Available online at www.sciencedirect.com

ScienceDirect

Tetrahedron Letters 47 (2006) 6569–6572

Tetrahedron Letters

Microwave-assisted synthesis of (η^6-arene)tricarbonylchromium complexes

Young Tak Lee,[a] Soo Young Choi,[a] Sang Ick Lee,[a]
Young Keun Chung[a,*] and Tae Jin Kang[b]

[a]*Intellectual Textile System Research Center, and Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Republic of Korea*
[b]*Intellectual Textile System Research Center, and School of Materials Science and Engineering, Seoul National University, Seoul, Republic of Korea*

Received 20 June 2006; revised 4 July 2006; accepted 6 July 2006
Available online 31 July 2006

Abstract—We have undertaken a study of the microwave-assisted synthesis of (η^6-arene)tricarbonylchromium complexes. Under microwave irradiation, the reactions of hexacarbonylchromium with arenes gave high yields of (η^6-arene)chromium tricarbonyl complexes.

For the last three decades, an extensive exploration of (η^6-arene)chromium carbonyl complexes has been carried out.[1] One of the stumbling blocks in the study of (η^6-arene)chromium carbonyl complexes is their synthesis. In many cases, a lengthy reaction time is required and the yields are not high enough. The greatest limitation to the thermal synthesis of (η^6-arene)tricarbonylchromium compounds is the high temperatures and long reaction times required. For this reason, many useful complexation reagents have been developed to overcome these difficulties. For example, the development of complexation reagents such as [(η^6-naphthalene)$Cr(CO)_3$],[2] [$(pyridine)_3Cr(CO)_3$],[3] [$(NH_3)_3Cr(CO)_3$],[4] and [$(CH_3CN)_3Cr(CO)_3$][5] has been reported. Although these complexation reagents are reliable, the overall process requires a step involving derivatization of chromium hexacarbonyl followed by its transformation into the complexation reagents. Atom and step economy would be greatly improved if a direct reaction between the arene and chromium hexacarbonyl could be developed.

Recently, microwave radiation has been widely used as a source of energy.[6] When microwaves are used as a source of energy, the reaction time can be shortened and, in some cases, much higher yields than those obtained in the conventional thermal reactions have been achieved. The yield of microwave-assisted reactions can be affected by several factors, such as the reaction medium, the rate of heating, and so on. Recently, a paper describing the use of microwaves in the synthesis of (η^6-arene)tricarbonylchromium compounds has been published.[7] However, they were unable to solve the problems of the lengthy reaction time and poor yields, presumably due to their inappropriate choice of the reaction medium (diglyme/THF).

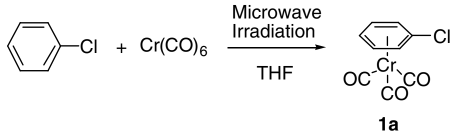
While we were studying the microwave-assisted synthesis of η^6-(arene)tricarbonylchromium compounds using chromium Fischer carbonyl compounds as a source of chromium carbonyl,[8] we found that chromium hexacarbonyl was obtained as a byproduct. Thus, although we were indisposed to use this method due to the conclusion of the recent paper,[7] we decided to proceed. Fortunately, the use of THF as a reaction solvent highly improved the yield of the reaction. Moreover, the use of chromium hexacarbonyl in the microwave-assisted synthesis of (η^6-arene)tricarbonylchromium compounds in THF provided a reasonable to high yield of (η^6-arene)tricarbonylchromium compounds. The yields obtained are sometimes comparable to those obtained in the conventional prolonged thermal reactions. Herein we report our preliminary results.

---

* Corresponding author. Tel.: +82 2 880 6662; fax: +82 2 889 0310; e-mail: ykchung@plaza.snu.ac.kr

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.07.011

Table 1. Screening the reaction conditions[a]



1a (1)

Entry	Temperature (°C)	Time (h)	Yield (%)[b]
1	130	0.5	12
2	140	0.5	15
3	150	0.5	25
4	160	0.5	35
5	160	1	46
6	160	1.5	62

[a] Chlorobenzene (1.0 mL) and THF (1.0 mL) used.

[b] Isolated yield.

In the beginning, we studied the microwave-assisted complexation of chlorobenzene. When a solution of $Cr(CO)_6$ (0.1 g, 0.45 mmol) in ClC_6H_5 (1.0 mL) and THF (1.0 mL) was heated at 130 °C under microwave irradiation for 30 min, a poor yield of [(η^6-chlorobenzene)$Cr(CO)_3$](**1a**) was obtained (Eq. 1). Therefore, we screened the reaction conditions in order to obtain a higher yield (Table 1). As the reaction temperature and time increased, the yield increased and the best (62%) was obtained at 160°C for a 1.5 h reaction time. The yield was quite close to that (64%) obtained in the thermal reaction.[9] It has been known[10] that the synthesis of [(η^6-haloarene)$Cr(CO)_3$] derivatives in refluxing Bu_2O frequently resulted in the hydro-dehalogenation and the formation of (benzene)tricarbonylchromium, which was difficult to separate from the desired product. However, no arene byproducts were observed. When the reaction temperature increased to 170 °C, it resulted in the explosion of the reaction mixture. The reaction time was quite long compared to other microwave-assisted reactions, presumably due to the insolubility of chromium hexacarbonyl in chlorobenzene/THF. The best yield (99%) had been described by McCarthy et al. two decades ago.[11] However, they had to heat the reaction mixture at reflux for four days.

Table 2. Complexation of various arenes[a]

Entry	Arene	THF (mL)	Bu_2O (mL)	Yield (%)[b]
1[c]	Benzene	0.5	1	59 (**1b**)
2	Anisole	1	—	77 (**1c**)
3	Toluene	1	—	79 (**1d**)
4	Mesitylene	1	—	79 (**1e**)
5	Acetophenone	1	—	70 (**1f**)
6	Propiophenone	1	—	61 (**1g**)
7	Methylbenzoate	1	—	53 (**1h**)
8[d]	*N*,*N*-Dimethylaniline	1	—	71 (**1i**)
9	α-Tetralone	1	—	66 (**1j**)
10[e]	Fluorene	1	1	70 (**1k**)
11[f]	Biphenyl	0.8	1	48 (**1l**)
12[g]	2,2′-Methoxybiphenyl	1	1	68 (**1m**)
13[h]	**2**	1	1	78 (**1n**)

[a] Reaction conditions: arene (1.0 mL), 160 °C, and 1 h.

[b] Isolated yield.

[c] 0.5 mL of benzene used.

[d] Reaction time: 0.5 h.

[e] 91 mg of fluorine used.

[f] 84 mg of biphenyl used.

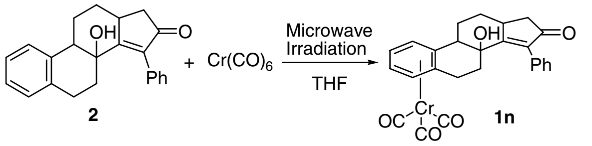
[g] 117 mg of 2,2′-dimethoxybiphenyl used.

[h] 50 mg of steroid-like compound (**2**) used.

We next investigated the microwave-assisted complexation of other aromatic compounds (Table 2).[12] A variety of arenes could be used in the microwave-assisted synthesis of [(η^6-arene)$Cr(CO)_3$]. When benzene was complexed with $Cr(CO)_6$ for 1 h, the expected chromium compound (**1b**) was obtained in 59% (entry 1). For this reaction, a mixed solvent system of benzene/THF/dibutyl ether (0.5 mL:0.5 mL:1.0 mL) was used because of the low boiling points of benzene and THF. In the conventional thermal synthesis, the yield of **1b** was 89%. Various synthetic methods have been devised and used. For example, Bicketlhaupt et al.[13] reported a medium pressure mercury lamp-irradiation of a stirred suspension of arene and $Cr(CO)_6$ in THF for 40 h at room temperature. However, they obtained **1b** in 50% yield. Toma et al.[14] reported a complexation of arene with $Cr(CO)_6$ in the presence of butyl acetate in refluxing decalin using a special apparatus. After refluxing for 5 h, they isolated **1b** in 93% yield. Treatment of anisole with $Cr(CO)_6$ at 160 °C under microwave irradiation for 1 h gave [(η^6-anisole)-$Cr(CO)_3$](**1c**) in 77% yield (entry 2). Recently, Hogarth et al. reported[7] a microwave-assisted synthesis of **1c** from the reaction of anisole with $Cr(CO)_6$ in diglyme and THF. After irradiation of microwaves for 4 h, they obtained **1c** in 45% yield. The difference between these processes was the reaction medium. Thus, this study has been demonstrated that the choice of the reaction medium is very important in microwave-assisted reactions. In the conventional thermal reaction over 24 h, Pauson et al.[15] obtained a pure **1c** in 80%. Arenes such as mesitylene, acetophenone, propiophenone, methylbenzoate, *N*,*N*-dimethylaniline, and α-tetralone were good substrates in the microwave-assisted synthesis of [(η^6-arene)$Cr(CO)_3$] complexes. Yields were 53–71% (entries 3–9). It is noteworthy that the reaction of mesitylene with chromium hexacarbonyl in diglyme under microwave irradiation did not yield any product.[7] In the cases of propiophenone and methyl benzoate, a prolonged irradiation (1.5 h) did not significantly increase the yield.

When solid arenes such as fluorine, biphenyl, and 2,2′-dimethoxybiphenyl were complexed, a mixture of THF and dibutyl ether was used as a solvent (entries 10–12). There were two possible reaction products- mono- or bis-chromium carbonyl compound. In fact, monochromium tricarbonyl compounds were obtained as the sole product with 48–70% yields. The structure of [(2,2′-dimethoxybiphenyl)$Cr(CO)_6$] (**1m**) was confirmed by an X-ray diffraction study (Fig. 1).[16]

When the new method for the synthesis of tricarbonylchromium complexes of arenes was applied to the synthesis of a tricarbonylchromium complex of a steroid-like compound (**2**) (entry 13),[16] the expected chromium compound was isolated in 78% (Eq. 2).



(2)

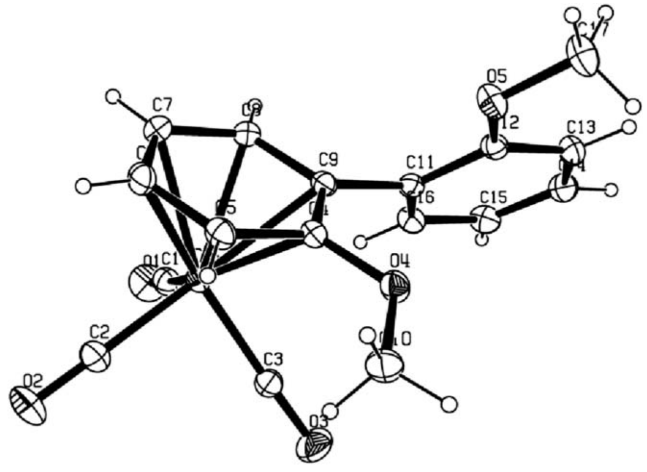


Figure 1. X-ray structure of **1m**.

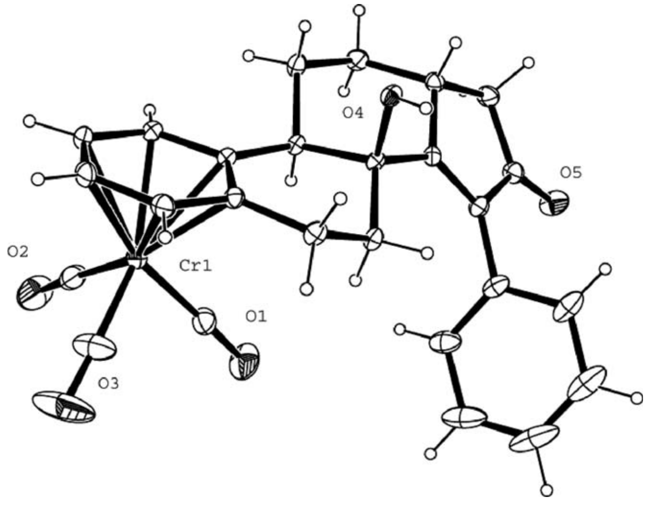


Figure 2. X-ray structure of **1n**.

The complexation was confirmed by an X-ray diffraction study (Fig. 2).[16]

In conclusion, we have demonstrated the usefulness of microwave irradiation in the synthesis of (η^6-arene)chromium tricarbonyl complexes from hexacarbonylchromium and arenes.

Acknowledgements

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-070-C00072) and the Korea Science and Engineering Foundation (KOSEF) for sponsoring this research through the SRC/ERC Program of MOST/KOSEF (R11-2005-065).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.07.011.

References and notes

1. For selected reviews, see: (a) Bringmann, G.; Mortimer, A. J. P.; Keller, P. A.; Gresser, M. J.; Garner, J.; Breuning, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 5384–5427; (b) Dötz, K. H.; Wenzel, B.; Jahr, H. C. *Topics Current Chem.* **2004**, *248*, 63–103; (c) Salzer, A. *Coord. Chem. Rev.* **2003**, *242*, 59–72; (d) *New Aspects of Transition Metal Arene Complexes*; Kündig, E. P., Ed.; Springer: Berlin, 2004; For recent papers, see: (e) Kamikawa, K.; Kinoshita, S.; Matsuzaka, H.; Uemura, M. *Org. Lett.* **2006**, *8*, 1097–1100; (f) Kündig, E. P.; Chaudhuri, P. D.; House, D.; Bernardinelli, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 1092–1095; (g) Kamikawa, K.; Harada, K.; Uemura, M. *Tetrahedron: Asymmetry* **2005**, *16*, 1419–1423; (h) Jahr, H. C.; Nieger, M.; Dötz, K. H. *Chem. Eur. J.* **2005**, *11*, 5333–5342; (i) Watanabe, T.; Tananka, Y.; Shoda, R.; Sakamoto, R.; Kamikawa, K.; Uemura, M. *J. Org. Chem.* **2004**, *69*, 4152–4158; (j) Englert, U.; Hu, C.; Salzer, A.; Alberico, E. *Organometallics* **2004**, *23*, 5419–5431.
2. (a) Dötz, K. H.; Stendel, J.; Muller, S.; Nieger, M.; Ketrat, S.; Dolg, M. *Organometallics* **2005**, *24*, 3219–3228; (b) Englert, U.; Hu, C.; Salzer, A.; Alberico, E. *Organometallics* **2004**, *23*, 5419–5431; (c) Kamikawa, K.; Sakamoto, T.; Tanaka, Y.; Uemura, M. *J. Org. Chem.* **2003**, *68*, 9356–9363; (d) Mitchell, R. H.; Brkic, Z.; Berg, D. J.; Barclay, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 11983–11988; (e) Kündig, E. P.; Perret, C.; Spichinger, S.; Bernardinelli, G. *J. Organomet. Chem.* **1985**, *286*, 183; (f) Desobry, V.; Kündig, E. P. *Helv. Chim. Acta* **1981**, *64*, 1288–1297.
3. (a) Oprunenko, Y.; Gloriozov, I.; Lyssenko, K.; Malyugina, S.; Mityuk, D.; Mstislavsky, V.; Günther, H.; von Firks, G.; Ebener, M. *J. Organomet. Chem.* **2002**, *656*, 27–42; (b) Oprunenko, Y. F.; Malugina, S. G.; Ustynyuk, Y. A.; Ustynyuk, N. A.; Kravtsov, D. N. *J. Organomet. Chem.* **1988**, *338*, 357–368.
4. (a) Amor, A. B. H.; Top, S.; Meganem, F.; Jaouen, G. *J. Organomet. Chem.* **2005**, *690*, 847–856; (b) Zabalov, M. V.; Gloriozov, I. P.; Oprunenko, Y. F.; Lemenovski, D. A. *Russ. Chem. Bull.* **2003**, *52*, 1567–1572; (c) Kündig, E. P.; Lomberget, T.; Bragg, R.; Poulard, C.; Bernardinelli, G. *Chem. Commun.* **2004**, 1548–1549.
5. (a) Edelmann, F. T. *Inorg. Chim. Acta* **2004**, *357*, 4592–4595; (b) Merlic, C. A.; Miller, M. M.; Hietbrink, B. N.; Houk, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 4904–4918.
6. Recent reviews, see: (a) de la Hoz, A.; Díaz-Ortiz, Á.; Moreno, A. *Chem. Soc. Rev.* **2005**, *34*, 164–178; (b) Hayes, B. L. *Aldrichim. Acta* **2004**, *37*, 66; (c) Blackwell, H. E. *Org. Biomol. Chem.* **2003**, *1*, 1251–1255; (d) Larhed, M.; Moberg, C.; Hallberg, A. *Acc. Chem. Res.* **2002**, *35*, 717–727; (e) Kuhnert, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 1863–1866; (f) Lindström, P.; Tierney, J.; Wathey, B.; Westman, J. *Tetrahedron* **2001**, *57*, 9225–9283; (g) Gabriel, C.; Gabriel, S.; Grant, E. H.; Halstead, B. S.; Mingos, D. M. P. *Chem. Soc. Rev.* **1998**, *27*, 213–224.

7. Ardon, M.; Hogarth, G.; Oscroft, D. T. W. *J. Organomet. Chem.* **2004**, *689*, 2429–2435.
8. Kim, S. J.; Choi, S. Y.; Chung, Y. K., in preparation.
9. Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154–158.
10. Heppert, J. A.; Morgenstern, M. A.; Scherubel, D. M.; Takusagawa, F.; Shaker, M. R. *Organometallics* **1988**, *7*, 1715–1723.
11. McCarthy, J. R.; Wiedeman, P. E.; Schuster, A. J.; Whitten, J. P.; Barbuch, R. J. *J. Org. Chem.* **1985**, *50*, 3095–3103.
12. General procedures for microwave-assisted complexation of (η^6-arene)chromium tricarbonyl complexes: microwave-assisted reactions were carried out on a CEM Discover microwave reactor with a circular (1.3 cm (d) × 8 cm (l), volume: 10 mL), single mode, self-tuning microwave applicator operating at 2450 MHz (300 W). Into a 10 mL glass tube of a microwave reactor, 1 mL of THF was added via a syringe. A suitable arene was added and 0.1 g of $Cr(CO)_6$ was added in one portion and the tube was sealed. After microwave irradiation for 1.5 h at 160 °C, the tube was cooled to room temperature. A column chromatography (eluted with hexane/ethyl acetate) gave the (η^6-arene)chromium tricarbonyl complexes.

    Compound **2**: ^{1}H NMR ($CDCl_3$): δ 7.31–7.18 (m, 4H), 7.13–7.04 (m, 3H), 6.99–6.96 (m, 2H), 3.43–3.35 (m, 1H), 2.90–2.78 (m, 2H), 2.70 (dd, $J = 6.7$, 19.1 Hz, 1H), 2.59–2.51 (m, 1H), 2.42–2.35 (m, 2H), 2.10 (d, $J = 19.1$ Hz, 1H), 1.88 (qd, $J = 3.1$, 12.7 Hz, 1H), 1.82 (s, 1H), 1.65–1.61 (m, 2H), 1.35 (qd, $J = 3.8$, 12.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 208.6, 176.8, 138.4, 135.7, 135.0, 129.8, 129.29, 129.0, 128.1, 127.8, 127.0, 126.5, 126.5, 71.6, 47.5, 41.1, 37.1, 35.6, 33.1, 25.3, 24.9; IR $\nu_{C=O}$ 1698 cm^{-1}; HRMS for $C_{23}H_{22}O_2$: calcd. 330.1620, obsd 330.1617.

    Compound **1m**: ^{1}H NMR ($CDCl_3$): δ 3.68 (s, 3H), 3.78 (s, 3H), 4.87 (s, 1H), 5.08 (s, 1H), 5.63 (m, 2H), 6.91 (m, 2H), 7.37 (m, 2H) ppm; Elemental Anal. Calcd for $C_{17}H_{14}O_5Cr_1$: C 58.29; H 4.03. Found: C 58.28; H 4.03. IR $\nu_{C=O}$ (in $CHCl_3$) 1877, 1955 cm^{-1}.

    Compound **1n**: ^{1}H NMR ($CDCl_3$): δ 1.26 (m, 2H), 1.60–2.38 (m, 6H), 2.80 (s, 1H), 2.87 (m, 2H), 3.38 (m, 1H), 4.11 (m, 1H), 5.21–5.47 (m, 4H), 7.07 (m, 2H), 7.35 (m, 3H) ppm; Elemental Anal. Calcd for $C_{26}H_{22}O_5Cr_1$: C 66.94; H 4.76. Found: C 66.92; H 5.03. IR $\nu_{C=O}$ (in $CHCl_3$) 1962, 1888, 1698 cm^{-1}.
13. Kostemans, G. B. M.; Bobeldijk, M.; Kwakman, P. J.; de Wolf, W. H.; Bickelhaupt, F. *J. Organomet. Chem.* **1989**, *363*, 291–296.
14. Hudeček, M.; Toma, Š. *J. Organomet. Chem.* **1991**, *406*, 147–151.
15. Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1990**, *28*, 136–140.
16. Single crystals were grown by the slow evaporation of CH_2Cl_2 solution. (**1m**) Crystal data: crystal system, monoclinic, P21/*n*, unit cell dimensions, $a = 7.6094(5)$ Å, $b = 15.2373(10)$ Å, $c = 13.5676(9)$ Å, $\alpha = 90°$, $\beta = 104.6800(10)°$, $\gamma = 90°$. Final R indices [$I > 2\text{sigma}(I)$], $R1 = 0.0650$, $wR2 = 0.1212$. CCDC reference number: 611497. (**1n**) Crystal data: crystal system, monoclinic, P21/*n*, unit cell dimensions, $a = 11.7535(8)$ Å, $b = 12.6540(10)$ Å, $c = 15.1559(10)$ Å, $\alpha = 90°$, $\beta = 94.756(2)°$, $\gamma = 90°$. Final R indices [$I > 2\text{sigma}(I)$], $R1 = 0.0538$, $wR2 = 0.368$. CCDC reference number: 611498.