

Novel Pyranylidene Complexes from Group 6 Transition Metals and β -Ethynyl α,β -Unsaturated Carbonyl Compounds

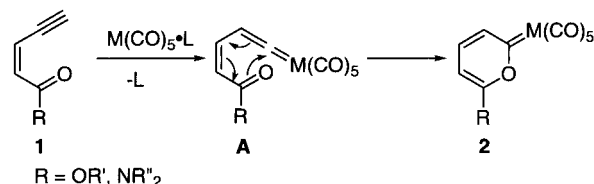
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Summary: The reaction of conjugated enyne–carbonyl compounds such as 1-(alkoxycarbonyl)-2-ethynylcycloalkenes and 1-carbamoyl-2-ethynylcycloalkenes with $\text{Mo}(\text{CO})_5\text{NEt}_3$ and $\text{W}(\text{CO})_5\text{THF}$ gave the corresponding 6-alkoxy- and 6-amino-2H-pyranylidene–molybdenum and –tungsten complexes, respectively. The cycloisomerization reaction of the conjugated vinylidene–ene–carbonyl complexes generated from 1-(alkoxycarbonyl)- or 1-carbamoyl-2-ethynylcycloalkenes and metals is a key route to these Fischer-type oxacarbene complexes. The crystal structure of the 6-methoxy-2H-pyranylidene–tungsten complex **2b** has been determined by X-ray diffraction. New pyranylidene complexes undergo [4 + 2] cycloaddition reactions with acetylenes to give aromatic rings together with the liberation of metal hexacarbonyls.

Scheme 1



structure of **2** represents the α -metallo analogue of α -pyrone.⁶ Although the reactivity as well as the structural feature is of much interest, the studies on pyranylidene–metal complexes are still limited.^{7,8} Thus, we also describe the synthetic application of these pyranylidene–metal complexes **2** as an enophile to [4 + 2] cycloaddition reactions.

Introduction

Fischer-type carbene complexes of the group 6 metals Cr, Mo, and W are versatile and useful organometallic reagents in organic synthesis.¹ Typical oxacarbene complexes ($\text{M}=\text{C}(\text{OR})\text{R}$) are readily prepared by the reaction of the metal hexacarbonyl with a range of organolithium reagents. It has also been demonstrated that nucleophilic addition of an alcoholic O–H bond to the α - and β -carbons of a vinylidene–metal complex ($\text{M}=\text{C}_\alpha=\text{C}_\beta$, M = Cr, Mo, W), generated from an ω -alkynol, provides new access to oxacarbene complexes as intermediates in catalytic reactions and isolable intermediates in stoichiometric reactions.^{2,3} We report herein a new approach for the pyranylidene–metal compound **2** as a group 6 oxacarbene complex via a nucleophilic attack with a carbonyl oxygen at an α -carbon of a vinylidene–metal species (**A**) produced from the conjugated compound **1** (Scheme 1).^{4,5} The

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(2) For a review, see: McDonald, F. E. *Chem. Eur. J.* **1999**, 5, 3103.

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(4) For reviews on vinylidene transition-metal complexes, see: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, 22, 59. (b) Bruce, M. I. *Chem. Rev.* **1991**, 91, 197. (c) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, 32, 311.

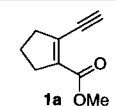
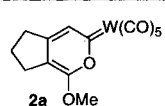
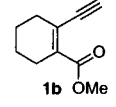
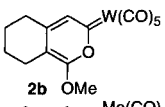
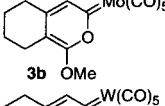
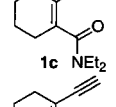
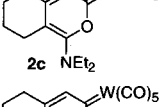
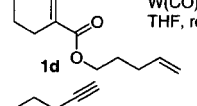
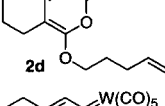
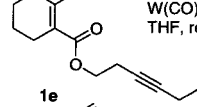
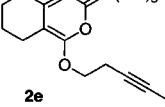
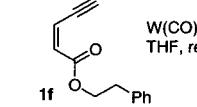
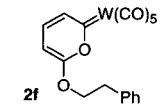
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(7) Moretó reported that the reaction of diethoxyacrylate with alkynylalkoxycarbene–metal complexes eventually leads to 6-ethoxy-2H-pyranylidene–chromium and –tungsten carbene complexes; see: Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Molins, E.; Miravittles, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1560. Jordi, L.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Molins, E.; Miravittles, C. *J. Organomet. Chem.* **1993**, 444, C28. For preparation of other pyran-2-ylidene carbene complexes which have mainly alkyl or aryl moieties as substituents on the pyranylidene ring, see: (a) Rees, C. W.; von Angerer, E. *J. Chem. Soc., Chem. Commun.* **1972**, 420. (b) Gilchrist, T. L.; Livingston, R.; Rees, C. W.; von Angerer, E. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2535. (c) Juneau, K. N.; Hegedus, L. S.; Roepke, F. W. *J. Am. Chem. Soc.* **1989**, 111, 4762. For preparation from Fischer-type oxacarbene complexes, see: (d) Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, 120, 537. (e) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, 112, 6419. (f) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, 112, 4550. (g) Aumann, R.; Roths, K.; Läge, M.; Krebs, B. *Synlett* **1993**, 667. (h) Aumann, R.; Roths, K.; Jasper, B.; Fröhlich, R. *Organometallics* **1996**, 15, 1257. (i) Aumann, R.; Meyer, A. G.; Fröhlich, R. *J. Am. Chem. Soc.* **1996**, 118, 10853. (j) Yu, Z.; Aumann, R.; Fröhlich, R.; Roths, K.; Hecht, J. *J. Organomet. Chem.* **1997**, 541, 187.

(8) In the course of our study Iwasawa and co-workers have reported the formation of benzopyranylidene–tungsten complexes from *o*-ethynylphenyl ketones and tungsten carbonyl and its application to [4 + 2] cycloaddition reactions with electron-rich alkenes; see: Shido, M.; Maeyama, K.; Kusama, H.; Iwasawa, N. 78th Annual Meeting of the Chemical Society of Japan, Funabashi, Japan, March 29, 2000; Abstracts Vol. II, p 1026. Note Added in Proof: Iwasawa, N.; Shido, M.; Maeyama, K.; Kusama, H. *J. Am. Chem. Soc.* **2000**, 122, 10226.

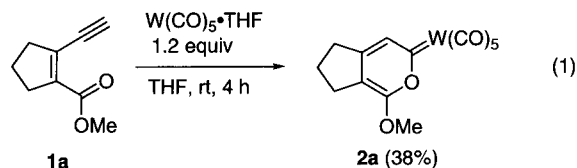
Table 1. Preparation of Pyranylidene–Metal Complexes from Conjugated Enyne–Carbonyls and the Group 6 Metals^a

entry	1	conditions ^b	product	isolated yield
1		W(CO) ₅ •THF (1.2 equiv) THF, rt, 4 h		38%
2	1a	W(CO) ₅ •THF (2.0 equiv) THF, rt, 4 h	2a	51%
3	1a	W(CO) ₅ •THF (3.0 equiv) THF, rt, 4 h	2a	75%
4		W(CO) ₅ •THF (2.0 equiv) THF, reflux, 0.5 h		63%
5	1b	Mo(CO) ₅ •NEt ₃ (1.2 equiv) Et ₂ O, Et ₃ N, rt, 3 h		35%
6		W(CO) ₅ •THF (3.0 equiv) THF, reflux, 0.5 h		68%
7		W(CO) ₅ •THF (3.0 equiv) THF, reflux, 0.5 h		55%
8		W(CO) ₅ •THF (2.0 equiv) THF, reflux, 0.5 h		71%
9		W(CO) ₅ •THF (3.0 equiv) THF, reflux, 0.5 h		58%

^a Reactions were carried out with **1** (0.2–0.5 mmol) under Ar.^b The solution of M(CO)₅•L was prepared by irradiating a THF or Et₂O solution of M(CO)₆ for 4 h with a high-pressure Hg lamp.

Results and Discussion

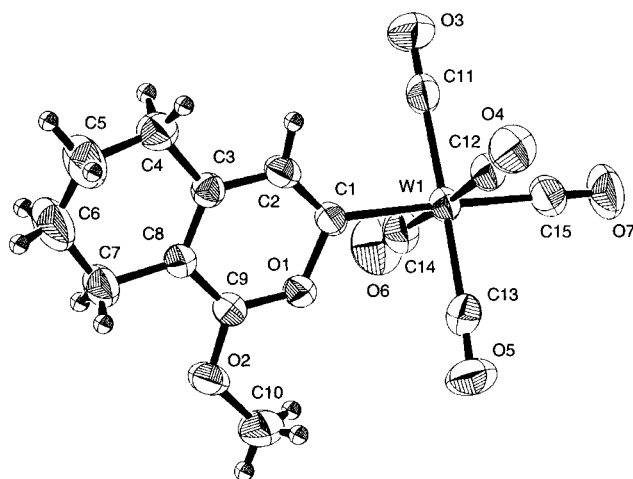
As a first attempt to investigate our idea, we undertook the reaction of a conjugate β -ethynyl α,β -unsaturated carbonyl compound with group 6 metals, which are capable of the formation of stable Fischer-type carbene complexes. When 2-ethynyl-1-(methoxycarbonyl)cyclopent-1-ene (**1a**,⁹ 0.5 mmol) was treated with 1.2 equiv of preformed W(CO)₅•THF¹⁰ at room temperature, the corresponding pyranylidene–tungsten complex **2a** was isolated in 38% yield (eq 1). The complex **2a** is stable



enough to be purified by silica gel column chromatography. The reaction conditions were further optimized, and the generality of the reaction of β -ethynyl α,β -unsaturated carbonyl compounds with group 6 metal carbonyls was examined. The results are shown in Table 1. Reactions of **1a** with excess amounts of W(CO)₅•THF

(9) β -Ethynyl α,β -unsaturated carbonyl compounds were prepared from the corresponding 2-bromo-1-cycloalkenecarboxylic acids. Procedures for the preparation of these compounds and their spectral data are reported in the Supporting Information.

(10) Strohmeier, W.; Gerlach, K. *Chem. Ber.* **1961**, *94*, 398.

**Figure 1.** ORTEP drawing of the complex **2b**.

gave better yields of **2a**, in 51% (2.0 equiv of W) and 75% yields (3.0 equiv of W), respectively (entries 2 and 3). Although the condition of THF reflux was required, the reaction of 2-ethynyl-1-(methoxycarbonyl)cyclohex-1-ene (**1b**) with W(CO)₅•THF was complete within 0.5 h to give the corresponding pyranylidene–tungsten complex **2b** in 63% yield as well (entry 4). Among other group 6 metals examined, the similar pyranylidene–molybdenum complex **3b** was obtained in 35% yield from **1b** and preformed Mo(CO)₅•NEt₃¹¹ (entry 5), while the reaction with the chromium complex Cr(CO)₅•NEt₃¹¹ gave only a trace amount of an isolable complex. An amide compound, 2-ethynyl-1-(*N,N*-diethylcarbamoyl)-cyclohex-1-ene (**1c**), also reacted with W(CO)₅•THF at reflux temperature in THF to give the 6-(diethylamino)-pyranylidene complex **2c** in 68% yield (entry 6). The formation of pyranylidene–metal complexes **2d,e** from **1d,e** demonstrated the tolerance of an ω -alkenyl or an internal alkynyl moiety in the substrate (entries 7 and 8). The simplest substrate, 2-phenylethyl (*Z*)-pent-2-en-4-ynoate (**1f**), was reacted with W(CO)₅•THF to give the 6-((2-phenylethyl)oxy)pyranylidene–tungsten complex **2f** in 58% yield (entry 9).

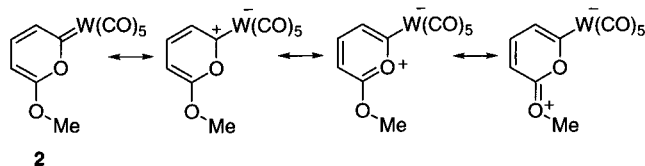
These are all new α,γ -dienyl Fischer-type carbene complexes, and the structure of one of them was unambiguously determined by X-ray diffraction. An ORTEP drawing of the complex **2b** is shown in Figure 1. The figure shows that the tungsten pentacarbonyl fragment presents the carbene carbon with a wall of CO. The W–C_{carb} bond length (2.215(6) Å) is almost equal to the W–C_{carb} bond (2.02–2.22 Å) in typical tungsten-oxacarbene complexes.¹² The C_{carb}–O bond length of 1.430(7) Å indicates the lack of multiple bonding between pyran oxygen and the carbene carbon, other typical oxacarbene complex C_{carb}–O bond lengths being in the range of 1.30–1.35 Å.^{12,13} On the other hand, the O(1)–C(9) and C(9)–O(2) bond lengths, 1.321(7) and 1.316(7) Å, respectively, indicate substantial multiple

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(12) (a) Guy, M. P.; Guy, J. T.; Bennett, D. W. *Organometallics* **1986**, *5*, 1696. (b) Alvarz, C.; Pacreau, A.; Parlier, A.; Rudler, H.; Daran, J.-C. *Organometallics* **1987**, *6*, 1057.

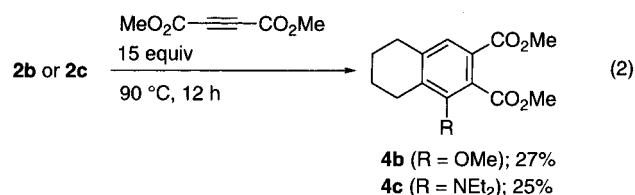
(13) Typical organic ethers exhibit C–O bond lengths of around 1.43 Å, while the C=O distances in ketones average about 1.22 Å: Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; p 108.

Scheme 2



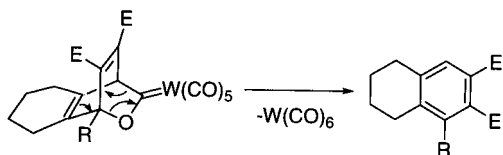
bonding in complex **2b**. ^{13}C NMR chemical shifts of carbene carbons of the complexes **2** were all observed in the higher field range of 220–235.4 ppm compared with those observed at 321–347 ppm for typical oxacarbene complexes.¹² These data strongly support the contribution of the resonance structures shown in Scheme 2.

The structure of **2b** represents a canonical form of α -pyrone. Therefore, we envisaged cycloaddition reactions of these pyranilidene complexes with dienophiles. The reaction of **2b** with an excess amount of dimethyl acetylenedicarboxylate (DMAD; 15 equiv) gave the tetralin derivative **4b** in 27% isolated yield (eq 2). The



use of solvent, i.e., toluene, did not positively affect the reaction, giving the product only in 9% yield. The carbene complex **2c** also reacted with DMAD to give the corresponding tetralin derivative **4c** in 25% yield. The transformation was explained by assuming a [4 + 2] cycloaddition reaction between **2** and the acetylene followed by a pericyclic demetalation of a tungsten hexacarbonyl (Scheme 3). The demetalation step is quite similar to the decarboxylation step in the [4 + 2] cycloaddition of α -pyrones.

Scheme 3



In conclusion, we have demonstrated that a nucleophilic attack of carbonyl oxygen at a vinylidene–metal intermediate, generated from terminal acetylenes and the group 6 metal carbonyls, provides new entry to a pyranilidene–metal complex. Further, we have disclosed the reactivity of newly prepared pyranilidene complexes in [4 + 2] cycloadditions. Considering the facile formation of a vinylidene–metal complex from a terminal alkyne and the regeneration of a metal hexacarbonyl with [4 + 2] cycloaddition, this reaction protocol will be applicable to catalytic reactions.

Experimental Section

General Procedures. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone–ketyl under argon. Analytical thin-layer chromatography (TLC) was per-

formed with silica gel 60 Merck F-254 plates. Column chromatography was performed with Merck silica gel 60. The NMR spectra were measured for solutions in CDCl_3 with Me_4Si as an internal standard (^1H and ^{13}C), and the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. IR spectra were recorded with an FT-IR spectrometer. Melting points are uncorrected. Elemental analyses were performed at the Microanalytical Center of Kyoto University. All new compounds **1** were prepared and fully characterized. Procedures for the preparation of **1** and the precursors of **1** are reported in the Supporting Information.

Typical Procedure for Synthesis of the Pyranilidene–Tungsten Complex **2**. Pyranilidene–Tungsten Complex **2a**.

A solution of $\text{W}(\text{CO})_6$ (0.53 g, 1.5 mmol) in THF (10 mL) under Ar was irradiated by an Hg lamp (350 nm) at room temperature for 4 h. To this yellow solution under Ar was added a solution of **1a** (75 mg, 0.50 mmol) in THF (1 mL) by a syringe. The solution was stirred at room temperature for 4 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (10:1 v/v) as an eluent to afford **2a** (0.18 g, 0.38 mmol, 75% yield) as a yellow solid: mp 106.1 °C dec; IR (KBr) 1909, 1957, 2058 cm^{-1} ; ^1H NMR (300 MHz, 25 °C) δ 2.10 (quint, $J = 7.8$ Hz, 2H), 2.75 (t, $J = 7.8$ Hz, 2H), 2.81 (t, $J = 7.8$ Hz, 2H), 4.30 (s, 3H), 7.61 (s, 1H); ^{13}C NMR (75 MHz, 25 °C) δ 23.8, 27.0, 33.8, 56.9, 114.4, 132.2, 166.0, 170.1, 199.1, 204.0, 235.4. Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{O}_7\text{W}$: C, 35.47; H, 2.13. Found: C, 36.39; H, 2.28. HRMS (FAB): calcd for $\text{C}_{14}\text{H}_{10}\text{O}_7\text{W}$ (M^+), 473.9933; found, 473.9938.

Pyranilidene–Tungsten Complex **2b.** The reaction was carried out in THF at reflux temperature for 0.5 h: yellow solid, 63% yield; mp 103.8–105.6 °C; IR (KBr) 1882, 1920, 1962, 2059 cm^{-1} ; ^1H NMR (300 MHz, 25 °C) δ 1.77–1.78 (m, 4H), 2.43–2.50 (m, 2H), 2.55–2.65 (m, 2H), 4.30 (s, 3H), 7.34 (s, 1H); ^{13}C NMR (75 MHz, 25 °C) δ 20.5, 21.1, 21.3, 29.2, 57.1, 109.3, 135.7, 157.1, 171.1, 199.2, 203.9, 228.1. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_7\text{W}$: C, 36.91; H, 2.48. Found: C, 36.82; H, 2.57.

Pyranilidene–Tungsten Complex **2c:** yellow solid, 68% yield; mp 99.0–101.8 °C; IR (KBr) 1881, 1894, 1922, 1964, 2053 cm^{-1} ; ^1H NMR (300 MHz, 25 °C) δ 1.35 (t, $J = 7.2$ Hz, 6H), 1.70–1.77 (m, 4H), 2.45–2.53 (m, 2H), 2.53–2.61 (m, 2H), 3.60 (q, $J = 7.2$ Hz, 4H), 6.97 (s, 1H); ^{13}C NMR (100 MHz, 25 °C) δ 13.7, 21.1, 22.6, 25.6, 29.6, 44.9, 109.4, 133.1, 153.1, 169.1, 199.7, 204.3, 220.0. Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_6\text{W}$: C, 40.85; H, 3.62; N, 2.65. Found: C, 41.10; H, 3.70; N, 2.64.

Pyranilidene–Tungsten Complex **2d:** yellow liquid, 55% yield; IR (neat) 1907, 1915, 1965, 2058 cm^{-1} ; ^1H NMR (300 MHz, 25 °C) δ 1.74–1.80 (m, 4H), 1.99 (quint, $J = 6.9$ Hz, 2H), 2.20–2.27 (m, 2H), 2.35–2.42 (m, 2H), 2.45–2.55 (m, 2H), 4.65 (t, $J = 6.9$ Hz, 2H), 5.02–5.09 (m, 2H), 5.75–5.88 (m, 1H), 7.31 (s, 1H); ^{13}C NMR (75 MHz, 25 °C) δ 20.6, 21.1, 21.3, 27.7, 29.1, 29.7, 70.2, 109.3, 116.1, 135.5, 136.5, 157.1, 170.8, 199.2, 204.0, 227.4. Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_7\text{W}$: C, 42.09; H, 3.35. Found: C, 43.50; H, 3.57. HRMS (FAB): calcd for $\text{C}_{19}\text{H}_{18}\text{O}_7\text{W}$ (M^+), 542.0562; found, 542.0554. (This complex is unstable to air and light to obtain the correct elemental analytical data.)

Pyranilidene–Tungsten Complex **2e:** yellow solid, 71% yield; mp 73.6–75.4 °C dec; IR (KBr) 1896, 1923, 1976, 2059, 2366 ($\text{C}\equiv\text{C}$) cm^{-1} ; ^1H NMR (300 MHz, 25 °C) δ 1.10 (t, $J = 7.6$ Hz, 3H), 1.78–1.79 (m, 4H), 2.15 (qt, $J = 2.6, 7.6$ Hz, 2H), 2.39–2.53 (m, 2H), 2.53–2.71 (m, 2H), 2.75 (tt, $J = 2.6, 6.2$ Hz, 2H), 4.69 (t, $J = 2.6$ Hz, 2H), 7.35 (s, 1H); ^{13}C NMR (75 MHz, 25 °C) δ 12.3, 13.9, 19.6, 20.5, 21.1, 21.3, 29.2, 68.7, 73.5, 84.5, 109.4, 135.8, 157.2, 170.6, 199.7, 203.9, 228.2. Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_7\text{W}$: C, 43.34; H, 3.27. Found: C, 43.26; H, 3.18.

Pyranilidene–Tungsten Complex **2f:** orange solid, 58% yield; mp 78.4–79.8 °C; IR (KBr) 1904, 1921, 1939, 1981, 2059 cm^{-1} ; ^1H NMR (400 MHz, 25 °C) δ 3.12 (t, $J = 6.8$ Hz, 2H), 4.77 (t, $J = 6.8$ Hz, 2H), 6.14 (d, $J = 8.0$ Hz, 1H), 7.10–7.30 (m, 6H), 7.56 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (75 MHz, 25 °C) δ

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 2b

Bond Lengths			
W(1)–C(1)	2.215(6)	W(1)–C(11)	2.023(8)
W(1)–C(12)	2.018(8)	W(1)–C(13)	2.042(8)
W(1)–C(14)	2.054(8)	W(1)–C(15)	2.021(7)
O(1)–C(1)	1.430(7)	O(1)–C(9)	1.321(7)
O(2)–C(9)	1.316(7)	O(2)–C(10)	1.448(9)
O(3)–C(11)	1.146(9)	O(4)–C(12)	1.153(9)
O(5)–C(13)	1.138(8)	O(6)–C(14)	1.136(9)
O(7)–C(15)	1.145(8)	C(1)–C(2)	1.362(9)
C(2)–C(3)	1.404(8)	C(3)–C(8)	1.383(8)
C(8)–C(9)	1.382(9)		
Bond Angles			
C(1)–W(1)–C(11)	89.4(3)	C(1)–W(1)–C(12)	92.8(3)
C(1)–W(1)–C(13)	88.5(3)	C(1)–W(1)–C(14)	87.8(3)
C(1)–W(1)–C(15)	177.1(3)	C(11)–W(1)–C(12)	86.4(3)
C(11)–W(1)–C(13)	177.9(3)	C(11)–W(1)–C(14)	90.3(3)
C(11)–W(1)–C(15)	92.5(3)	C(12)–W(1)–C(13)	93.3(3)
C(12)–W(1)–C(14)	176.7(3)	C(12)–W(1)–C(15)	89.6(3)
C(14)–W(1)–C(15)	90.0(3)	C(1)–O(1)–C(9)	123.0(5)
C(9)–O(2)–C(10)	119.5(6)	W(1)–C(1)–O(1)	113.8(4)
W(1)–C(1)–C(2)	133.2(5)	O(1)–C(1)–C(2)	112.9(5)
C(1)–C(2)–C(3)	124.5(6)	C(2)–C(3)–C(8)	120.1(6)
C(3)–C(8)–C(9)	115.6(6)	O(1)–C(9)–O(2)	115.8(6)
O(1)–C(9)–C(8)	123.8(5)	O(2)–C(9)–C(8)	120.3(6)
W(1)–C(11)–O(3)	178.1(8)	W(1)–C(12)–O(4)	176.7(6)
W(1)–C(13)–O(5)	177.4(6)	W(1)–C(14)–O(6)	179.3(7)
W(1)–C(15)–O(7)	178.7(7)		

35.0, 71.2, 98.5, 127.2, 128.8, 128.9, 135.3, 136.1, 142.4, 173.7, 198.7, 203.0, 242.3. Anal. Calcd for $C_{18}H_{12}O_7W$: C, 41.25; H, 2.31. Found: C, 40.76; H, 2.27. HRMS (FAB): calcd for $C_{18}H_{12}O_7W$ (M^+), 524.0096; found, 524.0078.

Synthesis of Pyranilidene–Molybdenum Complex 3b.

A solution of $Mo(CO)_6$ (82 mg, 0.31 mmol) in Et_2O (25 mL) and Et_3N (4 mL) under Ar was irradiated by an Hg lamp (350 nm) at room temperature for 1 h. A solution of **1b** (42 mg, 0.26 mmol) in Et_2O (1 mL) was added to this yellow solution. The mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/ $AcOEt$ (10:1 v/v) as an eluent to afford **3b** (35 mg, 0.090 mmol, 35% yield) as a yellow solid: mp 89.5–90.8 °C; IR (KBr) 1884, 1927, 1968, 2060 cm^{-1} ; 1H NMR (300 MHz, 25 °C) δ 1.76–1.79 (m, 4H), 2.42–2.46 (m, 2H), 2.58–2.62 (m, 2H), 4.31 (s, 3H), 7.30 (s, 1H); ^{13}C NMR (75 MHz, 25 °C) δ 20.5, 21.2, 21.3, 29.1, 56.9, 109.1, 134.7, 155.8, 171.5, 207.4, 213.6. Anal. Calcd for $C_{15}H_{12}O_7Mo$: C, 45.02; H, 3.02. Found: C, 44.54; H, 2.87. HRMS (FAB): calcd for $C_{15}H_{12}O_7Mo$ (M^+), 401.9637; found, 401.9644.

X-ray Crystallography of 2b. Yellow prismatic crystals were obtained from a hexane solution at 23 °C. A crystal of dimensions 0.20 × 0.20 × 0.20 mm was mounted on a glass fiber. Bond lengths and bond angles are given in Table 2. Main features of the refinement appear in Table 3. The intensity data were measured on a Rigaku AFC-7R four-circle automated diffractometer with $Mo\ K\alpha$ radiation and a graphite monochromator at 23 °C using the ω –2 θ scan technique. The structure was solved by direct methods (SIR92)¹⁴ and expanded using Fourier techniques. All the calculations were performed using the teXsan crystallographic software package. The final cycle of full-matrix least-squares refinement was based on 3142 observed reflections ($I > 3.00\sigma(I)$) and 220 variable parameters and gave $R = 0.031$ and $R_w = 0.034$. The value of the goodness-of-fit indicator was 3.07. Lorentz and polarization corrections and secondary extinction were applied for the structure.

(14) Altomare, A.; Casciarano, G.; Giacovazzo, C.; Guagliardi, A. J. *Appl. Crystallogr.* **1993**, *26*, 343.

Table 3. Summary of Crystallographic Data of 2b

empirical formula	$C_{15}H_{12}O_7W$
fw	488.11
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
cryst color	yellow
lattice params	
<i>a</i> (Å)	16.141(6)
<i>b</i> (Å)	5.909(6)
<i>c</i> (Å)	18.592(5)
β (°)	114.17(2)
<i>V</i> (Å ³)	1617(1)
<i>Z</i>	4
<i>D</i> _{calcd} (g cm ^{−3})	2.004
μ ($Mo\ K\alpha$) (cm ^{−1})	71.80
<i>F</i> (000)	928
diffractometer	Rigaku AFC7R
radiation	$Mo\ K\alpha$ ($\lambda = 0.71069$ Å), graphite monochromated
temp (°C)	23.0
scan type	ω –2 θ
max 2 θ (deg)	55
no. of rflns measd	total, 1280; unique, 1239 ($R_{int} = 0.045$)
no. of observns ($I > 3.00\sigma(I)$)	3142
structure soln	direct methods (SIR92)
refinement	full-matrix least squares
no. of variables	220
rfln/param ratio	14.28
residuals: <i>R</i> ; <i>R</i> _w	0.031; 0.034
goodness of fit (GOF)	3.07
max shift/error in final cycle	0.03
max peak in final diff map (e Å ^{−3})	1.21
min peak in final diff map (e Å ^{−3})	−1.82

Typical Procedure for [4 + 2] Cycloaddition of 2 with Acetylene. Dimethyl 5,6,7,8-Tetrahydro-1-methoxy-2,3-naphthalenedicarboxylate (4b). A mixture of complex **2b** (0.15 g, 0.30 mmol) and dimethyl acetylenedicarboxylate (0.55 mL, 4.5 mmol) in a sealed tube was stirred at 90 °C for 12 h under N_2 . The mixture was subjected to column chromatography on SiO_2 with hexane/ $AcOEt$ (10:1 v/v) as an eluent to afford **4b** (22 mg, 0.080 mmol, 27% yield) as a colorless liquid: IR (neat) 791, 1042, 1146, 1274, 1294, 1328, 1727 (C=O), 1738 (C=O), 2861, 2947, 3430 cm^{-1} ; 1H NMR (300 MHz, 25 °C) δ 1.77–1.84 (m, 4H), 2.74–2.82 (m, 4H), 3.79 (s, 3H), 3.86 (s, 3H), 3.94 (s, 3H), 7.52 (s, 1H); ^{13}C NMR (75 MHz, 25 °C): δ 22.2, 22.4, 23.7, 29.3, 52.3, 52.6, 61.7, 125.3, 126.6, 127.2, 136.9, 140.4, 155.0, 165.8, 168.4. Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.79; H, 6.64.

Dimethyl 1-(Diethylamino)-5,6,7,8-tetrahydro-2,3-naphthalenedicarboxylate (4c): yellow liquid, 25% yield; IR (neat) 1141, 1277, 1731 (C=O), 1738 (C=O), 1916, 2341, 2360, 2859, 2933, 3436 cm^{-1} ; 1H NMR (300 MHz, 25 °C) δ 1.00 (t, *J* = 7.2 Hz, 6H), 1.72–1.82 (m, 4H), 2.65–2.75 (m, 2H), 2.75–2.86 (m, 2H), 2.90–3.12 (m, 4H), 3.85 (s, 3H), 3.89 (s, 3H), 7.57 (s, 1H); ^{13}C NMR (75 MHz, 25 °C) δ 14.4, 22.4, 22.6, 26.6, 29.6, 47.4, 52.1, 52.2, 124.7, 128.1, 134.9, 139.4, 144.2, 146.8, 166.2, 169.8. Anal. Calcd for $C_{18}H_{25}NO_4$: C, 67.69; H, 7.89; N, 4.39. Found: C, 67.67; H, 7.86; N, 4.30.

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Supporting Information Available: Text giving synthesis details and characterization data for precursors of **1** and tables of all X-ray crystal data, refinement parameters, atomic coordinates, and bond distances and angles for **2b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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