

Chemoselective Stepwise Demetalation of Unusually Stable Fischer Biscarbene Complexes by Domino [4+2]/[2+2] Cycloaddition of 2-Isopropenyl-2-oxazoline to 1-Alkynyl Fischer Carbene Complexes of Chromium and Tungsten

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Domino [4+2]/[2+2] cycloaddition of 2-isopropenyl-2-oxazoline **2** to 1-alkynyl Fischer carbene complexes (CO)₅M=C(OEt)C≡CPh **1** (**a**, M = Cr; **b**, W) in a 1:2 molar ratio afforded unusually stable biscarbene complexes **3a** and **3b** containing a novel four-, five-, and six-membered tricyclic core in 99.6% and 45.2% yields, respectively. Chain-opening β-aminoalkenyl monocarbene complex **4b** and β-amidoalkenyl monocarbene complex **5b** of tungsten were also isolated from the cycloaddition upon treatment of the reaction mixture of **1b** and **2** on silica gel. Partial and full oxidation of **3a,b** with pyridine *N*-oxide underwent efficient chemoselective stepwise demetalation to afford the corresponding monocarbene complexes **6a,b** and organic diester **7**, respectively, under mild conditions. The X-ray crystallographic study revealed the presence of a four-, five-, and six-membered tricyclic core in compounds **3**, **6**, and **7**, and the methyl and oxazolindinyl groups derived from oxazoline **2** are positioned *syn* with respect to the azabicyclo[4.2.0]octadiene bicyclic moiety, which is oriented in the opposite direction. X-ray crystal structural data are reported for the bis- and monocarbene complexes **3a**, **5b**, and **6b** as well as for diester **7**.

Introduction

A rich chemistry of Fischer carbene complexes has evolved since they were first described by Fischer.¹ However, the major effort has been contributed to development and applications of Fischer mononuclear carbene complexes² in organic synthesis, although the first Fischer-type biscarbene complex was reported in 1982.³ Until recently, very limited work has been directed toward synthesis and reactions of bis- and polycarbene complexes. Biscarbene complexes of tungsten were synthesized by photochemical double-bond metathesis of alkenylcarbene complexes.⁴ Transforma-

tion of simple bimetallic complexes into structurally more complicated biscarbenes was documented.⁵ Macomber synthesized biscarbene complexes by reactions of group 6 carbene complexes with α,ω-dihaloalkanes.⁶ Hegedus reported homo-biscarbene complexes in his approach to synthesize cyclams.⁷ Wulff studied the synthesis and reactions of bisalkyl-tethered phenyl-substituted carbene complexes of chromium.⁸ Alkynediyl-bridged biscarbene complexes were also prepared.⁹ Bis-bridge-tethered Fischer carbene complexes were obtained from Pd-catalyzed carbene transfer reactions.¹⁰ Tetraakis-Fischer-type carbene complexes of chromium were

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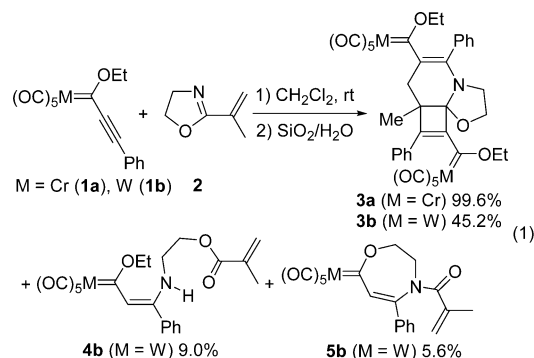
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synthesized from reactions of 1-alkenyl carbene complexes with pentaerythritol.¹¹ Cyclophanic chromium biscarbene complexes have been prepared by double addition of diamines to bimetallic Fischer carbene complexes.¹² Aumann reported synthesis of 1-alkoxy-2-azabicyclo[*n*.2.0]alkenyl biscarbene complexes¹³ by reactions of *O*-alkyl lactams $\sim(\text{CH}_2)_n\text{-N}=\text{C}(\text{OR})_n$ with **1a,b** and azabicyclo[4.2.0]octadiene biscarbene tungsten complexes¹⁴ by cycloaddition of **1b** to in-situ-generated alkenyl imidates $\text{RCH}=\text{CHC}(\text{OEt})=\text{NR}'$. The first type of Aumann's biscarbene complexes are not stable and decomposed by water, and the second are rearranged to ring-opened isomers on silica gel during column chromatography.^{13,14} Alkenyl oxazolines excluding **2** were reported as achiral substrates for cyclopropanation with 1-alkenyl and 1-alkyl chromium Fischer carbene complexes.¹⁵ Keeping in mind the structural similarity between alkenyl imidates and **2**, we studied the reactions of **1** and **2**. Herein, we report the synthesis of Fischer biscarbene complexes **3** of chromium and tungsten containing a novel four-, five-, and six-membered tricyclic core and their stepwise demetalation to diester **7** by pyridine *N*-oxide.

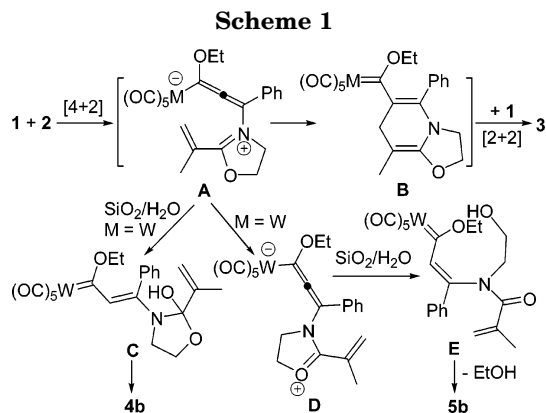


Results and Discussion

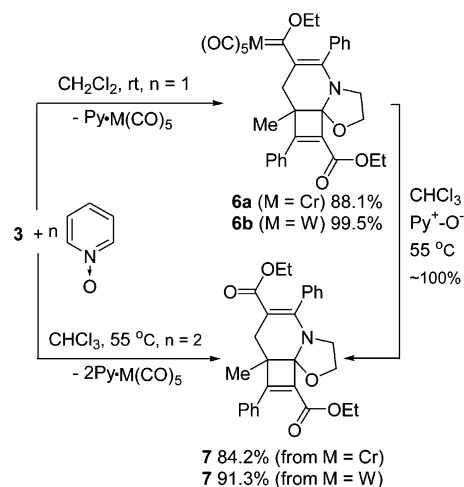
1. Synthesis of Fischer Biscarbene Complexes

3. Treatment of **2** with 2.0 equiv of **1a** in CH_2Cl_2 at ambient temperature followed by column chromatography on silica gel afforded complex **3a** in 99.6% yield. In the same fashion **3b** was obtained in 45.2% yield with two minor products, i.e., **4b** (9.0%) and **5b** (5.6%) (eq 1). Complexes **3** are rationalized to be formed by domino [4+2]/[2+2] cycloaddition of **2** to **1** as shown in Scheme 1. **3a** is unusually stable on silica gel and can be prepared in nearly quantitative yield (99.6%). Complexes **4b** and **5b** are presumably generated via reactions of the intermediates **A** and **D** with water on silica gel, respectively (Scheme 1).

2. Oxidative Stepwise Demetalation of Complexes 3 with Pyridine *N*-Oxide. At ambient temperature **3** were selectively transformed into monocarbene complexes **6a** (88.1%) and **6b** (99.5%), respectively, by oxidative demetalation with 1.0 equiv of pyridine



Scheme 2



N-oxide ($\text{Py}^+\text{-O}^-$). It was found that only the metal carbene bound to the cyclobutenyl had been demetalated (Scheme 2) under the conditions. With 2.0 equiv of the oxidant in CHCl_3 at an elevated temperature, i.e., 55°C , **3** were completely demetalated to organic diester **7** in 84.2% yield from **3a** and 91.3% yield from **3b**, respectively. **7** was also quantitatively obtained by further demetalation of **6** with $\text{Py}^+\text{-O}^-$ (1.0 equiv) in CHCl_3 at 55°C . During demetalation the $\text{M}(\text{CO})_5$ moieties were removed by formation of complexes $\text{Py}\cdot\text{M}(\text{CO})_5$.

Demetalation of Fischer monocarbene complexes can be achieved by employment of different oxidants,^{2a,16} but disadvantages are often accompanied in terms of low yields of the products (e.g., using DMSO,^{16a,b} oxone and PhIO ,^{16b} ceric ammonium nitrate,^{16b,c} dimethyldioxirane^{16d}) and/or formation of byproducts (e.g., using pyridine *N*-oxide^{16e,f} and KI/NaBO_3 ^{16g}). In our case, pyridine *N*-oxide is an excellent oxidant for demetalation. Interestingly, the two carbene centers in **3** exhibit different reactivity to pyridine *N*-oxide such that the

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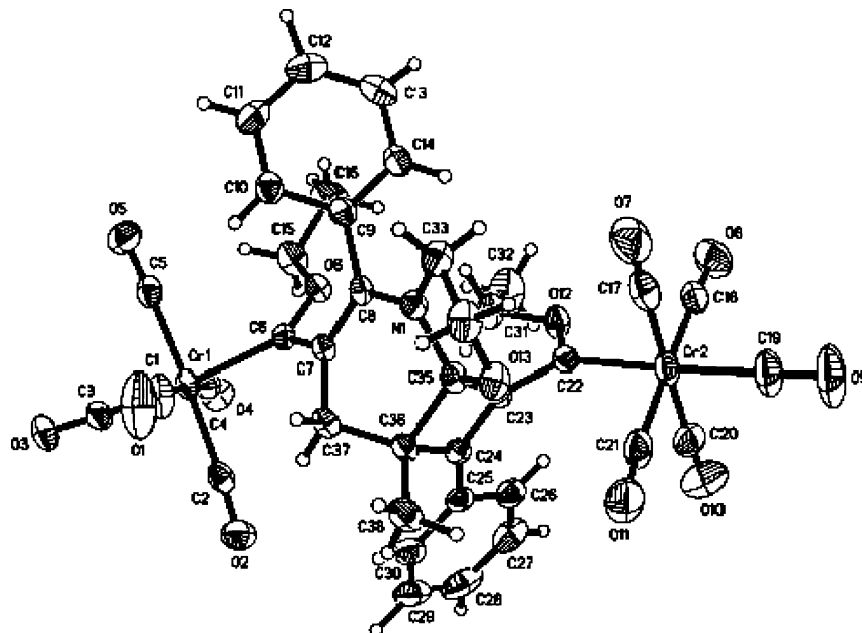


Figure 1. Perspective view of **3a**. Selected bond length (Å) and angles (deg): Cr(1)–C(6) 2.106(2), Cr(2)–C(22) 2.003(2), C(6)–C(7) 1.446(3), C(7)–C(8) 1.384(3), C(22)–C(23) 1.472(3), C(23)–C(24) 1.347(3), C(6)–C(7)–C(8) 121.4(2), C(22)–C(23)–C(24) 135.8(2), C(23)–C(24)–C(36) 95.26(19), C(23)–C(35)–C(36) 86.73(17).

metallocarbene bound to the cyclobutenyl, i.e., the alkenylcarbene $M=C$, is more reactive than the β -aminoalkenylcarbene $M=C$ and demetalated first at ambient temperature, while the latter is demetalated by another equivalent of the oxidant only at an elevated temperature. Their reactivity difference seems to be relevant to their stability. The β -aminoalkenylcarbene is stabilized by two heteroatoms (the ethoxy oxygen and oxazolindinyl nitrogen), while the alkenylcarbene is stabilized by only one heteroatom (the ethoxy oxygen). The ^{13}C NMR shifts of the carbene carbons described below account well for their different nature. To the best of our knowledge, stepwise demetalation has never been investigated for a Fischer bis- or polycarbene complex. Tricyclic building blocks are very important in construction of polycyclic natural products,¹⁷ and heteroatom-containing tricyclic compounds usually exhibit bioactivity and have potential medical applications.¹⁸ As one of the highlighted points of the present work, formation of the tricyclic core in **3**, **6**, and **7** has never been reported and these compounds may have potential medical applications due to some skeletal similarity between them and known bioactive tricyclic compounds.^{17,18}

3. Spectroscopic Characterization. The ^{13}C NMR spectra exhibit two signals for the metal carbene ($M=C$) at 345.4 and 317.5 ppm for **3a** and 315.9 and 292.9 ppm for **3b**. Two sets of resonances of $M(\text{CO})_5$ moieties with 1:4 ratios of *trans*- and *cis*-CO at 225.5/216.9 and 223.9/218.4 ppm for **3a** and 204.4/194.1 and 203.2/198.9 ppm for **3b** were observed, respectively. Complexes **4b** and **5b** show signals at 272.6 and 307.4 ppm for $W=C$, respectively, and 167.0 ppm for the ester $C=O$ in **4b** and 173.9 ppm for the amide $C=O$ in **5b**. The N–H proton signal appears at 9.24 ppm as a singlet

in the ^1H NMR spectrum of **4b**. Complex **6a** shows a ^{13}C signal of the $\text{Cr}=C$ at 315.3 ppm and **6b** that of the $W=C$ at 290.0 ppm, shifting upfield 2.2 and 2.9 ppm, respectively, as compared with those of **3**. This indicates that demetalation of the first $M=C$ does not obviously affect the other $M=C$ due to the long distance and rigid tricyclic structure between the two metal carbene centers. Diester **7** exhibits a ^{13}C NMR spectrum similar to those of **3** with the diester $C=O$ signals at 168.8 and 163.6 ppm, respectively.

4. X-ray Crystallographic Study of Complexes 3a, 5b, and 6b and Diester 7. Figures 1–4 show perspective views of complexes **3a**, **5b**, and **6b** and diester **7** along with selected bond lengths and angles, respectively. The molecule of **3a** consists of a four-, five-, and six-membered tricyclic core bridging two ethoxy pentacarbonylchromium carbene moieties via C7 of the six-membered heterocycle and C23 of the cyclobutenyl. Both $\text{Cr}(\text{CO})_5$ moieties are arranged *exo* with respect to the tricyclic core to reduce steric hindrance. The methyl group (C38) and the oxazolindinyl moiety are positioned *syn* with respect to the azabicyclo[4.2.0]octadiene moiety, which is oriented in the opposite direction (Figure 1). The bond lengths $\text{Cr}2=C22 = 2.003(2)$ Å, $\text{C}22-\text{C}23 = 1.472(3)$ Å, and $\text{C}23-\text{C}24 = 1.347(3)$ Å indicate that only little (or even no) π -conjugation is expected to operate within the (cyclobutenyl)carbene chromium(0) unit, and the other chromium carbene bond $\text{Cr}1=C6$ is 2.106(2) Å. The shorter $\text{Cr}=C$ bond demonstrates higher reactivity to pyridine *N*-oxide. The X-ray single-crystal structure of **5b** presents a seven-membered heterocyclic structure, and the $W=C$ bond length is 2.162(9) Å (Figure 2). The molecular structure of **6b** is similar to that of **3a** except that the alkenylcarbene $W=C$ was oxidatively demetalated to $O=C$ in **6b** (Figure 3). The methyl and oxazolindinyl in **6b** are also arranged *syn*

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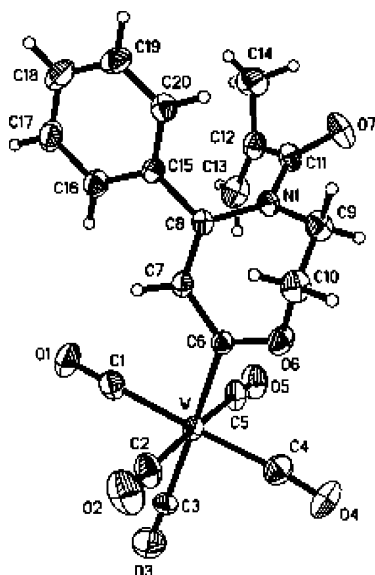


Figure 2. Perspective view of **5b**. Selected bond length (Å) and angles (deg): W–C(6) 2.162(9), C(6)–C(7) 1.446(12), C(7)–C(8) 1.351(12), O(6)–C(6) 1.324(11), O(7)–C(11) 1.198(12), N(1)–C(8) 1.398(10), N(1)–C(9) 1.464(12), C(12)–C(13) 1.308(15), C(12)–C(14) 1.477(16), O(6)–C(6)–C(7) 116.5(8), O(6)–C(6)–W 120.0(7), C(7)–C(6)–W 123.5(6).

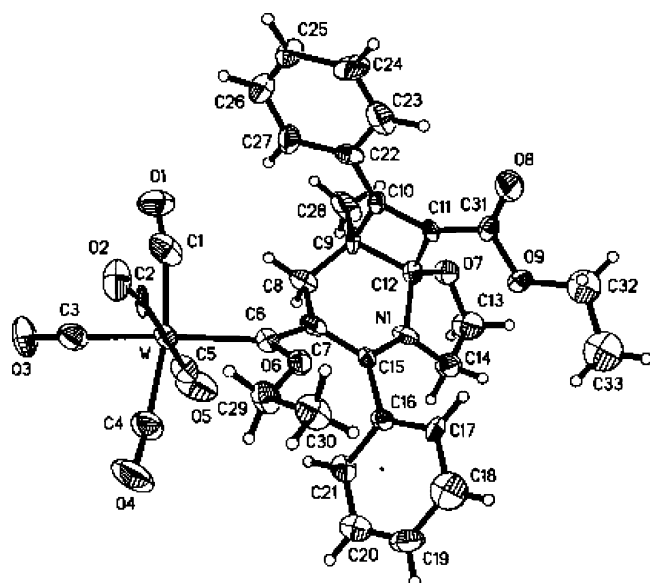


Figure 3. Perspective view of **6b**. Selected bond length (Å) and angles (deg): W–C(6) 2.237(15), C(6)–C(7) 1.43(2), C(7)–C(15) 1.38(2), C(31)–O(8) 1.21(3), C(31)–C(11) 1.42(3), C(10)–C(11) 1.358(19), C(6)–C(7)–C(15) 122.9(14), C(10)–C(11)–C(31) 140.3(17), C(9)–C(10)–C(11) 94.5(11), C(9)–C(12)–C(11) 89.1(11).

to each other. The W=C bond length in **6b** is 2.237(15) Å, longer than the corresponding Cr=C (2.106(2) Å) in **3a**. The molecular structure of **7** resembles that of **6b** except that the β -aminoalkenylcarbene M=C was also oxidized to O=C in **7**. In all the structures of **3a**, **6b**, and **7** the tricyclic core stays unchanged.

Summary

In conclusion, the domino [4+2]/[2+2] cycloaddition of 2-alkenyl-2-oxazoline to 1-alkynyl Fischer carbene complexes affords unusually stable Fischer bis-carbene

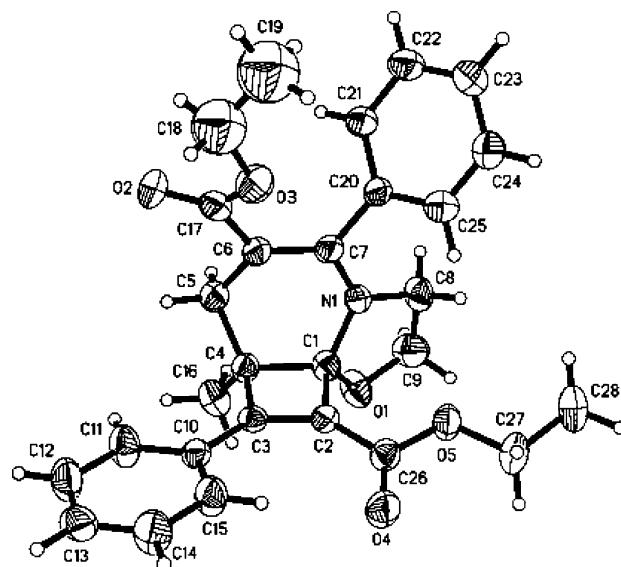


Figure 4. Perspective view of diester **7**. Selected bond length (Å) and angles (deg): O(2)–C(17) 1.210(5), O(4)–C(26) 1.205(4), C(6)–C(17) 1.448(5), C(6)–C(7) 1.364(5), C(2)–C(26) 1.459(5), C(2)–C(3) 1.340(3), C(1)–C(2)(3) 93.8(3), C(1)–C(4)–C(3) 84.9(3).

complexes containing a novel four-, five-, and six-membered tricyclic core. Chemoselective stepwise demetalation of these complexes has been efficiently realized with pyridine *N*-oxide for the first time.

Experimental Section

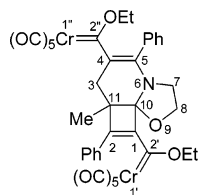
All manipulations of air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried and distilled prior to use by the literature methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer, and all chemical shift values refer to $\delta_{\text{TMS}} = 0.00$ ppm. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer. Elemental analysis was achieved by the Analysis Center, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Analytical TLC plates, Sigma-Aldrich silica gel 60 $_{\text{F200}}$, were viewed by UV light (254 nm). Chromatographic purifications were performed on SDZF silica gel 160.

Synthesis of Fischer Biscarbene Complexes 3. 1-Alkynyl carbene complex **1** (1 mmol) was reacted with alkenyl oxazoline **2** (0.5 mmol) in 3 mL of dry dichloromethane in a 5 mL screwtop vessel with stirring at ambient temperature, and the reaction was monitored by TLC on silica gel. After **1** was completely consumed, all the volatiles were removed under reduced pressure. The resultant residue was purified to afford complex **3a** by flash chromatography on silica gel (v/v, hexanes/dichloromethane = 10:1). When **1b** was used as the starting carbene complex, complexes **3b**, **4b**, and **5b** were isolated by flash chromatography on silica gel (v/v, hexanes/dichloromethane = 10:1), respectively.

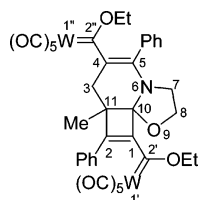
Oxidative Stepwise Demetalation of 3. Complex **3** (1 mmol) was reacted with pyridine *N*-oxide (1 mmol) in 3 mL of dry dichloromethane in a 5 mL screwtop vessel with stirring at ambient temperature, and the reaction was monitored by TLC on silica gel. After **3** was completely consumed, all the volatiles were removed under reduced pressure. The resultant residue was purified to afford complex **6** by flash chromatography on silica gel (v/v, hexanes/dichloromethane = 1:1). **3** (1 mmol) was reacted with pyridine *N*-oxide (2 mmol) in 3 mL of dry chloroform in a 5 mL screwtop vessel with stirring at 55 °C. After **3** was completely consumed, all the volatiles were

removed under reduced pressure. The resultant residue was purified to afford compound **7** by chromatography on silica gel (v/v, hexanes/diethyl ether = 4:1).

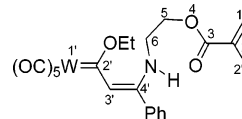
1,4-Bis(2-ethoxy-1,1,1,1-pentacarbonyl-1-chroma-1-ethen-2-yl)-2a-methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[d]indene (3a): dark red crystals (404 mg, 99.6%); single crystals were obtained by recrystallization from dichloromethane and pentane at $-20\text{ }^{\circ}\text{C}$; mp $134\text{ }^{\circ}\text{C}$ (dec); ^1H NMR (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 7.41, 7.33, 7.23, and 7.08 (m each, 3:3:2:2 H, 2 Ph), 4.65 and 4.47 (br each, 1:1 H, $2'\text{-OCH}_2$), 4.32 (q, 2 H, $2''\text{-OCH}_2$), 3.86 (m, 2 H, 3-H), 3.76 (d, $J = 13.8\text{ Hz}$) and 3.55 (dd, $J = 10.6, 4.96\text{ Hz}$) (1:1 H, 8-H), 3.14 (dd, $J = 10.4, 4.96\text{ Hz}$) and 2.79 (d, $J = 13.8\text{ Hz}$) (1:1 H, 7-H), 1.72 (s, 3 H, 11- CH_3), 1.53 and 0.50 (t each, 3:3 H, $2'\text{-OCH}_2\text{CH}_3$ and $2''\text{-OCH}_2\text{CH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 345.37 and 317.52 (s each, Cq each, Cr=C, C2' and C2''), 225.54 and 216.96 (s each, Cq each, 1:4, *trans*- and *cis*-CO, C2'-Cr(CO) $_5$), 223.89 and 218.38 (s each, Cq each, 1:4, *trans*- and *cis*-CO, C2''-Cr(CO) $_5$), 150.71 (s, Cq, C=C-N, C5), 138.02 (s, Cq, *i*-C of Ph), 134.33 and 131.15 (s each, Cq each, C1 and C4), 130.35, 129.75, 129.66, and 128.86 (s each, 1:3:4:2 CH of 2 Ph), 97.47 (s, Cq, C10), 76.45 and 74.48 (s each, C2'-OCH $_2$ and C2''-OCH $_2$), 66.92 (s, C8), 63.24 (s, Cq, C11), 48.89 and 39.80 (s each, C7 and C3), 20.48 (s, C11- CH_3), 15.85 and 14.56 (s each, C2''-OCH $_2\text{CH}_3$ and C2'-OCH $_2\text{CH}_3$); IR (KBr) cm^{-1} 2044.2 (76), 2050.2 (80), 1924.8 (100), 1889.3 (100) [$\nu(\text{C}\equiv\text{O})$], 1475.5 (60), 1423.4 (50) [$\nu(\text{C}=\text{C})$]. Anal. Calcd for $\text{C}_{38}\text{H}_{29}\text{Cr}_2\text{NO}_{13}$: C, 56.23; H, 3.60; N, 1.72. Found: C, 55.51; H, 3.66; N, 1.60.



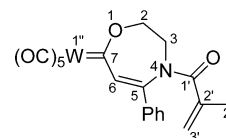
1,4-Bis(2-ethoxy-1,1,1,1-pentacarbonyl-1-tungsta-1-ethen-2-yl)-2a-methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[d]indene (3b): dark red crystals (243 mg, 45.2%); single crystals were obtained by recrystallization from dichloromethane and pentane at $-20\text{ }^{\circ}\text{C}$; mp $153\text{ }^{\circ}\text{C}$ (dec); ^1H NMR (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 7.40, 7.32, 7.23 and 7.17 (m each, 3:3:2:2 H, 2 Ph), 4.82 and 4.74 (br each, 1:1 H, $2'\text{-OCH}_2$), 4.19 (q, 2 H, $2''\text{-OCH}_2$), 3.95 and 3.69 (m each, 1:1 H, 3-H), 3.57 (m, 2 H, 8-H), 3.21 (m) and 2.66 (d, $J = 13.5\text{ Hz}$) (1:1 H, 7-H), 1.72 (s, 3 H, 11- CH_3), 1.65 and 0.54 (t each, 3:3 H, $2'\text{-OCH}_2\text{CH}_3$ and $2''\text{-OCH}_2\text{CH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 315.87 and 292.89 (s each, Cq each, W=C, C2' and C2''), 204.38 and 194.14 (s each, Cq each, 1:4, *trans*- and *cis*-CO, C2'-W(CO) $_5$), 203.21 and 198.87 (s each, Cq each, 1:4, *trans*- and *cis*-CO, C2''-W(CO) $_5$), 151.96 (s, Cq, C=C-N, C5), 137.66 (s, Cq, *i*-C of Ph), 133.96 and 130.86 (s each, Cq each, C1 and C4), 129.75, 129.64, 129.13, 128.95, 128.87, and 128.80 (s each, 1:1:2:2:2:2 CH of 2 Ph), 95.94 (s, Cq, C10), 75.94 (s, C2'-OCH $_2$), 66.30 (s, C8), 62.90 (s, Cq, C11), 48.08 and 40.24 (s each, C7 and C3), 20.01 (s, C11- CH_3), 15.33 and 14.00 (s each, C2''-OCH $_2\text{CH}_3$ and C2'-OCH $_2\text{CH}_3$); IR (KBr) cm^{-1} 2056.0 (90), 1911.3 (95) [$\nu(\text{C}\equiv\text{O})$], 1469.7 (85), 1425.3 (80) [$\nu(\text{C}=\text{C})$]. Anal. Calcd for $\text{C}_{38}\text{H}_{29}\text{NO}_{13}\text{W}_2$: C, 42.44; H, 2.72; N, 1.30. Found: C, 42.13; H, 2.86; N, 1.28.



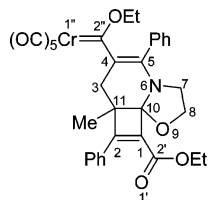
(2-Ethoxy-1,1,1,1-pentacarbonyl-4-phenyl-1-tungsta-4-buta-1,3-dienylamino) ethyl ester (4b): orange oil (55 mg, 9.0%); ^1H NMR (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 9.24 (s and br, 1H, NH), 7.49 and 7.38 (m each, 3:2 H, Ph), 6.36 (s, 1H, 3'-H), 6.16 and 5.69 (s each, 1:1 H, 1-H), 4.76 (q, 2H, OCH $_2$), 4.22 and 3.49 (t each, 2:2 H, 5-H and 6-H), 1.99 (s, 3H, CH $_3$, 2'-H), 1.57 (t, 3H, OCH $_2\text{CH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 272.61 (s, Cq, C2', W=C), 203.95 and 199.25 (s each, Cq each, 1:4, *trans*- and *cis*-CO, W(CO) $_5$), 167.02 (s, Cq, C3, C=O), 157.59 (s, Cq, C4'), 135.75 and 134.43 (s, Cq, *i*-C of *E*- and *Z*-Ph), 130.46, 129.03, and 127.78 (s each, 1:2:2 CH, Ph), 126.65 (s, CH, C3'), 122.63 (s, C1), 76.97 (s, OCH $_2$), 63.32 (s, OCH $_2$, C5), 41.52 (s, C6, NCH $_2$), 15.80 and 13.76 (s each, 2 CH $_3$). No satisfactory elemental analysis was obtained due to its decomposition at ambient temperature.



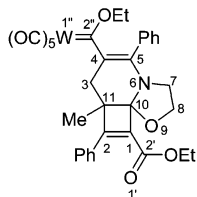
7-(1,1,1,1-Pentacarbonyl-1-tungsta-4-(2-methylacryloyl)-5-phenyl-2,3-dihydro-7H-[1,4]oxazepine (5b): black crystals (30 mg, 5.6%); single crystals were obtained by recrystallization from dichloromethane/pentane at $-20\text{ }^{\circ}\text{C}$; mp $132\text{--}134\text{ }^{\circ}\text{C}$; ^1H NMR (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 7.41 and 7.32 (m each, 3:2 H, Ph), 7.06 (s, 1H, 6-H), 5.22 and 5.10 (s each, 1:1 H, 3'-H), 4.90 and 4.42 (t each, 2:2 H, 2-H and 3-H), 1.32 (s, 3H, 2'-H, CH $_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 307.44 (s, Cq, W=C), 205.10 and 197.64 (s each, Cq each, 1:3, *trans*- and *cis*-CO, W(CO) $_5$), 173.86 (s, Cq, C1', C=O), 141.93 (s, Cq, C5), 139.14 (s, Cq, C2'), 135.13 (s, Cq, *i*-C of Ph), 132.02 (s, CH, C6), 130.47, 129.50, and 128.30 (s each, 1:2:2 CH of Ph), 120.77 (s, =CH $_2$, C3'), 73.42 (s, OCH $_2$, C2), 54.76 (s, NCH $_2$, C3), 18.27 (s, C2'', CH $_3$); IR (KBr) cm^{-1} 2063.5 (70), 1943.9 (80) [$\nu(\text{C}\equiv\text{O})$], 1673.9 (55) [$\nu(\text{C}=\text{O})$], 1531.2 (50), 1452.2 (50) [$\nu(\text{C}=\text{C})$]. Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{NO}_6\text{W}$: C, 42.48; H, 2.81; N, 2.61. Found: C, 42.37; H, 2.65; N, 2.34.



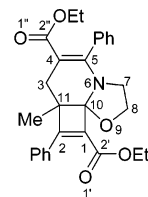
4-(2-Ethoxy-1,1,1,1-pentacarbonyl-1-chroma-1-ethen-2-yl)-2a-methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[d]indene-1-carboxylic acid ethyl ester (6a): orange crystals (560 mg, 88.1%); single crystals were obtained by recrystallization from pentane at $-20\text{ }^{\circ}\text{C}$; mp $121\text{--}123\text{ }^{\circ}\text{C}$; ^1H NMR (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 7.93, 7.38, and 7.17 (m each, 2:6:2 H, 2 Ph), 4.35 and 4.12 (m each, 3:1 H, $2'\text{-OCH}_2$ and $2''\text{-OCH}_2$), 4.03 and 3.94 (q each, 1:1 H each, 3-H), 3.83 (m) and 3.64 (d, $J = 13.5\text{ Hz}$) (1:1 H, 8-H), 3.22 (m) and 2.76 (d, $J = 13.5\text{ Hz}$) (1:1 H, 7-H), 1.61 (s, 3H, 11- CH_3), 1.42 and 0.56 (t each, 3:3 H, $2'\text{-OCH}_2\text{CH}_3$ and $2''\text{-OCH}_2\text{CH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 315.30 (s, Cq, C2', Cr=C), 223.83 and 218.08 (s each, Cq each, 1:4, *trans*- and *cis*-CO, C2'-Cr(CO) $_5$), 163.77 (C=O, C2'), 161.79 (s, Cq, C=C-N, C5), 149.73 (s, Cq, C1), 137.35 and 132.25 (s each, Cq each, *i*-C of 2 Ph), 131.22, 130.05, 129.33, 129.26, 128.78, and 128.60 (s each, 1:2:1:2:2:2 CH of 2 Ph), 130.32 (s, Cq, C4), 123.38 (s, Cq, C2), 94.18 (s, Cq, C10), 73.95 (s, C2''-OCH $_2$), 66.46 (s, C8), 63.47 (s, Cq, C11), 60.75 (C2'-OCH $_2$), 47.81 and 38.20 (s each, C7 and C3), 19.83 (s, C11- CH_3), 14.46 and 14.22 (s each, C2''-OCH $_2\text{CH}_3$ and C2'-OCH $_2\text{CH}_3$); IR (KBr) cm^{-1} 2046.4 (95), 1909.4 (95) [$\nu(\text{C}\equiv\text{O})$], 1708.8 (90) [$\nu(\text{C}=\text{O})$], 1629.8 (70), 1454.2 (90), 1427.2 (80) [$\nu(\text{C}=\text{C})$]. Anal. Calcd for $\text{C}_{33}\text{H}_{29}\text{CrNO}_9$: C, 62.36; H, 4.60; N, 2.20. Found: C, 62.20; H, 4.73; N, 2.11.



4-(2-Ethoxy-1,1,1,1-pentacarbonyl-1-tungsta-1-ethen-2-yl)-2a-methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[d]indene-1-carboxylic acid ethyl ester (6b): orange crystals (764 mg, 99.5%); single crystals were obtained by recrystallization from pentane at $-20\text{ }^{\circ}\text{C}$; mp $146\text{--}147\text{ }^{\circ}\text{C}$; $^1\text{H NMR}$ (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 7.94, 7.38, and 7.20 (m each, 2:6:2 H, 2 Ph), 4.37 and 4.18 (m each, 3:1 H each, $2''\text{-OCH}_2$ and $2'\text{-OCH}_2$), 4.03 and 3.97 (q each, 1:1 H, 3-H), 3.73 (m, 1H) and 3.66 (d, $J = 13.5\text{ Hz}$) (1:1 H, 8-H), 3.23 (m, 1H) and 2.69 (d, $J = 13.5\text{ Hz}$) (1:1 H, 7-H), 1.61 (s, 3 H, 11- CH_3), 1.43 and 0.55 (t each, 3:3 H each, $2'\text{-OCH}_2\text{CH}_3$ and $2''\text{-OCH}_2\text{CH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 290.04 (s, Cq, $\text{W}=\text{C}$, $\text{C}2''$), 203.28 and 198.99 (s each, Cq each, 1:4, *trans*- and *cis*-CO, $\text{C}2''\text{-W}(\text{CO})_5$), 163.87 (C=O, $\text{C}2'$), 161.70 (s, Cq, $\text{C}=\text{C}-\text{N}$, C5), 152.86 (s, Cq, C1), 137.61 and 132.95 (s each, Cq each, *i*-C of 2 Ph), 131.17, 130.05, 129.24, 129.11, 128.72, and 128.59 (s each, 1:2:1:2:2:2 CH of 2 Ph), 130.34 (s, Cq, C4), 123.54 (s, Cq, C2), 94.15 (s, Cq, C10), 75.86 (s, $\text{C}2''\text{-OCH}_2$), 66.30 (s, C8), 63.27 (s, Cq, C11), 60.75 ($\text{C}2'\text{-OCH}_2$), 47.95 and 39.61 (s each, C7 and C3), 19.79 (s, C11- CH_3), 14.42 and 13.83 (s each, $\text{C}2''\text{-OCH}_2\text{CH}_3$ and $\text{C}2'\text{-OCH}_2\text{CH}_3$); IR (KBr), cm^{-1} 2054.1 (90), 1899.8 (95) [$\nu(\text{C}=\text{O})$], 1706.9 (90) [$\nu(\text{C}=\text{O})$], 1629.8 (60), 1454.2 (80), 1425.3 (70) [$\nu(\text{C}=\text{C})$]. Anal. Calcd for $\text{C}_{33}\text{H}_{29}\text{NO}_9\text{W}$: C, 51.65; H, 3.81; N, 1.82. Found: C, 51.72; H, 3.83; N, 1.76.



2a-Methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[d]indene-1,4-dicarboxylic acid diethyl ester (7): pale yellow crystals (from M = Cr, 387 mg, 84.2%; from M = W, 419 mg, 91.3%); single crystals were obtained by recrystallization from diethyl ether at $-20\text{ }^{\circ}\text{C}$; mp $120\text{--}121\text{ }^{\circ}\text{C}$; $^1\text{H NMR}$ (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 7.98, 7.37 and 7.24 (m each, 2:6:2 H, 2 Ph), 4.38–4.26 (m) and 4.02 (q) (3:1 H, $2'\text{-OCH}_2$ and $2''\text{-OCH}_2$), 3.80 and 3.73 (m each, 1:1 H, 3-H), 3.65 (m) and 3.30 (d, $J = 14.5\text{ Hz}$) (1:1 H, 8-H), 3.14 (m) and 2.17 (d, $J = 14.5\text{ Hz}$) (1:1 H, 7-H), 1.51 (s, 3H, 11- CH_3), 1.39 and 0.70 (t each, 3:3 H each, $2'\text{-OCH}_2\text{CH}_3$ and $2''\text{-OCH}_2\text{CH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , $23\text{ }^{\circ}\text{C}$, 400 MHz) δ 168.80 (C=O, $\text{C}2''$), 163.58 (C=O, $\text{C}2'$), 162.05 (s, Cq, $\text{C}=\text{C}-\text{N}$, C5), 153.85 (s, Cq, C1), 137.07 and 131.00 (s each, Cq each, *i*-C of 2 Ph), 130.69, 129.90, 128.79, 128.44, and 128.11 (s each, CH of 2 Ph), 123.37 and 101.48 (s each, Cq each, C2 and C4), 93.92 (s, Cq, C10), 66.31 (s, C8), 64.87 (s, Cq, C11), 60.56 ($\text{C}2'\text{-OCH}_2$), 59.06 (s, $\text{C}2''\text{-OCH}_2$), 46.90 and 32.83 (s each, C7 and C3), 19.61 (s, C11- CH_3), 14.39 and 13.73 (s each, $\text{C}2''\text{-OCH}_2\text{CH}_3$ and $\text{C}2'\text{-OCH}_2\text{CH}_3$); IR (KBr) cm^{-1} 1705.3 (94), 1664.5 (100) [$\nu(\text{C}=\text{O})$], 1627.3 (85), 1568.0 (90), 1492.8 (75), 1446.5 (75) [$\nu(\text{C}=\text{C})$]. Anal. Calcd for $\text{C}_{28}\text{H}_{29}\text{NO}_5$: C, 73.18; H, 6.36; N, 3.05. Found: C, 73.20; H, 6.42; N, 2.92.



X-ray Crystallographic Studies. Single-crystal X-ray diffraction studies for complexes **3a**, **5b**, and **6b** and diester **7** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in

Table 1. Crystal Data and Refinement Details for Compounds 3a, 5b, 6b, and 7

	3a	5b	6b	7
empirical formula	$\text{C}_{38}\text{H}_{29}\text{NO}_{13}\text{Cr}_2$	$\text{C}_{20}\text{H}_{15}\text{NO}_7\text{W}$	$\text{C}_{33}\text{H}_{29}\text{NO}_9\text{W}$	$\text{C}_{28}\text{H}_{29}\text{NO}_5$
fw	811.62	565.18	767.42	459.52
temperature (K)	293(2)	293(2)	293(2)	293(2)
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2(1)/c$	$P\bar{1}$	$P2(1)$	$C2/c$
a (\AA)	12.5659(9)	7.4353(7)	11.1571(9)	38.242(9)
b (\AA)	20.5264(14)	12.1255(11)	13.6990(11)	7.1774(17)
c (\AA)	14.4656(10)	12.5732(12)	11.3873(10)	17.705(4)
α (deg)	90	65.069(2)	90	90
β (deg)	90.1920(10)	82.996(2)	113.103(2)	92.733(5)
γ (deg)	90	79.906(2)	90	90
V (\AA^3)	3731.1(5)	1010.55(16)	1600.9(2)	4854.1 (19)
Z	4	2	2	8
D_c (gcm^{-3})	1.445	1.857	1.592	1.258
μ (mm^{-1})	0.649	5.757	3.662	0.086
$F(000)$	1664	544	760	1952
cryst size (mm^3)	$0.54 \times 0.49 \times 0.47$	$0.42 \times 0.20 \times 0.09$	$0.28 \times 0.17 \times 0.12$	$0.38 \times 0.15 \times 0.07$
θ limits (deg)	1.62–28.29	1.79–27.00	1.94–27.00	2.13–26.00
no. of data collected	22 520	5994	9521	12 758
no. of unique data	8666	4294	6185	4754
$R(\text{int})$	0.0458	0.1375	0.0674	0.0837
no. of data observed with $I > 2\sigma(I)$	8666	4294	6185	4754
no. of refined params	573	263	386	300
goodness-of-fit on F^2	0.870	1.037	0.912	0.707
R (all data/obsd data)	0.0856/0.0471	0.0757/0.0719	0.0804/0.0519	0.1657/0.0583
R_w^2 (all data/obsd data)	0.1089/0.0977	0.1776/0.1744	0.1752/0.1181	0.1543/0.1318
residual ρ_{max} (e \AA^{-3})	0.294 (–0.217)	4.217 (–3.525)	1.632 (–0.690)	0.572 (–0.276)

calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. Crystal data and refinement details for complexes **3a**, **5b**, and **6b** and diester **7** are summarized in Table 1.

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and the “Hundred Talented Program” Funding of CAS for support of this research.

Supporting Information Available: Crystallographic data for **3a**, **5b**, **6b**, and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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