The *ansa*-effect in permethyltantalocene chemistry: a [Me_2Si] *ansa* bridge promotes olefin-insertion and reductive-elimination reactions for [$Me_2Si(C_5Me_4)_2$]Ta(η^2-C_2H_4)H and [$Me_2Si(C_5Me_4)_2$]TaH_3

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The *ansa*-effect, as it applies to tantalocene chemistry, has been investigated by a comparison of the chemistry of [$Me_2Si(C_5Me_4)_2$]TaH_3 and [$Me_2Si(C_5Me_4)_2$]Ta(η^2-C_2H_4)H with their permethyltantalocene counterparts; these studies demonstrate that incorporation of the [Me_2Si] *ansa* bridge substantially enhances the rates of both reductive elimination of H_2 and ethylene-insertion into a Ta–H bond.

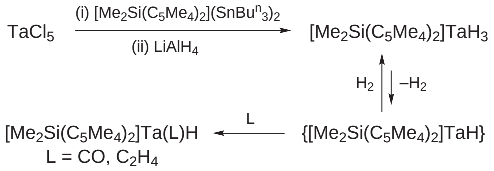
The ability of an *ansa* bridge to modify the chemistry of a metallocene system has recently found important applications. For example, the stereoregularity of polymers obtained using metallocene catalysts is influenced considerably by the presence of such bridges.[1] The majority of studies on *ansa*-metallocene complexes, however, has principally been concerned with identifying the manner in which the *ansa*-bridge effects a product distribution, with relatively little attention having been given to defining, and quantifying, its effect on fundamental organometallic transformations.[2] Here, we describe quantitative aspects of the *ansa*-effect as it applies to two of the most important reactions in organometallic chemistry, namely olefin-insertion and reductive-elimination.

By comparison with unsubstituted tantalocene complexes, Cp_2TaX_n, their permethylated counterparts $Cp^*{}_2TaX_n$ (Cp^* = η^5-C_5Me_5) have provided a most valuable system for studying a variety of elementary organometallic transformations.[3] An investigation of the chemistry of the corresponding permethylated *ansa*-tantalocene complexes [$Me_2Si(C_5Me_4)_2$]TaX_n should, therefore, allow for a quantitative evaluation of the influence of an *ansa* bridge on elementary transformations at a tantalum center. Single atom bridged *ansa*-tantalocene complexes are, however, most uncommon. For example, the only structurally characterized *ansa*-tantalocene complexes with η^5,η^5-coordination listed in the Cambridge Structural Database[4] are the imido derivatives, [$Me_2C(C_5H_4)_2$]Ta(NBu^t)Cl[5] and [$Me_2C(C_5H_4)_2$]Ta[$N(C_6H_3Pr^i{}_2)$]Cl.[6,7] In view of the large number of *ansa*-metallocene complexes of Ti, Zr, and Hf, the paucity of studies in *ansa*-tantalocene chemistry may be a reflection of synthetic difficulties in obtaining the requisite compounds; indeed, even the literature synthesis of $Cp^*{}_2TaCl_2$[8] is considerably more complicated than those of the Group 4 analogues, $Cp^*{}_2MCl_2$ (M = Ti, Zr, Hf). It is, therefore, noteworthy that we have been able to access the *ansa* bridged {[$Me_2Si(C_5Me_4)_2$]Ta} system. Specifically, the trihydride complex [$Me_2Si(C_5Me_4)_2$]TaH_3 may be obtained *via* reaction of $TaCl_5$ with [$Me_2Si(C_5Me_4)_2$]$(SnBu^n{}_3)_2$,[9] followed by treatment with $LiAlH_4$ (Scheme 1).

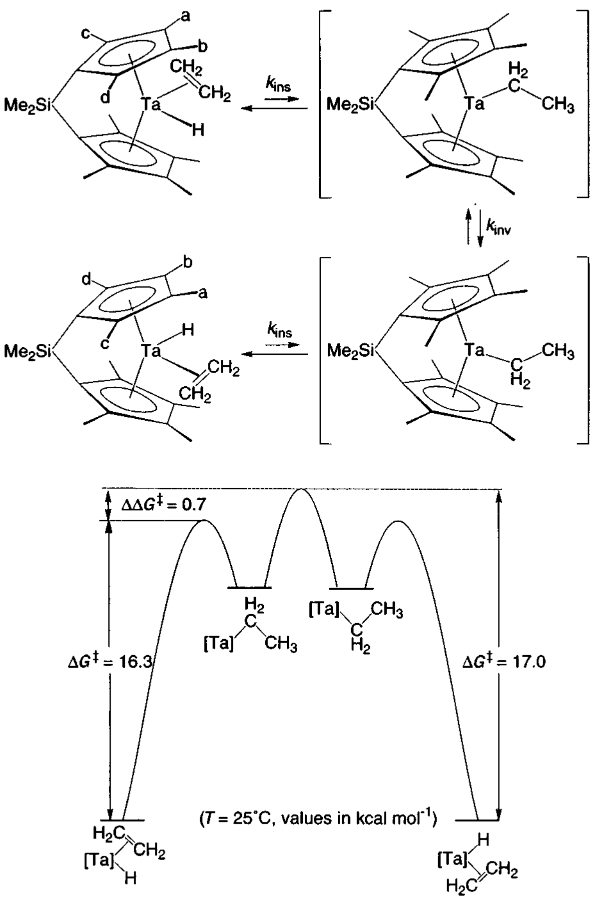
[$Me_2Si(C_5Me_4)_2$]TaH_3 is a convenient precursor to other derivatives, including the ethylene and carbonyl complexes, [$Me_2Si(C_5Me_4)_2$]Ta(η^2-C_2H_4)H and [$Me_2Si(C_5Me_4)_2$]Ta(CO)H (Scheme 1). While the pentamethylcyclopentadienyl analogues, $Cp^*{}_2$Ta(η^2-C_2H_4)H and $Cp^*{}_2$Ta(CO)H, have likewise been prepared from $Cp^*{}_2TaH_3$,[8] an important distinction between the two systems resides with the conditions required to effect reaction. For example, [$Me_2Si(C_5Me_4)_2$]Ta(η^2-C_2H_4)H is readily obtained over a period of hours at 80 °C, whereas the literature synthesis of the pentamethylcyclopentadienyl analogue requires prolonged heating for 10 days at 140 °C.[8] A more detailed comparison indicates that the *ansa* complex [$Me_2Si(C_5Me_4)_2$]TaH_3 reacts with C_2H_4 *ca.* 4000 times faster than does $Cp^*{}_2TaH_3$ under identical conditions.[10] Likewise, (i) the reaction of [$Me_2Si(C_5Me_4)_2$]TaH_3 with CO and (ii) H/D exchange with D_2 are also enhanced over the corresponding reactions of $Cp^*{}_2TaH_3$. These comparisons clearly demonstrate that the [Me_2Si] *ansa* bridge strongly promotes reductive elimination of H_2 in this system, a most notable result because a completely opposite effect is observed in a related tungsten system. Specifically, Green and coworkers demonstrated that the [Me_2C] *ansa* bridge in [$Me_2C(C_5H_4)_2$]W(R)H totally inhibits reductive elimination of alkane, an observation that was rationalized in terms of the *ansa* bridge preventing adoption of the parallel ring geometry favored for a tungstenocene intermediate.[11] The tantalum systems, however, do not require a parallel ring geometry since both monohydride intermediates, {[$Me_2Si(C_5Me_4)_2$]TaH} and [$Cp^*{}_2$TaH], are expected to have a bent sandwich structure.[12] Other factors are, therefore, responsible for dictating the influence of the [Me_2Si] *ansa* bridge on reductive elimination reactions in tantalocene complexes. One possible explanation is associated with the notion that the [Me_2Si] *ansa* bridge reduces the electron donating capability of the attached cyclopentadienyl groups (*vide infra*).[2b,13] As such, the Ta(V) trihydride would be stabilized with respect to the Ta(III) monohydride intermediate to a lesser degree for the *ansa* system than that for the unbridged system and so their interconversion would be more facile.

Dynamic NMR spectroscopic studies (line broadening and magnetization transfer) indicate that the ethylene hydride complex [$Me_2Si(C_5Me_4)_2$]Ta(η^2-C_2H_4)H is in rapid equilibrium with its ethyl tautomer {[$Me_2Si(C_5Me_4)_2$]$TaCH_2CH_3$} (Scheme 2).[14] Significantly, the [Me_2Si] *ansa* bridge also enhances the rate of ethylene insertion in [$Me_2Si(C_5Me_4)_2$]Ta(η^2-C_2H_4)H by a factor of *ca.* 760 (at 100 °C)[15] over that for its non-bridged counterpart, $Cp^*{}_2$Ta(η^2-C_2H_4)H.[16] As with the reductive elimination reactions described above, it is likely that the origin of the effect on the olefin insertion reaction is also attributable to an electronic influence resulting from the reduced electron donating properties of the *ansa* bridged ligand. Indeed, a similar argument has been made by Bercaw to rationalize the observation that olefin insertion within $Cp_2M(\eta^2$-$C_2H_4)H$ is more facile than that within $Cp^*{}_2M(\eta^2$-$C_2H_4)H$ (M = Nb, Ta).[3b]

In addition to olefin insertion, the barrier to 'inversion',[17] *i.e.* the combined barrier to cleaving any potential agostic interaction, passing the alkyl group through the center of the wedge, and rotating about a M–C bond (Scheme 2), is of most relevance



Scheme 1



Scheme 2

to the use of metallocene derivatives as polymerization catalysts. Specifically, depending on the catalyst system, the polymer stereochemistry will depend critically on the relative rates of such ‘inversion’ and olefin insertion.[18] While it is not possible to study inversion within $Cp^*_2Ta(\eta^2\text{-}C_2H_4)H$ because of the lack of a suitable diagnostic technique, it is possible to detect the occurrence of this process for the *ansa* analogue $[Me_2Si(C_5Me_4)_2]Ta(\eta^2\text{-}C_2H_4)H$ by virtue of the diasterotopic methyl substituents of the $[Me_2Si(C_5Me_4)_2]$ ligand. In particular, the barrier for ethylene–hydride site interchange within $[Me_2Si(C_5Me_4)_2]Ta(\eta^2\text{-}C_2H_4)H$ may be conveniently measured by monitoring exchange of the aforementioned diasterotopic methyl substituents (a ↔ b and c ↔ d) by using ^1H NMR spectroscopy. These experiments indicate that there is indeed an additional barrier required to effect ‘inversion’ in this system. The additional barrier ($\Delta\Delta G^\ddagger$) is, however, modest, with a value of only *ca.* 0.7 kcal mol^{-1} at 25 °C (Scheme 2), corresponding to a factor of *ca.* 4 in rate constant.[15]

Spectroscopic studies are in accord with the notion that the $[Me_2Si]$ *ansa* bridge causes a reduction in the electron density at the tantalum centers in $\{[Me_2Si(C_5Me_4)_2]Ta\}$ complexes as compared with their $[Cp^*_2Ta]$ counterparts. Thus, the ν(CO) stretch of $[Me_2Si(C_5Me_4)_2]Ta(CO)H$ (1887 cm^{-1}) in pentane is substantially greater than that of $Cp^*_2Ta(CO)H$ (1868 cm^{-1}). X-Ray diffraction studies[19] suggest that these spectroscopic differences are a result of the $[Me_2Si]$ *ansa* bridge displacing the cyclopentadienyl groups from their preferred positions with respect to tantalum. For example, the Cp_{cent}–Ta–Cp_{cent} angle in $[Me_2Si(C_5Me_4)_2]Ta(CO)H$ [139.7°] is significantly reduced from that in $Cp^*_2TaH_3$ [148.3°].[20] More importantly, the angle between the ring normals in $[Me_2Si(C_5Me_4)_2]Ta(CO)H$ [131.3°] is reduced to an even greater extent, so that the ring normals lose coincidence with the Ta–Cp_{cent} vectors and there is an increase in the asymmetry of the Ta–Cp interactions.[21] The binding mode thus approaches η^3,η^3-coordination and thereby reduces the electron density transferred to the metal center.

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Notes and references

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10 Rate constants for reaction with C_2H_4 at 90 °C: $[Me_2Si(C_5Me_4)_2]TaH_3$ [9.8(9) × 10^{-4} s^{-1}], $Cp^*_2TaH_3$ [2.5(2) × 10^{-7} s^{-1}]. Rate constants for reaction with CO at 90 °C: $[Me_2Si(C_5Me_4)_2]TaH_3$ [6.1(6) × 10^{-4} s^{-1}], $Cp^*_2TaH_3$ [2.2(2) × 10^{-7} s^{-1}].

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15 For ethylene insertion, $\Delta H^\ddagger$ = 15.49(33) kcal mol^{-1} and $\Delta S^\ddagger$ = −2.60(10) cal mol^{-1} K^{-1} corresponding to k_{ins} = 1.83 × 10^3 s^{-1} and $\Delta G^\ddagger$ = 16.44 kcal mol^{-1} at 100 °C. For inversion, $\Delta H^\ddagger$ = 17.96(24) kcal mol^{-1} and $\Delta S^\ddagger$ = 3.3(8) cal mol^{-1} K^{-1}.

16 Data for $Cp^*_2Ta(\eta^2\text{-}C_2H_4)H$ at 100 °C: k_{ins} = 2.4 s^{-1}; $\Delta G^\ddagger$ = 21.3 kcal mol^{-1}. See ref. 3(*b*).

17 The term ‘inversion’ in this sense is being used to refer to ethylene–hydride site (or alkyl–vacancy) interchange. Since the molecule is not chiral, it is not intended to refer to enantiomer interconversion.

18 See, for example: C. P. Casey, M. A. Fagan and S. L. Hallenbeck, *Organometallics*, 1998, **17**, 287 and references therein.

19 See supplementary data for the structures of $[Me_2Si(C_5Me_4)_2]Ta(CO)H$, $[Me_2Si(C_5Me_4)_2]Ta(\eta^2\text{-}C_2H_4)H$, and $Cp^*_2TaH_3$. The C_2H_4 and hydride ligands of $[Me_2Si(C_5Me_4)_2]Ta(\eta^2\text{-}C_2H_4)H$ are statistically disordered about a crystallographic mirror plane that lies in the Cp_{cent}–Ta–Cp_{cent} plane. CCDC 182/1209. See http://www.rsc.org/suppdata/cc/1999/887/ for crystallographic files in .cif format.

20 Cp_{cent}–Ta–Cp_{cent} = 148.3°; Cp_{norm}/Cp_{norm} = 148.2°.

21 Individual Ta–C_{Cp} bond lengths for $[Me_2Si(C_5Me_4)_2]Ta(CO)H$ range from 2.32 Å to 2.45 Å. The difference between the Cp_{cent}–Ta–Cp_{cent} angle and the angle between the ring normals is 8.2° for $[Me_2Si(C_5Me_4)_2]Ta(CO)H$, but only 0.1° for $Cp^*_2TaH_3$.

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