

system. Also, attempted hydrogenation of olefins, such as stilbene or reduction of benzonitrile with our reagents resulted in recovery of the starting materials respectively. The source of this unexpected reactivity of activated molybdenum powder for the reduction of nitroarenes may be from the high surface area, some unique surface species which we are currently under investigation. In conclusion, the high yields, short reaction times, mild conditions and simplicity of workup are noteworthy of this system. We are presently exploring the scope of activated molybdenum to a variety of functional group transformation.

Experimental

Commercial nitro compounds (Aldrich, Junsei, Yakuri) and solvents were purified and dried prior to use when deemed necessary. Anhydrous molybdenum (V) chloride and zinc dust (-325 mesh) were purchased from Aldrich chemical and used without any further treatment. Hydrazine monohydrate was purchased from Junsei Chemicals. Dimethoxyethane (DME) was distilled over sodium. Amino compounds were identified by comparison of their physical and chemical properties with those of authentic samples.

General procedure for the preparation of activated molybdenum powder. A typical preparation of activated molybdenum powder is as follows. Into a 100 ml of two-necked round bottom flask equipped with nitrogen septum inlet and condenser were placed anhydrous molybdenum chloride (0.38 g, 1.4 mmol), zinc (0.23 g, 3.5 mmol) and dry DME (10 ml). The exothermic reaction took place immediately and dark red solution turned to black. The mixture was then heated to reflux for 1h to complete reduction. When the heating was stopped, the very finely divided black metal powder was settled down in a black solution. This slurry was ready for this investigation without any further treatment after cooled to room temperature.

General procedure of reduction of nitroarenes with activated metal powder. Nitroarenes (1.2 mmol) and hydrazine monohydrate (1 ml, 20.6 mmol) were added to the stirred slurry. After initial effervescence had ceased, the resulting reaction mixture was then heated to reflux for 2 h. The dark solution mixture became clear and dark powder (presumably activated molybdenum) was settled down. Product isolation was straightforward. After filtration, solvent removal, and flash chromatography on a short silica gel column (4 cm x 1.5 dia.) using methylene chloride or methylene chloride-ethanol (8 : 2, v/v) as a eluant, the expected aminoarenes were obtained in 83-92% (see Table 1). Assignments of the simple amino compounds are based on NMR, IR and GLC-Mass spectral data.

Benzo[c]cinnoline was isolated as followed; after filtration and evaporation of solvent, silica gel column chromatography of the residue using ethyl acetate-hexane (1 : 1) as eluent provided benzo[c]cinnoline as reddish yellow crystalline solid. mp. 155-156 °C (lit.¹¹, mp. 157-158 °C); ¹H NMR (CDCl₃) δ 7.78-7.90 (m, 4H), 8.43-8.76 (m, 4H); MS (m/z): 180 (m⁺).

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Hydride Reduction of $\text{diag}(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{Br}_2$: Ring Attack vs. Metal-Halogen Exchange

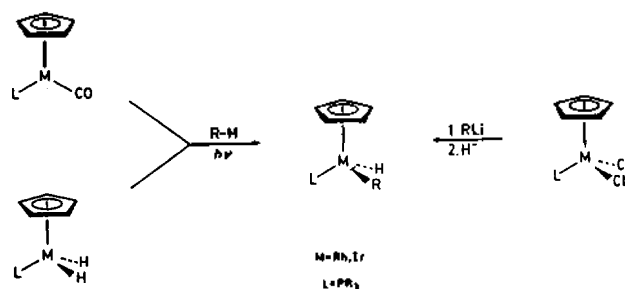
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The activation of alkanes by soluble cyclopentadienyl metal complexes has been shown to afford stable hydrido (alkyl) metal complexes in the case of rhenium, rhodium, and iridium systems.¹⁻³ The same products of these intermolecular oxidative addition reactions have also been independently prepared from the corresponding cyclopentadienyl rhodium and iridium dihalides by sequential halide reduction (Scheme 1).⁴ In contrast, the reaction of reducing agents with analogous cyclopentadienyl rhenium dihalides has not been extensively studied.⁵⁻⁷ This paper reports the results on the reaction of $\text{diag-CpRe}(\text{CO})_2\text{Br}_2$ (1: $\text{diag} = \text{diagonal}$; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$)



Scheme 1.

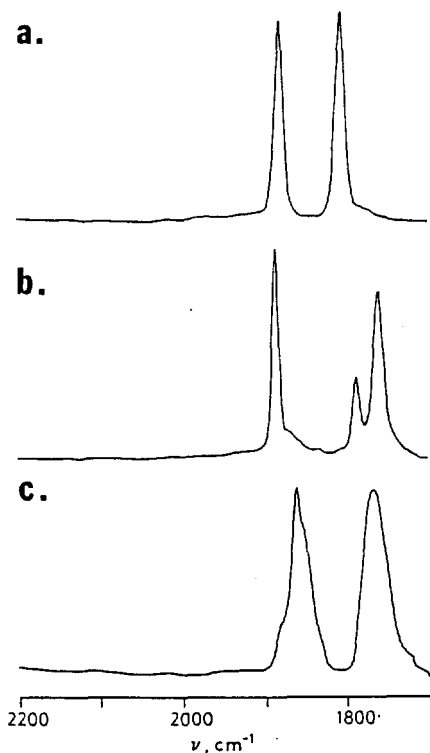


Figure 1. Infrared spectra of the carbonyl region for (a) $\text{CpRe}(\text{CO})_2\text{Br}^-$ (**2**), (b) $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{Br}_2^-$ (**3**), and (c) $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{Br}_2^-$ (**3**) with 5 eq. of 15-Crown-5. All spectra were recorded in THF at -78°C .

with reducing agents and shows that cyclopentadienyl ring attack and metal-halogen exchange occur in preference to direct metathetical replacement of the bromide moiety in **1**.

Reaction of **1** in THF with various RLi reagents (1.1 eq; R=Me, Ph, *t*-Bu) at -78°C affords a yellow colored solution containing $[\text{CpRe}(\text{CO})_2\text{Br}][\text{Li}]$ (**2**)⁹. Compound **2** exhibits carbonyl stretching bands at 1881 and 1806 cm^{-1} which are consistent with the ascription of **2** as an anionic complex possessing two carbonyl ligands (Figure 1a). A d_8 -THF solution of **2** displays a single ^1H NMR resonance at 4.87 ppm along with two ^{13}C NMR resonances at 87.2 and 214.3 ppm for the cyclopentadienyl and carbonyl groups, respectively.¹⁰ When these reactions were monitored by low-temperature FT-IR and NMR techniques no other complexes or intermediates were observed.^{11,12} **2** appears to be indefinitely stable under an inert atmosphere, but slowly decomposes upon exposure to oxygen to give $\text{CpRe}(\text{CO})_3$ in 25-35% yield.

We next treated a THF solution of **1** at -78°C with a stoichiometric amount of LiEt_3BH and observed a yellow colored solution whose infrared spectrum correspond to neither $[\text{CpRe}(\text{CO})_2\text{Br}]^-$ (*vide infra*), a Li^+/Br^- exchange product, nor $\text{CpRe}(\text{CO})_2\text{Br}(\text{H})$, a H^-/Br^- exchange product. The low-temperature FT-IR spectrum exhibited three carbonyl stretching bands at 1884, 1785, and 1758 cm^{-1} (Figure 1b) that are replaced by two new carbonyl bands at 1862 and 1768 cm^{-1} upon addition of 5 eq. of 15-Crown-5(1,4,7,10,13-pentaoxacyclopentadecane) as shown in Figure 1c. This latter spectrum is also obtained when a THF solution of **1** containing 5 eq. of 15-Crown-5 is treated with LiEt_3BH at

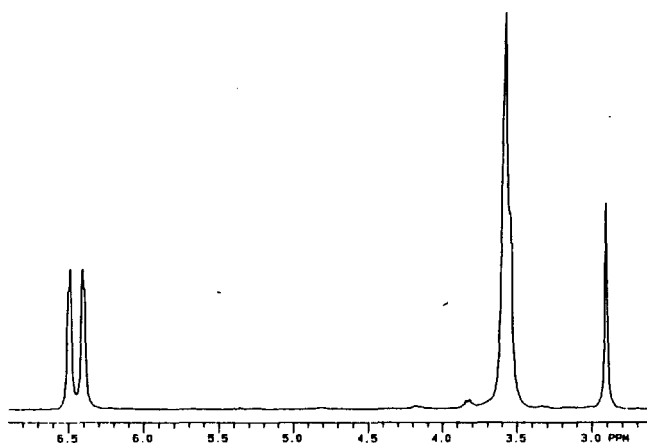


Figure 2. ^1H NMR spectrum of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{Br}_2^-$ (**3**) at -78°C in d_8 -THF. The resonance at 3.58 ppm belongs to the THF solvent from the LiEt_3BH reducing agent.

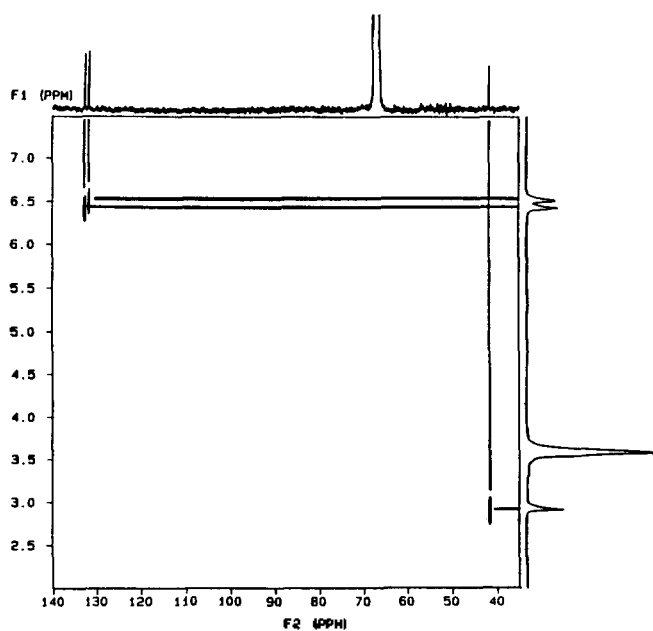


Figure 3. Heteronuclear chemical shift correlation spectrum of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{Br}_2^-$ (**3**) at -78°C in d_8 -THF.

-78°C . These results are consistent with the formation of an anionic cyclopentadienylrhenium complex that displays extensive carbonyl oxygen-lithium ion pairing in the absence of 15-Crown-5.¹³

The identity of this new complex was ascertained by low-temperature NMR spectroscopy. When a d_8 -THF solution of **1** was treated with LiEt_3BH at -78°C the starting cyclopentadienyl ^1H NMR resonance of **1** was replaced by three new resonances at 6.53, 6.43, and 2.90 ppm with an integral ratio of 2 : 2 : 2 (Figure 2). The use of LiEt_3BD in place of LiEt_3BH led to a decrease in the intensity of the resonance at 2.90 ppm; the low-field resonances associated with the AA'BB' spin system were unaffected yielding an observed integral ratio of 2 : 2 : 1. A ^{13}C [^1H] NMR spectrum revealed two low-field resonances at 134.3 and 133.1 ppm along with a single resonance at 42.6 ppm which suggested the presence

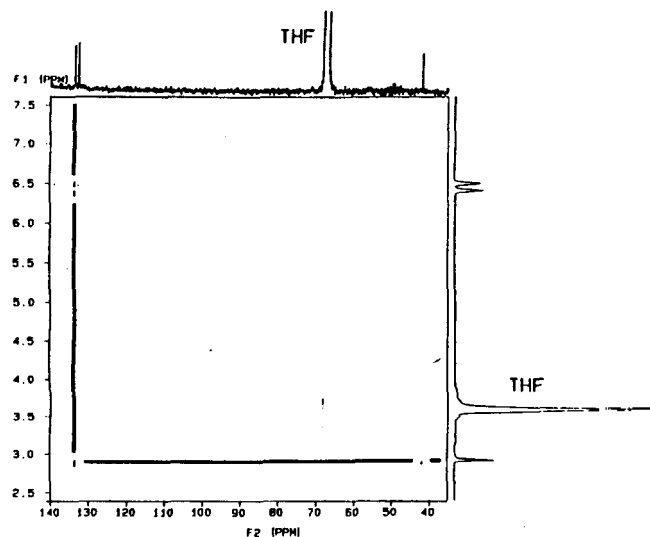
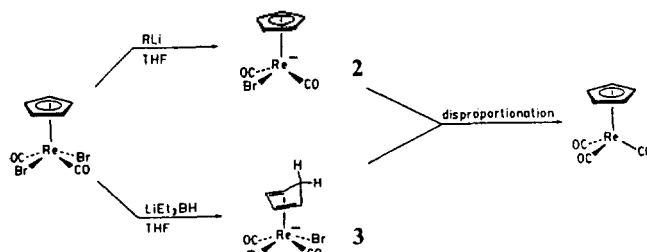
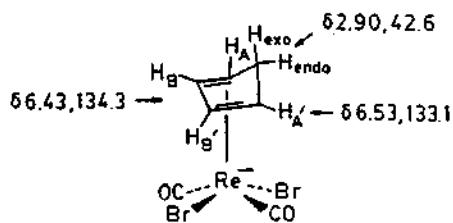


Figure 4. Long-range heteronuclear chemical shift correlation spectrum of $(\eta^4\text{-C}_5\text{H}_6)\text{Re}(\text{CO})_2\text{Br}_2^-$ (**3**) at $-78\text{ }^\circ\text{C}$ in $d_8\text{-THF}$.

of two types of olefinic carbons and a methylene moiety that are derived from the Cp ring of **1**.¹⁴ Finally, a ^1H - ^{13}C chemical shift correlation spectrum (HETCOR) was recorded to provide an accurate proton/carbon relationship¹⁵ in Figure 3. The ^1H NMR resonances at 6.53, 6.43 and 2.90 were shown to correlate with the ^{13}C NMR resonances at 133.1, 134.3 and 42.6 ppm, respectively. Based on these results we propose that the reduction with LiEt_3BH proceeds *via* hydride attack on the Cp ring of **1** to yield $(\eta^4\text{-C}_5\text{H}_6)\text{Re}(\text{CO})_2\text{Br}_2^-$ (**3**).¹⁶

Additional NMR experiments were conducted in an attempt to demonstrate that **3** resulted from Cp-ring attack.^{17,18} The easiest experiment would have involved the observation of NOE between the methylene protons and the adjacent olefinic protons (H_A and H_A'). Unfortunately, no NOE was observed in the olefinic protons when the methylene resonance at 2.90 ppm was irradiated. A selective ^{13}C NOE experiment was then performed using the ^1H resonance at 2.90 ppm to provide information concerning the adjacent olefinic carbons. The ^{13}C resonance at 133.1 ppm displayed about 15% enhancement in signal intensity relative to the 134.3 ppm resonance. This indicates that the low-field resonance of the proton AA'BB' spin system (6.53 ppm) is adjacent to the methylene moiety. Finally, the relationship between the methylene group and the remaining olefinic carbons (134.3 ppm) was established by long-range ^1H - ^{13}C chemical shift correlation spectroscopy using magnetization transfer delays optimized for three-bond coupling (10 Hz).¹⁹ Figure 4 shows the long-range coupling between the methylene protons and the olefinic resonance at 134.3 ppm. These data collectively support the existence of a $\eta^4\text{-C}_5\text{H}_6$ cyclopentadiene ring in **3**. The results are summarized below.²⁰



Scheme 2.

3 was observed to be stable for a period of six months when maintained at $-78\text{ }^\circ\text{C}$. However, decomposition of **3** is noticeable upon warming to $-30\text{ }^\circ\text{C}$, being complete by $0\text{ }^\circ\text{C}$ to afford a green colored solution. FT-IR analysis revealed the presence of only $\text{CpRe}(\text{CO})_3$ which we have been able to routinely isolate in 25-35% yield. While the exact mechanism associated with this disproportionation is unknown at this time, the observation of $\text{CpRe}(\text{CO})_3$ (in part) provides insight into the stereochemistry attendant upon hydride attack. If we assume that the *endo* hydrogen of the $\eta^4\text{-C}_5\text{H}_6$ ring is transferred to rhenium during decomposition,²¹ then the *exo* hydrogen must become incorporated into the cyclopentadienyl ring of $\text{CpRe}(\text{CO})_3$. This was demonstrated by isolation and ^2H NMR examination of the $\text{CpRe}(\text{CO})_3$ that was formed from a reaction using LiEt_3BD . The ^2H NMR spectrum exhibited a singlet at 5.48 ppm consistent with a cyclopentadienyl moiety. Integration against added C_6D_6 or the natural abundance solvent resonance supports the presence of one deuterium per Cp ring and an initial *exo* attack of the reducing agent.²²

The reaction of reducing agents with *diag*- $\text{CpRe}(\text{CO})_2\text{Br}_2^-$ has been shown to proceed via cyclopentadienyl ring attack or metal-halogen exchange. Under no circumstances was a metathetical replacement of bromide observed. Anions **2** and **3** are currently being examined as cluster building blocks and in CO_2 reduction studies. These results along with our work in progress on the reduction reactions involving the lateral isomer of **1** and the analogous rhenium MeCp derivatives will be reported shortly.

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9. Complete details on the X-ray crystal structure of **2** (Li^+ /15-Crown-5) will be presented in the full paper describing the reactivity differences between the lateral and diagonal isomer of $\text{CpRe}(\text{CO})_2\text{Br}_2$.
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A Facile Synthetic Route to 2-[p-(2',2',3',3'-Tetracyanocyclopropyl)phenoxy]ethanol

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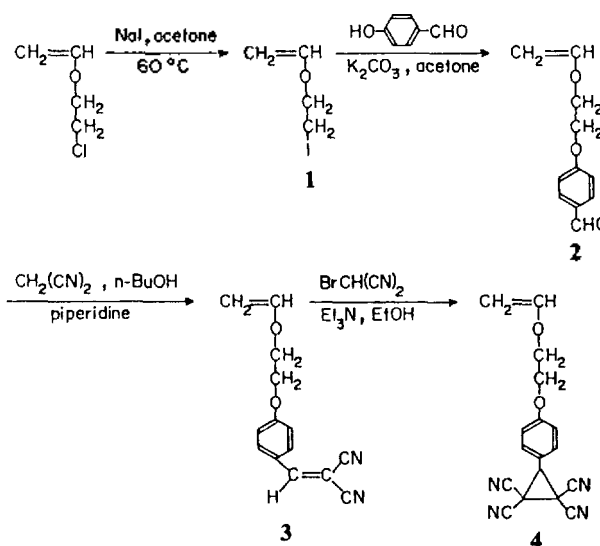
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1,1,2,2-Tetracyanocyclopropane can be obtained easily by reaction of aqueous formaldehyde and malononitrile¹, tetracyanoethylene with diazomethane² or tetracyanoethylene with bromoketene acetals.³ A large number of substituted 1,1,2,2-tetracyanocyclopropanes are prepared by the Wideqvist reaction,^{4,5} in which a carbonyl compound react with excess bromomalononitrile. A similar cyclopropanation procedure was reported by Hart.^{6,7} 1,1,2-Tricyanocyclopropanes can be prepared from ylidenecyanoacetate and bromomalononitrile.⁸ Recently, we extended the Wideqvist reaction to prepare substituted 1,2-dicyanocyclopropanes.⁹

In the course of our study of tetracyanocyclopropane,^{10,11} we found that benzylidenemalononitrile or benzylidencyanoacetate containing vinyl ether moiety shows an abnormal cyclopropanation. In this work we investigated the cyclopropanation behaviors of p-(2-vinyloxyethoxy)benzylidenemalononitrile **3** and methyl (2-vinyloxyethoxy)benzylidencyanoacetate **6**. We now report the results of the initial phase of the work.

2-Iodoethyl vinyl ether **1** was prepared by the well known halogen exchange reaction¹² from 2-chloroethyl vinyl ether and sodium iodide. Compound **1** was reacted with 4-hydroxy-



Scheme 1.