Attack by Allenes on a Bridging Alkylidyne Ligand at a Ditungsten Centre: Formation of a Bridging Allyl-η^3-W^1,σ-W^2-alkylidene Ligand

Malcolm H. Chisholm,* Kirsten Folting, Joseph A. Heppert, and William E. Streib

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405, U.S.A.

The alkylidyne bridged compounds $[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2$ (**1**), $[(Me_3SiCH_2)(Bu^tO)W(\mu\text{-}CSiMe_3)]_2$ (**2**), and $[(Pr^iO)_2W(\mu\text{-}CSiMe_3)]_2$ (**3**) each react with allenes $R^1CH{=}C{=}CHR^2$, where $R^1 = R^2 = H$, Me or R^1 = Me, Ph and R^2 = H, to give, by C–C bond formation between the tertiary carbon atom of the allene and the bridging carbon atom of one of the μ-CSiMe$_3$ ligands, a bridging ligand which is formally a π-allyl to one tungsten atom and a terminal alkylidene to the other; the rate of reaction follows the order (**1**) > (**2**) > (**3**); $CH_2{=}C{=}CH_2 \geqslant RCH{=}C{=}CH_2 > RCH{=}C{=}CHR$, and the C–C bond formation is stereoselective.

There is current interest in the chemical reactivity of bridging hydrocarbon ligands in part because μ-CR and μ-CR$_2$ ligands may represent soluble models for reactive intermediates in heterogeneous catalytic processes and also because their reactivity may differ with respect to the chemistry of the terminal (σ) bound moieties.[1] Within this context we have initiated a study of the reactivity of 1,3-dimetallacyclobutadienes which may be supported by a variety of ligands and have different d^n–d^n configurations at the metal centres.[2—5] We describe here reactions between $W_2(\mu\text{-}CSiMe_3)_2$, d^1–d^1, containing compounds and allenes which proceed to generate, by C–C bond formation, a new type of bridging hydrocarbyl ligand.

In hydrocarbon solutions $[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2$ (**1**),

$[(Me_3SiCH_2)(Bu^tO)W(\mu\text{-}CSiMe_3)]_2$ (**2**), which may be isolated as *syn*- and *anti*-isomers, and $[(Pr^iO)_2W(\mu\text{-}CSiMe_3)]_2$ (**3**) react with allenes $R^1CH{=}C{=}CHR^2$ to give compounds containing a $W_2(\mu\text{-}CSiMe_3)[\mu\text{-}R^1CH(R^2CH)CCSiMe_3]$ moiety where $R^1 = R^2 = H$ or Me or R^1 = Me or Ph and R^2 = H. The relative rate of reaction follows the order (**1**) > (**2**) > (**3**) and allene $\geqslant$ $RCH{=}C{=}CH_2 > RCH{=}C{=}CHR$. The reaction between (**1**) and allene is rapid even at −50 °C while the analogous reaction employing (**3**) proceeds only over several days at room temperature. In the case of reactions employing (**3**) a second addition (insertion) of allene occurs at comparable rate to the first addition.

$[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2$
(**1**)

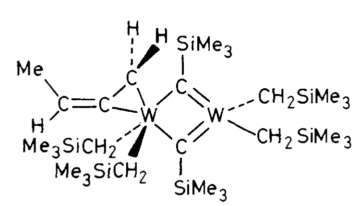
$[(Me_3SiCH_2)(Bu^tO)W(\mu\text{-}CSiMe_3)]_2$
(**2**)

$[(Pr^iO)_2W(\mu\text{-}CSiMe_3)]_2$
(**3**)

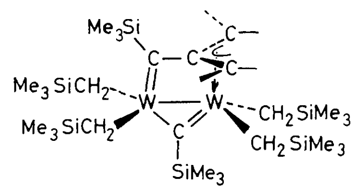
Studies of the reaction between (**1**) and MeCH=C=CHMe reveal the initial formation at −20 °C of an intermediate, whose n.m.r. spectroscopic properties are consistent with a 1 : 1 π-complex of the type shown in (**4**). This would be analogous to the structurally characterized 1 : 1 adduct involving (**1**) and PhC≡CMe which is formed prior to insertion into a $\mu\text{-}CSiMe_3$ ligand.[6] In this regard, the reactions involving alkynes and allenes with compounds (**1**)—(**3**) are probably related and require the d^1–d^1 centre since adduct formation is tantamount to an asymmetric oxidative-addition to the dinuclear centre. No similar reactions occurred between allenes and analogous tantalum d^0–d^0 compounds.[3]

The products of allene addition to one of the $\mu\text{-}CSiMe_3$ ligands are air-sensitive, extremely hydrocarbon-soluble, waxy solids and only one example of a crystalline derivative has yielded to single crystal *X*-ray studies.† The molecular structure of the product of the reaction between (**1**) and $MeCH{=}C{=}CH_2$ is shown in Figure 1. The ^1H and ^{13}C n.m.r. data for the other compounds leave no doubt that they are structurally related.‡ In particular for each compound there is one alkylidyne $\mu\text{-}CSiMe_3$ resonance at δ *ca.* 350 with coupling to two different ^{183}W nuclei, *J* (W^1–C) *ca.* 110 Hz and *J*(W^2–C) *ca.* 90 Hz, and one alkylidene carbon resonance at δ *ca.* 240 which shows coupling to only one type of ^{183}W atom. All of the addition compounds have the common template shown in the valence bond description (**5**).

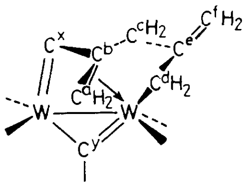
Reactions employing $CH_2{=}C{=}CH_2$ generate molecules having a mirror plane containing the W–W axis while reactions employing $RCH{=}C{=}CH_2$ give molecules with no element of symmetry. This is easily determined by an examination of the ^1H n.m.r. signals associated with the other ligands.



(**4**)



(**5**)



(**6**)

Rather interestingly reactions employing $MeCH{=}C{=}CH_2$ with (**1**) yield initially the *anti*-isomer of the allyl ligand, *i.e.*, the one found by crystallography and shown in Figure 1. However, with time in solution an equilibrium is established between the *anti*- and *syn*-forms of the allyl ligand.

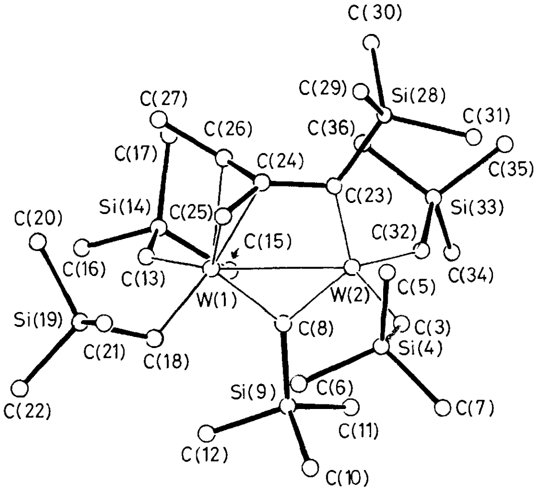


Figure 1. Selected bond distances (Å) and angles (°) for the $(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)[\mu\text{-}MeCH(CH_2)CCSiMe_3]$ molecule: W–W 2.8585(7), W(1)–C(8) 1.918(7), W(2)–C(8) 1.944(7), W(2)–C(23) 1.928(7), W(1)–C(24) 2.275(7), W(1)–C(25) 2.243(5), W(1)–C(26) 2.260(7), W(1)–$C(CH_2SiMe_3)$ 2.13(1) (av.), W(2)–$C(CH_2SiMe_3)$ 2.10(2) (av.), C(23)–C(24) 1.47(1), C(24)–C(25) 1.44(1), C(24)–C(26) 1.41(3); W(1)–C(8)–W(2) 95.5(3), W(1)–W(2)–C(23) 80.8(2), W(2)–C(23)–C(24) 103.1(4), W(2)–C(23)–Si(28) 133.8(4), C(23)–C(24)–C(25) 121.1(7), C(23)–C(24)–C(26) 123.7(7), C(25)–C(24)–C(26) 113.4(7), C(24)–C(26)–C(27) 122.9(7), C(13)–W(1)–C(18) 98.6(3), C(3)–W(2)–C(32) 104.0 (3).

Reactions employing either *anti*- or *syn*-$[(Bu^tO)(Me_3SiCH_2)W(\mu\text{-}CSiMe_3)]_2$ with allene proceed to give a single but different isomer of the addition product implying that the insertion reaction proceeds with either complete retention or inversion of stereochemistry at tungsten. The latter seems most implausible while the former (retention of stereochemistry at tungsten) is understandable if the addition–insertion of allene is faster than a pseudorotation about W^1 in the proposed intermediate π-complex (**4**).

Reaction between (**3**) and allene (>2 equiv.) yields a compound lacking a plane of symmetry but retaining one $\mu\text{-}CSiMe_3$ ligand. Based on n.m.r. data the most likely

---

† *Crystal data* for $(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)[\mu\text{-}MeCH(CH_2)CCSiMe_3]$ at −158 °C: monoclinic, *a* = 12.367(3), *b* = 11.036(3), *c* = 30.502(10) Å, β = 93.59(2)°, D_c = 1.501 g cm^{-3}, *Z* = 4, space group $P2_1/c$. All atoms except hydrogens were refined anisotropically. H atoms were included in fixed idealized positions in the full matrix least squares refinement. Present residuals are *R* = 0.031 and R_w = 0.033. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

structure of the product involves formation of the bridging ligand depicted by (**6**).‡ This is related to (**5**) by a formal insertion of an allene molecule into one of the methylene groups of the allyl ligand.

While addition to the central carbon atoms of allenes is a well documented route to π-allyl ligands in mononuclear complexes,[7] the attack on a bridging alkylidyne seen in this work provides with a new twist the generation of both π-allyl and alkylidene functionalities at a dinuclear centre.

We thank the National Science Foundation, the donors of the Petroleum Research Fund administered by the American Chemical Society and the Wrubel Computing Center for support.

Received, 17th July 1985; Com. 1045

---

‡ N.m.r. data for representative addition compounds: *anti*-$W_2[\mu\text{-}(CH_2)(CHMe)CC(SiMe_3)](\mu\text{-}CSiMe_3)(CH_2SiMe_3)_4$, ^{1}H ($CD_3C_6D_5$, 23 °C) δ 4.23 [1H, m, *J* (H^b–H^x) 2.9 Hz, $\mu\text{-}(CH^b\mathit{H}^x)(CH^aMe)CC(SiMe_3)$], 2.56 [1H, qd, *J* ($H^a$–$H^b$) 2.8 Hz, *J* ($H^a$–Me) 6.5 Hz, $\mu\text{-}(CH^bH^x)(C\mathit{H}^aMe)CC(SiMe_3)$], 1.95 [1H, dd, *J* ($H^a$–$H^b$) 2.8 Hz, ($H^b$–$H^x$) 2.9 Hz, $\mu\text{-}(C\mathit{H}^bH^x)(CH^aMe)CC(SiMe_3)$], 1.44 [3H, d, *J* ($H^a$–Me) 6.5 Hz, $\mu\text{-}(CH^bH^x)(CH^a\mathit{Me})CC(SiMe_3)$], 0.59, 0.58 [9H, s, $\mu\text{-}CSi\mathit{Me}_3$ and $\mu\text{-}(CH^bH^x)(CH^aMe)CC(Si\mathit{Me}_3)$], 0.14, 0.12, 0.08, −0.01 (9H, s, $CH_2Si\mathit{Me}_3$), 0.63, 0.32, 0.30, 0.24, 0.22, 0.19, −0.05, −0.22 (1H, d, J_{HH} 11.5 Hz, $C\mathit{H}_2SiMe_3$); ^{13}C ($CD_3C_6D_5$, 23 °C) δ 326.6 [*J* (^{183}W–^{13}C) 114 and 93 Hz, $\mu\text{-}\mathit{C}SiMe_3$], 238.2 [*J* ($^{183}W$–$^{13}C$) 93 Hz, $\mu\text{-}(CH_2)(CHMe)C\mathit{C}(SiMe_3)$], 85.8 [$\mu\text{-}(CH_2)(CHMe)\mathit{C}C(SiMe_3)$], 62.3, 51.7 [$\mu\text{-}(\mathit{C}H_2)(\mathit{C}HMe)CC(SiMe_3)$], 69.6, 64.8, 60.6, 55.8 ($\mathit{C}H_2SiMe_3$), 19.9 [$\mu\text{-}(CH_2)(CH\mathit{Me})CC(SiMe_3)$], 3.2, 3.2, 3.1, 2.2, 1.6, 0.2 [$CH_2Si\mathit{Me}_3$, $\mu\text{-}CSi\mathit{Me}_3$, $\mu\text{-}(CH_2)(CHMe)CC(Si\mathit{Me}_3)$].

$W_2[\mu\text{-}(CH_2)_2CC(SiMe_3)](\mu\text{-}CSiMe_3)(CH_2SiMe_3)_4$, ^{1}H (C_6D_6, 23 °C) δ 3.33 [2H, s, *anti*-$\mu\text{-}(C\mathit{H}^aH^b)_2CC(SiMe_3)$], 1.77 [2H, s, *syn*-$\mu\text{-}(CH^a\mathit{H}^b)_2CC(SiMe_3)$], 0.63, 0.58 [9H, s, $\mu\text{-}CSi\mathit{Me}_3$, $\mu\text{-}(CH_2)CC(Si\mathit{Me}_3)$], 0.08, 0.00 (18H, s, $CH_2Si\mathit{Me}_3$), 0.41, 0.17, 0.03, −0.40 (2H, d, J_{HH} 11.8 Hz, $C\mathit{H}_2SiMe_3$); ^{13}C (C_6D_6, 23 °C) δ 323.4 [*J*(^{183}W–^{13}C) 110.1 and 90.8 Hz, $\mu\text{-}\mathit{C}SiMe_3$], 234.5 [*J*($^{183}W$–$^{13}C$) 83.1 Hz, $\mu\text{-}(CH_2)_2C\mathit{C}(SiMe_3)$], 84.1 [$\mu\text{-}(CH_2)_2\mathit{C}C(SiMe_3)$], 63.6, 63.4 ($\mathit{C}H_2SiMe_3$), 54.8 [$\mu\text{-}(\mathit{C}H_2)CC(SiMe_3)$], 3.2, 2.8 ($CH_2Si\mathit{Me}_3$), 1.4, 0.2 [$\mu\text{-}CSi\mathit{Me}_3$, $\mu\text{-}(CH_2)_2CC(Si\mathit{Me}_3)$].

$W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4\cdot(MeCH{=}C{=}CHMe)$ (intermediate allene adduct), ^{1}H (partial, Me_3Si region; $CD_3C_6D_5$, −20 °C) δ 0.58, 0.32, 0.19, 0.14, 0.11, 0.16 (9H, s, $CH_2Si\mathit{Me}_3$, $\mu\text{-}CSi\mathit{Me}_3$).

$W_2[\mu\text{-}(C^fH_2)(C^dH_2)C^e(C^cH_2)(C^aH_2)C^bC^y(SiMe_3)](\mu\text{-}C^xSiMe_3)(OPr^i)_4$, letter superscripts refer to structure (**6**), ^{13}C (partial, $CD_3C_6D_5$, 23 °C) δ 306 (C^x), 161 (C^y), 111.5 (C^b), 106.9 [C^a, dd, *J* (^{13}C–^{1}H) 154 Hz], 69.4 [C^d, dd, *J* (^{13}C–^{1}H) 121.9 Hz], 65.6 (C^e), 62.4 [C^f, dd, *J* (^{13}C–^{1}H) 144.3 Hz], 38.2 [C^c, dd, *J* (^{13}C–^{1}H) 142.6 Hz].

References

1 J. Holton, M. F. Lappert, R. Pearce, and P. I. W. Yarrow, *Chem. Rev.*, 1983, **83**, 135; W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 159; W. A. A. Van Barneveld and V. Ponec, *J. Catal.*, 1978, **51**, 426; K. M. Motyl, J. R. Norton, C. K. Schauer, and O. P. Anderson, *J. Am. Chem. Soc.*, 1982, **104**, 7325; J. Levisalles, H. Rudler, F. Rose-Munch, J. C. Daran, Y. Dromzee, Y. Jearin, D. Ades, and M. Fontanille, *J. Chem. Soc., Chem. Commun.*, 1981, 1055; P. Q. Adams, D. L. Davies, A. F. Dyke, S. A. R. Knox, K. A. Mead, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1983, 222; L. L. Kesmodel, L. H. Dubois, and G. A. Somorjai, *Chem. Phys. Lett.*, 1978, **56**, 267; R. J. Koestner, J. C. Frost, P. C. Stair, M. A. Van Hove, and G. A. Somorjai, *Surf. Sci.*, 1982, **116**, 85; P. J. Fagan and C. P. Casey, *J. Am. Chem. Soc.*, 1982, **104**, 4950; C. P. Casey, W. H. Miles, R. J. Fagan, and K. J. Haller, *Organometallics*, 1985, **4**, 559; F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 89.

2 F. Huq, W. Mowat, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1971, 1477 (Ta^V–Ta^V, d^0–d^0).

3 R. A. Anderson, A. L. Gayler, and G. Wilkinson, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 609 (W^V–W^V, d^1–d^1).

4 M. H. Chisholm, F. A. Cotton, M. W. Extine, and C. A. Murillo, *Inorg. Chem.*, 1978, **17**, 696; 1976, **15**, 2252 (W^V–W^V, d^1–d^1).

5 M. Bochmann, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, and K. M. Abdul-Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 1797 (Re^V–Re^V, d^2–d^2).

6 M. H. Chisholm, J. A. Heppert, and J. C. Huffman, *J. Am. Chem. Soc.*, 1985, **107**, 5116; 1984, **106**, 1151.

7 J. P. Collman and L. S. Hegedus in 'Principles and Applications of Organotransition Metal Chemistry,' University Science Books, Mill Valley, CA 1980, p. 137; M. H. Chisholm and W. S. Johns, *Inorg. Chem.*, 1975, **14**, 1189.