Journal of Organometallic Chemistry, 235 (1982) 197—200
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

A DIRECT AND EFFICIENT COMPLEXATION OF SOME INDENES AND DIHYDRONAPHTHALENES WITH $(NH_3)_3Cr(CO)_3$

J. VEBREL *, R. MERCIER,
Université de Franche-Comté, Faculté des Sciences et des Techniques, Laboratoires de Chimie Appliquée et d'électrochimie des solides, La Bouloie, Route de Gray, 25030 Besançon Cedex (France)

and J. BELLENEY
Université René Descartes, Faculté des Sciences Pharmaceutiques et Biologiques, Laboratoire de Chimie organique, 4 Avenue de l'Observatoire, 75006 Paris Cedex (France)

(Received March 2nd, 1982)

Summary

In contrast to hexacarbonylchromium, tricarbonylchromiumtriammine (I) readily yields complexes of some indenes and dihydronaphthalenes. A high yield and reproducible preparation of I is described.

No efficient method of preparing indenic and dihydronaphthalenic tricarbonylchromium complexes is currently available. The complexation with $Cr(CO)_6$ requires high reaction temperatures (140, 160°C), long reaction times (48 to 72 h) and complex apparatus [1] to avoid sublimation of the reagent. Furthermore, the complexes are usually obtained in poor yields. For example, complex II is obtained in only 7% yield [2] while the starting material is partially polymerized. Recently, Khand et al. [3] have described a technique using a mixture of dibutyl ether with sufficient THF to "catalyse" the reaction and to wash back most of the $Cr(CO)_6$ which sublimes into the condenser. With this method the authors produce complexes of aromatic compounds bearing an unsaturated side chain; for example, indenetricarbonylchromium (reaction time 24 h, yield 69%, m.p. 92—94°C) and styrenetricarbonylchromium (70 h, 52%, 78°C).

In order to prevent the polymerisation, we can also use precursors of the complexes [4]. Then, a multistep sequence involving supplementary cautions (inert atmosphere, darkness, numerous purification stages) is necessary to obtain the desired complexes in rather poor yields.

Other complexing agents [5,6] proved to be unsatisfactory, but Rausch and coworkers [7] have shown that styrene can be directly complexed without

0022-328X/82/0000—0000/$02.75

polymerisation in a 50—65% yield, with tricarbonylchromiumtriammine (I) prepared according to Hieber's method [8]. In this paper, we would report:

(1) An improved procedure for the preparation of $(CO)_3Cr(NH_3)_3$ giving excellent and reproducible yields (92—93%) on a 10 g scale.

(2) Use of this now easily prepared chromium derivative in a very efficient complexation of indenes and dihydronaphthalenes (Scheme 1) (65 to 85% yields) in refluxing dioxane. Under these conditions, $(NH_3)_3Cr(CO)_3$ does not sublime out and only a simple apparatus is required.

The advantages of this procedure is that there is no need to use a large excess of arene, and the reaction times are shorter.

Scheme 1

(II : X = H ;
III : X = CO_2Me)

(IV : X = H , R = H ;
V ; X = CO_2Me, R = H ;
VI ; X = CO_2Me, R = Me
(two diastereoisomers))

Experimental

Synthesis of $(NH_3)_3Cr(CO)_3$

An ethanolic potassium hydroxyde solution (21.5 g of KOH in 250 cm^3 of deoxygenated ethanol) is introduced under nitrogen into a 500 cm^3 autoclave fitted with a magnetic stirrer, a pressure regulator, a heating mantle and a cooling device supplied with cold water inside the reactor. Then 13 g of commercial hexacarbonylchromium are added. The mixture is heated at 100°C at 7.5 bars pressure for 6 h. After cooling and removal of carbon monoxide the mixture is poured under inert atmosphere into a one liter Erlenmeyer flask. Then, 500 cm^3 of 20% NH_4OH (*d* 0.92) are added and the mixture is stirred at room temperature for 1 h under nitrogen. The yellow solid obtained is filtered off under nitrogen, washed twice with a 10% ammonia solution and then with nitrogen-saturated EtOH. After drying under inert atmosphere, 10.2 to 10.3 g of a yellow powder (yield 92—93%) is obtained. The complex is relatively stable in air, but is better stored in a Schlenk tube under nitrogen in the dark.
F 105°C (déc).

Analysis. Found: C, 19.23; H, 4.70; N, 22.25; Cr, 27.81. $C_3H_9N_3O_3Cr$ calcd.: C, 19.25; H, 4.85; N, 22.45; Cr, 27.80%. IR (KBr) ν (cm^{-1}): 3380 and 3295 (N—H); 1875 and 1885 (C═O).

TABLE 1

YIELDS, PHYSICAL CONSTANTS AND ANALYSES OF PRODUCTS II—VI

Product	Reaction time (h)	Purification (cryst. solvent)	m.p. (°C)	Yield (%)	Molecular formula [a]
II	6	A [c] (Hexane/Et_2O 80/20)	97	78	$C_{12}H_8O_3Cr$
III	8	B (Hexane/Benzene 60/40)	147	72	$C_{14}H_{10}O_5Cr$
IV	6	A (Hexane/Et_2O 80/20)	108	85	$C_{13}H_{10}O_3Cr$
V	8	B (Hexane/Benzene 60/40)	133	81	$C_{15}H_{12}O_5Cr$
VI-*exo* [b] (82%)	10	C (Et_2O/Hexane 70/30)	104	65	$C_{16}H_{14}O_5Cr$
VI-*endo* [b] (18%)		C (Et_2O/Hexane 80/20)	133		$C_{16}H_{14}O_5Cr$

[a] The microanalyses, performed by Service Central de Microanalyses du CNRS (Lyon) were in satisfactory agreement with the calculated values (C ± 0.3, H ± 0.2). [b] TLC on silica gel with 4/1 hexane/ether as eluent. (VI-*exo*: R_f 0.32/VI-*endo*: R_f 0.23). [c] A, B and C see experimental.

TABLE 2

SPECTRAL DATA FOR COMPOUNDS II—VI

Product	IR (KBr) ν (cm^{-1})	^1H NMR (solvent/internal standard) δ (ppm), J (Hz)
II	1950, 1860 (C=O)	100 MHz (C_6D_6/TMS) 2.48—3.24(m, 2H) [a]; 5.85—6.15(m, 2H) [a]; H arom: 4.40—4.80 (2H); 5.00—5.30 (2H)
III	1955, 1875, 1842 (C=O) 1695 (C=O ester) 1630 (C=C)	270 MHz (C_6D_6/HMDS) 2.95 and 3.26 (AB system, 2H); ^2J 24.0, ^4J 2.0; 3.24 (s, 3H); H arom: 4.05 (td, 1H); 4.33 (t, 1H); 4.53 (dt, 1H); 4.71 (d, 1H); J 6.3 and 0.8; 6.69 (d, 1H); ^4J 2.0
IV	1950, 1860, 1830 (C=O) 1630 (C=C)	100 MHz ($CDCl_3$/TMS) 250 (m, 4H); H arom: 5.20 (m, 4H); 6.05 (m, 2H)
V	1955, 1875, 1842 (C=O) 1695 (C=O ester) 1630 (C=C)	270 MHz (C_6H_6/HMDS) 1.90—2.38 (m, 4H); 3.25 (s, 3H); H arom: 4.10 (m, 2H) and 4.27 (m, 2H); 6.80 (s, 1H)
VI-*exo*	1952, 1890, 1860 (C=O) 1700 (C=O ester) 1620 (C=C)	270 MHz (C_6D_6/HMDS) 0.67 (d, 3H); J 6.8; 3.29 (s, 3H); 2.67 (m, 2H), 1.62 (dd, 1H); ^2J 14.5 and ^3J 1.2; H arom: 4.02 (td, 1H); 4.28 (dd, 1H); 4.38 (td, 1H); 4.48 (dd, 1H); J 6.3 and 1.2; 6.80 (s, 1H)
VI-*endo*	1955, 1884, 1862 (C=O) 1710 (C=O ester) 1630 (C=C)	270 MHz (C_6D_6/HMDS) 1.31 (d, 3H); J 7.0; 3.29 (s, 3H); 1.82 (dd, 1H); ^2J 16.5 and ^3J 1.2; 2.31 (dd, 1H) ^2J 16.5 and ^3J 9.0; 2.71 (m, 1H); H arom: 4.20 (m, 3H), 4.37 (td, 1H) J 6.5 and 1.2; 6.87 (s, 1H)

[a] First order analysis is not possible.

Complexation reactions

In the dark and under nitrogen, a mixture of 2×10^{-2} mol of benzo-condensed olefin and 1.3 equivalent of tricarbonylchromiumtriammine in 250 cm^3 of dioxane (anhydrous, deoxygenated and deperoxydized) is refluxed for 6 to 10 h with stirring. The residue after solvent removal is either purified by direct crystallisation (A) or is dissolved in a 1/1 hexane/diethyl ether mixture, the solution being passed through silica gel (70—230 mesh) before being crystallized (B).

The two diastereoisomers VI-*exo* and VI-*endo* are separated (C) by liquid chromatography on silica gel Si 60 Merck (230—400 mesh) using hexane/Et_2O (70/30) as eluent.

The complexation of 2-methyl-3-methoxycarbonyl-1,2-dihydronaphthalene is diastereoselective. VI-*exo* (with $Cr(CO)_3$ and the methyl group in anti positions, with respect to the plane of the aromatic ring) is the major isomer (82%, NMR). VI-*exo* and VI-*endo* stereochemistry was established by X-ray diffraction [9].

Characteristic data are given in Tables 1 and 2.

Acknowledgment

The authors thank the E.R.A. C.N.R.S. No. 389 from Rennes (France) for support.

References

1 W. Strohmeier, Chem. Ber., 94 (1961) 2490.
2 E.O. Fischer and N. Kriebitzsch, Z. Naturforsch. B, 15 (1960) 465.
3 I.U. Khand, C.A.L. Mahaffy and P.L. Pauson, J. Chem. Res., (1978) (S) 352, (M) 4454, and ref. cited.
4 H. Falk, K. Schlögl and W. Steyrer, Monatsh. Chem., 97 (1966) 1029. Preparation of compound IV starting from α-tetralonechrometricarbonyle; 1,2-dihydronaphthalenechrometricarbonyle (oil) is obtained with a 11% yield.
5 R.B. King, J. Organometal. Chem., 8 (1967) 139.
6 W.E. Silverthorn, Adv. Organometal. Chem., 13 (1975) 47.
7 M.D. Rausch, G.A. Moser, E.J. Zaiko and A.L. Lipman, J. Organometal. Chem., 23 (1970) 185.
8 W. Hieber, W. Abeck and H.K. Platzer, Z. Anorg. Allg. Chem., 280 (1955) 252.
9 R. Mercier, R. Douglade and J. Vebrel, Acta Crystallogr., submitted for publication.