(O)OEt), 174.3 (MeC(O)CH*C*(O)OEt), 85.4 (MeC(O)*C*HC(O)OEt), 64.2 (O*C*HMe$_2$), 60.2 (MeC(O)CHC(O)O*C*H$_2$CH$_3$), 26.3 (*Me*C(O)CHC(O)OEt), 24.3 (OCH*Me*$_2$), 14.7 (MeC(O)CHC(O)OCH$_2$*C*H$_3$). Anal. Calcd for $C_{30}H_{50}Al_2O_{14}$: C, 52.32; H, 7.32. Found: C, 52.24; H, 7.42.

[Al(OMe)(etac)$_2$]$_2$ (12). Compound **12** was prepared from "[Al(OMe)$_2$(etac)]$_x$" and ethyl acetoacetate. "[Al(OMe)$_2$(etac)]$_x$" was prepared by the addition of MeOH (20 g, 0.624 mol) to **5** (62.9 g, 0.115 mol). After having been stirred for 1 h, the volatiles were removed in vacuo. This procedure was repeated with 10 g of MeOH. This reaction mixture was then dissolved in 100 mL of pentane, and ethyl acetoacetate (29.8 g, 0.229 mol) was slowly added. After having been stirred for 12 h, a copious amount of a white solid precipitated from the solution. This product was collected by filtration and dried in vacuo (66 g, 91%). Compound **12** was recrystallized from CH_2Cl_2/pentane solution at −30 °C: ^{1}H NMR (CDCl$_3$) 4.89 (s, 2, MeC(O)C*H*C(O)OEt), 4.11 (br m, 4, MeC(O)CHC(O)OC*H*$_2$CH$_3$), 3.13 (s, 3, OCH$_3$), 1.90 (s, 6, *Me*C(O)CHC(O)OEt), 1.24 (br t, 6, $^3J_{HH}$ = 7.0 Hz, MeC(O)CHC(O)OCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$) 187.0 (Me*C*(O)CH(O)OEt), 174.6 (MeC(O)CH*C*(O)OEt, 85.3 (MeC(O)*C*HC(O)OEt), 60.4 (MeC(O)CHC(O)O*C*H$_2$CH$_3$), 49.6 (OCH$_3$), 26.2 (*Me*C(O)CHC(O)OEt), 14.5 (MeC(O)CHC(O)OCH$_2$*C*H$_3$); mass spectrum (FD) *m/e* 632 (M$^+$), 503 (M$^+$ − etac). Anal. Calcd for $C_{26}H_{42}Al_2O_{14}$: C, 49.37; H, 6.69. Found: C, 49.37; H, 6.29.

Kinetics of Ligand Disproportionation of 9. Stock solutions (0.01 M and 0.1 M) of **9** were prepared in toluene-d_8. The disproportionation reaction was monitored by 200-MHz ^{1}H NMR. The MeC(O)C*H*C(O)Me resonance of **9** can be clearly distinguished from those of the products, **1** and Al(acac)$_3$. The kinetics were determined by the relative integration of the respective resonances. After several minutes were allowed for temperature equilibration in the NMR probe, at least 10 spectra were recorded over a period of 2–4 half-lives. After each kinetic run, the temperature of the NMR probe was calibrated with use of an ethylene glycol standard. The k_{obsd}, $t_{1/2}$, correlation coefficient for each run, and the Arrhenius plot data are listed in Table III. The kinetic plot of the reaction at 72.7 °C is shown in Figure 6. The error of these kinetics is estimated to be ±5% based on the precision of the integration technique.

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Study of the Formation of a σ,π-Vinyl Ligand by Hydrogen Atom Transfer from a Coordinated Dimethylamide to a Perpendicularly Bonded Ethyne Ligand. Preparation and Characterization of $(PMe_2Ph)Cl_2W(\mu\text{-}NMe_2)(\mu\text{-}\eta^1,\eta^2\text{-}CHCH_2)(\mu\text{-}\eta^2,\eta^1\text{-}CH_2NMe)WCl(NMe_2)(PMe_2Ph)$

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Abstract: Addition of ethyne (1 equiv) to hydrocarbon solutions of $W_2Cl_3(NMe_2)_3L_2$ yields μ-perpendicular alkyne adducts $W_2Cl_3(NMe_2)_3L_2(\mu\text{-}C_2H_2)$ where L = PMe$_2$Ph, I, and PMe$_3$, Ia. Compound Ia may also be obtained by the displacement of PMe$_2$Ph from I upon addition of PMe$_3$ (>2 equiv). The molecular structure of Ia, deduced from a single-crystal X-ray analysis, shows the presence of one μ-Cl, one μ-NMe$_2$, and the μ-C$_2$H$_2$ ligand. Each tungsten is also coordinated to three terminal ligands, NMe$_2$, Cl, and PMe$_3$, such that if the μ-C$_2$H$_2$ ligand is viewed to occupy a single coordination site, then the dinuclear compound can be considered to contain a central confacial bioctahedral core. ^{1}H and ^{13}C NMR data for I and Ia are entirely reconcilable with the structure found in the solid state for Ia. Of note are the small values of $J_{^{13}C-^{13}C}$, ca. 18 Hz in the labeled μ-*C$_2$H$_2$ containing compounds (*C represent 92.5 g-atom % ^{13}C) and the large chemical shift difference between the two types of μ-C nuclei, ca. 40 ppm. The compounds I and Ia react in benzene or toluene at and above room temperature to give compounds II and IIa, respectively, which contain a $W_2(\mu\text{-}C_2H_3)(\mu\text{-}CH_2NMe)$ core. The compounds II and IIa can be considered to have a $(W-W)^{10+}$ core supported by a bridging σ,π-vinyl(3−) and a bridging imine(2−) ligand. The structural characterization of II, by a single-crystal study, provides the first example of a μ-CH$_2$NMe ligand. The conversions of I to II and Ia to IIa have been followed by ^{1}H NMR spectroscopy as a function of time and temperature. A double-labeling experiment shows that transfer of an H atom to the μ-C$_2$H$_2$ carbon atom involves an intramolecular process. The rate of reaction is independent of added phosphine and shows a large primary kinetic isotope effect, k_H/k_D, of ca. 6 at +60 °C and a small but positive secondary isotope effect, k_H/k_D, of ca. 1.4 when the reaction rates are followed involving $N(CH_3)_2/N(CD_3)_2$ and $\mu\text{-}C_2H_2/\mu\text{-}C_2D_2$ labeled compounds, respectively. The entropy of activation is of medium magnitude and negative. Taken together, the data conform to a model in which C–H bond breaking (NMe$_2$) and forming (μ-C$_2$H$_2$) are of approximately equal importance in the transition state. A direct tranference of the H atom via a five-membered ring is thus favored over a reaction pathway involving initial β-hydrogen atom transfer to a metal atom. These reactions are compared to related findings reported in the literature. Crystal data are as follows: for (i) $W_2Cl_3(NMe_2)_3(PMe_3)_2(\mu\text{-}C_2H_2)\cdot{}^1/_2C_7H_8$ at −162 °C, a = 18.069 (7) Å, b = 14.108 (4) Å, c = 11.204 (3) Å, β = 106.09 (2)°, Z = 4, d_{calcd} = 2.01 g cm^{-3}, and space group $P2_1/a$; for (ii) $W_2(NMe_2)_2Cl_3(\mu\text{-}CH_2NMe)(\mu\text{-}C_2H_3)(PMe_2Ph)_2\cdot{}^1/_2C_7H_8$ at −160 °C, a = 16.929 (7) Å, b = 17.766 (8) Å, c = 11.108 (4) Å, α = 103.31 (2)°, β = 91.76 (2)°, γ = 78.59 (2)°, Z = 4, d_{calcd} = 2.01 g cm^{-3}, and space group $P\bar{1}$.

Previous studies of the reactions between alkynes and ditungsten hexaalkoxides have revealed a rich and varied chemistry.[1] The principle reactions discovered thus far include metathesis-like alkylidyne formation, alkyne adduct formation, carbon–carbon bond forming reactions, and the formation of alkylidyne-capped cluster compounds. There is also evidence for a kinetically facile equilibrium involving $W_2(\mu\text{-}C_2R_2)$- and W≡CR-containing compounds. The position of the equilibrium appears very sensitive to the nature of the alkoxide ligands and the substituent, R, on the alkyne.

We have been interested in how changes in the ligands bonded to tungsten would influence the reactivity of the W≡W bond toward alkynes. With that view, we have started to investigate

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[1] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Chem. Soc. Rev.* **1985**, *14*, 69 and references cited therein.

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the reactivity of $(W{\equiv}W)^{6+}$ containing compounds with a variety of supporting ligands, e.g., alkyls–alkoxides[2] and amides–halides.[3,4] During the course of these studies, we have prepared several alkyne adducts of general formula $W_2(NMe_2)_{6-x}Cl_x(\mu\text{-}RCCR')L_2$ where L = neutral donor ligand, R and R′ are H, alkyl, or phenyl, and x = 2, 3, and 4.[3,4] Rather interestingly, no alkylidyne formation was seen in these reactions. The details of this study will be published elsewhere, but one finding which we feel should be highlighted is reported here. This involves the formation of a so-called σ,π-vinyl ligand by hydrogen atom transfer from a coordinated dimethylamido ligand. The latter is transformed to a bridging methylimine ligand. The structure and bonding in the $W_2(\mu\text{-}CHCH_2)(\mu\text{-}CH_2NMe)$-containing compound and the reaction pathway leading to its formation warrant special attention and are reported here in detail.

Results and Discussion

Syntheses. Reactions between $W_2Cl_3(NMe_2)_3L_2$ and 1 equiv of ethyne in toluene produce $W_2Cl_3(NMe_2)_3L_2(\mu\text{-}C_2H_2)$ where L = PMe_2Ph (I) and PMe_3 (Ia). The ^1H NMR spectra of the crude reaction mixtures show that both compounds are formed essentially quantitatively. Compound I, which is only sparingly soluble in toluene, can be isolated from the reaction mixture by filtration within $^1/_2$ h of the addition of ethyne when the reaction is carried out at 22 °C. Compound Ia is formed more slowly at 22 °C and requires a reaction time of ca. 3 h. It is more soluble in toluene and can be isolated by low-temperature crystallizations from concentrated solutions. We believe that the longer reaction time involved in the preparation employing the PMe_3 adduct reflects the order of phosphine lability in the $W_2Cl_3(NMe_2)_3L_2$ compounds and the phosphine dissociation is required before alkyne uptake. Compound Ia can also be prepared by the addition of PMe_3 to a warm toluene solution of I with substitution of PMe_2Ph.

The 1:1 ethyne adducts, I and Ia, are thermally unstable in aromatic hydrocarbon solutions and react to form $W_2Cl_3(NMe_2)_2(\mu\text{-}CHCH_2)(\mu\text{-}CH_2NMe)L_2$ compounds: II where L = PMe_2Ph and IIa where L = PMe_3. The formation of II is essentially complete in 45 min at 65 °C while formation of IIa requires roughly twice as long at this temperature. Compounds II and IIa have been isolated as green crystalline solids by crystallization from toluene.

The overall reaction sequence is shown in eq 1. In the first step, an unbridged W–W triple bond is converted to a bridged dimer.

(i)

$$W_2Cl_3(NMe_2)_3L_2 + C_2H_2 \xrightarrow[\text{toluene}]{22\ ^\circ C} W_2Cl_3(NMe_2)_3L_2(\mu\text{-}C_2H_2)$$

$$\text{(ii)}\quad W_2Cl_3(NMe_2)_3L_2(\mu\text{-}C_2H_2) \xrightarrow[\text{toluene}]{65\ ^\circ C} W_2Cl_3(NMe_2)_2L_2(\mu\text{-}C_2H_3)(\mu\text{-}CH_2NMe) \qquad (1)$$

In the second step, a hydrogen atom from a coordinated dimethylamido ligand is transferred to one of the carbon atoms of the bridging ethyne ligand.

It should be noted that in the preparation of I and Ia, only 1 equiv of ethyne must be added since a further reaction occurs with more acetylene.

Physicochemical Properties. The new compounds, I, Ia, II, and IIa, are all air-sensitive and must be handled in dry and oxygen-free inert atmospheres (N_2) and solvents. The compounds appeared indefinitely stable when stored in sealed vials. All the compounds are moderately soluble in aromatic hydrocarbon solvents but more so in methylene chloride, the deuterated form of which was used as a solvent for spectroscopic studies. Elemental analyses, infrared data, and NMR data are given in the Experimental Section. Various aspects of the NMR data, particularly those pertaining to the structural identity of the compounds in solution, are discussed in the section on NMR studies.

Table I. Fractional Coordinates and Isotropic Thermal Parameters for $W_2Cl_3(NMe_2)_3(PMe_3)_2(C_2H_2){\cdot}{}^1/_2C_7H_8$

atom	10^4x	10^4y	10^4z	$10B_{iso}$
W(1)	6406.0 (3)	1389.1 (3)	3786.4 (4)	17
W(2)	6300.8 (3)	1924.3 (3)	1462.0 (4)	16
Cl(3)	6889 (2)	−154 (2)	4758 (3)	35
Cl(4)	6676 (2)	988 (2)	−181 (3)	27
Cl(5)	7535 (2)	1258 (2)	2850 (3)	24
N(6)	5910 (6)	587 (7)	2080 (8)	22
C(7)	5076 (8)	417 (10)	1801 (11)	30
C(8)	6235 (9)	−342 (9)	1843 (11)	31
C(9)	5685 (7)	2381 (8)	2695 (11)	22
C(10)	6413 (7)	2785 (8)	3046 (10)	21
P(11)	7369 (2)	2062 (2)	5681 (3)	21
C(12)	7687 (8)	1352 (10)	7090 (12)	35
C(13)	8292 (8)	2410 (9)	5467 (12)	30
C(14)	6999 (8)	3121 (9)	6243 (11)	29
N(15)	5663 (6)	1465 (8)	4787 (9)	26
C(16)	5002 (10)	2093 (17)	4616 (14)	69
C(17)	5731 (9)	913 (11)	5932 (12)	39
P(18)	7127 (2)	3246 (3)	982 (3)	26
C(19)	6612 (9)	4364 (10)	634 (14)	44
C(20)	7976 (9)	3559 (10)	2195 (13)	37
C(21)	7548 (10)	3095 (12)	−329 (13)	46
N(22)	5401 (6)	2412 (7)	155 (8)	23
C(23)	5438 (7)	2562 (9)	−1134 (12)	28
C(24)	4621 (8)	2668 (11)	196 (13)	38
C(25)	4845 (26)	4981 (32)	5428 (38)	66 (9)
C(26)	5697 (11)	5079 (13)	5446 (18)	7 (3)
C(27)	4282 (24)	4942 (29)	5760 (39)	66 (9)
C(28)	4851 (13)	5022 (16)	6847 (22)	76 (5)
C(29)	5614 (20)	5127 (24)	6522 (32)	50 (7)

Table II. Bond Distances for the $W_2Cl_3(NMe_2)_3(PMe_3)_2(\mu\text{-}C_2H_2)$ Molecule

A	B	distance
W(1)	W(2)	2.6674 (10)
W(1)	Cl(3)	2.482 (3)
W(1)	Cl(5)	2.546 (3)
W(1)	P(11)	2.527 (3)
W(1)	N(6)	2.189 (9)
W(1)	N(15)	1.977 (10)
W(1)	C(9)	2.066 (11)
W(1)	C(10)	2.138 (12)
W(2)	Cl(4)	2.508 (3)
W(2)	Cl(5)	2.520 (3)
W(2)	P(18)	2.537 (3)
W(2)	N(6)	2.193 (10)
W(2)	N(22)	1.985 (10)
W(2)	C(9)	2.102 (11)
W(2)	C(10)	2.113 (11)
P(11)	C(12)	1.823 (13)
P(11)	C(13)	1.818 (13)
P(11)	C(14)	1.819 (13)
P(18)	C(19)	1.818 (16)
P(18)	C(20)	1.801 (15)
P(18)	C(21)	1.844 (13)
N(6)	C(7)	1.470 (16)
N(6)	C(8)	1.490 (16)
N(15)	C(16)	1.456 (20)
N(15)	C(17)	1.475 (16)
N(22)	C(23)	1.479 (16)
N(22)	C(24)	1.469 (17)
C(9)	C(10)	1.388 (17)

Solid-State Molecular Structures and Bonding Considerations. Compounds Ia and II yielded crystals suitable for single-crystal X-ray studies. NMR studies leave no doubt that I and Ia and II and IIa are related in a pairwise manner.

$W_2Cl_3(NMe_2)_3(PMe_3)_2(\mu\text{-}C_2H_2)$, Ia. Final atomic coordinates and isotropic thermal parameters are given in Table I, and selected bond distances and angles are given in Tables II and III, respectively. An ORTEP view of the molecule is shown in Figure 1. This view emphasizes the perpendicular mode of bonding for the ethyne ligand. If the ethyne is considered to occupy a single

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Table III. Bond Angles (deg) for the $W_2Cl_3(NMe_2)_3(PMe_3)_2(C_2H_2)$ Molecule

A	B	C	angle	A	B	C	angle
W(2)	W(1)	Cl(3)	126.72 (8)	Cl(5)	W(2)	C(9)	104.4 (3)
W(2)	W(1)	Cl(5)	57.77 (7)	Cl(5)	W(2)	C(10)	80.4 (3)
W(2)	W(1)	P(11)	124.06 (8)	P(18)	W(2)	N(6)	163.55 (28)
W(2)	W(1)	N(6)	52.56 (25)	P(18)	W(2)	N(22)	89.9 (3)
W(2)	W(1)	N(15)	131.5 (3)	P(18)	W(2)	C(9)	111.3 (3)
W(2)	W(1)	C(9)	50.8 (3)	P(18)	W(2)	C(10)	80.2 (3)
W(2)	W(1)	C(10)	50.7 (3)	N(6)	W(2)	N(22)	105.2 (4)
Cl(3)	W(1)	Cl(5)	83.84 (12)	N(6)	W(2)	C(9)	77.3 (4)
Cl(3)	W(1)	P(11)	83.36 (11)	N(6)	W(2)	C(10)	101.2 (4)
Cl(3)	W(1)	N(6)	86.51 (27)	N(22)	W(2)	C(9)	84.5 (4)
Cl(3)	W(1)	N(15)	90.6 (3)	N(22)	W(2)	C(10)	106.8 (4)
Cl(3)	W(1)	C(9)	160.3 (4)	C(9)	W(2)	C(10)	38.5 (5)
Cl(3)	W(1)	C(10)	159.8 (3)	W(1)	Cl(5)	W(2)	63.53 (8)
Cl(5)	W(1)	P(11)	85.96 (10)	W(1)	P(11)	C(12)	120.0 (5)
Cl(5)	W(1)	N(6)	77.50 (27)	W(1)	P(11)	C(13)	115.7 (4)
Cl(5)	W(1)	N(15)	170.3 (3)	W(1)	P(11)	C(14)	111.5 (5)
Cl(5)	W(1)	C(9)	104.6 (3)	C(12)	P(11)	C(13)	100.4 (6)
Cl(5)	W(1)	C(10)	79.3 (3)	C(12)	P(11)	C(14)	102.1 (6)
P(11)	W(1)	N(6)	161.44 (28)	C(13)	P(11)	C(14)	105.2 (6)
P(11)	W(1)	N(15)	85.5 (3)	W(2)	P(18)	C(19)	112.8 (5)
P(11)	W(1)	C(9)	114.7 (4)	W(2)	P(18)	C(20)	116.7 (5)
P(11)	W(1)	C(10)	84.4 (3)	W(2)	P(18)	C(21)	118.7 (5)
N(6)	W(1)	N(15)	110.2 (4)	C(19)	P(18)	C(20)	103.2 (7)
N(6)	W(1)	C(9)	78.1 (4)	C(19)	P(18)	C(21)	103.2 (8)
N(6)	W(1)	C(10)	100.5 (4)	C(20)	P(18)	C(21)	100.1 (7)
N(15)	W(1)	C(9)	83.3 (4)	W(1)	N(6)	W(2)	75.0 (3)
N(15)	W(1)	C(10)	104.4 (4)	W(1)	N(6)	C(7)	114.7 (7)
C(9)	W(1)	C(10)	38.5 (5)	W(1)	N(6)	C(8)	121.6 (8)
W(1)	W(2)	Cl(4)	127.39 (8)	W(2)	N(6)	C(7)	118.3 (8)
W(1)	W(2)	Cl(5)	58.70 (7)	W(2)	N(6)	C(8)	121.6 (8)
W(1)	W(2)	P(18)	121.86 (8)	C(7)	N(6)	C(8)	104.4 (10)
W(1)	W(2)	N(6)	52.43 (23)	W(1)	N(15)	C(16)	128.2 (9)
W(1)	W(2)	N(22)	129.85 (27)	W(1)	N(15)	C(17)	123.9 (9)
W(1)	W(2)	C(9)	49.6 (3)	C(16)	N(15)	C(17)	107.7 (11)
W(1)	W(2)	C(10)	51.6 (3)	W(2)	N(22)	C(23)	121.4 (8)
Cl(4)	W(2)	Cl(5)	83.31 (10)	W(2)	N(22)	C(24)	131.2 (8)
Cl(4)	W(2)	P(18)	86.38 (11)	C(23)	N(22)	C(24)	107.4 (10)
Cl(4)	W(2)	N(6)	87.42 (26)	W(1)	C(9)	W(2)	79.6 (4)
Cl(4)	W(2)	N(22)	88.5 (3)	W(1)	C(9)	C(10)	73.6 (7)
Cl(4)	W(2)	C(9)	160.9 (4)	W(2)	C(9)	C(10)	71.2 (6)
Cl(4)	W(2)	C(10)	159.5 (3)	W(1)	C(10)	W(2)	77.7 (4)
Cl(5)	W(2)	P(18)	86.15 (11)	W(1)	C(10)	C(9)	67.9 (7)
Cl(5)	W(2)	N(6)	77.99 (27)	W(2)	C(10)	C(9)	70.3 (7)
Cl(5)	W(2)	N(22)	171.11 (28)				

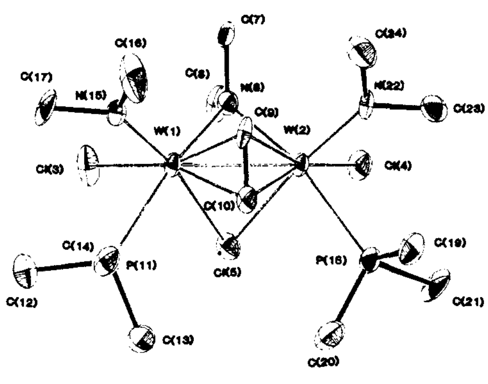

Figure 1. ORTEP view of the $W_2Cl_3(NMe_2)_3(PMe_3)_2(\mu\text{-}C_2H_2)$ molecule giving the atom number scheme used in the tables.

coordination site, X, then the PNClW(μ-X)(μ-N)(μ-Cl)WClNP unit corresponds quite closely to a confacial bioctahedron.

The W–W distance, 2.667 (1) Å, and the C–C distance, 1.39 (2) Å, are comparable to those seen for $W_2(\mu\text{-}C_2)$-containing compounds supported by alkoxide ligands.[5] The choice of one bridging NMe_2 group and one bridging Cl ligand satisfies electroneutrality within the molecule and gives rise to a virtual mirror plane containing the bridging atoms. The specific arrangement of the ligands such that all three NMe_2 groups lie on one side of the molecule may well result from trans influences[6] of the PMe_3, Cl, and NMe_2 ligands.

The W–N distances associated with the terminal NMe_2 groups are ca. 0.2 Å shorter than those involving the μ-NMe_2 ligand, which taken together with the planarity of the terminal WNC_2 units and observation of restricted rotations about the W–N bonds in solution[7] (see NMR Studies section) are indicative of Me_2N-to-W π-bonding.

$W_2Cl_3(NMe_2)_2(CH_2NMe)(CHCH_2)(PMe_2Ph)_2$, II, crystallizes in the space group $P\bar{1}$ along with a molecule of solvent. There are two independent molecules of II in the unit cell differing very little in terms of pertinent distances and angles. A ball-and-stick drawing of one of the molecules is given in Figure 2. There is no element of symmetry in either molecule. Stereoviews, space-filling drawings, and a superposition of the two independent molecules are given in the supplementary material. Atomic positional parameters are given in Table IV, and selected bond distances and angles are reported in Tables V and VI, respectively. A summary of crystal data for the two compounds structurally characterized, Ia and II, is given in Table VII.

Each tungsten atom can be considered to be in a distorted octahedral environment if the atoms C(27)–C(28) and N(29)–C(30) are considered to occupy a single coordination site of W(1) and W(2), respectively. The W–W distance, 2.606 (1) Å, though slightly shorter than that in Ia (2.667 (1) Å), is still in the range

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Table IV. Fractional Coordinates and Isotropic Thermal Parameters for $W_2Cl_3(NMe_2)_2(CH_2NMe)(CHCH_2)(PMe_2Ph)_2 \cdot {}^1/_2C_7H_8$[a]

atom	10^4x	10^4y	10^4z	$10B_{iso}$
W(1A)	3660.5 (3)	1641.1 (3)	2540.8 (5)	14
W(2A)	3077.2 (3)	927.6 (3)	4018.1 (5)	13
N(3A)	4791 (6)	1486 (6)	2008 (11)	20
C(4A)	5050 (9)	1698 (9)	885 (14)	29
C(5A)	5523 (9)	1181 (9)	2601 (12)	28
Cl(6A)	3166 (2)	1584 (2)	424 (3)	23
P(7A)	3426 (2)	3103 (2)	2437 (3)	24
C(8A)	3609 (11)	3338 (9)	972 (15)	20
C(9A)	2248 (18)	3612 (14)	2596 (28)	90
C(10A)	3778 (16)	3796 (13)	3584 (22)	68
C(11A)	4520 (17)	3750 (15)	3408 (24)	76
C(12A)	4936 (22)	4359 (18)	4451 (31)	104
C(13A)	5575 (19)	5135 (20)	4532 (27)	98
C(14A)	3569 (20)	4766 (15)	5518 (30)	95
C(15A)	2933 (33)	4190 (13)	4519 (22)	180
Cl(16A)	1876 (2)	318 (2)	3896 (3)	24
Cl(17A)	3848 (2)	−294 (2)	4495 (3)	22
P(18A)	2921 (2)	1167 (2)	6369 (3)	16
C(19A)	3881 (9)	1098 (10)	7140 (14)	34
C(20A)	2477 (9)	474 (8)	6914 (13)	25
C(21A)	2369 (9)	2119 (8)	7229 (11)	22
C(22A)	1569 (10)	2206 (10)	7621 (15)	38
C(23A)	1135 (11)	2958 (11)	8283 (18)	48
C(24A)	1501 (13)	3594 (12)	8443 (19)	55
C(25A)	2285 (13)	3518 (11)	8051 (16)	49
C(26A)	2738 (11)	2780 (9)	7405 (14)	36
C(27A)	4048 (8)	1448 (7)	4473 (12)	18
C(28A)	4041 (8)	2237 (8)	4393 (11)	17
N(29A)	2409 (7)	1806 (6)	3104 (11)	24
C(30A)	2251 (8)	2056 (7)	4438 (10)	14
C(31A)	1671 (8)	1797 (9)	2406 (11)	25
N(32A)	3499 (6)	420 (6)	2156 (10)	18
C(33A)	2930 (8)	97 (8)	1238 (12)	24
C(34A)	4279 (9)	−122 (8)	1928 (13)	24
W(1B)	6787.2 (3)	3281.5 (3)	−1582.9 (4)	12
W(2B)	7504.9 (3)	3094.5 (3)	462.6 (5)	14
N(3B)	5715 (6)	3107 (7)	−2139 (11)	23
C(4B)	5180 (9)	3486 (9)	−2951 (13)	31
C(5B)	5287 (9)	2533 (9)	−1788 (13)	29
Cl(6B)	6457 (2)	4566 (2)	−2109 (3)	24
P(7B)	7319 (2)	2877 (2)	−3832 (3)	15
C(8B)	6717 (8)	2285 (8)	−4855 (13)	24
C(9B)	7329 (9)	3663 (8)	−4630 (12)	26
C(10B)	8344 (8)	2292 (8)	−4138 (11)	17
C(11B)	8466 (9)	1465 (8)	−4489 (12)	24
C(12B)	9249 (10)	1038 (9)	−4763 (13)	33
C(13B)	9897 (10)	1418 (11)	−4627 (15)	40
C(14B)	9773 (9)	2240 (11)	−4257 (16)	38
C(15B)	8995 (8)	2687 (9)	−3975 (12)	24
Cl(16B)	8212 (2)	3964 (2)	1982 (3)	31
Cl(17B)	6755 (2)	2924 (2)	2201 (3)	22
P(18B)	8420 (2)	1937 (2)	1126 (3)	22
C(19B)	7906 (9)	1176 (8)	1403 (13)	30
C(20B)	8954 (10)	2182 (10)	2548 (13)	38
C(21B)	9227 (8)	1360 (8)	32 (12)	22
C(22B)	9056 (8)	801 (8)	−983 (13)	22
C(23B)	9647 (9)	367 (9)	−1871 (13)	28
C(24B)	10430 (8)	516 (9)	−1707 (12)	24
C(25B)	10612 (9)	1065 (10)	−703 (14)	33
C(26B)	10013 (8)	1504 (9)	202 (14)	27
C(27B)	7047 (7)	2214 (7)	−684 (11)	15
C(28B)	7213 (7)	1961 (7)	−1976 (11)	14
N(29B)	7961 (7)	3517 (6)	−979 (10)	20
C(30B)	8527 (8)	2864 (8)	−749 (10)	20
C(31B)	8306 (9)	4236 (9)	−982 (13)	28
N(32B)	6495 (6)	4005 (6)	291 (10)	16
C(33B)	6587 (9)	4832 (8)	721 (13)	27
C(34B)	5678 (8)	3966 (7)	700 (11)	18
C(1S)	375 (28)	4441 (28)	2756 (71)	259
C(2S)	1150 (35)	4701 (23)	5331 (59)	244
C(3S)	321 (25)	3880 (23)	3739 (49)	162
C(4S)	772 (29)	3992 (35)	5224 (43)	192
C(5S)	991 (40)	5051 (43)	4645 (58)	242
C(6S)	861 (61)	4793 (74)	3456 (58)	429

[a] Atoms labeled A and B refer to the two independent molecules in the unit cell; atoms labeled S are solvent.

Table V. Selected Bond Distances (Å) for the $W_2Cl_3(NMe_2)_2(CH_2NMe)(CHCH_2)(PMe_2Ph)_2$ Molecules

A	B	distance
W(1A)	W(2A)	2.6130 (11)
W(1A)	Cl(6A)	2.458 (3)
W(1A)	P(7A)	2.578 (4)
W(1A)	N(3A)	1.968 (11)
W(1A)	N(29A)	2.172 (11)
W(1A)	N(32A)	2.184 (10)
W(1A)	C(27A)	2.307 (12)
W(1A)	C(28A)	2.226 (12)
W(2A)	Cl(16A)	2.472 (3)
W(2A)	Cl(17A)	2.461 (3)
W(2A)	P(18A)	2.560 (3)
W(2A)	N(29A)	2.170 (11)
W(2A)	N(32A)	2.140 (11)
W(2A)	C(27A)	2.037 (12)
W(2A)	C(30A)	2.167 (11)
W(1B)	W(2B)	2.6014 (12)
W(1B)	Cl(6B)	2.440 (3)
W(1B)	P(7B)	2.574 (3)
W(1B)	N(3B)	1.958 (10)
W(1B)	N(29B)	2.166 (11)
W(1B)	N(32B)	2.193 (11)
W(1B)	C(27B)	2.303 (12)
W(1B)	C(28B)	2.257 (11)
W(2B)	Cl(16B)	2.465 (3)
W(2B)	Cl(17B)	2.450 (3)
W(2B)	P(18B)	2.558 (4)
W(2B)	N(29B)	2.141 (10)
W(2B)	N(32B)	2.146 (10)
W(2B)	C(27B)	2.043 (12)
W(2B)	C(30B)	2.140 (13)
P(7A)	C(8A)	1.820 (14)
P(7A)	C(9A)	2.02 (3)
P(7A)	C(10A)	1.736 (21)
P(18A)	C(19A)	1.810 (15)
P(18A)	C(20A)	1.784 (14)
P(18A)	C(21A)	1.825 (14)
P(7B)	C(8B)	1.799 (13)
P(7B)	C(9B)	1.822 (13)
P(7B)	C(10B)	1.835 (13)
P(18B)	C(19B)	1.832 (15)
P(18B)	C(20B)	1.803 (13)
P(18B)	C(21B)	1.834 (14)
N(3A)	C(4A)	1.484 (17)
N(3A)	C(5A)	1.454 (18)
N(29A)	C(30A)	1.463 (16)
N(29A)	C(31A)	1.450 (17)
N(32A)	C(33A)	1.478 (16)
N(32A)	C(34A)	1.463 (17)
N(3B)	C(4B)	1.441 (18)
N(3B)	C(5B)	1.487 (17)
N(29B)	C(30B)	1.418 (17)
N(29B)	C(31B)	1.507 (16)
N(32B)	C(33B)	1.475 (16)
N(32B)	C(34B)	1.488 (16)

encountered for single-bond distances[8] and is consistent with the view that a central $(W-W)^{10+}$ moiety is ligated by a μ-$CHCH_2(3-)$ ligand and a μ-$CH_2NMe(2-)$ ligand in addition to $Cl(1-)$, $Me_2N(1-)$, and neutral PMe_2Ph ligands.

Although the so-called σ,π-vinyl ligand has been seen several times in organometallic chemistry,[9] its occurrence here is with

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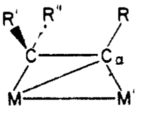
Table VI. Selected Bond Angles (deg) for the $W_2Cl_3(NMe_2)_2(CH_2NMe)(CHCH_2)(PMe_2Ph)_2$ Molecules[a]

A	B	C	angle	A	B	C	angle	A	B	C	angle
W(2A)	W(1A)	Cl(6A)	121.42 (8)	W(2B)	W(1B)	N(29B)	52.40 (27)	C(9A)	P(7A)	C(10A)	97.7 (12)
W(2A)	W(1A)	P(7A)	131.88 (9)	W(2B)	W(1B)	N(32B)	52.32 (26)	W(2A)	P(18A)	C(19A)	112.4 (5)
W(2A)	W(1A)	N(3A)	127.4 (3)	W(2B)	W(1B)	C(27B)	48.8 (3)	W(2A)	P(18A)	C(20A)	116.0 (5)
W(2A)	W(1A)	N(29A)	53.0 (3)	W(2B)	W(1B)	C(28B)	78.1 (3)	W(2A)	P(18A)	C(21A)	119.0 (4)
W(2A)	W(1A)	N(32A)	52.1 (3)	Cl(6B)	W(1B)	P(7B)	80.94 (11)	C(19A)	P(18A)	C(20A)	102.1 (7)
W(2A)	W(1A)	C(27A)	48.4 (3)	Cl(6B)	W(1B)	N(3B)	88.5 (3)	C(19A)	P(18A)	C(21A)	101.7 (7)
W(2A)	W(1A)	C(28A)	77.5 (3)	Cl(6B)	W(1B)	N(29B)	89.4 (3)	C(20A)	P(18A)	C(21A)	103.3 (6)
Cl(6A)	W(1A)	P(7A)	78.28 (12)	Cl(6B)	W(1B)	N(32B)	82.10 (26)	W(1B)	P(7B)	C(8B)	112.8 (5)
Cl(6A)	W(1A)	N(3A)	92.6 (3)	Cl(6B)	W(1B)	C(27B)	168.5 (3)	W(1B)	P(7B)	C(9B)	117.3 (5)
Cl(6A)	W(1A)	N(29A)	86.7 (3)	Cl(6B)	W(1B)	C(28B)	155.2 (3)	W(1B)	P(7B)	C(10B)	118.0 (4)
Cl(6A)	W(1A)	N(32A)	83.5 (3)	P(7B)	W(1B)	N(3B)	90.8 (4)	C(8B)	P(7B)	C(9B)	101.3 (7)
Cl(6A)	W(1A)	C(27A)	168.3 (3)	P(7B)	W(1B)	N(29B)	89.1 (3)	C(8B)	P(7B)	C(10B)	103.0 (6)
Cl(6A)	W(1A)	C(28A)	154.8 (3)	P(7B)	W(1B)	N(32B)	159.39 (26)	C(9B)	P(7B)	C(10B)	102.1 (6)
P(7A)	W(1A)	N(3A)	90.6 (3)	P(7B)	W(1B)	C(27B)	110.3 (3)	W(2B)	P(18B)	C(19B)	115.0 (5)
P(7A)	W(1A)	N(29A)	89.5 (3)	P(7B)	W(1B)	C(28B)	74.5 (3)	W(2B)	P(18B)	C(20B)	115.9 (6)
P(7A)	W(1A)	N(32A)	159.1 (3)	N(3B)	W(1B)	N(29B)	177.9 (4)	W(2B)	P(18B)	C(21B)	116.4 (4)
P(7A)	W(1A)	C(27A)	112.7 (3)	N(3B)	W(1B)	N(32B)	100.4 (4)	C(19B)	P(18B)	C(20B)	102.4 (8)
P(7A)	W(1A)	C(28A)	76.6 (3)	N(3B)	W(1B)	C(27B)	93.9 (4)	C(19B)	P(18B)	C(21B)	102.3 (7)
N(3A)	W(1A)	N(29A)	179.2 (5)	N(3B)	W(1B)	C(28B)	88.6 (4)	C(20B)	P(18B)	C(21B)	102.8 (7)
N(3A)	W(1A)	N(32A)	100.5 (4)	N(29B)	W(1B)	N(32B)	79.1 (4)	W(1A)	N(3A)	C(4A)	124.3 (9)
N(3A)	W(1A)	C(27A)	91.4 (5)	N(29B)	W(1B)	C(27B)	88.1 (4)	W(1A)	N(3A)	C(5A)	129.2 (9)
N(3A)	W(1A)	C(28A)	86.7 (5)	N(29B)	W(1B)	C(28B)	93.4 (4)	C(4A)	N(3A)	C(5A)	106.4 (10)
N(29A)	W(1A)	N(32A)	79.2 (4)	N(32B)	W(1B)	C(27B)	86.4 (4)	W(1A)	N(29A)	W(2A)	74.0 (3)
N(29A)	W(1A)	C(27A)	89.3 (4)	N(32B)	W(1B)	C(28B)	122.6 (4)	W(1A)	N(29A)	C(30A)	115.4 (8)
N(29A)	W(1A)	C(28A)	94.1 (5)	C(27B)	W(1B)	C(28B)	36.3 (4)	W(1A)	N(29A)	C(31A)	132.3 (9)
N(32A)	W(1A)	C(27A)	84.9 (4)	W(1B)	W(2B)	Cl(16B)	131.42 (10)	W(2A)	N(29A)	C(30A)	70.2 (6)
N(32A)	W(1A)	C(28A)	121.4 (4)	W(1B)	W(2B)	Cl(17B)	120.96 (8)	W(2A)	N(29A)	C(31A)	129.5 (9)
C(27A)	W(1A)	C(28A)	36.6 (4)	W(1B)	W(2B)	P(18B)	134.23 (9)	C(30A)	N(29A)	C(31A)	112.0 (11)
W(1A)	W(2A)	Cl(16A)	132.30 (9)	W(1B)	W(2B)	N(29B)	53.3 (3)	W(1A)	N(32A)	W(2A)	74.4 (3)
W(1A)	W(2A)	Cl(17A)	121.43 (8)	W(1B)	W(2B)	N(32B)	54.0 (3)	W(1A)	N(32A)	C(33A)	123.9 (8)
W(1A)	W(2A)	P(18A)	134.45 (8)	W(1B)	W(2B)	C(27B)	58.0 (3)	W(1A)	N(32A)	C(34A)	110.5 (8)
W(1A)	W(2A)	N(29A)	53.0 (3)	W(1B)	W(2B)	C(30B)	79.7 (3)	W(2A)	N(32A)	C(33A)	118.5 (8)
W(1A)	W(2A)	N(32A)	53.59 (27)	Cl(16B)	W(2B)	Cl(17B)	87.76 (13)	W(2A)	N(32A)	C(34A)	119.5 (8)
W(1A)	W(2A)	C(27A)	57.9 (4)	Cl(16B)	W(2B)	P(18B)	86.94 (13)	C(33A)	N(32A)	C(34A)	107.5 (10)
W(1A)	W(2A)	C(30A)	80.1 (3)	Cl(16B)	W(2B)	N(29B)	89.0 (3)	W(1B)	N(3B)	C(4B)	128.9 (10)
Cl(16A)	W(2A)	Cl(17A)	86.96 (12)	Cl(16B)	W(2B)	N(32B)	95.12 (28)	W(1B)	N(3B)	C(5B)	125.5 (9)
Cl(16A)	W(2A)	P(18A)	86.05 (11)	Cl(16B)	W(2B)	C(27B)	169.8 (3)	C(4B)	N(3B)	C(5B)	105.6 (11)
Cl(16A)	W(2A)	N(29A)	89.0 (3)	Cl(16B)	W(2B)	C(30B)	87.9 (4)	W(1B)	N(29B)	W(2B)	74.3 (3)
Cl(16A)	W(2A)	N(32A)	97.1 (3)	Cl(17B)	W(2B)	P(18B)	77.05 (12)	W(1B)	N(29B)	C(30B)	115.7 (8)
Cl(16A)	W(2A)	C(27A)	169.0 (4)	Cl(17B)	W(2B)	N(29B)	166.0 (3)	W(1B)	N(29B)	C(31B)	128.5 (9)
Cl(16A)	W(2A)	C(30A)	86.7 (4)	Cl(17B)	W(2B)	N(32B)	86.0 (3)	W(2B)	N(29B)	C(30B)	70.6 (7)
Cl(17A)	W(2A)	P(18A)	76.32 (11)	Cl(17B)	W(2B)	C(27B)	89.5 (4)	W(2B)	N(29B)	C(31B)	132.9 (8)
Cl(17A)	W(2A)	N(29A)	164.7 (3)	Cl(17B)	W(2B)	C(30B)	154.6 (4)	C(30B)	N(29B)	C(31B)	114.8 (11)
Cl(17A)	W(2A)	N(32A)	85.6 (3)	P(18B)	W(2B)	N(29B)	116.4 (3)	W(1B)	N(32B)	W(2B)	73.7 (3)
Cl(17A)	W(2A)	C(27A)	89.6 (4)	P(18B)	W(2B)	N(32B)	162.8 (3)	W(1B)	N(32B)	C(33B)	125.0 (8)
Cl(17A)	W(2A)	C(30A)	154.6 (3)	P(18B)	W(2B)	C(27B)	82.8 (3)	W(1B)	N(32B)	C(34B)	111.4 (7)
P(18A)	W(2A)	N(29A)	118.2 (3)	P(18B)	W(2B)	C(30B)	77.8 (4)	W(2B)	N(32B)	C(33B)	118.0 (8)
P(18A)	W(2A)	N(32A)	161.5 (3)	N(29B)	W(2B)	N(32B)	80.7 (4)	W(2B)	N(32B)	C(34B)	119.8 (7)
P(18A)	W(2A)	C(27A)	83.0 (4)	N(29B)	W(2B)	C(27B)	95.9 (4)	C(33B)	N(32B)	C(34B)	106.8 (10)
P(18A)	W(2A)	C(30A)	78.7 (3)	N(29B)	W(2B)	C(30B)	38.7 (5)	W(1A)	C(27A)	W(2A)	73.7 (4)
N(29A)	W(2A)	N(32A)	80.2 (4)	N(32B)	W(2B)	C(27B)	94.5 (4)	W(1A)	C(27A)	C(28A)	68.6 (7)
N(29A)	W(2A)	C(27A)	96.8 (4)	N(32B)	W(2B)	C(30B)	119.3 (5)	W(2A)	C(27A)	C(28A)	122.2 (9)
N(29A)	W(2A)	C(30A)	39.4 (4)	C(27B)	W(2B)	C(30B)	90.4 (5)	W(1A)	C(28A)	C(27A)	74.8 (7)
N(32A)	W(2A)	C(27A)	93.0 (5)	W(1A)	P(7A)	C(8A)	118.5 (5)	W(2A)	C(30A)	N(29A)	70.4 (6)
N(32A)	W(2A)	C(30A)	119.6 (4)	W(1A)	P(7A)	C(9A)	111.9 (6)	W(1B)	C(27B)	W(2B)	73.3 (4)
C(27A)	W(2A)	C(30A)	91.9 (5)	W(1A)	P(7A)	C(10A)	121.1 (8)	W(1B)	C(27B)	C(28B)	70.1 (7)
W(2B)	W(1B)	Cl(6B)	121.93 (9)	C(8A)	P(7A)	C(9A)	96.5 (9)	W(2B)	C(27B)	C(28B)	124.0 (9)
W(2B)	W(1B)	P(7B)	130.66 (8)	C(8A)	P(7A)	C(10A)	106.5 (10)	W(1B)	C(28B)	C(27B)	73.6 (7)
W(2B)	W(1B)	N(3B)	128.8 (3)					W(2B)	C(30B)	N(29B)	70.7 (7)

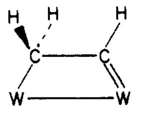
[a] Atoms labeled A and B refer to the two independent molecules in the unit cell.

an unusual set of ligands and some of its structural features are different from those seen previously. There is a short W(2)–C(27) distance, 2.04 (1) Å, and two longer distances, 2.32 (1) and 2.25 (1) Å, between W(1)–C(27) and W(1)–C(28), respectively. In previously characterized compounds containing the μ-CRCR′R″ ligand (R, R′, and R″ are H or alkyl), the M–C(α) distances are shorter than the M–C(β) distances using the stereochemical representation shown in III below.

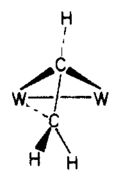


III

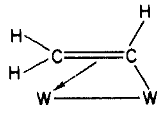
The structural data emphasize the importance of the VB (valence bond) descriptions shown below in IV and V at the expense of the more conventional VB description VI. Note that the C(27)–C(28) distance of 1.42 (2) Å is very markedly longer than that in ethylene, 1.34 Å.[10]



IV



V



VI

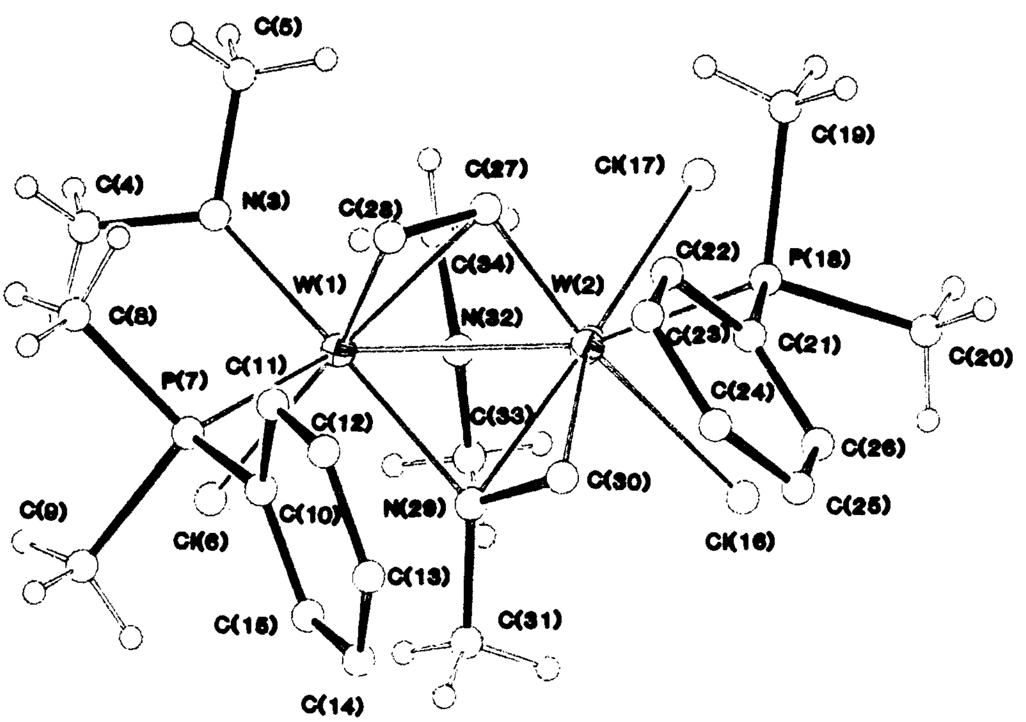
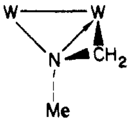


Figure 2. Ball and stick drawing of one of the $W_2Cl_3(NMe_2)_2(\mu\text{-}CH_2\text{–}NMe)(\mu\text{-}CHCH_2)(PMe_2Ph)_2$ molecules giving the atom number scheme used in the tables.

The nitrogen atom, N(29), of the $W_2(\mu\text{-}CH_2NMe)$ moiety is bound to both tungsten atoms by W–N bonds of essentially equal distance which in turn are the same as found for the single bridging amido ligand. The N(29)–C(30) distance, 1.44 (2) Å, of the η^2-CH_2NMe ligand is approaching a N_{sp^3}–C_{sp^3} single-bond distance, and the coordination environment about the nitrogen atom is close to tetrahedral. The W(2)–C(30) distance of 2.16 (1) Å falls within the range commonly seen for W–C_{sp^3} single-bond distances.[11] It is also within 3σ of the distance seen in the W-η_2-(Me_2C—N-*t*-Bu) core of the W($\overline{N(t\text{-}Bu)CMe_2}$)Me(N-*t*-Bu)(N(*t*-Bu)CMe=CMe_2) molecule.[12] The structural features of the $W_2(\mu\text{-}CH_2NMe)$ moiety may therefore be represented by the VB description shown in VII.



VII

As in the molecular structure of Ia, we find short W–N distances, 1.97 (1) Å, for the terminal amido ligands, and the alignment of the NC_2 blades and their restricted rotation in solution are indicative of Me_2N-to-W π-bonding. The W–P and W–Cl distances are normal.

NMR Studies

Ethyne Adducts I and Ia. The ^1H NMR spectra for both compounds are essentially identical and consistent with expectations based on the molecular structure seen for Ia in the solid state. The bridging NMe_2 group shows two *N*-methyl signals, and the two terminal NMe_2 groups, which are symmetry related by the molecular mirror plane, also have two *N*-methyl signals due to restricted rotation about the W–N bond. This is frozen out on the NMR time scale at 360 MHz and at 21 °C and below. Rather interestingly, one of the *N*-methyl signals assignable to the terminal W–NMe_2 group shows a coupling to ^{31}P. We suggest that this is a four-bond coupling, $^4J_{^{31}P-^1H} = 3.6$ Hz, and that this arises because the W=N bond is analogous to an olefinic double bond[13] and that the couplings P–W = N–C will be in the order trans > cis with the latter being too small to be resolved. The ^1H NMR spectrum of I is shown in Figure 3.

The acetylinic protons are in different environments, one lying over the μ-Cl ligand, the other over the μ-NMe_2 group, and this causes a sizable chemical shift separation, >2 ppm, for the two protons. Again one proton shows a sizable coupling to phosphorus, $J_{^{31}P-^1H}$ ca. 9 Hz, while coupling to the other is much smaller $J_{^{31}P-^1H}$ ca. 2.5 Hz. The H–H coupling, 2.4 Hz, is comparable to those in other $W_2(\mu\text{-}C_2H_2)$-containing compounds supported by alkoxide ligands.[5]

The ^{13}C NMR spectrum of the labeled compound $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2(\mu\text{-}{}^*C_2H_2)$, where *C represents 92 g-atom % ^{13}C, in the μ-ethyne region is shown in Figure 4. The two carbon atoms have chemical shift values separated by ca. 40 ppm. Again only one carbon atom shows a sizable coupling to phosphorus which we assign to the carbon atom having the larger P–W–C angle. The value of $^1J_{^{13}C-^{13}C} = 18$ Hz is greatly reduced from the value found in the free ethyne molecule, 172 Hz, but is similar to those in other $W_2(\mu\text{-}C_2H_2)$-containing compounds supported by alkoxide ligands which we have previously described as dimetallatetrahedranes.[5] A similar bonding description seems applicable here. Small C–C couplings are generally observed in strained ringed systems[14] and a value of ca. 9 Hz has recently been reported for the central C_4-tetrahedral unit in $C_4(t\text{-}Bu)_4$.[15]

σ,π-Vinyl Compounds, II and IIa. The ^1H NMR spectra of these compounds are remarkable in terms of the range of chemical shift and complexity, though, as we show specifically for compound II, they are entirely consistent with expectations based on the observed molecular structure in the solid state.

The ^1H NMR spectrum for II in CD_2Cl_2 at 21 °C is shown in Figure 5, and each region of the spectrum is shown at scale

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(10) Kutchitsu, K. *J. Chem. Phys.* **1966**, *44*, 906.

(11) E.g., in $W_2R_2(NMe_2)_4$ or $W_2R_2(O_2CX)_4$ compounds: Chisholm, M. H.; Haitko, D. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046. Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *Inorg. Chem.* **1977**, *16*, 603. Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C.; Van Der Sluys, W. G.; Russo, S. *J. Am. Chem. Soc.* **1984**, *106*, 5386.

(12) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galan, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 2088.

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(15) Loerzer, T.; Machinek, R.; Luttke, W.; Franz, L. H.; Malsh, K. D.; Maier, G. *Angew. Chem., Ed. Engl.* **1983**, *22*, 878.

Table VII. Summary of Crystal Data

	compound Ia	compound II
empirical formula	$C_{14}H_{38}Cl_3N_3P_2$-$W_2 \cdot {}^1/_2C_7H_8$	$C_{24}H_{42}Cl_3N_3P_2W_2 \cdot {}^1/_2C_7H_8$
color of crystal	reddish-brown	black
crystal dimensions, mm	0.064 × 0.064 × 0.144	0.072 × 0.148 × 0.272
space group	$P2_1/a$	$P\bar{1}$
cell dimensions		
temp, C	−162	−160
a, Å	18.069 (7)	16.929 (7)
b, Å	14.108 (4)	17.766 (8)
c, Å	11.204 (3)	11.108 (4)
α, deg		103.31 (2)
β, deg	106.09 (2)	91.76 (2)
γ, deg		78.59 (2)
Z (molecules/cell)	4	4
vol, $Å^3$	2744.50	3186.63
calcd density, g/cm^3	2.010 (with $^1/_2$ toluene)	2.007
wavelength, Å	0.71069	0.71069
M_r	784.48	962.71
linear absorption coeff, cm^{-1}	89.843	77.514
detector to sample distance, cm	22.5	22.5
sample to source distance, cm	23.5	23.5
av ω scan width at half height	0.25	0.25
scan speed, deg/min	6.0	5.0
scan width, deg + dispersion	1.6	1.4
individual background, s	6	5
aperture size, mm	3.0 × 4.0	3.0 × 4.0
2θ range, deg	6–45	6–45
total no. of reflections collected	3887	8397
no. of unique intensities	3601	8299
no. with $F > 0.0$	3407	7841
no. with $F > 3.0\sigma(F)$	3216	7487
$R(F)$	0.0411	0.0483
$R_w(F)$	0.0425	0.0482
goodness of fit for the last cycle	1.327	1.412
max Δ/σ for last cycle	0.05	0.05

Table VIII. Rate Constants, *k*, at Various Temperatures for the Conversion of I and Ia to II and IIa, Respectively

$W_2Cl_3(NMe_2)_3(C_2H_2)$-$(PMe_2Ph)_2 \rightarrow$ vinyl		$W_2Cl_3(NMe_2)_3(C_2H_2)$-$(PMe_3)_2 \rightarrow$ vinyl	
temp, °C	*k*, s^{-1}	temp, °C	*k*, s^{-1}
43	2.66×10^{-5}	45	5.09×10^{-5}
57	1.67×10^{-4}	55	9.05×10^{-5}
63	4.03×10^{-4}	65	1.58×10^{-4}
68	4.83×10^{-4}	77	4.99×10^{-4}
72	6.42×10^{-4}		

expansion. The use of the labeled compound, I, containing three $N(CD_3)_2$ groups allowed identification of five NMe signals in the spectrum of II and also the $N-CH_2$ moiety which gives rise to the high-field resonances above Me_4Si. The appearance of the NCH_aH_b resonances as two doublets is due to coupling to one ^{31}P nucleus (as shown by $^1H\{^{31}P\}$ NMR spectrum) and not due to a geminal $^1H-^1H$ coupling which must be close to zero (not resolved). A reaction involving the use of I, labeled with $*C_2H_2$ (*C represents 92.5 g-atom % ^{13}C), generates II* for which the ^1H NMR spectrum reveals $^{13}C-H$ couplings to the resonances at 14.75 and 4.95 ppm. By integration, the signals were estimated to be equivalent to one H atom each. This still leaves one hydrogen atom unaccounted for in the ^1H NMR spectrum, and the following experiments were carried out in order to locate it.

(1) A $^1H\{^{31}P\}$ NMR spectrum of the compound, II, showed that the resonance at 14.75 ppm (1 H, originally a triplet of triplets) collapsed to a 1:2:1 triplet; see Figure 6. This suggested that the H atom was coupled equally to two H atoms, $J_{^1H-^1H} = 8.3$ Hz.

(2) Although the spectral integration suggested that the resonance of 4.95 ppm corresponded to one H atom, there can be some unreliability about integration especially when using high-field NMR spectrometers. In order to eliminate any doubt concerning the integral intensities of the two resonances (14.75 and 4.95 ppm), a single-frequency ^1H-decoupling experiment was carried out (see Figure 6). When the ^1H NMR spectrum is recorded with proton decoupling of the resonance at 4.95 ppm, the low-field signal, assignable to $C_\alpha H$ appears as a 1:3:3:1 (or doublet of triplets) pattern. This indicates that $C_\alpha H$, in addition to being coupled to two ^{31}P nuclei (and the H atom with a resonance at 4.95 ppm), is still coupled to yet another hydrogen atom. This experiment rules out the possibility that the two H atoms attached to C_β of the σ,π-vinyl ligand are accidentally magnetically degenerate, thereby confirming the integration experiment.

(3) In order to locate the missing ^1H resonance, a reaction employing I-($N(CD_3)_2$) labeled was carried out, and in the ^2H NMR spectrum of II, a resonance at 1.75 ppm was located of approximate integral intensity one ^2H. This part of the ^1H NMR spectrum is obscured by one of the doublets of a PMe_2Ph methyl resonance. Using the isotopically ^{13}C-labeled compound II*, the $^{13}C-H$ and $^{13}C-^{13}C$ coupling constants associated with the μ-$CHCH_2$ ligand can be evaluated, and the spectra clearly show that the C_β atom is bonded to two H atoms. When using a single-frequency proton-decoupling experiment with the decoupling frequency set at δ 1.75, the C_β resonance shows coupling to only one H, which is an added proof of the presence of the "missing" $C_\beta H$ resonance at δ 1.75. See Figure 7.

Certain points of this NMR study are worthy of note: (1) The $^{13}C-^{13}C$ coupling in the μ-$CHCH_2$ moiety is 27 Hz, notably reduced from the value of 69 Hz seen for ethylene and closer to values seen for C–C single bonds, c.f., 35 Hz in ethane.[14] (2) The chemical shift values of the C_α and C_β atoms are in the range of alkylidene and alkyl tungsten bound carbon atoms, respectively.[16] (3) The $^3J_{H-H}$ couplings in the μ-$CHCH_aH_b$ ligand show that the hydrogen atom on C_α is coupled equally to H_a and H_b, which is in contrast to prior observations for σ,π-vinyl ligands and, of course, substituted olefins, including mononuclear metal vinyl complexes, where $^3J_{H-H}$ trans > $^3J_{H-H}$ cis.[17] These observations indicate the importance of the contributions of the VB descriptions IV and V.

Mechanistic Considerations Concerning the Conversion of I to II. The formation of the σ,π-vinyl compounds II and IIa from the ethyne adducts I and Ia has been followed by NMR spectroscopy, yielding the following observations.

(1) The reactions obey first-order rate expressions in benzene-d_6 in the temperature range ca. +40 to ca. +80 °C. The reactions were monitored up to their three half-lives. The rate constants, *k*, at different reaction temperatures are given in Table VIII. From the Arrhenius plots, the following activation parameters were obtained: (i) for L = PMe_2Ph, $\Delta H^* = 23.7 \pm 2.1$ kcal mol^{-1} and $\Delta S^* = -4 \pm 6$ eu; (ii) for L = PMe_3, $\Delta H^* = 17.2 \pm 2.9$ kcal mol^{-1} and $\Delta S^* = -25 \pm 8$ eu.

(2) The rates of the reactions were found to be independent of added phosphine (10 equiv).

(3) A large primary kinetic isotope effect, $k_H/k_D = 6.0 \pm 1.0$ at 60 °C, was observed for the reactions involving $W_2Cl_3(N(CH_3)_2)_3(PMe_2Ph)_2(\mu-C_2H_2)$ vs. $W_2Cl_3(N(CD_3)_2)_3(PMe_2Ph)_2(\mu-C_2H_2)$.

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[16] For a listing of W—C, W=C, and W≡C ^{13}C resonances, see ref 5.

[17] For coupling information in σ,π-vinyl complexes, see: (a) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417. (b) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29. (c) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614. (d) Deeming, A. J.; Underhill, M. *J. Organomet. Chem.* **1974**, *80*, C53. (e) Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc., Chem. Commun.* **1970**, 1333. (f) King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3600.

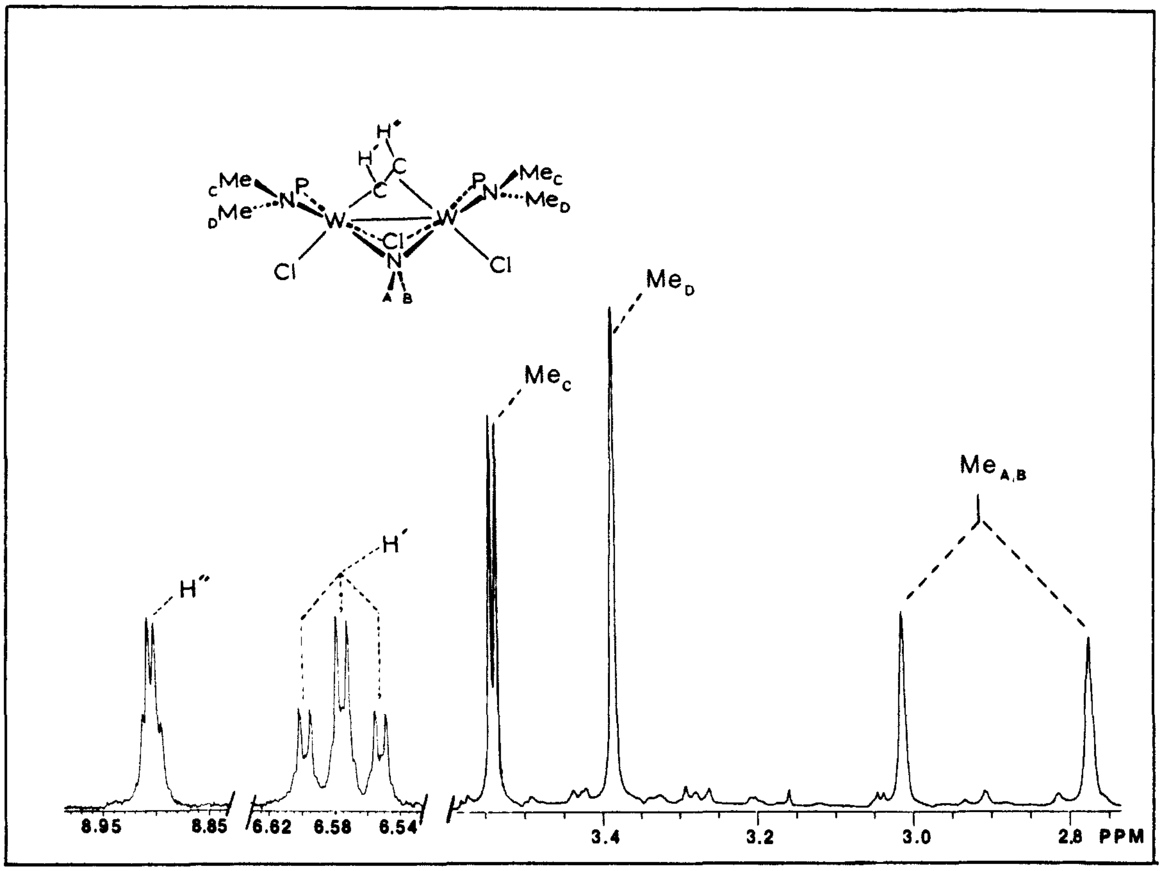


Figure 3. ^{1}H NMR spectrum of $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2(\mu\text{-}C_2H_2)$ recorded in CD_2Cl_2 at 360 MHz and 21 °C, showing the NMe_2 signals and those of the $\mu\text{-}C_2H_2$ ligand.

(4) A significant and relatively large secondary isotope effect was observed, $k_H/k_D = 1.4 \pm 0.1$, in comparing the rates of the reactions involving $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2(\mu\text{-}C_2H_2)$ vs. $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2(\mu\text{-}C_2D_2)$.

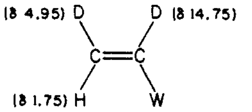
(5) The following double-labeling experiment was carried out and monitored by ^{13}C NMR spectroscopy. A 1:1 mixture of $W_2Cl_3(N(CH_3)_2)_3(PMe_2Ph)_2(\mu\text{-}{}^*C_2H_2)$ and $W_2Cl_3(N(CD_3)_2)_3(PMe_2Ph)_2(\mu\text{-}C_2H_2)$, where *C represents 92.5 g atom % ^{13}C, was allowed to react to form the σ,π-vinyl complex. The $^*C_\beta$ carbon resonance showed only the presence of bonded H atoms; no evidence for the formation of the *CH*CHD ligand could be seen in the ^{13}C NMR spectrum.

(6) The reaction of $W_2Cl_3(N(CH_3)_2)_3(PMe_2Ph)_2(\mu\text{-}C_2D_2)$ to form the σ,π-vinyl complex was monitored by ^{2}H NMR spectroscopy. The spectra showed the initial formation of the deuterated vinyl ligand with signals at 14.7 and 4.9 ppm of equal intensity. After the reaction was complete, the temperature was raised from +50 to +70 °C, and ^{2}H NMR spectra were periodically recorded. Over 24 h, the resonance at ca. 4.9 ppm decreased in intensity as the resonance at ca. 1.7 ppm grew. After 24 h at +70 °C, these were of roughly equal intensity and remained unchanged thereafter. The ^{2}H signal at 14.7 ppm remained unaffected by these changes. In the ^{1}H NMR spectrum of this sample, there was no resonance at δ 14.75. The rate of H/D scrambling at C_β was not influenced by added PMe_2Ph.

Interpretations

(1) The reaction is intramolecular. This rules out a reaction pathway involving β-hydrogen atom elimination from a coordinated amide followed by reductive elimination of HCl (or $HNMe_2$) and subsequent HCl (or $HNMe_2$) addition to the $W_2(\mu\text{-}C_2H_2)(CH_2NMe)$-containing compound.

(2) The formation of the μ-$CHCH_2$ ligand is stereospecific. From previous studies of σ,π-vinyl complexes,[17] the lowest field resonance is always assigned to the H atom on the α-carbon atom, while the highest field signal is assigned to the cis-hydrogen atom with respect to the metal atom bonded to C_α. If this assignment holds for our compounds, then the initially formed σ,π-vinyl ligand involving μ-C_2D_2H will be analogous to that shown in VIII. This



VIII

implies a cis addition of the H atom to the coordinated alkyne and is believed to be kinetically favored. However, with time and an increase in temperature, there is H/D scrambling over the formally cis and trans positions at the β-carbon but no scrambling with the C_α H/D atom. The seemingly simplest explanation for this isomerization is the reversible interconvertion of a σ,π-vinyl with a σ-vinyl ligand, the equilibrium position lying well in favor of the σ,π-vinyl compound. The σ-vinyl reactive intermediate may then undergo rotation about the C–C bond, formally the double bond of a σ,π-vinyl ligand in VI, which upon reconversion to the σ,π-complex will scramble the H/D atoms on the C_β atom.

(3) The large primary isotope effect at +60 °C, k_H/k_D of ca. 6, is appreciably larger than any ratio previously found for β-hydrogen atom transfer from a coordinated alkyl ligand.[18] Indeed the value is close to the limiting situation in organic chemistry for C---H---C bond forming/breaking in which both forming and breaking are equally important in the transition state.[19]

(4) There is a significant secondary isotope effect $k_{(C_2H_2)}/k_{(C_2D_2)}$ of ca. 1.4. This is suggestive that C–H bond formation is also

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(18) (a) Baird, M. C.; Hommeltoft, S. I. J. Am. Chem. Soc. 1985, 107, 2548. (b) Ikariya, T.; Yamamoto, A. J. Organomet. Chem. 1976, 120, 257. (c) Evans, J.; Schwartz, J.; Urquatt, P. W. J. Organomet. Chem. 1974, 81, C37. (d) Ozawa, F.; Ito, T.; Yamamoto, A. J. Am. Chem. Soc. 1980, 102, 6457. (e) Collman, J. P.; Hegedus, L. S. In "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; p 294.

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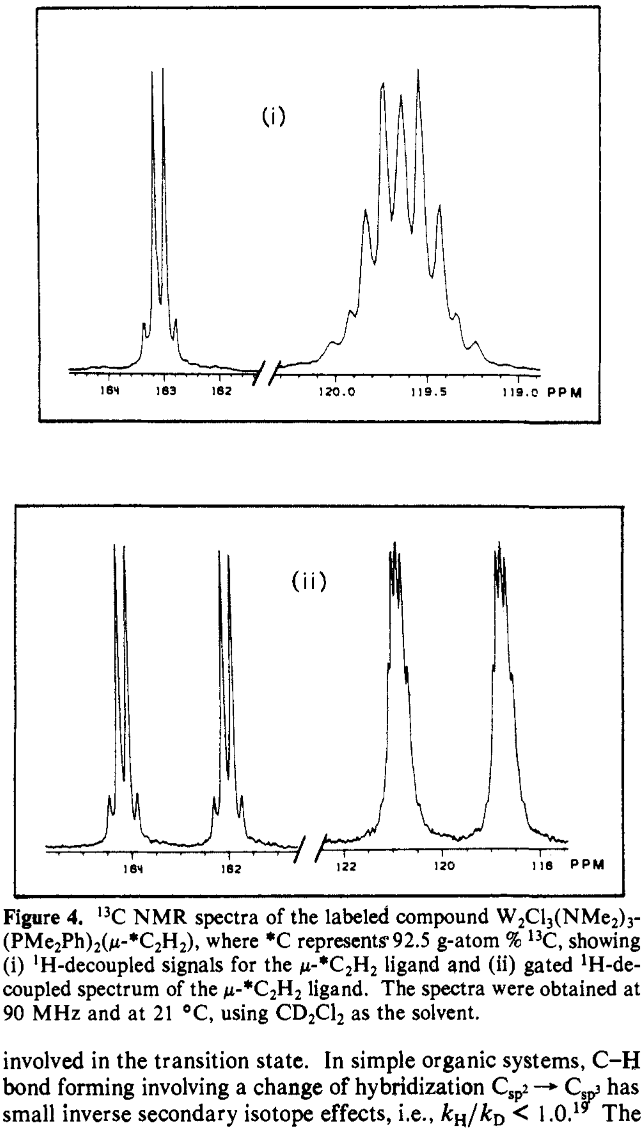
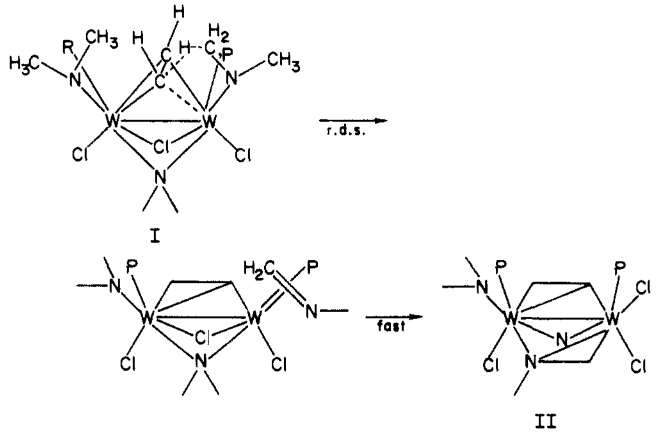


Figure 4. ^{13}C NMR spectra of the labeled compound $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2(\mu\text{-}^*C_2H_2)$, where *C represents 92.5 g-atom % ^{13}C, showing (i) ^1H-decoupled signals for the $\mu\text{-}^*C_2H_2$ ligand and (ii) gated ^1H-decoupled spectrum of the $\mu\text{-}^*C_2H_2$ ligand. The spectra were obtained at 90 MHz and at 21 °C, using CD_2Cl_2 as the solvent.

involved in the transition state. In simple organic systems, C–H bond forming involving a change of hybridization $C_{sp^2} \rightarrow C_{sp^3}$ has small inverse secondary isotope effects, i.e., $k_H/k_D < 1.0$.[19] The origin of the positive secondary isotope effect observed in the present study is clearly open to debate but provides strong evidence for the importance of C(ethyne)–H(dimethylamide) bond forming in the transition state.

(5) The arguments presented in 3 and 4 above lead us to suggest that there is probably a direct hydrogen atom transfer from a coordinated dimethylamide to the μ-C_2H_2 ligand, and it is not appropriate to invoke the intermediacy of a metal hydride. We cannot, of course, determine whether or not the hydrogen atom donor is a terminal or a bridging amido group, and the subsequent ligand rearrangements must be fast relative to the hydrogen-atom-transfer process. No intermediates are detected in the conversion of I to II. A plausible mechanism is shown below.



I

II

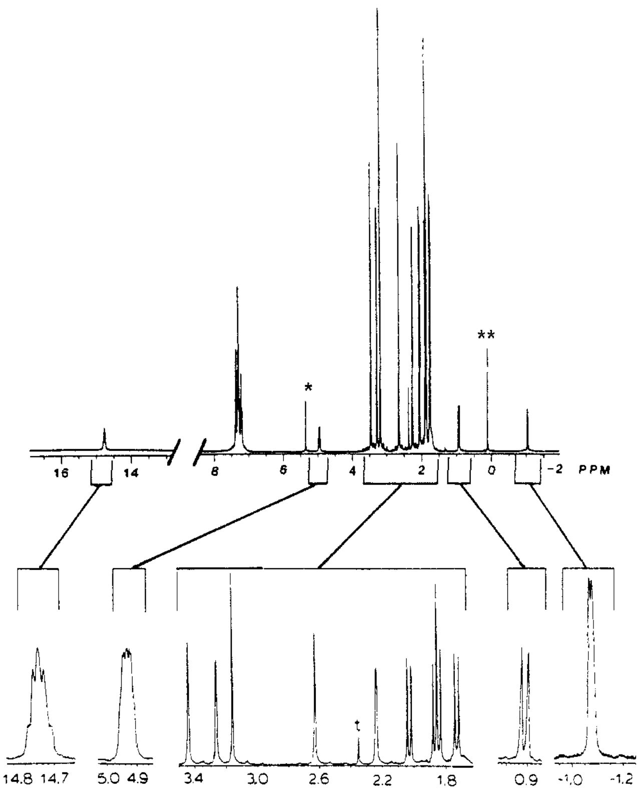


Figure 5. ^1H NMR spectra of $W_2Cl_3(NMe_2)_2(\mu\text{-}CH_2NMe)(\mu\text{-}CHCH_2)(PMe_2Ph)_2$ recorded at 360 MHz, 21 °C, and in CD_2Cl_2 solvent. The protio impurities denoted by * are residual protons in the CD_2Cl_2 solvent, t represents the toluene–methyl signal of the $^1/_2$ molecule of toluene of crystallization, and ** represents an impurity due to Dow Corning grease. The resonances of significance, namely, the μ-$CHCH_2$, μ-CH_2NMe, NMe_2, and PMe_2Ph groups are shown at scale expansion in the lower portion of the figure.

(6) Commenting on the significance of the activation parameters must be most speculative since the degree of accuracy is not good. It appears that $\Delta H^{‡}$ is less for L = PMe_3 than for PMe_2Ph, perhaps because PMe_3 is a better donor ligand making the alkyne ligand more carbanionic and thus receptive to protonation or proton abstraction from a coordinated Me_2N ligand. The $\Delta S^{‡}$ values are in the inverse order, $\Delta S^{‡}$ (−4 ± 6 eu) is small for L = PMe_2Ph, but for PMe_3, $\Delta S^{‡}$ (−25 ± 8 eu) is quite definitely of medium magnitude and negative. This may reflect a well-ordered transition state as would be expected for a direct C---H---C atom transfer in the transition state, and the relative conformational degrees of freedom in the ground-state molecules for L = PMe_3 vs. PMe_2Ph may account for their respective differing $\Delta S^{‡}$ values.

Concluding Remarks

σ,π-Vinyl ligands are now well-documented in organometallic chemistry and have been prepared from (i) insertion of an alkyne into a M–H bond,[20] (ii) protonation of a coordinated alkyne,[21] and (iii) degradation of an olefin at a dinuclear or more commonly trinuclear center.[22] The example of the σ,π-vinyl ligand reported here is unusual in both its sets of attendant ligands and in some of its structural features. The isomerization of the C(β)H atoms (substituents) has been seen before, and in dinuclear metal systems, a mechanism other than that offered here has been proposed.[23] This former mechanism involves the π-bond of the σ,π-vinyl ligand

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[20] See ref 9c, 17c, 17d, 17e: Jackson, W. G.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Schorpp, K. T. *J. Organomet. Chem.* **1975**, *87*, C27.

[21] See ref 9a, 9d, 17a: Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1980**, 441.

[22] See ref 17b: Cooksey, C. J.; Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1981**, 1718.

[23] See ref 17a.

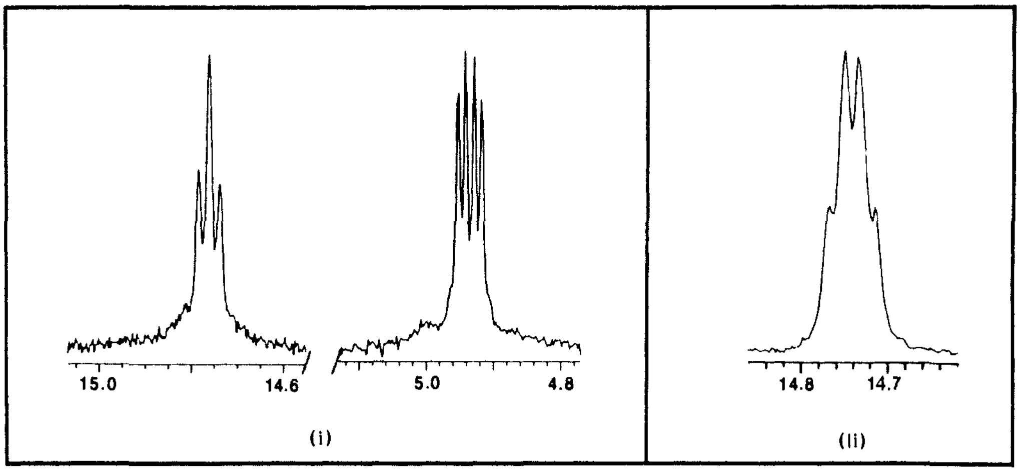

Figure 6. ^1H NMR spectra of the μ-$CHCH_2$ ligand in $W_2Cl_3(NMe_2)_2(\mu\text{-}CH_2NMe)(\mu\text{-}CHCH_2)(PMe_2Ph)_2$ recorded in CD_2Cl_2 at 360 MHz and at 21 °C under various decoupling conditions. Shown in (i) are the $C_\alpha H$ and one of the $C_\beta H$ protons (see text for an assignment) when decoupled to ^{31}P. Shown in (ii) is the $C_\alpha H$ proton when the ^1H resonance at 4.95 ppm is selectively decoupled.

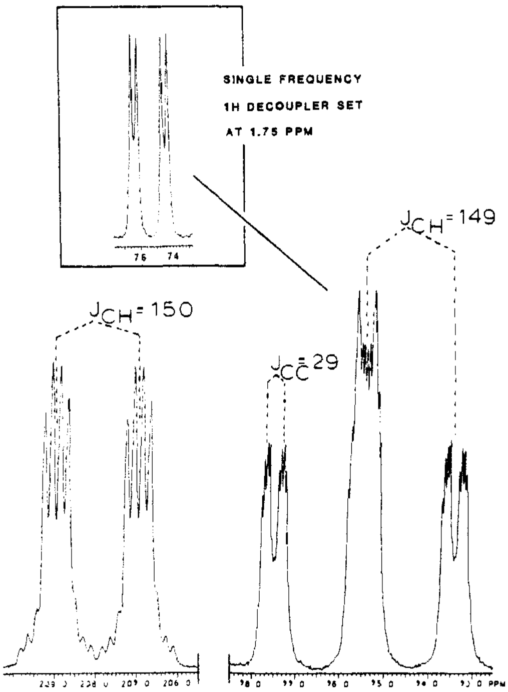

Figure 7. ^{13}C NMR spectra of the labeled compound $W_2Cl_3(NMe_2)_2(\mu\text{-}CH_2NMe)(\mu\text{-}{}^*CH{}^*CH_2)(PMe_2Ph)_2$, where *C represents 92.5 g-atom % ^{13}C, at 75 MHz and at 21 °C, in CD_2Cl_2 solvent, showing only the resonances associated with the μ-$^*CH^*CH_2$ ligand with proton coupling allowing assignment of C_α and C_β and $J_{^{13}C-^{13}C}$, J_{C-H}, and $J_{^{13}C-^{31}P}$ values. The inset shows the C_β signal with selective ^1H decoupling at δ 1.75.

oscillating between the two metal atoms and is clearly not the one responsible for H atom scrambling on C_β in our case. Deeming[24] has also noted that isomerization of the σ,π-vinyl ligand in triangular metal systems may be promoted by Lewis bases and has suggested a reversible Lewis base coordination to the C_β carbon atom which would in turn generate a η^1- or η^2-alkylidene intermediate. The lack of dependence of the rate of isomerization on added PMe_2Ph suggests that this is not the operative mechanism for compounds II.

The experimental observations relevant to the hydrogen-atom-transfer mechanism are consistent with a scheme that does not involve β-hydrogen atom migration to the metal but involves a five-membered ring for a transition state. This is little different from the four-center transition states now commonly proposed in C–H activations at d^0 metal centers.[25]

Formation of η^2-imine complexes in the thermal decomposition of amide ligands is now well-established.[26] In most instances, the η^2-imino ligand is best counted as a 2– ligand as it is in the present study. To our knowledge, however, this work provides the first example of a structurally characterized μ-CH_2NMe ligand. It is now easy to see how such intermediates could be important in the H/D scrambling reported by Nugent and coworkers[27] in their studies of the reaction between $W_2(N(CH_3)_2)_6$ and $DN(CH_3)_2$ which led to C–D bond formation.

Experimental Section

All operations were carried out in dry and oxygen-free solvents and atmospheres (N_2). $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2\cdot{}^1/_2C_7H_8$ and $W_2Cl_3(NMe_2)_3(PMe_3)_2$ were prepared according to literature methods.[28] Nicolet 360 MHz, Varian XL-300, and Varian XL-100 instruments were used to obtain ^1H, ^{13}C, and ^{31}P NMR spectra, respectively. A Perkin-Elmer 283 infrared spectrometer was used to record IR spectra from Nujol mulls between NaCl plates.

$W_2Cl_3(NMe_2)_3(\mu\text{-}C_2H_2)(PMe_2Ph)_2\cdot{}^1/_2C_7H_8$. A suspension of $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2\cdot{}^1/_2C_7H_8$ (0.62 g, 0.7 mmol) in toluene (5 mL) was cooled to −196 °C. $HC{\equiv}CH$ (1 equiv) was transferred onto this frozen mixture with the help of a calibrated vacuum manifold and quickly brought to 0 °C. Stirring was continued at that temperature for $^1/_2$ h by which time purple microcrystalline solids start to form. The mixture was brought to 10 °C and stirred for another 15 min. The solid was then isolated by filtration and washed with cold toluene (5 mL), dried under vacuum, and then redissolved in a minimum volume of toluene. Deep purple needles of $W_2Cl_3(NMe_2)_3(\mu\text{-}C_2H_2)(PMe_2Ph)_2\cdot{}^1/_2C_7H_8$ were obtained by cooling this solution to −15 °C for 5 days: yield, 0.4 g, 65%. Anal. Calcd for $W_2Cl_3N_3P_2C_{27.5}H_{46}$: C, 34.3; H, 4.8; Cl, 11.1; N, 4.4. Found: C, 34.2; H, 4.9; Cl, 11.3; N, 4.5. IR (cm^{-1}) 1430 (s), 1254 (s), 1090 (br, s), 1015 (br, s), 935 (m), 900 (s), 795 (br, s), 740 (m), 689 (m); ^1H NMR (CD_2Cl_2, 21 °C, relative to Me_4Si) δ 1.62 (d, 6 H, $J = 9.0$ Hz, PMe_2Ph), 1.91 (d, 6 H, $J = 8.6$ Hz, PMe_2Ph), 2.77 (s, 3 H, μ-NMe_2), 3.01 (s, 3 H, μ-NMe_2), 3.38 (s, 6 H, NMe_2), 3.54 (d, 6 H, $J = 3.6$ Hz, NMe_2), 6.57 (td, 1 H, $J_{PH} = 7.9$, $J_{HH} = 2.5$, $J_{W-H} = 2.2$ Hz, $CH'CH''$), 8.92 (dt, 1 H, $J_{PH} = 2.0$, $J_{WH} = 5.3$ Hz, $CH'CH''$); $^{31}P\{^1H\}$ NMR data (CD_2Cl_2, 22 °C) δ −7.41 (s, $J_{WP} = 217.5$, $J_{PP} = 3.8$ Hz); ^{13}C NMR (μ-$^{13}C_2H_2$ ligand) (gated ^1H decoupled, CD_2Cl_2, −35 °C) δ 163.1 ($J_{CC} = 17.6$, $J_{WC} = 34.9$, $J_{CH} = 195.5$ Hz, J_{CP} = unobserved), 119.8 ($J_{WC} = 34.4$, $J_{CH} = 193.7$, $J_{CP} = 9.2$ Hz).

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$W_2Cl_3(NMe_2)_3(\mu\text{-}C_2H_2)(PMe_3)_2\cdot{}^1/_2C_7H_8$. The compound is best prepared by ligand substitution of PMe_2Ph by PMe_3 in $W_2Cl_3(NMe_2)_3(\mu\text{-}C_2H_2)(PMe_2Ph)_2$, although reactions between 1 equiv of $HC{\equiv}CH$ and $W_2Cl_3(NMe_2)_3(PMe_3)_2$ at 21 °C yield the μ-ethyne adduct after ca. 2 $^1/_2$ h along with significant amounts of decomposition products.

PMe_3 (2.5 equiv) was added to a suspension of $W_2Cl_3(NMe_2)_3(\mu\text{-}C_2H_2)(PMe_2Ph)_2\cdot{}^1/_2C_7H_8$ (0.35 g, 0.4 mmol) in toluene (5 mL) via a calibrated vacuum manifold and stirred at 45 °C for $^1/_2$ h. The color darkened considerably and the reaction mixture was stripped. The resulting purple solid was redissolved in a minimun amount of warm toluene and allowed to cool slowly to room temperature. Black rectangular bars of $W_2Cl_3(NMe_2)_3(\mu\text{-}C_2H_2)(PMe_3)_2\cdot{}^1/_2C_7H_8$ were collected after 1 day: yield 0.2 g, 60%. Anal. Calcd for $W_2Cl_3N_3P_2C_{17.5}H_{42}$: C, 25.3; H, 5.1; Cl, 12.8; N, 5.1. Found: C, 25.3; H, 5.0; Cl, 13.0; N, 5.1. IR (cm^{-1}) 1435 (m), 1360 (m), 1285 (w), 1279 (w), 1160 (m), 1180 (w), 1086 (br, m), 1020 (s), 950 (vs), 918 (s), 795 (br, m), 735 (w), 725 (w); ^1H NMR (CD_2Cl_2, 21 °C, relative to Me_4Si) δ 1.50 (d, 18 H, J = 8.7 Hz, $P\mathit{Me}_3$), 2.74 (s, 3 H, $\mu\text{-}N\mathit{Me}_2$), 2.92 (s, 3 H, $\mu\text{-}N\mathit{Me}_2$), 3.66 (d, 6 H, J = 3.0 Hz, $N\mathit{Me}_2$), 3.87 (d, 6 H, J = 1.3 Hz, $N\mathit{Me}_2$), 6.37 (td, 1 H, J_{PH} = 8.7, J_{W-H} = 2.7, J_{HH} = 2.4 Hz, $C\mathit{H}'CH''$), 8.78 (dt, 1 H, J_{PH} = 2.1, J_{WH} = 5.0 Hz, $CH'\mathit{CH''}$).

$W_2Cl_3(NMe_2)_2(CH_2NMe)(CHCH_2)(PMe_2Ph)_2\cdot{}^1/_2C_7H_8$. $W_2Cl_3(NMe_2)_3(\mu\text{-}C_2H_2)(PMe_2Ph)_2$ (0.51 g, 0.53 mmol) was dissolved in toluene (10 mL) and stirred at 60 °C for 12 h. The color changed from purple to dark green. After the reaction was complete, the green solution was reduced in volume and cooled to −15 °C for 5 days. Dark-green needles of $W_2Cl_3(NMe_2)_2(\mu\text{-}CH_2NMe)(\mu\text{-}CHCH_2)(PMe_2Ph)_2\cdot{}^1/_2C_7H_8$ formed and were separated by filtration: yield 0.41 g, 77%. Anal. Calcd for $W_2Cl_3N_3P_2C_{27.5}H_{46}$: C, 34.3; H, 4.8; Cl, 11.1; N, 4.4. Found: C, 34.3; H, 4.9; Cl, 11.0; N, 4.4; IR (cm^{-1}) 1430 (s), 1255 (m), 1095 (br, m), 1070 (m), 1015 (br, s), 945 (s), 920 (m), 908 (s), 795 (s), 735 (s), 705 (w), 690 (s), 670 (w); ^1H NMR (CD_2Cl_2, 21 °C, relative to Me_4Si) δ −1.05 (d, 1 H, J = 3.9 Hz, $MeNC\mathit{H}_2$), 0.92 (d, 1 H, J = 11.5 Hz, $MeNC\mathit{H}_2$), 1.73 (d, 3 H, J = 9.0 Hz, $P\mathit{Me}_2Ph$), 1.84 (d, 3 H, J = 9.4 Hz, $P\mathit{Me}_2Ph$), 1.86 (d, 3 H, J = 8.3 Hz, $P\mathit{Me}_2Ph$), 2.03 (d, 3 H, J = 9.4 Hz, $P\mathit{Me}_2Ph$), 2.23 (d, 3 H, J = 2.2 Hz, $N\mathit{Me}_2$), 2.63 (s, 3 H, $N\mathit{Me}_2$), 3.16 (s, 3 H, $N\mathit{Me}_2$), 3.26 (unresolved d, 3 H, $N\mathit{Me}_2$), 3.44 (s, 3 H, $N\mathit{Me}_2$), 4.93 (unresolved multiplet, 1 H, $CHC\mathit{H}_2$), 14.75 (tt, 1H, J_{PH} = 6.5, J_{HH} = 8.3 Hz, $C\mathit{H}CH_2$); ^2H NMR (CH_2Cl_2, 21 °C) δ 14.7 (br, $C\mathit{D}CD_2$), 4.9 (br, $CDC\mathit{D}_2$), 1.7 (br, $CDC\mathit{D}_2$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C, relative to H_3PO_4 as external standard) δ −12.3 (d, J_{PP} = 2.0 Hz), −14.2 (d); ^{13}C NMR data ($^{13}CH{-}^{13}CH_2$ ligand) (gated ^1H decoupled, CD_2Cl_2, 22 °C) δ 208.0 ($^1J_{CH}$ = 150, $^2J_{CH}$ = 4, J_{CW} = 83, J_{CC} = 29, J_{CP} = 14 Hz, $\mathit{C}HCH_2$), 75.5 ($^1J_{CH}$ = 149, J_{CW} = unobserved, J_{CP} = 8 Hz, $CH\mathit{C}H_2$).

$W_2Cl_3(NMe_2)_2(CH_2NMe)(CHCH_2)(PMe_3)_2$ can be prepared in an analogous manner from $W_2Cl_3(NMe_2)_3(C_2H_2)(PMe_3)$ in toluene at 65 °C, employing a reaction time of ca. 36 h: ^1H NMR (benzene-d_6, 21 °C, relative to Me_4Si) δ 14.70 (dt, J = 6.5 Hz, 1 H, $C\mathit{H}CH_2$), 4.58 (m, 1 H, $CHC\mathit{H}H$), 3.95 (s, 3 H, $N\mathit{Me}$), 3.49 (s, 3 H, $N\mathit{Me}$), 3.08 (s, 3 H, $N\mathit{Me}$), 2.94 (s, 3 H, NMe), 1.86 (s, 3 H, $N\mathit{Me}$), 1.37 (d, J = 7.2 Hz, 9 H, $P\mathit{Me}_3$), 0.97 (d, J = 7.4 Hz, 9 H, PMe_3), −0.20 (d, J = 5.0 Hz, 1 H, $C\mathit{H}_2NMe$) (the other $C\mathit{H}_2NMe$ signal was not observed); $^{31}P\{^1H\}$ NMR data (C_6D_6, 22 °C, relative to H_3PO_4 as the external standard) −15.8 (d, J_{PP} = 16 Hz), −25.0 (d, J_{PP} = 16 Hz).

Measurements of the reaction rates for the conversion of I to II and Ia to IIa were followed by ^1H NMR spectroscopy using benzene-d_6 as the solvent. The decrease in the NMe signals of I and Ia were monitored as a function of time at a given temperature, using a constant-temperature bath and a cooled ^1H probe, whilst the growth of the product NMe signals was simultaneously monitored.

Whenever labeling experiments were carried out, the protio and deuterio samples were made up at the same time and at similar concentrations and monitored with time using the same temperature control bath. For the determination of k_H/k_D for the primary isotope effect (i.e., $N(CH_3)_2$ vs. $N(CD_3)_2$), the relative intensities of the $P\mathit{Me}_2Ph$ signals were monitored. For the determination of k_H/k_D in the secondary isotope experiments, involving $\mu\text{-}C_2H_2$ and $\mu\text{-}C_2D_2$ labeled compounds, the NMe_2 signals were followed.

Analyses of the data conformed to first-order kinetics for the disappearance of I and Ia and the formation of II and IIa, respectively. The standard deviations in ΔH^* and ΔS^* were determined by a statistical least-squares program written by Prof. J. Gajewski for use on an IBM PC.

X-ray Structural Determinations. General operating facilities have been described previously.[29] Crystal data for the two compounds studied in this work are given in Table VII.

$W_2Cl_3(NMe_2)_3(\mu\text{-}C_2H_2)(PMe_3)_2\cdot{}^1/_2C_7H_8$. The sample studied was cleaved from a very large crystal using standard inert atmosphere techniques and transferred to the goniostat where it was cooled to −161 °C. The unit cell for this sample was determined to be monoclinic, space group $P2_1/a$.

The structure was solved by direct methods and heavy atom Fourier techniques. All non-hydrogen atoms were readily located; $^1/_2$ molecule of solvent (toluene) was located at a center of symmetry. The data were corrected for absorption, and the structure was refined by full-matrix least squares by using anisotropic thermal parameters on the non-hydrogen atoms. Hydrogen atoms were not located, but were introduced in calculated positions, except for those on the bridging acetylene.

The final difference Fourier was essentially featureless; several peaks of about 1.0 e/Å were located in the vicinity of the heavy atoms.

$W_2Cl_3(NMe_2)_2(\mu\text{-}CH_2NMe)(\mu\text{-}CHCH_2)(PMe_2Ph)_2\cdot{}^1/_2C_7H_8$. A suitable small crystal was selected and transferred to the goniostat where it was cooled to −160 °C. The crystal was characterized in the usual manner; a systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited no symmetry or systematic absences. The crystal was triclinic, and the centrosymmetric space group $P\bar{1}$ was selected and confirmed by the subsequent solution and refinement of the structure.

The structure was solved by using a combination of direct methods and standard heavy atom techniques. Preliminary calculations of the density had indicated the presence of four W atoms, and four W atoms were located in the E-map from the best solution of MULTAN. The remaining atoms were located in successive Fourier maps phased with the known atoms. The asymmetric unit contains two essentially similar molecules and one molecule of solvent (presumably toluene). The two molecules are distinguished by the labels A and B. Molecule A appears to be slightly disordered; one phenyl group in a dimethylphenylphosphine occupies approximately the same space as the solvent molecule. The disorder was not completely resolved; the methyl group on the solvent toluene was not located. Another indication of the disorder problem is the poor distances. The structure was refined by full-matrix least squares using anisotropic thermal parameters. Hydrogen atoms were not located. Selected hydrogen atoms were introduced in calculated positions during refinement. The data were corrected for absorption.

The final difference Fourier was essentially featureless; a few peaks of approximately 1.0 e/Å were located in close proximity of the W atoms.

Although refinement converged normally, several of the peripheral atoms exhibited large anisotropic motion, specifically those associated with the solvent and the four phenyl rings. All ORTEP diagrams were therefore drawn by using isotropic thermal parameters.

Acknowledgment. We thank the National Science Foundation and the Wrubel Computing Center for support.

Supplementary Material Available: Anisotropic thermal parameters, complete listings of bond distances and angles, and listing of F_o and F_c (126 pages). Ordering information is given on any current masthead page. The complete structural reports are available from the Indiana University Chemistry Library in microfische form only at a cost of $2.50 per copy. For $W_2Cl_3(NMe_2)_3(C_2H_2)(PMe_3)_2$ and $W_2Cl_3(NMe_2)_2(CH_2NMe)(CHCH_2)(PMe_2Ph)_2$ request I.U. MSC Reports 84086 and 84073, respectively.

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