or unit **1**) + 62 (3e,4a; or unit **3**) + 16 (2e,4a; or unit **7**) = +140 (observed +133).

Entries 5–11 in Table I are tribenzoates involving 6-OBz. As in classes V and VI, the conformations of the 6-benzoates are oriented toward the right or left depending on whether the 4 substituent is equatorial or axial. That this is so was supported by the good agreement between the observed and calculated *A* values in all cases; e.g., for entry 6 (2e,3e,6-): +62 (2e,3e; or unit **1**) – 7(2e,6; or unit **10**) + 11 (3e,6; or unit **9**) = +66 (observed +69).

The additivity relation still holds satisfactorily for the tetrabenzoates (entries 12–16) despite the fact that there are now *six component interactions* (involving also the 6-OBz group), e.g., for entry 14 (2e,3e,4a,6-): +62 (2e,3e; or unit **1**) + 16 (2e,4a; or unit **7**) – 4 (2e,6; or unit **14**) + 62 (3e,4a; or unit **3**) – 9 (3e,6; or unit **13**) – 15(4a,6; or unit **12**) = +112 (observed +100). Although the *A* values for the two anomeric methyl glycosides are usually in good agreement (entries 10/11 and 14/15), this was not so for the methyl glucosides, entries 12/13, in which the ratio of *A* values was 1.33; however, the ratio of the integrated values was satisfactory and was 1.1.[9]

The values summarized in Figure 1 for the various units can be regarded as *constants which are dependent only on the benzoate substitution pattern and are independent of the nature of the pyranose or other substituents*. This aspect together with the fact that only microgram quantities of the sugar derivatives are required forms the basis of a new method for determining oligosaccharide structures currently under investigation. The *A* value additivity relation, which has been found to hold for as many as six interacting units, and which is not confined to the benzoate chromophore, greatly simplifies the interpretations of CD data and also has general applicabilities in the studies of complex natural products.[10,11]

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(10) It has been applied to structural studies of trichilin, a limonoid insect antifeedant (by Dr. M. Nakatani) and a new compound related to ecdysteroids (by Dr. D. A. Trainor): manuscripts in preparation.

(11) The work was supported by NIH Grant CA 11572.

Allylic Rearrangements in the Thermal Decarbonylation of (2-Cyclopropene-1-carbonyl)rhenium Compounds; Nonfluxional η^1-Cyclopropenylrhenium Compounds

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Hanover, New Hampshire 03755

Received April 20, 1981

Two examples of fundamental organometallic reaction pathways which have stimulated the attention of synthetic and theoretical chemists involve (a) the migration of σ-bonded organic ligands to and from an adjacent coordinated carbon monoxide ligand[1] and (b) the migration of metals around the periphery of coordinated cyclic polyenyl ligands.[2] The former area is of intense interest because of its crucial role in many homogeneously catalyzed organometallic reactions;[3] in every defined case reported to date such migrations proceed via simple 1,2 shifts. The latter area has generated some controversy concerning the mechanism of metal migrations; the question of whether they are sigmatropic rearrangements which are subject to the constraints of conservation of orbital symmetry[4] or whether a simple least-motion migration pathway for the metal is operative has been raised.[5] η^1-Cyclopentadienyl compounds have been studied extensively; metal migrations around the periphery of the ring are invariably fast on the ^{1}H NMR time scale and have been shown to occur by a sequence of 1,2 shifts for both main group[6] and transition-metal derivatives.[2,5] Unfortunately the 1,2 shift of least motion is indistinguishable from an allowed [1,5]-sigmatropic shift in these molecules. Two examples of such metal migrations in η^1-cycloheptatrienyl compounds have been studied. The main group derivative $SnPh_3(\eta^1\text{-}C_7H_7)$ has been shown to undergo a 1,5 shift,[7] which is not the least motion pathway but which is consistent with an orbital-symmetry-allowed [1,5]-sigmatropic rearrangement. In contrast, $Re(CO)_5(\eta^1\text{-}C_7H_7)$ undergoes a 1,2 shift of the metal,[8] which appears to be consistent with a least motion pathway but which would correspond to a formally forbidden [1,7]-sigmatropic rearrangement were orbital symmetry the sole controlling factor. η^1-Cyclopropenyl compounds represent a class of molecule in which the least motion 1,2 shift pathway for metal migration corresponds to an orbital-symmetry-forbidden [1,3]-sigmatropic rearrangement; yet no studies of the dynamic behavior of such compounds have been reported.[9] This communication details the synthesis and characterization of *nonfluxional* η^1-cyclopropenyl compounds of rhenium; these are formed by clean, quantitative thermal decarbonylations of (2-cyclopropene-1-carbonyl)(pentacarbonyl)rhenium compounds, which proceed exclusively with *allylic rearrangement* of the migrating group.

We have reported previously the reaction of the acyl chloride **1** with $Co(CO)_4^-$ to afford η^3-cyclobutenonyl complexes of cobalt; an unstable acyl(tetracarbonyl)cobalt intermediate was detected in these reactions.[10] A similar reaction of **1** with $Re(CO)_5^-$ (THF, –78 °C), followed by warming to –20 °C and removal of the solvent at this temperature, allows the isolation of the rhenium acyl compound **2**.[11] In contrast to its cobalt analogue, **2** undergoes a smooth thermal decarbonylation in solution at 20 °C[12] to afford quantitatively the η^1-cyclopropenyl compound **3**.[11] Similarly, reaction of the deuterium labeled acyl chloride **4** with $Re(CO)_5^-$ under identical conditions affords the thermally unstable acyl complex **5a**,[11,13] which undergoes rapid decarbonylation at 20 °C to give exclusively **6a**;[11] the analogous conversion of **4b** → **5b** →

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† Alfred P. Sloan Research Fellow, 1980–1982.

(1) For reviews of the CO insertion/extrusion reaction, see: (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87–145. (b) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195–225.

(2) For a review, see: Cotton, F. A. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, **1975**; Chapter 10.

(3) For leading references, see ref 1b.

(4) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1971.

(5) Fabian, B. D.; Labinger, J. A. *J. Organomet. Chem.* **1981**, *204*, 387–392 and references cited therein. Free energies of activation for transition-metal migrations in η^1-C_5H_5 systems usually lie in the range of 8–11 kcal·mol^{-1}.[2]

(6) Holmes-Smith, R. D.; Stobart, S. R. *J. Am. Chem. Soc.* **1980**, *102*, 382–384 and references cited therein.

(7) Larrabee, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 1510–1512. Mann, B. E.; Taylor, B. F.; Taylor, N. A.; Wood, R. *J. Organomet. Chem.* **1978**, *162*, 137–144.

(8) Heinekey, D. M.; Graham, W. A. G. *J. Am. Chem. Soc.* **1979**, *101*, 6115–6116. The free energy of activation for this process is $\Delta G^{\ddagger} = 19.8 \pm 0.1$ kcal·mol^{-1} at 300 K.

(9) Some η^1-cyclopropenyl compounds of iron have been characterized: Gompper, R.; Bartmann, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 456–457. Gompper, R.; Bartmann, E.; Noth, H. *Chem. Ber.* **1979**, *112*, 218–233.

(10) Chidsey, C. E.; Donaldson, W. A.; Hughes, R. P.; Sherwin, P. F. *J. Am. Chem. Soc.* **1979**, *101*, 233–235.

(11) Compound **2** is isolated as pale yellow crystals (30%) after recrystallization: mp 92–94 °C; ν_{CO} (hexane) 2122 w, 2054 w, 2009 vs, 1984 s, 1592 w cm^{-1} ($\nu_{C=C}$ is too weak to be observed); ^{1}H NMR (60 MHz, $CDCl_3$, 20 °C) δ 2.98 (s, CH), 7.37–7.72 (m, Ph); mass spectrum *m/e* 546 (P$^+$, using ^{187}Re). **3**: mp 100–103 °C; ν_{CO} (hexane) 2137 w, 2045 w, 2025 vs, 1993 s cm^{-1}; $\nu_{C=C}$ 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$, 20 °C) δ 6.43 (s, C=CH), 6.98–7.61 (m, Ph); mass spectrum, *m/e* 518 (P$^+$, using ^{187}Re). **5a**: ^{1}H NMR ($CDCl_3$, 20 °C) δ 2.92 (s, CH), 1.15 (s, *t*-Bu). **6a**: ^{1}H NMR ($CDCl_3$, 20 °C) δ 6.20 (s, C=CH), 1.20 (s, *t*-Bu). **6b**: ^{1}H NMR ($CDCl_3$, 20 °C) δ 2.20 (d, $J = 1.2$ Hz, CH), 6.20 (d, $J = 1.2$ Hz, C=CH), 1.20 (s, *t*-Bu). IR and mass spectral data for compounds **5** and **6** are compatible with those quoted for **2** and **3**. Satisfactory microanalysis data have been obtained for all compounds reported.

(12) The rate of decarbonylation is qualitatively faster in more polar solvents. If THF solutions of **2** are warmed to 20 °C the rate of conversion of **2** → **3** is sufficiently fast so as to preclude isolation of pure **2**; **2** is moderately stable in C_6H_6 solution at 20 °C.

(13) Compounds **5** are much more labile toward decarbonylation than is **2**.

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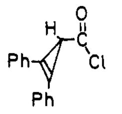
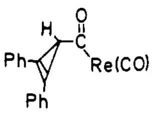
6b provides compounds for ^{1}H NMR spectroscopic comparison.[11]



1



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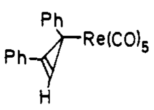

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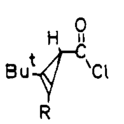
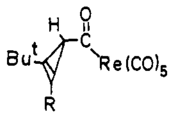
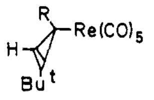


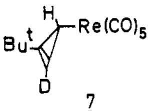
4a. R = D
4b. R = H



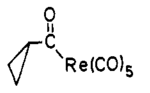
5a. R = D
5b. R = H



6a. R = D
6b. R = H



7



8

The regioselective formation of **6a** from **5a** clearly illustrates that the cyclopropenyl migration from CO to Re occurs with allylic rearrangement of the migrating group and provides the first example of such a migration by other than a simple 1,2 shift. The absence of **7** precludes any dissociative migration pathway or a sequence of steps involving a 1,2 shift of the cyclopropenyl group from CO to Re followed by a shift of Re(CO)$_5$ around the ring. The facility with which **2** and **5** undergo thermal decarbonylation is noteworthy. The saturated acyl compound **8** has been reported to be thermally and photochemically inert with respect to cyclopropyl migration;[14] clearly, participation of the cyclopropene olefin in an allylic rearrangement provides a lower energy migration route.

Compound **6a** does not rearrange to produce detectable amounts of its isomer **7** over a period of 24 h (CDCl$_3$, 20 °C),[15] demonstrating quite unambiguously that migration of the Re(CO)$_5$ moiety around the cyclopropenyl periphery is not a chemically significant event at this temperature.[16] We note that the qualitative order of increasing activation energy for 1,2 migration of a ReL$_n$ moiety around cyclopolyenyl ligands is η^1-C$_5$H$_5$[17] < η^1-C$_7$H$_7$[8] < η^1-C$_3$H$_2$-*t*-Bu; this ordering is consistent with the expected ordering of activation energies for a sigmatropic rearrangement ([1,5] < [1,7] < [1,3]),[4,18] but it is not clear why a least motion mechanism should produce such widely differing rates. Even more unclear is the reason for the different migration pathways adopted by SnPh$_3$(η^1-C$_7$H$_7$)[7] and Re(CO)$_5$(η^1-C$_7$H$_7$).[8] Clearly the mechanisms of all such metal shifts require further experimental and theoretical elucidation.

Studies of the generality of allylic rearrangements in the migrations of cyclopropenyl and allyl moieties to and from coordinated CO, and of the chemistry of η^1-cyclopropenyl compounds, are currently in progress.

Acknowledgment. We gratefully acknowledge generous support of our research by the National Science Foundation (Grants CHE7717877 and CHE8022854), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Alfred P. Sloan Foundation.

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(14) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Organomet. Chem.* **1969**, *20*, 161-168.

(15) Barring an unprecedented isotope effect, this would constitute a degenerate arrangement.

(16) This corresponds to a *minimum* free energy of activation of ca. 30 kcal·mol^{-1} for this migration.

(17) The compound Re(CO)(NO)(PMe$_3$)$_2$(CH$_3$)(η^1-C$_5$H$_5$) is reported to be fluxional at -100 °C: Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* **1980**, *102*, 6156-6157.

(18) This ordering assumes that the metal orbital involved in the transition state for a sigmatropic rearrangement is isolobal with, for example, a methyl group. Molecular orbital calculations on a square-pyramidal Re(CO)$_5$ fragment indicate that this may be the case: Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058-1076.

Spherands, the First Ligand Systems Fully Organized during Synthesis Rather than during Complexation[1]

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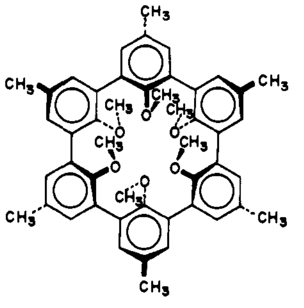
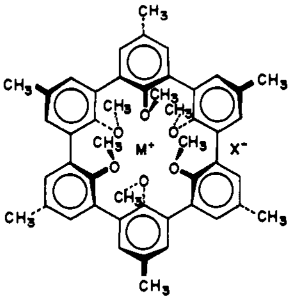
Received March 26, 1981

We report here four new syntheses of spherand **1**,[2] its crystal structure, and the crystal structures of its lithiospherium chloride complex **2**[2] and sodiospherium methylsulfate complex **3**.[3] The results establish that, unlike any organic ligand system previously prepared, **1** possesses the same conformational organization as that of its complexes, **2** and **3**. Thus the full burden of binding-site collection and organization in this spherand is transferred from the complexation process to the synthesis of the ligand system, whose conformation is enforced by its rigid support structure.

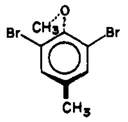


1

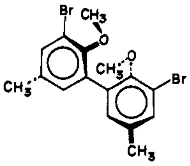


2, M$^+$ = Li$^+$; X$^-$ = Cl$^-$
3, M$^+$ = Na$^+$; X$^-$ = CH$_2$SO$_4^-$

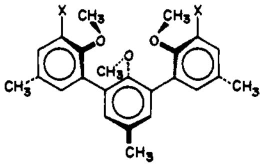
The cyclohexametaarylene oligomeric system **2** was synthesized in a single experiment by coupling the *six* individual *monomeric units* of **4**[4] by its metalation with 3 mol of *sec*-butyllithium at -80 °C in THF. The mixture was cannulated into a refluxing solution of 4 mol of Fe(AcAc)$_3$ in benzene. After refluxing for 1 h, the mixture was cooled and stirred (3 h) with 3 N HCl aqueous solution containing FeCl$_3$·6H$_2$O. The organic solvent of the mixture was evaporated at 50 °C under vacuum. The remaining material after 8 h at 25 °C was collected, dried at 25 °C, and triturated with dry Et$_2$O to give crude **1**·LiFeCl$_4$. This material was converted directly to **2** as before[2] (2% overall). Similar lithiation and oxidative coupling of *three dimeric units* of **5**,[3,5] and *two trimeric units* of **6**[2] gave **2** in 7 and 25% yields, respectively. In a fourth new synthesis of **2**, **7**[6] was directly lithiated



4



5



6, X = Br
7, X = H

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(1) Support for the X-ray crystal structure determinations by the National Science Foundation Grants GP-28248 and 77-18748 is gratefully acknowledged by K. N. Trueblood, C. B. Knobler, and E. Maverick. Support for the syntheses by the Division of Basic Sciences of the Department of Energy (Contract AT(04-3)34, P.A. 218) is gratefully acknowledged by R. C. Helgeson, S. B. Brown, and D. J. Cram.

(2) Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Lein, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 6752-6754.

(3) Carbon and hydrogen analyses were within 0.30% of theory. Mass spectra and ^{1}H NMR spectra (200 MHz, Bruker) were as expected.

(4) Kohn, M.; Segel, A. *Monatsh. Chem.* **1925**, *46*, 661-669.

(5) We thank Dr. P. Stückler for preparing this new compound (mp 84-85 °C) by conventional reactions[2] from 2,2'-dihydroxy-5,5'-dimethylbiphenyl.

(6) Koenig, K. E.; Lein, G. M.; Stückler, P.; Kaneda, T.; Cram, D. J., *J. Am. Chem. Soc.* **1979**, *101*, 3553-3566.

0002-7863/81/1503-5594$01.25/0