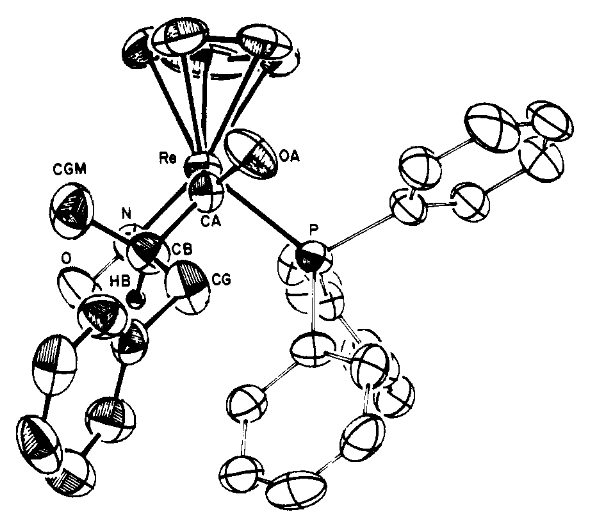
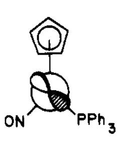


Figure 1. Molecular structure of (*SR,RS*)-(η^5-C_5H_5)Re(NO)(PPh_3)($COCH(CH_3)CH_2C_6H_5$)·$(THF)_{0.5}$. Important bond lengths (Å) and angles (deg): Re–C(A), 2.081 (7); Re–P, 2.358 (3); Re–N, 1.758 (7); C(A)–O(A), 1.252 (10); C(A)–C(B), 1.531 (11); C(B)–C(GM), 1.452 (20); C(B)–C(G), 1.524 (11); N–O, 1.181 (9); N–Re–P, 93.4 (3); C(A)–Re–P, 88.3 (3); C(A)–Re–N, 95.6 (3); Re–C(A)–O(A), 122.7 (6); Re–C(A)–C(B), 121.4 (5); C(A)–C(B)–C(GM), 106.8 (9); C(A)–C(B)–C(G), 108.9 (7); Re–N–O, 177.0 (6). The hydrogen is assigned an arbitrary radius.

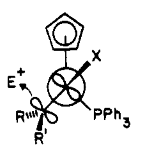
C_5H_5)Re(NO)(PPh_3)($COCH(CH_3)CH_2C_6H_5$) ((*SR,RS*)-**8**)[4] was subsequently isolated in 71% yield (eq 2). The stereochemistry of a 0.5 THF solvate of (*SR,RS*)-**8** was established by X-ray crystallography as described in the supplementary material. Complex **7** was similarly treated with CH_3I (CH_2Cl_2; 25 °C, 12 h, and then 50 °C, 2 h). The opposite acyl complex diastereomer (*SS,RR*)-**8**[4] was subsequently isolated in 88% yield (eq 3). Diastereomers (*SR,RS*)-**8** and (*SS,RR*)-**8** showed no tendency to interconvert under the workup conditions employed. HPLC analyses of the reaction mixtures from eq 2 and 3 prior to workup indicated diastereomer ratios of (99 ± 1):(1 ± 1). Hence, efficient 1,3-asymmetric induction occurred.

The molecular structure of (*SR,RS*)-**8**, and important bond lengths and angles, are given in Figure 1. The torsion angle between the planes defined by N–Re–CA and Re–CA–OA is 0.5°, indicating an almost perfectly antiperiplanar relationship of the NO ligand to the acyl C=O moiety. In this conformation, overlap of C=O π^* acceptor orbital with the rhenium d orbital HOMO (shown in I)[10] is maximized. Together with our earlier X-ray crystal structure of (η^5-C_5H_5)Re(NO)(PPh_3)(CHO),[11] this study provides the second[12] direct structural comparison of homologous acyl and formyl complexes.

The configuration of the asymmetric carbon in (*SR,RS*)-**8** is that which would be expected if eq 2 proceeded



I



II

via transition state II—our previously proposed model for electrophilic attack upon (η^5-C_5H_5)Re(NO)(PPh_3)(C(X)=CRR′) complexes.[1] In this transition state, the Re–C_α conformation is such that overlap of the C=C π^* acceptor orbital with I is maximized. This should, by analogy to enamine C-alkylation reactions,[13] maximize the nucleophilicity of C_β. The electrophile then attacks C_β opposite the bulky PPh_3 ligand.[14]

In summary, we have shown that chiral (α-methoxyvinyl)rhenium complexes undergo facile C_β electrophilic attack with highly efficient 1,3-asymmetric induction. In addition, we have defined the stereochemistry of these transformations. The development of other highly stereoselective carbon–carbon bond forming reactions involving these complexes is in progress.

Acknowledgment. We thank the NIH for support of this research and Dr. J. P. Hutchinson for assistance with the X-ray crystal structure determination.

Supplementary Material Available: Characterization of new compounds and crystallographic data (43 pages).[4] Ordering information is given on any current masthead page.

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[10] Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

[11] Wong, W.-K.; Tam, W.; Strouse, C. E.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1979**, 530.

[12] Casey, C. P.; Meszaros, M. W.; Neumann, S. M.; Cesa, I. G.; Haller, K. J. *Organometallics* **1985**, *4*, 143.

[13] Bláha, K.; Gerinka, D. *Adv. Heterocycl. Chem.* **1966**, *6*, 147.

[14] There is a second Re–C_α conformation (besides the one in II) in which overlap of I with the C=C π^* acceptor orbital is maximized. Data from our previous study[1] indicate this to be a far less reactive Re–C_α conformer than the one in II. Note that the two conformers give different Re^+=C geometric isomers upon electrophilic attack.

An NOE Difference NMR Study of a Conformationally Labile Organometallic Compound

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Summary: An NOE difference NMR study of the compound CpFe(CO)(PPh_3)CH_2SiMe_3 suggests that the (trimethylsilyl)methyl group preferentially oscillates between the cyclopentadienyl and triphenylphosphine ligands.

There is currently considerable interest in stereospecific and stoichiometric reactions of organotransition-metal compounds, especially with respect to reactions of metal–carbon σ-bonds[1] and the utilization of chiral organometallic compounds to effect stoichiometric[2] and catalytic[3] organic syntheses. While various attempts have been made to rationalize the stereochemical consequences of specific reactions on the basis of steric and/or electronic factors,[4,5] however, progress in this area is at present seriously hampered by lack of knowledge of the conformational properties in solution of many types of flexible organometallic compounds.

An attempt to deal with the problem of conformational preferences of coordinated alkyl groups of a series of compounds was reported by us in the early 1970s.[6] For

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[1] For a comprehensive review, see: Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37.

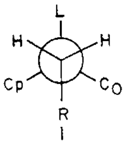
[2] Davies, S. G. "Organotransition Metal Chemistry: Application to Organic Synthesis"; Pergamon Press: Oxford, 1982.

[3] Bosnich, B.; Fryzuk, M. D. *Top. Stereochem.* **1981**, *12*, 119.

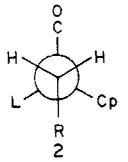
[4] Davies, S. G.; Seeman, J. I. *Tetrahedron Lett.* **1984**, *25*, 1845.

[5] Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

example, it was noted that the ^1H NMR spectra of compounds of the type $CpFe(CO)(PPh_3)CH_2R$ (I) (R = alkyl, aryl) exhibit temperature dependencies characteristic of systems undergoing conformational changes which are rapid on the NMR time scale. It was shown that the conformational changes in question involve restricted rotation about the iron–carbon σ-bonds, and, by assuming both a preference for staggered energy minima and a Karplus-type relation for the vicinal coupling constants between the phosphorus atom and the diastereotopic hydrogen atoms on the α-carbon ($^3J(P\text{-}H)$), it was possible to suggest that compounds of type I exist as three staggered rotamers, **1**, **2**, and **3**.[6]



1



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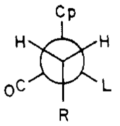

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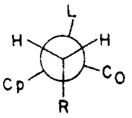

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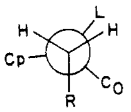

5

It was also shown that the low-energy rotamer of I has very unequal values of $^3J(P\text{–}H)$, as would be expected for **2** or **3**, and it was argued on steric grounds that **3** would be less crowded than **2** and therefore more stable (i.e., that steric requirements decrease in the order Cp > PPh_3 > CO). It was clear from the data, however, that all three rotamers are significantly populated at room temperature in the case of the benzyl compound (R = Ph) and that two are significantly albeit quite unequally populated even for as bulky an alkyl group as (trimethylsilyl)methyl (R = $SiMe_3$).

We were intrigued, therefore, by recent communications by Seeman and Davies,[7] who reported the results of extended Hückel (EH) calculations which purported to show that our above-mentioned conclusions are incorrect and that a rotamer similar to **1** but better described as **4** is the only rotamer significantly populated when R = Ph and $SiMe_3$. We have dealt elsewhere[8] with the claims of Seeman and Davies, showing that several of our earlier conclusions were misquoted and that their calculated energy profiles fail to rationalize adequately many of our experimental data. However, EH calculations are known[9] to be successful in at least qualitatively rationalizing relative conformational energies in other organometallic systems, and we had never been completely satisfied with the notion that the Cp group has greater steric requirements than does PPh_3. Thus we decided to reinvestigate the conformational preference(s) of I, utilizing the recently developed nuclear Overhauser enhancement difference (NOED) methodology.[10,11]

The power of the NOE experiment to deduce information regarding structures and conformations of complex molecules has been known for many years and has been reviewed extensively.[11-13] The approach should be applicable to systems such as I, and we now present the preliminary results from an NOED study on the compound $CpFe(CO)(PPh_3)CH_2SiMe_3$ (A) (I, R = $SiMe_3$), chosen because our earlier experiments had suggested that it exhibits a relatively strong preference for one rotamer. Thus any measured NOE's should reflect largely the properties of the low-energy rotamer and should not be skewed unduly by the averaging in of large contributions from other rotamers.

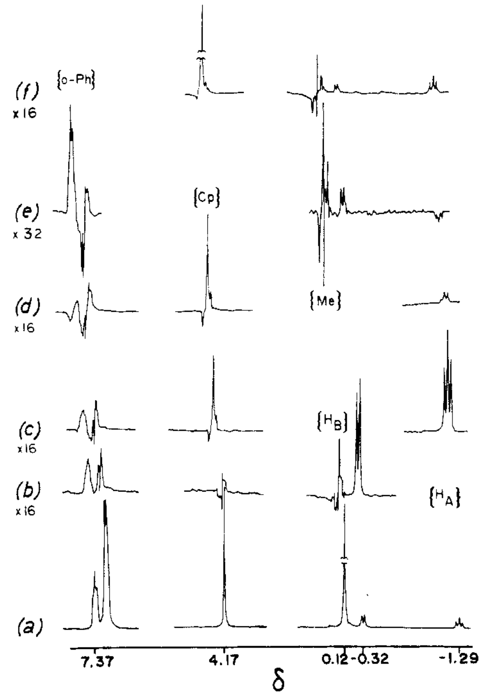

Figure 1. Difference spectra obtained on irradiating the five resonances indicated in b–f. Note that each spectrum is offset somewhat to lower field so as to avoid overlap.

The investigation described here[14] involved experiments carried out with irradiations of 2-s duration, too short to allow quantitative measurements of any NOE's which develop very slowly but sufficient to obtain the signs and relative magnitudes of the dominant NOE's. The key results from these experiments are illustrated in Figure 1, which shows (a) a normal spectrum and difference spectra obtained during irradiation at the resonance frequencies of (b) H_A (at δ −1.29) (the α-hydrogen which is to higher field and which exhibits the larger value of $^3J(P\text{–}H)$), (c) H_B (at δ −0.32) (the low field α-hydrogen, exhibiting the smaller $^3J(P\text{–}H)$), (d) the $SiMe_3$ group (at δ 0.12), (e) the Cp group (at δ 4.17), and (f) the *o*-phenyl hydrogens (at δ ~7.37).

Several observations should be immediately noted from the data. (1) Irradiation of H_A results in large enhancement of the H_B resonance and small enhancements of the phenyl resonances but little or no enhancement of the Cp

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(6) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 4292.

(7) Seeman, J. I.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1019, and manuscript submitted for publication. We thank Dr. Seeman for sending us a preprint of the latter document.

(8) Cameron, A. D.; Baird, M. C. *J. Chem. Soc., Dalton Trans.*, in press.

(9) Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149.

(10) Hall, L. D.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1980**, *102*, 5703.

(11) Sanders, J. K. M.; Mersh, J. D. *Prog. Nucl. Magn. Reson. Spectrosc.* **1983**, *15*, 353.

(12) Noggle, J. H.; Schirmer, R. E. "The Nuclear Overhauser Effect"; Academic Press: New York, 1971.

(13) Bell, R. A.; Saunders, J. K. *Top. Stereochem.* **1973**, *7*, 1.

(14) The NOE's were measured at 18 °C from a single experiment which included six on-resonance irradiations (at the frequencies shown in Figure 1) and two off-resonance blanks. In each individual irradiation, the decoupler was gated on for 2 s (at a power setting of 25-dB attenuation from 200 mW) prior to acquisition of the spectrum and then turned off during the irradiation. Eight transients were acquired at each irradiation frequency, and the cycle through the list of nine frequencies was repeated 20 times with the spectra at each frequency being coadded. Each spectrum is the average of 160 transients collected over the time required to perform the experiment. Thus the small phase and frequency errors which accumulate with time were averaged uniformly through the data set.

or Me resonances. (2) Irradiation of H_B results in large enhancement of the H_A resonance and lesser enhancement of the Cp and phenyl resonances. (3) Irradiation of the Me resonance resulted in enhancement of the H_A, Cp, and part of the phenyl multiplet. (4) Irradiation of the Cp resonance resulted in enhancements of the H_B, Me, and *o*-phenyl resonances but in a *negative* NOE for the H_A resonance. (5) Irradiation of the *o*-phenyl multiplet resulted in enhancements of the H_A, H_B, and Cp resonances, but not in the Me resonance.

In a spin system such as that under consideration here, all nuclei can in principle experience dipolar relaxation by (and hence gain NOE from irradiation of) all other nuclei, the relative effects being inversely proportional to the sixth power of the distance between pairs of nuclei.[10-13] The fact that the two α-hydrogen atoms gain almost as much total enhancement from irradiation of the Cp, Me, and phenyl resonances as they do from irradiation of their geminal partner demonstrates this fact. It is also to be expected that the Cp and PPh_3 ligands may well be undergoing rotational motions which are rapid relative to the various dipolar relaxation rates, and it becomes clear that a comprehensive description of the NOED experiments in terms of molecular geometry is a far from trivial task.

However, if one assumes that the rapidly rotating Cp group can be treated as a net dipole acting from the mean of all possible orientations (see ref 13 for similar treatment of rapidly rotating methyl groups), then the question of orientation of the alkyl ligand becomes answerable. The key lies in the experiment (Figure 1e) which involves irradiation of the Cp resonance, where a large, positive enhancement was observed for the H_B resonance, but a small, negative NOE was observed for the H_A resonance. This type of behavior is uniquely characteristic of three-spin systems in which the three nuclei in question are aligned in a more or less linear fashion and provides direct evidence that the Cp–H_B–H_A assemblage defines an obtuse angle.[11-13] This conclusion is reinforced by the observation of a positive NOE for the Cp resonance on irradiation of H_B (Figure 1c) but not on irradiation of H_A (Figure 1b), suggesting that the former is indeed closer to the Cp group. These results are clearly incompatible[15] with a conformation such as **3** and appear to be most consistent with conformations such as **1** ($\simeq$**4**) or **2** (which can probably be ruled out because of the close proximity of the bulky groups L, R, and Cp.

As discussed above, however, our earlier variable-temperature NMR data for compounds of the type I are generally best interpreted in terms of a most stable rotamer having one large and one small ^3J(P–H), a conclusion inconsistent with both **1**, which should exhibit two small (gauche) coupling constants, and **4**, which should exhibit one small (gauche) and one almost zero (90°) coupling constant. While we had originally assumed staggered energy minima such that the large and small vicinal coupling constants are to be related to antiperiplanar and gauche couplings,[6] respectively, it now seems that the assumption of a maximum degree of staggering was not warranted. The conformation most consistent with the NOED and variable-temperature coupling constant data *and* the EH calculations is **5**, with the large vicinal coupling constant to be attributed to an α-hydrogen atom which is eclipsed or nearly eclipsed with the phosphorus atom and the small coupling constant to a hydrogen atom which is gauche to or possibly at approximately a 90° angle with the phosphorus. Thus R preferentially occupies a position which places it as far as possible from both the Cp and the L groups, a conclusion which is supported by molecular models.[16]

The relative chemical shifts of H_A and H_B are also consistent with **5** being a good approximation to the low-energy conformation. The difference between the two, 1.01 ppm, with the higher field resonance being assigned to the α-hydrogen atom eclipsing the PPh_3, is most consistent with the latter (H_A) being strongly affected by the ring current[17] of the aryl rings. This conclusion is quite consistent with the conformation illustrated as **5**, as H_A would spend on average considerable time close to a face of a phenyl ring.[18]

The remaining NOE data cannot unfortunately be interpreted in terms of relative internuclear distances, in part because the total NOE's have not been fully developed, in part because of the averaging effects related to rotation about the Cp–Fe, the P–aryl, and the Fe–P bonds. Various other "three-spin" sets of mutually relaxing nuclei must also be present, leading to alterations in enhancements. However, it seems clear that most of the pairs of the ligand hydrogen atoms effect mutual dipolar relaxation, consistent with their being resonably contiguous in space, i.e., with the above-mentioned rotations and the probable degree of steric congestion.

The approach to conformational analysis of flexible organometallic compounds described here would appear to have wide utility. Experiments to determine the NOE growth rates are expected to provide information on internuclear distances[11] and are in progress.

Acknowledgment. Financial assistance from Queen's University and the Natural Sciences and Engineering Research Council is gratefully acknowledged.

Registry No. I (R = $SiMe_3$), 32761-84-5.

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[15] Reference 12, p 77.

[16] The alternate "eclipsed" structure, involving eclipsing of the other methylene hydrogen atom with L, can be ruled out on the basis of both anticipated steric effects and the NOED data.

[17] Bovey, F. A. "Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1969, p 64.

[18] A list of references dealing with the conformation of a coordinated PPh_3 molecule may be found in: Davies, S. G.; Seeman, J. I. *Tetrahedron Lett.* 1984, *25*, 1845.

Binuclear Carbonylates $[Ru_2(CO)_8]^{2-}$ and $[Os_2(CO)_8]^{2-}$: Syntheses and Crystal Structures

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Received April 10, 1985

Summary: The new dianion $[Ru_2(CO)_8]^{2-}$ has been prepared from the reaction of CO_2 with $[Ru(CO)_4]^{2-}$ in a 1:1 molar ratio. In a similar manner $[Os_2(CO)_8]^{2-}$ has been prepared. X-ray crystal structures of tetraphenylphosphonium salts of these ions have been determined. The structure of $[Ru_2(CO)_8]^{2-}$ represents a previously unobserved and apparently unanticipated configuration for homodinuclear carbonylates and carbonyls. It consists of a trigonal-bipyramidal fragment ($Ru(CO)_4$) joined to a four-sided pyramidal fragment ($Ru(CO)_4$). The structure of $[Os_2(CO)_8]^{2-}$ is like that of $[Fe_2(CO)_8]^{2-}$.