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Reactions of Delocalized Dianions with Transition Metal Complexes. Electron Transfer in the Reaction of the Isobutylene Dianion with Molybdenum Carbonyl Dihalides

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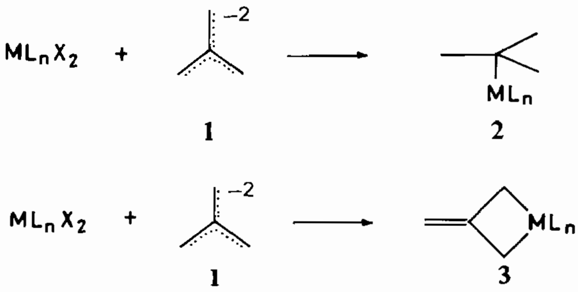
Abstract

Reaction of the dianion of isobutylene with $Mo(CO)_3(PPh_3)_2X_2$ results in the reduction of the metal and concomitant oxidation of the dianion. The reduction parallels the previously reported electrochemical reduction. Reaction of the dianion with $Mo(CO)_4X_2$ results in reduction of the metal presumably to coordinatively unsaturated $Mo(CO)_x$ (x = 5, 4) which is then trapped by solvent or tertiary amines in solution to give $Mo(CO)_4L_2$ (L_2 = $(THF)_2$, TMEDA). The reduction potentials for $Mo(CO)_3(PPh_3)_2X_2$ allow an estimate of the oxidation potential of the isobutylene dianion to be greater than −0.35 V *versus* SCE. Cp_2TiCl_2, which is not reduced by the isobutylene dianion, allows the estimate of the upper limit of the oxidation potential to be evaluated as less that −0.88 V *versus* SCE. The dianion is therefore by this criterion, less stable than the cyclopentadienyl anion (Ep = −0.18 V *versus* SCE) but more stable than the allyl anion (Ep = −1.40 V *versus* SCE).

Introduction

The preparation of organometallic complexes by the reaction of delocalized 'anions' [1] with transition metal halides is well established. Because of our interest in acyclic delocalized dianions [2–4], we have begun examining their reactions with transition metal halides.

The dianion of isobutylene (**1**) might be expected to add to a transition metal halide in one of two ways as shown in Scheme 1, depending on the number of electrons surrounding the metal. Alternatively, reaction of the electron-rich dianion with transition metal complexes may result in oxidation of the dianion with concomitant reduction of the transition metal complex. If the reduction potential of the transition metal complex is known, the minimum value of the oxidation potential of the dianion can be deduced from it. Because of current interest in the stability of the isobutylene dianion [5, 6] which could be evaluated from its oxidation potential, and because of the difficulty in obtaining the oxidation potential directly, indirect determination of that potential might be the most feasible approach in an assessment of the stability of **1**. With these outcomes in mind, we began our investigations with the group VIb carbonyl halides, $M(CO)_4X_2$ (**4**) and $M(CO)_3(PPh_3)_2X_2$ (**5**), where M = Mo, W and X = Br, Cl. Compound **4** is formally a 16 electron complex and might be expected to give **2** upon treatment with **1**; **5** is an 18 electron complex, whose reaction with **1** could give **3**. Labilization of a carbonyl ligand either *in situ* or photochemically should allow conversion of **3** to **2**.



Scheme 1.

Experimental

General Techniques and Chemicals

All manipulations of air-sensitive compounds were carried out under an inert gas using Schlenk techniques. Transfer of solvents was by cannula with solvent removal by high vacuum techniques. The preparations of $Mo(CO)_4Br_2$ and $Mo(CO)_3(PPh_3)_2Br_2$ were based on procedures previously described [7, 8]. All solvents used for this work were distilled under nitrogen from the sodium/benzophenone ketyl. Potassium t-butoxide was used as obtained

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from Aldrich Chemical Company. Isobutylene was obtained from Matheson and distilled prior to use. n-Butyllithium was used as obtained from Alfa.

Instrumentation

IR spectra were taken on a Perkin-Elmer 283 grating spectrophotometer and proton and carbon-13 NMR spectra were taken on a JEOL-FX-90Q spectrometer.

General Procedure for Metallation

(A) With Lochman's base [9]

Potassium t-butoxide (2.48 g, 22 mmol) in pentane and n-butyllithium (9.2 ml, 22 mmol) were combined in a septum-capped test-tube under argon to form a beige complex. To the metallating system at 0 °C was added isobutylene (1 ml, 11 mmol) which had been condensed at –78 °C. The bright yellow dianion was ready for reaction after 60 min. The supernatant was removed by cannula and the precipitated dianion washed with benzene. The precipitate was suspended in 20 ml THF and added to 11 mmol of the molybdenum dihalide (**4** or **5**) in 30 ml THF at 0 °C. After 60 min, the solvent was removed under vacuum and the reddish-brown sludge extracted with 50 ml benzene. $Mo(CO)_4(PPh_3)_2$ (from reaction of the dianion with **5**) was isolated by chromatography with benzene on alumina under N_2 or by trituration of the benzene solution with pentane.

(B) With n-butyllithium/TMEDA

N,N,N′,N′-tetramethylethylenediamine(TMEDA) (3.2 ml, 22 mmol) and n-butyllithium (9.2 ml, 22 mmol) were combined in a septum-capped test tube under argon. To the metallating system was added isobutylene (1 ml, 11 mmol) condensed at –78 °C. The yellow–orange dianion was ready for reaction after 3–5 days. The supernatant was removed by cannula, the precipitate dissolved in THF and reacted with molybdenum dihalides **4** and **5** as described in (A). $Mo(CO)_4(PPh_3)_2$ (from reaction with **5**) was isolated from the benzene solution as described above. $Mo(CO)_4$(TMEDA) (from reaction of the dianion with 4) was isolated by trituration of the benzene solution with pentane and identified by comparison with an authentic sample prepared by the method of Cotton* [10].

(C) With Lochman's base followed by replacement of potassium cations with lithium cations [11]

The dianion was prepared as in (A) and the supernatant removed. The precipitate was washed with benzene to remove lithium t-butoxide and suspended in 15 ml THF. Addition of a solution of lithium bromide (22 mmol) in 15 ml THF resulted in the rapid deposition of potassium bromide. The dianion solution was removed and reacted with molybdenum dihalides **4** and **5** as in (A).

Results

Treatment of a THF solution of $Mo(CO)_3(PPh_3)_2X_2$ [7, 8] (X = Cl or Br) with an equimolar solution of **1**, prepared by metallating isobutylene with two equivalents of n-butyllithium/potassium t-butoxide, (Lochman's base) [9] resulted in the formation of a brownish solution from which only one stable product, *trans*-$Mo(CO)_4(PPh_3)_2$ (**6**), could be isolated, by treatment with benzene. The presence of **6** [12] in the reaction mixture within an hour of the addition of the solution of the isobutylene dianion to a solution of **5** was established by infrared spectroscopy and verified by isolation of the product. Product **6** was the major metal carbonyl species formed in the reaction. Confirmation of the formation of **6** by electron transfer from dianion **1** was obtained through the isolation of two oxidation products of **1**, methylenecyclopropane and 1,4-dimethylenecyclohexane. In an analogous reaction, Bond *et al.* [13] isolated **6** by the electrochemical reduction of **5** (X = Cl). Interestingly, Bond reports that reduction of **5** (X = Br), (5×10^{-3} M $Mo(CO)_3(PPh_3)_2Br_2$) occurs to give $[Mo(CO)_5Br]^-$ which decomposed without substitution by PPh_3 to give a non-carbonyl-containing product. Our observation of substitution by PPh_3 in solutions which are 0.233 M in $Mo(CO)_3(PPh_3)_2Br_2$, rather than formation of $[Mo(CO)_5Br]^-$, suggests that the proclivity for substitution is primarily a concentration dependent phenomenom.

Reasoning that the reactivity of dianion **1** might be modified by association with a less electropositive cation, we then prepared and reacted two dilithio isobutylene dianions with **5**. Dianion **1** can be prepared by metallation of isobutylene by a 1:1 complex of n-butyllithium/tetramethylenediamine (TMEDA) [14]. Alternatively, the dipotassio **1** can be treated with LiBr [11] to afford the dilithiated species in the absence of coordinating ligands. Infrared spectra of the reaction mixtures from the addition of either dilithated isobutylene to **5** (M = Mo) were very similar and showed primarily the strong peak at 1905 cm^{-1} characteristic of $Mo(CO)_4(PPh_3)_2$. In all cases, formation of **6** was accompanied by the formation of a thick sludge containing molybdenum, which was not soluble in organic solvents.

During this time, we had also begun investigating the reaction of **1** with **4** (M = Mo, X = Br). Only

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*The identity of the product was confirmed by an independent synthesis from $Mo(CO)_6$.

when **1**, produced by metallation with n-butyllithium/TMEDA, was reacted with **4** (M = Mo) could a stable product be isolated. That product was $Mo(CO)_4$TMEDA [10], produced by reduction of **4** by **1** with concomitant loss of halide ions and complexation by the TMEDA initially associated with the lithium cation. Again the involvement of **1** as a reducing agent was confirmed by isolation of its oxidation products, methylenecyclopropane and 1,4-dimethylenecyclohexane.

Addition of dipotassio or dilithio-isobutylene, prepared by initial metallation with potassium t-butoxide/n-butyllithium, to **4** (M = Mo) gave a reaction mixture with strong carbonyl absorptions in the infrared spectrum, at 1930, 1860 and 1790 cm^{-1}. Extraction with benzene gave a solution with essentially the same absorbances. However, removal of the solvent under argon led to decomposition of the complex with concomitant formation of $Mo(CO)_6$. We theorize that reduction of **4** (M = Mo) gives coordinatively unsaturated $Mo(CO)_x$ species which react with electron donors present, forming unstable adducts.

Discussion

Although the reaction of the isobutylene dianion with the molybdenum(II) carbonyl halides resulted in reduction through electron transfer from **1**, rather than substitution to give **2** or **3**, knowledge of the reduction potentials of $Mo(CO)_3(PPh_3)_2X_2$ (X = Cl, Br) allows us to begin to assess the oxidation potential of the dianion. Bond *et al.* [13] report the half-wave potentials for reduction of $Mo(CO)_3(PPh_3)_2Cl_2$ ($E_{1/2}$ = −0.38 V *versus* Ag/Ag Cl; −0.36 V *versus* SCE) and $Mo(CO)_3(PPh_3)Br_2$ ($E_{1/2}$ = −0.49 V *versus* Ag/AgCl; −0.47 V *versus* SCE). The electron transfer from dianion **1** to the molybdenum dihalide reflects not only the reduction potential of the metal dihalide but also the corresponding oxidation potential must be at least as negative as the of an organolithium reagent is directly related to its reluctance to be oxidized, the more stable organolithium compound has a less negative (more positive) oxidation potential.

For dianion **1** to reduce $Mo(CO)_3(PPh_3)_2X_2$, its oxidation potential must be at least as negative as the reduction potential of the molybdenum dichloride [13]; it must be more negative than −0.38 V *versus* SCE. An organolithium with a more positive oxidation potential, like the cyclopentadienyl anion (*Ep* of cyclopentadienyllithium [15] = −0.18 V *versus* SCE at 25 °C) would not be capable of reducing $Mo(CO)_3(PPh_3)_2X_2$. Since the more stable organolithium reagent should have the less negative oxidation potential, it comes as no surprise that cyclopentadienyllithium is more stable than dilithio-isobutylene.

With these results, we have begun to establish indirectly, the range of values for the oxidation potential of dilithio-**1**, with the oxidation potential equal to or more negative than −0.36 V *versus* SCE. To obtain a sense of the maximum negative potential, one must identify a reaction in which the dianion does not react by electron transfer. The most nearly similar substrate for comparison purposes should also be a covalent transition metal dihalide, such as biscyclopentadienyl titanium dichloride. The reaction of **1** with $(C_5H_5)_2TiCl_2$ ($Ep_{\text{reduction}}$ = −0.88 V *versus* SCE [16]) gives titanocyclobutane **3** [17] ($L_n = Cp_2$) as the major product. Since there was no apparent electron transfer, the oxidation potential of **1** must be less than the reduction potential of $Ti(C_5H_5)_2Cl_2$, less than −0.88 V *versus* SCE. To summarize, the oxidation potential of **1** must be between −0.88 V and −0.36 V *versus* SCE.

By this criterion dilithio-**1** is more stable, less susceptible to electron transfer, than organolithium compounds with more negative oxidation potentials, such as allyllithium ($Ep_{\text{oxidation}} = -1.40$ V *versus* SCE) [15].

Dianion **1** has been considered as a potentially 'Y-aromatic' species [5, 6, 18, 19]. The current results suggest additional [2] evidence to support its enhanced stability.

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