Asian Journal of Chemistry Vol. 17, No. 2 (2005), 1304–1306

NOTE

Synthesis of Tricarbonylchromium Complex of 1,2;5,6;9,10-Tribenzododeca-1,5,9-triene

A. MOSHTAGHI ZENOUZ
Chemistry Department, Faculty of Science
Azarbaijan University of Tarbiat Moallem, Tabriz, Iran
E-mail: adelehmz@yahoo.com

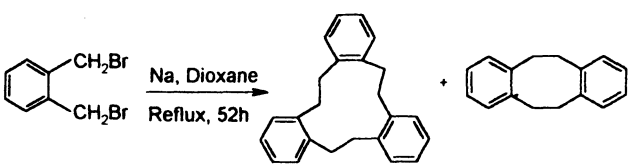
The mono(tricarbonylchromium) complex of [2.2.2]orthocyclophane have been synthesized. The structure of this complex has been determined by ^{1}H and ^{13}C NMR spectroscopy.

Key Words: Synthesis, Tricarbonylchromium complex.

There are usually three general methods for preparation of arenechromium complexes on practical scale: (a) thermal reaction of Cr(CO)6 with arene, which involves heating Cr(CO)6 with arene in mixture of refluxing di-n-butylether and tetrahydrofuran (THF) (9 : 1 v/v), is now established as the best way to prepare $[Cr(CO)_3$ (η-arene) complexes routinely[1]; (b) thermal reaction of $[Cr(CO)_3L_3]$ species with arene, in which replacement of three carbonyls of $[Cr(CO)_6]$ by more labile ligands enables subsequent thermal reactions with arenes to be carried out at lower temperatures. Particular attention has been given to those complexes[2] (where L = MeCN, py or NH_3; (c) arene exchange reaction, treating (naphthalene)-$Cr(CO)_3$ complex with different arenes, leads, in some cases, to arene exchange reactions, a procedure which goes under mild conditions[3, 4].

The [2.2.2] orthocyclophane **1** had been prepared many years ago[5] but its tricarbonylchromium complex has not yet been described. The synthesis of this complex is described here.

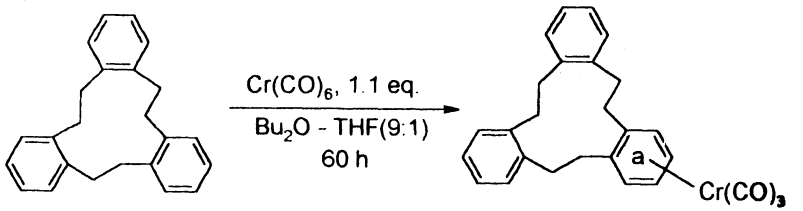
Compound **1** was prepared by treating α,α'-dibromo-*o*-xylene with sodium in dioxane[5] **(Scheme-1).**



Scheme-1

The synthesis and crystal structures of mono- and bis-(tricarbonylchromium) complexes of **2** has been previously described[6]. Heating **1** with equimolecular

amount of $Cr(CO)_6$ in di-*n*-butyl ether (Bu_2O) and tetrahydrofuran (THF) (9 : 1 v/v) at reflux temperature afforded 35% unreacted compound **1**, 56% of complex **3** and 9% the mixture of bis- and tris-(tricarbonylchromium) complexes of **1**, which were separated on a column of alumina **(Scheme-2)**.



Scheme-2

All manipulations involving chromium complexes were performed under an atmosphere of purified argon and using gas/vacuum double manifold and standard Schlenk technique[7]. THF and Bu_2O were distilled from sodium/benzophenone ketyl immediately prior to use. $Cr(CO)_6$ was purchased from Aldrich and sublimed prior to use. Elemental analyses: Carlo-Erba Modell 1104; IR: Bruker IFS 25; ^1H and ^{13}C NMR: Bruker AM-400, Bruker AC-200; MS: Varian MAT 311A, Varian MAT 111; melting points: Büchi SMP-20.

Preparation of 1,2;5,6;9,10-tribenzododeca-1,5,9-triene 1: To a solution of α,α′-dibromo-*o*-xylene (5520 mg, 20 mmol) in dry dioxane (600 mL) was added sodium (3700 mg, 160 mmol), finely dispersed in dry dioxane. The resultant suspension was stirred at reflux temperature for 36 h, acquiring a deep blue colour. The reaction mixture was filtered and evaporated. To the residue was added petrol ether at 30–50°C and heated and then filtered and evaporated. Column chromatography on silica-gel with hexane gave the products **2** (50%) and **1** (30%) respectively.

[2.2.2]orthocyclophane 1: m.p. 179–180°C, ^1H NMR (400 MHz, $CDCl_3$): δ = 3.05 (s, 12H), 7.2–7.37 (AA′BB′, 12H, ArH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 37.36 (6 × CH_2), 126.73 (6 × CH), 130.47 (6 × CH), 140.12 (6 × C) ppm; MS (EI): m/z (%) = 314 (13) [M^+ + 2], 313 (51) [M^+ + 1], 208 (18), 207 (100), 193 (22), 178 (15), 165 (6), 129 (9), 115 (25), 104 (30), 91 (19), 78 (14).

Preparation of $Cr(CO)_3$[2.2.2]orthocyclophane 3: A mixture of [2.2.2]orthocyclophane **1** (500mg, 1.6 mmol) and freshly sublimed $Cr(CO)_6$ (360 mg, 1.76 mmol) in Bu_2O (15 mL) and THF (2 mL) was heated under reflux (bath temperature: 160°C) for 60 h. Volatiles were removed *in vacuo* and the crude yellow solid purified by column chromatography [Al_2O_3 Grade, dichloromethane/pentane (1 : 1.5) and then dichloromethane]. Three fractions separated, fraction was unreacted **1** (35%), fraction was complex **3** (56%), and fraction that eluted with dichloromethane was the mixture of bis- and tris-(tricarbonylchromium) complexes of **2**. Crystallization of fraction from dichloromethane/hexane gave the complex **3** as yellow crystals; m.p. 218°C (Decomp.); IR (KBr): ν = 3056 (w), 3024 (w), 2971–2867 (w), 1963 (s), 1881 (br, s), 1488 (m), 1474 (m), 1450 (m), 755 (s), 668 (s), 628 (s) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 2.5–2.6

(m, 2H), 2.7–3.0 (m, 8H), 3.1–3.2 (m, 2H), 5.7–5.8 (AA'BB', 2H, ArH^a), 5.8–6.0 (AA'BB', 2H, ArH^a), 7.1–7.3 (m, 4H, ArH), 7.3–7.5 (m, 4H, ArH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 36.28 (2 × CH_2), 37.26 (2 × CH_2), 37.73 (2 × CH_2), 92.17 (2 × CH), 94.74 (2 × CH), 110.50 (2 × C), 126.99 (2 × CH), 127.21 (2 × CH), 130.37 (2 × CH), 130.61 (2 × CH), 138.32 (2 × C), 139.75 (2 × C), 234 (3 × CO) ppm; MS (70 eV): m/z (%) = 448 (9) [M^+], 364 (100) [M^+ 3CO], 312 (37) [$M^+Cr(CO)_3$], 260 (12), 207 (71), 193 (15), 182 (15), 117 (13), 105 (18), 52 (69) [Cr^+]; CHN: ($C_{27}H_{24}CrO_3$) Calcd.: C 72.31, H 5.39%; found: C 71.85, H 5.06%.

REFERENCES

1. C.A.L. Mahaffy and P. Pauson, *Inorg. Synth.*, **28**, 137 (1990).
2. J. Vebrel, R. Mercier and J. Belleney, *J. Organomet. Chem.*, **235**, 197 (1982).
3. E.P. Kundig, C. Perret, S. Spichiger and G. Bernardinelli, *J. Organomet. Chem.*, **286**, 183 (1985).
4. B. Ohlsson, C. Ullenius and S. Jagner, *J. Organomet. Chem.*, **365**, 243 (1989).
5. D. Paolo, P. Cozzini, R.M. Claramunt, J.L. Lavandera, C. Sanz and J. Elguero, *J. Chem. Soc. Perkin Trans. 2*, 1609 (1992).
6. S.A. Fakhri and A.M. Zenouz, *J. Organomet. Chem.*, **608**, 6 (2000).
7. D.F. Shriver and M.A. Drezdon, The Manipulation of Air Sensitive Compounds, 2nd Edn., John Wiley & Sons, New York (1986).

(*Received:* 17 June 2004; *Accepted:* 3 November 2004) AJC-4088