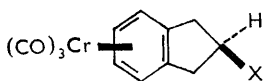


## 206. Intramolecular Hydrogen Bonds in Some Arene-Metal Carbonyl Compounds.

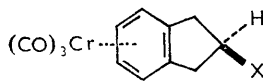
By W. R. JACKSON and C. H. McMULLEN.

The infrared absorptions of *cis*-tricarbonyl-(1- and 2-hydroxyindane)-chromiums suggest that an intramolecular hydrogen bond between hydroxyl and carbonylchromium groups is present in each compound.

In a preliminary account of some work<sup>1</sup> on tricarbonylchromium complexes of substituted indanes, we reported the preparation of *cis*- (I; X = OH) and *trans*- (II; X = OH)tricarbonyl-(2-hydroxyindane)chromiums. Stereochemical assignments were based on the following evidence. The lower-melting alcohol was eluted slightly more easily than the higher-melting from alumina, while the order of elution of their acetates was reversed. A 10<sup>-3</sup>M solution of the higher-melting alcohol in carbon tetrachloride showed a single sharp peak at 3625 cm.<sup>-1</sup> in its infrared spectrum. The other alcohol gave peaks of almost equal intensity at 3617 and 3540 cm.<sup>-1</sup>, their relative intensity being only slightly (<3%) affected by increase in concentration to 2 × 10<sup>-3</sup>M. The lower-melting alcohol was assigned the *cis*-structure (I; X = OH) as it was assumed that the intramolecular hydrogen bond at 3540 cm.<sup>-1</sup> was due to the carbonyl chromium group. Recent work<sup>2-6</sup> has provided evidence of hydrogen bonding in α- and β-metalloenyl alcohols directly to the metal atom and the Δν (non-bonded-bonded) of 77 cm.<sup>-1</sup> shown by the *cis*-alcohol (I; X = OH) is



(I)



(II)

comparable in strength with Δν 99 cm.<sup>-1</sup> shown by 2-ferrocenylethanol.<sup>5</sup> Exact comparisons are uncertain owing to differences in molecular bonding geometry. Justification that the intramolecular hydrogen bond in the more easily eluted alcohol is to the chromium carbonyl residue and not a π-bond to the uncomplexed face of the aromatic ring may be found in the work of Nicholls and Whiting<sup>7</sup> who showed from dissociation constants of tricarbonyl(benzoic and phenylacetic acid)chromiums that the π-bound tricarbonylchromium residue accepts electrons at least as strongly as a *p*-nitro-group. In contrast, the free ligand indan-2-ol showed a shoulder at 3592 cm.<sup>-1</sup> as well as its main peak at 3620 cm.<sup>-1</sup>. This may be due to the hydroxyl group's interacting with the aromatic π-electron system.

An accurate model of the *cis*-alcohol (I; X = OH) gave no certain site for hydrogen bonding to the -CrCO group, the hydrogen being about equidistant from the chromium and oxygen atoms. The spectra of cobalt<sup>8</sup> and manganese<sup>9,10</sup> carbonyl hydrides suggest that each hydrogen atom, which carries some negative charge, could be more strongly bonded to the metal atom than to the carbonyl group. In the case of hydroxylic hydrogen bonding to a metal carbonyl residue the converse may be expected to hold, *i.e.*, a bond to the carbonyl group would be preferred. Examination of the carbonyl region of the spectra of the *cis*- and *trans*-alcohols (I and II; X = OH) was of no assistance as both isomers had virtually identical spectra (see Table).

<sup>1</sup> Henbest, Jackson, and McMullen, Lecture to XIth I.U.P.A.C. Congress, London, 1963.

<sup>2</sup> Richards and Hill, *J. Amer. Chem. Soc.*, 1959, **81**, 3484.

<sup>3</sup> Hill and Richards, *J. Amer. Chem. Soc.*, 1961, **83**, 3840.

<sup>4</sup> Hill and Richards, *J. Amer. Chem. Soc.*, 1961, **83**, 4216.

<sup>5</sup> Trifan and Backsai, *J. Amer. Chem. Soc.*, 1960, **82**, 5010.

<sup>6</sup> Trifan and Backsai, *Tetrahedron Letters*, 1960, **13**, 1.

<sup>7</sup> Nicholls and Whiting, *J.*, 1959, 551.

<sup>8</sup> Edgell and Summitt, *J. Amer. Chem. Soc.*, 1961, **83**, 1772.

<sup>9</sup> Edgell, Asato, Wilson, and Angell, *J. Amer. Chem. Soc.*, 1959, **81**, 2022.

<sup>10</sup> Cotton, Down, and Wilkinson, *J.*, 1959, 833.

O-H Fundamentals (cm.<sup>-1</sup>).

Compound	Main peak	Shoulder	2nd peak
Benzyl alcohol .....	3612 <sup>a</sup>	3628 <sup>d</sup>	
1-Phenylethanol .....	3615 <sup>b</sup>		
2-Phenylethanol .....	3629 <sup>c</sup>	3615	3602
Indan-1-ol .....	3594	3610	
Indan-2-ol .....	3620	3592	
Tricarbonyl(benzyl alcohol)chromium .....	3610		
Tricarbonyl(1-phenylethanol)chromium .....	3607		
Tricarbonyl(2-phenylethanol)chromium .....	3625		
<i>trans</i> -Tricarbonyl(indan-1-ol)chromium (IV; X = OH) .....	3610		
<i>cis</i> -Tricarbonyl(indan-1-ol)chromium (III; X = OH) .....	3612		3584
<i>trans</i> -Tricarbonyl(indan-2-ol)chromium (II; X = OH) .....	3626		
<i>cis</i> -Tricarbonyl(indan-2-ol)chromium (I; X = OH) .....	3617		3540
<i>trans</i> -Tricarbonyl(2-hydroxymethylindane)chromium (II; X = CH <sub>2</sub> OH) .....	3642		
<i>cis</i> -Tricarbonyl(2-hydroxymethylindane)chromium (I; X = CH <sub>2</sub> OH) ...	3640		

## C=O Fundamentals

Compound	Main peak	2nd peak
<i>trans</i> -Tricarbonyl(indan-2-ol)chromium (II; X = OH) .....	2000	1916
<i>cis</i> -Tricarbonyl(indan-2-ol)chromium (I; X = OH) .....	2000	1918

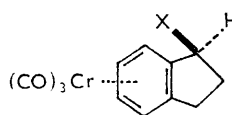
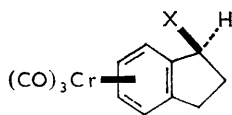
Lit. values: <sup>a</sup> 3616 (ref. 13); <sup>b</sup> 3617 (ref. 12); <sup>c</sup> 3630 (ref. 12); <sup>d</sup> 3636 (ref. 13); <sup>e</sup> 3601 (ref. 12).

In the hope of obtaining evidence on the site of hydrogen bonding, the homologous complexes (I and II; X = CH<sub>2</sub>OH) were prepared and their spectra examined. A mixture of the two compounds was prepared as usual from 2-hydroxymethylindane and hexacarbonylchromium; separate compounds were obtained by chromatography of the mixed acetates followed by hydrolysis. The spectra of both isomers were almost identical (Table), both having the normal hydroxyl fundamental associated with a primary alicyclic alcohol.<sup>11</sup>

The stereochemistry of these compounds was assigned by preparing the *cis*- and *trans*-tricarbonyl(methyl 2-indancarboxylate)chromiums (I and II; X = CO<sub>2</sub>Me). The dipole moments of these two compounds were 5.9 ± 0.15D (*cis*-isomer) and 4.9 ± 0.2D (*trans*). Reduction of the higher-melting *cis*-ester with aluminium lithium hydride gave the higher-melting *cis*-hydroxymethyl isomer.

Models of the *cis*-hydroxymethyl isomer showed no geometric limitations to hydrogen bonding. In the most advantageous conformations the hydroxyl hydrogen could approach the -CrCO group more easily than in the *cis*-2-hydroxy compound. Strong intramolecular hydrogen bonding in the hydroxymethyl compound would however cause the loss of entropy of rotation of a further -C-C- bond over that of the 2-hydroxy-compound, and this may be sufficient to discourage hydrogen bonding.

The *cis*- and *trans*-tricarbonyl(1-hydroxyindane)chromiums (III and IV; X = OH) were separated as their acetates on alumina. The higher-melting, more difficultly eluted acetate, gave an alcohol whose infrared spectrum showed two hydroxyl fundamentals at



3612 and 3584 cm.<sup>-1</sup>, the latter being approximately twice as intense as the former. This was assigned the *cis*-structure and it can be seen that the strength of the intramolecular

<sup>11</sup> Cole, in Bentley (ed.), "Elucidation of Structures by Physical and Chemical Methods," Interscience, New York and London, 1963, Pt. 1, p. 146.

<sup>12</sup> Trifan, Weinmann, and Kuhn, *J. Amer. Chem. Soc.*, 1957, **79**, 6566.

<sup>13</sup> Fox and Martin, *Trans. Faraday Soc.*, 1940, **36**, 897.

hydrogen bond as measured by the separation  $\Delta\nu$  (non-bonded-bonded) is less than that of the 2-substituted compound: 28 against 77  $\text{cm}^{-1}$ . This reduction in bond strength is similar to that recorded in going from a  $\beta$ - to an  $\alpha$ -hydroxymetallophenyl system.<sup>5</sup> Indan-1-ol had a main absorption at 3595  $\text{cm}^{-1}$ , with a shoulder of roughly half intensity at 3610  $\text{cm}^{-1}$ . This is similar to the spectrum of 2-phenylethanol<sup>12</sup> in that two bands are visible, the lower one being attributed to a hydroxyl group  $\pi$ -bonded to the aromatic sextet. The increase in  $\Delta\nu$  (non-bonded-bonded) on forming the *cis*-tricarbonylchromium compound of indan-1-ol is probably due to this  $\pi$ -bond's being replaced by a stronger bond to the carbonylchromium residue.

$\alpha$ - and  $\beta$ -Ferrocenylethanols showed hydrogen bonds of increasing strength but 3-ferrocenylpropan-1-ol did not form a detectable hydrogen bond, probably because of unfavourable entropy factors.<sup>5</sup> The tricarbonyl(benzyl, 1-phenylethanol, and 2-phenylethanol)chromiums were prepared; in each case a single hydroxyl fundamental was observed. The spectra of the first two compounds were almost identical to that of the parent ligand, but the shoulder at 3628  $\text{cm}^{-1}$  in the benzyl alcohol spectrum had disappeared. This shoulder has been attributed to an alternative conformation of benzyl alcohol.<sup>13</sup> The spectrum of 2-phenylethanol shows a peak at 3610  $\text{cm}^{-1}$  attributed to the  $\pi$ -bonded hydroxyl-group. This disappears when the tricarbonylchromium compound is formed indicating that  $\pi$ -bonding to the rear side of the aromatic ring is then not possible.

Compared with related ferrocenes, hydroxytricarbonylarene-chromium compounds are less prone to form intramolecular hydrogen bonds. Only when a *cis*-hydroxyl group is constrained by direct union to a small ring, where the molecular geometry holds the hydroxyl and tricarbonylchromium groups close together, can such bonds be formed.

#### EXPERIMENTAL

All m. p.s were determined on a hot stage. Light petroleum refers to the fraction of b. p. 40—60°. Alumina (Spence, grade H) deactivated with aqueous acetic acid<sup>14</sup> was used for chromatography. Indan-2-ol, m. p. 68—68.5°, was prepared by the method of Horan and Schiessler,<sup>15</sup> indan-1-one, m. p. 39—41°, by the method of Snyder and Werber,<sup>16</sup> and indan-1-ol, m. p. 52—53° from light petroleum, by aluminium lithium hydride reduction of the above ketone (lit.,<sup>17</sup> m. p. 52.5°).

*cis*- and *trans*-Tricarbonyl-(2-acetoxyindane)chromium (I and II; X = OAc).—Hexacarbonylchromium (2 g.) and indan-2-ol (5 g.) were heated for 3.5 hr. in boiling diglyme under conditions similar to those of Nicholls and Whiting.<sup>7</sup> The cooled solution was filtered and the diglyme and most of the indan-2-ol distilled off at 100°/0.1 mm. The residue was dissolved in pyridine (50 ml.), acetic anhydride (12.5 ml.) was added, and the solution kept overnight at 20°. The acetylated compounds were chromatographed on alumina (300 g.), when elution with light petroleum-ether (5 : 1) gave *trans*-tricarbonyl-(2-acetoxyindane)chromium (1.45 g.; 46%), m. p. 116—117° from light petroleum-ether (Found: C, 53.9; H, 4.1.  $\text{C}_{14}\text{H}_{12}\text{CrO}_5$  requires C, 53.9; H, 3.85%). Elution with light petroleum-ether (1 : 1) and ether gave *cis*-tricarbonyl-(2-acetoxyindane)chromium (0.63 g., 20%), m. p. 160—161° from light petroleum-ether (Found: C, 53.9; H, 4.05%).

*cis*-Tricarbonyl-(2-hydroxyindane)chromium (I; X = OH).—The *cis*-acetate (0.3 g.) was treated with potassium hydroxide (0.5 g.) dissolved in aqueous methanol (5%) (10 ml.) for 12 hr. at 20°. Isolation in ether gave *cis*-tricarbonyl-(2-hydroxyindane)chromium (0.21 g.; 80%), m. p. 96—97° from light petroleum-isopropyl ether (Found: C, 53.2; H, 3.85.  $\text{C}_{12}\text{H}_{10}\text{CrO}_4$  requires C, 53.4; H, 3.7%). Other samples of this compound had varying m. p.s in one instance as high as 103—104°. On melting and resolidifying all specimens gave m. p. 96—97°.

*trans*-Tricarbonyl-(2-hydroxyindane)chromium (II; X = OH).—The *trans*-acetate (0.3 g.) was hydrolysed as above to yield *trans*-tricarbonyl-(2-hydroxyindane)chromium (0.2 g.; 77%), m. p. 132—133° from light petroleum-ether (Found: C, 53.9; H, 4.05%).

<sup>14</sup> Farrar, Hamlet, Henbest, and Jones, *J.*, 1952, 2657.

<sup>15</sup> Horan and Schiessler, *Organic Syntheses*, 1961, **41**, 53.

<sup>16</sup> Snyder and Werber, *J. Amer. Chem. Soc.*, 1950, **72**, 2965.

<sup>17</sup> Whitmore and Gebhart, *J. Amer. Chem. Soc.*, 1942, **64**, 912.

*Chromatography of Alcohols.*—In other experiments mixtures of *cis*- and *trans*-tricarbonyl-(2-hydroxyindane)chromiums were chromatographed on alumina. In all cases the *cis*-alcohol was first eluted, followed by many mixed fractions and finally pure *trans*-alcohol. A clean separation was never attained.

*cis*- and *trans*-Tricarbonyl-(1-acetoxyindane)chromiums (III and IV; X = OAc).—Hexacarbonylchromium (2 g.) and indan-1-ol (5 g.) were heated for 3.25 hr. in boiling diglyme (10 ml.) and the products isolated as before. The residue was dissolved in pyridine (50 ml.), acetic anhydride (12.5 ml.) added, and the solution kept for 12 hr. at 20°. The acetates were isolated in ether and chromatographed on alumina (350 g.). Elution with light petroleum gave 1-acetoxyindane (0.4 g.). Elution with light petroleum-ether (9 : 1) gave *trans*-tricarbonyl-(1-acetoxyindane)chromium (0.94 g.; 31%), m. p. 78–79°, from light petroleum-ether (Found: C, 54.2; H, 4.0.  $C_{14}H_{12}CrO_5$  requires C, 53.9; H, 3.85%). Elution with light petroleum-ether (1 : 1) gave *cis*-tricarbonyl-(1-acetoxyindane)chromium (0.81 g.; 27%), m. p. 104–106° from light petroleum-ether (Found: C, 53.75; H, 3.8%).

*trans*-Tricarbonyl-(1-hydroxyindane)chromium (IV; X = OH).—*trans*-Tricarbonyl-(1-acetoxyindane)chromium (150 mg.) was added to a solution of potassium hydroxide (500 mg.) in aqueous methanol (10 ml.), and kept overnight at 20°. Isolation in ether gave *trans*-tricarbonyl-(1-hydroxyindane)chromium (90 mg.; 70%), m. p. 87–88° from light petroleum-ether (Found: C, 53.2; H, 3.9.  $C_{12}H_{10}CrO_4$  requires C, 53.4; H, 3.7%). Recrystallisation of the mother-liquors yielded a further sample (10 mg.; 8%), m. p. 86–87°.

*cis*-Tricarbonyl-(1-hydroxyindane)chromium (III; X = OH).—The *cis*-acetate (150 mg.) was hydrolysed as above to give *cis*-tricarbonyl-(1-hydroxyindane)chromium (90 mg.; 70%), m. p. 104–106° from light petroleum-ether (Found: C, 53.55; H, 4.0%). The mother-liquors yielded a further sample (12 mg., 12%), m. p. 104–105°.

*cis*- and *trans*-Tricarbonyl-(2-acetoxymethylindane)chromium (I and II; X =  $CH_2OAc$ ).—Hexacarbonylchromium (2.2 g.) and 2-hydroxymethyleneindane (5.9 g.) were heated for 3 hr. in boiling diglyme (10 ml.). The products were acetylated with acetic anhydride (12.5 ml.) and pyridine (100 ml.) and chromatographed on alumina (300 g.). Elution with light petroleum-ether (9 : 1) gave *trans*-tricarbonyl-(2-acetoxymethylindane)chromium (0.84 g.; 26%), m. p. 81–81.5° from light petroleum-ether (Found: C, 55.35; H, 4.5.  $C_{15}H_{14}CrO_5$  requires C, 55.2; H, 4.3%). Further elution with light petroleum-ether (9 : 1) gave *cis*-tricarbonyl-(2-acetoxymethylindane)chromium (0.30 g.; 9%), m. p. 139–139.5° from light petroleum-ether (Found: C, 55.35; H, 4.6%). Elution with light petroleum-ether (1 : 1) gave a yellow solid (0.42 g.; 15%), m. p. 70–80°, which was shown to be a mixture of *cis*- and *trans*-tricarbonyl-(2-hydroxymethylindane)chromiums.

*cis*-Tricarbonyl-(2-hydroxymethylindane)chromium (I; X =  $CH_2OH$ ).—The *cis*-acetate (50 mg.) was dissolved in aqueous methanol (5 ml.) containing potassium hydroxide (250 mg.). Isolation in ether gave *cis*-tricarbonyl-(2-hydroxymethylindane)chromium (35 mg.; 81%), m. p. 120.5–121° from light petroleum-ether (Found: C, 54.7; H, 4.2.  $C_{13}H_{12}CrO_4$  requires C, 54.9; H, 4.25%).

*trans*-Tricarbonyl-(2-hydroxymethylindane)chromium (II; X =  $CH_2OH$ ).—The *trans*-acetate (150 mg.) was hydrolysed as above to give *trans*-tricarbonyl-(2-hydroxymethylindane)chromium (84 mg.; 65%), m. p. 91–92° from light petroleum-ether (Found: C, 54.9; H, 4.3%). The mother-liquors yielded more material, m. p. 90–92° (20 mg.; 16%).

Methyl indane-2-carboxylate, b. p. 85–86°/0.3 mm.,  $n_D^{18}$  1.5288 was prepared as by Perkin and Revay<sup>18</sup> who quote b. p. 170°/60 mm.

*cis*- and *trans*-Tricarbonyl(methyl indane-2-carboxylate)chromiums (I and II; X =  $CO_2Me$ ).—Methyl indane-2-carboxylate (3.4 g.) and hexacarbonylchromium (1.1 g.) were heated for 5 hr. in boiling diglyme (10 ml.). The esters were chromatographed on alumina (200 g.) and traces of unchanged ester and diglyme washed off the column in light petroleum. Elution with light petroleum-ether (10 : 1) gave *trans*-tricarbonyl(methyl indane-2-carboxylate)chromium (0.81 g.; 52%), m. p. 95–96° from light petroleum-ether (Found: C, 53.62; H, 3.9.  $C_{14}H_{15}CrO_5$  requires C, 53.9; H, 3.9%). Elution with light petroleum-ether (5 : 1) gave *cis*-tricarbonyl(methyl indane-2-carboxylate)chromium (0.38 g.; 24.5%), m. p. 131–132° from light petroleum-ether (Found: C, 54.1; H, 4.0%). A small yellow band persisted at the top of the column; extraction of the alumina with dilute sulphuric acid followed by extraction with ether gave yellow acidic material (60 mg.) with infrared bands at 1990 and 1915  $cm^{-1}$ .

<sup>18</sup> Perkin and Revay, *Ber.*, 1893, **26**, 2251.

*Reduction of trans-Tricarbonyl(indane-2-carboxylate)chromium.*—The *trans*-ester (100 mg.) was dissolved in ether (25 ml.) and added slowly to a stirred suspension of lithium aluminium hydride (200 mg.) in ether (30 ml.). The stirred mixture was boiled for 12 hr., cooled, dilute sulphuric acid was added and the product isolated in ether as a yellow solid (91 mg.; 98%), m. p. 82—91°. Crystallisation from ether—light petroleum gave *trans*-tricarbonyl-(2-hydroxymethyl-indane)chromium (II; X = CH<sub>2</sub>OH), m. p. and mixed m. p. 92.5—93.5°.

Tricarbonyl(benzyl alcohol)chromium, m. p. 95.5—96°, was obtained by the method of Nicholls and Whiting,<sup>7</sup> who quote m. p. 95.5—96.5°.

*Tricarbonyl-(2-phenylethanol)chromium.*—Hexacarbonylchromium (1 g.) and 2-phenylethanol (4 ml.) were heated in diglyme (7 ml.) for 3 hr. Removal of solvents and excess of 2-phenylethanol under reduced pressure gave a solid (0.6 g.; 63%), m. p. 49—51°. Crystallisation from ether—light petroleum gave *tricarbonyl-(2-phenylethanol)chromium*, m. p. 51—52° (Found: C, 51.5; H, 4.0. C<sub>11</sub>H<sub>10</sub>CrO<sub>4</sub> requires C, 51.2; H, 3.9%).

*Tricarbonyl-(1-phenylethanol)chromium.*—Hexacarbonylchromium (2 g.), 1-phenylethanol (8 ml.), and diglyme (10 ml.) were heated under reflux for 2.5 hr.; the solution was evaporated to dryness and the resulting oil treated with acetic anhydride (12 ml.) and pyridine (25 ml.) for 12 hr. at 20°. Isolation in ether gave *tricarbonyl-(1-phenyl-1-acetoxyethane)chromium* (1.35 g.; 50%), m. p. 76—77° after one crystallisation from light petroleum—ether. Further crystallisation gave a sample, m. p. 77—78° (Found: C, 52.3; H, 4.2. C<sub>13</sub>H<sub>12</sub>CrO<sub>5</sub> requires C, 52.0; H, 4.0%).

The above acetate (0.75 g.) was dissolved in aqueous methanol (10%; 35 ml.) containing potassium hydroxide (3.0 g.) and the solution kept for 12 hr. at 18°. Isolation in ether gave *tricarbonyl-(1-phenylethanol)chromium* as a gum (0.62 g.; 96%) (Found: C, 51.8; H, 4.3. C<sub>11</sub>H<sub>10</sub>CrO<sub>4</sub> requires C, 51.2; H, 3.9%). After standing in air the compound could be crystallised from light petroleum—ether as a hydrate, m. p. 32—35° (Found: C, 48.5; H, 4.35. C<sub>11</sub>H<sub>10</sub>CrO<sub>4</sub>·H<sub>2</sub>O requires C, 47.8; H, 4.25%). The hydrate was readily converted into the liquid anhydrous compound by storing in an evacuated desiccator for several minutes. Spectra were recorded for the anhydrous compound.

*Spectra.*—Spectra were determined in a Perkin-Elmer S.21 spectrophotometer with lithium fluoride optics. The hydroxyl region of the spectrum was calibrated against a water spectrum and the carbonyl region against a polystyrene film. All spectra were recorded using 10<sup>-3</sup>M solutions of the compounds in dry carbon tetrachloride in a 2 cm. cell.

*Dipole Moments.*—The dipole moments of *cis*- and *trans*-tricarbonyl(methyl indane-2-carboxylate)chromiums were determined in carbon tetrachloride solution by the method of Guggenheim and Smith<sup>19</sup> using a Wissenschaftlich-Technische Werkstätten, DMO1 dipolemeter. The rather large errors in measurements were due to the limited solubility of these compounds in carbon tetrachloride.

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<sup>19</sup> Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714; Smith, *ibid.*, 1950, **46**, 394.