

# Arene-Metal Complexes. VI. Hindered Rotations in Mono(tricarbonylchromium) Complexes of Diarylmethanes and Related Compounds<sup>1</sup>

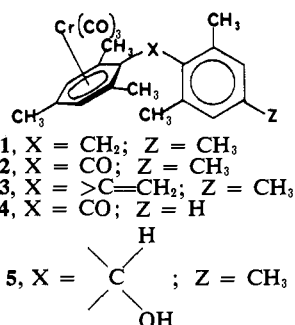
Walter S. Trahanovsky,\* David J. Kowalski, and Michael J. Avery

Contribution from the Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010, Received May 21, 1973

**Abstract:** Mono(tricarbonylchromium) complexes of dimesitylmethane (1), dimesityl ketone (2), 1,1-dimesitylethene (3), 2,6-dimethylphenyl mesityl ketone (with the mesityl ring complexed) (4), and dimesitylmethanol (5) are described. By nmr spectroscopy the barriers of rotation of the uncomplexed rings, complexes 1-5, were found to be (in kcal/mol) 14.3 at 18°, 19.6 at 118°, 14.2 at 14°, 19.4 at 115°, and 13.9 at 22°, respectively. The higher barriers for the ketone complexes are attributed to increased stabilization of the ground-state conformation of the ketone complexes by conjugation of the  $\pi$  electrons of the uncomplexed ring with those of the carbonyl group. It is suggested that the approximately equal barrier for the methane (1) and ethene (3) complexes means that there is very little interaction between the  $\pi$  electrons of the uncomplexed ring and those of the carbon-carbon double bond. Also reported are the ir absorption bands for the carbonyl group of some aryl ketones and their tricarbonylchromium complexes.

## Results and Discussion

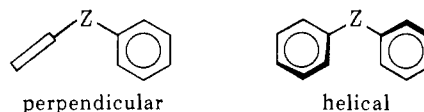
Mono(tricarbonylchromium) complexes of dimesitylmethane (1), dimesityl ketone (2), 1,1-dimesitylethene



(3), and 2,6-dimethylphenyl mesityl ketone (4) were prepared from the free arene and hexacarbonylchromium by standard procedures. The mono complex of dimesitylmethanol (5) was prepared by reducing 2 with lithium aluminum hydride. The nmr spectrum and elemental analysis of each complex are consistent with its assigned structure, and the nmr spectrum of 4 indicates that the mesityl ring is the one that is complexed.

The rings of uncomplexed diarylmethanes with four ortho substituents and related compounds are thought to rotate with the same angular velocity about the bonds which connect them to the central atom and are arranged so that when one ring is in the plane of the aryl-central atom-aryl plane, the other ring is perpendicular to this plane.<sup>2</sup> This so called "cogwheel mechanism" enables the four ortho positions to become equivalent rapidly. From steric considerations alone the coplanar conformation seems very unlikely but experi-

mental results,<sup>2d</sup> such as the ultraviolet spectrum of dimesityl ketone,<sup>3</sup> also indicate that only one ring is coplanar with the central atom. The conformations of uncomplexed diarylmethanes and related compounds and their interconversions have recently been analyzed in detail by Gust and Mislow.<sup>2d</sup> They call the two most stable conformations the perpendicular and helical conformations and these terms will be used below to describe the conformation of our complexed compounds.



In Figure 1, the cogwheel mechanism for the mono(tricarbonylchromium) complexed tetra ortho-substituted diarylmethane derivatives is presented. The nmr spectra of complexes 1-3 at low temperatures indicate that the *o*-methyl groups of the complexed rings give identical signals which is consistent with these groups being in equivalent environments. The same situation is noted for the aromatic protons of these rings. However, the *o*-methyl groups and the aromatic protons of the uncomplexed rings are in nonequivalent environments since each member of both sets gives a separate signal. This is illustrated by the nmr spectrum of 1 at -45° which is shown in Figure 2.<sup>4</sup>

These nmr results are consistent with rapid rotation of the rings of these complexes *via* the cogwheel mechanism shown in Figure 1 since the ortho positions indicated by A and B become equivalent but those indicated by C and D do not. However, inspection of models shows that conformation 8 is very unlikely since there is severe steric interaction between the metal moiety and one of the *o*-methyl groups (D) of the uncomplexed ring. Thus, a more likely interpretation of the low tempera-

(1) (a) Part V: R. J. Card and W. S. Trahanovsky, *Tetrahedron Lett.*, 3823 (1973). (b) Based on work by D. J. K. and M. J. A. in partial fulfillment of the requirements for the M.S. degree at Iowa State University. (c) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. (d) Presented at the 5th International Conference on Organometallic Chemistry, Moscow, USSR, Aug 1971, Abstracts, I, 216.

(2) (a) M. Allen and R. H. Moore, *Can. J. Chem.*, 37, 1799 (1959); (b) H. Kwart and S. Alekman, *J. Amer. Chem. Soc.*, 90, 4482 (1968); (c) G. Montaudo, S. Caccamese, and P. Finocchiaro, *ibid.*, 93, 4202 (1971); (d) D. Gust and K. Mislow, *ibid.*, 95, 1535 (1973), and references cited therein.

(3) M. T. O'Shaughnessy and W. H. Rodebush, *J. Amer. Chem. Soc.*, 62, 2906 (1940).

(4) The <sup>13</sup>C nmr spectrum of 2 is also consistent with the two sides of the complexed ring being in equivalent environments, and also requires that the two sides of the uncomplexed ring are in nonequivalent environments.<sup>5</sup>

(5) D. J. Thoennes, C. L. Wilkins, and W. S. Trahanovsky, *J. Magn. Resonance*, in press.

ture nmr spectra is that these complexes exist predominantly in conformation **6**, a perpendicular conformation, or rock back and forth rapidly from some conformation between **6** and **8** going through **6** to the enantiomeric conformation. In the latter case, the preferred conformations could be **7** and **9** or some pair of helical conformations between **6** and **8**.

Conformation **6** is favored as the most stable one because steric interactions of the metal moiety are minimized in this conformation. Based on an nmr study of ortho-substituted diphenylmethanes<sup>2c,6</sup> the predicted position of the signal for the methyl group in position C of **6** is  $\delta$  1.8–1.9 and that for the methyl group in position D of **6** is  $\delta$  2.5–2.6 for complex **1** if the shielding effects of the metal moiety are negligible. From the nmr data in Table I it is seen that the signals for these

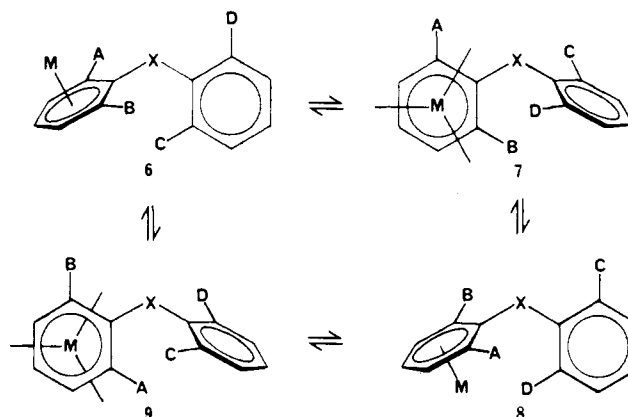


Figure 1. The cogwheel mechanism for complexed tetra (ortho-substituted) diarylmethane derivatives.

Table I. Nmr Signals<sup>a</sup> for the Tricarbonylchromium Complexes of Dimesitylmethane (**1**), Dimesityl Ketone (**2**), 1,1-Dimesitylethene (**3**), 2,6-Dimethylphenyl Mesityl Ketone (**4**), and Dimesitylmethanol (**5**)

Complex (solvent)	Temp, °C	Nmr shifts, $\delta^b$						
		Complexed ring			Central Atom, X	Uncomplexed ring		
		<i>p</i> -Methyl	Aromatic protons	<i>o</i> -Methyls			<i>o</i> -Methyls	Aromatic Protons
<b>1</b> (CDCl <sub>3</sub> )	-45	2.16	5.02	2.06	3.89	2.42	6.89	2.26
<b>1</b> (C <sub>2</sub> Cl <sub>4</sub> )	105	2.08	4.80	2.02	3.91	1.89	6.77	
<b>2</b> (CDCl <sub>3</sub> )	40	2.22	4.83	2.05		2.14	6.72	2.20
<b>2</b> ( <i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> )	133	2.08 <sup>c</sup>	4.70	2.00		2.38	6.92	
<b>3</b> (CDCl <sub>3</sub> )	-10	2.18	4.97	2.11	5.92	2.01	6.75	
					(d, <i>J</i> = 2 Hz)	2.08 <sup>c</sup>	<i>d</i>	2.18
					5.66	2.48	6.97	2.28
					(d, <i>J</i> = 2 Hz)			
<b>3</b> (C <sub>2</sub> Cl <sub>4</sub> )	102	2.14	4.76	2.09	5.90	2.19	6.76	2.22
					(d, <i>J</i> = 2 Hz)			
					5.60			
					(d, <i>J</i> = 2 Hz)			
<b>4</b> ( <i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> )	38	2.04	4.58	1.95		2.33	<i>d</i>	
						1.91		
<b>4</b> ( <i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> )	140	2.10	<i>e</i>	2.04		2.18	<i>d</i>	
<b>5</b> (CDCl <sub>3</sub> )	-36	2.27 <sup>f</sup>	4.95	2.20 <sup>f</sup>	6.60	2.58	6.89	2.36 <sup>f</sup>
			(d, <i>J</i> = 2 Hz)		(d, <i>J</i> = 4 Hz)			
				1.96 <sup>f</sup>		2.00		
			4.86		1.81		6.76	
			(d, <i>J</i> = 2 Hz)		(d, <i>J</i> = 4 Hz)			
<b>5</b> ( <i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> )	142°	2.17 <sup>f</sup>	4.77	2.04 <sup>f</sup>	<i>d</i>	2.23	<i>d</i>	2.35 <sup>f</sup>
			4.72	1.90 <sup>f</sup>	1.62			
					(d, <i>J</i> = 4 Hz)			

<sup>a</sup> All spectra were taken on a 100-MHz spectrometer. <sup>b</sup> All signals were singlets (some broad) unless marked otherwise. <sup>c</sup> The signals for the *p*-methyl group of the complexed ring and the *o*-methyl groups of the uncomplexed ring could not be resolved even at 162°. <sup>d</sup> These signals were obscured by the solvent signals. <sup>e</sup> This signal was not recorded. <sup>f</sup> These assignments may be interchanged and are based on analogy to the other spectra.

methyl groups are at  $\delta$  1.89 and 2.42 and are thus quite consistent with conformation **6** being the most stable one.

When the CH<sub>2</sub> is replaced with a CO (complex **2**), the higher field signal shifts 0.12 ppm downfield and the lower field signal shifts 0.04 ppm upfield while the signals for the *p*-methyl group of the uncomplexed ring and *o*-methyl groups of the complex ring shift  $\leq 0.02$  ppm and those for the *p*-methyl group of the complex ring shifted downfield by 0.06 ppm (none of these shifts are corrected for temperature changes). This inequality of shifts of the signals for the *o*-methyl groups of the uncomplexed ring when going from **1** to **2** is readily accounted for by conformation **6** being the most stable one

for both complexes, but the directions and magnitudes are not obvious from considerations of the long-range shieldings by the carbonyl group.<sup>7</sup> Of course, the exact geometries of these congested molecules cannot be estimated accurately.

In an effort to get more information about the ground-state conformation of these mono complexes, an ir study of various aryl ketones and their mono- and bis(tricarbonylchromium)<sup>8</sup> complexes was undertaken. However, the carbonyl absorption bands of the model compounds acetophenone, whose carbonyl group is

(7) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, p 89–90.

(8) W. S. Trahanovsky, D. J. Kowalski, R. S. Hansen, and J. C. Clardy, unpublished results.

(6) G. Montaudo, P. Finocchiaro, S. Caccamese, and F. Bottino, *J. Chem. Eng. Data*, **16**, 249 (1971).

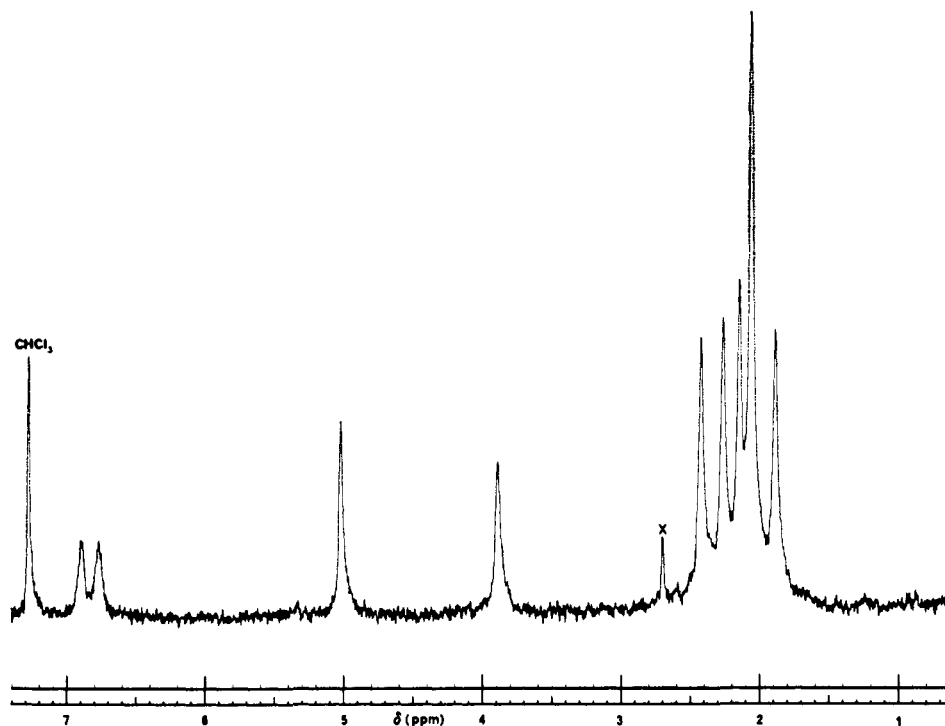
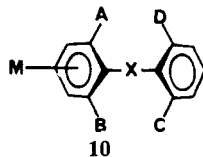


Figure 2. Nmr spectrum of ((mesityl)tricarboxylchromium)mesitylmethane (1) at  $-45^{\circ}$  in  $\text{CDCl}_3$  (a spurious peak is indicated by x).

conjugated with the aromatic ring,<sup>9</sup> and 2,4,6-trimethylacetophenone, whose carbonyl group is not conjugated with the aromatic ring,<sup>9</sup> were only slightly affected by complexation<sup>10</sup> and thus there are no predictable differences between the carbonyl absorption bands for conformations 6 and 7 (or 9) of the mono complex of dimesityl ketone (2). The ir spectra of the mono- and bis(tricarboxylchromium) complexes of dimesityl ketone are somewhat unusual in that the ir bands for the ketone groups of the complexes are doublets shifted about  $10\text{--}20\text{ cm}^{-1}$  from the main peak for the ketone group of the uncomplexed ketone, but we have no good explanation for these changes. These ir absorptions are given in Table III.

At high temperatures, the separate signals for the *o*-methyl groups and the aromatic protons of the uncomplexed rings of complexes 1–3 coalesce. This is illustrated by the nmr spectrum of 1 at  $105^{\circ}$  which is shown in Figure 3. In order for the two sides of the uncomplexed rings to become equivalent, these complexes are most likely going through conformation 10 in



which both rings are perpendicular to the ring–central atom–ring plane. Conformation 10 appears to be the

(9) A. G. Pinkus and H. C. Custard, Jr., *J. Phys. Chem.*, **74**, 1042 (1970), and references cited therein.

(10) In the solid state the complex of acetophenone is orange whereas the 2,4,6-trimethylacetophenone complex is yellow. This observation coupled with the fact that 2 is orange and 1 and 3 are yellow (4 is also orange and 5 is yellow) suggest that the carbonyl group of 2 is conjugated with the complexed ring. However, it is difficult to interpret these color changes since one does not know how the ultraviolet–visible absorption of a complexed ring changes as conjugation with an adjacent carbonyl group is increased and other factors could affect the ultraviolet–visible absorption to an equal or even greater extent.

one with minimum steric interaction which permits the interchange of positions C and D. This mechanism of interchange has been called a one-ring flip.<sup>2d</sup>

The nmr spectra of 4 at various temperatures are similar to those of 2 except that the signals from the aromatic protons of the free ring are more complex since the free ring of 2 contains three protons, not two. The nmr spectra of 5 at various temperatures are similar to those of 1 except that the *o*-methyl groups and aromatic protons of the complexed ring give separate signals. This behavior is expected since there is no plane of symmetry through the middle carbon atom, X, of 5. The nmr spectra of complexes 1–5 at various temperatures are summarized in Table I.

The nmr signals of the *o*-methyl groups of uncomplexed dimesitylmethane and dimesityl ketone<sup>11</sup> remain sharp singlets even at  $-90^{\circ}$ . These results are consistent with the rings rotating about the central atom–ring bond relatively freely by the cogwheel mechanism.<sup>2</sup> If one assumes that the chemical shift difference of the *o*-methyl groups on the ring which is in the plane of the aryl–central atom–aryl plane of the perpendicular conformation of uncomplexed dimesitylmethane derivatives would be about 50 Hz, which is the difference obtained from the data of Montaudo and coworkers<sup>2c</sup> as well as from the spectra of the complexes, the barrier of rotation by the cogwheel mechanism for the uncomplexed dimesitylmethane derivatives is calculated<sup>12</sup> to be  $<9\text{ kcal/mol}$ .

Free energies of activation for the rotation of the uncomplexed rings for complexes 1–5 were calculated from the temperature dependence of the nmr signals of these complexes<sup>12</sup> and are listed in Table II. The barriers obtained from the signals of the aromatic protons

(11) D. Lauer and H. A. Staab, *Chem. Ber.*, **102**, 1631 (1969).

(12) M. T. Rodgers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

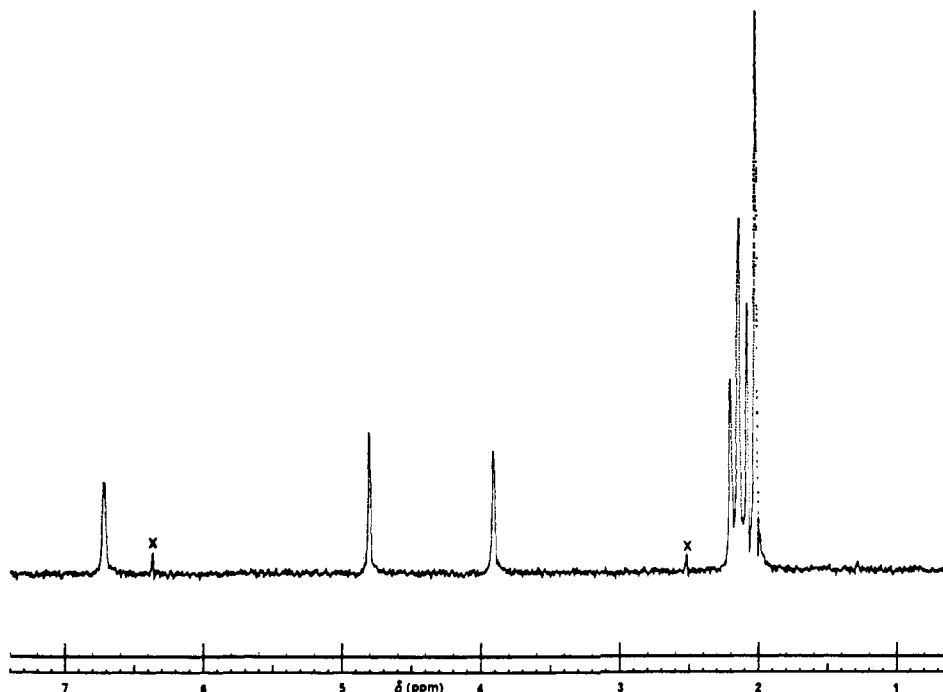


Figure 3. Nmr spectrum of ((mesityl)tricarbonylchromium)mesitylmethane (1) at 105° in C<sub>2</sub>Cl<sub>4</sub> (spurious peaks are indicated by x's).

Table II. Free Energies of Activation of the Rotation of the Uncomplexed Ring of Tricarbonylchromium Complexes 1-5

Compd (solvent)	$T_c$ for aro- matic pro- tons, °C <sup>a</sup>	$T_o$ for <i>o</i> - methyl groups, °C <sup>b</sup>	$\Delta\nu_{AB},^c$ Hz	$\Delta G_{T_c}^\ddagger,$ kcal/mol <sup>d</sup>
1 (CHCl <sub>2</sub> CHCl <sub>2</sub> )	-5		11	13.9
1 (CHCl <sub>2</sub> CHCl <sub>2</sub> )		18	54	14.3
2 (CHCl <sub>2</sub> CHCl <sub>2</sub> )	98		17	19.2
2 ( <i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> )		118	42	19.6
3 (CDCl <sub>3</sub> )	8		22	14.2
3 (CDCl <sub>3</sub> )		14	58	14.2
4 ( <i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> )		115	42	19.4
5 (CDCl <sub>3</sub> )	-8		13	13.7
5 (CDCl <sub>3</sub> )		22	58	13.9

<sup>a</sup> Error is  $\pm 2^\circ$ . <sup>b</sup> Error is  $\pm 5^\circ$ . <sup>c</sup> Separation of the two coalescing peaks below their coalescence temperature. <sup>d</sup> The estimated errors for these values are no greater than  $\pm 0.6$  kcal/mol.

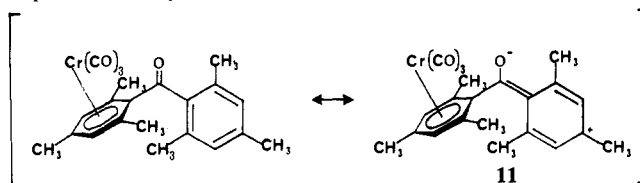
agree quite well with those obtained from the signals of the *o*-methyl groups.

The most striking feature of the results presented in Table II is that the barriers of rotation of the uncomplexed ring of the ketone complexes, 2 and 4, are *ca.* 5 kcal/mol higher than those for the methane (1), ethene (3), and methanol (5) complexes. Although the coalescence temperatures for 1, 3, and 5 are *ca.* 100° lower than those for 2 and 4, the 5 kcal difference in free energy of activation is a significant one.<sup>13</sup>

Since the central atoms, X, of both the ketone and ethene complexes are trigonal, the higher barriers in the ketone complexes cannot be due to a change in the

(13) The  $\Delta G^\ddagger$  changes only slightly with temperature for processes whose rates vary by usual amounts with temperature. For example, if one makes the simple assumption that the rate of a process doubles every 10°, the  $\Delta G^\ddagger$  for this reaction will change from 14.0 kcal at 290°K to 13.7 kcal at 390°K. A similar calculation for a process whose rate increases by 1.5 every 10° shows that the  $\Delta G^\ddagger$  will change from 14.0 kcal at 290°K to 15.1 at 390°K.

hybridization of the orbitals of the central atom. We believe that the larger barriers of the ketone complexes are a result of increased stabilization of the ground state by delocalization of the  $\pi$  electrons of one or both rings into the carbonyl group. For conformation 6 only the uncomplexed ring is in conjugation with the carbonyl group, for conformation 7 and 9 only the complexed ring is in conjugation with the carbonyl group, and for some enantiomeric pair of helical conformations between 6 and 8, the  $\pi$  electrons of both rings can partially overlap with those of the carbonyl group. For the sake of discussion we will assume that conformation 6 is the most stable one. Delocalization of the  $\pi$  electrons of the uncomplexed ring into the carbonyl group can be represented by resonance structures such as 11. The



equal barriers of the methane (1) and the ethene (3) complexes indicate that resonance structures analogous to 11 for the ethene complex are relatively unimportant. Recent molecular orbital calculations by Dewar, *et al.*,<sup>14</sup> and Pople, *et al.*,<sup>15</sup> support this conclusion since they show that the delocalization between the phenyl ring and the carbon-carbon double bond of styrene is small.

Pople, *et al.*,<sup>15</sup> have calculated that the barrier to rotation of the formyl group of benzaldehyde is 6.6 kcal/mol. This value is in good agreement with our observed difference of 5 kcal for the barriers of rotation of the uncomplexed rings of the ketone and methane or ethene complexes.

Experimentally, the barrier to rotation about the

(14) M. J. S. Dewar and A. J. Harget, *Proc. Roy. Soc., Ser. A*, **315**, 443 (1970).

(15) W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 1496 (1972).

phenyl-carbon bond in benzaldehyde has been determined to be  $4.90 \pm 0.43$  kcal/mol by microwave spectroscopy,<sup>16</sup> 4.66 kcal/mol by infrared spectroscopy,<sup>17,18</sup> and 7.9 kcal/mol by nmr spectroscopy<sup>19</sup> and our value is in excellent agreement with these.

The barrier of rotation of the uncomplexed ring of complex **4**, which is identical with complex **2** except that the para position of the uncomplexed ring contains a hydrogen atom instead of a methyl group, is the same within experimental error as that of complex **2**. One might have expected these two complexes to have different barriers considering resonance structure **11** and the difference in electron donating ability of the hydrogen atom and the methyl group. However, the substituent effects on the barriers of rotation about the phenyl-oxygen bond of phenols<sup>20</sup> and about the phenyl-carbonyl bond of protonated benzaldehydes<sup>21</sup> have been shown to be small. For example, the barrier of rotation for protonated *p*-methylbenzaldehyde is 16.3 kcal/mol whereas the barrier for the *p*-chloro compound is 14.8 kcal/mol.<sup>21</sup> The largest substituent effect reported is the 2.8 kcal/mol increase in the barrier to rotation about the phenyl-carbonyl bond as one goes from benzaldehyde to *p*-*N,N*-dimethylaminobenzaldehyde.<sup>19</sup> Even in this case the change in the barrier is not great despite the much greater electron-donating ability of the amino group compared to the hydrogen atom.

If the most stable conformation of the complexes is not **6** but is one in which the complexed ring is partial or fully conjugated with the carbonyl group, then our analysis suggests that the delocalization of  $\pi$  electrons between carbonyl groups or carbon-carbon double bonds and phenyl rings is not significantly affected by complexation of the phenyl ring with a tricarbonylchromium group.

### Experimental Section

Most equipment and materials have been previously described.<sup>22</sup> Nmr spectra were taken on a Varian Associates HA-100 nmr spectrometer which was equipped with a V-6040 variable-temperature controller and V-4333 probe. Ir spectra were taken on a Beckman IR 12 dual beam spectrophotometer. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Chemalytics, Inc., Tempe, Ariz. Mesitylene was obtained from Baker Co., bromomesitylene was obtained from Eastman, acetophenone and 1,1,1-trichloroethane were obtained from Matheson Coleman and Bell, 2,6-dimethylaniline was obtained from Aldrich, and hexacarbonylchromium from Strem.

**Dimesitylmethane** was prepared<sup>23</sup> in 57% yielded; mp 126–130.5° (lit.<sup>23</sup> mp 134–135.5°); nmr (CCl<sub>4</sub>)  $\delta$  6.65 (s, 4), 3.9 (s, 2), 2.19 (s, 6), and 2.04 (s, 12).

**Dimesityl ketone** was prepared from mesitylene, mesityl chloride,<sup>24</sup> and aluminum trichloride in carbon disulfide. After an

ether extraction the crude product was crystallized from 95% ethanol to give 87% of white crystals: mp 137.5–138.5° (lit.<sup>25</sup> mp 139–139.5°); nmr (CCl<sub>4</sub>)  $\delta$  6.75 (s, 2), 2.25 (s, 3), and 2.06 (s, 6); ir, see Table III.

**Table III.** Infrared Data for Certain Aryl Ketones and Their Tricarbonylchromium Complexes

Compound	Solvent	Concn, <i>M</i>	C=O stretch, <sup>a</sup> cm <sup>-1</sup>
Acetophenone	CCl <sub>4</sub>	$2.85 \times 10^{-2}$	1692.3 <sup>b</sup>
	CHCl <sub>3</sub>	$3.07 \times 10^{-2}$	1684.0
(Acetophenone)tricarbonylchromium	CCl <sub>4</sub>	$5.33 \times 10^{-3}$	1693.2
	CHCl <sub>3</sub>	$5.46 \times 10^{-3}$	1684.6
2,4,6-Trimethylacetophenone	CCl <sub>4</sub>	$4.51 \times 10^{-2}$	1706.2 <sup>c</sup>
	CHCl <sub>3</sub>	$3.49 \times 10^{-2}$	1698.4
(2,4,6-Trimethylacetophenone)tricarbonylchromium ( <b>12</b> )	CCl <sub>4</sub>	$6.7 \times 10^{-3}$	1704.3
	CHCl <sub>3</sub>	$7.27 \times 10^{-3}$	1699.4
	CHCl <sub>3</sub>	$3.9 \times 10^{-2}$	1650.4 <sup>d,e</sup>
Dimesityl ketone (Mesityl)tricarbonylchromium mesityl ketone ( <b>2</b> )	CHCl <sub>3</sub>	$1.53 \times 10^{-2}$	1660.7 <sup>f</sup> 1665.2
	CHCl <sub>3</sub>	$9.33 \times 10^{-2}$	1667.1 <sup>f</sup> 1671.3

<sup>a</sup> Error limit is  $\pm 1$  cm<sup>-1</sup>. <sup>b</sup> Lit.<sup>9</sup> value, 1688 cm<sup>-1</sup> (neat). <sup>c</sup> Lit.<sup>9</sup> value, 1692 cm<sup>-1</sup> (neat). <sup>d</sup> Lit. value, 1651.2 cm<sup>-1</sup> (CHCl<sub>3</sub>); A. M. De Roos, *Recl. Trav. Chim. Pays-Bas*, **87**, 1359 (1968). <sup>e</sup> Shoulders occurred at 1644.2 and 1655.9 cm<sup>-1</sup>. <sup>f</sup> Shoulder occurred at 1650.5 cm<sup>-1</sup>. <sup>g</sup> See ref 8.

**1,1-Dimesitylethane** was prepared from mesitylene, 1,1,1-trichloroethane, and aluminum trichloride. After an ether extraction the yellow residue was recrystallized from propanol-water to give 17% of colorless needles: mp 97–97.5° (lit.<sup>26</sup> mp 98°); nmr (CCl<sub>4</sub>)  $\delta$  6.72 (s, 4), 5.45 (s, 2), 2.23 (s, 6), and 2.10 (s, 12).

**2,4,6,2',6'-Pentamethylbenzophenone**, 2,6-Dimethylaniline was converted to the bromide<sup>27</sup> and then to 2,6-dimethylbenzoic acid *via* the Grignard reagent.<sup>28</sup> The acid was converted to the acid chloride<sup>29</sup> which was dissolved in carbon disulfide and then dropped into excess mesitylene and aluminum chloride in carbon disulfide with stirring. The mixture was stirred overnight and the crude product, obtained by an ether extraction, was recrystallized from ethanol-water to give a 73% yield of colorless needles: mp 83.5–85° (lit.<sup>30</sup> mp 86°); nmr (CDCl<sub>3</sub>)  $\delta$  7.10 (m, 3), 6.84 (s, 2), 2.27 (s, 3), 2.14 (s, 6), and 2.12 (s, 6).

**2,4,6-Trimethylacetophenone** was prepared from mesitylene, acetyl chloride, and aluminum trichloride: bp 113–114° (10 mm) (lit.<sup>31</sup> bp 90° (3 mm)); nmr (CDCl<sub>3</sub>)  $\delta$  6.83 (s, 2), 2.43 (s, 3), 2.27 (s, 3), and 2.22 (s, 6); ir, see Table III.

**Tricarbonylchromium Complexes.** Most of these were prepared by the method used to prepare **1**. Experimental details and data for each complex are given in Table IV.

**((Mesityl)tricarbonylchromium)mesitylmethane (1).** Dimesitylmethane and hexacarbonylchromium in freshly distilled diglyme were heated to reflux for 1.5 hr under nitrogen in a flask fitted with a Strohmeier apparatus.<sup>32</sup> Ether was added to the cooled reaction

(16) R. K. Kakar, E. A. Reinhart, C. R. Quade, and T. Kojima, *J. Chem. Phys.*, **52**, 3803 (1970).

(17) W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, **21**, 231 (1965).

(18) The value 4.66 kcal/mol is for the gas phase. A value of 6.69 kcal/mol was obtained for the liquid phase, but the authors believe that their value for the liquid phase is unreliable.

(19) F. A. L. Anet and M. Ahmad, *J. Amer. Chem. Soc.*, **86**, 119 (1964).

(20) D. L. Radom, W. J. Hehre, J. A. Pople, G. L. Carlson, and W. G. Fateley, *J. Chem. Soc., Chem. Commun.*, 308 (1972).

(21) R. Jost, P. Rimmelin, and J. M. Sommer, *J. Chem. Soc., Chem. Commun.*, 879 (1971).

(22) W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).

(23) J. Cornell, Jr., and M. H. Gollis, *Org. Syn.*, **42**, 57 (1962).

(24) "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955: (a) D. M. Bowen, p 553; (b) R. P. Barnes, p 555.

(25) R. F. Rekker and W. Nauta, *Recl. Trav. Chim. Pays-Bas*, **73**, 969 (1954).

(26) R. J. Snyder and R. W. Roeske, *J. Amer. Chem. Soc.*, **74**, 2493 (1952).

(27) A. I. Vogel, "Elementary Practical Organic Chemistry, Part 1: Small Scale Preparations," 2nd ed, Wiley, New York, N. Y., 1966, p 282.

(28) R. W. Hufford and W. A. Noyes, *J. Amer. Chem. Soc.*, **43**, 925 (1921).

(29) G. Lock and K. Schmidt, *J. Prakt. Chem.*, **140**, 229 (1934).

(30) J. Coops, W. T. Nauta, M. J. E. Ernsting, and A. C. Faber, *Recl. Trav. Chim. Pays-Bas*, **59**, 1112 (1940).

(31) C. R. Noller and R. Adams, *J. Amer. Chem. Soc.*, **46**, 1889 (1924).

(32) W. Strohmeier, *Chem. Ber.*, **94**, 2490 (1961).

**Table IV.** Experimental Details, Melting Points, Elemental Analyses, and Nmr Signals for Tricarbonylchromium Complexes<sup>a</sup>

Complex	Reaction time, hr	Chromatography eluent	Mp, <sup>b</sup> °C	Anal., %				Nmr
				Calcd		Found		
				C	H	C	H	
1	1.5	10% PhH, 90% <i>n</i> -C <sub>8</sub> H <sub>14</sub>	180.5–181.8	68.03	6.23	67.86	6.14	See Figures 2 and 3; Table I
2	4	PhH, <i>n</i> -C <sub>8</sub> H <sub>14</sub>	177–177.5	65.66	5.51	65.54	5.60	See Table I
3	11.5	<i>n</i> -C <sub>8</sub> H <sub>14</sub>	142–143.5	68.98	6.04	68.84	5.83	See Table I
4 <sup>c</sup>	3	93% <i>n</i> -C <sub>8</sub> H <sub>12</sub> , 7% Et <sub>2</sub> O	169–171	64.94	5.19	65.09	5.10	(CDCl <sub>3</sub> ) δ 7.02 (m, 3), 4.84 (s, 2), 2.42 (s, 3), 2.23 (s, 3), 2.06 (s, 9); see Table I for nmr in <i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>
5	<i>d</i>	PhH, <i>n</i> -C <sub>8</sub> H <sub>14</sub>	150–152	65.33	5.98	65.24	5.97	See Table I
12	20	20% CH <sub>2</sub> Cl <sub>2</sub> , 80% <i>n</i> -C <sub>8</sub> H <sub>12</sub>	131–132.5	56.38	4.73	56.35	4.72	(CDCl <sub>3</sub> ) δ 4.81 (s, 2), 2.56 (s, 3), 2.18 (s, 3), 2.17 (s, 6)

<sup>a</sup> See Table III for ir data for **2** and **12**. <sup>b</sup> Complexes were recrystallized from methylene chloride–pentane. <sup>c</sup> The desired complex was obtained in higher yield and was purified by careful recrystallization. <sup>d</sup> Prepared by the lithium aluminium hydride reduction of **2**.

mixture and the resultant mixture was then filtered through a bed of Celite. The filtrate was washed with water, dried (MgSO<sub>4</sub>), and concentrated to give a yellow solid which was chromatographed on a column of silica gel using a 1:9 benzene–hexane mixture as the eluent. The chromatographed material was recrystallized; see Table IV for properties and analyses.

**(Acetophenone)tricarbonylchromium.** The complex of the diethyl ketal of acetophenone<sup>33</sup> was prepared in dibutyl ether and glyme by the procedure used to prepare **1** except that the reaction mixture was heated for 35 hr. After work-up a quantity of orange crystals of the complex of  $\alpha$ -ethoxystyrene was obtained which was recrystallized from methylene chloride–hexane: mp 103.5–105.5°; nmr (CDCl<sub>3</sub>) δ 5.5 (m, 5), 4.4 (AB pattern,  $J_{AB} = 2$ –4 Hz, 2), 3.9 (q,  $J = 7$  Hz, 2), and 1.3 (m, 3). This complex was dissolved in nitrogen-saturated absolute ethanol and treated with nitrogen-saturated 0.5 *M* hydrochloric acid under nitrogen for 14 hr. After work-up, the residue was recrystallized from hexane to give orange crystals: mp 85.5–87.5° (lit.<sup>34</sup> mp 91.5–92°); nmr (CDCl<sub>3</sub>) δ 6.2–5.2 (m, 5) and 2.5 (s, 3)

**Nmr Procedure.** Solutions of the complexes were filtered through activated charcoal immediately before being placed into the nmr tubes. Either immediately before or after a variable-temperature study, the range that was observed was calibrated by methanol for low temperatures or ethylene glycol for high temperatures. At the coalescence temperature,  $T_c$ , the temperature at which the two

peaks became a singlet peak with a flat top, the free energy of activation,  $\Delta G_{T_c}^\ddagger$ , is given by the equation

$$\Delta G_{T_c}^\ddagger = (4.5756)(10^{-3})(T_c)[9.972 + \log(T_c/\Delta\nu_{AB})]$$

where  $\Delta\nu_{AB}$  is the width of the peak at its half-height.<sup>12</sup> The  $\Delta\nu_{AB}$  was determined by measuring the separation of the two peaks well below the coalescence temperature (method A) and measuring the width of the coalesced peak at its half-height (method B). Both methods were used for both the methyl signals and the aromatic proton signals<sup>35</sup> and the barriers calculated from the two methods differed by 0.2 kcal/mol or less in all cases except for **4** where a barrier of 19.0 kcal/mol was calculated by method B compared to 19.4 kcal/mol calculated by method A. Since it was difficult to use method B for the methyl signals because of the signals from the other methyl groups, the results from method A are felt to be more reliable and are those reported.

**Ir Procedure.** The solutions were placed in ir cells that were 0.5 mm thick. The carbonyl absorptions were measured by recording spectra of the expanded carbonyl region using a slow scan speed and measuring the absorptions relative to the 1583.1- and 1601.4-cm<sup>-1</sup> peaks of polystyrene.

**Acknowledgment.** We thank Darrell K. Wells for the preparation of (acetophenone)tricarbonylchromium.

(33) R. C. Fuson and D. M. Burness, *J. Amer. Chem. Soc.*, **68**, 1270 (1946).

(34) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

(35) This was done for all the complexes except **5** since method B could not be used for the methyl signals since this region of the spectrum was too complex.