Journal of Organometallic Chemistry, 221 (1981) 317—321
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CONVENIENT SYNTHETIC ROUTES TO THE CYCLOPENTADIENYLRUTHENIUM DICARBONYL CHLORIDE AND BROMIDE

AMIHAI EISENSTADT, RINA TANNENBAUM and AVI EFRATY *

Department of Organic Chemistry, The Weizmann Institute of Science Rehovot (Israel)

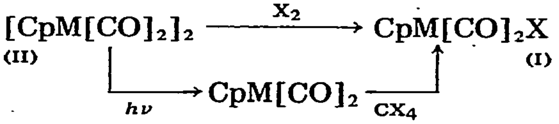
(Received July 21st, 1981)

Summary

The reactions of $[CpRu(CO)_2]_2$ with CX_4 (X = Cl, Br) were found to take place under indoor light conditions as well as in the dark to afford $CpRu(CO)_2X$ (X = Cl, Br) in excellent yields. Another convenient synthetic route to such ruthenium halide complexes involves the reaction of $CpRu(CO)_2H$, prepared "in situ" from $Ru_3(CO)_{12}$ and cyclopentadiene, with CX_4 (X = Cl, Br).

Introduction

Cyclopentadienylmetal carbonyl halides of the type $CpM(CO)_2X$ (I) are synthetically useful organometallic reagents. Commonly, such halides are prepared by the cleavage of the dimers $[CpM(CO)_2]_2$ (II: M = Ru [1], Fe [2]) with halogens (X_2). The photochemical homolytic cleavage of II: M = Ru [3], Fe [4] in the presence of halogenated hydrocarbons (e.g. CX_4) also leads to such complexes (I) by halogen abstraction from the solvent. This procedure, which avoids the use of free halogens, is particularly attractive for the preparation of the chloride and bromide derivatives of I. The current study describes convenient synthetic routes to I: M = Ru; X = Cl, Br starting with either II or $Ru_3(CO)_{12}$, which do not require photochemical equipment and/or free halogens.



$Cp = \eta^5 - C_5H_5$

Results and discussion

In the development of a facile synthetic route to I: M = Ru; X = Cl by the reaction of the ruthenium dimer (II) with CX_4 (X = Cl, Br), it was thought of

0022-328X/81/0000—0000/$02.50

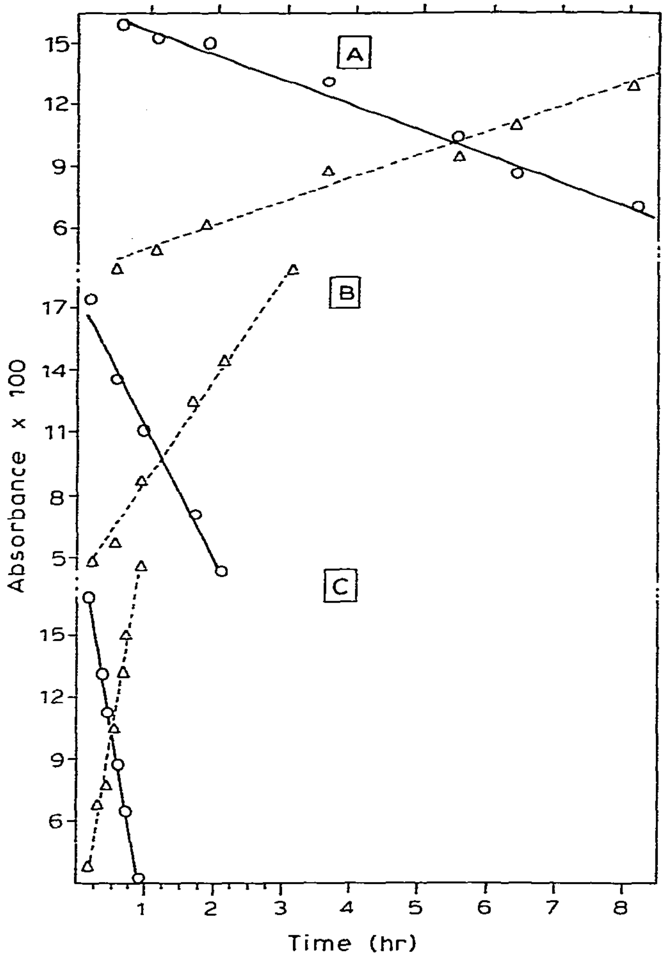


Fig. 1. Change in absorbances of the bridging carbonyl in $[CpRu(CO)_2]_2$ (———) and the $\nu(A')$ carbonyl band in $CpRu(CO)_2X$ (------) as determined from the IR spectra during the reaction of the dimer (0.015 *M*) with CX_4 (0.15 *M*) in $ClCH_2CH_2Cl$ at 25°C: (A) Reaction with CCl_4 in light [5]; last point (~8 h) corresponds to ~68% conversion; (B) Reaction with CBr_4 in the dark (100% conversion); (C) Reaction with CBr_4 in light [5] (100% conversion).

interest to see whether such processes can take place in the dark or under typical indoor light conditions. The ruthenium dimer II dissolved in $ClCH_2$-CH_2Cl (0.015 *M*) was treated with a ten-fold molar excess of CX_4 ($X = Cl, Br$) at 25°C in the dark as well as under indoor light (day time) conditions, and the IR spectra of this homogeneous system was periodically monitored. Progress made in these reactions was determined by following the disappearance of the bridging carbonyl band of II: M = Ru (1771 cm^{-1}) and the formation of the $\nu(A')$ bands of I: M = Ru; X = Cl (2052 cm^{-1}), Br (2054 cm^{-1}) from the IR spectra. Plots of absorbance $[\log(I_c/I)]$ against time (h) are shown in Fig. 1 (A, B, C).

In light [5], the reaction of the ruthenium dimer with CCl_4 requires ~13 h for completion (Fig. 1), while a similar dark reaction needs several weeks

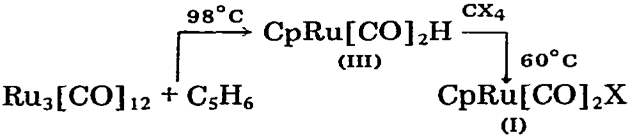
(3—4). The reactions of the ruthenium dimer with CBr_4 were found to be considerably faster than those with CCl_4. For instance, the dark reaction with CBr_4 (Fig. 1B) is complete in ~3 h, compared with less than 60 min for an analogous reaction in the light [5] (Fig. 1C). Noteworthy are the approximately zero-oder disappearance of the starting ruthenium dimer (II) and appearance of the halide products (I) under these conditions. The complexes $[CpRu(CO)_2]_2$ and $CpRu(CO)_2X$, but no other ruthenium carbonyl complexes and/or intermediates, were detected from the IR spectra recorded during the reactions.

The cleavage of the dimer with halogen abstraction reactions in light [5] were observed to be faster at higher temperatures. For example, in toluene at 75—85°C the reaction of the ruthenium dimer (II) with CCl_4 is complete in ~5 h, while only 15 min is required for the analogous reaction with CBr_4.

The reactions considered above provide a viable synthetic route to the ruthenium halide complexes I: M = Ru; X = Cl, Br, which were isolated in 85—96% yields. In most cases, the halides are obtained relatively pure directly from the reaction mixtures, and further purification may not be necessary for most purposes. This simple procedure avoids the need for free halogens, and does not require photochemical equipment. Moreover, these reactions can be carried out in air without any decrease in the yield.

The reactions of the iron dimer II: M = Fe with CX_4 (X = Cl, Br) were also examined. The reactions were found to be faster than those of the ruthenium dimer, but the yields (41—60%) of the iron halide products I: M = Fe; X = Cl, Br were lower because of decomposition.

The preparation of the ruthenium halides I: M = Ru; X = Cl, Br from $Ru_3(CO)_{12}$ was investigated as an alternative synthetic procedure. A fairly short (1—2 h) reaction between $Ru_3(CO)_{12}$ and freshly distilled cyclopentadiene in boiling n-heptane (~98°C) under an inert atmosphere was reported to afford the hydrido-ruthenium complex III as the only product [6]. The hydrido complex III, prepared "in situ", underwent a rather fast (several minutes) reaction with CX_4 (X = Cl, Br) at 60°C to give the halide complexes I: M = Ru; X = Cl, Br in better than 85% overall yields, most of the product crystallizing when the reaction mixture is cooled to ambient temperature. If not carried out under a rigorously air-free atmosphere, some ruthenium dimer II: M = Ru is formed along with the halides I: M = Ru; X = Cl, Br. Separation of these complexes may be achieved by chromatography on alumina. This synthetic route is particularly convenient if commercially available $Ru_3(CO)_{12}$ is used. Alternatively, $Ru_3(CO)_{12}$ can be prepared in a resonable yield by an atmospheric pressure carbonylation of $RuCl_3 \cdot 3\ H_2O$ in the presence of Zn by an established procedure [7].



The hydrido ruthenium complex III was also found to be a useful intermediate for the preparation of the iodide derivative I; X = I. Addition of CH_3I to the yellow n-heptane solution of III at 80°C resulted in an immediate color change to red followed by extensive gas (CH_4) evolution. When the mixture cooled to ambient temperature the orange product I; X = I crystallized out in 75% yield. This procedure, which affords a relative pure sample of the iodide I; X = I, is faster and more convenient than the route involving the preparation of the ruthenium dimer II and its cleavage with iodine.

Experimental

Ruthenium dimer $[CpRu(CO)_2]_2$ was prepared by a published procedure [6]. Ruthenium carbonyl $Ru_3(CO)_{12}$ was purchased from Strem Chemicals Inc. (U.S.A.). Carbon tetrabromide (BDH, reagent) and carbon tetrachloride (Fluka, spectroquality) were used without purification. Solvents were redistilled before use.

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 467 grating IR spectrometer using 0.4 mm path NaCl cells.

Reactions of $[CpRu(CO)_2]_2$ with CX_4 (X = Cl, Br)

(A) Reactions in $ClCH_2CH_2Cl$ at 25°C. Two stock solutions of $[CpRu(CO)_2]_2$ (0.025 *M*) and CX_4 (0.375 *M*) in $ClCH_2CH_2Cl$ were prepared. A typical reaction was started by mixing 3 ml of the ruthenium dimer solution with 2 ml of the CX_4 solution. The initial concentrations in this reaction were 0.015 *M* $[CpRu(CO)_2]_2$ and 0.15 *M* CX_4. Monitoring by IR spectroscopy showed the disappearance of the bridging carbonyls in $[CpRu(CO)_2]_2$ and the appearance of the $\nu(A')$ carbonyl band in $CpRu(CO)_2X$. The results of several reactions with CCl_4 and CBr_4 carried out in the dark or under normal indoor light conditions [5], are summarized in Fig. 1 (A, B and C). All these reactions proceed to completion, and the products $CpRu(CO)_2X$ (X = Cl, Br) can be isolated in >90% yield.

The products described here and below were identified by comparison of their melting points and infrared spectra with those of the authentic samples [1]. The purity of the products was checked by TLC.

(B) Reactions in toluene at elevated temperatures. A mixture of $[CpRu(CO)_2]_2$ (0.28 g, 0.63 mmol) and CCl_4 (2 ml) in toluene (10 ml) was heated to 75°C for 5 h under normal indoor light conditions [5]. After being cooled to ambient temperature, the mixture was filtered and the filtrate was evaporated under reduced pressure (0.1 Torr./25°C) to give a fairly pure sample of $CpRu(CO)_2Cl$ (0.28 g; m.p. 100—101°C) (~86%).

A similar reaction with CBr_4 was complete in about 15 min, and gave $CpRu(CO)_2Br$ (m.p., 88—89°C) (~95%). Separation of the product from the excess of CBr_4 is best achieved by chromatography on neutral alumina.

Reaction of $CpRu(CO)_2H$ with CX_4 (X = Cl, Br)

A mixture of freshly prepared cyclopentadiene (0.8 ml; 9.72 mmol) and $Ru_3(CO)_{12}$ (0.205 g, 0.32 mmol) in n-heptane (62 ml) was refluxed for 2 h. The mixture, which consists mainly of $CpRu(CO)_2H$, was then cooled to 60°C and treated with a n-heptane solution (2 ml) of CBr_4 (0.52 g, 1.57 mmol). The mixture was stirred for a further 20 min at this temperature, during which the yellow $CpRu(CO)_2Br$ precipitated out. The mixture was cooled to room temperature and $CpRu(CO)_2Br$ (0.28 g; m.p., 87—88°C) was isolated by filtration in ~96% yield.

A similar reaction with CCl_4 gave the chloride $CpRu(CO)_2Cl$ (m.p., 99—100°C) (85%).

In the above procedure an air-free atmosphere (e.g. Ar) must be used. The presence of even trace amounts of oxygen leads to formation of the dimer $[CpRu(CO)_2]_2$.

Reaction of $CpRu(CO)_2H$ with CH_3I

A mixture of freshly prepared cyclopentadiene (0.9 ml; 10.93 mmol) and $Ru_3(CO)_{12}$ (0.3 g, 0.47 mmol) in n-heptane (70 ml) was refluxed for 1.5 h. The temperature of the mixture was lowered to 80°C and neat CH_3I (0.6 ml; 14.0 mmol) was added. After several minutes at 80°C, the mixture was cooled slowly to room temperature and the orange product $CpRu(CO)_2I$ (0.37 g; m.p. 120—122°C) was isolated by filtration in 75% yield.

Acknowledgement

This research program was supported by a grant from the U.S.-Israel Binational Science Foundations.

References

1 R.J. Haines and A.L. duPreez, J. Chem. Soc. Dalton, (1972) 944; D.H. Gibson, W.L. Hsu and A.L. Steinmetz, J. Organometal. Chem., 208 (1981) 89.

2 R.J. Haines and A.L. duPreez, J. Amer. Chem. Soc., 91 (1969) 769; J. Chem. Soc. (A), (1970) 2341; and pertinent references therein.

3 H.B. Abrahamson, M.C. Palazzotto, C.L. Reichel and M.S. Wrighton, J. Amer. Chem. Soc., 101 (1979) 4123; and pertinent references therein.

4 J.V. Caspar and T.J. Meyers, J. Amer. Chem. Soc., 102 (1980) 7794; and pertinent references therein.

5 The term light stands for normal indoor light conditions during day time.

6 A.F. Humphries and S.A.R. Knox, J. Chem. Soc. Dalton, (1975) 1710.

7 J.L. Dawes and J.D. Holmes, Inorg. Nucl. Chem. Lett., 7 (1971) 847; A. Mantovani and S. Cenini, Inorg. Synth. 15 (1976) 47.