

none gave better analysis of variance than did unit weights, which were therefore retained. Programs and packages used were SHELXTL¹⁵ on a Nova 45 minicomputer for initial structure solution, SHELX76¹⁶ on an Amdahl 470 V/8 computer for final refinement, CALC¹⁷ for molecular geometry calculations, and EASYORTEP¹⁸ for plotting. For Co, coefficients for an analytical form of the scattering curve were taken from ref 19, while inlaid¹⁶

scattering factors were used for all other atoms.

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Supplementary Material Available: Coding of the program for the computerized simulation of the hydrolysis of propylene carbonate with H₂¹⁸O (3 pages); a listing of observed and calculated structure factors for I (1 page). Ordering information is given on any current masthead page.

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Formation and Characterization of Stable Alkylidyne(alkene)tungsten Complexes

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Reaction of the alkylidyne complexes [W(CPh)Cl(CO)₂(py)₂], [Kat][W(CR)Cl₂(CO)₂(py)], and [W-(CPh)Cl(CO)₂(tmeda)] with maleic anhydride and fumaronitrile results in substitution of carbon monoxide and affords the alkylidyne(alkene)tungsten complexes [W(CPh)Cl(CO)(η^2 -alkene)(py)₂] (4 and 5), [Kat][W(CR)Cl₂(CO)(η^2 -alkene)(py)] (6 and 7; R = Me, Kat = NEt₄; 8 and 9, R = Ph, Kat = NEt₄, PPN), and [W(CPh)Cl(CO)(η^2 -alkene)(tmeda)] (10 and 11), respectively. Compounds 10 and 11 can also be obtained by reaction of 4 and 5 with tmeda. The reactions are conducted in THF or CH₂Cl₂ at room temperature or slightly elevated temperatures. In all complexes the coordination site trans to the alkylidyne ligand is occupied by chloride. ¹H NMR NOE difference studies show that in the anionic complexes the second chloride ligand is coordinated trans to the alkene. The fumaronitrile complexes are obtained as mixtures of diastereomers due to coordination of the two enantiotopic faces of the alkene to the asymmetric metal complex fragments. The molecular structure of 4 was determined by X-ray crystallography: space group P2₁/n, a = 11.522 (2) Å, b = 16.026 (3) Å, c = 11.680 (2) Å, β = 102.97 (1)°, Z = 4, R = 3.28%, R_w = 3.57%. Substitution of carbon monoxide in the formation of the title complexes is postulated to occur indirectly by initial substitution of pyridine or chloride and subsequent trans labilization of carbon monoxide by the alkene.

Introduction

Reactions of alkenes and alkynes with multiple metal-carbon bonds play a prominent role in the chemistry of transition-metal alkylidene⁴ and alkylidyne⁵ complexes. High-valent transition-metal alkylidene complexes are established as the active species in olefin metathesis⁶ and polymerization of olefins and acetylenes,⁷ and high-valent

transition-metal alkylidyne complexes are involved in acetylene metathesis.⁸ Transition-metal carbene complexes in lower formal oxidation states were found to participate in a variety of reactions.⁹ For example, they were demonstrated to be useful for the cyclopropanation of olefins¹⁰ and to generate many different organic products in reactions with acetylenes.¹¹ The Fischer-type carbyne complexes [M(CR)Br(CO)₄] were shown to induce the polymerization of certain olefins¹² and acetylenes (M = W)¹³ and to react with α,ω -diynes to form phenols (M = Cr, W).¹⁴ We have recently begun to investigate reactions of substituted Fischer-type carbyne complexes with un-

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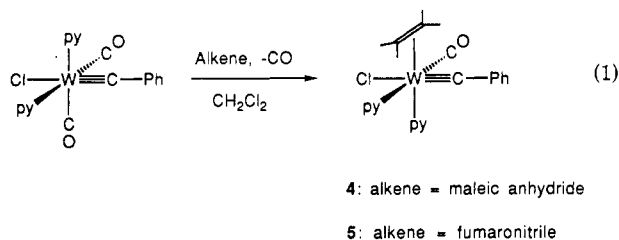
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saturated organic substrates. One of the objectives of this work is to gain insight into the basic interactions of metal carbyne complexes with alkenes and alkynes. This knowledge may provide a basis for the further development of reactions of low-valent transition-metal carbyne complexes with unsaturated organic substrates. Here we give a full account¹⁵ on the formation and characterization of stable alkylidyne(alkene)tungsten complexes.

Very little is known about the interaction of metal-carbon triple bonds in any type of alkylidyne complex with alkenes. Schrock et al. reported the formation of the methylidyne ethylene tungsten complex $[W(CH)(CF_3SO_3)(\eta^2-C_2H_4)(PMe_3)_3]$ from $[W(CH)(CF_3SO_3)(PMe_3)_4]$ and ethylene.¹⁶ The unusual dialuminated tungsten methylidyne complex $[W(CAl_2Me_4Cl)(CH_3)(PMe_3)_2(\eta^2-C_2H_4)]$ was obtained by reaction of $[W(CHAlMe_2Cl)(Cl)(PMe_3)_3]$ with C_2H_4 and $AlMe_3$; Churchill et al. determined its structure by X-ray crystallography.¹⁷ Very recently, the formation and structure of the molybdenum complex $[Mo(CCH_2CMe_3)(\eta^5-C_5H_5)(C_2(CN)_4)\{P(OMe)_3\}]$ was reported by Green et al.¹⁸

Results and Discussion

Synthesis of $[W(CC_6H_5)Cl(CO)(\eta^2\text{-alkene})(py)_2]$ (4, Alkene = Maleic Anhydride; 5, Alkene = Fumaronitrile). The alkylidyne complex $[W(CC_6H_5)Cl(CO)_2(py)_2]$,¹⁹ 1, reacts in methylene chloride solution with maleic anhydride to give the alkylidyne(alkene)tungsten complex $[W(CC_6H_5)Cl(CO)(\text{maleic anhydride})(py)_2]$, 4, and free carbon monoxide (eq 1). The reaction is complete

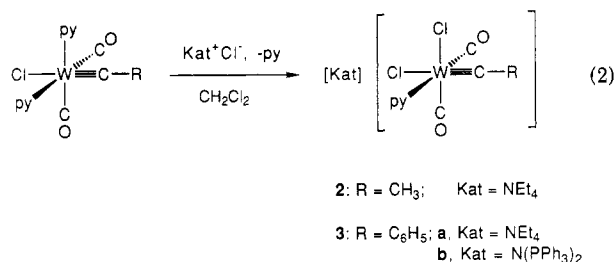


within a few hours at room temperature. The product forms orange-yellow crystals from CH_2Cl_2 /pentane. The simultaneous presence of a carbyne ligand and an alkene ligand in the product is evident from spectroscopic information. The carbyne carbon gives rise to a characteristic ¹³C NMR resonance at δ 268.0. The signals for the olefinic carbon atoms of maleic anhydride appear at δ 55.4 and 51.8. A single resonance for coordinated carbon monoxide is present at δ 207.1. The ¹H NMR spectrum shows the presence of two inequivalent pyridine ligands. Two separate signals for the ortho-hydrogen atoms of the pyridine ligands appear at δ 9.30 and 9.21. The olefinic protons give rise to widely separated doublets at δ 4.42 and 3.19 (³J = 5.3 Hz). The two infrared absorptions in the carbonyl region of starting complex 1 at 1985 and 1897 cm^{-1} are replaced by a single absorption at 2044 cm^{-1} . These spectroscopic data are consistent with a product derived from $[W(CC_6H_5)Cl(CO)_2(py)_2]$ by substitution of

one carbon monoxide ligand by maleic anhydride.

In a very similar manner 1 reacts with fumaronitrile to give $[W(CC_6H_5)Cl(CO)(\text{fumaronitrile})(py)_2]$, 5 (eq 1). The reaction with fumaronitrile is slower than the reaction with maleic anhydride, requiring several hours at 45 °C. The noncrystalline, light yellow product is obtained as an approximate 1:1 mixture of two diastereomers. The two diastereomers arise due to coordination of the two enantiotopic faces of fumaronitrile to the asymmetric metal complex fragment $[W(CC_6H_5)Cl(CO)(py)_2]$ (vide infra). Different fractions of the product obtained by chromatography (silica gel, CH_2Cl_2 /THF) contained varying relative ratios of the isomers, but full separation has not been attempted. The ¹³C NMR signals for the carbyne carbon atoms of the two diastereomers are found at δ 264.7 and 264.3, and the signals for the alkene carbon atoms are at δ 35.4, 33.7, 32.6, and 30.0. The olefinic protons give rise to two AB patterns (Figure 3). In diastereomer A the resonances are widely separated (δ 3.37 and 2.40), while diastereomer B shows a very small chemical shift difference (δ 3.43 and 3.31). In the infrared an absorption at 2218 cm^{-1} is observed for the cyano groups, and an absorption at 2049 cm^{-1} for the carbonyl ligand. The relative orientation of the fumaronitrile ligand in the two isomers will be discussed further below.

Synthesis of $[NEt_4][W(CR)Cl_2(CO)(\eta^2\text{-alkene})(py)]$ (6, R = CH₃, Alkene = Maleic Anhydride; 7, R = CH₃, Alkene = Fumaronitrile) and $[Kat][W(CC_6H_5)Cl_2(CO)(\eta^2\text{-alkene})(py)]$ (8a,b, Alkene = Maleic Anhydride; 9a,b, Alkene = Fumaronitrile (a, Kat = NEt₄; b, Kat = N(PPh₃)₂)). The anionic alkylidynedihalotungsten complexes $[NEt_4][W(CR)Cl_2(CO)_2(py)]$, 2 (R = CH₃) and 3 (R = C₆H₅), are generated from the bispyridine-substituted compounds $[W(CR)Cl(CO)_2(py)_2]$ by reaction with excess tetraethylammonium chloride in methylene chloride solution (eq 2).²⁰ Other chlorides, e.g.,



bis(triphenylphosphine)iminium chloride, may be employed as well. These salts are not isolated in pure form as they are only stable in the presence of excess chloride ions. Substitution of chloride for pyridine causes a shift of the carbonyl stretching frequencies by about 20–30 cm^{-1} to lower energies. The ¹H NMR spectrum shows the presence of only one pyridine ligand, and the ¹³C NMR spectrum reveals the presence of two inequivalent CO ligands. Thus, compounds 2 and 3 are formulated as the anionic carbyne complexes $[W(CR)Cl_2(CO)_2(py)]^-$ in which one chloride ligand and the pyridine ligand are trans to the two carbonyl ligands, while the second chloride is coordinated trans to the carbyne ligand.

Complexes 2 and 3 react in methylene chloride with maleic anhydride and fumaronitrile to give the anionic alkylidyne(alkene)tungsten complexes $[Kat][W(CR)Cl_2(CO)(\eta^2\text{-alkene})(py)]$, 6–9. The methylcarbyne complex $[NEt_4][W(CMe)Cl_2(CO)_2(py)]$ reacts faster than the phe-

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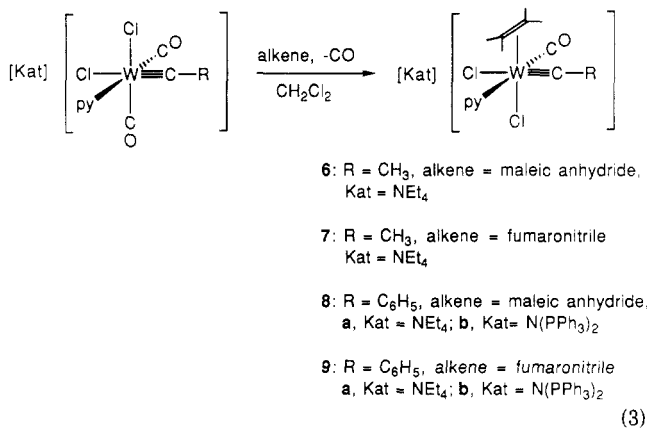
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Table I. Crystallographic Data for 4

(a) Crystal Parameters			
formula	C ₂₂ H ₂₅ ClN ₂ O ₄ W	Z	4
cryst syst	monoclinic	D(calc), g cm ⁻³	1.87
space	P2 ₁ /n	μ(Mo Kα), cm ⁻¹	59.8
group		T, K	295
a, Å	11.522 (2) ^a	color	yellow
b, Å	16.026 (3)	size, mm	0.26 × 0.31 × 0.35
c, Å	11.680 (2)	T(max)/T(min)	1.50
β, deg	102.97 (1)		
V, Å ³	2101.7 (6)		
(b) Data Collection			
diffractometer	Nicolet R3m		
radiation	Mo Kα		
wavelength, Å	0.71073		
monochromator	graphite		
scan limits, deg	4 ≤ 2θ ≤ 50		
scan method	θ/2θ		
no. of rflns collected	4045		
no. of indep rflns	3695		
R(int), %	3.1		
no. of obs rflns (3σF _o)	3218		
std rflns	3 std/197 rflns		
decay, %	<1		
(c) Refinement			
R(F)	3.28		
R(wF)	3.57		
GOF	1.517		
Δ/σ	0.043		
Δ(ρ), e Å ⁻³	0.98		
N _o /N _v	11.8		

^aUnit cell parameters obtained from the angular settings of 25 reflections (21° ≤ 2θ ≤ 26°).

nylcarbyne complex [NEt₄][W(CPh)Cl₂(CO)₂(py)], and in all cases reaction of maleic anhydride proceeds faster than reaction with fumaronitrile. The reaction times range from 15 min at room temperature for the formation of the methylcarbyne maleic anhydride complex 6 to 1.5 h at 40 °C for formation of the phenylcarbyne fumaronitrile complex 9. The anionic complexes 2 and 3 react faster than

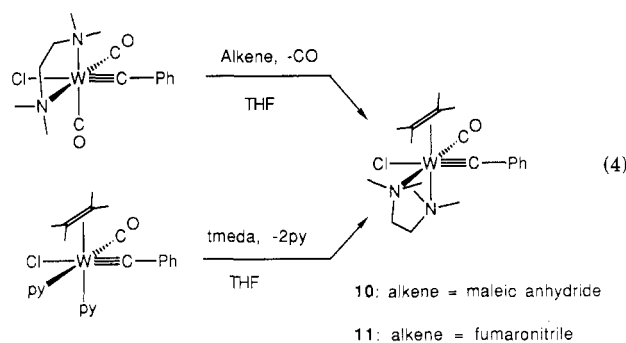


the neutral complex 1. When the reactions are completed, the solvent is removed and excess olefin is washed away with ether. Repeated extractions with cold (0 °C) THF separate the products from excess chloride salts. The anionic alkylidyne(alkene)tungsten complexes 6–9 could not be crystallized but were purified by multiple precipitations from CH₂Cl₂/ether with yields between 40 and 91%. Both methylcarbyne complexes 6 and 7 are thermally labile, but all phenylcarbyne alkene complexes do not show signs of decomposition, even after several weeks in air. The relative arrangement of the ligands was determined by ¹H NOE difference NMR experiments (vide infra). The two chloride ligands are trans to the carbyne and the alkene ligands; the pyridine ligand is trans to the

carbonyl ligand. The fumaronitrile complexes are again mixtures of two diastereomers. These are obtained in approximately 1:1 ratios, with slight variations observed for different fractions of precipitation or column chromatography (silica gel, CH₂Cl₂/THF).

In a modified synthesis of 8a the anionic complex 3 is not prepared separately. Reaction of 1 with maleic anhydride and excess NEt₄Cl in CH₂Cl₂ gives 8a in a single procedure. It was also demonstrated in spectroscopic experiments that 8a and 9a may be obtained by reaction of 4 and 5 with excess NEt₄Cl in CH₂Cl₂.

Synthesis of [W(CC₆H₅)Cl(CO)(η²-alkene)(tmeda)] (10, Alkene = Maleic Anhydride; 11, Alkene = Fumaronitrile). The tmeda-substituted compounds [W(CC₆H₅)Cl(CO)(η²-alkene)(tmeda)] were obtained by two independent routes. Method A: In analogy to the previously described syntheses the carbyne complex [W(CC₆H₅)Cl(CO)₂(tmeda)]¹⁸ is allowed to react with maleic anhydride or fumaronitrile in THF solution at 60 °C for prolonged reaction times (several hours to days) to give the carbyne(alkene)tungsten complexes 10 and 11. The



products are purified by chromatography on short silica gel columns (CH₂Cl₂/THF) and recrystallized from CH₂Cl₂/ether. Method B: The same products are obtained by substitution of the pyridine ligands in 4 and 5 by tmeda. The spectroscopic data for the fumaronitrile complex 11 (¹H and ¹³C NMR) indicate the presence of only a single isomer (vide infra). No evidence for a second (expected) isomer could be found.

Solid-State Structure of [W(CC₆H₅)Cl(CO)(η²-maleic anhydride)(py)₂] (4). The molecular structure of 4 is shown in Figure 1. Final atomic positional parameters are listed in Table II; selected bond distances and angles are presented in Table III. The geometry of the molecule is best described in terms of octahedral coordination with the η²-olefin ligand occupying one coordination site. The structure is typical of a low-valent monohalo group 6 transition metal alkylidyne complex. The chloride ligand occupies the coordination site trans to the phenylcarbyne ligand, and the two pyridine ligands are trans to carbon monoxide and maleic anhydride. The maleic anhydride ligand is oriented nearly perpendicular with respect to the metal-carbon triple-bond axis (dihedral angle C(2)-M-W-C(6) = 95.2°, M = midpoint between C(2) and C(3)) and is bonded slightly asymmetrical to the metal center (W-C(2) = 2.215 (6), W-C(3) = 2.272 (6) Å). The carbon atom that is located on the side of the carbonyl ligand has the longer bonding distance. The length of the C(2)-C(3) bond is 1.408 (8) Å. This is considerably longer than the C=C bond length in free maleic anhydride (1.303 Å).²¹ In the (phenylacetylene)(maleic anhydride)tungsten complex [W(S₂CNEt₂)₂(PhC₂H)(maleic anhydride)] the C=C dis-

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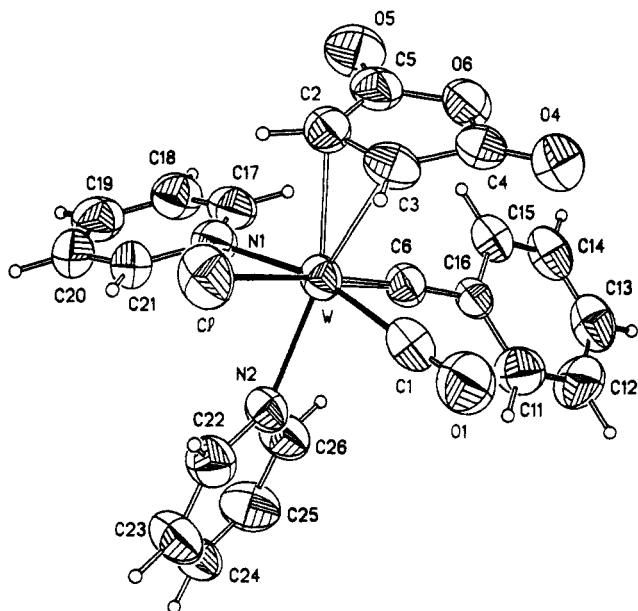


Figure 1. ORTEP drawing of $[W(CC_6H_5)Cl(CO)(\text{maleic anhydride})(py)_2]$ (4).

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U^a
W	2292.8 (2)	6929.3 (2)	8889.3 (2)	45.2 (1)
Cl	2711 (1)	6974 (1)	11117 (1)	71 (1)
C(1)	2926 (5)	5741 (4)	9068 (5)	57 (2)
C(2)	3794 (5)	7821 (4)	9094 (5)	51 (2)
C(3)	4309 (5)	7020 (4)	9228 (6)	59 (2)
C(4)	4760 (5)	6844 (4)	8193 (6)	62 (2)
C(5)	3947 (5)	8153 (4)	7981 (5)	60 (2)
C(6)	2098 (5)	6741 (3)	7338 (5)	48 (2)
C(11)	1628 (6)	5680 (4)	5791 (5)	68 (3)
C(12)	1470 (7)	5434 (5)	4636 (6)	81 (3)
C(13)	1664 (5)	5992 (5)	3809 (5)	73 (3)
C(14)	2005 (5)	6802 (4)	4136 (5)	64 (2)
C(15)	2165 (5)	7050 (4)	5272 (5)	56 (2)
C(16)	1965 (4)	6483 (4)	6127 (4)	44 (2)
C(17)	988 (5)	8570 (4)	7875 (5)	62 (2)
C(18)	213 (5)	9239 (4)	7722 (6)	69 (3)
C(19)	-381 (6)	9414 (4)	8588 (7)	73 (3)
C(20)	-161 (6)	8924 (4)	9583 (6)	70 (3)
C(21)	621 (5)	8275 (4)	9673 (5)	59 (2)
N(1)	1196 (4)	8085 (3)	8819 (4)	53 (2)
C(22)	153 (6)	6150 (4)	9880 (5)	63 (2)
C(23)	-969 (6)	5883 (5)	9892 (6)	74 (3)
C(24)	-1834 (5)	5893 (4)	8867 (6)	67 (3)
C(25)	-1537 (5)	6169 (5)	7883 (6)	77 (3)
C(26)	-381 (5)	6413 (4)	7912 (5)	64 (2)
N(2)	481 (4)	6414 (3)	8919 (4)	48 (2)
O(1)	3286 (4)	5080 (3)	9138 (5)	85 (2)
O(4)	5280 (4)	6260 (3)	7922 (5)	87 (2)
O(6)	4498 (3)	7527 (3)	7432 (4)	64 (2)
O(5)	3703 (4)	8804 (3)	7495 (4)	80 (2)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

cance of coordinated maleic anhydride is very similar, 1.41 (1) \AA .²² This (alkyne)(alkene)metal complex is related to complex 4 in the sense that in both molecules maleic anhydride is coordinated to a metal center containing a multiply bonded ligand, alkyne and alkylidyne, respectively. The dihedral angle between the mean plane of the four maleic anhydride ring carbon atoms (C(5), C(2), C(3), C(4)) and the plane defined by the metal center and the

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Table III

(a) Bond Distances (\AA)			
W-Cl	2.538 (1)	W-C(1)	2.033 (6)
W-C(2)	2.215 (6)	W-C(3)	2.272 (6)
W-C(6)	1.801 (6)	W-N(1)	2.233 (5)
W-N(2)	2.253 (4)	C(1)-O(1)	1.133 (8)
C(2)-C(3)	1.408 (8)	C(2)-C(5)	1.451 (9)
C(3)-C(4)	1.448 (10)	C(4)-O(4)	1.192 (8)
C(4)-O(6)	1.400 (8)	C(5)-O(6)	1.415 (8)
C(5)-O(5)	1.191 (8)	C(6)-C(16)	1.448 (8)
(b) Bond Angles (deg)			
Cl-W-C(1)	86.6 (2)	Cl-W-C(2)	84.7 (2)
C(1)-W-C(2)	109.9 (2)	Cl-W-C(3)	82.4 (2)
C(1)-W-C(3)	73.3 (2)	C(2)-W-C(3)	36.5 (2)
Cl-W-C(6)	171.2 (2)	C(1)-W-C(6)	84.7 (2)
C(2)-W-C(6)	97.7 (2)	C(3)-W-C(6)	94.5 (2)
Cl-W-N(1)	89.4 (1)	C(1)-W-N(1)	165.4 (2)
C(2)-W-N(1)	83.7 (2)	C(3)-W-N(1)	120.1 (2)
C(6)-W-N(1)	99.2 (2)	Cl-W-N(2)	87.6 (1)
C(1)-W-N(2)	88.1 (2)	C(2)-W-N(2)	159.9 (2)
C(3)-W-N(2)	159.3 (2)	C(6)-W-N(2)	92.7 (2)
N(1)-W-N(2)	77.7 (2)	W-C(6)-C(16)	173.0 (4)
W-C(1)-O(1)	178.1 (6)	W-C(2)-C(3)	73.9 (3)
W-C(2)-C(5)	112.9 (4)	W-C(3)-C(2)	69.5 (3)
W-C(3)-C(4)	112.7 (4)	C(3)-C(2)-C(5)	107.5 (6)
C(2)-C(3)-C(4)	107.8 (6)	C(3)-C(4)-O(4)	132.1 (6)
C(3)-C(4)-O(6)	108.2 (5)	O(4)-C(4)-O(6)	119.7 (7)
C(2)-C(5)-O(6)	107.7 (5)	C(2)-C(5)-O(5)	133.2 (6)
O(6)-C(5)-O(5)	119.1 (6)		

two alkene carbon atoms (W, C(2), C(3)) is 109.5° . The anhydride ring is oriented toward the side of the carbyne ligand, possibly for steric reasons. Orientation in the opposite direction would bring the central anhydride oxygen atom close to the chlorine atom. The distance between the central oxygen atom of the anhydride ring and the carbyne carbon C(6)-O(6) is 3.019 (8) \AA , only slightly shorter than the sum of standard van der Waals radii.²³ The displacement of O(6) from the mean plane of the four ring carbon atoms is only 0.048 \AA . Similarly small deviations from ring planarity were observed for the maleic anhydride ligands in $[M(\text{arene})(\text{maleic anhydride})(CO)_2]$ ($M = Cr$, arene = mesitylene, 0.09 \AA ;²⁴ $M = Mo$, arene = C_6Et_6 , 0.10 \AA).²⁵ Nonbonded interactions between the anhydride ring and the carbyne ligand thus appear to be small. The phenylcarbyne ligand is slightly bent ($W-C(6)-C(16) = 173.0 (4)^\circ$), to a similar extent as found in other complexes.^{26,27} The metal-carbon triple-bond length $W-C(6)$ is 1.801 (6) \AA . This is within the established range for metal carbynes and close to the value found for $[W(CPh)Br(CO)_2(py)_2]$ (1.84 (2) \AA),²⁸ the most closely related structurally characterized alkylidyne complex. The metal-carbonyl bond distance ($W-C(1) = 2.033 (6) \text{\AA}$) and the $W-N$ pyridine distances [$W-N(1) = 2.233 (5)$, $W-N(2) = 2.253 (4) \text{\AA}$] are also similar to those found in $[W(CPh)Br(CO)_2(py)_2]$ ($W-C = 2.00 (2)$, $W-N = 2.263 (12)$ and $2.283 (12) \text{\AA}$). The $W-Cl$ distance (2.538 (1) \AA) is somewhat longer than in the tetracarbonyl complexes $[W(C-C_6H_5-Cr(CO)_3)Cl(CO)_4]$ (2.485 (8) \AA)²⁹ and $[W(CCH_3)Cl(CO)_4]$ (2.48 (1) \AA).²⁶ A slight lengthening of the metal-halide distance upon going from tetracarbonylmetal car-

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byne complexes to donor ligand substituted derivatives (two pyridine ligands in the case of **4**) is generally observed.²⁶ The pyridine ligands (C(6)-W-N(1) = 99.2 (2)°, C(6)-W-N(2) = 92.7 (2)°) and the maleic anhydride ligand (C(6)-W-M = 96.4 (2)°) are bent away from the carbyne ligand while the carbon monoxide ligand is leaning slightly toward the carbyne ligand (84.7 (2)°). There is also a distinct bending back of the pyridine ligand cis to maleic anhydride away from maleic anhydride (M-W-N(1) = 102.1 (2)°). The bonding angle between the maleic anhydride carbon monoxide ligands (M-W-C(1)) is 91.4 (2)°.

Qualitative Bonding Considerations. The bonding in the alkylidyne(alkene)metal complexes is easily understood in qualitative terms as the effects of σ and π bonding are well separated in octahedral coordination geometry.³⁰ For the following discussion the carbyne ligand is assumed to be oriented along the z axis. Two of the three metal d_π orbitals, d_{xz} and d_{yz} , are engaged in formation of the metal-carbon triple bond. The corresponding M-C π orbitals are low lying due to strong contributions of carbon p orbitals. These orbitals are therefore not easily accessible to typical π -acceptor ligands, such as carbon monoxide or olefins. The d_{xy} orbital is more or less the only metal d_π orbital available for π bonding to the remaining ligands. As this orbital is orthogonal to the z axis, single-faced π -acceptor ligands, such as alkenes, are necessarily oriented perpendicular with respect to the metal-carbon triple bond as found in compounds **4-11**, in [W(CAl₂Me₄Cl)(CH₃)(PMe₃)₂(η^2 -C₂H₄)],¹⁷ and in [Mo(CCH₂CMe₃)(η^5 -C₅H₅)(C₂(CN)₄)]P(OMe)₃.¹⁸ Due to this bonding situation, a high barrier of activation is expected for rotation of the alkene ligands. This is in agreement with the failure to observe rotation of the fumaronitrile ligand in complex **5** on the NMR time scale.³¹

The alkylidyne(alkene)metal complexes described in this work are electronically related to oxo(alkene)- and imido(alkene)metal complexes.³² In those compounds, the alkene ligands are also oriented perpendicular with respect to the metal-ligand multiple bonds.

This bonding picture also helps to explain the unusually high shift of the ν_{CO} IR stretching frequency upon substitution of one CO ligand by maleic anhydride and fumaronitrile. The average ν_{CO} stretching frequency of [W(CPh)Cl(CO)₂(py)₂] (**1**) is 1941 cm⁻¹, while **4** and **5** have values of 2044 and 2049 cm⁻¹, respectively. This is a shift of about 100 cm⁻¹. Thus, in a situation where a carbonyl ligand can effectively utilize only one π^* orbital for π back-bonding with the metal center, maleic anhydride and fumaronitrile act as π -acceptor ligands significantly stronger than carbon monoxide. Even though a strict comparison is not possible due to the different number of carbonyl ligands involved, this shift of the ν_{CO} stretching frequencies may be compared with the shift occurring when one of the CO ligands in [W(CO)₄(bis(dimethylphosphino)ethane)] (2013 m, 1921 m, 1901 w, 1896 s cm⁻¹) is replaced by maleic anhydride to give [W(CO)₃(maleic

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(31) In the fumaronitrile complexes the olefin hydrogen atoms could in principle become equivalent by fast rotation of the olefin on the NMR time scale. The ¹H NMR spectrum of **5**, however, does not change significantly at temperatures up to 80 °C. In contrast, the NMR data for [Mo(CCH₂CMe₃)(η^5 -C₅H₅)(C₂(CN)₄)]P(OMe)₃ indicate that the tetracyanoethylene ligand is rotating fast on the NMR time scale.¹⁸

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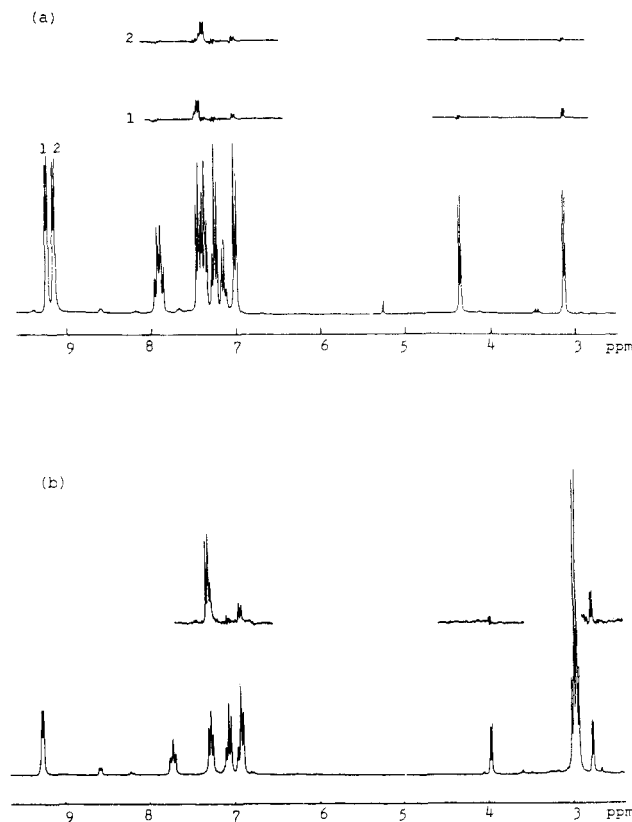


Figure 2. ¹H NMR spectra and ¹H NMR NOE difference spectra (inset) of (a) complex **4** and (b) complex **8**.

anhydride)(bis(dimethylphosphino)ethane)] (2007 w, 1944 m, 1897 s cm⁻¹). In this compound all CO ligands are able to interact well with two metal d orbitals, and the average ν_{CO} stretching frequency shifts by less than 20 cm⁻¹ to higher energy.

The bending away of cis ligands from metal-ligand multiple-bond systems strengthens the metal-ligand multiple bonds due to increased mixing of p and d orbitals.³³ This effect could thus explain the large coordination angles between the carbyne ligand and the pyridine ligands (99.2 and 92.7°) as well as the maleic anhydride ligand (96.4°). As indicated above, steric interactions are likely to contribute little to the widening of the bonding angle between the carbyne and maleic anhydride ligands. In contrast, the carbonyl ligand is bent toward the carbyne ligand. It is the only ligand possessing an empty π -acceptor orbital with the proper orientation to interact with the M≡C π system. Even though this interaction is expected to be quite weak, it may be sufficient to induce a slight approach of the carbonyl ligand toward the carbyne ligand (84.7°).

¹H NMR Studies. The basic nature of compounds **4-9** as alkylidyne(alkene)tungsten complexes could be deduced from routine spectroscopic information and was confirmed by an X-ray crystal structure analysis of **4**. The infrared and NMR spectroscopic data are consistent with a facial arrangement of the three π -bonded ligands, carbyne, alkene, and carbon monoxide, in all complexes, as expected for electronic reasons. However, the relative arrangement of the donor ligands in the anionic complexes [Kat][W-(CR)(Cl)₂(CO)(η^2 -alkene)(py)] could be determined only with further investigations. These compounds are formally derived from the bis(pyridine)-substituted complexes [W-

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(CR)(Cl)(CO)(η^2 -alkene)(py)₂] by replacement of one pyridine ligand by chloride. In particular, it remained unclear whether the second chloride ligand is coordinated trans to the alkene or trans to carbon monoxide. To answer this question, ¹H NMR NOE experiments were carried out. The resulting data also allowed a more precise assignment of ¹H NMR resonances to individual protons in the metal complexes.

Figure 2a shows the ¹H NMR spectrum of 4. The NOE difference ¹H NMR spectrum is shown as an inset in Figure 2a. Irradiation of the sample at the low-field resonance of the pyridine α -hydrogen atoms at δ 9.30 enhances the upfield doublet (δ 3.19) of the olefin ligand. Therefore, the downfield α -hydrogen resonance belongs to the pyridine ligand cis to maleic anhydride and the enhanced peak must be the resonance of the olefin proton which is oriented toward the pyridine ligand. Irradiation of the pyridine resonance at δ 9.21 showed no effect on the olefin hydrogen atoms. This resonance is thus assigned to the pyridine ligand trans to maleic anhydride. The double-resonance experiments also cause significant enhancement of the respective pyridine β -hydrogen resonances and moderate enhancement of the *o*-hydrogen resonance of the phenylcarbyne ligand.

The NOE difference ¹H NMR spectrum of [NEt₄][W-(CPh)Cl₂(CO)(maleic anhydride)(py)] (8) is shown as the upper trace in Figure 2b. Irradiation of an NMR sample of 8 at the resonance frequency of the pyridine α -protons at δ 9.43 leads to enhancement of the alkene proton signal at δ 2.93. This result shows that pyridine is coordinated cis to maleic anhydride. Since the π -bonded ligands, carbyne, alkene, and carbon monoxide, are in a facial arrangement, it follows that pyridine is coordinated trans to carbon monoxide and the second chloride trans to the olefin. The signal at δ 2.93 is consequently assigned to the alkene CH proton which is oriented toward the pyridine ligand and the resonance at δ 3.09 to the olefinic proton located on the side of the carbonyl ligand. A strongly enhanced triplet at δ 7.45 is assigned to the β -hydrogen atoms of the pyridine ligand. Some enhancement is also seen for a signal in the region of the phenyl group ligand (doublet at δ 7.06), which is assigned to the *o*-hydrogen atoms. The spectroscopic information available for all anionic complexes 6–9 is consistent with the formulation of the structures as the geometric isomers in which the two chloride ligands are trans to the alkene and trans to the carbyne ligands, and the pyridine ligand is trans to carbon monoxide. The presence of two isomers for the fumaronitrile complexes is therefore a consequence of coordination of the enantiotopic faces of fumaronitrile to the asymmetric metal complex fragments, which gives rise to two diastereomers, each existing as two enantiomers (Figure 4).

The ¹H NMR spectrum of [W(CPh)Cl(CO)(fumaronitrile)(py)₂] (5) is shown in Figure 3a. The two isomers differ most characteristically in the appearance of the AB patterns of the olefin protons. For one diastereomer the doublets are widely separated (A); in the other diastereomer the chemical shift difference is small (B). Figure 4 shows projections along the alkene–metal axis for the two diastereomers I and II, which are possible for the fumaronitrile complexes. The NOE enhancements of the olefinic hydrogen resonances caused by irradiation of the pyridine α -hydrogen atoms are shown in the inset of Figure 3a. Irradiation of the low-field doublet at δ 9.52 enhances only the high-field olefin resonance at 2.39 of diastereomer A. Irradiation of the next doublet at δ 9.48 enhances only the higher field doublet of diastereomer B at δ 3.32. Irradiation

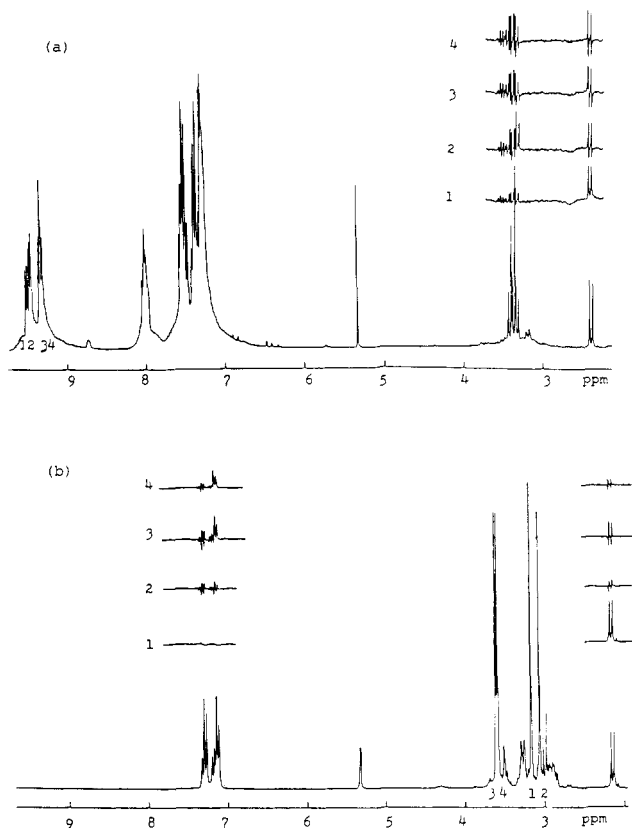


Figure 3. ¹H NMR spectra and ¹H NMR NOE difference spectra (inset) of (a) complex 5 and (b) complex 11.

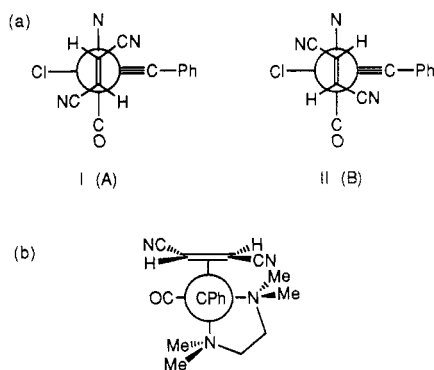
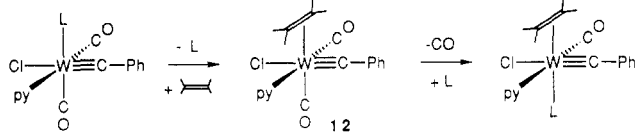


Figure 4. (a) Pair of diastereomers of the alkylidyne fumaronitrile complexes generated by coordination of the two enantiotopic faces of fumaronitrile to one enantiomer of the metal complex fragment. (b) Projection showing the arrangement of the tmeda and fumaronitrile ligands in 11.

at the frequencies of the overlapping doublets at δ 9.35 and 9.31 does not affect the intensities of the olefinic hydrogen resonances. Thus, in both diastereomers A and B the olefin hydrogen on the side of the pyridine ligand resonates at higher field than the olefin hydrogen on the side of the carbonyl ligand. It also follows that, as in complex 4, the α -hydrogen atoms on the pyridine ligands trans to carbon monoxide resonate at lower field than those of the pyridine trans to the alkene ligand. However, these results do not yet allow us to correlate diastereomers A and B with structures I and II. Attempts to determine the relative orientation of the fumaronitrile ligand in 5 by measuring the NOE enhancement of the phenyl hydrogen resonances upon irradiation of the olefin hydrogen resonances were not conclusive.

Additional steric information was obtained from NOE experiments on the tmeda-substituted complex [W-

Scheme I



(CPh)Cl(CO)(fumaritrile)(tmeda)] (11). According to the spectroscopic information available, this compound was obtained only as a single diastereomer. No evidence for the presence of the second, expected diastereomer could be detected. The results of NOE difference ^1H NMR experiments on 11 are shown in Figure 3b. Irradiation was carried out at the resonance frequencies of the tmeda methyl groups. Irradiation of the methyl group at δ 3.16 (1) strongly enhances the olefin peak at δ 2.14 but shows no enhancement in the phenyl region. Thus, in this isomer the olefin proton that is adjacent to one end of the tmeda ligand must be on the side opposite to the carbyne ligand. It follows that the orientation of fumaritrile in 11 is that of isomer I in Figure 4a. This isomer of the tmeda complex 11 is drawn in a different perspective in Figure 4b, showing the relative arrangement of the tmeda and olefin substituents. This assignment is corroborated by the other double-resonance experiments shown in Figure 3b. Irradiation of the methyl resonance at δ 3.05 (2) has no effect on the olefin and phenyl peaks. This methyl group therefore belongs to the tmeda terminus trans to fumaritrile and is located on the side opposite to the carbyne ligand. Irradiation of the methyl groups at δ 3.60 (3) and 3.57 (4) enhances the intensity of the phenyl *o*-hydrogen resonances. These methyl groups are therefore located on the side of the carbyne ligand. The fumaritrile hydrogen atoms in 11 appear as widely separated doublets at δ 2.99 and 2.14, similar to the resonances of diastereomer A of the other fumaritrile complexes. We therefore assume that the relative arrangement of the fumaritrile substituents with respect to the four *cis* ligands (carbyne, carbonyl, chloride, and nitrogen donor) is the same in 11 and in diastereomers A. If this assumption is correct, then the structures of the diastereomers A and B of the fumaritrile complexes can be considered fully established and correspond to presentations I and II in Figure 4, respectively.

Mechanistic Considerations. Several pieces of information from the synthetic work point toward a stepwise mechanism of formation of the carbyne(alkene)tungsten complexes as shown in Scheme I. According to this proposed mechanism one of the donor ligands L is substituted in the first step by alkene to afford the intermediate 12, in which the alkene is occupying a coordination site trans to one of the carbonyl ligands. In the intermediate the CO trans to the strongly π -bonding alkene is labilized and subsequently substituted by the ligand L. The rates of formation of the alkyldiene(alkene)tungsten complexes depend strongly on the nature of the donor ligands. Qualitatively, the rates increase with the lability of these ligands, indicating that the first step in Scheme I is rate determining and dissociative in nature. Formation of the products occurs faster with the anionic dichloro phenylcarbyne complexes 2 than with the neutral bis(pyridine)-substituted complex [W(CPh)Cl(CO)₂(tmeda)] is much slower. In an independent experiment it was shown that the rate of formation of 4 is decreased by addition of excess pyridine. The lack of reaction of unactivated alkenes may be rationalized by failure of the second step. Labilization of CO is only achieved by elec-

tron-poor olefins such as maleic anhydride or fumaritrile. With less activated olefins substitution of a donor ligand may occur, at least to some extent,³⁴ but is not followed by dissociation of carbon monoxide. Slower formation of the fumaritrile complexes may indicate a somewhat less effective *trans* labilization of carbon monoxide by fumaritrile than by maleic anhydride.

To probe this mechanism, we attempted to determine whether the ligand L entering in the second step shows a preference for the coordination site *trans* to the alkene or *trans* to carbon monoxide. The reaction of [W(CPh)Cl(CO)₂(py)₂] (1) with excess maleic anhydride in CD₂Cl₂ was allowed to proceed in the presence of 1 equiv of pyridine-*d*₅, and the reaction was monitored by ^1H NMR spectroscopy. The signals for the α -hydrogen atoms of the pyridine ligands *trans* to maleic anhydride and *trans* to carbon monoxide in product 4 were found to be of equal intensity, although in the initial phase of the reaction the signal of the α -hydrogen atoms on the pyridine *trans* to maleic anhydride was marginally lower in intensity. According to the proposed mechanism, a significantly lower intensity of the signal for the pyridine *trans* to maleic anhydride would have been expected. To determine the effects of pyridine exchange in starting complex 1 and 4 on the distribution of the label in 4, these exchange reactions were studied independently. Pyridine exchange in the starting complex 1 ($\sim 0.6 \times 10^{-3} \text{ s}^{-1}$) was found to be about 10 times faster than formation of the product 4 ($\sim 0.06 \times 10^{-3} \text{ s}^{-1}$). Pyridine exchange in product 4 ($\sim 0.006 \times 10^{-3} \text{ s}^{-1}$) was found to occur about 10 times more slowly than its formation. It was furthermore determined that pyridine exchange in the position *trans* to maleic anhydride occurs about 1.1 times faster than in the position *trans* to carbon monoxide. Due to the relative substitution inertness of 4 any unequal distribution of the label in product 4 arising as a consequence of the reaction mechanism would be preserved. Unfortunately, even if the substitution steps were to occur with the postulated stereoselectivity, the faster rate of pyridine exchange in starting complex 1 would obscure a clear manifestation of this mechanism in the labeling experiment.

For the reactions of the anionic dihalotungsten carbyne complexes 2 and 3 with alkenes the postulated mechanism in Scheme I would directly predict formation of the observed isomers with the chloride ligand *trans* to the alkene, if chloride is assumed to be L. We believe this is the operating mechanism; however, other experiments show that the existence of the anionic complexes 6–9 as single geometric isomers is a consequence of their thermodynamic stability. When excess tetraethylammonium chloride is added to the bis(pyridine)-substituted fumaritrile complex 4, only a single product, whose spectroscopic properties are identical with those of complex 8a, is obtained. Since the measured relative rates of pyridine exchange in 4 are 1.1:1 for the pyridine ligands *trans* to maleic anhydride and *trans* to carbon monoxide, respectively, we would expect that substitution of the two pyridine ligands in 4 by chloride proceeds with similar relative rates in both positions. Thus, we conclude that the isomer with chloride *trans* to the alkene and pyridine *trans* to carbon monoxide is thermodynamically more stable than the isomer with the reverse arrangement of these ligands.

The results just mentioned may be seen as a manifestation of the relative *trans* effects and *trans* influences of maleic anhydride and carbon monoxide ligands in this

(34) However, no evidence for such a species could be detected by infrared spectroscopy even in the presence of a large excess of unactivated alkenes (*n*-hexene, cyclohexene).

system. The pyridine ligand trans to maleic anhydride is kinetically about 1.1 times more labile than the pyridine trans to carbon monoxide as determined by the relative exchange rates (trans effect). In the anionic complexes the weaker chloride ligand is coordinating trans to maleic anhydride while the stronger pyridine ligand is coordinating trans to carbon monoxide (trans influence). The relative trans influence is also manifested in the longer W-N distance of the pyridine ligand trans to maleic anhydride (W-N(2) = 2.253 (4) Å) compared to the pyridine trans to carbon monoxide (W-N(1) = 2.233 (5) Å).

Comments and Conclusions

This study shows that low-valent Fischer-type carbyne complexes can coordinate alkene ligands to give stable alkylidyne(alkene)metal complexes. The alkene ligands in the new compounds are bound perpendicular with respect to the metal-carbon triple-bond axis to maximize π bonding. Infrared spectroscopic data indicate strong competition for π back-bonding among the equatorial ligands. In fact, formation of stable alkylidyne(alkene)-metal complexes has only been observed when no competing π -acceptor ligands were present^{16,17} or when the alkenes themselves were strong π acceptors (this work). In another case, both of these requirements were met.¹⁸ It seems clear that the electronic situation in low-valent alkylidyne complexes strongly disfavors a parallel arrangement of alkene and alkylidyne ligands. Therefore, formation of carbon-carbon bonds by direct interaction of alkene and alkylidyne ligands can generally not be expected to occur easily in Fischer-type carbyne complexes. On the other hand, suitable functional alkenes may be useful to introduce carbyne ligands into larger organic ligands. A pertinent example is the formation of vinylcarbene ligands from metal carbynes and allyl halides and subsequent coupling with carbon monoxide to give a coordinated vinylketene.³⁵

In contrast to the preparation of stable alkylidyne(alkene)metal complexes, attempts to isolate alkylidyne(alkyne)metal complexes have not yet been successful. A major reason for the lower stability of alkylidyne complexes containing alkyne ligands appears to be a repulsive electronic interaction between the second alkyne π bond and the metal-carbon π system.³³ This situation favors transformations of alkylidyne(alkyne)metal complexes. Protonation of the alkylidyne ligand to form an alkylidene ligand allows the alkyne to interact with the metal as a four-electron-donor ligand.³⁶ In the absence of a proton source the alkylidyne ligand may be activated toward coupling with other ligands, for example with alkyne and carbon monoxide to give a metallacyclopentadienone.³⁷

The present study leads us to believe that reactions of low-valent metal alkylidyne complexes with simple alkenes will not easily lead to carbon-carbon bond formation. However, utilization of suitably functionalized alkenes may provide many opportunities to incorporate carbyne ligands into organic molecules. We also expect that reactions of Fischer-type carbyne complexes with alkynes will be inherently more complex than reactions with alkenes.

Experimental Section

All experiments were performed with use of standard inert-atmosphere techniques. The solvents CH_2Cl_2 (P_2O_5), tetra-

hydrofuran, and diethyl ether (Na/benzophenone) were dried and distilled prior to use. The tungsten carbyne complexes were prepared as described in the literature.¹⁸ Reagents were used as obtained from commercial sources. The NMR spectra (CDCl_3 , -20°C , unless otherwise noted) were recorded on a Bruker WM250 spectrometer; the IR spectra were recorded on a Digilab FT-20 spectrometer. Elemental analyses were performed by Schwarzkopf Micro Analytical Laboratory.

[Net_4][$\text{W}(\text{CCH}_3)_2(\text{CO})_2(\text{py})$] (2). A 6-fold excess of dry Net_4Cl (0.244 g, 1.5 mmol) is added to a solution of [$\text{W}(\text{CCH}_3)_2\text{Cl}(\text{CO})_2(\text{py})_2$] (0.108 g, 0.24 mmol) in 20 mL of CH_2Cl_2 . The temperature is raised to 40°C for 1 h. The yellow color of the starting solution becomes lighter as the reaction proceeds. After the reaction is complete, as determined by IR spectroscopy, the solvent is removed under reduced pressure. The residue is washed with pentane to remove liberated pyridine and dried under vacuum. The product is only stable in the presence of excess chloride ions. IR: ν_{CO} 1961 (s), 1857 (s) cm^{-1} . ^1H NMR (CD_2Cl_2): δ 8.97 (d, 2 H, α -py), 7.70 (t, 1 H, γ -py), 7.23 (t, 2 H, β -py), 3.27 (q, NCH_2CH_3), 2.16 (s, 3 H, CCH_3), 1.18 (t, NCH_2CH_3). ^{13}C NMR (CD_2Cl_2): δ 277.6 (CCH_3), 222.8, 219.9 (CO), 152.8, 137.3, 123.8 (py), 51.7 (CH_2CH_3), 35.4 (CCH_3), 7.2 (CH_2CH_3).

[Net_4][$\text{W}(\text{CC}_6\text{H}_5)_2(\text{CO})_2(\text{py})$] (3). A 10-fold excess of dry Net_4Cl (6.56 g, 39.6 mmol) is added to a solution of [$\text{W}(\text{CC}_6\text{H}_5)_2\text{Cl}(\text{CO})_2(\text{py})_2$] (2.07 g, 3.96 mmol) in 100 mL of CH_2Cl_2 . The temperature is raised to 40°C for 40 min. The solution turns from orange to red-orange as the reaction proceeds. The solvent is removed under reduced pressure and the residue washed with pentane to remove liberated pyridine. The residue is redissolved in 100 mL of CH_2Cl_2 and the solution warmed to 40°C for another 40 min to ensure completion of the reaction. The solvent is removed and the residue washed with pentane and dried. The product is only stable in the presence of excess chloride ions. IR: ν_{CO} 1965 (s), 1867 (s) cm^{-1} . ^{13}C NMR (CD_2Cl_2): δ 267.2 (CC_6H_5), 224.2, 221.8 (CO).

In an analogous fashion the bis(triphenylphosphine)nitrogen-(1+) salt [PPN][$\text{W}(\text{CC}_6\text{H}_5)_2(\text{CO})_2(\text{py})$] was prepared from [$\text{W}(\text{CC}_6\text{H}_5)_2\text{Cl}(\text{CO})_2(\text{py})_2$] and [PPN] Cl .

[$\text{W}(\text{CC}_6\text{H}_5)_2\text{Cl}(\text{CO})(\text{maleic anhydride})(\text{py})_2$] (4). An excess of maleic anhydride (3.167 g, 32.3 mmol) is added to a solution of 1 (2.07 g, 3.96 mmol) in 100 mL of CH_2Cl_2 . The solution is stirred at room temperature for 2.5 h. During this time the evolving CO is removed by repeated application of vacuum or by blowing nitrogen over the reaction solution. The solution lightens from orange to yellow. After the reaction is complete, as determined by IR spectroscopy, the solvent is removed and the residue washed several times with diethyl ether (combined volume 125 mL). The product is recrystallized from CH_2Cl_2 /ether to give orange-yellow crystals (1.29 g, 67%): mp 135 – 139°C dec; IR ν_{CO} 2044 (s), $\nu_{\text{C=O}}$ 1806 (s), 1738 (s) cm^{-1} ; ^1H NMR δ 9.30 (d, 2 H, cis α -py), 9.21 (d, 2 H, trans α -py) (cis and trans refer to maleic anhydride ligand), 7.99–7.05 (m, 11 H, py and Ph), 4.42 (d), 3.19 (d) ($^3J = 5.3$ Hz, $\text{CH}=\text{CH}$); ^{13}C NMR δ 268.0 ($J_{\text{CW}} = 208.2$ Hz, CPh), 207.1 ($J_{\text{CW}} = 140.0$ Hz, CO), 175.3, 173.1 (C=O), 154.1, 153.0, 145.4, 139.8, 139.6, 129.6, 128.8, 127.9, 125.9 (py, Ph), 55.4 (d, $J_{\text{CH}} = 179.6$ Hz), 51.8 (d, $J_{\text{CH}} = 175.3$ Hz, $\text{CH}=\text{CH}$). Anal. Calcd for $\text{C}_{22}\text{H}_{17}\text{ClN}_2\text{W}$: C, 44.54; H, 2.87; N, 4.72. Found: C, 44.48; H, 2.76; N, 4.51.

[$\text{W}(\text{CC}_6\text{H}_5)_2\text{Cl}(\text{CO})(\text{fumaronitrile})(\text{py})_2$] (5). A solution of 1 (3.523 g, 6.8 mmol) and fumaronitrile (5.554 g, 71 mmol) in 150 mL of THF is stirred for 12 h at 45°C . Evolving CO is allowed to escape through a bubbler. After the solvent is removed, the residue is washed with a combined volume of 500 mL of ether. The product is chromatographed on silica gel (10 \times 2 cm) at -20°C with use of first a 3:1 mixture of CH_2Cl_2 /THF and finally pure THF as the eluant. Further purification by precipitation from CH_2Cl_2 /pentane affords 3.39 g (88%) of a pale yellow solid. The product is a mixture of two diastereomers: mp 122 – 125°C dec; IR ν_{CN} 2218 (m), ν_{CO} 2049 (s) cm^{-1} ; ^1H NMR δ 9.52 (d), 9.48 (d) (2 H, cis α -py), 9.35–9.31 (m, 2 H, trans α -py), 8.3–7.2 (m, 11 H, py, Ph), 3.43 (d), 3.31 (d) ($^3J = 9.3$ Hz, $\text{CH}=\text{CH}$, one diastereomer), 3.37 (d), 2.40 (d) ($^3J = 9.4$ Hz, $\text{CH}=\text{CH}$, one diastereomer); ^{13}C NMR δ 264.7, 264.3 (CPh) 208.2, 206.7 (CO), 155–120 (py, Ph, CN), 35.4, 33.7, 32.6, 30.0 ($J_{\text{CH}} = 168$ – 170 Hz, $\text{CH}=\text{CH}$).

[Net_4][$\text{W}(\text{CCH}_3)_2(\text{CO})(\text{maleic anhydride})(\text{py})$] (6). [Net_4][$\text{W}(\text{CCH}_3)_2(\text{CO})_2(\text{py})$] is prepared as described above

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from $[\text{W}(\text{CCH}_3\text{Cl}(\text{CO})_2(\text{py})_2)]$ (0.343 g, 0.75 mmol) and NEt_4Cl (1.235 g, 7.5 mmol) in 25 mL of CH_2Cl_2 . The dried salt is redissolved in 25 mL of CH_2Cl_2 , and maleic anhydride (0.110 g, 1.13 mmol) is added. Evolution of CO is immediately observed, and the reaction is complete in 15 min. The solvent is removed and the residue washed with ether to remove excess olefin. The product is extracted with a combined amount of 50 mL of THF. The volume of the solution is reduced, and the solution is filtered. When the solution is cooled to -78°C , the product separates either as a yellow oil or as a light yellow powder. The supernatant is removed and the product dried in vacuo (0.231 g, 50%): mp $115\text{--}116^\circ\text{C}$ dec; IR ν_{CO} 2037 (s), $\nu_{\text{C=O}}$ 1793 (s), 1727 (s) cm^{-1} ; ^1H NMR δ 9.24 (s, 2 H, α -py), 7.89 (t, 1 H, γ -py), 7.42 (t, 2 H, β -py), 3.99 (d, 2.79 (d) ($^3J = 4.9$ Hz, $\text{CH}=\text{CH}$), 3.32 (q, 8 H, NCH_2CH_3) 2.40 (s, 3 H, $^3J_{\text{WH}} = 8.35$ Hz, CH_3), 1.33 (t, 12 H, NCH_2CH_3); ^{13}C NMR δ 285.8 ($J_{\text{CW}} = 211.83$ Hz, CCH_3), 207.2 ($J_{\text{CW}} = 136.43$ Hz, CO), 175.2, 174.7 (C=O), 152.8, 138.0, 124.3 (py), 51.9 NCH_2CH_3), 49.8 (d, $J_{\text{CH}} = 177.3$ Hz), 48.0 (d, $J_{\text{CH}} = 175.4$ Hz) ($\text{CH}=\text{CH}$), 32.0 ($J_{\text{CH}} = 128.1$ Hz, CH_3), 7.3 (NCH_2CH_3).

[NEt_4][$\text{W}(\text{CCH}_3\text{Cl}_2(\text{CO})(\text{fumaritrile})(\text{py}))$] (7). $[\text{NEt}_4][\text{W}(\text{CCH}_3\text{Cl}_2(\text{CO})_2(\text{py}))]$ is prepared from $[\text{W}(\text{CCH}_3\text{Cl}(\text{CO})_2(\text{py})_2)]$ (0.232 g, 0.5 mmol) and NEt_4Cl (0.920 g, 5.0 mmol) in 25 mL of CH_2Cl_2 . The dried salt is redissolved in 25 mL of CH_2Cl_2 , and fumaritrile (0.060 g, 0.75 mmol) is added. The color of the solution darkens slightly while CO is evolving. After 30 min the solvent is removed and the residue washed with ether. The product is extracted with THF (50 mL). The combined extracts are reduced in volume until cloudiness appears, and the solution is filtered. Cooling to 5°C for 24 h affords a noncrystalline precipitate (0.120 g, 40%). The product is obtained as two diastereoisomers: mp $103\text{--}105^\circ\text{C}$ dec; IR ν_{CN} 2208 (m), ν_{CO} 2037 (s) cm^{-1} ; ^1H NMR δ 9.40 (d), 9.31 (d) (2 H, α -py), 7.89 (t, 1 H, γ -py), 7.43 (t, 2 H, β -py), 3.30 (q, 8 H, NCH_2CH_3), 2.92 (d), 2.82 (d) ($^3J = 8.3$ Hz, $\text{CH}=\text{CH}$, one diastereomer), 2.80 (d), 1.97 (d, $^3J = 8.5$ Hz, $\text{CH}=\text{CH}$, one diastereomer), 2.52 (d, 3 H, CH_3), 1.29 (t, 12 H, NCH_2CH_3); ^{13}C NMR δ 285.1, 281.2 (CCH_3), 210.0, 207.7 (CO), 155–119 (py, CN), 52.7 (CH_2CH_3), 33.33, 29.86, 28.02, 26.59 ($\text{CH}=\text{CH}$), 7.7 (CH_2CH_3). Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{Cl}_2\text{N}_4\text{O}$: C, 40.19; H, 5.02; N, 9.38. Found: C, 39.92; H, 5.44, N, 9.83.

[NEt_4][$\text{W}(\text{CC}_6\text{H}_5\text{Cl}_2(\text{CO})(\text{maleic anhydride})(\text{py}))$] (8a). $[\text{NEt}_4][\text{W}(\text{CC}_6\text{H}_5\text{Cl}_2(\text{CO})_2(\text{py}))]$ is prepared from 1 (2.07 g, 3.96 mmol) and NEt_4Cl (6.56 g, 39.6 mmol) in 100 mL of CH_2Cl_2 . The dried salt is redissolved in 100 mL of CH_2Cl_2 , and maleic anhydride (0.582 g, 5.9 mmol) is added. The orange color of the solution turns yellow as CO gas is evolved. After 1 h the solvent is removed and the residue washed with ether. The product is extracted with THF (250 mL). The combined extracts are reduced in volume until a slight cloudiness appears. The solution is filtered and cooled to -78°C for 24 h. A yellow oil forms, which is further treated with CH_2Cl_2 /ether to give a noncrystalline solid (1.80 g, 68%): mp $80\text{--}85^\circ\text{C}$; IR ν_{CO} 2041 (s), $\nu_{\text{C=O}}$ 1796 (m), 1728 (s) cm^{-1} ; ^1H NMR δ 9.43 (d, 2 H, α -py), 7.90 (t, 2 H, γ -py), 7.48–7.05 (m, 6 H, py, Ph), 4.13 (d, 1 H), 2.93 (d, 1 H) ($^3J = 5.06$ Hz, $\text{CH}=\text{CH}$), 3.09 (q, 8 H, CH_2CH_3), 1.15 (t, 12 H, CH_2CH_3); ^{13}C NMR δ 273.8 (CPh), 206.5 (CO), 175.6, 174.9 (C=O), 152.8, 146.3, 138.2, 128.6, 127.1, 124.4 (py, Ph), 51.5 (CH_2CH_3), 51.5 (d, $J_{\text{CH}} = 177$ Hz), 50.2 (d, $J_{\text{CH}} = 175$ Hz, $\text{CH}=\text{CH}$), 7.0 (CH_2CH_3). Anal. Calcd for $\text{C}_{25}\text{H}_{32}\text{Cl}_2\text{N}_4\text{O}_4$: C, 44.20; H, 4.71; N, 4.13; Cl, 10.45. Found: C, 44.22; H, 4.92; N, 4.41; Cl, 10.40.

Complex **8a** was also prepared by combining 1 (0.904 g, 2.0 mmol), maleic anhydride (0.192 g, 2.0 mmol), and NEt_4Cl (2.65 g, 16 mmol) in 100 mL of CH_2Cl_2 at room temperature. The color of the solution turns lighter as the reaction proceeds and CO gas is allowed to escape. After 45 min the solvent is removed and the product is isolated as described above (1.1 g, 89%).

A sample of **8a** was prepared by adding NEt_4Cl (0.166 g, 1 mmol) to a solution of 4 (0.059 g, 0.1 mmol) in 5 mL of CH_2Cl_2 and stirring for 18 h at room temperature. IR and ^1H NMR spectroscopy show the presence of **8a** and residual starting material.

[PPN][$\text{W}(\text{CC}_6\text{H}_5\text{Cl}_2(\text{CO})(\text{maleic anhydride})(\text{py}))$] (8b). The PPN salt was prepared in a manner analogous to that for the NEt_4 salt **8a** from 2.113 g (4.0 mmol) of $[\text{W}(\text{CC}_6\text{H}_5\text{Cl}(\text{CO})_2(\text{py})_2)]$. Slightly higher reaction temperatures and longer reaction times were required for the reaction to go to completion. Cooled (0°C) THF is used for the extraction of the product, which

is obtained as a pale yellow noncrystalline solid (4.03 g, 91%): mp $64\text{--}70^\circ\text{C}$; IR ν_{CO} 2046 (s), $\nu_{\text{C=O}}$ 1796 (m), 1727 (s); ^1H NMR δ 9.54 (d, 2 H, α -py), 7.8–7.0 (m, 38 H, py, Ph), 4.16 (d, 1 H), 2.96 (d, 1 H) ($^3J = 4.98$ Hz) ($\text{CH}=\text{CH}$); ^{13}C NMR δ 274.1 (CPh), 206.3 (CO), 176.8, 175.7 (C=O), 153.8–124.3 (py, Ph), 51.6, 50.46 (C–H=CH).

[NEt_4][$\text{W}(\text{CC}_6\text{H}_5\text{Cl}_2(\text{CO})(\text{fumaritrile})(\text{py}))$] (9a). $[\text{NEt}_4][\text{W}(\text{CC}_6\text{H}_5\text{Cl}_2(\text{CO})_2(\text{py}))]$ is prepared from 1 (1.554 g, 3.0 mmol) and NEt_4Cl (5.47 g, 33 mmol) in 75 mL of CH_2Cl_2 . The dried salt is redissolved in 75 mL of CH_2Cl_2 , and fumaritrile (0.348 g, 4.5 mmol) is added. The solution turns yellow as gas is evolved. Upon completion of the reaction (IR) the solvent is removed and the residue washed with ether. The product is extracted with THF (250 mL). The combined extracts are reduced in volume until a slight cloudiness appears. The solution is filtered and the solvent removed. The product is precipitated several times from CH_2Cl_2 /ether to give a noncrystalline solid (1.57 g, 80%). The product is obtained as two diastereomers: mp $56\text{--}62^\circ\text{C}$; IR ν_{CN} 2210 (m), ν_{CO} 2046 (s) cm^{-1} ; ^1H NMR δ 9.51 (one diastereomer), 9.42 (one diastereomer) (d, 2 H, α -py), 7.84–7.04 (m, 8 H, py, Ph), 3.21 (q, 8 H, CH_2CH_3), 3.07 (d), 3.00 (d) ($^3J = 8.8$ Hz, $\text{CH}=\text{CH}$, one diastereomer), 3.06 (d), 2.08 (d) ($^3J = 9.0$ Hz, $\text{CH}=\text{CH}$, one diastereomer), 1.22 (t, 12 H, CH_2CH_3); ^{13}C NMR δ 271.6, 270.4 ($J_{\text{CW}} = 208$ Hz, CPh), 208.8, 207.1 ($J_{\text{CW}} = 129$ Hz, CO), 155–115 (py, Ph, CN), 52.4 (CH_2CH_3), 30.9 (d, $J_{\text{CH}} = 164$ Hz), 30.6 (d, $J_{\text{CH}} = 184$ Hz), 28.8 (d, $J_{\text{CH}} = 166$ Hz), 27.9 (d, $J_{\text{CH}} = 185$ Hz) ($\text{CH}=\text{CH}$), 7.5 (CH_2CH_3). Anal. Calcd for $\text{C}_{25}\text{H}_{32}\text{Cl}_2\text{N}_4\text{O}$: C, 45.54; H, 4.85; N, 8.50; Cl, 10.76. Found: C, 45.36; H, 5.06; N, 8.43; Cl, 10.52.

A sample of **9a** was prepared by adding NEt_4Cl (2.36 g, 14 mmol) to a solution of 5 (0.815 g, 1.4 mmol) in 50 mL of CH_2Cl_2 and stirring for 3 h at room temperature. IR and ^1H NMR spectroscopy show the presence of **9a** and residual starting material.

[PPN][$\text{W}(\text{CC}_6\text{H}_5\text{Cl}_2(\text{CO})(\text{fumaritrile})(\text{py}))$] (9b). The PPN salt was prepared in a manner analogous to that for the NEt_4 salt **9a** from 2.00 g (3.8 mmol) of $[\text{W}(\text{CC}_6\text{H}_5\text{Cl}(\text{CO})_2(\text{py})_2)]$. Cooled (0°C) THF is used for the extraction of the product. Successive precipitations with CH_2Cl_2 /ether afford a noncrystalline solid, also as a mixture of two diastereomers (3.02 g, 73%): mp $95\text{--}96^\circ\text{C}$; IR ν_{CN} 2210 (m), ν_{CO} 2046 (s) cm^{-1} ; ^1H NMR δ 9.67 (d, one diastereomer), 9.59 (d, one diastereomer) (2 H, α -py), 7.8–7.0 (m, 38 H, py, Ph), 3.10 (d), 3.05 (d) ($^3J = 8.9$ Hz, one diastereomer), 3.04 (d), 2.16 (d) ($^3J = 8.9$ Hz, one diastereomer) ($\text{CH}=\text{CH}$); ^{13}C NMR δ 269.8, 269.1 (CPh), 207.5, 205.9 (CO), 154–124 (py, Ph, CN), 30.5, 30.3, 28.7, 27.7 ($\text{CH}=\text{CH}$).

[$\text{W}(\text{CC}_6\text{H}_5\text{Cl}(\text{CO})(\text{maleic anhydride})(\text{tmeda}))$] (10). Method A. A solution of $[\text{W}(\text{CC}_6\text{H}_5\text{Cl}(\text{CO})_2(\text{tmeda}))]$ (0.448 g, 0.93 mmol) and maleic anhydride (0.914 g, 9.3 mmol) is warmed to 60°C for 3 days. The solvent is removed and the product purified by chromatography on silica gel (5×1.5 cm). The product is eluted with CH_2Cl_2 and finally with a small amount of THF. The yellow solid is recrystallized from CH_2Cl_2 /ether (0.20 g, 40%): mp $138\text{--}142^\circ\text{C}$; IR ν_{CO} 2032 (s), $\nu_{\text{C=O}}$ 1806, 1736 cm^{-1} ; ^1H NMR δ 7.27 (t, 2 H, *m* phenyl), 7.15 (t, 1 H, *p* phenyl), 6.92 (d, 2 H, *o* phenyl), 4.11 (d, 1 H), 3.05 (d, 1 H, $^3J = 5.7$ Hz, $\text{CH}=\text{CH}$), 3.51 (s, 3 H), 3.46 (s, 3 H), 3.05 (s, 3 H), 3.04 (s, 3 H, NCH_3), 3.1–2.9 (m, NCH_2); ^{13}C NMR δ 269.7 ($J_{\text{CW}} = 208.2$ Hz, CPh), 208.7 ($J_{\text{CW}} = 140.0$ Hz, CO), 176.1, 173.1 (C=O), 144.5, 129.2, 128.7, 127.8 (Ph), 53.1 ($J_{\text{CH}} = 179.8$ Hz), 48.1 ($J_{\text{CH}} = 172.7$ Hz, $\text{CH}=\text{CH}$), 61.6, 60.8, 60.0, 58.3, 53.7, 52.0 (NCH_3 and NCH_2).

Method B. *tmeda* (0.5 mL, 3.0 mmol) is added to a solution of $[\text{W}(\text{CC}_6\text{H}_5\text{Cl}(\text{CO})(\text{maleic anhydride})(\text{py}))_2]$ (0.424 g, 0.72 mmol) in 30 mL of THF. At 40°C , the reaction is complete in 2 h. The solution is filtered through a pad of cellulose and the solvent removed. The residue is recrystallized from CH_2Cl_2 /ether to give fine pale yellow crystals (0.244 g, 62%): mp $155\text{--}158^\circ\text{C}$ dec.

[$\text{W}(\text{CC}_6\text{H}_5\text{Cl}(\text{CO})(\text{fumaritrile})(\text{tmeda}))$] (11). Method A. *tmeda* (0.75 mL, 4.5 mmol) is added to a solution of $[\text{W}(\text{CC}_6\text{H}_5\text{Cl}(\text{CO})(\text{fumaritrile})(\text{py}))_2]$ (0.485 g, 0.84 mmol) in 30 mL of THF. The reaction mixture is warmed to 50°C for 8 h, after which time the solution is filtered and the solvent removed. The product is purified by chromatography on a silica gel column, which is prepared with CH_2Cl_2 /pentane (1:1), and the product is eluted with THF. Recrystallization from CH_2Cl_2 affords yellow crystals (0.27 g, 60%; only one major diastereomer could be

Table IV

reactn	amt of ligand, equiv	rate const, 10^{-3} s^{-1}
1 + pyridine- d_5	5 ^a	0.59
	10 ^a	0.56
	20 ^a	0.63
	40 ^a	0.79
4 + pyridine- d_5	5 ^a	0.015
	10 ^a	0.006
	20 ^a	0.006
	40 ^a	0.007
1 + maleic anhydride + 1 pyridine	10 ^b	0.034
	15 ^b	0.052
	20 ^b	0.089

^aPyridine- d_5 . ^bMaleic anhydride.

distinguished): mp 155–158 °C; IR ν_{CN} 2218, 2210, ν_{CO} 2030 cm^{-1} ; ^1H NMR δ 7.33–7.11 (m, 5 H, Ph), 3.60 (s), 3.57 (s), 3.16 (s), 3.05 (s) (12 H, NCH_3), 3.6–2.7 (m, NCH_2), 2.99 (d), 2.14 (d) (2 H, $^3J = 8.9 \text{ Hz}$, $\text{CH}=\text{CH}$); ^{13}C NMR δ 266.9 (CPh), 210.8 (CO), 145.4, 129.5, 128.8, 127.8 (Ph), 126.6, 122.8 (CN), 61.6, 61.4, 60.1, 57.4, 53.8, 52.8 (NCH_3 and NCH_2), 32.5, 29.6 (d, $J_{\text{CH}} = 167 \text{ Hz}$, $\text{CH}=\text{CH}$).

Method B. This reaction was conducted only as an NMR experiment. $[\text{W}(\text{CC}_6\text{H}_5)\text{Cl}(\text{CO})(\text{fumaritrile})(\text{py})_2]$ was allowed to react with excess tmeda in CDCl_3 at room temperature. Only one diastereomer (same as in method A) could be observed.

Structure Determination for 4. Crystal data are collected in Table I. The monoclinic space group $P2_1/n$ was uniquely determined from systematic absences. The data were empirically corrected for absorption (216 data fitted to a six-parameter pseudoellipsoid). The structure was solved by heavy-atom methods and completed by difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were placed in idealized locations ($d_{\text{CH}} = 0.96 \text{ \AA}$). All computations used SHELXTL software.³⁸

(38) Sheldrick, G. SHELXTL; Nicolet XRD Corp.: Madison, WI, 1985.

Atomic coordinates are given in Table II and selected bond distances and angles in Table III.

Kinetic Studies. Pyridine Exchange Reactions. The experiments are conducted in 5-mm NMR tubes at 25 °C. NMR tubes containing constant millimolar samples (0.084 mmol) of either 1 or 4 are filled with nitrogen; then CD_2Cl_2 and pyridine- d_5 are added via microliter syringe to a total volume of 0.75 mL. During sample preparation the NMR tubes are cooled in an ice bath. The data are generated by integration of the pyridine α -hydrogen peaks, which are significantly shifted downfield from the resonances of the other aromatic hydrogen atoms. The peak for the α -hydrogen atom of free pyridine at δ 5.58 is also unobserved, allowing both sets to be clearly integrated. Comparison of the relative areas of the peaks for coordinated and free pyridine is used to monitor the reactions. The rates of ligand exchange were determined for high ligand concentrations and by considering initial rates of reaction to suppress the influence of the back-reaction (equilibration). The reactions are considered to be first order.

Measured rate constants are given in Table IV.

The reaction of 1 with maleic anhydride in the presence of 1 equiv of pyridine- d_5 was conducted with 10 and 20 equiv of maleic anhydride. The preference of pyridine- d_5 incorporation in the position trans to maleic anhydride was evident in both cases but was too small to be quantified.

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Supplementary Material Available: Supplementary material regarding the structure determination is given in ref 15.

Registry No. 1, 99630-91-8; 2, 99595-36-5; 3a, 99595-34-3; 4, 99595-45-6; 5 (isomer I), 99595-46-7; 5 (isomer II), 125610-97-1; 6, 99595-40-1; 7 (isomer I), 99595-44-5; 7 (isomer II), 99630-64-5; 8a, 99595-38-7; 8b, 125640-02-0; 9a (isomer I), 99595-42-3; 9a (isomer II), 99630-93-0; 9b (isomer I), 125712-36-9; 9b (isomer II), 125712-37-0; 10, 125610-95-9; 11, 125640-15-5; $[\text{W}(\text{CCH}_3)\text{Cl}(\text{CO})_2(\text{py})_2]$, 99630-62-3; $[\text{PPN}][\text{W}(\text{CC}_6\text{H}_5)\text{Cl}_2(\text{CO})_2(\text{py})]$, 125610-96-0; $[\text{W}(\text{CC}_6\text{H}_5)\text{Cl}(\text{CO})_2(\text{tmeda})]$, 94929-43-8; maleic anhydride, 108-31-6; fumaritrile, 764-42-1.