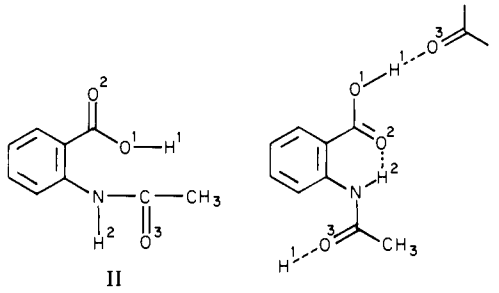
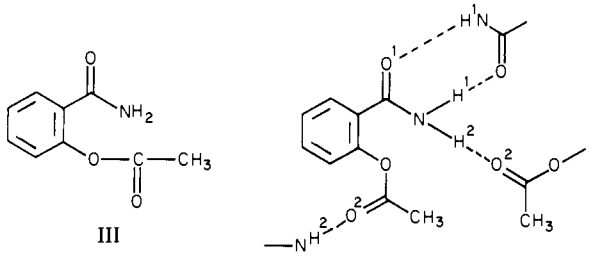


II

there are no doubly hydrogen-bonded oxygens present.

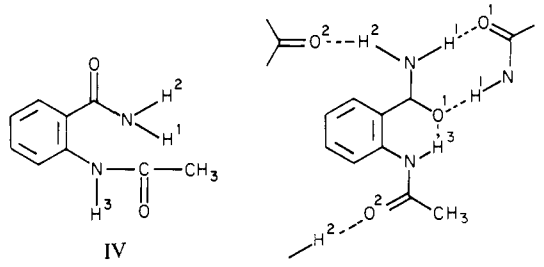
The structure of II could also be accounted for on the basis that amide oxygens are stronger proton acceptors than carboxyl oxygens, so one would expect H1 to bond to O3. In the structure of O-acetylsalicylamide (III), however, the ester carbonyl is linked



III

to an amide hydrogen,[9] consistent with criterion 3 but yet contrary to the expected hydrogen acceptor strengths of the two carbonyl groups in this compound. In benzamide, and in many other primary amides, the amide carbonyl bonds to both H1 and H2.[10] It may be that the important point here is *not* that the weaker acceptor was used but that relative acceptor strengths derived from solution experiments do not necessarily correlate with the bonding characteristics of these functional groups in the solid state.

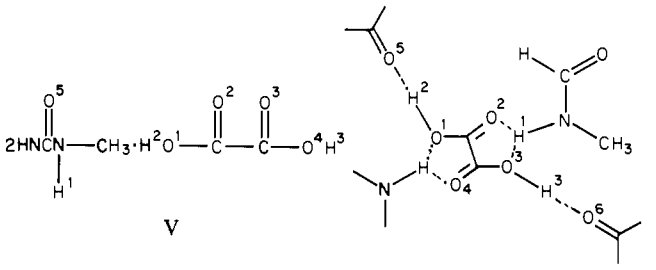
In a related example, which we reported recently[5] there are two polymorphs of *N*-acetylanthranilamide (IV), both of which have hydrogen bonds to all the avilable hydrogen acceptors. Since there are more hydrogens than acceptor sites in these structures (3:2), it is not surprising that they both contain cyclic dimer H-bond patterns. The α form of IV has the H-bonding features of both I and II in that there is an intramolecular H bond in addition to the cyclic dimer (like I) and also a hydrogen bond to the acetyl carbonyl (H2-O2) like II. Upon heating, this polymorph rearranges in such a way that all the acceptor sites remain H bonded even though the intramolecular H bond is broken, suggesting that criterion 3 may supercede 2 in importance in this case.



IV

An intriguing example which supports this new packing criterion is that of the structure of the 2:1 adduct of *N*-methylformamide with oxalic acid (V).[8] In this complex there are six acceptor sites and only four available hydrogens. The H-bonding pattern found has the oxalic acid hydrogens bonded to the two formamide oxygens (H2, H3-O5, O6). This leaves only two hydrogens to bond to the remaining four oxygens of the acid. In order to involve all of the oxygens the formamide hydrogen becomes bifurcated.

From a literature survey of approximately 50 structures which contain only amide and/or acid groups, we have found that



V

criterion 3 is satisified in all but two structures. In addition, all structures surveyed which contain phenol oxygens or amine nitrogens in addition to the acid and amide groups have hydrogen-bonding networks which incorporate the phenol and amines as hydrogen-bond acceptors also. On the other hand, groups like esters, nitro groups, sulfones, sulfonic acids, and furans while capable of forming hydrogen bonds are not always used as acceptor sites for hydrogen bonding.

As seen by structures II-IV, one result of incorporating the maximum number of acceptor sites into the H-bonding schemes is that extended polymer-like chains and networks are formed. We are interested in seeing whether or not there is evidence that these chains form in solution as well as in solid state. In addition, we are pursuing the possibility that solid-gas reactions of acids and amides with water vapor may be related to whether or not there are "free" hydrogen acceptor sites in the crystal. Indeed this may play a part in whether or not crystalline hydrates of amides and acids can be grown from solution.

Registry No. I, 119-68-6; II, 89-52-1; III, 5663-71-8; IV, 33809-77-7; V, 80399-20-8.

(9) V. Mohan Rao and H. Manohar, Abstract 04.4-06, 12th IUCr Meeting, Ottawa, Canada, Aug 1981.
(10) B. R. Penfold and J. C. B. White, *Acta Crystallogr.* **12**, 180, (1959).

Retention of Configuration during Ligand-Substitution Reactions of Cyclopentadienylrhodium Complexes Containing an Acyl Ligand

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There is considerable interest in the stereochemical fate of chiral centers in organometallic complexes during simple reactions. These centers can be either chiral ligands or complexes where the optical activity is due to asymmetry at the metal atom. Pseudotetrahedral complexes of the type CpMLL'L'' are examples of the latter whose preparation and resolution has been studied extensively by Brunner[2] and co-workers. The stereochemical fate of an optical center is a powerful mechanistic probe. Specific studies of the stereochemistry at the metal have been reported for reactions such as the photochemical decarbonylation of acyl ligands,[3] the insertion of SO_2 into iron-carbon bonds,[4] electrophilic cleavage of the latter,[5] asymmetric induction,[6] and ligand sub-

(1) Camille and Henry Dreyfus Teacher-Scholar.
(2) Brunner, H. *Top. Curr. Chem.* **1975**, *56*, 67-90.
(3) Davidson, A.; Martinez, N. *J. Organomet. Chem.* **1974**, *74*, C17-C20.
(4) Miles, S. L.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7278-7282.
(5) Attig, T. G.; Teller, R. G.; Wu, S. M.; Bau, R.; Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 619-628.

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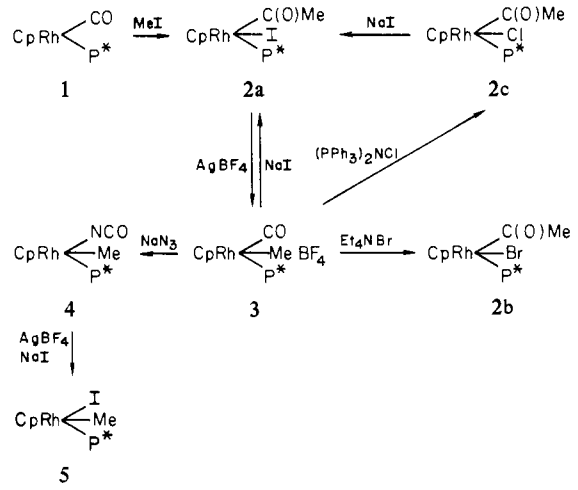
Scheme I



stitution.[7] We have prepared and separated diastereomers of some chiral cyclopentadienylrhodium complexes and find that they undergo highly stereospecific ligand-substitution reactions when an acyl ligand is present.

Graham and Oliver[8] reported the chiral complex CpRh[C(O)Me](PPhMe$_2$)I, the NMR spectrum of which resolved the diastereotopic methyl groups of the phosphine, consistent with configurational stability on the NMR time scale. We have introduced a resolved optical center by replacing the PPhMe$_2$ ligand with the chiral phosphine[9] (*S*)-[PPh$_2$NHCH(Me)Ph] (P*). Treatment of CpRh(CO)P* (**1**)[10] with MeI gave CpRh[C(O)Me](P*)I (**2a**)[10] as a 1:1 mixture of diastereomers which were separated by fractional crystallization. The peaks in the NMR spectrum of the individual diastereomers were easily resolved[11] in a mixture,[12] and the CD spectra[13] of the separated isomers were mirror images of each other.

The reaction of a diastereomer of **2a** with AgBF$_4$ in acetone (Scheme I) gave the salt [CpRh(CO)(Me)P*]BF$_4$ (**3**)[10] with only one diastereomer observed in the NMR spectrum.[14] The complexes **2a-c**[10] were prepared with high stereospecificity[12] from **3** by treatment with a salt of the appropriate anion (NaI, Et$_4$NBr, and (PPh$_3$)$_2$NCl, respectively). The NMR and CD spectra of **2a** prepared in this manner were identical with those of the **2a** used to prepare **3**. The chloro-complex **2c** was converted to the iodo-compound **2a** by metathesis with NaI in acetone, and the CD and NMR spectra were consistent with overall retention (i.e., **2a** → **3** → **2c** → **2a**).

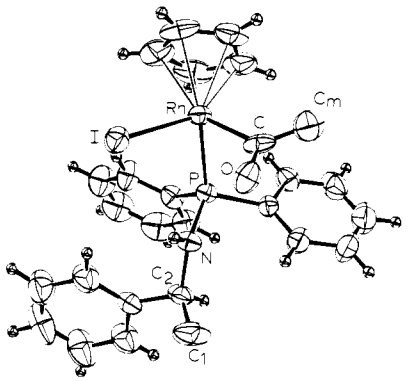


Figure 1. Perspective ORTEP drawing of the solid-state structure of (η^5-C$_5$H$_5$)Rh[C(O)Me][(*S*)-(PPh$_2$NHCH(Me)Ph)]I (**2a**). All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density; hydrogen atoms are represented by arbitrarily sized spheres which are in no way representative of their true thermal motion. Bond lengths (A) and angles (deg) of interest include Rh-I, 2.691(1); Rh-P, 2.269 (2) Å; (acyl)Rh-C, 2.139 (8) Å; (cyclopentadienyl) Rh-C, 2.252 (10, 28, 65, 5);[25] C-O, 1.190 (9); C-C$_m$, 1.361 (12); P-N, 1.650 (6); N-C$_2$, 1.482 (8); C$_1$-C$_2$, 1.508 (12); C$_g$-Rh-I,[25] 118.7; C$_g$-Rh-P, 129.1; C$_g$-Rh-C, 125.0; I-Rh-P, 95.7 (1); I-Rh-C, 94.6 (2); P-Rh-C, 84.2 (2); Rh-C-O, 117.0 (5); Rh-C-C$_m$, 115.0 (6); C$_m$-C-O, 127.8 (7)°.

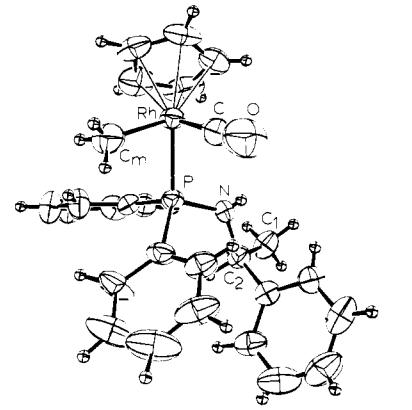


Figure 2. Perspective drawing similar to that of Figure 1 for the {(η^5-C$_5$H$_5$)Rh(CO)(Me)[(*S*)-(PPh$_2$NHCHMePh]}$^+$ cation in **3**. Bond lengths (Å) and angles (deg) of interest include Rh-C$_m$, 2.120 (8); Rh-P, 2.285 (1); (carbonyl) Rh-C, 1.876 (8); (cyclopentadienyl) Rh-C, 2.223 (7, 11, 26, 5);[25] C-O, 1.128 (11); P-N, 1.636 (5); N-C$_2$, 1.475 (8); C$_1$-C$_2$, 1.508 (9); C$_g$-Rh-C$_m$,[25] 122.0; C$_g$-Rh-P, 123.6; C$_g$-Rh-C, 129.7; C$_m$-Rh-P, 88.3 (2); C$_m$-Rh-C, 86.7 (3); P-Rh-C, 94.6 (2); Rh-C-O, 175.8 (7).

Treatment of **3** with NaN$_3$/acetone gave the isocyanate[15] complex CpRh(Me)(P*)NCO (**4**)[10] with high stereospecificity.[12] Complex **4**, which does not have an acyl ligand, was reacted with AgBF$_4$/acetone and the filtrate treated directly with NaI to give CpRh(Me)(P*)I (**5**)[10] as 1:1 mixture of diastereomers as shown by its NMR spectrum.[16] The separated diastereomers of **5**, prepared by an alternate route,[17] epimerized rapidly when treated with AgBF$_4$ and then NaI in acetone. Thus, racemization at the rhodium center occurred in the absence of the acyl ligand.

The NMR analyses of the reactions of **2** and **3** indicate they proceed with a very high degree of stereospecificity. The determination of the stereochemical fate of the chiral rhodium center

(6) (a) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1977**, *99*, 1808-1812. (b) Brunner, H. *Acc. Chem. Res.* **1979**, *12*, 250-257.

(7) (a) Faller, J. W.; Shvo, Y. *J. Am. Chem. Soc.* **1980**, *102*, 5396-5398. (b) Brunner, H. *J. Organomet. Chem.* **1975**, *94*, 189-194.

(8) Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 243-247.

(9) Brunner, H.; Rambold, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 1013-1014.

(10) Satisfactory elemental analysis and spectroscopic characterization were obtained for this compound.

(11) **2a**, diastereomer A: NMR (CDCl$_3$) δ 7.88-7.03 (15 H, m, C$_6$H$_5$), 5.16 (5 H, dd, C$_5$H$_5$, *J*(P-H) = 1.7 Hz, *J*(Rh-H) = 0.6 Hz), 4.00 (2 H, m, CH-NH), 2.96 (3 H, s, CH$_3$C(O)), 1.29 (3 H, d, CCH$_3$, *J*(H-H) = 6.4 Hz). **2a**, diastereomer B: NMR (CDCl$_3$) δ 7.88-7.03 (15 H, m, C$_6$H$_5$), 5.16 (5 H, dd, C$_5$H$_5$, *J*(P-H) = 1.7 Hz, *J*(Rh-H) = 0.6 Hz), 3.95 (2 H, m, CH-NH), 3.04 (3 H, s, CH$_3$C(O)), 1.08 (3 H, d, CCH$_3$, *J*(H-H) = 6.4 Hz).

(12) The NMR spectra were measured in CDCl$_3$ by using a Varian XL-200 FT spectrometer. The estimated limit of detection of a low concentration of one diastereomer as a percentage of the major isomer is 3%.

(13) The CD spectra were measured in CHCl$_3$ solvent by using a Jasco ORD/UV-5.

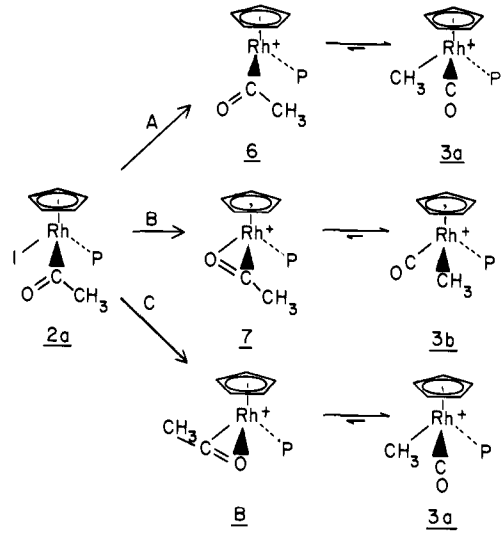
(14) **3**, diastereomer A: NMR (CDCl$_3$) δ 7.78-6.81 (15 H, m, C$_6$H$_5$), 5.60 (5 H, d, C$_5$H$_5$, *J*(P-H) = 1.5 Hz), 4.83 (1 H, dd, NH, *J*(P-H) = 18.5 Hz, *J*(H-H) = 9.2 Hz), 3.76 (1 H, m, CH), 1.60 (3 H, d, CCH$_3$, *J*(H-H) = 6.8 Hz), 0.95 (3 H, dd, RhCH$_3$, *J*(P-H) = 4.7 H z, *J*(Rh-H) = 2.2 Hz). **3**, diastereomer B (isolated from diastereomer B of 2a): NMR (CDCl$_3$) δ 7.77-6.84 (15 H, m, C$_6$H$_5$), 5.61 (5 H, d, C$_5$H$_5$, *J*(P-H) = 1.5 Hz), 4.78 (1 H, dd, NH, *J*(P-H) = 18.5 Hz, *J*(H-H) = 9.2 Hz), 3.71 (1 H, m, CH), 1.49 (3 H, d, CCH$_3$, *J*(H-H) = 6.8 Hz), 1.05 (3 H, dd, RhCH$_3$, *J*(P-H) = 4.5 Hz, *J*(Rh-H) = 2.2 Hz).

(15) Faraone, F.; Cusmano, F.; Piraino, P.; Pietropaolo, R. *J. Organomet. Chem.* **1972**, *44*, 391-397.

(16) **6**, diastereomer A: NMR (CDCl$_3$) δ 7.50-6.86 (15 H, m, C$_6$H$_5$), 5.03 (5 H, dd, C$_5$H$_5$, *J*(P-H) = 1.7 Hz, *J*(Rh-H) = 0.5 Hz), 3.82 (2 H, m, CH-NH), 1.48 (3 H, d, CCH$_3$, *J*(H-H) = 6.5 Hz), 1.29 (3 H, dd, RhCH$_3$, *J*(P-H) = 5.1 Hz, *J*(Rh-H) = 2.4 Hz). **6**, diastereomer B: NMR (CDCl$_3$) δ 8.20-6.80 (15 H, m, C$_6$H$_5$), 5.09 (5 H, dd, C$_5$H$_5$, *J*(P-H) = 1.8 Hz, *J*(Rh-H) = 0.6 Hz), 3.74 (2 H, m, CH-NH), 0.83 (3 H, d, CCH$_3$, *J*(H-H) = 6.5 Hz), 1.24 (3 H, dd, RhCH$_3$, *J*(P-H) = 5.1 Hz, *J*(Rh-H) = 2.4 Hz).

(17) Complex **6** was also prepared from CpRh(P*)I$_2$ and MeMgI as a 1:1 mixture of diastereomers which were separated by fractional crystallization.

Scheme II



during these transformations depends upon the analysis of the CD spectra of the complexes. The criterion that P*, the resolved center, does not contribute to the CD spectrum[18] is satisfied since the CD spectra of the separated diastereomers of **2a**, **3**, and **5** are approximate mirror images of each other. It has also been shown that complexes of the type $CpFe(CO)(PPh_3)X$ with the same configuration at iron have similar CD spectra if the anionic ligands X are similar.[19] The NMR and CD analysis of **2a** during the reaction sequence **2a** → **3** → **2a** provide unambiguous evidence that the two steps proceed with retention overall.[20] The complexes **2a–c** are very similar; thus, the conclusions that their preparations via **3** and the conversion of **2c** to **2a** proceed with retention seems justified. However, the structural relationship between **2** and **3** is somewhat distant; therefore, stereochemical assignments based on their CD spectra must be considered tentative. The CD spectra of **2a** and **3** are neither identical nor mirror images; however, the spectrum of **4** is a mirror image of that of **2a**. The reaction of NaN_3 with **3** to give **4** should have frozen the chirality of the salt snce the metal was not affected.[21] Thus, **4** corresponds to that isomer of **3** where the methyl group has occupied the site of the departed iodide and the carbonyl is at the original site of the acyl ligand in **2**. X-ray structural determinations[22] of **2a** and **3** confirm this (Figures 1 and 2, respectively).[23]

Stereospecificity in other systems has been attributed to asymmetric induction by the resolved optically active ligand.[6,26] This seems unlikely here since the ligand P* has been shown[27] to be very weak in this respect in the structurally related complexes $CpCo(R_F)(P^*)I$, where $R_F = CF_3$, C_2F_5, and C_3F_7. Induction was not observed in the preparations of **2a** and **5**[17] in contrast to the high stereospecificity observed for the reactions of **2a**, **2c**, and **3**. The epimerization observed for **4** and **5** confirms the role of the acyl group. Thus, the ability of the acyl ligand to undergo stereospecific reversible methyl migration accounts for the stereochemistry observed during the reactions of **2** and **3**.

The stereochemistry of the conversion of **2a** to **3** is consistent with the so-called "methyl migration" pathway whereby loss of I^- is assumed[28,29] to produce a chiral coordinatively unsaturated intermediate such as **6**[30,31] which is trapped before it can racemize by migration of the methyl group to the vacant site[32] (Scheme II, path A). Davison and Martinez[3] have shown that photochemical decarbonylation of $CpFe[C(O)Et](CO)PPh_3$ also proceeds such that the ethyl group occupies the site vacated by the departing terminal CO. However, Brunner has recently reported[33] that carbonylation of $CpFe(CO)(CH_3)L$, where L = (*S*)-$[PPh_2N(Me)CH(Me)Ph]$, proceeds such that the methyl group remains stationary and that a η^2-acyl intermediate is formed by insertion of the carbonyl into the iron–methyl bond. The chirality of the intermediate is preserved by the oxygen of the acyl group which occupies the position vacated by the carbonyl carbon. The reverse of this "carbonyl migration" mechanism applied to **2a** (Scheme II, path B) leads to the η^2-acyl **7** where the position of the departed iodide ligand has been occupied by the oxygen atom. Carbonyl migration would give **3** in the opposite configuration from that observed. However, if the oxygen atom became attached to the metal from the side opposite the departing iodide group (path C), this would give **8** and lead to the observed chirality at **3**. The principle of microscopic reversibility applied to paths A and C indicates that addition of an anion to **3**, perhaps forming a contact ion pair,[4,5,34] would ensure recapture of the original coordination position of the anion in **2**.

The reactions above illustrate the role of an acyl group as a type of chiral memory whereby the stereochemistry of a complex can be maintained throughout a series of catalytically important reactions such as dissociative ligand substitution. This is accomplished by the acyl group decarbonylating and temporarily filling a vacant coordination site. The complement to this process can be envisioned whereby certain polyhapto ligands such as η^3-allyl[7a,35] could stereospecifically reduce the number of sites they occupied

(18) (a) Reger, D. L. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1095–1097. (b) Flood, T. C.; Miles, D. L. *J. Am. Chem. Soc.* **1973**, *95*, 6460–6462.

(19) Chou, C.-K.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7271–7278 and references cited therein.

(20) This could result from both steps going with retention or both with inversion.

(21) In a similar reaction, Faller reported retention of configuration at molybdenum when the ion $CpMo(NO)(CO)(\eta^3\text{-}C_3H_5)^+$ was treated with N_3^- to form the isocyanate $CpMo(NO)(NCO)(\eta^3\text{-}C_3H_5)^+$. Faller, J. W.; Murray, H. Tenth International Conference on Organometallic Chemistry, Toronto, Canada, 1981.

(22) Single crystals of compounds **2a** and **3** are orthorhombic, space group $P2_12_12_1\text{-}D_2^4$ (No. 19), with a = 8.471 (1) Å, b = 17.429 (3) Å, c = 17.740 (2) Å, and Z = 4 for **2a**; a = 9.644 (2) Å, b = 10.171 (2) Å, c = 27.827 (6) Å, and Z = 4 for **3**. Three-dimensional X-ray diffraction data were collected for those [3393 (**2a**) and 5228 (**3**)] independent reflections having $2\theta_{MoK\alpha} < 55°$ (**2a**) or $2\theta_{MoK\alpha} < 63.7°$ (**3**) using graphite-monochromated $MoK\bar{\alpha}$ radiation and full (1.0° wide) ω scans on a Nicolet P$\bar{1}$ autodiffractometer. The solid-state structures of both compounds were solved by using the "heavy-atom" technique. The resulting structural parameters have been refined to convergence [R(unweighted, based on F) = 0.032 (**2a**) and R = 0.041 (**3**) for 2701 (**2a**) and 3381 (**3**) independent absorption-corrected reflections having $I > 3\sigma(I)$] by using empirically weighted full-matrix least-squares techniques with anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms of both compounds. Hydrogen atoms of **2a** (except those bonded to methyl carbon atoms C_1 and C_m) were placed in their idealized positions and fixed during least-squares refinement; positions for all hydrogen atoms of the cation in **3** were determined from a difference Fourier synthesis and varied during least-squares refinement.

(23) The stereochemical designation of the rhodium center of **2a** and **3** are *R* and *S*, respectively.[24]

(24) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598–6599.

(25) The first number in parentheses following an averaged value for a bond length or angle is the root-mean-square estimated standard deviation of the individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively; the fourth number is the number of individual values included in the average. C_g refers to the center of gravity for the five-membered ring of the cyclopentadienyl ligand.

(26) (a) Reich-Rohrwig, P.; Wojcicki, A. *Inorg. Chem.* **1974**, *13*, 2457–2464. (b) Attig, T. G.; Wojcicki, A. *J. Am. Chem. Soc.* **1974**, *96*, 262–263.

(27) Brunner, H.; Doppelberger, J.; Dreischl, P.; Möllenberg, T. *J. Organomet. Chem.* **1977**, *139*, 223–233.

(28) Both complexes **2** and **3** satisfy the 18-electron rule and are expected to undergo ligand substitution by a dissociative-type mechanism.[7b]

(29) (a) Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337–353. (b) Brunner, H.; Rackl, F. *J. Organomet. Chem.* **1976**, *118*, C19–C22.

(30) Calculations[31] have shown that 16-electron complexes of the type CpMLL′ are pyramidal but nothing is known about the barriers to inversion of these proposed structures.[7b,29b]

(31) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536–537.

(32) Rapid methyl migration has recently been reported for other acyl Rh(III) complexes. See: Werner, H.; Klingert, B. *J. Organomet. Chem.* **1981**, *218*, 395–407. Bennett, M. A.; Jeffery, J. C.; Robertson, G. B. *Inorg. Chem.* **1981**, *20*, 323–330.

(33) Brunner, H.; Vogt, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536–537.

(34) (a) Jacobson, S. E.; Wojcicki, A. *J. Am. Chem. Soc.* **1973**, *95*, 6962–6970. (b) Jacobson, S. E.; Reich-Rohrwig, P.; Wojcicki, A. *Inorg. Chem.* **1973**, *12*, 717–723.

(35) Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227–231.

and direct the stereochemistry of a reaction. Thus, the nature of the ligands in a chiral complex could have a profound effect on its chiroptical properties.

Acknowledgment. The support of the Natural Sciences and Engineering Research Council of Canada and the Ministère de l'Education du Québec is acknowledged. S.Q. acknowledges an NSERC 1967 Science Scholarship (1976-1980) and is a Boursière du Ministère de l'Education du Québec (1978-1981). We are particularly grateful to Engelhard Industries of Canada for the generous loan of $RhCl_3 \cdot (H_2O)_x$.

Registry No. 1, 80422-24-8; **2a**, diasteriomer A, 80422-25-9; **2a**, diasteriomer B, 80446-90-8; **2b**, 80422-26-0; **2c**, 80422-27-1; **3**, diasteriomer A, 80422-29-3; **3**, diasteriomer B, 80446-92-0; **4**, 80422-30-6; **5**, diasteriomer A, 80422-31-7; **5**, diasteriomer B, 80446-93-1.

Long-Range Proton-Carbon-13 NMR Spin Coupling Constants

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We propose a new NMR technique for the detection and assignment of long-range proton-carbon-13 spin coupling constants. It is based on an existing two-dimensional Fourier transform[1,2] experiment which detects carbon-13 spin echoes modulated by heteronuclear spin-spin coupling,[3-5] but it uses a frequency-selective 180° radio frequency pulse applied to an isolated proton resonance. The resulting carbon-13 spin multiplets are simple, well-defined, and readily assigned, and the sensitivity of this experiment can be higher than in the corresponding conventional proton-coupled carbon-13 spectrum. The technique provides precise measurements of long-range CH couplings, useful for studies of molecular conformation and for the assignment of carbon-13 spectra, particularly the quaternary sites.

Spin echoes are modulated by spin-spin coupling provided that both coupled spins experience the effects of the 180° refocusing pulse.[3-5] This phenomenon permits proton-carbon couplings to be separated from carbon-13 chemical shifts[6-8] by making use of the extra frequency dimension provided by two-dimensional Fourier transform NMR spectroscopy. A carbon-13 spin echo is generated at the end of a variable evolution period (t_1) and the second half of the echo detected under conditions of broadband proton decoupling. The new frequency dimension (F_1) displays the fine structure due to all the proton-carbon couplings.

The innovation is to make the 180° proton pulse frequency selective (Figure 1) by reducing its intensity ($\gamma B_1/2\pi = 25$ Hz) and increasing its duration (20 ms).[9,10] Its effectiveness for spin inversion is thereby restricted to a frequency range of the order ±25 Hz about the exact resonance condition for a chosen proton so that the outer satellite lines due to $^1J_{CH}$ are unaffected while the inner satellites due to long-range coupling are inverted. The proton site is selected so as to have a resonance frequency well separated from other proton lines, usually at least 50 Hz away. Thus only long-range couplings to this chosen proton modulate the carbon-13 spin echo, and there is *only one* such splitting on each carbon-13 resonance. No large one-bond CH couplings are involved so that very fine digitization can be used to display these spin multiplets, giving precise values for the long-range couplings. The process is then repeated to characterize long-range coupling to another proton site.

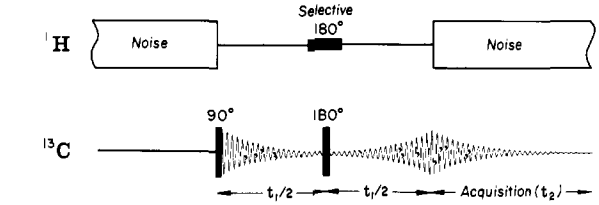

Figure 1. Pulse sequence used to detect long-range CH couplings.

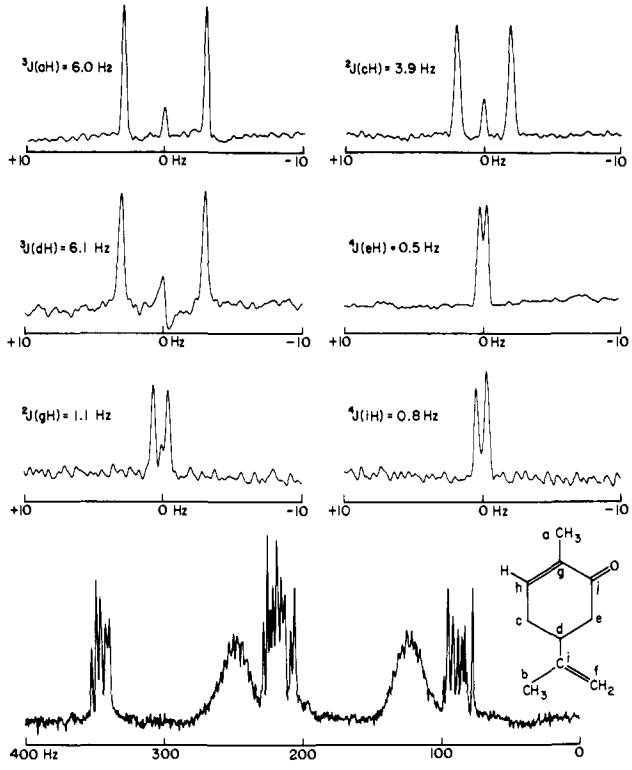

Figure 2. Long-range CH couplings observed between the various carbon sites of carvone (inset) and the proton at site h. The bottom trace shows the conventional proton-coupled carbon-13 spectrum for sites d and e obtained in the same total experimental time.

The pulse sequence (Figure 1) contains a preparation period for establishment of a nuclear Overhauser enhancement (8 s in practice) followed by a variable evolution period incremented in 64 equal steps up to a maximum of 3.2 s, giving a spectral width in the F_1 dimension of ±10 Hz. After the first Fourier transformation the data matrix contains useful information only at the carbon-13 chemical shift frequencies, known from an earlier conventional spectrum; the second Fourier transformation is therefore restricted to these sections through the data matrix, thus displaying only those F_1 traces which carry the desired coupling information. A complete two-dimensional spectrum is not computed.

Carbon-13 spectra were recorded at 50 MHz on a Varian XL-200 spectrometer, using carvone (Figure 2) to illustrate the technique, concentrating on the long-range CH couplings to the proton at site h. The assignment follows Bohlmann et al.[11]

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