Journal of Organometallic Chemistry, 365 (1989) 347–350
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09522

Rapid and convenient sonochemically-assisted alkyl-metal synthesis

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(Received October 8th, 1988)

Abstract

Sonochemically-activated potassium metal is a powerful and stoicheiometric reducing reagent and quickly produces the metallates $[M(C_5Me_5)(CO)_n]^-K^+$ from the dimers $[M(C_5Me_5)(CO)_n]_2$ (M = Fe, Ru, $n = 2$; M = Mo, $n = 3$). The reductions were carried out on a scale of 1 to 20 mmol with a 100 or 600 W acoustic power generator and a titanium horn directly immersed in the solution, and were complete in 15–20 min. In situ alkylation with one equivalent of a electrophile RX (CH_3I, CH_3CH_2I, CH_3OCH_2Cl, CH_3OCH_2Br) reagent provides a facile synthesis of metal alkyl $M(C_5Me_5)(CO)_nR$.

Introduction

The known procedures for the reductive cleavage of metal carbonyl dimers $[M(C_5Me_5)(CO)_n]_2$, I, (M = Fe, Ru, $n = 2$, M = Mo, $n = 3$) involve the use of hazardous and toxic reducing agents such as sodium or potassium amalgam [1], sodium–potassium alloy [2], potassium in refluxing THF [3], or a potassium mirror [4]. Moreover, whatever the reagent employed for the preparation of transition metal anion $[M(C_5Me_5)(CO)_n]^-M'^+$, II (M′ = K, Na; eq. 1), it must be used in a large excess for kinetic reasons [5*]. Indeed, although electron transfer is thermodynamically favored owing to the very low value of the redox potential of these reagents ($E_0 \approx -3$ V/e.c.s.), these reactions usually proceed slowly, mainly because of surface effects. For instance, preparation of the anionic Ru complex $[Ru(C_5Me_5)(CO)_2]^-K^+$ has proved to be difficult; the synthesis by reduction of the dimer $[Ru(C_5Me_5)(CO)_2]_2$ in THF with a large excess of Na/K alloy requires 3 d

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* Reference number with asterisk indicates a note in the list of references.

at 20 °C [2], and even with potassium metal (in 5-fold excess) in refluxing THF (65 °C) 12 h are still needed [3].

$$\underset{\text{(I)}}{[\mathrm{M(C_5Me_5)(CO)}_n]_2} + 2e^- \rightarrow 2\underset{\text{(II)}}{[\mathrm{M(C_5Me_5)(CO)}_n]^-} \qquad (1)$$

These transition metal anions II are important species because they are starting materials for the synthesis of the transition metal alkyl complexes $\mathrm{M(C_5Me_5)(CO)}_n\mathrm{R}$ (III) (eq. 2) [7].

$$\underset{\text{(II)}}{[\mathrm{M(C_5Me_5)(CO)}_n]^-} + \mathrm{RX} \rightarrow \underset{\text{(III)}}{\mathrm{M(C_5Me_5)(CO)}_n\mathrm{R}} + \mathrm{X}^- \qquad (2)$$

Since these metal alkyl compounds are important reagents or intermediates in most stoicheiometric or catalytic reactions involving transition metal compounds, a convenient synthesis is very desirable. In general the direct alkylation of the anionic compounds II in the presence of an excess of the reducing reagent is accompanied by side reactions and formation of by-products, and because of this a better route to the alkyl complexes III requires prior separation of the THF slurry of the highly reactive intermediates II from the excess of the reducing agent [4]. This hazardous step, often difficult and time consuming, has been found to be responsible for low yields. We now describe an alternative one-pot procedure for preparing compounds III from dimers I in THF at room temperature using ultrasound-activated potassium as a stoicheiometric reducing reagent [8].

Experimental

General data

All manipulations were performed under argon by use of standard Schlenk techniques or in a BS531 Jacomex dry-box filled with nitrogen. Solvents were dried, distilled, and de-aerated before use. Reagent grade tetrahydrofuran (THF), diethyl ether, and pentane, were distilled from sodium benzophenone ketyl immediately before use; CH_2Cl_2 was distilled first from P_2O_5 and then from Na_2CO_3. All other chemicals were used as received. Infrared spectra were recorded on a Pye Unicam SP 1100 spectrophotometer and calibrated with a polystyrene film; 0.1 mm cells with KBr windows were used for solutions and KBr pellets for Nujol mulls. The ^{1}H, and ^{13}C NMR spectra were recorded on a Brucker WP 80 FT or AM 300 Wb instrument. All chemical shifts are in parts per million (ppm) relative to TMS. Ultrasonic irradiations involved a collimated 20 kHz beam from a 600 W generator and a titanium amplifying horn (Vibra-Cell Model VC 600) introduced into the solution through a rubber septum. The reactions were performed in a 100 ml Schlenk tube equipped with a side arm for introduction of the reagents. Small scale reactions were performed with a 100 W equipment (Ultrasons Annemasse, Model Sonimasse S20) with a 20 ml vessel. Iron [1], ruthenium [9], and molybdenum [10] dimers were prepared as described below.

General procedure

In a typical experiment, clean potassium (20 mmol, 800 mg) was added to a 80 ml of THF, and the mixture was sonicated for a 5 min to give a grey blue colloidal dispersion. Dimer I (10 mmol) was carefully introduced under argon and the suspension was sonicated for an additional period (see Table 1). The mixture was then cooled to -80 °C and 20 mmol of the alkylating reagent RX was added. After 5 min of additional sonication, the temperature was allowed to warm up to 20 °C. The metal alkyl complexes was isolated by the literature procedures. All spectroscopic properties were in agreement with literature data. Reactions on 1 mmol scale were carried out for the same times with similar yields.

*$Fe(C_5Me_5)(CO)_2CH_2CH_3$ (**1b**).* Yellow solid, m.p. 50 °C. IR (CH_2Cl_2) 2040, 1985 cm^{-1}. ^1H NMR ($CDCl_3$, 36 °C) δ 1.72 (s, 15H, C_5Me_5), 1.25 (t, J 6.2 Hz, 3H, CH_3); 1.03 (q, J 6.5 Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 36 °C) δ 6.72 (t, CH_2), 9.3 (q, C_5Me_5), 21.6 (q, CH_3), 94.8 (s, C_5Me_5), 219.5 (s, CO). Anal. Found: C, 60.65; H, 7.38. $C_{14}H_{20}FeO_2$ calc: C, 60.89; H, 7.30%.

*$Mo(C_5Me_5)(CO)_3CH_3$ (**3a**) [1a].* (^1H)^{13}C NMR ($CDCl_3$, 20 °C) δ -12.2 (CH_3); 10.4 (C_5Me_5); 104.1 (C_5Me_5); 232.2, 243.1 (CO).

*$Mo(C_5Me_5)(CO)_3CH_2OCH_3$ (**3b**) [13].* (^1H)^{13}C NMR (C_6D_6, 20 °C) δ 10.0 (C_5Me_5), 64.5 (CH_3), 68.3 (CH_2), 105.0 (C_5Me_5), 230, 243 (CO).

Results and discussion

Ultrasound irradiation (20 kHz) of clean potassium metal with an immersion titanium horn to focus the ultrasonic energy into the liquid [8*] affords an activated grey blue colloidal dispersion of potassium. A half-equivalent of dimer I is introduced under argon and the THF slurry is sonicated for additional 15 min (M = Fe, Mo) or 30 min (M = Ru) before addition of a stoicheiometric amount of the electrophilic RX. After work up, the alkyl compounds III are isolated in 80 to 95% yield (Table 1). These yields are either equal to or, most often, higher than the literature values.

The use of ultrasound to accelerate chemical reactions, in heterogeneous systems is becoming widespread [11,14]. The advantages of this technique are again clearly illustrated by the results described here. To our knowledge, there is only one previous example of the synthetic application of sonochemically-activated potassium metal, that in the preparation of cycloalkanes from dihalogenoalkanes [15]. The physical phenomena which are responsible of the kinetic activation mainly include cavitational erosion, cleaning at the liquid solid interfaces, enhancement of

Table 1

Synthesis of the metal alkyl complexes $M(C_5Me_5)(CO)_nR$ under sonochemical conditions

	M	RX	Yield (%)	Time (min)	Ref.
1a	Fe	CH_3I	80	15	[4]
1b	Fe	CH_3CH_2I	85	15	This work
1c	Fe	CH_3OCH_2Cl	95	15	[4]
1c	Fe	CH_3OCH_2Br	95	15	[4,12*]
2a	Ru	CH_3I	90	30	[2]
2b	Ru	CH_3OCH_2Cl	89	30	[2,3]
3a	Mo	CH_3I	90	15	[1a], This work
3b	Mo	CH_3OCH_2Cl	95	15	[13], This work

surface area by fragmentation of the solid into microscopic particles, and improvement in mass transport through turbulent mixing and acoustic streaming [14].

From a synthetic view point the sonochemically assisted reduction of organometallic dimers, which enables rapid formation of metallate complexes free from reducing reagent, saves time, avoids the need for isolation of the very reactive anions II, and permits precise control of the stoicheiometry of the reagents. Moreover, the sonochemical procedure removes the need to use the toxic mercury to form sodium or potassium amalgam, or to use a hazardous potassium mirror. Finally, with ultrasound a few minutes of irradiation (20 kHz, 100 W) have similar effects to several hours of heating at 65 °C, as evidenced by comparison of the results we present with those in the literature.

Acknowledgements

We thank Laboratoires Standa (Caen) for financial support to C.R., BASF (Ludwigshafen, West Germany) for a generous gift of iron and molybdenum carbonyl, and Dr J.-R. Hamon for helpful discussions.

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