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The fluxional behaviour of hexaphenylbenzene chromium tricarbonyl: a variable-temperature ^{13}C NMR spectroscopic study

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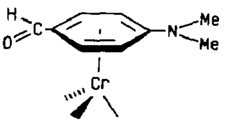
Abstract

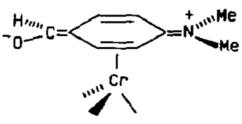
The 125 MHz ^{13}C NMR spectrum of $(C_6Ph_6)Cr(CO)_3$ reveals that the metal is π-bonded to a peripheral ring. At −80 °C this chromium-bonded phenyl exhibits slowed rotation on the NMR time-scale and is effectively orthogonal to the central ring. The fluxional process is shown to involve rotation of the $Cr(CO)_3$-complexed phenyl ring; the activation energy barrier is ≈ 12.2 kcal mol^{-1}, a value much lower than those previously reported for non-complexed hexa-aryl benzenes bearing *ortho* or *meta* methyl or methoxy substituents.

Introduction

In recent years NMR spectroscopy has been employed to investigate hindered rotation around the arene–R bond in a variety of substituted π-bonded arene–metal complexes. For example, the barrier to rotation around the bond between the formyl group and the complexed ring in [*para*-dimethylaminobenzaldehyde]Cr$(CO)_3$, **1**, has been estimated as 8.6 kcal mol^{-1} from variable temperature and line shape analysis [1]. The decrease in rotational barrier compared to the free arene ($\Delta G^{\#} = 10.3$ kcal mol^{-1}) is perhaps best attributed to the stabilization by the $Cr(CO)_3$ moiety of resonance form **1(a)** in which the ring is clearly aromatic and can function as a six-electron donor. Thus, resonance contributors such as **1(b)** in which delocalization of electron density from the dimethylamino group

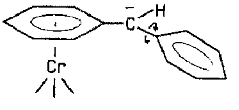


1(a)



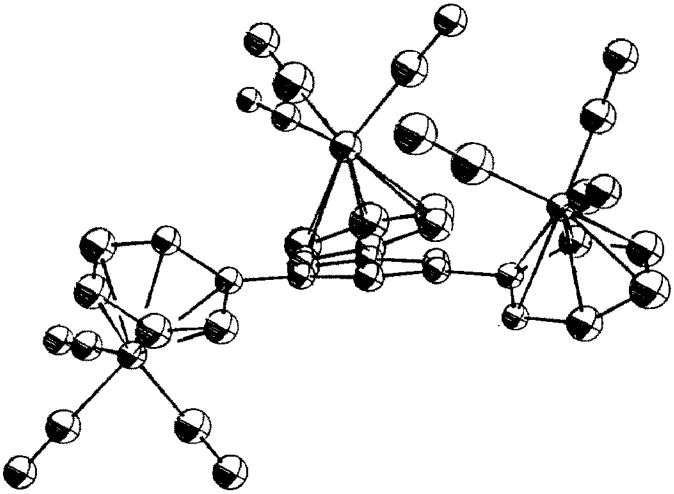
1(b)

has engendered some carbon–carbon double bond character in the formyl unit would be disfavored. In a related study using the bulky arene $(t\text{-}Bu)_2CHC_6H_5$, **2**, a similar decrease of the rotational barrier about the alkyl–arene ring bond upon complexation to $Cr(CO)_3$ ($\Delta G^{\#}$ decreases from 22 to 17 kcal mol^{-1}) was ascribed to additional steric strain between the alkyl and $Cr(CO)_3$ groups in **2** [2]. This effect has also been observed in diarylmethyl anions where the barrier to phenyl rotation in Ph_2CH^- itself is 11.2 kcal mol^{-1} but falls to 8.5 kcal mol^{-1} when both rings bear π-$Cr(CO)_3$ substituents [3,4]. It is noteworthy, however, that when only one $Cr(CO)_3$ is present, as in **3**, the phenyl ring spins freely but the linkage between the π-complexed ring and the anionic center exhibits considerable double bond character and the rotational barrier is large [4].



(3)

Studies of the molecular dynamics of highly substituted arenes have attracted considerable attention for a number of years [5]. Among the more fascinating studies of molecular crowding one could include the work of Gust on derivatives of hexaphenylbenzene [6,7]. The parent molecule, $C_6(C_6H_5)_6$ itself, has been crystallographically characterized and it has been shown that in the solid state the peripheral phenyl substituents are oriented so as to make dihedral angles of approximately 67° with the central ring [8]. A gas phase electron diffraction study showed the peripheral rings to be approximately perpendicular to the central ring, with oscillations of ±10° [9]. In order to evaluate the barriers to peripheral ring rotation, Gust labelled one, or more, phenyls with *ortho*- or *meta*-substituents. This technique allows one to generate a number of stereoisomers the rates of interconversion of which may be followed by dynamic NMR (DNMR) spectroscopy. The general conclusions drawn from Gust's elegant studies are (i) that these interconversions occur via mechanisms involving uncorrelated rotation of single aryl rings and (ii) the



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incorporation of an *ortho* methyl or methoxy group brings about an activation energy barrier of ≈ 33 kcal mol^{-1} while in the corresponding *meta*-substituted systems the barrier is ≈ 17 kcal mol^{-1} [7]. In that study Gust labelled the peripheral rings by effectively "painting the edges different colors" whereas our approach has been to "paint the faces differently" [10]. Typically, the attachment of tricarbonylchromium moieties to all three peripheral rings of 1,3,5-triphenylbenzene, as in **4**, yields a relatively crowded molecule the solid state structure of which has been determined X-ray crystallographically [10]. Despite the apparent molecular crowding in **4**, its low temperature NMR spectra did not provide unequivocal proof of hindered rotation of the π-$Cr(CO)_3$–C_6H_5 rings. We have reported some preliminary data on the products obtained from the reaction of hexaphenylbenzene (HPB) with $Cr(CO)_6$ [10]. However, at that time we were unable to obtain pure samples in sufficient quantity to permit the reliable assignment of their NMR spectra. We now describe the results of our continuing efforts in this area.

Results and discussion

Some years ago, Gust and Mislow developed a general and systematic approach to the topological analysis of isomerism and isomerization for compounds belonging to such triaryl systems as Ar_3CH, Ar_3N, Ar_3P, Ar_3B and Ar_3C^+ [11]. Subsequently, it was noted that the motions of these aryl rings are coupled in such a way that none of the rings moves independently of the others; such processes are termed *correlated rotations* [12]. In a recent elegant extension of this concept Mislow has demonstrated that molecules containing a closed cyclic array of securely meshed gears have parity constraints entirely analogous to mechanical systems [13].

In Gust's definitive series of papers on hexa-arylbenzenes, it was shown that interconversions of the stereoisomers are best rationalized in terms of a mechanism involving uncorrelated rotation of only one peripheral ring at a time through $\approx \pi$ radians. In an attempt to study the effects of π-bonded addenda on polyphenylarenes, we examined the DNMR spectra of the 1,3,5-triphenylbenzene complex **4** in which each of the peripheral rings bears a π-bonded $Cr(CO)_3$ moiety. Although in the solid state the bulky substituents in **4** orient themselves so as to avoid each other, the low temperature NMR spectra show no definitive evidence for slowed rotation of the peripheral rings. Consequently, we focussed our efforts on obtaining a $Cr(CO)_3$ complex of the more sterically demanding ligand hexaphenylbenzene (HPB).

The reaction of hexaphenylbenzene with $Cr(CO)_6$ gives a mixture of chromium complexes in low yields. Separation of the mixture was by no means trivial and was finally achieved by using high pressure liquid chromatography. The products were identified by Fast Atom Bombardment mass spectrometry as the mono- and bis-tricarbonylchromium complexes of HPB. However, the yields were such that sufficient material for variable-temperature ^{13}C NMR studies was available only for the mono-chromium complex. The 500 MHz ^1H NMR spectrum of $(HPB)Cr(CO)_3$, **5**, indicates very clearly that the $Cr(CO)_3$ moiety is bonded to a peripheral phenyl ring. The protons of the complexed ring lie in the range δ 4.7–5.4 while the non-complexed ring protons resonate between δ 6.8 and δ 7.1. Measurement of the proton peak intensities gave a ratio of 1 : 5 for the complexed versus non-complexed ring environments.

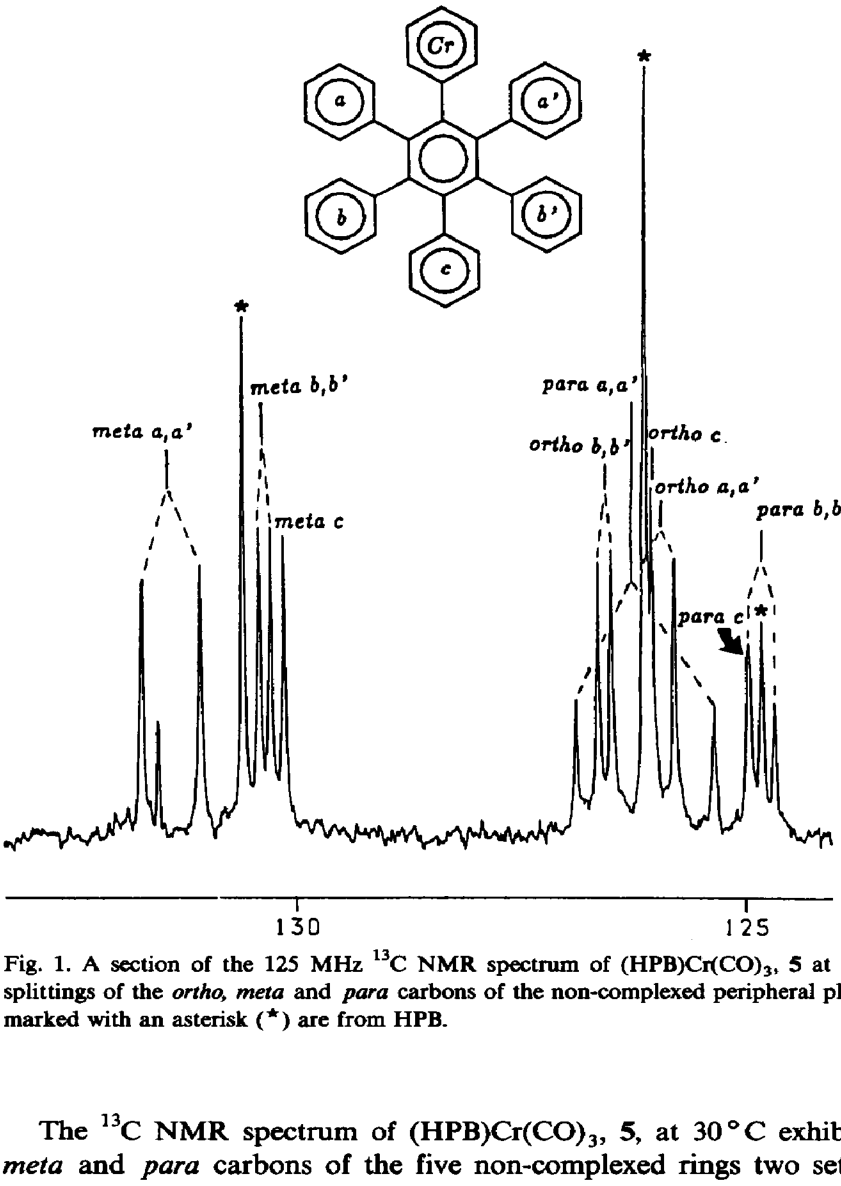

Fig. 1. A section of the 125 MHz ^{13}C NMR spectrum of $(HPB)Cr(CO)_3$, 5 at −80 °C, showing the splittings of the *ortho*, *meta* and *para* carbons of the non-complexed peripheral phenyl rings. The peaks marked with an asterisk (*) are from HPB.

The ^{13}C NMR spectrum of $(HPB)Cr(CO)_3$, 5, at 30 °C exhibits for the *ortho*, *meta* and *para* carbons of the five non-complexed rings two sets of 4:4:2 peak patterns corresponding to the a,a′ and b,b′ rings and a 2:2:1 peak pattern for the c ring. Likewise, the chromium-complexed ring shows a 2:2:1 pattern in the δ 85–105 region typical of π-coordinated arenes. We can therefore deduce that at room temperature the molecule has effective C_{2v} symmetry.

However, as shown in Fig. 1, on cooling the sample to −80 °C a number of the various *ortho*, *meta* and *para* carbons split into doublets indicating some type of slowed peripheral ring rotation on the NMR time scale. The ^{13}C NMR data are collected in Table 1, and Fig. 2 shows two viable limiting structures, **5(a)** and **5(b)**, for $(HPB)Cr(CO)_3$. In **5(a)**, the five non-complexed rings are orthogonal to the centre ring but the complexed ring is coplanar with the central ring, whereas in **5(b)** the complexed and the non-complexed rings are all orthogonal to the central ring. In assigning either of these structures to the low temperature spectrum the peak patterns of the various *ortho*, *meta* and *para* carbons must be taken into considera-

Table 1

^{13}C NMR data for hexaphenylbenzene (HPB) and for (HPB)Cr(CO)$_3$, 5, at −80 °C in CD$_2$Cl$_2$

	ortho	*meta*	*para*	*ipso*
HPB [a]	126.09	130.57	124.80	140.65 141.12
(HPB)Cr(CO)$_3$				
Cr ring	88.14	99.50	93.81	111.82
Rings a,a′	126.09 125.76	131.69 131.05	126.86 125.32	139.80 [b] 137.22
Rings b,b′	126.61 126.46	130.40 130.27	124.93 124.66	141.54 139.92
Ring c	126.09	130.12	124.93	140.64
Central ring	–	–	–	141.77/139.90 139.74/139.70 139.92 131.50

[a] These shifts are almost identical to those reported in ref. 19. [b] The assignments of the *ipso* carbons are tentative. We do, however, show the pairs of carbon resonances which coalesce.

tion. Of the three types, the *para* carbons are the simplest to consider. In the case of 5(a) the a_{para} and a'_{para} (also the b_{para} and b'_{para}) carbons are symmetrically disposed about the molecular mirror plane and so a 2 : 2 : 1 pattern is expected. In

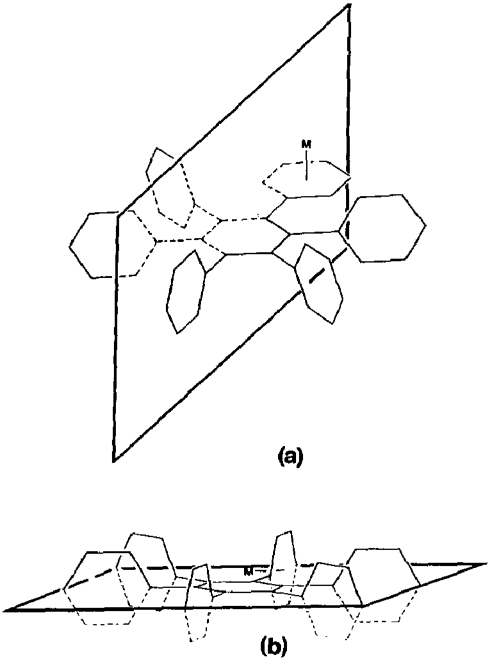

Fig. 2. Views of two rotamers of 5 possessing C_s symmetry in which (a) the molecular mirror plane bisects the central ring and the complexed ring, or (b) the central arene lies in the mirror plane while all six peripheral rings are orthogonal.

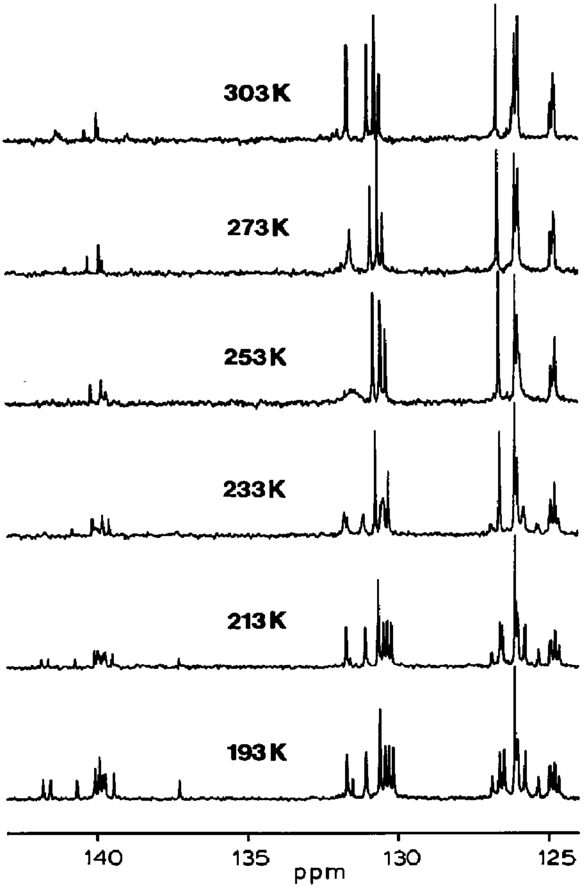

Fig. 3. Sections of the 125 MHz ^{13}C variable-temperature NMR spectra of (HPB)Cr(CO)$_3$, 5, over the range −80 °C to +30 °C showing six sets of peak coalescences.

contrast, for **5(b)**, the five *para* carbons of the non-complexed rings lie in the molecular mirror plane and so should be magnetically nonequivalent; in the limit this will produce a 1 : 1 : 1 : 1 : 1 peak pattern. The experimentally observed spectrum at −80 °C (Fig. 3) shows the 1 : 1 : 1 : 1 : 1 pattern for the *para* carbons in accord with conformation **5(b)**. Figure 3 depicts the beautiful coalescence pattern observed in this system on warming the sample from −80 to 30 °C.

The *ortho, meta* and *para* ^{13}C NMR resonances for ring c are readily assigned not only on the basis of intensities but also because these environments are not split at low temperatures. The *ortho, meta* and *para* resonances of rings a/a′ and b/b′ have been differentiated on the basis of the magnitude of their chemical shift separation at low temperature. We make the reasonable assumption that the proximity of the a/a′ rings to the Cr(CO)$_3$ fragment will lead to a greater chemical shift discrimination. Ideally, one would prefer to make the ^{13}C NMR assignments for the a, b and c rings on the basis of unequivocal 2-D correlations between the protons and their attached carbons. Such experiments were not viable in this instance because of the limited quantities of sample available. Each regular 1-D ^{13}C NMR spectrum required 3–4 hours even on the AM 500.

It is apparent that in each of the *ortho*, *meta* and *para* carbon regions there are two sets of coalescences. For each of these exchange processes, the activation energy barrier is readily evaluated from a knowledge of the chemical shift separations and coalescence temperatures. These six independently measured $\Delta G^{\#}$ values lie in the range 12.2 ± 0.2 kcal mol^{-1} which suggests that they are all manifestations of a single fluxional process.

These results are rationalizable in terms of conformation **5(b)** in which all the peripheral phenyl rings are orthogonal to the centre ring and the molecule possesses C_s symmetry whereby the single mirror plane contains all six atoms of the central ring. This renders equivalent the edges of any given phenyl ring. For example, the two *ortho* carbons of ring a are equivalent but the *ortho* carbons of rings a and a′ are not. The fluxional process must involve rotation of the chromium-complexed ring relative to the central ring; this would lead to effective C_{2v} symmetry thus equilibrating the four *ortho*, the four *meta* and the two *para* environments in the a/a′ and b/b′ rings. Since the two *ortho* and the two *meta* carbons in any particular aryl ring are always equivalent, it is not possible to say whether the non-complexed phenyl rings are undergoing rapid rotation. However, in the light of Gust's work on substituted hexa-arylbenzenes, it is a reasonably safe assumption that these phenyl moieties can rotate relatively freely.

To summarize, therefore, although incorporation of three π-$Cr(CO)_3$ fragments into 1,3,5-triphenylbenzene does not provide evidence for slowed peripheral ring rotation, use of the more sterically demanding hexaphenylbenzene requires only a single $Cr(CO)_3$ group in order to display restricted rotation of the complexed ring. Nevertheless, the rotational barrier of ≈ 12.2 kcal mol^{-1} is considerably lower than that encountered for non-complexed HPB derivatives with methyl substituents in *meta* positions. In order to gain some understanding of the electronic and steric factors involved, we carried out EHMO calculations on a series of rotamers of $(HPB)Cr(CO)_3$.

A combination of molecular modelling studies and EHMO calculations revealed that, as anticipated from the X-ray data on HPB, the favored orientations of the peripheral rings are at $\approx 65°$ to the plane of the central ring. This conformation provides the best compromise between the unfavorable steric interactions arising

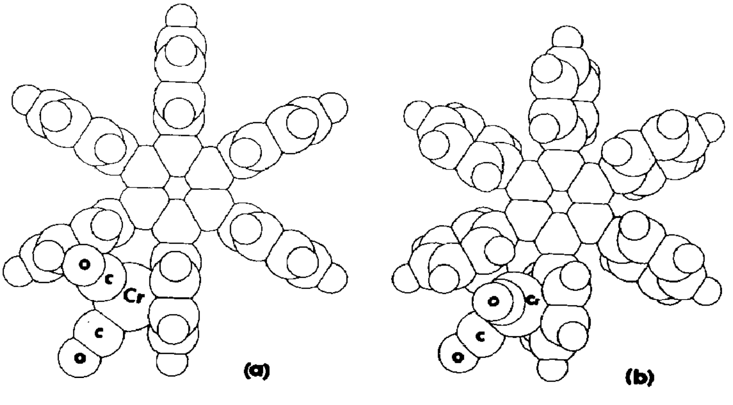

Fig. 4. Space-filling models of **5(b)** where (a) all six peripheral rings are orthogonal to the central ring and (b) all six outer rings are oriented at a dihedral angle of 70°.

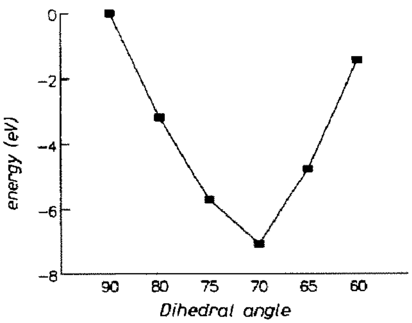

Fig. 5. Energy level diagram showing the effect of conrotation of the peripheral rings with respect to the central arene in 5.

from the *ortho*-hydrogens and the preference for maintaining the optimum orbital overlap between the central and peripheral π-systems. It is readily apparent from Fig. 4 that in (HPB)Cr(CO)$_3$, 5, the rotamer with all peripheral rings orthogonal to the central ring poses severe steric problems because of the proximity of the carbonyl ligands to the neighboring phenyl ring.

By using the EHMO approach, one finds that conrotatory movement of all the peripheral rings leads to a pronounced minimum in the sum of the one-electron energies for a dihedral angle of $\approx 70°$, as shown in Fig. 5. The orientation of the tripod with respect to the complexed arene ring follows that found in the crystal for the tris-Cr(CO)$_3$ complex of 1,3,5-triphenylbenzene where all three tripods eclipse carbon–carbon bonds rather than eclipsing ring carbon atoms [10].

Experimental

^{13}C NMR spectra were recorded at 5° intervals by using a Bruker AM 500 spectrometer operating at 125.7 MHz. All spectra were measured in methylene chloride-d_2 and chemical shifts are reported relative to tetramethylsilane. Fast Atom Bombardment (FAB) mass spectrometry was performed on a VG analytical micromass ZAB-E reversed-geometry double-focusing mass spectrometer with an accelerating potential of 8 kV and a resolving power of 10,000 and VG11/250 data system. 3-Nitrobenzyl alcohol was used as the sample matrix and Xe as the bombarding gas. Infrared data were obtained on a Perkin–Elmer 283 spectrometer using NaCl solution cells. All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures before use [14]. Micro-analytical data are from Guelph Chemical Laboratories, Guelph, Ontario.

Preparation of tricarbonyl(hexaphenylbenzene)chromium(0), 5

Hexaphenylbenzene itself is not readily soluble in any of the common solvents. Consequently, hexaphenylbenzene (0.677g, 1.27 mmol) and Cr(CO)$_6$ (0.316 g, 1.44 mmol) were heated under reflux in n-Bu$_2$O (90 cm^3) and THF (10 cm^3) during 7 days. The initial suspensions gave a milky yellow solution which eventually turned black. This solution was allowed to cool and was then filtered under vacuum to give a bright yellow filtrate and an unidentified black solid; the excess solvent was removed on a rotary evaporator at 60 °C. Thin layer chromatography on silica showed the product to contain a number of yellow complexes. Two of these complexes were isolated by using Reverse Phase High Pressure Liquid Chromatography on a Vydac RP C_{18} column with 80/20 methanol/water as eluent. The first yellow band collected was identified as $(C_6Ph_6)[Cr(CO)_3]_2$ only by FAB mass spectrometry: m/z (%) 722 (8) $C_{45}H_{30}Cr_2O_3$ $(M-3CO)^+$, 670 (10) $C_{45}H_{30}CrO_3$ $(M-3CO-Cr)^+$, 586 (100) $C_{42}H_{30}Cr$, 534 (35) $(HPB)^+$. The major product collected was $(C_6Ph_6)Cr(CO)_3$, **5**, (43 mg; 5%), m.p. > 300 °C. FAB mass spectrum: m/z (%) 670 (10) $C_{45}H_{30}CrO_3$ $(M)^+$, 586 (70) $C_{42}H_{30}Cr$ $(M-3CO)^+$, 534 (26) $C_{42}H_{30}$ $(HPB)^+$. The ^{13}C NMR data are collected in Table 1. IR (CH_2Cl_2): ν_{CO} 1975 and 1900 cm^{-1}. Anal. Found: C, 80.27; H, 4.22. $C_{45}H_{30}CrO_3$ calcd: C, 80.58; H, 4.51%.

Molecular orbital calculations. All calculations were carried out within the Extended Hückel formalism [15,16] using the weighted H_{ij} formula [17]. The bond lengths (phenyl rings: C–C = 1.39, complexed phenyl ring: C–C = 1.40, $Cr-C_{Ar}$ = 2.21, Cr–C(O) = 1.83, C–O = 1.16 Å, C–H = 1.1 Å) were taken from the idealized X-ray crystal structure of (1,3,5-triphenylbenzene)$[Cr(CO)_3]_3$ [10]. The atomic parameters used were taken from reference [18].

Acknowledgments

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