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STEREOCHEMISTRY AT SECONDARY CARBON IN ORGANOMETALLIC INSERTION REACTIONS†

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Summary

The stereochemistry of insertion reactions occurring at secondary carbon atoms bound to transition metals has been probed by examination of ^{13}C and ^{1}H spectra of 1,4-disubstituted cyclohexyl systems. The reaction of neat sulfur dioxide with *cis* and *trans* -4-methylcyclohexyl (pyridine)-cobaloxime leads to the *trans* and *cis* -4-methylcyclohexyl-S-sulfinate cobaloximes respectively, indicating inversion of configuration at the reacting carbon atom. A similar inversion is observed in the reaction of sulfur dioxide with [*cis*-4-methylcyclohexyl $Fe(CO)_2(\eta^5\text{-}C_5H_5)$], but the triphenylphosphine-induced insertion of carbon monoxide in acetonitrile proceeds with retention of configuration.

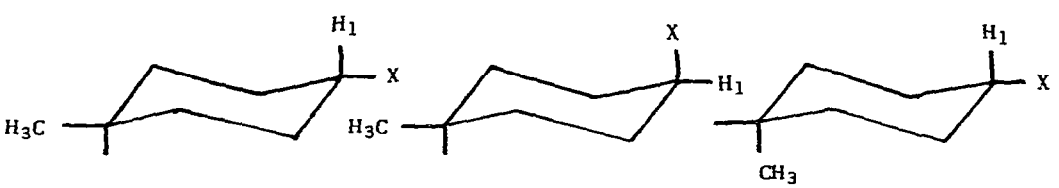
Introduction

Several recent studies have used the relative configuration of two asymmetric centres in ligands such as -CHDCHDR (R = ^{t}Bu [1] or Ph [2]) as a stereochemical probe for retention or inversion in reactions at the primary carbon atom bound to a transition metal. Specifically, the method has been used to demonstrate (on the basis of the characteristic proton coupling constants in the *erythro* and *threo* forms of the ligand)

† No reprints available.

that the "insertion" reaction of sulfur dioxide with $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$, which yields $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(SO_2R)]$, proceeds with inversion, and the triphenylphosphine-induced insertion of carbon monoxide, with the same compound, with retention of configuration.[1]

In this paper we report our attempts to establish the stereochemistry of similar insertion reactions at secondary carbon by identifying the relative geometry (*cis* or *trans*) of the substituents in 4-methylcyclohexylmetal systems before and after reaction. As the substituents have a significant steric influence, the arrangements accessible to the chair form of the cyclohexyl ring are the *trans* form (I) and the *cis* forms (II) and (III), (see diagram), where substituent X refers either to a transition metal group (e.g. $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ or the appropriate moiety after the insertion reaction (e.g. the acyl group $[C(O)Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]$. The *trans* arrangement with both substituents axial should be sterically unfavourable.



(I) (II) (III)

The *cis* or *trans* disposition of substituents X and CH_3 can be probed by consideration of the ^{13}C chemical shift of the 4-methyl carbon together with the coupling of proton H_1 with protons on the adjacent carbon atoms 2 and 6. The basis of the method is as follows. If the 4-methyl substituent is axial, as in the *cis* form (III), its ^{13}C chemical shift has a characteristic value of around 17 ppm downfield from TMS, whereas the value is around 23 ppm for equatorial substitution as in *cis* (II) or *trans* (I).[3] This information is clearly insufficient to characterise the ring geometry and is potentially even less definitive because of the possibility of conformational rearrangement of the two

cis forms which could serve to average the methyl carbon resonances on the NMR time scale. The necessary further evidence of ring geometry can be obtained from the resonance for proton H_1 which, particularly when the substituent group X is electron-withdrawing, can be clearly observed below the envelope associated with other ring protons. In the *trans* structure (I), where H_1 is axial, the overall coupling to the axial and equatorial protons on C_2 and C_6 reflects the influence of the larger axial-axial coupling constant, and the signal is observed as a triplet of triplets.[4] The *cis* structure (II), which is formally indistinguishable from (I) on the basis of ^{13}C NMR, has H_1 equatorial. The overall proton-proton couplings (equatorial-axial and equatorial-equatorial) are smaller, and a narrower H_1 peak is observed as a seven line multiplet. In the *cis* structure (III), which is readily distinguishable by its ^{13}C NMR, a triplet of triplets is again expected for H_1. Where conformational interconversion between (II) and (III) occurs, a seven line multiplet pattern is seen. The overall envelope of the remaining ring protons is complex and of little assistance in the determination of ring geometry. However the greater number of axial-axial couplings which can occur in the *trans* form (I) causes the envelope to broaden significantly.

The geometrical properties of the 4-methylcyclohexyl substituent attached to a transition metal have been applied in an earlier study [5] which established that the oxidatively-induced ligand transfer process, represented by the general equation,

$$MR + CuCl_2 \xrightarrow[CO]{R^1OH} RCOOR^1 + CuCl,$$

proceeds with retention of configuration at the secondary carbon in R. The analysis, in this case, was based on the characteristic ^1H NMR spectra of the *cis*- and *trans*- 4-methylcyclohexyl $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ derivatives and on the stereochemistry of the carboxylates formed in the reaction.

Results and Discussion

Few well-characterised cyclohexyl derivatives of transition metals have been reported and our test reactions have been limited to the (pyridine)cobaloxime and η^5-cyclopentadienyldicarbonyliron systems. The desired *cis* (and *trans*)-4-methylcyclohexyl(pyridine) cobaloxime compounds were prepared by displacement of tosylate ion from *trans* (and *cis*)-4-methylcyclohexyltosylate respectively by the Co(I) nucleophile by Schrauzer's method. [6] Although the *cis* compound contained (^{13}C NMR) a small amount (5%) of *trans*, we believe that it is presently inappropriate to attach any mechanistic significance to the observation, in view of the possibility that its formation may simply reflect a preferred reaction pathway with *cis*-tosylate impurities and/or a specific enhancement in yield because of solubility differences. The *trans*-cobaloxime was, within the limits of experimental measurement, isomerically pure. [*Cis*-4-methylcyclohexylFe(CO)$_2$(η^5-C_5H_5)] was prepared by nucleophilic displacement by [(η^5-C_5H_5)(CO)$_2$Fe]$^-$ from the *trans*-tosylate, but, as reported elsewhere, [5] only very small amounts of the corresponding *trans*-compound were produced by this method. Corresponding η^5-cyclopentadienyltricarbonylmolybdenum complexes were unsuccessfully sought by a similar synthetic route. However no evidence for the formation of cyclohexyl-molybdenum compounds was obtained; the lack of reaction may reflect the substantially lower nucleophilicity of the η^5-cyclopentadienyltricarbonylmolybdenum anion.[7]

The reaction of neat sulfur dioxide at room temperature with both isomers of 4-methylcyclohexyl(pyridine)cobaloxime yielded the expected S-sulfinates (by IR[8]), with overall inversion of configuration. The *trans*- insertion product was obtained isomerically pure (which was surprising in view of the small *trans*-impurity in the *cis* starting material), but the *cis* product contained a 15% *trans* impurity, indicating a significant loss of specificity in the reaction. A similar reaction with the *trans*-4-methylcyclohexyliron compound cleanly yielded the *cis*-S-sulfinate; the inversion of configuration at the reacting secondary

carbon atom thus observed parallels that previously noted for the primary carbon system.[1] Retention of configuration was observed in the triphenylphosphine-induced insertion of carbon monoxide into the iron-carbon bond in acetonitrile, which yielded [*cis*-4-methylcyclohexyl-C(O)Fe(CO)(PPh_3)(η^5-C_5H_5)]. Again the result parallels that for the primary carbon compound.[1] The specific spectroscopic parameters on which the configurational assignment is based are outlined below.

Because of the substantial size of the (pyridine)cobaloxime group compared with methyl, it was anticipated that the *cis*-4-methylcyclohexyl-cobaloxime starting material would have the *cis* structure(III) which has an axial methyl group. This was confirmed by the ^{13}C NMR spectrum which showed a methyl resonance at 17.65 ppm in $CDCl_3$ at room temperature, which was unchanged on lowering the temperature to 213K. The assignment is supported by the observation of H_1 in the proton spectrum at 1.86 ppm, slightly to high field of the dimethylglyoxime protons, as a triplet of triplets (J_{ae} = 3.8 Hz, J_{aa} = 11.4 Hz) appropriate to its expected axial situation. The S-sulfinate insertion product in CD_2Cl_2 solution had a ^{13}C methyl resonance at 22.15 ppm, which is appropriate either to a *trans*(I) or *cis*(II) structure. However, that the *trans* derivative had formed was clearly indicated by the triplet of triplets at 3.03 ppm in the proton spectrum, characteristic of axial H_1. The corresponding *trans*-4-methylcyclohexylcobaloxime starting material was characterised by a ^{13}C resonance at 22.0 ppm associated with an equatorial methyl group. (In this case, the H_1 signal is insufficiently separated from the cyclohexyl ring protons to be observed, but the possibility that the 22.0 ppm signal is associated with the *cis*(II) form is ruled out from the observations already described for the *cis*(III) product, which demonstrated the significantly greater conformational preference of the (pyridine) cobaloxime group for an equatorial position). The product of reaction of the *trans*-cobaloxime isomer with sulfur dioxide had a ^{13}C methyl resonance, in CD_2Cl_2 at room temperature, at 19.2 ppm which is intermediate between the characteristic axial and equatorial values and

suggestive of a conformational change between *cis*(II) and *cis*(III). The low temperature (193 K) spectrum supports this; two signals (at 17.4 and 22.0 ppm) appropriate to the axial and equatorial methyl groups in the two "frozen" *cis* forms were observed. The room temperature ^1H NMR spectrum for this *cis* product showed the expected seven line multiplet (average peak separation 4.6 Hz), centred at 3.16 ppm.

The S-sulfinate produced by insertion into the *cis*-4-methylcyclohexyliron complex gave a ^{13}C resonance for the methyl substituent at 22.3 ppm which, on the basis of expected conformational preferences, suggested the formation of a *trans* product. The observation of a triplet of triplets (3.27 ppm, J_{aa} = 12.4 Hz, J_{ae} = 3.5 Hz) for ^1H in the proton spectrum confirmed this. For the acyl product derived from the triphenylphosphine-induced insertion of carbon monoxide into the *cis*-iron compound, the ^{13}C methyl resonance at 19.9 ppm, in CD_2Cl_2 at room temperature, was characteristic of time-averaged signals of the *cis*-forms (II) and (III), where the two substituent groups exhibit similar steric influences. This was supported by the observation, at 173K, of two resonances, at 17.4 ppm (assigned to axial methyl in *cis*(III), and 22.4 ppm (equatorial methyl, *cis*(II)). Appropriately, the room temperature proton spectrum exhibited a seven line multiplet for H_1 (centred at 3.35 ppm, average separation 4.1 Hz). In this compound, the central iron atom is asymmetric, and separate ^{13}C signals were observed for the non-equivalent cyclohexyl ring carbon atoms. In addition, a resonance at 70.7 ppm at room temperature, which is tentatively assigned to C_1, is split into peaks at 65.3 and 72.8 ppm at 173K. The observation may again reflect the conformational equilibrium between the two *cis* forms.

Experimental

Manipulation of air-sensitive materials was carried out under nitrogen using Schlenk techniques. Reaction solvents were dried and distilled under nitrogen immediately prior to use. NMR spectra for the configurational studies were recorded at the National NMR Centre,

Australian National University, Canberra on a Bruker HX-270 spectrometer. Routine NMR spectra were measured on a Jeol MH100 spectrometer and IR spectra on a PE457 spectrometer.

Cis and *trans*-4-methylcyclohexyltosylates were prepared from pure (98%) *cis* and *trans* 4-methylcyclohexyl alcohol (Aldrich Chemical Co.).

Cis-4-methylcyclohexylpyridine bis(dimethylglyoximato)cobalt(III). The cobalt(I) nucleophile was prepared according to Schrauzer's method,[6] and treated with an equimolar amount of *trans*-4-methylcyclohexyltosylate in methanol at room temperature. The brown solid so obtained was filtered off, dissolved in pyridine and reprecipitated by the addition of hexane. The solid was filtered off, washed with hexane and dried. Yield 20%. Found: C. 51.5; H, 6.8%. The *trans* derivative was prepared by the same procedure from the *cis*-tosylate. Yield 24%. Found: C, 51.2; H, 6.7%. Calculated for $C_{20}H_{32}CoN_5O_4$: C, 51.6; H, 6.9%.

Reaction of SO_2 with (*Cis*-4-methylcyclohexyl(pyridine)cobaloxime The cobaloxime was dissolved in a large excess of sulfur dioxide and the solution allowed to stand for 5 days at room temperature in a pressure vessel. The brown solid remaining after evaporation of sulfur dioxide was dissolved in CH_2Cl_2, separated from starting material by a passage down a Florisil column in acetonitrile. The brown product (νSO_2: 1220, 1064 cm^{-1} in Nujol) was obtained after removal of solvent was the *trans* S-sulfinate. Yield 39%. Found: C, 44.4; H, 6.0; N, 12.8%. The *cis*-sulfinate was obtained similarly from the *trans*-cobaloxime. Found: C, 44.6; H, 6.0; N, 13.1%. Calculated for $C_{20}H_{32}CoN_5O_6S$: C, 45.4; H, 6.0; N, 13.2%.

Cis-4-methylcyclohexylpentahaptocyclopentadienyldicarbonyliron A slight excess of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ anion in THF, prepared by the traditional sodium amalgam reduction method, was added dropwise to a solution of the *trans*-tosylate in THF, at -78° and stirred for 4 hours. The THF was evaporated off at around 10° and the residue extracted

with hexane. The hexane extracts were concentrated and chromatographed on a short Florisil column using hexane as eluant. Removal of hexane under vacuum gave a thermally unstable yellow oil (Yield 22%) which was used directly in further reactions. The ^1H NMR (100 MHz) in $CDCl_3$ corresponded closely to that reported elsewhere [5] for the *cis*-product. [4.67 (s,Cp); 2.63 (m, FeCH); 1.20-2.10 (m, CH_2, CH); 1.00 ppm (d, J = 7Hz, CH_3)]

Reaction of Triphenylphosphine with *cis*-4-methylcyclohexylpentahaptocyclopentadienyldicarbonyliron.

Equimolar amounts of the 4-methylcyclohexyliron compound and triphenylphosphine were stirred in acetonitrile at 39°C for 18 h. Solvent was evaporated off and the resulting solid extracted with chloroform and chromatographed on Florisil. A yellow band was eluted with chloroform, concentrated, and treated with hexane to produce the acyl product as a cream solid. Yield 56%. Found: C, 71.9; H, 6.7%. Calculated for $C_{32}H_{33}FeO_2P$: C, 71.7; H, 6.2%. The complex was further characterised by ^1H NMR in $CHCl_3$ (7.56 (PPh_3); 4.52 (s, η^5-C_5H_5); 2.65(m, COCH); 0.80-2.00 (m, CH_2); 0.83 ppm (d, J = 7 Hz, CH_3), and by infrared spectroscopy in CH_3CN (ν_{CO}, 1911 cm^{-1}; $\nu_{acyl\ CO}$ 1594 cm^{-1}).

Reaction of Sulfur Dioxide with *cis*-4-methylcyclohexylpentahaptocyclopentadienyldicarbonyliron.

The 4-methylcyclohexyliron complex was reacted with a large excess of liquid sulfur dioxide in an ampoule at room temperature over 18 h. The sulfur dioxide was removed and the residue extracted with CH_2Cl_2 and chromatographed on Florisil. Elution with CH_2Cl_2 gave unreacted starting material while THF gave a yellow band, which, after concentration and treatment with hexane, gave the S-sulfinate insertion product. (Yield 19%) as a yellow solid. Found: C, 49.8; H 5.4%. Calculated for $C_{14}H_{18}FeO_4S$: C, 49.7; H, 5.3%.

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