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Tricarbonylchromium(0) complexes of 1,3,5-triphenylbenzene: an X-ray crystallographic and high field NMR spectroscopic study

Bavani Mailvaganam, Brian E. McCarry, Brian G. Sayer, Richard E. Perrier, Romolo Faggiani and Michael J. McGlinchey *

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1 (Canada)

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Abstract

The reaction of 1,3,5-triphenylbenzene (TPB) with $Cr(CO)_6$ yields products in which a $Cr(CO)_3$ moiety is bonded to the central ring or to one, two or all three peripheral phenyl rings. The structure of the TPB · $3Cr(CO)_3$ complex has been determined by single crystal X-ray diffraction techniques. The complex crystallizes in the space group $P2_1/n$ with unit cell parameters a 8.316(2) Å, b 15.498(5) Å, c 22.254(4) Å, β 92.18(2)°, V 2865.8(11) Å^3 and $Z = 4$. The structure has been solved by direct and Fourier methods and refined by block diagonal matrix least squares to R_1 and R_2 values of 0.053 and 0.053, respectively, for 2830 observed reflections. The structure reveals that the chromium tricarbonyl groups are bonded to the three peripheral phenyls and these aryl rings adopt dihedral angles of 35°, −26° and 14° with respect to the central ring; these dihedral angles are remarkably similar to those in the free ligand itself. All three $Cr(CO)_3$ tripods are oriented to within a few degrees of being perfectly staggered with respect to the aryl carbon atoms. The 500 MHz ^1H and 125 MHz ^{13}C NMR spectra of these complexes reveal that the peripheral rings do not exhibit restricted rotation even at −90 °C. This contrasts with the situation for (hexaphenylbenzene)$Cr(CO)_3$ the ^1H NMR spectrum of which may indicate slowed rotation of the phenyl rings even at room temperature.

Introduction

In continuation of our studies on organometallic complexes of potentially sterically demanding ligands [1], we decided to extend the early work on π-complexes of polyphenylarenes. In a very fine series of papers [2–7], Nöth and his co-workers demonstrated that 1,3,5-triphenylbenzene formed a set of $Cr(CO)_3$ complexes, **1**, **3** and **4**, containing one, two and three metal fragments, respectively [2]. Even with the 60 MHz NMR instruments then available he was able to show that the chromium

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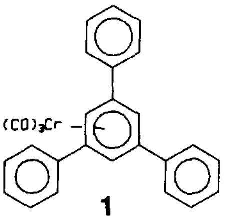
tricarbonyl moiety could π-bond to the central arene ring or to two or even all three of the peripheral aryl groups; he did not, however, observe the complex **2** bearing a single $Cr(CO)_3$ unit on a peripheral phenyl substituent.



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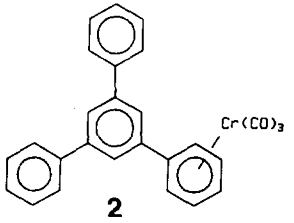

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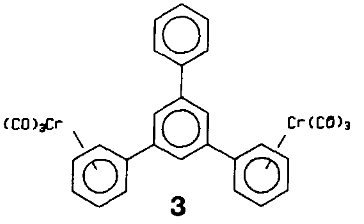

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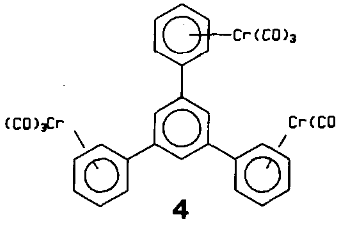

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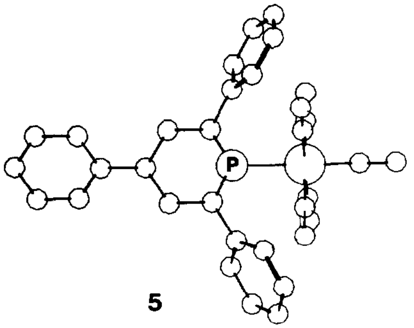
In contrast, reaction of $Cr(CO)_6$ with the 2,4,6-triphenylphosphabenzene system led initially to a pentacarbonylchromium(0) complex, **5**, in which the phosphabenzene functioned merely as a σ-bonded phosphine ligand [3]. Under more forcing conditions, however, the π-bonded complex **6** was obtained [4,5]. The analogous molybdenum complexes are also known [6].



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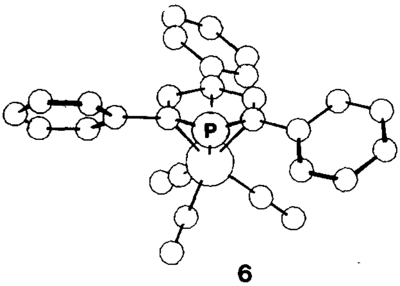

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The reaction with 2,4,6-triphenylpyridine yields complexes in which one, two or three peripheral phenyl rings bear π-bonded $Cr(CO)_3$ moieties but the metal fragment apparently does not complex to the central pyridine ring [7]. Of course, pyridine is not a good π-base and, even under the conditions of metal vapor synthesis [8], it is by no means trivial to prepare η^6-pyridine complexes [9]. Typically, co-condensation of chromium vapor, pyridine and trifluorophosphine leads to a mixture of the σ- and π-complexes, i.e. $(C_5H_5N)Cr(PF_3)_5$ and $(C_5H_5N)Cr(PF_3)_3$, respectively [10]. Clearly, in the case of 2,4,6-triphenylpyridine, the aryl rings are much more attractive targets for a chromium than is the heterocyclic system.

We here describe the synthesis, separation and high field NMR spectra of the molecules **1** through **4** together with the X-ray crystal structure of the tris-$\mathrm{Cr(CO)_3}$ molecule, **4**, and we discuss the conformational equilibria involved.

Results and discussion

The reaction of 1,3,5-triphenylbenzene (TPB) with chromium hexacarbonyl is reported to give a 4% yield of $\mathrm{(TPB)Cr(CO)_3}$ (**1**) in which the metal atom is π-bonded to the central ring of the ligand. This compound is obtained in very small quantities as orange prismatic crystals and was separated from the remaining product (a yellow powder) by careful selection under a microscope [2]. We repeated the reaction under the experimental conditions described by Nöth but we purified the products using reverse phase low pressure liquid chromatography with methanol/water as the eluent. We also obtained tiny quantities of **1**, but the major product was a yellow micro-crystalline material readily assignable as the isomeric $\mathrm{(TPB)Cr(CO)_3}$ complex, viz. **2**. Presumably, this product is the same material as the yellow powder described by Nöth and Deberitz. The identity of the product was easily established by the mass spectrum (which was essentially identical to that previously reported for **1**) and by the NMR spectra. Figure 1(b) shows the 500 MHz ^{1}H NMR spectrum of **2** and the assignments are collected in Table 1. In the whole series of organochromium complexes described herein the aromatic protons of π-complexed rings are in their expected resonance positions in the range δ 5.6–6.3 ppm while the non-complexed ring protons lie in the region δ 7.3–8.0 ppm. At this very high field, the *ortho*, *meta* and *para* protons are clearly resolved and the peak intensities unequivocally demonstrate that one peripheral phenyl ring bears a $\mathrm{Cr(CO)_3}$ unit. We note also that the three protons of the central arene ring in **2** are now split into a 1.7 Hz doublet (2H) and a 1.7 Hz triplet (1H) in accordance with the lowered symmetry. The NMR spectrum also reveals the presence of the minor

Table 1

500 MHz ^{1}H NMR data for triphenylbenzene-$\mathrm{Cr(CO)_3}$ complexes

Compound	Central ring	Peripheral rings		
		Complexed		Non-complexed
TPB	7.90(s)[3H]	–	*ortho*	7.84(d.d)[6H]
			meta	7.52(d.d)[6H]
			para	7.41(t.t)[3H]
$\mathrm{TPB\cdot Cr(CO)_3}$ (1)	6.52(s)[3H]	–	*ortho*	7.93(d)[6H]
			meta	7.51(t)[6H]
			para	7.45(t)[3H]
$\mathrm{TPB\cdot Cr(CO)_3}$ (2)	7.91(d)[2H]	6.32(d)[2H]	*ortho*	7.82(d)[4H]
	7.92(t)[1H]	5.86(t)[2H]	*meta*	7.50(t)[4H]
		5.69(t)[1H]	*para*	7.41(t)[2H]
$\mathrm{TPB\cdot 2Cr(CO)_3}$ (3)	7.93(d)[2H]	6.27(d)[4H]	*ortho*	7.80(d)[2H]
	7.92(t)[1H]	5.86(t)[4H]	*meta*	7.50(t)[2H]
		5.69(t)[2H]	*para*	7.42(t)[1H]
$\mathrm{TPB\cdot 3Cr(CO)_3}$ (4)	7.96(s)[3H]	6.24(d)[6H]	*ortho*	–
		5.87(t)[6H]	*meta*	
		5.71(t)[3H]	*para*	

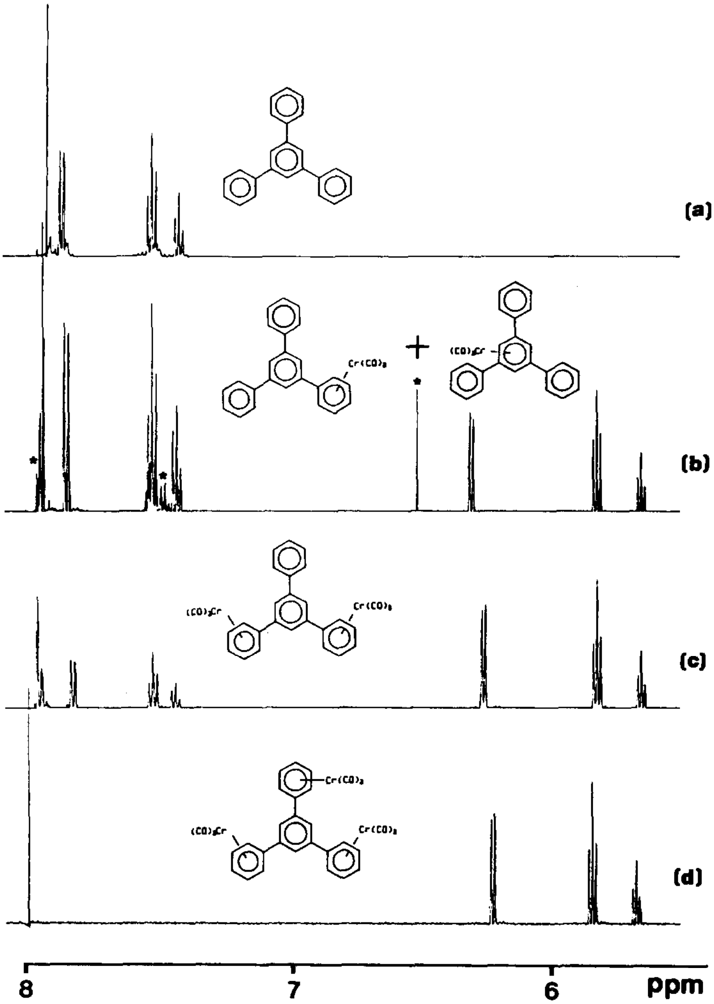


Fig. 1. 500 MHz ^1H NMR spectra of 1,3,5-triphenylbenzene and of (1,3,5-triphenylbenzene)[$Cr(CO)_3]_n$, where $n = 1, 2, 3$; in Fig. 1(b) peaks marked with an asterisk are attributable to the centrally-bonded isomer **1**.

isomer, **1**, in which the metal atom is now attached to the central ring and consequently gives rise to a singlet at δ 6.52 ppm as well as the peaks attributable to the non-complexed peripheral rings.

Furthermore, as previously reported by Nöth and Deberitz, TPB and excess $Cr(CO)_6$ gave the bis- and tris-$Cr(CO)_3$ complexes which were separable only with difficulty by fractional crystallization. These molecules can now be obtained in an almost pristine state by reverse phase low pressure liquid chromatographic techniques. The ^1H NMR spectra of the complexes **3** and **4** are presented in Fig. 1(c) and 1(d) and once more the superb peak resolution achievable at a magnetic field of 11.7 Tesla is clearly demonstrated. The ^{13}C NMR spectral data for molecules **1** through **4** (see the Experimental Section) are completely consistent with the above assignments. The ^1H–^{13}C shift-correlated two-dimensional NMR spectrum of **3**

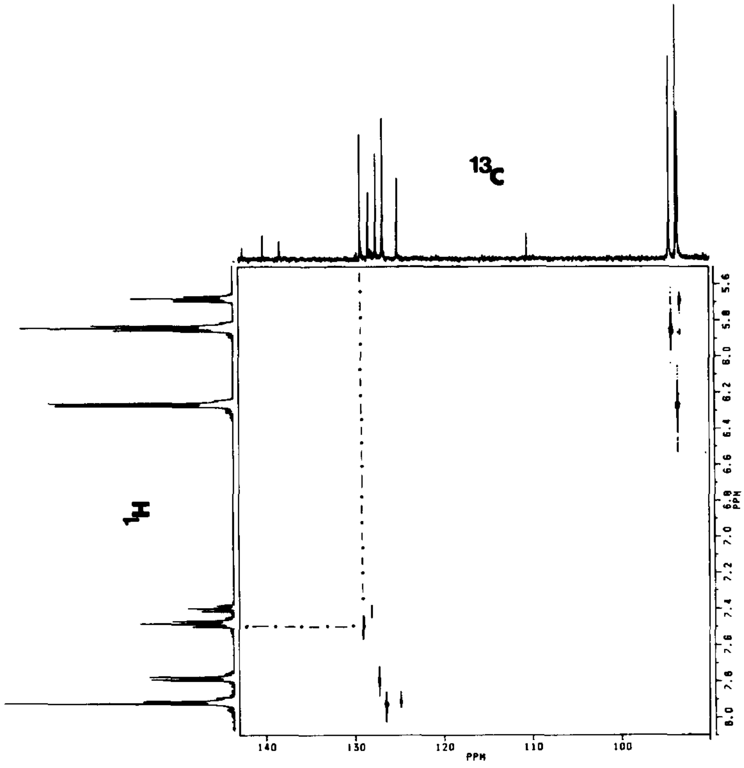
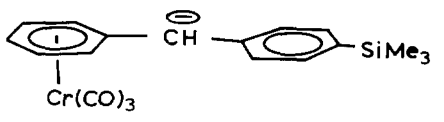


Fig. 2. ^1H–^{13}C Shift-correlated NMR spectrum of (1,3,5-triphenylbenzene)[$Cr(CO)_3$]$_2$ (3); a typical correlation is indicated showing the connectivity of the *meta* carbon of a non-complexed phenyl ring with its attached proton.

appears in Fig. 2 and allows the unambiguous assignment of the carbon shifts. We also recorded the ^1H and ^{13}C spectra of these molecules at −90 °C and found that they were essentially unchanged from their +30 °C counterparts. Clearly, despite the possibility of hindered rotations of the phenyl rings, the aryl rotational barriers must be so small as to preclude the slowing of any fluxional processes on the NMR time scale, at least using line-broadening techniques. This contrasts with the situation in the $Cr(CO)_3$ complexes of the diphenylmethyl anion and related species, such as 7 in which rotation of the phenyl rings can be stopped on the NMR time scale at low temperature [11].



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Indeed, since it is not possible to split the degeneracies of the *ortho* and *meta* protons and carbon nuclei, one has no real information on the conformations of these TPB complexes. This is reminiscent of the problem of the structure of hexaphenylbenzene which in the solid state has been shown by X-ray diffraction to adopt a propeller conformation in which the peripheral rings make angles of ≈ 65°

with the plane of the central ring [12]; an electron diffraction study [13] found that, in the gas phase, the peripheral rings were approximately perpendicular to this plane, with oscillations of ±10°. In a number of elegant studies, Gust has shown that hexaarylbenzenes exist in conformations in which the peripheral rings are perpendicular to the central ring on the NMR time scale [14]. By preparing molecules in which the aryl rings possessed substituents at the *ortho* or *meta* positions, he showed that the interconversions of the multitude of stereoisomers could be accounted for by a mechanism in which only one peripheral ring at a time rotated by $\approx \pi$ radians [15]. The general area of rotation dynamics of polyaryl compounds in solution has been extensively reviewed recently [16].

While it is clear that the potential steric hindrance in 1,3,5-triphenylbenzene is unlikely to be as severe as that encountered in hexaphenylbenzene, the incorporation of rather bulky $Cr(CO)_3$ groups as π-bonded substituents will certainly exacerbate the situation. Moreover, instead of differentiating between edges of aryl rings by using *ortho-* or *meta*-substituents, we are now effectively "painting the faces different colors" by incorporating π-bonded addenda. The steric interaction between peripheral phenyl rings is evident not only in 1,3,5-triphenylbenzene itself but also in the organometallic derivatives of related molecules. Thus, the X-ray crystal structure of TPB itself reveals that the peripheral phenyls are not aligned coplanar with the central ring but instead are rotated through torsion angles of +34°, −27° and +24° [17]; that is, the phenyls are not arranged as in a propeller but rather the pitch of one ring is in the opposite sense to that of the other two. In contrast, the phenyls in (2,4,6-triphenylphosphabenzene)$Cr(CO)_3$ (**6**), in which the chromium is attached to the central ring, are all twisted in the same sense (i.e., like a propeller) and the torsional angles are 43°, 28° and 34° [5]. However, in the analogous pentacarbonylchromium complex, **5**, in which the metal carbonyl fragment is σ-bonded to the phosphorus atom, the peripheral phenyls are not all rotated in the same sense. The phenyls positioned *ortho* to the $Cr(CO)_5$ unit are oriented so as to avoid the large organometallic substituent and adopt relatively large torsion angles of +61° and −74°. The *para* phenyl ring is, of course, too far away to be affected by the metal carbonyl unit and adopts its "normal" torsional angle of +31°. It would seem that torsional angles in the range 30 to 40° are the best compromise so as to minimise steric interactions between the *ortho* hydrogens yet not lose the benefits of conjugation of the rings which is, of course, maximized when the rings are coplanar. Interestingly, an energy minimization using Allinger's Molecular Mechanics calculation [18] on 1,3,5-triphenylbenzene itself yields torsion angles of approximately 38°.

In order to clarify the situation, the X-ray crystal structure of (TPB)$[Cr(CO)_3]_3$ (**4**) was determined and a view of the molecule is shown in Fig. 3. The first and most obvious result was that the metal atoms were indeed coordinated to the peripheral phenyls as had already been deduced from the NMR data. The orientation of the phenyls with respect to the plane of the central arene ring is shown clearly in Fig. 3; the torsional angles are remarkably similar to those in the free ligand itself, in fact, two of them are almost identical (+35° versus +34°; −26° versus −27°) while the third differs only by 10° (+14° versus +24° for TBP). It is also noteworthy that the phenyl rings in **4** which have torsional angles of +35° and −26° (and which are thus facing towards each other) bear $Cr(CO)_3$ groups which are oriented in a distal fashion and hence minimize steric interactions. Likewise, the third

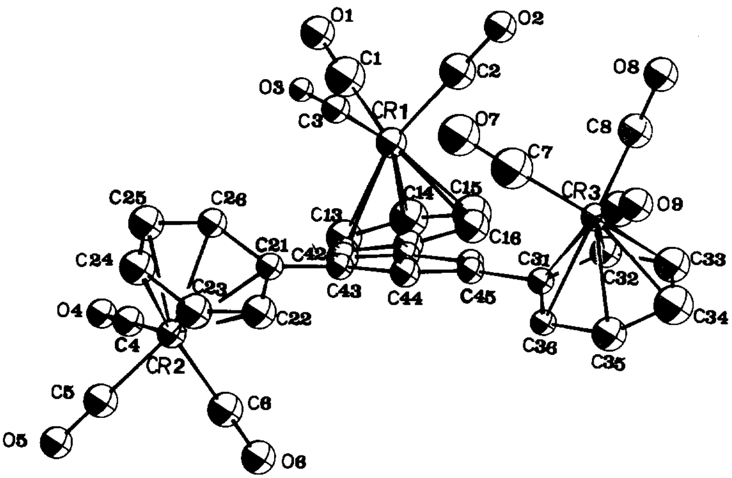


Fig. 3. SNOOPI plot of (1,3,5-triphenylbenzene)[Cr(CO)$_3$]$_3$ (4).

chromium tricarbonyl moiety is positioned so as to avoid the other two. A computer-drawn space-filling model based on the crystallographic data appears as Fig. 4.

The crystallographic data and important bond lengths and angles are collected in Tables 2 through 5. The ring-carbon to chromium distances average 2.212 Å but the bonds to C(11), C(21), and C(31) are significantly longer than this. The phenyl carbon–carbon distances are, as expected, longer than those in the uncomplexed ring (average 1.402 Å versus 1.388 Å). It is noteworthy that the C–C–C angles centred on the ring junction carbons are significantly smaller than the remaining

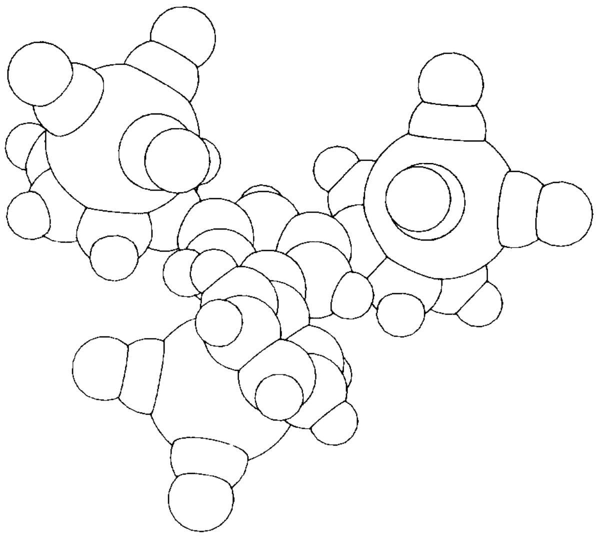


Fig. 4. Computer-drawn space-filling model of 4.

Table 2

Crystal data

Compound	$Cr_3C_{33}H_{18}O_9$
fw (daltons)	714.5
Crystal size, mm	0.27×0.17×0.17
Systematic absences	$h0l$, $h+l=2n$, $0k0$, $k=2n$
Space group	$P2_1/n$
Unit cell	
a, Å	8.316(2)
b, Å	15.498(5)
c, Å	22.254(4)
β, deg	92.18(2)
V, Å^3	2865.8(11)
Z	4
ρ_{calcd}, g/cm^3	1.65
ρ_{obsd}, g/cm^3	1.65
Temperature, °C	22
Linear abs coeff μ, cm^{-1}	12.22
Number of reflections measured	4245
Number of independent reflections	3469
$2\theta_{max}$ reflections measured	45°, $+h$, $+k$, $\pm l$
Number with $I > 3\sigma$	2830
Standard reflections (esd, %)	1.53, 1.42
Final R_1, R_2 ^{a} for $I > 0$	0.0528, 0.0526
Final shift/error, max (av)	0.1 (0.024)
χ (secondary extinction)	−0.00002
Final difference map max peak	0.40
(valley), e Å^3	−0.39
Weighting scheme	$\omega = (\sigma(F^2)+0.00073F_0^2)^{-1}$
Error in an observation of unit weight	1.15

^{a} $R_1 = (\Sigma||F_0| - |F_c||/\Sigma|F_0|)$; $R_2 = [\Sigma\omega(|F_0| - |F_c|)^2/\Sigma\omega F_0^2]^{1/2}$.

intra-ring angles. The average Cr–C and C≡O lengths are 1.83 Å and 1.16 Å, respectively. The angles between carbonyl groups are 88° ± 2°, and the Cr–C–O angles are close to linear.

In each case the disposition of the tripodal fragment is such as to place the carbonyls within a few degrees of being perfectly staggered with respect to the aryl carbon atoms. For exact staggering, the dihedral angles made by the carbonyl vectors with the bonds which join the peripheral and central rings should be +30, +150 and −90°. As shown in Fig. 5, these criteria are well satisfied and the largest deviation from ideality is 11°. We note that in (biphenyl)[Cr(CO)$_3$]$_2$ (**8**) the tripodal units are oriented in exactly this same fashion (see Fig. 6) and furthermore the Cr(CO)$_3$ groups are disposed on opposite faces of the planar biphenyl system [19]. In contrast, we note that the crystal structure of (1,3,5-tripyrrolidinobenzene)Cr-(CO)$_3$ shows the carbonyls to be almost eclipsing the three carbons bearing the amino substituents [20]. The factors influencing the orientation of the metal carbonyl ligands have been extensively discussed [21].

It is now clear that although molecule **4** has C_1 symmetry in the solid state and is chiral, the NMR spectra in solution are consistent with much higher effective symmetry. The magnetic equivalence of all the *ortho* and *meta* protons and

Table 3

Atomic positional parameters and temperature factors ($\mathrm{\AA}^2$) for molecule 4

Atom	x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)	U_{eq} ($\times 10^3$)
Cr(1)	2195.8(8)	1397.4(4)	990.7(3)	29.1(4)
Cr(2)	−3526.8(8)	8654.4(4)	5686.4(3)	30.5(4)
Cr(3)	3784.2(8)	6103.7(4)	7643.8(3)	29.4(4)
C(1)	3489(6)	6895(3)	3319(2)	47(3)
O(1)	3977(6)	7213(3)	2888(2)	78(3)
C(2)	4933(6)	6312(3)	4241(2)	42(3)
O(2)	6279(5)	6242(3)	4379(2)	72(3)
C(3)	2735(5)	7483(3)	4346(2)	38(3)
O(3)	2656(4)	8154(2)	4564(2)	63(3)
C(4)	−3795(6)	8653(3)	4862(2)	45(3)
O(4)	−3959(5)	8653(3)	4347(2)	79(3)
C(5)	−5642(6)	8994(3)	5716(2)	43(3)
O(5)	−6964(4)	9207(3)	5735(2)	71(3)
C(6)	−4271(6)	7532(4)	5704(2)	47(3)
O(6)	−4751(5)	6837(3)	5727(2)	81(3)
C(7)	3681(7)	7232(4)	7426(3)	60(4)
O(7)	3658(7)	7960(3)	7290(2)	107(4)
C(8)	5900(7)	6173(4)	7512(3)	61(4)
O(8)	7259(5)	6215(4)	7416(3)	121(5)
C(9)	4208(6)	6431(4)	8425(2)	52(3)
O(9)	4472(6)	6617(3)	8924(2)	85(3)
C(11)	1089(5)	5948(3)	4692(2)	30(2)
C(12)	199(5)	6267(3)	4176(2)	31(3)
C(13)	475(6)	5963(3)	3600(2)	40(3)
C(14)	1629(6)	5313(3)	3512(2)	42(3)
C(15)	2464(6)	4978(3)	4005(2)	40(3)
C(16)	2220(5)	5293(3)	4592(2)	34(3)
C(21)	−1073(5)	8260(3)	6017(2)	32(3)
C(22)	−2068(6)	8398(3)	6510(2)	36(3)
C(23)	−2862(6)	9184(3)	6583(2)	43(3)
C(24)	−2730(6)	9839(3)	6167(2)	47(3)
C(25)	−1772(6)	9716(3)	5673(2)	47(3)
C(26)	−953(5)	8931(3)	5600(2)	40(3)
C(31)	1953(5)	5753(3)	6919(2)	28(2)
C(32)	3294(5)	5203(3)	6881(2)	32(3)
C(33)	3858(6)	4725(3)	7388(2)	35(3)
C(34)	3109(6)	4795(3)	7926(2)	41(3)
C(35)	1776(6)	5340(3)	7972(2)	39(3)
C(36)	1196(5)	5819(3)	7482(2)	32(3)
C(41)	853(5)	6314(3)	5298(2)	27(2)
C(42)	8(5)	7074(3)	5387(2)	32(3)
C(43)	−209(5)	7423(3)	5944(2)	30(2)
C(44)	460(5)	7002(3)	6448(2)	32(3)
C(45)	1306(5)	6237(3)	6383(2)	28(2)
C(46)	1479(5)	5901(3)	5811(2)	27(2)

carbon-13 nuclei of the peripheral rings militate for the presence of a molecular mirror plane; this, together with the single resonance for the three central arene protons (and carbons), suggests overall C_{3h} symmetry. The most probable time-averaged conformation is the one in which the complexed phenyl rings are perpendicular

Table 4

Selected bond distances (Å) and angles (°)

(a) Chromium – carbon distances					
Cr(1)–C(1)	1.828(5)	Cr(1)–C(2)	1.830(5)	Cr(1)–C(3)	1.844(5)
Cr(1)–C(11)	2.234(4)	Cr(1)–C(12)	2.221(4)	Cr(1)–C(13)	2.214(5)
Cr(1)–C(14)	2.218(5)	Cr(1)–C(15)	2.217(5)	Cr(1)–C(16)	2.212(4)
Cr(2)–C(4)	1.840(5)	Cr(2)–C(5)	1.839(5)	Cr(2)–C(6)	1.847(5)
Cr(2)–C(21)	2.228(4)	Cr(2)–C(22)	2.195(4)	Cr(2)–C(23)	2.208(5)
Cr(2)–C(24)	2.214(5)	Cr(2)–C(25)	2.200(5)	Cr(2)–C(26)	2.198(5)
Cr(3)–C(7)	1.815(6)	Cr(3)–C(8)	1.798(6)	Cr(3)–C(9)	1.832(6)
Cr(3)–C(31)	2.242(4)	Cr(3)–C(32)	2.222(4)	Cr(3)–C(33)	2.212(4)
Cr(3)–C(34)	2.202(5)	Cr(3)–C(35)	2.194(5)	Cr(3)–C(36)	2.213(4)
(b) Carbon – oxygen distances					
C(1)–O(1)	1.165(7)	C(2)–O(2)	1.154(6)	C(3)–O(3)	1.149(6)
C(4)–O(4)	1.148(7)	C(5)–O(5)	1.150(6)	C(6)–O(6)	1.150(7)
C(7)–O(7)	1.168(8)	C(8)–O(8)	1.159(7)	C(9)–O(9)	1.159(7)
(c) Carbon – carbon distances					
C(11)–C(12)	1.430(6)	C(12)–C(13)	1.393(6)	C(13)–C(14)	1.410(7)
C(14)–C(15)	1.377(7)	C(15)–C(16)	1.416(7)	C(16)–C(11)	1.407(6)
C(21)–C(22)	1.415(6)	C(22)–C(23)	1.397(7)	C(23)–C(24)	1.381(7)
C(24)–C(25)	1.396(8)	C(25)–C(26)	1.407(7)	C(26)–C(21)	1.399(7)
C(31)–C(32)	1.408(6)	C(32)–C(33)	1.413(6)	C(33)–C(34)	1.375(7)
C(34)–C(35)	1.401(7)	C(35)–C(36)	1.390(6)	C(36)–C(31)	1.426(6)
C(41)–C(42)	1.389(6)	C(42)–C(43)	1.372(6)	C(43)–C(44)	1.395(6)
C(44)–C(45)	1.389(6)	C(45)–C(46)	1.388(6)	C(46)–C(41)	1.393(6)
C(11)–C(41)	1.481(6)	C(21)–C(43)	1.494(6)	C(31)–C(45)	1.492(6)
(d) Angles involving chromium					
C(1)–Cr(1)–C(2)	86.5(2)	C(2)–Cr(1)–C(3)	89.8(2)	C(3)–Cr(1)–C(1)	88.4(2)
Cr(1)–C(1)–O(1)	177.7(5)	Cr(1)–C(2)–O(2)	178.6(5)	Cr(1)–C(3)–O(3)	178.2(4)
C(4)–Cr(2)–C(5)	87.5(2)	C(5)–Cr(2)–C(6)	87.0(2)	C(6)–Cr(2)–C(4)	89.6(2)
Cr(2)–C(4)–O(4)	179.8(2)	Cr(2)–C(5)–O(5)	179.9(4)	Cr(2)–C(6)–O(6)	178.6(5)
C(7)–Cr(3)–C(8)	86.3(3)	C(8)–Cr(3)–C(9)	89.1(3)	C(9)–Cr(3)–C(7)	89.5(3)
Cr(3)–C(7)–O(7)	178.2(5)	Cr(3)–C(8)–O(8)	178.8(6)	Cr(3)–C(9)–O(9)	178.3(5)
(e) Angles in phenyl rings					
C(11)–C(12)–C(13)	121.6(4)	C(12)–C(13)–C(14)	120.3(4)	C(13)–C(14)–C(15)	119.0(4)
C(14)–C(15)–C(16)	121.3(4)	C(15)–C(16)–C(11)	121.0(4)	C(16)–C(11)–C(12)	116.8(4)
C(21)–C(22)–C(23)	120.9(4)	C(22)–C(23)–C(24)	120.9(5)	C(23)–C(24)–C(25)	119.3(5)
C(24)–C(25)–C(26)	120.1(5)	C(25)–C(26)–C(21)	121.3(5)	C(26)–C(21)–C(22)	117.4(4)
C(31)–C(32)–C(33)	120.6(4)	C(32)–C(33)–C(34)	120.4(4)	C(33)–C(34)–C(35)	119.9(4)
C(34)–C(35)–C(36)	121.0(4)	C(35)–C(36)–C(31)	120.0(4)	C(36)–C(31)–C(32)	118.2(4)
C(41)–C(42)–C(43)	123.3(4)	C(42)–C(43)–C(44)	118.7(4)	C(43)–C(44)–C(45)	120.3(4)
C(44)–C(45)–C(46)	119.1(4)	C(45)–C(46)–C(41)	122.1(4)	C(46)–C(41)–C(42)	116.6(4)

to the plane of the central ring and all three chromium atoms are oriented in the same sense, as in **9**. Indeed, conformations in which two tricarbonylchromium moieties are coplanar and point toward each other possess unacceptably short non-bonded interactions. This situation has been simulated using the program CHEM-X [22] by commencing with the crystallographic data and rotating the peripheral phenyls as in **10**. To render equivalent the *ortho* or the *meta* carbons or protons it is not necessary to allow complete rotation of the complexed phenyl rings

Table 5

Selected dihedral angles

C(11)–center 1–Cr(1)–C(1)	−33.4
C(11)–center 1–Cr(1)–C(2)	86.2
C(11)–center 1–Cr(1)–C(3)	−153.6
C(21)–center 2–Cr(2)–C(4)	−84.5
C(21)–center 2–Cr(2)–C(5)	155.2
C(21)–center 2–Cr(2)–C(6)	37.0
C(31)–center 3–Cr(3)–C(7)	19.2
C(31)–center 3–Cr(3)–C(8)	−98.9
C(31)–center 3–Cr(3)–C(9)	142.1
ring 1–ring 4	−35.0
ring 2–ring 4	−14.4
ring 3–ring 4	26.3

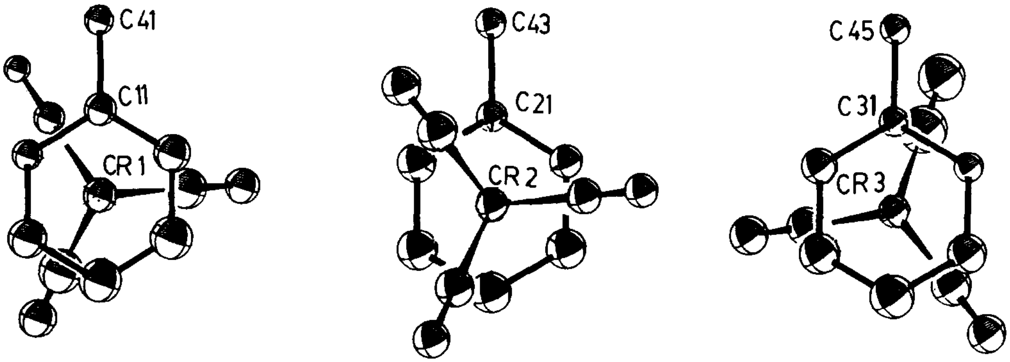
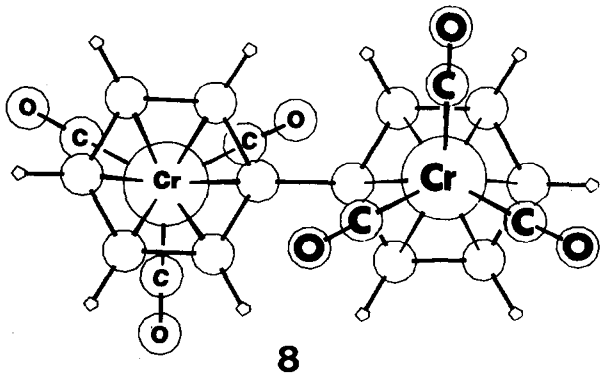


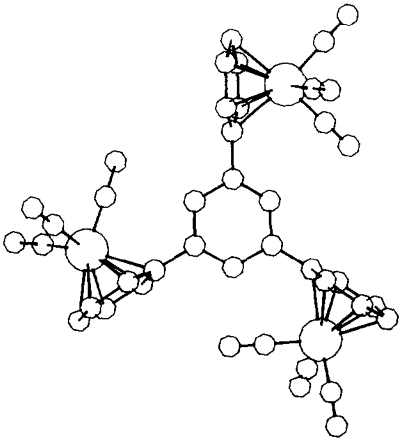
Fig. 5. The almost perfectly staggered orientations of the $Cr(CO)_3$ groups attached to the phenyl rings in **4**.



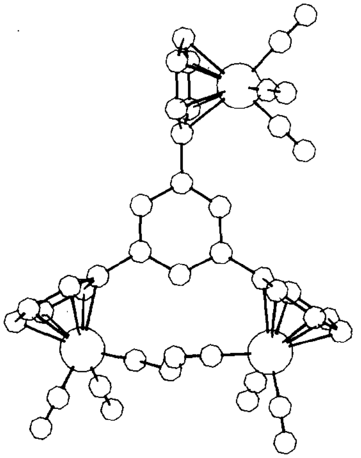
8

Fig. 6. The fully staggered orientations of the $Cr(CO)_3$ groups in **8**, as originally shown in ref. 19.

through 2π radians, one needs merely an oscillation above and below the plane of the central ring.

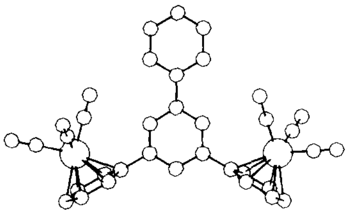


9

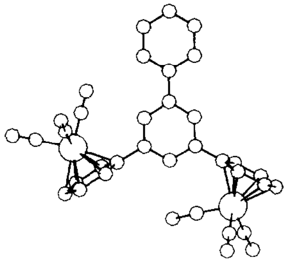


10

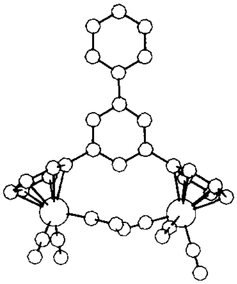
However, the situation is slightly different for the mono- and bis-$Cr(CO)_3$ complexes **2** and **3** which each exhibit effective C_{2v} symmetry. For the latter, one can envisage two rotamers **3a** and **3b** which do not place the $Cr(CO)_3$ substituents uncomfortably close to each other while a third, **3c**, would appear to be unacceptable. Nevertheless, the NMR evidence tells us that the rotational energy barriers are below the levels detectable by line-broadening techniques.



3a



3b



3c

A further point worthy of some comment is the very minor yield of complex **1** which bears a centrally bonded chromium atom. This isomer is presumably the kinetic product which then rearranges to **2** in which the metal is bonded to a peripheral ring. There would appear to be no a priori reason to exclude complexes in which chromium was bonded to both the central and a peripheral ring. Indeed, the existence of the biphenyl$[Cr(CO)_3]_2$ complex, **8** bears testimony to this fact and it may well be the case that such molecules are initially formed under the reaction conditions but subsequently rearrange to give the observed products. A number of recent studies [23–25] have elucidated some of the factors involved in the migration of tricarbonylchromium groups between aryl rings.

Finally, we report that the reaction of hexaphenylbenzene with $Cr(CO)_6$ gives a low yield of a mono-chromium complex **11**. This molecule was identified mass spectrometrically; the 500 MHz ^1H NMR spectrum of **11** is very complex even at room temperature suggesting not only that the metal is bonded to a peripheral ring but also that there is considerable restriction of aryl rotation. We have tentatively assigned all the proton resonances using two-dimensional NMR spectroscopy but, at this time, we prefer not to speculate as to the detailed molecular conformation. Hence, discussion of the structure of this complex is deferred until we can obtain crystals suitable for X-ray diffraction.

To conclude, the reaction of chromium hexacarbonyl with 1,3,5-triphenylbenzene yields complexes in which a single $Cr(CO)_3$ unit binds to either the central or a peripheral ring; the other products possess two or three organometallic fragments on the phenyl rings. The X-ray structure of the tris-$Cr(CO)_3$ complex reveals that the solid state conformation is remarkably similar to that of the free ligand but, in solution, rapid rotation of the phenyl groups equilibrates the *ortho* and *meta* protons and carbon-13 nuclei on the NMR time scale, even at a magnetic field of 11.7 Tesla and a temperature of $-90\,^\circ C$.

Experimental

^1H and ^{13}C NMR spectra were acquired using a Bruker AM500 spectrometer operating at 500 and 125.72 MHz, respectively. All spectra were measured in acetone-d_6. Fast Atom Bombardment (FAB) mass spectrometry was performed on a VG analytical ZAB-SE spectrometer with an accelerating potential of 8 kV and a resolving power of 10000. 3-Nitrobenzyl alcohol was used as the sample matrix and Xe as the bombarding gas.

Reaction of 1,3,5-triphenylbenzene with $Cr(CO)_6$

Following a minor modification of the method of Deberitz and Nöth [2] 1,3,5-triphenylbenzene (2.00 g, 6.5 mmol) and $Cr(CO)_6$ (0.88 g, 4.0 mmol) in freshly distilled di-n-butyl ether (50 ml) and THF (10 ml) were heated under reflux for 24 h under an atmosphere of dry nitrogen. The reaction mixture was allowed to cool to room temperature, filtered under nitrogen and the solvent removed under vacuum. Reverse phase low pressure liquid chromatography (Merck Lobar RP-8 column) was used to separate the mono-chromium products (isolated yield 13%) from the starting material using a mobile phase of methanol/water 80/20 at a flow rate of 4 ml/min on the Merck Size B column. The yellow microcrystalline product was shown by ^1H NMR spectroscopy to be the previously unreported isomer **2** (m.p. 160 °C) but small quantities of isomer **1** were also detectable. The ^{13}C NMR spectrum of **2**, in $CDCl_3$, exhibits peaks at δ (ppm) 233.1 (CrCO), 142.1 (central ring, 2C), 140.6 (phenyls, 2C), 137.3 (central ring, 1C), 128.9 (phenyls, 4 *meta*-CH), 127.8 (phenyls, 2 *para*-CH), 127.5 (central ring, 1CH), 127.2 (phenyls, 4 *ortho*-CH), 125.2 (central ring, 2CH), 109.9 (Cr-phenyl, 1C), 93.5 (Cr-phenyl), 2 *meta*-CH), 92.0 (Cr-phenyl, 2 *ortho*-CH), 91.5 (Cr-phenyl), 1 *para*-CH). The mass spectrum of **2** showed major peaks at m/z (%) 442 (5) $C_{27}H_{18}CrO_3$; 386 (7) $C_{25}H_{18}CrO$; 358 (26) $C_{24}H_{18}Cr$; 306 (100) $C_{24}H_{18}$.

The reaction was repeated using a six-fold excess of $Cr(CO)_6$ and heating under reflux for 24 h. The product mixture was separated via reverse phase low pressure liquid chromatography as described above using an 80/20 methanol/water mobile phase. The products eluted in the order of decreasing molecular weight. The fractions collected were concentrated using a rotary evaporator and the fraction containing **4** was recrystallized from THF/pentane by the vapor diffusion technique to give orange parallelepipeds which were subsequently used for the crystal structure determination. The products **2**, **3** and **4** were obtained pure in isolated yields of 6, 14 and 5%, respectively. No attempt was made to optimize these yields. ^{13}C NMR data: **3**: (in acetone-d_6) δ (ppm) 227.0 (CrCO), 143.0 (phenyl, 1C), 140.7 (central ring, 2C), 138.8 (central ring, 1C), 129.8 (phenyl, 2 *meta*-CH), 128.9 (phenyl, 1 *para*-CH), 128.1 (phenyl, 2 *ortho*-CH), 127.3 (central ring, 2CH), 125.7 (central ring, 1CH), 111.1 (Cr-phenyl, 2C), 95.1 (Cr-phenyl, 4 *meta*-CH), 94.4 (Cr-phenyl, 4 *ortho*-CH), 94.1 (Cr-phenyl, 2 *para*-CH). **4**: (in acetone-d_6) δ (ppm) 226.8 (CrCO), 138.5 (central ring, 3C), 128 (central ring, 3CH), 110.0 (Cr-phenyls, 3C), 94 (overlapping Cr-phenyl CH's).

Reaction of hexaphenylbenzene with $Cr(CO)_6$

Although hexaphenylbenzene itself is not readily soluble in dibutyl ether/THF, it was heated under reflux with an equimolar quantity of $Cr(CO)_6$ for 7 days after which time the reaction mixture had become deep yellow. The solution was allowed to cool, filtered and the solvent removed under vacuum. The resulting orange solid exhibited FAB mass spectral peaks at m/z (%) 670 (6) $C_{45}H_{30}CrO_3$; 614 (5) $C_{43}H_{30}CrO$; 586 (100) $C_{42}H_{30}Cr$; 534 (30) $C_{42}H_{30}$. The 500 MHz ^{1}H NMR spectrum (in acetone-d_6) exhibited peaks at δ (ppm) 7.82 (d, 2H), 7.78 (d, 2H), 7.66 (t, 2H), 7.55 (mult, 4H), 7.0–6.8 (mult, 5H), 6.34 (d, 2H), 6.32 (d, 2H), 6.22 (d, 2H), 6.0 (mult, 2H), 5.87 (t, 2H), 5.7 (mult, 5H).

Collection of the X-ray data

A crystal of **4** was selected and sealed in a Lindemann glass capillary tube. Precession photographs showed the compound to be monoclinic. Accurate unit cell parameters were obtained from a least-squares fit of χ, ϕ and 2θ for 15 well-centered reflections in the range $20° < 2\theta < 28°$. Data were collected on a Nicolet P3 diffractometer using Mo-K_α radiation (λ 0.71069 Å) at 22°C. Crystal data and other parameters related to data collection are summarized in Table 2. Corrections were made for Lorentz and polarization effects but not for absorption. This will introduce a maximum error in F_0 of 2.5%. The density was determined by flotation in aqueous zinc chloride solution.

Solution of the structure

Systematic absences were consistent with the space group $P2_1/n$ (a non-standard setting of $P2_1/c$, No. 14). The structure was solved by direct methods using 50 reflections with $|E| > 1.4$ and 12 sets of starting phases. The chromium atoms were found in the resulting E map and the coordinates were refined. All non-hydrogen atoms were revealed in subsequent three-dimensional difference syntheses. Further refinement using block-diagonal matrices terminated at a maximum shift/error of 0.1. Throughout the refinement, the scattering curves were taken from ref. 26 and anomalous dispersion corrections from ref. 27 were applied to the curve for chromium. The atomic positional parameters are listed in Table 3. All calculations were carried out on a VAX 8600 computer and the structure was solved using programs from the SHELX package (Sheldrick, 1976). Lists of hydrogen atom positions, thermal parameters, and calculated and observed structure factors (19 pages) are available from the authors.

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