

# Notes

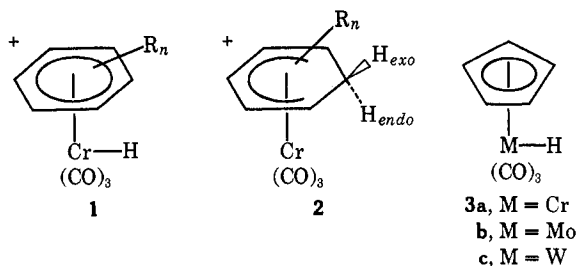
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## Tricarbonyl(arene)chromium Hydride Cations. Structure and Proton Exchange

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Tricarbonyl(arene)chromium hydride cations (1) were first reported by Davison, McFarlane, Pratt, and Wilkinson,<sup>2</sup> who studied tricarbonyl(arene)chromium compounds dissolved in  $\text{BF}_3 \cdot \text{H}_2\text{O} - \text{CF}_3\text{CO}_2\text{H}$  by nmr spectroscopy. The hydrido hydrogen signals were observed at  $\tau$  13.5–14 as singlets broadened (40–90 Hz width at half-height) by exchange with solvent protons. Thus, observation of spin–spin coupling involving the hydrido hydrogen was not possible.<sup>2a</sup> These data are still open to interpretation in terms of a C-protonated structure (2) in which  $\text{H}_{\text{endo}}$  migrates rapidly around the ring (possibly *via* 1 as an intermediate) as suggested by Ware and Traylor for protonated ferrocene.<sup>3</sup> In the case of structure 2,  $\text{H}_{\text{endo}}$



should be strongly coupled to the ring hydrogens<sup>4,5</sup> and significantly coupled to substituent hydrogens when  $\text{R}_n = (\text{CH}_3)_6$ . In the many *bona fide* neutral and cationic organo(transition metal) hydrides which have been characterized, the hydrido hydrogen is typically coupled to ligand hydrogens by  $J \leq 1.5$  Hz.<sup>6,7</sup> Complexes 3a–c, which are isoelectronic with tricarbonyl(arene)chromium hydride cations, possess the hydride structure shown and exhibit little or no coupling between the hydrido hydrogen and cyclopentadienyl

hydrogens.<sup>8</sup> Spin–spin coupling offers a basis for distinguishing between structures 1 and 2 as well as being a potential source of information on bonding. Therefore we have studied a series of cations 1 under rapid and slow-exchange conditions.

Addition of excess  $\text{FSO}_3\text{H}$  to liquid  $\text{SO}_2$  solutions of mesitylene-, hexamethylbenzene-, and 1,3,5-trimethoxybenzenechromium tricarbonyl<sup>9–11</sup> complexes (4, 5, and 6, respectively) caused a color change from deep red to light red. Protonation was apparent from the downfield shifts of the arene hydrogens and the appearance of high-field signals for the hydrido hydrogen (Table I). Excess  $\text{FSO}_3\text{H}$  gave a signal at *ca.*  $\tau$  0. Use of  $\text{FSO}_3\text{D}$  with 4 gave identical results except that the high- and low-field signals were absent. Decomposition to paramagnetic material, which caused broadening of the nmr lines, occurred at rates which increased in the order  $6 < 5 < 4$ . Tricarbonyl(benzene)chromium decomposed immediately and could not be examined.<sup>12</sup>

The hydrido hydrogen signals are much sharper than in  $\text{BF}_3 \cdot \text{H}_2\text{O}$ ,<sup>2a</sup>  $W_{1/2}$  (Table I) increasing with decreasing sample stability. That much of the observed signal width can be attributed to traces of paramagnetic material and/or to field inhomogeneity can be seen from the TMS signal widths. Coupling of the hydrido hydrogen with ligand hydrogens is clearly small or zero. For compounds 5 and 6 C-protonation, if it occurs, should occur preferentially on the three unsubstituted carbons.<sup>5</sup> Neglecting coupling between  $\text{H}_{\text{endo}}$  and methyl hydrogens when  $\text{R}_n = (\text{CH}_3)_6$  and estimating  $J_{\text{exo,endo}}$  as 15–18 Hz,<sup>4</sup> we predict that the upfield signal of protonated 5 and 6 should appear as a quartet ( $J_{\text{av}} = 5$ –6 Hz) if C-protonation occurred. The observed  $W_{1/2}$  values are 8 and 2.5 Hz, respectively. The methine hydrogen of C-protonated hexamethylbenzene is coupled to 18 methyl hydrogens,  $J_{\text{av}} = 2.1$  Hz,<sup>5</sup> but protonated tricarbonyl(hexamethylbenzene)chromium (5) has a hydrido hydrogen  $W_{1/2}$  of only 5.5 Hz. The C-protonated structures (2) cannot be the major species in solution in any of these cases. For the trimethoxy derivative (6) no coupling of the hydrido hydrogen can be occurring. Thus, 1 where  $\text{R}_n = 1,3,5$ -methoxy is the only species in solution in this case.

Addition of less than 1 equiv of  $\text{FSO}_3\text{H}$  to  $\text{ArCr}(\text{CO})_3$  ( $\text{Ar} = \text{arene}$ ) solutions resulted in complete ( $\geq 96\%$ ) transfer of acidic hydrogen to chromium (no  $\text{FSO}_3\text{H}$  signal observed). At low temperatures separate nmr signals of protonated and unprotonated  $\text{ArCr}(\text{CO})_3$  were observed. These lines broadened and then col-

(1) Alfred P. Sloan Foundation Fellow, 1969–1971.  
(2) (a) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962). See this reference for a discussion of the expected effects of exchange on the nmr spectra of cations 1. (b) Tricarbonyl(benzene)molybdenum and -tungsten have also been protonated in strong acidic media: D. A. Young, Ph.D. Thesis, University of California, Los Angeles, Calif., 1969.  
(3) J. C. Ware and T. G. Traylor, *Tetrahedron Lett.*, 1295 (1965).  
(4) Geminal coupling in a methylene group flanked by two  $\pi$ -electron systems is expected to be large. Cf. A. A. Bothner-By, *Advan. Magn. Resonance*, 1, 196 (1965).  
(5) For nmr spectra of uncomplexed benzenonium ions see D. M. Brouwer, E. L. Mackor, and C. Maclean in "Carbonium Ions," Vol. 2, G. A. Olah and P. von R. Schleyer, Ed., Interscience, New York, N. Y., 1970, p 837.  
(6) Cf. J. C. Kotz and D. G. Pedrotty, *Organometal. Chem. Rev., Sect. A*, 4, 479 (1969). These are often average coupling constants owing to rapid rotation of  $\pi$ -cyclopentadienyl ligands, etc.  
(7) An exception is the tricarbonyl(norbornadiene)iron hydride cation in which the hydride hydrogen is coupled to two ligand hydrogens by  $J = 13$  Hz: D. R. Falkowski, D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Amer. Chem. Soc.*, 89, 6387 (1967); H. D. Kaesz, unpublished results.

(8) Cf. J. C. Kotz and D. G. Pedrotty, *Organometal. Chem. Rev., Sect. A*, 4, 504 (1969).  
(9) The very basic arene nucleus<sup>10</sup> of this compound should enhance the tendency for C-protonation. The methoxy group has been shown to be electron donating in tricarbonyl(arene)chromiums.<sup>11</sup>  
(10) A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *J. Amer. Chem. Soc.*, 84, 4343 (1962); W. M. Schubert and R. H. Quacchia, *ibid.*, 85, 1278 (1963); D. M. Brouwer, E. L. Mackor, and C. MacLean, *Recl. Trav. Chim. Pays-Bas*, 85, 109 (1966).  
(11) G. Klopman and F. Calderazzo, *Inorg. Chem.*, 6, 977 (1967); G. Klopman and K. Noack, *ibid.*, 7, 579 (1968).  
(12) The apparent increase of stability in acid as electron-releasing substituents are attached to the arene ring parallels the qualitative basicity order pointed out by Davison, *et al.*<sup>2</sup>

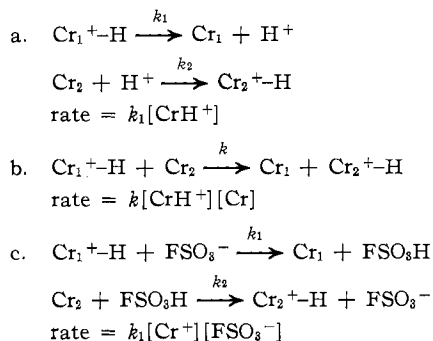
TABLE I  
NMR SPECTRA OF TRICARBONYL(ARENE)CHROMIUM COMPOUNDS IN SO<sub>2</sub>(l), CHEMICAL SHIFTS AND HALF-HEIGHT PEAK WIDTHS<sup>a-c</sup>

Compd	FSO <sub>3</sub> H	Ar-H	ArCH <sub>3</sub>	ArOCH <sub>3</sub>	Cr-H	W <sub>1/2</sub> <sup>d</sup> (TMS)
4	None	5.3 <sup>b</sup>	7.9			
4	Excess	3.75 (7) <sup>c</sup>	7.5 (10)		14.25 (8)	4
5	None		7.9			
5	Excess		7.4 (7.5)		14.6 (5.5)	5
6	None	4.9		6.2		
6	Excess	4.1 (2.5)		6.0 (4)	13.9 (2.5)	2

<sup>a</sup> At -40° in the absence of FSO<sub>3</sub>H; at -60° in the presence of FSO<sub>3</sub>H. <sup>b</sup> Chemical shifts in  $\tau$  units. <sup>c</sup> Half-height peak widths (Hz) given in parentheses after the chemical shift value. <sup>d</sup> Half-height width of the tetramethylsilane signal in the same sample.

lapsed to weighted averages of the separate low-temperature spectra as the temperature was raised.<sup>13</sup> The changes were reversible except in the case of **4** where partial decomposition occurred at higher temperatures and are indicative of intermolecular exchange of hydrido hydrogen. Possible mechanisms for exchange and the consequent rate laws are listed in Scheme I.

SCHEME I  
MECHANISMS FOR PROTON EXCHANGE  
(Cr = ArCr(CO)<sub>3</sub>; CrH<sup>+</sup> = ArCr(H)(CO)<sub>3</sub><sup>+</sup>)



The first-order mechanism a predicts that the lifetime of CrH<sup>+</sup> and hence the coalescence temperature ( $T_c$ ) for sets of collapsing lines<sup>14</sup> will be concentration independent. Mechanism b predicts an inverse dependence of  $T_c$  on [Cr] only, while mechanism c predicts an inverse dependence of  $T_c$  on [FSO<sub>3</sub><sup>-</sup>] only. Runs 1-6 in Table II show that  $T_c$  is concentration dependent,

TABLE II  
COALESCENCE TEMPERATURE FOR METHYL SIGNALS OF  
PROTONATED AND UNPROTONATED  
TRICARBONYL(MESITYLENE)CHROMIUM (**4**)<sup>a</sup>

Run	[CrH <sup>+</sup> ] <sup>b,d</sup> M	[Cr] <sup>c,d</sup> M	$T_c$ , °C	Run	[CrH <sup>+</sup> ] <sup>b,d</sup> M	[Cr] <sup>c,d</sup> M	$T_c$ , °C
1	0.02	0.12	+10	5	0.23	0.22	-50
2	0.04	0.19	-10	6	0.25	0.27	-54
3	0.05	0.35	-15	7 <sup>f</sup>	0.02	0.12	-30
4	0.10	0.13	-30				

<sup>a</sup> In 4:1 (v:v) CDCl<sub>3</sub>-SO<sub>2</sub>. <sup>b</sup> Concentration of protonated **4** ( $\pm 20\%$ ). <sup>c</sup> Concentration of unprotonated **4** ( $\pm 20\%$ ). <sup>d</sup> Measured by comparative integration vs. TMS as internal standard (see Experimental Section). <sup>e</sup> Coalescence temperature; error  $\pm 5^\circ$ . <sup>f</sup> KFSO<sub>3</sub> added to sample from run 1.

eliminating mechanism a. No correlation between [Cr] and  $T_c$ , as predicted by mechanism b, is observed. Runs 2 and 5 show that  $T_c$  can vary widely while [Cr]

(13) At higher temperatures the hydrido hydrogen signal was not observed. This could be caused by rapid exchange with 3-5% free FSO<sub>3</sub>H at these temperatures.

(14) Cf. L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon, London, 1969, p 56.

remains almost constant. Thus, mechanism b must be eliminated. Since [FSO<sub>3</sub><sup>-</sup>] = [CrH<sup>+</sup>], the inverse relationship between  $T_c$  and [FSO<sub>3</sub><sup>-</sup>] predicted by the remaining mechanism, c, is observed. As a direct demonstration of  $T_c$  dependence on [FSO<sub>3</sub><sup>-</sup>], a small amount of KFSO<sub>3</sub> was added to the sample solution from run 1. This, entered as run 7, caused the expected decrease in  $T_c$  at approximately constant [CrH<sup>+</sup>] and [Cr]. Thus, fluorosulfonate ion acts as a general base abstracting the hydrido hydrogen from one ArCr(CO)<sub>3</sub> molecule in a slow step and donating it to another ArCr(CO)<sub>3</sub> molecule in a fast second step.

Exchange is obviously slower in the presence of excess acid. This is consistent with the expected reduction in FSO<sub>3</sub><sup>-</sup> basicity if this ion is solvated by FSO<sub>3</sub>H. Addition of KFSO<sub>3</sub> to a solution of FSO<sub>3</sub>H in SO<sub>2</sub> caused the <sup>1</sup>H nmr signal to shift downfield, suggesting formation of a hydrogen-bonded species, e.g., FSO<sub>3</sub><sup>-</sup> ··· H-OSO<sub>2</sub>F.<sup>15</sup>

#### Experimental Section

Tricarbonyl(arene)chromium compounds were prepared according to methods described in the literature: **4**,<sup>16</sup> **5**,<sup>17</sup> **6**.<sup>17</sup> Technical fluorosulfonic acid, obtained from Allied Chemical, was distilled before use. Anhydrous sulfur dioxide was obtained from J. T. Baker Chemical Co. and was used without further purification.

Nmr spectra were recorded using a Varian Associates A-60 spectrometer equipped with a variable-temperature accessory which was calibrated at 10° intervals from -10 to -80° using the chemical shift difference between the two types of hydrogens in methanol. Samples (Table I) were prepared by addition of FSO<sub>3</sub>H dropwise to SO<sub>2</sub> solutions of the substrates at -78°. For the exchange work (Table II) CDCl<sub>3</sub>-SO<sub>2</sub> (4:1 v:v) was used to increase the solubility of unprotonated substrate. Solutions of **4** in CDCl<sub>3</sub> (0.2 ml) containing 1% tetramethylsilane by volume were added to an nmr tube cooled in Dry Ice-acetone, and 0.05 ml of SO<sub>2</sub> was added. The resulting slurry was warmed briefly in the air and shaken to mix the components, the mixture was recooled to -78°, and 1-2 drops FSO<sub>3</sub>H was added from a capillary dropper. The solution process was often not quantitative, and an insoluble residue was removed. The molarities of protonated and unprotonated **4** were calculated using eq 1

$$M = \frac{12}{9} \frac{A_{\text{com}}}{A_{\text{TMS}}} \frac{mM_{\text{TMS}}}{V} \quad (1)$$

where  $A_{\text{com}}$  is the integral of the methyl signal of **4**,  $A_{\text{TMS}}$  is the integral of the TMS signal,  $mM_{\text{TMS}}$  is the millimoles of TMS in the solution, and  $V$  is the volume of the solution in milliliters. Relative concentrations should be more accurate than absolute concentrations. For run 7 (Table II) 0.01 g of KFSO<sub>3</sub> was added to the solution from run 1, and the solution was agitated at -80° with a thin glass rod. Some of the KFSO<sub>3</sub> did not dissolve.  $T_c$  was redetermined immediately.

The effect of fluorosulfonate ion on the <sup>1</sup>H chemical shift of fluorosulfonic acid was determined as follows. A solution of 1 drop of FSO<sub>3</sub>H and 3 drops of TMS in 0.3 ml of SO<sub>2</sub> at -60°

(15) See ref 14, p 103.

(16) B. Nichols and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

(17) W. McFarlane and S. O. Grim, *J. Organometal. Chem.*, **5**, 147 (1966).

gave a  $^1\text{H}$  signal at  $\tau -0.25$ . Potassium fluorosulfonate (0.01 g) was added, most of the salt settling to the bottom of the tube. Redetermination of the  $^1\text{H}$  nmr spectrum showed that the fluorosulfonic acid signal had broadened and shifted to  $\tau -0.66$ .

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## Orbital Following and Hyperconjugation in Borane Adducts

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It is the purpose of this article to comment on the hybrid orbital force field (HOFF) model of Mills<sup>1</sup> as it applies to the compliance constants<sup>2</sup> of a series of borane adducts. Compliance constants are the elements of the inverse force constant matrix for a molecule and the HOFF model has been developed for the purpose of estimating the signs and magnitudes of interaction force constants. The HOFF model envisions hybrid orbital following of nuclear motions as the source of interaction force constants which are involved in the definition of compliance matrix elements. The latter are in turn related to interaction coordinates.

Jones and Ryan have shown<sup>3</sup> how the interaction coordinates may be obtained from the elements of  $\mathbf{C} = \mathbf{F}^{-1}$ .  $(S_3)_2$ , for example, is defined as  $(dS_3/dS_2)_{v=\min}$  and has the value  $C_{32}/C_{22}$ . According to Mills' formulation<sup>1</sup> in terms of hybrid orbital following,  $dS_3/dS_2 = (dS_3/d\lambda_x)(d\lambda_x/dS_2)$ .  $\lambda_x$  is the hybridization parameter in  $\phi_h = (1 + \lambda_x^2)^{-1/2}(\phi_s + \lambda_x\phi_p)$  for the B-X bond. In the cases which are to be discussed,  $S_3$  refers to the B-X stretching coordinate and  $S_2$  refers to the  $\text{BH}_3$  bending coordinate, both of  $A_1$  symmetry.

Before discussing the  $(S_3)_2$  interaction coordinates for the  $\text{BH}_3\text{X}$  adducts in detail, it is of interest to examine the compliance constant for  $S_3$ . In general, if there are interaction force constants between  $S_3$  and the other  $A_1$  coordinates  $C_{33} \neq 1/F_{33}$ . The difference is due to relaxational effects within the  $\text{BH}_3$  fragment which arise when the molecule is subjected to a force along  $S_3$ .  $C_{33}$  (units are  $\text{\AA}/\text{mdyn}$ ), then, measures the response of  $S_3$  to that force while allowing the other coordinates to achieve their minimum energy configuration.

Table I gives the values of  $C_{33}$  for a series of adducts which have recently been subjected to the HOFF treatment of the normal modes.<sup>4</sup> Compare, with regard to the comments in the last paragraph, the closeness of  $F_{33}$  for  $\text{X} = \text{PF}_3$  and  $\text{NMe}_3$  but the greater difference in  $C_{33}$ .

TABLE I  
COMPLIANCE AND FORCE CONSTANTS FOR  $S_3$  OF  $\text{BH}_3\text{X}^-$

	$C_{33}^a$	$F_{33}^b$	$\Delta = C_{33} - 1/F_{33}$
$\text{F}^-$	0.204	5.68	+0.028 (+14%)
$\text{CN}^-$	0.256	4.56	+0.037 (+14%)
$\text{NC}^-$	0.306	3.36	+0.008 (+3%)
$\text{CO}$	0.388	2.78	+0.023 (+6%)
$\text{NH}_3^c$	0.397	2.90	+0.053 (+13%)
$\text{PF}_3$	0.444	2.39	+0.026 (+6%)
$\text{NMe}_3^c$	0.494	2.36	+0.070 (+14%)

<sup>a</sup> Units are  $\text{\AA}/\text{mdyn}$ . <sup>b</sup> Units are  $\text{mdyn}/\text{\AA}$ . <sup>c</sup> See R. C. Taylor, *Advan. Chem. Ser.*, No. 42, 67 (1964).

Comparison of the B-X displacements per unit force with those calculated from  $F_{33}^{-1}$  shows that reorganization at  $\text{BH}_3$  facilitates B-X displacement by +14% for all but CO and  $\text{PF}_3$  (and  $\text{NC}^-$ ). The enhancement is thus small but detectable. The low values for CO and  $\text{PF}_3$  may be attributed to hyperconjugation in those adducts, hyperconjugation playing a resistive role to B-X elongation. The effect is small<sup>5</sup> however ( $\sim 8\%$ ) and of minor importance to the adduct bonds and probably the chemistries of  $\text{BH}_3\text{CO}$  and  $\text{BH}_3\text{PF}_3$ .

The low value of  $C_{33} - F_{33}^{-1}$  for  $\text{BH}_3\text{NC}^-$  would imply a singularly unresponsive  $\text{BH}_3$  fragment in that adduct. This value is subject to some question, however, since there are several possibilities for small errors in the force field of this molecule, not the least of which is the difficulty in assigning band positions with high accuracy.<sup>4</sup>

Another feature of the compliance matrix which is interesting to examine is the ratio  $C_{32}/C_{22}$  which gives the interaction coordinate  $(S_3)_2 = dS_3/dS_2$ . According to the HOFF model of Mills,  $(S_3)_2$  may be calculated from the set of orthogonality conditions for the boron hybrids ( $\lambda_i\lambda_j \cos \alpha_{ij} + 1 = 0$ ) and the definition of  $S_2 = c[\alpha_1 + \alpha_2 + \alpha_3 - b(\beta_1 + \beta_2 + \beta_3)]$ . The quantities  $c$  and  $b$  are chosen to ensure orthonormality of  $S_2$  and the angle redundancy coordinate, the latter being null to first order. With

$$\frac{dS_3}{dS_2} = \frac{dS_3}{d\lambda_x} \frac{d\lambda_x}{dS_2}$$

we find for  $d\lambda_x/dS_2$  from  $S_2$  and the orthogonality equations

$$\frac{d\lambda_x}{dS_2} = \lambda_x K$$

where

$$K = -\frac{1}{6} \sqrt{3 + \frac{\cos^2 \alpha/2}{\cos^2 \beta}} \left[ \tan \beta - \frac{\sqrt{3} \cos \beta \tan \alpha}{2 \cos \alpha/2} \right] \text{rad}^{-1}$$

Here  $\alpha = \angle \text{HBH}$  and  $\beta = \angle \text{HBX}$ . To evaluate  $dS_3/d\lambda_x$  we may try  $dS_3/d\lambda_x = d\phi_h/d\lambda_x$ , where

$$\phi_h = \frac{1}{1 + \lambda_x^2} [\phi_s + \lambda_x\phi_p]$$

(5) For the series  $\text{CH}_3\text{X}$ , we find (unpublished) enhancement of  $C_{33}$  by 11% for  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ . With  $\text{X} = \text{CN}, \text{CCH}, \text{CCCl}, \text{CCBr}$ , the enhancement is only 5%, while it is 8% for  $\text{X} = \text{NC}$ . Thus, as far as electron rearrangement following nuclear displacement is concerned, hyperconjugation is hardly more important to  $\text{BH}_3$  than it is to  $\text{CH}_3$ . For the force fields of  $\text{CH}_3\text{X}$ , see J. Aldous and I. M. Mills, *Spectrochim. Acta*, **18**, 1073 (1962), and J. L. Duncan, *ibid.*, **20**, 1197 (1964).

(1) I. M. Mills, *Spectrochim. Acta*, **19**, 1585 (1963).  
(2) J. C. Decius, *J. Chem. Phys.*, **38**, 241 (1963).  
(3) L. H. Jones and R. R. Ryan, *ibid.*, **52**, 2003 (1970).  
(4) J. R. Berschied and K. F. Purcell, in press.