of observed temperature-independent isotope effects giving rise to large anomalous A_H/A_D values the possibility of alternative mechanisms should be carefully considered.

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Deprotonation and Anionic Rearrangements of Organometallic Compounds. 1. Reactions of Cyclopentadienylrhenium Acyl and Alkyl Complexes with Strong Bases

Poh Choo Heah and J. A. Gladysz*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

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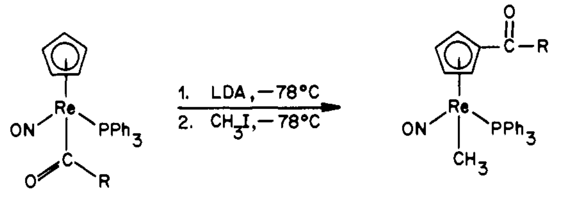
Carbanions generated by reactions of organometallic complexes with strong, nonnucleophilic bases are seeing increased applications in organic and organometallic synthesis.[1,2] However, few if any parallels[3] have been noted to the rich migration chemistry observed upon deprotonation of ligands attached to main-group elements[4] (e.g., Wittig,[4a] Stevens,[4b] and Brook[4d] rearrangements). We disclose herein (1) a novel sequence of reactions which occurs upon treatment of rhenium acyl complexes (η^5-C_5H_5)Re(NO)(PPh$_3$)(COR) with strong bases, (2) mechanistic details thereof, and (3) related chemistry of alkyl complexes (η^5-C_5H_5)Re(NO)(PPh$_3$)(R). These observations presage a new class of organometallic reactions[5] of potentially broad generality and utility.[3,6]

Treatment of acetyl complex (η^5-C_5H_5)Re(NO)(PPh$_3$)(COCH$_3$)[7] (**1a**) with Li$^+$ (i-Pr)$_2$N$^-$ (LDA) (1.6–2.1 equiv) in THF at −78 °C (5 min), followed by CH$_3$I (2 equiv) gave, after workup, methyl complex (η^5-C_5H_4COCH$_3$)Re(NO)(PPh$_3$)(CH$_3$) (**2a**) in 76% yield (eq i). The structure of **2a** was evident from its spectral features,[8] which included ^{1}H and ^{13}C NMR patterns characteristic of monosubstituted cyclopentadienyl complexes. No products derived from the methylation of (η^5-C_5H_5)Re(NO)(PPh$_3$)(COCH$_2$Li) were detected. Bases n-BuLi and n-BuLi·TMEDA gave chemistry identical with LDA.

The generality of this transformation was probed with additional substrates. Similar treatment of benzoyl complex **1b**[7] and phenylacetyl complex **1c**[7] (eq i) with LDA and CH$_3$I gave methyl complexes **2b**[8] and **2c**[8] in 50% and 78% yields, respectively. Substitution of Br$_2$ for CH$_3$I in the latter reaction gave bromide complex (η^5-C_5H_4COCH$_2$C$_6$H$_5$)Re(NO)(PPh$_3$)(Br) (58%).[8]

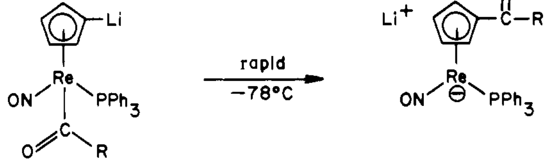


(i)

1a, R = CH$_3$
b, R = C$_6$H$_5$
c, R = CH$_2$C$_6$H$_5$

2a, R = CH$_3$ (76%)
b, R = C$_6$H$_5$ (50%)
c, R = CH$_2$C$_6$H$_5$ (78%)

via:



3 **4**

Plausible steps in the transformations **1** → **2** would include initial cyclopentadienyl ring deprotonation to give (η^5-C_5H_4Li)-Re(NO)(PPh$_3$)(COR) (**3**), followed by acyl ligand migration to give rhenium anion Li$^+$[(η^5-C_5H_4COR)Re(NO)(PPh$_3$)]$^-$ (**4**). We sought evidence for and mechanistic data on these processes. First, reaction of (η^5-C_5D_5)Re(NO)(PPh$_3$)(COCH$_3$) (**1a**-d_5; ca. 90:10 d_5/d_4)[8] with LDA and CH$_3$I as described above gave **2a**-d_4 (<2% d_3), as assayed by careful mass spectrometric analysis. This indicates that LDA initially abstracts a cyclopentadienyl proton of **1**; also, since the product **2a**-d_4 is of greater isotopic purity than the starting material, deprotonation must occur with a substantial k_H/k_D. Second, the reaction of **1a** with LDA was monitored by ^{31}P NMR at −78 °C. A new resonance (43.8 ppm, br m) appeared immediately, and did not diminish upon warming to −5 °C. Addition of CH$_3$I gave **2a**; hence, the resonance was assigned to **4a**. Also, **2a** was isolated in good yield following addition of LDA to a −78 °C *mixture* of **1a** and CH$_3$I. These observations indicate that the rearrangement **3** → **4** is rapid at −78 °C. Finally, coreaction of a mixture of **1b** and (η^5-C_5D_5)Re(NO)(PPh$_3$)(COC$_6$D$_5$) (**1b**-d_{10})[8] with LDA and CH$_3$I as above gave *exclusively* **2b**-d_0 and **2b**-d_9. Hence, **3** → **4** is intramolecular.

Before attempting stereochemical experiments, the deprotonation of analogous rhenium alkyl complexes was studied. Treatment of (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_2$C$_6$H$_5$)[9] with 1.5 equiv of n-BuLi·TMEDA in THF at −78 °C gave rapid (<5 min) and quantitative conversion to (η^5-C_5H_4Li)Re(NO)(PPh$_3$)(CH$_2$C$_6$H$_5$) (**5**), as assayed by ^{31}P NMR (25.8 ppm) and subsequent methylation (CH$_3$I, −78 °C) to (η^5-C_5H_4CH$_3$)Re(NO)(PPh$_3$)(CH$_2$C$_6$H$_5$) (**6**, 74%, eq ii).[8] Treatment of (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_3$) (**7**)[10] with 2.1 equiv of n-BuLi·TMEDA in THF at −78 °C gave a slower (10 min) but still quantitative conversion to (η^5-C_5H_4Li)Re(NO)(PPh$_3$)(CH$_3$) (**8**), as assayed by ^{31}P NMR (28.2 ppm) and subsequent acylation (acetic anhydride, −24 °C, 38%) to **2a** and (benzoic anhydride, −78 °C, 60%) **2b**. In separate ^{31}P NMR experiments, neither **5** nor **8** showed any appreciable rearrangement or decomposition over the course of 30 min at 25 °C.

With two distinct routes to **2a** established, the stereochemistry of the rearrangement **3a** → **4a** could be probed. First, it was determined that addition of the chiral shift reagent tris[(trifluoromethyl)hydroxymethylene-d-camphorato]europium to CD$_2$Cl$_2$ solutions of **2a** differentiated the CH$_3$ ^{1}H NMR reso-

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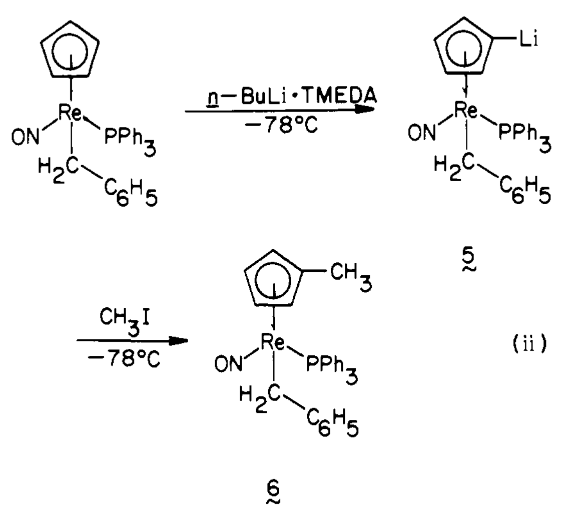
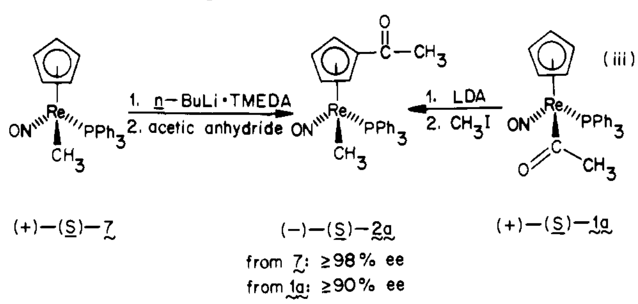


nances of each enantiomer. With this optical purity assay available, the reaction of methyl complex **7** with *n*-BuLi·TMEDA and acetic anhydride was repeated with (+)-(*S*)-**7**, (≥98% ee, prepared from (+)-(*S*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$).[11] Levorotatory **2a**, ≥98% ee, was obtained. Since this transformation occurs without apparent rupture of any metal–ligand bonds, we assign the product as (−)-(*S*)-**2a** (eq iii), corresponding



to retention of configuration at rhenium. Next eq i was repeated with (+)-(*S*)-**1a** (≥98% ee, also prepared from (+)-(*S*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$).[7] This gave (−)-(*S*)-**2a**, ≥90% ee (eq iii). Hence the rearrangement **3a** → **4a** proceeds with a high degree of *retention*.

The above results are important in several contexts. First, migrations of $Mo\text{–}Ge(C_6H_5)_3$[3a] and $Fe\text{–}Si(CH_3)_3$[3c] to coordinated $\eta^5\text{-}C_5H_4Li$ have been previously reported. Our data indicate that such rearrangements (1) are likely to be of appreciable generality with regard to the metal and migrating ligand[6] and (2) can be intramolecular and highly stereoselective. Some conceptually related organometallic rearrangements have been recently analyzed by Hoffmann.[5] Also, note the intriguing parallel of eq i to the Wittig rearrangement,[4a] in which an alkyl ligand of an ether oxygen is α-deprotonated to $R'O\bar{C}HR$, followed by ligand′ migration to give oxygen anion $^-OCHRR'$. Finally, other cyclopentadienylmetal acyl complexes are deprotonated by LDA on the *acyl* ligand.[2] Is the contrasting chemistry of **1a** and **1c** kinetically or thermodynamically controlled? We estimate, on the basis of previously noted parallels,[7,11] that the pK_a's of the $ReCOCH_2R$ protons of **1a** and **1c** are similar to those found in amides.[12] The pK_a of $CH_3CON(CH_3)_2$ is, depending upon solvent, 31–34, and α-phenyl substitution enhances amide acidity by ca. 7 pK_a units.[12] The pK_a's of $\eta^5\text{-}C_5H_5$ C–H bonds in $(\eta^5\text{-}C_5H_5)Fe(CO)_2(R)$ complexes are in the range 29–30.[13] Hence, it is highly probable that the deprotonation of **1c** is kinetically controlled. Experiments designed to probe this point, and other aspects of the above reactions, are in progress.

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Supplementary Material Available: Table of characterization of new compounds (3 pages).[8] Ordering information is given on any current masthead page.

Force Constants for the Cyclopropenyl Cation

Norman C. Craig,* Julianto Pranata, Julian R. Sprague, and Philip S. Stevens

Department of Chemistry, Oberlin College
Oberlin, Ohio 44074

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Although the unsubstituted cyclopropenyl cation ($C_3H_3^+$) has been known since the experiments of Breslow and co-workers in the late 1960s,[1] the bonds in this simplest of aromatic systems (Hückel $4n + 2$, $n = 0$) are not experimentally well characterized. We now report empirical force constants for the bonds of this ion, as derived from normal coordinate calculations applied to the fundamental vibration frequencies of $C_3H_3^+$, $C_3D_3^+$, and $C_3H_2D^+$. The force constants for CC stretching, CH stretching, and in-plane CH bending of the cyclopropenyl cation are larger than the corresponding ones in benzene. The notably high value for the CC stretching force constant supports the value obtained in the ab initio calculation of Takada and Ohno.[2]

The precursors of the $C_3H_3^+$ and $C_3D_3^+$ ions were 3-chlorocyclopropene-d_0 and -d_3.[1c,3] The precursor of the new species, $C_3H_2D^+$, was prepared by a two-step reduction process in which perchlorocyclopropene was treated with tributyltin hydride, and the product was treated with tributyltin deuteride. For all of the cation preparations BF_3 was used as the Lewis acid. Samples for Raman spectroscopy at −50 °C were prepared in SO_2 solution, and samples for infrared spectroscopy at −196 °C were prepared as polycrystalline deposits on a cesium iodide window by a bilayer reaction technique.[4]

Table I summarizes the observed fundamental vibration frequencies and assignments for the in-plane modes of the three cations. Assignments for the out-of-plane modes, which are incomplete at the present time, are not included. The assignments of the IR bands of $C_3H_3^+$ and $C_3D_3^+$ are in reasonable agreement with the observations of Breslow et al. for Nujol mulls of the $SbCl_6^-$ salts.[1b] Except for the a_2' modes of the two ions of D_{3h} symmetry, which are neither infrared nor Raman active, and ν_9 of the $C_3H_2D^+$ ion, all of the in-plane fundamental frequencies have been observed for the three ions in one or both spectroscopies.

Normal coordinate calculations were carried out in the harmonic approximation in internal coordinate space with well-known matrix formalisms and standard computer programs.[5,6] A nonredundant set of internal coordinates [three CC stretching, three CH(D) stretching, and three CH(D) bending] were used.[7] The three simple valence force constants and four of the seven possible interaction force constants of the general valence force field were employed. Table II contains a comparison of the fitted and observed frequencies. The good quality of the fit is reflected in

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