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Evidence for Rhenaphenanthrene Formation and Its Conversion to Fluorenone

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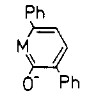
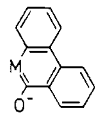
Introduction of 2,2′-dilithiobiphenyl to $PPh_3(CO)_4ReBr$ gives 9-fluorenone. 9-Fluorenone may be formed via a reductive elimination from a rhenaphenanthrene intermediate. Reaction of 2,2′-dilithiobiphenyl with $(CO)_5ReBr$ also gives 9-fluorenone. A mechanism consistent with this conversion involves formation of a rhenacycloheptatetraene followed by ring contraction to the rhenaphenanthrene **4**. Reductive elimination from **3** gives the product. Reaction of 2,2′-dilithiobiphenyl with $(CO)_5ReBr$ followed by low-temperature oxidative quenching generates 9,10-phenanthrenequinone and 9-fluorenone. Isolation of 9,10-phenanthrenequinone supports the mechanistic route that incorporates the rhenacycloheptatetraene intermediate.

Introduction

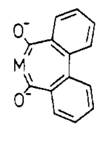
Transition metallabenzenes and metallacyclohexatrienes are of interest due to their possible involvement in alkyne metathesis[1] and their potential in studies concerning aromaticity.[2] We have recently reported reactions of (1*E*,3*E*)-1,4-dilithio-1,4-diphenylbutadiene with transition-metal halide carbonyls. Metallabenzenes **1** and **2** were proposed as intermediates leading to substituted cyclopentadienyl metal complexes.[3] We now report a study of the reaction of 2,2′-dilithiobiphenyl with $PPh_3(CO)_4ReBr$ and $(CO)_5ReBr$. These reactions support the intermediacy of higher $(4n + 2)\pi$ electron metallacyclic homologues—the 14π-electron rhenaphenanthrenes **3** and **4**. Low-temperature oxidative quenching of a 2,2′-dilithiobiphenyl and $(CO)_5ReBr$ reaction mixture implicates the seven-membered rhenacyclic intermediate **5**.



1 M=Cp(CO)Fe
2 M=PPh$_3$(CO)$_3$Re

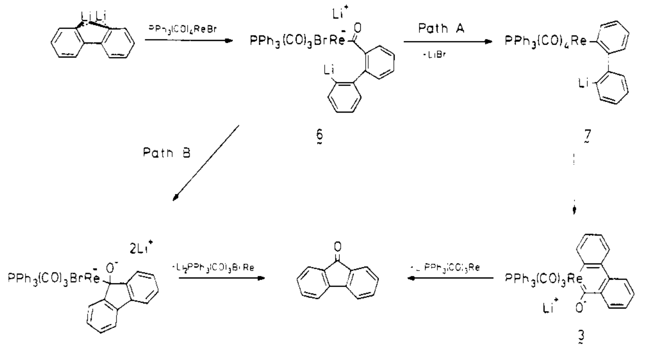


3 M=PPh$_3$(CO)$_3$Re
4 M=(CO)$_4$Re



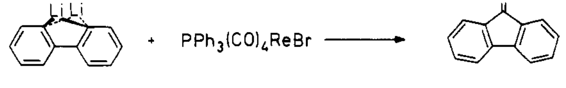
5 M=Br(CO)$_3$Re

Scheme I



Results and Discussion

Addition of an ether solution of 2,2′-dilithiobiphenyl to a cold ether solution of $PPh_3(CO)_4ReBr$ gave after chromatography 9-fluorenone (89%, eq 1). No organometallic complexes were observed. The formation of 9-fluorenone could proceed via two fundamentally different mechanistic routes. One mechanism (A, Scheme I) involves the formation of metallaphenanthrene **3** via reaction of the first aryllithium moiety with a terminal carbonyl followed by aryl migration. Reaction of the remaining aryllithium moiety with a terminal carbonyl gives **3**. Reductive elimination from **3** forms the product. A second mechanism



(1)

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[1] (a) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554–1562. (b) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563–1573. (c) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574–1583.

[2] Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39–45.

[3] (a) Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463–465. (b) Ferede, R.; Hinton, J. F.; Korfmacher, W. A.; Freeman, J. P.; Allison, N. T. *Oganometallics* **1985**, *4*, 614–616.

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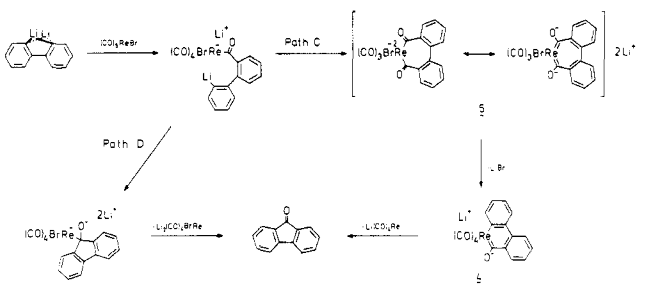
Scheme II



(B, Scheme I) involves sequential direct attack of an alkyllithium moiety on the acyl ligand in lieu of metallacyclic formation. Elimination of the transition metal gives 9-fluorenone.

Our earlier results from reactions between 1,4-dilithio-1,4-diphenylbutadiene and $PPh_3(CO)_4ReBr$ supported a mechanism similar to A, Scheme I, exclusive of the B mechanism.[3] A test, therefore, to probe the viability of mechanism B (or other alternate mechanistic paths) in similar complexes was designed. Thus we chose to react 2,2′-dilithiobiphenyl with a selected transition-metal carbonyl halide that would *not* facilitate aryl migration as shown in path A. In an earlier report by Lukehart and co-workers, reaction of $(CO)_5ReBr$ with 2 mol of CH_3Li leads to the bis(acyl) complex $(RCO)_2Re(CO)_3Br^{-2}$ (R = CH_3) with no apparent methyl migration.[4] We thus chose $(CO)_5ReBr$ to test for these alternate routes. In fact, addition of an ethereal solution of 2,2′-dilithiobiphenyl to a cold THF solution of $(CO)_5ReBr$ followed by warming to room temperature and column chromatography does give 9-fluorenone in 50% yield. Again, no organometallic products could be isolated from the chromatography. With the assumption that aryl migration does not occur, two alternate mechanisms shown in Scheme II could be operating. Mechanism D is analogous to B, Scheme I. Path C involves sequential attack with both aryllithium moieties at terminal carbonyls to form the rhenacycloheptatetraene **5**.[5] Ring contraction to rhenaphenanthrene **4** followed by reductive elimination gives fluorenone.

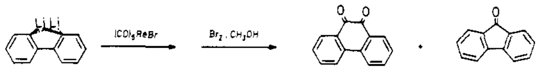
Attempts at isolating or observing stable organometallic products prior to chromatographic workup were performed on reactions of 2,2-dilithiobiphenyl with $(CO)_4PPh_3ReBr$ and $(CO)_5ReBr$. In both cases, reactions aimed at protonation or methylation of the reaction products gave fluorenone and metal carbonyls as the only observable (^{13}C NMR, IR) products in crude reaction mixtures. In reactions that were not protonated or methylated, detection of **3** or **4** from an expected IR acyl absorption in the crude product was not successful.

To test for the kinetically unstable metallacycloheptatetraene intermediate **5**, shown in mechanism C, low-temperature oxidative quenching of reaction mixtures were carried out.[6] Introduction of 2,2′-dilithiobiphenyl to cold (−78 °C) ether solution of $(CO)_5ReBr$ was followed by warming to selected temperatures. Cooling again to −78 °C, addition of Br_2/methanol, and then workup gave a new product, 9,10-phenanthrenequinone, along with 9-fluorenone as shown in eq 2. The percent yield of products vs selected warming temperatures is summarized in Table I.

Table I. Summary of Low-Temperature Quenching Reactions

	% yield^b	
temp (°C)^a	9-fluorenone	9,10-phenanthrene-quinone
25	72	0
−20	68	6
−25	68	13

^{a} Highest temperature obtained prior to low temperature quench. Solutions < −40 °C were heterogeneous. ^{b} % Yield based on recrystallized product of which no melting point depression was observed upon mixing with authentic samples.



(2)

These data support the following. Oxidative quenching of reaction mixtures at low temperatures followed by isolation of 9,10-phenanthrenequinone implicates the intermediate seven-membered metallacycle **5**.[6] Secondly, some 9-fluorenone isolated from the reactions of 2,2′-dilithiobiphenyl and $(CO)_5ReBr$ could be formed via the seven-membered metallacycle as shown in C, Scheme II. Although this mechanism proposes a migration that is unprecedented with $(RCO)_2Re(CO)_3Br^{-2}$ (R = CH_3)[4] and may be predicted to be even slower with aryl groups,[7] ring constraints inherent in **5** could ameliorate ring contraction to **4**. On the other hand, these data do not exclude the possibility of both mechanisms C and D operating as shown in Scheme II. Finally, although no further direct evidence could be obtained from the conversion of 2,2′-dilithiobiphenyl and $(CO)_4PPh_3ReBr$ to 9-fluorenone, a mechanistic route analogous to path C is reasonable.

Conclusion

The reactions of 2,2′-dilithiobiphenyl with the rhenium carbonyl halides $(CO)_4PPh_3ReBr$ and $(CO)_5ReBr$, as in the case of our earlier reports of reactions between (1*E*,3*E*)-1,4-dilithio-1,4-diphenylbutadiene and late transition metal carbonyl halides, do not yield stable aromatic metallacycles. The question of the relative stabilities of such metallaaromatics as compared to their five membered products (fluorenone or other cyclopentadienyl type products) is currently under investigation.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen by using standard Schlenk tube techniques. Nitrogen gas was purified by passing it first through a copper catalyst (Catalyst R3-11, cat. no. 18-3000-00, Chemical Dynamics Corp.) to remove oxygen followed by anhydrous calcium sulfate to remove residual water. THF and diethyl ether for reactions were predried with calcium hydride and transferred to a still, where they were distilled from benzophenone ketyl immediately prior to use. Reaction temperatures were monitored with an Omega type J digital thermocouple thermometer.

Reagent grade pentane and diethyl ether eluents were saturated with nitrogen gas before use. $Re(CO)_4PPh_3Br$,[8] $Re(CO)_5Br$,[9] and diiodobiphenyl[10] were prepared following published procedures. Baker silica gel (60–200 mesh) was used for column chromatography.

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(4) Darst, K. P.; Lenhert, P. G.; Lukehart, C. M.; Warfield, L. T. *J. Organomet. Chem.* **1980**, *195*, 317–324.

(5) For examples of bis(carbene)metallacycles formed by reaction of 1,2-dilithiobenzene and $M(CO)_6$ (M = Cr, Mo, W): cf. Fischer, E. O.; Röll, W.; Schubert, W.; Ackermann, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 611–612.

(6) Oxidative quenching (Br_2/MeOH) of manganese bis(acyl) complexes gives diones in excellent yields: cf. Casey, C. P.; Bunnell, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 436.

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(9) Michels, G. D.; Svec, H. J. *Inorg. Chem.* **1981**, *20*, 3445.

(10) Sandin, J. B. *J. Org. Chem.* **1968**, *34*, 456.

9-Fluorenone and 9,10-phenanthrenequinone products were analyzed by ^1H NMR, ^{13}C NMR, IR, and melting points except where noted. IR spectra were obtained on a Perkin-Elmer Model 283 spectrophotometer. ^1H NMR spectra were obtained either at 60 MHz on a Varian EM-360 spectrometer or at 90 MHz on a JEOL FX-90Q (FT) spectrometer using tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained at 22.6 MHz on a JEOL FX-90Q (FT) spectrometer. All ^{13}C spectra were obtained with complete broad-band proton decoupling. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

2,2′-Dilithiobiphenyl.[11] In a typical reaction, 8.7 mL of *tert*-butyllithium in pentane (14.8 mmol, 1.7 M solution) was added dropwise (15 min) to a cold (−78 °C) stirred ethyl ether solution (40 mL) of 2,2′-diiodobiphenyl (1.5 g, 3.7 mmol). The resulting yellow mixture was stirred at −78 °C for 0.5 h and then slowly (1.5 h) warmed to room temperature. After being stirred for 1 h, the solution was used immediately.

Reaction of 2,2′-Dilithiobiphenyl with $Re(CO)_4PPh_3Br$. To a stirred, cold (0 °C) solution of $Re(CO)_4PPh_3Br$ (1.48 g, 2.21 mmol) in 100 mL of ethyl ether was added dropwise via cannula an ether solution (30 mL) of 2,2′-dilithiobiphenyl (2.20 mmol). The temperature was increased gradually (2 h) to room temperature. The solvent was removed in vacuo while the products were coated on 5 g of silica gel. Chromatography on silica gel (eluted first with pentane then gradually increasing ether content to 3%), collection of the yellow band, and removal of solvent on the rotary evaporator gave 0.356 g (89%) of 9-fluorenone as a yellow solid.

Reaction of 2,2′-Dilithiobiphenyl with $Re(CO)_5Br$. To a stirred, cold (−78 °C) solution of $Re(CO)_5Br$ (1.5 g, 3.7 mmol) in 40 mL of THF was added dropwise an ether solution (30 mL) of 2,2′-dilithiobiphenyl (3.7 mmol) over 0.5 h. The yellow suspension slowly (3 h) warmed to a brown-green color at room temperature. Silica gel (5 g) was added and the solvent removed in vacuo. The coated silica gel was transferred to the top of a silica gel column (160 g of silica gel; 125 × 25 cm; pentane/ether, 8:2). Collection of the yellow band and removal of solvent on the rotary evaporator gave 9-fluorenone. Recrystallization from ethanol gave 0.273 g of yellow needles (71%, mp 81–82 °C).

Reaction of 2,2′-Dilithiobiphenyl with $Re(CO)_5Br$ Followed by Oxidative Quenching. To a stirred, cold (−78 °C) solution of $Re(CO)_5Br$ (1.5 g, 3.7 mmol) in 40 mL of THF was added dropwise an ether solution (30 mL) of 2,2′-dilithiobiphenyl (3.7 mmol) over 0.5 h. The reaction mixture was slowly warmed to the desired temperature (Table I) and then stirred for 0.5 h. After the solution was cooled again to −78 °C, 0.4 mL of bromine in 25 mL of methanol was added via syringe. The mixture was then slowly (1.5 h) warmed to room temperature and the solvent removed in vacuo with reaction products coated on silica gel (5 g). Chromatography on silica gel, collection of the yellow band (pentane/ethyl ether, 8:2) and then, if observed, a second yellow band (pentane/ethyl ether, 75:25), gave 9-fluorenone and 9,10-phenanthrenenquinone, respectively. Purification by recrystallization from ethanol gave yellow needles of mp 81–82 °C and orange crystals of mp 207–209 °C, respectively. See Table I for yields.

Acknowledgment. We wish to thank the National Science Foundation (CHE-8312644) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Interaction of Organoaluminum Compounds and Crown Ethers. Formation in Solution of $R_2Al(crown)^+$ and $RAl(halide)(crown)^+$ Ions[1]

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^1H NMR studies indicate that solutions prepared from R_2AlX (X = Br and I) and 15-crown-5 contain significant amounts of $R_2Al(crown)^+$ and $RAlX(crown)^+$ ions. These cations are thought to have pentagonal-bipyramidal structures in which all oxygens of the crown ether occupy equatorial positions about the Al, and R and X occupy apical positions. ^1H NMR spectra of solutions prepared from R_3Al and 15-crown-5 give no evidence for formation of ions.

We recently reported that addition of an appropriate cryptand to a dialkylmagnesium compound leads to disproportionation to ions, for example, as indicated in eq 1.[2]

$$2R_2Mg + \text{cryptand} \rightleftharpoons RMg(\text{cryptand})^+ + R_3Mg^- \text{ (or } R_6Mg_2^{2-}\text{)} \quad (1)$$

In favorable cases disproportionation is quantitative in solutions, and solids containing $RMg(\text{cryptand})^+$ and either R_3Mg^- or $R_6Mg_2^{2-}$ ions have been isolated and characterized by single-crystal X-ray diffraction techniques.[2,3] Crown ethers can induce a similar disproportionation. In solutions, however, the average size of the species accompanying the $RMg(\text{crown})^+$ ion has never been smaller than $R_5Mg_2^{2-}$; the one solid that has been characterized contains $RMg(\text{crown ether})^+$ and polymeric $(R_5Mg_2^-)_n$ ions.[4]

We decided to investigate if a similar disproportionation could be induced in organoaluminum compounds by such additives. Enhanced conductivities observed when some mono- or bidentate coordinating agents are added to solutions of trialkylaluminum compounds have been attributed to partial formation of ions, for example, as in eq 2.[5]

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