2354 *Organometallics* **1993**, *12*, 2354-2359

Notes

Carbon–Carbon Coupling of a μ-Ethynyl Ligand with an Isocyanide at a Ditungsten Center. Preparation and Structure of $W_2(\mu\text{-CCCNHXyl})(OSiMe_2Bu^t)_5(CNXyl)_4$, Where Xyl = $2,6\text{-}Me_2C_6H_3$

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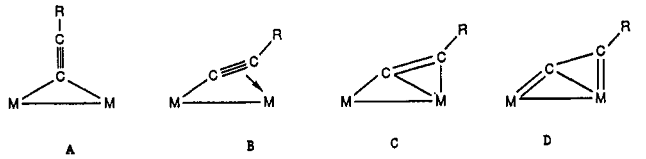
Summary: The ethynyl-bridged complex $W_2(\mu\text{-CCH})(OSiMe_2Bu^t)_5$ reacts in hydrocarbon solvents with xylyl isocyanide, $2,6\text{-}Me_2C_6H_3NC$, to give $W_2(\mu\text{-CCCNHXyl})(OSiMe_2Bu^t)_5(CNXyl)_4$ which has been characterized by NMR spectroscopy and a single-crystal X-ray study. The bridging μ-CCCNHXyl ligand may be viewed as an η^2-aminoalkyne to one tungsten and an alkylidyne to the other. One tungsten is in a pseudooctahedral environment being coordinated to four isocyanide ligands, one siloxide, and an η^2-alkyne moiety while the other is a five-coordinate pseudo-square-based pyramid having four siloxides in the basal plane and the alkylidyne carbon at the apical site. Crystal data for $W_2(\mu\text{-CCCNHXyl})(OSiMe_2Bu^t)_5(CNXyl)_4\cdot{}^1/_2(\text{toluene})$ at −158 °C: a = 21.354(7) Å, b = 17.095(6) Å, c = 24.288(9) Å, β = 100.18(2)°, d_{calcd} = 1.347 g cm^{-3}, Z = 4, and space group $P2_1/n$.

Introduction

The alkynyl ligand, C≡CR, is known to bridge two metal atoms in either a μ-perpendicular mode, A, or a μ-σ,π (side-on) bonding mode, shown in B.[1] In the side-on μ-σ,π bonding mode the alkynyl ligand can be considered a 3-electron donor but other valence bond descriptions (resonance forms) can be written, such as those in C and D.



In A and B the alkynyl ligand is formally a uninegative ligand, while in C the formation of the metallacyclopropene to one metal generates a $(\mu\text{-CCR})^{3-}$ ligand. In D further carbon–metal bonding implies an additional reduction to give a 5^- ligand. The bonding in $W_2(\mu\text{-CCH})(OSiMe_2Bu^t)_5$ is best described by C and D relative to B on the basis of the extensive W_2 to C_2H back-bonding.[2] Supporting arguments for this description based on an analysis of the structural data and the ^{13}C NMR data for the $W_2(\mu\text{-CCH})$ moiety have been expressed previously.[2]

In dinuclear carbonyl chemistry there are numerous μ-σ,π-alkynyl complexes. Carty and co-workers[3] at Waterloo have shown that the μ-σ,π-alkynyl ligand can be readily formed from alkynylphosphines by cleavage of the phosphorus–carbon sp bond, as in eq 1.

$$Fe_2(CO)_9 + RC{\equiv}CPR'_2 \rightarrow Fe_2(\mu\text{-}PR'_2)(\mu\text{-}\sigma,\pi\text{-}CCR)(CO)_6 + 3CO \quad (1)$$

These σ,π-alkynyl ligands are known to undergo reactions with nucleophiles such as amines,[4] phosphines,[5] phosphites[6] and isocyanides,[7] as shown in Scheme I. The μ-σ,π-alkynyl ligand in $HOs_3(\mu\text{-CCPh})(CO)_{10}$ shows similar reactivity with amines, phosphines, and isocyanides.[8] We were naturally interested in what type of reactivity the $W_2(\mu\text{-CCH})(OSiMe_2Bu^t)_5$ compound might show, and we describe here a rather unusual reaction involving an isocyanide addition.

Results and Discussion

Syntheses. The $W_2(\mu\text{-CCH})(OSiMe_2Bu^t)_5$ compound, 1, is prepared by the decomposition of the respective μ-ethyne complex, as shown in eq 2 in ca. 90% isolated yield.[2] The ^{13}C-labeled compound containing the $W_2(\mu\text{-}^{13}C^{13}CH)$ moiety, 1*, is readily prepared from the $\mu\text{-}^{13}C_2H_2$ precursor.[2]

$$W_2(\mu\text{-}C_2H_2)(OSiMe_2Bu^t)_6(py) \xrightarrow[\text{hexane}]{22\ °C,\ 5\ h} \underset{\mathbf{1}}{W_2(\mu\text{-CCH})(OSiMe_2Bu^t)_5} + Bu^tMe_2SiOH + py \quad (2)$$

Compound 1 is unreactive toward PMe_3 and H_2 (3 atm) in hydrocarbon solutions at 22 °C. With CO (0.5 atm) a reaction occurs, but $W(CO)_6$ is the only characterizable product. The fate of the μ-CCH group is unknown. A

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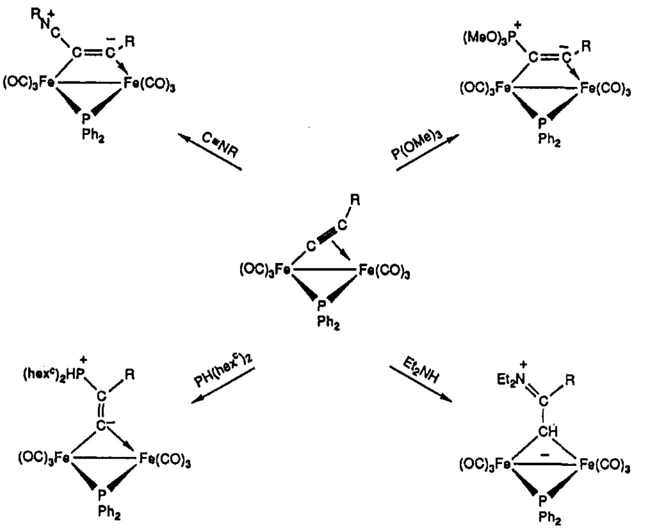
Scheme I. Addition Reactions of Weak Nucleophiles to the Alkynyl Ligand in $Fe_2(\mu\text{-}PPh_2)(\mu\text{-}CCR)(CO)_6$ Complexes Where R = Bu^t or Ph



reaction occurs with isocyanides, and that reaction involving xylyl isocyanide was followed most closely.

Compound 1* in pentane or toluene solution reacts at room temperature with xylyl isocyanide (5 equiv) to give compound 2 over a period of 1.5 h. The reaction is apparently quantitative. From reactions employing 1*, ^{13}C NMR spectroscopy showed that all the ^{13}C-labeled carbon atoms were present in 2*. Compound 2* is sparingly soluble in pentane and precipitates as a red-orange microcrystalline solid during the course of the reaction when pentane is employed as a solvent. Compound 2 is extremely soluble in toluene, and from concentrated solutions in toluene deep orange-red crystals were obtained for the X-ray study. Compound 2 is stable in solution and the solid-state at room temperature under a dry and oxygen-free N_2 atmosphere.

Crystal and Molecular Structure of $W_2(\mu\text{-}CCCNHXyl)(OSiMe_2Bu^t)_5(CNXyl)_4\cdot{}^1/_2$(toluene). A summary of crystal data is given in Table I, and two views of the molecule are given in Figures 1 and 2. Atomic coordinates are given in Table II. Selected bond distances and bond angles are given in Table III.

In the space group $P2_1/n$ there are four crystallographically equivalent molecules of 2 and two noninteracting toluene molecules per unit cell. The toluene molecules are disordered about a center of inversion. The crystallographic data yielded a structural determination with metrical parameters that were poorly defined. Nevertheless the structural determination is of sufficient quality to uniquely define the coordination geometry of complex 2.

One tungsten atom is coordinated to four siloxide ligands and a carbon atom of the bridging CCCNHXyl ligand. The local geometry may be described as a distorted square-based pyramid with the carbon at the apical position. The W(2)–C(3) distance of 1.75(2) Å is short, rather typical of a W–C triple bond.[9] The other W(2)–O distances fall in the range 1.93–1.97 Å and are as expected for W–OSiR$_3$ distances involving a five-coordinate W^{6+} center.

Table I. Summary of Crystal Data for $W_2(\mu\text{-}CCCNHXyl)(OSiMe_2Bu^t)_5(CNXyl)_4\cdot{}^1/_2$(toluene)

empirical formula	$C_{77}H_{121}N_5O_5Si_5W_2\cdot 0.5C_7H_8$
color of cryst	red
cryst dimens (mm)	0.28 × 0.30 × 0.44
space group	$P2_1/n$
cell dimens	
temp (°C)	−158
a (Å)	21.354(7)
b (Å)	17.095(6)
c (Å)	24.288(9)
β (deg)	100.18(2)
Z (molecules/cell)	4
vol (Å^3)	8726.63
calcd dens (g/cm^3)	1.347
wavelength (Å)	0.710 69
mol wt	1769.05
linear abs coeff (cm^{-1})	28.048
detector to sample dist (cm)	22.5
sample to source dist (cm)	23.5
av ω scan width at half-height	0.25
scan speed (deg/min)	6.0
scan width (deg + dispersion)	1.5
individual bckgd (s)	6
aperture size (mm)	3.0 × 4.0
2θ range (deg)	6–45
total no. of reflns collcd	13 180
no. of unique intensities	11 443
no. with $F > 0.0$	9908
no. with $F > 2.33\sigma(F)$	6642
$R(F)$	0.0871
$R_w(F)$	0.0850
goodness of fit for the last cycle	2.142
max δ/σ for last cycle	0.92

The other tungsten atom, W(1), is separated from W(2) by 5.20 Å, and clearly the dinuclear nature of the molecule is a result of the bridging ligand and not a result of M–M bonding. The coordination geometry about W(1) is that of a pseudooctahedron with the η^2-C$_2$ moiety and the unique siloxide ligand in trans positions to one another. The W(1)–O(55) distance of 2.06(14) Å is notably longer than the W(2)–O distances which is consistent with the view that W(1) is in a lower oxidation state and is possibly an indication of a relatively high trans influence of the η^2-C$_2$ moiety.[10] The W(1) to C(4) and C(5) distances, 2.05(2) and 2.02(2) Å, respectively, are notably shorter than those to the isocyanide carbons which span a range 2.11–2.15 Å. The short W(2) to C(4) and C(5) distances, taken together with the C(4)–C(5) distance, 1.38(4) Å, and the angles N(6)–C(5)–C(4) = 128° and C(5)–C(4)–C(3) = 125° are characteristic of an η^2-alkyne bound to a strongly back-bonding early transition metal.[11] The W(2)–C(3)–C(4) angle of 167° is close to linear, and the C(3)–C(4) bond distance of 1.42 Å compares favorably with C_{sp}–C_{sp^2} bond lengths of 1.43 Å for compounds such as vinylacetylene and acrylonitrile.[12] The C(5)–N(6) distance of 1.35 Å is analogous to the C–N bond distance in formamide,[13a] indicative of some multiple-bond character.[13b] This too is implicated by the C(7)–N(6)–C(5) angle of 121° and the fact that the C(7) atom of the aryl ring is only 0.12 Å out

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[9] E.g. for the complexes $[(Bu^tO)_3W{\equiv}CR]_2$ the W≡C distances are ca. 1.77 Å: (a) (R = Me) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903. (b) (R = NMe$_2$) Chisholm, M. H.; Huffman, J. C.; Marchant, N. S. *J. Am. Chem. Soc.* **1983**, *105*, 6162.

[10] Appleton, T. G.; Clark, H. C.; Manzer, L. M. *Coord. Chem. Rev.* **1973**, *10*, 351.

[11] For example, see the W$_2$-η^2-C$_2$R$_2$ metric parameters in $W_2(OPr^i)_6(\mu\text{-}C_4R_4)(\eta^2\text{-}C_2R_2)$ where R = H and Me: Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C.; Leonelli, J. *J. Chem. Soc., Chem. Commun.* **1983**, 589. Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806.

[12] Gordon, A. J.; Ford, R. A. *The Chemists Companion*; John Wiley and Sons: New York, 1972; pp 244–336 (see also references therein).

[13] (a) Lide, D. R. *Tetrahedron* **1962**, *17*, 125. (b) Dotz, K. H.; Fischer, H.; Hoffmann, P.; Kreissl, F. R.; Schubert, V.; Weiss, K. *Transition Metal Carbene Complexes* Verlag Chemie: Weinheim, FRG, 1983 (see also references therein).

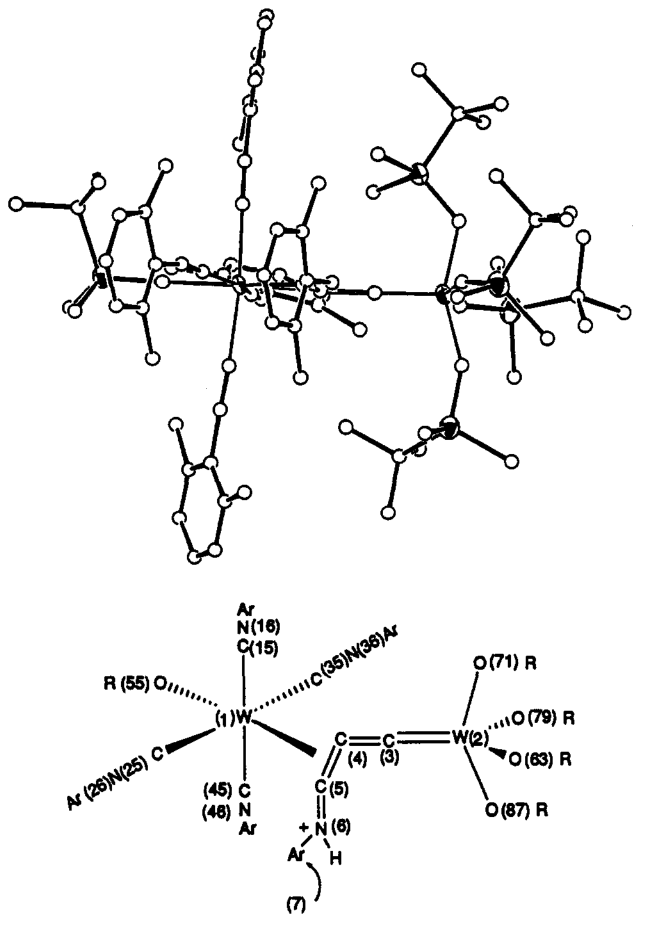


Figure 1. Top: ball-and-stick representation for the solid-state structure of $W_2(\mu\text{-CCCNHXyl})(OSiMe_2Bu^t)_5(CNXyl)_4$. Hydrogen atoms have been omitted for clarity. Bottom: stick figure representation showing the atom label scheme. R = $SiMe_2Bu^t$ and Ar = Xylyl.

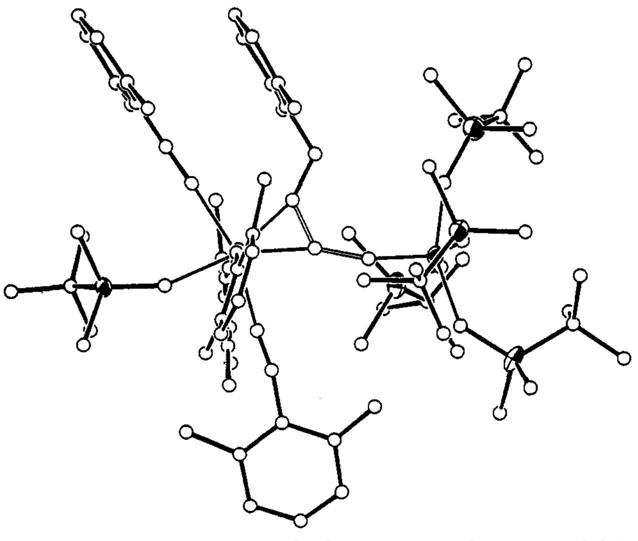
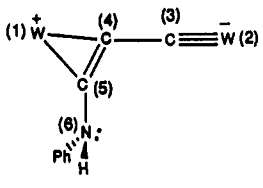
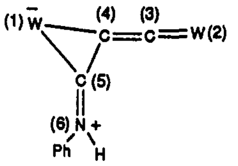


Figure 2. Ball-and-stick drawing of the $W_2(\mu\text{-CCC-NHXyl})(OSiMe_2Bu^t)_5(CNXyl)_4$ molecule showing the η^2-alkyne-like nature of the bridging ligand to W(1) and the near linearity of W(2)–C(3)–C(4). The atom number scheme is given in Figure 1.

of the plane containing W(1), C(4), C(5), and N(6). The hydrogen atom, though not located crystallographically, can be reasonably placed on the sp^2-hybridized nitrogen atom. (This is consistent with NMR data presented later.) Consequently, the bonding in this rather unusual molecule can be represented by two resonance forms, shown in E and F.



E



F

Clearly, there is delocalized π bonding involving N(6), C(5), C(4), C(3), and W(2). W(2) may be most easily viewed as a W^{6+} center, while the oxidation state of W(1) is more subjective, depending largely on ones preference for various valence bond/resonance structures. In this regard it is instructive to examine the NMR data and particularly the ^{13}C NMR data for the labeled compound **2*** (**2** prepared from **1***).

NMR Data for the Bridging CCCNHXyl Ligand. The ^1H and ^{13}C NMR data for compound **2** are given in the Experimental Section. It is sufficient here to confine our discussion to those data pertaining to the bridging CCCNHXyl ligand. For the carbon atoms C(3), C(4), and C(5) (see Figure 1) we can identify their respective ^{13}C signals at δ 260, 214, and 218. From the ^{13}C spectra of the labeled compound **2*** the signals at δ 260 and 214 are clearly derived from the original μ-CCH moiety in **1*** and are still directly bonded because of the observed $^1J_{^{13}C-^{13}C}$ = 53 Hz. This value is between that of ethane, 36 Hz, and ethene, 67 Hz.[14] The signal at δ 218 which is not enhanced in the labeled compound **2*** is thus the carbon derived from the isocyanide ligand, and this is coupled to C(4) (from the ethynyl ligand) with $^1J_{^{13}C-^{13}C}$ = 33 Hz. None of the ^{13}C signals assignable to C(3), C(4), and C(5) show coupling to H atoms. In the ^1H NMR spectrum a broad signal at δ 10.3 is assigned to the N*H* proton of the bridging ligand. In the deuterium-labeled compound derived from $W_2(\mu\text{-CCD})(OSiMe_2Bu^t)_5$ this signal is absent. The signal at δ 10.3 shows no coupling to ^{183}W and is thus unlikely to be due to a W—H moiety. Its broadness most likely arises from being bound to the quadrupolar ^{14}N nucleus. The chemical shift value, δ 10.3, is similar to values seen for NH protons in μ-C=NHPh ligands.[15] From this we are confident in the assignment of the connectivity of the bridging ligand as μ-CCCNHXyl where the α and β carbons are derived from the μ-CCH ligand in **1**.

The coupling constants involving ^{183}W, $I = {}^1/_2$, 14.5% natural abundance, are also informative. The α carbon C(3) shows $^1J_{^{183}W-^{13}C}$ = 273 Hz, which taken together with the chemical shift of δ 260 is rather typical of a W≡C carbon. Compare, for example, $(Bu^tO)_3W{\equiv}CR$ compounds having carbyne carbons which occur at δ ca. 250 and have $^1J_{^{183}W-^{13}C}$ = ca. 300 Hz.[9,16] The β carbon C(4) shows coupling to two ^{183}W nuclei. One coupling constant is 48 Hz, which is typical of the $^2J_{^{183}W-^{13}C}$ in $W{\equiv}CC_{\beta}H_2R$ containing compounds.[16] The other coupling of 33 Hz is more typical of a π-bonding interaction, e.g. as in the alkyne in $W_2(OPr^i)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}C_2H_2)$ where $J_{^{183}W-^{13}C}$ = 28 Hz.[11]

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(15) Lin, Y.-W.; Gau, H.-M.; Wen, Y.-S.; Lu, K.-L. *Organometallics* **1992**, *11*, 1445.

(16) Schrock, R. R.; Listemann, M. L. *Organometallics* **1985**, *4*, 74.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for $W_2(\mu\text{-CCCNHXyl})(OSiMe_2Bu^t)_5(CNXyl)_4\cdot{}^1/_2(\text{toluene})$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2	atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	811.6(4)	3981(1)	2521.4(4)	15(3)	C(51)	2841(12)	3110(16)	482(11)	34(6)
W(2)	−1005.9(5)	2083(1)	1673.5(4)	18(3)	C(52)	2966(13)	2921(18)	1049(12)	43(6)
C(3)	−359(10)	2674(13)	1963(9)	19(4)	C(53)	2550(12)	3136(15)	1386(10)	30(5)
C(4)	74(10)	3296(13)	2138(9)	15(4)	C(54)	2641(12)	2925(16)	1985(11)	34(5)
C(5)	−59(10)	4077(13)	2039(9)	16(4)	O(55)	1686(7)	4271(8)	2986(6)	19(3)
N(6)	−595(9)	4407(11)	1741(8)	22(4)	Si(56)	2251(3)	4818(4)	3264(3)	20(4)
C(7)	−636(11)	5241(15)	1639(10)	26(5)	C(57)	2360(11)	5672(15)	2812(10)	27(5)
C(8)	−953(11)	5692(14)	1989(10)	25(5)	C(58)	3016(11)	4276(14)	3377(10)	27(5)
C(9)	−1202(14)	5333(19)	2469(13)	48(7)	C(59)	2104(11)	5204(14)	3969(9)	22(5)
C(10)	−989(12)	6508(15)	1888(11)	30(5)	C(60)	1519(12)	5711(15)	3890(11)	31(5)
C(11)	−775(12)	6818(16)	1427(11)	33(5)	C(61)	2032(13)	4524(16)	4346(11)	35(6)
C(12)	−494(12)	6341(15)	1080(11)	30(5)	C(62)	2683(13)	5700(17)	4254(12)	40(6)
C(13)	−421(11)	5535(14)	1180(10)	25(5)	O(63)	−1641(7)	2871(9)	1381(6)	24(3)
C(14)	−95(13)	5040(16)	811(11)	36(6)	Si(64)	−2255(3)	3216(4)	978(3)	30(4)
C(15)	460(11)	3968(15)	3296(10)	25(5)	C(65)	−2440(14)	2628(18)	317(13)	49(7)
N(16)	285(9)	3926(12)	3710(8)	25(4)	C(66)	−2108(13)	4240(16)	784(11)	36(6)
C(17)	86(12)	3765(14)	4225(10)	28(5)	C(67)	−2982(13)	3179(16)	1345(11)	35(6)
C(18)	−376(12)	4280(15)	4375(10)	29(5)	C(68)	−3114(17)	2370(23)	1455(16)	70(9)
C(19)	−636(12)	5014(16)	4039(11)	36(6)	C(69)	−3553(16)	3553(20)	997(14)	54(7)
C(20)	−600(12)	4112(16)	4863(11)	35(6)	C(70)	−2810(16)	3611(21)	1901(15)	59(8)
C(21)	−372(13)	3451(17)	5165(12)	40(6)	O(71)	−1448(7)	1975(9)	2310(6)	23(3)
C(22)	106(13)	2968(17)	5008(12)	40(6)	Si(72)	−1207(3)	2221(4)	2966(3)	27(4)
C(23)	335(11)	3149(15)	4526(10)	28(5)	C(73)	−1209(12)	3301(16)	3059(11)	32(5)
C(24)	849(12)	2623(16)	4375(11)	35(6)	C(74)	−373(11)	1830(14)	3250(10)	23(5)
C(25)	703(11)	5233(15)	2463(10)	26(5)	C(75)	−1774(12)	1807(16)	3419(11)	33(5)
N(26)	662(9)	5908(12)	2446(8)	25(4)	C(76)	−1601(13)	2177(17)	4004(11)	38(6)
C(27)	661(12)	6710(16)	2340(11)	32(5)	C(77)	−2441(14)	1988(19)	3152(13)	49(7)
C(28)	393(13)	7175(17)	2760(11)	37(6)	C(78)	−1673(14)	913(18)	3476(12)	44(6)
C(29)	92(13)	6830(17)	3185(12)	38(6)	O(79)	−711(7)	1003(10)	1830(6)	26(3)
C(30)	384(16)	7996(22)	2609(15)	62(8)	Si(80)	−973(4)	94(4)	1750(3)	32(4)
C(31)	626(17)	8268(22)	2162(15)	63(8)	C(81)	−780(13)	−368(16)	2460(11)	35(5)
C(32)	886(15)	7783(20)	1826(13)	51(7)	C(82)	−518(12)	−477(16)	1280(11)	33(6)
C(33)	898(14)	6974(18)	1911(12)	42(6)	C(83)	−1854(12)	−26(15)	1456(10)	30(5)
C(34)	1187(13)	6425(17)	1542(12)	41(6)	C(84)	−2013(16)	−934(22)	1294(14)	63(8)
C(35)	1179(11)	2857(15)	2744(10)	25(5)	C(85)	−2270(14)	223(18)	1896(13)	47(7)
N(36)	1333(8)	2232(11)	2850(7)	19(4)	C(86)	−2056(16)	455(20)	947(14)	56(8)
C(37)	1536(10)	1521(13)	3124(9)	20(4)	O(87)	−906(7)	1929(9)	907(7)	28(3)
C(38)	1226(11)	815(14)	2900(10)	23(5)	Si(88)	−550(3)	2016(4)	362(3)	25(4)
C(39)	780(12)	808(16)	2373(11)	35(6)	C(89)	−951(14)	1341(18)	−170(13)	47(7)
C(40)	1427(12)	128(15)	3207(11)	31(5)	C(90)	−648(14)	3036(18)	113(12)	46(7)
C(41)	1886(12)	179(16)	3682(11)	32(5)	C(91)	324(12)	1762(15)	527(11)	30(5)
C(42)	2195(11)	852(15)	3893(10)	29(5)	C(92)	674(13)	2323(17)	983(12)	39(6)
C(43)	2025(10)	1565(13)	3592(9)	20(4)	C(93)	651(15)	1868(19)	19(13)	51(7)
C(44)	2349(12)	2333(15)	3752(11)	32(5)	C(94)	401(13)	920(17)	757(12)	41(6)
C(45)	1286(10)	3924(14)	1825(9)	21(4)	C(95)	629(33)	−521(45)	4494(30)	156(14)
N(46)	1598(8)	3854(10)	1486(7)	18(4)	C(96)	216(40)	−252(55)	4880(40)	87(14)
C(47)	2029(10)	3602(13)	1130(9)	19(4)	C(97)	−56(32)	565(40)	4703(29)	145(14)
C(48)	1905(11)	3822(14)	579(10)	26(5)	C(98)	347(42)	218(57)	4310(37)	94(13)
C(49)	1380(13)	4359(17)	339(12)	39(6)	C(99)	526(61)	−1041(83)	4859(57)	148(9)
C(50)	2343(12)	3568(16)	246(11)	32(5)					

Collectively, the NMR data are supportive of the X-ray structure and our formulation of the bridging ligand as having alkylidyne character to one tungsten, W(2), and η^2-alkyne character to W(1).

Concluding Remarks. The disruption of a M—M bond in the reaction with a strong π-acceptor ligand such as an isocyanide or CO is well-known,[17] but the formation of the μ-CCCNHXyl ligand is to our knowledge a new perturbation on the reactivity of μ-σ,π-alkynyl ligands shown in Scheme I. The insertion of isocyanide ligands into one of the Pd—C bonds in a Pd—C≡C—Pd-containing compound has been recently reported.[18]

Experimental Section

The preparation of $W_2(\mu\text{-CCH})(OSiMe_2Bu^t)_5$ (1) and the ^{13}C-labeled derivative 1* have been described previously.[2] ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-300 or a Bruker AM-500 NMR spectrometer. ^{1}H and ^{13}C NMR chemical shifts were referenced to the protio impurity of benzene-d_6 at δ 7.15 and the downfield aromatic signal of toluene-d_8 at δ 137.5, respectively (coupling constants are in hertz). Xylyl isocyanide (Fluka), hydrogen (Air Products), and ^{13}CO (99% ^{13}C; Cambridge Isotopes) were used without purification. Elemental analyses were obtained from Oneida Research Services, Inc., New York, NY. PMe_3 was prepared by a published procedure.[19]

Preparation of $W_2(\mu\text{-CCCNHXyl})(OSiMe_2Bu^t)_5(CNXyl)_4$. Toluene (10 mL) was added via cannula to a 30-mL Schlenk flask charged with the deep red crystalline solid $W_2(\mu\text{-CCH})(OSiMe_2Bu^t)_5$ (413 mg, 0.394 mmol), CNXyl (255 mg, 1.98 mmol), and a stir bar. The solution color immediately began turning orange-red. After the solution was stirred for 3 h, the volume was reduced in vacuo to 4 mL and the flask was placed at −20 °C. Red-orange crystals were formed after 2 days and were isolated by removing the supernatant liquid to a separate flask via cannula. Combined crystallizations gave a 44% yield (305 mg, 0.172 mmol). Anal. Calcd for $C_{77}H_{121}N_5O_5Si_5W_2$: C, 54.25; H, 7.15; N, 4.10. Found: C, 54.28; H, 6.82; N, 3.53. Note

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(17) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley Interscience: New York, 1982.

(18) Onitsuka, K.; Joh, T.; Takahashi, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 851.

(19) Luetkens, M. L.; Sattelberger, A. P.; Murray, H. H.; Basil, J. D.; Fackler, J. P. *Inorg. Synth.* **1990**, *28*, 305.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $W_2(\mu\text{-CCCNHXyl})(OSiMe_2Bu^t)_5(CNXyl)_4 \cdot {}^1/_2(\text{toluene})$

	Distances		
W(1)–O(55)	2.07(1)	W(2)–O(71)	1.96(2)
W(1)–C(4)	2.05(2)	W(2)–O(79)	1.97(2)
W(1)–C(5)	2.02(2)	W(2)–O(87)	1.93(2)
W(1)–C(15)	2.15(2)	W(2)–C(3)	1.76(2)
W(1)–C(25)	2.15(2)	C(3)–C(4)	1.42(3)
W(1)–C(35)	2.11(3)	C(4)–C(5)	1.38(3)
W(1)–C(45)	2.12(3)	C(5)–N(6)	1.35(3)
W(2)–O(63)	1.96(2)	N(6)–C(7)	1.45(3)
	Angles		
O(55)–W(1)–C(4)	159.0(7)	O(63)–W(2)–O(87)	86.0(6)
O(55)–W(1)–C(5)	161.4(7)	O(63)–W(2)–C(3)	101.3(8)
O(55)–W(1)–C(15)	86.9(7)	O(71)–W(2)–O(79)	86.6(6)
O(55)–W(1)–C(25)	82.8(7)	O(71)–W(2)–O(87)	154.2(6)
O(55)–W(1)–C(35)	79.6(7)	O(71)–W(2)–C(3)	101.1(8)
O(55)–W(1)–C(45)	86.2(7)	O(79)–W(2)–O(87)	88.4(6)
C(4)–W(1)–C(5)	39.5(8)	O(79)–W(2)–C(3)	105.2(8)
C(4)–W(1)–C(15)	91.9(9)	O(87)–W(2)–C(3)	104.6(9)
C(4)–W(1)–C(25)	118.2(9)	W(1)–O(55)–Si(56)	157.5(9)
C(4)–W(1)–C(35)	79.5(9)	W(2)–O(63)–Si(64)	156.3(10)
C(4)–W(1)–C(45)	92.7(8)	W(2)–O(71)–Si(72)	129.1(9)
C(5)–W(1)–C(15)	94.6(8)	W(2)–O(79)–Si(80)	140.5(9)
C(5)–W(1)–C(25)	78.7(9)	W(2)–O(87)–Si(88)	155.5(10)
C(5)–W(1)–C(35)	119.0(9)	W(2)–C(3)–C(4)	166.7(18)
C(5)–W(1)–C(45)	93.5(8)	W(1)–C(4)–C(3)	165.6(17)
C(15)–W(1)–C(25)	91.0(9)	W(1)–C(4)–C(5)	69.2(12)
C(15)–W(1)–C(35)	86.4(9)	C(3)–C(4)–C(5)	124.6(19)
C(15)–W(1)–C(45)	171.4(9)	W(1)–C(5)–N(6)	160.2(18)
C(25)–W(1)–C(35)	162.3(9)	W(1)–C(5)–C(4)	71.3(13)
C(25)–W(1)–C(45)	93.1(9)	W(1)–C(15)–N(16)	176.7(23)
C(35)–W(1)–C(45)	87.4(9)	W(1)–C(25)–N(26)	117.8(21)
O(63)–W(2)–O(71)	87.3(6)	W(1)–C(35)–N(36)	175.0(20)
O(63)–W(2)–O(79)	153.6(6)	W(1)–C(45)–N(46)	172.4(20)

the sample sent for elemental analysis was dried under a dynamic vacuum and sent by mail under vacuum. We believe that the half molecule of solvent of crystallization is lost under these conditions since the ^{1}H NMR spectrum of similarly treated samples does not reveal the presence of toluene. ^{1}H NMR (benzene-d_6, 22 °C, 300 MHz): 10.3 (s, NH, 1 H), 6.81 (m (ovlp), toluene H and xyl H, 14 H), 6.61 (d, xyl H, 2 H), 6.41 (t, xyl H, 1 H), 2.64 (s, xyl Me, 6 H), 2.50 (s, xyl Me, 24 H), 2.09 (s, toluene Me, 1.5 H), 1.2 (s, CMe_3, 36 H), 1.08 (s, CMe_3, 9 H), 0.27 (s, Me_2, 24 H), 0.21 (s, Me_2, 6 H). $^{13}C\{^1H\}$ NMR (toluene-d_8, 22 °C, 125 MHz) [C_a–C_c in the $C_aC_bC_c$NHXyl ligand only]: 260.7 (C_a, J_{WC} = 273 with I = 14%), 218.2 (C_a, J_{WC} = 33 with I – 14%), 214.3 (C_c, $^2J_{WC}$ = 48 with I = 14%, J_{WC} = 28 with I = 14%). No change in these signals was observed upon coupling to ^{1}H. ^{13}C NMR (toluene-d_8, 22 °C, 125 MHz) [C_a–C_c in the $^{13}C_a{}^{13}C_bC_c$NHXyl ligand only]: 260.7 (d, C_a, $J_{C_aC_b}$ = 53), 218.2 (d, C_c, $J_{C_cC_b}$ = 33), 214.3 (C_b, $J_{C_bC_a}$ = 53). IR (cm^{-1}, Nujol mull): 2048 (m), 2042 (m), 1599 (m), 1242 (vs), 1210 (m), 1140 (m), 1060 (s, br), 1008 (s), 960–810 (vs, br), 830 (s), 818 (vs), 799 (vs), 772 (vs), 718 (m), 690 (m), 670 (s), 659 (m), 620 (vw), 600 (w), 580 (vw), 563 (vw), 563 (vs), 460 (w), 390 (w), 365 (w), 350 (w), 322 (w), 315 (vw), 305 (vw), 290 (vw), 280 (vw), 270 (vw).

Preparation of $W_2(\mu\text{-CCCNHMes})(OSiMe_2Bu^t)_5(CNMes)_4$. Pentane (10 mL) was added via cannula to a 30-mL Schlenk flask charged with the deep red crystalline solid $W_2(\mu\text{-CCH})(OSiMe_2Bu^t)_5$ (125 mg, 0.119 mmol), CNMes (Mes = mesityl) (87 mg, 0.595 mmol), and a stir bar. The solution color immediately began turning orange-red, and an orange-red microcrystalline precipitate began forming. After the solution was stirred for 3 h, the volume was reduced in vacuo to 4 mL and the flask was placed at −20 °C for 2 h. The red-orange precipitate was isolated by removing the supernatant liquid to a separate flask via cannula in 52% yield (110 mg, 0.062 mmol). ^{1}H NMR (benzene-d_6, 22 °C, 500 MHz): 10.30 (s, NH, 1 H), 6.64 (s, Mes H, 8 H), 6.49 (s, Mes H, 2 H), 2.69 (s, Mes Me, 6 H), 2.55 (s, Mes Me, 24 H), 1.98 (s, Mes Me, 12 H), 1.74 (s, Mes Me, 3 H), 1.19 (s, CMe_3, 36 H), 0.94 (s, CMe_3, 9 H), 0.38 (s, Me_2, 24 H), 0.03 (s, Me_2, 6 H). $^{13}C\{^1H\}$ NMR (toluene-d_8, 22 °C, 75 MHz) [C_a–C_c in the $C_aC_bC_c$NHMes ligand only]: 260.3 (C_a, J_{WC} = 263 with I = 14%), 218.1 (C_a, no J_{WC} observed), 214.2 (C_c, $^2J_{WC}$ = 54 with I = 14%, no other J_{WC} observed). No change in these signals was observed upon coupling to ^{1}H. ^{13}C NMR (toluene-d_8, 22 °C, 125 MHz) [C_a–C_b in the $^{13}C_a{}^{13}C_b$CNHMes ligand only]: 260.3 (d, C_a, $J_{C_aC_b}$ = 54), 214.2 (C_b, $J_{C_bC_a}$ = 54).

NMR Study of the Reaction of $W_2(\mu\text{-}^{13}C^{13}CH)(OSiMe_2Bu^t)_5$ with PMe_3. The deep red crystalline compound $W_2(\mu\text{-}^{13}C^{13}CH)(OSiMe_2Bu^t)_5$ (30 mg, 0.029 mmol) was weighed into an extended 5-mm NMR tube equipped with a Kontes vacuum line adapter. Toluene-d_8 (0.5 mL) was added via a 1-mL syringe. PMe_3 (2.5 µL, 0.029 mmol) was added via a 10-µL syringe. The solution was frozen at −196 °C, the NMR tube was evacuated, and the tube was flame sealed. The NMR tube was allowed to warm to room temperature. No reaction was observed by ^{13}C NMR spectroscopy after 2 weeks at room temperature.

NMR Study of the Reaction of $W_2(\mu\text{-CCH})(OSiMe_2Bu^t)_5$ with H_2. The deep red crystalline compound $W_2(\mu\text{-CCH})(OSiMe_2Bu^t)_5$ (17 mg, 0.016 mmol) was weighed into an extended 5-mm NMR tube equipped with a Kontes vacuum line adapter. Toluene-d_8 (0.5 mL) was added via a 1-mL syringe. The solution was frozen at −196 °C, the NMR tube was evacuated, and H_2 was added via a calibrated vacuum manifold. The NMR tube was then flame sealed and the NMR tube allowed to warm to room temperature. At 23 °C, the pressure of the added H_2 was calculated to be 3 atm. No reaction was observed by ^{1}H NMR spectroscopy after 4 weeks at room temperature.

NMR Study of the Reaction of $W_2(\mu\text{-}^{13}C^{13}CH)(OSiMe_2Bu^t)_5$ with ^{13}CO. The deep red crystalline compound $W_2(\mu\text{-}^{13}C^{13}CH)(OSiMe_2Bu^t)_5$ (20 mg, 0.019 mmol) was weighed into an extended NMR tube equipped with a Kontes vacuum line adapter. Toluene-d_8 (0.5 mL) was added via a 1-mL syringe. The solution was frozen at −196 °C, the NMR tube was evacuated, and ^{13}CO (0.019 mmol) was added via a calibrated vacuum manifold. After addition of the gas, the tube was flame sealed. The NMR tube was allowed to warm to room temperature. After 1 h the red color of the solution had faded to orange. ^{13}C NMR spectroscopy revealed the signals for $W_2(\mu\text{-}^{13}C^{13}CH)(OSiMe_2Bu^t)_5$ and $W(^{13}CO)_6$ (δ 191.1 J_{WC} = 126 with I = 14%). In an analogous reaction employing 0.5 atm of ^{13}CO, only $W(^{13}CO)_6$ was observed by ^{13}C NMR spectroscopy.

X-ray Study of 2·$^1/_2$(toluene). General operating procedures and a listing of programs have been previously given.[20]

A single crystal was separated from a cluster of crystals, affixed to the end of a glass fiber with silicon grease, and transferred to a goniostat where it was cooled to −158 °C for characterization and data collection. Standard inert atmosphere techniques were employed.

A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited monoclinic symmetry. A secondary fragment with an intensity of less than 5% of the primary crystal's intensity was also observed. The systematic absences of all $h0l$, $h + l = 2n + 1$ except the −6,0,1, −6,0,−1, and −10,0,−5, and all $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, $00l$, $l = 2n + 1$ reflections indicated a possible space group ambiguity. However, subsequent refinement confirmed the choice of the space group $P2_1/n$, suggesting the anomalous $h0l$ reflections were artifacts. Unit cell dimensions were determined from 70 unique reflections with 18° < 2θ < 28°.

Data collection was undertaken as described in Table I. A total of 13 180 reflections were collected including space group extinctions and standards. The reflections −2,3,−1, 2,0,−4, −6,0,0, and −2,−3,−1 were chosen as standard reflections which were measured every 300 reflections. Between the first 600 and 900 reflections three of the four reflections dropped significantly. It was not possible to recover the initial intensity. However, no further loss in the standards intensity occurred until after a complete data set had been obtained. The intensity of the initial

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[20] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

900 reflections was adjusted by 12.6% to account for the average drop in intensity. Following the data collection, when the crystal was measured for an absorption correction, a large fracture along the −2,0,2 face was observed. This crystal fracture may well account for the above loss in intensity. An absorption correction was performed by using the dimensions described in the supplementary materials. Following the usual data reduction, absorption correction, and averaging of equivalent reflections, a set of 11 443 unique reflections was obtained. The R for averaging was 0.163 for 356 redundant data.

The structure was solved by using a combination of direct methods (SHELXS-86) and Fourier techniques. The two W atoms were located in the initial, E map. The remainder of the non-hydrogen atoms were located in successive Fourier transforms. A toluene solvent molecule disordered across a center of inversion was also located. Hydrogen atoms were placed in calculated fixed positions. The full-matrix least-squares refinement was completed using anisotropic thermal parameters on the two tungsten and five silicon atoms and isotropic thermal parameters on all other atoms. The final $R(F)$ was 0.0871 and $R_w(F)$ was 0.0850 when only the data with intensities greater than 2.33σ were used. Thus 6642 data were used for the refinement of 433 variables.

The final difference map contained several peaks of up to 4 e/Å^3. All of these peaks were in the immediate vicinity (within 1.2 Å) of the tungsten atoms, likely a result of an insufficient absorption correction of the fractured crystal.

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Supplementary Material Available: A table of anisotropic parameters, full listings of bond distances and angles, a summary of absorption correction, and VERSORT drawings (14 pages). Ordering information is given on any current masthead page.

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