Journal of Organometallic Chemistry, 281 (1985) 119–122
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

FORMATION OF LITHIUM CYCLOPENTADIENIDE BY THE REACTION OF $Li(C_2H_5)_3BH$ WITH CYCLOPENTADIENE, AND A CONVENIENT PREPARATION OF $[M(CO)_3(C_5H_5)]^-$ (M = Cr, Mo AND W)

MAHMOUD A. EL-HINNAWI * and ARAB K. EL-QASEER
Department of Chemistry, Yarmouk University, Irbid (Jordan)

(Received August 20th, 1984)

Summary

Commercially available lithium triethylborohydride, $Li(C_2H_5)_3BH$, (1 *M*, THF) reacts with C_5H_6 in THF solution at room temperature to give a yellow-orange solution of $Li(C_5H_5)$ with gas evolution. Molybdenum hexacarbonyl, $Mo(CO)_6$, reacts with this solution to give $Li[Mo(CO)_3(C_5H_5)]$ in a high yield after 12 h reflux. Both $W(CO)_6$ and $Cr(CO)_6$ give the corresponding cyclopentadienyl carbonyl anions after 15 h reflux in a somewhat lower yield. The corresponding cyclopentadienyl carbonyl dimers, $[M(CO)_3(C_5H_5)]_2$ have also been prepared and characterized.

Introduction

Trialkylborohydrides, especially $Li(C_2H_5)_3BH$ (super-hydride), are well known as potent hydride donors toward a variety of organic electrophiles [1]. Lithium cyclopentadienide was prepared from alkyllithium compounds and cyclopentadiene as a white precipitate in ether solution [2]. Metal carbonyl anions such as $[M(CO)_3(C_5H_5)]^-$ (M = Cr, Mo, W) are conventionally prepared either by the reaction of $M(CO)_6$ with $Na(C_5H_5)$ [3] or $K(C_5H_5)$ [4] in diglyme or by treating the dimers, $[M(CO)_3(C_5H_5)]_2$ with 1% Na/Hg amalgam [5], Na/K alloy [6] or Na dispersion [7]. Recently $Li(C_2H_5)_3BH$ was used to synthesise the anion, $[Mo(CO)_3(C_5H_5)]^-$ and other metal carbonyl anions from corresponding dimers [8]. Since the anions $[M(CO)_3(C_5H_5)]^-$ are extremely useful intermediates for preparation of other carbonyl derivatives, there is a need for a simple synthesis of these metal carbonyl anions from $M(CO)_6$ employing easily handled reagents. We report below that the anions, $[M(CO)_3(C_5H_5]^-$ (M = Cr, Mo, W) can be conveniently prepared in THF solution in moderate to good yield by the one-pot sequence shown below:

---

* To whom correspondence should be addressed.

0022-328X/85/$03.30

$$C_5H_6 + Li(C_2H_5)BH \xrightarrow{THF} Li(C_5H_5) + (C_2H_5)_3B + H_2$$

$$Li(C_5H_5) + M(CO)_6 \xrightarrow{THF} Li[M(CO)_3(C_5H_5)] + 3CO$$

Experimental

Materials and methods. Infrared spectra were obtained on Pye-Unicam SP3-100 spectrometer. ^{1}H NMR spectra were recorded on Bruker WP 80 SY spectrometer with TMS as internal standard. All reactions were performed under nitrogen using Schlenk glassware [9]. Solution transfer under nitrogen was performed by use of cannula. Ether and tetrahydrofuran (THF) were distilled from sodium and benzophenone under nitrogen. Petroleum ether was purified over $LiAlH_4$ and transferred upon vacuum. Acetone-d_6 was dried over activated 4A molecular sieves and vacuum distilled.

$Li(C_2H_5)_3BH$ and $M(CO)_6$ were purchased from Aldrich. Cyclopentadiene was freshly prepared by cracking of the dimer.

Reaction of $Li(C_2H_5)_3BH$ with cyclopentadiene, C_5H_6, and the preparation of $[M(CO)_3(C_5H_5)]^-$ (M = Cr, Mo and W)

A 1 ml (0.80 g, 12 mmol) of freshly cracked cyclopentadiene was introduced into a 100 ml Schlenk flask containing 30 ml THF. Addition of 12 ml of 1 *M* THF solution of $Li(C_2H_5)_3BH$ (12 mmol) without cooling gave a homogeneous yellow-orange solution within 10 min, with evolution of gas. To this solution was added 2.64 g (10 mmol) of $Mo(CO)_6$ and the mixture was then refluxed under nitrogen for 12–15 h. The color changed to dark red-violet. The mixture was cooled to room temperature and the infrared spectra was recorded; this showed the formation of $Li[Mo(CO)_3(C_5H_5)]$ (IR ν(CO): 1905s, 1805s 1780m and 1715s cm^{-1}) and the disappearence of $Mo(CO)_6$ (IR ν(CO): 1975 cm^{-1}).

Similarly $Li[Cr(CO)_3(C_5H_5)]$ (IRν(CO): 1895s, 1800s, 1780sh and 1711s cm^{-1}) and $Li[W(CO)_3(C_5H_5)]$ (IR ν(CO): 1900s, 1800s, 1780sh and 1713s) were generated during 15 h reflux and the infrared spectra of the reaction mixtures indicated the presence of unreacted $Cr(CO)_6$ and $W(CO)_6$, respectively (ν(CO): 1975–1980 cm^{-1}). Further reflux in THF did not convert the remaining $Cr(CO)_6$ or $W(CO)_6$ into the corresponding anions. However, when a 6/4 v/v ratio of diglyme to THF was used as the reaction medium, all of the $Cr(CO)_6$ and $W(CO)_6$ was converted into the corresponding cyclopentadienyl carbonyl anion during 10 h reflux.

Preparation of $[M(CO)_3(C_5H_5)]_2$ (M = Mo, Cr and W)

A solution of 10 mmol of $Li[Mo(CO)_3(C_5H_5)]$ in THF was prepared as described above. The method of Birdwhistell et al. [10], involving the direct oxidative coupling of $[Mo(CO)_3(C_5H_5)]^-$ by means of iron(III) sulphate, was used to prepare the dimer $[Mo(CO)_3(C_5H_5)]_2$. The dimer was isolated as a purple-red crystalline compound (2.08 g, 85% yield based on $Mo(CO)_6$), which was characterized by IR and ^{1}H NMR spectroscopy IR (THF) ν(CO): 2015w, 1960s, 1915s cm^{-1}. ^{1}H NMR δ 5.53 ppm, acetone-d_6.

The compounds $[Cr(CO)_3(C_5H_5)]_2$ and $[W(CO)_3(C_5H_5)]_2$ were prepared by the method used for $[Mo(CO)_3(C_5H_5)]_2$. Thus $[Cr(CO)_3(C_5H_5)]^-$ (10 mmol) in 60%

diglyme/THF was used to prepare the chromium dimer. The crude product was twice sublimed at 90–100°C (0.05 mmHg) to give deep green crystals of $[Cr(CO)_3(C_5H_5)]_2$ (0.89 g, 32% yield based on $Cr(CO)_6$). IR (THF) ν(CO): 2010m, 1945s, 1925s 1912sh cm^{-1}. IR (Nujol) ν(CO): 1935s, 1920s, 1880s.

The tungsten dimer $[W(CO)_3(C_5H_5)]_2$ was ioslated as deep purple-red crystals with 65% yield. IR (THF) ν(CO): 2015w, 1959s, 1915s cm^{-1}.

Results and discussion

The reaction of lithium triethylborohydride with cyclopentadiene in THF as solvent at room temperature gives a homogeneous yellow-orange solution with gas evolution. Since $Li(C_2H_5)_3BH$ is a strong hydride donor, the yellow-orange solution contains mainly lithium cyclopentadienide, and was utilized directly in the preparation of cyclopentadienyl tricarbonyl dimers, $[M(CO)_3(C_5H_5)]_2$ of chromium, molybdenum and tungsten. Lithium cyclopentadienide has previously been prepared by the reaction of butyllithium (15% in hexane) with cyclopentadiene in THF as white precipitate, which is extremely air-sensitive and pyrophoric; the reaction is also highly exothermic and so a H_2O-ice bath must be used and strict precautions have to taken during its preparation and reactions. Use of THF as a solvent has many advantages, and it is widely used in many organometallic reactions [11]. The reaction of $Li(C_2H_5)BH$ (1 *M* THF) with cyclopentadiene in THF was found to be slightly exothermic, the temperature rising only by about 5°C during the 5-min addition of the $Li(C_2H_5)_3BH$ solution, and cooling was unnecessary. The homogeneous orange solution of $Li(C_5H_5)$ was found to be relatively insensitive to air, and elaborate precautions were unnecessary; for example, we found that either addition of undegassed solid $M(CO)_6$ to the solution of $Li(C_5H_5)$ or cannula transfer of the $Li(C_5H_5)$ solution to undegassed solid $M(CO)_6$ under nitrogen was possible without complications, whereas cannula transfer of insoluble lithium cyclopentadienide which is formed from the reaction of butyllithium and cyclopentadiene is not recommended, and degassing of solid $M(CO)_6$ before its addition to the $Li(C_5H_5)$ solution is necessary [2].

The reaction of the THF orange solution of $Li(C_5H_5)$ with $Mo(CO)_6$ was complete within 12 h under reflux, i.e. all the $Mo(CO)_6$ was converted to anion $[Mo(CO)_3(C_5H_5)]^-$, and the direct oxidative coupling of the anion by iron(III)-sulfate produced the corresponding dimer, $[Mo(CO)_3(C_5H_5)]_2$ in high yield. On the other hand refluxing of $Li(C_5H_5)$ which had been generated from LiBu and C_5H_6, with $Mo(CO)_6$ in THF for 15 h did not convert all the $Mo(CO)_6$ into the corresponding anion $[Mo(CO)_3(C_5H_5)]^-$.

The reaction of the orange THF solution of $Li(C_5H_5)$ with either $Cr(CO)_6$ or $W(CO)_6$ produced the corresponding cyclopentadienyl carbonyl anion in lower yield, and some $M(CO)_6$ remained after the reaction time used. A higher yield was obtained when the reaction medium consisted of diglyme/THF 6/4 v/v, and no $M(CO)_6$ remained. The yield obtained for $[M(CO)_3(C_5H_5)]_2$ (M = Cr, W) was lower than that for M = Mo indicating that the yield of the anion $[M(CO)_3(C_5H_5)]^-$ for M = Mo was higher than of that for M = Cr and W. We believe that our method provides the best route to $[M(CO)_3(C_5H_5)]_2$ in THF solution from the readily available $M(CO)_6$, especially when M = Mo.

Acknowledgment

The authors gratefully acknowledge the research grant support from the graduat school at Yarmouk University.

References

1 S. Krishnamurthy, Aldrichim. Acta, 7 (1974) 55.
2 M.A. Lyle and S.R. Stobart, Inorg. Synth. 17 (1977) 178.
3 T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.
4 A.P. Hagen and P.J. Russo, Inorg. Synth., 17 (1977) 104.
5 R.B. King, Acc. Chem. Res., 3 (1970) 417.
6 J.E. Ellis and E.A. Flom, J. Organomet. Chem., 99 (1975) 263.
7 D.L. Reger, D.J. Fauth and M.D. Dukes, Synth. React. Inorg. Met-Org. Chem., 7 (1977) 151.
8 J.A. Gladysz, G.M. Williams, W. Tam, D.L.J. Johnson, D.W. Parker and J.C. Selover, Inorg. Chem., 18 (1979) 553.
9 D.F. Shriver, The Manipulation of Air-Sensitive compounds, McGraw Hill, New York, N.Y., 1969, pp. 141–163.
10 R. Birdwhistell, P. Hackett and A.R. Manning, J. Organomet. Chem., 157 (1978) 239.
11 R.B. King, Transition-Metal Organometallic Chemistry, Academic Press, New York, 1966.