TaCl_2Cp^*(\eta^4$-*supine*-$C_4H_6)$ (**11a**) with two equivalents of benzyl-Grignard reagent in THF.[45] The thermolysis of **10** in the presence of PMe_3 afforded a benzylidene complex $Ta(=CHPh)Cp^*(\eta^4$-*supine*-$C_4H_6)(PMe_3)$ (**5**) whose benzylidene moiety was found to be the *anti*-rotamer with the phenyl group pointing away from the Cp* ligand.[45] The PMe_3 ligand was required to stabilize the benzylidene complex. The complex **5** was characterized in solution by NMR spectroscopy: its ^1H NMR spectrum exhibited a doublet resonance due to an α-benzylidene proton at $\delta = 9.67$ ($J_{P,H} = 5.9$ Hz) and its Cα benzylidene resonance was observed at $\delta = 237.3$ ($J_{C,H} = 112$ Hz, $J_{C,P} = 19$ Hz). In sharp contrast, the reaction of $TaCl_2Cp^*(\eta^4$-*supine*-DMBD) (**11b**) with 1 equivalent of $Mg(CH_2Ph)_2$ in toluene did not afford a dibenzyl complex, instead a smooth α-hydrogen abstraction of one of the two benzyl groups followed by the release of toluene proceeded spontaneously to give **6**.[47] The observed difference in reactivity can be attributed to the steric congestion around the metal center and the increased electron-donor character induced by the methyl groups on the ligand. Complex **6** was found to be the *syn*-rotamer where the phenyl group points upward to the Cp* ligand. The ^1H NMR spectrum of **6** displayed a singlet resonance at $\delta = 5.88$ due to an α-benzylidene proton and the ^{13}C NMR spectrum showed a signal at $\delta = 242.8$ ($J_{C,H} = 90$ Hz) due to the benzylidene carbon.

A dichloro-*o*-xylylene complex $TaCl_2[\eta^4$-*o*-$(CH_2)_2$-$C_6H_4]Cp^*$ (**12**) reacted with 2 equivalents of $PhCH_2MgCl$ in THF to give the corresponding dibenzyl complex $Ta(CH_2Ph)_2[\eta^4$-*o*-$(CH_2)_2C_6H_4]Cp^*$ (**13**).[46] Thermolysis of **13** resulted in the smooth α-hydrogen abstraction accompanied by the elimination of toluene to give a benzylidene complex $Ta(=CHPh)[\eta^4$-*o*-$(CH_2)_2$-$C_6H_4]Cp^*$ (**7**), whose stereochemistry around the Ta=CHPh moiety was determined by X-ray analysis to be a *syn*-rotamer. The benzylidene complex **7** was able to be isolated without any phosphine ligand, similar to the isolation of phosphine-free benzylidene complexes such as **6**[47] and **4**.[6] The ^1H NMR spectrum of **7** showed a singlet at $\delta = 4.99$ due to the α-benzylidene proton. We observed the benzylidene carbon atom at $\delta = 230.8$ ($J_{C,H} = 85$ Hz), whose chemical shift value and coupling constant are comparable to those found for **4** ($\delta = 220$, $J_{C,H} = 82$ Hz).[6]

3 Ring Opening Metathesis Polymerization of Norbornene and Related Reactions

Since alkylidene complexes of early transition metals have been used as catalysts for olefin metathesis and ring-opening metathesis polymerization (ROMP) of cyclic olefins,[51,52] at first we applied the isolated benzylidene complexes as catalysts for ROMP of norbornene. Results were that the isolated benzylidene complexes **5** and **6** did not show any catalytic activity, presumable due to the presence of the phosphine ligand and the steric congestion between the monomer and the two methyl groups at the 2,3-positions of the butadiene ligand, both severely preventing the coordination of norbornene to the tantalum center. Additionally, the complex **5** did not react with unsaturated hydrocarbons, while the phosphine-free complex **6** reacted with unsaturated hydrocarbons such as ethylene and cyclopentene to give metallacyclic compounds **15** and **16**, respectively.[47]

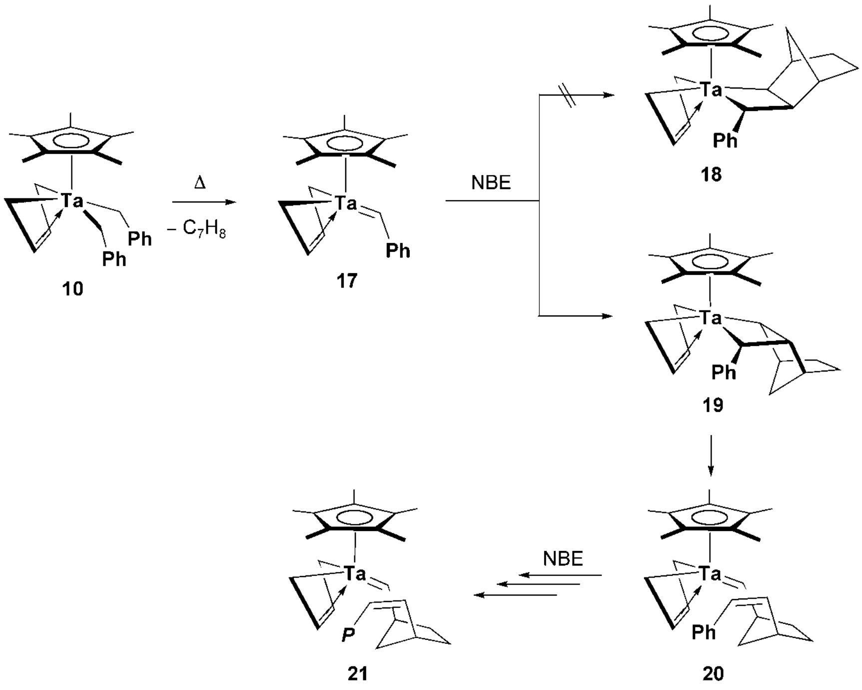
At elevated temperature, the dibenzylbutadiene complex **10** gave 97–99% *cis* polymers, while the *o*-xylylene-dibenzyl complex **13** and the isolated benzylidene complex **7** gave polymers with 92–95% *trans* double bonds. Phosphine-free benzylidenebutadiene species **17**, generated *in situ* from the thermolysis of dibenzyl complex **10**, were able to initiate the polymerization of norbornene (Scheme 1). The addition of norbornene to **17** resulted in the formation of a metallacyclobutane **19** while keeping the direction of the phenyl group and successive metathesis cleavage afforded the *cis* polymer. Another metallacycle **18** was unfavorable due to the steric repulsion between the monomer and Cp* ligand. The geometry of the propagating chain end with the butadiene ligand is mostly *anti* (Scheme 1), while the polymer chain end with the *o*-xylylene ligand is much more sterically demanding and thus a meta-stable *anti*-alkylidene species **24**, derived from metathesis reaction of metallacycle **23**, turns into the *syn*-species **26** (see Scheme 2). Thus, the stereoselectivity (*cis*/*trans* ratio) of the C=C bond of poly(norbornene) was highly controlled by the geometry of the Ta=CHPh group towards to the Cp* ligand, depending on the ancillary ligands bound to the tantalum center: Schrock et al. already demonstrated that *syn* and *anti* rotamers of molybdenum complexes of the type $Mo(NAr)(=CHMe_2Ph)(OR)_2$ [$Ar = 2,6\text{-}Me_2C_6H_3$, $2,6\text{-}i\text{-}Pr_2C_6H_3$; $OR = O\text{-}t\text{-}Bu$, $OCMe(CF_3)_2$, etc.] play a major role in determining the stereochemistry of polymer C=C bonds.[53]



[Ta] = TaCp*(DMBD)

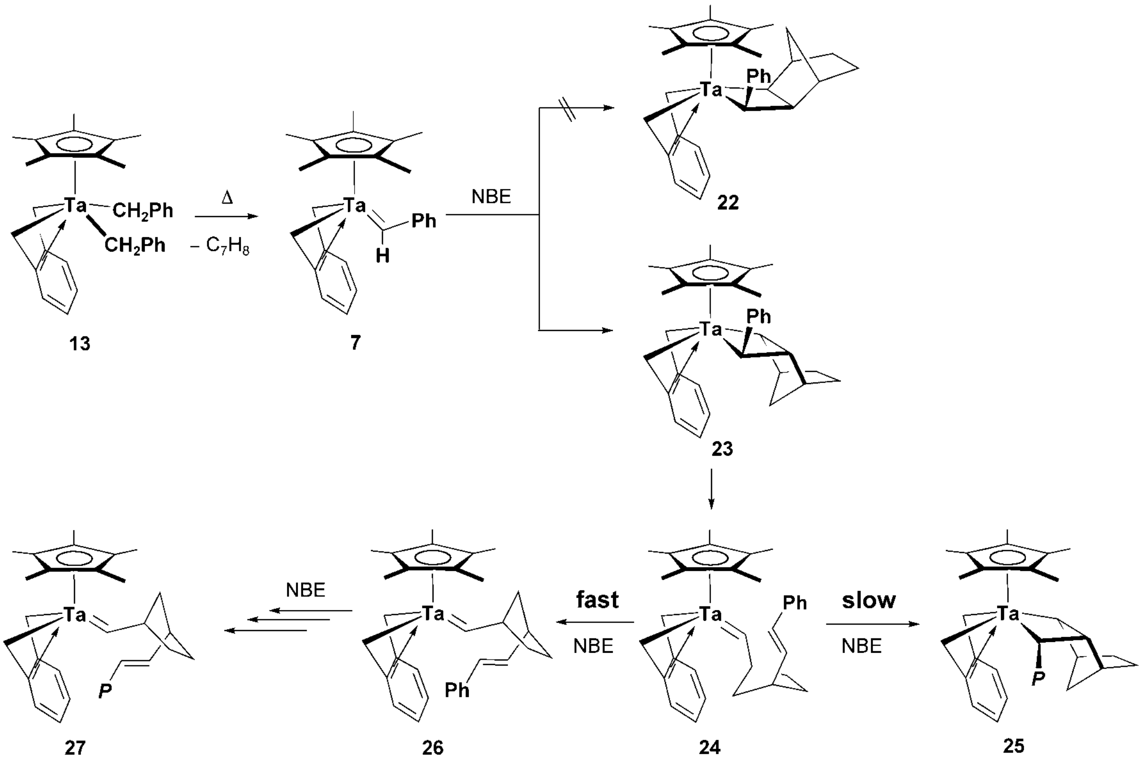
4 Benzylidene Complexes of Tantalum with 1,4-Diazadiene or 1-Azadiene Ligands and their Reactions

The nitrogen atom donates more electron density to the metal center than the carbon atom.[54,55] We used 1,4-diazadiene (DAD) and 1-azadiene (AD) as nitrogen li-



P = *cis*-poly(norbornene)

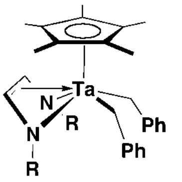
Scheme 1.



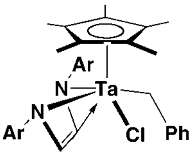
P = *trans*-poly(norbornene)

Scheme 2.

gands. A notable feature of these ligands is the mutability and flexibility of the DAD and AD ligands. The DAD-dibenzyl complexes of tantalum, $Ta(CH_2Ph)_2Cp^*(\eta^4$-*prone*-dad) (**28a**: dad = *p*-$MeOC_6H_4$-dad; **28b**: dad = Cy-dad), were obtained from the reactions of the corresponding dichloro compounds $TaCl_2Cp^*(\eta^4$-*supine*-dad) (**29a**: dad = *p*-$MeOC_6H_4$-dad; **29b**: dad = Cy-dad), with $Mg(CH_2Ph)_2$ in THF. In contrast, the reaction of the *o*-Tol-dad complex, $TaCl_2Cp^*(\eta^4$-*supine*-*o*-Tol-dad) (**29c**), with an excess of $Mg(CH_2Ph)_2$ in diethyl ether did not give the corresponding dibenzyl complex $Ta(CH_2Ph)_2Cp^*(\eta^4$-*prone*-*o*-Tol-dad) (**28c**); however, a mono(benzyl) complex $Ta(CH_2Ph)ClCp^*(\eta^4$-*supine*-*o*-Tol-dad) (**30**) was obtained. The dad ligands of the complexes **28** preferred the *prone*-orientation, while the complexes **29** and **30** were found to be in the *supine*-one. Thus, the dibenzylation caused the change of the dad ligand from the *supine*-conformation to the *prone*-one.



28a: R = *p*-MeO-C_6H_4
28b: R = Cy

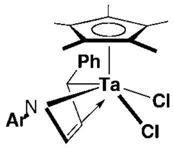


30: Ar = *o*-Tol

The complexes **28** thus isolated in solution gradually decomposed to give the corresponding benzylidene complexes $Ta(=CHPh)Cp^*(\eta^4$-*prone*-dad) (**8a**: dad = *p*-$MeOC_6H_4$-dad; **8b**: dad = Cy-dad), with the release of toluene. The ^1H NMR and ^{13}C NMR spectra of **8a** [$\delta_H = 7.95$; $\delta_C = 222.6$ ($J_{C,H} = 124$ Hz)] and **8b** [$\delta_H = 7.95$; $\delta_C = 222.9$ ($J_{C,H} = 129$ Hz)] indicated that they adopted an *anti*-isomer form.

The AD ligand may have both the characters of the diene and the DAD ligand. The starting dichloro complexes $TaCl_2Cp^*$(*supine*-η^4-ad) (**31a**: ad = Ph-ad; **31b**: ad = *p*-$MeOC_6H_4$-ad; **31c**: ad = *o*-Tol-ad) were prepared by the reaction of a dinuclear Ta(III) complex, $[TaCl_2Cp^*]_2$ (**32**)[56,57] with the corresponding AD ligands.[49,50] Benzylation of the dichloro complexes **31** gave several interesting tantalum complexes having the AD ligand, depending on the reaction conditions, i.e., stoichiometry and solvent. The reaction of **31a** with 1 equivalent of $Mg(CH_2Ph)_2$ in *toluene* afforded a dibenzyl complex $Ta(CH_2Ph)_2Cp^*(\eta^2$-*C,N*-Ph-AD) (**33a**) in quantitative yield. In contrast, the same reaction in *THF* afforded a mixture of **33a** (77%) and a metallacyclic tantalum-carbene complex **34a** (23%). Similarly, reaction of **31b** with $Mg(CH_2Ph)_2$ gave the same result, producing a dibenzyl complex **33b** in toluene and a mixture of **33b** and the metallacyclic tantalum-carbene complex **34b** in THF. A similar cyclic carbene complex has been reported for a half-titanocene azadiene complex, TiMeCp-

(*supine*-η^4-CyN=CHCMe=CHPh) (**35**), which gradually decomposed *via* α-hydrogen elimination to give a metallacyclic titanium-carbene complex **36**.[58] During the dibenzylation of **31** in toluene, the transformation from the *supine*-η^4-AD coordination mode to the η^2-*C,N*-imine mode took place.



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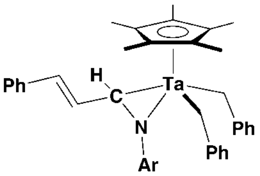

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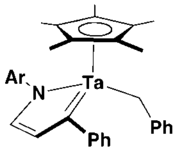

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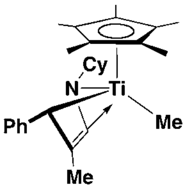
a: Ar = Ph
b: Ar = C_6H_4OMe-4
c: Ar = C_6H_4Me-2



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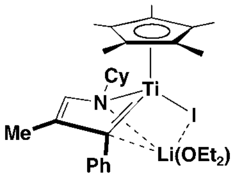

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A similar reaction of **31c** with $Mg(CH_2Ph)_2$ in toluene afforded a dibenzyl complex **33c**,[59] which released toluene to give the corresponding benzylidene complex Ta(=CHPh)Cp*(η^4-*supine*-*o*-Tol-AD) (**9c**). The ^{1}H NMR spectrum of **9c** exhibited a characteristic α-benzylidene proton signal in the downfield region ($\delta = 8.14$) and in the ^{13}C NMR spectrum the benzylidene carbon atom appeared at $\delta = 243.4$ with a coupling constant $^1J_{C,H} = 123$ Hz, indicating that the phenyl group of the benzylidene moiety pointed in the direction opposite to the Cp* ligand, an *anti*-rotamer. It is also interesting that the coordination mode of the AD ligand tuned from the η^2-fashion to the η^4-*supine* fashion.

5 Conclusion

We have systematically synthesized benzylidene complexes of half-metallocene tantalum complexes bearing butadiene, 2,3-dimethylbutadiene, *o*-xylylene, diazadiene, and azadiene auxiliary ligands, and we discussed the coordination mutability and feasibility of the benzylidene moiety caused by choice of the auxiliary ligands including electronic and steric factors. Butadiene and *o*-xylylene complexes serve as unique catalysts for the stereoselective ROMP of norbornene.

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