

# Stereoelectronic effects on arene rotation: the structure and fluxionality of $[1,4\text{-C}_6\text{H}_4(\text{SiMe}_3)_2]\text{Cr}(\text{CO})_2\text{PPh}_3$ and $[1,3,5\text{-C}_6\text{H}_3^t\text{Bu}_3]\text{Cr}(\text{CO})_2\text{PPh}_3$

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## Abstract

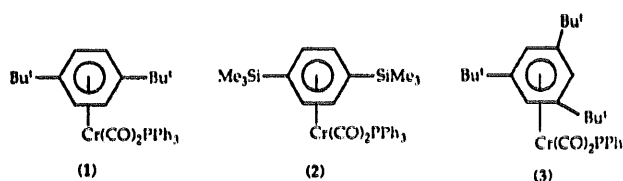
Barriers to metal–arene ring rotation in  $[1,4\text{-C}_6\text{H}_4(\text{SiMe}_3)_2]\text{Cr}(\text{CO})_2\text{PPh}_3$  and  $(1,3,5\text{-C}_6\text{H}_3^t\text{Bu}_3)\text{Cr}(\text{CO})_2\text{PPh}_3$  are lowered relative to a previously reported barrier of  $32\text{ kJ mol}^{-1}$  for  $(1,4\text{-C}_6\text{H}_4^t\text{Bu}_2)\text{Cr}(\text{CO})_2\text{PPh}_3$ . Reasons for the decreased barriers are discussed in the light of crystal structure determinations of these complexes.

**Keywords:** Chromium; Arene; Fluxionality; Carbonyl; Phospine

## 1. Introduction

There has been considerable interest in the study of rotational barriers in metal–arene complexes in recent years, concentrating mainly on slowed tripod rotation in  $(\text{arene})\text{Cr}(\text{CO})_3$  and related derivatives. For  $(\text{benzene})\text{Cr}(\text{CO})_3$  and its simpler derivatives, the computed low energy barriers to rotation ( $\leq 5\text{ kJ mol}^{-1}$ ) [1,2] have been confirmed by electron diffraction measurements in the gas phase [3] and  $^{13}\text{C}$  spin lattice relaxation measurements in solution [4]. Higher barriers which are amenable to study by variable temperature NMR methods may be generated either electronically by partial localisation of the arene ring [5] or sterically through introduction of demanding groups either on the ring or on the metal (for a comprehensive review which includes all leading references, see Ref. [6]). Though substitution of CO by phosphine might be expected to increase the barrier to rotation, in practice steric congestion in  $\text{C}_6\text{Et}_6$  complexes is relieved through an increase in the distal/proximal ratio of the methyl groups and arene–M rotation remains rapid on the NMR time scale at low temperature. Only in three cases have barriers

been measured for  $(\text{arene})\text{Cr}(\text{CO})_2\text{PPh}_3$  complexes [7,8], and for several other molecules [9], restricted M–P rotation is the process of highest energy. We have recently determined the molecular structure and barrier to rotation in  $(1,4\text{-C}_6\text{H}_4^t\text{Bu}_2)\text{Cr}(\text{CO})_2\text{PPh}_3$  (1) [8], and wish to report here our results on the structure and fluxionality of  $[(1,4\text{-C}_6\text{H}_4(\text{SiMe}_3)_2)]\text{Cr}(\text{CO})_2\text{PPh}_3$  (2) and  $(1,3,5\text{-C}_6\text{H}_3^t\text{Bu}_3)\text{Cr}(\text{CO})_2\text{PPh}_3$  (3) which shed further light on the influence of stereoelectronic effects on rotational barriers in complexes of this type.



## 2. Results and discussion

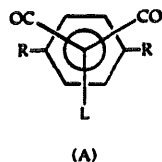
Complexes 2 and 3 were prepared from the tricarbonyls by photolysis (complex 3 has previously been prepared, but not studied by VT NMR methods, see

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Ref. [10]).  $^{13}\text{C}$  NMR spectra of the tricarbonyls are temperature invariant down to  $-115^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$ . The molecular structures of complexes 1–3 are shown in Fig. 1, and important geometrical data are given in Table 1.

### 2.1. Structure and fluxionality of complex 2

Complexes 1 and 2 both exhibit the staggered conformation (A) which is favoured on both electronic and steric grounds.



Sterically, the large  $\text{PPh}_3$  ligand is placed furthest from the  $\text{EMe}_3$  ( $\text{E} = \text{C}, \text{Si}$ ) substituents. Electronically, the  $\text{ML}_3$  fragment may be regarded as having two interpenetrating trios of orbitals, three of which are lone pair and parallel to the  $\text{M-L}$  axes and three of which are empty and localised in regions of space which stagger the  $\text{M-L}$  axes. Thus, the  $\text{ML}_3$  moiety will orient itself such that the empty hybrids point towards the region of highest electron density. For a *para*-disubstituted electron donor complex, this is best satisfied by conformation (A) [2]. A comparison of 1 and 2 reveals reduced steric distortion in 2. Whereas in 1 both the arene C1/4 and  $\text{CMe}_3$  carbons are displaced away from the C2/3/5/6 plane by 0.07 and 0.35 Å respectively, the arene ring in 2 is essentially planar, with the silicon atoms displaced by 0.29 Å from the arene plane. Si-C bond lengths are comparable with those in  $(\text{C}_6\text{H}_3\text{SiMe}_3)\text{M}(\text{CO})_3$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) [11].

One other minor structural variation between 1 and 2 may be noted, in that if viewed down the C1–C4 axis the arrangement of the methyl groups is approximately staggered in 2 but eclipsed in 1. Crystal structure determinations of both free ligands [12] reveal a staggered configuration in the solid state, though MM2 calculations on the free ligands show less than  $0.5 \text{ kJ mol}^{-1}$  difference between the eclipsed and staggered conformations. In 1 and 2, the methyl groups adopt positions which minimise interactions with the  $(\text{CO})_2\text{PPh}_3$  moiety. However, the conformations of the phosphines are likely to be determined by crystal packing forces as they reach into the crystal structure.

NMR studies also reveal a reduced rotational barrier for 2 compared with 1. Whereas in 1 the  $^{13}\text{C}(2,3,5,6)$  resonance is resolved into two at  $-115^\circ\text{C}$ , the analogous resonance for complex 2 is only substantially

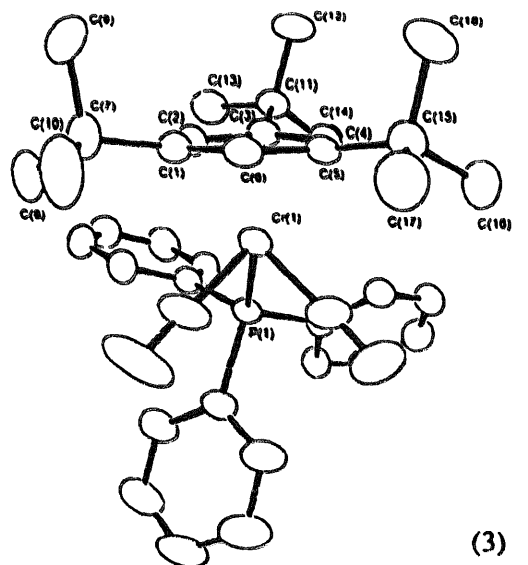
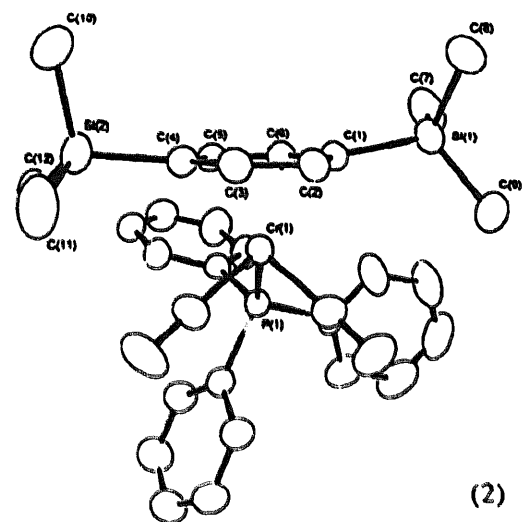
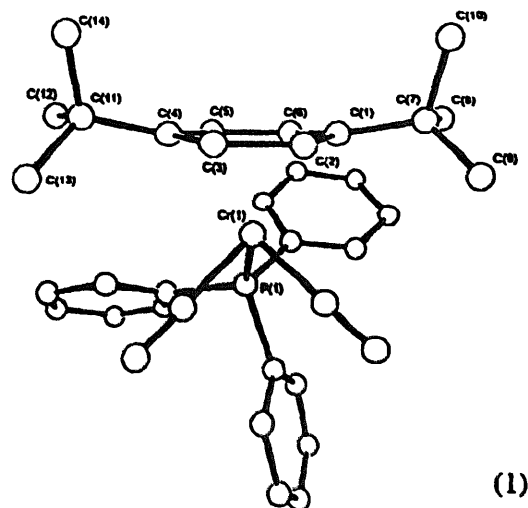


Fig. 1. Molecular structures of complexes 1 to 3.

Table 1  
Important geometrical data for complexes 1 to 3<sup>a</sup>

	1	2	3
Cr–P	2.328(2)	2.332(1)	2.339(1)
Cr–CO (av)	1.813(8)	1.828(2)	1.812(4)
Cr–C(arene)			
	C1	2.274(1)	2.251(3)
	C2	2.168(1)	2.260(3)
	C3	2.188(1)	2.345(3)
	C4	2.236(2)	2.258(3)
	C5	2.201(2)	2.212(3)
	C6	2.222(1)	2.205(3)
C–O (av)	1.174(8)	1.157(2)	1.163(5)
C(arene)–EMe <sub>3</sub> (av)	1.51(1)	1.888(2)	1.535(4)
E–Me (av) (E = C, Si)	1.51(1)	1.864(3)	1.526(6)
P–C (av)	1.842(7)	1.837(2)	1.848(3)
OC–Cr–CO	82.9(3)	86.7(1)	84.4(2)
P–Cr–CO	89.5(3)	87.6(1)	86.5(1)
	91.5(3)	88.4(1)	85.6(1)
Me–E–Me (av)	107.9(9)	109.9(1)	108.5(3)
C–P–C (av)	100.4(3)	101.8(1)	101.0(2)

<sup>a</sup> Bond lengths in Å, bond angles in deg.

broadened at this temperature. Assuming, however, that the chemical shift difference for the C(2,3)/C(5,6) pairs is the same for both 1 and 2, a barrier of  $29 \pm 2 \text{ kJ mol}^{-1}$  may be estimated compared with  $31.6 \text{ kJ mol}^{-1}$  for complex 1 [assuming  $\Delta\delta = 513 \text{ Hz}$ , rate constants ( $\text{s}^{-1}$ ) and  $\Delta G^\ddagger$  values ( $\text{kJ mol}^{-1}$ ) are 59000, 28.9 (193 K), 11000, 28.1 (173 K) and 860, 28.9 (158 K); an uncertainty factor of two in the chemical shift difference corresponds to an error margin of  $2 \text{ kJ mol}^{-1}$  in  $\Delta G^\ddagger$ ]. An analogy with organic chemistry may be found in the reduced barrier for rotation found in  $\text{CH}_3\text{SiH}_3$  ( $7.1 \text{ kJ mol}^{-1}$ ) compared with  $\text{CH}_3\text{CH}_3$  ( $12.1 \text{ kJ mol}^{-1}$ ) [13].

## 2.2. Structure and fluxionality of complex 3

Surprisingly, NMR studies of 3 also reveal a reduced rotational barrier relative to 1, with the C(2,4,6) resonance exhibiting only a substantially broadened resonance at  $-115^\circ\text{C}$  (Fig. 2) rather than the 2:1 pair expected for any conformation which is static on the NMR time scale. Assuming a value of 5–10 ppm for the chemical shift difference between limiting low temperature resonances (the spectrum of  $[(\text{C}_6\text{Et}_6)\text{Cr}(\text{CO})(\text{CS})(\text{NO})]^+$  at 168 K shows six ring resonances spread over a 6–7 ppm range, see Ref. [14]), a rotational barrier of  $28 \pm 3 \text{ kJ mol}^{-1}$  may be calculated [using  $\Delta\delta = 5 \text{ ppm}$ , rate constants ( $\text{s}^{-1}$ ) and  $\Delta G^\ddagger$  ( $\text{kJ mol}^{-1}$ ) values are 92000, 29.5 (193 K), 34000, 27.7 (173 K) and 4500, 27.9 (158 K)].

A rationalisation for this result may be obtained through analysis of the molecular structure. There are two independent molecules in the asymmetric unit and their structures are almost identical, with only minor differences in geometry. Maximum steric pressure is

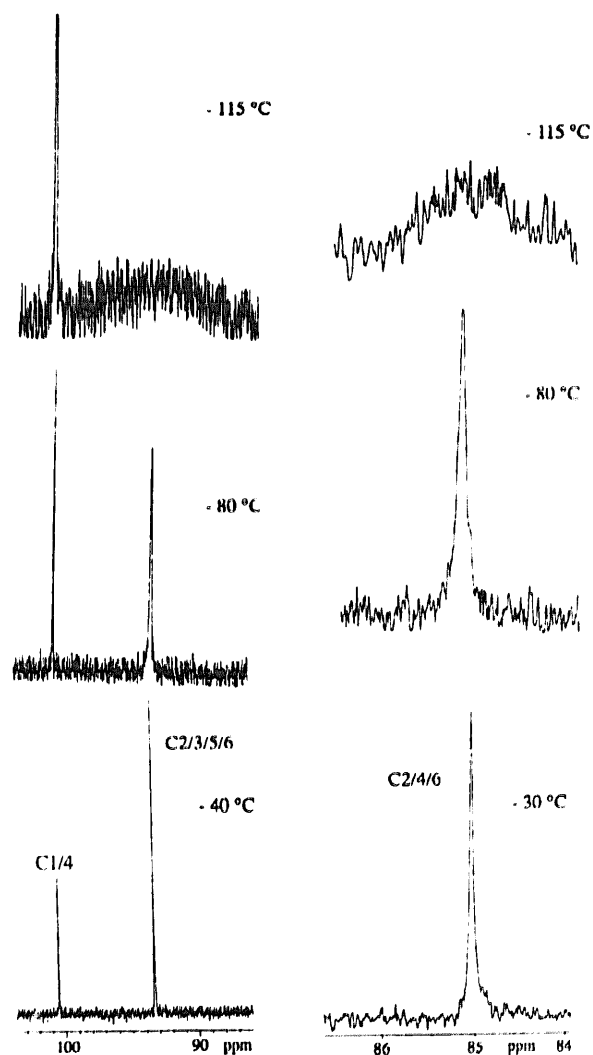


Fig. 2. Variable temperature  $^{13}\text{C}$  NMR spectra of 2 and 3 ( $\text{CD}_2\text{Cl}_2$ ).

observed in the interaction between the butyl group on C(3) and the phosphine. The aromatic rings bonded to chromium are essentially planar, with a maximum deviation from the plane of 0.037 Å; maximum deviations in both rings are shown by the atoms C(3) and C(103) which bear the substituent which is directly above the phosphine. The chromium–ring carbon distances are normal for all except Cr(1)–C(3) and Cr(2)–C(103) which unusually are longer than the Cr–P bonds. The effect of steric pressure is also clear when the deviations of the tertiary carbons in the butyl groups from the planes of the aromatic rings are examined; C(7), C(11) and C(15) are 0.243, 0.446 and 0.208 Å out of the plane away from the chromium (the corresponding figures for the other molecule are 0.195, 0.434 and 0.236 Å). Considerable compression of the interligand angles ( $L-Cr-L(av) = 86^\circ$ ) is also observed. The electronic preference for the eclipsed configuration is thus substantial, providing a ground state molecule which appears much closer in energy to the steric demands of the transition state for arene rotation than the staggered ground states of **1** and **2**, where stereoelectronic influences reinforce a much deeper ground state energy well. [(Mesitylene)M(CO)<sub>2</sub>L complexes also exhibit eclipsed structures, though displacement of methyl groups from the arene plane is not above 0.07 Å, see Ref. [15]; the structure of (1,3,5-C<sub>6</sub>H<sub>3</sub>(Bu<sub>3</sub>)Mo(CO)<sub>3</sub> is characterised by longer M–C(arene) bonds (2.39 Å) and a smaller displacement of

the CMe<sub>3</sub> carbon from the arene plane (0.18 Å), see Ref. [16].]

Finally, it may be noted that in contrast to **1** and **2**, where the <sup>13</sup>C subspectrum of the PPh<sub>3</sub> ligand remains sharp at –115 °C, this subspectrum for **3** is also substantially broadened at –115 °C, indicative of restricted Cr–P rotation. We have not been able to estimate this barrier, and therefore cannot comment on the possibility that this process may be correlated with Cr–arene rotation.

### 3. Experimental

NMR spectra were recorded using a JEOL GSX270 spectrometer; temperatures were measured using the built-in copper–constantan thermocouple previously calibrated with a platinum resistance thermometer. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P spectra were measured at 270, 68 and 109 MHz respectively. Chemical shifts were measured relative to SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C) and 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P).

#### 3.1. Synthesis

1,4-C<sub>6</sub>H<sub>4</sub>((SiMe<sub>3</sub>)<sub>2</sub>) was prepared by a literature method [17]: white solid, m.p. 75–79 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.49 (4H, s, H<sub>2,3,5,6</sub>), 0.23 (9H, s, SiMe<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 140.9 (C<sub>1,4</sub>), 132.6 (C<sub>2,3,5,6</sub>), –1.20 (SiMe<sub>3</sub>).

Table 2  
Crystal data and data collection parameters for **2** and **3**

Compound	<b>2</b>	<b>3</b>
Empirical formula	C <sub>32</sub> H <sub>37</sub> CrO <sub>3</sub> PSi <sub>2</sub>	C <sub>38</sub> H <sub>45</sub> CrO <sub>3</sub> P
Formula weight	592.77	616.71
Temperature	293(2) K	293(2) K
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
Unit cell dimensions	<i>a</i> = 8.4810(7) Å, $\alpha$ = 90° <i>b</i> = 18.672(2) Å, $\beta$ = 90.790(8)° <i>c</i> = 19.614(3) Å, $\gamma$ = 90°	<i>a</i> = 10.311(3) Å, $\alpha$ = 86.60(1)° <i>b</i> = 10.527(2) Å, $\beta$ = 88.42(2)° <i>c</i> = 37.739(6) Å, $\gamma$ = 60.19(2)°
Volume	3105.7(6) Å <sup>3</sup>	3548.0(14) Å <sup>3</sup>
Z	4	4
Density (calc.)	1.268 Mg m <sup>-3</sup>	1.155 Mg m <sup>-3</sup>
Absorption coefficient	0.524 mm <sup>-1</sup>	0.397 mm <sup>-1</sup>
<i>F</i> (000)	1248	1312
Crystal size	0.40 × 0.45 × 0.38 mm <sup>3</sup>	0.38 × 0.42 × 0.44 mm <sup>3</sup>
Theta range for data collection	2 to 30°	2 to 30°
Index ranges	0 ≤ <i>h</i> ≤ 11; 0 < <i>k</i> ≤ 26; –27 ≤ <i>l</i> ≤ 27	0 ≤ <i>h</i> ≤ 13; –12 ≤ <i>k</i> ≤ 13; –53 ≤ <i>l</i> ≤ 49
Reflections collected	9915	18520
Independent reflections	9023 [ <i>R</i> ( <i>j</i> ) = 0.0157]	17106 [ <i>R</i> ( <i>j</i> ) = 0.0338]
Data/restraints/parameters	9023/0/349	17106/0/775
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.056	0.902
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0369, <i>wR</i> <sub>2</sub> = 0.1258	<i>R</i> <sub>1</sub> = 0.0841, <i>wR</i> <sub>2</sub> = 0.2506
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0491, <i>wR</i> <sub>2</sub> = 0.1357	<i>R</i> <sub>1</sub> = 0.1096, <i>wR</i> <sub>2</sub> = 0.2844
Largest diff. peak and hole	0.386 and –0.223 e Å <sup>-3</sup>	1.379 and –1.180 e Å <sup>-3</sup>

*R* indices:  $R_1 = [\sum ||F_o| - |F_c||] / \sum |F_o|$  (based on *F*),  $wR_2 = \{[\sum_w (|F_o|^2 - |F_c|^2)^2] / [\sum_w (|F_o|^2)^2]\}^{1/2}$  (based on *F*<sup>2</sup>).

$w = 1 / [(σF_o)^2 + (a \cdot P)^2 + b \cdot P + d + e \cdot \sin(\theta)]$ .

Goodness-of-fit  $[\sum_w (F_o^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$ .

Table 3  
Atomic coordinates for complexes 2 and 3

Atom	x	y	z
<b>Complex 2</b>			
Cr(1)	4406(1)	8470(1)	3218(1)
P(1)	5349(1)	7318(1)	3438(1)
Si(2)	2854(1)	8843(1)	1417(1)
Si(1)	7705(1)	9730(1)	3954(1)
O(1)	3443(3)	8559(1)	4671(1)
O(2)	1196(2)	7859(1)	2957(1)
C(1)	6300(2)	9328(1)	3305(1)
C(2)	4747(2)	9620(1)	3254(1)
C(3)	3737(2)	9465(1)	2702(1)
C(4)	4183(2)	8974(1)	2188(1)
C(5)	5675(2)	8643(1)	2261(1)
C(6)	6712(2)	8816(1)	2807(1)
C(7)	9754(2)	9429(1)	3787(2)
C(8)	7581(3)	10720(1)	3814(1)
C(9)	7128(3)	9533(1)	4848(1)
C(10)	3451(4)	9543(2)	798(1)
C(11)	755(3)	8997(2)	1661(1)
C(12)	3079(3)	7931(1)	1055(1)
C(13)	3851(2)	8517(1)	4114(1)
C(14)	2456(2)	8081(1)	3056(1)
C(15)	3855(2)	6626(1)	3589(1)
C(16)	2637(2)	6777(1)	4040(1)
C(17)	1495(2)	6275(1)	4182(1)
C(18)	1518(3)	5615(1)	3874(1)
C(19)	2699(3)	5456(1)	3425(1)
C(20)	3866(2)	5952(1)	3286(1)
C(21)	6542(2)	6904(1)	2772(1)
C(22)	5865(2)	6832(1)	2128(1)
C(23)	6714(3)	6550(1)	1591(1)
C(24)	8241(3)	6341(1)	1696(1)
C(25)	8935(3)	6409(2)	2328(1)
C(26)	8087(2)	6688(1)	2871(1)
C(27)	6612(2)	7214(1)	4203(1)
C(28)	6442(3)	6667(2)	4671(1)
C(29)	7386(3)	6644(2)	5261(1)
C(30)	8526(3)	7153(2)	5371(1)
C(31)	8757(4)	7675(1)	4899(2)
C(32)	7794(4)	7712(1)	4321(1)
<b>Complex 3</b>			
Cr(1)	2044(1)	819(1)	3869(1)
Cr(2)	8768(1)	8299(1)	1243(1)
P(1)	2041(1)	-713(1)	3444(1)
P(2)	8334(1)	7556(1)	1802(1)
O(1)	-1278(4)	2502(5)	3796(1)
O(2)	1888(7)	2810(5)	3262(1)
O(101)	7921(6)	11148(4)	1546(1)
O(102)	5479(4)	9746(6)	1130(1)
C(1)	3887(4)	1131(3)	4076(1)
C(2)	4417(4)	-384(3)	4076(1)
C(3)	3681(3)	-1037(3)	4272(1)
C(4)	2316(4)	-125(3)	4432(1)
C(5)	1707(3)	1429(3)	4428(1)
C(6)	2535(4)	2016(3)	4255(1)
C(7)	4859(5)	1778(5)	3935(1)
C(8)	5735(6)	1046(5)	3597(1)
C(9)	6008(6)	1401(8)	4231(2)
C(10)	3994(7)	3398(5)	3860(2)
C(11)	4503(4)	-2687(3)	4372(1)
C(12)	4984(5)	-2838(4)	4760(1)
C(13)	5914(5)	-3541(4)	4151(1)
C(14)	3522(5)	-3373(4)	4344(1)

Table 3 (continued)

Atom	x	y	z
C(15)	371(4)	2367(4)	4667(1)
C(16)	-835(5)	1933(5)	4672(1)
C(17)	-360(5)	3998(4)	4552(1)
C(18)	980(6)	2140(6)	5042(1)
C(19)	21(5)	1810(5)	3827(1)
C(20)	1979(6)	2003(5)	3494(1)
C(21)	958(3)	-1666(3)	3529(1)
C(22)	324(4)	-1652(4)	3855(1)
C(23)	-403(5)	-2452(5)	3927(1)
C(24)	-503(5)	-3272(5)	3669(1)
C(25)	84(4)	-3256(5)	3333(1)
C(26)	792(4)	-2448(4)	3264(1)
C(27)	1226(4)	190(4)	3007(1)
C(28)	-284(5)	1210(5)	2988(1)
C(29)	-953(6)	1911(6)	2665(1)
C(30)	-124(7)	1581(6)	2359(1)
C(31)	1357(7)	569(7)	2372(1)
C(32)	2069(6)	-138(6)	2697(1)
C(33)	3897(4)	-2192(3)	3315(1)
C(34)	4310(4)	-3665(4)	3317(1)
C(35)	5770(5)	-4722(4)	3236(1)
C(36)	6825(5)	-4294(5)	3144(1)
C(37)	6410(4)	-2831(5)	3132(1)
C(38)	4972(4)	-1796(4)	3219(1)
C(101)	9008(4)	7817(4)	673(1)
C(102)	9665(4)	6439(4)	868(1)
C(103)	10824(4)	6012(4)	1109(1)
C(104)	11278(4)	7032(4)	1180(1)
C(105)	10694(4)	8402(4)	988(1)
C(106)	9575(4)	8760(4)	733(1)
C(107)	7949(6)	8141(6)	362(1)
C(108)	6953(7)	9754(6)	278(2)
C(109)	8932(9)	7462(9)	47(1)
C(110)	6942(7)	7470(7)	426(2)
C(111)	11763(5)	4376(4)	1229(1)
C(112)	12495(6)	3558(5)	890(1)
C(113)	10831(6)	3757(4)	1402(1)
C(115)	11460(6)	9321(5)	1018(1)
C(114)	13018(5)	4079(5)	1488(1)
C(116)	11938(7)	9335(6)	1398(1)
C(117)	10451(8)	10917(6)	880(2)
C(118)	12864(7)	8616(8)	787(2)
C(119)	8271(6)	10026(4)	1435(1)
C(120)	6777(5)	9155(5)	1174(1)
C(121)	7334(4)	6509(4)	1840(1)
C(122)	7119(5)	5918(5)	1543(1)
C(123)	6447(6)	5055(7)	1570(2)
C(124)	5949(6)	4810(6)	1901(2)
C(125)	6115(5)	5407(5)	2192(1)
C(126)	6797(5)	6264(5)	2164(1)
C(127)	9986(4)	6495(3)	2088(1)
C(128)	10311(4)	5206(4)	2287(1)
C(129)	11559(5)	4523(4)	2505(1)
C(130)	12474(5)	5116(5)	2530(1)
C(131)	12181(4)	6363(5)	2336(1)
C(132)	10946(4)	7054(4)	2112(1)
C(133)	7155(4)	9016(4)	2105(1)
C(134)	7661(5)	9213(5)	2420(1)
C(135)	6704(6)	10277(5)	2647(1)
C(136)	5242(6)	11172(5)	2560(1)
C(137)	4699(6)	11003(6)	2246(2)
C(138)	5646(5)	9933(5)	2020(1)

1,3,5-C<sub>6</sub>H<sub>3</sub><sup>1</sup>Bu<sub>3</sub>, <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.25 (3H, s, H<sub>2,4,6</sub>), 1.30 (12H, s, CMe<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 150.0 (C<sub>1,3,5</sub>), 119.5 (C<sub>2,4,6</sub>) (from Ref. [18]).

The (arene)Cr(CO)<sub>3</sub> complexes were prepared by standard methods [18–20].

(a) [1,4-C<sub>6</sub>H<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>]Cr(CO)<sub>3</sub>: yellow solid, m.p. 114–115°C. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1959, 1983. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) 4.76 (4H, s, H<sub>2,3,5,6</sub>), 0.14 (9H, s, SiMe<sub>3</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) 102.8 (C<sub>1,4</sub>), 98.1 (C<sub>2,3,5,6</sub>), 1.47 (SiMe<sub>3</sub>), 234.1 (CO).

(b) (1,3,5-C<sub>6</sub>H<sub>3</sub><sup>1</sup>Bu<sub>3</sub>)Cr(CO)<sub>3</sub>: yellow solid, m.p. 125–128°C. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1947, 1871. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) 5.72 (3H, s, H<sub>2,4,6</sub>), 1.09 (12H, s, CMe<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 118.4 (C<sub>1,3,5</sub>), 93.2 (C<sub>2,4,6</sub>) (from Ref. [18]).

Complexes **2** and **3** were prepared by photolysis of the tricarbonyls in toluene using a literature procedure [18].

(a) Complex **2**: red crystals, m.p. 190–93°C. Anal. Found: C, 65.0; H, 6.43. C<sub>32</sub>H<sub>37</sub>CrO<sub>2</sub>PSi<sub>2</sub> Calc.: C, 64.6; H, 6.23%. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1879, 1819. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) 4.48 (4H, d, H<sub>2,3,5,6</sub>, J<sub>P-H</sub> = 2.9 Hz), 0.20 (9H, s, SiMe<sub>3</sub>), 6.9–7.8 (15H, m, PPh<sub>3</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, J<sub>P-C</sub> values in parentheses) 100.3 (C<sub>1,4</sub>), 93.3 (C<sub>2,3,5,6</sub>), 140.1 (32.3), 133.2 (10.7), 129.0 (1.4), 128.0 (8.7) (PPh<sub>3</sub>), 242.3 (20.8) (CO); <sup>31</sup>P NMR (CDCl<sub>3</sub>) 89.5.

(b) Complex **3**: red crystals, m.p. 129–132°C (decomp.). Anal. Found: C, 74.3; H, 9.69. C<sub>38</sub>H<sub>45</sub>CrO<sub>2</sub>P Calc.: C, 74.0; H, 9.87%. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1867, 1803. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) 5.21 (3H, s, H<sub>2,4,6</sub>), 1.13 (12H, s, CMe<sub>3</sub>), 6.9–7.8 (15H, m, PPh<sub>3</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, J<sub>P-C</sub> values in parentheses) 120.4 (C<sub>1,3,5</sub>), 84.9 (C<sub>2,4,6</sub>), 31.1, 34.8 (CMe<sub>3</sub>), 140.8 (31.6), 134.0 (10.7), 128.8, 127.8 (8.8) (PPh<sub>3</sub>), 242.8 (20.5) (CO); <sup>31</sup>P NMR (CDCl<sub>3</sub>) 88.0.

### 3.2. Crystallography

Suitable crystals of **2** and **3** for X-ray analysis were obtained by crystallisation from petroleum ether (60–80). The crystal and refinement data are given in Table 2. Intensity data were collected at room temperature on an Enraf–Nonius CAD4F diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) using the  $\omega$ - $2\theta$  scan method. Data were corrected for Lorentz and polarisation effects, but not for absorption. Crystals of **3** were all twinned and too large for data collection. The crystal piece for data collection was cut from a larger twinned one until the remaining piece showed no twinning as judged by examination on a polarising microscope. The standard deviations on the bond lengths are quite satisfactory, and the largest peaks in the final difference map are small and close to chromium. However, the *R* indices are larger than might have been expected, and this is possibly due to slight internal damage which the

crystal suffered on being cut. The structure was solved by direct methods, SHELXS-86 [21], and refined by full-matrix least-squares using SHELXL-93 [22]. Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. All calculations were performed on a VAX 6610 computer. The ORTEX program was used to obtain the drawings [23]. Atomic coordinates are listed in Table 3. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre.

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