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

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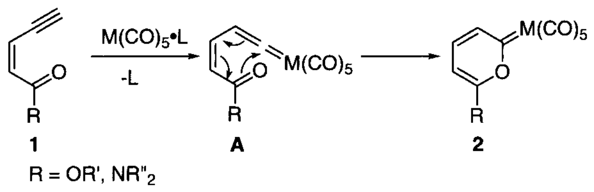
Summary: The reaction of conjugated enyne−carbonyl compounds such as 1-(alkoxycarbonyl)-2-ethynylcycloalkenes and 1-carbamoyl-2-ethynylcycloalkenes with $Mo(CO)_5 \cdot NEt_3$ *and* $W(CO)_5 \cdot THF$ *gave the corresponding 6-alkoxy- and 6-amino-2H-pyranylidene−molybdenum and −tungsten complexes, respectively. 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.*

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 (M=C(OR′)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 ($M{=}C_\alpha{=}C_\beta$, 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 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.

Scheme 1



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[1] Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994; p 151.

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

[3] For leading references, see: (a) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326. (b) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895. (c) Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1986**, 514. (d) Dötz, K. H.; Sturm, W.; Alt, H. G. *Organometallics* **1987**, *6*, 1424. (e) McDonald, F. E.; Connolly, C. B.; Gleason, M. M.; Towne, T. B.; Treiber, K. D. *J. Org. Chem.* **1993**, *58*, 6952. (f) Quayle, P.; Rahman, S.; Ward, E. L. M.; Herbert, J. *Tetrahedron Lett.* **1994**, *35*, 3801. (g) McDonald, F. E.; Gleason, M. M. *J. Am. Chem. Soc.* **1996**, *118*, 6648. (h) Schmidt, B.; Kocienski, P.; Reid, G. *Tetrahedron* **1996**, *52*, 1617. (i) Bernasconi, C. F. *Chem. Soc. Rev.* **1997**, *26*, 299. (j) McDonald, F. E.; Zhu, H. Y. H. *J. Am. Chem. Soc.* **1998**, *120*, 4246. (k) McDonald, F. E.; Reddy, K. S.; Díaz, Y. *J. Am. Chem. Soc.* **2000**, *122*, 4304.

[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) Bruneauu, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311.

[5] For leading references dealing with transformation of vinylidene−metal intermediates in conjugate systems, see: (a) Wang, Y.; Finn, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 8045. (b) Ohe, K.; Kojima, M.; Yonehara, K.; Uemura, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1823. (c) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319. (d) Manabe, T.; Yanagi, S.; Ohe, K.; Uemura, S. *Organometallics* **1998**, *17*, 2942. (e) Maeyama, K.; Iwasawa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1928. (f) Maeyama, K.; Iwasawa, N. *J. Org. Chem.* **1999**, *64*, 1344.

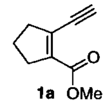
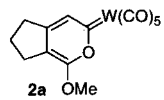
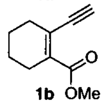
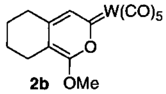
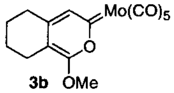
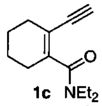
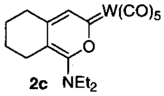
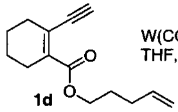
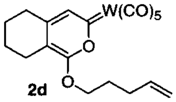
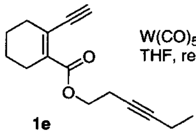
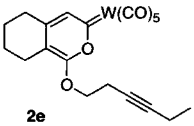
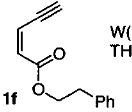
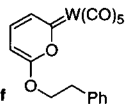
[6] For reviews, see: (a) Afarinkia, K.; Vinader, V.; Nelson, T. D.; Posner, G. H. *Tetrahedron* **1992**, *48*, 9111. (b) Woodard, B. T.; Posner, G. H. *Advances in Cycloaddition*; JAI: Greenwich, CT, 1999; Vol. 5, p 47.

[7] Moretó reported that the reaction of diethoxyacrylate with alkynylalkoxycarbene−metal complexes eventually leads to 6-ethoxy-2*H*-pyranylidene−chromium and −tungsten carbene complexes; see: Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Molins, E.; Miravitlles, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1560. Jordi, L.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Molins, E.; Miravitlles, 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.

10.1021/om0006763 CCC: $19.00

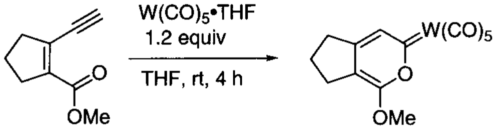
Table 1. Preparation of Pyranylidene−Metal Complexes from Conjugated Enyne−Carbonyls and the Group 6 Metals[a]

entry	1	conditions[b]	product	isolated yield
1	 **1a**	W(CO)$_5$•THF (1.2 equiv) THF, rt, 4 h	 **2a**	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	 **1b**	W(CO)$_5$•THF (2.0 equiv) THF, reflux, 0.5 h	 **2b**	63%
5	**1b**	Mo(CO)$_5$•NEt$_3$ (1.2 equiv) Et$_2$O, Et$_3$N, rt, 3 h	 **3b**	35%
6	 **1c**	W(CO)$_5$•THF (3.0 equiv) THF, reflux, 0.5 h	 **2c**	68%
7	 **1d**	W(CO)$_5$•THF (3.0 equiv) THF, reflux, 0.5 h	 **2d**	55%
8	 **1e**	W(CO)$_5$•THF (2.0 equiv) THF, reflux, 0.5 h	 **2e**	71%
9	 **1f**	W(CO)$_5$•THF (3.0 equiv) THF, reflux, 0.5 h	 **2f**	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 Et$_2$O 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)$_5$·THF[10] 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 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)$_5$·NEt$_3$[11] (entry 5), while the reaction with the chromium complex Cr(CO)$_5$·NEt$_3$[11] 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).



1a **2a** (38%) (1)

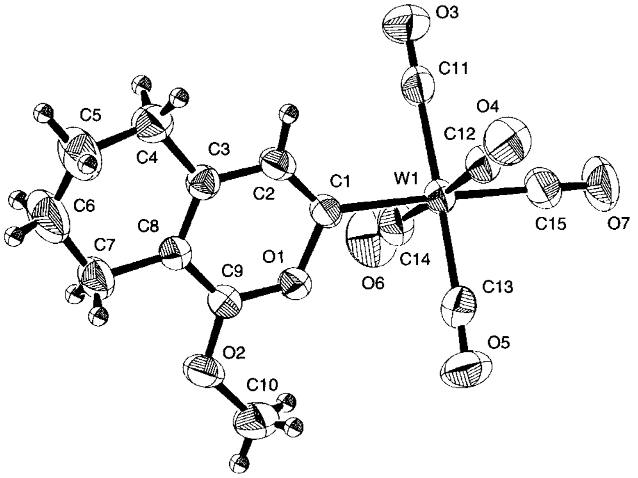


Figure 1. ORTEP drawing of the complex **2b**.

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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(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.

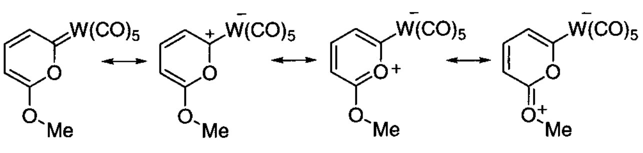
(10) Strohmeier, W.; Gerlach, K. *Chem. Ber.* **1961**, *94*, 398.

(11) (a) Wrighton, M. *Chem. Rev.* **1974**, *74*, 401. (b) McDonald, F. E.; Schultz, C. C. *J. Am. Chem. Soc.* **1994**, *116*, 9363.

(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.

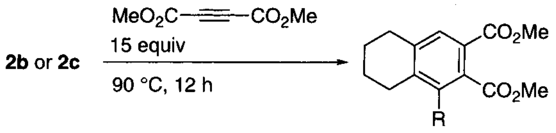
Scheme 2



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 oxa-carbene complexes.[12] These data strongly support the contribution of the resonance structures shown in Scheme 2.

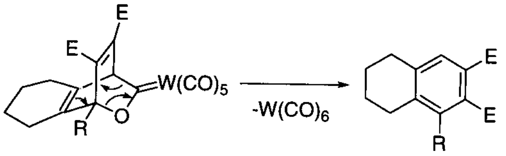
The structure of **2b** represents a canonical form of α-pyrone. Therefore, we envisaged cycloaddition reactions of these pyranylidene complexes with dienophiles. The reaction of **2b** with an excess amount of dimethyl acetylenedicarboxylate (DMAD; 15 equiv) gave the tetralin derivative **4b** in 27%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



(2)

4b (R = OMe); 27%
4c (R = NEt$_2$); 25%

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 pyranylidene−metal complex. Further, we have disclosed the reactivity of newly prepared pyranylidene 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 performed 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 Pyranylidene−Tungsten Complex 2. Pyranylidene−Tungsten Complex 2a. A solution of $W(CO)_6$ (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 $C_{14}H_{10}O_7W$: C, 35.47; H, 2.13. Found: C, 36.39; H, 2.28. HRMS (FAB): calcd for $C_{14}H_{10}O_7W$ (M^+), 473.9933; found, 473.9938.

Pyranylidene−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 $C_{15}H_{12}O_7W$: C, 36.91; H, 2.48. Found: C, 36.82; H, 2.57.

Pyranylidene−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 $C_{18}H_{19}NO_6W$: C, 40.85; H, 3.62; N, 2.65. Found: C, 41.10; H, 3.70; N, 2.64.

Pyranylidene−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 $C_{19}H_{18}O_7W$: C, 42.09; H, 3.35. Found: C, 43.50; H, 3.57. HRMS (FAB): calcd for $C_{19}H_{18}O_7W$ (M^+), 542.0562; found, 542.0554. (This complex is unstable to air and light to obtain the correct elemental analytical data.)

Pyranylidene−Tungsten Complex 2e: yellow solid, 71% yield; mp 73.6−75.4 °C dec; IR (KBr) 1896, 1923, 1976, 2059, 2366 (C≡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 $C_{20}H_{18}O_7W$: C, 43.34; H, 3.27. Found: C, 43.26; H, 3.18.

Pyranylidene−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 Pyranylidene−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 Kα radiation and a graphite monochromator at 23 °C using the $\omega-2\theta$ 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.

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	
a (Å)	16.141(6)
b (Å)	5.909(6)
c (Å)	18.592(5)
β (Å)	114.17(2)
V (Å^3)	1617(1)
Z	4
D_{calcd} (g cm^{-3})	2.004
μ(Mo Kα) (cm^{-1})	71.80
F(000)	928
diffractometer	Rigaku AFC7R
radiation	MoKα ($\lambda = 0.71069$ Å), graphite monochromated
temp (°C)	23.0
scan type	$\omega-2\theta$
max 2θ (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: R; R_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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(14) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.