α-halocarboxylates may serve as a source of carbene. However, attempts to trap CF_2 by converting I to II in the presence of olefins have proven unsuccessful to date. Further efforts in this direction are in progress.

The appearance of the $-CHF_2$ group in I and II was somewhat unexpected, and, in light of the aprotic nature of the solvent, the source of the proton proved of interest. It seems that although the diglyme had been dried by refluxing over $LiAlH_4$, sufficient water remained to serve as the proton source. This was demonstrated by drying diglyme to which D_2O had been added and repeating the reaction outlined above. The deuterium analog of II, $IrCl_2(CDF_2)(CO)L_2$, was thus obtained (ν_{C-H} 2940, ν_{C-D} 2200 cm^{-1}). The abstraction of a proton from water to yield difluoromethyl is taken as evidence for the intermediacy of a metallocarbanion, and the reaction sequence given in Scheme I is proposed to explain the formation of I. Support

Scheme I
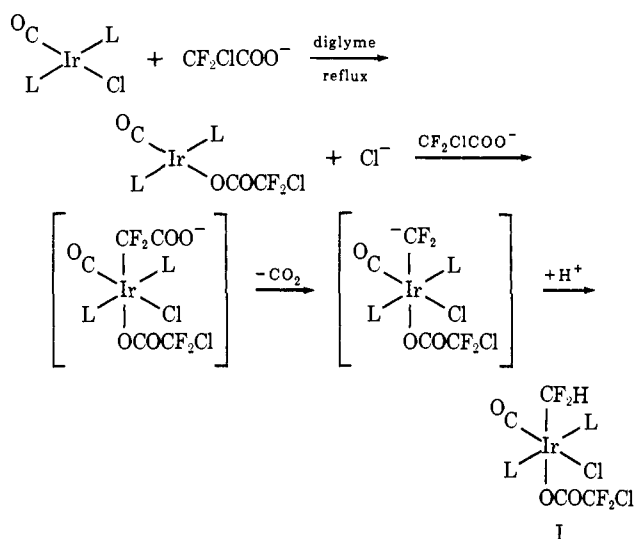
for the initial step involving replacement of the chloride in the parent complex by the acetate is obtained from the reports[6-8] of a number of closely related complexes which were synthesized by different routes. However, attempts to synthesize the directly analogous complex $Ir(OCOCF_3)(CO)L_2$ by allowing $IrCl(CO)L_2$ to react with $NaCF_3COO$ were unsuccessful.

Finally, we note that continued refluxing of II in diglyme yields a mixture of $IrCl(CO)L_2$ and $IrHCl_2-(CO)L_2$ after 1 hr indicating the possibility of a cyclic reaction sequence between the Ir(I) complex and excess $NaCF_2ClCOO$. Such a sequence is being investigated to determine its synthetic utility.

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(8) S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Chem. Commun.*, 1047 (1972).
(9) Alfred P. Sloan Foundation Fellow, 1972–1973.

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Reverse Osmosis in Organometallic Synthesis

Sir:

When a solution of a dissociable complex is forced against a selectively permeable membrane under pressure, ligand and solvent diffuse through the membrane but the metal-containing species are retained. Thus, reverse osmosis concentration of a solution of the equilibrium mixture results in selective removal of the free ligand and provides a solution to the long-standing problem of removal of nonvolatile dissociated ligands from solutions of organometallic complexes.[1]

Solutions of homogeneous catalysts often contain detectable quantities of coordinatively unsaturated species, as illustrated for dihydridotetrakis(triphenylphosphine)ruthenium(II).[3] Ligand-deficient complexes such as 2[3] are commonly the active species for

$$RuH_2(PPh_3)_4 \rightleftharpoons RuH_2(PPh_3)_3 + PPh_3$$
$$\text{1} \qquad\qquad \text{2}$$
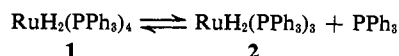
catalysis.[4] Removal of the dissociated ligand by reverse osmosis enhances catalytic activity. Whether or not the ligand-deficient complex can be isolated depends on the particular system and the conditions employed. For example, 2 is too unstable to be isolated but if nitrogen is used as the pressuring gas, the dinitrogen complex $RuH_2(N_2)(PPh_3)_3$[5] (3) can be readily isolated. This illustrates the use of reverse osmosis to replace a dissociated ligand (triphenylphosphine) by a more labile one (dinitrogen). The dinitrogen complex 3 had been previously detected in nitrogen-saturated solutions of 1 but could not be isolated from these solutions because of the presence of the dissociated triphenylphosphine.[3] Preparation and isolation required a different route.[5]

In an illustrative experiment, a 0.02 *M* tetrahydrofuran solution (200 ml) of 1 was pressured with nitrogen (80–100 atm) in a reverse osmosis cell[6] fitted with a membrane[7] of the polyimide obtained from *p,p'*-diaminodiphenyl ether and pyromellitic dianhydride. A solution (170 ml) of triphenylphosphine in tetrahydrofuran (THF) was removed by permeation. Slow addition of hexane to the residual solution precipitated crystalline $RuH_2(N_2)(PPh_3)_3$ in 41% yield.

In addition, two new dinitrogen complexes have been isolated by this technique. Both new complexes were

(1) The principles of reverse osmosis, many kinds of reverse osmosis apparatus, and diverse membrane forms have been discussed recently.[2] These publications provide a detailed introduction to many qualitative and mathematical aspects of reverse osmosis and membrane technology. However, in our experience, the use of reverse osmosis for preparative purposes requires neither elaborate apparatus nor complex mathematics.
(2) (a) C. E. Reid in "Desalination by Reverse Osmosis," J. Merton, Ed., Massachusetts Institute of Technology Press, Cambridge, Mass., 1966; (b) A. S. Michaels and H. H. Bixler, *Progr. Separation Purification*, 1, 143 (1968); (c) A. S. Michaels, *ibid.*, 1, 297 (1968); (d) N. N. Li and R. B. Long, *ibid.*, 3, 153 (1970); (e) H. K. Lonsdale, *ibid.*, 3, 191 (1970); (f) R. E. Kesting, "Synthetic Polymeric Membranes," McGraw-Hill, New York, N. Y., 1971; (g) S. Sourirajan, "Reverse Osmosis," Academic Press, New York, N. Y., 1970.
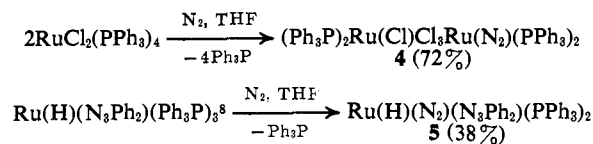(3) T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 92, 3011 (1970).
(4) C. A. Tolman, *Chem. Soc. Rev.*, 1, 337 (1972).
(5) W. H. Knoth, *J. Amer. Chem. Soc.*, 94, 104 (1972).
(6) We have used both a commercially available Amicon Model 420 device and a functionally similar cell described by J. W. Richter and H. H. Hoehn, U. S. Patent 3,567, 632 (1971).
(7) C. W. Alegranti and M. Panar, manuscript submitted for publication.

$$2RuCl_2(PPh_3)_4 \xrightarrow[-4Ph_3P]{N_2,\ THF} (Ph_3P)_2Ru(Cl)Cl_3Ru(N_2)(PPh_3)_2$$
$$\textbf{4}\ (72\%)$$

$$Ru(H)(N_3Ph_2)(Ph_3P)_3{}^8 \xrightarrow[-Ph_3P]{N_2,\ THF} Ru(H)(N_2)(N_3Ph_2)(PPh_3)_2$$
$$\textbf{5}\ (38\%)$$

characterized by elemental analysis.[9] Complex **4** has $\nu_{N\equiv N}$ 2165 cm^{-1} (Nujol) and reacts with $N_2B_{10}H_8S$-$(CH_3)_2{}^9$ to form the previously reported[10] $(Ph_3P)_2Ru$-$(Cl)Cl_3Ru(PPh_3)_2N_2B_{10}H_8S(CH_3)_2$. Passage of argon through a tetrahydrofuran solution of **4** causes loss of nitrogen; however, the $[(Ph_3P)_2RuCl_2]_2$ species reported by Gilbert and Wilkinson[11] was not obtained.

The yellow complex **5** has $\nu_{N\equiv N}$ 2000 cm^{-1} (Nujol) and exhibits a hydride resonance at δ −13.58 (triplet, $J_{P-H} = 21$ Hz) in a benzene-d_6 solution. In sharp contrast to the behavior of $RuH_2(N_2)(Ph_3P)_3$, dinitrogen is not lost from **5** when its solutions are swept with argon or with hydrogen.

Acknowledgment. We are indebted to Mrs. C. W. Alegranti for the membranes used in this work.

(8) W. H. Knoth, *Inorg. Chem.*, **12**, 38 (1973).
(9) Complex **4**: *Anal.* Calcd for $C_{72}H_{60}Cl_4N_2P_4Ru_2$: C, 60.84; H, 4.25; Cl, 9.97; N, 1.97; P, 8.71. Found: C, 61.11; H, 4.54; Cl, 9.71; N, 1.82; P, 8.56. Complex **5**: *Anal.* Calcd for $C_{48}H_{41}$-N_5P_2Ru: C, 67.75; H, 4.86; N, 8.23; P, 7.28. Found: C, 68.62; H, 4.96; N, 7.98; P, 6.94.
(10) W. H. Knoth, *J. Amer. Chem. Soc.*, **88**, 935 (1966).
(11) J. D. Gilbert and G. Wilkinson, *J. Chem. Soc. A*, 1749 (1969).

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Conformational Analysis of Cyclononatrienyl Anions

Sir:

A number of nmr spectra of simple hydrocarbon anions have been reported[1] in recent years but in most cases these species have been acyclic and presumably planar. Little is known about the molecular distortions of cyclic anions (or cations) which possess substantial conformational strain. In this communication we report the first examples of cyclononatrienyl anions and also present the first analysis of the conformation of a medium ring cyclic anion.

Treatment of 1,3,6-cyclononatriene (**1**)[2] with potassium amide in liquid ammonia gave a light-red solution of anion **2** (see nmr data in Figure 1)[3] which was quenched into pentane–water to afford **1** as the sole product. This anion is also rapidly produced at 25° starting with 1,4,7-cyclononatriene.[4]

The observation of only one signal for the C_8 and C_9 protons indicates that either **2** is planar or that it is non-

(1) Reviews: (a) J. M. Brown, *Org. React. Mech.*, 127 (1969); (b) *ibid.*, 119 (1970); (c) R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Fortsch. Chem. Forsch.*, **24**, 33 (1971).
(2) W. H. Okamura, T. I. Ito, and P. M. Kellett, *Chem. Commun.*, 1317 (1971). A similar reduction was discovered independently in these laboratories by T. J. Henry utilizing potassium instead of sodium.
(3) The nmr spectrum of **2** is completely different from that of the unknown species obtained by treatment of **1** with *n*-butyllithium in TMEDA–hexane; R. B. Bates, S. Brenner, and B. I. Mayall, *J. Amer. Chem. Soc.*, **94**, 4765 (1972).
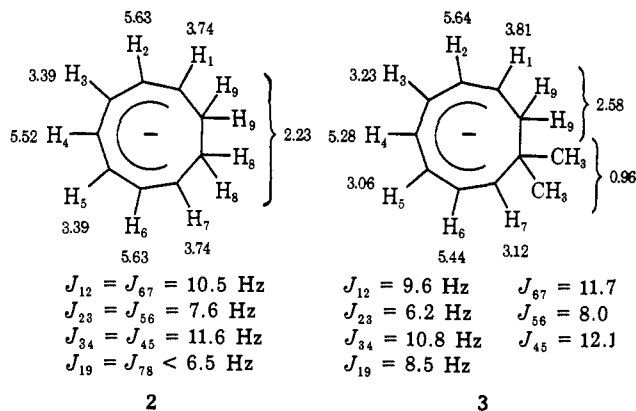(4) Prepared by the method of P. Radlick, Ph.D. Thesis, University of California at Los Angeles, 1964.

Figure 1. Nmr spectral data for the (potassium) cyclononatrienyl (**2**) and 8,8-dimethylcyclononatrienyl (**3**) anions in potassium amide–liquid ammonia at −55° with trimethylamine ($\delta_{NH_3}^{TMS}$ 2.135) as internal standard.

planar and rapidly flipping on the nmr time scale. The relatively low value for J_{23} (7.6 Hz)[5] tends to support the latter interpretation.

Additional evidence concerning this point is provided by the preparation of the 8,8-dimethylcyclononatrienyl anion (**3**) by the addition of either 8,8- or 9,9-dimethyl-1,3,6-cyclononatriene[2] (**4** and **5**, respectively) to potassium amide in liquid ammonia. The chemical shift of the methyl protons was obtained by using ammonia-$d_3{}^6$ as the solvent. Analysis of the nmr spectrum of **3** was aided by the fact that H_3 and H_5 undergo exchange in potassium amide–ammonia-d_3 (*ca.* 1 hr at room temperature) with the result that H_4 becomes a broadened singlet and H_2 and H_6 become doublets. The fact that exchange occurs primarily at these positions is in accord with the quenching of **3** into pentane–water to afford a mixture consisting only of **4** and **5**.[7]

The remarkable observation that the values of J_{12}, J_{23}, and J_{34} in **3** are each 1–2 Hz smaller than J_{45}, J_{56}, and J_{67}, respectively, suggests that **3** is nonplanar, even though the methylene protons at C_9 and the two methyl protons are each equivalent at −55°. This point is strongly supported by the large value of J_{19} (8.5 Hz) which requires that the methylene group at C_9 be substantially twisted with respect to the adjacent π bond so that H_1 and one of the protons at C_9 are nearly *s-trans* to each other.[8]

We suggest that the above points are uniquely accommodated by **6** as the predominant conformation. The latter is perhaps best described in terms of eight carbons (C_1–C_8) located near a common plane and forming a shallow twisted tub with C_9 bent substantially above the other ring carbons. Some features of this conformation are (1) the geminate methyl groups are at C_8 rather than at the sterically more crowded C_9, (2) the substituents at C_8 are more or less staggered with respect to those at C_9 and also with H_7, in accord with the low value (<4.5 Hz) estimated for J_{78} (average) in

(5) The C_2–C_3 bond is the most likely π bond to be twisted since it has the lowest HMO π bond order.
(6) I. Melczynski, *Angew. Chem.*, **74**, 32 (1962). We thank Dr. John Morrison for assistance with the preparation of ammonia-d_3.
(7) A 72:28 ratio of triene B to triene A (same designation as in ref 2) was obtained. It has not been established which isomer is which; W. H. Okamura, personal communication.
(8) For an analysis of a similar coupling in 1,3,5-cycloheptatriene, see H. Günther and R. Wenzl, *Z. Naturforsch. B*, **22**, 389 (1967).