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Communications

The *Ansa* Effect in Permethylmolybdenocene Chemistry: A $[Me_2Si]$ *Ansa* Bridge Promotes Intermolecular C−H and C−C Bond Activation

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Summary: Access to the $[Me_2Si]$ ansa-bridged permethylmolybdenocene system is provided by the synthesis of $[Me_2Si(C_5Me_4)_2]MoCl_2$ from the reaction of $MoCl_5$ with a mixture of $[Me_2Si(C_5Me_4)_2]Li_2$ and $NaBH_4$, followed by treatment with $CHCl_3$. Comparison with the chemistry of the non-ansa $Cp^*{}_2MoX_2$ system indicates that incorporation of the $[Me_2Si]$ ansa bridge promotes intermolecular C−H and C−C bond activation reactions.

Recent studies have demonstrated that the incorporation of an *ansa* bridge may have a profound influence on the chemistry of a metallocene system.[1] We are particularly interested in delineating the origin of these effects by studying well-defined permethylated[2] *ansa* metallocene complexes, $[A(C_5Me_4)_2]MX_n$. For example, we recently demonstrated that the $[Me_2Si]$ *ansa* bridge in $[Me_2Si(C_5Me_4)_2]ZrX_2$ derivatives creates more electrophilic metal centers than those in $Cp^*{}_2ZrX_2$ counterparts.[3] In this paper, we report that incorporation of the $[Me_2Si]$ *ansa* bridge into the permethylmolybdenocene system promotes intermolecular C−H and C−C bond activation reactions.

Access to the $[Me_2Si]$ *ansa*-bridged permethylmolybdenocene system is conveniently provided by the synthesis of $[Me_2Si(C_5Me_4)_2]MoCl_2$ via reaction of $MoCl_5$ with a mixture of $[Me_2Si(C_5Me_4)_2]Li_2$ and $NaBH_4$, followed by treatment with $CHCl_3$ (Scheme 1).[4,5] $[Me_2Si(C_5Me_4)_2]MoCl_2$ is a useful precursor for other derivatives. Thus, reaction of $[Me_2Si(C_5Me_4)_2]MoCl_2$ with MeLi and $LiAlH_4$ yields $[Me_2Si(C_5Me_4)_2]MoMe_2$ and $[Me_2Si(C_5Me_4)_2]MoH_2$, respectively, while Na(Hg) reduction in the presence of CO and C_2H_4 yields $[Me_2Si(C_5Me_4)_2]Mo(CO)$ and $[Me_2Si(C_5Me_4)_2]Mo(C_2H_4)$, respectively (Scheme

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(1) For leading reports describing differences in the chemistry of *ansa* and non-*ansa* systems, see: (a) Conway, S. L. J.; Dijkstra, T.; Doerrer, L. H.; Green, J. C.; Green, M. L. H.; Stephens, M. L. H. *J. Chem. Soc., Dalton Trans.* **1998**, 2689−2695. (b) Labella, L.; Chernega, A.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1995**, 395−402. (c) Chernega, A.; Cook, J.; Green, M. L. H.; Labella, L.; Simpson, S. J.; Souter, J.; Stephens, A. H. H. *J. Chem. Soc., Dalton Trans.* **1997**, 3225−3243 and references therein. (d) Wochner, F.; Brintzinger, H. H. *J. Organomet. Chem.* **1986**, *309*, 65−75. (e) Smith, J. A.; Brintzinger, H. H. *J. Organomet. Chem.* **1981**, *218*, 159−167. (f) Dorer, B.; Diebold, J.; Weyand, O.; Brintzinger, H. H. *J. Organomet. Chem.* **1992**, *427*, 245−255. (g) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828−1838 and references therein.

(2) Our reason for studying permethylated *ansa*-metallocenes is associated with the fact that such substitution frequently allows isolation of complexes that have no counterparts in the corresponding unsubstituted cyclopentadienyl system. For reviews of heavily substituted cyclopentadienyl ligands, see: (a) Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291−393. (b) Okuda, J. *Top. Curr. Chem.* **1991**, *160*, 97−145.

(3) Lee, H.; Desrosiers, P. J.; Guzei, I.; Rheingold, A. L.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 3255−3256.

(4) The diiodide $[Me_2Si(C_5Me_4)_2]MoI_2$ may also be obtained by treatment of $[Me_2Si(C_5Me_4)_2]MoH_2$ with $(CH_2I)_2$.

(5) The molecular structures of $[Me_2Si(C_5Me_4)_2]MoCl_2$, $[Me_2Si(C_5Me_4)_2]MoI_2$, $[Me_2Si(C_5Me_4)_2]MoMe_2$, $[Me_2Si(C_5Me_4)_2]MoH_2$, $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$, $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C_2H_4)$, $[Me_2Si(C_5Me_4)_2]Mo(Me)CN$, $[Me_2Si(C_5Me_4)_2]Mo(CO)$, $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}Bu^tCN)$, and $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}Bu^tCP)$ have been determined by X-ray diffraction. See the Supporting Information.

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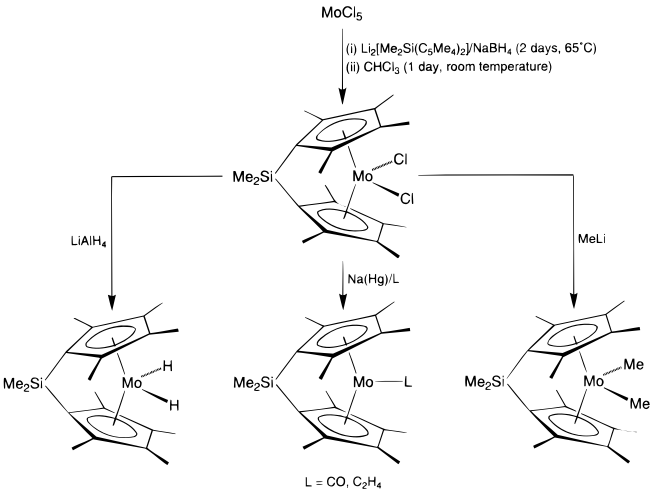
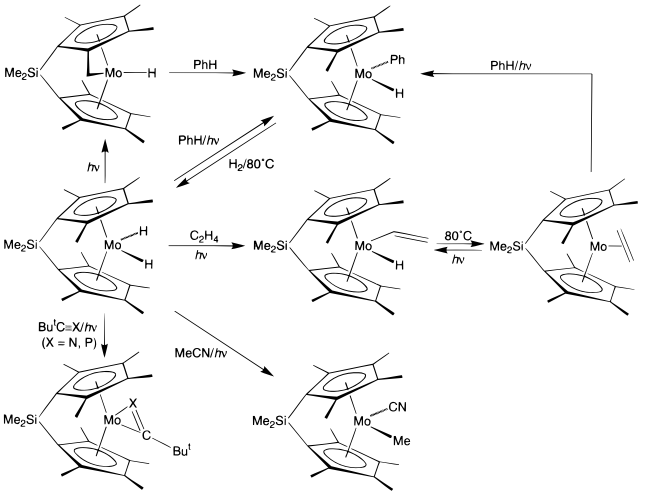
Scheme 1



Scheme 2



1).[5] The dihydride is of particular interest to the present study, since it is capable of participating in a variety of C−H bond activation reactions (Scheme 2). For example, photolysis of $[Me_2Si(C_5Me_4)_2]MoH_2$ in the presence of C_6H_6 cleanly gives the phenyl hydride complex $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$, which has been structurally characterized by X-ray diffraction (Figure 1).[5] While the formation of a phenyl hydride complex itself is not unprecedented,[1b] it is most remarkable in the sense that the corresponding reaction of its non-*ansa* counterpart, $Cp^*_2MoH_2$,[6] does *not* result in *intermolecular* C−H bond activation: thus, photolysis of $Cp^*_2MoH_2$ in benzene yields only a product of *intramolecular* C−H bond activation, namely $Cp^*(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)MoH$.[7]

Interestingly, the *ansa* analogue of the latter complex, $[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]MoH$, which may be generated by photolysis of $[Me_2Si(C_5Me_4)_2]MoH_2$ in cyclohexane,[8] reacts thermally with benzene to give the phenyl−hydride complex $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$ (Scheme 2). This observation provides strong evidence that the [Me2Si] *ansa* bridge exerts a *thermodynamic* influence which destabilizes the product of intramolecular C−H bond activation relative to that of intermolecular C−H bond activation.[9]

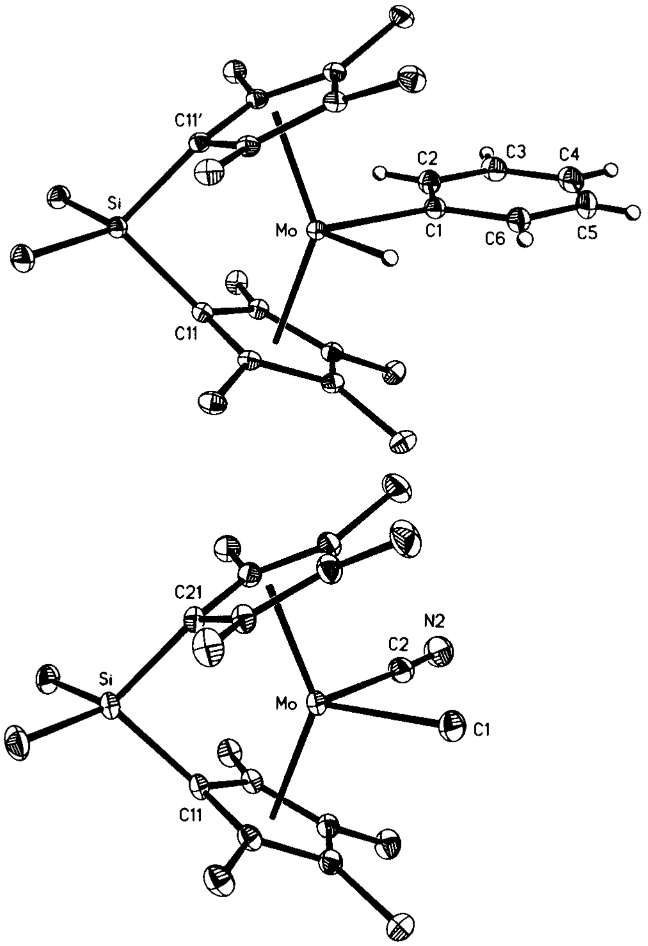


Figure 1. Molecular structures of $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$ (upper) and $[Me_2Si(C_5Me_4)_2]Mo(Me)CN$ (lower).

A further example which demonstrates that the [Me2Si] *ansa* bridge promotes intermolecular C−H bond activation is provided by photolysis of $[Me_2Si(C_5Me_4)_2]MoH_2$, in the presence of C_2H_4, to give the vinyl−hydride complex $[Me_2Si(C_5Me_4)_2]Mo(CHCH_2)H$;[10] the latter reaction is, however, complicated by thermal equilibration with the olefin adduct, $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}CH_2CH_2)$ (Scheme 2).[11] Under comparable conditions, $Cp^*_2MoH_2$ is inert to reaction with the C−H bonds of C_2H_4 and yields only the product of intramolecular metalation, $Cp^*(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)MoH$.

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(6) $Cp^*_2MoH_2$ is prepared by a modification of the literature method. See: Thomas, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 1838−1848.

(7) The formation of $Cp^*(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)MoH$ by photolysis of $Cp^*_2MoH_2$ in cyclohexane has been previously described. See: Cloke, F. G. N.; Day, J. P.; Green, J. C.; Morley, C. P.; Swaim, A. C. *J. Chem. Soc., Dalton Trans.* **1991**, 789−796.

(8) $[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]MoH$ has not been isolated due to the ease of its reversible reaction with H_2, and has only been spectroscopically characterized.

(9) The data available at present do not allow us to comment on the relative kinetic preferences of inter- and intramolecular C−H bond activation reactions of the *ansa* and non-*ansa* systems, although it is possible that the ratio of the rates of inter- to intramolecular C−H bond activation for $\{[Me_2Si(C_5Me_4)_2]Mo\}$ is greater than that for $[Cp^*_2Mo]$.

(10) Furthermore, $[Me_2Si(C_5Me_4)_2]MoH_2$ reacts photochemically with C_2H_2 to give a mixture of spectroscopically characterized $[Me_2Si(C_5Me_4)_2]Mo(CCH)H$ and $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C_2H_2)$, but under comparable conditions $Cp^*_2MoH_2$ yields only $Cp^*(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)MoH$.

(11) For a discussion of the factors which influence the interconversion of olefin and vinyl−hydride complexes, see: (a) Jiménez-Cataño, R.; Niu, S.; Hall, M. B. *Organometallics* **1997**, *16*, 1962−1968 and references therein. (b) Siegbahn, P. E. M.; Blomberg, M. R. A.; Svensson, M. *J. Am. Chem. Soc.* **1993**, *115*, 1952−1958.

In addition to C−H bond activation, $[Me_2Si(C_5Me_4)_2]MoH_2$ is also capable of C−C bond activation. Specifically, photolysis of $[Me_2Si(C_5Me_4)_2]MoH_2$ in the presence of CH_3CN yields the methyl−cyanide complex $[Me_2Si(C_5Me_4)_2]Mo(Me)CN$;[12,13] as with the aforementioned reactions with C_6H_6 and C_2H_4, $Cp^*{}_2MoH_2$ exhibits no reactivity toward MeCN and yields only $Cp^*(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)MoH$. The methyl−cyanide complex $[Me_2Si(C_5Me_4)_2]Mo(Me)CN$ has been structurally characterized by X-ray diffraction (Figure 1), and the cyanide ligand is spectroscopically characterized by a signal at 156.0 ppm in the ^{13}C NMR spectrum and an absorption at 2094 cm^{-1} in the IR spectrum.

The ability of the *ansa* system to cleave the C−C bond in MeCN is of 2-fold interest. Firstly, C−C bond activation has long been recognized to be more difficult to achieve than C−H bond activation;[14] indeed, while C−H bond activation of MeCN yielding the cyanomethyl−hydride complex $L_nM(CH_2CN)H$ is well-documented,[15,16] we are not aware of any reports of isolation of methyl−cyanide derivatives $L_nM(Me)CN$ by cleavage of the C−C bond.[17−20] Secondly, neither C−H nor C−C bond cleavage has been observed for the parent molybdenocene and tungstenocene systems, which react with acetonitrile to give only η^2-MeCN adducts, $Cp_2M(\eta^2\text{-}MeCN)$.[21] An η^2-RCN complex for the *ansa* system, however, has been isolated by the use of a bulky substituent. Thus, photolysis of $[Me_2Si(C_5Me_4)_2]MoH_2$ in the presence of Bu^tCN yields $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}Bu^tCN)$. Furthermore, the analogous η^2-phosphaalkyne complex, $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}Bu^tCP)$,[22] is obtained by photolysis of $[Me_2Si(C_5Me_4)_2]MoH_2$ in the presence of Bu^tCP.[23]

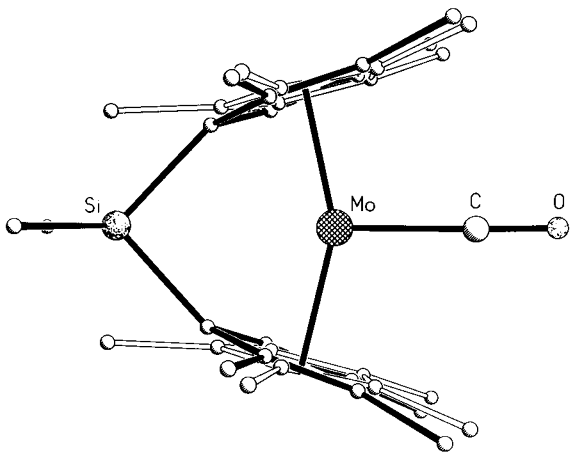

Figure 2. Superposition of the molecular structures of $[Me_2Si(C_5Me_4)_2]Mo(CO)$ and $Cp^*{}_2Mo(CO)$.

Although the aforementioned observations indicate that the *ansa* bridge promotes intermolecular C−X bond (X = H, C) activation, thermally induced elimination of benzene from $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$ is, nevertheless, kinetically facile, as indicated by exchange with C_6D_6 and by reaction with H_2 to give $[Me_2Si(C_5Me_4)_2]MoH_2$.[24] Evidence that these reactions proceed via a reductive-elimination pathway, as opposed to a mechanism involving direct abstraction of a ring methyl hydrogen atom, includes the observation that elimination of benzene from $[Me_2Si(C_5Me_4)_2]Mo(C_6D_5)D$ gives C_6D_6, rather than C_6D_5H.[25,26] Accordingly, the kinetics of the reductive elimination of PhH from $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$, as judged by exchange with C_6D_6, are first order and are independent of $[C_6D_6]$.[27]

The ability of $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$ to undergo reductive elimination of benzene is also noteworthy, since Green has demonstrated that the $[Me_2C]$ *ansa* bridge in $[Me_2C(C_5H_4)_2]W(R)H$ completely inhibits loss

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(12) Small quantities of a complex which may be tentatively identified as the η^2-MeCN adduct $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}MeCN)$ are also formed, but this product has only been characterized by ^1H NMR spectroscopy.

(13) A reviewer has questioned the use of the term "intermolecular" to describe the C−C bond activation reaction between $[Me_2Si(C_5Me_4)_2]MoH_2$ and Me-CN, suggesting that the *initial* interaction of MeCN with photochemically generated $\{[Me_2Si(C_5Me_4)_2]Mo\}$ may not involve C−C bond activation: possible initial steps include (i) formation of the η^2-MeCN adduct, $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}MeCN)$, and (ii) formation of $[Me_2Si(C_5Me_4)_2]Mo(CH_2CN)H$ by C−H bond activation. While we agree that it is possible for the initial interaction not to involve C−C bond cleavage, so that the activation step may be intramolecular, we nevertheless feel that it is appropriate to describe the overall reaction as intermolecular.

(14) For examples of C−C bond activation reactions, see: (a) Wick, D. D.; Northcutt, T. O.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4484−4492. (b) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406−12415. (c) Liou, S.-Y.; Van der Boom, M. E.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1998**, 687−688. (d) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699−701. (e) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1986**, *108*, 4679−4681. (f) Suggs, J. W.; Jun, C.-H. *J. Chem. Soc., Chem. Commun.* **1985**, 92−93. (g) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. **1986**, *108*, 7222−7227. (h) Suzuki, H.; Takaya, Y.; Takemori, T.; Tanaka, M. *J. Am. Chem. Soc.* **1994**, *116*, 10779−10780.

(15) For example, $(dmpe)_2M(Np)H$ (M = Fe, Ru; Np = 2-naphthyl)[15a] and $[(R_3P)_4Ir]^+$ [15b] react with MeCN to give $(dmpe)_2Fe(CH_2CN)H$ and $[(R_3P)_4Ir(CH_2CN)H]^+$, respectively: (a) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577−7585. (b) English, A. D.; Herskovitz, T. *J. Am. Chem. Soc.* **1977**, *99*, 1648−1649.

(16) C−H bond activation reactions of MeCN involving σ-bond metathesis pathways are also known. For example, $Cp^*{}_2LnCH(SiMe_3)_2$ reacts with MeCN to give $[Cp^*{}_2Ln(CH_2CN)]_2$ (Ln = La, Ce). See: Heeres, H. J.; Meetsma, A.; Teuben, J. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 420−422.

(17) In this regard, the reactions of $\{(Cy_3P)_2Ni\}$ with RCN (R = Me, Et, Pr, Ph) have been suggested to generate $(Cy_3P)_2Ni(R)CN$, but the products were unstable and could not be isolated. See: (a) Morvillo, A.; Turco, A. *J. Organomet. Chem.* **1981**, *208*, 103−113. (b) Favero, G.; Morvillo, A.; Turco, A. *Gazz. Chim. Ital.* **1979**, *109*, 27−28.

(18) Aryl−cyanide complexes have, however, been obtained via oxidative addition. For example, $(Et_3P)_3Pt$ reacts with PhCN to give $(Et_3P)_2Pt(Ph)CN$,[18a] and $(Et_3P)_4M$ (M = Ni, Pd, Pt) reacts with ArCN (Ar = C_6H_4F) to give *trans*-$(Et_3P)_2M(Ar)CN$.[18b] Furthermore, an early example of C−CN bond cleavage was reported for $MeC(CN)_3$:[18c] (a) Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543−3544. (b) Parshall, G. W. *J. Am. Chem. Soc.* **1974**, *96*, 2360−2366. (c) Burmeister, J. L.; Edwards, L. M. *J. Chem. Soc. A* **1971**, 1663−1666.

(19) While not a simple oxidative-addition reaction, thermolysis of the alkylcyanide complexes $Cp_3U(NCR)$ (R = Me, Pr^n, Pr^i, Bu^t) has been reported to give a mixture of Cp_3UCN and Cp_3UR. See: Adam, R.; Villiers, C.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1993**, *445*, 99−106.

(20) For a review of the chemistry of coordinated RCN complexes, see: Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299−338.

(21) (a) Wright, T. C.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 2017−2019. (b) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897−3908.

(22) For recent reviews on phosphaalkyne complexes, see: (a) Nixon, J. F. *Chem. Soc. Rev.* **1995**, 319−328. (b) Nixon, J. F. *Coord. Chem. Rev.* **1995**, *145*, 201−258.

(23) A sample of Bu^tCP was kindly provided by Professor F. G. N. Cloke.

(24) In contrast, dissociation of C_2H_4 does not occur thermally but is observed to occur photochemically (Scheme 2).

(25) Elimination of C_6D_6 was demonstrated by mass spectroscopic investigation of the product of exchange between $[Me_2Si(C_5Me_4)_2]Mo(C_6D_5)D$ and C_6H_6.

(26) Furthermore, ^1H and ^{13}C NMR spectroscopy demonstrates that reaction of $[Me_2Si(C_5Me_4)_2]Mo(C_6H_5)H$ with D_2 in C_6D_{12} yields $[Me_2Si(C_5Me_4)_2]MoD_2$ and C_6H_6.

(27) The activation parameters over the range 40−90 °C are $\Delta H^\ddagger = 27.3(2)$ kcal mol^{-1} and $\Delta S^\ddagger = -2(1)$ eu.

of alkane.[1a,b] The origin of this kinetic barrier to reductive elimination has been attributed to geometrical constraints of the [Me_2C] bridge preventing the metallocene fragment from adopting a parallel configuration.[28] As such, the difference between the [Me_2Si] and [Me_2C] *ansa*-bridged systems is most likely attributed to the larger size of silicon, which relaxes the geometrical constraints of the bridge. The [Me_2Si] *ansa* bridge does, nevertheless, exert a subtle structural influence, with the cyclopentadienyl groups being forced to tilt such that the ring normals lose coincidence with the Mo−Cp_{cent} vector, as illustrated by comparison of the carbonyl complexes (Figure 2). For example, the difference between the Cp_{cent}−Mo−Cp_{cent} angle and the angle between the ring normals is 6.0° for [$Me_2Si(C_5Me_4)_2$]Mo(CO) but only 0.6° for Cp^*_2Mo(CO). Such perturbation presumably reduces the degree of electron donation to the Mo center in the *ansa* system, analogous to that observed for the related zirconium system.[3] In accord with this notion, the ν(CO) stretching frequency for [$Me_2Si(C_5Me_4)_2$]Mo(CO) (1900 cm^{-1}) is higher than that in Cp^*_2Mo(CO) (1890 cm^{-1}).[29,30]

In summary, a [Me_2Si] *ansa* bridge promotes intermolecular C−H and C−C bond activation reactions in permethylmolybdenocene chemistry, as evidenced by the photochemical reactivity of [$Me_2Si(C_5Me_4)_2$]MoH_2 toward C_6H_6 and MeCN.

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Supporting Information Available: Text and tables giving experimental details and spectroscopic data and tables and figures giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[28] Green, J. C.; Jardine, C. N. *J. Chem. Soc., Dalton Trans.* **1998**, 1057−1061.

[29] Shin, J. H.; Parkin, G. Unpublished results.

[30] For comparison, the ν(CO) stretching frequencies in the chromium complexes [$Me_2Si(C_5Me_4)_2$]Cr(CO) (1876 cm^{-1}) and Cp^*_2Cr(CO) (1857 cm^{-1}) show a similar trend. See: Schaper, F.; Rentzsch, M.; Prosenc, M.-H.; Rief, U.; Schmidt, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1997**, *534*, 67−79.