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η^2-Alkynyl and Vinylidene Transition Metal Complexes. 5.[1] Reaction of the Metal−Acetylide $[(\eta^5\text{-}C_5H_5)(CO)(NO)WC{\equiv}CR]^-$ with Ethyl Iodoacetate as Electrophile. Preparation and Crystal Structure Analysis of a Metallacyclic Complex

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Treatment of η^1-acetylide complexes $[(\eta^5\text{-}C_5H_5)(CO)(NO)WC{\equiv}CR]^-$ (R = $C(CH_3)_3$ (**2a**), C_6H_5 (**2b**), $p\text{-}CH_3C_6H_4$ (**2c**)) with ethyl iodoacetate in THF at −78 °C afforded, after protonation with diluted acids, the corresponding oxametallacyclopentadienyl complexes $(\eta^5\text{-}C_5H_5)W(I)(NO)\text{-}[\eta^2\text{-}O{=}C(CH_2COOC_2H_5)CH{=}CR]$ (**3a**−**c**). The formation of these metallafuran derivatives is rationalized by the electrophilic attack of ethyl iodoacetate on the metal center of **2** to create first $[(\eta^5\text{-}C_5H_5)(I)(CO)(NO)WC{\equiv}CR]$. Subsequent nucleophilic addition of the ester enolate anion of $[CH_2COOC_2H_5]Li$ and a reductive-elimination step followed by protonation lead to the product **3**. One of the reaction intermediates was trapped by the addition of $CF_3SO_3CH_3$.

Introduction

Transition metal η^1-acetylide complexes are known to be involved in a number of catalytic and stoichiometric reactions of alkynes.[2,3] The metal−acetylide catalysts have been widely employed in basic chemical transformations,[4] industrial alkyne coupling reactions such as the preparation of N-alkyl-substituted aminoalkynes,[2i] the dimerization of acetylene,[3a] and the coupling of acetylene with formaldehyde.[3d] A well-characterized rhodium−acetylide complex has recently been shown to promote the living polymerization of phenylacetylene.[2h] Interest in the metal-coordinated η^1-acetylide complexes has also grown in recent years because of their role as precursors of molecules containing a linear array of delocalized π-systems[5] and because such complexes have emerged as key components in generating materials for nonlinear optics,[6] molecular conductors,[7] and liquid crystals.[8] Transition metal σ-acetylide complexes have also attracted a great deal of attention because their strict relationship to organometallic vinylidene chemistry.[3e,9,10]

It is well-recognized that the reactivity of transition metal η^1-acetylide complexes can be rationalized on the basis of resonance forms **A** and **B**, with form **B** becoming more prevalent with increasing electron density on the

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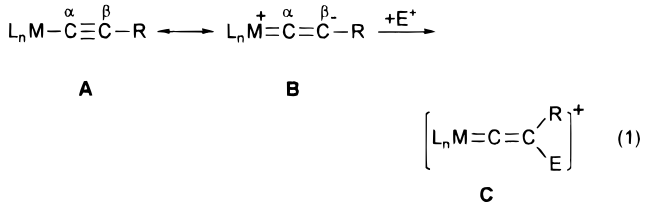
complex upon moving from cationic to anionic complexes. The importance of the resonance form **B** is indicated by the general attack of electrophiles on the β-carbon atom to form vinylidene complexes **C** (eq 1).[9,10] While this kind of reaction has been well-established, electrophilic attacks on the metal center are observed only very rarely.[10g]



(1)

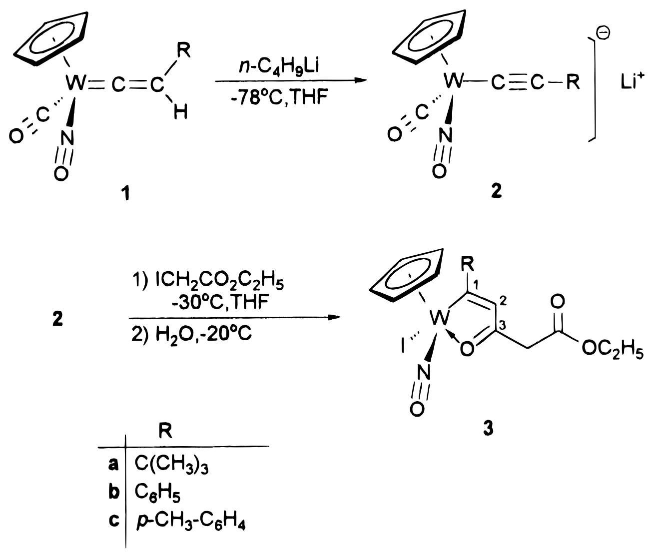
Addition at the metal center is more likely by using anionic η^1-acetylide complexes and "soft" electrophiles, where the reaction is favored by a HOMO−LUMO interaction and has a late transition state.[11] Spectroscopic evidence suggests that the protonation of the anionic acetylide complex *trans*-$[RhCl(C{\equiv}CCO_2Et)(P^iPr_3)_2]^-[^nBu_4N]^+$ with nitromethane as a weak and soft acid occurs on rhodium and not on the alkynyl ligand.[12]

In an attempt to explore the reactivity of the metal atom of the transition metal η^1-acetylide complexes, we have begun searching for appropriate electrophiles which react preferentially on the metal center. Recently we reported the reaction of tungsten−acetylide complexes **2** with a variety of allyl iodides to give the corresponding η^3-allyl derivatives, which were the results of initial alkylation on the metal center.[1] In this study, we describe the synthesis of the oxametallacyclopentadienyl complexes $(\eta^5\text{-}C_5H_5)W(I)(NO)[\eta^2\text{-}O{=}C(CH_2COOC_2H_5)CH{=}CR]$ (**3**) by addition of ethyl iodoacetate to the anion **2** and subsequent protonation by dilute acid. Replacement of acid by $CF_3SO_3CH_3$ gave rise to the η^3-allenyl complex **4**. The transformation of **2** to **3** starts presumably via an electrophilic attack on the metal center of **2** and proceeds via a multistep reaction to **3**.

Results and Discussion

Synthesis of Metallacycles 3a−c. The emerald green solutions of lithium metalates **2a**−**c** were generated, as described before,[1] by treatment of the corresponding tungsten vinylidene complexes **1a**−**c** with 1.0 equiv of *n*-BuLi in THF at −78 °C. After addition of ethyl iodoacetate the solutions turned immediately red. Protonation by dilute acids gave rise to the oxametallacyclopentadienyl complexes **3a**−**c** in 47−54% yield (Scheme 1). These were isolated as red crystals which could be stored without decomposition under an argon atmosphere for several months. The structures of the products were fully characterized by spectroscopic methods, elemental analysis, and X-ray crystallographic studies of **3a**.

Scheme 1



Spectroscopy. In agreement with the structure, the infrared spectrum of **3a** shows an absorption at 1728 cm^{-1} for the ester carbonyl group; the nitrosyl group gives rise to a strong absorption at 1629 cm^{-1}, and the IR band at 1538 cm^{-1} can be assigned to a coordinated carbonyl group. This stretching frequency is comparable to the C=O absorption in similar metallacycles.[13] On the other hand, there is no sign of any signal for a carbonyl ligand in the IR spectra. Likewise, the metallacycles **3b** and **3c** show absorptions very similar to those of **3a** in the infrared spectra (see Experimental Section).

The ^{1}H and ^{13}C NMR spectra of compounds **3a**−**c** consist of sharp and well-resolved resonance signals. The most informative features from the ^{1}H and ^{13}C NMR spectra are the signals for H2 and C1 with the corresponding satellite signals caused by the coupling with the ^{183}W atom (14% ^{183}W abundance; $I = {}^1/_2$). The ^{1}H NMR spectrum of compound **3a** shows, exemplary for the compounds **3a**−**c**, for H2 a singlet at δ 7.26 ppm with $^3J_{W-H} = 6$ Hz of the satellite signals and for the Cp protons a signal situated at δ 6.02. The methylene hydrogen atoms have the appearance of an AB spin system pattern in the region δ 3.70−3.80 ($^2J_{H-H} = 16$ Hz). In the ^{13}C NMR spectrum, C1 is observed as a singlet at δ 271.5 and the corresponding tungsten satellite signals have $^1J_{W-C} = 91$ Hz. The C2 and C3 signals appear at δ 203.0 and 133.5 ppm, respectively.

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Table 1. Comparison of ^{13}C NMR Chemical Shifts of Selected Carbon Atoms of 3a-c with Those of Similar Tungsten Metallacyclic Complexes

complex	δ(C1) (ppm)	δ(C2) (ppm)	δ(C3) (ppm)	$\Delta\delta$ (ppm)
$[\mathrm{CpW(I)(NO)}[\eta^2\text{-}O{=}\mathrm{C(CH_2COOC_2H_5)CH{=}}C\mathrm{C(CH_3)_3}]$ (**3a**)	271.5	133.5	203.0	138.0
$[\mathrm{CpW(I)(NO)}[\eta^2\text{-}O{=}\mathrm{C(CH_2COOC_2H_5)CH{=}}C\mathrm{C_6H_5}]$ (**3b**)	250.1	149.9	204.0	100.2
$[\mathrm{CpW(I)(NOI)}[\eta^2\text{-}O{=}\mathrm{C(CH_2COOC_2H_5)CH{=}}C(p\text{-}\mathrm{CH_3{-}C_6H_4}]$ (**3c**)	250.1	146.9	204.6	103.2
$[\mathrm{CpW(CO)_2}[\eta^2\text{-}O{=}\mathrm{C(C_2H_5)CH{=}}C\mathrm{C_6H_5}]^{15c}$	251.6	129.4	204.9	122.2
$[\mathrm{CpW(CO)_2}[\eta^2\text{-}O{=}\mathrm{C(CH_3)CH{=}}C\mathrm{CH_3}]^{15c}$	256.7	132.9	200.7	123.8
$[\mathrm{CpW(CO)_2}[\eta^2\text{-}O{=}\mathrm{C(CH_3)C(CH_3){=}}C\mathrm{CH_3}]^{15c}$	249.7	136.7	199.5	113.0

Table 2. Crystal Data and Conditions for Crystallographic Data Collection and Structure Refinement for 3a

formula	$C_{16}H_{22}INO_4W$
fw	603.109
color, habit	red, transparent
cryst syst	red, transparent
space group	$P\bar{1}$ (No. 2)
lattice constants	$a = 9.321(6)$ Å $b = 10.877(8)$ Å $c = 11.741(7)$ Å $\alpha = 105.10(5)°$ $\beta = 102.62(5)°$ $\gamma = 112.46(5)°$
V	992.3(2) Å^3
formula units per unit cell	$Z = 2$
density (calcd)	1.944 g/cm^3
linear abs coeff	73.89 cm^{-1}
diffractometer	image plate diffractometer system (STOE)
radiation	Mo Kα ($\lambda = 0.710$ 69 Å)
monochromator	graphite
scan range	$9.5 \le 2\theta \le 56.5°$ $-12 \le h \le 12$, $-14 \le k \le 14$, $-15 \le l \le 15$
no. of rflns collected	8841
R_{int}	0.063
no. of indep rflns	4335
no. of indep reflns	
no. of indep rflns with $F_o > 4\sigma(F_o)$	3487
applied corrections	Lorentz and polarization coefficients
structure determination and refinement	W positional parameters from Patterson synthesis (program SHELXS-86[a]); further atoms from *F* synthesis (program SHELXL-93[b]), structure refinement by anisotropic full-matrix least-squares procedure for all non-hydrogen atoms; atomic scattering factors from lit.[c]
no. of params	208
$R(F^2)$	0.175
$R(\lvert F\rvert)$	0.074 for all 4335 rflns
$R(\lvert F\rvert)$	0.062 for 3487 rflns with $F_o > 4\sigma(F_o)$

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The large difference between the chemical shifts of the two olefinic carbon atoms C1 and C2 ($\Delta\delta = \delta(\mathrm{C1}) - \delta(\mathrm{C2}) = 138$ ppm) can be assigned to a high polarity difference of the carbon atoms in this bond. In Table 1 the ^{13}C NMR chemical shifts of complexes **3a**−**c** are compared with those of similar tungsten metallacyclic complexes.

The structure of **3a** was further confirmed by a single-crystal X-ray diffraction analysis. The crystallographic data for **3a** are collected in Table 2. An ORTEP view of **3a** is shown in Figure 1, and selected bond distances and bond angles are summarized in Table 3.

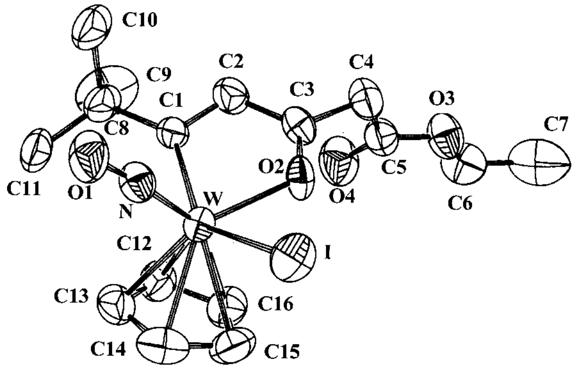
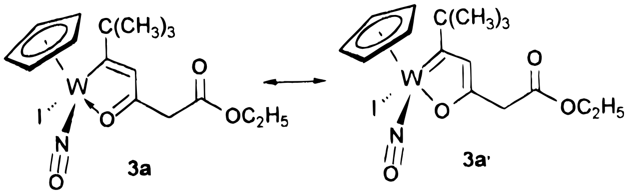


Figure 1. ORTEP drawing of (η^5-C$_5$H$_5$)W(I)(NO)[η^2-$O{=}\mathrm{C(CH_2COOC_2H_5)CH{=}}C\mathrm{C(CH_3)_3}$] (**3a**) with thermal ellipsoids shown at the 40% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 3a

W−O2	2.11(1)	C1−C8	1.51(2)
W−C1	2.19(1)	C2−C3	1.43(2)
W−I	2.8230(9)	C3−O2	1.26(2)
C1−C2	1.36(2)	C3−C4	1.50(2)
N−W−O2	121.0(4)	C1−W−I	137.3(2)
N−W−C(1)	84.0(5)	C1−C2−C3	116(1)
N−W−I	84.8(3)	C2−C1−C8	117(1)
O2−W−C1	75.0(3)	C2−C1−W	112.1(7)
O2−W−I	76.0(2)	C2−C3−C4	123(2)
O2−C3−C2	117.1(9)	C(3)−O(2)-W	118.5(6)
O2−C3−C4	120(1)	C(8)−C(1)-W	130.6(9)

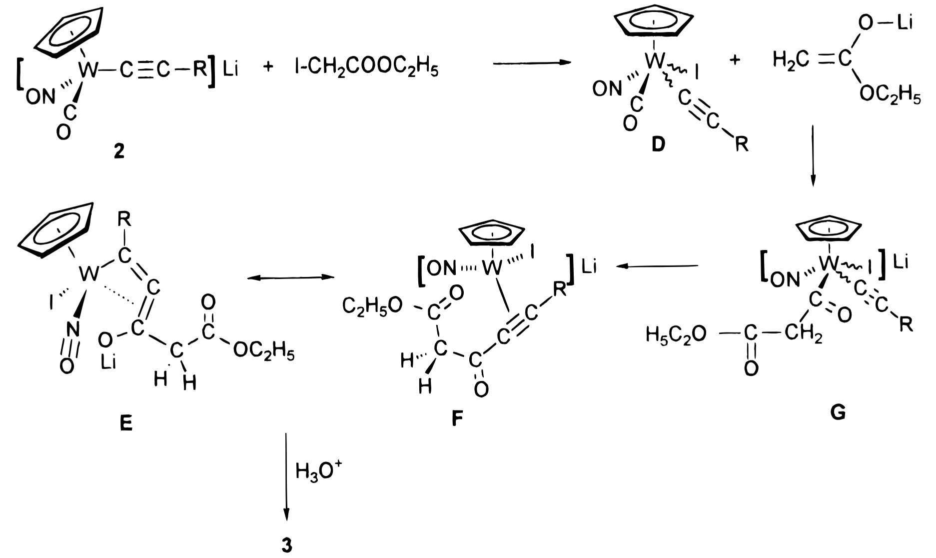
Scheme 2



Molecular Structure of Complex 3a. The four-legged piano-stool arrangement of ligands in the solid-state molecular structure of **3a** has been established by an X-ray crystallographic analysis. The nitrosyl group and the acyl function are trans-disposed in the metal's coordination sphere, and concomitantly also the iodo group is situated trans to the σ-bonded alkenyl group. The data indicate that the vinyl ligand is coordinated through the α-carbon atom (W−C(1) = 2.19(1) Å) and the carbonyl oxygen (W−O(2) = 2.11(1) Å), forming a five-membered metallacycle which can be represented as a hybrid of the mesomeric forms **3a** and **3a**' (Scheme 2).

Of particular note is the short−long-short pattern of bond lengths for the O(2)=C(3)−C(2)=C(1) fragment (1.26(2), 1.43(2), and 1.36(2) Å), respectively, which is typical for an oxametallacyclopentadiene ring system.[15] The resonance **3a** ↔ **3a'** in the five-membered ring

Scheme 3

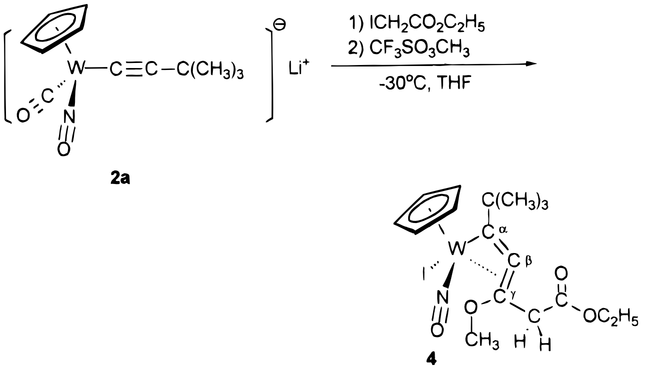


contributes to the unpronounced difference (0.07 Å) between the C−C bond lengths in the ring and to the elongated C═O bond (C(3)−O(2) = 1.26(2) Å) relative to the average value of 1.21 Å expected for an α,*β*-unsaturated ketone.[15b,16] The carbene structure **3a'** corresponds with the low-field ^{13}C NMR signal for the α-carbon atom at δ 271.5 ppm with a large $^{183}W-^{13}C$ coupling constant ($^1J_{W-C}$ = 91 Hz)[14] and with the significantly low wavenumbers for the stretching frequencies of the coordinated carbonyl group in the infrared spectra.

The above-mentioned structural features of **3a** are comparable with those indicated for similar five-membered metallacyclic complexes such as $(\eta^5\text{-}C_5Me_5)W(CO)_2[\eta^2\text{-}O{=}C(CH_3)C(CH_3){=}C(CH_3)]$,[15c] $[(dppe)_2Fe(\eta^2\text{-}O{=}C(OCH_3)CH{=}CH)][BF_4]$,[13] and $(CO)_4Mn[\eta^2\text{-}O{=}(CH_3)\text{-}CH{=}CFc]$,[17] (Fc = ferrocenyl).

Mechanistic Considerations. As a working hypothesis for the formation of **3** by the addition of ethyl iodoacetate to the η^1-acetylide complexes **2**, we propose a multistep process as presented in Scheme 3. In the first step the anionic η^1-acetylide complex **2** undergoes an electrophilic iodination on the metal center and leads to the neutral η^1-acetylide complex $(\eta^5\text{-}C_5H_5)(I)(CO)(NO)WC{\equiv}CR$ (**D**). Nucleophilic addition of the ester enolate anion of $[CH_2COOC_2H_5]Li$, the leaving group in the first step, to the CO ligand of **D** generates the anionic η^1-acetylide-η^1-acyl complex **G**. In the subsequent step a reductive-elimination reaction leads to the structures **E**/**F**. Protonation of **E** and tautomerization finally produces the oxametallacyclopentadienyl complexes **3**. Attempts to isolate the neutral iodo complex **D** and to study its chemical behavior were not successful until now. Using $CF_3SO_3CH_3$ instead of protonation by H_3O^+ prevents the tautomerization to **3** and leads in good yield to the η^3-allenyl complex **4** (vide infra).

Scheme 4



Synthesis of η^3-Allenyl Complex 4. To support the mechanistic consideration proposed in Scheme 3, we have tried to isolate or to detect some of the intermediates. We have, up to now, succeeded only in the transformation of intermediate **E** to the η^3-allenyl complex **4** (Scheme 4). After treatment of η^1-acetylide complex **2a** with ethyl iodoacetate at −30 °C, addition of 1.0 equiv of $CF_3SO_3CH_3$ gave rise in 68% yield to the η^3-allenyl complex **4** as an orange oil. The structure of **4** was determined fully by spectroscopic techniques.

The ^{13}C NMR spectrum of **4** exhibited a signal at δ 137.5, which was assigned to the carbon atom σ-bonded to tungsten, e.g. the α-carbon atom. This carbon atom showed a coupling to tungsten of $^1J_{W-H}$ = 28 Hz. The β-carbon atom is observed at δ 204.7, and the signal at δ 166.9 ppm can be attributed to C_γ. In the ^1H NMR spectrum compound **4** shows an AB spin system at δ 3.67−3.55 for the nonequivalent methylene hydrogen of the methylene group with $^2J_{H-H}$ = 15 Hz. In the infrared spectra of **4**, two strong absorptions for the ester carbonyl group and nitrosyl group are observed at 1733 and 1665 cm^{-1}, respectively.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere (99.99%, by Messer-Griesheim)

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with the use of standard Schlenk techniques. Solvents were purified by standard methods and distilled under argon prior to use. Literature methods were used to prepare [(η^5-$\mathrm{C_5H_5}$)(CO)(NO)W=C=CHR] (**1a**−**c**).[1,10h] All other compounds were commercially available. NMR spectra were obtained on Bruker AM 400 and AC 200 spectrometers. Proton and carbon chemical shifts are referenced to tetramethylsilane. MS measurements (70 eV) were performed on a Varian MAT 311-A. IR spectra were recorded on a Bruker FT-IR IFS 85. Microanalyses were done on Carlo Erba 1104 elemental analyzer.

(η^5-$\mathrm{C_5H_5}$)W(I)(NO)[η^2-*O*=C($\mathrm{CH_2COOC_2H_5}$)CH=*C*C($\mathrm{CH_3}$)$_3$] (3a). At −78 °C, to a THF solution (20 mL) of the tungsten vinylidene complex **1a** (389 mg, 1 mmol) was added 1 mmol of *n*-BuLi (a solution of 1.5 mmol/mL in hexane); the color changed immediately from orange to green. After the mixture was stirred for 0.5 h, 0.13 mL (236 mg, 1.1 mmol) of ethyl iodoacetate was added to the green reaction mixture, whereby the color changed immediately to orange-red. The temperature was raised to −20 °C. After 15 min 1 mL of a precooled mixture of THF and water (6:1) was added. The solvent was removed under reduced pressure, and the oily residue was chromatographed (silica gel; pentane−ether 1:1) to yield 325 mg (54%) of **3a** as dark red crystals (mp 101−105 °C dec) from $\mathrm{CH_2Cl_2}$ and pentane. Anal. Calcd for $\mathrm{C_{16}H_{22}INO_4W}$: C, 31.86; H, 3.68; N, 2.32. Found: C, 31.47; H, 3.24; N, 2.28. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.26 (1H, $^3J_{\mathrm{W-H}} = 6$ Hz), 6.02 (s, 5H, Cp), 4.21 (q, $^3J = 7$ Hz, 2H, $\mathrm{CH_3C}H_2$), 3.80 (d, $^2J = 16$ Hz, 1H, $\mathrm{CH_2}$), 3.70 (d, $^2J = 16$ Hz, 1H, $\mathrm{CH_2}$), 1.33 (s, 9H, $\mathrm{C(CH_3)_3}$), 1.31 (t, $^3J = 7$ Hz, 3H, $\mathrm{C}H_3\mathrm{CH_2}$). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 271.5 ($\mathrm{C_1}$, $^1J_{\mathrm{W-C}} = 91$ Hz), 203.0 ($\mathrm{C_3}$), 166.9 (C=O), 133.5 ($\mathrm{C_2}$), 101.8 ($\mathrm{C_5H_5}$), 61.9 ($C\mathrm{H_2CH_3}$), 49.4 ($C\mathrm{(CH_3)_3}$), 44.3 (CO−$\mathrm{CH_2}$−CO), 31.9 ($\mathrm{C(}C\mathrm{H_3)_3}$), 14.1 ($C\mathrm{H_3CH_2}$). IR (KBr; cm^{-1}): 1728 (s, C=O), 1629 (s, N≡O), 1538 (m, C=O, ring). MS (70 eV): *m/e* 603 (M$^+$, ^{184}W), 588 (M$^+$ − $\mathrm{CH_3}$), 573 (M$^+$ − NO).

(η^5-$\mathrm{C_5H_5}$)W(I)(NO)[η^2-*O*=C($\mathrm{CH_2COOC_2H_5}$)CH=*C*$\mathrm{C_6H_5}$] (3b). The preparation was carried out as described for **3a**, but instead of **1a**, tungsten vinylidene complex **1b** was used. Crystallization from $\mathrm{CH_2Cl_2}$ and pentane yielded 305 mg (49%) of **3b** as dark red crystals, mp 171−173 °C. Anal. Calcd for $\mathrm{C_{18}H_{18}INO_4W}$: C, 34.70; H, 2.91; N, 2.24. Found: C, 34.85; H, 2.31; N, 2.57. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.54−7.37 (m, 5H, $\mathrm{C_6H_5}$), 7.26 (s, 1H), 5.72 (s, 5H, Cp), 4.25 (q, $^3J = 7$ Hz, 1H, $\mathrm{CH_3C}H_2$), 4.24 (q, $^3J = 7$ Hz, 1H, $\mathrm{CH_3C}H_2$), 3.90 (d, $^2J = 17$ Hz, 1H, $\mathrm{CH_2}$), 3.83 (d, $^2J = 17$ Hz, 1H, $\mathrm{CH_2}$), 1.32 (t, $^3J = 7$ Hz, 3H, $\mathrm{C}H_3\mathrm{CH_2}$). ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$): δ 250.1 ($\mathrm{C_1}$), 204.0 ($\mathrm{C_3}$), 166.5 (C=O), 149.9 ($\mathrm{C_2}$), 132.3, 129.9, 128.7, 125.8 (arom C), 101.8 ($\mathrm{C_5H_5}$), 62.0 ($C\mathrm{H_2CH_3}$), 44.9 ($\mathrm{CO}C\mathrm{H_2CO}$), 14.2 ($\mathrm{CH_2}C\mathrm{H_3}$). IR (KBr; cm^{-1}): 1738 (s, C=O), 1631 (s, N≡O), 1532 (m, C=O, ring). MS (70 eV): *m/e* 623 (M$^+$, ^{184}W), 593 (M$^+$ − NO).

(η^5-$\mathrm{C_5H_5}$)W(I)(NO)[η^2-*O*=C($\mathrm{CH_2COOC_2H_5}$)CH=*C*(*p*-$\mathrm{CH_3}$−$\mathrm{C_6H_4}$)] (3c). The preparation was carried out as described for **3a**, but instead of **1a**, tungsten vinylidene complex **1c** was used. Crystallization from $\mathrm{CH_2Cl_2}$ and pentane yielded 300 mg (47%) of **3c** as dark red crystals, mp 124−127 °C. Anal. Calcd for $\mathrm{C_{19}H_{20}INO_4W}$: C, 35.82; H, 3.16; N, 2.20. Found: C, 35.88; H, 2.80; N, 2.07. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.46−740 (m, 2H, $\mathrm{C_6H_5}$), 7.29−7.25 (m, 3H), 5.79 (s, 5H, Cp), 4.24 (q, $^3J = 7$ Hz, 1H, $\mathrm{CH_3C}H_2$), 4.23 (q, $^3J = 7$ Hz, 1H, $\mathrm{CH_3C}H_2$), 3.90 (d, $^2J = 17$ Hz, 1H, $\mathrm{CH_2}$), 3.81 (d, $^2J = 17$ Hz, 1H, $\mathrm{CH_2}$), 2.43 (s, 3H, $\mathrm{CH_3}$), 1.32 (t, $^3J = 7$ Hz, 3H, $\mathrm{C}H_3\mathrm{CH_2}$). ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$): δ 250.1 ($^1J_{\mathrm{W-C}} = 87$ Hz, $\mathrm{C_1}$), 204.6 ($\mathrm{C_3}$), 166.6 (C=O), 146.9 ($\mathrm{C_2}$), 140.7, 131.7, 129.5, 126.3 (arom C), 101.8 ($\mathrm{C_5H_5}$), 62.0 ($C\mathrm{H_2CH_3}$), 44.9 ($\mathrm{CO}C\mathrm{H_2CO}$), 21.3 ($C\mathrm{H_3C_6H_4}$), 14.2 ($\mathrm{CH_2}C\mathrm{H_3}$). IR (KBr; cm^{-1}): 1734 (s, C=O), 1617 (N≡O), 1535 (C=O, ring). MS (70 eV): *m/e* 637 (M$^+$, ^{184}W), 607 (M$^+$ − NO).

(η^5-$\mathrm{C_5H_5}$)W(NO)(I)[η^3-*C*($\mathrm{CH_3}$)$_3$=*C*=*C*($\mathrm{OCH_3}$)($\mathrm{CH_2COOC_2H_5}$)] (4). At −78 °C, to a THF solution (20 mL) of tungsten vinylidene complex **1a** (389 mg, 1 mmol) was added 1 mmol of *n*-BuLi (a solution of 1.5 mmol/mL in hexane); the color changed immediately from orange to green. After the mixture was stirred for 0.5 h, 0.13 mL (236 mg, 1.1 mmol) of ethyl iodoacetate was added to the green reaction mixture, whereby the color changed immediately to orange-red. Then 0.11 mL of $\mathrm{CF_3SO_3CH_3}$ (160 mg, 1 mmol) was added. After 2 h at room temperature, the solvent was removed under reduced pressure, the oily residue was dissolved in 1 mL of $\mathrm{CH_2Cl_2}$, and this solution was chromatographed very quickly (silica gel; ether) to yield 420 mg (68%) of **4**, as a brown oil. Anal. Calcd for $\mathrm{C_{17}H_{24}INO_4W}$: C, 33.09; H, 3.92; N, 2.27. Found: C, 33.35; H, 3.43; N, 2.56. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 6.22 (s, 5H, Cp), 4.15 (q, $^3J = 7$ Hz, 2H, $\mathrm{CH_3C}H_2$), 3.86 (s, 3H, $\mathrm{OCH_3}$), 3.67 (d, $^2J = 15$ Hz, 1H, $\mathrm{CH_2}$), 3.58 (d, $^2J = 15$ Hz, 1H, $\mathrm{CH_2}$), 1.37 (s, 9H, $\mathrm{C(CH_3)_3}$), 1.27 (t, $^3J = 7$ Hz, 3H, $\mathrm{C}H_3\mathrm{CH_2}$). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 204.7 (s, C_β), 166.9 (C=O), 166.6 (C_γ), 137.5 ($^1J_{\mathrm{W-C}} = 28$ Hz, C_α), 103.7 (Cp), 66.2 ($\mathrm{OCH_3}$), 60.9 ($\mathrm{CH_3}C\mathrm{H_2}$), 50.5 ($C\mathrm{H_2CO}$), 38.4 ($C\mathrm{(CH_3)_3}$), 31.1 ($\mathrm{C(}C\mathrm{H_3)_3}$), 14.1 ($C\mathrm{H_3CH_2}$). IR (KBr; cm^{-1}): 1733 cm^{-1} (C=O), 1665 (N≡O). MS (70 eV): *m/e* 617 (M$^+$, ^{184}W), 587 (M$^+$ − NO).

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Supporting Information Available: Tables giving crystal data and crystal structure determination and refinement details, atomic coordinates, bond lengths and angles, and thermal parameters for **3a** (6 pages). Ordering information is given on any current masthead page.

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