3566 *Organometallics* **1999,** *18,* 3566−3568

Addition of Aromatic C−H Bonds to Terminal Metal−Carbonyl Groups. A New Method for Cyclocarbonylation of Aromatic Groups

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Received May 11, 1999

Summary: Treatment of $CpW(CO)_3[\eta^1\text{-}CH_2C{\equiv}C(CH_2)_n\text{-}Ar]$ *(*$n = 0-1$*) with triflic acid catalysts (25 mol %) in cold* CH_2Cl_2 *(−95 °C) effects a new cyclocarbonylation reaction to give* $CpW(CO)_2$*(π-cyclopentenonyl) and* $CpW(CO)_2$*(π-cyclohexenonyl) compounds; these results provide direct evidence for addition of neutral aryl C−H bonds to coordinated carbonyl groups.*

Substitutive carbonylation of the aryl C−H bond to form an aryl ketone group is a useful reaction in organic synthesis.[1] Such syntheses are generally carried out through treatment of aromatic compounds with carboxylic acid derivatives in the presence of acid catalysts (Friedel−Crafts acylation) as shown in Scheme 1 (eq 1).[1] Intramolecular Friedel−Crafts reaction is an important tool for the syntheses of natural pericyclic ketones.[2] Nucleophilic attack of a metal-coordinated carbonyl group is an important step in metal-mediated organic syntheses.[3,4] Although this synthetic method covers a wide range of nucleophiles,[3,4] to our best knowledge, there is no precedent for attack of a neutral aryl group at a metal−carbonyl ligand to effect a substitutive carbonylation (Scheme 1, eq 2). A cationic metal−carbonyl group may serve as a good candidate to realize this carbonylation reaction because its structure resembles the intermediate in Friedel−Crafts reaction. We report here a new cyclocarbonylation for propargyltungsten compounds having a tethered aryl group. These cyclizations show the feasibility for addition of aryl C−H bonds at coordinated carbonyl groups.

As shown in Scheme 2, alkynyltungsten compound **2** was conveniently prepared from the corresponding propargyl tosylate **1** and $CpW(CO)_3Na$ in 80% yield.[5] Treatment of compound **2** with triflic acid (25 mol %) in cold CH_2Cl_2 (−95 °C) gave tungsten−π-allyl compound **3a** and **3b** in 40% and 32% yields, respectively, after separation from a silica column. The molecular structure[6] of **3b** shows that the molecule has a cyclopentenone fragment fused with a phenyl ring, and the $CpW(CO)_2$ fragment is bound to the ketone ring in a metal−π-allyl fashion. This information indicates that the aryl C−H bond of compound **2** is cleaved and inserted by a CO group to effect a substitutive carbonylation. We also examined the same operation on alkynyltungsten complex **4** (triflic acid, 0.25 equiv, −95 °C) to give two cyclohexenonyl derivatives, **5a** and **5b**, in 21% and 24% yields, respectively, after separation on a silica column. The molecular structures of **5a** and **5b**[7,8] are also elucidated by X-ray diffraction studies to confirm the formation of a tungsten−π-cyclohexenonyl complex.

We also prepared various alkynyltungsten compounds **6**−**11** tethered with an aromatic group to generalize the cyclizations; the yields in Table 1 are estimated after separation on a silica column. Cyclocarbonylation of these alkynyl compounds **6**−**11** follows the same reaction sequence involving the use of triflic acid catalyst (0.25 equiv) in cold CH_2Cl_2 (−95 °C). Entry 1 shows an intramolecular carbonylation of a tethered 2,5-dimethoxyphenyl group to yield the tungsten−π-cyclopentenonyl complex **12** in 55% yield. The same reaction sequence on compound **7** gave a 44% yield of π-cyclohexenonyl complex **13**, as shown in entry 2. Similarly, treatment of alkynyltungsten species **8** and **9** with triflic acid catalysts (0.25 equiv) gave the cyclocarbonylation products **14** and **15** in 52% and 45% yields, respectively.

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(1) (a) Friedel. C.; Crafts, J. M. *Compt. Rend.* **1877**, *84*, 1392. (b) Olah, G. A. *Friedel−Crafts Chemistry*; Wiley: New York, 1973; p 40.

(2) (a) Reddy, P. A.; Krishna-Rao, G. S. *J. Chem Soc., Perkin Trans. 1* **1974**, 450. (b) Katsui, N.; Matsunaga, A.; Imaizumi, K.; Masamune, T.; Tomiyama, K. *Tetrahedron Lett.* **1971**, 83. (c) McCombie, S. W.; Shankar, B. B.; Ganguly, A. K. *Tetrahedron Lett.* **1987**, *28*, 4123.

(3) Bates, R. W. In *Comprehensive Organometallic Chemistry, Vol 12: Transition Metal Organometallics In Organic Synthesis*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Chapter 4, p 349.

(4) Collman, J. P., Hegedus, L. S., Norton, J. R., Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 7, p 403.

(5) (a) Bell, P. B.; Wojcicki, A. *Inorg. Chem.* **1981,** *20*, 1585. (b) Wang, S.-H.; Shiu, L.-H.; Liao, Y.-L.; Wang, S.-L..; Lee, G.-H., Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1996,** 118, 530. (c) Madhushaw, R. J.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics*, **1999**, *18*, 748.

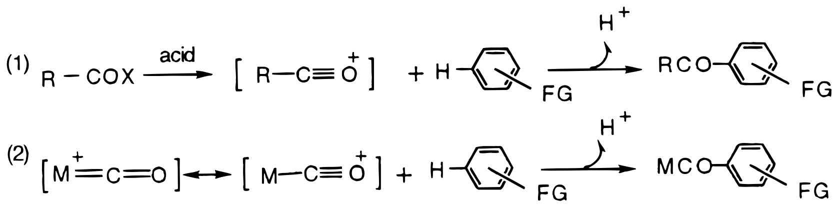
(6) Compound **3b** crystallizes in the monoclinic space group $C2/c$, $a = 27.2181(8)$ Å, $b = 8.7445(2)$ Å, $c = 15.1753(4)$ Å, $\beta = 121.192(2)°$, $V = 3089.7(8)$ Å^3, $Z = 8$. Data were collected on a Siemens Smart-CCD diffractometer, using Mo Kα radiation. Final $R = 0.0264$, $R_w = 0.0294$ for 2768 reflections $> 3\sigma(I)$ out of 3346 unique reflections.

(7) Compound **5a** crystallizes in the monoclinic space group $P2_1/c$, $a = 7.4008(4)$ Å, $b = 17.8675(9)$ Å, $c = 12.3853(6)$ Å, $\beta = 90.591(1)°$, $V = 1637.7(5)$ Å^3, $Z = 4$. Data were collected on a Siemens Smart-CCD diffractometer, using Mo Kα radiation. Final $R = 0.0262$, $R_w = 0.0255$ for 2586 reflections $> 3.0\sigma(I)$ out of 3613 unique reflections.

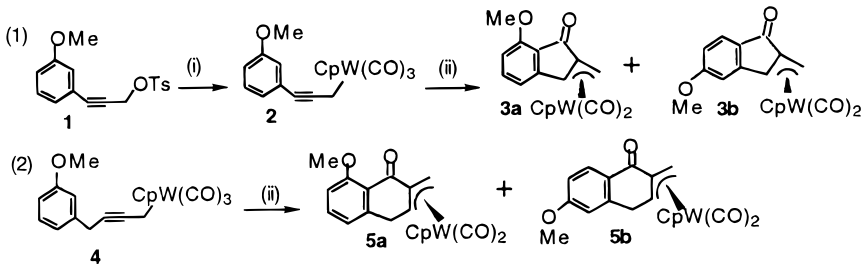
(8) Compound **5b** crystallizes in the triclinic space group $P\bar{1}$, $a = 7.9912(2)$ Å, $b = 8.2813(2)$ Å, $c = 12.4342(3)$ Å, $\alpha = 82.061(0)°$, $\beta = 85.265(1)°$, $\gamma = 89.076(1)°$, $V = 812.2(3)$ Å^3, $Z = 2$. Data were collected on a Siemens Smart-CCD diffractometer, using Mo Kα radiation. Final $R = 0.0323$, $R_w = 0.0304$ for 2498 reflections $> 3.0\sigma(I)$ out of 3496 unique reflections.

10.1021/om990352i CCC: $18.00

Scheme 1

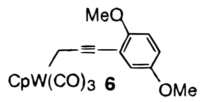
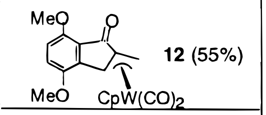
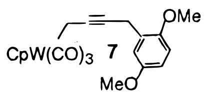
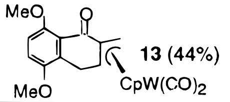
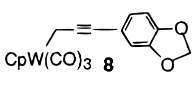
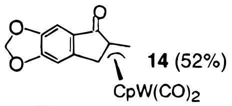
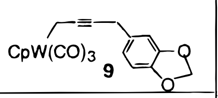
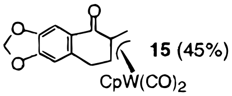
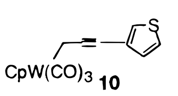
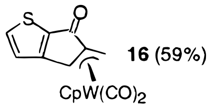
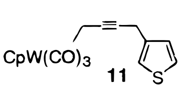
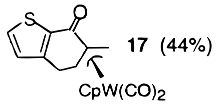


Scheme 2

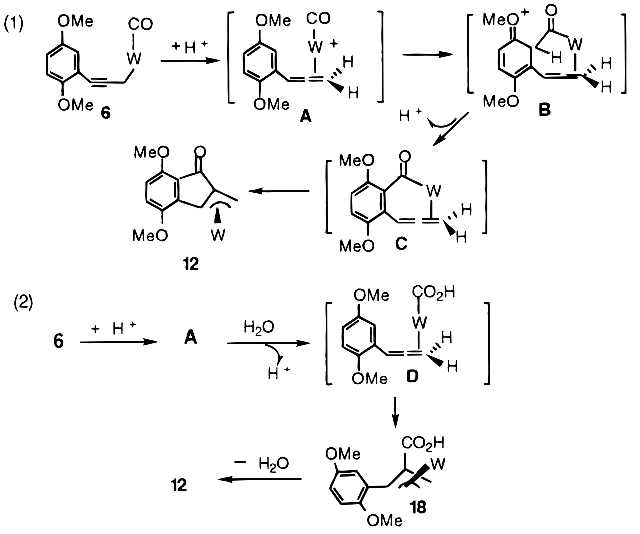


Condition (i) NaCpW(CO)$_3$, THF, 25°C, 10 hr (ii) CF$_3$SO$_3$H (25 mol %),.CH$_2$Cl$_2$, - 95°C, 2h

Table 1. Acid-Catalyzed Cyclocarbonylation Reaction

Entry 1	Alkynyl Compounds	Products
1	 6	 12 (55%)
2	 7	 13 (44%)
3	 8	 14 (52%)
4	 9	 15 (45%)
5	 10	 16 (59%)
6	 11	 17 (44%)

Scheme 3



The heterocyclic thiophenes of compounds **10** and **11** can also be carbonylated intramolecularly, as shown in entries 5 and 6, and the yields of the cyclocarbonyltion products **16** and **17** were 59% and 44% yields, respectively. The observed products **16** and **17** are consistent with our expectation because the thienyl C$_2$-carbon is generally more reactive toward electrophiles than its C$_3$-carbon. The conjugated effect of the sulfur atom is responsible for this effect. For **14** and **15**, the absence of the ortho-carbonylation product is probably due to its more congested structure compared to its para-carbonylation product.

The results shown in Scheme 2 and Table 1 clearly demonstrate a substitutive carbonylation for the C–H bonds of various aromatic compounds. Two possible mechanisms are shown in Scheme 3. Previously, Rosenblum reported[9] that protonation of propargylmetal compounds yielded metal–η^2-cis-allene cation[10] **A** as the kinetically favorable intermediate. This cis-configuration of **A** is very important because it allows intramolecular attack of its tethered 2,5-dimethoxybenzene group at the coordinated CO group to effect an electrophilic substitution, yielding species **B** and **C** sequentially. Further insertion of the η^1-acyl group of **C** gave the observed product **12**. An alternative mechanism involves a conventional electrophilic attack of a syn-π-allylic acid **18** at its tethered 2,5-dimethoxy benzene as shown in eq 2. The species **18** can be generated from the intermediate **D** via attack of H$_2$O at the tungsten–cis-allene cation **A**;[5c] commercial triflic acid normally contains a small amount of H$_2$O that may furnish such a catalytic cyclocarbonylation.

We therefore prepared the tungsten–π-allyl complex **18** in a separate experiment. Compound **6** was treated with triflic acid (1.0 equiv) in anhydrous diethyl ether

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(9) Rosenblum, M.; Raghu, S. *J. Am. Chem. Soc.* **1973**, *95*, 3062.

(10) (a) Memour, J. Y.; Charrier, C,; Benaim, J.; Roustan, J. L. *J. Organomet. Chem.* **1972**, *39*, 321. (b) Vinson, N. A.; Day, C. S.; Welker, M. E.; Guzei, I.; Rheingold, A. L. *Organometallics* **1999**, *18*, 1824.

at −95 °C for 2 h to yield a dark yellow precipitate, presumably the η^2-allene cation **A**. Subsequent treatment of this salt with an aqueous Na_2CO_3 solution afforded the expected acid **18** in 61% yield. The structure of **18** was confirmed by X-ray diffraction studies.[11] Treatment of compound **18** with CF_3SO_3H (1.0 equiv) in CH_2Cl_2 over various temperatures (−95 t*o* 23 °C) for 24 h did not give the desired product **12** at all, and in this case compound **18** was recovered in significant amount (50−71% yields). This information supports a direct attack of the aryl C−H bond at the coordinated CO group of species **A**.

In a summary, we have shown a new intramolecular cyclization via treatment of various alkynyltungsten compounds with a triflic acid catalyst. The key step of this cyclization is proposed to involve addition of the tethered aryl C−H bond of a cis-η^2-allene species **A** at its coordinated CO group. This cyclization is a useful tool in organic synthesis because the resulting tungsten−π-allyl compounds have chemical versatilities in organic syntheses.[12]

Acknowledgment. We gratefully acknowledge financial support of this work from the National Science Council, Republic of China.

Supporting Information Available: Tables of crystal data, atomic coordinates, bond distances and angles, and thermal parameters of compounds **3a, 5a, 5b**, and **18** This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] Compound **18** crystallizes in the monoclinic space group $P2_1/n$, $a = 12.6211(2)$ Å, $b = 8.9088(2)$ Å, $c = 17.3164(5)$ Å, $\beta = 95.180(2)°$, $V = 1939.1(6)$ Å^3, $Z = 4$. Data were collected on a Siemens Smart-CCD diffractometer, using Mo Kα radiation. Final $R = 0.0429$, $R_w = 0.0419$ for 2148 reflections > $3.0\sigma(I)$ out of 3496 unique reflections.

[12] Liu, R.-S. In *Advances in Metal-Organic Chemistry;* Liebeskind, L. S., Ed.; JAI Press: London, 1998; Vol 5, pp 145−187.