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1,3-Ditungstacyclobutadienes. 4.[1] 1:1 Diphenyldiazomethane Adducts $W_2(\mu\text{-}CSiMe_3)_2X_4{\cdot}(N_2CPh_2)$. A Comparison of the Effects of the Supporting Ligands, $X = CH_2SiMe_3$ versus $X = O\text{-}i\text{-}Pr$

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Hydrocarbon solutions of $W_2(\mu\text{-}CSiMe_3)_2X_4(W\text{–}W)$ compounds, where X = CH_2SiMe_3 and O-*i*-Pr, have been found to react with diphenyldiazomethane, N_2CPh_2, at room temperature to give the 1:1 adducts $W_2(\mu\text{-}CSiMe_3)_2X_4(N_2CPh_2)$ (1, X = CH_2SiMe_3; 2, X = O-*i*-Pr). The dinuclear center of the alkylidyne compound acts as a source of electrons reducing the diazoalkane to a $NNCPh_2$ hydrazonido(2−) ligand. Both compounds have been characterized by ^1H, ^{13}C, and IR spectroscopy. The molecular structure of $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$ (1) shows that $NNCPh_2$ is terminally bound to one W atom resulting in a pseudo-trigonal-bipyramidal geometry at that W atom wherein the coordinated $NNCPh_2$ ligand and one of the alkylidyne bridges occupy the axial positions. The other W atom is in a pseudotetrahedral environment. The W–N distance of 1.767 (10) Å together with the WNN angle of 158.2 (8)° suggests partial donation of the nitrogen lone pair to give significant W≡N character. Thermolysis of 1 at 120 °C in toluene solution results in loss of $Si(CH_3)_4$ (1 equiv) and generates, via C–H bond activation, a compound which we formulate, on the basis of ^1H and ^{13}C NMR spectroscopic data, as $(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)_2W(CH_2SiMe_3)(NN{=}C(Ph)\text{-}o\text{-}C_6H_4)$. At no time was alkylidene formation observed from either thermolysis or photolysis of solutions of 1. On the basis of low-temperature ^1H NMR, ^{13}C NMR, and IR spectroscopic data, we formulate that 2 is structurally related to 1. The molecule is fluxional on the ^1H NMR time scale due to a pseudorotational process occurring about the trigonal-bipyramidal W atom, ΔG^{*}_{rot} = 13.4 kcal/mol. Neither thermolysis at 120 °C nor photolysis of hydrocarbon solutions of 2 generate alkylidene-containing products, but rather dissociation of N_2CPh_2 occurs with regeneration of $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4$. Crystal data for 1 at −159 °C: a = 21.163 (5) Å, b = 22.639 (4) Å, c = 10.403 (1) Å, β = 91.73 (1)°, Z = 4, d_{calcd} = 1.441 g cm^{-3}, and space group $P2_1/a$.

Introduction

In previous studies of the chemistry of $W_2(\mu\text{-}CSiMe_3)_2X_4$ compounds (X = CH_2SiMe_3 and/or OR) we have observed carbon–carbon bond-forming reactions with alkynes, allene, alkyl and aryl isocyanides, and carbon monoxide.[2] In the previous paper in this series, we reported[1] upon a comparative study of the reactions involving alkynes (C_2H_2 and Me_3SiCCH) and $W_2(\mu\text{-}CSiMe_3)_2X_4$ compounds. This revealed that for X = CH_2SiMe_3 1:1 adduct formation was more rapid than for X = O-*i*-Pr, an observation that was explained in terms of the different electronic properties of X. However, subsequent to 1:1 alkyne adduct formation, carbon–carbon bond formation involving alkylidyne–alkyne coupling was in the inverse order, namely, X = O-*i*-Pr > X = CH_2SiMe_3.

We describe here a comparative study of the reactions between $W_2(\mu\text{-}CSiMe_3)_2X_4$ compounds (X = CH_2SiMe_3 and O-*i*-Pr) and diphenyldiazomethane which was prompted by the possibility of carbene–metal bond formation and subsequent carbon–carbon coupling reactions.[3]

Results and Discussion

Synthesis and Physicochemical Properties. Hydrocarbon solutions of the alkylidyne-bridged compound $W_2(\mu\text{-}CSiMe_3)_2X_4$ (X = CH_2SiMe_3, O-*i*-Pr) react with solutions of N_2CPh_2 to generate the 1:1 diphenyldiazomethane adducts $W_2(\mu\text{-}CSiMe_3)_2X_4{\cdot}(N_2CPh_2)$ as indicated in eq 1. The reactions proceed rapidly at room temperature and NMR studies indicate that the formation of the 1:1 adducts is quantitative. The basic course of the reaction appears to be one in which the d^2 (M–M) electrons have been utilized to reduce the diazoalkane ligand to a hydrazonido(2−) ligand. Indeed, formation of the 1:1 diazoalkane adducts $W_2(\mu\text{-}CSiMe_3)_2X_4{\cdot}(N_2CPh_2)$ parallels the formation of the previously observed 1:1 η^2-alkyne adducts $W_2(\mu\text{-}CSiMe_3)_2X_4{\cdot}(\eta^2\text{-}C_2R_2)$.[4] In the reactions of $W_2(\mu\text{-}CSiMe_3)_2X_4(M\text{–}M)$ with alkynes, the dinuclear center serves as a reservoir of electrons for reduction of the alkyne to a 2− ligand forming a metallacyclopropene unit. In both cases the formation of a 1:1 adduct can thus be viewed as an oxidative addition reaction.

$$W_2(\mu\text{-}CSiMe_3)_2X_4 + N_2CPh_2 \xrightarrow[\text{2 h, 22 °C}]{\text{hexane}} W_2(\mu\text{-}CSiMe_3)_2X_4{\cdot}(N_2CPh_2) \quad (1)$$

$$1, X = CH_2SiMe_3$$
$$2, X = O\text{-}i\text{-}Pr$$

The 1:1 diphenyldiazomethane adducts are red-orange crystalline compounds when pure and in the solid state and are air- and moisture-sensitive. Due to their extreme solubility in various organic solvents (e.g. hydrocarbons, ethers), compounds 1 and 2 are initially isolated as viscous red oils. Crystals can be obtained by slow recrystallization from hexane, and, in the case of compound 1, these crystals are suitable for X-ray structural analysis (vide infra). Elemental analyses of both 1 and 2 indicated that the compounds were indeed diphenyldiazomethane adducts in that the diazoalkane nitrogen atoms had been retained.

Solid-State Structural and Bonding Considerations. $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$. Fractional

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Table I. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$
W(1)	7367.2 (2)	918.2 (2)	6885.0 (4)	15
W(2)	6466.4 (2)	1418.7 (2)	8644.1 (4)	14
N(3)	7987 (4)	397 (4)	7018 (8)	18
N(4)	8400 (4)	16 (4)	7591 (9)	21
C(5)	8755 (5)	−336 (5)	6955 (12)	21
C(6)	8737 (5)	−400 (5)	5553 (11)	18
C(7)	8171 (6)	−448 (5)	4822 (11)	31
C(8)	8168 (6)	−520 (5)	3502 (11)	28
C(9)	8727 (7)	−523 (6)	2864 (12)	31
C(10)	9274 (7)	−472 (7)	3544 (13)	40
C(11)	9298 (6)	−411 (6)	4878 (13)	35
C(12)	9200 (5)	−703 (5)	7728 (11)	21
C(13)	9388 (6)	−544 (5)	8978 (13)	27
C(14)	9801 (7)	−899 (7)	9716 (14)	41
C(15)	10009 (7)	−1426 (7)	9226 (15)	41
C(16)	9801 (6)	−1603 (5)	8027 (13)	31
C(17)	9412 (6)	−1241 (6)	7255 (13)	30
C(18)	7901 (6)	1668 (6)	6322 (14)	32
Si(19)	8661 (2)	1642 (2)	5568 (4)	31
C(20)	9260 (8)	1375 (9)	6718 (29)	106
C(21)	8872 (7)	2411 (7)	5054 (18)	50
C(22)	8607 (14)	1172 (8)	4086 (20)	107
C(23)	6830 (5)	454 (5)	5439 (11)	20
Si(24)	6366 (2)	−250 (2)	5648 (3)	21
C(25)	5605 (6)	−100 (6)	6448 (12)	35
C(26)	6788 (6)	−823 (6)	6652 (13)	34
C(27)	6196 (7)	−570 (8)	4002 (13)	46
C(28)	7166 (5)	884 (5)	8756 (11)	18
Si(29)	7502 (2)	520 (1)	10236 (3)	19
C(30)	8343 (6)	732 (5)	10520 (12)	24
C(31)	7422 (6)	−294 (5)	10073 (12)	25
C(32)	7029 (7)	756 (6)	11643 (12)	34
C(33)	6491 (5)	1571 (5)	6932 (11)	14
Si(34)	6107 (2)	1974 (2)	5572 (3)	20
C(35)	5882 (7)	2717 (6)	6147 (12)	30
C(36)	5381 (6)	1555 (6)	5065 (12)	31
C(37)	6593 (7)	2063 (6)	4116 (12)	33
C(38)	6578 (6)	2194 (5)	9714 (11)	23
Si(39)	7266 (2)	2716 (1)	9903 (3)	22
C(40)	7079 (7)	3258 (6)	11173 (13)	34
C(41)	7390 (8)	3114 (6)	8350 (14)	39
C(42)	8010 (6)	2336 (6)	10415 (16)	38
C(43)	5594 (6)	1006 (5)	9047 (10)	21
Si(44)	4925 (2)	1419 (2)	9759 (3)	22
C(45)	5137 (8)	1654 (7)	11411 (13)	40
C(46)	4705 (6)	2073 (7)	8773 (15)	41
C(47)	4228 (7)	925 (7)	9819 (13)	37

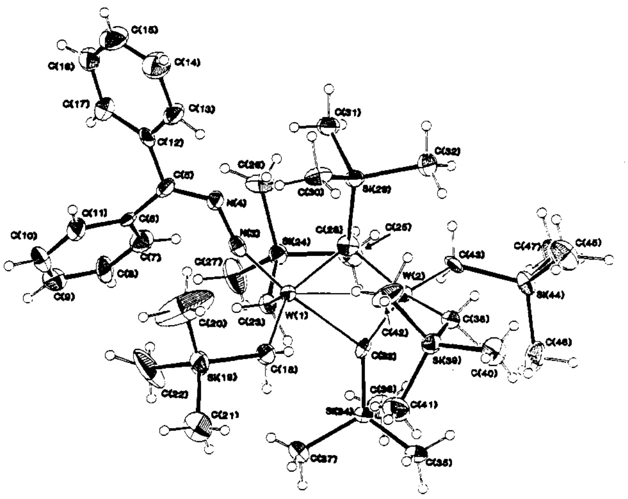


Figure 1. ORTEP view of the $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$ molecule giving the atom numbering scheme used in the tables.

Table II. Selected Bond Distances (Å) for the $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$ Molecule

A	B	dist
W(1)	N(3)	1.767 (10)
W(1)	C(18)	2.130 (13)
W(1)	C(23)	2.134 (12)
W(1)	C(28)	2.007 (11)
W(1)	C(33)	2.372 (10)
W(2)	C(28)	1.914 (12)
W(2)	C(33)	1.816 (11)
W(2)	C(38)	2.089 (12)
W(2)	C(43)	2.122 (11)
Si(29)	C(28)	1.867 (12)
Si(34)	C(33)	1.851 (11)
N(3)	N(4)	1.355 (13)
N(4)	C(5)	1.291 (15)
C(5)	C(6)	1.464 (17)
C(5)	C(12)	1.475 (16)
C(6)	C(7)	1.404 (17)
C(6)	C(11)	1.398 (17)
C(7)	C(8)	1.383 (18)
C(8)	C(9)	1.373 (19)
C(9)	C(10)	1.343 (20)
C(10)	C(11)	1.394 (20)
C(12)	C(13)	1.397 (18)
C(12)	C(17)	1.392 (18)
C(13)	C(14)	1.399 (19)
C(14)	C(15)	1.375 (21)
C(15)	C(16)	1.369 (20)
C(16)	C(17)	1.398 (19)

Table III. Selected Bond Angles for the $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$ Molecule

A	B	C	angle
N(3)	W(1)	C(18)	98.9 (5)
N(3)	W(1)	C(23)	96.0 (4)
N(3)	W(1)	C(28)	94.4 (4)
N(3)	W(1)	C(33)	173.3 (4)
c(18)	W(1)	C(23)	118.3 (5)
C(18)	W(1)	C(28)	115.3 (5)
C(18)	W(1)	C(33)	86.0 (4)
C(23)	W(1)	C(28)	122.7 (4)
C(23)	W(1)	C(33)	85.5 (4)
C(28)	W(1)	C(33)	79.4 (4)
C(28)	W(2)	C(33)	97.7 (5)
C(28)	W(2)	C(38)	115.1 (5)
C(28)	W(2)	C(43)	112.7 (5)
C(33)	W(2)	C(38)	110.9 (5)
C(33)	W(2)	C(43)	109.2 (4)
C(38)	W(2)	C(43)	110.5 (5)
W(1)	N(3)	N(4)	158.2 (8)
N(3)	N(4)	C(5)	123.0 (10)
N(4)	C(5)	C(6)	125.0 (11)
N(4)	C(5)	C(12)	116.1 (11)
C(6)	C(5)	C(12)	119.0 (10)
W(1)	C(18)	Si(19)	125.4 (7)
W(1)	C(23)	Si(24)	127.0 (6)
W(1)	C(28)	W(2)	95.9 (5)
W(1)	C(28)	Si(29)	136.9 (7)
W(2)	C(28)	Si(29)	127.1 (6)
W(1)	C(33)	W(2)	87.0 (4)
W(1)	C(33)	Si(34)	128.1 (6)
W(2)	C(33)	Si(34)	144.9 (6)
W(2)	C(38)	Si(39)	131.2 (6)
W(2)	C(43)	Si(44)	122.1 (6)

coordinates are given in Table I, and selected bond distances and bond angles are given in Tables II and III, respectively. An ORTEP view of the molecule giving the atomic number scheme used in the tables is shown in Figure 1.

This view is nearly perpendicular to the W–W axis and emphasizes the pseudo-trigonal-bipyramidal geometry about W(1) and the tetrahedral-like geometry about W(2). The two halves of the molecule are joined together through the two μ-$CSiMe_3$ bridging ligands. The N_2CPh_2 ligand occupies one of the axial coordination sites of the trigonal bipyramid as does one of the μ-$CSiMe_3$ ligands. The equatorial sites are occupied by the two CH_2SiMe_3 ligands

Table IV. ^{1}H and ^{13}C NMR Spectral Data

compd	^{1}H NMR	^{13}C NMR
W$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_4$ (N$_2$CPh$_2$) (1) (^{1}H NMR [benzene-d_6, 23 °C); ^{13}C NMR [toluene-d_8, 23 °C]	μ-CSiMe_3 (0.684, 0.498, s, 9 H) CH$_2$SiMe_3 (0.208, −0.012, s, 18 H) CH_2SiMe$_3$ (1.636, 0.925, 0.804, 0.774, d, 2 H, J_{AB} = 10.1 Hz) N$_2$CPh_2 (7.847, 7.790, 7.200, 7.086, m, 10 H)	μ-CSiMe$_3$ (359.98, s, $J_{^{183}W-^{13}C}$ = 125 Hz) μ-CSiMe$_3$ (338.54, s, $J_{^{183}W-^{13}C}$ = 88.9 Hz) N$_2$$CPh_2$ (163.06 s) N$_2$CPh_2 ipso (138.52, 137.30, s) N$_2$CPh_2 partial (130.52, 130.04, 129.30, 128.64, d?) CH_2SiMe$_3$ (66.06, 61.83, dd, $J_{^{13}C-^1H}$ = 110 Hz) μ-CSiMe_3 (4.869, 3.768, q, $J_{^{13}C-^1H}$ = 118.7 Hz) CH$_2$SiMe_3 (3.128, 3.000, q, $J_{^{13}C-^1H}$ = 118.8 Hz)
W$_2$(μ-CSiMe$_3$)$_2$(O-i-Pr)$_4$(N$_2$CPh$_2$) (2) [toluene-d_8, −40 °C]	μ-CSiMe_3 (0.810, 0.501, s, 9 H) OCH(Me)$_2$ (1.306, 1.279 and 1.149, 1.134 d, 6 H, J_{CH-Me} = 6.14 Hz) OCH(Me)$_2$ (4.828, 4.173, dq, 4 H, J_{CH-Me} = 6.14 Hz) N$_2$CPh_2 (7.943, 7.144, 7.190, 7.135, m, 10 H)	μ-CSiMe$_3$ (320.78, s) μ-CSiMe$_3$ (281.80, s) N$_2$$CPh_2$ (163.07, s) N$_2$CPh_2 partial (136.38, 130.21, 129.05, 128.90, 128.68) OCH(Me)$_2$ (84.88, 78.46 d, $J_{^{13}C-^1H}$ = 142.9 Hz) OCH(Me)$_2$ (27.24, 27.20, 26.78, 26.65, q, $J_{^{13}C-^1H}$ = 126.2 Hz) μ-CSiMe_3 (4.47, 3.72, q, $J_{^{13}C-^1H}$ = 118.5 Hz)
W$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_3$(NNC(Ph)C$_6$H$_4$) (3) [toluene-d_8, 23 °C]	μ-CSiMe_3 (0.687, 0.659, s, 9 H) CH$_2$SiMe_3 (0.201, −0.073, −0.430, s, 9 H) NNC(Ph)C$_6$$H_4$ (6.57–7.76, m, 9 H)	μ-CSiMe$_3$ (342.4, s, $J_{^{183}W-^{13}C}$ = 73.0, 33.7 Hz) μ-CSiMe$_3$ (339.7, s, $J_{^{183}W-^{13}C}$ = 102.4, 54.3 Hz) NNC(Ph)(C$_6$H$_4$) (167.2, s) C$_\alpha$ of C$_6$H$_4$ (150.3, s, $J_{^{183}W-^{13}C}$ = 23.2 Hz) NNC(Ph)C_6H$_4$ partial (138.8, 136.9, 131.0, 121.6, 119.3) CH$_2$SiMe$_3$ (67.0, dd, $J_{^{183}W-^{13}C}$ = 79 Hz, $J_{^{13}C-^1H}$ = 107 Hz) CH$_2$SiMe$_3$ (62.61, dd, $J_{^{183}W-^{13}C}$ = 75.6 Hz, $J_{^{13}C-^1H}$ = 107 Hz) CH$_2$SiMe$_3$ (51.75, dd, $J_{^{183}W-^{13}C}$ = 104.7 Hz, $J_{^{13}C-^1H}$ = 113 Hz) CH$_2$SiMe_3 and μ-CSiMe_3 (5.02, 3.96, 3.15, 3.02, 1.17, q, $J_{^{13}C-^1H}$ = 119 Hz)

and the other μ-CSiMe$_3$ ligand. That the coordination geometry about W(1) is nearly an idealized trigonal bipyramid is emphasized by (1) the trans N–W–C angle is 173.3 (4)° and (2) the sum of the three equatorial C–W–C angles (115.3 (5), 118.3 (5), and 122.7 (4)°) is 356.3°.

The molecular structure (Figure 1) reveals that the mode of bonding of the N$_2$CPh$_2$ ligand is through the terminal nitrogen atom and that coordination occurs only to one tungsten atom. This mode of bonding has been previously observed in dinuclear systems, as for example, in Mo$_2$(O-i-Pr)$_6$(N$_2$CPh$_2$)$_2$(py)[5] and Cp$_2$Mo$_2$(CO)$_3$[≡C(C$_6$H$_4$-p-Me)$_2$][N$_2$C(C$_6$H$_4$-p-Me)$_2$].[6] Steric constraints arising from the bulky μ-CSiMe$_3$ and CH$_2$SiMe$_3$ ligands undoubtedly act in preventing either symmetrically bridged diazoalkane coordination as found in Cp$_2$Mo$_2$(CO)$_4$(N$_2$CPh$_2$)[7] or an asymmetric μ-η^2-N,N′ type of coordination as found in [(CpTiCl)$_2$(μ-Ph$_2$C=NN)$_2$].[8] In fact, upon coordination of the bulky N$_2$CPh$_2$ ligand, steric congestion results in one of the μ-CSiMe$_3$ groups being tilted toward W(2) and in a slight bending back of the two neighboring CH$_2$SiMe$_3$ ligands.

The C=N distance of 1.291 (15) Å and the N—N distance of 1.355 (13) Å are indicative of double and single bonds, respectively, and can be directly compared to those found in Cp$_2$Mo$_2$(CO)$_4$(N$_2$CPh$_2$).[7] The W=N distance of 1.767 (10) Å is clearly indicative of multiple-bond character and is comparable in length to the W=N distance (1.763 (6)) found in the imido complex W$_2$(μ-CSiMe$_3$)(μ-CCSiMe$_3$)(O-i-Pr)$_4$(=NC$_6$H$_3$Me$_2$)[9] but is slightly longer than the 1.740 (15) Å W≡N distance found in the nitrido complex [(^{t}BuO)$_3$W≡N]$_x$.[10] The W–N distance together with the WNN angle of 158.2 (8)° indicate a structure that is intermediate in valence bond description between I and II. The W–W distance, 2.91 Å, is characteristic of a

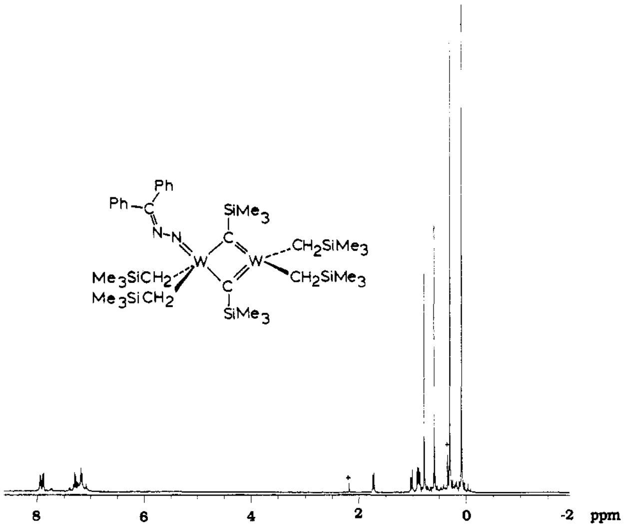
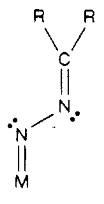


Figure 2. 360-MHz ^{1}H NMR spectrum of W$_2$(μ-CSiMe$_3$)$_2$-(CH$_2$SiMe$_3$)$_4$(N$_2$CPh$_2$) in toluene-d_8 at 22 °C.



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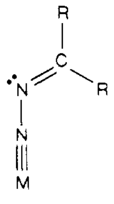

II

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nonbonding distance and is comparable to that found both in the d^0–d^0 dinuclear compound, $Nb_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$,[11] or in the alkyne adduct, $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4{\cdot}C_2(Me)(Ph)$.[4] This is consistent with the formulation of the diazoalkane as a hydrazonido(2–) ligand generating a (W^{VI}–W^{VI}) d^0–d^0 center.

Coordination of N_2CPh_2 at W(1) results in a significant elongation of the W(1)–C(33) bond, thereby producing a gross asymmetry within the central W_2C_2 core. The bridging carbon atoms C(28) and C(33) form shorter distances to W(2) than to W(1) [C(28)–W(2) = 1.914 (12) Å and C(33)–W(2) = 1.816 (11) Å] and may be considered double bonds as in the asymmetric W_2C_2 core of the alkyne adduct $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4{\cdot}C_2(Me)(Ph)$.

NMR Studies. $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$ (1). Complete ^1H and ^{13}C NMR data for the diazoalkane adducts are given in Table IV. Figure 2 shows the 360-MHz ^1H NMR spectrum of $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$ at room temperature.

The ^1H NMR spectrum of 1 in toluene-d_8 shows that a molecular plane of symmetry exists in solution and is entirely consistent with the observed solid-state structure. Specifically, there are two types of CH_2SiMe_3 ligands in a 2:2 ratio each possessing diastereotopic methylene protons. The μ-$CSiMe_3$ protons appear as two singlets in a 1:1 ratio at 0.68 and 0.49 ppm and do not exchange on the NMR time scale in the temperature range −60 to +90 °C.

In the ^{13}C NMR spectrum, the ipso-carbon resonance, δ(NNC), is found at 163 ppm and is in a range typically observed for diaryldiazomethane complexes of this type.[5,6] It is also worth noting that the alkylidyne carbon resonances, μ-$CSiMe_3$, each show significant coupling to only one tungsten atom as a result of the asymmetric central W_2C_2 core (μ-$CSiMe_3$, $^1J_{^{183}W-^{13}C}$ = 125 and 88.9 Hz).

$W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4(N_2CPh_2)$ (2). ^1H NMR spectroscopy reveals that 2 is fluxional on the NMR time scale. A low-temperature-limiting spectrum can be obtained at −40 °C which is consistent with expectations based on considerations of the solid-state structure of 1 and that 2 and 1 are structurally related by the mere interchange of X = CH_2SiMe_3 vs X = O-*i*-Pr. Figure 3 shows the methyl region of the ^1H NMR spectra of $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4(N_2CPh_2)$ in toluene-d_8 as a function of temperature. At −40 °C, the protons of each of the μ-$CSiMe_3$ ligands appear as two distinct singlets at 0.81 and 0.50 ppm. Downfield from these resonances are the diastereotopic methyl resonances of each set of isopropoxide ligands that appear as overlapping doublets of doublets. As the temperature is raised, the set of diastereotopic methyl resonances centered at 1.31 ppm broaden and reappear as a doublet while the two signals corresponding to the μ-$CSiMe_3$ ligands go into the base line ($\Delta G_c^{\ddagger}$ = 13.4 ± 0.2 kcal/mol). At 50 °C, the ^1H NMR spectrum reveals a time-averaged signal for the μ-$CSiMe_3$ resonances, indicating that these ligands have become equivalent.

These NMR data are interpretable if one imagines a pseudorotational process occurring at the five-coordinate trigonal-bipyramidal tungsten center as shown in Scheme I. Pseudorotation of the ligands at W(1) causes the μ-$CSiMe_3$ ligands to become equivalent and creates an additional plane of symmetry within the molecule causing the methyl groups of the isopropoxide ligands at W(2) to lose their diastereotopic character. The methyl groups of the isopropoxide ligands at W(1), however, remain diastereotopic at all times.

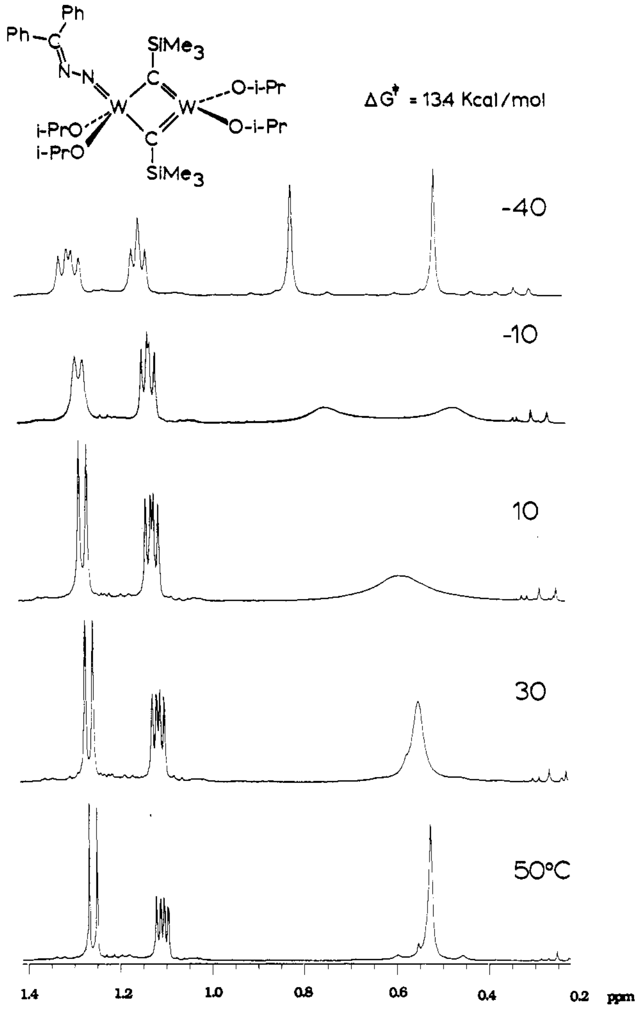
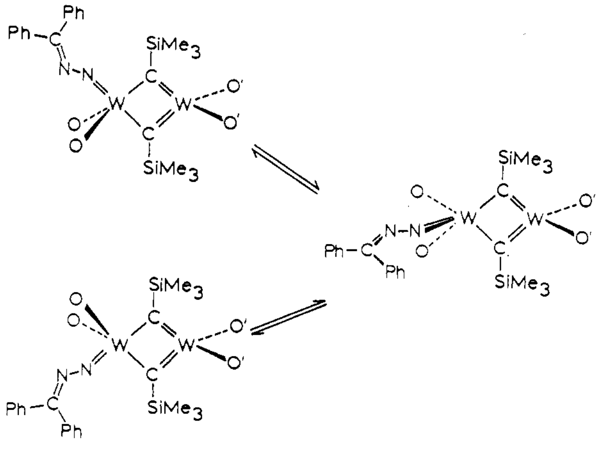


Figure 3. 360-MHz variable-temperature ^1H NMR spectra of the methyl region of $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4(N_2CPh_2)$.

Scheme I



The ^{13}C NMR resonance for the unique diazoalkane carbon (δ(NNC)) appears at 163 ppm and is unaffected by the supporting ligands, i.e. alkoxide for alkyl substitution.

Thermolysis and Photolysis Reactions. Since one of the most important reactions of transition-metal diazoalkane complexes involves the formation of transition-metal alkylidene complexes via dinitrogen loss, we undertook thermolysis and photolysis reactions of both 1 and 2. In this regard we hoped to generate either (1) a stabilized alkylidene–alkylidyne species such as that shown in IIIa or IIIb or (2) an alkylidene intermediate which might eventually lead to C–C bond formation by insertion

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[11] Huq, F.; Mowat, W.; Skapski, A. C.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* 1971, 1477.

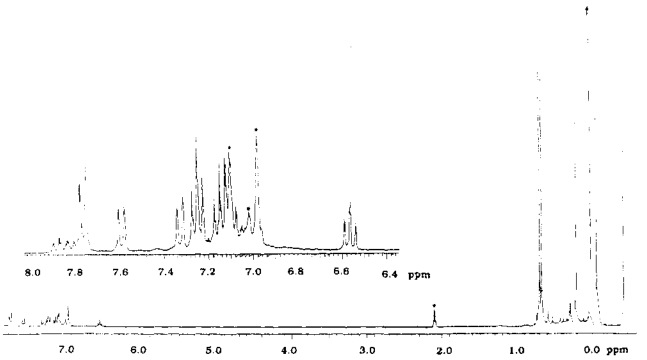
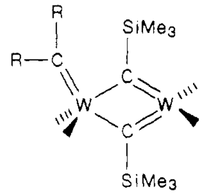
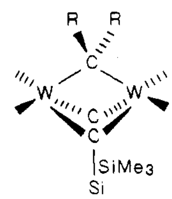
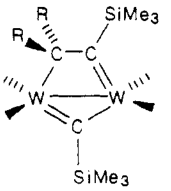


Figure 4. 300-MHz ^1H NMR spectrum of toluene-d_8 solution of $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$ after 24 h at 120 °C. The asterisk (*) denotes protio impurities in toluene-d_8; the dagger (†) denotes $SiMe_4$ evolved during reaction.

of the carbenoid species into a μ-$CSiMe_3$ bridge as shown in IV.


IIIa


IIIb


IV

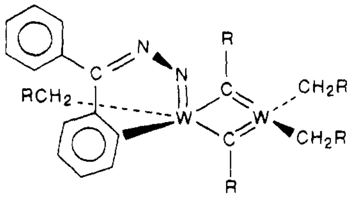
A toluene-d_8 solution of $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$ was gradually heated in a temperature-controlled oil bath and periodically monitored by ^1H NMR. No change in the sample was detected at any time at temperatures below 120 °C. At 120 °C, the solution began to darken considerably from an orange-red to a deep brown. ^1H NMR spectroscopy after 24 h at 120 °C revealed a spectrum containing six methyl singlets of approximately equal intensity along with a complex pattern of multiplets in the phenyl region (see Figure 4). One of these singlets (0.0 ppm) is due to $Si(CH_3)_4$ (~1 equiv) which is evolved during the reaction. Its identity was confirmed by the addition of a small amount of an authentic sample of $SiMe_4$ to the reaction mixture which resulted in the enhancement of the signal at 0.0 ppm in the ^1H NMR spectrum. The remaining five methyl singlets are due to two inequivalent μ-$CSiMe_3$ ligands and three inequivalent CH_2SiMe_3 ligands. The diastereotopic methylene protons appear to be buried under the methyl proton resonances. Through controlled selective decoupling experiments, the phenyl protons could be assigned as belonging either to a C_6H_5 ring or to a C_6H_4 ring.

^{13}C NMR spectroscopy confirmed the presence of three inequivalent CH_2SiMe_3 ligands in the thermolysis product and allowed the identification of the diazoalkane carbon $NNC(Ph)(C_6H_4)$ (167.2 ppm) and of C_α of the C_6H_4 ring (δ 150.3 ($^1J_{^{183}W-^{13}C}$ = 23.2 Hz)). Complete ^1H and ^{13}C NMR data are given in Table IV.

On the basis of these observations, we postulate that thermolysis of $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$ at 120 °C results in orthometalation via aromatic C–H bond activation with concomitant elimination of $SiMe_4$ (eq 2).

$$W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2) \xrightarrow[120\ °C,\ 24\ h]{toluene} W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_3({=}NN{=}C(Ph)\text{-}o\text{-}C_6H_4) + SiMe_4 \quad (2)$$

The orthometalation product, which was isolated as a black tar, proved to be extremely hydrocarbon soluble and could neither be recrystallized nor obtained analytically pure. Although the specific orientation of the ligands is not known, NMR spectroscopic data indicate that the product formed possesses no elements of symmetry. One plausible structure is that shown in V in which the molecule contains a metallapyridazine unit cis to the unique CH_2SiMe_3 ligand.


V (R = $SiMe_3$)

In this instance, cyclometalation is a preferred pathway of decomposition over alkylidene formation. This is undoubtedly due to the very strong W–N linkage present in the 1:1 adduct, thereby making $SiMe_4$ formation kinetically if not thermodynamically favored over dinitrogen formation. The thermally robust nature of $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$ is exemplified by the harsh reaction conditions necessary for cyclometalation to occur. In contrast, photolysis for 4 h produced no change in solutions of 1.

In the thermolysis of 1 there was at no time any evidence for alkylidene formation. Additionally, we can also rule out the formation of a metallacyclobutene species which might be formed by cyclometalation of an alkylidene intermediate. One would expect alkylidene carbon resonances to be found at ~230–290 ppm in the ^{13}C NMR spectrum with $^1J_{W-C} \approx$ 140–200 Hz. While several unidentified resonances were present in the ^{13}C NMR spectrum of the thermolyzed product, these were not of significant intensity and were not located in the region expected for alkylidene carbons. The possibility that toluene-d_8 was acting as a D source leading to the formation of Me_3SiCH_2D cannot be ruled out, though such a reaction pathway is considered unlikely.

Solutions of $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4(N_2CPh_2)$ (2) were also thermolyzed at 120 °C and monitored periodically by ^1H NMR spectroscopy. In contrast to compound 1, $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4(N_2CPh_2)$ readily undergoes dissociation of diphenyldiazomethane with subsequent decomposition to generate $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4$ and benzophenone azine. Further reaction between $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4$ and benzophenone azine is not observed after 24 h at room temperature.

Photolysis of solutions of $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4(N_2CPh_2)$ for 4 h results in complete dissociation of N_2CPh_2 *without decomposition* and generates $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4$ as determined by ^1H NMR. It was hoped that photolysis of solutions of 1 would also result in dissociation of N_2CPh_2 with decomposition and that any resultant carbene would be preferentially trapped by $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4$ to form III or IV prior to the formation of the azide $Ph_2C{=}NN{=}CPh_2$. However, neither III, IV, or the azide was observed *under the conditions indicated.* It should also be noted that dissociation of diazoalkanes without decomposition is rare and to our knowledge has been cited in only one other instance.[12]

The differences in reactivity between compounds 1 and 2 can be attributed to the effect of the supporting ligands. The presence of σ- and π-donating O-i-Pr ligands act to destabilize the 1:1 diazoalkane adduct. Competition for interaction with the same metal-based orbitals presumably

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[12] Woodcock, C.; Eisenberg, R. *Organometallics* **1985**, *4*, 4.

occurs between filled p orbitals of both the diazoalkane nitrogen atom and the oxygen atoms of the O-*i*-Pr ligands. The result of this competition is a weakening of the W–N interaction in the diazoalkane adduct when the supporting ligands are O-*i*-Pr. Thus on thermodynamic grounds, cleavage of the weak W—N bond proceeds more readily than does cleavage of the nitrogen–carbon (NN═C) bond, and diazoalkane is regenerated.

Concluding Remarks

The formation of 1:1 diaryldiazomethane adducts of 1 and 2 parallels the formation of 1:1 alkyne adducts in the reactions between $W_2(\mu\text{-}CSiMe_3)_2X_4$ compounds and alkynes in that the stability of the adduct is in the order X = CH_2SiMe_3 > O-*i*-Pr. This effect of the ancillary ligand is understandable in terms of alkoxide oxygen p_π-to-tungsten d_π donation. The reversible formation of compound 2 is quite noteworthy, as are the thermal and photochemical decompositions of 1, neither of which involve alkylidene formation.

Experimental Section

All reactions were carried out under dry N_2 gas by using a standard Schlenk apparatus. Solids were isolated and transferred in a N_2-filled Vacuum Atmospheres drybox. $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$,[13] $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4$,[4] and N_2CPh_2[14] were prepared according to published procedures. Hexanes and toluene were dried and deoxygenated by refluxing over Na/benzophenone. NMR solvents were dried over 3-Å molecular sieves and degassed using a dry N_2 purge.

^1H and ^{13}C NMR spectra were acquired on either a Nicolet 360 MHz spectrometer or a Varian 300 MHz spectrometer. ^1H NMR spectra were referenced against the residual protio impurity in the aromatic hydrogens of benzene-d_6 (7.15 ppm) or in the methyl group hydrogens of toluene-d_8 (2.09 ppm). ^{13}C NMR spectra were referenced against the methyl group of toluene-d_8 at 20.4 ppm. Infrared spectra were obtained as Nujol mulls between CsI plates by using a Perkin-Elmer 283 IR spectrophotometer. Microanalytical data were supplied by Analytical Laboratories, Engelskirchen, West Germany. All analytical samples were ignited with V_2O_5 due to silicon content. Photolyses were performed by using a focused beam Photochemical Research Association (PRA) high-pressure 100-W Hg lamp with all samples placed ca. 15 cm from the source.

Preparation of $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$ (1). $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$ (0.50 mmol) was introduced into a Schlenk flask and dissolved in toluene (5 mL). N_2CPh_2 (0.50 mmol) in toluene (5 mL) was added via cannula, and the solution was allowed to stand for 3 h at room temperature. During this time the color of the solution changed from brown to red-orange. The solvent was removed in vacuo, leaving a dark red oily residue which showed evidence of crystallization after several hours under vacuum. The residue was dissolved in a minimum volume of warm hexanes (0.3 mL) and cooled to -20 °C to produce 390 mg of red-black crystals. These crystals were identified as $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)$ (1) by ^1H and ^{13}C NMR spectroscopy (Table IV), elemental analysis, IR spectrophotometry, and X-ray crystallography. Yield (as crystals): 72%. Anal. Calcd: C, 41.44; H, 6.67; N, 2.59 Found: C, 41.09; H, 6.56; N, 2.54. IR data (cm^{-1}): 1365 (shoulder on Nujol), 1265 w, 1241 m, 1100 w, 980 w, 930 w, 831 s, 750 w, 738 w, 720 w, 700 w, 689 w, 630 vw.

Preparation of $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4(N_2CPh_2)$ (2). A procedure identical with that described above was used in the formation of 2. Red-orange crystals (350 mg, 0.39 mmol) isolated from the reaction of $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4$ with N_2CPh_2 were identified as $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4(N_2CPh_2)$ (2) by ^1H and ^{13}C NMR spectroscopy at -40 °C (Table IV), elemental analysis, and IR spectrophotometry. Yield (as crystals): 78%. Anal. Calcd: C, 40.91; H, 5.78; N, 2.89. Found: C, 40.88; H, 5.79; N, 2.92. IR data (cm^{-1}): 1362 m, 1322 m, 1236 m (1161 sh), 1147 m (1128 sh), 1106 s, 1001 m, 978 s (960 sh), 836 s, 783 m, 750 w, 738 w, 712 w, 695 w, 688 w, 675 w, 610 m, 589 vw.

Table V. Summary of Crystal Data for 1

empirical formula	$W_2C_{37}H_{72}N_2Si_6$
color of cryst	black
cryst dimens (mm)	0.12 × 0.13 × 0.14
space group	$P2_1/a$
cell dimens	
temp, °C	-159
a, Å	21.163 (5)
b, Å	22.639 (4)
c, Å	10.403 (1)
β, deg	91.73 (1)
Z, molecules/cell	4
V, Å^3	4981.82
D(calcd), g cm^{-3}	1.442
wavelength, Å	0.710 69
mol wt	1081.21
linear abs coeff, cm^{-1}	48.797
detector to sample dist, cm	22.5
sample to source dist, cm	23.5
average ω scan width at half-height	0.25
scan speed, deg/min	4.0
scan width, deg + dispersion	2.0
individual background, s	2.0 + dispersion
aperture size, mm	3.0 × 4.0
2θ range, deg	6–45
total no. of reflctns collected	7059
no. of unique intensities	6542
no. of $F > 3.00\sigma(F)$	5335
$R(F)$	0.0473
$R_w(F)$	0.0451
goodness of fit for the last cycle	0.915
max Δ/σ for last cycle	0.05

Thermolysis and Photolysis of 1. In a 5-mm o.d. NMR tube fitted with a Pyrex extension was placed 100 mg of 1 and ca. 0.5 mL of toluene-d_8. The tube was closed to the atmosphere by means of a vacuum stopcock and then flame sealed following two freeze–pump–thaw cycles. The solution was heated at 120 °C for 24 h at which time the color had changed from red-orange to brown. A ^1H NMR spectrum taken at this time revealed that 1 had been completely converted to 3 (Table IV). While being held at -196 °C, the tube was opened to the vacuum line and an authentic sample of $Si(CH_3)_4$ (ca. 5 μL) was condensed into the reaction vessel resulting in enhancement of the resonance at 0.0 ppm in the ^1H NMR spectrum. The black oily residue obtained (84 mg) from the thermolysis of 1 has been formulated as $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_3(NNC(Ph)C_6H_4)$ based on ^1H and ^{13}C NMR spectroscopy (Table IV).

Photolysis of a solution of 1 (40 mg in 0.5 mL of toluene-d_8) for 4 h resulted in no change as determined by ^1H NMR spectroscopy.

Thermolysis and Photolysis of 2. 2 (40 mg, 0.0456 mmol) was placed in a 5-mm NMR tube; toluene-d_8 (0.5 mL) was added, and the tube was flame-sealed as described previously. Heating for 2 h at 120 °C caused the solution to change from orange to red. ^1H NMR spectroscopy revealed that partial dissociation of 2 had occurred generating $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4$. After several hours, yellow needles had precipitated from the solution and were identified as $Ph_2C{=}NN{=}CPh_2$ (mp 159–160 °C; ^1H NMR in toluene-d_8, complex multiplets 6.7–7.8 ppm).

Photolysis of a solution of 2, prepared as above, for 1 h resulted in partial dissociation of 2 as determined by ^1H NMR spectroscopy. Continued photolysis of the sample for 4 h resulted in complete dissociation of 2 producing $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4$ and N_2CPh_2.

Crystallographic Studies. General operating procedures and a listing of programs used at the Indiana University Molecular Structure Center have been previously described.[15] Crystal data are summarized in Table V.

A suitable crystal was cleaved from a larger aggregate and transferred to the goniostat using standard inert-atmosphere

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(13) Chisholm, M. H.; Cotton, F. A.; Extine, M.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 2252.

(14) Smith, L. I.; Howard, K. L. *Organic Synthesis*; Wiley: New York, 1955; Collect. Vol. III, p 351.

(15) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *24*, 1021.

handling techniques. After transfer, the crystal was cooled to −159 °C for characterization and data collection. A systematic search of a limited hemisphere located a set of diffraction maxima with monoclinic symmetry and extinction corresponding to the unique space group $P2_1/a$ (alternate setting of $P2_1/c$). Subsequent solution and refinement of the structure confirmed this choice.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques and refined by a blocked full-matrix least squares. Hydrogen atoms were present in a difference Fourier phased on the non-hydrogen parameters and were included in the final cycles. Their positions are poorly determined as seen by the scatter in the C–H distances and angles but are qualitatively correct.

Since the crystal was nearly equidimensional, no absorption correction was performed ($\mu = 48.8$ cm^{-1}).

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Supplementary Material Available: A listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

Reactions of (*N*,*N'*-Diisopropyl-1,4-diaza-1,3-butadiene)ironruthenium Hexacarbonyl with Alkynes[1]

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$FeRu(CO)_6$(*i*-Pr-DAB) (1) [R-DAB = RN=CHCH=NR] reacts at 20 °C with dimethyl acetylenedicarboxylate in heptane solution to give the complexes $FeRu(CO)_5$(*i*-Pr-DAB)[μ_2,η^2-MeOC(O)C≡CC(O)OMe] (2), with DAB chelating the Ru center and the alkyne in perpendicular bridging position, and $FeRu(CO)_5$[*i*-PrN=CHCH(N-*i*-Pr)C(C(O)OMe)=CC(O)OMe] (4) in which the alkyne is C—C coupled with the η^2-C=N coordinated imine C atom of the DAB ligand (in 1). In 4 both N atoms are bonded to Fe whereas in 1 they are bonded to Ru which suggests that the formation of 4 is preceded by an isomerization of 1 involving the migration of the η^2-C=N coordinated imine fragment from Fe to Ru. The X-ray crystal structure of 4 has been determined. Dark brown crystals of 4 ($FeRuC_{19}H_{22}N_2O_9$, mol wt 579.31, $Z = 4$) are monoclinic, space group $P2_1/a$, and have cell constants $a = 14.858$ (1) Å, $b = 17.055$ (1) Å, $c = 9.4289$ (8) Å, and $\beta = 94.215$ (8)°. A total of 3092 reflections (Mo Kα, $\mu = 12.77$ cm^{-1}) were used in the refinement which converged to a final R of 0.053 ($R_w = 0.096$). Complex 2 shows a thermally induced (70 °C) isomerization which involves the migration of one of the isopropyl methine protons to the alkyne which is transformed into an η^1-vinyl fragment in $FeRu(CO)_5$[MeOC(O)C=CHC(O)OMe][Me_2C=NCHCHN-*i*-Pr] (3). Reaction of 1 at 20 °C with methyl propynoate produces a mixture of two pairs of isomeric complexes, $FeRu(CO)_5$(*i*-Pr-DAB)(μ_2-HC≡CC(O)OMe) (8, 9) and $FeRu(CO)_4$(*i*-Pr-DAB)(μ_2-HC≡CC(O)OMe) (10, 11). The isomeric complexes differ with respect to the coordination of the alkyne relative to the Fe–Ru core. In all complexes 8–11 the DAB ligand is bonded as a σ,σ-N,N′, η^2,η^2-C=N,C=N′ bridging 8e donor with the N atoms σ-bonded to Ru and the alkyne as a μ_2-parallel bridging ligand. In 8 and 9 a fifth CO ligand is bonded to Ru and the metal centers are at a long nonbonding distance of 3.089 (2) Å. The reaction of 10 and 11 with CO at 20 °C yields 8 and 9, respectively, in quantitative yield. Both 8 and 9 again easily lose a CO ligand when a solution of these compounds is purged with N_2. The X-ray crystal structure of 8 has been determined. Yellow crystals of 8 ($FeRuC_{17}H_{20}N_2O_7$, mol wt 521.27, $Z = 8$) are orthorhombic, space group *Pnab*, and have cell constants $a = 15.263$ (2) Å, $b = 18.458$ (2) Å, and $c = 15.130$ (2) Å. A total of 4027 reflections (Mo Kα, $\mu = 14.57$ cm^{-1}) were used in the refinement which converged to a final R of 0.050 ($R_w = 0.081$). In the reaction of 1 in *n*-octane at 90 °C with ethyne four products are formed, of which three are the isomeric metallacyclopentadienyl complexes FeRu[HC=CHCH=CH]$(CO)_4$(*i*-Pr-DAB) (12–14). In 14 (yield 20%) the DAB ligand is chelating Fe which is bonded to the RuC_4 metallacycle. In 12 and 13 (both obtained in 15–20% yield) the DAB ligand is bonded to Ru and Fe, respectively, which metal atom is also part of the metallacycle. The fourth complex (15) (yield 5%) has the composition $FeRu(CO)_6$(*i*-Pr-DAB)(C_2H_2) and probably has a flyover structure in which a CO molecule is C–C coupled to the alkyne which is N–C coupled to DAB. When the reaction is performed in refluxing heptane at 98 °C, $FeRu(CO)_4$(*i*-Pr-DAB(8e))(μ_2-HC≡CH) (6) is also formed in 5–10% yield. It is shown that the product distribution of reactions of complexes $M_2(CO)_6$(α-diimine) with alkynes is largely determined by the nature of the η^2-C=N—M interaction.

Introduction

The formation and the chemical properties of the homodinuclear Fe and Ru carbonyl α-diimine complexes $M_2(CO)_6$(L) [M_2 = Fe_2, Ru_2; L = R-DAB (= 1,4-diaza-1,3-butadiene; RN=CHCH=NR), R-Pyca (= pyridine-2-carbaldimine; C_5H_4N-2-CH=NR)] in which the α-diimine ligand is bonded as a σ-N, μ_2-N′, η^2-C=N′ bridging 6e

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[1] Reactions of Dinuclear Metal Carbonyl α-Diimine Complexes with Alkynes. Part 6: see ref 2.

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