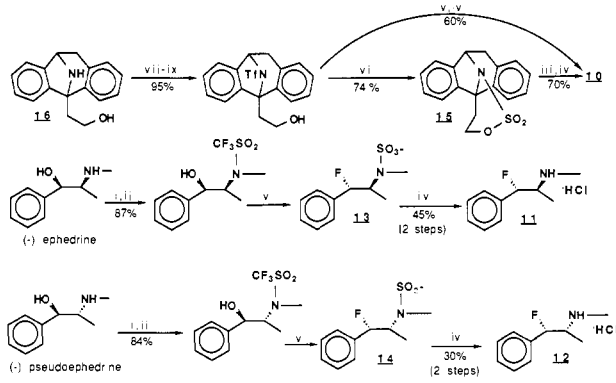
Scheme II[a]



[a] (i) TMS-imidazole/CH_2Cl_2; (ii) $(CF_3SO_2)_2O$/*t*-Bu_2Me-pyridine/CH_2Cl_2, 0 °C (H_3O^+ workup); (iii) *n*-$Bu_4N^+F^-/CH_3CN$, 70 °C, 20 min; (iv) 3.0 M HCl, 70 °C, 15 min; (v) *n*-$Bu_4N^+F^-/CH_3CN$, 70 °C, 60 min; (vi) NaH/THF reflux; (vii) TBDMS-Cl/imidazole/DMF; (viii) $(CF_3SO_2)_2O$/TEA/*t*-Bu_2Me-pyridine/CH_2Cl_2, 0 °C; (ix) TsOH/MeOH.

acid. The overall reaction pathway is summarized in Scheme I.

Reaction of tertiary sulfonamides with alkoxide under vigorous conditions normally results in cleavage of the S–N bond.[13] Indeed, when the triflamide derivative of MK-801 (**9**) is treated with sodium methoxide in refluxing acetonitrile, the only observed reaction is the slow removal of the sulfonyl group from nitrogen rather than loss of trifluoromethide. If this mechanism applied to the intramolecular reaction of the alkoxide oxygen with the sulfonyl group of **5**, one would not expect to observe the product **7** retaining the S–N bond. Therefore, it is likely that the intramolecular nature of the process as well as the stability of the trifluoromethide leaving group (pK_a = 25 for CHF_3)[14] leads to this unique observation. As shown in Scheme I, a transition state or intermediate involving a pentacoordinate sulfur should require that the incoming oxygen occupy an axial position of the trigonal bipyramid. Because the N and incoming O atoms are part of a five-membered ring, the N must occupy an equatorial position, thus giving rise to two possible isomers *a* and *b*. By the same token, the highly electronegative CF_3^- leaving group should occupy an axial position (isomer *a*) which would lead to the product **7**. Therefore if isomer *b* is formed first, it must isomerize to isomer *a* via pseudorotation or turnstile rotation.[15d]

To further define the scope of this reaction we have prepared the γ-fluoroamine **10**[6a,9,7a–c] and the acyclic β-fluoroamines **11**[6b,9,7a,c,d] and **12**[6b,9,7a,c,d] derived from (–)-ephedrine and (–)-pseudoephedrine, respectively (Scheme II). In these cases, transient protection of the hydroxyl groups as their silyl ethers was required in order to direct the sulfonation to nitrogen. In all cases, we have shown the intermediacy of cyclic sulfamates by the isolation of the acyclic (e.g., **13**[7a] and **14**[7a]) or cyclic sulfamate (e.g., **15**[6b,9,7a,e]) intermediates. In contrast to the previous syntheses in which **11** and **12** were obtained as a mixture of epimers at the carbon-bearing fluorine,[16] our methodology provides a stereospecific[17] route to these compounds which is also amenable to ^{18}F labeling. Attempts to convert the amino alcohol **16** to the triflate **17** by using triflic anhydride or to the cyclic sulfamate **15** by using sulfuryl diimidazole led only to azetidine formation. Also treatment of the disulfonylated material **18** with F^- caused elimination.

For preparative purposes, the cyclic sulfamates **7** and **15** may also be generated by treating the hydroxy triflamides with NaH in THF, thus avoiding the possibility of further reaction with F^-. Because **7** and **15** are stable, crystalline materials and give rise to the fluoro compounds **6** and **10** in a short period of time, they are currently being evaluated in radioactive labeling experiments for producing the ^{18}F analogues with encouraging initial results.[18]

In summary, the facile formation of cyclic sulfamates from hydroxy triflamides involving the unusual expulsion of CF_3^- has been documented. In this reaction, the trifluoromethanesulfonyl group serves as a protecting group for nitrogen as well as a means of activating the hydroxyl carbon toward nucleophilic attack. Until now, cyclic sulfamates have been relatively inaccessible.[19] We have also demonstrated the nucleophilic ring opening of these compounds to afford fluoroamines in a stereospecific manner.[20] This method provides an attractive addition to the existing synthetic methods for cyclic sulfamates and fluoroamines[16] and seems well suited for the requirements of ^{18}F labeling. In order to extend this methodology to primary amines, it is likely that transient protection of the triflamide N–H proton will be necessary.

Acknowledgment. We thank Dr. Paul Anderson for his support, interest, and encouragement during this work. We also thank Dr. Susan Britcher, Dr. Wayne Thompson, and Prof. Barry Trost for their comments, Dr. Samuel Graham for several helpful discussions, and Vera Finley for preparing the manuscript.

Supplementary Material Available: Selected spectral data (^1H NMR, ^{19}F NMR, ^{13}C NMR) for compounds **3–8** and **10–15** (2 pages). Ordering information is given on any current masthead page.

(13) Searles, S.; Nukina, S. *Chem. Rev.* **1959**, *59*, 1077–1103.
(14) Edgecombe, K. E.; Boyd, R. J. *Can. J. Chem.* **1984**, *62*, 2887–2891.
(15) For a discussion of nucleophilic displacement at sulfonyl centers, see: (a) Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, *17*, 156. (b) March, J. *Advanced Organic Chemistry*, 3rd ed.; McGraw Hill: 1985; pp 442–446. (c) White, E. H.; Linn, H. M. *J. Org. Chem.* **1987**, *52*, 2162–2166. (d) Schwoebel, A.; Kresze, G.; Perez, M. A. *Liebigs Ann. Chem.* **1985**, 72–77.
(16) (a) Alvernhe, G.; Lacombe, S.; Laurent, A.; Rousset, C. *J. Chem. Res. (Synop.)* **1983**, 246–247. (b) Kollonitsch, J.; Marburg, S.; Perkins, L. M. *J. Org. Chem.* **1979**, *44*, 771–777.
(17) The assigned stereochemistry is based on the assumed overall inversion at the benzylic carbon. Examination of the ^1H NMR of crude **11** and **12** indicates stereochemical homogeneity. In both cases, the diastereomer which would result from partial racemization at either chiral center could not be detected.
(18) Private communication from Dr. V. W. Pike, MRC Cyclotron Unit, Hammersmith Hospital, London.
(19) (a) Deyrup, J. A.; Moyer, C. L. *J. Org. Chem.* **1969**, *34*, 175–179. (b) Benson, G. A.; Spillane, W. J. *Chem. Rev.* **1980**, *80*, 151–186.
(20) This reaction resembles the nucleophilic fluoride opening of cyclic sulfates: cf. Tewson, T. J.; Soderlind, M. *J. Carbohydr. Chem.* **1985**, *4*, 529–543.

Reactions of Ammonium Salts with Butyllithium and with Lithium Hydride: New Routes to Fully Anhydrous Inorganic Lithium Complexes

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Lithium halide complexes, $(LiHal{\cdot}xL)_n$, L = a nonmacrocyclic ligand, whether fully or partly ion-separated monomers, $Li(L)_x^+\cdots Hal^-$, or intact oligomers, $(LiHal)_n{\cdot}(xL)_n$,[1] often have understandably low melting points and good solubility in organic media. As such, their likely applications are as low-energy

(1) Setzer, W.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. A review of the structures of lithium compounds, including lithium halide complexes.

0002-7863/87/1509-7891$01.50/0

Table I

complex[a]	route[b]	yield (%)	mp (°C)
1 $(LiCl{\cdot}HMPA)_4$	Hal = Cl, x = 1, 2, 3, or 4	83	142–144 (lit.[6] 142–144)
2 $(LiBr{\cdot}2HMPA)_n$	Hal = Br, x = 2	53	70–72
3 $(LiBr{\cdot}4HMPA)_n$	Hal = Br, x = 4	49	50–52
4 $(LiI{\cdot}2HMPA)_n$	Hal = I, x = 2	64	63–65
5 $(LiI{\cdot}4HMPA)_n$	Hal = I, x = 4	94	141–143

[a] Analyses: **1** $(C_6H_{18}ClLiN_3OP)_4$, H, Li, N; C: calcd, 32.51; found, 32.03. Cl: calcd, 16.03; found, 15.40. **2** $(C_{12}H_{36}BrLiN_6O_2P_2)_n$, Li, N; C: calcd, 32.36; found, 31.19. H: calcd, 8.09; found, 7.53. **3** $(C_{24}H_{72}BrLiN_{12}O_4P_4)_n$, H, Li; C: calcd, 35.87; found, 35.05. N: calcd, 20.92; found, 20.30. **4** $(C_{12}H_{36}ILiN_6O_2P_2)_n$, H, Li; C: calcd, 29.27; found, 28.53. I: calcd, 25.81; found, 25.37. N: calcd, 17.07; found, 17.52. **5** $(C_{24}H_{72}ILiN_{12}O_4P_4)_n$, C, H, I, Li, N. [b] All via eq 1, with L = HMPA.

electrolytic sources of Li metal,[2] and as soluble, pre-isolable (thus stoichiometrically controllable) halogenating agents, cf. current uses of, e.g., a CsF suspension in sulfolane.[3] Furthermore, these complexes hold promise as fast-ion conductors, e.g., most recently, LiI·4MeOH,[4] and, in effect, are used now in numerous organic transformations by reacting $(LiHal)_\infty$ in various donors with organic precursors, e.g., $(LiI)_\infty$ in pyridine or DMF, to carry out decarboxylations, ether cleavages, and dechlorinations.[5] Direct routes to such complexes, through dissolution of $(LiHal)_\infty$ in neat donors or donor/hydrocarbon mixes, have drawbacks: first, total exclusion of H_2O is difficult, even supposedly anhydrous Li^+ salts requiring vigorous in vacuo dehydration prior to use, and, second, the energies of *preformed* lattices often prevent dissolution.[6] Recently, in situ routes have been described, whereby lattice growth of small $(LiHal)_n$ units formed at low temperatures from organolithiums with metallic or organic halides is arrested by donor, e.g., $(LiCl{\cdot}HMPA)_4$ [HMPA = $O{:}P(NMe_2)_3$] from *t*-$Bu_2C{=}NLi + AlCl_3$ + HMPA[6] and $(LiBr{\cdot}PMDETA)_2$ [PMDETA = $Me_2N(CH_2)_2{\cdot}NMe{\cdot}(CH_2)_2NMe_2$] from *n*-BuLi + *n*-BuBr + PMDETA.[7] Here we outline a very simple preparative system for these complexes [eq 1] in which *ammonium* salts $(NH_4Hal)_\infty$ are used as the Hal^- source, so removing hydration problems (and probably offsetting lattice energy ones). Furthermore, reaction 1 allows syntheses of different complexes, $(LiHal{\cdot}xL)_n$, with a common Hal^- and L, but, when L = HMPA, with x = 2 or 4, and seems equally applicable to pseudo halide complexes, e.g., SCN^- ones. We also note preliminary work on a totally inorganic route to these complexes [eq 2].[8]

$$BuLi + NH_4Hal + xL \rightarrow BuH + NH_3 + {}^1/_n(LiHal{\cdot}xL)_n \quad (1)$$

$$LiH + NH_4Hal + xL \rightarrow H_2 + NH_3 + {}^1/_n(LiHal{\cdot}xL)_n \quad (2)$$

Details of some lithium halide–HMPA complexes, **1–5**, synthesised via route 1 are given in Table I. In a typical reaction, 10 mmol of a 1.7 mol dm^{-3} *n*-BuLi solution in hexane (5.9 cm^3) was taken under nitrogen, the hexane was removed (see below) and replaced by toluene, and HMPA (1. 2, 3, or 4 molar equiv as indicated) was added[9] to give a deep red solution (presumably a charge-transfer complex). The ammonium halide solid (10 mmol) was then added, and the mixture was heated to 40–60 °C when vigorous gas evolution (BuH, NH_3) occurred along with color changes, usually from deep red to violet-purple, to orange, then yellow, then colorless (still yellow for iodide complexes), and with gradual total disappearance of the solid.

Refrigeration of the solution gave crystals of the products. Recorded yields, where relatively low (e.g., for **2**, **3** especially, and **4**), reflect the high solubility of complexes (e.g., for **3**, >2 g per cm^3 of toluene) rather than incomplete reaction: IR spectra of filtrates reduced in volume lacked ν(N–H) absorptions. If hexane is not removed from the *n*-BuLi solution, reactions in ensuing hexane/toluene mixtures are much slower and incomplete. Interestingly, also, gas evolution then occurs in two stages, BuH before NH_3.

Their simplicity apart, key points for these syntheses are, firstly, that **1–5** show no evidence of hydration, even though no efforts were made to dry, or otherwise purify (e.g., by sublimation), ammonium halide precursors: in contrast, direct dissolution of, e.g., supposedly anhydrous $(LiCl)_\infty$ in HMPA gives, even at 100 °C and after extensive prior heating of the halide in vacuo, very low yields of a complex which contains H_2O.[6] Second, complexes **2** and **3**, and **4** and **5** illustrate that this in situ route allows some control of final product identity/stoichiometry, with x = 2 or 4;[10] again, in contrast, direct dissolution does not allow such control, e.g., $(LiI)_\infty$ or $(LiI{\cdot}H_2O)_\infty$ suspended in toluene dissolve on addition of 4 equiv of HMPA—but not less—so giving **5** but not **4**.

A similar route to $(LiF{\cdot}xHMPA)_n$ was attempted by adding $(NH_4F)_\infty$ to deep red *n*-BuLi·4HMPA in toluene. Heating the mix to 110 °C caused fading of the color to red and then yellow. After 2 h, the powdered $(NH_4F)_\infty$ had disappeared, giving a pale yellow solution from which a microcrystalline material was slowly deposited. This solid was shown to be essentially $(LiF)_\infty$ [e.g., Li found, 25.2%; LiF requires 26.9%] in ~100% yield, though its IR spectrum showed traces of HMPA (but none of NH_4^+). Although a distinct, soluble LiF complex for use in fluorinations is seemingly out of reach, thermodynamically,[11] formation here of a $(LiF)_\infty$ lattice from a $(NH_4F)_\infty$ one presumably involves at some stage breakdown of the latter prior to growth of the former, whether in solution or at a solid surface: such a mixture at that stage might therefore be a promising fluorinating agent.

Finally, we have initiated experiments to open up an all-inorganic route [eq 2] to alkali metal halide complexes with use of $(LiH)_\infty$ as the Li^+ source; in a different context, it was noted many years ago that reaction of $(BaH_2)_\infty$ with $(NH_4I)_\infty$ in pyridine produces a $BaI_2{\cdot}pyr$ complex.[12] Thus, addition of $(NH_4Cl)_\infty$ to a suspension of $(LiH)_\infty$ in HMPA (2 equiv) and toluene, followed by heating at 110 °C for 4 days, caused most of the solids to dissolve. After filtration, cooling of the filtrate gave **1** in 51% yield. Although this is a relatively low yield, the unreactivity of commercially supplied $(LiH)_\infty$ is well known,[13] and this route certainly holds promise for syntheses of, e.g., NaHal and KHal complexes, with use of more reactive $(NaH)_\infty$ and $(KH)_\infty$, and furthermore avoiding [see eq 1] *n*-BuNa and *n*-BuK.[14]

Further applications of these routes are known, e.g., for Hal = Cl, Br, I, complexes with L = TMEDA($Me_2N{\cdot}CH_2CH_2{\cdot}NMe_2$) have been isolated, while thiocyanate complexes, $(LiSCN{\cdot}xL)_n$

(2) *Lithium: Current Applications in Science, Medicine and Technology*; Bach, R. O., Ed.; Wiley: Chichester, 1985.

(3) (a) Bayliff, A. E.; Bryce, M. R.; Chambers, R. D.; Matthews, R. S. *J. Chem. Soc., Chem. Commun.* **1985**, 1018. (b) Brown, S. J.; Clark, J. H. *Ibid.* **1985**, 672.

(4) Weppner, W.; Welzel, W.; Kniep, R.; Rabenau, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1087.

(5) Fieser, M. *Fieser's Reagents for Organic Synthesis*; Wiley-Interscience: New York, 1986; Vol. 12 and earlier volumes give specific uses arranged according to individual lithium halide compounds.

(6) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 79.

(7) Hall, S. R.; Raston, C. L.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1983**, *22*, 4070.

(8) Routes (1) and (2) are the subjects of a preliminary patent filed by the Associated Octel Co. Ltd., Ellesmere Port, U.K.

(9) HMPA is a cancer suspect agent and should be handled with due care, e.g., wearing gloves, within a fume hood.

(10) Apart from mp and analyses (see Table I), IR and ^1H, ^7Li NMR spectroscopic and cryoscopic RMM measurements showed differences for the complexes mentioned.

(11) (a) Clark, J. H.; Hyde, A. J.; Smith, D. K. *J. Chem. Soc., Chem. Commun.* **1986**, 791. (b) Ichihara, J.; Matsuo, T.; Hanafusa, T.; Ando, T. *Ibid.* **1986**, 793.

(12) Taylor, M. D.; Grant, L. R. *J. Am. Chem. Soc.* **1955**, *77*, 1507.

(13) Klusener, P. A. A.; Brandsma, L.; Verkruijsse, H. D.; Schleyer, P. v. R.; Friedl, T.; Pi, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 465. This notes the preparation of highly active alkali metal hydrides.

(14) These organometallics give suspensions in hydrocarbons, though soluble complexes result on addition of TMEDA. However, to prevent metalation of the TMEDA, the resulting solutions must be stored or used below 0 °C and −40 °C, respectively, and so could not be used in a reaction akin to (1). See: (a) Schade, C.; Bauer, W.; Schleyer, P. v. R. *J. Organomet. Chem.* **1985**, *295*, C25. (b) Pi, R.; Bauer, W.; Brix, B.; Schade, C.; Schleyer, P. v. R. *Ibid.* **1986**, *306*, C1.

with $x = 2$, L = HMPA, $x = 1$, L = TMEDA or PMDETA, result in 83–95% yields from *n*-BuLi + NH_4SCN + L reactions in hexane/toluene; thermodynamic (enthalpic and, possibly more important, entropic) parameters are also being calculated.

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Electrochemically Induced Reversible Insertion of Ruthenium Atoms into an Eight-Carbon Chain†

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We report remarkable redox chemistry of an organodiruthenium complex in which reversible opening and closing of an eight-carbon chain is accompanied by formation and cleavage, respectively, of a metal–metal bond. A net two-electron transfer, accomplished either electrochemically or with a chemical redox agent, is an integral part of the reaction. This redox-initiated C–C bond activation may have relevance to the mechanism of the nickel-catalyzed tetramerization of acetylene.[1,2]

Earlier studies[3] demonstrated that the pseudo-triple-decker[4] complexes $Cp_2M_2(cot)$[5] (**1**: M = Co, Rh; see Scheme I) undergo substantial flattening of the bridging cyclooctatetraene ligand when oxidized by two electrons to give **2** (M = Co, Rh; $n = 2$). The two butadiene-like halves of the cot ring remain slightly twisted from coplanarity in **2**.[3b] In a search for even more electron-deficient members of this series, the oxidation of $Cp_2Ru_2(cot)$ (**3**) was investigated. This diruthenium complex is isoelectronic and isostructural[6] with **2** but is more readily oxidized since it is neutral.

Solutions of **3** at 298 K in acetone/0.1 M Bu_4NPF_6 display an anodic wave of two-electron height at +0.04V versus SCE when scanned in CV[5] experiments. A cathodic wave at −0.25 V arises from re-reduction of the oxidation product. Bulk coulometric oxidation of **3** released 2 faradays of charge and resulted in stable solutions of a red-brown dication, **4**. The dication was isolated either from acetone with 2 equiv of $[Cp_2Fe][PF_6]$ as oxidant or from dichloromethane with low-temperature electrolysis (**4** precipitated nearly quantitatively from CH_2Cl_2 solutions of **3** electrolyzed at 220 K).

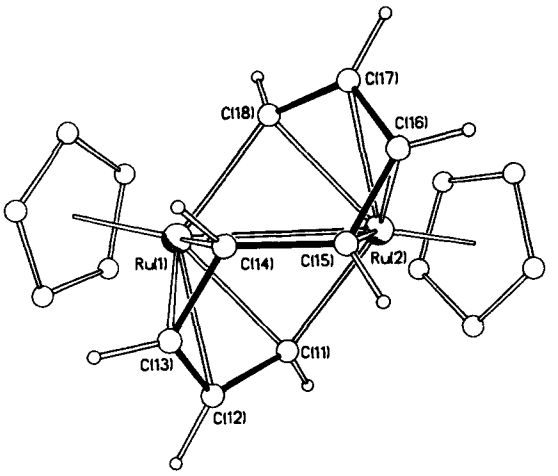
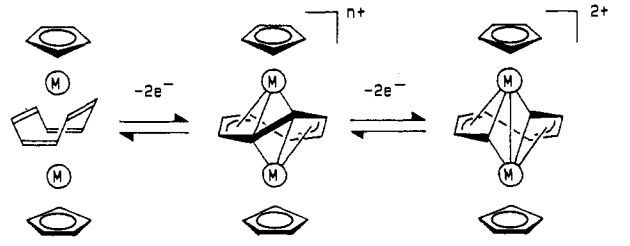


Figure 1. Molecular structure and labeling scheme for $[C_{18}H_{18}Ru_2][PF_6]_2 \cdot 0.5C_6H_6$ (distances in Å, angles in deg): Ru(1)–Ru(2), 2.7291 (4); Ru(1)–CNT(1), 1.868 (5); Ru(2)–CNT (2), 1.881 (5); Ru(1)–Cu(11), 2.131 (4); Ru(1)–C(12), 2.213 (5); Ru(1)–C(13), 2.181 (7); Ru(1)–Cu(14), 2.233 (8); Ru(1)–C(18), 2.066 (4); Ru(2)–C(11), 2.063 (4); Ru(2)–Cu(15), 2.228 (7); Ru(2)–C(16), 2.174 (7); Ru(2)–C(17), 2.216 (6); Ru(2)–C(18), 2.143 (5); C(11)–C(12), 1.417 (8); C(12)–C(13), 1.407 (10); C(13)–C(14), 1.400 (8); C(14)–C(15), 1.491 (7); C(15)–C(16), 1.366 (8); C(16)–C(17), 1.408 (10); C(17)–C(18), 1.414 (8); C(11)···C(18), 3.195 (8). C(11)–Ru(1)–C(18), 99.1 (2); C(11)–Ru(2)–C(18), 98.8 (2); Ru(1)–C(11)–Ru(2), 81.2 (2); Ru(1)–C(18)–Ru(2), 80.8 (2); Ru(1)–C(11)–C(12), 74.1 (3); Ru(2)–C(11)–C(12), 132.5 (4); Ru(1)–C(18)–C(17), 131.8 (4); Ru(2)–C(18)–C(17), 73.9 (3); C(11)–C(12)–C(13), 121.3 (4); C(12)–C(13)–C(14). 118.0 (5); C(13)–C(14)–C(15), 120.5 (5); C(14)–C(15)–C(16), 120.3 (5); C(15)–C(16)–C(17), 118.2 (5); C(16)–C(17)–C(18), 121.9 (5). CNT(1)–Ru(1)–Ru(2)–CNT(2), −31.5 (4); C(11)–C(12)–C(13)–C(14), −13.3 (6); C(12)–C(13)–C(14)–C(15), −38.3 (6); C(13)–C(14)–C(15)–C(16), 152.3 (6); C(14)–C(15)–C(16)–C(17), −36.7 (6); C(15)–C(16)–C(17)–C(18), −14.8 (6).

Scheme I



1, M = Co, Rh 2, M = Co, Rh, n = 2 4
3, M = Ru, n = 0

NMR spectra of the dication displayed an unusually low-field resonance in both ^1H (δ 13.4) and ^{13}C (δ 195) experiments.[7] The carbon resonance was reminiscent of those observed for bridging carbons in "flyover" complexex[8] and suggested that the eight-carbon ring had been fractured in the dication. This suspicion was confirmed by X-ray crystallography on crystals grown from nitromethane/benzene.[9]

† Structural Consequences of Electron-Transfer Reactions. Part 16. Part 15: Van Order, N., Jr., et al. *J. Am. Chem. Soc.* **1987**, *109*, 5680.

(1) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *560*, 1.

(2) Leading references to the Reppe synthesis of carbocycles may be found in the following: Colborn, R. E.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1981**, *103*, 6259.

(3) (a) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1978**, *100*, *1978*, 7429. (b) Edwin, J.; Geiger, W. E.; Rheingold, A. L. *Ibid.* **1984**, *106*, 3052.

(4) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

(5) Abbreviations used in this paper are the following: cot = cyclooctatetraene; Cp = η^5-cyclopentadienyl; CV = cyclic voltammetry.

(6) (a) Bieri, J. H.; Egolf, T.; von Philipsborn, W.; Piantini, U.; Prewo, R.; Ruppli, U.; Salzer, A. *Organometallics* **1986**, *5*, 2413. (b) **3** has been characterized by X-ray crystallography.

(7) NMR data for **4** (acetone-d_6): δ 13.40 (d, $J = 6.8$ Hz, 2 H, $Ru_2CHCHCHCH$), 7.30 (dd, $J = 6.8$, 5.4 Hz, 2 H, $Ru_2CHCHCHCH$), 6.37 (m, 2 H, $Ru_2CHCHCHCH$), 6.03 (s, 10 H, C_5H_5), and 4.64 (d, $J = 7.6$ Hz, 2 H, $Ru_2CHCHCHCH$).

(8) (a) Knox, S. A. R.; Stansfield, F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1978**, 221. (b) Knox, S. A. R.; Stansfield, F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 173. (c) Boileau, A. M.; Orpen, A. G.; Stansfield, R. F. D.; Woodward, P. *Ibid.* **1982**, 187; (d) Green, M.; Kale, P. A.; Mercer, R. J. *J. Chem. Soc., Chem. Commun.* **1987**, 375.

0002-7863/87/1509-7893$01.50/0