A Dynamic Nuclear Magnetic Resonance Study of the Effects of Methyl Group Substitution of the Hexahapto-arene on the Intramolecular Rotations of (η^6-Arene)dicarbonyl(triphenylphosphine)-chromium(0) and -molybdenum(0) Complexes

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The variable-temperature 75.49 MHz ^{13}C-{^1H} n.m.r. spectra of (η^6- arene)-dicarbonyl(triphenylphosphine)metal(0) complexes (arene = $C_6H_{6-n}Me_n$, n = 0—6, metal = Cr; arene = 1,3,5-trimethylbenzene, metal = Mo) have been observed down to 145 K. The steric requirements for intramolecular rotations for these complexes are visualised as two cones with a common apex at the centre of the metal atom. Methyl substitution of the benzene ring can lead to restricted rotation of the triphenylphosphine ligand about the metal–phosphorus bond, with $\Delta G^{\ddagger}_{200}$ *ca.* 36.6 kJ mol^{-1}. However, if two adjacent positions on the benzene ring are unsubstituted then rapid interconversion of the phenyl-group environments of the PPh_3 ligand occurs even at the lowest experimentally accessible temperature. Slowed rotation about the metal–arene bond is not observed in any of the complexes.

We have recently reported[1] the results of a variable-temperature n.m.r. study whose aim was to quantify the effect induced by the alkyl substituents of homosubstituted hexa-alkylbenzenes, C_6R_6, on the barrier to rotation about the chromium–phosphorus bond axis in the series of complexes $[Cr(\eta^6\text{-}C_6R_6)(CO)_2(PPh_3)]$ [R = H, (**1**); Me, (**14**); Et, (**15**); or Pr^n, (**16**)]. It was found that steric, rather than electronic, factors are dominant and that the steric requirements for the intramolecular rotations for these complexes can be modelled by two cones with a common apex at the centre of the chromium atom: an arene cone with the rotating co-ordinated arene as its base, and the triphenylphosphine cone (Figure 1). Significant interaction between the two cones can lead to slowed rotation of the triphenylphosphine moiety, such that a decoalescence phenomenon was observed in the low-temperature ^{13}C-{^1H} n.m.r. spectrum of, for example, the η^6-hexamethylbenzene complex, (**14**), whereas it was not observed for its η^6-benzene homologue (**1**). It was thus possible to calculate a maximum possible cone angle of 141° for PPh_3, closely comparable to the value of 145° originally measured by Tolman[2] from space-filling (CPK) molecular models, lending credence to our model of two interacting cones. This simple model suggested that even for $[Cr(C_6H_5Me)(CO)_2(PPh_3)]$, (**2**), the single methyl substituent might sweep out a cone sufficiently large as to cause significant interference with the rotation of the triphenylphosphine ligand.

As recognised from the outset, regular solid cone angles take no account of the intermeshing of adjacent ligands and under these circumstances a bulky phosphine ligand is better described as a 'conic cog',[3] this modified description also applying to the arene cone. Provided therefore that the notches of the conic cogs are of sufficient depth, a complex of this type with an arene of three-fold symmetry, such as 1,3,5-trimethylbenzene, might conceivably behave as an analogue of a pair of meshed bevel gears.[4] Such analogues have recently gained more attention with the emergence of the concept of 'nanotechnology' whose pundits predict the application of mechanical principles at the molecular level perhaps to produce the ultimate in miniaturised machines.[5]

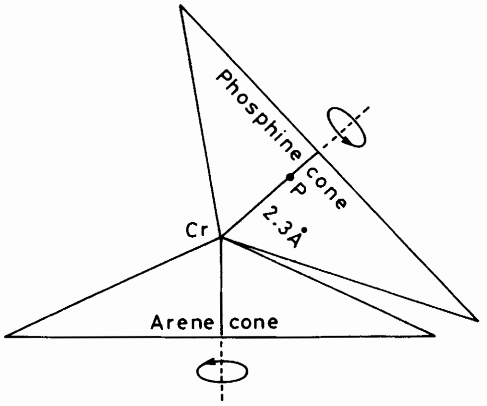


Figure 1. Cross-sectional illustration of the arene and triphenylphosphine cones of the complexes

This paper reports the results of an extension of the variable-temperature n.m.r. study of the series of complexes $[M(\eta^6\text{-arene})(CO)_2(PPh_3)]$ (M = Cr, arene = $C_6H_{6-n}Me_n$; M = Mo, arene = 1,3,5-trimethylbenzene) to include all methyl-substituted benzenes and presents our conclusions concerning their intramolecular rotational dynamics.

Results and Discussion

Variable-temperature N.M.R. Spectra.—Solutions of the complexes (Table 1) in CD_2Cl_2 ($CDFCl_2$) were cooled to 158 K (145 K) and their 75.49-MHz ^{13}C-{^1H} n.m.r. spectra recorded. N.m.r. data for the complexes are reported in Table 2. Although the *X*-ray crystal structures of the methyl-substituted arene complexes are unknown, from the close similarity of their ambient-temperature PPh_3 subspectra to those of (**15**) and (**16**) it would appear that they also have static molecular structures with staggered conformations about the P–Cr bonds and that one of the phenyl rings is remote from, and the other two are

Table 1. The $[M(\eta^6\text{-arene})(CO)_2(PPh_3)]$ complexes

Complex	Arene	Metal	Decoalescence?[a]	$\Delta G^{\ddagger}_{200}$[b]	$\Delta H^{\ddagger}_{200}$[b]
(1)	C_6H_6	Cr	No	—	—
(2)	C_6H_5Me	Cr	No	—	—
(3)	$C_6H_4Me_2$-1,2	Cr	No	—	—
(4)	$C_6H_4Me_2$-1,3	Cr	No	—	—
(5)	$C_6H_4Me_2$-1,4	Cr	No	—	—
(6)	$C_6H_3Me_3$-1,2,3	Cr	No	—	—
(7)	$C_6H_3Me_3$-1,2,4	Cr	No	—	—
(8)	$C_6H_3Me_3$-1,3,5	Cr	Yes	34.7 ± 1.8	30.0 ± 1.2
(9)	$C_6H_3Me_3$-1,3,5	Mo	Yes	36.3 ± 1.9	30.3 ± 1.4
(10)	$C_6H_2Me_4$-1,2,3,4	Cr	No	—	—
(11)	$C_6H_2Me_4$-1,2,3,5	Cr	Yes	38.5 ± 2.0	24.6 ± 1.5
(12)	$C_6H_2Me_4$-1,2,4,5	Cr	Yes	33.9 ± 1.3	28.5 ± 0.7
(13)	C_6HMe_5	Cr	Yes	37.5 ± 2.7	17.1 ± 1.4
(14)	C_6Me_6	Cr	Yes	38.4 ± 1.5[c]	28.2 ± 3.0[c]
(15)	C_6Et_6	Cr	Yes	38.2 ± 1.5[c]	30.8 ± 0.5[c]
(16)	$C_6Pr^n{}_6$	Cr	Yes	37.7 ± 1.5[c]	—

[a] Decoalescence observed in the PPh_3 ^{13}C-{^1H} n.m.r. subspectrum. [b] In kJ mol^{-1}. [c] Data from ref. 1.

Table 2. ^{13}C-{^1H} N.m.r. data for the complexes (δ values, J_{PC} in Hz in parentheses)

Complex	Solvent	T/K	C_{methyl}	C_{arene}	CO	*i*-C	*o*-C	*m*-C	*p*-C
(1)	$CDFCl_2$	170		90.71	242.10(26.2)[a]	138.81(34.8)[b]	132.73	127.95	129.07
(2)	CD_2Cl_2	200	20.42	88.24, 88.72, 92.21, 106.20	241.60(16.8)[a]	138.84(34.0)[b]	132.46(11.1)[c]	127.60(8.3)[d]	128.64
(3)	CD_2Cl_2	275	18.88	91.56, 93.27, 101.69	241.67(16.9)[a]	140.26(33.22)[b]	133.08(9.8)[c]	128.01(7.5)[d]	129.03
(4)	CD_2Cl_2	295	20.87	87.50, 90.41, 94.53, 105.37	242.30(22.2)[a]	140.37(33.2)[b]	133.28(9.8)[c]	128.14(7.5)[d]	129.19
(5)	CD_2Cl_2	275	19.99	91.54, 104.05	242.28(19.4)[a]	140.48(33.2)[b]	133.16(10.6)[c]	128.11(8.3)[d]	129.12
(6)	CD_2Cl_2	250	14.81, 19.83	92.41, 93.26, 97.14, 104.41	242.0(22.2)[a]	140.01(34.0)[b]	132.75(11.0)[c]	127.76(11.1)[d]	128.72
(7)	CD_2Cl_2	250	18.20, 18.72, 19.82	90.43, 93.26, 95.69, 100.60, 103.06, 105.34	242.20(13.8)[a]	140.33(32.5)[b]	132.90(11.1)[c]	127.86(8.3)[d]	128.87
(8)	CD_2Cl_2	303	20.37	90.48, 105.99	240.20(15.5)[a]	139.90(31.7)[b]	129.14(16.3)[c]	127.89(8.2)[d]	128.56
	CD_2Cl_2	163	19.57	89.55, 105.58	241.53(16.6)[a]	141.28(45.2)[b], 136.50(26.6)[b]	133.32(9.0)[c], 130.21	126.74	128.41
(9)	$CDFCl_2$	250	20.34	90.53, 109.22	230.66(14.6)[a]	139.15(37.7)[b]	133.51(12.8)[c]	127.84	129.08
	$CDFCl_2$	160	20.55	91.13, 110.82	231.43(11.6)[a]	141.20(43.6)[b], 136.96(34.9)[b]	134.24, 131.55	127.95	129.46
(10)	CD_2Cl_2	295	15.91, 19.87	95.13, 99.20, 104.92	242.35(19.4)[a]	141.14(31.7)[b],	133.26(9.8)[c]	128.12	128.97
(11)	CD_2Cl_2	270	14.67, 19.52, 19.68	94.70, 98.20, 104.12, 105.83	242.51(17.5)[a]	140.00(32.5)[b],	133.49	127.94	128.95
	CD_2Cl_2	180	13.93, 17.27, 19.14	94.50, 96.87, 103.62, 104.99	242.89(23.3)[a]	141.48(45.3)[b], 136.9(27.2)[b]	133.34, 130.40	127.15	128.45
(12)	$CDFCl_2$	250	17.75	96.97, 108.34	243.41(17.4)[a]	139.90(31.7)[b]	133.19(10.6)[c]	127.91(6.0)[d]	128.87
	$CDFCl_2$	155	17.82	97.66, 107.88	243.91(15.1)[a]	141.41(36.2)[b], 137.97(33.2)[b]	133.32, 131.30	127.88	128.96
(13)[e]	$CDFCl_2$	250	15.67, 15.92, 19.17	99.90, 100.50, 104.64	243.06(23.3)[a]	140.00(32.5)[b]	133.16(11.6)[c]	127.81(5.8)[d]	128.79
	$CDFCl_2$	160	15.73, 15.96, 19.33	100.21	243.68(14.6)[a]	141.28(40.5)[b], 137.96(22.4)[b]	133.63, 131.74	127.87	128.94
(14)[f]	CD_2Cl_2	Ambient	15.60	101.66	242.84(21.2)[a]	138.81(30.0)[b]	132.58(11.0)[c]	126.96(8.1)[d]	127.82
	CD_2Cl_2	158				142.23(43.8)[b], 136.10(19.9)[b]	132.85, 130.60	127.17	128.13, 127.86
(15)[f]	CD_2Cl_2	Ambient	—	108.98	243.84(22.0)[a]	139.90(29.6)[b]	133.40(10.6)[c]	127.63(8.0)[d]	128.53
	CD_2Cl_2	158	—			142.05(45.8)[b], 136.56(21.5)[b]	132.84, 130.48	127.16	128.06
(16)[f]	CD_2Cl_2	Ambient	—	107.51	243.42(21.5)[a]	139.10(31.6)[b]	132.90(10.8)[c]	127.52(8.0)[d]	128.10
	CD_2Cl_2	158	—			142.53(50.8)[b], 136.69(22.0)[b]	133.59, 131.07	127.65	128.69, 128.39

[a] $^2J_{PC}$. [b] $^1J_{PC}$. [c] $^2J_{PC}$. [d] $^3J_{PC}$. [e] Not all arene resonances observed as some are obscured by the solvent resonances. [f] Data from ref. 1.

closer to, the steric and electronic influences of the η^6-arene ligand.[1] No decoalescence phenomena were revealed in the alkyl, hexahapto arene, or carbonyl subspectra of any of the complexes, indicating that rotation about the metal–arene bond remains rapid even at the lowest temperatures observed. However, a decoalescence phenomenon in the triphenylphosphine subspectrum, starting at 205 K, was observed for $[Cr(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(CO)_2(PPh_3)]$, **(8)**, $[Mo(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(CO)_2(PPh_3)]$, **(9)**, $[Cr(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,3,5)(CO)_2(PPh_3)]$, **(11)**, $[Cr(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,5)(CO)_2(PPh_3)]$, **(12)**, and $[Cr(\eta^6\text{-}C_6HMe_5)(CO)_2(PPh_3)]$, **(13)**, as well as for **(14)** as previously reported.[1] No decoalescence phenomenon was observed for any of the other methyl-substituted complexes down to 145 K, the lowest temperature attained. The low-

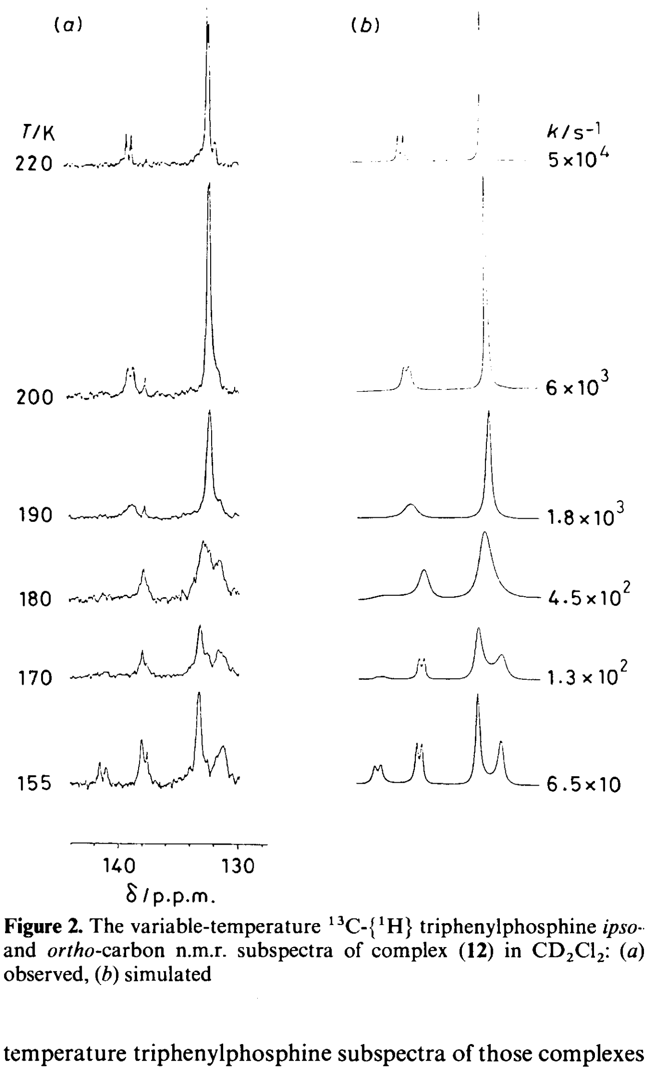


Figure 2. The variable-temperature $^{13}C-\{^1H\}$ triphenylphosphine *ipso*- and *ortho*-carbon n.m.r. subspectra of complex (**12**) in CD_2Cl_2: (*a*) observed, (*b*) simulated

temperature triphenylphosphine subspectra of those complexes in which the decoalescence phenomenon occurred were almost identical to those previously reported for (**14**)—(**16**), and the decoalescence can therefore with confidence be attributed to slowed rotation about the metal–phosphorus bond, with the major contribution to the rotational barrier arising from the passage of the phenyl rings past the co-ordinated arene. The decoalescence of the signals assigned to the *ipso*-C and *ortho*-C atoms was simulated as a two-site exchange problem with superimposed splitting due to ^{31}P coupling. Simulated and observed variable-temperature n.m.r. spectra for those carbons of (**12**) are illustrated in Figure 2. There were no significant differences in the PPh_3 rotational barrier for any of the complexes displaying this decoalescence phenomenon and the mean value calculated for $\Delta G^{\ddagger}_{200}$ was 36.6 kJ mol^{-1}. It is of interest that increasing the metal–arene and metal–phosphorus distances on going from Cr to Mo in (**8**) and (**9**) makes no appreciable difference to the metal–phosphorus rotational barrier.

Down to 145 K, *i.e.* 60° below the temperature at which decoalescence started to appear in the spectra of the complexes listed above, there was no indication of slowed PPh_3 rotation for the toluene complex, (**2**), or the three xylene complexes, (**3**)—(**5**). The complexes of 1,3,5-trimethylbenzene, (**8**) and (**9**), were the only ones of trimethyl-substituted benzenes to show a decoalescence. In contrast, that of 1,2,3,4-tetramethylbenzene, (**10**), was the only complex of a tetramethyl-substituted benzene for which slowed PPh_3 rotation was *not* observed.

Clear conclusions can thus be drawn concerning the major intramolecular rotations of these complexes of the methyl-substituted benzenes. In none of the examples examined is there any evidence for slowed rotation about the metal–arene bond axis even though methyl substitution of the benzene ring can lead to slowed rotation of the PPh_3 ligand. However, if two adjacent positions on the benzene ring are unsubstituted then rapid interconversion of the phenyl-group environments of the PPh_3 ligand occurs even at the lowest experimentally accessible temperature.

The crystal and molecular structures of complexes (**8**) and (**10**) are unknown, but it is reasonable to assume that, as with (**15**) and (**16**),[1] electronic effects will favour staggered over eclipsed conformations about the metal–arene bond. Figure 3 illustrates the expected rotamers about the metal–arene bond for complexes (**8**) and (**10**). For (**10**), rotation about the metal–phosphorus bond is rapid at all experimentally accessible temperatures only in rotamer (**I**), whereas in all the others interference occurs between the triphenylphosphine cone and the methyl groups substituting the arene. However, no matter that the PPh_3 rotation may be slowed in these latter rotamers, the observed triphenylphosphine spectrum is controlled by rapid rotation of this ligand in metal–arene rotamer (**I**). Moreover, as unequal rotamer populations can be anticipated, slowed PPh_3 rotation might not therefore be observed even if metal–arene rotation were to become slowed, as metal–arene rotamers other than (**I**) may be only negligibly populated. In contrast, for (**8**) and (**9**) all the metal–arene rotamers illustrated are required to be equally populated and in each of them there is interference between the phosphine cone and the arene-methyl groups. For these latter complexes under conditions of slowed PPh_3 rotation, but rapid metal–arene rotation, two different environments are expected for the three phenyl groups and this is reflected in the observed decoalescences of the *ipso*-C and *ortho*-C resonances each into two signals in a 2:1 ratio.

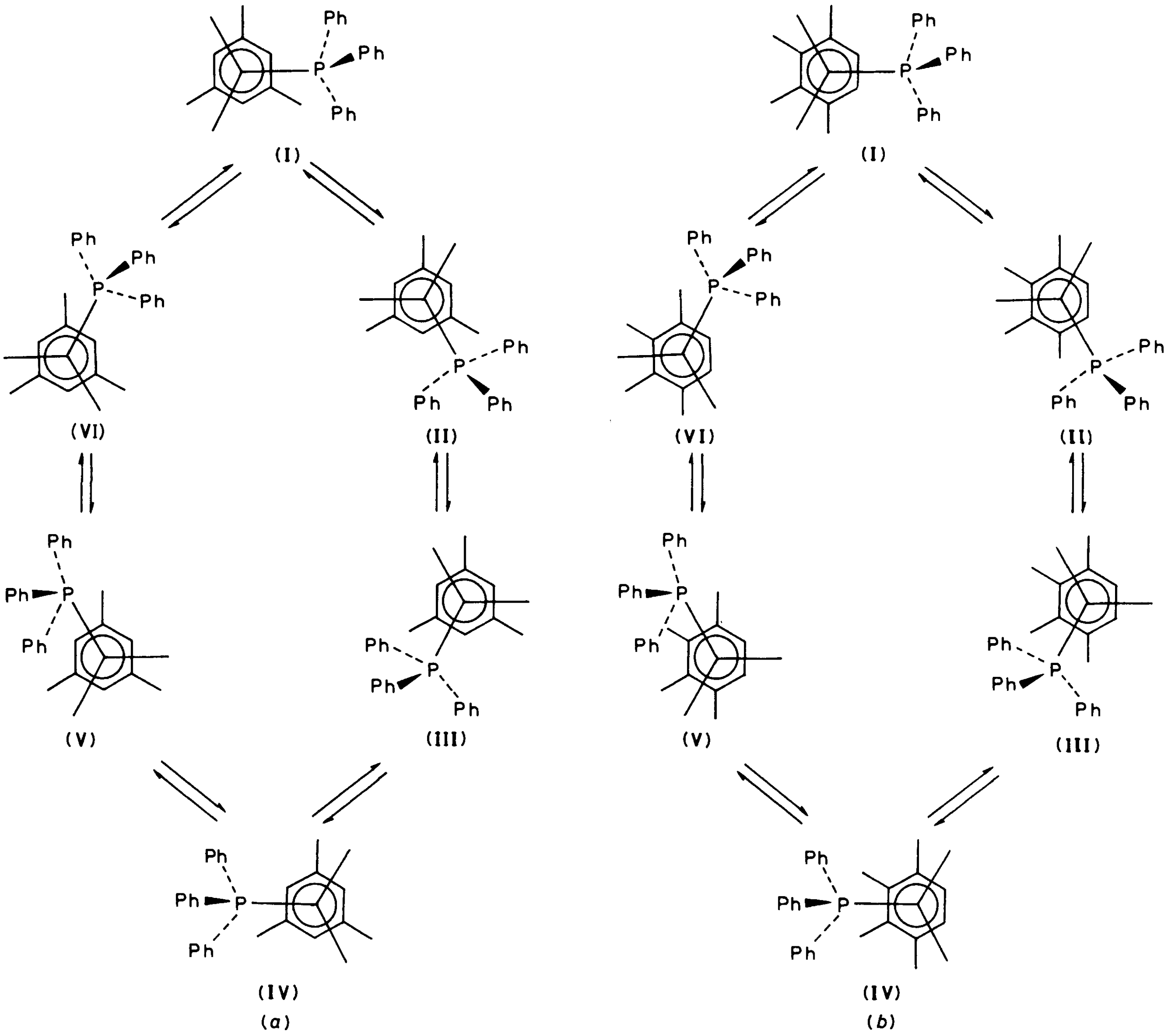
Finally, there is no evidence that any member of this particular class of molecules behaves as an analogue of a pair of meshed bevel gears, as in such a situation slowed rotation of the phosphine ligand about the metal–phosphorus bond would inevitably lead to slowed rotation about the metal–arene bond.

Experimental

Variable-temperature N.M.R. Measurements.—Variable-temperature n.m.r. spectra were recorded at 75.49 MHz (^{13}C) on a Bruker AM300WB spectrometer operating in the Fourier transform mode. Those n.m.r. samples dissolved in CD_2Cl_2 were filtered under nitrogen, degassed, and sealed in 10-mm (outside diameter) tubes. Concentrations of the sample CD_2Cl_2 solutions were approximately 75 mmol dm^{-3}. Provided that they were carefully filtered, degassed, and the tube sealed, it was possible to supercool the solutions to at least 20 °C below the nominal freezing point of the solvent CD_2Cl_2, the samples remaining liquid for several hours at this temperature. The n.m.r. tubes were not spun at temperatures below 178 K. N.m.r. samples dissolved in $CDFCl_2$ were not filtered, only freeze-thaw degassed and sealed in 10-mm (outside diameter) tubes. Concentrations of these latter solutions were approximately 40 mmol dm^{-3} and their n.m.r. spectra were observed down to 145 K.

Spectral simulations were performed using the DNMR3 program.[6] Satisfactory fits of simulated to observed spectra were judged by visual comparison. Values of $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ were calculated from a linear least-squares fit to the Eyring equation.

Syntheses.—(*η*^{6}-*Arene*)*tricarbonylchromium*(0). Typically these complexes were prepared by refluxing the arene (*ca.* 3 mmol) and $[Cr(CO)_6]$ (0.73 g, 3.3 mmol) in dibutyl ether–



(a) (b)

Figure 3. The expected rotamers about the metal–arene bond for compounds (**8**) (*a*) and (**10**) (*b*)

Table 3. Yields and carbonyl stretches in the i.r. spectra of the complexes $[M(\eta^6\text{-}C_6H_{6-n}Me_n)(CO)_3]$ and $[M(\eta^6\text{-}C_6H_{6-n}Me_n)(CO)_2(PPh_3)]$

	$[M(\eta^6\text{-arene})(CO)_3]$			$[M(\eta^6\text{-arene})(CO)_2(PPh_3)]$		
Arene	Metal	Yield (%)	$\nu_{CO}(cm^{-1})$ [a]	Complex	Yield (%) [b]	$\nu_{CO}(cm^{-1})$ [a]
C_6H_5Me	Cr	97	1 962, 1 893	(**2**)	15	1 859, 1 803
$C_6H_4Me_2$-1,2	Cr	99	1 959, 1 888	(**3**)	23	1 863, 1 792
$C_6H_4Me_2$-1,3	Cr	77	1 959, 1 889	(**4**)	13	1 857, 1 800
$C_6H_4Me_2$-1,4	Cr	97	1 959, 1 888	(**5**)	22	1 872, 1 857, 1 803
$C_6H_3Me_3$-1,2,3	Cr	64	1 954, 1 887, 1 879	(**6**)	8	1 869, 1 862, 1 800
$C_6H_3Me_3$-1,2,4	Cr	68	1 955, 1 883	(**7**)	13	1 854, 1 792
$C_6H_3Me_3$-1,3,5	Cr	62	1 973, 1 875	(**8**)	24	1 837, 1 785
$C_6H_3Me_3$-1,3,5	Mo	58	1 970, 1 932, 1 865	(**9**)	—	1 847, 1 795
$C_6H_2Me_4$-1,2,3,4	Cr	38	1 950, 1 880, 1 873	(**10**)	8	1 875, 1 812
$C_6H_2Me_4$-1,2,3,5	Cr	61	1 958, 1 871	(**11**)	15	1 840, 1 782
$C_6H_2Me_4$-1,2,4,5	Cr	75	1 944, 1 882, 1 854	(**12**)	23	1 872, 1 840, 1 790
C_6HMe_5	Cr	85	1 947, 1 850	(**13**)	28	1 845, 1 791
C_6Me_6	Cr	77	1 942, 1 849	(**14**)	34	1 843, 1 790

[a] Nujol mulls. [b] Based on $M(CO)_6$.

tetrahydrofuran (6:1, 35 cm^3) for 1 week. The solvents were stripped off under reduced pressure and unreacted $[Cr(CO)_6]$ removed by sublimation [85 °C at 0.5 Torr (*ca.* 67 Pa)]. The yellow-green complexes were recrystallised from dichloromethane solution under N_2. Yields and CO stretches in the i.r. spectra of the complexes are reported in Table 3.

Tricarbonyl(1,3,5-*trimethylbenzene*)*molybdenum*(0). This was prepared by refluxing 1,3,5-trimethylbenzene (0.36 g, 3 mmol) and $[Mo(CO)_6]$ (0.87 g, 3.3 mmol) in decalin for 3 h. The cooled solution was diluted with diethyl ether when the desired product was precipitated as yellow-green crystals.

(η^6-*Arene*)*dicarbonyl*(*triphenylphosphine*)*metal*(0). Typically these complexes were prepared by u.v. irradiation of a freeze-thaw degassed toluene solution of $[M(\eta^6\text{-arene})(CO)_3]$ (1.0 mmol) and triphenylphosphine (0.26 g, 1.0 mmol) for 2 h during which N_2 was bubbled through the solution. The orange-yellow solution was filtered under N_2, the solvent evaporated, and residue extracted with toluene. Removal of the solvent gave orange crystals which were purified by medium-pressure chromatography under N_2 [n-hexane–10% ethyl ethanoate on silica gel at a pressure of 2 bar (2×10^5 Pa), flow rate 20 cm^3 min^{-1}].

Satisfactory elemental analyses and/or mass spectral data were obtained for all of the complexes. Yields and CO stretches in the i.r. spectra of the complexes are reported in Table 3.

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