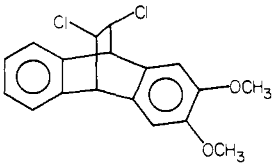
uncharacterizable materials). Thus these cyclopropylcarbinyl to homoallyl systems (which are also homobenzyl) also require an anti position relationship between chromophore and nucleofuge.



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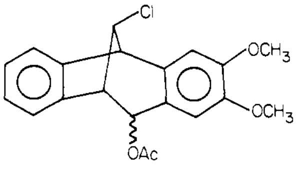

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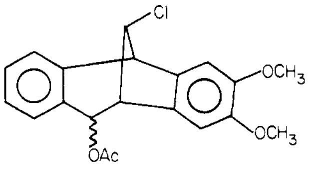

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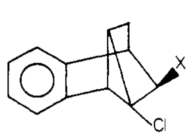

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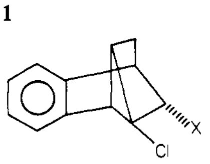

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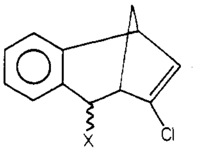
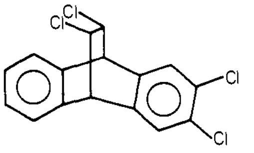


14

Similarly, irradiation of **15** in acetic acid at 285–290 nm (where **6** is transparent) gave [3.2.1] photosolvolysis and photorearrangement products **17**, while the isomeric cis dichloride **16** did not react similarly.



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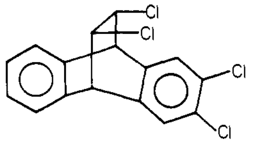

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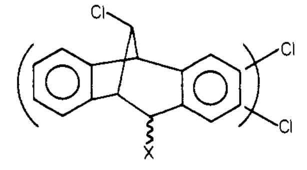

17

These photoreactions, unlike those reported earlier,[1,4] clearly require that the nucleofuge be positioned anti to the chromophoric aromatic ring. Although this is, in a sense, like the stereochemical requirements for similar ground-state reactions,[6,8] anchimeric assistance by the anti ring in the ground-state reaction is accompanied by participation of that ring in the Wagner–Meerwein rearrangement,[8] while in these photochemical reactions, we observe largely migration of the syn ring. We envisage the "anti" activation as an intramolecular electron transfer[1,4,9] which occurs from the excited (π–π^*) state of the aromatic ring to the σ^* orbital of the carbon–nucleofuge bond[10,11] to give a zwitterionic diradical. The mode by which this species decays to an ion pair with predominant syn migration of the unactivated ring or with ring opening of the cyclopropyl ring in **12** to give the observed products remains unclear.

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(8) Cristol, S. J.; Kochansky, M. C. *J. Org. Chem.* **1975**, *40*, 2171.

(9) Lin, C.-I.; Singh, P.; Ullman, E. F. *J. Am. Chem. Soc.* **1976**, *98*, 6711.

(10) Examination of molecular models shows that the σ^* orbital is close to the π system of the anti aromatic ring.

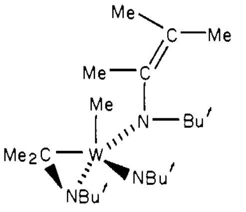
(11) Another possibility is that the activating electron occupies an orbital which combines the overlapping π^* and σ^* orbitals.

Reaction of *tert*-Butyl Isocyanide with Hexamethyltungsten. Synthesis and X-ray Crystal Structure of $\overline{\mathrm{WN(Bu^{t})C}}\mathrm{Me_2(Me)(NBu^{t})\{N(BU^{t})(CMe{=}CMe_2)\}}$

Sir:

Isocyanides are known to insert into transition-metal–alkyl bonds to give acylimidoyl, $\mathrm{MC(R){=}NR'}$, metal complexes;[1,2] coupling of the ligands via C–C bond formation between adjacent ligands has also been observed.[1,3] However, there are no reports of reactions in which the C–N bond of the CNR group is cleaved yielding a metal organoimido, M=NR, group[4] with concomitant C–C bond formation between carbon atoms of the CNR groups.

The interaction of hexamethyltungsten[5] in isopentane–diethyl ether at −78 °C with excess *tert*-butyl isocyanide yields yellow air-stable crystals, soluble in petroleum ether of $\overline{\mathrm{WN(Bu^{t})C}}\mathrm{Me_2(Me)(NBu^{t})[N(Bu^{t})(CMe{=}CMe_2)]}$ (**1**). Analytical and spectroscopic data[6] are compatible with the structure determined[7] by X-ray diffraction (Figure 1). The unique five-coordinate tungsten(VI) complex contains $\mathrm{CH_3}$, $\mathrm{NBu^{t}}$, η^2-$\mathrm{NBu^{t}CMe_2}$, and an unusual dialkylamido $\mathrm{N(Bu^{t})(CMe{=}CMe_2)}$ group all bound to tungsten.



1

Although the detailed mechanism of this transfer reaction, which involves transfer of five methyl groups, is not known, it seems reasonable to assume that transfer to coordinated isocyanide leads first to a $\mathrm{WC(Me){=}NBu^{t}}$ group.[1,2] Migration of a second methyl group on to the carbon atom will lead to an azatungsten cyclopropane unit as found in **1** (eq 1).

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(1) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21.

(2) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 2928.

(3) Lam, C. T.; Corfield, P. W. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 619.

(4) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

(5) Galyer, A. L.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 2235.

(6) Calcd: C, 48.18; H, 8.60; N, 8.03. Found: C, 48.28; H, 8.74; N, 8.04. Mp 128–129 °C; mol wt calcd 523, found 520 ± 50 (benzene); ^{1}H NMR ($\mathrm{C_6D_6}$, 250 MHz) δ 1.92 (s, 3 H), 1.87 (s, 3 H), 1.73 (s, 3 H), 1.47 (s, 9 H), 1.46 (s, 9 H), 1.43 (s, 3 H), 1.28 (s, 9 H), 1.25 (s, 6 H). Apart from the Bu^t groups the other peaks in the spectrum cannot be assigned with certainty. However, the two sharp singlets at δ 1.92 and 1.87 may be due to the two nonequivalent $\overline{\mathrm{WNBu^{t}}C}Me_2$ methyls. (A chemical shift of δ 1.88 was assigned to Me in the $\overline{\mathrm{WNEtC}}\mathrm{H}Me$ group of an unisolated $\mathrm{W^{VI}}$ complex.[8])

(7) The structure was solved and refined by using 4069 observed [$I > 1.50(I)$] data (out of 4417 measured) recorded on a Nonius CAD4 diffractometer using Mo Kα radiation. Crystal data are a = 8.829 (2) Å, b = 10.265 (1) Å, c = 14.324 (5) Å, α = 90.87 (2)°, β = 101.47 (2)°, γ = 82.44 (2)°, space group $P\bar{1}$, Z = 2, D_c = 1.38 g cm^{-3}, and μ(Mo Kα) = 43.84 cm^{-1}. R = 0.056 with all nonhydrogen atoms anisotropic.

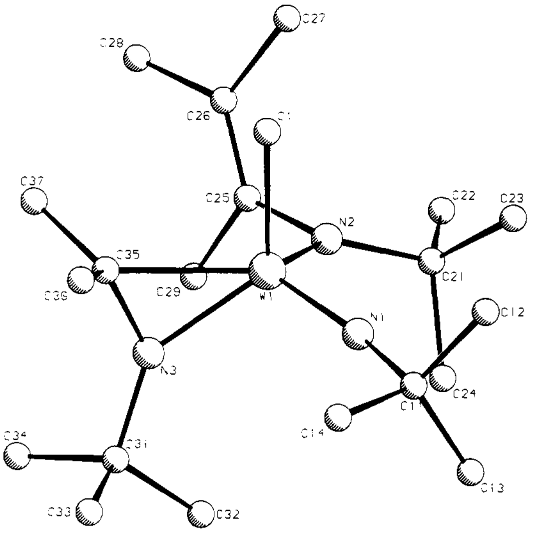
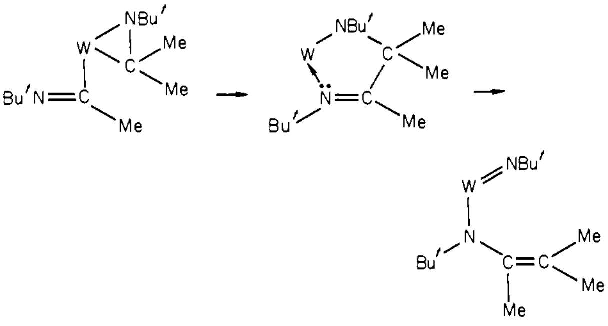


Figure 1. Molecular structure of **1**. Bond lengths (Å) and angles (deg) in the coordination sphere are as follows: W–N(1) = 1.74 (1), W–N(2) = 1.94 (1), W–N(3) = 1.92 (1), W–C(35) = 2.19 (1), W–C(1) = 2.14 (1), W···C(25) = 2.79 (1); N(1)–W–C(1) = 99 (1), N(1)–W–N(2) = 109 (1), N(1)–W–N(3) = 110 (1), N(1)–W–C(35) = 123 (1), N(2)–W–C(1) = 106 (1), N(2)–W–N(3) = 110 (4), N(2)–W–C(35) = 126 (1), N(3)–W–C(35) = 40 (1).

(1)

A similar $\overline{\text{WN(Et)C}}$HMe group has been detected in the reaction products from WCl_6 and $LiNEt_2$.[8] Migration of two methyl groups to coordinated carbon monoxide to give acetone via the acyl has been demonstrated in reactions of CO with $(\eta^6\text{-}C_6H_6)Mo(CO)(PR_3)Me_2$[9] and $CoMe_3(PMe_3)_3$,[10] while $(\eta^5\text{-}C_5Me_5)TaMe_4$ gives an (η^2-acetone)(oxatantallacyclopropane) complex, $(\eta^5\text{-}C_5Me_5)TaMe_2(\eta^2\text{-}OCMe_2)$,[11] which provides an analogue for the η^2-NBu^tCMe_2 group.

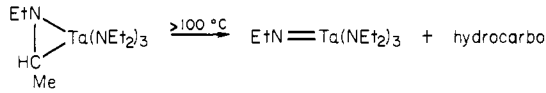
Further methyl transfer to isocyanide and intramolecular rearrangement of adjacent azacyclopropane and $WC(Me){=}NBu^t$ groups with C–C bond formation could then lead to the dialkylamido and *tert*-butylimido groups (eq 2). Note that the



(2)

reaction of $(\eta^5\text{-}C_5Me_5)Me_2Ta(\eta^2\text{-}OCMe_2)$ with a second CO molecule yields a product which appears to contain Ta=O and $TaOC(Me){=}CMe_2$ groups—analogous to the $W{=}NBu^t$ and $WN(Bu^t)C(Me){=}CMe_2$ units found in **1**.[11]

Although thermolysis of an azatantallacyclopropane complex has been reported to yield an organomido group[12] it seems unlikely that a similar process occurs in our case since **1** is formed in high



(3)

yield under mild conditions and no gaseous hydrocarbons are evolved.

Further reaction of two of the remaining WMe groups with 1 mol of Bu^tNC would then give rise to the final $\overline{\text{WC(Me)}_2\text{N}}Bu^t$ group. Steric factors may be responsible for the retention of one WMe group in the molecule which does not react with the excess Bu^tNC present under the reaction conditions employed.

Hexamethyltungsten reacts with CO (3 atm) in isopentane to give $W(CO)_6$ and acetone (NMR, GLC).

Acknowledgment. We thank the S.R.C. (U.K.) for support.

Supplementary Material Available: Tables of fractional coordinates and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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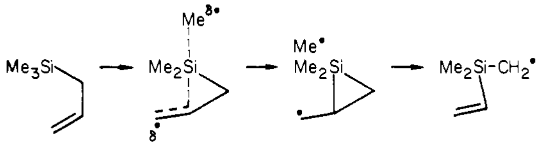
Radical Rearrangements in the Pyrolysis of Allyldisilanes

Sir:

Jones[1] has recently presented surprising evidence that a major mode of thermal decomposition of allyltrimethylsilane, to ultimately afford trimethylvinylsilane, is through direct loss of the methyl radical. As simple homolysis of Si–Me rather than Si–allyl



bonds should not be at all competitive,[2] we would suggest that these results argue for π participation in the loss of methyl radical.

Since the Si–Si bond is almost 10 kcal/mol weaker than the Si–Me bond,[3] alkylsilyl should be a considerably better leaving group than methyl. Thus, in order to favor the formation of the silahomoallyl/silacyclopropylcarbinyl radical, we undertook the thermolysis of 1,2-diallyl-1,1,2,2-tetramethyldisilane (**1**).[4,5] However, we were surprised to find that vacuum-flow pyrolysis of **1** (800° C, 10^{-4} torr, 1-ft quartz-packed horizontal tube) cleanly produces 1,1,3,3-tetramethyl-1,3-disilacyclopentene (**2**)[7] in 51%

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(1) Neider, S. M.; Chambers, G. R.; Jones, M., Jr. *Tetrahedron Lett.* **1979**, 3793.

(2) Assuming that ΔE_{act} for Me· loss vs. C_3H_5· loss is simply $\Delta\Delta H$, then Me· loss would be ~16 kcal/mol > E_{act} for allyl loss. Thus, even at the reported 600 °C, allyl radicals should be produced more than 3000 times faster than methyl radicals. Of course this argument is only necessary if the process is unimolecular. No evidence has been presented to date which rules out a bimolecular origin of trimethylvinylsilane.

(3) Sakurai, H. "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 25.

(4) All starting materials and products reported here were established by both their mass and NMR spectra.

(5) Prepared in 77% yield from the coupling of 1,2-dichlorotetramethyldisilane and excess allylmagnesium bromide; bp 95–100° (34 mm) [lit. bp 86 °C (24 mm)].[6]

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