Organometallics 1992, *11*, 563-573

[4.4]nona-2,7-diene (**3**), obtained in 23% yield, and silole dimer **5**, obtained in 22% yield.

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Supplementary Material Available: Figures of original NMR, infrared, ultraviolet, and mass spectra for methoxytris(trimethylsilyl)silane, NMR, infrared, and mass spectra for 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene and 1,1-bis(trimethylsilyl)-1-silacyclopent-3-ene, and NMR and mass spectra for the silole dimer 3,8-disila-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene and a table of gas chromatographic mass spectral data for the silole dimer (24 pages). Ordering information is given on any current masthead page.

Insertion of Acetylenes into *trans*,*trans*-$WH(CO)_2(NO)(PMe_3)_2$

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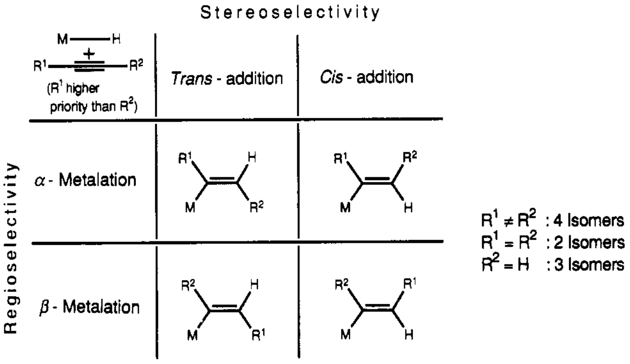
The insertion reactions of *trans*,*trans*-$WH(CO)_2(NO)(PMe_3)_2$ with activated acetylenes of the type $RC{\equiv}CCO_2R'$ (R = H, Me, Ph, $R'O_2C$) were investigated. In all cases selective α-metalation occurs, affording tungsten-vinyl compounds, and except for R = Ph, selective trans insertion is observed as well. Thus, from the reaction of $RC{\equiv}CCO_2Me$ (R = H, Me) the products $W[Z\text{-}C(CO_2Me){=}CH(R)](CO)_2(NO)(PMe_3)_2$, where R = H (**1**) and Me (**2**), were isolated in high yield. The reaction with $PhC{\equiv}CCO_2Et$ initially yields the trans- and cis-insertion products $W[Z\text{-}C(CO_2Me){=}CH(Ph)](CO)_2(NO)(PMe_3)_2$ (**3a**) and $W[E\text{-}C(CO_2Me){=}CH(R)](CO)_2(NO)(PMe_3)_2$ (**3b**) in a 85:15 ratio. Compound **3a** slowly and reversibly loses CO affording the four-membered metallacycle $W\{Z\text{-}C[C(O)OEt]{=}CH(Ph)\}(CO)(NO)(PMe_3)_2$ (**3c**). Heating equilibrium solutions of **3a** and **3c** and CO results in complete, irreversible conversion of these compounds to **3b**. Insertion reactions of $RO_2CC{\equiv}CCO_2R$ initially afford $W[Z\text{-}C(CO_2R){=}CH(CO_2R)](CO)_2(NO)(PMe_3)_2$, where R = Me (**4a**) and tBu (**5a**). These compounds have half-lives of ca. 10 min at room temperature, as irreversible CO loss produces the isolable five-membered-ring compounds $W\{Z\text{-}C(CO_2R){=}CH[C(O)OR]\}(CO)(NO)(PMe_3)_2$ (**4b**, **5b**). Remarkably enough, these compounds are also only metastable, since a PMe_3-catalyzed isomerization occurs in which the NO and CO ligands switch positions, affording **4c** and **5c**, respectively. The X-ray structures of three complexes were determined: **3c**, orthorhombic, space group $P2_12_12_1$, a = 15.985 (5) Å, b = 16.000 (4) Å, c = 9.167 (3) Å, Z = 4; **5b**, monoclinic, space group $P2_1/c$, a = 12.282 (5) Å, b = 11.238 (4) Å, c = 19.463 (8) Å, β = 98.87 (3)°; **5c**, monoclinic, space group $P2_1/c$, a = 10.537 (4) Å, b = 12.319 (4) Å, c = 21.606 (8) Å, β = 95.20 (3)°. Comparison of structures **5b** and **5c** provides direct insight into the difference in electronic effects between CO and NO ligands.

Introduction

The insertion of activated acetylenes into metal–hydride bonds represents a general route to metal–vinyl complexes.[1] Statistically, the insertion of asymmetrically substituted acetylenes can give rise to four different isomers (Scheme I).

Usually, however, these reactions produce only one stereoisomer, and much effort has gone into the elucidation of the factors influencing the regio- and stereoselectivity. Several insertion reactions, which were initially thought to proceed in a cis fashion,[2,3] are now being recognized as trans insertions, followed by a cis/trans isomerization of the kinetic product to a more stable thermodynamic product.[4-6] For asymmetrically substituted acetylenes the regioselective choice between α- and β-metalation is less well understood. Reaction of the monosubstituted acetylenes $HC{\equiv}CCO_2R$, $HC{\equiv}CCF_3$, or $HC{\equiv}CCN$ with $MnH(CO)_5$,[7] $ReH(CO)_5$,[8] Cp_2ReH,[9] $[Os(\eta^6\text{-}C_6H_6)(PiPr_3)\text{-}$

Scheme I



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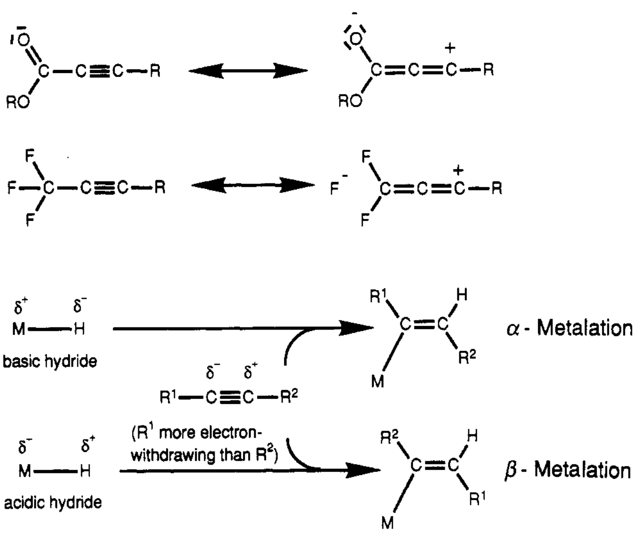
Scheme II



H]$^+$,[10] RuClH(CO)(PPh$_3$)$_3$,[11] and RuClH(CO)(PPh$_3$)$_2$(3,5-dimethylpyrazole)[12] exclusively yields β-metalated products, whereas that with Cp$_2$Nb(CO)H,[6,13] Cp$_2$MoH$_2$,[14] Cp$_2$WH$_2$,[14] and PtH$_2$(PR$_3$)$_2$[15] yields α-metalated products. It is noticed that α-metalated products are especially formed from the relatively basic early-transition-metal hydrides, which suggests at least a dependence on the polarization of the metal–hydride bond. If one considers the extreme canonical forms of activated acetylenes, which puts a positive charge on the β-carbon (Scheme II), one can expect basic, i.e. hydridic, hydrides to yield α-metalated products and acidic, i.e. protonic, hydrides, which are related to each other by the "Umpolung" formalism,[16] to yield β-metalated products.

In previous papers we reported on the trans-labilizing effect of nitrosyl ligands in a complex of the type *trans,trans*-WH(CO)$_2$(NO)[P(OiPr)$_3$]$_2$,[17-19] resulting in a rather basic tungsten–hydride bond. We were interested to what extent this polarization would influence regioselectivity during the insertion of activated acetylenes. We therefore set out to thoroughly investigate the reaction of the even more basic[19] tungsten hydride *trans,trans*-WH(CO)$_2$(NO)(PMe$_3$)$_2$ with acetylenes of the type RC≡CCO$_2$R′ (R = H, Me, Ph, R′O$_2$C).

Experimental Part

All preparations and manipulations were carried out under an atmosphere of dry nitrogen, by conventional Schlenk techniques. Solvents were dried and freshly distilled before use. All acetylene reagents were purchased from commercial suppliers and used without further purification. *trans,trans*-WH(CO)$_2$(NO)(PMe$_3$)$_2$ and -WH(CO)$_2$(NO)(PPh$_3$)$_2$ were prepared by previously described procedures.[19,20]

IR spectra were recorded in solution on a Biorad FTS-45 instrument. MS spectra were run on a Finnigan MAT-8230 mass spectrometer, *m/e* based on ^{184}W. ^{1}H and ^{13}C NMR spectra were run on a Varian Gemini-200 instrument operating at 200 and 50.3 MHz, respectively, and ^{31}P NMR spectra, on a Varian XL-200 spectrometer at 81 MHz.

***trans,trans*-W[C(CO$_2$Me)═CH$_2$](CO)$_2$(NO)(PMe$_3$)$_2$ (1).** To a solution of WH(CO)$_2$(NO)(PMe$_3$)$_2$ (0.29 g, 0.69 mmol) in 20 mL of hexane was added HC≡CCO$_2$Me (65 μL, 1.2 equiv). After 5 min the yellow solution was filtrated over Celite, concentrated, and chilled to −80 °C to afford a yellow precipitate. A second recrystallization from hexane afforded 0.33 g (0.65 mmol, 95%) of yellow crystals of 1. Anal. Calcd for $C_{12}H_{23}NO_5P_2W$: C, 28.42; H, 4.57; N, 2.76. Found: C, 28.43; H, 4.73; N, 2.85. MS (EI): *m/e* 507 (M$^+$), 479 (M$^+$ − CO), 451 (M$^+$ − 2CO), 423 (M$^+$ − HC≡CCO$_2$Me or M$^+$ − 3CO), 347 (M$^+$ − HC≡CCO$_2$Me − PMe$_3$ or M$^+$ − 3CO − PMe$_3$).

***trans,trans*-W[*Z*-C(CO$_2$Me)═CH(Me)](CO)$_2$(NO)(PMe$_3$)$_2$ (2).** A solution of WH(CO)$_2$(NO)(PMe$_3$)$_2$ (0.50 g, 1.18 mmol) and MeC≡CCO$_2$Me (0.3 mL, 2.5 eq) in hexane (20 mL) was stirred for 4 h at room temperature. Workup as described for 1 afforded 2 as a yellow solid (0.52 g, 85%). Anal. Calcd for $C_{13}H_{25}NO_5P_2W$: C, 29.96; H, 4.84; N, 2.69. Found: C, 30.22; H, 5.08; N, 2.81. MS (EI): *m/e* 521 (M$^+$), 493 (M$^+$ − CO), 465 (M$^+$ − 2CO), 425 [W(CO)(NO)(PMe$_3$)$_2$OMe$^+$], 397 [W(NO)(PMe$_3$)$_2$OMe$^+$], 367 (M$^+$ − MeC≡CCO$_2$Me − 2CO), 361 (M$^+$ − 3CO − PMe$_3$), 321 [W(NO)(PMe$_3$)OMe$^+$].

***trans,trans*-W[*E*-C(CO$_2$Et)═CH(Ph)](CO)$_2$(NO)(PMe$_3$)$_2$ (3b).** A solution of WH(CO)$_2$(NO)(PMe$_3$)$_2$ (0.20 g, 0.47 mmol) and PhC≡CCO$_2$Et (95 μL, 1.2 equiv) was stirred for 3 days at 40–50 °C in toluene under an atmosphere of carbon monoxide. The reddish solution was then filtered and evaporated to dryness, and the residue was extracted with hexane. The combined extracts were concentrated and cooled to −80 °C, upon which orange-red plates of 3b were deposited in 65% yield. Anal. Calcd for $C_{19}H_{29}NO_5P_2W$: C, 38.21; H, 4.89; N, 2.35. Found: C, 37.91; H, 4.96; N, 2.21.

***trans*-W{*Z*-C[C(O)OEt]═CH(Ph)}(CO)(NO)(PMe$_3$)$_2$ (3c).** A solution of WH(CO)$_2$(NO)(PMe$_3$)$_2$ (0.15 g, 0.36 mmol) and PhC≡CCO$_2$Et (53 μL, 0.9 equiv) in hexane was stirred for 1 week at room temperature in vacuo. The red solid that precipitated was filtered off and identified as pure 3c. Yield: 65%. Anal. Calcd for $C_{18}H_{29}NO_4P_2W$: C, 37.98; H, 5.13; N, 2.46. Found: C, 38.22; H, 5.11; N, 2.29. MS (EI): *m/e* 569 (M$^+$), 541 (M$^+$ − CO), 513 (M$^+$ − 2CO), 437 (M$^+$ − 2CO − PMe$_3$), 411 [W(NO)(PMe$_3$)$_2$OEt$^+$].

W{*Z*-C(CO$_2$Me)═CH[C(O)OMe]}(CO)(NO)(PMe$_3$)$_2$ LT Isomer (4b). To a solution of WH(CO)$_2$(NO)(PMe$_3$)$_2$ (0.19 g, 0.45 mmol) in hexane (15 mL) was added 60 μL of MeO$_2$CC≡CCO$_2$Me (4.9 mmol). After being stirred for 1 h, the intense brown solution was worked up as described for 1, producing red-brown 4b in 90% yield. Anal. Calcd for $C_{13}H_{25}NO_6P_2W$: C, 29.07; H, 4.69; N, 2.61. Found: C, 29.33; H, 4.88; N, 2.87.

W{*Z*-C(CO$_2$Me)═CH[C(O)OMe]}(CO)(NO)(PMe$_3$)$_2$ HT Isomer (4c). To the reaction mixture, as described for 4b, was added an excess of PMe$_3$. The solution was stirred overnight at room temperature, filtered, and evaporated to dryness. Recrystallization of the residue from hexane afforded purple microcrystaline 4c in 80% yield. Anal. Calcd for $C_{13}H_{25}NO_6P_2W$: C, 29.07; H, 4.69; N, 2.61. Found: C, 29.43; H, 4.76; N, 2.76.

W{*Z*-C(CO$_2$tBu)═CH[C(O)OtBu]}(CO)(NO)(PMe$_3$)$_2$ LT isomer (5b) and W{*Z*-C(CO$_2$tBu)═CH[C(O)OtBu]}(CO)(NO)(PMe$_3$)$_2$ HT isomer (5c) were synthesized as described for 4b,c from WH(CO)$_2$(NO)(PMe$_3$)$_2$ and tBuO$_2$CC≡CCO$_2$tBu in 80 and 65% yield, respectively. Anal. Calcd for $C_{19}H_{37}NO_6P_2W$: C, 36.73; H, 6.00; N, 2.25. Found for 5b: C, 36.57;

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Table I. Crystal Data for 3c, 5b, and 5c

complex	3c	5b	5c
formula	$C_{18}H_{29}NO_4P_2W$	$C_{19}H_{37}NO_6P_2W$	$C_{19}H_{37}NO_6P_2W$
mol wt	569.2	621.3	621.3
cryst system	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a, Å	15.985 (5)	12.282 (5)	10.537 (4)
b, Å	16.000 (4)	11.238 (4)	12.319 (4)
c, Å	9.167 (3)	19.463 (8)	21.606 (8)
β, deg	90	98.87 (3)	95.20 (3)
V, Å^3	2345 (1)	2654 92)	2793 (2)
Z	4	4	4
d_c, g/cm^2	1.613	1.555	1.477
μ, cm^{-1} (Mo K*α*)	51.87	45.93	43.65
cryst size, mm^3	0.32 × 0.18 × 0.78	0.33 × 0.34 × 0.59	0.50 × 0.15 × 0.25
temp, K	236	236	235
no. of reflcns	3055	6708	7546
no. of unique reflcns	3031	6101	6402
no. of obsd reflcns [$F > 6\sigma(F)$]	2819	5018	4179
no. of variables	246	268	265
R, R_w, %	4.87, 4.91	5.56, 6.23	4.78, 5.18

H, 6.28; N, 1.99. Found for **5c**: C, 36.67; H, 6.26; N, 2.05.

***trans,trans*-W[C(CO$_2$Me)=CH$_2$](CO)$_2$(NO)(PPh$_3$)$_2$ (6).** A solution of $WH(CO)_2(NO)(PPh_3)_2$ (0.29 g, 0.36 mmol) in toluene (10 mL) was allowed to react with $HC{\equiv}CCO_2Me$ (0.2 mL, excess) for 1 h, after which the red reaction mixture was filtered. The filtrate was evaporated to dryness to afford a sticky brown residue, which upon washing with ethanol and hexane yielded **6** as a yellow powder (0.18 g, 55%). Compound **6** is unstable, even when stored under nitrogen at 0 °C; it decomposes to a brown oily substance within a few weeks. Anal. Calcd for $C_{42}H_{35}NO_5P_2W$: C, 57.36; H, 4.01; N, 1.59. Found: C, 57.60; H, 3.93; N, 1.49. IR (CH_2Cl_2): $\nu(C{\equiv}O)$ 1940 (vs), $\nu(C{=}O)$ 1682 (w), $\nu(N{\equiv}O)$ 1621 cm^{-1} (s). MS (FAB): *m/e* 851 ($M^+ - CO$), 823 ($M^+ - 2CO$), 794 ($M^+ - HC{\equiv}CCO_2Me$), 766 ($M^+ - HC{\equiv}CCO_2Me - CO$), 588 ($M^+ - CO - PPh_3$), 531 ($M^+ - HC{\equiv}CCO_2Me - PPh_3$). ^1H NMR (C_6D_6): δ 3.03 (s, 3 H, CO_2CH_3), 5.48 (t × d, $^4J(HP)$ = 2.1 Hz, $^2J(HH)$ = 4.5 Hz, 1 H, vinylic H cis to W), 6.70 (t × d, $^4J(HP)$ = 2.3 Hz, $^2J(HH)$ = 4.5 Hz, 1 H, vinylic H trans to W), 7.05 (m, 18 H, aryl *m,p*-H), 7.7 (m, 12 H, aryl *o*-H). ^{31}P NMR (C_6D_6): δ +21.6 ($^1J(PW)$ = 277 Hz). ^{13}C NMR (C_6D_6): δ 50.6 (CO_2CH_3), 128.8 (t, $^3J(CP)$ = 6.6 Hz, W–C(CO$_2$Me)=CH_2), 128.0 (s, aryl), 130.0 (s, aryl), 134.3 (t, $J(CP)$ = 5.6 Hz, aryl), 135.0 (t, $J(CP)$ = 21.1 Hz, aryl), 172.4 (t, $^2J(CP)$ = 11.1 Hz, W–C(CO$_2$Me)=CH$_2$), 214.4 (t, $^2J(CP)$ = 6.1 Hz, W–CO).

Reaction of 1 with HO$_2$CCF$_3$: Synthesis of *trans,trans*-W(O$_2$CCF$_3$)(CO)$_2$(NO)(PMe$_3$)$_2$ (7). To a solution of **1** (generated in situ from $WH(CO)_2(NO)(PMe_3)_2$ (0.10 g, 0.24 mmol) and $HC{\equiv}CCO_2Me$ (25 μL, 1.2 equiv)) in hexane (5 mL) was added a small excess of HO_2CCF_3. The pale yellow reaction mixture was then filtered over Celite, reduced in volume, and chilled to produce yellow crystals of **7** (0.08 g, 80%). Anal. Calcd for $C_{10}H_{18}F_3NO_5P_2W$: W, 34.4. Found: W, 32.4. MS (EI): *m/e* 535 (M^+), 507 ($M^+ - CO$), 479 ($M^+ - 2CO$), 449 ($M^+ - 2CO - NO$), 422 ($M^+ - O_2CCF_3$), 385 [$WF(NO)(PMe_3)_2^+$], 309 [$WF(NO)(PMe_3)^+$]. IR (hexane): 1951 (vs, C≡O), 1704 (w, C=O), 1641 cm^{-1} (s, N≡O).

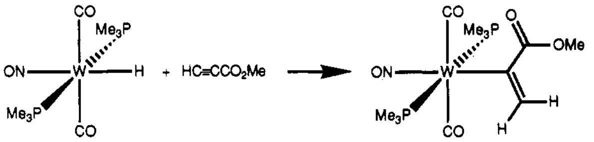
The reaction of **2** with HO_2CCF_3 also yields **7**. No reaction was observed between either **1** or **2** and water or acetic acid.

Reaction of 4b and 4c with HO$_2$CCF$_3$. The reactions of **4b** and **4c** with HO_2CCF_3 in $CDCl_3$ were monitored by ^1H and ^{13}C NMR spectroscopy. Both reactions resulted in the deposition of an unidentified black oil and formation of an organic product left in solution, which was identified as $MeO_2CCH_2CH_2CO_2Me$ [^1H NMR δ 2.72 (s, 4 H, CH_2), 3.75 (s, 6 H, Me); ^{13}C NMR δ 28.6 (CH_2), 51.3 (Me), 173.1 (RCO_2R)].

X-ray Diffraction Studies on 3c, 5b, and 5c. Crystals of **3c** were precipitated within 1 week upon standing of a solution of equimolar amounts of $WH(CO)_2(NO)(PMe_3)_2$ and $PhC{\equiv}CCO_2Et$ in hexane. Crystals of **5b** and **5c** were grown by slow cooling of a saturated hexane solution from room temperature to −85 °C within 2 days. Each crystal was sealed in a thin-walled glass capillary and placed in the cold nitrogen stream of the Siemens P3 diffractometer. Cell constants and the orientation matrix were obtained and refined from the settings of 30–35 centered reflections in the range $10 < \theta < 25°$. Data were collected over the range $4.0° \leq 2\theta \leq 55.0°$ using the Wyckoff scan technique with a variable scan rate of 2.0–15.0°/min in *ω*. Graphite-monochromated Mo K*α* radiation was used. Three reference reflections were checked every 97 measurements, showing no appreciable loss of intensity. Further details of the crystals data for the three compounds are given in Table I. The tungsten atom was located from a Patterson search; all other non-hydrogen atoms were found from a series of difference Fourier syntheses. Discrimination of CO and NO ligands during refinement was based on several grounds: (1) spectroscopic data of the three compounds in solution indicate the presence of a single isomer, making CO/NO disorder problems in the solid state highly improbable; (2) refining the structure with the C and N atoms exchanged resulted in anomalous temperature factors for these atoms; (3) M–N(O) bonds are always significantly shorter than M–C(O) bonds; (4) CO bond lengths are usually shorter than NO bond lengths. The structure was further refined after an empirical absorption correction had been applied, which was based on ca. 10 reflection measurements at different azimuthal angles. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, except for the vinylic H atoms, were fixed on idealized positions (d_{C-H} = 0.96 Å) and allowed to ride on their carrier atoms. Common isotropic temperature factors were refined for the 18 PMe$_3$ hydrogens and for the 5 phenyl hydrogens in **3c** and the 18 tBu hydrogens in **5b** and **5c**; other hydrogens were given individual isotropic temperature factors. During the final stages of convergence full-matrix least-squares refinement was applied.

Results and Discussion

Insertion Reactions of *trans,trans*-WH(CO)$_2$(NO)(PMe$_3$)$_2$. (a) HC≡CCO$_2$Me. $WH(CO)_2(NO)(PMe_3)_2$ reacts instantaneously with $HC{\equiv}CCO_2Me$ at room temperature resulting in clean formation of the insertion product **1** (eq 1), which can be isolated in high yield.



(1)

1

Identification of this and most other insertion products is based on infrared (Table II) and NMR (Tables III and IV) spectroscopic data, as well as combustion analyses and mass spectra.

The geometry around W is easily deduced from (a) IR data, showing a trans configuration of CO ligands, (b) ^{13}C NMR spectra, showing equivalent carbonyls with coupling to two equivalent ^{31}P nuclei ($^2J(CP)$ = 7.0 Hz), and (c) one ^{31}P resonance, also indicating symmetrically positioned

Table II. IR Data for 1–8[a]

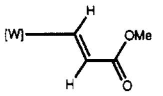
complex	ν(C≡O)	ν(N≡O)	ν(C=O)
1	1926, 2017	1633	1696
2	1922, 2016	1633	1687
3a	1930, 2016	1634	1686
3b	1928, 2016	1634	1681
3c	1899	1598	1586
4a	1936, 2026	1638	1700
4b	1886	1615	1598, 1708
4c	1910	1608	1553, 1710
5a	1933, 2024	1635	1700
5b	1881	1611	1583, 1691
5c	1906	1602	1545, 1690
8[b]	1918	1610	1687, 1706

[a] In hexane solution; data are given in cm^{-1}. Complexes **1**, **2**, **3a**, **3b**, **4a**, and **5a** have a very strong and a weak ν(C≡O) band; other have one very strong band; ν(N≡O) and ν(C=O) have strong and weak intensities, respectively. [b] ν(N≡C) at 1930 cm^{-1} (medium intensity).

PMe$_3$ ligands. The IR spectra also indicate the presence of a *noncoordinated* carboxylate group (ν(C=O) = 1696 cm^{-1} in **1**, as compared to 1720 cm^{-1} for methyl propiolate).

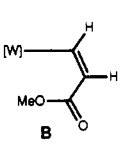
There are three different possible isomers (**A**–**C**) for the geometry of the vinylic unit in **1**, the correct assignment of which could be made by NMR spectroscopy.

In the ^{1}H-coupled ^{13}C NMR spectrum of **1**, one of the vinylic carbons appears as a triplet at 170.3 ppm, with a ^2J(CP) coupling of 11.5 Hz to two equivalent phosphorus atoms; the other vinylic carbon at 130.6 ppm appears as a triplet of doublet of doublets with ^3J(CP) = 5.6 Hz and ^1J(C–H) = 152 and 158 Hz. These data unambiguously prove isomer **C** to be the correct structure for **1**.



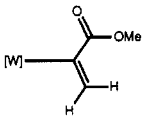
A

β-metalation, *cis*-insertion



B

β-metalation, *trans*-insertion



C

α-metalation, *cis*- or *trans*-insertion

The resonances of the two vinylic H atoms appear as triplet of doublets at 5.60 ppm, with ^4J(HP) = 3.4 Hz, and at 6.43 ppm, with ^4J(HP) = 3.9 Hz, and with a geminal ^2J(HH) coupling of 4.8 Hz. The two signals may be discriminated by the magnitude of the ^4J(HP) coupling, since it is anticipated that a coupling that is trans across the double bond is larger than a cis coupling. Thus, the signal at 5.60 ppm is associated with the vinylic H atom cis to the W moiety, which is corroborated by labeling studies (vide infra).

Although it has now been established that the reaction of HC≡CCO$_2$Me with WH(CO)$_2$(NO)(PMe$_3$)$_2$ yields an α-metalated product, deuterium labeling is required to

Table III. ^{1}H and ^{31}P NMR Data for 1–8[a]

complex	PMe$_3$	vinyl[b]	ester	other	^{31}P[c]
1	1.34 (3.9)	6.43 (3.9)[b]	3.44	5.60 (3.4)[d] (vinylic H cis to W)	−31.5 (274)
2	1.35 (3.9)	6.50 (4.0)[e]	3.47	1.74 (2.4)[e] (methyl cis to W)	−30.1 (274)
3a	1.39 (3.8)	7.58 (3.8)	1.11 (t),[f] 4.13 (q)[f]	7.20 (s), 7.23 (s) (phenyl)	−30.9 (274)
3b	1.40 (3.9)	6.85 (3.3)	0.98 (t),[f] 4.07 (q)[f]	6.95 (t), 7.11 (t), 7.30 (d) (phenyl)	−30.1 (273)
3c	1.14 (3.5)	9.02 (3.6)	0.92 (t),[f] 3.78 (q)[f]	7.12 (t), 7.44 (t), 8.05 (d) (phenyl)	−13.7 (289)
4a	1.58 (3.9)[g]	6.29 (3.5)[g]	3.60, 3.61[g]		−29.0 (275)[i]
4b	1.22 (3.7)	6.87 (3.6)	3.26, 3.46		−18.0 (292)[i]
4c	1.25 (3.8)	6.69 (2.6)	3.10, 3.66		−18.4 (296)[i]
5b	1.30 (3.6)	6.86 (3.6)	1.23, 1.51		−18.1 (285)
5c	1.34 (3.6)	6.63 (2.8)	1.10, 1.63		−19.5 (297)
8	1.61 (3.8)	6.75 (2.9)	1.14, 1.38, 1.55[h]		

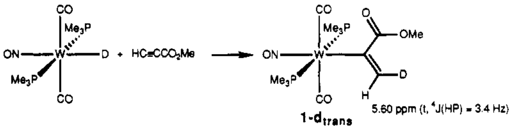
[a] In C$_6$D$_6$ solution, unless stated otherwise; ^{1}H chemical shifts are given in ppm relative to C$_6$D$_5$H (7.15 ppm); triplet coupling to ^{31}P is given in parentheses. [b] Vinylic H atom, all, except for **3b**, trans to W. [c] ^{31}P chemical shifts are relative to H$_3$PO$_4$; coupling to ^{183}W in parentheses. [d] ^2J(HH) = 4.8 Hz. [e] ^3J(HH) = 6.6 Hz. [f] ^3J(HH) = 7.1 Hz. [g] At −50 °C in CDCl$_3$. [h] One of 3 signals belongs to the tBuN≡C group. [i] In CDCl$_3$.

Table IV. ^{13}C NMR Data for 1–8[a]

complex	PMe$_3$	CO	α-C(vinylic)	β-C(vinylic)	ester	other
1	17.8 (14.9) [129]	213.9 (7.0)	170.3 (11.5)	130.6 (5.6) [152, 158]	50.0 [145], 180.6	
2	18.2 (14.7) [129]	209.9 (br), 214.2 (br)	163.3 (11.3)	137.6 (5.3) [148]	49.9 [146], 181.8	23.3 [125]
3a	18.4 (13.1) [128]	209.8 (br), 211.3 (br)	167.9 (11.2)	141.4 (5.1) [149]	14.4 [126], 59.1 [146], 181.8	144.7 (1.8), 128.9, 126.9, ...
3b	17.9 (14.3)	213.9 (7.0)	166.0 (11.4)	139.3 (5.4)	14.1, 58.8, 180.3	141.2 (2.6), 128.9, 126.3, ...
3c	16.1 (13.1)	249.2 (4.2)	165.9 (10.8)	146.4 (4.0)	13.9, 61.1, 186.9 (1.8)	141.6 (2.2), 129.1, 127.2, ...
4a[b]	18.2 (15.2)	208.3 (7.0), 211.4 (6.4)	188.3 (11.0)	128.9 (4.0)	50.7, 51.1, 169.4, 181.5	
4b	15.0 (13.5) [129]	248.7 (3.9)	228.4 (10.4) {4.7}	124.8 (4.0) [167]	50.3 [146], 53.0 [148], 177.2 {7.6 × 3.9}, 182.6 {3.4 × 3.4}	
4c	15.3 (13.5) [128]	240.7 (5.2)	249.8 (7.6) {3.8}	113.2 (2.4) [167]	50.3 [147], 52.7 [148], 177.9 {6.9 × 3.7}, 185.5 {3.2 × 3.2}	
5b	15.8 (13.2) [129]	249.3 (4.1)	227.6 (10.1) {4.0}	127.0 (4.1) [163]	27.9 [128], 28.3 [126], 79.7, 82.9, 177.0 {7.2}, 182.5 {7.5}	
5c	16.1 (13.3) [129]	242.2 (5.1)	248.0 (7.6) {3.5}	115.9 (2.6) [167]	28.6 [127], 29.0 [127], 80.1, 82.5, 177.7 {7.3}, 185.9 {6.9}	
i[g]	18.5 (14.3)	225.3 (5.5)	196.7 (10.3)	131.1 (3.3)	28.5, 28.6, 77.5, 78.9, 169.3, 181.9 (4.2)	

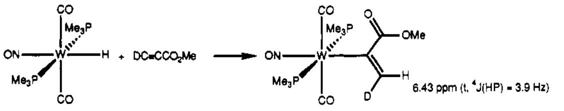
[a] In C$_6$D$_6$ solution; chemical shifts are given in ppm relative to C$_6$D$_6$ (128.0 ppm); triplet coupling to ^{31}P is given in parentheses; ^1J(CH) given in brackets; $^{2,3}J$(CH) given in braces. [b] In CDCl$_3$ at −50 °C. [g] tBuNC: 30.3, 55.9, 156 (br).

distinguish between cis and trans insertion. For this reason additional reactions, as depicted in eqs 2 and 3, were carried out.



(2)

1-d_{trans}

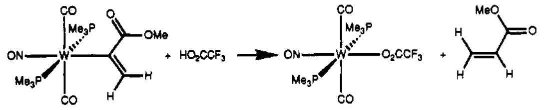


(3)

1-d_{cis}

Thus, the reaction of WD(CO)$_2$(NO)(PMe$_3$)$_2$ with HC≡CCO$_2$Me results in a product, 1-d_{trans}, in which the ^{1}H resonance at 6.43, assigned to the trans-W vinylic H atom, is missing. The complementary reaction of WH(CO)$_2$(NO)(PMe$_3$)$_2$ with DC≡CCO$_2$Me consequently results in a product 1-d_{cis} in which the signal at 5.60 ppm, assigned to the cis-W vinylic H atom, is absent. Both reactions indicate that the addition reaction across the triple bond of HC≡CCO$_2$Me proceeds in a trans fashion. However, it is noticed that this deduction is based on the weakly founded assignments of the two vinylic H atoms. Therefore, a more reliable method was sought in order to definitely determine the regioselectivity of the reaction.

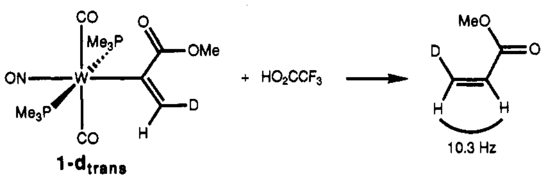
It was found that reaction of 1 with HO$_2$CCF$_3$[21] results in a selective cleavage of the W–C bond with formation of W(O$_2$CCF$_3$)(CO)$_2$(NO)(PMe$_3$)$_2$ (7, 80% isolated yield) and methylacrylate[22] (eq 4). Moreover, it was found that this reaction is *not* accompanied by cis/trans scrambling of the olefinic H atoms of methylacrylate; under these acidic conditions, however, methylacrylate slowly polymerizes.



(4)

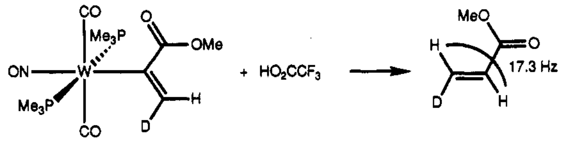
1 7

Treatment of the monodeuterated insertion products 1-d_{trans} and 1-d_{cis} with HO$_2$CCF$_3$ resulted in formation of two different isomers of monodeuterated methylacrylate (eqs 5 and 6). In the former methylacrylate the presence of a D atom cis to the carboxylate unit results in the appearance of two doublets in the ^{1}H NMR spectrum arising from two cis-coupled olefinic H atoms, whereas in the latter case the two doublets arise from trans-positioned olefinic H atoms.



(5)

1-d_{trans}

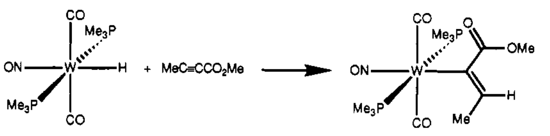


(6)

1-d_{cis}

These observations unambiguously prove (a) the insertion of HC≡CCO$_2$Me into the W–H bond of WH(CO)$_2$(NO)(PMe$_3$)$_2$ proceeds in a trans fashion and (b) the correct assignment was made for the two vinylic H atoms in the ^{1}H NMR spectrum of 1.

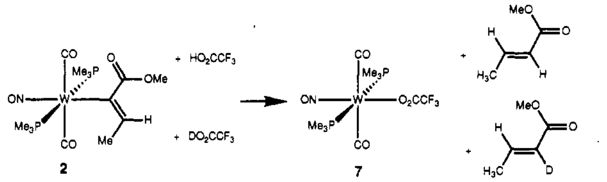
(b) MeC≡CCO$_2$Me. The reaction of WH(CO)$_2$(NO)(PMe$_3$)$_2$ with MeC≡CCO$_2$Me is complete within 4 h at room temperature (eq 7). Again, only one product (2) is observed, although four isomers are theoretically possible.



(7)

2

The IR and NMR data suggest a structure very similar to that of 1. The reactions of 2 with HO$_2$CCF$_3$ (eq 8) and DO$_2$CCF$_3$ (eq 9) unambiguously reveal the regiochemistry of the reaction.



(8)

(9)

2 7

Thus, the organic product resulting from the reaction of 2 with HO$_2$CCF$_3$ is identified as the known compound methyl crotonate; the trans positions of the olefinic H atoms are reflected in their ^3J(HH) coupling of 15.5 Hz.[23] Obviously, this product is a result of an initial trans insertion of MeC≡CCO$_2$Me into the W–H bond. Reaction of 2 with DO$_2$CCF$_3$ affords monodeuterated methyl crotonate, in which the ^{1}H resonance of the vinylic H atom, which is adjacent to the carboxylate group, is now absent. This clearly proves that the insertion of MeC≡CCO$_2$Me results in the formation of an α-metalated product.

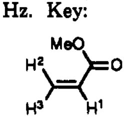
A striking difference between the spectroscopic data of 1 and 2 can be found in the ^{13}C NMR spectra (Table IV). Whereas for 1 only one resonance for the two C≡O carbons is observed, for 2 two, broad resonances at 209.9 and 214.2 ppm are seen. In contrast, both compounds 1 and 2 show only one sharp resonance in the ^{31}P NMR spectrum, at −31.5 and −30.1 ppm, respectively, both with ^1J(PW) = 274 Hz. These observations are indicative of a hindered rotation of the vinylic moiety in 2 around the W–C bond; that is, this group can rotate more easily past the coordinated carbonyl ligands than it can past the phosphorus ligands (see Scheme III). This hindered rotation apparently stems from the cis-W orientated methyl group, since in 1, where a H atom is in a cis-W position, free rotation is observed, *even at −80 °C* (^{13}C NMR).

(c) PhC≡CCO$_2$Et. The reaction of WH(CO)$_2$(NO)(PMe$_3$)$_2$ with PhC≡CCO$_2$Et takes a more complicated course. A sealed NMR tube containing equivalent amounts of the reagents in C$_6$D$_6$ was monitored by ^{1}H, ^{13}C,

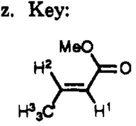
---

[21] 1 and 2 did not react with water or acetic acid.

[22] ^{1}H NMR (C$_6$D$_6$): δ 3.32 (s, 3 H, CO$_2$CH_3), 5.26 (d × d, 1 H, H^2), 5.89 (d × d, 1 H, H^1), 6.22 (d × d, 1 H, H^3), ^3J(H^{1}H^2) = 10.4 Hz, ^3J(H^{1}H^3) = 17.3 Hz, ^2J(H^{2}H^3) = 1.7 Hz. Key:



[23] ^{1}H NMR (C$_6$D$_6$): δ 1.35 (d × d, 3 H, H$_3$), 3.41 (s, 3 H, CO$_2$CH_3), 5.74 (d × q, 1 H, H^1), 6.86 (d × q, 1 H, H^2), ^3J(H^{1}H^2) = 15.5 Hz, ^4J(H^{1}H^3) = 1.8 Hz, ^3J(H^{2}H^3) = 7.0 Hz. Key:



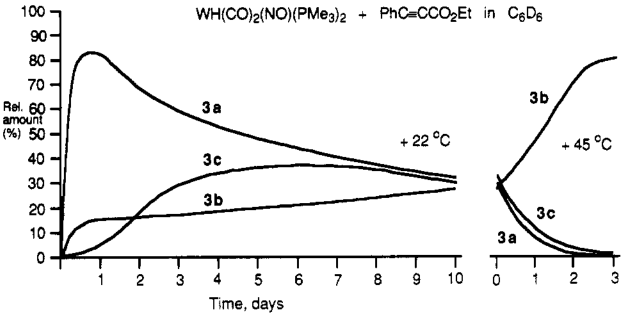
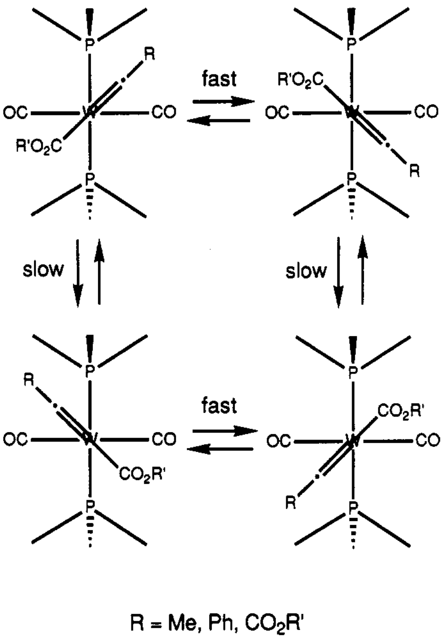


Figure 1. Product distribution during the reaction of WH$(CO)_2(NO)(PMe_3)_2$ (0.2 mmol) and $PhC{\equiv}CCO_2Et$ (0.2 mmol) in C_6D_6 (0.5 mL).

Scheme III



and ^{31}P NMR spectroscopy over a period of weeks; see Figure 1. After ca. 4 h most of the tungsten hydride had been consumed and two new compounds **3a** and **3b** had formed in an approximate 85 to 15 ratio. Thereafter, resonances of a third compound **3c** grew in, whereby at the same time the relative amount of **3a** gradually decreased from ca. 85% to 35% after 10 days. The amount of **3c** reached a maximum of ca. 40% after 1 week, whereupon it slowly decreased again. The amount of **3b**, which initially stabilized at ca. 20%, *slowly* increased to ca. 30% after 10 days. After 10 days the reaction mixture was heated to 45 °C, after which compounds **3a** and **3c** both disappeared within a few days in favor of **3b**.

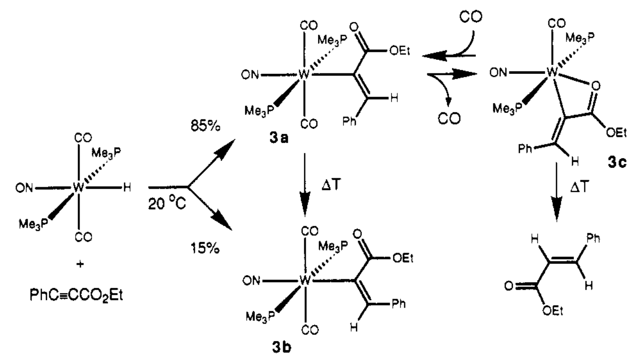
The final product **3b** can therefore be isolated in pure form (65% yield) after prolonged heating of a reaction mixture containing $WH(CO)_2(NO)(PMe_3)_2$ and 1 or more equiv of $PhC{\equiv}CCO_2Et$ in toluene or benzene.

If the insertion reaction was done in hexane, red crystals of **3c** (65% yield) are precipitated from the solution after a few days at room temperature. It is recalled that when the reaction is done in benzene, the amount of **3c** does not exceed 40%.

These curious observations fit the reaction sequences, as depicted in Scheme IV. The structure of the reaction products **3a–c** were determined by NMR spectroscopic methods (vide infra).

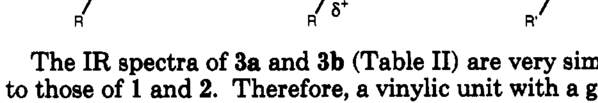
The primary reaction between $WH(CO)_2(NO)(PMe_3)_2$ and $PhC{\equiv}CCO_2Et$ produces the α-metalated trans- and cis-insertion products **3a** and **3b**, respectively. Apparently, **3a** is formed at a rate ca. 5.5 times faster than **3b**, since the **3a**:**3b** ratio is approximately 85:15, after $WH(CO)_2(NO)(PMe_3)_2$ has been used up.

Scheme IV



Thus, in contrast to the 100% trans selectivity observed for the insertion reactions of $HC{\equiv}CCO_2Me$ and $MeC{\equiv}CCO_2Me$, 15% cis byproduct is formed for the present $PhC{\equiv}CCO_2Et$ case. The bigger size of the phenyl group, as compared to a H atom or methyl group, and probably not electronic reasons must be responsible for this atypical behavior. Thus, the kinetic product **3a**, although presenting the major component of the insertion reaction, is quite unstable with respect to the byproduct **3b**. This is due to severe internal sterical hindrance between the cis W positioned phenyl group and adjacent carbonyl and phosphorus ligands. For the same reason, but in contrast to the analogous compounds **1** and **2**, **3a** slowly loses carbon monoxide forming the four-membered metalacyclic compound **3b**. Over a period of days an equilibrium between **3a**, **3b**, and free carbon monoxide is reached at room temperature in benzene. However, in hexane **3b** is dragged out of this equilibrium, because of its insolubility in this solvent, which contrasts the properties of **3a** and **3c**. When isolated **3b** is dissolved in benzene under an atmosphere of carbon monoxide, the equilibrium between **3a** and **3b** and free carbon monoxide is slowly reestablished within a few days at room temperature.

Over longer periods of time (shortened by heating) **3a** isomerizes irreversibly to **3b** and, while **3c** and free carbon monoxide are in equilibrium with **3a**, both **3a** and **3c** disappear from the solution in favor of **3b**. Isolated **3c**, when heated to 45 °C, in the absence of carbon monoxide, disproportionates and produces only trace amounts of **3b**, whereas larger amounts of the organic decomposition product ethyl cinnamate are formed. To check whether **3b** is really produced by direct cis/trans isomerization of **3a** or perhaps via a *reversible* insertion of $WH(CO)_2(NO)(PMe_3)_2$ and $PhC{\equiv}CCO_2Et$, isolated **3c** was heated to 45 °C in the presence of carbon monoxide and $MeO_2CC{\equiv}CCO_2Me$ for a few days. Only **3b** was observed under these conditions with no insertion products arising from the other acetylene, suggesting that **3a** indeed directly isomerizes to **3b**. Further examples of cis/trans isomerizations of transition-metal–vinyl compounds are reported in the literature.[5,6] They are probably facilitated through the intermediacy of a carbenoid species (eq 10).



(10)

The IR spectra of **3a** and **3b** (Table II) are very similar to those of **1** and **2**. Therefore, a vinylic unit with a geminal *trans,trans*-$W(CO)_2(NO)(PMe_3)_2$ group and a nonco-

Table V. Selected Bond Lengths (Å) for 3c

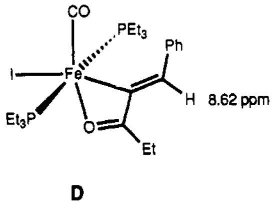
W-P(1)	2.483 (4)	O(3)-C(3)	1.29 (2)
W-P(2)	2.465 (5)	O(4)-C(3)	1.30 (2)
W-N	1.78 (1)	O(4)-C(4)	1.53 (2)
W-O(3)	2.242 (9)	C(1)-C(2)	1.35 (2)
W-C(2)	2.20 (2)	C(1)-C(6)	1.50 (2)
W-C(18)	1.99 (2)	C(2)-C(3)	1.40 (2)
(P-C)$_{av}$	1.78 (2)	C(4)-C(5)	1.53 (3)
O(1)-N	1.24 (2)	(C$_{Ph}$-C$_{Ph}$)$_{av}$	1.37 (2)
O(2)-C(18)	1.14 (2)		

Table VI. Selected Bond Angles (deg) for 3c

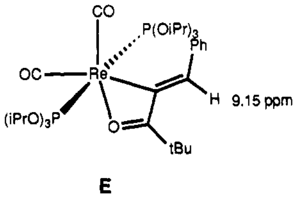
P(1)-W-P(2)	171.4 (2)	C(2)-W-C(18)	154.0 (6)
P(1)-W-O(3)	89.4 (3)	(W-P-C)$_{av}$	116 (2)
P(1)-W-N	91.7 (4)	(C-P-C)$_{av}$	103 (4)
P(1)-W-C(2)	83.8 (4)	W-C(18)-O(2)	176 (2)
P(1)-W-C(18)	95.7 (5)	W-O(3)-C(3)	92.3 (9)
P(2)-W-O(3)	87.0 (3)	C(3)-O(4)-C(4)	117 (1)
P(2)-W-N	91.1 (4)	W-N-O(1)	177 (1)
P(2)-W-C(2)	87.6 (4)	C(2)-C(1)-C(6)	126 (1)
P(2)-W-C(18)	92.2 (5)	W-C(2)-C(1)	152 (1)
O(3)-W-N	174.3 (5)	W-C(2)-C(3)	91 (1)
O(3)-W-C(2)	61.7 (5)	C(1)-C(2)-C(3)	117 (1)
O(3)-W-C(18)	92.4 (6)	O(3)-C(3)-O(4)	119 (2)
N-W-C(2)	112.9 (6)	O(3)-C(3)-C(2)	115 (1)
N-W-C(18)	93.1 (7)	O(4)-C(3)-C(2)	126 (2).

ordinated carboxylate group is anticipated. The trans- and cis-W positions of the vinylic H atoms in **3a** and **3b**, respectively, may be deduced from the magnitude of the ^{4}J(HP) couplings. For **3a** (3.8 Hz) and **3b** (3.3 Hz) they exactly match those for the trans- and cis-W vinylic H atoms in compound **1** (3.9 and 3.4 Hz). Moreover, the ^{4}J(CP) couplings on the α-carbons of the phenyl groups in **3a** and **3b** follow the expected reverse trend (1.8 vs 2.6 Hz). The cis-W position of the vinylic H atom in **3b** is further corroborated by the presence of only one ^{13}C resonance for the two metal–carbonyl ligands, indicating free rotation of the vinylic moiety around the W–C bond. In contrast, the cis-positioned phenyl group in **3a**, like the methyl group in **2**, caused a hindered rotation, which is expressed in the observation of two ^{13}C signals for the metal carbonyls at room temperature.

The structural assignment for **3c** on spectroscopic grounds is less straightforward. Coordination of the carboxylate group through the ketonic oxygen atom can be deduced from ν(C=O), showing a shift of more than 100 cm^{-1} to lower energy, compared to that in **3a** and **3b**. The remarkable low-field shift for the ^{1}H resonance of the vinylic H atom (9.02 ppm) seems to be characteristic for a four-membered cyclic structure, since in compounds like D[24] and E[25] similar low-field resonances are observed.



D



E

X-ray Structure of 3c. In order to definitely establish the structure of **3c**, an X-ray diffraction study was undertaken. Important data are given in Tables V and VI. The tungsten center carries trans-positioned phosphine ligands (see Figure 2), whereas the equatorial plane contains linearly coordinated CO and NO groups, as well as a (C, O)-bidentate-coordinated vinyl moiety, forming a W—O=C—C four-membered ring. The NO ligand is arranged trans to the O atom of this ring, and the CO ligand is found trans to the C atom; this was an unexpected result, since in the starting compound **3a** the NO ligand occupied a position trans to the C atom. The four-membered ring imposes an acute O–W–C angle of 61.7 (5)°, as well as severe angular distorsions around the ring atoms C(2) and O(3). The C(2)–C(3) bond length of 1.41 (2) Å is rather short for a single bond (compare 1.49 (2) Å in D[24] and 1.48 (1) Å in E[25]). The entire vinyl moiety, including the C and O atoms of the phenyl and ethoxy groups, lies in the equatorial plane.

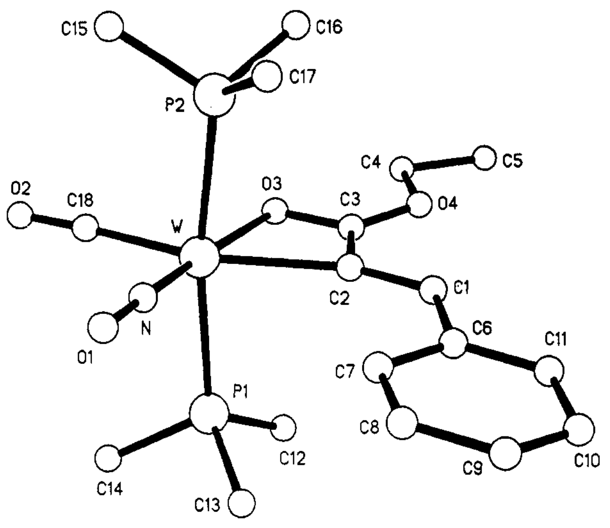
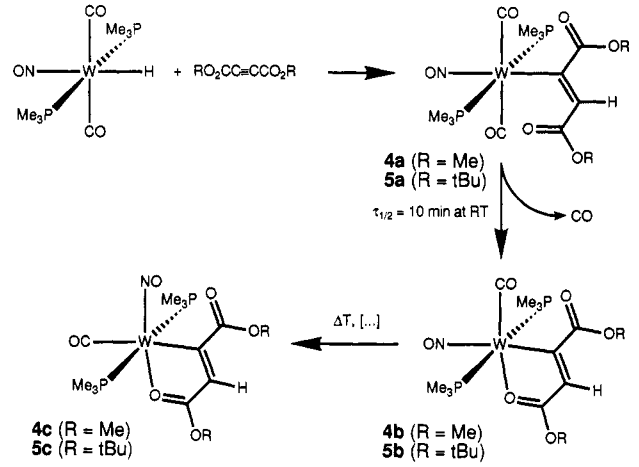


Figure 2. Molecular structure of **3c**.

Scheme V



It is noticed that, compared to the numerous compounds containing five-membered M—O=C—C=C rings, relatively few compounds with four-membered M—O=C—C rings and an exocyclic double bond exist (see structures D and E). This is certainly due to the strained nature of the latter configuration. Only specific steric circumstances will therefore permit such a structural peculiarity. Compound **3c**, and also D and E and some others,[12,26] probably owe their existence to the presence of a large substituent (a phenyl group for the three cases) at the vinylic C atom cis to the complexed metal moiety. This group exerts such a repulsive force on the ligands cis to the metal vinyl bond that the ketonic oxygen is forced in the coordination sphere

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(24) Kölbener, P.; Hund, H.-U.; Bosch, H. W.; Sontag, C.; Berke, H. *Helv. Chim. Acta* **1990**, *73*, 2251.

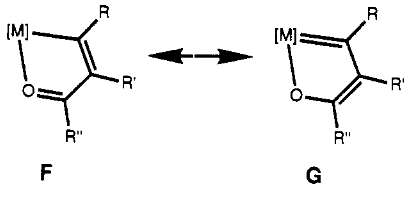
(25) Feracin, S.; Hund, H.-U.; Berke, H. Manuscript in preparation.

(26) Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1987**, *326*, 413.

of the metal atom (thereby expelling one of the other ligands).

(d) $RO_2CC{\equiv}CCO_2R$ (R = Me, tBu). A very fast reaction is observed (even at −80 °C) between $WH(CO)_2(NO)(PMe_3)_2$ and $RO_2CC{\equiv}CCO_2R$, affording the orange insertion products **4a** (R = Me) and **5a** (R = tBu) (Scheme V). The structural analogy of **4a** and **5a** with **1**, **2**, **3a**, and **3b** is obvious, if one compares the respective IR spectra (Table II). The two ester groups are not coordinated (ν(C=O) = 1700 cm^{-1}). Although we do not have clear spectroscopic evidence, we assume trans insertion had occurred. This is supported by the fact that succeeding reactions of **4a** and **5a** described below cannot occur, if the vinylic H atom were in a cis-W position. By the observation of two ^{13}C signals for the metal carbonyls of **4a** (Table IV) it became clear that, just as for **2** and **3a**, the rotation around the W–C(vinyl) bond in these compounds is hindered.

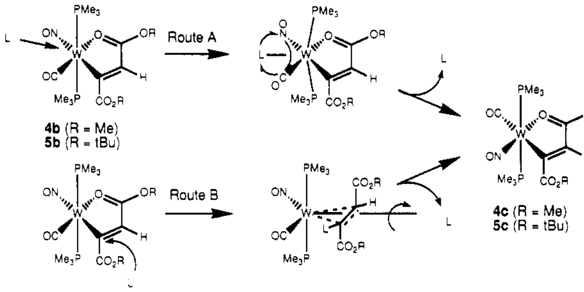
Compounds **4a** and **5a** have half-lives of ca. 10 min at room temperature and therefore cannot be isolated. Irreversible loss of carbon monoxide is observed, and the red-brown complexes **4b** and **5b** are selectively formed, which can be obtained in high yield (Scheme V). The presence of a coordinated and a noncoordinated ester group in **4b**/**5b** is indicated by a ν(C=O) resonance at ca. 1590 cm^{-1} and another one at ca. 1700 cm^{-1}. The ν(C≡O) absorption at ca. 1885 cm^{-1} is typical for a trans-O position of the tungsten-coordinated carbonyl group,[18] which leaves the NO ligand at a position trans to the vinylic C atom. The IR and ^{1}H and ^{31}P NMR data do not in principle distinguish between the presence of a four-membered W—O=C—C ring (through the α-carboxylate group, as in **3c**) or a five-membered W—O=C—C=C ring (through the β-carboxylate group) in **4b**/**5b**. Inspection of the ^{13}C NMR data, however, shows they are in favor of the latter configuration. The resonances for the vinylic α-carbon in **4b** (228.4 ppm) and **5b** (227.6 ppm) show a remarkable low-field shift of ca. 40 ppm, as compared to that for the starting compound (188.3 ppm in **4a**). Similar low-field shifts have also been encountered in a number of other five-membered M—O=C—C=C ring compounds,[10,24,27] which is explained by a mesomeric formulation of this ring structure:



If resonance structure G contributes to the electronic description of **4b** and **5b**, the α-vinylic carbons attain more carbenoid character and therefore their ^{13}C resonances shift to lower field. These spectroscopic findings of **4b** and **5b** were mirrored in the structural properties of **5b** as derived by an X-ray diffractive study (vide infra).

Curiously, compounds **4b** and **5b** are also not stable and irreversibly isomerize to the purple products **4c** and **5c** (Scheme V), which can be isolated in good yield. The rearrangement may be induced by heating solutions of **4b** and **5b** to ca. 50–90 °C, but it appeared difficult to reproduce these experiments. Sometimes even an induction period seemed to be necessary to initiate the reaction. It was found that this isomerization is catalyzed by trace amounts of impurities (vide infra). The spectroscopic data of **4b**/**5b** and **4c**/**5c** are very similar and suggest very analogous structures. From these data it is easily seen that the trans position of the two PMe_3 ligands as well as the five-membered W—O=C—C=C ring are still intact, which leaves the possibility that the CO and NO ligands might have switched positions in going from **4b**/**5b** to **4c**/**5c**. This is confirmed by the X-ray diffraction study on **5c**·(vide infra).

Scheme VI



Apparently, **4c** and **5c** are more stable than **4b** and **5b**, probably because of the better π-acceptor properties of NO as opposed to CO. From the resonance structures of **4b**/**5b** (see F and G; vide supra) it is seen that through the W–C(vinyl) bond, π-electron density is built up trans to the NO ligand but not trans to the CO ligand. Obviously, it would be better if the W–C(vinyl) bond is positioned trans to the weaker π-acceptor, i.e. the CO ligand, and apparently this represents the thermodynamic driving force for the **4b**/**5b** to **4c**/**5c** conversion. After the isomerization the W–N bond should be stronger in **4c**/**5c** than it was in **4b**/**5b** and the NO bond weaker, which is consistent with the ν(N≡O) data. Vice versa, the W–C(carbonyl) bond in **4c**/**5c** should be weaker than in **4b**/**5b** and the CO bond stronger, which is also in agreement with the ν(C≡O) data. The conversion also results in a larger share of resonance structure G for **4c**/**5c** as compared to **4b**/**5b**. This is nicely reflected in the ^{13}C NMR spectra, which show that the α-vinylic carbon attains more carbenoid character, since a low-field shift from ca. 228 ppm in **4b**/**5b** to 249 ppm in **4c**/**5c** is observed. Consistent with this it can be seen that the double-bond character of the coordinated C=O ester group is reduced, since ν(C=O) changes to lower energy (from 1598 to 1553 cm^{-1} in **4** and from 1583 to 1545 cm^{-1} in **5**).

Exchange of two adjacent ligands in electronically saturated octahedral complexes is not a feasible process and usually either a dissociative or associative mechanism is operative. It was noted before that the conversions are catalyzed by certain impurities. A systematic investigation revealed that water, oxygen, and excess acetylene were not the catalysts but that in fact trace amounts of free PMe_3 accelerated the conversion. Apparently, heating solutions of **4b**/**5b** results in minor decomposition of these complexes and in liberation of some PMe_3, which then catalyses the **4b**/**5b** to **4c**/**5c** conversion. Later we found that tBuN≡C is an even better catalyst than PMe_3, whereas PMe_2Ph and CO are somewhat less active and PEt_3 and $HNEt_2$ were inactive. It is noted that all catalysts represent molecules with very small cone angles.

Two mechanisms for the conversion can be put forward, which are depicted in Scheme VI. Route A is based on the possibility that a linearly coordinated NO ligand in our saturated 18e W(0) complex **4b**/**5b** might be able to bend, thereby creating a formally unsaturated 16e W(II) com-

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(27) Alt, H. G.; Engelhardt, H. E.; Thewalt, U.; Riede, J. *J. Organomet. Chem.* **1985**, *288*, 165. Alt, H. G.; Hayen, H. I. *J. Organomet. Chem.* **1986**, *315*, 337. Alt, H. G.; Herrmann, G. S.; Engelhardt, H. E.; Rogers, R. D. *J. Organomet. Chem.* **1987**, *331*, 329.

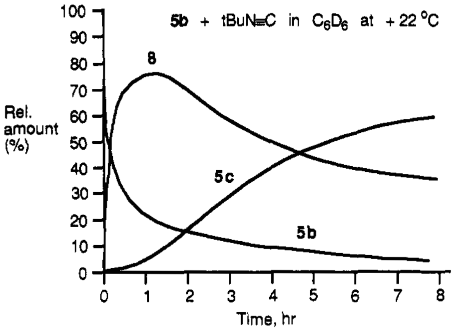
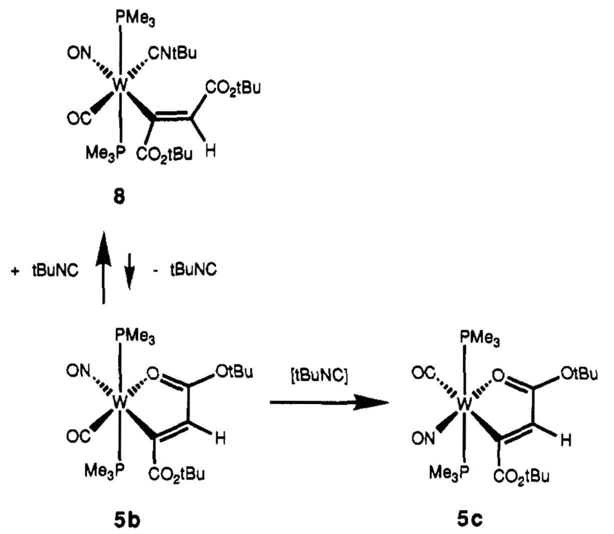


Figure 3. Product distribution during the conversion of **5b** to **5c** catalyzed by $tBuN{\equiv}C$ in C_6D_6.

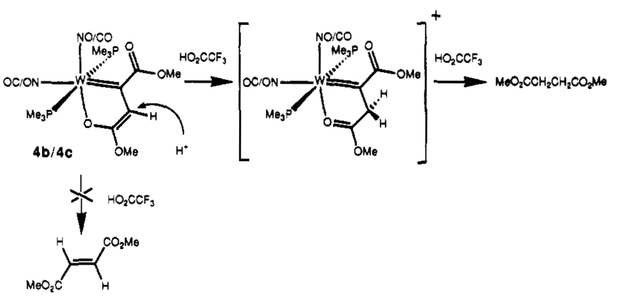
Scheme VII



plex. In this situation another ligand can enter the coordination sphere, forming a seven-coordinate 18e W(II) complex,[28] which are known to be very dynamic molecules. Thus, scrambling of ligands may occur, whereupon a ligand is lost and the NO ligand bends back forming the rearranged compounds **4c**/**5c**. In this context it is noted that the substitution of CO in related W(CO)$_4$(NO)X (X = Cl, Br, I) with P(nBu)$_3$ proceeds in a partly associative way.[29]

An alternative mechanism is based on the existence of two resonance structures for **4b**/**5b** (F and G; vide supra). Carbenoid structure G makes the α-carbon susceptible to nucleophilic attack. Nucleophiles like PMe$_3$ and PMe$_2$Ph can react in this way to yield an ylid type intermediate.[30] The vinylic moiety, now transformed to an ordinary η^2-bound olefin, may than rotate 180 degrees around its coordination axis, whereupon phosphine is reversibly lost to produce the isomerized products **4c**/**5b**. At the moment we do not know which of two mechanisms is operative for these isomerizations.

Scheme VIII



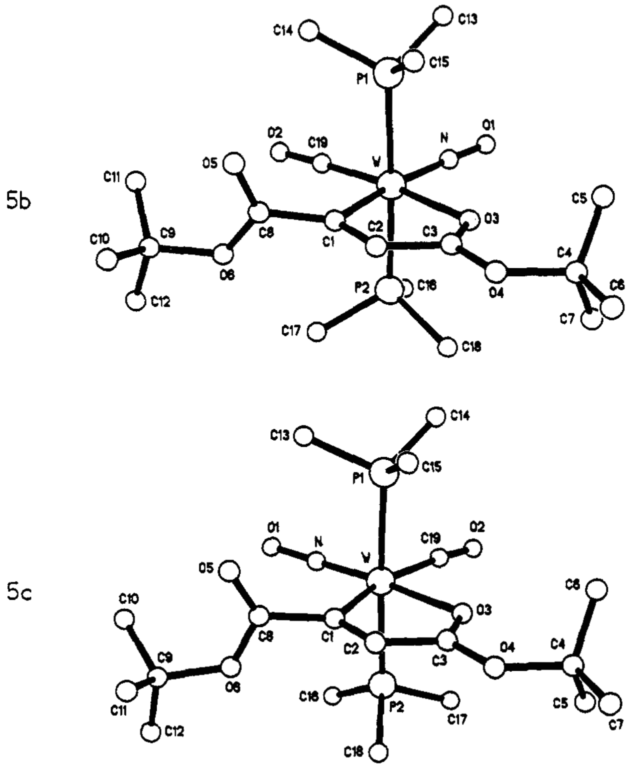


Figure 4. Molecular structures of **5b** and **5c**.

For the $tBuN{\equiv}C$-catalyzed isomerization, an intermediate **8** can be observed by IR and NMR spectroscopy; see Figure 3. Thus, when $tBuN{\equiv}C$ is added to a solution of **5b** in C_6D_6 at room temperature, about 80% of **5b** is consumed within the first $^1/_2$ h and an equilibrium between **5b** and the new compound **8** sets in. Thereafter, both **5b** and **8** disappear at the same rate to produce **5c** as the final product within ca. 24 h. Spectroscopic characterization of **8** (see Tables II–IV) suggests that this compound is probably *not* one of the hoped-for intermediates as depicted in Scheme VI. In fact **8** is very similar to **5a**, the only difference being the substitution of a CO ligand by a $tBuN{\equiv}C$ molecule; see Scheme VII. And, since **5b** and **8** seem to be in equilibrium, it is the former compound which actually isomerizes via an intermediate different from that of **8**.

The carbenoid resonance structures of **4b** and **4c** are also reflected in their reactions with HO$_2$CCF$_3$. However, in contrast to the analogous reactions of **1** and **2**, electrophilic protonic attack does not occur on the α-carbon atom of the vinylic atom but on the β-carbon atom, representing a typical reaction for transition-metal carbene compounds. Thus, the organic product observed after the reaction is the saturated methyl succinate[31] and not methyl fumarate; see Scheme VIII. The fate of the inorganic part is yet unclear.

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[28] Quite a number of seven-coordinate W(II) complexes are known; see e.g.: Carmona, E.; Doppert, K.; Marin, J. M.; Poveda, M. L.; Sánchez, L.; Sánchez-Delgado, R. *Inorg. Chem.* **1984**, *23*, 530. Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Pérez, P. J.; Sánchez, L. J. *Inorg. Chem.* **1989**, *28*, 2120.

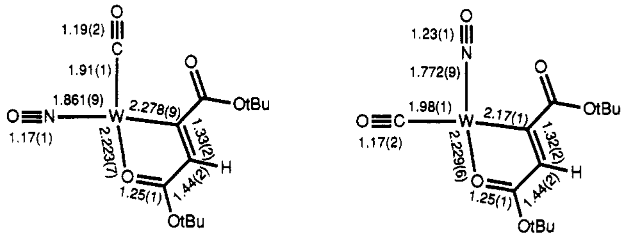
[29] Sulfab, Y.; Basolo, F.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2139.

[30] There is precedent for such an attack; see: Alt, H. G.; Thewalt, U. *J. Organomet. Chem.* **1984**, *286*, 235. Alt, H. G.; Hayen, H. I. *J. Organomet. Chem.* **1986**, *316*, 301.

[31] NMR data for MeO$_2$CCH$_2$CH$_2$CO$_2$Me are as follows: ^{1}H NMR (C_6D_6): δ 2.72 (s, 4 H, CH_2), 3.75 (s, 6 H, CH_3). ^{13}C NMR: δ 28.6 (CH$_2$), 51.6 (CH$_3$), 173.1 (CO$_2$Me).

Table VII. Selected Bond Lengths (Å) for 5b and 5c

	5b	5c
W-P(1)	2.488 (3)	2.498 (3)
W-P(2)	2.469 (3)	2.486 (3)
W-N	1.861 (9)	1.772 (9)
W-O(3)	2.223 (7)	2.229 (6)
W-C(1)	2.278 (9)	2.17 (1)
W-C(19)	1.91 (1)	1.98 (1)
$(P-C)_{av}$	1.81 (1)	1.78 (6)
O(1)-N	1.17 (1)	1.23 (1)
O(2)-C(19)	1.19 (2)	1.17 (2)
O(3)-C(3)	1.25 (1)	1.25 (1)
O(4)-C(3)	1.32 (1)	1.30 (1)
O(4)-C(4)	1.47 (1)	1.50 (1)
O(5)-C(8)	1.21 (1)	1.19 (1)
O(6)-C(8)	1.34 (1)	1.32 (1)
O(6)-C(9)	1.46 (1)	1.46 (2)
C(1)-C(2)	1.33 (2)	1.32 (2)
C(1)-C(8)	1.48 (1)	1.51 (2)
C(2)-C(3)	1.44 (2)	1.44 (2)



5b **5c**

Figure 5. Comparison of X-ray data of structures **5b** and **5c**.

Table VIII. Selected Bond Angles (deg) for 5b and 5c

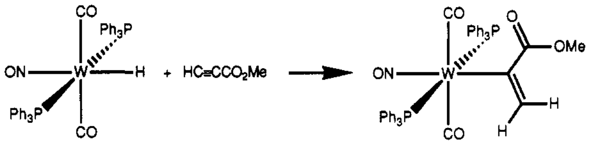
	5b	5c
P(1)-W-P(2)	175.2 (1)	174.7 (1)
P(1)-W-O(3)	90.7 (2)	89.0 (2)
P(1)-W-N	93.1 (3)	92.0 (3)
P(1)-W-C(1)	84.0 (3)	87.5 (3)
P(1)-W-C(19)	90.4 (3)	92.7 (3)
P(2)-W-O(3)	88.0 (2)	85.9 (2)
P(2)-W-N	91.6 (3)	92.9 (3)
P(2)-W-C(1)	91.2 (3)	89.5 (3)
P(2)-W-C(19)	90.3 (3)	88.9 (3)
O(3)-W-N	94.0 (3)	174.6 (3)
O(3)-W-C(1)	72.7 (3)	72.9 (3)
O(3)-W-C(19)	171.8 (3)	90.7 (4)
N-W-C(1)	166.3 (4)	101.8 (4)
N-W-C(19)	94.0 (4)	94.6 (4)
C(1)-W-C(19)	99.3 (4)	163.6 (4)
$(W-P-C)_{av}$	116 (1)	116 (3)
$(C-P-C)_{av}$	102 (1)	103 (2)
W-O(3)-C(3)	117.1 (6)	115.4 (6)
C(3)-O(4)-C(4)	122.8 (8)	123.4 (8)
C(8)-O(6)-C(9)	121.3 (7)	121.3 (9)
W-N-O(1)	176.0 (9)	176.3 (8)
W-C(1)-C(2)	113.2 (8)	116.9 (8)
W-C(1)-C(8)	125.9 (7)	124.5 (8)
C(2)-C(1)-C(8)	120.5 (9)	118.4 (9)
C(1)-C(2)-C(3)	118 (1)	115.1 (9)
O(3)-C(3)-O(4)	125.0 (9)	123.0 (9)
O(3)-C(3)-C(2)	119.4 (9)	119.6 (9)
O(4)-C(3)-C(2)	115.6 (9)	117.4 (9)
O(5)-C(8)-O(6)	125 (1)	126 (1)
O(5)-C(8)-C(1)	121 (1)	124 (1)
O(6)-C(8)-C(1)	113.7 (8)	110.6 (9)
W-C(19)-O(2)	177 (1)	175 (1)

X-ray Structures of 5b and 5c. The single-crystal structures of the isomers **5b** and **5c** offer the unique opportunity to directly compare the different electronic effects associated with CO and NO ligands. Bond lengths and angles of the two compounds are listed in Tables VII and VIII. The molecular structures are depicted in Figure 4, illustrating their very close similarity. Both consist of slightly distorted octahedrons, the largest distortion resulting from the five-membered chelate ring that imposes an acute O-W-C angle of 72.7 (3)° in **5b** and 72.9 (3)° in **5c**. The rings are planar within experimental error, the noncoordinated CO_2tBu group forming an angle of 77° with this plane in **5b** and 85° in **5c**. The central C atom of the other tBu group is forced into the plane of the five-membered ring.

The major differences between **5b** and **5c** are found in the bond lengths in the plane of the five-membered ring; see Figure 5. On spectroscopic grounds it was concluded that the double-bond character of W–C(1) in **5c** should be bigger than in **5b**. This is clearly reflected in the respective bond lengths: 2.17 (1) and 2.278 (9) Å. There are, on the other hand, no significant differences between the other four bond lengths of the five-membered ring.

It was also argued that the double-bond character of the W–C(vinyl) bond provides the driving force for the **4b**/**5b** to **4c**/**5c** conversion, since it forces the stronger π-acceptor ligand NO, which is initially trans to this W–C bond, into the cis position. This is very clearly reflected in the crystal data of both compounds. Thus, the W–N distance in **5c** is 0.09 Å shorter than in **5b**, whereas the NO bond length in **5c** is 0.06 Å longer than in **5b**, unambiguously demonstrating that the W–NO bond is stronger in **5c** than in **5b**. Opposite trends in data are found for the coordinated CO ligand. Thus, the W–C(carbonyl) distance in **5c** is 0.07 Å longer than in **5b**, whereas the CO bond length is 0.02 Å shorter, obviously reflecting the fact that the W–CO bond is weaker in **5c** than in **5b**. These observations are also in accord with the ν(C≡O) and ν(N≡O) IR data for the complexes (vide supra).

Reactions of Other Tungsten Hydrides with Acetylenes. Although we have restricted ourselves to the $WH(CO)_2(NO)(PMe_3)_2$ system, some reactions of acetylenes were performed with other complexes of the type $WH(CO)_2(NO)(PR_3)_2$. Preliminary results indicate that the reaction rate with $HC{\equiv}CCO_2Me$ follows Tolman's electronic series for phosphorus ligands,[32] up to ligands with cone angles of ca. 140°. Thus, tungsten hydrides with phosphite ligands react slower with $HC{\equiv}CCO_2Me$ than those with phosphines. The compound $WH(CO)_2(NO)(PPh_3)_2$, however, reacts relatively slowly because of the bulkier size of the phosphorus ligands. The insertion product **6**, analogous to **1**, is formed (eq 11).



6 (11)

No reaction at all was observed between $WH(CO)_2(NO)(PPh_3)_2$ and $MeC{\equiv}CCO_2Me$ or $PhC{\equiv}CCO_2Et$, whereas reaction with $MeO_2CC{\equiv}CCO_2Me$ affords a multitude of unidentified products. Obviously, the outcome of the acetylene insertion reaction is also very sensitive to steric factors.

Conclusions

The reaction of $WH(CO)_2(NO)(PMe_3)_2$ with $RC{\equiv}CCO_2R'$ (R = H, Me, Ph, $R'O_2C$) affords preferably α-metalated trans-insertion products; due to the large size of the phenyl group, only the reaction of $PhC{\equiv}CCO_2Et$ yields a small amount of α-metalated cis-insertion product.

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[32] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

The exclusive formation of α-metalated products can be attributed to the strong basic polarization of the W–H bond in complexes of the type $WH(CO)_2(NO)(PR_3)_2$ (see also Scheme II).

The reaction rate of $WH(CO)_2(NO)(PMe_3)_2$ with $RC\equiv CCO_2R'$ is strongly dependent on the kind of R group; the sequence is $R'O_2C > H \gg Ph \approx Me$. The series roughly follows Hammett's parameter σ_p^+ for phenyl substituents, which, according to Swain and Lupton, contains a large degree of resonance contribution *R* (R = 0.11, 0, –0.13, and –0.18 for the aforementioned substituents, respectively).[33] Especially the large difference in reaction rate between the acetylenes $HC\equiv CCO_2Me$ and $MeC\equiv CCO_2Me$, cannot be explained by field effects alone, since these are almost identical for H and Me group. However, steric effects may also play a role, and more research is needed to elucidate the electronic and steric influences for C≡C addition reactions.

Acknowledgment. We thank the Swiss National Science Foundation for financial support.

Supplementary Material Available: For **3c**, **5b**, and **5c**, tables of positional and thermal parameters and complete bond lengths and angles (12 pages); tables of structure factors (56 pages). Ordering information is given on any current masthead page.

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[33] Swain, C. G.; Lupton, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 4328. See also: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

Pronounced Effect of Substituents on the Intramolecular Electron-Transfer Rates in Mixed-Valence Biferrocenium Triiodide Complexes

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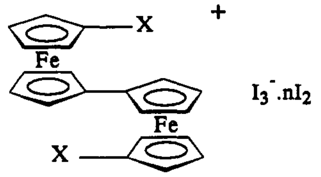
The factors controlling the rate of intramolecular electron transfer in the solid state have been studied for a series of binuclear mixed-valence 1′,1‴-bis(substituted benzyl)biferrocenium triiodide salts, where the substituents in the benzyl unit are *p*-iodo (**1**), *p*-bromo (**2**), *p*-chloro (**3**), *o*-iodo (**4**), and *o*-bromo (**5**). The X-ray structure of neutral 1′,1‴-bis(*p*-bromobenzyl)biferrocene has been determined at 298 K: $P\bar{1}$, a = 5.853 (4) Å, b = 8.380 (3) Å, c = 14.2295 (18) Å, α = 74.622 (15)°, β = 83.940 (23)°, and γ = 86.69 (4)°; Z = 1, D_{calcd} = 1.758 g cm^{-3}, R_F = 0.036, and R_{wF} = 0.038. The Fe–Fe distance is 5.119 (3) Å. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a unit cell with dimensions a = 9.5505 (24) Å, b = 10.984 (3) Å, c = 11.248 (5) Å, α = 119.71 (3)°, β = 116.04 (3)°, and γ = 76.946 (22)°. The final discrepancy factors are R_F = 0.052 and R_{wF} = 0.039. A decrease in Fe–Fe distance (5.058 (7) Å) has been observed when 1′,1‴-bis(*p*-bromobenzyl)biferrocene is oxidized. The solid-state structure of **2** is composed of parallel sheets of cations and polyiodide ions which contain zigzag chains of alternate I_3^- and I_2 units. The distance of 3.487 (2) Å between neighboring iodine atoms in I_2 and I_3^- units within a chain indicates a nonnegligible interaction. Compound **4** crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a unit cell with dimensions a = 8.149 (4) Å, b = 9.567 (3) Å, c = 12.491 (4) Å, α = 111.78 (3)°, β = 85.97 (4)°, and γ = 108.39 (3)°. The final discrepancy factors for **4** and R_F = 0.056 and R_{wF} = 0.04. The Fe–Fe distance in **4** is 5.082 (8) Å. As expected, the triiodide anion in **4** is situated differently. In contrast to compound **2**, the I_3^- anion in **4** is perpendicular to the fulvalenide ligand. The features in the variable-temperature (77–300 K) ^{57}Fe Mössbauer spectra of **1** include two doublets, which are expected for a mixed-valence cation localized on the time scale of the Mössbauer technique (electron-transfer rates less than ~10^7 s^{-1}). The valence-trapped electronic structure is also seen for compound **3**. In the case of **2**, at temperatures below 150 K it shows two doublets in the ^{57}Fe Mössbauer spectra and increasing the temperature causes two doublets to become a single "average-valence" doublet at a temperature of ~200 K. In comparison with compounds **1**–**3**, a single "average-valence" doublet ($\Delta E_Q \approx$ 1.1 mm s^{-1}) is seen even at 77 K for **4** and **5**. Thus, there is a dramatic change in electron-transfer rate as the position of halide substituent in the benzyl unit is changed from the para position to the ortho position. EPR and IR data are also presented for **1**–**5**.

Introduction

Recently, there has been considerable progress made in understanding the factors which control the rate of intramolecular electron transfer in the solid state for mixed-valence compounds.[1] In the case of binuclear mixed-valence biferrocenium compounds,[2–14] it has been found that the nature of the solid-state environment about a

Scheme I



1. X=p-iodobenzyl n=0
2. X=p-bromobenzyl n=1
3. X=p-chlorobenzyl n=0
4. X=o-iodobenzyl n=0
5. X=o-bromobenzyl n=0
6. X=H n=0
7. X=C_2H_5 n=0
8. X=C_3H_7 n=0
9. X=C_4H_9 n=0
10. X=benzyl n=0

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[1] For recent reviews, see: (a) Day, P. *Int. Rev. Phys. Chem.* **1981**, *1*, 149. (b) Brown, D. B., Ed. *Mixed-Valence Compounds, Theory and Applications in Chemistry, Physics, Geology and Biology*; Reidel Publishing Co.: Boston, MA, 1980. (c) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1–73. (d) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107–129.

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